APPENDIX A: Full Text of Some Cited References

Reference documents not readily available online are included in Appendices A, B, and C. The reference documents are split into three Appendices to accommodate the SEPA Register upload size limit.

Appendix A contains the full text of the following references:

Andrade, N. A., Lozano, N., McConnell, L. L., Torrents, A., Rice, C.P., & Ramirez, M. (2015). Long-term trends of PBDEs, triclosan, and triclocarban in biosolids from a wastewater treatment plant in the Mid-Atlantic region of the US. Journal of Hazardous Materials, 282(2015) 68-74. https://doi.org/10.1016/j.jhazmat.2014.09.028

Blaine, A. C., Rich, C. D., Hundal, L. S., Lau, C., Mills, M. A., Harris, K. M., & Higgins, C.P. (2013). Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: field and greenhouse studies. Environmental Science & Technology, 47(24), 14062–14069. https://doi.org/10.1021/es403094q

Blaine A. C., Rich, C. D., Sedlacko E. M., Hundal, L. S., Kumar, K., Lau, C., Mills, M. A., Harris, K. M., & Higgins, C.P (2014) Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended soils. Environmental Science & Technology, 48 (14), 7858-7865. https://doi.org/10.1021/es500016s

Bothfeld, F. & C. Mathieu. (2022). PFAS Concentrations in Influent, Effluent, Solids, and Biosolids of Three Wastewater Treatment Plants. Washington State Department of Ecology. https://apps.ecology.wa.gov/publications/SummaryPages/2203028.html

Brown, S., Beecher, N., & Carpenter, A. (2010). Calculator Tool for Determining Greenhouse Gas Emissions for Biosolids Processing and End Use. Environmental Science and Technology, 44, 9509-9515, https://doi.org/10.1021/es101210k

Brown, S., & Henry, C. (2015). Using Biosolids for Reclamation/Remediation of Disturbed Soils. https://www.epa.gov/sites/default/files/2015-05/documents/biosolidswhitepaper-uwash.pdf

Brusseau M. L., (2023). Influence of chain length on field-measured distributions of PFAS in soil and soil porewater. Journal of Hazardous Materials Letters, 4 (2023) 1000080. https://doi.org/10.1016/j.hazl.2023.100080

Calafat, A. M., Wong, L.-Y., Kuklenyik, Z., Reidy, J. A., & Needham, L. L. (2007). Polyfluoroalkyl Chemicals in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 2003–2004 and Comparisons with NHANES 1999–2000. Environmental Health Perspectives, 115, 1596–1602. https://doi.org/10.1289/ehp.10598

California Association of Sanitation Agencies. (2022). Response to “Sludge in the Garden: Toxic PFAS in Home Fertilizers Made from Sewage Sludge”.

Christian, A. E., & Koper, I. (2023). Microplastics in biosolids: A review of ecological implications and methods for identification, enumeration, and characterization. Science of the Total Environment, 864. https://doi.org/10.1016/j.scitotenv.2022.161083

Hale, R. C., La Guardia M. J., Harvey, E., Chen D., Mainor T. M., & Luellen D. R. (2012). Polybrominated Diphenyl Ethers in U.S. Sewage Sludges and Biosolids: Temporal and Geographical Trends and Uptake by Corn Following Land Application. Environmental Science and Technology, 46(4), 2055-2063. https://doi.org/10.1021/es203149g

Harrad, S., & Hunter, S. (2006). Concentrations of Polybrominated Diphenyl Ethers in Air and Soil on a Rural-Urban Transect Across a Major UK Conurbation. Environmental Science and Technology, 40(15), 4548-4553. https://doi.org/10.1021/es0606879

Lono-Batura, M., Beecher, N., Franciosi, F., Riggs, M., (2018). Proposed ADEC Amendments to 18 AAC 75-Setting Cleanup Levels for PFAS, https://static1.squarespace.com/static/54806478e4b0dc44e1698e88/t/5be06915cd83666b73a1054c/1541433624189/NWBiosolidsNEBRAUSCCWORCCommentsAK_DECSoilStndsPFAS-2Nov2018.pdf

Ma, Y., Stubbings, W. A., Abdallah, M. A., Cline-Cole, R., & Harrad, S. (2023). Temporal trends in concentrations of brominated flame retardants in UK foodstuffs suggest active impacts of global phase-out of PBDEs and HBCDD. Science of the Total Environment, 863(2023). https://doi.org/10.1016/j.scitotenv.2022.160956

Journal of Hazardous Materials 282 (2015) 68–74

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Long-term trends of PBDEs, triclosan, and triclocarban in biosolids from a wastewater treatment plant in the Mid-Atlantic region of the US

Natasha A. Andrade[a,*], Nuria Lozano[a,1], Laura L. McConnell[b,2], Alba Torrents[a], Clifford P. Rice[b], Mark Ramirez[c]

[a] Department of Civil and Environmental Engineering, University of Maryland, College Park, MD 20742, USA
[b] Environmental Management and Byproduct Utilization Laboratory, BARC, ARS/USDA, 10300 Baltimore Avenue, Beltsville, MD 20705, USA
[c] DC Water, District of Columbia Water and Sewer Authority, 5000 Overlook Avenue, S.W., Washington, DC 20032, USA

HIGHLIGHTS

- From 2005 to 2011, BDE-47 + BDE-99 concentrations in biosolids decreased by 42%.
- BDE-209 concentrations remained constant.
- TCC decreased by 47% while TCS showed no temporal trend.
- Contaminant concentrations did not correlate with seasons or with WWTP inflow.
- Decreasing concentrations could be due to phase-out or usage/production reduction.

ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form 18 July 2014
Accepted 12 September 2014
Available online 28 September 2014

Keywords:
Biosolids
Sewage sludge
PBDEs
Triclosan
Triclocarban

ABSTRACT

In the US, land application of biosolids has been utilized in government-regulated programs to recycle valuable nutrients and organic carbon that would otherwise be incinerated or buried in landfills. While many benefits have been reported, there are concerns that these practices represent a source of organic micropollutants to the environment. In this study, biosolids samples from a wastewater treatment plant in the Mid-Atlantic region of the US were collected approximately every 2 months over a 7-year period and analyzed for brominated diphenyl ethers (BDE-47, BDE-99, and BDE-209), triclosan, and triclocarban. During the collection period of 2005–2011, concentrations of the brominated diphenyl ethers BDE-47 + BDE-99 decreased by 42%, triclocarban decreased by 47%, but BDE-209 and triclosan remained fairly constant. Observed reductions in contaminant concentrations could not be explained by different seasons or by volumetric changes of wastewaters arriving at the treatment plant and instead may be the result of the recent phaseout of BDE-47 and BDE-99 as well as potential reductions in the use of triclocarban.

1. Introduction

In 2001, production of biosolids in the US was estimated to be 5.1–6.4 million metric dry tons [1]. Methods for disposal of this wastewater treatment byproduct in the US have typically been land application, incineration, and landfilling [1,2]. Biosolids are applied to approximately 0.1% of US available agricultural land on an annual basis [1]. While land application of this nutrient and carbon-rich material has been shown to be a beneficial method of utilization [3,4], reports on the presence of organic pollutants in biosolids has led to concerns over potential exposure to humans and wildlife. Several organic pollutants have been identified in biosolids, including pesticides, flame retardants, hormones, and other manufactured compounds [5]. Some classes of chemicals have received increased attention as exposure can cause disruption of the endocrine system in some species; these chemicals are called endocrine disrupting chemicals (EDCs) [6]. Among EDCs that have

* Corresponding author at: Department of Civil and Environmental Engineering, University of Maryland, College Park, MD 20742, USA. Tel.: +1 301 405 7768; fax: +1 301 405 2585.
E-mail address: nandrade@umd.edu (N.A. Andrade).
[1] Address: Department of Water and Environmental Science and Technology, University of Cantabria, Santander, Cantabria 39005, Spain.
[2] Address: Bayer CropScience, 2 T.W. Alexander Dr., Research Triangle Park, NC 27709, USA.

http://dx.doi.org/10.1016/j.jhazmat.2014.09.028
0304-3894/

gained notoriety in the last decade are polybrominated diphenyl ethers (PBDEs) and commonly used antibacterial and fungicidal agents, such as triclosan (TCS) and triclocarban (TCC).

PBDEs are flame retardants used in electronics, consumer products, plastics, textiles, vehicles, etc. [7]. These chemicals have been recognized as bioaccumulative, endocrine disruptors, and toxic [8]. Three commercial formulations of PBDEs were originally produced: penta-BDE, octa-BDE, and deca-BDE. In December of 2004, in the US, the penta-BDE and octa-BDE formulations have been voluntarily phased out of production and, as of January 2005, EPA requires notification and will evaluate the intent of any company to manufacture, import, or use these commercial products [9]. Manufacturers and importers of the deca-BDE formulation announced their commitment to stop production and use by the end of 2013 [10]. BDE-209 is the fully brominated PBDE congener and the main component of the deca-BDE commercial formulation. BDE-47 and BDE-99 are the major components of the penta-BDE commercial formulation, which contains a variety of congeners, from tetra- to hepta-brominated compounds and are listed as persistent organic pollutants by the Stockholm Convention [11]. BDE-209, -47, and -99 are the congeners most frequently observed in the environment and have been observed in sediments [12], soils and biosolids [13], house dust and indoor air [14,15], polar bears [16], and humans [17].

TCS and TCC are fungicidal and bactericidal chemicals used in a wide variety of consumer products like soaps, toothpastes, and lotions. Both chemicals have been detected in human plasma, urine, and milk [18–20] and have been shown to bioaccumulate in aquatic species [21–23] and plants [24,25]. Furthermore, both TCC and TCS have shown to possess endocrine disrupting properties [26–29]. Previous reports have indicated that biosolids can be a source of these chemicals to receiving soils when biosolids are land applied [30–33].

PBDEs, TCS, and TCC are present in biosolids throughout the world, with the highest levels observed in the United States [13,34–37] and Australia [38,39]. PBDEs enter wastewater treatment plants (WWTPs) via the disposal of wash water from contaminated indoor dust, leachate from landfilled PBDE-containing products, and discharge from industrial sites processing PBDE containing material [40]. As production of PBDEs is discontinued, and they are replaced with other chemicals, it is unclear if their presence in environmental matrices, such as biosolids, will follow the production and usage trend or whether a significant lag phase will exist. As TCC and TCS are used in personal care products, their pathway to WWTPs is more straightforward through hand washing and showering.

The present study was conducted over a 7-year period, from 2005 to 2011. Selected PBDEs (BDE-47, BDE-99, and BDE-209), TCS, and TCC were measured in samples of lime-stabilized biosolids from a single large municipal WWTP located in the Mid-Atlantic region of the US. The plant is largely fed by residential wastewater but part of its influent also comes from combined sewer/stormwater pipes. The goal of this project was to observe long term trends in concentrations of the target analytes in an area generally typical of other suburban/urban areas of the US and to examine the distribution pattern and the potential effects of the plant's inflow and seasonal changes in contaminant concentrations.

While a number of survey investigations have been conducted [5,37], there have been few studies of EDCs in biosolids published in the scientific literature [41–45] that address the temporal trends associated with chemical production and usage. Similar to studies that examine wastewater for illicit drugs to estimate their community drug usage [46,47], biosolids analysis has the potential of being used to estimate the relative usage of some chemicals, the release of chemicals from consumer products, the lag phase between their production phase-out and their presence in the environment, and formation and fate of their degradation products. As the target chemicals of this study are mostly hydrophobic, examination of biosolids can be an effective approach to observe trends in the use and release of persistent organic compounds from residential and industrial products into wastewater. Results of the present study, focused on a single site in a large metropolitan area over a longer period, rather than a large number of sites, will serve as an important study for future investigations and will be useful in assessing the influence of the withdrawal of penta-BDE and deca-BDE from the market, and the continued use of TCC and TCS on their presence in biosolids.

2. Experimental methods

2.1. Target compounds

Eight PBDE congeners (BDE28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209), 5-chloro-2-(2,4-dichlorophenoxy)phenol (TCS), and 3-(4-chlorophenyl)-1-(3,4-dichlorophenyl)urea (TCC) were selected for analysis. Analytes were chosen for their routine presence in environmental samples as well as their presence in commercial formulations of PBDEs [5,7,12–25,30–39].

2.2. Sample collection

Biosolids samples were collected approximately every two months from July 2005 until June 2011 from a large Mid-Atlantic WWTP. In this plant, the approximately 1100 wet metric tons (330 dry metric tons) of biosolids produced daily are stabilized with addition of lime (approximately 15% on a dry weight basis). Samples analyzed here were collected at the final stage of lime stabilization and were then transferred to 250 mL amber, wide-mouth jars and were kept frozen (−30 °C) until processing. Average moisture content of samples was 67.4 ± 3.43% (n = 62).

2.3. Sample analysis

2.3.1. PBDEs

Biosolids samples for the analysis of PBDEs were processed and analyzed as described previously [13]. Samples were kept in the dark or under the protection of a light filter to prevent possible photodegradation of PBDEs. Briefly, a 1.0-g aliquot was weighed and mixed with anhydrous sodium sulfate (J.T. Baker, Phillipsburg, NJ) using a mortar and pestle. Samples were extracted twice with a total 100 mL of dichloromethane (DCM) (99.9%, Acros, Morris Plains, NJ) utilizing a vortex mixer (Fisher Scientific, Fairlawn, NJ) at a speed of 2500 rpm for 2 min. The extraction surrogate, used for calculating the efficacy of the methodology, was 40 ng of 2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl (PCB-209). The solvent was then separated from the sample via centrifugation, concentrated with a stream of N_2 in a water bath and cleaned up with a 2-g alumina Superclean N-alumina SPE cartridge (pre-rinsed with 6 mL of DCM) (Supelco, Bellefonte, PA).

All samples extracts were analyzed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5975 mass selective detector (MSD) in electron capture negative ionization (ECNI) mode. A 15-m Agilent capillary column (DB5-MS), nominal diameter of 0.25 mm, and nominal film thickness of 0.1 μm (J&W Scientific, Folsom, CA) was used with a constant flow of 1.6 mL/min. The oven started at a temperature of 48 °C and ended with 310 °C. The inlet was a programmable temperature vaporizing inlet that also carried a temperature program starting at 48 °C and increasing to 310 °C at a rate of 600 °C/s. The interface and source

temperatures were 300 °C and 250 °C, respectively. Quantification of the analytes was obtained in selective ion monitoring (SIM) and with a 5-point calibration curve with an internal standard. A total of 4 ng of the internal standard, PCB $^{13}C_{12}$ 2,2′,3,4,4′,5′-hexachlorobiphenyl ($^{13}C_{12}$ PCB-138), was added prior to analysis. The methodology was carefully selected to reflect ion selectivity, availability of instrumentation, and samples' quality. A detailed review of possible advantages and disadvantages of selected methodology is available elsewhere [48].

2.3.2. TCC and TCS

Details of TCC and TCS analysis methods have been published previously [30]. Briefly, 0.3–0.5 g (wet weight) of biosolids was placed into an accelerated solvent extraction (ASE) cell. The ASE cell was packed and extracted (Dionex Corp. Sunnyvale, CA, USA) using water/isopropyl alcohol (IPA) (20:80, v/v). The target compounds were isolated from the recovery extracts using solid phase Oasis®HLB cartridges (Waters Corporation, Milford, MA, USA). A dichloromethane (DCM)/diethyl ether (DEE) (80:20) solution was used to elute TCC and TCS from the cartridges. The solvent in the final extract was removed by nitrogen blow down and the sample was reconstituted with methanol to a final volume of 1.5 mL. Finally, TCC and TCS concentrations were obtained through liquid chromatography–tandem mass spectrometry LC–MS/MS analysis. LC-chromatographic separation was performed on a reverse-phase liquid chromatographic column (Waters Xterra 5 μm MS C18 column – 150 × 2.1 mm) using a Waters 2695 XE LC instrument (Waters Corp., Milford, MA, USA). Atmospheric pressure ionization tandem mass spectrometry analysis was performed on a benchtop triple quadrupole mass spectrometer (Quattro Ultima from Micromass Ltd., Manchester, UK) operated using a electrospray ionization source (ESI-) in negative mode. All samples were spiked with 100 ng of $^{13}C_{13}$-TCC and $^{13}C_{12}$-TCS internal standards before extraction to allow for isotope dilution quantitation.

2.4. Quality control

Results were statistically analyzed and linear regression was applied to the temporal data and a one-way ANOVA was applied to the seasonal analysis using GraphPad Prism software (GraphPad Software, Inc., San Diego, CA, USA). Linear regression was also applied to test the influence of wastewater inflow to biosolids contaminant concentration. Method detection limits (MDLs) were: BDE-28: 0.57, BDE-47: 0.56, BDE-99: 0.50, BDE-100: 0.38, BDE-153: 0.62, BDE-154: 0.6, BDE-183: 0.50, BDE-209: 6.02, TCS: 13.9, and TCC: 7.9 μg/kg d.w. All biosolids samples had detectable levels of all target BDE congeners, however, BDE-28, BDE-154, BDE-153, and BDE-183 were below quantification limit (BQL) (quantification limits were 3× the MDLs) while 32.3% of samples had BDE-100 concentrations that were BQL. The method detection limits were calculated according to EPA guidelines [49]. Results presented here are limited to BDE-47, BDE-99, and BDE-209 as these congeners had levels that were well above the MDLs. One laboratory blank was run for each batch of 20 samples and contamination was not found in the blanks during this study. Average sand surrogate (PCB-209) recoveries were 90.7 ± 5.34% (n = 6) while biosolids matrix surrogate recoveries averaged 72.6 ± 6.97% (n = 56). Results were not corrected for recovery. Samples were processed in duplicates and the differences for all eight PBDE congeners ranged from 0 to 14.7% (n = 62). TCC spike recovery averaged 99.9 ± 13.3% and TCS 99.3 ± 17.0% (n = 22). Differences between duplicates ranged from none to 19.0% for TCC and from 2.9 to 17.5% for TCS (n = 48).

3. Results and discussion

3.1. Overall concentration

The concentration of BDE-209 averaged 1490 ± 503 μg/kg d.w. while the sum of BDE-47 and BDE-99 averaged 255 ± 78.0 μg/kg d.w. (n = 31) resulting in an average total PBDE concentration of 1790 ± 528 μg/kg d.w. over the collection period of 2005–2011. Total BDE concentrations ranged from 563 to 2900 μg/kg d.w. Observed concentrations generally fell within the same order of magnitude found in other US studies, particularly for BDE-209 [5,37]. In the Targeted National Sewage Sludge Survey (TNSSS) [37], the mean BDE-209 concentration was 2181 ± 3463 μg/kg d.w. Another study analyzed the samples collected for the TNSSS for a wider range of PBDEs and found the mean BDE-209 to be higher than the present study at 5360 ± 5163 μg/kg d.w. [50]. Results of these surveys indicate that concentrations across the US are highly variable and the results obtained in the present study for BDE-209 are within this range. In Chicago [41], the average BDE-209 concentration from 2006 to 2007 was 6870 μg/kg d.w. which is almost 4× higher than observed in the present study perhaps due to higher use rates in the region or a greater contribution from industrial sources.

The mean of the sum of BDE-47 and BDE-99 observed in the TNSSS [37] was approximately 1425 μg/kg d.w., which is about 5.5× higher than the average in this study (255 ± 78.0 μg/kg d.w.) However, the standard deviation for the mean presented by the TNSSS is ~500 μg/kg d.w. for each of the congeners, and the concentrations found in the present study are within the range reported by the Survey. PBDE concentrations are highly variable in European countries as well, for example, in Italy, Cincinelli et al. [51] reported mean total PBDE concentrations of 2763 μg/kg d.w. for eight different WWTPs with PBDEs concentrations ranging from 158 to 9427 μg/kg d.w. This widespread variability reported in the US and other parts of the world reflect the heterogeneous quality of the matrix, the impact of different sources to the receiving WWTPs [52], and possibly the different use of consumer products that contains these chemicals in the different geographical regions.

TCC and TCS measured concentrations were approximately 8× higher than those of PBDEs. The mean concentrations were 14,300 ± 3710 μg/kg d.w. for TCC and 16,600 ± 3540 μg/kg d.w. for TCS (n = 31). TCC concentrations ranged from 8850 to 22,900 μg/kg d.w. and TCS concentrations ranged from 9880 to 25,800 μg/kg d.w. In the TNSSS, which included 80 publicly owned treatments works [37], the mean concentration of TCC was more than 2x that found in the present study at 39,400 μg/kg d.w. (n = 84), and the median was 21,700 μg/kg d.w. TCC concentration ranges found by the TNSSS were from 187 to 441,000 μg/kg d.w., showing the high variability of TCC concentrations that can be observed in different WWTPs.

In previous research in the US and Canada, TCC ranged from 7190 [54] to 51,000 μg/kg d.w. [55]. The lower end of TCC concentration (7190 μg/kg d.w.) was found in 3 WWTP in Michigan in 2007 and 2008. Two of the three WWTPs sampled had activated sludge treatment and one rotating biological contactors. The highest end of TCC concentration (51,000 μg/kg d.w.) was analyzed in a WWTP sited in the Mid-Atlantic region in 2004. The main removal process in this plant was activated sludge. The TNSSS [37] report shows a TCS mean of 16,100 μg/kg d.w., which is similar to the value found in the present study (16,600). TCS maximum and minimum concentrations found in the US were 133,000 and 344 μg/kg d.w., respectively [37]. In other studies, the range of TCS mean concentrations found in US WWTPs was from 1870 [55] to 30,000 μg/kg d.w. [56]. TCS mean concentrations found in European WWTPs are generally lower than concentrations found in US WWTPs [5,37]. TCS has been observed at levels of 0.46 μg/kg d.w. in a WWTP in Greece [55] to 2830 μg/kg d.w. in Spain [56].

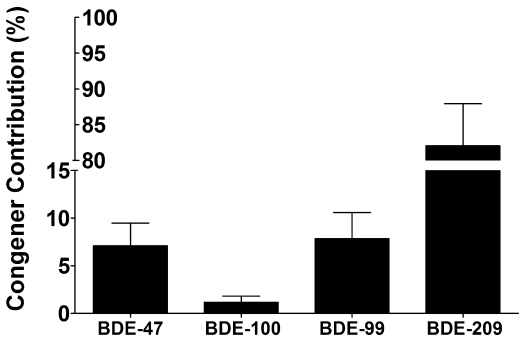


Fig. 1. Average PBDE congener profile of biosolids samples collected from 2005 to 2011 from the large Mid-Atlantic WWTP analyzed in this study ($n = 31$; $n = 22$ for BDE-100).

3.2. Detection frequency and pattern of detection

The contribution of each congener to the total PBDE concentration is important, and generally correlates to commercial formulations that were produced in the past. The fully brominated BDE-209 was the dominant congener, representing $83.7 \pm 5.83\%$ ($n = 31$) of the total PBDE concentration of biosolids samples collected from the WWTP from July 2005 until June 2011. Other significant congeners were BDE-47 and BDE-99, which combined represented $15.2 \pm 5.28\%$ ($n = 31$) of the total concentration. The profile of the congeners and the presence of other congeners in significantly smaller amounts suggest that the penta- and deca-BDE commercial formulations were the major source of PBDEs for this particular biosolids (Fig. 1). This trend has been observed by others in the US as well as in other parts of the world [5,37]. When BDE-209 is included in the analysis, it is the dominant congener in all studies, generally contributing to more than 50% of the total concentration. In Italy, a survey of eight WWTPs resulted in BDE-209 contributing between 75% and 99.8% of the total concentration of all plants [51]. Hale et al. [41] also reported that penta- and deca-BDE commercial mixtures main congeners were the major contributors in sewage sludge samples collected since the 1970s in Chicago. All biosolids samples presented mesearuble levels of BDE-209, BDE-47, BDE-99, TCC, and TCS which were always above MDLs.

3.3. Temporal trends

A linear regression analysis (Fig. 2) of concentration versus time from 2005 to 2011 was applied to all datasets ($n = 31$ for each chemical). No correlation between concentration and time was observed for BDE-209 ($p = 0.868$) and for TCS ($p = 0.283$). However, a statistically significant decrease in concentration over time was identified for BDE-47 + BDE-99 ($p < 0.0001$, $R^2 = 0.4523$) and for TCC ($p < 0.0001$, $R^2 = 0.4354$). Results indicate that overall usage of penta-BDE has decreased since the voluntary phase-out at the end of 2004. While TCC has not been banned in the US, it appears that usage of this compound has decreased over the study period.

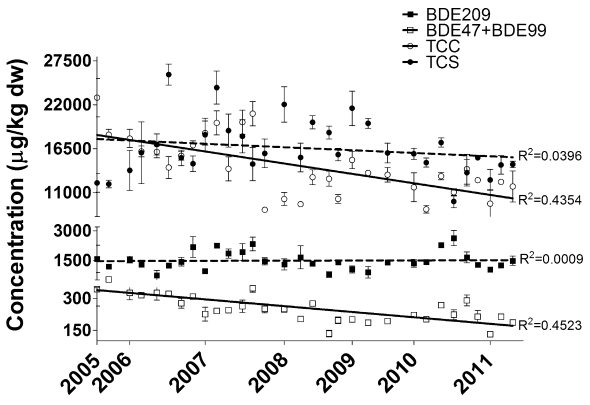


Fig. 2. Concentration of BDE-209, BDE-47 + BDE-99, TCC, and TCS in biosolids over the collection period. Each point represents the mean and standard deviation for each sampling day. Linear regression was applied to all datasets and solid lines represent statistically significant correlations, while dotted lines represent not significant regressions. R^2 are provided for each contaminant to the right of its regression line.

Similar trends have been observed by other researchers. Zennegg et al. [44] reported no significant trend in a period of 20 years in Switzerland biosolids ($n = 4$) for BDE-209 or for the major congeners of the penta-BDE formulation. However, for penta-BDE, concentrations measured in 2012 were lower than those from the beginning of their study indicating usage has decreased. In Sweden, where biosolids from several WWTPs were analyzed between 2004 and 2010, an increase in BDE-209 concentrations ($n = 54$) was observed and the authors attributed this increase to a higher global use of BDE-209 after the European ban of the penta-BDE formulation in 2004 [45,57]. Temporal analysis of BDE-99 concentrations in the same Swedish study did not reveal a corresponding decrease over the same period but a decrease in BDE-154 was observed. In the US, biosolids from several WWTPs were analyzed from the 1970s to the 2000s and concentrations of BDE-209 increased from 1994 to 2007 ($n = 48$) while the penta-BDE related congeners presented an increase from the mid-1970s until the mid-1990s, leveling off around year 2000 with a possible decrease after that [41].

The WWTP included in the present study treats wastewater collected from approximately 2.2 million people and the composition of wastewater received is mostly from residential sources. During the study, approximately 7% of its inflow was pre-treated industrial wastewater, and the remaining was a mixture of sanitary, combined, and storm waters. Since the majority of wastewater treated by this plant came from residential sanitary sewers, the observed decrease in BDE-47 + BDE-99 concentrations over the study period indicates a decrease in the release of the penta-BDE related congeners from consumer products. To further examine the change in concentration over time, annual averages with standard deviation were plotted (Fig. 3). It is clear that BDE-209 annual averages for the 7-year period were variable but relatively stable. However, for BDE-47 + BDE-99, as mentioned above, average concentrations decreased over time, *e.g.*, the 2006 average was 17% lower than the 2005 average and the 2007 average was 8.8% lower than 2006. An increase in annual average concentration was observed from 2009 to 2010 (10%) but then decreased by 14% between 2010 and 2011. Over the entire sampling period, the decrease in BDE-47 + BDE-99 average concentration was approximately 42%. If the decreasing trend in concentrations continues at the same rate, BDE-47 + BDE-99 concentrations should fall below MDLs by approximately 2017 (Fig. 2).

Previous studies have indicated that TCS and TCC will degrade under biological treatment in WWTPs. Bester [58] found that TCS can be removed in percentages higher than 90% from wastewater treatment. However, other studies that examined TCS and TCC fate in WWTPs using a mass balance approach have found that concentrations in final biosolids represented more than 50% of the incoming load [33,54,56]. Therefore, while different WWTPs may be more or less effective at degrading TCC and TCS, the overall temporal trend in their concentrations in biosolids at a single plant can be used to examine changes in the use or environmental release of TCC and TCS.

Linear regression results from the present study suggest a decrease in TCC concentration over time ($p < 0.0001$, $R^2 = 0.4354$) and no change in TCS concentration ($p = 0.283$) over the 7-year period (Fig. 2). At the beginning of the sampling period (2005/2006), TCC concentrations were generally higher than TCS concentrations,

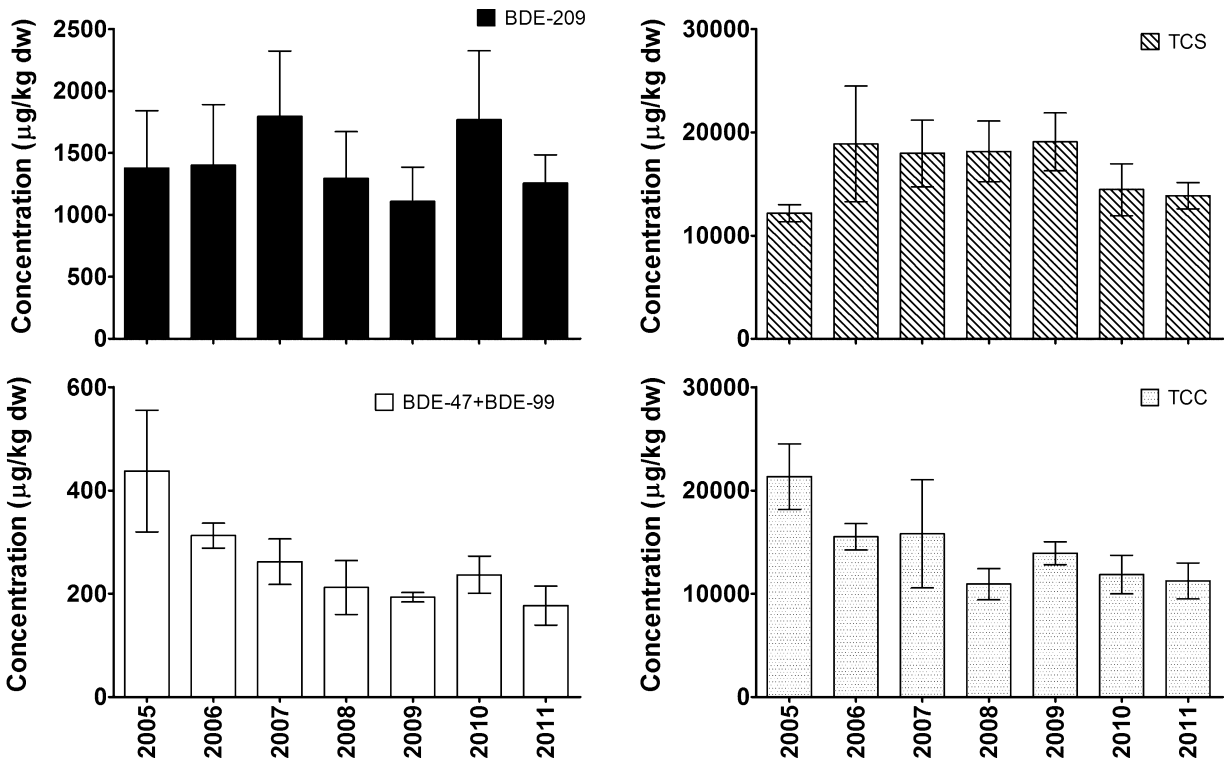


Fig. 3. Yearly average and standard deviation for BDE-209, BDE-47 + BDE-99, TCC, and TCS. This illustrative bar plot shows the decreasing concentration trend for BDE-47 + BDE-99 and TCC and the relatively stable concentrations of BDE-209 and TCS during the 2005–2011 sample collection period.

however, at the end of the sample collection period (2009/2011), TCC concentrations were generally lower than TCS. The overall TCC reduction in annual average concentration was 47% between 2005 and 2011 (Fig. 3), which indicates that TCC concentration at the end of the present study was approximately half the concentration observed in the first year. Earlier research at the same WWTP found that approximately 80% of the TCC load was found in the biosolids [33]. Thus the observed decreasing trend is a clear indication of lower loads in the WWTP influent. According to US EPA, in 2002, the annual US production/import volume of TCC was 250–500 metric tons/year [59], while in 2006 it was reported as less than 250 metric tons [60]. Although this information was based on estimates, it supports the findings of decreasing TCC concentrations.

3.4. Seasonal variations and WWTP flow relationship

There are several factors that could influence contaminant concentrations in biosolids over time, such as changes in the wastewater treatment processes, industrial and residential output, population changes, and climate of the region. During the study period, this WWTP did not undergo any major changes in treatment. Industrial input to the plant accounted for less than 7% of total inflow and did not change significantly over the study period. Population in the region is gradually increasing over time, but there were no drastic changes in population during the study. Changes in climate are more difficult to examine over a short period. Other factors which may be important are changes in temperature with season which could influence degradation rates or changes in influent flow in response to large storms or lack of rain due to drought.

The bimonthly resolution of the dataset was not sufficient to identify any seasonal influences on the concentration of the target analytes. Statistical analysis of BDE-209, BDE-47 + BDE-99, TCC, and TCS levels with season resulted in no discernible trend. Contaminant concentrations were grouped per season (fall, winter, summer, and spring) and an analysis of variance (one-way ANOVA) showed no statistical differences between the levels found in each season ($p > 0.05$). Another study, conducted in a WWTP in China, also did not detect seasonal changes in biosolids samples and in influent wastewater, though their study lasted only one year [43]. Changes over time loads to the WWTP in response to use patterns appear to be more important than seasonal differences.

Part of the sewer lines that lead to this WWTP are combined with stormwater lines. The variability in the inflow to the plant depends not only on residential usage and industrial input, but also rainfall events. Atmospheric deposition of PBDEs has been shown to be of importance in their environmental transport both in rural and urban areas [61–63]. As this WWTP receives stormwater from combined stormwater/sewer lines, the atmospheric deposition input can be two-fold, from direct deposition to the surface of the treatment tanks as well as deposition to the surrounding region which is then transported to the plant via combined stormwater/sewer lines. Both residential water use and stormwater can contain residues of the target analytes, therefore inflow (in million liters per day, ML/d) to this WWTP was plotted against measured biosolids contaminant concentrations (Fig. 4). To account for the solids retention time for this WWTP, we have used the average inlet flow for the two days that preceded the biosolids samples collection.

Regression analysis of BDE-47 + BDE-99 results did not correlate strongly with inflow ($p > 0.05$, $R^2 = 0.0031$). However, BDE-209 concentrations did correlate to the influent flow of the plant. The relationship is statistically significant ($p < 0.05$), however the correlation was weak likely due to the combined variability of the concentrations and flows ($R^2 = 0.1002$). When the same analysis was conducted for TCC and TCS concentrations and the 2-d average influent flow to the WWTP (data not shown), no correlation ($p > 0.05$) was observed.

The WWTP in the present study received wastewater mostly from residential regions, however, at the center of the collection ducts, there were connections to the stormwater collection

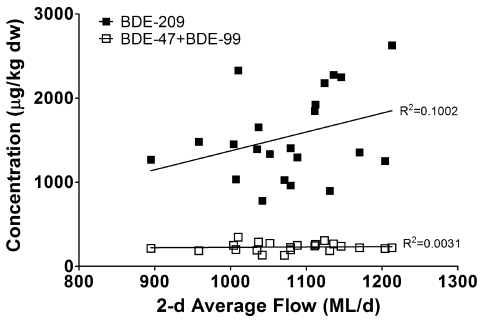


Fig. 4. Relationship between concentrations of BDE-209 and BDE-47 + BDE-99 and a 2-day average of influent wastewater flow (chosen to represent biosolids retention time at the WWTP).

system, and therefore the plant received a considerable amount of stormwater throughout the years. This WWTP was located in a heavily urban area. Previous studies have found higher atmospheric concentrations of PBDEs and other contaminants in urban areas (vapor, particle, and precipitation phases) [62,63] suggesting stormwater could be an important source of PBDEs. While high flow events could act to dilute contaminants in the influent water, the hydrophobic contaminants would partition onto particles during wastewater treatment and would be captured in the biosolids material. In addition, large storm events would be expected to deliver more contaminated particulate matter and precipitation-associated contaminants to the WWTP leading to greater concentrations in the biosolids. The weak correlation between BDE-209 concentrations and flow suggests that storm events resulted in an increased load of BDE-209 to the plant. Further research is needed to investigate atmospheric deposition and stormwater runoff sources of BDE-209 as compared to sanitary sewer loads to the WWTP.

4. Conclusions

This study provides a large dataset on the temporal monitoring of emerging contaminants present in lime-stabilized biosolids from a single wastewater treatment plant over a period of seven years. The average BDE-209 concentration in biosolids from this Mid-Atlantic WWTP was within what is generally observed in other parts of the US, while BDE-47 + BDE-99 concentrations were lower than average US values but within the range of values observed in other parts of the world. TCC and TCS measured concentrations were approximately 8× higher than those of PBDEs, and were within the range observed in the US and Europe. Over the 7-year period of this study, concentrations of BDE-209 remained constant while BDE-47 + BDE-99 concentrations decreased in the biosolids from the target WWTP by a total of 42%. The decrease in concentration of these penta-BDE related compounds indicates that the input of these chemicals to this plant from the combined residential sewer and stormwater pipes decreased over the study period. TCS concentrations showed no decreasing or increasing trend and TCC concentrations decreased over the study period, which could be reflecting a decrease in this chemical's production as suggested by EPA information. During the 7-year period, contaminant biosolids concentrations did not illustrate any seasonal trends or any correlation with wastewater inflows, which for this specific plant also reflects rainfall events. Samples collected for this study have been archived and collection is scheduled to continue to provide the option for future analysis of other emerging contaminants for an even more comprehensive longer term temporal investigation.

Disclaimer

Mention of specific products is for identification and does not imply endorsement by the US Department of Agriculture to the exclusion of other suitable products or suppliers.

Acknowledgments

This study was partially supported by the District of Columbia Water and Sewer Authority, Washington DC, and the Agricultural Research Service – US Department of Agriculture laboratories at Beltsville, MD. The authors want to acknowledge and thank the reviewers of this article for their thoughtful and thorough review which undoubtedly produced a higher quality manuscript.

References

[1] North East Biosolids and Residuals Association (NEBRA), A National Biosolids Regulations, Quality, End Use & Disposal Survey – Final Report, 2007.
[2] US EPA, Standards for the Use or Disposal of Sewage Sludge, 40CRF Part 257, 1993.
[3] C.G. Cogger, A.I. Bary, A.C. Kennedy, A.-M. Fortuna, Long-term crop and soil response to biosolids applications in dryland wheat, J. Environ. Qual. 42 (2013) 1872–1880.
[4] P.F. Jaramillo-López, M.A. Powell, Application of stabilized biosolids and fly ash mixtures as soil amendments and their impact on free living nematodes and carrot (*Daucus carota*) yield, Int. J. Recycl. Org. Waste Agric. 2 (2013) 22–32.
[5] B.O. Clarke, S.R. Smith, Review of 'emerging' organic contaminants in biosolids and assessment of international research proorities for the agricultural use of biosolids, Environ. Int. 37 (2011) 226–247.
[6] T.A. McDonald, A perspective on the potential health risks of PBDEs, Chemosphere 46 (2002) 745–755.
[7] C.A. de Wit, An overview of brominated flame retardants in the environment, Chemosphere 46 (2002) 583–624.
[8] USDHHS, Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers, US Department of Human Health & Human Services, Agency for Toxic Substance and Disease Registry, 1994.
[9] US EPA, Certain Polybrominated Diphenylethers; Significant New Use Rule and Test Rule, 40CRF Parts 721, 795, 799, 2012.
[10] US EPA, DecaBDE Phaseout Initiative, 2009, http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/deccadbe.html; http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/Albemarle.DecaBDE.pdf; http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/Chemtura.DecaBDE.pdf; http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/ICL.DecaBDE.pdf
[11] The New POPs Under the Stockholm Convention, 2011, http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx
[12] J. de Boer, P.G. Wester, A. van der Horst, E.G. Leonards, Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plants and effluents and biota from the Netherlands, Environ. Pollut. 122 (2003) 63–74.
[13] N.A. Andrade, L.L. McConnell, A. Torrents, M. Ramirez, Persistence of polybrominated diphenyl ethers in agricultural soils after biosolids applications, J. Agric. Food Chem. 58 (2010) 3077–3084.
[14] H.M. Stapleton, N.G. Dodder, J.H. Offenberg, M.M. Schantz, S.A. Wise, Polybrominated diphenyl ethers in house dust and clothes dryer lint, Environ. Sci. Technol. 39 (2005) 925–931.
[15] S. Harrad, C. Ibarra, M. Diamond, L. Melymuk, M. Robson, J. Douwes, L. Roosens, A.C. Dirtu, A. Covaci, Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States, Environ. Int. 34 (2008) 232–238.
[16] W.A. Gebbink, C. Sonne, R. Dietz, M. Kirkegaard, F.F. Riget, E.W. Born, D.C.G. Muir, R.J. Letcher, Tissue-specific congener composition of organohalogen and metabolite contaminants in East Greenland polar bears (*Ursus maritimus*), Environ. Pollut. 152 (2008) 621–629.
[17] D. Trudel, M. Scheringer, N. von Goetz, K. Hungerbühler, Total 214 consumer exposure to polybrominated diphenyl ethers in North America and Europe, Environ. Sci. Technol. 45 (2011) 2391–2397.
[18] G. Sandborgh-Englund, M. Adolfsson-Erici, G. Odham, J. Ekstrand, Pharmacokinetics of triclosan following oral ingestion in humans, J. Toxicol. Environ. Health A 69 (2006) 1861–1873.
[19] M. Allmyr, M.S. McLachlan, G. Sandborgh-Englund, M. Adolfsson-Erici, Determination of triclosan as its pentafluorobenzoyl ester in human plasma and milk using electron capture negative ionization mass spectrometry, Anal. Chem. 78 (2006) 6542–6546.
[20] X. Ye, X. Zhou, J. Furr, K.C. Ahn, B.D. Hammock, E.L. Gray, et al., Biomarkers of exposure to triclocarban in urine and serum, Toxicology 286 (2011) 69–74.
[21] M. Adolfsson-Erici, M. Pettersson, J. Parkkonen, J. Sturve, Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden, Chemosphere 46 (2002) 1485–1489.

[22] M.A. Coogan, R.E. Edziyie, T.W. La Point, B.J. Venables, Algal bioaccumulation of triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment plant receiving stream, Chemosphere 67 (2007) 1911–1918.
[23] J.W. Kim, B.R. Ramaswamy, K.H. Chang, T. Isobe, S. Tanabe, Multiresidue analytical method for the determination of antimicrobials, preservatives, benzotriazole UV stabilizers, flame retardants and plasticizers in fish using ultra high performance liquid chromatography coupled with tandem mass spectrometry, J. Chromatogr. A 1218 (2011) 3511–3520.
[24] N. Aryal, D.M. Reinhold, Phytoaccumulation of antimicrobials from biosolids: impacts on environmental fate and relevance to human exposure, Water Res. 45 (2011) 5545–5552.
[25] P.A. Herklotz, P. Gurung, B.V. Heuvel, C.A. Kinney, Uptake of human pharmaceuticals by plants grown under hydroponic conditions, Chemosphere 78 (2010) 1416–1421.
[26] N. Veldhoen, R.C. Skirrow, H. Osachoff, H. Wigmore, D.J. Clapson, M.P. Gunderson, et al., The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development, Aquat. Toxicol. 80 (2006) 217–227.
[27] K.M. Crofton, K.B. Paul, M.J. DeVito, J.M. Hedge, Short-term in vivo exposure to the water contaminant triclosan: evidence for disruption of thyroxine, Environ. Toxicol. Pharmacol. 24 (2007) 194–197.
[28] K.C. Ahn, B. Zhao, J. Chen, G. Cherednichenko, E. Sanmarti, M.S. Denison, et al., In vitro biologic activities of the antimicrobials triclocarban, its analogs, and triclosan in bioassay screens: receptor-based bioassay screens, Environ. Health Perspect. 116 (2008) 1203–1210.
[29] L.M. Zorrilla, E.K. Gibson, S.C. Jeffay, K.M. Crofton, W.R. Setzer, R.L. Cooper, et al., The effects of triclosan on puberty and thyroid hormones in male Wistar rats, Toxicol. Sci. 107 (2008) 56–64.
[30] N. Lozano, C.P. Rice, M. Ramirez, A. Torrents, Fate of triclosan in agricultural soils after biosolid applications, Chemosphere 78 (2010) 760–766.
[31] N. Lozano, C.P. Rice, M. Ramirez, A. Torrents, Fate of Triclosan and Methyltriclosan in soil from biosolids application, Environ. Pollut. 160 (2012) 103–108.
[32] K. Xia, L.S. Hundal, K. Kumar, K. Armbrust, A.E. Cox, T.C. Granato, Triclocarban, triclosan, polybrominated diphenyl ethers, and 4-nonylphenol in biosolids and in soil receiving 33-year biosolids application, Environ. Toxicol. Chem. 29 (2010) 597–605.
[33] N. Lozano, C.P. Rice, M. Ramirez, A. Torrents, Fate of Triclocarban, Triclosan and Methyltriclosan during wastewater and biosolids treatment processes, Water Res. 47 (2013) 4519–4527.
[34] R.C. Hale, M.J. La Guardia, E.P. Harvey, M.O. Gaylor, T. Matteson Mainor, W.W.H. Duff, Persistent pollutants in land-applied sludges, Nature 412 (2001) 140–141.
[35] D.C. McAvoy, B. Schatowitz, M. Jacob, A. Hauk, W.S. Eckoff, Measurement of triclosanin wastewater treatment systems, Environ. Toxicol. Chem. 21 (2002) 1323–1329.
[36] A. Sapkota, J. Heidler, R.U. Halden, Detection of triclocarban and two co-contaminating chlorocarbanilides in US aquatic environments using isotope dilution liquid chromatography tandem mass spectrometry, Environ. Res. 103 (2007) 21–29.
[37] US EPA, Targeted National Sewage Sludge Survey Statistical Analysis Report, United States Environmental Protection Agency, Office of Water, Washington, DC, 2009, EPA-822-R-08-018.
[38] B. Clarke, N. Porter, R. Symons, P. Marriott, P. Ades, G.G. Stevensen, J. Blackbeard, Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge, Chemosphere 73 (2008) 980–989.
[39] G.-G. Ying, R.S. Kookana, Triclosan in wastewaters and biosolids from Australian wastewater treatment plants, Environ. Int. 33 (2007) 199–205.
[40] US EPA, An Exposure Assessment of Polybrominated Diphenyl Ethers, National Center for Environmental Assessment, Office of Research and Development, Washington, DC, 2010, EPA-600-R-08-086F.
[41] R.C. Hale, M.J. La Guardia, E. Harvey, D. Chen, T.M. Mainor, D.R. Luellen, Polybrominated diphenyl ethers in U.S. sewage sludge and biosolids: temporal and geographical trends and uptake by corn following land application, Environ. Sci. Technol. 46 (2012) 2055–2063.
[42] E.F. Davis, S.L. Klosterhaus, H.M. Stapleton, Measurement of flame retardants and triclosan in municipal sewage sludge and biosolids, Environ. Int. 40 (2012) 1–7.
[43] N. Xiang, L. Chen, X.-Z. Meng, Y.-L. Li, Z. Liu, B. Wu, L. Dai, X. Dai, Polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) in a conventional wastewater treatment plant (WWTP) in Shanghai: seasonal variations and potential sources, Sci. Total Environ. 487 (2014) 342–349.
[44] M. Zennegg, M. Munoz, P. Schmid, A.C. Gerecke, Temporal trends of persistent organic pollutants in digested sewage sludge (1993–2012), Environ. Int. 60 (2013) 202–208.
[45] U. Olofsson, A. Bignert, P. Haglund, Time-trends of metals and organic contaminants in sewage sludge, Water Res. 46 (2012) 4841–4851.
[46] C. Postigo, M.J.L. Alda, D. Barcelo, Drugs of abuse and their metabolites in the Ebro River basin: occurrence in sewage and surface water, sewage treatment plants removal efficiency, and collective drug usage estimation, Environ. Int. 36 (2010) 75–84.
[47] C. Metcalfe, K. Tindale, H. Li, A. Rodayan, V. Yargeau, Illicit drugs in Canadian municipal wastewater and estimates of community drug use, Environ. Pollut. 158 (2010) 3179–3185.
[48] H.M. Stapleton, Instrumental methods and challenges in quantifying polybrominated diphenyl ethers in environmental extracts: a review, Anal. Bioanal. Chem. 386 (2006) 807–817.
[49] US EPA, Subchapter D – Water Programs, Guidelines establishing test procedures for the analysis of pollutants, EPA 40 CFR Part 136 Appendix B.
[50] A.K. Venkatesan, R.U. Halden, Brominated flame retardants in US biosolids from the EPA national sewage sludge survey and chemical persistence in outdoor soil mesocosms, Water Res. 55 (2014) 133–142.
[51] A. Cincinelli, T. Martellini, L. Misuri, E. Lanciotti, A. Sweetman, S. Laschi, I. Palchetti, PBDEs in Italian sewage sludge and environmental risk of using sewage sludge for land application, Environ. Pollut. 161 (2012) 229–234.
[52] M.J. LaGuardia, R.C. Hale, E. Harvey, D. Chen, Flame-retardants and other organohalogens detected in sewage sludge by electron capture negative ion mass spectrometry, Environ. Sci. Technol. 44 (2010) 4658–4664.
[54] J. Heidler, A. Sapkota, R.U. Halden, Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment, Environ. Sci. Technol. 40 (2006) 3634–3639.
[55] P. Pothitou, D. Voutsa, Endocrine disrupting compounds in municipal and industrial wastewater treatment plants in Northern Greece, Chemosphere 73 (2008) 1716–1723.
[56] J. Heidler, R.U. Halden, Mass balance assessment of triclosan removal during conventional sewage treatment, Chemosphere 66 (2007) 362–369.
[57] EU, Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restriction on the marketing and use of certain dangerous substances and preparations (pentabromoduphenyl ether, octabromodiphenyl ether), Off. J. Eur. Union L 42/45 (2003).
[58] K. Bester, Triclosan in a sewage treatment process – balances and monitoring data, Water Res. 37 (2003) 3891–3896.
[59] US EPA, High Production Volume (HPV) Chemical Challenge Program Data Availability and Screening Level Assessment for Triclocarban CAS#:101-20-2, 2002.
[60] US EPA, Initial Risk-based Prioritization of High Production Volume (HPV) Chemicals – Triclocarban (CASRN 101-20-2), 2009.
[61] A. Goel, L.L. McConnell, A. Torrents, J.R. Scudlark, S. Simonich, Spray irrigation of treated municipal wastewater as a potential source of atmospheric PBDEs, Environ. Sci. Technol. 40 (2006) 2142–2148.
[62] L. Melymuk, M. Robson, P.A. Helm, M.L. Diamond, PCBs, PBDEs, and PAHs in Toronto air: spatial and seasonal trends and implications for contaminant transport, Sci. Total Environ. 429 (2012) 272–280.
[63] Y. Ma, A. Salamova, M. Venier, R.A. Hites, Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere, Environ. Sci. Technol. 47 (2013) 11457–11464.

Environmental Science & Technology

Article

pubs.acs.org/est

Uptake of Perfluoroalkyl Acids into Edible Crops via Land Applied Biosolids: Field and Greenhouse Studies

Andrea C. Blaine,[†] Courtney D. Rich,[†] Lakhwinder S. Hundal,[‡] Christopher Lau,[§] Marc A. Mills,[§] Kimberly M. Harris,[∥] and Christopher P. Higgins*[,†]

[†]Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, Colorado 80401, United States

[‡]Metropolitan Water Reclamation District of Greater Chicago, [§]U.S. EPA Office of Research and Development, [∥]U.S. EPA Region 5, Ralph Metcalfe Federal Building, 77 West Jackson Boulevard, Chicago, Illinois 60604-3590, United States

Supporting Information

ABSTRACT: The presence of perfluoroalkyl acids (PFAAs) in biosolids destined for use in agriculture has raised concerns about their potential to enter the terrestrial food chain via bioaccumulation in edible plants. Uptake of PFAAs by greenhouse lettuce (*Lactuca sativa*) and tomato (*Lycopersicon lycopersicum*) grown in an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil was measured. Bioaccumulation factors (BAFs) were calculated for the edible portions of both lettuce and tomato. Dry weight concentrations observed in lettuce grown in a soil amended (biosolids:soil dry weight ratio of 1:10) with PFAA industrially contaminated biosolids were up to 266 and 236 ng/g for perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA), respectively, and reached 56 and 211 ng/g for PFBA and PFPeA in tomato, respectively. BAFs for many PFAAs were well above unity, with PFBA having the highest BAF in lettuce (56.8) and PFPeA the highest in tomato (17.1). In addition, the BAFs for PFAAs in greenhouse lettuce decreased approximately 0.3 log units per CF_2 group. A limited-scale field study was conducted to verify greenhouse findings. The greatest accumulation was seen for PFBA and PFPeA in both field-grown lettuce and tomato; BAFs for PFBA were highest in both crops. PFAA levels measured in lettuce and tomato grown in field soil amended with only a single application of biosolids (at an agronomic rate for nitrogen) were predominantly below the limit of quantitation (LOQ). In addition, corn (*Zea mays*) stover, corn grains, and soil were collected from several full-scale biosolids-amended farm fields. At these fields, all PFAAs were below the LOQ in the corn grains and only trace amounts of PFBA and PFPeA were detected in the corn stover. This study confirms that the bioaccumulation of PFAAs from biosolids-amended soils depends strongly on PFAA concentrations, soil properties, the type of crop, and analyte.

INTRODUCTION

Perfluoroalkyl acids (PFAAs), which have been used in a myriad of consumer and industrial products (e.g., stain repellents, nonstick food packaging, and fire-fighting foams),[1] are ubiquitous and persistent in the environment; they have been detected in air, house dust, water, sediment, soil, wildlife, and humans.[2−4] In addition, longer chain PFAAs are poorly eliminated by many higher trophic level organisms, with elimination half-lives of more than five years in humans for some PFAAs.[5] Toxicity to wildlife and laboratory animals is well established for perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), including adverse effects such as reduced survival rates, infertility, and abnormal maturation.[3] The toxicity of shorter-chain PFAAs is less well documented. The persistence, bioaccumulation, and potential toxicity of PFAAs make them high priority contaminants of emerging concern.

PFAAs entering conventional wastewater treatment plants (WWTPs) or produced from precursors during treatment can exit the plant in either the aqueous or sludge phase.[6] The presence of PFAAs in municipal biosolids is well documented.[7−9] The land application of biosolids has been practiced for decades; in the United States, approximately 60% of biosolids are land applied.[10] Nutrient-rich biosolids are particularly attractive as a fertilizer for crop production. Currently, the United States Environmental Protection Agency (U.S. EPA) regulates the land application of biosolids based on pathogen, metal, and nutrient content under the U.S. 40 Code of Federal Regulations Part 503.[11] However, PFAAs in biosolids are not currently regulated in the U.S.[10] Furthermore, due to the persistence of PFAAs, repeated agricultural applications of PFAA-contaminated biosolids may present a potential exposure route for terrestrial food webs if PFAAs contaminate surface or groundwater destined for animal or

Received: July 12, 2013
Revised: October 29, 2013
Accepted: November 8, 2013
Published: November 8, 2013

human consumption[12] or are transferred to (i.e., bioaccumulate in) the edible portion of crops.

Previous studies have documented the potential for PFAA bioaccumulation into crops, particularly for PFOS and PFOA.[13,14] While growing corn, wheat, potato, and oats in PFAA-spiked soils, Stahl et al. found PFOA and PFOS in the vegetative plant portions,[13] a finding that was confirmed in follow-up studies.[15] In a similar study using PFAA-spiked soils, Lechner and Knapp found carryover of PFOA and PFOS in carrots, cucumbers, and potato, with the highest transfer factors for the vegetative portions.[14] Both studies found higher PFOA than PFOS levels; however, spiked soil systems are known to be problematic with respect to contaminant bioavailability,[16,17] and thus these studies may not adequately describe PFAA uptake from nonspiked, biosolids-amended soils. Wen et al. conducted hydroponic studies with corn, which revealed that there are potentially different uptake mechanisms for PFOA and PFOS.[18] In a more relevant study, the transfer of PFAAs from industrially contaminated biosolids-amended soils into grass was observed,[19] with PFOA again bioaccumulating more than PFOS. Although grass may be consumed by animals, thereby enabling PFAA entry into the terrestrial food chain, it does not represent a direct human exposure scenario. PFAA uptake in hydroponically grown lettuce has also been observed,[20] though again, this does not likely describe the bioavailability of PFAAs to plants grown in biosolids-amended soils.[21,22]

Concerns about the potential bioaccumulation of PFAAs into crops grown in biosolids-amended soils are also supported by limited data on their plant uptake and transport behavior.[13,19,20] While some predictions about plant uptake and transfer potential can be made based on plant physiology models[23−25] and contaminant parameters such as octanol−water partition coefficients (K_{ow}),[26] a very limited number of plant uptake studies have focused specifically on PFAAs. Initial models correlating the transpiration stream concentration factor[25] (TSCF), or the concentration ratio of the compound in the xylem to the solution around the roots, to K_{ow} suggested maximal TSCFs for compounds with log K_{ow} values of 1.8. However, a more recent model[24] suggests hydrophilic compounds (e.g., sulfolane) may actually be preferentially accumulated. Moreover, ionized contaminants are very soluble and nonvolatile and thus have the potential to accumulate high concentrations in plants.[27]

The objective of this study was to examine PFAA bioaccumulation in lettuce (*Lactuca sativa*) and tomato (*Lycopersicon lycopersicum*) grown in biosolids-amended soils using a combination of greenhouse and field-scale experiments. Plant bioaccumulation was studied with unspiked biosolids-amended soils known to contain residual PFAAs. In addition, corn (*Zea mays*) samples were also collected from several biosolids-amended farm fields. Lettuce and tomato were chosen because they represent common edible crops eaten fresh. This scenario represents the most direct route of human exposure from plants, thus avoiding complicating factors from processing and packaging. Although lettuce and tomato are not commonly grown in biosolids-amended soils, they represent crops from the scenario of a home gardener using commercial biosolids as fertilizer. Greenhouse studies were conducted to avoid confounding environmental factors, and pilot-scale field studies were performed to verify greenhouse results. Data from an existing full-scale system were also collected for comparison; however, the crop availability was limited to corn. To our knowledge, this study is the first to look at PFAA uptake in lettuce and tomato from biosolids-amended soils.

MATERIALS AND METHODS

Chemicals. Perfluorinated standards as well as stable-isotope labeled standards (Supporting Information (SI) Table S1) were obtained from Wellington Laboratories (Guelph, ON, Canada). Analytes in this study include perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), PFOS, and perfluorodecane sulfonate (PFDS). All standards were prepared in a 70/30 (v/v) methanol/water with 0.01% ammonium hydroxide solution. HPLC-grade methanol and high purity Chromasolv dichloromethane from Sigma Aldrich (St. Louis, MO) were used for extractions. All other solvents were reagent grade from Sigma Aldrich. Water used in extractions was obtained from a Milli-Q system (Millipore, Billerica, MA), and HPLC-grade water was used for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. For extraction cleanup, Chromabond diamino from Macherey-Nagel Inc. (Bethlehem, PA) and Supelclean ENVI-Carb from Sigma-Aldrich were used.

Greenhouse Study. Accumulation was studied from three soils: industrially impacted soil (soil amended with PFAA contaminated biosolids), municipal soil (soil receiving a long-term field application of municipal biosolids), and an unamended control soil. The industrially impacted soil was created by mixing composted biosolids from a small municipal (but impacted by PFAA manufacturing) WWTP with the control soil on a 10% mass basis. Composted biosolids were prepared at the utility by mixing dewatered biosolids with woody material (e.g., woodchips, saw dust, etc.) to achieve a 30:1 carbon to nitrogen ratio. Although this application rate is 10 times higher than an average recommended agronomic rate (approximately 25 Mg/ha, on dry weight basis) of biosolids application, it was chosen to represent multiple applications or industrially impacted PFAA-contaminated soil. The municipal soil came from a reclamation site in Illinois where municipal biosolids were applied at reclamation rates for 20 years, reaching the cumulative biosolids application rate of 1654 Mg/ha. This field was planted with rotations of cereal crops such as corn, wheat, and sorghum. The control soil was taken from a nearby field that had a similar cropping system to the reclamation site but only received commercial fertilizers. Both the amended and control soils were classified as Lenzburg silt loams. All three soils were sieved (6.3 mm), and pots were filled on a dry weight basis. The fraction of organic carbon (f_{oc}), determined by the Walkley−Black Method (SI Table S2), and other soil characteristics (SI Table S3) measured by Agvise Laboratories (Northwood, ND) can be found in the SI.

Pots were seeded with either leaf lettuce (*Lactuca sativa* 'Multy') or tomato (*Lycopersicon lycopersicum* 'Stupice') to achieve a density of two lettuce plants/pot and one tomato plant/pot. Edible portions (lettuce leaves or tomato fruits) from each pot were combined as one experimental replicate. Each of the three soils was evaluated for each crop with five replicates. Pots were randomly arranged to account for any spatial variations in light and temperature within the greenhouse. Crops were harvested at maturation and frozen at −20 °C in sealed plastic bags until extraction. Detailed information

about propagation, environmental conditions, and sampling are given in the SI.

Field Studies. A limited-scale field study was conducted in the Midwestern U.S. Eighteen plots (3.0 m × 4.6 m) were established, and each was planted with lettuce (*Lactuca sativa* 'Black-Seeded Simpson') and tomato (*Lycopersicon lycopersicum* 'Burpee Big Boy Hybrid'). Fertilization via biosolids occurred at five application rates (plus control) with three replicate plots per application rate. The soil treatments included an unamended control (CTRL), one-half of the agronomic rate of biosolids application to meet nitrogen (N) requirements of the crop (0.5×), agronomic rate (1×), two times the agronomic rate (2×), and four times the agronomic rate (4×). Crops were grown and harvested following normal agricultural practices. Lettuce and tomato were harvested at maturity (lettuce ∼45 days; tomato ∼100 days) using a sample collection protocol (detailed in the SI) developed to minimize cross-contamination. Duplicate soil samples as well as lettuce and tomato samples from each plot were collected, placed on ice, and shipped to the laboratory where they were frozen at −20 °C until extraction.

In addition, a full-scale field sampling campaign was conducted in the Midwestern U.S. Because corn (*Zea mays*) is the most commonly grown crop in this region, several paired samples of corn grain, corn stover, and soil were collected from three agricultural fields amended (0.5×, 1×, and 2×) with municipal biosolids (rural or urban). Rural biosolids (0.5× field) were from a WWTP receiving domestic waste only, and urban biosolids (1×, 2× fields) were from a WWTP receiving both domestic and industrial waste. In addition, control samples of corn plant tissues and soil were collected from two nonamended fields (each proximal to the rural and urban amended field sites). All samples were collected in triplicate using the above-mentioned protocol, placed on ice after collection, and shipped to the laboratory where they were frozen at −20 °C until extraction. A summary of both the greenhouse and field studies is shown in Table 1.

Table 1. Summary of Experimental Framework for Each Phase of Study

study phase	soils and amendment rates	plant tissue analyzed for each soil condition
greenhouse experiments	field-collected control (unamended) soil (5 replicate pots)	lettuce leaves; tomato fruit
	field-collected control + industrially impacted biosolids (10%) (5 replicate pots)	
	field-collected amended municipal soil (£1654 Mg/ha) (5 replicate pots)	
field-scale trial plots	control (unamended) (3 replicate plots)	lettuce leaves; tomato fruit
	0.5× agronomic rate for nitrogen (N) (12.5 Mg/ha) (3 replicate plots)	
	1× agronomic rate for N (25 Mg/ha) (3 replicate plots)	
	2× agronomic rate for N (50 Mg/ha) (3 replicate plots)	
	4× agronomic rate for N (100 Mg/ha) (3 replicate plots)	
full-scale field study	urban site (control) (3 replicate samples)	corn stover; corn grain
	urban site (1× agronomic rate for N) (3 replicate samples)	
	urban site (2× agronomic rate for N) (3 replicate samples)	
	rural site (control) (3 replicate samples)	
	rural site (0.5× agronomic rate for N) (3 replicate samples).	

Extraction and PFAA Analysis. *Sample Extractions.* Plant material was homogenized prior to extraction using a food processor. An aliquot of the homogenized plant tissue (0.5−2 g) was transferred to a 50 mL polypropylene vial, to which a surrogate spiking solution containing 2 ng of each isotopically labeled surrogate standard was added. A solvent mixture of 50/50 dichloromethane (DCM) and 99:1 (v/v) methanol (MeOH) and ammonium hydroxide was chosen based on the exhaustive extraction results of Yoo et al.[19] The solvent mixture (7 mL) was added to the sample and heated (30 °C) in a sonication bath (Fisher Scientific FS110H, Pittsburgh, PA) for 30 min followed by shaking (VWR 5000 STD 120 V, West Chester, PA) for 1 h. The sample was centrifuged (Eppendorf 5810, Hamburg, Germany) at 2700 rpm (1467 RCF) for 20 min, and the extract was decanted into a separate 50 mL tube. This procedure was repeated twice for a total of three extraction cycles. The combined extract was evaporated at 50 °C under nitrogen (Organomation Associates Inc. N-EVAP 112, Berlin, MA) to dryness. To minimize matrix effects, the extract was cleaned up via oxidation with 1 mL of a basic hydrogen peroxide solution (20 μL ammonium hydroxide and 980 μL 30% hydrogen peroxide), vortexed, and sonicated in a heated (30 °C) bath for 2 h. An additional aliquot (7 mL) of the basic DCM/MeOH mixture was added to each oxidized extract, vortexed, and heated in a sonication bath for 30 min. The extract was centrifuged at 2700 rpm (1467 RCF) for 20 min and decanted into a glass 20 mL scintillation vial. This re-extraction procedure was repeated twice for a total of three cycles. The combined extract was evaporated at 50 °C under nitrogen to dryness and reconstituted with 1 mL of 99:1 (v/v) MeOH and acetic acid. The extract was run through a cleanup column packed with 100 mg of diamino and 100 mg of ENVI-Carb. To analyze, 105 μL of the cleaned extract was transferred to an autosampler vial, along with 1350 μL of water and 45 μL of dilution water consisting of 0.01% ammonium hydroxide. All results are reported on a dry weight basis, which was determined by drying separate aliquots of plant tissue at 70 °C overnight (at which time no additional change in mass was observed). Soil samples were extracted as per established protocols.[28] Additional details as to the soil extraction procedure can be found in the SI.

PFAA Analysis. All PFAAs were analyzed using isotope dilution LC-MS/MS under conditions similar to those previously described.[28] Briefly, chromatography was performed using an aqueous ammonium acetate (10 mM) and MeOH (10 mM) gradient delivered at a flow rate of 800 μL/min by a Shimadzu LC-20AD unit (Kyoto, Japan). Samples and standards were injected (1 mL) by a Shimadzu SIL-5000 auto injector onto a 50 mm × 4.6 mm Gemini C18 column with a 3 μm particle size (Phenomenex, Torrance, CA) also equipped with a C18 guard column and cartridge. Initial eluent conditions were 50% MeOH and 50% water. The percent MeOH was ramped to 95% over 4 min, held at 95% over 4 min, ramped back down to 50% over 1.5 min, and re-equilibrated at 50% until 13 min. An MDS Sciex Applied Biosystems API 3200 (MDS Sciex, Ontario) operating in negative electrospray ionization scheduled multiple reaction monitoring (MRM)

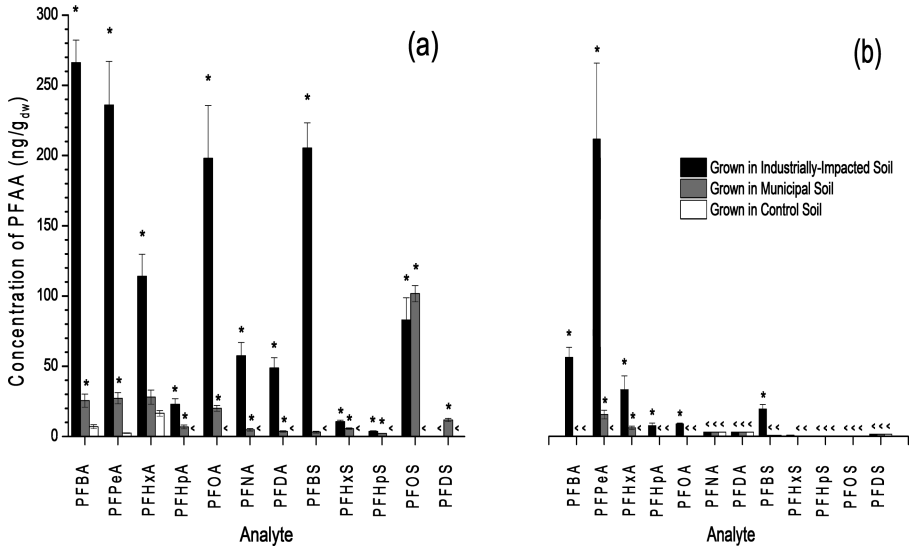


Figure 1. Concentrations of PFAAs in greenhouse lettuce (a) and tomato (b) grown in biosolids-amended soils. Mean and standard error are shown (n = 5). Values marked with an asterisk are significantly different (α = 0.05) than the control. Values less than the LOQ are denoted by <; LOQs for respective matrix and analyte are listed in SI Table S5.

mode was used to monitor two MRM transitions for all analytes.

Quality Control. Quantitation was performed using the software Analyst. A minimum of 20% of all samples in each matrix were extracted and analyzed in triplicate. In general, the relative standard deviation for analytical replicates was less than 25%. Values presented in this study are averages of experimental (greenhouse) or field (outdoor) replicates (n = 3−18). Limits of quantitation (LOQs) were derived from the lowest calibration standard calculated to be within 30% of its actual value and were analyte, matrix, and run-dependent. LOQs, in general, ranged from 0.01 to 1.5 ng/g$_{dw}$. Field, experimental, and analytical blanks were employed to monitor contamination. Sample values that were not at least twice the level of the highest concentration in a blank were reported as <LOQ. Internal surrogate standards were used for each analyte (SI Table S1) to correct for any losses during extraction. Plant surrogate recovery varied with matrix and analyte but typically ranged from 10% to 60%, and samples with less than 8% were excluded from any calculations. These recoveries are low in comparison to soil recoveries,[28] however, are somewhat typical in plant matrices[19,20] due to matrix ion suppression.

The results of additional spike-recovery experiments (accounting for surrogate losses) resulted in an average of 85% recovery for all analytes across all matrices (SI Figure S1) with no clear chain length dependent trends among analytes.

Bioaccumulation Metrics. To enable meaningful comparisons across soils and crops, bioaccumulation factors (BAFs) were calculated for each crop and PFAA for which plant tissue concentrations were above the LOQ. The BAF[29] was calculated by dividing the concentration in the plant tissue on a dry weight basis by the concentration in the soil on a dry weight basis:

$$\mathrm{BAF} = \frac{\text{PFAA concentration in plant (ng g}_{dw}^{-1})}{\text{PFAA concentration in soil (ng g}_{dw}^{-1})} \quad (1)$$

When calculating BAFs, several assumptions were made including (1) absence of any chemical transformation in the plant or plant extraction process and (2) negligible atmospheric exchange, thereby presuming the dominant uptake pathway for PFAAs was from the soil via the roots. As PFAAs are extremely stable and generally ionized at environmental pH values,[30] these assumptions appear quite reasonable. In addition, given the propensity of PFAAs to sorb to organic carbon,[30] organic-carbon normalized BAFs (i.e., BAF$_{oc}$) were calculated by normalizing the PFAA soil concentrations to the soil f_{oc} to explore the impacts of soil organic carbon on bioaccumulation:

$$\mathrm{BAF}_{oc} = \mathrm{BAF} \times f_{oc} \quad (2)$$

Because TSCFs are a widely used plant uptake parameter, for comparative purposes, BAFs were also converted to TSCFs. Briefly, TSCFs were obtained by converting concentrations in plant tissues to concentrations in the xylem using an average rate of water transpired per mass of plant tissue and by converting the soil concentrations to pore water concentrations using soil-water partitioning coefficients and soil f_{oc} values. Detailed information concerning the TSCF calculations can be found in the SI.

Statistical Analysis. Data are presented as means with standard errors. Statistical analysis, including calculation of regression equations, was completed using OriginPro 8.6. Statistical difference was determined by using an analysis of variance (ANOVA) with Tukey's Test (α = 0.05); homogeneity of variance was assessed by Levene's Test (α = 0.05). Regression equation slopes were compared by first fitting a line across the difference of values for each analyte and then comparing the slope of the resulting line to zero at an α of 0.05.

RESULTS AND DISCUSSION

Greenhouse Study. Although the control soil was obtained from an unamended field, trace levels of PFAAs (<0.5 ng/g; SI Table S5) were observed. Biosolids have long been applied in the surrounding area, and minor cross-contamination may have resulted from cultivation practices such as plowing and planting or from atmospheric deposition.[31] In contrast, the industrially impacted soil resulting from combining industrially impacted biosolids with the control soil had a total of 335 ng/g PFAAs, with the largest contributors being PFDA (93.5 ng/g), PFOA (78.5 ng/g), PFOS (49.7 ng/g), and PFBS (48.6 ng/g). The

Table 2. Summary of Bioaccumulation Factors (BAFs) for PFAAs in All Three Phases of This Study and Previous Study (Values Not Measured Are Designated as NM)[a]

analyte	greenhouse lettuce (municipal soil)	greenhouse lettuce (industrially impacted soil)	field trial lettuce (4× soil)	greenhouse tomato (industrially impacted soil)	field trial tomato (4× soil)	field corn stover (2× soil)	previous study [19] grass
PFBA	28.4 ± 5.21	56.8 ± 3.45	40.0 ± 2.41	12.2 ± 1.71	18.2 ± 5.34	64.8 ± 15.35	NM
PFPeA	10.2 ± 1.52	20.4 ± 2.70	16.3 ± 2.35	17.1 ± 3.74	14.9 ± 1.96	41.1 ± 9.00	NM
PFHxA	11.7 ± 2.11	9.90 ± 1.37	<LOQ	2.90 ± 0.87	6.84 ± 0.81	<LOQ	3.40 ± 1.84
PFHpA	3.33 ± 0.72	2.66 ± 0.47	<LOQ	0.86 ± 0.23	<LOQ	<LOQ	0.90 ± 0.30
PFOA	1.34 ± 0.14	2.52 ± 0.48	<LOQ	0.11 ± 0.01	<LOQ	<LOQ	0.25 ± 0.10
PFNA	0.77 ± 0.15	2.85 ± 0.47	<LOQ	<LOQ	<LOQ	<LOQ	0.12 ± 0.04
PFDA	0.34 ± 0.05	0.52 ± 0.08	<LOQ	<LOQ	<LOQ	<LOQ	0.10 ± 0.04
PFBS	14.5 ± 3.84	4.22 ± 0.37	2.02 ± 0.32	0.42 ± 0.08	<LOQ	<LOQ	NM
PFHxS	1.08 ± 0.11	7.56 ± 0.86	1.51 ± 0.11	0.50 ± 0.04	<LOQ	<LOQ	NM
PFHpS	1.03 ± 0.02	6.57 ± 0.94	<LOQ	<LOQ	<LOQ	<LOQ	NM
PFOS	0.32 ± 0.02	1.67 ± 0.32	0.10 ± 0.01	<LOQ	<LOQ	<LOQ	0.07 ± 0.02
PFDS	0.19 ± 0.02	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	NM

[a]BAFs were not calculated if analyte concentrations were below LOQ and are denoted by < LOQ. Data are shown as means and standard errors (n = 3–5).

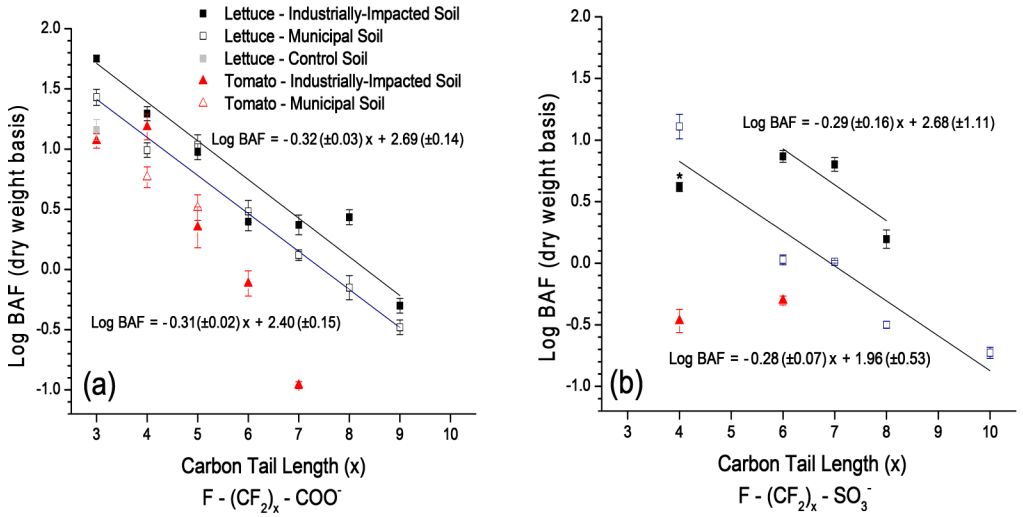


Figure 2. Correlations between log BAF for PFCAs (a) and PFSAs (b) and carbon tail length in greenhouse lettuce and tomato grown in biosolids-amended and control soils. Means and standard errors are shown (n = 5). Linear regressions with slopes, intercepts, and associated error values are shown for lettuce in industrially impacted and municipal soils; the data point marked with an asterisk is excluded from the regression calculation. Regressions for tomato BAFs were not performed.

municipal biosolids-amended soil had a total of 434 ng/g PFAAs, consisting primarily of PFOS (319.5 ng/g) and PFDS (61.2 ng/g). Both biosolids-amended soils had comparatively low levels of the shorter chain carboxylates (PFBA, PFPeA, PFHxA, PFHpA): <12 ng/g of each in the industrially impacted soil and <3 ng/g in the municipal biosolids-amended soil (SI Table S5).

Despite the relatively low soil concentrations of the short chain PFAAs, elevated levels were observed in the greenhouse lettuce for all soil treatments. For lettuce grown in the industrially impacted soil, concentrations were greatest for PFBA (266.1 ng/g), PFPeA (236.0 ng/g), and PFBS (205.2 ng/g), respectively (Figure 1a). Lettuce grown in the municipal soil had the highest concentrations of PFOS (101.6 ng/g), PFHxA (28.0 ng/g), PFPeA (27.2 ng/g), and PFBA (25.5 ng/g), respectively (Figure 1a). The preferential uptake of shorter chain PFAAs as has been previously observed[19,20] was also exemplified in this study, with the lettuce concentration of PFOS being only roughly 4-fold larger than the lettuce concentrations of the short chain perfluorocarboxylates (PFCAs) even though the initial soil concentration of PFOS was more than 100× greater than the soil concentrations of the short chain PFCAs. Even though control soil levels were below 0.5 ng/g for each PFAA, the lettuce grown in the control soil accumulated low levels of some PFAAs, notably PFHxA (16.4 ng/g) and PFBA (6.9 ng/g). The levels of all other PFAAs in the control lettuce were each less than 2.5 ng/g (Figure 1a). An ANOVA test was used to compare concentrations of PFAAs in the different lettuce treatments. Concentrations of PFAAs in lettuce grown in the industrially impacted soil were significantly different (α = 0.05) than the control for all 11 analytes detected above the LOQ (SI Table S5), and lettuce grown in the municipal soil was different than the control for 10 of the 12 analytes (Figure 1a).

In contrast to the lettuce results, only seven and two PFAAs were detected above the LOQs for tomatoes grown in industrially impacted soil and municipal soil, respectively. PFAAs in the control tomatoes were all less than LOQ (Figure 1b). In the tomatoes grown in industrially impacted soil, the highest levels were measured for PFPeA (211.4 ng/g), PFBA

(56.1 ng/g), and PFHxA (33.2 ng/g). For tomatoes grown in the municipal soil, PFPeA (15.5 ng/g) and then PFHxA (5.9 ng/g) were present at the highest levels. Very little accumulation of any of the perfluoroalkyl sulfonates (PFSAs) was observed in tomatoes (only 19.4 ng/g PFBS and 0.8 ng/g PFHxS in the industrially impacted soil, respectively), despite the fact that the soil concentration of PFOS in the municipal soil was 319 ng/g (SI Table S5).

Bioaccumulation Factors. Average BAFs for lettuce grown in the industrially impacted soil ranged from 56.8 for PFBA to 0.5 for PFDA, while values for the municipal soil lettuce ranged from 28.4 for PFBA to 0.2 for PFDS (Table 2). When log BAFs were plotted versus carbon chain length for PFCAs (Figure 2a) and PFSAs (Figure 2b), a linear correlation was evident, as was previously observed for PFCAs.[19] Within lettuce, the slopes of the regression equations are consistent in both biosolids-amended soils (Figure 2). The BAF decreases by approximately 0.3 log units per CF_2 group for PFCAs and PFSAs in both biosolids-amended soils, with no statistical differences between the slopes (α = 0.05). However, the BAF for PFBS in lettuce grown in industrially impacted soil was excluded from the regression calculation, as its value did not conform to the pattern displayed by the other data points. An increase in soil–water distribution coefficient of 0.5–0.6 log units per CF_2 group[30,32] could point to reduced bioavailability for plant uptake as chain-length increases. The linearity of the plant uptake response to soil concentration of PFAAs suggests that passive transport may be the primary mechanism for uptake and translocation. However, the lower than expected BAF for PFBS of 4.2 (Table 2) versus the calculated one of 33.1 (equation in Figure 2b) for lettuce grown in the industrially impacted soil where PFBS concentrations were much higher than in the municipal soil indicates that bioaccumulation capacity for some PFAAs may be limited.[27]

As is also apparent in Figure 2, BAFs for PFCAs and PFSAs in lettuce were, in general, slightly higher in the industrially impacted soil than in the municipal soil (~0.3–0.8 log units). Although the oxidation step in the plant extraction process could have potentially transformed precursors in one of the soils to several PFCAs,[33] the consistency of the chain length trend among all of the PFCAs suggests this is not a significant contributing factor. Given that neither soil was spiked with PFAAs, differences in this apparent bioavailability to the lettuce was likely due to differences in soil properties and/or aging of the biosolids–soil mixture. In an effort to examine whether the f_{oc} of the soils could account for the differences, organic-carbon normalized BAFs were calculated. While for PFCAs, normalizing the BAFs more than compensated for the difference between the two soil treatments, for PFSAs, normalizing only accounted for about half the log difference (SI Figure S2). It is possible that the difference in bioavailability of PFAAs may have also been due to the nature of the organic carbon, as the industrially impacted soil contained carbon from fresh biosolids-based compost, whereas organic carbon in the municipal soil was derived primarily from aged soil organic matter rich in recalcitrant clay–humic complexes. While organic carbon is likely a contributing factor to differences in PFAA bioaccumulation, other geochemical factors may be important as well.

Tomato BAFs in the industrially impacted soil ranged from 17.1 for PFPeA to 0.1 for PFOA (Figure 2a). No other studies have measured the uptake of PFAAs in tomato. However, the BAF for PFOA in a fruit (cucumber) estimated at 0.75 using the value reported on a wet weight basis of 0.03[14] and correcting for water content (assumed to be 96% for cucumber)[34] is on the same order of magnitude. Linear trends were not as apparent for PFAA log BAFs in tomato. However, for PFCAs in tomato grown in industrially impacted soil, the BAF decreases approximately 0.5–0.9 log units if PFBA is excluded. Again, the shortest chain PFAAs (PFBA and PFBS) may be slightly less bioaccumulative than would be expected from trends in BAFs for their longer chain homologues, particularly if there is a concentration ceiling on the passive transport process or if there are other contributing barriers to transport. Furthermore, the difference in uptake patterns of lettuce and tomato suggest that the type of crop, or perhaps more importantly, the type of vegetative structure, may play an important role in PFAA bioaccumulation. Contaminants must be transported much further in the plant to reach a fruit crop (tomato) than a stem/leaf crop (lettuce).

Transpiration Stream Concentration Factors. As no other studies have reported PFAA BAFs for lettuce grown in biosolids-amended soil, comparable TSCFs were calculated to enable comparisons with results from a hydroponic lettuce study.[20] Calculated TSCFs are plotted in Figure 3 alongside literature values.[20] As organic-carbon derived partition coefficients were used to estimate soil pore water concentrations, the strong agreement between the TSCFs generated from the present study and those published previously reiterates the importance of f_{oc} in affecting the bioavailability of PFAAs in biosolids-amended soils. These results also support the passive transport mechanism as, in general, PFAAs are taken up at a rate much lower than water (less than unity).[24]

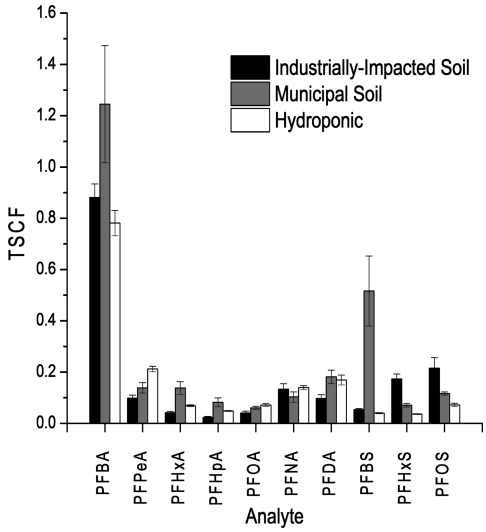


Figure 3. Comparison of transpiration stream concentration factors (TSCFs) for lettuce calculated from this study compared to TSCFs from a previous hydroponic lettuce study.[20] Mean and standard error (n = 5) are shown.

Pilot-Scale Field Trial. The five biosolids treatments used in the pilot-scale field trial plots were selected to represent increasing application rates; however, PFAA soil concentrations above background (i.e., >1.5 ng/g) were only observed for PFOA, PFNA, PFDA, PFOS, and PFDS (SI Table S6). The two highest concentrations were for PFOS (13.9 ng/g) and PFOA (5.2 ng/g) in the 4× amended soil. Soil concentrations of shorter chain PFAAs did not significantly increase with

increased biosolids amendment rate (SI Table S6). These field soil values of PFAAs were significantly lower (3−20 times) than the levels found in the soils used in the greenhouse study. As a result of low initial soil concentrations, limited plant uptake data from the field trials were obtained, restricting the comparisons that could be made. PFAA concentrations in field crops were averaged for the three replicate soil plots only if all three replicate values were above the LOQ (SI Table S6). In the lettuce, the highest concentrations found were for PFBA (27.5 ng/g) and PFPeA (16.4 ng/g) in the 4× amended soil plot. For tomato, the highest concentrations were for PFBA (17.0 ng/g) in the 0.5× plot and PFPeA (15.0 ng/g) in the 4× plot. Minimal accumulation was found in crops grown in the 1× and 2× plots; all lettuce and tomato PFAA concentrations can be found in SI Table S6. For the analytes that had concentrations above the LOQ in the 4× amended soil, lettuce and tomato BAFs were calculated. These values are shown alongside the respective greenhouse grown lettuce and tomato BAFs in Table 2.

A trend suggesting an inverse relationship between BAFs and chain length was seen for PFCAs in both the field trial lettuce and tomato (SI Figure S3). Although the field data are limited, the difference between the log BAFs (1.6 for PFBA and 1.2 for PFPeA) for the field trial lettuce is a decrease of 0.4, which correlates well with the greenhouse grown lettuce decrease of 0.3 per CF_2 moiety. In addition, the field BAF values for tomato decrease approximately 0.1−0.3 log units per CF_2 moiety, similarly but less closely correlated to the greenhouse grown tomatoes (0.5−0.9 log units per moiety).

Full-Scale Field Study. Soil concentrations of PFAAs for the full-scale crop−soil system were similar to concentrations in the field trial plots. All PFAAs were individually less than 2 ng/g except for PFOA (4.4 ng/g), PFDA (2.6 ng/g), and PFOS (4.3 ng/g) from the rural 0.5× field, and PFOS (2.8 ng/g) from the urban 2× field (SI Table S7). All PFAA corn grain concentrations were below the LOQ (SI Table S7). In the corn stover, only PFBA (4.2 ng/g) and PFPeA (0.3 ng/g) were above the LOQ for the Urban 2× plot (SI Table S7). This preferential accumulation in the vegetative compartment is consistent with the findings of Stahl et al.[13] In addition, the findings reiterate the consistent bioaccumulation of the short chain PFCAs as found in the greenhouse and field trial studies. From these limited data, BAFs for PFBA and PFPeA were calculated and are shown in Table 2 along with grass-soil accumulation factors from Yoo et al.[19] In the absence of other studies for comparison, the similarity of corn stover to grass was used to compare results. However, the longest PFCA detected in this study was PFPeA and the shortest PFCA that Yoo et al. reported was PFHxA, so no direct comparisons are possible. Trendwise, Yoo et al. reported a decrease of 0.2 log units per CF_2 group increase;[19] the limited log BAF data found for corn stover in the present study (1.8 for PFBA and 1.6 for PFPeA) also shows a decrease by 0.2 log units per CF_2 group. Stahl et al.[13] studied corn straw in spiked soil systems, and BAFs can be calculated from the data reported. BAFs for the only two PFAAs studied were 0.24 for PFOA and 0.16 for PFOS, which are in line with corn stover and grass trends provided in Table 2.

Implications. While some PFAA crop accumulation data are available from the literature, this is the first study examining PFAA accumulation in food crops grown in unspiked, biosolids-amended soils, although amendment rates were generally above typical agronomic application rates. From this study, it is clear that there is preferential uptake of PFCAs over PFSAs and accumulation of shorter chain PFAAs over longer chain PFAAs. In addition, uptake differences in crops suggest that the vegetative structure of the crop may affect the amount of bioaccumulation. In both the field and greenhouse studies, BAFs for shorter chain PFAAs were greater than than unity (i.e., 1), indicating accumulation in the plant tissues. In the context of the U.S. EPA's risk assessment framework for potential contaminant accumulation in crops from biosolids-amended soils, the default "conservative" value for BAFs is 1;[35] clearly, in light of these results, this estimate is not truly conservative for short chain PFAAs. This finding points to the need for more thorough research before full risk assessments can be completed for PFAAs. These results may also have important implications with respect to the potential routes of PFAA exposure in humans who might have repeatedly used biosolids to fertilize their home gardens, particularly if the biosolids were from a WWTP receiving industrially impacted wastewater with elevated levels of PFAAs. More work is needed to verify the trends observed in this study as plant accumulation of PFAAs varies with soil properties, crop type, biosolids application rate, and analyte.

■ ASSOCIATED CONTENT

Supporting Information

Additional details are available regarding analytical methods, soil characteristics, greenhouse experiment details, sampling details, the soil extraction procedure, PFAA concentrations in soils and crops, log and normalized plots of BAFs, and TSCF calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (720) 984-2116; fax: (303) 273-3413; E-mail: chiggins@mines.edu.

Notes

The information in this document has been funded by the U.S. Environmental Protection Agency. It has been subjected to review by the Region 5 Office and the Office of Research and Development (ORD) and approved for publication. Approval does not signify that the contents reflect the views of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was funded by a RARE grant from the U.S. EPA and was supported by efforts from the Metropolitan Water Reclamation District of Greater Chicago and the New Lenox Wastewater Department. We appreciate the help of various U.S. EPA staff and, in particular, Lee Thomas (Region 4), Carole Braverman, Bradley Grams, Gerald Golubski, Kenneth Gunter, Erin Newman, Thomas Poy, David Schroeder (Region 5), Andy Lindstrom, Mark Strynar, and John Washington (ORD). We also acknowledge the help of Erin Sedlacko, Lisa Kudryk, Amanda Hering, and Karen Kazor from CSM.

■ REFERENCES

(1) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. Perfluoroalkyl and polyfluoroalkyl substances in the environment:

terminology, classification, and origins. *Integr. Environ. Assess. Manage.* **2011**, *7* (4), 513−41.
(2) Kovarova, J.; Svobodova, Z. Perfluorinated compounds: occurrence and risk profile. *Neuroendocrinol. Lett.* **2008**, *29* (5), 599−608.
(3) Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. Perfluoroalkyl acids: a review of monitoring and toxicological findings. *Toxicol. Sci.* **2007**, *99* (2), 366−394.
(4) Haug, L. S.; Huber, S.; Schabach, M.; Becher, G.; Thomsen, C. Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from norwegian homes. *Environ. Sci. Technol.* **2011**, *45* (19), 7991−7998.
(5) Lau, C. Perfluorinated compounds. In *Molecular Clinical and Environmental Toxicology, Vol. 3: Environmental Toxicology*; Luch, A., Ed.; Birkhäuser-Verlag: Basel, Switzerland, 2012; pp 47−86.
(6) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry—characterization of municipal wastewaters. *Environ. Sci. Technol.* **2006**, *40* (1), 289−295.
(7) Guo, R.; Sim, W. J.; Lee, E. S.; Lee, J. H.; Oh, J. E. Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants. *Water Res.* **2010**, *44* (11), 3476−3486.
(8) Kunacheva, C.; Tanaka, S.; Fujii, S.; Boontanon, S. K.; Musirat, C.; Wongwattana, T.; Shivakoti, B. R. Mass flows of perfluorinated compounds (PFCs) in central wastewater treatment plants of industrial zones in Thailand. *Chemosphere* **2011**, *83* (6), 737−744.
(9) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* **2005**, *39* (11), 3946−3956.
(10) Lu, Q.; He, Z. L.; Stoffella, P. J. Land application of biosolids in the USA: a review. *Appl. Environ. Soil Sci.* **2012**, *2012*, 1−11.
(11) Standards for the use or disposal of sewage sludge. *Code of Federal Regulations*, Title 40, Part 503 , 2013.
(12) Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L. Polyfluorinated compounds: past, present, and future. *Environ. Sci. Technol.* **2011**, *45* (19), 7954−7961.
(13) Stahl, T.; Heyn, J.; Thiele, H.; Huther, J.; Failing, K.; Georgii, S.; Brunn, H. Carryover of perfluorooctanoic Acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plants. *Arch. Environ. Contam. Toxicol.* **2009**, *57* (2), 289−298.
(14) Lechner, M.; Knapp, H. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant and distribution to the different plant compartments studied in cultures of carrots (*Daucus carota* ssp Sativus), potatoes (*Solanum tuberosum*), and cucumbers (*Cucumis sativus*). *J. Agric. Food. Chem.* **2011**, *59* (20), 11011−11018.
(15) Stahl, T.; Riebe, R. A.; Falk, S.; Failing, K.; Brunn, H. Long-term lysimeter experiment to investigate the leaching of perfluoroalkyl substances (PFASs) and the carry-over from soil to plants: results of a pilot study. *J. Agric. Food Chem.* **2013**, *61* (8), 1784−1793.
(16) Loibner, A. P.; Szolar, O.; Schlegl, M.; Gartner, M.; Braun, R. Bioavailability of PAHs in soil and ecotoxicological considerations. *Contam. Soil 98, Proc. Int. FZK/TNO Conf.* **1998**, *1−2*, 797−799.
(17) Wu, X. M.; Yu, Y. L.; Li, M.; Long, Y. H.; Fang, H.; Li, S. N. Prediction of bioavailability of chlorpyrifos residues in soil to earthworms. *J. Soil Sci. Plant Nutr.* **2011**, *11* (1), 44−57.
(18) Wen, B.; Li, L. F.; Liu, Y.; Zhang, H. N.; Hu, X. Y.; Shan, X. Q.; Zhang, S. Z. Mechanistic studies of perfluorooctane sulfonate, perfluorooctanoic acid uptake by maize (*Zea mays* L. cv. TY2). *Plant Soil* **2013**, *370* (1−2), 345−354.
(19) Yoo, H.; Washington, J. W.; Jenkins, T. M.; Ellington, J. J. Quantitative determination of perfluorochemicals and fluorotelomer alcohols in plants from biosolid-amended fields using LC/MS/MS and GC/MS. *Environ. Sci. Technol.* **2011**, *45* (19), 7985−7990.
(20) Felizeter, S.; McLachlan, M.; Voogt, P. Uptake of perfluorinated alkyl acids by hydroponically grown lettuce (*Lactuca sativa*). *Environ. Sci. Technol.* **2012**, *46*, 11735−11743.
(21) Zabludowska, E.; Kowalska, J.; Jedynak, L.; Wojas, S.; Sklodowska, A.; Antosiewicz, D. M. Search for a plant for phytoremediation—what can we learn from field and hydroponic studies? *Chemosphere* **2009**, *77* (3), 301−307.
(22) Trapp, S. Fruit tree model for uptake of organic compounds from soil and air. *SAR QSAR Environ. Res.* **2007**, *18* (3−4), 367−387.
(23) Collins, C.; Fryer, M.; Grosso, A. Plant uptake of non-ionic organic chemicals. *Environ. Sci. Technol.* **2006**, *40* (1), 45−52.
(24) Dettenmaier, E. M.; Doucette, W. J.; Bugbee, B. Chemical hydrophobicity and uptake by plant roots. *Environ. Sci. Technol.* **2009**, *43* (2), 324−329.
(25) Trapp, S.; McFarlane, C.; Matthies, M. Model for uptake of xenobiotics into plants—validation with bromacil experiments. *Environ. Toxicol. Chem.* **1994**, *13* (3), 413−422.
(26) Michel, M.; Buszewski, B. Isolation, determination and sorption modelling of xenobiotics in plant materials. *Pol. J. Environ. Stud.* **2008**, *17* (3), 305−319.
(27) Swartjes, F. A., Ed. *Dealing with Contaminated Sites: From Theory Towards Practical Application*; Springer: London, 2011.
(28) Sepulvado, J. G.; Blaine, A. C.; Hundal, L. S.; Higgins, C. P. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. *Environ. Sci. Technol.* **2011**, *45* (19), 8106−8112.
(29) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: Hoboken, NJ, 2005.
(30) Higgins, C. P.; Luthy, R. G. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* **2006**, *40* (23), 7251−6.
(31) Strynar, M. J.; Lindstrom, A. B.; Nakayama, S. F.; Egeghy, P. P.; Helfant, L. J. Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils. *Chemosphere* **2012**, *86* (3), 252−257.
(32) Guelfo, J. L.; Higgins, C. P. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol.* **2013**, *47* (9), 4164−4171.
(33) Houtz, E. F.; Sedlak, D. L. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ. Sci. Technol.* **2012**, *46* (17), 9342−9349.
(34) Pennington, J. A. T.; Douglass, J. S. *Bowes and Church's Food Values of Portions Commonly Used*, 18th ed.; Lippincott Williams & Wilkins: Baltimore, MD, 2005.
(35) *Guidance for Developing Ecological Soil Screening Levels*; USEPA, Office of Solid Waste and Emergency Response: Washington, DC, 2003.

Environmental Science & Technology

Article

pubs.acs.org/est

Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended soils

Andrea C. Blaine,[†] Courtney D. Rich,[†] Erin M. Sedlacko,[†] Lakhwinder S. Hundal,[‡] Kuldip Kumar,[‡] Christopher Lau,[§] Marc A. Mills,[#] Kimberly M. Harris,[∥] and Christopher P. Higgins[†,*]

[†]Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, Colorado 80401, United States

[‡]Metropolitan Water Reclamation District of Greater Chicago, Chicago, Illinois 60611, United States

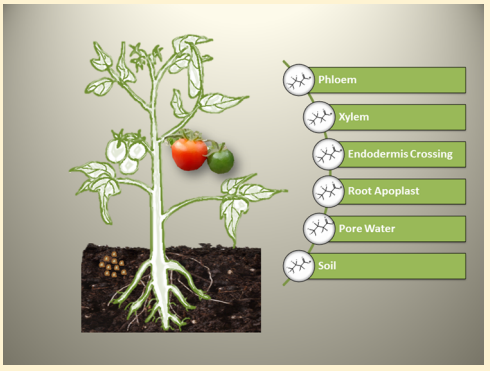
[§]U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina 27711, United States

[#]U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Office of Research and Development, Cincinnati, Ohio 45268, United States

[∥]U.S. Environmental Protection Agency, Region 5, Chicago, Illinois 60604, United States

Supporting Information

ABSTRACT: Crop uptake of perfluoroalkyl acids (PFAAs) from biosolids-amended soil has been identified as a potential pathway for PFAA entry into the terrestrial food chain. This study compared the uptake of PFAAs in greenhouse-grown radish (*Raphanus sativus*), celery (*Apium graveolens* var. *dulce*), tomato (*Lycopersicon lycopersicum*), and sugar snap pea (*Pisum sativum* var. *macrocarpon*) from an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil. Individual concentrations of PFAAs, on a dry weight basis, in mature, edible portions of crops grown in soil amended with PFAA industrially impacted biosolids were highest for perfluorooctanoate (PFOA; 67 ng/g) in radish root, perfluorobutanoate (PFBA; 232 ng/g) in celery shoot, and PFBA (150 ng/g) in pea fruit. Comparatively, PFAA concentrations in edible compartments of crops grown in the municipal biosolids-amended soil and in the control soil were less than 25 ng/g. Bioaccumulation factors (BAFs) were calculated for the root, shoot, and fruit compartments (as applicable) of all crops grown in the industrially impacted soil. BAFs were highest for PFBA in the shoots of all crops, as well as in the fruit compartment of pea. Root-soil concentration factors (RCFs) for tomato and pea were independent of PFAA chain length, while radish and celery RCFs showed a slight decrease with increasing chain length. Shoot-soil concentration factors (SCFs) for all crops showed a decrease with increasing chain length (0.11 to 0.36 log decrease per CF_2 group). The biggest decrease (0.54−0.58 log decrease per CF_2 group) was seen in fruit-soil concentration factors (FCFs). Crop anatomy and PFAA properties were utilized to explain data trends. In general, fruit crops were found to accumulate fewer long-chain PFAAs than shoot or root crops presumably due to an increasing number of biological barriers as the contaminant is transported throughout the plant (roots to shoots to fruits). These data were incorporated into a preliminary conceptual framework for PFAA accumulation in edible crops. In addition, these data suggest that edible crops grown in soils conventionally amended for nutrients with biosolids (that are not impacted by PFAA industries) are unlikely a significant source of long-chain PFAA exposure to humans.



INTRODUCTION

Perfluoroalkyl acids (PFAAs) are used extensively both in industrial and consumer products,[1] but resist degradation by conventional wastewater treatment plants (WWTPs) and persist in both aqueous effluent and treated biosolids.[2,3] Land-application of biosolids on crops can therefore facilitate the entry of PFAAs into the terrestrial food web. Although PFAAs are regulated in biosolids used as fertilizer for agriculture in some parts of Europe (e.g., Bavaria),[4] currently, there are no federal regulations in the U.S. that govern the use and application of biosolids based on PFAA concentrations.[5] Land-application of biosolids primarily occurs on grain crops; however, sustainability movements are encouraging more liberal use of biosolids on home gardens by consumers.

While several studies have demonstrated uptake of PFAAs into plants, the majority of these studies used either spiked systems or hydroponics which both differ from aged field soils.[4,6−8] Blaine et al.[9] have shown that edible crops can uptake PFAAs from authentic biosolids-amended soils. Both lettuce

Received: January 2, 2014
Revised: May 25, 2014
Accepted: June 11, 2014
Published: June 11, 2014

   dx.doi.org/10.1021/es500016s | Environ. Sci. Technol. 2014, 48, 7858−7865

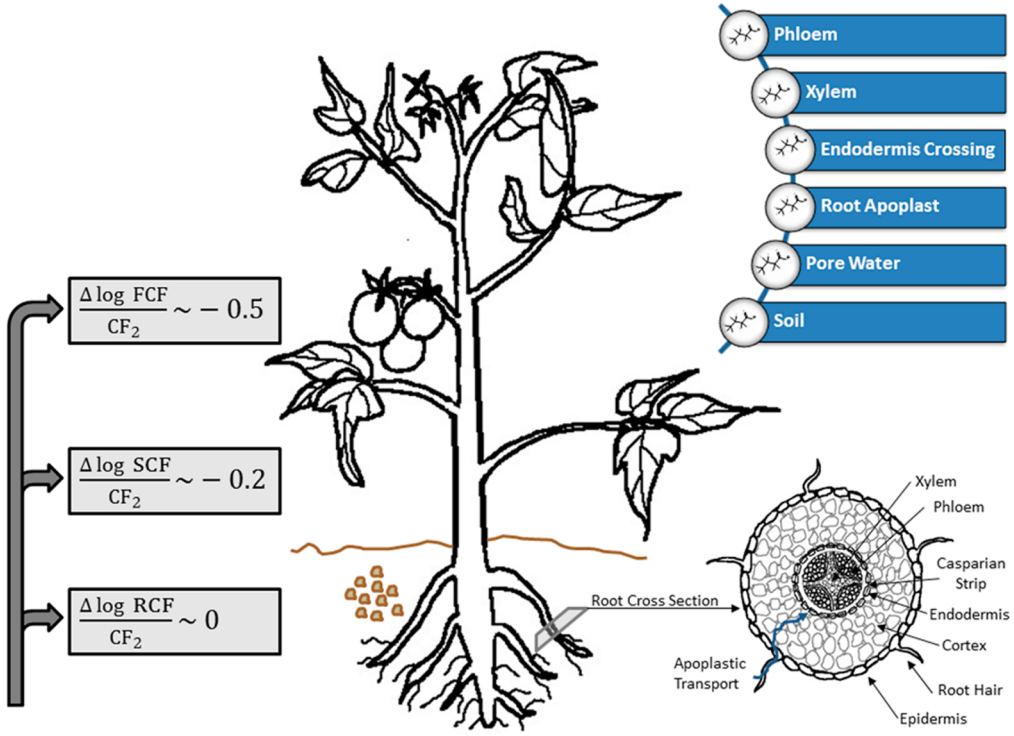


Figure 1. Conceptual model of perfluorocarboxylate uptake as exhibited in a tomato plant. Approximate values are shown for change in log bioaccumulation factor per CF_2 group. Root, shoot, and fruit concentration factors are RCF, SCF, and FCF, respectively. Uptake pathway is shown in the top right corner. Root cross-section modified from Taiz and Zeiger.[16]

leaves and tomato fruit had bioaccumulation factors (BAFs) greater than one for short-chain perfluorocarboxylates (PFCAs).[9] In addition, carbon chain length dependent trends were seen in lettuce leaves, resulting in an approximately 0.3 log decrease for each CF_2 group.[9] However, as only the edible portions were analyzed, more general correlations between plant compartment and PFAA accumulation were not made. In another recent greenhouse study, an inverse relationship between BAF and carbon chain length was also seen for PFCAs in alfalfa plants.[10] Felizeter et al.[8] studied accumulation of PFAAs in hydroponic lettuce and found that long-chain PFAAs accumulated more in the roots than in the foliage, whereas for short-chain compounds, there was more translocation from the roots to the foliage.[8] A more mechanistic study by Wen et al.[11] determined that PFOA and PFOS may have different uptake mechanisms in maize; potential active uptake and entry by anion channels were suggested for PFOA, while entry by aquaporins (water channels) or anion channels (different than the ones used by PFOA) were suggested for PFOS.

The translocation and partitioning behavior of a chemical in a plant is highly varied and complex. Various plant uptake models have been explored over the years with the majority focusing on uptake of neutral hydrophobic chemicals based on the octanol–water partition coefficient (K_{ow}).[12−14] In these models, chemical uptake from soil is usually driven by passive diffusion, as only natural or structurally similar chemicals are actively transported,[13] and small, neutral substances are most easily carried into the roots.[15] Although early models indicated that plant uptake of hydrophilic (low log K_{ow}) chemicals was limited, a more recent empirical model indicates that hydrophilic chemicals are extensively taken up by plants.[14] Although there are some discrepancies among the various plant uptake models, the basic pathway of chemicals within a plant is fairly well-defined. Chemicals can travel across the root cortex through the apoplast (extracellular space) or symplast (intracellular space) until they reach the Casparian strip at the endodermis.[16] At this point, they must cross through a cell membrane (Figure 1). While neutral, hydrophobic chemicals may easily pass through a membrane, hydrophilic and/or ionized chemicals may have to pass through as neutral salts, through anion channels, or through water pores in the membrane.[11,17] The Casparian strip acts as an ion trap, allowing for higher concentrations of solutes in the xylem than in the pore water.[16]

While nonpolar chemicals are mostly confined to the surface of root membranes due to lipid partitioning, polar chemicals can enter the transpiration stream and migrate throughout the plant.[18,19] Once within the transpiration stream, a chemical can be transported throughout the plant, first to the shoot (i.e., stem and leaves) via the xylem and then to storage organs (e.g., fruit) via the phloem. The xylem and phloem are separated by the vascular cambium, a single row of cells. Accumulation of solutes in plant cells near the leaves helps drive translocation from source (e.g., leaf) to sink (e.g., fruit) via a pressure-flow[16] model. As the concentration in a cell escalates, water is absorbed osmotically thus building up hydrostatic pressure. The subsequent movement of the water and solutes through the system of phloem sieve tubes equalizes the pressure. The sieve tubes are separated by sieve plates which allow flow through transport pores (plasmodesmata). Eventually, chemicals may be stored in cell vacuoles or in intercellular spaces. Neutral and ionized polar chemicals with low lipophilicity, low volatility, and high persistence are particularly prone to accumulation in the leaves and other sinks by phloem transport.[20] PFAAs generally meet these criteria. In particular,

PFAAs, being anionic at environmental pH values,[21] are generally nonvolatile, thereby eliminating potential release into the air from the leaf stomata.

This study evaluated the PFAA distribution in various plant structural compartments by examining both the edible and nonedible portions of radish (*Raphanus sativus*), celery (*Apium graveolens* var. *dulce*), tomato (*Lycopersicon lycopersicum*), and sugar snap pea (*Pisum sativum* var. *macrocarpon*) grown in biosolids-amended soils. Radish represents an edible root crop (i.e., below ground crop), although radish tops are also edible. Celery represents an edible shoot crop (i.e., stem and leaf crop) although certain varieties of celery are also harvested for the bulb and seeds. Tomato represents an edible fruit crop. Sugar snap pea, a legume, also represents a fruit and edible seed crop. Bioaccumulation factors for the root, shoot, and fruit portions were calculated. To our knowledge, this is the first study to examine PFAA uptake in celery, snap pea, and radish; in addition, it is one of the most detailed studies addressing intercompartmental translocation of PFAAs in edible crops to date.

MATERIALS AND METHODS

Chemicals. Native perfluorinated standards and stable isotopes were obtained from Wellington Laboratories (Guelph, ON, Canada) and prepared as per established methods.[9] Analytes studied include perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), and perfluorooctanesulfonate (PFOS; Supporting Information (SI) Table S1). HPLC-grade methanol (MeOH), high purity Chromasolv dichloromethane (DCM), and all other reagent grade solvents were obtained from Sigma-Aldrich (St. Louis, MO). A Milli-Q system (Millipore, Billerica, MA) was used to provide water for extractions, and HPLC-grade water was used for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. Chromabond diamino from Macherey-Nagel Inc. (Bethlehem, PA) and Supelclean ENVI-Carb from Sigma-Aldrich were used in extract cleanup.

Greenhouse Study. Two biosolids-amended soils as well as an unamended control soil were used in this study: a soil amended with industrially impacted biosolids (industrially impacted soil), a soil receiving multiple applications of municipal biosolids over a span of 20 years (municipal soil), and an unamended control soil. Although the control soil was obtained from an unamended field, its proximity to biosolids-amended fields likely led to minor cross-contamination resulting in the detection of trace levels of PFAAs. Details on all three soils can be found in Blaine et al.;[9] PFAA concentrations in the soils are reported in the SI Table S2. In general, soils were sieved (6.3 mm) for homogeneity and pots were filled on a dry weight basis. Four edible crops including radish, celery, tomato, and pea were grown from seed. Five pot replicates were grown for each crop in each soil. Pots were randomly arranged to account for any spatial variations in light and temperature within the greenhouse. Additional information about propagation and greenhouse environmental conditions are given in the SI. Both edible and nonedible parts of all crops were harvested (SI Table S3) at maturity and frozen at −20 °C in sealed plastic bags until extraction.

Extraction and Analysis. *Sample Extraction.* Prior to sample preparation, plant material was homogenized using a food processor. Aliquots (0.5−2 g) of soil or plant material were transferred to 50 mL polypropylene vials. To each vial, 2 ng of isotopically labeled surrogate standard was added. Plant samples were then extracted with a 50/50 (v/v) solution of DCM and 99:1 (v/v) MeOH with ammonium hydroxide as detailed elsewhere;[9] soil samples obtained prior to planting were extracted based on the protocol from Sepulvado et al.[3] Results for both plants and soils are presented on a dry weight basis.

PFAA Analysis. All PFAAs were analyzed with isotope dilution using LC-MS/MS under conditions outlined in previous work,[9] though the method was validated for the wide variety of plant matrices included in the present study (SI Figure S1). Chromatography was performed using a Shimadzu LC-20AD unit (Kyoto, Japan). Samples were injected onto a Gemini C18 Column with a 3-μm particle size (Phenomenex, Torrance, CA). Two transitions for each analyte were observed using an MDS Sciex Applied Biosystems API 3200 (MDS Sciex, Ontario) with negative electrospray ionization operating in scheduled multiple reaction mode. No attempt to analytically differentiate between branched and unbranched isomers was made.

Data Analysis. *Quality Control.* The software Analyst was used for quantitation in this study. For each matrix, a minimum of 20 percent of the samples were extracted and analyzed in triplicate. The relative standard deviation for analytical replicates was less than 18%. Sample values are presented as the mean experimental replicate value (n = 3 to 5). One extraction blank with surrogate standard and one double blank without surrogate standard were prepared with each batch of samples. Limits of quantitation (LOQ) ranged from 0.03 to 0.71 ng/g; they were determined by the lowest calibration standard calculated to be within 30% of its actual value and were analyte, matrix, and run-dependent. LOQs were also required to be at least twice as high as the highest concentration in the corresponding blanks and have signal-to-noise ratios greater than 30. To account for any loss during the extraction process, each sample was fortified with isotopically labeled surrogate standards. PFBS was the only analyte that did not have a corresponding surrogate; therefore, PFHxS was used (SI Table S1). Surrogate recoveries for the samples averaged 35% for root tissues, 36% for shoot tissues, and 40% for fruit tissues across all analytes. While lower than typical soil surrogate recoveries,[3] this range is typical in plant matrices[8,22] due to matrix ion suppression. Native spike-recovery experiments (which account for surrogate losses) showed an average native recovery of 73% in root tissues, 80% in shoot tissues and 71% in fruit tissues for all analytes (SI Figure S1). PFBS showed lower native recovery than PFHxS despite the use of the same surrogate; this indicates that PFHxS may not have corrected for additional matrix suppression of PFBS and thus PFBS values in this study may be slightly underestimated. All data presented in this study are reported in terms of surrogate-corrected concentrations.

Statistical Analysis. Data are shown as means with standard errors. Statistical analyses and regression lines were calculated using OriginPro 9.0. Statistical difference of means was established by an analysis of variance (ANOVA) with Tukey's Test (α = 0.05); homogeneity of variance was assessed by Levene's Test (α = 0.05).

Bioaccumulation Metrics. Bioaccumulation factors (BAFs), ratios between the chemical determined on a dry weight basis in the respective plant tissue and soil, were

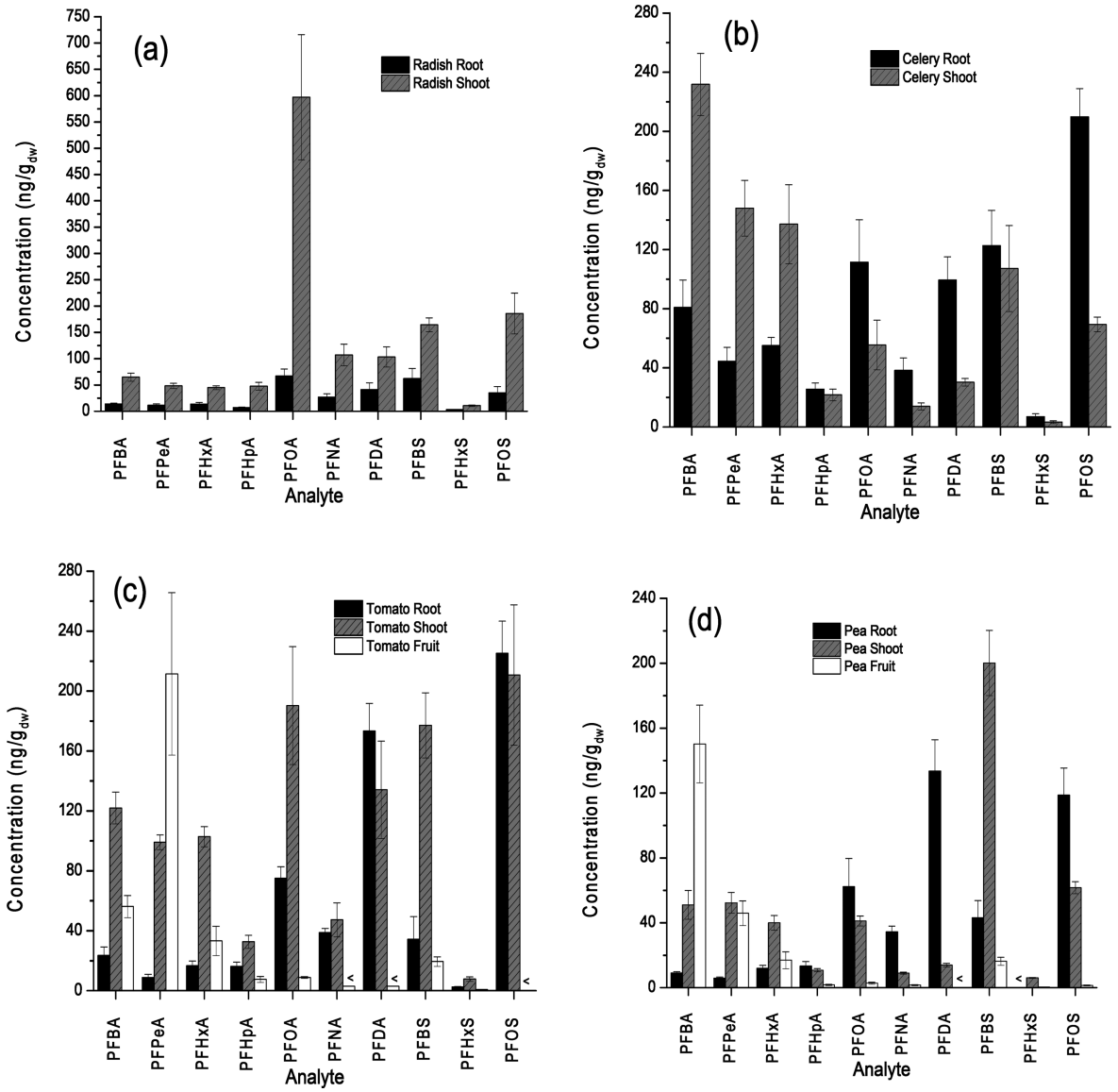


Figure 2. Concentrations of PFAAs in greenhouse radish (a), celery (b), tomato (c), and pea (d) grown in industrially impacted soil. Values for tomato fruit are from a previous study.[9] Bars represent means and standard errors of five determinations. Values less than the LOQ are denoted by <; LOQs for respective matrix and analyte are listed in SI Table S4 and Table S5.

calculated (eq 1) leading to estimations of root concentration factors (RCFs; SI eq S1), shoot concentration factors (SCFs; SI eq S2), and fruit concentration factors (FCFs; SI eq S3).

$$\text{BAF} = \frac{\text{PFAA concentration in plant tissue}(\text{ngg}^{-1})}{\text{PFAA concentration in soil}(\text{ngg}^{-1})} \quad (1)$$

Due to the ionized nature of PFAAs at environmental pH values (i.e., ~ 4 to 9), plant entry into the stomata from the air was assumed to be insignificant compared with uptake through the roots. BAFs were calculated using crops grown in the industrially impacted soil for each PFAA that had concentrations in the plant tissues above the LOQ.

Root-pore water concentrations (RCF_{pw}) were calculated (SI eq S4) by dividing the concentrations in the roots (ng/g) by the pore water concentrations (ng/mL) derived in previous work.[9] Briefly, pore water concentrations were obtained by dividing soil concentrations by the fraction of organic carbon in the soil and soil-water equilibrium partitioning coefficients obtained from Guelfo and Higgins.[23]

In addition, intercompartmental concentration factors (ratio of concentrations on a dry weight basis) were calculated for shoot to root (SRCFs; SI eq S5) and fruit to shoot (FSCFs; SI eq S6).

RESULTS AND DISCUSSION

Edible Portions. In the radish root grown in the industrially impacted soil, PFAA concentrations were highest for PFOA (67 ng/g), PFBS (62 ng/g), PFDA (41 ng/g), and PFOS (35 ng/g) (Figure 2a); these four analytes also had the highest concentrations in the soil. In the municipal and control soils, PFBS concentrations in the radish root were the highest at 24 ng/g and 22 ng/g, respectively (SI Table S4). For celery grown in the industrially impacted soil (Figure 2b), concentrations of PFAAs in the shoot were greatest for the short-chain (i.e., C6 and below) compounds, PFBA (232 ng/g), PFPeA (148 ng/g), PFHxA (137 ng/g), and PFBS (107 ng/g). Comparatively,

dx.doi.org/10.1021/es500016s | Environ. Sci. Technol. 2014, 48, 7858−7865

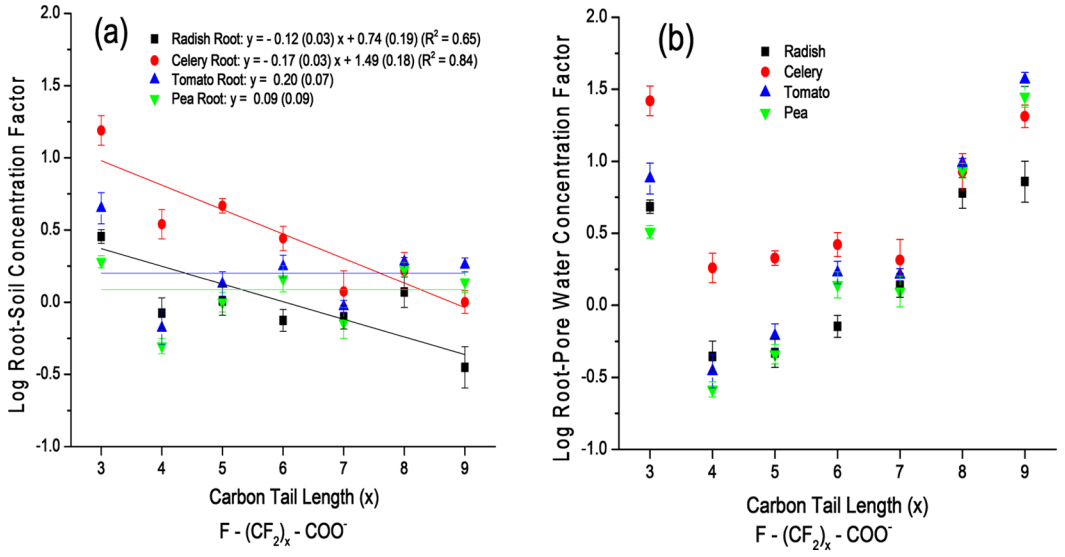


Figure 3. Correlations between log RCF for PFCAs based on soil (a) and calculated pore water (b) concentrations and carbon tail length in greenhouse radish, celery, tomato, and pea grown in industrially impacted soil. Means and standard errors are shown (n = 3 to 5). Linear regressions with slopes (if significantly different than zero at α = 0.05) and intercepts are shown; associated error values are shown parenthetically after each coefficient.

lettuce grown in the same soil had similar concentrations of the short-chain compounds: PFBA (266 ng/g), PFPeA (236 ng/g).[9] In the municipal soil, PFAA celery concentrations were all less than 8 ng/g with the exception of PFOS (17 ng/g), which is most likely due to the relatively high concentration of PFOS and low concentrations of short-chain PFAAs in the soil (SI Table S4). All PFAA concentrations in the celery grown in control soil were less than 6 ng/g (SI Table S4). Concentrations of PFAAs in the pea fruit grown in industrially impacted soil were highest for PFBA (150 ng/g) and PFPeA (46 ng/g); all PFAAs were below LOQ (0.03−0.71 ng/g) for pea fruit grown in municipal and control soils (SI Table S4). Although no quantifiable data was collected to measure overall plant health in each of the three soils, qualitatively, more robust growth was observed for the plants grown in biosolids-amended soils versus the control soil. This increased vigor, in turn, likely led to increased transpiration, which may have promoted additional uptake of PFAAs. PFAA concentrations in the crops grown in the industrially impacted and municipal soils were compared to the control (unamended) treatments by an ANOVA test; statistical differences are shown in SI Figure S2. Low PFAA concentrations in the municipal and control soils limited the ability to determine accumulation trends, and thus the remainder of the results and discussion focuses on the crops grown in the industrially impacted soil.

Plant Compartments. PFAA concentrations in nonedible plant compartments grown in the industrially impacted soil were also analyzed and plotted alongside edible compartment concentrations in Figure 2. The concentrations of PFAAs in the radish shoot follow the same trends as in the radish root (and the soil), but are approximately 5−10 times higher. Physiologically, radishes lack the typical barrier (Casparian strip) between the edible bulb and the above ground shoot.[24] The swollen edible portion of the radish is actually formed at the intersection of the hypocotyl (embryonic stem) and the fine roots below; as the fine roots below the bulb are not generally eaten, they were not analyzed as part of the edible root portion. Therefore, although the analytes accumulate in the same proportions, more accumulation is seen in the shoot, perhaps due to the unrestricted upward flow of PFAAs. For celery, the shoot and root portions do not have parallel concentration trends. The celery shoot has higher concentrations of short-chain PFCAs while the celery root has higher concentrations of long-chain PFCAs and perfluoroalkyl sulfonates (PFSAs). The tomato plant has three compartments: root, shoot, and fruit. Within the tomato plant, the root has the highest concentrations of PFDA and PFOS, the longest chain compounds analyzed, whereas the tomato shoot has the highest concentrations of all the other PFAAs except PFPeA. The majority of PFAAs in the tomato fruit, as reported in Blaine et al.,[9] are short-chain compounds. Pea roots and shoots exhibit similar results to the celery and tomato in that long-chain compounds are highest in the roots while short-chain compounds are highest in the shoots. Pea fruit is similar to tomato fruit in that it accumulates primarily the short-chain compounds.

Bioaccumulation. *PFCAs.* Root to soil concentration factors plotted versus carbon chain length of PFCAs for the four crops grown in the industrially impacted soil are shown in Figure 3a; linear trend lines with equations and associated errors are also shown. In general, the RCF values of celery are greater than the other three crops, indicating more overall accumulation in celery root. This could be due to the greater surface area of celery roots or could be correlated to the total water transpired during the duration of the crop. Tomato and pea have very similar RCF values, most likely resulting from similar root physiology and crop duration times. The slopes of the trend lines for tomato and pea root are not statistically different from zero (α = 0.05), indicating no preferential accumulation of short- or long-chain PFCAs in the root tissues as compared to soil. Both of these crops have thicker tap root systems which may allow larger contaminants to cross the epidermis into the apoplast and yet be retained in the root tissue.[17] The trend line for radish shows a slope of −0.12, indicating a slight preference for uptake of the short-chain compounds. Taking into consideration that the edible portion of the radish root exhibits characteristics of both root and stem as a hypocotyl, this difference could reflect the prior impeded

dx.doi.org/10.1021/es500016s | Environ. Sci. Technol. 2014, 48, 7858−7865

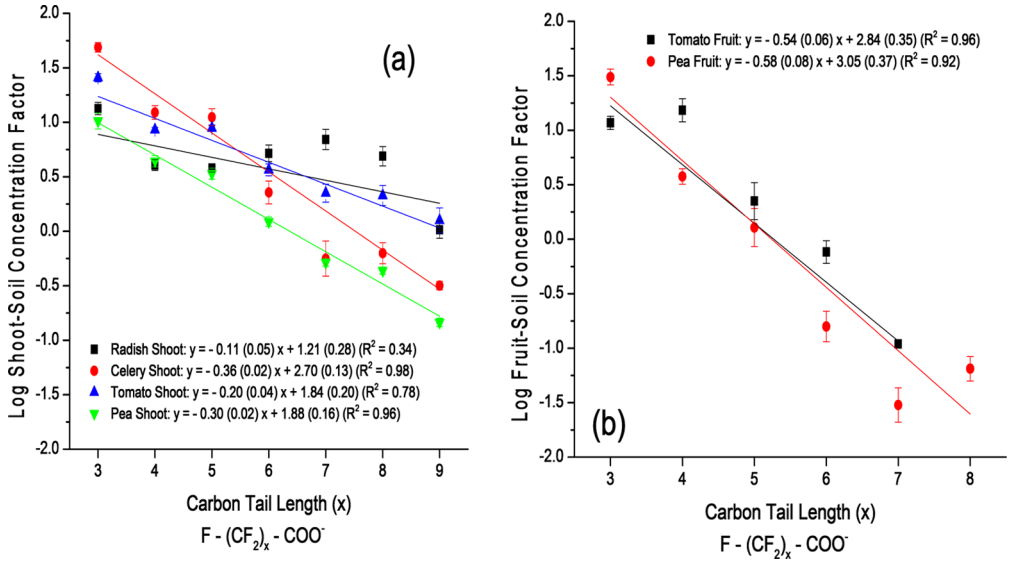


Figure 4. Correlations for PFCAs between log SCF (a) and log FCF (b) and carbon tail length in greenhouse radish, celery, tomato, and pea grown in industrially impacted soil. Means and standard errors are shown (n = 3−5). Linear regressions with slopes and intercepts; associated error values are shown parenthetically after each coefficient.

movement of long-chain compounds by the Casparian strip during translocation from the fine roots to the bulb. In this way, the radish data resemble more of a shoot trend than the expected root trend. However, other entryways into the hypocotyl may be possible (aquaporins or direct diffusion through hypocotyl endodermis) thus allowing more long-chain compounds than seen in the other crops.[24] The trend line for celery has a more obvious downward slope of −0.17, showing preferential entry for short-chain PFCAs. This could be due to the fact that celery has a very finely branched root system that is more likely to filter out larger contaminants by the Casparian strip at an early entry point. RCF_{pw} values were also calculated for PFCA accumulation in the four crops (Figure 3b). When plotted versus chain length, all four crops exhibit a U-shape that is consistent with the trend reported by Felizeter et al.[8] for hydroponically grown lettuce and by Krippner et al.[7] for maize. PFBA as well as the long-chain PFCAs have higher sorption tendencies to organic carbon,[23] thus reducing their concentrations in the pore water and driving up the RCF_{pw}.

Shoot to soil concentration factors plotted versus PFCA chain length are shown in Figure 4a with corresponding linear trend lines, equations and associated errors. Comparing among crops, celery shoots have higher accumulation of the short-chain PFCAs, likely due to exclusion of long chain PFCAs by the roots, while radish and tomato shoots have higher accumulation of the long-chain PFCAs. Pea shoots have the least amount of accumulation; perhaps the woody, dry characteristics of its stem and its minimal leaves reduce the available accumulation area in the shoots. Celery, tomato and pea SCFs show a decrease of 0.36, 0.20, and 0.30 log units, respectively, per CF_2 moiety. As these SCFs encompass the movement of PFCAs traveling from soil through the root to the shoots, the slightly larger value for celery (0.36) may reflect the fact that the preferential accumulation of short-chain length compounds in the celery root is compounded by additional increased selectivity from the root to shoots. When shoot-to-root (intercompartmental) factors are compared (SI Figure S3a), relative PFCA accumulation from roots to shoots are similar for celery and tomato; pea shows the greatest log decrease per CF_2 moiety. Overall, the preferential exclusion of long-chain PFCAs seen in celery, tomato, and pea shoots is consistent with the trend found for lettuce shoots (decrease of 0.3 log units) in Blaine et al.[9] and for maize shoots in Krippner et al.[7] Relative PFCA accumulation in radish shoots, however, is an exception: the trend of log SCF vs chain length is significantly flatter and the slope is statistically equivalent (α = 0.05) to the log RCF trend line (Figure 4a), resulting in no preferential accumulation of long- or short-chain PFCAs in the radish shoot as compared to the root (SI Figure S3a). Considering that once PFCAs are in the radish root (hypocotyl), no Casparian strip prevents upward translocation to the shoot; this lack of a trend is consistent with the Casparian strip serving as an important barrier to the interplant movement of long-chain PFCAs. Although, trend-wise, the radish root and shoot accumulation patterns correlate, more overall accumulation is seen in the shoot since after entry into the edible bulb, contaminants are subsequently transported upward with the flow of xylem and then accumulate in the leaves. There is potential for some of the smaller PFCAs to return to the bulb via the phloem as the plant stores nutrients for the winter in the bulb; however, this translocation is likely insignificant as radish is harvested before dormancy. In addition, small increases of PFAA concentration in the bulb may be obscured by growth dilution.

Fruit to soil concentration factor values for tomato and pea fruits for each PFCA are generally similar (i.e., on the same order of magnitude); however, variations in the values still exist due to the myriad of differences in the physiology of the roots and shoots encountered during translocation. In both tomato and pea plants, contaminants encounter additional membrane barriers (e.g., the cambium) in order to be loaded into the phloem and transported to their final destination (i.e., the fruit compartment). Additional chain length exclusion is evidenced by the decrease of 0.2 to 0.3 log units per carbon chain length for fruit to shoot concentration factors (SI Figure S3b) resulting in cumulative decreases of 0.54 and 0.58 log units per carbon chain length for fruit to soil accumulation factors (Figure 4b).

dx.doi.org/10.1021/es500016s | Environ. Sci. Technol. 2014, 48, 7858−7865

PFSAs. Bioaccumulation factors for PFSAs were also calculated (SI Table S6); however, as only three analytes were studied, chain length trends were not calculated with linear regressions. Differences between PFCAs and PFSAs seem to magnify from the roots upward. In the roots, all analyte RCFs are below 5, with the exception of PFBA. Values for SCFs for PFSAs are all below 8, compared to the SCFs for the short-chain PFCAs which reach up to 50. In tomato and pea, values of FCFs for PFSAs are all below 1, while values for short-chain PFCAs are primarily greater than 1. A more direct comparison can be made by comparing similar chain length analytes (e.g., PFPeA to PFBS or PFNA to PFOS). PFPeA has significantly higher values than PFBS for the celery and tomato SCFs as well as for both tomato and pea FCFs; PFNA compares fairly well to PFOS with the only significant difference being slightly higher SCF values in celery, tomato, and pea for PFOS. As the core structures of PFCAs and PFSAs are almost identical, the larger size of the sulfonate headgroup may be a contributing factor to the accumulation differences in the shoots and fruits for short-chain analytes. For larger analytes that are already restricted based on size, the larger headgroup may not matter as much. Other differences in accumulation patterns may be due to differing uptake mechanisms between PFCAs and PFSAs.[11]

Conceptual Model and Implications. Figure 1 shows a conceptual model of PFCA accumulation in tomato, a typical three compartment crop. The primary translocation pathway for PFCAs is illustrated via an enlarged root cross section and an outline showing movement of PFCAs from the soil all the way to the phloem. In addition, approximate bioaccumulation factors are shown for a tomato plant indicating increasing discrepancy in PFCA accumulation per CF_2 moiety with acropetal movement. Although the scope of this study was not fully mechanistic, uptake and distribution factors likely include specific plant physiology and transpiration rate parameters.

In general, chain length dependent accumulation is seen as PFCAs translocate upward from the roots. Each crop is anatomically different, presenting unique biological barriers in the translocation process; however, some common barriers do exist, namely the Casparian strip and in general, the permeation of membranes. To effectively model plant uptake of PFAAs, these various crop-specific factors as well as contaminant-specific factors must be considered. Plant factors examined in this paper were root structure and number of compartments, while the contaminant-specific factors examined included chain length and headgroup. Without plant-specific data, the best prediction that can be made consists of a generalization about plant compartment accumulation. In general, the data presented here suggest edible fruit crops accumulate fewer long-chain PFCAs than do edible shoot or root crops. For example, one would expect that 5 g of peas or tomatoes would contain roughly 5−25 times less PFOA than 5 g of celery or radish grown in the same soil. With a good understanding of plant physiology, it may be possible to extrapolate these generalizations to other crops; however, caution is warranted since visually similar crops can have anatomical or physiological differences that can significantly alter uptake potential. In terms of analytes, there is a much larger discrepancy; one could expect that shoot and fruit crops may have 1−3 orders of magnitude more PFBA than PFOA if these two analytes are present in equal concentrations in the soil. With industry trends shifting toward the use of short-chain PFAAs, it is important to recognize this increased potential of PFAA entry into the terrestrial food chain via plants.

With respect to overall exposure, it is unlikely that edible crops grown in soils conventionally amended for nutrients with biosolids (that are not impacted by PFAA industries) are a primary source of long-chain PFAA exposure to humans; this has also been suggested from recent food basket studies.[25] However, in the absence of comprehensive toxicological data on short-chain PFAAs, precaution may be warranted for production of fruit or shoot crops grown in PFAA contaminated soils. More work is needed to discern all applicable factors needed to comprehensively mechanistically model PFAA uptake in plants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional details are available regarding analytical methods, greenhouse experiment details, experimental design, PFAA concentrations in soils and crops, and plots of intercompartmental concentration factors. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chiggins@mines.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research is funded by a RARE grant from the U.S. EPA, and is supported by efforts from the Metropolitan Water Reclamation District of Greater Chicago. We appreciate the help of various U.S. EPA staff, and in particular, Lee Thomas (Region 4), Carole Braverman, Bradley Grams, Gerald Golubski, Kenneth Gunter, Erin Newman, Thomas Poy, David Schroeder (Region 5), Mark Strynar, Rebecca McMahan and Shuang Liang (ORD). We would also like to acknowledge the help of Kate Percival and Karen Kazor from CSM and Cecil Stushnoff from Colorado State University. The information in this document has been funded by the U.S. Environmental Protection Agency. It has been subjected to review by the Region 5 Office and the Office of Research and Development (ORD) and approved for publication. Approval does not signify that the contents reflect the views of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

■ REFERENCES

(1) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integr. Environ. Assess. Manage.* **2011**, *7* (4), 513−41.

(2) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry - Characterization of municipal wastewaters. *Environ. Sci. Technol.* **2006**, *40* (1), 289−295.

(3) Sepulvado, J. G.; Blaine, A. C.; Hundal, L. S.; Higgins, C. P. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. *Environ. Sci. Technol.* **2011**, *45* (19), 8106−8112.

(4) Lechner, M.; Knapp, H. Carryover of Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant and

distribution to the different plant compartments studied in cultures of carrots (*Daucus carota* ssp *Sativus*), potatoes (*Solanum tuberosum*), and cucumbers (*Cucumis Sativus*). *J. Agric. Food. Chem.* **2011**, *59* (20), 11011−11018.
(5) Lu, Q.; He, Z. L.; Stoffella, P. J. Land application of biosolids in the USA: A review. *Appl. Environ. Soil Sci.* **2012**, 1−11.
(6) Stahl, T.; Riebe, R. A.; Falk, S.; Failing, K.; Brunn, H. Long-term lysimeter experiment to investigate the leaching of perfluoroalkyl substances (PFASs) and the carry-over from soil to plants: Results of a pilot study. *J. Agric. Food Chem.* **2013**, *61* (8), 1784−1793.
(7) Krippner, J.; Brunn, H.; Falk, S.; Georgii, S.; Schubert, S.; Stahl, T. Effects of chain length and pH on the uptake and distribution of perfluoroalkyl substances in maize (*Zea mays*). *Chemosphere* **2014**, *94*, 85−90.
(8) Felizeter, S.; McLachlan, M.; Voogt, P. Uptake of perfluorinated alkyl acids by hydroponically grown lettuce (*Lactuca sativa*). *Environ. Sci. Technol.* **2012**, *46*, 11735−11743.
(9) Blaine, A. C.; Rich, C. D.; Hundal, L. S.; Lau, C.; Mills, M. A.; Harris, K. M.; Higgins, C. P. Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: Field and greenhouse studies. *Environ. Sci. Technol.* **2013**, *47* (24), 14062−14069.
(10) Lee, H.; Tevlin, A. G.; Mabury, S. A.; Mabury, S. A. Fate of polyfluoroalkyl phosphate diesters and their metabolites in biosolids-applied soil: Biodegradation and plant uptake in greenhouse and field experiments. *Environ. Sci. Technol.* **2013**, *48* (1), 340−349.
(11) Wen, B.; Li, L. F.; Liu, Y.; Zhang, H. N.; Hu, X. Y.; Shan, X. Q.; Zhang, S. Z. Mechanistic studies of perfluorooctane sulfonate, perfluorooctanoic acid uptake by maize (*Zea mays* L. cv. TY2). *Plant Soil* **2013**, *370* (1−2), 345−354.
(12) Trapp, S. Plant uptake and transport models for neutral and ionic chemicals. *Environ. Sci. Pollut. Res.* **2004**, *11* (1), 33−39.
(13) Collins, C.; Fryer, M.; Grosso, A. Plant uptake of non-ionic organic chemicals. *Environ. Sci. Technol.* **2006**, *40* (1), 45−52.
(14) Dettenmaier, E. M.; Doucette, W. J.; Bugbee, B. Chemical hydrophobicity and uptake by plant roots. *Environ. Sci. Technol.* **2009**, *43* (2), 324−329.
(15) Michel, M.; Buszewski, B. Isolation, determination and sorption modelling of xenobiotics in plant materials. *Polym. J. Environ. Stud.* **2008**, *17* (3), 305−319.
(16) Taiz, L.; Zeiger, E. *Plant Physiology*, 5th ed.; Sinauer Associates Inc.: Sunderland, MA, 2010.
(17) Trapp, S. Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. *Pest Manage. Sci.* **2000**, *56* (9), 767−778.
(18) Mench, M.; Schwitzguebel, J. P.; Schroeder, P.; Bert, V.; Gawronski, S.; Gupta, S. Assessment of successful experiments and limitations of phytotechnologies: Contaminant uptake, detoxification and sequestration, and consequences for food safety. *Environ. Sci. Pollut. Res.* **2009**, *16* (7), 876−900.
(19) Katayama, A.; Bhula, R.; Burns, G. R.; Carazo, E.; Felsot, A.; Hamilton, D.; Harris, C.; Kim, Y. H.; Kleter, G.; Koedel, W.; Linders, J.; Peijnenburg, J.; Sabljic, A.; Stephenson, R. G.; Racke, D. K.; Rubin, B.; Tanaka, K.; Unsworth, J.; Wauchope, R. D. Bioavailability of xenobiotics in the soil environment. In *Reviews of Environmental Contamination and Toxicology*; Whitcare, D. M., Ed.; Springer: New York, 2010; Vol. *203*, pp 1−86.
(20) Trapp, S.; Eggen, T. Simulation of the plant uptake of organophosphates and other emerging pollutants for greenhouse experiments and field conditions. *Environ. Sci. Pollut. Res.* **2013**, *20* (6), 4018−4029.
(21) Vierke, L.; Berger, U.; Cousins, I. T. Estimation of the acid dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport. *Environ. Sci. Technol.* **2013**, *47* (19), 11032−11039.
(22) Yoo, H.; Washington, J. W.; Jenkins, T. M.; Ellington, J. J. Quantitative determination of perfluorochemicals and fluorotelomer alcohols in plants from biosolid-amended fields using LC/MS/MS and GC/MS. *Environ. Sci. Technol.* **2011**, *45* (19), 7985−7990.
(23) Guelfo, J. L.; Higgins, C. P. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol.* **2013**, *47* (9), 4164−4171.
(24) Suga, S.; Murai, M.; Kuwagata, T.; Maeshima, M. Differences in aquaporin levels among cell types of radish and measurement of osmotic water permeability of individual protoplasts. *Plant Cell Physiol.* **2003**, *44* (3), 277−286.
(25) Herzke, D.; Huber, S.; Bervoets, L.; D'Hollander, W.; Hajslova, J.; Pulkrabova, J.; Brambilla, G.; De Filippis, S. P.; Klenow, S.; Heinemeyer, G.; de Voogt, P. Perfluorinated alkylated substances in vegetables collected in four European countries; occurrence and human exposure estimations. *Environ. Sci. Pollut. Res. Int.* **2013**, *20* (11), 7930−9.

DEPARTMENT OF ECOLOGY
State of Washington

PFAS Concentrations in Effluent, Influent, Solids, and Biosolids of Three Wastewater Treatment Plants

November 2022

Publication 22-03-028

Publication Information

This report is available on the Department of Ecology's website at:
https://apps.ecology.wa.gov/publications/SummaryPages/2203028.html.

Data for this project are available in Appendix B of this report.

The Activity Tracker Code for this study is 21-023.

Suggested Citation
Bothfeld, F. and C. Mathieu. 2022. PFAS Concentrations in Influent, Effluent, Solids, and Biosolids of Three Wastewater Treatment Plants. Publication 22-03-028. Washington State Department of Ecology, Olympia.
https://apps.ecology.wa.gov/publications/SummaryPages/2203028.html.

Contact Information

Publications Team
Environmental Assessment Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 360-407-6764

Washington State Department of Ecology – https://ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Shoreline 206-594-0000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

PFAS Concentrations in Influent, Effluent, Solids, and Biosolids of Three Wastewater Treatment Plants

by

Frances Bothfeld

Water Quality Program
Washington State Department of Ecology
Olympia, Washington

Callie Mathieu

Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington

Table of Contents

List of Tables

Acknowledgments

The authors of this report thank the following people for their contributions to this study:

- Washington State Legislature
- Staff of the three wastewater treatment plants sampled
- Washington State Department of Ecology staff:
  - Jakub Bednarek
  - Lisa Euster
  - Charles Hoffman
  - Emily Kijowski
  - Karen Dinicola
  - Christina Frans
  - Nancy Rosenbower

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals that have a wide range of commercial and industrial uses. However, they are also known as “forever chemicals” due to widespread ubiquity and persistence in the environment. While not considered a source themselves, wastewater treatment plants (WWTPs) are a known pathway for PFAS to enter surface water and groundwater.

In 2021, the Washington State Department of Ecology (Ecology) carried out a study to evaluate concentrations of PFAS from three municipal WWTPs that receive influent likely to contain PFAS. In February 2021, Ecology collected samples of influent, effluent, sludge, and biosolids for analysis of PFAS. The goals of this study were to (1) have an initial reconnaissance of PFAS concentrations along several points in a wastewater system in Washington state, (2) better understand how PFAS moves through WWTPs with varying treatment types, and (3) evaluate PFAS speciation in a WWTP.

The study found that the three WWTPs sampled generally contained PFAS concentrations consistent with levels typically found in non-industrial effluents in the United States. PFAS concentrations in the WWTP effluent were below the five state action levels (SALs) for drinking water, with the exception of perfluorooctanoate (PFOA) concentrations in the effluent of one WWTP that were above the SAL of 10 ng/L. PFAS concentrations in the solids were a magnitude higher than concentrations found in the influents and effluents (parts per billion vs parts per trillion) with longer chained PFAS often partitioning out into the solids.

A larger scale study with more data, both in frequency and location, is recommended before determining the need for WWTPs to monitor for PFAS. Also, more information is needed before determining if regular monitoring of PFAS in biosolids is necessary.

Introduction

Introduction to Per- and Polyfluoroalkyl Substances

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals that contain carbon-fluorine bonds. PFAS usually have a hydrophilic head, followed by a chain of carbon and fluorine bonds. Perfluoroalkyl carboxylic acids (PFCAs) with less than seven carbons, and perfluoroalkyl sulfonic acids (PFSAs) with less than six carbon chain lengths, are considered "short chain." Whereas PFCAs and PFSAs with carbon chain lengths greater than seven and six, respectively, are considered "long chain." Perfluoroalkyl substances are fully fluorinated and every hydrogen in the carbon chain has been replaced with a fluorine. Polyfluoroalkyl substances are not fully fluorinated and at least one hydrogen bond remains.

PFAS chemicals have been produced since the 1940s and over 6,000 substances have entered commerce since (US EPA, 2021). However, there are more PFAS than the known, commercially derived PFAS because they can degrade into breakdown products (Washington et al., 2015). Moreover, there is a class of PFAS chemicals known as precursors that are chemicals, both known and unknown, which break down to form perfluoroalkyl acids in the environment (Washington et al., 2015).

PFAS are useful chemicals because they repel oil, water, and grease. They are used in many applications, such as household products, clothing, food packaging, manufacturing processes, and firefighting foam. However, research now shows that PFAS can be bioaccumulative and toxic to human and aquatic life. Furthermore, PFAS received the moniker "forever chemicals" because they are persistent in the environment and not easily removed.

While there is a lot of research on common PFAS, the full extent of PFAS toxicity is not fully known (ITRC, 2020). A lot of information and data goes into developing a toxicity profile, which is hard to gather due to the sheer amount of PFAS in commerce. There are many PFAS chemicals, like precursors and terminal breakdown products, which are unknown and, therefore, have unknown toxicological effects. Furthermore, there is little information gathered about synergistic toxicological effects (Aherns & Bundschuh, 2014).

PFAS and Wastewater Treatment Plants

PFAS is widespread in surface water, but information on the sources, extent, and toxicological impacts is lacking. One potential environmental pathway that needs to be further explored is PFAS discharged from wastewater treatment plants (WWTPs) via effluent. WWTP effluent can contain PFAS contamination from industrial sources; personal care products, laundry and other household sources; and landfill leachate. It is anticipated that in comparison to household/domestic sources and landfill leachate, industrial sources can contribute much larger loads of PFAS by volume to WWTPs.

Once PFAS enter a WWTP, little is known about how PFAS transforms within the treatment plant (Liu & Mejia Avendaño, 2013). PFAS can either settle out into solids (sludge or biosolids) or end up in the effluent in its original form or as a breakdown or transformed chemical (Ebrahimi et al., 2021). Most WWTPs currently do not use treatment technologies that are able to remove PFAS from effluent. Removal requires advanced treatment technologies (e.g., reverse osmosis, ozonation plus granular activated carbon, ion resin exchange) that are not used at most WWTPs (Kucharzyk et al., 2017).

WWTPs are a central collection point for multiple wastewater/sanitary sewer streams that contain PFAS. Due to the lack of advanced treatment methods, PFAS can be found in the WWTPs' effluent and downstream receiving waters. A 2016 study of PFAS in Washington state surface waters found that PFAS were elevated in waterbodies receiving a large proportion of WWTP effluent and that WWTP effluent appears to be a significant pathway for short-chain PFAAs and PFOA into surface water under hydrological conditions of limited dilution (Mathieu & McCall, 2017).

Goals of This Study

The Washington State Department of Ecology (Ecology) developed a Chemical Action Plan (CAP) to address PFAS contamination in Washington's waters (Ecology, 2021). One of the recommendations of the CAP was to evaluate PFAS in wastewater. Ecology received funding to start this evaluation. Ecology sampled three WWTPs with differing treatment trains at the influent, effluent, sludge, and biosolids (when applicable).

The goals of this study were to:

- Characterize PFAS concentrations along several points of a wastewater treatment process.
- Better understand how PFAS moves through a WWTP in different wastewater treatment trains.
- Evaluate PFAS speciation in a WWTP.

This study will add to Ecology's growing list of PFAS studies supporting a broader perspective on PFAS in Washington state.

Methods

Sample Collection

In 2021, Ecology field staff collected samples of influent, effluent, waste activated sludge (WAS), and biosolids (when applicable) from three selected WWTPs. Sampling occurred on February 9 and February 11. Table 1 describes the sampling locations for each plant. Sampling occurred during a period of dry weather. Plant operators confirmed that no infiltration and inflow was occurring at the time of collection. Light snow was observed on the February 11 sampling date, but no accumulation occurred prior to or during sampling.

All aspects of sampling followed the Quality Assurance Project Plan (QAPP; Hoffman, 2021), including protocols to avoid PFAS cross contamination. Field equipment was decontaminated prior to and between sampling with the following protocol:

1. Rinse with tap water.
2. Hand wash/scrub with Liquinox soap.
3. Rinse with tap water.
4. Rinse with 100% methanol.

Field staff used new, clean nitrile gloves for each sampling point within a facility and followed practices for low-level contaminant sampling.

All samples were stored on ice until the end of the sample collection day, at which point they were placed inside Ecology Headquarters chain of custody room freezers. Samples were held frozen at -20 °C and shipped to AXYS SGS Analytical Services Ltd. laboratory for analysis. Chain of custody was maintained and recorded throughout the study.

Table 1. Collection dates and sampling point location descriptions

WWTP	Date of Sample Collection	Plant Type	Influent Sampling Point	Effluent Sampling Point	Sludge Sampling Point	Biosolids Sampling Point
Plant A	2/11/2021	Activated sludge, biological nitrogen removal	After headworks screens and grit tanks	Effluent channel before discharge/ outfall	WAS daylighted tank, post-secondary clarifier	Dewatered cake solids at conveyor belt
Plant B	2/11/2021	Activated sludge, pure oxygen	After headworks screen, post-sand/grit removal	Final effluent port before discharge/ outfall	WAS pump line before DAF thickeners, after secondary clarifier and return solids well	Dewatered cake solids at screw press
Plant C	2/9/2021	Reclaimed water facility, biological treatment and microfiltration	After headworks screen, before any treatment (no grit removal at this plant)	At final effluent sampler point, distribution pump/ clear well	WAS pump line	n/a

WAS = waste activated sludge; DAF = dissolved air flotation; n/a = not applicable

Influent and Effluent

Field staff collected individual grab samples in the morning, mid-day, and afternoon from each influent and effluent sampling point. Grab samples were then hand composited by equal volumes (about 166 mL) from each grab into laboratory-provided 500 mL HDPE containers. Grab samples and finished composite samples were kept in laboratory-provided enclosure bags and stored in coolers with bagged wet ice.

Influent and effluent samples were collected at, or as near as possible to, the plants' compositor sampling points. The plant composite samplers were not used for sample collection to avoid potential PFAS contamination from tubing or other parts inside the equipment. Field staff removed grates nearest to the plant sampling locations and lowered a clean, laboratory-provided transfer bottle attached to a sampling pole into the influent or effluent channel. Samples were collected from a representative, well-mixed location in the channel accessible from the grate at about 10-20 cm below the surface.

All influent and effluent samples were collected by sampling pole from the channel with the exception of effluent from Plant B. The Plant B effluent sample was collected from the final effluent port prior to discharge/outfall for accessibility reasons. The final effluent port was purged for about two minutes prior to sample collection.

Waste Activated Sludge

WAS samples were collected from each of the WWTPs as individual grab samples. WAS from Plants A and B was collected mid-day, and WAS from Plant C was collected mid-morning. Ecology field staff collected WAS from Plant A by lowering a decontaminated stainless steel dip sampler into a daylight WAS tank about 10-20 cm below the surface and filling all three sample jars from the first dip sample. At Plants B and C, WAS samples were collected via ports. For these samples, the plant operator purged the WAS sample port for two minutes, then Ecology field staff filled sampling jars directly from the port. WAS samples were placed into laboratory-provided 250 mL HDPE jars and enclosure bags and placed in coolers with bagged wet ice.

Biosolids

Biosolids samples were collected mid-day as individual grabs from only Plants A and B. No biosolids were sampled from Plant C because a representative sample was not possible at this plant. Biosolid samples consisted of dewatered cake solids at the final accessible sampling point prior to leaving the facility. For Plant A, biosolids were collected directly from the conveyor belt by hand. At Plant B, biosolids were collected from a screw press auger removed by the WWTP operator. Ecology field staff filled laboratory-provided 250 mL HDPE jars about 80% full of the solids, then placed the jars into enclosure bags and stored them in coolers with bagged wet ice.

Laboratory Analysis

AXYS SGS Analytical Services Ltd. analyzed all samples for 40 PFAS following their in-house method, MLA-110 Rev. 02 Ver. 11., *Analytical Procedure for the Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Samples, Solids, Tissues, AFF Products, Blood/Serums and Solvent Extracts by LC-MS/MS.* Appendix A lists the PFAS analyzed for, along with their CAS numbers, median reporting limits, and median detection limits.

Influent and effluent samples were extracted and cleaned up using solid phase extraction as required by the Department of Defense Quality Systems Manual (DOD QSM) Table B-15 criteria (DOD/DOE, 2019) with weak anion exchange cartridges. Extracts were then treated with carbon powder and spiked with recovery standards. Isotopically labeled surrogate standards (extracted internal standards) were added to all field and quality control (QC) samples prior to extraction.

WAS and biosolids samples were spiked with isotopically labeled surrogate standards then extracted by shaking with a methanolic ammonium hydroxide solution. The supernatants were then combined, treated with ultra-pure carbon powder and evaporated to remove methanol. The solutions were cleaned up by solid phase extraction using weak anion exchange cartridges and spiked with recovery standards.

All sample extracts were analyzed on an ultrahigh performance liquid chromatograph with a reversed phase C18 column coupled to a triple quadrupole mass spectrometer (LC-MS/MS). Final sample concentrations were determined by isotopic dilution/internal standard quantification. Samples were analyzed in three batches: (1) influent samples, (2) effluent samples, and (3) WAS and biosolid samples.

Limits of quantitation (LOQs) were based on the lowest calibration standard analyzed during calibration with adjustments for sample amount extracted and considerations to baseline noise levels. The sample-specific detection limit (SDL) was based on the signal to noise ratio (S/N > 3.0) of the instrument per target analyte. PFAS concentrations reported include the total of linear and branched isomers. An accreditation waiver was obtained from Ecology's Quality Assurance Officer for seven analytes, as these compounds are newly developed, and no laboratory currently holds accreditation with Washington state for them. These compounds are denoted in Appendix A by asterisk.

Data Quality

Manchester Environmental Laboratory's (MEL's) Quality Assurance Coordinator completed an independent party Stage 4 data validation on all lab results for this project. The data validation was conducted using manual review and verification per the technical specifications of the method, the QAPP (Hoffman, 2021), and validation guidance documents (DOD/DOE, 2019; DOD, 2020; EPA, 2016). MEL provided a written data validation report describing the analytical method used, holding times, initial and ongoing calibrations, and results of QC tests analyzed with each batch. All QC tests outlined in the QAPP were analyzed with each batch, including method blanks, laboratory control samples (LCS), matrix spikes, matrix spike duplicates, field replicates, and field/equipment blanks.

The data validation confirmed that the lab followed the analytical method for all samples, with no errors or omissions. All results were deemed usable as qualified for this study, with the following exception. The data validator recommended rejection of several samples based on corrective actions outlined in DOD (2020) for detected and non-detected analytes quantitated with surrogates having percent recoveries of less than 20%. The QC tests associated with the rejected results all had acceptable surrogate recoveries, suggesting that matrix effects in the samples were responsible for poor surrogate performance. The samples rejected include PFBA in all influent and effluent samples collected from Plant C, as well as several samples for N-EtFOSA, N-MeFOSA, and N-EtFOSE, N-MeFOSE, and one sample for PFTeDA.

Qualifiers were added to final results based on QC tests that fell outside of acceptance limits. All detected concentrations below the LOQ, but above the SDL were qualified "J" as estimated values. No results were reported below the SDL. Results that met all qualitative criteria for compound detection except for mass-ion ratios were qualified as "NJ" or tentatively identified and estimated.

Method Blanks

No target analytes were detected in any of the method blanks at or above the method detection limit. No results were qualified based on method blanks.

Laboratory Control Samples

All LCS percent recoveries were within MQOs outlined in the QAPP and requirements of the DOD QSM Table B-15.

Matrix Spikes/Matrix Spike Duplicates

Six results were qualified "J" as estimates based on a potential high bias indicated by matrix spike recoveries. The affected results included PFBS (A-EFF-3), PFDA (A-INF-3), PFOS (A-INF-3), PFTrDA (A-BIO-3), PFBS (A-BIO-3), and N-EtFOSAA (A-BIO-3). The relative

percent difference between matrix spikes and matrix spike duplicates were within MQOs and resulted in no qualifications to the data.

Field Blanks

At each influent and effluent sampling point, a field blank was collected prior to the morning grab sample. Field blanks consisted of laboratory-provided blank water poured into new laboratory-provided sampling bottles at the sampling site with the same sampling pole used for field sample collection. PFDA was detected at a concentration of 0.576 ng/L in one field blank collected alongside the Plant A effluent samples. PFDA results in the associated effluent samples were less than five times the field blank result, and thus qualified as not detected ("U"). No other analytes were detected in the field blanks.

An equipment rinseate blank was collected from the stainless-steel dip sampler used to sample WAS from Plant A. No PFAS analytes were detected in the equipment rinseate blank.

Field Replicates

Triplicate samples were collected at every sampling point for this study. Results of triplicate analysis were assessed by calculating relative standard deviation (RSD) of each analyte. For influent and effluent samples, the RSD control limit was 30% for results greater than 5 times the LOQ. For results less than five times the LOQ, the absolute difference between the sample and replicate had to be less than the LOQ for aqueous matrices and less than two times the LOQ for solid matrices. Six out of 440 replicate RSDs exceeded the control limit. Affected results were qualified "J" or "UJ" (if undetected), to indicate the value is an estimate.

Results

PFAS concentrations measured in influent, effluent, sludge, and biosolids from the three WWTPs are presented in Tables 2 through 7. Values given in the tables represent the average of triplicate results for each sample. Appendix B provides individual sample results of the full dataset. Aqueous samples are reported as ng/L (parts per trillion; ppt), and solids samples are reported on a ng/g dry weight (dw) basis (parts per billion; ppb).

Perfluoroalkyl Carboxylates

Table 2 presents average PFCA concentrations in influent and effluent and Table 3 presents PFCA concentrations measured in the sludge and biosolids sampled. Short chain PFCAs were generally detected more frequently in the influent and effluent and long chain PFCAs were mostly present in the sludge and biosolids samples. PFHxA and PFOA were detected in all samples and matrices.

The influent and effluent samples contained short chain PFCAs and PFOA in the range of 1.0 – 13 ng/L, with the exception of higher concentrations of PFPeA and PFHxA measured in the effluent of Plant C (231 and 133 ng/L, respectively). Concentrations of PFPeA and PFHxA in the influent of this plant were much lower (10.5 and 8.6 ng/L, respectively).

PFPeA, PFHxA, and PFDA were present in the sludge of Plant C at relatively higher concentrations (18.4 – 21.8 ng/g). PFHxA and long chain PFCAs were present in all biosolids samples, at relatively low concentrations (0.3 – 3.1 ng/g).

Table 2. Perfluoroalkyl carboxylate results in aqueous samples (ng/L, ppt).

Plant	Sample Type	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrDA	PFTeDA
Plant A	Influent	**7.02 J**	**5.09**	**7.31**	**1.77**	**3.85**	**0.88 NJ**	**0.55 J**	ND	ND	ND	ND
Plant A	Effluent	**12.6**	**6.03**	**13.5**	**2.22**	**5.00**	**0.64 J**	ND	ND	ND	ND	ND
Plant B	Influent	**6.89 J**	**5.70**	**11.81**	**3.34**	**6.33**	**1.42 J**	**0.55 J**	ND	ND	ND	ND
Plant B	Effluent	**7.95**	**6.53**	**18**	**3.38**	**7.13**	**1.09 J**	**0.58 J**	ND	ND	ND	ND
Plant C	Influent	REJ	**10.5**	**8.60**	**0.86 J**	**2.57**	ND	ND	ND	ND	ND	ND
Plant C	Effluent	REJ	**231**	**133**	**2.76**	**12.3**	**0.57 J**	**0.76 J**	ND	ND	ND	ND

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
REJ = Result was rejected.

Table 3. Perfluoroalkyl carboxylate results in solids samples (ng/g dw, ppb).

Plant	Sample Type	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrDA	PFTeDA
Plant A	Sludge	ND	ND	**2.50 J**	ND	**1.53 J**	ND	**2.28 J**	**1.23 NJ**	**1.66 J**	ND	ND
Plant A	Biosolids	ND	ND	**1.14 J**	ND	**0.99 J**	**1.87**	**3.13 J**	**1.32 J**	**1.91 J**	**1.12 J**	**0.84 J**
Plant B	Sludge	ND	ND	**8.19 J**	ND	**2.43 J**	ND	**2.03 NJ**	ND	ND	ND	ND
Plant B	Biosolids	ND	ND	**1.49 J**	ND	**0.34 J**	**0.91 J**	**1.84**	**0.82 J**	**1.32 NJ**	**0.579 J**	**0.73 J**
Plant C	Sludge	ND	**18.4**	**21.8**	ND	**6.96**	**1.80 J**	**18.6**	**1.43 NJ**	**4.21 J**	ND	ND

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
NJ = There is evidence the analyte is present and the associated numerical result is an estimate.

Perfluoroalkyl Sulfonates

Average PFSA concentrations in influent and effluent samples are provided in Table 4 and concentrations in sludge and biosolids are presented in Table 5. PFBS and PFOS were consistently detected in all samples and matrices. PFHxS was detected in all influent, effluent, and biosolids, but in only one sludge sample. Other PFSAs were infrequently detected, and at low concentrations.

In influent and effluent samples, PFBS was found at the highest concentrations (2.3 – 26.7 ng/L), followed by PFOS (2.0 – 11.9 ng/L), and PFHxS (0.99 – 6.9 ng/L). PFBS concentrations were higher in effluent than influent at all plants, and PFOS concentrations in the effluent were lower than in the influent at all plants.

PFOS was the dominant PFSA in the sludge and biosolids, with concentrations in the range of 22 – 37 ng/g in the sludge and 26 – 29 ng/g in the biosolids. PFDS and PFDoS were present at 5.0 and 8.8 ng/g in the sludge of Plant B, and all other detected PFSAs were present at less than 5 ng/g.

Table 4. Perfluoroalkyl sulfonate results in aqueous samples (ng/L, ppt).

Plant	Sample Type	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS
Plant A	Influent	**15.1**	**1.18 J**	**6.94**	ND	**11.9**	ND	**0.51**	ND
Plant A	Effluent	**26.7**	**1.15 J**	**5.98**	ND	**5.92**	ND	ND	ND
Plant B	Influent	**15.2**	**ND**	**4.43**	ND	**11.5 NJ**	ND	ND	ND
Plant B	Effluent	**22.7**	**0.54 NJ**	**3.92**	ND	**7.04**	ND	ND	ND
Plant C	Influent	**2.33**	**ND**	**2.37 NJ**	ND	**5.36 NJ**	ND	**0.51 NJ**	ND
Plant C	Effluent	**7.93**	**ND**	**0.99 J**	ND	**2.03**	ND	ND	ND

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
NJ = There is evidence the analyte is present and the associated numerical result is an estimate.

Table 5. Perfluoroalkyl sulfonate results in solids samples (ng/g dw).

Plant	Sample Type	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS
Plant A	Sludge	**1.69 J**	ND	ND	ND	**21.6**	ND	**1.15 NJ**	ND
Plant A	Biosolids	**4.49 NJ**	ND	**0.44 NJ**	ND	**28.5**	ND	**1.52 NJ**	ND
Plant B	Sludge	**2.34 J**	ND	**ND**	ND	**36.6**	ND	**5.01 J**	**8.83 NJ**
Plant B	Biosolids	**1.79 NJ**	ND	**1.51 NJ**	ND	**29.1**	**0.42 NJ**	**2.04 NJ**	**1.33 NJ**
Plant C	Sludge	**1.45 NJ**	ND	**3.94 NJ**	ND	**22.2**	ND	**ND**	ND

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
NJ = There is evidence the analyte is present and the associated numerical result is an estimate.

Perfluoroalkyl Acid Precursors

Tables 6 and 7 present the results of perfluoroalkyl acid precursors in aqueous and solids samples. Of the precursor analyte suite, 5:3 FTCA was the most frequently detected, and at the highest concentrations. Concentrations of 5:3 were highly variable, ranging from non-detect – 199 ng/L in the influent and effluent, and 151 – 329 ng/g in the sludge and biosolids. 7:3 FTCA was also detected in the solids of two of the plants, at concentrations of 23 – 46 ng/g.

6:2 FTS was detected in several aqueous samples (2.6 – 6.0 ng/L), but not in the sludge or biosolids. Several perfluoroalkane sulfonamido substances were detected, primarily in the sludge and biosolids samples: MeFOSAA, EtFOSAA, N-MeFOSE, and N-EtFOSE. Concentrations of the perfluoroalkane sulfonamidos ranged from non-detect – 29 ng/g in the solids samples.

Table 6. Perfluoroalkyl acid precursor results in aqueous samples (ng/L).

Plant	Sample Type	6:2 FTS	PFOSA	MeFOSAA	EtFOSAA	N-MeFOSE	N-EtFOSE	5:3 FTCA	7:3 FTCA
Plant A	Influent	**2.68 J**	ND	**0.66 J**	ND	ND	REJ	**199 J**	ND
Plant A	Effluent	ND	ND	**0.68 J**	ND	ND	ND	ND	ND
Plant B	Influent	**4.52 J**	ND	ND	ND	ND	REJ	**113**	ND
Plant B	Effluent	**6.01 J**	ND	ND	**0.78 J**	ND	ND	**27.4 J**	ND
Plant C	Influent	ND	ND	ND	ND	ND	ND	ND	ND
Plant C	Effluent	ND	ND	ND	ND	ND	ND	ND	ND

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit. REJ = Result was rejected.
Analytes in this group not shown because they were not detected in any samples: 4:2 FTS, 8:2 FTS, N-MeFOSA, N-EtFOSA, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, 3:3 FTCA, PFEESA, PFMPA, PFMBA, NFDHA.

Table 7. Perfluoroalkyl acid precursor results in solids samples (ng/g dw).

Plant	Sample Type	6:2 FTS	PFOSA	MeFOSAA	EtFOSAA	N-MeFOSE	N-EtFOSE	5:3 FTCA	7:3 FTCA
Plant A	Sludge	ND	ND	**9.77 J**	**3.29 J**	ND	**4.71 J**	**329**	**46.2 J**
Plant A	Biosolids	ND	**0.53 J**	**21.0**	**3.91**	ND	**4.90 J**	**267**	**23.3 J**
Plant B	Sludge	ND	**ND**	**3.51 J**	**11.6 J**	**29.3 J**	**10.6 J**	**307**	**ND**
Plant B	Biosolids	ND	**0.81 J**	**4.76**	**6.53**	**REJ**	**REJ**	**151**	**25.1 J**
Plant C	Sludge	ND	**2.89 J**	**7.33 J**	**4.10 J**	ND	ND	ND	**167**

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit. REJ = Result was rejected.

Analytes in this group not shown because they were not detected in any samples: 4:2 FTS, 8:2 FTS, N-MeFOSA, N-EtFOSA, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, 3:3 FTCA, PFEESA, PFMPA, PFMBA, NFDHA.

Discussion

Comparison to Other U.S. WWTPs

Table 8 presents a comparison of this study's PFAS concentrations in effluent with a nationwide, non-industrial average calculated by Thompson et al. (2022), as well as previous effluent sampling in Washington state.

PFAS concentrations in the effluents tested for this study were within the range of non-industrial WWTP effluent throughout the United States. Thompson et al. (2022) calculated nationwide mean PFOA and PFOS concentrations in effluents with no industrial source and outliers omitted as 8.4 ng/L and 10 ng/L, respectively. PFOA and PFOS concentrations measured for this study ranged from 5.0 – 12 ng/L (PFOA) and 2.0 – 7.0 ng/L (PFOS), which agree well with the nationwide non-industrial effluent averages. Other PFAS measured by this study had concentrations very close to national averages calculated by Thompson et al. (2022), including PFBA, PFHpA, PFNA, PFDA, and PFHxS. Concentrations of these PFAS were also quite similar to other WWTP effluent sampling conducted in previous Washington state studies (Furl and Meredith, 2010; Ecology and Herrera, 2010; Mathieu and McCall, 2017).

Concentrations of PFPeA and PFHxA in Plant C effluents were an order of magnitude higher than the non-industrial national average. PFBS concentrations were also slightly above the national average in the effluent of Plant A and B. It is unclear what the source of these analytes might be. These samples were also higher than previous Washington effluent sampling, with the exception of a similarly elevated PFHxA concentration from one of the WWTPs sampled in 2008.

Table 8. PFAS concentrations in WWTP effluents from the U.S. and previous Washington studies.

Analyte	U.S. WWTPs (mean*, ng/L)	WA WWTPs, 2008 (range, ng/L)	WA WWTPs, 2010 (range, ng/L)	WA WWTPs, 2016 (range, ng/L)	This study (range, ng/L)
PFBA	8.2	0.7 - 5.4	ND - 6.0	1.6 - 7.1	7.9 - 13
PFPeA	19	3.8 - 47	ND - 18	5.5 - 57	6.0 - 231
PFHxA	23	11 - 141	9.6 - 52	11 - 49	14 - 133
PFHpA	5.6	ND - 35	2.1 - 10	2.2 - 5.5	2.2 - 3.4
PFOA	8.4	17 - 128	11 - 70	6.6 - 20	5.0 - 12.3
PFNA	3.9	3.6 - 18	1.4 - 134	ND - 4.0	0.6 - 1.1
PFDA	1.9	3.6 - 13	1.4 - 10	ND - 5.0	ND - 0.8
PFBS	4.5	ND - 6.6	ND - 18	ND - 14	7.9 - 27
PFHxS	4.8	1.3 - 16	ND - 8.3	ND - 7.1	1.0 - 6.0
PFOS	10	3.9 - 31	ND - 55	ND - 6.5	2.0 - 7.0
reference:	Thompson et al., 2022	Furl and Meredith, 2010	Ecology and Herrera, 2010	Mathieu and McCall, 2017	

*See Thompson et al. (2022) for calculation of mean, simple random sample, no outliers.
ND = not detected

Fewer data were available to compare this study's PFAS concentrations in solids. Thompson et al. (2022) calculated a national biosolids and sludge mean for PFOA and PFOS with 0.1% industrial sources as 15.3 and 167 ng/g, respectively. The biosolids and sludges tested for this study were an order of magnitude lower, at 0.3 – 7.0 ng/g (PFOA) and 22 – 37 ng/g (PFOS). In addition, Michigan has adopted a biosolids PFOS concentration of 125 ng/g as a threshold to indicate that the solids are industrially impacted (EGLE, 2022). Michigan calculated an average PFOS concentration in their biosolids with industrially impacted samples removed as 18 ng/g (AECOM and EGLE, 2021). Biosolids collected for this study were very similar to the Michigan non-industrial mean and well below the 125 ng/g industrial threshold. However, Michigan does encourage investigation into sources of PFAS when biosolids contain over 20 ng/g of PFOS, a level that all of the Washington biosolids samples exceeded. None of these thresholds are risk-based; Michigan is waiting on EPA to establish risk-based thresholds for biosolids.

Comparison to Action Thresholds

Washington state currently has state action levels (SALs) for PFAS in drinking water. SALs are levels set by Washington State Department of Health for long-term daily drinking water to protect people's health. These SALs only cover five PFAS: PFOA, PFOS, PFNA, PFHxS, and PFBS (Table 9). All PFAS concentrations in aqueous samples analyzed for this study were below the SALs, with the exception of PFOA in the effluent of Plant C. The effluent samples from Plant C contained PFOA concentrations of 11.7 – 13.5 ng/L (mean = 12.3 ng/L), slightly above the SAL of 10 ng/L for PFOA. The influent samples from this WWTP were below the SAL, at concentrations ranging 2.5 – 2.64 ng/L (mean = 2.57 ng/L). Effluent from Plant C is considered reclaimed water and is the only plant in this study that had microfiltration as a tertiary treatment.

Table 9. PFAS state action levels for Washington

Type of PFAS	SAL (ng/L)
PFOA	10
PFOS	15
PFNA	9
PFHxS	65
PFBS	345

While Washington's SALs are not directly applicable to WWTP effluent, they provide an indication that the majority of effluent samples collected for this study do not contain the five PFAS in Table 9 at levels of concern for human health via drinking water. These thresholds are not protective of human health from exposure to PFAS in surface water via consumption of fish and other aquatic species. This consideration is particularly important for PFAS that are highly bioaccumulative, like PFOS. The EPA expects to draft recommended surface water quality criteria for human health that would be protective of both drinking water and fish consumption for PFOA and PFOS by Fall 2024 (EPA, 2021). That type of threshold would be helpful to determine the relevance of the concentrations observed in the WWTP effluents sampled for this study.

The EPA has proposed draft aquatic life criteria for PFOA and PFOS to provide surface water and biota-based levels protective of aquatic life against adverse effects (EPA, 2022a; EPA, 2022b). All effluents tested in this study contained PFOA and PFOS concentrations that were orders of magnitude below the draft aquatic life criteria. The draft aquatic life criteria for PFOA are 49 mg/L for acute effects and 0.094 mg/L for chronic effects. Draft PFOS aquatic life criteria are 3.0 mg/L (acute) and 0.0084 mg/L (chronic). Though surface water quality criteria are not applied to effluent concentrations, these thresholds indicate that the effluents would not cause direct adverse effects to aquatic biota themselves in receiving waters. This doesn't take into account wildlife that are consuming the aquatic biota, which is again a concern for the bioaccumulative PFAS.

PFAS Partitioning within WWTPs

Long chain PFAS concentrations were less frequently detected in the aqueous samples than in the sludge and biosolids samples of this study. This was expected because PFAS tends to partition to solids in a WWTP. Long chain PFAS partition into the solids as they are more hydrophobic compared to their shorter chain counter parts (Ebrahimi et al., 2021). The data in this study do not have the granularity to determine the effect of treatment type on PFAS partitioning. Other, more in-depth, studies have shown that there are many conditions that affect PFAS partitioning into solids, including: temperature, pH, chain length, solid and hydraulic retention time, sludge composition, sludge stabilization additive, ions present, and presence of oxygen (Ebrahimi et al., 2021).

With the data collected in this study, it is not possible to determine whether there is more total PFAS in the effluent than in the solids. There was an order of magnitude more of each type of PFAS sampled in the solids phase than the liquid for some compounds (ppb vs ppt). However, the solids are amassed over time, which allows for a higher concentration of PFAS to accumulate in the solid phases sampled. For example, a study from Australia estimated that effluent contained more PFOA and PFOS (65kg and 26kg per year) than biosolids (2kg and 8kg per year) on an annual volume basis (Gallen et al., 2018). Regardless, the presence of PFAS at concentrations in the ppb range indicate further research is needed to understand the relevance and impact of these levels.

The samples show concentration differences between influent concentrations and effluent for multiple PFAS compounds. This is especially true for 5:3 FTCA in Plant A and B and for PFPEA and PFHxA in Plant C. Fluorotelomers such as 5:3 FTCA are known to readily degrade and/or transform in a treatment plant and PFPEA and PFHxA are known degradation products of multiple other PFAS substances (Van Hees, 2013). These transformation products are also likely responsible for all three plants having species of PFAS in the solids that are not found in the influent or effluent.

Transformation of PFAS within a treatment plant is a well-known occurrence, though not well understood. There are multiple biotransformation pathways for PFAS in WWTPs. Abiotic transformation pathways include hydrolysis, photolysis, and oxidation. All of these processes create new PFAS rather than removing them (Houtz et al., 2016). Total organic fluorine (TOF) and total oxidizable precursor (TOP) assays would help to determine how much PFAS, if any at all, is removed. EPA approved methods for TOP and TOF are in development at the time of this report.

The data indicate that PFAS concentrations in influent, effluent, solids, and biosolids are unique to each treatment plant. Influent concentrations can vary due to industrial sources and other differences in the service area of each WWTP. While not investigated in this study, PFAS concentrations and speciation can also vary with time (Thompson et al., 2022).

Future Research Needs

PFAS is now considered a ubiquitous type of chemical because it is found wherever surface water and groundwater samples are analyzed for PFAS (CDC & NCEH, 2016). This study's preliminary reconnaissance shows that most of the WWTP effluents contain PFAS concentrations below the five existing SALs. However, little is known about the other PFAS species detected for which no SAL has been established. More toxicological information is needed about the other PFAS detected.

Concentrations of PFAS in biosolids also need more research. This study shows PFAS concentrations in biosolids that are an order of magnitude higher than in aqueous substances and contain types of PFAS that are not found in influent and effluent. This is in line with other literature values (Gallen et al., 2018). Little is known about transport of PFAS after biosolids are

land applied. One study in Arizona found that PFAS remained highly absorbed to solids with limited migration into the soil depths. The study concluded that PFAS in biosolids was not a large threat to groundwater contamination due to the low concentrations of PFAS in biosolids, low rainfall and the depth to groundwater (Pima County Wastewater Reclamation, 2020). However, conditions in Washington state are different and there are currently no thresholds for biosolids in soil. Therefore, it is not possible to assess localized effects of PFAS at biosolids land application sites.

Conclusions

In February 2021, Ecology conducted a reconnaissance survey of PFAS concentrations in influent, effluent, sludge, and biosolids from three WWTPs. This study evaluated PFAS concentrations at several points along a wastewater treatment process, as recommended in the state's PFAS Chemical Action Plan. Conclusions of this study include the following:

- Short chain PFCAs were generally detected more frequently in the influent and effluent and long chain PFCAs were mostly present in the sludge and biosolids samples. PFHxA, PFOA, PFBS, and PFOS were detected in all samples and matrices. PFAS precursors were also present, with 5:3 FTCA at the highest concentrations of all analytes measured. 6:2 FTS was detected in several influent and effluent samples, and perfluoroalkane sulfonamido substances were detected mostly in the sludge and biosolids.
- PFAA concentrations in the effluents tested for this study were within the range of non-industrial WWTP effluent found throughout the United States. Slightly elevated concentrations of PFPeA and PFHxA were found in the effluent of Plant C, and the source of those analytes are unknown. All PFAS concentrations in effluent samples analyzed for this study were below the drinking water state action levels (SALs) for five PFAS, except for PFOA in the effluent of Plant C which was slightly above.
- PFOS concentrations in the biosolids and sludges were (1) lower than what other states consider industrially impacted, and (2) similar to or lower than national and state averages of PFOS in biosolids lacking industrial PFAS sources.
- Information from this study does not, on its own, justify a need for widespread PFAS monitoring at WWTPs. Additional monitoring on a larger scale would be needed before making that determination.
- This study was not able to draw conclusions about treatment technologies and PFAS removal efficiency or partitioning within WWTPs.

Recommendations

Results of this 2021 study support the following recommendations:

- The limited sample size of this study precludes the ability to make recommendations on a WWTP PFAS monitoring program. A larger scale study with more data, both in frequency and location, is recommended before requiring WWTPs to regularly monitor influent, effluent, and/or biosolids for PFAS. It would be helpful to have (1) more data on PFAS concentrations found at WWTPs across Washington state, (2) samples taken across a larger time scale, and (3) sampling coordinated when there are known industrial releases.
- More research is needed to determine if PFAS from biosolids causes localized PFAS contamination.

References

AECOM and EGLE [Michigan Department of Environment, Great Lakes, and Energy]. 2021. Evaluation of PFAS in Influent, Effluent, and Residuals of Wastewater Treatment Plants (WWTPs) in Michigan. Project Number: 60588767.

Aherns, L., & Bundschuh, M. 2014. Fate and effects of poly- and perfluoroalkyl substances in the aquatic.pdf. 33(9), 1921–1929.

CDC, & NCEH. 2016. Fourth National Report on Human Exposure to Environmental Chemicals Update. March. https://www.cdc.gov/exposurereport/pdf/FourthReport_UpdatedTables_Volume1_Mar2018.pdf

DoD [Department of Defense]. 2020. Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-15. Environmental Data Quality Workgroup 05/01/2020. https://denix.osd.mil/edqw/documents/documents/module-3-data-validation/

DoD [Department of Defense] / DOE [Department of Energy]. 2019. Department of Defense (DoD) Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories. DoD Quality Systems Manual Version 5.3. https://denix.osd.mil/edqw/documents/manuals/qsm-version-5-3-final/

Ebrahimi, F., Lewis, A. J., Sales, C. M., Suri, R., & McKenzie, E. R. 2021. Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes. Chemosphere, 271. https://doi.org/10.1016/j.chemosphere.2020.129530

Ecology. 2021. Per- and Polyfluoroalkyl Substances Chemical Action Plan. Washington State Department of Ecology, Olympia, WA. Publication 21-04-048. https://apps.ecology.wa.gov/publications/summarypages/2104048.html

Ecology and Herrera. 2010. Control of Toxic Chemicals in Puget Sound - Summary Technical Report for Phase 3: Loadings from POTW Discharge of Treated Wastewater. Washington State Department of Ecology, Olympia, WA. Publication 10-10-057. https://apps.ecology.wa.gov. /publications/SummaryPages/1010057.html

EGLE [Michigan Department of Environment, Great Lakes, and Energy]. 2022. Land Application of Biosolids Containing PFAS, Interim Strategy Updated 2022. EGLE, Water Resources Division.

EPA [Environmental Protection Agency]. 2016. National Functional Guidelines for High Resolution Superfund Methods Data Review. Office of Superfund Remediation and Technology Innovation (OSRTI), Washington, DC. Publication OLEM 9200.3-115, EPA 542-B-16-001. https://www.epa.gov/sites/production/files/2016-05/documents/hrsm_nfg.pdf

EPA [Environmental Protection Agency]. 2021. PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024. https://www.epa.gov/system/files/documents/2021-10/pfas-roadmap_final-508.pdf

EPA [Environmental Protection Agency]. 2022a. Draft Aquatic Life Ambient Water Quality Criteria for Perfluorooctanoic Acid (PFOA). U.S. Environmental Protection Agency Office of Water, Washington D.C. Publication Number EPA-842-D-22-001.

EPA [Environmental Protection Agency]. 2022b. Draft Aquatic Life Ambient Water Quality Criteria for Perfluorooctane Sulfonate (PFOS). U.S. Environmental Protection Agency Office of Water, Washington D.C. Publication Number EPA-842-D-22-002.

Furl, C. and C. Meredith. 2010. Perfluorinated Compounds in Washington Rivers and Lakes. Washington State Department of Ecology, Olympia, WA. Publication 10-03-034. https://apps.ecology.wa.gov. /publications/summarypages/1003034.html

Gallen, C., Eaglesham, G., Drage, D., Nguyen, T. H., & Mueller, J. F. 2018. A mass estimate of perfluoroalkyl substance (PFAS) release from Australian wastewater treatment plants. Chemosphere, 208, 975–983. https://doi.org/10.1016/j.chemosphere.2018.06.024

Hoffman, C. 2021. Quality Assurance Project Plan: PFAS Concentrations in Influent, Effluent, and Solids in Three Municipal Wastewater Treatment Plants in Washington State. Washington State Department of Ecology, Olympia. Publication 21-10-006. https://apps.ecology.wa.gov/publications/SummaryPages/2110048.html

Houtz, E. F., Sutton, R., Park, J. S., & Sedlak, M. 2016. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. Water Research, 95, 142–149. https://doi.org/10.1016/j.watres.2016.02.055

ITRC. 2020. Human and Ecological Health Effects and Risk Assessment of Per- and Polyfluoroalkyl Substances (PFAS). 1–4. https://pfas-1.itrcweb.org/

Kucharzyk, K. H., Darlington, R., Benotti, M., Deeb, R., & Hawley, E. 2017. Novel treatment technologies for PFAS compounds: A critical review. Journal of Environmental Management, 204(August), 757–764. https://doi.org/10.1016/j.jenvman.2017.08.016

Liu, J., & Mejia Avendaño, S. 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. Environment International, 61, 98–114. https://doi.org/10.1016/j.envint.2013.08.022

Mathieu, C., & McCall, M. 2017. Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Rivers and Lakes, 2016. https://apps.ecology.wa.gov. /publications/SummaryPages/1703021.html

Pima County Wastewater Reclamation. 2020. PFAS in Biosolids: A Southern Arizona Case Study.

Thompson, K. A., Mortazavian, S., Gonzalez, D. J., Bott, C., Hooper, J., Schaefer, C. E., & Dickenson, E. R. V. 2022. Poly- and Perfluoroalkyl Substances in Municipal Wastewater Treatment Plants in the United States: Seasonal Patterns and Meta-Analysis of Long-Term Trends and Average Concentrations. ACS ES&T Water. https://doi.org/10.1021/acsestwater.1c00377

US EPA. 2021. Multi-Industry Per- and Polyfluoroalkyl Substances (PFAS) Study – 2021 Preliminary Report. September.

Van Hees, P. 2013. Analysis of the unknown pool of PFAS: Total Oxidizable Precursors (TOP), PFOS Precursor (PreFOS) and Telomer Degradation. https://cdnmedia.eurofins.com/european-east/media/1568225/top_precursor_short_facts_170613.pdf

Washington, J. W., Jenkins, T. M., Rankin, K., & Naile, J. E. 2015. Decades-scale degradation of commercial, side-chain, fluorotelomer-based polymers in soils and water. Environmental Science and Technology, 49(2), 915–923. https://doi.org/10.1021/es504347u

Glossary, Acronyms, and Abbreviations

Glossary

Anthropogenic: Human-caused.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a wastewater treatment plant.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Synergistic toxicological effect: Adverse effects caused by exposures to two or more toxic substances at a time, which is greater than would be caused by one substance alone.

Acronyms and Abbreviations

DOD	U.S. Department of Defense
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
MEL	Manchester Environmental Laboratory
NPDES	National Pollutant Discharge Elimination System (see glossary)
PFAS	Per- and polyfluoroalkyl substances
PFCA	Perfluoroalkyl carboxylates
PFSA	Perfluoroalkyl sulfonates
PFOA	Perfluorooctanoate

PFOS	Perfluorooctane sulfonate
QAPP	Quality Assurance Project Plan
QC	Quality control
QSM	Quality Systems Manual
RSD	Relative standard deviation
SAL	State action level
TOF	Total organic fluorine
TOP	Total oxidizable precursors
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
dw	dry weight
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)
ppb	parts per billion
ppt	parts per trillion

Appendices

Appendix A. Analytes and Reporting Limits

Table A-1. Analytes measured and median reporting limits for this study.

Analyte	CAS number	Abbreviation	QSM Analyte	Influent median LOQ (ng/L)	Influent median SDL (ng/L)	Effluent median LOQ (ng/L)	Effluent median SDL (ng/L)	Solids median LOQ (ng/g)	Solids median SDL (ng/g)
Perfluorobutanoate	45048-62-2	PFBA	•	6.5	1.6	6.5	1.6	16.1	4.0
Perfluoropentanoate	45167-47-3	PFPeA	•	3.3	0.8	3.2	0.8	8.1	2.0
Perfluorohexanoate	92612-52-7	PFHxA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluoroheptanoate	120885-29-2	PFHpA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorooctanoate	45285-51-6	PFOA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorononanoate	72007-68-2	PFNA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorodecanoate	73829-36-4	PFDA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluoroundecanoate	196859-54-8	PFUnA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorododecanoate	171978-95-3	PFDoA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorotridecanoate	862374-87-6	PFTrDA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorotetradecanoate	365971-87-5	PFTeDA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorobutane sulfonate	45187-15-3	PFBS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluoropentane sulfonate	175905-36-9	PFPeS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorohexane sulfonate	108427-53-8	PFHxS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluoroheptane sulfonate	146689-46-5	PFHpS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorooctane sulfonate	45298-90-6	PFOS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorononane sulfonate	474511-07-4	PFNS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorodecane sulfonate	126105-34-8	PFDS	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorododecane sulfonate	343629-43-6	PFDoS		1.6	0.4	1.6	0.4	4.0	1.0
4:2 fluorotelomer sulfonate	414911-30-1	4:2 FTS	•	6.5	1.6	6.5	1.6	16.1	4.0
6:2 fluorotelomer sulfonate	425670-75-3	6:2 FTS	•	5.9	2.5	5.8	2.5	14.5	3.6
8:2 fluorotelomer sulfonate	481071-78-7	8:2 FTS	•	6.5	1.6	6.5	1.6	16.1	4.0
N-Methylperfluorooctane sulfonamidoacetic acid	2355-31-9	N-MeFOSAA	•	1.6	0.4	1.6	0.4	4.0	1.0
N-Ethylperfluorooctane sulfonamidoacetic acid	2991-50-6	N-EtFOSAA	•	1.6	0.4	1.6	0.4	4.0	1.0
Perfluorooctane sulfonamide	754-91-6	PFOSA	•	1.6	0.4	1.6	0.4	4.0	1.0
N-Methylperfluorooctane sulfonamide	31506-32-8	N-MeFOSA	•	1.9	0.5	1.9	0.5	4.6	1.2
N-Ethylperfluorooctane sulfonamide	4151-50-2	N-EtFOSA	•	4.1	1.0	4.0	1.0	10.1	2.5
N-Methylperfluorooctane sulfonamidoethanol	24448-09-7	N-MeFOSE	•	16.3	4.1	16.2	4.0	40.3	10.1
N-Ethylperfluorooctane sulfonamidoethanol	1691-99-2	N-EtFOSE	•	12.2	3.1	12.1	3.0	30.3	2.5
Perfluoro-2-propoxypropanoate	122499-17-6	HFPO-DA	•	6.2	1.6	6.1	1.5	15.3	3.8
4-dioxa-3H-perfluorononanoate	2127366-90-7	ADONA	•	6.5	1.6	6.5	1.6	16.1	4.0
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	1621485-21-9	9Cl-PF3ONS	•	6.5	1.6	6.5	1.6	16.1	4.0
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	2196242-82-5	11Cl-PF3OUdS	•	6.5	1.6	6.5	1.6	16.1	4.0
3:3 perfluorohexanoic acid*	1169706-83-5	3:3 FTCA		6.5	1.6	6.5	1.6	16.1	4.0
5:3 perfluorooctanoic acid*	1799325-94-2	5:3 FTCA		40.8	10.2	40.4	10.1	101	25.2
7:3 perfluorodecanoic acid*	1799325-95-3	7:3 FTCA		40.8	10.2	40.4	10.1	101	25.2

Analyte	CAS number	Abbreviation	QSM Analyte	Influent median LOQ (ng/L)	Influent median SDL (ng/L)	Effluent median LOQ (ng/L)	Effluent median SDL (ng/L)	Solids median LOQ (ng/g)	Solids median SDL (ng/g)
Perfluoro (2-ethoxyethane)sulfonic acid*	220689-13-4	PFEESA		1.6	0.4	1.6	0.4	4.0	1.0
Perfluoro-4-methoxybutanoate*	1432017-36-1	PFMBA		1.6	0.4	1.6	0.4	4.0	1.0
Perfluoro-3-methoxypropanoate*	n/a	PFMPA		3.3	0.8	3.2	0.8	8.1	2.0
Perfluoro-3,6-dioxaheptanoate*	39187-41-2	NFDHA		3.3	0.8	3.2	0.8	8.1	2.0

LOQ = limit of quantitation
SDL = sample specific detection limit

Appendix B. PFAS Results Table

Table B-1. Individual PFAS results of all samples analyzed for this study.

This table is available only online, linked to this report at https://apps.ecology.wa.gov/publications/SummaryPages/2203028.html.

Environ. Sci. Technol. **2010,** *44,* 9509–9515

Calculator Tool for Determining Greenhouse Gas Emissions for Biosolids Processing and End Use

SALLY BROWN,[†,*] NED BEECHER,[‡] AND ANDREW CARPENTER[§]

School of Forest Resources, University of Washington Box 352100 Seattle, Washington 98195, United States, North East Biosolids and Residuals Association, PO Box 422 Tamworth, New Hampshire 03886, United States, Northern Tilth, P.O. Box 361 Belfast, Maine 04915, United States

Received April 15, 2010. Revised manuscript received October 21, 2010. Accepted October 25, 2010.

A greenhouse gas (GHG) calculator tool (Biosolids Emissions Assessment Model, BEAM) was developed for the Canadian Council of Ministers of the Environment to allow municipalities to estimate GHG emissions from biosolids management. The tool was developed using data from peer reviewed literature and municipalities. GHG emissions from biosolids processing through final end use/disposal were modeled. Emissions from nine existing programs in Canada were estimated using the model. The program that involved dewatering followed by combustion resulted in the highest GHG emissions (Mg CO_2e 100 Mg^{-1} biosolids (dry wt.). The programs that had digestion followed by land application resulted in the lowest emissions (−26 and −23 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.). Transportation had relatively minor effects on overall emissions. The greatest areas of uncertainty in the model include N_2O emissions from land application and biosolids processing. The model suggests that targeted use of biosolids and optimizing processes to avoid CH_4 and N_2O emissions can result in significant GHG savings.

Introduction

Wastewater treatment systems often constitute the single largest use of electricity within municipal governments with 3% of electricity use in the U.S consumed in water and wastewater treatment (*1*). GHG emissions from wastewater treatment have been classified as one of the larger minor sources of emissions (*2*). Energy use is often considered to be the primary source of GHG emissions related to wastewater (*3*−*6*). A recent re-examination of initial estimates resulted in a greater than 100% increase in emissions of N_2O and CH_4 (*7*). Biosolids treatment and end use can constitute up to 40% of total emissions associated with wastewater treatment (*8*). A range of different stabilization and end use technologies are widely available, each with different associated costs and environmental impacts (*9, 10*).

Decisions on end use/disposal of municipal biosolids have traditionally been based on cost, regulatory, environmental, and public acceptance considerations. Environmental concerns have generally focused on contaminants in the biosolids (*11*−*14*). Understanding the GHG emissions associated with different biosolids management practices is likely to influence public opinion and municipal decision-making. It can also be used as a model for management of other residuals including animal manures.

Different biosolids processing technologies require varying energy and chemical inputs. Fugitive emissions of CH_4 and N_2O during processing and end use of biosolids can result in significant debits. End use of biosolids may generate credits, through energy production, as a substitute for synthetic fertilizers, and through carbon sequestration in soils. These factors have been discussed to varying degrees in previous studies (*9, 15*−*19*). The Intergovernmental Panel on Climate Change (IPCC) includes limited discussion of these factors in separate sections of the documents on waste management, mitigation, and agriculture (*6, 20, 21*).

There have been few studies that effectively integrated the potential emissions/sequestration associated with the full range of biosolids management options, and those have often neglected fugitive emissions or potential credits (*4, 5, 9, 22*). The goal of the current study was to create a tool for modeling and calculating GHG emissions from different biosolids processing and end use options that includes default values but also provides for use of site specific data. The tool was designed to compare the GHG impact of different biosolids management options. Data provided by nine participating municipalities with different biosolids processing and end use programs were put through the model.

Materials and Methods

Biosolids management was divided into categories for solids processing and stabilization, and end use and disposal. Default values for each unit process, including inputs, energy use, and fugitive gas emissions, were developed based on values from published literature and data from individual treatment facilities. Potential credits for each process were also described. When multiple values were available for a unit process, preference was given to values from peer reviewed literature or scientific studies. The range of values considered for each process is shown in the Supporting Information (SI). Emissions related to electricity production were calculated using specific factors for Canadian provinces (*23*). These ranged from 10 CO_2e (g/kWh) in Manitoba, Newfoundland, and Quebec to 926 CO_2e (g/kWh) in Alberta. When available, facility-specific data is used in place of default values. Emissions/credits from each process were classified as Scope 1 (direct emissions), Scope 2 (purchased electricity, heat or steam), Scope 1 and 2 combined, or Scope 3 (indirect emissions from production of purchased materials and uses of end products). Carbon dioxide emissions as a result of aerobic decomposition of biosolids organics were considered biogenic in origin and not considered in the model. Calculations were made and are reported on a per dry Mg biosolids produced. Individual unit processes and values for municipalities will be discussed.

Aerobic Digestion. Aerobic digestion (activated sludge treatment, aerated lagoons, and trickling filters) is unlikely to be a source of significant CH_4 or N_2O emissions except for controlled nutrient removal via nitrification (*6*). The model includes default values for electricity use for aeration and mixing based on a sludge retention time of 15 days (*10*).

Storage Lagoons. Anaerobic lagoons storing organic residuals have been identified as sources of CH_4 (*6*). Both temperature and depth of the lagoon will influence the

* Corresponding author phone: (206) 616 1299; fax: (206) 685 3091; e-mail: slb@uw.edu.
† University of Washington.
‡ North East Biosolids and Residuals Association.
§ Northern Tilth.

10.1021/es101210k
Published on Web 11/16/2010

potential for CH_4 release. Minimal emissions are predicted at temperatures less than 15 °C for nonaerated lagoons. Emissions of 0.12 and 0.40 kg CH_4 kg BOD are predicted for lagoons less and greater than 2 m in depth, respectively (*6*). Aerated lagoons will have minimal CH_4 emissions. Emissions from electricity consumption by aeration blowers or mechanical mixers are included in the model.

Anaerobic Digestion. Anaerobic digestion is generally used to meet regulatory requirements for volatile solids (VS) reduction (*10*). The CH_4 generated during digestion can be flared or used to provide heat and power for facilities. In the model, total CH_4 is calculated as a function of the total VS destruction (*10, 24*). Biogas yields from VS destruction average 0.9 m^3/kg VS destroyed (*25*).

Digesters require energy for heating and operating pumps and mixers. Default values for electricity requirements and heat loss, based on a typical heat loss of 4.62 m^3 of natural gas/m^3 sludge treated (*10*), are included in the model. There are potential fugitive emissions from combustion or flaring of digester gas. A range of values for gas flare efficiency have been reported (*2, 3*). The model uses a default value of 0.3% (*26*). Emissions of N_2O from incomplete combustion are minimal per Mg dry biosolids (between 0.004 and 1.7 g N_2O/kg CH_4 burned) (*3, 6*). The model includes default values for VS destruction and composition of biogas and uses U.S. EPA values for biogas conversion to electricity.

Thickening, Conditioning, and Dewatering. Emissions from thickening, conditioning, and dewatering include emissions from polymer production and electricity use. Polymer manufacturing emissions (Scope 3) are approximately 9.0 Mg CO_2eq/Mg polymer (*27*). A default dosage of 5 kg of polymer per Mg dry solids was used (*23*). Centrifuges use considerably more electricity than belt filter presses. Default values in the model reflect this difference: 101.4 kWh for centrifuges and 4.9 kWh for presses, per Mg dry sludge treated (*28*).

Thermal Drying. Rotary dryers are the most common drying systems used in North America, generally operating at 340−370 °C (*23*). Default electricity for drying was set at 214 kWh/Mg dry solids, based on biosolids thermal drying data from Windsor, Ontario. Default fuel use for drying was calculated based on energy required to evaporate water from sludge and initial and final solids content (*10*).

Alkaline Stabilization. Lime stabilization is used to meet pathogen reduction prior to land application or landfill disposal. If the lime is processed specifically for biosolids stabilization, its production has significant embedded, supply chain (Scope 3) carbon emissions (*9*). The model uses a supply chain cost of 0.9 Mg CO_2e/Mg lime (*27*). If the liming agent used is a residual from another process, these debits do not apply. Use of lime stabilized biosolids in soils displaces agricultural lime and emissions associated with its use. IPCC estimated emissions of 0.12 Mg CO_2e per Mg agricultural limestone applied to the soil (*20*). The model includes production emissions for total quantity of lime used (*9, 28, 29*). Credits for displacement of agricultural lime are also included.

Composting. Composting results in emissions from energy use and fugitive gas release. Different systems have different energy requirements with lowest requirements associated with windrows (5 L of fuel per dry Mg feedstock) and highest for in-vessel systems (90 kWh per dry Mg) (*16*). The model includes fuel requirements for mixing (18.3 kg CO_2e) and turning (14 kg CO_2e) per dry Mg feedstock (*16, 30*). Average energy consumption, including requirements for aeration and odor control across 16 in-vessel composting facilities, was 40 kWh per Mg of waste, based on operating near full capacity (*31, 32*). The model also includes aerated static pile and windrow systems.

Methane emissions during composting have been reported (*16*). The Clean Development Mechanism (CDM) protocol for composting requires oxygen measures to document the absence of CH_4 (*33*). Studies have shown that CH_4 is oxidized in the upper portion of the windrow, with compost used to oxidize CH_4 (*34*). Storage of finished compost releases trace quantities of CH_4 and N_2O (*35*). Regulations for composting biosolids require internal pile temperature of 55 °C, which is associated with aerobic decomposition.

Nitrous oxide has also been detected during composting (up to 4.6% of total N released as N_2O) with increased emissions resulting from low C:N ratios and high moisture content (*36, 37*). Emissions are reduced by maintaining pile temperature at 55° and by incorporating finished compost into the pile (*36, 38, 39*). Default values for N_2O and CH_4 emissions are provided for piles with excess moisture and low C:N ratios. The model reduces emissions when a compost cover or biofilter is used.

End Use or Disposal

Landfill. In the model, fugitive emissions are the major debits associated with landfilling. Landfills are considered a significant source of CH_4 (*2, 40*). Decomposition rates are accelerated in sanitary landfills (*41*−*43*). Protocols exist for diversion of biosolids from landfills to composting facilities (*6, 33*). The decay rate constant for biosolids from the CDM protocol for CH_4 generation in warm wet environments (0.40) was used for default value as these temperatures are characteristic of sanitary landfills (*33, 41, 42*). Default values included consideration of gas collection efficiency and onset of collection systems (*44*−*49*). Nitrous oxide emissions from landfilled biosolids have also been reported (*40, 44, 50, 51*). The model includes a default debit for N_2O emissions equivalent to emissions from compost. The range of values associated with landfill gas emissions are reported in the SI. Biosolids used as a component of manufactured soil material for final landfill cover are considered as an agricultural application and not included in the landfill disposal section of the model.

Combustion. There is growing interest in combustion of biosolids as a disposal/end use option. Multiple hearth or fluidized bed technologies are the most prevalent, with higher efficiency in fluidized beds (*52*). There was insufficient data on pyrolysis/gasification facilities to model emissions from these facilities. Because of the high moisture content in biosolids, combustion operations often require supplemental energy. Use of waste heat will decrease energy requirements. The model uses the Btu value, percent solids, and the amount of energy required to evaporate water from sludge to calculate a default balance for combustion (*10*).

Fugitive Emissions. The IPCC default value of 4.85×10^{-5} kg CH_4 emitted/dry kg wastewater solids burned, was used in this model (*6*). Combustion temperature is the primary variable controlling N_2O emissions, with higher emissions observed at lower temperatures. The IPCC default value for N_2O release from combustion is based on moisture content with limited information provided on percent solids for each category and limited data forming the basis for the values (*6, 53, 54*). A study of emissions from fluidized bed combustion facilities for monoincineration using continuous monitoring showed significantly higher emissions factors ranging from 1520−6400 g N per dry Mg biosolids (*19*). The emissions were described as a function of total N in the material using the equation:

$$\eta = 161.3 - 0.140T_f$$

where η is the % of total N that is volatilized as N_2O, and T_f is the average highest freeboard temperature from the fluidized bed facilities. There is limited published data on cocombustion of coal or MSW and biosolids (*54*). There was no published data for emissions from multiple hearth

TABLE 1. Data from Nine Municipalities Used to Model Greenhouse Gas Emissions

municipality	population served	wastewater treated (MLD)	weighted GHG emissions for electricity generation g CO_2e/kWh	treatment processes	end use/disposal	GHG emissions Mg CO_2e/100 Mg dry solids
TB, Ontario	100 000	70	181	• anaerobic digestion • centrifuge dewatering	biosolids/soil landfill cover	46
AN, Quebec	330 000	295	10	• rotary press dewatering	• incineration/heat recovery • ash recycling	148
LA, Quebec	271 600	254	10	• rotary press dewatering • rotary drum high temperature drying	• landfilling dewatered cake • cement kiln incineration	49
WI, Ontario	181 350	161	181	• centrifuge dewatering • rotary drum high temperature drying	agricultural land application	10
MO, New Brunswick	125 000	79	352	• centrifuge dewatering • polymer addition • alkaline stabilization • composting	land application	5
VA, British Columbia	980 000	436	20	• gravity thickening • dissolved air floatation thickening • anaerobic digestion • centrifuge dewatering	restoration land application	−23
HX, Nova Scotia	54 000	27	733	• anaerobic digestion • Fournier press dewatering • alkaline stabilization	agricultural application	28
NA, British Columbia	25 000	10	20	• gravity thickening • aerobic digestion • centrifuge dewatering	silvicultural land application	12
HA, Ontario	165 000	96	181	• dissolved air floatation thickening • anaerobic digestion • polymer addition • belt filter press dewatering	liquid and dewatered biosolids agricultural application	−26

furnaces. These facilities have more frequent start-up and shut-down with associated temperature fluctuations (*52*). For this study, no distinction is made between mono- and cocombustion of biosolids or types of facilities. Nitrous oxide emissions are calculated using the equation presented above with reduction factors for drier biosolids. The model emissions factors for combustion at 850 °C, are similar to emissions from the IPCC default. The ash resulting from combustion can be used as a soil amendment or for cement manufacture. Beneficial use of ash is given a credit based on the quantity of lime or phosphorus it displaces (*9*).

Direct Land Application

The model includes CO_2 emissions debits for transport and land application.

Fugitive Emissions. Biosolids are generally applied to aerobic soils to meet the N requirements of a crop. Previous work has shown minimal CH_4 release, even in poorly drained soils (*15*, *55*). The model includes CH_4 emissions for storage prior to land application. A number of studies have quantified N_2O release from soils, with higher emissions on poorly drained soils in warmer climates (*56*−*59*). A majority of emissions associated with the production of agronomic crops has been attributed to N_2O release (*60*). The IPCC default factor for N_2O emissions for fertilizer, compost and biosolids use are 1% of the total N added. Published literature generally reports lower emissions for biosolids compared to fertilizer (*15*, *57*, *61*, *62*). The range of emissions is shown in the SI. The current model considers N_2O emissions from biosolids as equivalent to synthetic fertilizer for biosolids applied as a fertilizer replacement.

Offsets from Land Application. Using biosolids in lieu of synthetic fertilizers results in avoidance of Scope 3 emissions due to energy use from production of synthetic fertilizers. Different values for emissions have been reported (*9*, *30*). For this model, we used default values of 4 and 2 kg CO_2e/kg for N and P respectively, with no distinction made between total and available nutrients (*30*, *63*, *64*). As biosolids supply additional macro- and micronutrients, default values were considered conservative. Offsets associated with increased soil organic matter are included in the model. Increases in soil carbon have been observed in biosolids amended soils

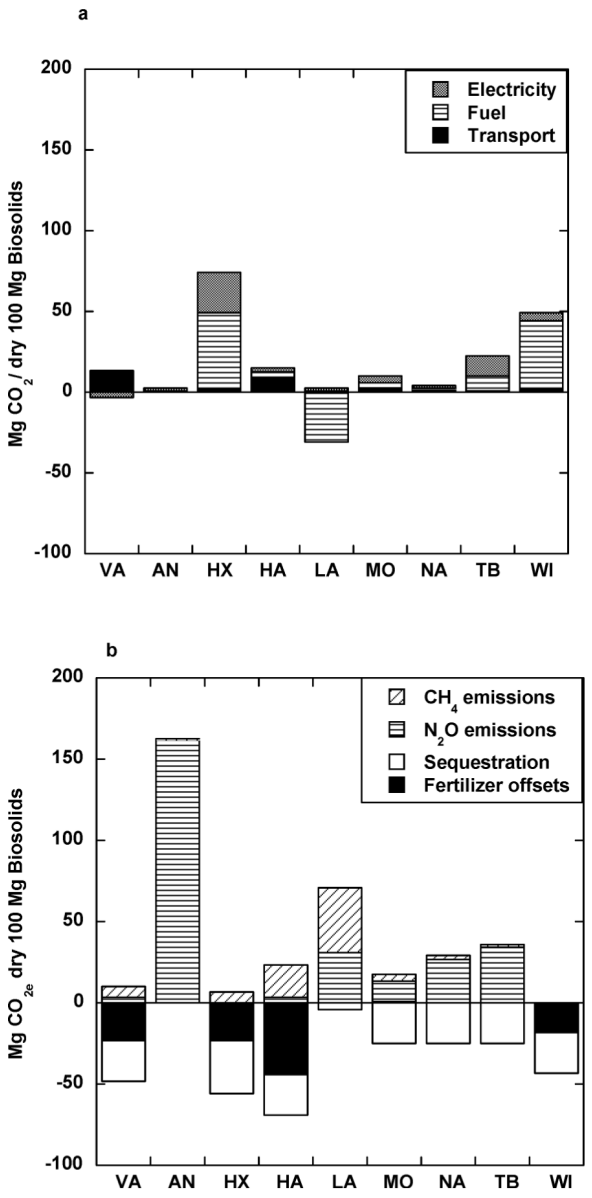


FIGURE 1. Greenhouse gas emissions or credits associated with (a) electricity, fuel and transport and (b) fugitive gas emissions, carbon sequestration, and fertilizer offsets for nine biosolids programs in Canada. Emissions include province-specific weighting factors for electricity.

(*18, 65, 66*). The current model provides a default credit of 25 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.). The range of reported values for fertilizer offsets and soil carbon sequestration are provided in the SI.

Applying the Model. Data from nine wastewater treatment facilities across Canada was applied to the spreadsheet. The facilities were selected to represent different treatment processes and end use/disposal programs. This enabled a direct comparison of different biosolids management scenarios with regard to GHG emissions. The programs evaluated, treatment and end use for biosolids, and associated GHG emissions are shown in Table 1.

Total GHG emissions per dry Mg of biosolids ranged from a low of −26 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.) for HA (anerobic digestion, polymer addition, belt filter press dewatering followed by liquid and dewatered land application) to 144 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.) for AN (rotary press dewatering followed by incineration with heat recovery and ash recycling). This difference was observed despite the fact that emissions associated with electricity

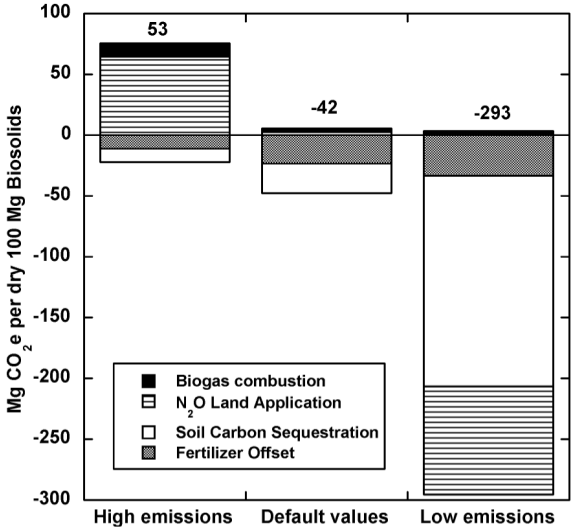


FIGURE 2. High, low, and default emissions factors for VA showing range of reported values for fertilizer offsets, soil carbon sequestration, CH_4 emissions from flaring biogas, and N_2O emissions following land application. Transport and electricity use are not included.

use in HA were significantly higher (181 g CO_2e kWh^{-1}) than those in AN (10 g CO_2e kWh^{-1}).

The bulk of emissions and credits for the different programs were associated with indirect factors. This illustrates the importance of considering a full range of potential GHG impacts when evaluating different biosolids treatment and end use options. Emissions associated with energy and transport are shown in Figure 1a. Emissions associated with fugitive gas release, credits from soil carbon sequestration, use of ash, fertilizer offset credits, or credits for heat recovery are shown in Figure 1b.

The wide range of GHG costs associated with electricity use across Canada shows the importance of considering province specific factors as well as future power needs when considering the benefits of an anaerobic digestion facility with energy capture. For provinces with low GHG costs for electricity, use of heat for drying to offset transport emissions could be preferable to generating electricity.

A sensitivity analysis was conducted for two municipalities to see how the range of reported factors would influence the outcomes of this analysis. Midrange values were used for the model as a means to show general trends while remaining conservative considering the high level of uncertainty (Figure 2). Transport and electricity use were not included in this estimate. Uncertainties related to soil carbon sequestration and N_2O emissions were associated with the largest differences in end values. The range in reported values were sufficient to alter the net balance in the VA program from a net credit per dry 100 Mg biosolids of 293 Mg CO_2e (low end factors) to a net emitter of 53 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.) (high range emissions factors). The default values for VA resulted in a net credit of 42 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.). For landfilled biosolids, the high-end emissions scenario used high decomposition rates with midrange gas capture efficiency. The low end coupled slower decomposition with more effective gas collection. As collection systems are not required for the first three years after material is deposited, these changes had a low impact on total emissions [range from 32−53 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.)].

A side-by-side comparison of two of the Canadian programs illustrates the importance of fugitive emissions, energy, minimal impact of transport, and the importance of Scope 3 factors in determining the potential GHG impacts of different biosolids management options (Table 2). VA, a municipality that uses anaerobic digestion followed by land

TABLE 2. Existing and Optimized GHG Emissions/Credits for the VA (Anaerobic Digestion Followed by Land Application) and AN (Dewatering, Combustion with Ash Use in Cement Production) Programs

		VA		AN	
		existing	optimized	existing	optimized
		kWh Mg^{-1} biosolids (dry wt.)			
conditioning	kWh Mg^{-1} biosolids (dry wt.)	5	5	5	5
anaerobic digestion		−1658	−2333	0	0
dewatering		171	171	11	11
combustion		0	0	1113	716
total electricity use		−1482	−2157	1129	732
		Mg CO_2e 100 Mg^{-1} biosolids (dry wt.)			
electricity	Mg CO_2e 100 Mg^{-1} biosolids (dry wt.)	−3	−4.3	1.1	0.7
polymer		5	5	5	5
fuel/not transport		0.6	0.6	−25	−10
fuel/transport		12.5	2	0.2	0.2
CH_4 emissions		7	7	0	0
N_2O emissions		3	3	163	0
carbon sequestration		−25	−25	0	0
ash use		0	0	−0.1	−0.1
fertilizer offset		−23	−23	0	0
total emissions		−23	−34	144	−4

application, and AN, an incineration facility, were used for this comparison. These programs feature very different end use options and represent the highest emissions (AN) and close to the lowest emissions of the programs modeled in this exercise. The CO_2e for electricity in both provinces are also similar at 20 and 10 g CO_2e kWh^{-1}, respectively.

Data from 1 of 5 treatment plants operated by VA was used for this model. The plant treats an average of 436 megaliters per day (MLD). Primary solids are gravity thickened and secondary solids are thickened by dissolved air floatation. Thickened solids are fed to thermophilic anaerobic digesters. Digester gas is burned for heat alone (18%) and heat plus electricity (60%), generating 61 MJ/yr of heat or 20×10^6 kWh/yr of electricity. A portion (22%) of the gas is flared. Biosolids are dewatered to 31% solids using polymer and centrifuges. Approximately 40 000 wet Mg of biosolids are generated and land applied with round trip distance to projects of 520−875 km.

At AN, the treatment plant services approximately 330 000 people with total inflow of 295 MLD. Sludge is dewatered using chemical mixing, flocculation, and settling. It is concentrated in thickening tanks and dewatered using rotary presses and polymer. The dewatered sludge is incinerated in a fluidized bed monocombustion facility at 760 °C. Process heat is used for process and facility heating. External electricity and fuel are also required. The ash (8 Mg per day) is used for cement production at a cement kiln 35 km from the treatment plant.

Emissions per dry Mg biosolids were similar for both municipalities for conditioning, dewatering, and thickening. Transport emissions were higher in VA [12.5 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.)] in comparison to AN [0.2 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.)]. VA derives a negative net GHG balance of −303 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.) from anaerobic digestion with heat and electricity generation and −48 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.) from land application of the biosolids for fertilizer replacement and soil carbon sequestration. This credit has the potential to increase with use of all digester gas for electricity generation. Decreasing transport distances would also decrease emissions.

Using the model, biosolids programs for both municipalities were optimized to reduce emissions and maximize credits. Results from this optimization are compared to current estimated emissions in Table 2. GHG credits related to net electricity use and generation were increased 40% for the VA program by expanding electricity production to include use of all CH_4. Reducing the one-way haul distance to 100 km resulted in a reduction of transport GHG emissions by 83%. These two optimization steps resulted in net negative GHG emissions (credits) for VA's biosolids program increasing from −23 to −34 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.).

Nitrous oxide was the primary emission associated with the combustion facility, result in a debit of 163 Mg CO_2e 100 Mg^{-1} biosolids (dry wt.). According to the model, increasing the combustion temperature to 880 °C effectively eliminated N_2O. This temperature increase was estimated to require an additional energy input of 54 GJ/day. This municipality reported using a portion of heat from the combustion process for heating buildings and reducing energy requirements for combustion. The theoretical optimization included increasing the fraction of waste heat used for combustion and increasing combustion temperature to eliminate N_2O emissions. This resulted in emissions per dry 100 Mg biosolids decreasing from 144 to −4 Mg CO_2e. As a result of this study, the municipality has increased the burn temperature at its facility to minimize N_2O emissions.

The BEAM spreadsheet tool provides a means for municipalities to evaluate GHG emissions associated with biosolids treatment and end use, considering both direct and indirect emissions. Because of their high CO_2e, emissions of CH_4 and N_2O have the potential to negate benefits associated with biosolids use or disposal. Focusing solely on CO_2e emissions related to energy use results in an incomplete understanding of net GHG emissions. Similarly, the high emissions and/or offset potentials associated with indirect (Scope 3) factors should be considered. The results from this study suggest that limiting considerations of emissions to Scope 1 and 2 factors has a high potential for generating misleading GHG estimates.

It must be emphasized that default factors used in the model for each unit process vary dramatically with regards to level of uncertainty. Factors used in the model range from those that can be predicted with a relatively high degree of accuracy (transport related emissions) to those with a greater degree of uncertainty (soil carbon credits and N_2O emissions). The factors with the greatest potential impact on net emissions include all sources of N_2O.

Results from applications of the BEAM model suggest that maximizing potential offsets, including energy capture and fertilizer and carbon sequestration value, while minimizing fugitive CH_4 and N_2O emissions associated with biosolids management practices such as landfilling, low

temperature combustion, or poor compost management, can significantly decrease the GHG emissions from biosolids management programs. The end use options associated with the highest credits were also those with the lowest capitol costs, suggesting a cost-effective means for wastewater treatment agencies to lower their GHG footprints without increasing capitol expenditures (*11*).

Acknowledgments

Funding for this work was provided by the Canadian Council of Ministers of the Environment.

Supporting Information Available

Additional information including the calculator spreadsheets, tables summarizing the literature for the range of reported values for different parameters, and a flow diagram for the wastewater treatment process. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) EPA. Sustainable water infrastructure. Available at http://water.epa.gov/infrastructure/sustain/ (Accessed on August 28, 2010).

(2) EPA. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990−2007; Washington, DC, 2009. EPA 430-R-09-004. Available at http://epa.gov/climatechange/emissions/usinventoryreport.html. usinventoryreport.html (Accessed on June 1, 2010).

(3) Barber, W. P. Influence of anaerobic digestion on the carbon footprint of various sewage sludge treatment options. *Water Environ. J.* **2009**, *23*, 170–179.

(4) Foley, J.; Lant, P. Fugitive greenhouse gas emissions from wastewater systems. In *WSAA Literature Review No. 1*; Water Services Association of Australia., 2007; Available at http://www.wsaa.asn.au.

(5) Poulsen, T. G.; Hansen, J. A. Assessing the impacts of changes in treatment technology on energy and greenhouse gas balances for organic waste and wastewater treatment using historical data. *Waste Manage. Res.* **2009**, *27*, 861–870.

(6) IPCC. Guidelines for National Greenhouse Gas Inventories Volume 5: Waste. Intergovernmental Panel on Climate Change. 2006. Available at http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html (Accessed on August 28, 2010).

(7) Scheehle, E.; Doorn, M. R. Improvements to the U.S. wastewater methane and nitrous oxide emissions estimates. U.S. EPA. Available at www.epa.gov/ttnchie1/conference/ei12/green/scheehle.pdf (Accessed on August 1, 2010).

(8) Shaw, A.; Coleman, A.; Nolasco, D.; Rosso, D.; Yuan, Z.; van Loosdrecht, M.; Shiskowski, D.; Chandran, K.; Houweling, D.; Willis, J.; Beecher, N.; Corominas, L.; Siegrist, H.; Porro, J.; Nopens, I. Workshop Summary: The Role of Modeling in Assessing Greenhouse Gas (GHG) Emissions. *Proceedings of 83rd Annual WEFTEC*, New Orleans, LA., 2010.

(9) Murray, A.; Horvath, A.; Nelson, K. L. Hybrid life-cycle environmental and cost inventory of sewage sludge treatment and end-use scenarios: a case study from China. *Environ. Sci. Technol.* **2008**, *42*, 3163–3169.

(10) *Wastewater Engineering: Treatment and Reuse*, 4th ed.; Metcalf & Eddy, McGraw-Hill: New York, 2003.

(11) Xia, K.; Bhandari, A.; Das, K.; Pillar, G. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. *J. Environ. Qual.* **2005**, *34*, 91–104.

(12) Gottschall, N.; Edwards, M.; Topp, E.; Bolton, P.; Payne, M.; Curnoe, W. E.; Ball Coelho, B.; Lapen, D. R. Nitrogen, phosphorus, and bacteria tile and groundwater quality following direct injection of dewatered municipal biosolids into soil. *J. Environ. Qual.* **2009**, *38*, 1066–1075.

(13) Rusin, P. A.; Maxwell, S. L.; Brooks, J. P.; Gerba, C. P.; Pepper, I. L. Evidence for the absence of Staphylococcus aureus in land applied biosolids. *Environ. Sci. Technol.* **2003**, *37*, 4027–4030.

(14) Brown, S. L.; Chaney, R. L.; Angle, J. S.; Ryan, J. A. Organic carbon and the phytoavailability of cadmium to lettuce in long term biosolids amended soils. *J. Environ. Qual.* **1998**, *27*, 1071–1078.

(15) Ball, B. C.; McTaggart, I. P.; Scott, A. Mitigation of greenhouse gas emissions from soil under silage production by use of organic manures or slow-release fertilizer. *Soil Use Manage.* **2004**, *20*, 287–295.

(16) Brown, S.; Kruger, C.; Subler, S. Greenhouse gas balance for composting operations. *J. Environ. Qual.* **2008**, *37*, 1396–1410.

(17) Sänger, M.; Werther, J.; Ogada, T. NOx and N_2O emission characteristics from fluidized bed combustion of semi-dried municipal sewage sludge. *Fuel* **2001**, *80*, 167–177.

(18) Spargo, J. T.; Alley, M.; Follett, R.; Wallace, J. V. Soil carbon sequestration with continuous no-till management of grain cropping systems in the Virginia Coastal Plain. *Soil Tillage Res.* **2008**, *100*, 133–140.

(19) Suzuki, Y.; Ochi, S.; Kawashima, Y.; Hiraide, R. Determination of emission factors of nitrous oxide from fluidized bed sewage sludge incinerators by long-term continuous monitoring. *J. Chem. Eng. Jpn.* **2003**, *36*, 458–463.

(20) IPCC. Guidelines for National Greenhouse Gas Inventories Volume 4: Agriculture Forestry and Other Land Uses. Intergovernmental Panel on Climate Change. 2006. Available at http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html (Accessed on August 28, 2010).

(21) IPCC. Climate change. 2007. Mitigation. Intergovernmental Panel on Climate Change. Available at http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html (Accessed on August 28, 2010).

(22) Barber, W. P. Influence of anaerobic digestion on the carbon footprint of various sewage sludge treatment options. *Water Environ. J.* **2009**, *23*, 170–179.

(23) The Climate Registry General Reporting Protocol, Canadian Emissions Factors for Grid Electricity by Province, March, 2, 2009 update, www.theclimateregistry.org.

(24) Novack, J. Volatile solids destruction. Personal communication, Beecher, N. 1/16/2009.

(25) *Design of Municipal Wastewater Treatment Plants*, 4th ed.; Water Environment Federation: Alexandria, VA, 1998.

(26) Smith, K. R.; Uma, R.; Kishore, V. V. N.; Lata, K.; Joshi, V.; Zhang, J.; Rasmussen, R. A.; Khalil, M. A. K. *Greenhouse Gases from Small-Scale Combustion Devices in Developing Countries, Phase IIa: Household Stoves in India*, 600/R-00-052; U.S. EPA.: Washington, DC, 2000.

(27) Carnegie Mellon Green Design Inst. Available at http://www.eiolca.net (Accessed on August 28, 2010).

(28) Gould, M.; Carpenter, A. CDM (http://www.cdm.com/). *Electricity use during lime stabilization* Personal communication, March 2009.

(29) Peot, C.; Beecher, N. Lime use for pathogen reduction, Personal communication, February 2009.

(30) *Recycled Organics Unit. Life Cycle Inventory and Life Cycle Assessment for Windrow Composting Systems*; The University of New South Wales: Sydney, Australia, 2006; http://www.recycledorganics.com/publications/reports/lca/lca.htm (Accessed March 5, 2008).

(31) Wannholt, L. Biological treatment of domestic waste in closed plants in Europe—Plant visit reports; RVF Report 98:8 for the Swedish Association of Solid Waste Management, 1998.

(32) Beecher, N.; Kuter, G.; Petroff, B. Another reason not to landfill: Composting can help reduce greenhouse gas emissions. *Water Environ. Technol.* **2009**, *21*, 4.

(33) Clean Development Mechanism. Tool to determine methane emissions avoided from disposal of waste at a solid waste disposal site, version 04, EB 41. 2008. UNFCC/CCNUCC: Available at http://cdm.unfccc.int/methodologies/PAmethodologies/approved.html (Accessed on August 28, 2010).

(34) *Solid waste management and greenhouse gases: A life-cycle assessment of emissions and sinks*, 3rd ed.; U.S. Environmental Protection Agency: Washington, DC, 2006; http://www.epa.gov/climatechange/wycd/waste/SWMGHGreport.html.

(35) Hao, X. Nitrate accumulation and greenhouse gas emissions during compost storage. *Nutr. Cycling Agroecosyst.* **2007**, *78*, 189–195.

(36) Fukumoto, Y.; Suzuki, K.; Osada, T.; Kuroda, K.; Hanajima, D.; Yasuda, T.; Haga, K. Reduction of nitrous oxide emission from pig manure composting by addition of nitrite-oxidizing bacteria. *Environ. Sci. Technol.* **2006**, *40*, 6787–6791.

(37) Czepiel, P.; Douglas, E.; Harriss, R.; Crill, P. Measurement of N_2O from composted organic wastes. *Environ. Sci. Technol.* **1996**, *30*, 2519–2525.

(38) Eklind, Y.; Sundberg, C.; Smårs, S.; Steger, K.; Sundh, I.; Kirchmann, H.; Jönsson, H. Carbon turnover and ammonia emissions during composting of biowaste at different temperatures. *J. Environ. Qual.* **2007**, *36*, 1512–1520.

(39) Zhang, H.; He, P.; Shao., L. N_2O emissions at municipal solid waste landfill sites: Effects of CH_4 emissions and cover soil. *Atmos. Environ.* **2009**, *43*, 2623–2631.

(40) *Canada's Fourth National Report on Climate Change*; Environment Canada: Ottawa, 2006; http://www.ec.gc.ca/climate/home-e.html.

(41) Koerner, G. R.; Koerner, R. M. Long-term temperature monitoring of geomembranes at dry and wet landfills. *Geotextiles Geomembr.* **2006**, *24*, 72–77.
(42) Lefebvre, X.; Lanini, S.; Houi, D. The role of aerobic activity on refuse temperature rise, I. Landfill experimental study. *Waste Manage. Res* **2000**, *18*, 444–452.
(43) Bäumler, R.; Kögel-Knabner, I. Spectroscopic and wet chemical characterization of solid waste organic matter of different age in landfill sites, Southern Germany. *J. Environ. Qual.* **2008**, *37*, 146–153.
(44) Börjesson, G.; Svensson, B. H. Nitrous oxide emissions from landfill cover soils in Sweden. *Tellus* **1997**, *49B*, 357–363.
(45) Lohila, A.; Laurila, T.; Tuovinen, J.; Aurela, M.; Hatakka, J.; Thum, T.; Pihlatie, M.; Rinne, J.; Vesala, T. Micrometeorological measurements of methane and carbon dioxide fluxes at a municipal landfill. *Environ. Sci. Technol.* **2007**, *41*, 2717–2722.
(46) Mosher, B. W.; Czepiel, P. M.; Harriss, R. C.; Shorter, J. H.; Kolb, C. E.; McManus, J. B.; Allwine, E.; Lamb, B. K. Methane emissions at nine landfill sites in the northeastern United States. *Environ. Sci. Technol.* **1999**, *33*, 2088–2094.
(47) Spokas, K.; Bogner, J.; Chanton, J. P.; Morcet, M.; Aran, C.; Graff, C.; Moreau-Le Golvan, Y.; Hebe, I. Methane mass balance at three landfill sites: what is the efficiency of capture by gas collection systems? *Waste Manage.* **2006**, *26*, 516–525.
(48) *Background Information Document for Updating AP42 Section 2.4 for Estimating Emissions from Municipal Solid Waste Landfills*; EPA, Office of Research & Development: Washington, DC, 2008.
(49) *Landfill Gas Emissions Model (LandGEM) Version 3.02 User'S Guide*, EPA-600/R-05/047; U.S. Environmental Protection Agency: Washington, DC, 2005.
(50) Rinne, J.; Lohila, A.; Aurela, M.; Laurila, T.; Pihlatie, M.; Thum, T.; Tuovinen, J.; Vesala, T. Nitrous oxide emissions from a municipal landfill. *Environ. Sci. Technol.* **2005**, *39*, 7790–7793.
(51) Zhang, H.; He, P.; Shao, L. N_2O emissions at municipal solid waste landfill sites: Effects of CH_4 emissions and cover soil. *Atmos. Environ.* **2009**, *43*, 2623–2631.
(52) Werther, J.; Ogada, T. Sewage sludge combustion. *Prog. Energy Combust. Sci.* **1999**, *25*, 55–116.
(53) Gutierrez, M. J. F.; Baxter, D.; Hunter, C.; Svoboda, K. Nitrous oxide (N_2O) emissions from waste and biomass to energy plants. *Waste Manage. Res.* **2005**, *23*, 133–147.
(54) Svoboda, K.; Baxter, D.; Martinec, J. Nitrous oxide emissions from waste incineration. *Versita* **2006**, DOI: 10.2478/s11696-00600016-x.
(55) Jones, S. K.; Rees, R. M.; Kosmas, D.; Ball, B. C.; Skiba, U. M. Carbon sequestration in a temperate grassland; management and climate controls. *Soil Use Manage.* **2006**, *22*, 132–142.
(56) Grant, R. F.; Pattey, E.; Goddard, T. W.; Kryzanowski, L. M.; Puurveen, H. Modeling the effects of fertilizer application rate on nitrous oxide emissions. *Soil Sci. Soc Am. J.* **2006**, *70*, 235–248.
(57) Jones, S. K.; Rees, R. M.; Skiba, U. M.; Ball, B. C. Influence of organic and mineral N fertiliser on N_2O fluxes from a temperate grassland. *Agric. Ecosys Environ.* **2007**, *121*, 74–83.
(58) Peterson, S. O. Nitrous oxide emissions from manure and inorganic fertilizers applied to spring barley. *J. Environ. Qual.* **1999**, *28*, 1610–1618.
(59) Rochette, P.; Angers, D. A.; Chantigny, M. H.; Bertrand, N. Nitrous oxide emissions respond differently to no-till in a loam and a heavy clay soil. *Soil Sci. Soc Am. J.* **2008**, *72*, 1363–1369.
(60) Kim, S.; Dale, B. E. Effects of nitrogen fertilizer application on greenhouse gas emissions and economics of corn production. *Environ. Sci. Technol.* **2008**, *42*, 6028–6033.
(61) Goodroad, L. L.; Keeney, D. R.; Peterson, L. A. Nitrous oxide emissions from agricultural soils in Wisconsin. *J. Environ. Qual.* **1984**, *13*, 557–561.
(62) Scott, A.; Ball, B. C.; Crichton, I. J.; Aitken, M. N. Nitrous oxide and carbon dioxide emissions from grassland amended with sewage sludge. *Soil Use Manage.* **2000**, *16*, 36–41.
(63) Cogger, C. G.; Bary, A. I.; Fransen, S. C.; Sullivan, D. M. Seven years of biosolids vs. inorganic nitrogen applications to tall fescue. *J. Environ. Qual.* **2001**, *30*, 2188–2194.
(64) Miller, M.; O'Connor, G. A. The longer-term phytoavailability of biosolids-phosphorus. *Agron. J.* **2009**, *101*, 889–896.
(65) Sukkariyah, B. F.; Evanylo, G.; Zelazny, L.; Chaney, R. L. Cadmium, copper, nickel, and zinc availability in a biosolids-amended Piedmont soil years after application. *J. Environ. Qual.* **2005**, *34*, 2255–2262.
(66) Tian, G.; Granato, T. C.; Cox, A. E.; Pietz, R. I.; Carlson, C. R.; Abedin, Z. Soil carbon sequestration resulting from long-term application of biosolids for land reclamation. *J. Environ. Qual.* **2009**, *38*, 61–74.

ES101210K

USING BIOSOLIDS FOR RECLAMATION/REMEDIATION OF DISTURBED SOILS

By:

Sally Brown and Chuck Henry
University of Washington

Table of Contents

USING BIOSOLIDS FOR RECLAMATION/REMEDIATION OF DISTURBED SOILS

What are Biosolids?

All municipal wastewater treatment plants produce biosolids; the stabilized residuals that settle from the water during the various treatment processes. Figure 1 outlines a typical wastewater treatment facility. Solids are produced during primary treatment, as heavy suspended solids settle out. In secondary treatment, microbes eat the dissolved and remaining suspended solids; then, being heavier than water, they also settle out in quiet water. In some cases, tertiary treatment can be used to clean the water even further, and a third type of solids is produced -- one that normally involves chemical and physical treatment.

Following wastewater treatment, the solids are then treated to stabilize the readily putrecible materials, reduce volume and destroy pathogens. Solids treatments are generally biologically based. Microbes use the organic carbon in the solids as an energy source. The material that is produced as a result of solids treatment is called biosolids. Biosolids are generally about 50% organic at the end of typical anaerobic digestion. All biosolids can be used for their fertilizer value. Total nitrogen in biosolids varies with the treatment process but generally ranges from 1-6% total N. Used in agriculture, they are generally applied at rates sufficient to meet the nitrogen requirements of the crop. They are also good soil conditioners, providing organic matter with each application.

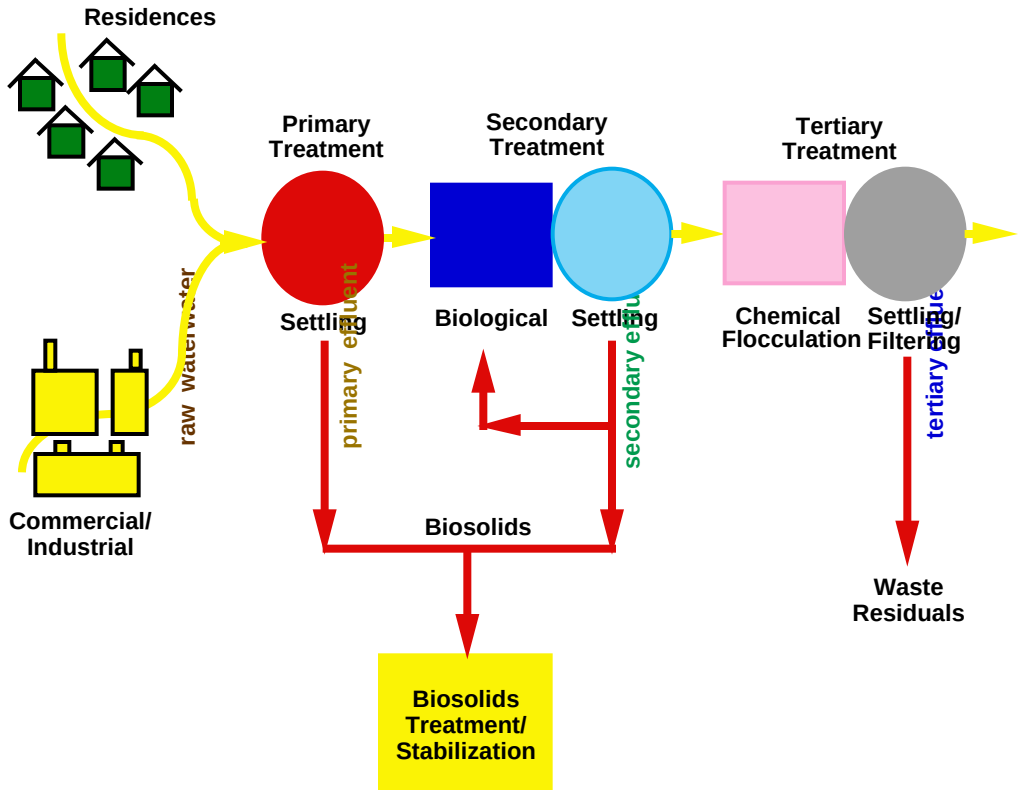


Figure 1. Schematic representation of wastewater collection and treatment.

High N biosolids

Biosolids can generally be divided into two categories: high N and low N biosolids. High N biosolids (total N content ranging from 3-6%) are generally more reactive, due to a shorter stabilization period. They are excellent fertilizer sources and will require generally a few months to stabilize when applied at high rates. They contain a high fraction of short chain organic compounds that are easily decomposed and so will encourage high rates of biological activity after application. These materials often contain organic polymers that have been added to aid in dewatering. Examples of high N biosolids include anaerobically digested, lime stabilized, and heat-treated materials. These are names of treatment processes that are used to stabilize biosolids and reduce pathogens to meet Class B application requirements (Line to 503 ergs). Lime addition to achieve Class B pathogen reduction will volatize a portion of the nitrogen and also result in higher solids content. While lime stabilized materials may have N concentrations and solids content typical of low N materials, they are still highly reactive and should be grouped with the high N materials.

Low N biosolids

Low N biosolids are generally more stable than high N biosolids with total N ranging from 1-3%. These materials are generally treated in lagoons or drying beds where average residence time may be several years. While low N biosolids are also excellent fertilizers, generally higher application rates are required to meet the N needs of a crop. They are less reactive and will be less readily decomposed. They also generally have a higher solids content then the high N materials and most of the polymers, if used, have decomposed..

Biosolids Composts

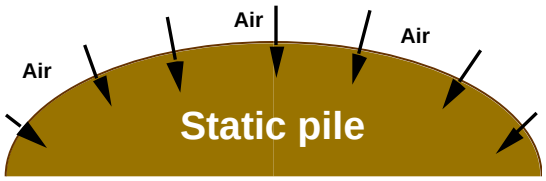
Both high and low N biosolids may be used as part of the feedstock for producing composts. Composting is often a portion of a municipalities biosolids program. Composting biosolids requires a long residence time (1-4 months). These materials are generally produced for the home gardener or landscaper so that the final product needs to be highly stable and screened to a small particle size. As a result of this, composts tend to be the most expensive of all types of biosolids so that the use of compost in restoration may not be the most cost effective option. Composts tend to have low fertilizer value and are used primarily as a soil conditioner. However, they can also be used to create a new soil horizon. High rates of compost are required for restoration (generally applying 3" of material is sufficient to create a new soil horizon). They are appropriate for use in high population areas and in areas bordering roads and streams where potential erosion of less stable materials is a concern. They can also be used as a border in projects that primarily use biosolids. Composts are also highly effective for use in wetland restoration or construction.

They are stable, highly organic materials that are similar to the muck found in naturally occurring wetlands.

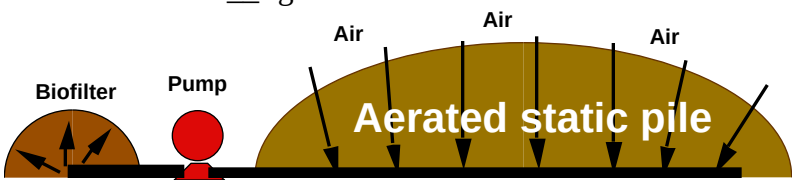
One way to lower the costs associated with compost use is to use compost that has not been screened or completely cured, as both long detention times and screening add significant costs to the process. These less stable materials are much cheaper to produce and can be obtained by working with a municipality or composting operation to specify the type of product that you require.

There are at least three relatively low-tech ways to produce compost from biosolids:

- **Static pile composting**. Biosolids (mixed with a low surface area carbonaceous material such as hog fuel as a bulking agen__t) can be set in piles and left to cure for 4 or more months. Little odor will be created except at pile building, and some amount at extraction of composted material for land application.



- **Aerated static pile**. A second method is similar to the first, with the exception that air is forced into or vacuumed from compost piles. This greatly reduces the composting time - for restoration use to within 1-2 months. Little odor will be created except at pile building. Continuous aeration should keep the pile mostly aerobic, and reduce odor production. Some odo__r generation can result if this is forced aerated. If air is pulled through the piles, it can easily be treated by a biofilter. No odor should be produced when the compost is finally extracted for application.



- **Windrow composting**. Biosolids and bulking agent can be set out in windrows. The windrows are turned by a specialized turner, or a loader as temperature dictates (generally 1 or 3 times per week) to insure adequate aeration. This type of composting also produces a product for restoration use within 1-2 months. Odor _will be produced at each turn of the compost pile. Similar odors will be produced when the compost is finally extracted for application.

Materials for composting. If biosolids are used as the primary ingredient to be composted, a bulking agent must be added to aid in aeration. A number of materials are suitable for this purpose, but commonly a carbon-rich material is used. Often materials are added simply to "dry out" the biosolids to about 40% solids. This can be accomplished with woodchips at a volume ratio of about 3:1 woodchips to biosolids, or a dry weight ratio of about 7.5:1 woodchips to biosolids. If a yard waste is used with higher moisture than woodchips, even a greater ratio is required. Raw materials that go into the compost piles will lose both volume and weight through the decomposition process. With biosolids and a woody bulking agent, somewhere between 25-50% volume loss can be expected.

What They can be Used for

Determining the problems

Biosolids can be used to remedy a number of factors that may potentially contribute to a soil's inability to support a vegetative cover. It is important to first understand what the problems are preventing plants to grow at a particular site. There are several soil tests that can help determine the nature of the problems. A history of a site can also be useful when attempting to figure out what is preventing plants from growing.

The primary things to test for are soil pH, soil fertility, soil physical properties, and potentially toxic concentrations of trace metals. All states have land grant colleges; these generally have soil testing labs that can do your analysis. Land grant universities have agricultural schools and are generally known as State University rather than the University of "XX". While the purpose of these labs is to test soils, generally they are testing agricultural rather than disturbed soils. It is very important to be clear that you are sending a sample from a disturbed site in for analysis. Specifying the tests to be run is also important. Soil testing labs at Land grant universities generally use extractions designed for the soils that are common in the state to determine fertility. Soils at disturbed sites may have very different properties that make these extractions less valuable.

pH

Appropriate soil pH for plant growth is generally between 5.5 and 7.5. A hand held pH meter can be used to measure soil pH. Mix soil and water at a 1:1 or 1:2 volume ratio and let it sit for 1 hour. The slurry will then be ready for a pH measurement. All soil testing labs are equipped to do this measurement. If you have a soil with high levels of trace metals (Zn, Pb, Cd) part of your remediation goal will be to increase soil pH to >7.0. Metals are much less soluble at high pH and, thus, less bioavailable. An appropriate way to determine a good pH goal (assuming that metals are not an issue) is to look at the pH of soils in the area. The soil test lab can usually provide this information and can tell you an appropriate amount of lime to add based on your soil type and soil pH.

An important factor to consider when looking at soil pH, is the potential for soils to get more acidic over time. For example, certain mine tailings have very high **sulfur** (S) content. Initially the S is in a reduced form. As the S is exposed to air and moisture, it will oxidize and generate sulfuric acid. If you are working with high S residuals you need to account for potential as well as actual acidity. There are special tests that can be run to determine potential acidity. Dennis Neuman (dneuman@montana.edu) and Douglas Dollhopf (dollhopf@montana.edu) at Montana State University and Lee Daniels (wdaniels@vt.edu) at Virginia Polytechnic specialize in remediating soils with high acid generating potential. Either one can test your soil for a lime requirement that takes into account acid generating potential.

Soil fertility

Soil fertility is the most common test performed by any soil test lab. The 3 macronutrients that are generally tested for are N, P, and K. Soil test results for these nutrients are generally reliable. Phosphorus is the only macronutrient whose test results may not be appropriate. Phosphorus is relatively stable in soils; it will generally precipitate and only a small fraction of total soil P is plant available at any time. In cases of mine tailings or metal contaminated soils, P is very often deficient. Adding sufficient P to provide excess for plant growth is important at these sites as plants can inadvertently access trace metals in their efforts to increase the P supply.

Soil physical properties

In many cases, disturbed soils have a very poor water holding capacity. This can make plants grown on the sites very susceptible to draught. Organic matter addition can greatly increase a soil's water holding capacity. Adding organic matter can also increase percolation, and enhance soil aggregation (cementing of particles into small clumps instead of being dispersed).

Soils generally contain between 1 and 8% organic matter; the higher values found in areas with colder climates, fine soil texture and high rainfall. If you are trying to reclaim a sand pit in New Mexico, your goal for total organic matter will be much less than if you are working with a soil in Wisconsin. Soil labs can test your soil for total C using a CHN analyzer. The results from this analysis can help to determine how deficient your soil is in organic matter. Generally extra organic matter can only benefit a soil. When you are working with mine tailings or overburden, organic matter always improves soil properties.

Trace metal concentrations

_ We often hear that high levels of metals can kill plants. However, many of these metals are also necessary micronutrients for plant growth. Soil labs routinely test for micronutrients like Zn, Mn, Cu, and Fe. These tests were developed to assess potentially deficient conditions, and normally are extraction procedures. They are not appropriate tests for potentially toxic conditions or conditions where you may have a nutrient imbalance. The best tests to use for these situations are procedures that measure total metals, such as a wet digestion. Total concentrations can tell you if you are in a potentially toxic range for certain elements or if you are deficient in others. Plant availability of these metals is highly pH dependent. As the soil gets more acid, the metals get more plant available. A non-toxic concentration of metals at pH 7.5 can be toxic at pH 5.0. pH must always be considered when determining whether metals concentrations are excessive. A range of metal concentrations for normal soils is as follows:

- Zn 10-300 (necessary nutrient)
- Pb <1 - 120
- Cd <0.01-2
- Cu 2-100 (necessary nutrient)
- Fe 10,000-100,000 (necessary nutrient)
- Mn 20-4,000 (necessary nutrient)

Metal toxicity

Metal toxicity can occur when a metal (often a necessary plant nutrient) is present in high concentrations. Toxicity becomes more severe at acidic soil pH or when coupled with other nutrient deficiencies. Certain metals are more toxic to plants than they are to humans. An example of this is Zn, which will kill plants in concentrations that are too low to cause any negative human health effects. Other metals, such as Pb, are generally not toxic to plants butcan cause negative human health effects when soil is ingested directly. Plant tissue tests can help to determine if you have a metal toxicity. Commercial labs and land grant universities can generally do plant tissue analysis. Grab samples from young leaves of several plants in a field can be combined for analysis. They should be washed in soapy water, rinsed and air-dried before being sent to a lab. While toxic concentrations of metals vary across plant species, generally Zn > 400, Mn > 1000, and Cu > 40 are potentially toxic.

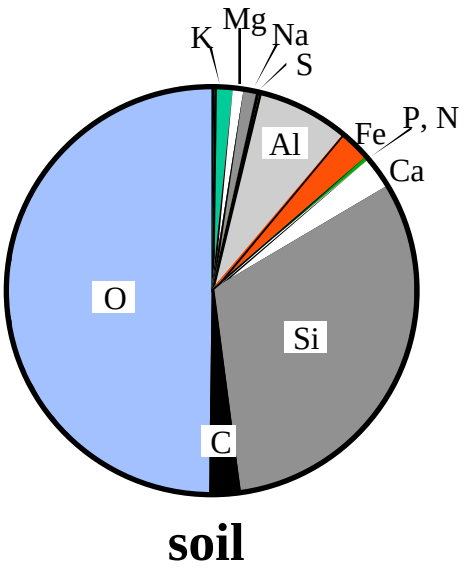
Combination of factors

In many cases, disturbed sites are barren for a combination of reasons. An example is the case of soils contaminated by smelter emissions. Aerial deposition of contaminants makes the soil surface toxic to new seedlings. As a result, only preexisting vegetation survives. The established growth is weakened by contaminants on leaves. Often, older growth gradually dies out or is killed by fire. Without plant roots to hold soil in place, erosion increases. To remediate this type of soil, there are a number of obstacles that need to be overcome. These obstacles include: poor physical properties due to erosion of the surface soil horizon, nutrient imbalances and deficiencies (again, due to the loss of a surface horizon), and acidic and potentially metal-toxic surface soils due to smelter deposition.

In all cases it is important to understand the range of factors that are contributing to a barren soil. While conventional approaches can be very effective at remedying a particular problem, they are often insufficient for fixing a combination of problems. Biosolids, alone or in combination with other products or residuals, are generally able to remedy a range of problems.

Why Use Biosolids?

While other materials, like manure, may also be effective, there are reasons to use biosolids. From a regulatory viewpoint, there are new EPA rules (40 CFR 503) that govern use of biosolids. On a scientific basis, there is an extensive body of research on the use of biosolids, including use of biosolids for reclamation. Then, from an economic viewpoint, all biosolids generators have an associated cost for management, meaning that use of biosolids for remediation can be partially subsidized by the generator. Also, since they have been practicing biosolids application for many years, generators, or their contractors, have an enormous amount of application expertise and equipment for biosolids application.

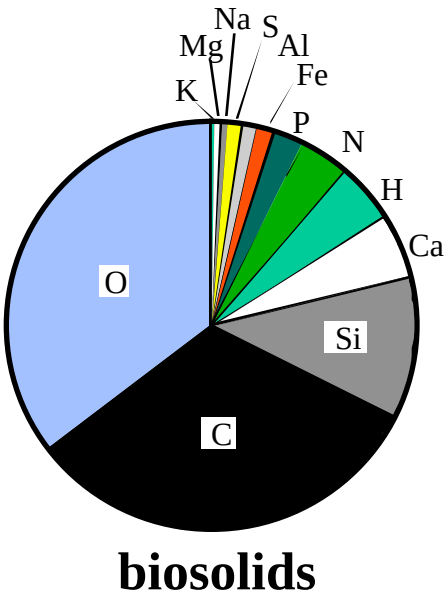


How biosolids work

Fertility

Biosolids are generally applied in agricultural soils to meet the N needs of a crop. By applying material to meet the N needs, sufficient P is also applied. Sufficient potassium is generally not provided for in an agricultural application of biosolids and commercial K may need to be

added. If the only problem with a site is lack of N or P, application of biosolids at agronomic rates will more than correct the deficiency. Most biosolids are applied to agricultural or forest soils for this purpose and appropriate rates are generally based on providing 150-200 lbs of plant available N per acre. Calculation of an appropriate application rate is common practice for people experienced with biosolids applications. The organic matter that is supplied along with the N and P will improve the physical properties of the soil as well, but, as an application at fertility rates is relatively small, improvement of physical properties happen only over many repeated applications.



When attempting to vegetate disturbed mine tailings, unexpected micronutrient deficiencies are not unusual, and nutrient imbalances are also common. In addition to macronutrients, biosolids also contain all other necessary micronutrients; thus an application of biosolids to meet the N needs of a crop will also provide sufficient concentrations of all other micronutrients -- and generally in balanced ratios. Rather than attempting to test for a full range of nutrients and develop a customized fertilizer blend, a biosolids application can function as an all purpose fertilizer. Some special cases exit, such as with lime stabilized biosolids added at high rates to light textured or sandy soils. If the lime added to the biosolids is primarily a Ca rich material, there may be a potential for a long-term Mg deficiency. This can be avoided by addition of a high Mg product, such as dolomitic limestone, to your application mixture.

pH

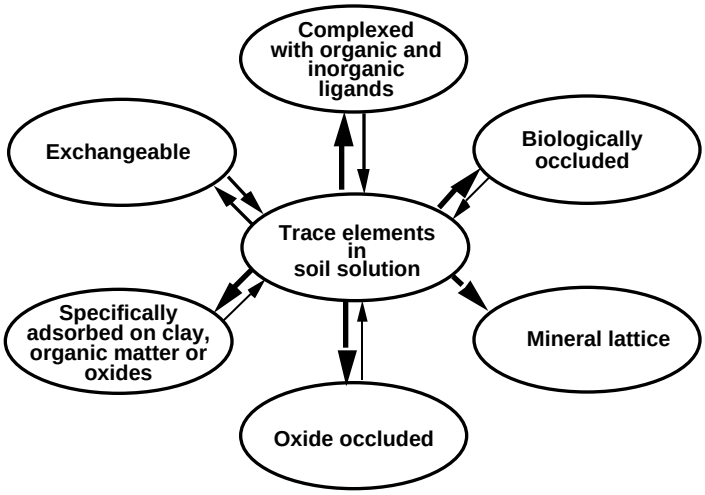
Biosolids can sometimes be applied to correct the pH of a soil. To meet requirements for pathogen and vector attraction reduction that is outlined in 40 CFR 503, some treatment plant operators will add lime to biosolids. Lime is generally added at a rate of 20-50% solids to reduce pathogens; generally referred to as lime stabilized materials. Application of lime stabilized biosolids can very effectively correct soil pH. Applied at high rates (> 100 dt/ac), these materials have been shown to correct subsoil as well as surface acidity. If locally available materials are not lime stabilized, limestone or a high lime residual such as coal fly ash (when burning high S coal), wood ash, cement kiln dust, or sugar beet lime can be mixed with the biosolids. Addition of a high calcium carbonate residual to biosolids will volatilize much of the ammonia in the biosolids, reducing the N value of the amendment.

Soil physical properties

In many cases, poor soil physical properties are responsible for poor plant growth. When you are trying to establish a plant cover on a disturbed site, poor water holding capacity and poor water infiltration/percolation can lead to droughty conditions. Addition of organic matter to soil will improve both of these properties. Organic matter also helps to form stable soil aggregates, which increase water infiltration and percolation. As biosolids are generally 50% organic matter, biosolids application will improve the physical properties of a soil.

Trace metal toxicity

Much of the initial research on biosolids centered on the potential for trace metals in biosolids to cause negative human health effects. A range of pathways that outline 14 major ways that metal in biosolids could potentially negatively impact human, animal and plant health was developed (link). The metal perceived to pose the greatest potential human health effect was Cd. One of the primary ways that Cd can potentially harm people is through people consuming plants grown on high Cd soils. Cadmium can accumulate in plants in concentrations that are potentially high enough to negatively effect people without affecting plant yield.



Early studies were done with Cd salts added to soils to predict what happens when Cd from biosolids was added to soils. What was shown in the studies, however, was that biosolids Cd does not behave at all like Cd added as salts. Plant uptake in biosolids amended soils was consistently lower than in salt-amended soils. This phenomenon has been attributed to the ability of biosolids to bind trace metals. Biosolids generally contain iron at > 1% as well as manganese ≥ 0.1%. These elements form highly amorphous minerals that are capable of forming specific bonds with trace metals. Once complexed, the trace metals are not plant available and so are rendered non-toxic in situ. As metals in biosolids have decreased due to pretreatment regulations, biosolids can now be used to bind trace metals. Biosolids and biosolids compost addition can reduce plant uptake and bioavailability of Zn, Pb, and Cd.

Can they be used with other materials?

Lime or residuals with high CCE

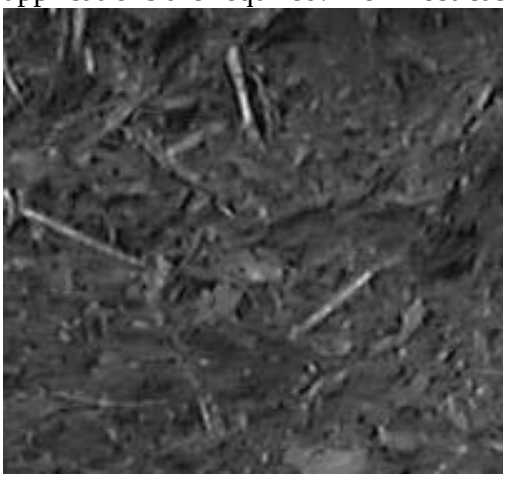
Blending biosolids with other residuals or with other products can result in an excellent soil treatment. The most common type of material to blend with biosolids is limestone or a residual with a high calcium carbonate equivalent (CCE). Materials are easily mixed using a low-tech approach. Once an appropriate dry loading rate of each material is determined, a front end loaded can mix materials by adding the proper number of scoops of each to a pile and giving the pile a few turns. Too much mixing can give the amendment a gel like consistency that makes spreading difficult with a vehicle with flinging or other throwing mechanism.

Commercial limestone is available as agricultural lime (primarily $CaCO_3$), or burnt or slaked lime (CaO or CaOH). Another form of ag lime is dolomitic limestone. This material has high Mg, as well as Ca, contents. These ag limes are generally slow reacting and are about pH 8.3. The other forms of lime are much more reactive and are generally greater than pH 10. Some examples of residuals with high CCEs include wood ash, coal fly ash from plants that burn high S coal, sugar beet lime, cement kiln dust, and ash from burning pulp and paper sludges. The pH of the amendment will vary depending on the form of Ca in the residual. The generator of the material often knows the CCE of the residual. It can also be easily calculated by looking at an elemental analysis of the material. The elemental analysis should list the total Ca (% weight x 2.5), Mg (% weight x 4.2), and K (% weight x 1.3) in the material to get CCE of the residual.

With less reactive materials, the amount of ammonia that is volatilized from the biosolids should not be critical to germination. It may be possible to add seed mixture directly into the amendment immediately prior to application. This approach has been successful at a NPL site in Palmerton, PA where fly ash was mixed with biosolids. In the case of more reactive forms of lime, however, the increase in pH will be sufficient to cause a sizeable fraction of the ammonia to rapidly volatilize, at a rate sufficient to kill any seeds added directly to the amendment. For these types of mixtures, a waiting period of several days is recommended before seeding amended areas.

Residuals with high C:N ratios

Other amendments to add to biosolids may include residuals with high C:N ratios. When biosolids are used for reclamation, rates generally higher than those used for agronomic applications are required. For most cases, excess N is added to the soil. Previous studies on sites where a range of rates of biosolids have been used for reclamation have shown that there is generally a one time spike in N concentration in surrounding waters following application. If there is concern about excess N entering neighboring streams or into groundwater, addition of a residual with a high C:N ratio may be appropriate. Examples of these types of materials include sawdust, straw, primary pulp and paper sludge, log yard debris, and cotton gin waste. By adding these materials to biosolids, the excess C in the high carbon residual will increase the C:N ratio of the mixture, and immobilize the N. While total C is not always an indication of how easily biodegradable a material may be, aiming for a C:N ratio of 30-40:1 for the mixture is a good ball park figure.



Correcting micronutrient imbalances

Generally, biosolids applications at restoration rates provide more than adequate levels of all necessary plant nutrients (with the possible exception of K, as noted). However, in special cases addition of a micronutrient source may also be required. Examples of this include cases of high Ni soils, where addition of Fe to reduce Ni availability may induce a Mn deficiency. Addition of Mn as commercial fertilizer salts can alleviate these deficiencies. Another example is cases of Cd contamination. When Cd alone is present in elevated concentrations, addition of materials with sufficient Zn is required to bring the Zn:Cd ratio to greater than 100:1. Addition of biosolids alone may be sufficient to accomplish this. If not, supplementing the biosolids amendment with a Zn fertilizer may be required.

How do You get Them?

All municipalities generate biosolids. As outlined in the Clean Water Act (PL 92-500), all municipalities are responsible for biosolids management -- use or disposal. Municipalities use a range of programs to meet this requirement. Programs can include direct application to agricultural land, composting, use in reclamation, surface disposal, incineration, or landfilling. Approximately 60% of all biosolids generated are beneficially used, and beneficial use is

encouraged under EPA 40 CFR 503. Most municipalities subsidize the costs of these use or disposal options.

EPA officials

Each EPA region has a biosolids coordinator. Biosolids coordinators are generally an excellent source of information on the availability of biosolids within a particular region. They can often provide direct contacts to generators and may be willing to assist in making arrangements for use of materials in reclamation projects. A list of these contacts follows. Those names followed by an asterisk have previously been actively involved in use of biosolids for reclamation projects.

EPA REGIONAL BIOSOLIDS COORDINATORS
January 1999

REGION 1

Thelma Hamilton-Murphy*
USEPA Region 1
Office of Ecco-System Protection
One Congress Street, Suite E1100 CMU)
Boston, MA 02114-2023
Tele: (617) 918-1615
Fax: (617) 918-1505

REGION 2

Alia Roufaeal
USEPA Region 2
Div. of Enforcement & Compliance Asst.
290 Broadway - 20th Floor
New York, NY 10007-1866
Tele: (212) 637-3864
Fax: (212) 637-3953

REGION 3

Ann Carkhuff*
USEPA Region 3 (3WP12)
Water Protection Div.
1650 Arch St.
Philadelphia, PA 19103
Tele: (215) 814-5735
Fax: (215) 814-2301

REGION 4

Madolyn Dominy
USEPA Region 4 - Water Mgmt Div.
Atlanta Federal Center
61 Forsyth Street SW
Atlanta, GA 30303-3104
Tele: (404) 562-9305
Fax: (404) 562-8692

REGION 6

Stephanie Kordzi
USEPA Region 6 (6WQ-PO)
Water Quality Protection Div.
1445 Ross Avenue
Dallas, TX 75202-2733
Tele: (214) 665-7520
Fax: (214) 665-2191

REGION 7

John Dunn/Cynthia Sans*
USEPA Region 7
Water, Wetlands & Pesticides Div.
726 Minnesota Ave.
Kansas City KS 66101
Tele: (913) 551-7594/551-7492
Fax: (913) 551-7765

REGION 8

Bob Brobst*
USEPA Region 8 (8WM-G)
999 18th St, Suite 500
Denver, CO 80202-2405
Tele: (303) 312-6129
Fax: (303) 312-7084

REGION 9

Lauren Fondahl*
USEPA Region 9 (WTR-7)
CWA Compliance Office
75 Hawthorne Street
San Francisco, CA 94105-3901
Tele: (415) 744-1909
Fax: (415) 744-1235

REGION 5

John Colletti/Ash Sajjad*
USEPA Region 5 (WN-16J)
NPDES & Technical Support
77 W. Jackson Blvd.
Chicago, IL 60604-3590
Tele: (312) 886-6106/886-6112
Fax: (312) 886-7804

REGION 10

Dick Hetherington
USEPA Region 10
NPDES Permits Unit (OW-130)
1200 Sixth Avenue
Seattle, WA 98101
Tele: (206) 553-1941
Fax: (206) 553-1280

INTERNET: Format for all EPA internet addresses:
(lastname).(firstname)@epa.gov
EXAMPLE: centilla.sharie@epa.gov

Survey

A national inventory of biosolids is being prepared by Bob Brobst, (brobst.bob@epamail.epa.gov) the Region 8 biosolids coordinator. This inventory includes information on biosolids currently being generated in the country. Information on treatment process, quantity, and quality is included. The survey provides information on the current uses of biosolids for each municipality as well as contact names. This survey can be used for identifying sources of materials.

Municipalities

Municipalities can also be contacted directly to procure biosolids. The wastewater treatment department of any city is where you will find the people that work with biosolids. Many municipalities operate biosolids use programs without the use of private companies. Some of their primary concerns are: (i) cost, (ii) developing long-term use sites, and (iii) public acceptance. If a municipality beneficially uses their material, obtaining biosolids for remediation is generally possible. It is important to understand that large municipalities -- the ones that will primarily be involved in restoration, as it requires a large amount of biosolids -- generate material on a daily basis. Most cities are not able to stockpile biosolids. So, from a generator's perspective, it is extremely important to preserve existing markets for materials, as they need to assure long-term use sites for biosolids. This needs to be considered when negotiating with a municipality. For instance, if, by working with a municipality, an arrangement can be made to get sufficient biosolids over time, rather than requiring them to abandon completely their existing practice, a mutually agreeable situation can be reached. This will require either stockpiling materials on site or prolonging the time period of reclamation activities while materials are being delivered. In the majority of cases, the municipality will arrange for transportation of materials, as part of their normal operations. Similarly, they can often arrange for application and incorporation of biosolids.

It is also important to understand that certain municipalities in areas of high population densities have difficulty identifying local use sites for their materials. These cities (for example New York and Boston) often use rail lines to transport biosolids as far as Texas and Colorado for agricultural use. If your project is far from a large municipality, but close to a rail line, materials from high population areas may be a cost-effective option.

If a municipality currently disposes of, rather than uses, their biosolids, acquiring material for beneficial use may require a number of extra steps. All biosolids that are used for land application are required to meet Class B criteria for pathogen reduction. If a municipality

landfills their biosolids, the biosolids may require additional processing and stabilization to be suitable for land application. While treatment facilities can often be retrofitted for additional processing, the additional expense and limited need for Class B materials may discourage treatment plant operators from doing so

There are a number of organizations that municipalities belong to that can be sources of information for obtaining biosolids. The best are ones like the Northwest Biosolids Management Association (http://www.nwbiosolids.org/), that can not only identify sources, but can help put projects together on a cooperative basis, and even arrange multiple sources of residuals for a project. There are a number of these organizations currently being formed throughout the US. They include:

Northeast NEBRA Ned Beecher ned.beecher@rscs.net

Middle Atlantic MABA Bill Toffey William.Toffey@phila.gov

Southern California SCAP Ray Kearney rjk@san.ci.la.ca.us

Other organizations can also provide leads to biosolids sources. The Water Environment Federation (http://www.wef.org/) is an organization of practitioners, wastewater plant operators and private contractors in the industry. Regional groups of WEF can be contacted (http://www.wef.org/docs/wclinkma.html) to identify sources of materials within a particular area. Additionally, large municipalities belong to an organization called Association of Metropolitan Sewage Agencies (http://www.amsa-cleanwater.org/), which can suggest possibilities. Currently, there is a National Biosolids Partnership among EPA, WEF and AMSA to help promote environmentally sound biosolids management, so help from each or all of these organizations is highly likely

Private companies

There are private companies that also handle biosolids. These companies will contract with a municipality for use of their biosolids. The companies are paid a fee by the municipality to apply biosolids. Companies can arrange for materials delivery and application. These companies are easily contacted through advertisements in wastewater, biosolids and organic residuals journals (i.e., the WEF journal, or BioCycle).

How much do biosolids cost?

Under the Clean Water Act, all municipalities that generate biosolids are responsible for their management -- use or disposal. Beneficial use for agriculture, silviculture, and restoration are recommended end-uses for biosolids under this act. Generally, a municipality will have developed a range of beneficial use options or will have paid a contractor to develop a beneficial use program. In all cases, the municipality has costs associated with biosolids use or disposal. It is also the goal of all municipalities to reduce these costs. When approaching a municipality, it is important to fully appreciate both of these facts. In certain cases, the municipality or contractor will willingly provide and incorporate biosolids at no charge. In many cases, a token payment will be required. Some municipalities may look at restoration projects, particularly those under the Superfund umbrella, as having very deep pockets. They may attempt to have the restoration project cover all transportation costs and even request payment for materials. In these cases, negotiations are necessary and it is important to have an understanding of the normal costs covered by municipalities when entering into these negotiations.

The beneficial use costs of a city with an award winning use program can be used as an example. Costs for biosolids use in this city have decreased by over 33% in the last ten years, due to increasing options and corresponding demand. Currently the city uses a three pronged approach for biosolids use. A portion of the biosolids is sent to a private company to be composted. Transportation costs as well as composting costs are covered by the municipality

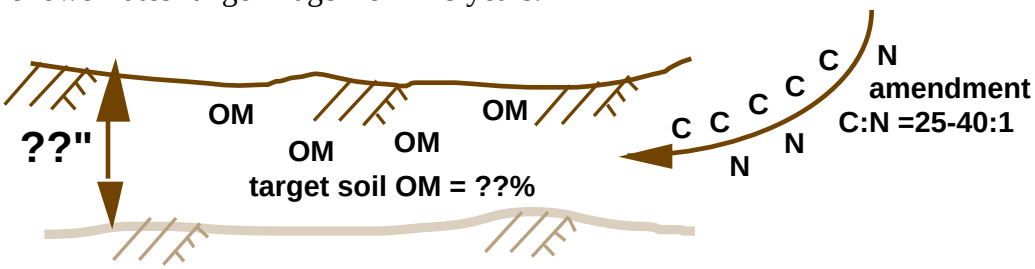
bringing the costs of this process to > $35 a wet ton. An additional portion of biosolids is used for forest application. The municipality pays about $12 a wet ton for transport and an additional $5 per ton for application. The bulk of the biosolids are used as a fertilizer in agricultural soils. Here transportation is approximately $30 per wet ton and incorporation costs are $2-3 per ton. The farmers pay the municipality $1-2 dollars per ton to the municipality in exchange for the biosolids.

It is important to work with a municipality to develop an appropriate time line for materials delivery and incorporation as well as to determine the amount of biosolids that can be provided within a particular timeframe. Working together and showing some flexibility can make the costs of biosolids application a reasonable fraction of total project costs. In addition, using the expertise and equipment of the biosolids generators for application can greatly reduce the cost of operations.

Design and Permitting Process

Determining appropriate biosolids rates

Determining an appropriate application rate, unfortunately, is not a matter of rigorous science at this point in time. Older restoration projects using biosolids generally used rates in excess of 100 dry tons/acre. There was generally the perception that more biosolids would result in longer-lasting and more effective restoration efforts. While often addition of high rates of materials will have a positive effect, cost concerns may outweigh that luxury. There has been some research to determine appropriate rates at the lower end of the scale. With only a shallow horizon of contaminated soil, application rates of 25 dry t/ac were found to be equivalent to 50 and 75 t/ac in Palmerton, PA. Application of 25 dry t/ac in combination with fly ash has maintained a stable vegetative cover for 8 years. A project in Silesia, Poland found that 100 t/ac was necessary to establish a vegetative cover on slag piles. Work in Bunker Hill, ID indicated that a higher application rate of a drier biosolids was required to achieve even coverage. As use of biosolids to restore metal contaminated sites is a relatively new practice, it is not yet possible to say whether lower rates are as effective as higher rates over the long-term. Areas that have received higher rates are showing a self-sustaining cover up to 30 years after biosolids application. Projects using the lower rates range in age from 2-8 years.



Factors to be considered in determining an appropriate application rate are depth and levels of contamination. The deeper and more contaminated a sites suggest that higher application rates be used. For example, in cases where a plant cover is to be established on mine tailings with Zn concentrations in excess of 10,000 mg kg^{-1} and acidic pH, a higher application rate of 100 t/ac or greater would be appropriate. Where tailings are calcareous and have lower metal concentrations, 25-50 t/ac should be sufficient. Brown fields sites with highly variable concentrations of contaminants should also be restored successfully with lower rates.

Rates determined by depth of application

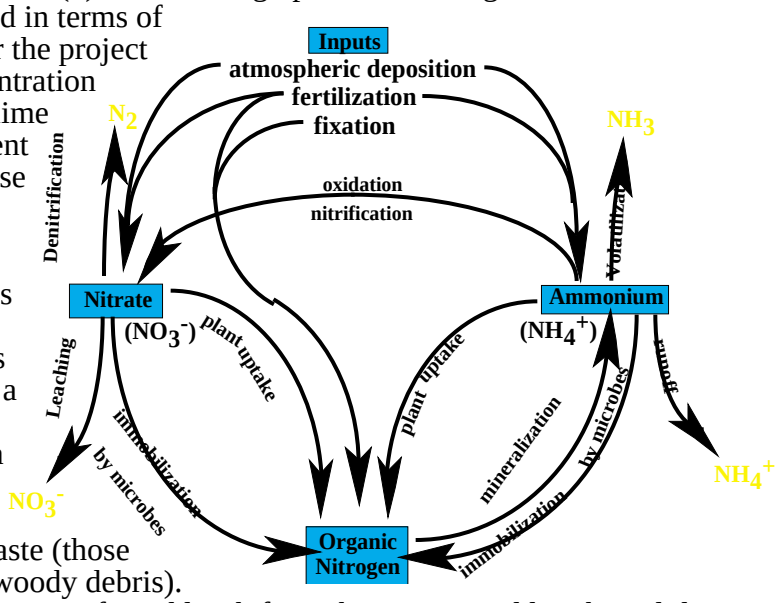
To create a "soil horizon" by biosolids or biosolids products, requires approximately 115 dt/ac of stable material for every inch of soil built up. However, over the first year or so, a large

portion of the fresh biosolids mass may be lost to decomposition, say up to 25% depending upon the biosolids stability at time of application. Thus, the applied amount required may be about 150 dt/ac. Then, since biosolids generally range from 15-30% solids, every inch of soil requires a wet depth of biosolids over 6 inches (assuming 20% solids).

Similarly, one must consider the reduction of volume of compost material in the years following application as the organics decompose - depending upon the characteristics of the compost, greater than 25% of the volume. Thus, a desired depth of compost of 1" should receive an application of 1.3", or about 180 cy per acre. In terms of dry weight loading, this is about 50 dt/ac (at a bulk density of about 20 lbs/cf) per desired final inch of soil compost.

Nitrogen management

One major consideration of heavy applications of biosolids is nitrogen management. An application of 100 dt/ac may contribute up to 10,000 lbs-N/ac (at 5% N); half of that may be in an available form during the first year. This amount of available N (initially in an ammonium form) will either volatilize, or be transformed into nitrate. Two associated concerns exist: (1) nitrification is an acidifying process, and (2) there is a high potential for high rates of nitrate leaching. This needs to be considered in terms of groundwater impacts. If biosolids for the project are lime stabilized, the total N concentration will be lowered by dilution, and the lime added to the biosolids during treatment will maintain soil pH and also increase N volatilization.



An alternative to high biosolids only applications, which both reduces the N loading and may actually conserve excess N from the biosolids through immobilization, is co-use of a carbon-rich residual. In this case, biosolids can be applied to the soil in combination with sawdust, primary pulp and paper sludge, paper waste, or even some types of yard waste (those that include a significant amount of woody debris). This limits the potential for excess N to nitrify and leach from the site. By adding biosolids in combination with a high C material directly to the soil, you are essentially letting it compost in place. Total cost for this option would be transportation of materials to the site and direct application of the materials. In normal practice, either: (a) alternate layers of biosolids and C-rich material are laid down, then incorporated, or (b) materials are mixed on site prior to application. Because a C-rich residual is often considerably drier than biosolids, it if much easier to work the soil after application.

pH adjustment

Determining the appropriate application rate for lime is very important in cases of metal contamination. Plants generally require a pH > 5.5 for good growth. In cases of metal contamination, pH > 7.0 will limit the solubility of metals by both increasing the number and strength of binding sites and decreasing the potential for soluble stable species. It is important to add sufficient limestone to raise soil pH in the surface 18" of soil and to keep it well buffered.

Procedure

Soil samples can be collected in 6" increments. pH measurements should be made on the dried and sieved subsamples. There are standard EPA procedures to determine the lime requirement of a soil. An alternative test is as follows: base (such as 1 M KOH) should then be added to 10 g subsamples of the soils that have been mixed with 20 mls of water. A good starting point is addition of **1** ml of 0.8 M KOH, which is equivalent to the addition of 8 t/ac of limestone for the 6" portion of the soil profile. Take the pH of the soil/water slurry 1 hour after water addition. Then add the base and put the sample on a side to side shaker for 24 hrs. The pH of the sample after shaking will be comparable to the pH of the field soil after limestone application. If this is sufficient to bring the pH> 8.5, that should be sufficient lime to add to neutralize that portion of the soil. If the base brings the pH of the sample to >10.5 then the CCE tested was more than is required. Redo the incubation using a lower rate of KOH addition. Add the adjusted lime requirements for all horizons tested and you will have your lime requirement for the profile. This is a relatively quick procedure to determine the lime requirement for a site where acidity is an obstacle to revegetation. It is appropriate to use this type of procedure, rather than simply consulting the soil test lab or an agricultural extension agent when you are working with heavily disturbed soils or mine tailings.

High sulfur sites

In cases where soils were contaminated with high S minerals or where tailings that contain high concentrations of S are present, it is also necessary to account for the acidity that can be generated when the S oxidizes when determining the appropriate rate of limestone addition. Sulfur is often present in mine tailings when high S ores have been processed. These ores are stable under anaerobic conditions. As the rocks are ground to small particles and exposed to O_2, the minerals are no longer stable and the reduced S will oxidize. When S oxidizes, it generates sulfuric acid. This is never good for plant growth.

There are a number of procedures to test for the acid generating potential of these types of soils. The best way to test a soil for this type of acidity is to consult with scientists who work with these types of materials. Douglas Dollhopf (dollhopf@montana.edu) at Montana State University and Lee Daniels (wdaniels@vt.edu) at Virginia can test your soil for a lime requirement that takes into account acid generating potential.

Regulations and guidelines

40 CFR 503

Contaminants – metals and organics. The national regulations that define appropriate use of biosolids are detailed in 40 CFR part 503 (link). These guidelines define the maximum metal concentrations that biosolids can have and still be suitable for land application. The basis for 40 CFR 503 is primarily the agronomic use of biosolids. The exposure risk assessment (that used a pathway approach to evaluate any potential negative impacts as a result of biosolids use) also considered soil reclamation in its analysis. They also define the maximum metal concentrations that biosolids may have to be considered exceptional quality materials (Table 3). These materials may be used without restriction. Currently the vast majority of biosolids produced in the country

have metal concentrations well below the Table 3 requirements. Organic contaminants are not regulated under 40 CFR 503 as concentrations of these materials were well below concentrations that were deemed to pose a potential risk. Radionucleide concentrations were not regulated in the 503's. EPA is currently surveying the radionucleide concentration in biosolids and may issue an advisory or site specific guidelines for these materials. The technical basis for the 503 regulations is outlined in one of the support documents (LINK). *******

Pathogens. Part 503 also regulates pathogen reduction requirements that are necessary to achieve Class A and Class B standards. Class B biosolids have undergone a Process to Significantly Reduce Pathogens (PSRP). Use of Class B materials has some restrictions. For example, no vegetable crops may be grown on the soil for 18 months following application. Material may not be applied within 10 m of streams or rivers. Public entry in applied areas is restricted immediately following application. Full details of these restrictions are outlined in the regulations. Most generators and contractors are familiar with these restrictions and can make sure that application is in compliance with the regulations. Most biosolids from larger municipalities that have anaerobic digestion and high N biosolids generally fall under Class B standards. Class A materials have undergone a Process to Further Reduce Pathogens (PFRP), such a high temperature digestion, composting or heat drying. These materials may be used without any restrictions, so long as they also meet the Table 3 limits.

State regulations

The 40 CFR Part 503 regulations are the minimum standards for biosolids application. Each state has the freedom to apply more stringent standards above and beyond those outlined in 503. The EPA regional biosolids coordinator will be familiar with any additional regulations. Many additional regulations relate primarily to agricultural use of biosolids. Use of material for restoration purposes (generally a one-time application) may be exempt from these additional regulations.

Permitting process

Permits are generally required for all biosolids applications. This is a good means to gain public acceptance of a proposed remedy even though permitting can be a time consuming process. Use of biosolids for reclamation is also a recommended use in the regulations. A provision is made within the regulations for application in excess of agricultural rates for restoration objectives: 503.14(d) “Bulk sewage sludge shall be applied…. at agronomic rates…unless, in the case of a reclamation site, otherwise specified by the permitting authority. Permits may be required on several levels, depending on the particular region of the country. Generally, the permitting process is best left to the experts. If biosolids are being obtained through a municipality, generators can often walk the necessary permits through. Another way to obtain appropriate permits is by working with the regional biosolids coordinator.

Public acceptance

The public has generally accepted the use of biosolids on agricultural lands. This has not always been the case and in some local areas there are still citizens that need to have the benefits of biosolids use demonstrated before public acceptance is achieved. Years of practice in dealing with public acceptance issues have made many biosolids generators public acceptance professionals. Generally, a successful biosolids project requires a pro-active approach. It is necessary to be very open with local citizens groups about the nature of the restoration project. This includes being straightforward about the materials to be used as well as their origins. Low-keyed informational meetings (as opposed to formal public meetings or hearings) and articles in local papers are very effective means for gaining public acceptance. A large body of educational materials exists that is excellent for use in public meetings. These include videos and pamphlets that describe what biosolids are, the regulations governing their use, and the benefits associated

with biosolids use. The generator or contractor providing biosolids for a project may have access to these types of materials. The Northwest Biosolids Management Association (NBMA - contact Leah Taylor 206 684-1145 www.nwbiosolids.org) is also an excellent source of general educational material and can also provide detailed literature reviews on the environmental effects of biosolids use.

One of the most often heard objections of those near a biosolids use site is to its unique aroma. Odor can be a challenging obstacle to public acceptance. There are two stages of odor from biosolids: 1) The strongest smell happens immediately after application and is caused by volatilization of ammonia and anaerobic decomposition of sulfur compounds. This dissipates after a day or two. Evolution of different sulfur compounds will result in some less-intense lingering odor that will depend upon climatic conditions. Dry and hot or cold conditions will reduce odor intensity in a relatively short period of time, while moist, warm conditions prolong odors. Incorporation also reduces odors. Generally in an agricultural community, familiarity with the use of manure will make acceptance of any odors less of a problem. Use of materials in isolated areas also eliminates this as an issue.

How are They Applied?

Application of biosolids usually requires special equipment to match the characteristics of the biosolids to the individual site. The amount of moisture in biosolids, commonly reported as % solids (a weight measurement of the amount of solids and water in a biosolids sample), is the predominant characteristic that dictates the type of machinery required, the application procedures and application timing. The solids content of sludge will vary from a dark liquid at 2-3% solids to a semi-solid moist cake-like material at up to 40% solids. Increasing the solids content of biosolids at the WWTP is expensive, and a generator whose use sites are within a reasonable distance will generally be satisfied with a more liquid product. Dewatered biosolids, sometimes called cake, have had polymers or lime added prior to belt filter press or centrifuge processing to achieve a 15-30% solids content. They are generally the consistency of gelatinous mud.

Typical ranges of biosolids solids content which have been applied to restoration sites include liquid sludge at 2-3% or 6-8% which can easily be pumped, semi-solid biosolids at 8-18% solids which can also be pumped, although less efficiently than liquids, and solid biosolids cake at 20-40% solids which may be flung from a manure-type spreader or end-dumped.

Application rates are typically calculated on a dry weight basis. This means that, for an average dewatered biosolids (20% solids), application of 100 dry t/ac would involve applying 500 wet t/ac of material. This is a significant amount of material - almost 5" deep! This quantity suggests simplicity and speed -- a feature of direct spreading! A variety of equipment technologies are available to perform direct spreading including farm manure wagons, all terrain vehicles with rear tanks and dump trucks.

Heavy applications such as this can be accomplished using two basic techniques, both of which are relatively easy in concept and relatively inexpensive, but that require significant waiting periods for the biosolids to dry out.

- **Single application**. The fastest and most cost-effective method is to make the total application in a single lift. Depending upon application rate and % solids, this may be as little as 1" to up to 30" in depth! Drying of the biosolids at higher depths may require a complete summer period; drying can be enhanced by seeding with a grass that can germinate and withstand the anaerobic conditions of the biosolids. A cereal grass such as annual rye or wheat is generally very effective for this purpose. Once the biosolids have dried, normal farm disks can be used to incorporate biosolids into the subsoils.

- **Multiple lifts**. Applications of biosolids can also be made in smaller "lifts", or partial applications. Biosolids are then immediately incorporated into the soil. In fact, in some states, incorporation within a certain time period is a requirement of biosolids management. Incorporation into the soil helps solidify the mixture by dilution of the wet biosolids with the relatively dry soil. However, unless a cover crop is grown before a second application, drying of this mixture may be slower than if the biosolids were simply surface applied. In the case of multiple heavy applications needed within a short period of time, working the soil becomes a definite challenge, as repeated applications following by mixing without drying will turn the soil into a deep quagmire (potentially far deeper than the actual depth of biosolids added). Because the soil is worked many more times in this method, costs will be significantly higher.

There are several technologies that are effective for applying and even incorporating these rates of materials. Site topography, soil strength, evenness (including debris), and waterways are the physical features that affect equipment selection. Easy access, stable soils and a clear site favors the simple methods, while obstructions or steep slopes require specific equipment. Also important is the application rate, as light applications require a more precise method. The following table summarizes the common types of equipment available to make applications to disturbed soils.

Comparison of different application systems used in remediation sites.

System	Range	% Solids	Relative Costs	Advantages	Disadvantages
Biosolids dump truck discharge, spreading with dozer	10'	> 12%	Low capital, low O&M	Simple to operate, fast for high application rates	Need cleared, relatively flat site, acceptable to heavy equipment, difficult to get even applications for low application rates
Application vehicle with mounted cannon	125'	< 12%	Moderate capital, high O&M	Can make even applications for low rates, any terrain.	May need special trails with strength for repeated trips, slow.
Application vehicle with rear splash plate	10'	15-35%	Moderate capital, moderate O&M	Can make even applications for low rates, moderate terrain.	May need special trails with strength for repeated trips, slow.
Application vehicle with side discharge	200'	15-50%	Moderate capital, moderate O&M	Can make even applications for low rates, any terrain.	May need special trails with strength for repeated trips, moderate speed.
Manure-type spreader - rear discharge	10'-30'	> 25%	Low capital, low O&M	Can make even applications for low rates, moderate terrain.	Limited to high % solids, trails may need to be close together, moderate speed.

Dump truck and dozer

The most basic (and simple) application technologies use dump trucks and bulldozers. Dump trucks can transport materials directly to the application site and end dump accurately, i.e., without the need for additional equipment for spreading. (In other words, the biosolids will "flow" out of a truck to evenly spread to an average depth -- if, say over 4" wet depth is required -- if the trucks are spaced appropriately.) If the soils can not withstand heavy trucks, either dump trucks or other equipment with high flotation tires can be used between the point that the long-haul vehicles can access and where the biosolids will be used. This equipment may be available from the POTW that supplies the biosolids, potentially for the price of transportation and a small fee.. The capacity of the dump truck combined with the loading or application rate can be used to determine how much ground one load of material should cover. A bulldozer can then spread the biosolids over that amount of ground. With the right kind of ground (level to gently sloping and sufficiently dry soils, this can be a quick and cost effective application technology. The bulldozer will have sufficient traction to drive on ground that has already received application. The process should be staged so that the dump trucks (which will not have sufficient traction) dump at the far end of the site first, then move forward.

Application vehicle with cannon

_An application system suited to liquid biosolids is a vehicle with a tank and spray nozzle mounted on the rear. Depending on the site needs, a specially designed all-terrain vehicle may be used or a simple heavy-duty truck chassis with rear mounted tank may be acceptable. Each of these types of systems has been demonstrated to be effective in the Pacific Northwest. The operation of these systems is relatively simple. A biosolids source, where biosolids are transferred into the application vehicle, is available either at the treatment plant, through a delivery truck or from onsite storage. Once full, the vehicle moves into the site and unloads the biosolids in uniform layers while the vehicle is moving or stationary. When empty, the vehicle

returns to the biosolids source for a refill and repeats the cycle. The vehicle-tank spray system is patterned after a combination of fire-fighting systems and log skidders (in the case of the all-terrain vehicle). Key features of the vehicular system include: 1) high ground clearance, 2) suspension that increases tire contact with the ground, 3) articulated steering to reduce vehicle turning radius, and 4) low ground pressure, high flotation, high traction and puncture resistant tires. Key parts of the tank-spray system include: 1) as large a tank as possible, mounted low on the chassis for a low center of gravity to reducing roll-over potential, 2) a pressure-vacuum system for biosolids transfer, and 3) a biosolids or solids pump supplying material to a remotely controlled spray nozzle.

Application vehicle with rear discharge

There are also vehicles that have been specifically designed to apply biosolids to agricultural sites. These typically have flotation tires and a carrying capacity of about 18 yards of material.

They spread biosolids from the rear of the box with a fan or splash plate. The width of the spread is comparable to the width of the vehicle. Changing the speed of the vehicle as well as the speed of the fan can alter application rates. These vehicles are excellent for operating on wet soils. The flotation tires give generally excellent traction and enable access to areas that may not be possible with conventional equipment. They can spread high or low rates of biosolids or biosolids mixtures onto the surface of a soil. In cases where incorporation is required, additional equipment is required. Rear-discharge application vehicles can also be set up with sub-surface injection equipment. Sub-surface injection requires a low solids content to function properly. Water can be added to biosolids before application to achieve sufficiently low % solids. The subsurface injection is generally used for agricultural fields that are under a no-till system. It may be appropriate for reclamation projects with relatively low application rates.

Side cast spreader

Another type of biosolids application vehicle is a side cast spreader, capable of throw distances of up to 200 ft. Throw distance is dependent on the moisture content of the biosolids,

with wetter (15-20% solids) biosolids having a greater throw distance than drier materials such as composts. Application rates can be controlled with this spreader by adjusting the speed of the vehicle as well as the speed of the fan. The spreader can be mounted on a range of vehicles, ranging from simple truck chassis to agricultural application vehicle with high floatation tires to all-terrain logging forwarders. The reclamation effort at Palmerton, PA used an Aerospread mounted on surplus army vehicles. The type of vehicle that is required is especially useful on very steep or debris-filled sites.

_Manure-type spreader

Farm equipment that has been designed for manure spreading also works well for many types of soil reclamation projects. A common design is a wagon pulled by a tractor. Typically, these discharge out the back with a big rotary brush.

Incorporation

_Incorporation of high rates of biosolids mixtures similarly requires the proper equipment and equipment operators. The low % solids of the biosolids means that when you are making a 100 dry t/ac application, you may actually be applying over 500 wet t/ac of material. Generally a large track bulldozer (such as a Caterpiller D7) pulling a 36" disk is required. Smaller equipment will just float on the surface of the biosolids mixture. Large chisel plows also exist that are capable of inc

orporating the amendments. When you are incorporating high rates of amendments it will not be possible to achieve a completely homogenous mixture. Although not always necessary, maximizing soil – amendment content will increase the effectiveness of the amendment and should be done where practical.

Operator

In most cases, the municipality or private contractor that has applied the biosolids for the municipality will have appropriate application equipment and operators. Arranging for application and incorporation as part of the agreement to use biosolids from a municipality may be the best way to assure appropriate and cost effective application of materials. If the particular municipality that you are working with does not have appropriate equipment, others will. Examples of municipalities that have large scale application equipment include Chicago (contact Thomas Granato (708)222 4063), Virginia (contact Lee Daniels wdaniels@vt.edu), Denver, CO (contact Bob Brobst USEPA , brobst.bob@epamail.epa.gov) and Philidelphia (contact Bill Toffee William.Toffey@phila.gov). Bob Bastian (US EPA Washington, DC bastian.robert@epamail.epa.gov) can be contacted as a source of information on application equipment across the country.

Seeding/planting

Immediate seeding

There are several options for establishing a vegetative cover on a biosolids amended site. The simplest process involves adding seeds directly to the amendment immediately prior to application. This approach was successfully used at the Palmerton, PA NPL site. Thirty lbs/ac of a grass vetch mixture was hand scattered on the amendment before loading into application vehicles. This is a very efficient and cost effective approach. It is appropriate to use this type of seeding technique with a relatively low cost seed mixture. As only a small portion of the added seed is close enough to the surface after application and incorporation, germination rates of 10-20% are not uncommon. Seeding with an annual rye would be an example of a low cost option that is appropriate for this type of approach.

Delayed seeding

This approach will not be effective in cases where a highly reactive lime (slaked or burnt lime or a high CCE residual with pH>9) is added to a high N biosolids. These mixtures will

release sufficient ammonia to kill any seeds added directly to the mix immediately prior to application. For these situations, seeds can be hand thrown on the surface of the amended soil anytime after sufficient ammonia has volatilized (generally a waiting period of 3 days is sufficient). The surface of a biosolids amended site will be sufficiently irregular that seeds spread on the surface will fall into cracks and crevices and be able to germinate. It should be noted that use of conventional equipment to spread seed 3 days after application of high rates of high moisture materials might not be effective. In these cases, the simpler the approach, the more effective and efficient. Hand seeding, using a whirly bird seeder is one approach. Using snowshoes or driving on a vehicle with floatation tires will allow early access to these sites. Biosolids amended soils are sufficiently moist and sticky or adhesive that it is not necessary to hydroseed or to use any tackifiers or mulches. The one exception is when biosolids are being applied in areas where it can be very hot during the growing season. The dark color of the material will increase surface temperature and may kill seedlings. In this case, use of light colored mulch is recommended. On the other hand, the dark color of the biosolids can effectively extend the growing season in cooler areas.

Appropriate seed mixtures

In many areas, there is increasing concern with reestablishing native plants on previously disturbed sites. This goal has to be combined with the more immediate goal of establishing a vegetative cover. When high rates of biosolids potentially in combination with other materials have been added to a soil, there are several approaches that may be followed to achieve a healthy stand of native species. Ongoing research to fine-tune these approaches may give different answers over time, but certain approaches seem reasonable.

Initial seeding with high rates (>20 lb/ac) of an annual cereal is generally a very effective approach. Annual cereals such as wheat or rye are inexpensive. There are also varietals that are salt tolerant (high rates of biosolids will increase the electrical conductivity of the soil for a finite period). These materials will germinate quickly and can provide a cover while the amendment stabilizes. Use of lower rates of native species seeds the following season will permit a succession to naturally occurring vegetation. If the area that has been amended is relatively small and is bordered by healthy vegetation, it is also possible to let this vegetation naturally colonize the amended area. If there is no potential for erosion and it is acceptable to leave the amended surface bare for several months, the bordering vegetation will invade the amended areas over time.

A relatively new approach involves cutting mature hay from neighboring fields and using the hay as mulch for the amended areas. The hay should be cut so that viable seeds are included in the hay. These seeds will germinate and the hay will decompose. This is a relatively inexpensive way to establish a native cover.

Links or contacts for information on successful projects

Palmerton, PA (http://WWW.EPA.GOV/OERRPAGE/SUPERFUND/WEB/SITES/CURSITES/C3PA/)

Bunker Hill, ID (http://weber.u.washington.edu/~clh/bunker.html)

Coeur d'Alene Wetlands, ID (http://weber.u.washington.edu/~clh/wet.html)

Leadville, CO (http://weber.u.washington.edu/~clh/leadville.html)

Journal of Hazardous Materials Letters 4 (2023) 100080

Contents lists available at ScienceDirect

Journal of Hazardous Materials Letters

journal homepage: www.sciencedirect.com/journal/journal-of-hazardous-materials-letters

Influence of chain length on field-measured distributions of PFAS in soil and soil porewater

Mark L. Brusseau

Environmental Science Department, University of Arizona, Tucson, AZ 85721, USA

ARTICLE INFO

Keywords:
PFOS
PFOA
Leaching
Adsorption
Retention

ABSTRACT

Soil and porewater concentrations measured for multiple PFAS were compiled from three field studies. The soil: porewater concentration ratios were shown to be functions of molar volume for all three data sets. Remarkable consistency was observed between the three sets of field-based measurements, indicating that PFAS distributions in the three soil systems exhibited similar magnitudes of overall retention. The relative contributions of solid-phase sorption and air-water interfacial adsorption to total retention were examined. The contribution of air-water interfacial adsorption was greater than that of solid-phase sorption for the longer-chain PFAS, whereas it was less than that of solid-phase sorption for the shorter-chain PFAS. These results show that the relative contributions of the two processes can vary as a function of the particular PFAS when the solid-phase sorption functionality deviates from that of air-water interfacial adsorption. This might occur for example when sorption is influenced by addition mechanisms beyond hydrophobic interaction, or when sorption and/or adsorption are nonlinear. Based on the results from all three data sets, soil concentrations are likely to be smaller than porewater concentrations for the shortest-chain PFAS. Conversely, soil concentrations will generally be significantly greater than porewater concentrations for longer-chain PFAS. The results from this study have implications for characterizing and evaluating PFAS distributions in vadose-zone soils.

1. Introduction

Per and polyfluorinated alkyl substances (PFAS) have been documented to be prevalent in soils across the globe (Rankin et al., 2016; Brusseau et al., 2020). Concentrations of different PFAS in soil range from ng/kg levels to 100's of mg/kg, depending upon the type of site (Brusseau et al., 2020). For example, higher concentrations are typically observed for sites that involved repeated releases of aqueous film-forming foam (e.g., Anderson et al., 2019; Brusseau et al., 2020) compared to secondary-source sites such as those receiving land application of biosolids (e.g., Washington et al., 2010; Pepper et al., 2021; Johnson, 2022). The leaching of PFAS from soil to groundwater at sites with extensive soil contamination is a critical concern, and has generated great interest among scientists, regulators, industry, and other stakeholders. Issues related to the soil-to-groundwater exposure pathway and associated risks of groundwater contamination have been discussed recently (e.g., Anderson, 2021; Brusseau and Guo, 2023; Pepper et al., 2023).

Different approaches have been deployed to investigate and evaluate PFAS leaching, including theoretical/conceptual analyses, mathematical modeling, and field-based studies. Integral to these investigations is the determination of PFAS concentrations in soil porewater. The mass in porewater is that which is directly subject to transport during water flow and groundwater recharge. Several recent works have reported measured PFAS porewater concentrations determined from field studies (Felizeter et al., 2021; Quinnan et al., 2021a; Anderson et al., 2022; Schaefer et al., 2022). Equally important is characterizing the distribution of PFAS within the entire soil volume sampled, i.e., determining the relationship between soil and porewater concentrations. This is relevant for a number of reasons, including that most field investigations report soil rather than porewater concentrations, that regulatory or reference levels are typically developed in terms of soil concentrations, and the need to quantify total masses and mass balances within the soil volume. Brusseau and Guo (2022) developed a comprehensive model to characterize the distribution of PFAS within soil, and the associated relationship between soil and porewater concentrations.

The purpose of this research is to investigate the relationship between measured soil and porewater concentrations using data obtained from three recent field studies (Felizeter et al., 2021; Schaefer et al.,

E-mail address: Brusseau@arizona.edu.

https://doi.org/10.1016/j.hazl.2023.100080
Received 25 May 2023; Received in revised form 25 July 2023; Accepted 26 July 2023
Available online 27 July 2023

2022; Quinnan et al., 2021b). Measured concentrations reported for several PFAS from each study are examined to determine if the porewater-soil concentration relationship is a function of PFAS chain length. Quantitative structure-property relationship (QSPR) analysis, employing molar volume as the molecular descriptor, is used to characterize the data sets. Consistency among the three field data sets is assessed. The field data sets are used to evaluate the representativeness of the Brusseau and Guo (2022) distribution model. The relative contributions of solid-phase sorption and air-water interfacial adsorption to overall retention and PFAS distribution within the soils are examined by comparing composite versus actual K_d values.

2. Materials and methods

2.1. Data analysis

The soil concentration of a given constituent (C_s) represents the total mass of that constituent present in all phases of the soil sample, while the porewater concentration (C_{pw}) represents the mass of dissolved constituent present in the porewater. The ratio of C_s to C_{pw} is given as (Brusseau and Guo, 2022):

$$\frac{C_s}{C_{pw}} = \frac{\theta_w}{\rho_b} R_d \tag{1}$$

where ρ_b is soil bulk density (g/cm^3), θ_w is volumetric water content (cm^3/cm^3), and R_d is the nondimensional distribution coefficient. The full definition of R_d, accounting for all potential retention processes, is presented in the source paper. For the application herein it is assumed that solid-phase sorption and air-water interfacial adsorption are the two relevant retention processes. This is supported by the results of the predictions discussed in the Supplemental Information (SI). Under these conditions R_d can be simplified to:

$$R_d = \left(1 + K_d \frac{\rho_b}{\theta_w} + K_{aw} \frac{a_{aw}}{\theta_w}\right) \tag{2}$$

where K_d is the solid-phase adsorption coefficient (cm^3/g), K_{aw} is the air-water interfacial adsorption coefficient (cm^3/cm^2), and a_{aw} is the specific air-water interfacial area (cm^2/cm^3). Information regarding the determination of a_{aw} is presented in Brusseau (2023). The R_d term quantifies the distribution of all constituent mass within the system, comprising mass in porewater (represented by "1"), mass sorbed by the soil grains (second term on r.h.s.), and mass adsorbed at the air-water interface (third term on r.h.s.). The contributions of solid-phase sorption and air-water interfacial adsorption can be individually quantified using nondimensional retention coefficients. These are defined as $K_d^0 = K_d \frac{\rho_b}{\theta_w}$ and $K_{aw}^0 = K_{aw} \frac{a_{aw}}{\theta_w}$ for solid-phase sorption and air-water interfacial adsorption, respectively.

Quantitative structure-property relationship (QSPR) analysis, as described in Brusseau (2019a), is used to characterize the data sets. Molar volume (V_m) is employed as the single descriptor. This descriptor characterizes the influence of molecular size on cavity formation and destruction in solution, the process mediating the hydrophobic-interaction mechanism that drives interfacial adsorption processes. Values of molar volume were obtained from a prior work (Brusseau, 2019a).

2.2. Field data sets

The studies serving as the sources of the data sets analyzed herein are described in the SI. This includes brief descriptions of the study objectives and approach, along with methods used for soil extraction and analysis. The PFAS from each of the three source works that are included in the present study are listed in Table SI-1, along with their acronyms. The standardized definition of short-chain and long-chain PFAS is used herein, wherein perfluoroalkyl carboxylic acids and perfluoroalkane sulfonates containing ≥ 7 and ≥ 6 fluorinated carbons, respectively, are considered long-chain (Buck et al., 2011). Information on soil properties reported in the source works is presented in Table SI-2 in the SI.

A factor to consider for any field test is the potential magnitude and impacts of heterogeneity. Spatial variability of soil properties (e.g., texture, structure, geochemical constituents) and system conditions (e.g., PFAS concentrations, water saturations) is present to some degree for all sites. One commonality among the three source studies is the relatively small scale of the test systems. The test plot for the Schaefer et al. study comprised an area of 18.5 m^2. They treated the system as homogeneous, using mean soil and porewater concentrations for their assessments. The data from the Quinnan et al. study represent samples from a pair of co-located lysimeters. Hence, relatively smaller magnitudes of heterogeneity may be anticipated for these two systems. The data from the Felizeter et al. study represent samples from several 1 m^2-area test lysimeters for which the soil was initially mixed and homogenized, effectively eliminating spatial heterogeneity effects in this case. These conditions support an assessment of the impact of PFAS physicochemical properties on retention in the absence of significant heterogeneity effects.

3. Results and discussion

3.1. Comparison of measured data sets

The ratios of the soil and porewater concentrations measured for several PFAS are presented in Fig. 1 for all three data sets. Remarkable consistency is observed between the three sets of field-based measurements. Recall that C_s/C_{pw} correlates to the nondimensional distribution coefficient R_d (equation 1), which quantifies the combined contributions of the relevant retention processes to PFAS distribution within the soil. The congruency of the three data sets indicates that PFAS distributions in the three soil systems exhibit relatively similar magnitudes of overall retention. Exact comparisons will be influenced by differences in extant water contents and bulk densities (i.e., $\frac{\theta_w}{\rho_b}$).

Inspection of Fig. 1 shows that the C_s/C_{pw} ratio is approximately 1 for a molar volume of 200, meaning that soil and porewater concentrations are equivalent. Soil concentrations are actually smaller than porewater concentrations for PFAS with molar volumes < 200, i.e., the shorter-chain PFAS. This is a combined function of comparatively small R_d values typical for short-chain PFAS and the $\frac{\theta_w}{\rho_b}$ term, which is always < 1. Conversely, soil concentrations are significantly greater than porewater concentrations for the longer-chain PFAS, and the difference increases with increasing molar volume.

The C_s/C_{pw} values for all three data sets exhibit strong log-linear correlations to molar volume, which is representative of molecular size. The regression function determined for the Brusseau and Guo data set reasonably represents the other two data sets. This indicates that the slopes of the C_s/C_{pw}-V_m relationships are similar for the three data sets. In fact, the slope for the Schaefer et al. data set is essentially identical to that of the Brusseau and Guo data. The slope for the Quinnan et al. data set is slightly larger, but within the 95% confidence intervals of the other two data sets. The similarity of the slopes demonstrates equivalent distribution behavior of the various PFAS between soil and porewater for the three studies. Recalling that the Felizeter et al. data set employed by Brusseau and Guo (2022) were obtained from a short-term field study of a few months, the similar results observed for these data compared to the results from the other two long-term field studies indicates that representative equilibrium conditions were obtained for the former system. This is consistent with the results of the C_s/C_{pw} predictions discussed in the SI.

As noted, C_s/C_{pw} is a function of R_d and, therefore, the C_s/C_{pw}-V_m correlations observed in Fig. 1 are equivalent to correlations between R_d and V_m. R_d was demonstrated previously to be a function of molar volume for the Brusseau and Guo data set (Brusseau and Guo, 2022). The

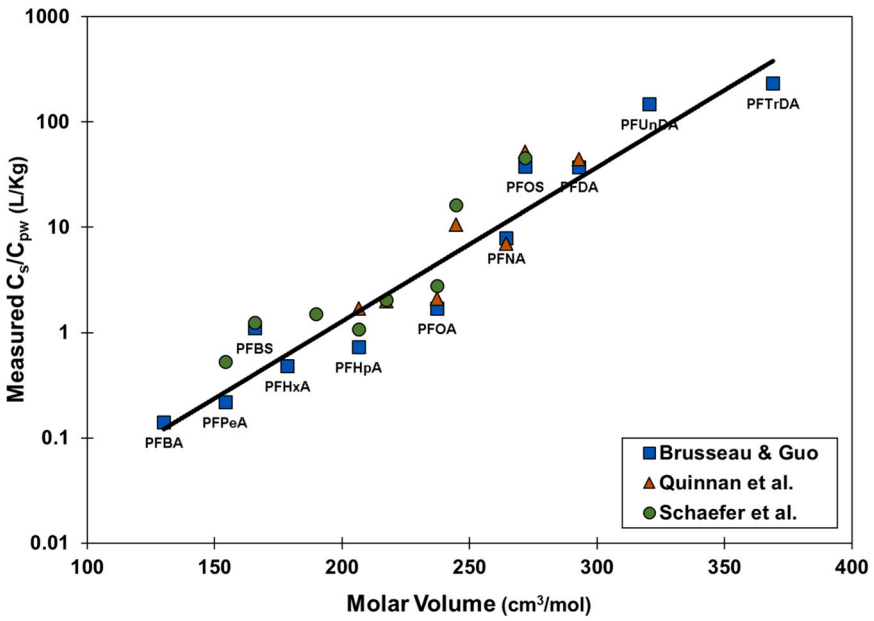


Fig. 1. Measured soil (C_s) and soil porewater (C_{pw}) concentrations for several PFAS as a function of molar volume (V_m). From equation 1, $\frac{C_s}{C_{pw}} = \frac{\theta_w}{\rho_b} R_d$. The three data sets represent measurements conducted for field studies as described in the text. The black solid line represents a regression function developed for only the Brusseau and Guo data set. Statistics for aggregated data (log C_s/C_{pw} vs V_m): slope = 0.0146 (0.0124–0.0168); r^2 = 0.89; p-value < 0.001. Slopes for the individual data sets: Brusseau and Guo- 0.0146 (0.0117–0.0175); Quinnan et al.- 0.0184 (0.008–0.029); Schaefer et al.- 0.0144 (0.007–0.022). Values in parentheses are 95% confidence intervals.

results in Fig. 1 confirm that similar relationships are also observed for the other two field data sets. Such a correlation is predicted based on the comprehensive distribution model developed by Brusseau and Guo (2022). Hence, the measured PFAS distributions between soil and porewater are consistent with that expected from theory for all three field studies. This indicates that the model provides an accurate representation of PFAS retention and distribution in soil for these data sets. In addition, the high degree of representativeness provided by the QSPR model along with the congruency to the distribution-model predicted behavior suggests that relatively ideal conditions mediated the distribution of the various PFAS within the soil.

Solid-phase sorption and air-water interfacial adsorption are the two primary retention processes considered to mediate the distribution of PFAS in the three soil systems. The two processes are represented by their respective distribution coefficients, K_d and K_{aw}. Both parameters have been shown to be log-linear functions of molar volume (Brusseau, 2019a, 2019b; Brusseau and Van Glubt, 2021). This is illustrated in Fig. 2, in which are presented the K_d and K_{aw} values used to quantify R_d values of the respective PFAS for the Brusseau and Guo data set. Hence, the log-linear relationships observed for the data sets in Fig. 1 are consistent with the functional dependencies of the individual retention parameters.

3.2. *Composite versus actual K_d values*

Field-determined or "in-situ" K_d values are reported in some characterization studies. These are typically calculated using soil and porewater concentrations determined for co-located or adjacent soil and porewater samples. Such calculations can provide useful information regarding the distribution of the constituent of interest within the sampled domain. However, this approach can be influenced by a number of uncertainties. One primary one of particular relevance for PFAS in

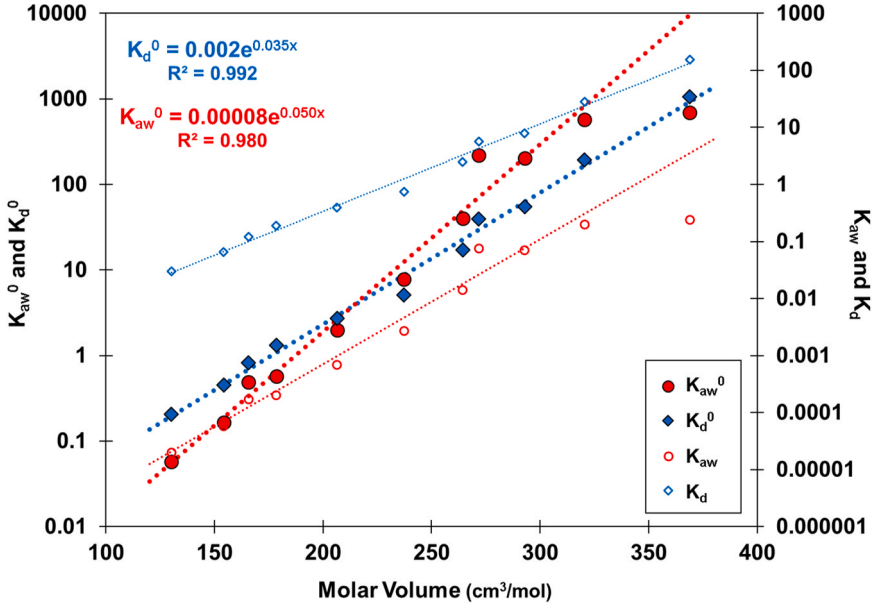


Fig. 2. Dimensional and nondimensional distribution coefficients for air-water interfacial adsorption (K_{aw}, K_{aw}^0) and solid-phase sorption (K_d, K_d^0) as a function of molar volume for the Brusseau and Guo data set.

vadose-zone systems is the potential contribution of other retention processes such as air-water interfacial adsorption. When additional processes contribute to PFAS retention, the calculated field-based K_d becomes a composite parameter that aggregates the contributions of all relevant retention processes. In this case, all retained mass is incorrectly assumed implicitly to be sorbed mass.

The R_d values determined from the measured C_s/C_{pw} data sets were used to calculate composite K_ds as: $K_d^C = (R_d\text{-}1)\ \frac{\theta_w}{\rho_b}$. The calculated values are presented in Fig. 3 as a function of molar volume. The K_d^C values are observed to correlate well with molar volume for all three data sets. This is consistent with the fact that both K_d and K_{aw} correlate to molar volume as discussed above, and that the definition of K_d^C and $\frac{C_s}{C_{pw}}$ are comparable. These results illustrate that the observation of good correlations between field-determined K_d values and PFAS molecular descriptors such as molar volume or fluorinated carbon number (chain length) does not necessarily indicate that the underlying retention processes have been accurately identified or characterized. This point is especially important to keep in mind when applying this or similar methods to vadose-zone soil samples.

3.3. Relative contributions of solid-phase sorption and air-water interfacial adsorption

Characterizing the relative contributions of solid-phase sorption and air-water interfacial adsorption to overall retention is important to an accurate understanding of how the distribution and transport of PFAS may be influenced by different factors and conditions. This issue was examined recently, and it was shown that the relative contributions of the two processes will depend in part upon specific properties of the soil and their impacts on magnitudes of retention (Brusseau, 2019b). It was further shown that the relative contributions of the two processes will be similar for any given PFAS under ideal conditions wherein the K_d-V_m and K_{aw}-V_m relationships are consistent (i.e., essentially identical correlation slopes). This could occur for example when sorption is dominated by hydrophobic interaction, the same mechanism mediating air-water interfacial adsorption (Brusseau, 2019b).

The relative contributions of solid-phase sorption and air-water interfacial adsorption to overall retention can be assessed by plotting the ratios of the composite and actual K_ds as a function of molar volume. The ratios are presented in Fig. 4 for the Brusseau and Guo and Schaefer et al. data sets. Measured or estimated K_ds are not available for the Quinnan et al. data set. Inspection of Fig. 4 shows that the ratio is generally close to 1 for PFAS with molar volumes < 200. This indicates that the contribution of air-water interfacial adsorption is relatively minimal for the short-chain PFAS. Conversely, the ratio is greater than 1 for the PFAS with larger molar volumes, and it increases approximately monotonically with V_m up to PFUnDA for the Brusseau and Guo data set. Interestingly, the ratios for PFOS for both data sets and PFHpS for the Schaefer et al. data set deviate from the trend observed for the other longer-chain PFAS. It is unclear if this is a consequence of measurement variability or greater relative significance of air-water interfacial adsorption.

As larger ratios represent greater proportional contributions of air-water interfacial adsorption, the results in Fig. 4 indicate that air-water interfacial adsorption contributes to retention at increasingly greater proportions as molar volume increases. For example, a ratio of 2 equates to equal contributions of both processes, whereas a ratio of 4 equates to a 75% contribution by air-water interfacial adsorption. The PFAS-specific dependency of the relative retention contributions observed for these data differs from the results reported in Brusseau (2019b), wherein the relative contributions were independent of the specific PFAS. This disparity is explained by the results presented in Fig. 2. Close inspection reveals that the slopes of the K_d-V_m and K_{aw}-V_m functions differ, in contrast to the results presented in the prior work. The impact of these differences on the relative contributions of the two processes to retention can be further elucidated by examining the nondimensional retention coefficients for solid-phase sorption and air-water interfacial adsorption, K_d^0 and K_{aw}^0, respectively, as a function of V_m (Fig. 2).

First, it is observed that the two sets of values are relatively similar, meaning that both processes are relevant to the overall retention of the majority of the PFAS. Second, because the two functions exhibit different slopes, the magnitudes of the two sets of values diverge. The cross-over point occurs at a molar volume between those of PFOA and PFHpA. Notably, the contributions of the two processes are approximately equal for PFOA. Third, due to the specific slopes, the contribution of air-water interfacial adsorption is greater than that of solid-phase sorption for PFAS with V_ms larger than that of PFOA. Conversely, the contribution of solid-phase sorption is greater than that of air-water interfacial adsorption for PFAS with V_ms smaller than that of PFOA. These results show that the PFAS-specific dependency of the relative

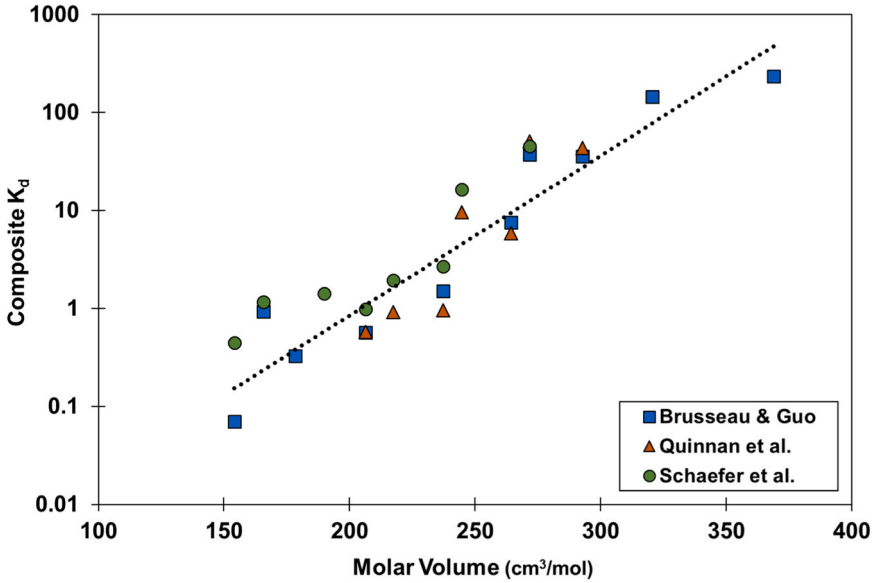


Fig. 3. Composite K_d values determined from the measured C_s/C_{pw} data sets. PFBA for the Brusseau and Guo data set is not included because the back-calculated K_d is 0 (the measured retardation factor is <1). Statistics for aggregated data (log K_d vs V_m): slope = 0.0157 (0.0127–0.0187); r^2 = 0.84; p-value < 0.001.

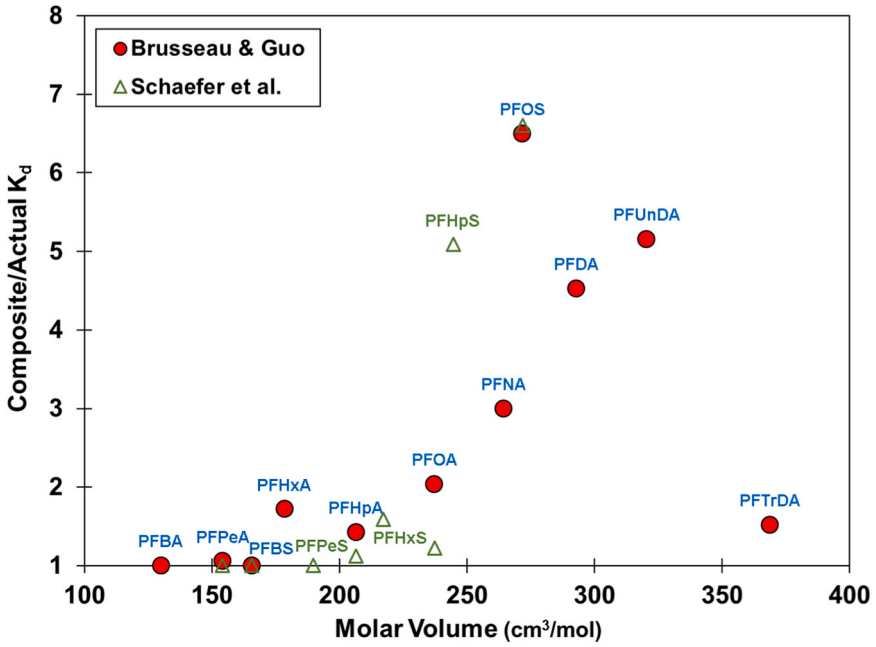


Fig. 4. Composite versus actual K_d values for the Brusseau & Guo and Schaefer et al. data sets. Note that a single data label is used for cases where two data points are reported for the same PFAS (vertically stacked data points).

contributions of the two processes may be soil specific, and in particular depend upon the operative solid-phase sorption functionality for the specific set of PFAS and the relevant soil.

The results for PFTDA are an exception to the behavior observed for the other PFAS. The measured K_{aw} value deviates significantly from the correlation representing the values for the other PFAS. As a result, the K_d^0 and K_{aw}^0 values are similar. This explains the deviation observed for PFTDA in Fig. 4. As discussed in the SI, a very good prediction of the measured C_s/C_{pw} value was obtained for PFTDA, suggesting that the values used for K_d and K_{aw} are robust.

4. Conclusions

The measured ratios of soil and porewater concentrations for a series of PFAS were shown to be functions of molar volume for data sets obtained from three field studies. Remarkable consistency was observed between the three sets of field-based measurements, indicating that PFAS distributions in the three soil systems exhibited relatively similar magnitudes of overall retention. These results are consistent with the behavior expected from theory, and indicates that the comprehensive distribution model developed by Brusseau and Guo (2022) provides an accurate representation of PFAS retention and distribution in soil. Thus, the model is anticipated to be a useful tool for characterizing PFAS distributions and associated relationships between porewater and soil concentrations in vadose-zone systems.

As discussed above and in the SI, the results of the QSPR analyses and the distribution-model predictions indicate that the distribution of PFAS within the tested soils was mediated by apparently ideal conditions for the measurements assessed herein. However, it should be noted that the relationship between soil and porewater concentrations can be influenced by factors that may result in deviations from expected behavior, as discussed previously by Brusseau and colleagues (Brusseau, 2019b; Brusseau and Guo, 2022, 2023). For example, mass-transfer constraints may affect distributions, particularly under dynamic conditions wherein water contents are changing rapidly. In addition, nonlinear-adsorption, competitive interactions, aggregation, or other nonideal processes may be relevant in some cases, particularly for systems with comparatively high concentrations. Anderson et al. (2022) measured soil and porewater concentrations for several PFAS in a study conducted at a large AFFF-impacted site. The reported soil:porewater concentration ratios were smaller than would be expected for the longer-chain PFAS, suggesting potential impacts of nonideal processes. Notably, the measured porewater concentrations are significantly higher for the Anderson et al. study compared to those measured for the Quinnan and Schaefer studies. For example, mean concentrations of approximately 1100, 3000, and 600 μg/L were reported by Anderson et al. for PFOA, PFHxS, and PFOS, respectively, in contrast to concentrations ranging between 0.6 and 26 μg/L for those three PFAS in the other two studies. In addition, spatial heterogeneity of soil properties and system conditions may affect the characterization of PFAS distributions. The test systems for the three data-source studies examined herein comprised small spatial scales that are anticipated to have comparatively smaller impacts of heterogeneity. Conversely, the test site for the Anderson et al. study comprised ~14, 000 m^2. The influence of heterogeneity on characterization of soil and porewater concentrations needs further investigation.

The relative contributions of solid-phase sorption and air-water interfacial adsorption to total retention was examined. The contribution of air-water interfacial adsorption was greater than that of solid-phase sorption for the longer-chain PFAS, whereas it was less than that of solid-phase sorption for the shorter-chain PFAS. These results show that the relative contributions of the two processes can vary as a function of the particular PFAS when the solid-phase sorption functionality deviates from that of air-water interfacial adsorption. This might occur for example when sorption is influenced by addition mechanisms beyond hydrophobic interaction, or when solid-phase sorption and/or air-water interfacial adsorption are nonlinear.

Based on the results from all three data sets, soil concentrations are likely to be smaller than porewater concentrations for the shortest-chain PFAS. This is a combined function of comparatively small R_d values typical for short-chain PFAS and the $\frac{\theta_w}{\rho_b}$ term, which is always < 1. Conversely, soil concentrations will generally be greater than porewater concentrations for longer-chain PFAS. These results serve as a useful rule-of-thumb guide for characterizing and evaluating PFAS distributions in vadose-zone soils.

Funding Information

This research was supported by the Environmental Security Technology Certification Program (Project ER21-5041).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data are reported in the source papers.

Acknowledgements

This research was supported by the Environmental Security Technology Certification Program (Project ER21-5041). The reviewers are thanked for their constructive comments.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2023.100080.

References

Anderson, R.H., 2021. The case for direct measures of soil-to-groundwater contaminant mass discharge at AFFF-impacted sites. Environ. Sci. Technol. 2021 (55), 6580–6583.

Anderson, R.H., Feild, J.B., Dieffenbach-Carle, H., Elsharnouby, O., Krebs, R.K., 2022. Assessment of PFAS in collocated soil and porewater samples at an AFFF-impacted source zone: field-scale validation of suction lysimeters. Chemosphere 308, 136247.

Anderson, R.H., Adamson, D.T., Stroo, H.F., 2019. Partitioning of poly-and perfluoroalkyl substances from soil to groundwater within aqueous film-forming foam source zones. J. Contam. Hydrol. 220, 59–65.

Brusseau, M.L., 2019a. The influence of molecular structure on the adsorption of PFAS to fluid-fluid interfaces: using QSPR to predict interfacial adsorption coefficients. Water Res 152, 148–158.

Brusseau, M.L., 2019b. Estimating the relative magnitudes of adsorption to solid-water and air/oil-water interfaces for per- and poly-fluoroalkyl substances. Environ. Pollut. 254, Artic., 113102

Brusseau, M.L., 2023. Determining air-water interfacial areas for the retention and transport of PFAS and other interfacially active solutes in unsaturated porous media. Sci. Total. Environ. 884, 163730.

Brusseau, M.L., Guo, B., 2022. PFAS concentrations in soil versus soil porewater: mass. distributions and the impact of adsorption at air-water interfaces. Chemosphere 302, 134938.

Brusseau, M.L., Guo, B., 2023. Revising the EPA dilution-attenuation soil screening model for PFAS. J. Hazard. Mat. Lett. 4, 100077.

Brusseau, M.L., Anderson, R.H., Guo, B., 2020. PFAS concentrations in soils: background levels versus contaminated sites. Sci. Total Environ. 740, 140017 (article).

Brusseau, M.L., Van Glubt, S., 2021. The influence of molecular structure on PFAS adsorption at air-water interfaces in electrolyte solutions. Chemosphere 281, 130829.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A., van Leeuwen, S.P., 2011. Perfluoroalkyl and polyfluoroalkyl. substances in the environment: terminology, classification, and origins. Integr. Environ. Assess. Manag 7 (4), 513–541.

Felizeter, S., Jürling, H., Kotthoff, M., De Voogt, P., McLachlan, M.S., 2021. Uptake of perfluorinated alkyl acids by crops: results from a field study. Environ. Sci. Proc. Impacts 23, 1158.

Johnson, G.R., 2022. PFAS in soil and groundwater following historical land application of biosolids. Wat. Res. 211, 118035.

Pepper, I.L., Brusseau, M.L., Prevatt, F.J., Escobar, B.A., 2021. Incidence of PFAS in soil following long-term application of class B biosolids. Sci. Total Environ. 793, 148449.

Pepper, I.L., Kelley, C., Brusseau, M.L., 2023. Is PFAS from land applied municipal biosolids a significant source of human exposure via groundwater? Sci. Total Environ. 864, 161154.

Quinnan, J., Rossi, M., Curry, P., Lupo, M., Miller, M., Korb, H., Orth, C., Hasbrouck, K., 2021a. Application of PFAS- mobile lab to support adaptive characterization and flux- based conceptual site models at AFFF releases. Remediation 31, 7–26.

Rankin, K., Mabury, S., Jenkins, T., Washington, J., 2016. A North American and global survey of perfluoroalkyl substances in surface soils: distribution patterns and mode of occurrence. Chemosphere 161, 333–341.

Schaefer, C.E., Lavorgna, G.M., Lippincott, D.R., Nguyen, D., Christie, E., Shea, S., O'Hare, S., Lemes, M.C.S., Higgins, C.P., Field, J., 2022. A field study to assess the role of air-water interfacial sorption on PFAS leaching in an AFFF source area. J. Contam. Hydrol. 248, 104001 (article).

Washington, J., Yoo, H., Ellington, J., Jenkins, T., Libelo, E., 2010. Concentrations, distribution. and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. Environ. Sci. Technol. 44, 8390–8396.

Quinnan, J., Curry, P., Lupo, M., Miller, M., Rossi, M., 2021b. Validation of Streamlined Mobile Lab-Based Real Time PFAS Analytical Methods. Final Report ESTCP Project ER19–5203.

Polyfluoroalkyl Chemicals in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 2003–2004 and Comparisons with NHANES 1999–2000

Antonia M. Calafat, Lee-Yang Wong, Zsuzsanna Kuklenyik, John A. Reidy, and Larry L. Needham

Division of Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, Georgia, USA

Background: Polyfluoroalkyl chemicals (PFCs) have been used since the 1950s in numerous commercial applications. Exposure of the general U.S. population to PFCs is widespread. Since 2002, the manufacturing practices for PFCs in the United States have changed considerably.

Objectives: We aimed to assess exposure to perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorohexane sulfonic acid (PFHxS), perfluorononanoic acid (PFNA), and eight other PFCs in a representative 2003–2004 sample of the general U.S. population ≥ 12 years of age and to determine whether serum concentrations have changed since the 1999–2000 National Health and Nutrition Examination Survey (NHANES).

Methods: By using automated solid-phase extraction coupled to isotope dilution–high-performance liquid chromatography–tandem mass spectrometry, we analyzed 2,094 serum samples collected from NHANES 2003–2004 participants.

Results: We detected PFOS, PFOA, PFHxS, and PFNA in > 98% of the samples. Concentrations differed by race/ethnicity and sex. Geometric mean concentrations were significantly lower (approximately 32% for PFOS, 25% for PFOA, 10% for PFHxS) and higher (100%, PFNA) than the concentrations reported in NHANES 1999–2000 ($p < 0.001$).

Conclusions: In the general U.S. population in 2003–2004, PFOS, PFOA, PFHxS, and PFNA serum concentrations were measurable in each demographic population group studied. Geometric mean concentrations of PFOS, PFOA, and PFHxS in 2003–2004 were lower than in 1999–2000. The apparent reductions in concentrations of PFOS, PFOA, and PFHxS most likely are related to discontinuation in 2002 of industrial production by electrochemical fluorination of PFOS and related perfluorooctanesulfonyl fluoride compounds.

Key words: biomonitoring, C8, exposure, PFCs, PFOA, PFOS, prevalence, serum. *Environ Health Perspect* 115:1596–1602 (2007). doi:10.1289/ehp.10598 available via *http://dx.doi.org/* [Online 29 August 2007]

Concern about exposure of the ecosystem, including humans, to halogenated persistent organic pollutants (POPs) has existed for several decades. Many of these chemicals are persistent and toxic, tend to bioaccumulate, and can undergo long range atmospheric transport; for these reasons, their production has been banned or reduced worldwide, leading to their decreased concentrations in the ecosystem. In addition, adherence to provisions set forth in the Stockholm Convention on POPs for 12 organochlorine chemicals (United Nations Environment Programme 2004) probably will result in continued decreasing environmental concentrations. More recently, the focus of environmental and public health concern has shifted from chlorinated chemicals to brominated and fluorinated chemicals.

Among the fluorinated chemicals, the polyfluoroalkyl chemicals (PFCs) have been used extensively since the 1950s in commercial applications, including surfactants, lubricants, paper and textile coatings, polishes, food packaging, and fire-retarding foams. Some of these PFCs, including perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), persist in humans and the environment and have been detected worldwide in wildlife (Houde et al. 2006 and references therein). Exposure to PFOS and PFOA in the general population also is widespread, although demographic, geographic, and temporal differences may exist (Calafat et al. 2006b, 2007; Fromme et al. 2007; Guruge et al. 2005; Hansen et al. 2001; Harada et al. 2007; Kannan et al. 2004; Karrman et al. 2006; Olsen et al. 2005; Taniyasu et al. 2003; Yeung et al. 2006).

No definite association has been established between exposure to PFOS and PFOA and adverse health effects in several occupational studies (Alexander et al. 2003; Gilliland and Mandel 1993; Grice et al. 2007; Olsen et al. 2004a) and in one population exposed to PFOA through contaminated drinking water (Emmett et al. 2006). Negative associations between cord serum concentrations of both PFOS and PFOA and birth weight and ponderal index, but not newborn length or gestational age, have been reported in a nonoccupational population (Apelberg et al. 2007). By contrast, no association has been reported between employment in jobs with high exposure to PFOS before the end of pregnancy and maternally reported birth weight (Grice et al. 2007). In animals, exposure to PFOS and PFOA is associated with adverse health effects (Kennedy et al. 2004; Lau et al. 2004; Organisation for Economic Co-operation and Development 2002) albeit at serum concentrations orders of magnitude higher than the concentrations observed in the general population (Butenhoff et al. 2004; Luebker et al. 2005). Because of these compounds' known toxicity to animals, their ubiquitous presence, and their persistence in humans, wildlife, and the environment, PFCs research is of interest to toxicologists, epidemiologists, and environmental and public health scientists.

Biomonitoring data for these PFCs in the general population are needed to assess current exposures and to determine whether technologic changes affect human exposures to these compounds. As part of the continuous U.S. National Health and Nutrition Examination Survey (NHANES), urine and serum samples are collected and analyzed for selected environmental chemicals [Centers for Disease Control and Prevention (CDC) 2005]. NHANES participants also provide sociodemographic information and medical history and undergo standardized physical examinations (CDC 2003). We recently reported the concentrations of PFOS, PFOA, and nine other PFCs in 1,562 participants from NHANES 1999–2000 (Calafat et al. 2007). The high frequency of detection of PFOS and PFOA suggested highly prevalent exposures to these compounds at a time when both were being manufactured in the United States. In 2002, the 3M Company (St. Paul, MN), the sole U.S. producer of PFOS, discontinued its production of PFOS and related perfluorooctanesulfonyl fluoride

Address correspondence to A.M. Calafat, Division of Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, 4770 Buford Hwy, NE, Mailstop F53, Atlanta, GA 30341, USA. Telephone: (770) 488-7891. Fax: (770) 488-4371. E-mail: Acalafat@cdc.gov

Supplemental Material is available online at http://www.ehponline.org/docs/2007/10598/suppl.pdf

The authors thank J. Pirkle for useful discussions, and J. Tully, K. Kato, A. Wanigatunga, and J. Ekong for technical assistance.

The findings and conclusions in this article are those of the authors and do not necessarily represent the views of the Centers for Disease Control and Prevention.

The authors declare they have no competing financial interests.

Received 25 June 2007; accepted 29 August 2007.

(POSF)–based chemistries by electrochemical fluorination. Although PFOA and its salts and precursors still are manufactured by others by a different process, reductions in their manufacturing emissions have been proposed [Prevedouros et al. 2006; U.S. Environmental Protection Agency (EPA) 2006]. We now report the serum concentrations of 12 PFCs, including PFOS and PFOA, in 2,094 participants from NHANES 2003–2004 and compare these data with data from NHANES 1999–2000 (Calafat et al. 2007). The 2003–2004 data provide the first estimates of serum PFC concentrations in a representative U.S. population since implementation of the changes in manufacturing practices for some PFCs in the United States.

Materials and Methods

We obtained serum samples analyzed for PFCs from 2,094 participants ≥ 12 years of age from NHANES 2003–2004. The National Centers for Health Statistics Institutional Review Board reviewed and approved the study protocol. All participants provided informed written consent; parents or guardians provided consent for participants < 18 years of age (CDC 2006a).

We measured perfluorooctane sulfonamide (PFOSA), 2-(*N*-ethyl-perfluorooctane sulfonamido) acetic acid (Et-PFOSA-AcOH), 2-(*N*-methyl-perfluorooctane sulfonamido) acetic acid (Me-PFOSA-AcOH), perfluorobutane sulfonic acid (PFBuS), perfluorohexane sulfonic acid (PFHxS), PFOS, PFOA, perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDeA), perfluoroundecanoic acid (PFUA), and perfluorododecanoic acid (PFDoA) in 1 mL of serum, using a modification of the method of Kuklenyik et al. (2004), which involved automated solid-phase extraction coupled to reversed-phase high-performance liquid chromatography–tandem mass spectrometry. We used $^{18}O_2$-PFOS (for all sulfonic acids and all amides) and $^{13}C_2$-PFOA (for all carboxylic acids) for quantification. To compensate for the lack of isotope-labeled internal standards for the other analytes and to partially account for matrix effects, the calibration standards were spiked into calf serum. The limits of detection (LODs) ranged from 0.1 to 1.0 μg/L; the accuracy ranged from 84 to 135% at three concentrations (Kuklenyik et al. 2004); and the precision ranged from around 10 to 26% at two different levels (Table 1). Low-concentration (~ 3 μg/L to ~ 9 μg/L) and high-concentration (~ 10 μg/L to ~ 30 μg/L) quality-control (QC) materials, prepared from a base calf serum pool, were analyzed with reagent blank, serum blank, and NHANES samples (Kuklenyik et al. 2004). Standard, blank, QC, and NHANES samples were analyzed by the procedure described above.

We analyzed the data using SAS (version 9.1.3; SAS Institute Inc., Cary, NC) and SUDAAN (version 9.0.1; Research Triangle Institute, Research Triangle Park, NC). SUDAAN calculates variance estimates after incorporating the sample population weights, designed for the one-third subset of the full survey, which account for unequal selection probabilities and planned oversampling of certain subgroups resulting from the complex multistage area probability design of NHANES. Race/ethnicity was defined on the basis of self-reported data as non-Hispanic black, non-Hispanic white, and Mexican American. Persons not defined by these groups were included only in the total population estimate. Age was reported in years at the most recent birthday. We estimated the weighted percentage of detection and calculated weighted geometric means and percentiles for the serum concentrations (in micrograms per liter) of the various PFCs. For concentrations below the LOD, as recommended for the analysis of NHANES data (CDC 2006b), we used a value equal to the LOD divided by the square root of 2 (Hornung and Reed 1990). Parametric statistics were computed only for analytes for which the frequency of detection was ≥ 60%. Because PFC concentrations were not normally distributed, we used the natural log transformation. Weighted Pearson correlation coefficients and related *p*-values were calculated in SAS. Statistical significance was set at $p < 0.05$.

We used analysis of covariance to examine the influence of demographic and socioeconomic variables on the log-transformed serum concentrations of PFOS, PFOA, PFHxS, and PFNA. For multiple regression, we calculated the least square geometric means (LSGM) and compared them for each categorical variable. The variables included in the initial model were as follows: age as a continuous variable, sex, race/ethnicity, smoking status (yes/no), and education (less than high school, high school diploma, more than high school). Participants were categorized as smokers if their serum cotinine concentrations were > 10 μg/L. We chose to include education in the model without household income to minimize the possibility of collinearity because *a*) income and education are strongly associated (chi-square $p = 0.001$) and *b*) the final model yielded comparable results with either variable separately (except for PFOS, which included one additional significant term between income and smoking status). We assessed all possible two-way interaction terms in the model.

To reach the final reduced model, we used backward elimination with a threshold of $p < 0.05$ for retaining the variable in the model, using Satterwaite adjusted *F* statistics. We evaluated for potential confounding by adding each of the excluded variables back into the final model one by one and examining changes in the β coefficients of the statistically significant main effect. If addition of one of these excluded variables caused a change in a β coefficient by ≥ 10%, the variable was re-added to the model.

Results

The distribution of PFC serum concentrations is reported stratified by age, sex, and race/ethnicity (Tables 2–5). Four analytes were detected in > 98% of the samples (PFOS, 99.9%; PFOA, 99.7%; PFHxS, 98.3%; PFNA, 98.8%). Concentrations of these four PFCs ranged from < 0.4 μg/L to 435 μg/L (PFOS), < 0.1 μg/L to 77.2 μg/L (PFOA), < 0.3 μg/L to 82.0 μg/L (PFHxS), and < 0.1 μg/L to 11.5 μg/L (PFNA). Six other analytes were detected at lower frequencies: PFDeA (31.3%), Me-PFOSA-AcOH (27.5%), PFOSA (22.2%), PFUA (9.7%),

Table 1. LOD and precision data for the 12 polyfluoroalkyl compounds included in this study and a comparison of these parameters to the previously reported data for NHANES 1999-2000.

	LOD (μg/L)[b]		Precision[a] QCL		Precision[a] QCH	
Analyte	NHANES 2003–2004	NHANES 1999–2000	NHANES 2003–2004	NHANES 1999–2000	NHANES 2003–2004	NHANES 1999–2000
PFOSA	0.2	0.05	2.7 (14.9)	2.4 (14.1)	13.0 (16.3)	12.4 (12.5)
Me-PFOSA-AcOH	0.6	0.2	3.4 (15.5)	3.1 (14.2)	9.1 (16.7)	9.0 (13.5)
Et-PFOSA-AcOH	0.4	0.2	3.8 (17.2)	3.5 (14.3)	8.3 (19.2)	8.1 (15.6)
PFBuS	0.4	ND	4.4 (18.2)	ND	14.6 (15.1)	ND
PFHxS	0.3	0.1	2.5 (16.4)	2.1 (16.6)	11.9 (12.9)	11.2 (12.3)
PFOS	0.4	0.2	8.9 (10.4)	8.8 (8.4)	31.4 (10.1)	31.6 (7.1)
PFHpA	0.3	0.4	7.6 (17.0)	6.8 (13.5)	15.8 (14.3)	15.5 (12.0)
PFOA	0.1	0.1	3.2 (10.0)	3.1 (8.5)	14.7 (10.9)	15.1 (7.3)
PFNA	0.1	0.1	2.5 (15.0)	2.6 (15.4)	12.7 (13.2)	13.0 (10.9)
PFDeA	0.3	0.2	2.4 (17.5)	2.2 (13.9)	8.5 (18.2)	8.4 (13.1)
PFUA	0.3	0.2	1.9 (22.0)	2.0 (19.1)	9.9 (19.8)	10.6 (16.2)
PFDoA	1.0	0.2	2.2 (25.6)	2.4 (22.4)	8.5 (25.7)	9.1 (19.3)

ND, not determined.
[a]Mean concentration (% coefficient of variation) of repeated measurements (minimum of 20) over time of quality-control calf serum materials of low (QCL) and high (QCH) concentrations. [b]The NHANES 1999–2000 samples were analyzed by using the approach described in Kuklenyik et al. (2005), whereas the NHANES 2003–2004 samples were analyzed by using the Kuklenyik et al. (2004) approach.

PFHpA (6.2%), and Et-PFOSA-AcOH, (3.4%); their geometric mean and selected percentile concentrations are given as Supplemental Material in Tables S1–S6 (online at http://www.ehponline.org/docs/2007/10598/suppl.pdf). For the two analytes detected in < 1% of the samples (PFDoA, < 0.1%; PFBuS, 0.4%), we could not calculate the 95th percentile of concentrations.

Statistically significant correlations ($p < 0.001$) existed between the log-transformed concentrations of PFOS and PFOA (Pearson correlation coefficient $r = 0.66$), PFHxS ($r = 0.56$), and PFNA ($r = 0.50$); between PFOA and PFHxS ($r = 0.46$) and PFNA ($r = 0.55$); and between PFHxS and PFNA ($r = 0.17$).

The final models included sex ($p < 0.01$), age, race/ethnicity, and age-by-race/ethnicity interaction ($p = 0.01$) for PFOS; sex, race/ethnicity, age, education, sex-by-age ($p < 0.01$), sex-by-race/ethnicity ($p = 0.03$), and education-by-age ($p = 0.04$) interactions for PFOA; sex, race/ethnicity ($p = 0.01$), age, and sex-by-age interaction ($p = 0.02$) for PFHxS; and sex ($p < 0.01$), race/ethnicity, age, education ($p = 0.02$), smoking status ($p = 0.02$), and race/ethnicity-by-age ($p < 0.01$) and

Table 2. Geometric mean and selected percentiles (95% confidence intervals) of perfluorooctanesulfonate (PFOS) concentrations in serum (μg/L) for the U.S. population 12 years of age and older: data from NHANES 2003–2004.

Variable	Geometric mean	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	95th percentile	No.
All	20.7 (19.2–22.3)	9.8 (9.0–10.8)	14.6 (13.8–15.2)	21.1 (19.8–22.4)	29.9 (27.5–32.8)	41.2 (35.5–48.9)	54.6 (44.0–65.9)	2,094
12–19 years	19.3 (17.5–21.4)	9.9 (9.5–10.9)	14.4 (12.5–15.7)	19.9 (17.6–21.9)	27.1 (23.6–30.2)	36.5 (28.6–45.6)	42.2 (35.1–52.1)	640
20–39 years	18.7 (17.3–20.1)	8.9 (8.2–10.2)	12.6 (11.2–14.2)	18.7 (17.7–20.4)	27.4 (24.9–29.7)	36.9 (33.6–41.3)	44.3 (38.6–60.8)	490
40–59 years	22.0 (19.7–24.5)	10.6 (9.2–12.3)	15.3 (14.1–18.0)	22.2 (20.2–24.2)	32.2 (27.4–35.4)	43.8 (33.5–62.7)	61.5 (43.8–81.8)	387
≥ 60 years	23.2 (20.8–25.9)	9.9 (7.7–13.0)	16.6 (15.0–17.9)	23.9 (20.9–27.2)	34.7 (30.0–39.3)	50.3 (40.8–68.9)	69.4 (49.6–90.0)	577
Mexican American	14.7 (13.0–16.6)	7.4 (5.6–7.9)	10.3 (8.3–11.8)	15.9 (13.4–17.9)	21.1 (18.7–23.5)	28.1 (24.1–35.0)	35.5 (28.9–38.5)	485
Non-Hispanic black	21.6 (19.1–24.4)	9.9 (7.5–11.9)	14.8 (12.5–16.8)	22.0 (19.5–24.9)	32.2 (28.1–36.2)	43.8 (37.2–57.3)	57.5 (43.8–78.4)	538
Non-Hispanic white	21.4 (19.9–23.1)	10.5 (9.5–11.5)	15.0 (14.4–16.0)	21.9 (20.5–23.0)	30.2 (27.7–33.0)	41.3 (35.7–49.6)	55.9 (44.0–69.4)	962
Female	18.4 (17.0–20.0)	9.0 (7.8–9.9)	12.4 (11.5–13.8)	18.2 (16.8–19.7)	27.3 (23.6–30.0)	39.7 (34.4–42.6)	45.7 (42.3–61.5)	1,041
Male	23.3 (21.1–25.6)	12.3 (10.4–13.5)	17.7 (15.9–18.9)	23.9 (22.3–25.3)	32.1 (28.7–35.7)	45.3 (35.5–62.7)	62.7 (43.8–81.8)	1,053

Table 3. Geometric mean and selected percentiles (95% confidence intervals) of perfluorooctanoate (PFOA) concentrations in serum (μg/L) for the U.S. population 12 years of age and older: data from NHANES 2003–2004.

Variable	Geometric mean	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	95th percentile	No.
All	3.9 (3.6–4.3)	1.9 (1.8–2.1)	2.7 (2.6–3.0)	4.0 (3.8–4.4)	5.8 (5.2–6.3)	7.8 (6.7–9.6)	9.8 (7.4–14.1)	2,094
12–19 years	3.9 (3.5–4.4)	2.2 (1.9–2.3)	2.9 (2.6–3.2)	3.9 (3.3–4.4)	5.4 (4.6–6.1)	6.9 (5.6–9.2)	8.6 (5.9–12.6)	640
20–39 years	3.9 (3.6–4.2)	1.8 (1.5–2.1)	2.7 (2.5–3.0)	4.1 (3.7–4.5)	5.8 (5.4–6.1)	7.6 (7.3–8.4)	9.6 (8.4–11.1)	490
40–59 years	4.2 (3.8–4.8)	2.0 (1.8–2.4)	2.9 (2.6–3.2)	4.2 (3.9–4.8)	6.3 (5.3–7.2)	8.2 (6.8–10.7)	10.6 (7.4–16.9)	387
≥ 60 years	3.7 (3.3–4.1)	1.8 (1.5–2.1)	2.7 (2.4–2.9)	3.9 (3.5–4.3)	5.4 (4.9–5.9)	7.2 (6.0–9.5)	9.5 (6.9–14.1)	577
Mexican American	3.1 (2.8–3.4)	1.4 (1.1–1.8)	2.2 (1.9–2.5)	3.3 (3.0–3.6)	4.4 (4.1–5.1)	6.7 (5.7–7.3)	7.6 (6.7–10.5)	485
Non-Hispanic black	3.4 (3.0–3.8)	1.2 (1.1–1.6)	2.2 (1.9–2.5)	3.7 (3.1–4.2)	5.1 (4.4–6.1)	7.7 (5.3–10.9)	9.3 (6.5–13.9)	538
Non-Hispanic white	4.2 (3.9–4.5)	2.1 (2.0–2.3)	3.0 (2.6–3.2)	4.2 (3.9–4.6)	5.9 (5.4–6.6)	7.8 (7.2–9.1)	9.8 (7.6–13.3)	962
Female	3.5 (3.2–3.8)	1.6 (1.5–1.9)	2.5 (2.2–2.7)	3.6 (3.2–3.9)	5.2 (4.6–5.7)	7.1 (6.3–8.2)	8.4 (7.4–10.6)	1,041
Male	4.5 (4.1–4.9)	2.3 (2.0–2.4)	3.2 (3.1–3.5)	4.6 (4.2–5.0)	6.3 (5.6–7.1)	8.3 (6.8–11.8)	10.4 (7.4–17.5)	1,053

Table 4. Geometric mean and selected percentiles (95% confidence intervals) of perfluorohaxanesulfonate (PFHxS) concentrations in serum (μg/L) for the U.S. population 12 years of age and older: data from NHANES 2003–2004.

Variable	Geometric mean	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	95th percentile	No.
All	1.9 (1.7–2.2)	0.7 (0.6–0.7)	1.0 (0.9–1.2)	1.9 (1.6–2.1)	3.3 (2.8–3.9)	5.9 (4.8–7.2)	8.3 (7.1–9.7)	2,094
12–19 years	2.4 (2.1–2.9)	0.6 (0.5–0.8)	1.2 (1.0–1.4)	2.3 (1.7–3.0)	4.8 (3.9–6.0)	9.5 (6.8–12.5)	13.1 (9.9–19.6)	640
20–39 years	1.8 (1.6–2.0)	0.5 (0.5–0.6)	1.0 (0.9–1.2)	1.7 (1.5–2.0)	2.8 (2.5–3.3)	4.8 (3.9–6.1)	6.7 (4.9–9.4)	490
40–59 years	1.9 (1.6–2.2)	0.7 (0.5–0.8)	1.0 (0.9–1.2)	1.6 (1.4–2.0)	3.1 (2.3–4.5)	5.5 (4.3–6.9)	6.7 (5.5–8.2)	387
≥ 60 years	2.0 (1.7–2.4)	0.8 (0.5–0.9)	1.1 (1.0–1.3)	1.9 (1.6–2.1)	3.2 (2.6–3.7)	7.2 (4.3–9.7)	10.2 (7.0–12.6)	577
Mexican American	1.4 (1.2–1.7)	0.5 (0.3–0.7)	0.7 (0.5–0.9)	1.4 (1.2–1.7)	2.3 (1.9–2.7)	4.2 (3.1–5.1)	5.4 (4.0–8.9)	485
Non-Hispanic black	1.9 (1.6–2.3)	0.5 (0.3–0.7)	1.1 (0.9–1.3)	1.9 (1.5–2.2)	3.4 (2.7–4.3)	6.0 (5.0–7.1)	8.2 (6.3–12.0)	538
Non-Hispanic white	2.0 (1.8–2.3)	0.7 (0.6–0.8)	1.1 (1.0–1.3)	1.9 (1.6–2.1)	3.3 (2.8–4.0)	6.0 (4.6–7.8)	8.1 (6.9–10.1)	962
Female	1.7 (1.6–1.9)	0.6 (0.5–0.6)	0.9 (0.8–1.0)	1.5 (1.4–1.8)	2.9 (2.5–3.5)	5.8 (4.6–6.9)	8.2 (6.7–10.0)	1,041
Male	2.2 (1.9–2.5)	0.8 (0.7–1.0)	1.3 (1.1–1.4)	2.0 (1.8–2.4)	3.3 (2.8–4.4)	6.1 (4.6–8.1)	8.5 (6.4–10.5)	1,053

Table 5. Geometric mean and selected percentiles (95% confidence intervals) of perfluorononanoate (PFNA) concentrations in serum (μg/L) for the U.S. population 12 years of age and older: data from NHANES 2003–2004.

Variable	Geometric mean	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	95th percentile	No.
All	1.0 (0.8–1.1)	0.4 (0.3–0.4)	0.6 (0.5–0.6)	1.0 (0.9–1.1)	1.5 (1.2–1.7)	2.2 (1.6–3.8)	3.2 (1.8–7.7)	2,094
12–19 years	0.9 (0.7–1.0)	0.3 (0.3–0.4)	0.5 (0.5–0.6)	0.7 (0.6–0.9)	1.2 (0.9–1.5)	1.9 (1.2–3.3)	2.7 (1.3–6.3)	640
20–39 years	1.0 (0.8–1.1)	0.3 (0.2–0.5)	0.6 (0.6–0.7)	0.9 (0.8–1.1)	1.4 (1.2–1.7)	2.1 (1.7–2.7)	2.8 (1.9–6.1)	490
40–59 years	1.1 (0.9–1.4)	0.5 (0.4–0.5)	0.7 (0.6–0.7)	1.0 (0.9–1.2)	1.7 (1.2–2.4)	2.7 (1.6–5.9)	4.3 (1.7–9.3)	387
≥ 60 years	0.8 (0.7–1.0)	0.3 (0.2–0.3)	0.5 (0.5–0.6)	0.9 (0.8–1.0)	1.3 (1.1–1.5)	1.9 (1.5–3.0)	3.0 (1.6–6.5)	577
Mexican American	0.7 (0.6–0.8)	0.2 (0.1–0.2)	0.5 (0.4–0.5)	0.7 (0.5–0.8)	1.0 (0.9–1.3)	1.6 (1.2–1.8)	2.0 (1.6–2.8)	485
Non-Hispanic black	1.1 (0.8–1.5)	0.4 (0.3–0.6)	0.6 (0.5–0.8)	1.0 (0.8–1.4)	1.6 (1.2–2.7)	3.1 (1.5–6.5)	4.7 (2.1–9.3)	538
Non-Hispanic white	1.0 (0.8–1.1)	0.4 (0.3–0.4)	0.5 (0.5–0.6)	0.8 (0.8–0.9)	1.5 (1.2–1.7)	2.2 (1.6–3.4)	2.9 (1.8–6.2)	962
Female	0.9 (0.7–1.0)	0.4 (0.3–0.4)	0.6 (0.5–0.6)	0.9 (0.7–0.9)	1.2 (1.0–1.6)	2.2 (1.4–3.3)	3.0 (1.7–6.1)	1,041
Male	1.1 (0.9–1.3)	0.5 (0.4–0.5)	0.6 (0.6–0.7)	1.0 (0.9–1.2)	1.6 (1.3–1.8)	2.4 (1.7–4.8)	4.0 (1.8–8.7)	1,053

age-by-smoking status ($p = 0.04$) interactions for PFNA. Because of these interactions with age, concentrations were compared at the 25th (age = 26 years), 50th (age = 41 years), 75th (age = 55 years), and 90th (age = 70 years) percentiles of age.

LSGM concentrations provide geometric mean estimates for a demographic variable after adjustment for the model covariates (Table 6). The statistical significance values when comparing these LSGM concentrations are shown in the Supplemental Material, Table S7 (online at http://www.ehponline.org/docs/2007/10598/suppl.pdf). PFOS LSGM concentrations were significantly higher ($p < 0.01$) in males than in females. Similarly, for PFOA and PFHxS, males had significantly higher LSGM concentrations than females except at the 90th percentile of age (Table 6). LSGM concentrations of PFHxS were significantly lower for Mexican Americans than for non-Hispanic blacks ($p = 0.01$) and non-Hispanic whites ($p < 0.01$); LSGM concentrations did not differ significantly between non-Hispanic whites and non-Hispanic blacks ($p = 0.49$). PFOS and PFNA LSGM concentrations were significantly lower in Mexican Americans than in non-Hispanic blacks (PFOS, $p < 0.01$; PFNA, $p < 0.01$–0.03) and non-Hispanic whites (PFOS, $p < 0.01$; PFNA, $p < 0.01$–0.02), regardless of age; LSGM concentrations between non-Hispanic whites and non-Hispanic blacks differed significantly only at the 75th and 90th percentiles of age (Table 6). Non-Hispanic whites had significantly higher PFOA LSGM concentrations ($p < 0.01$), regardless of sex, than Mexican Americans. The differences between Mexican-American males and non-Hispanic black males and between non-Hispanic white males and non-Hispanic black males were not statistically significant.

We used a two-sample *t*-test to compare the difference of the two geometric mean concentrations (on the log scale) of PFOS, PFOA, PFHxS, and PFNA during NHANES 1999–2000 and NHANES 2003–2004 (Table 7), taking into account their associated standard errors and degrees of freedom, by age, sex, and race/ethnicity, using SAS. The differences were all statistically significant ($p < 0.05$), except for PFHxS in Mexican Americans ($p = 0.21$) (Table 7). We analyzed the NHANES 2003–2004 samples first and then the NHANES 1999–2000 samples (Calafat et al. 2007) using two methods that differed in the manner in which PFCs were extracted and preconcentrated from the serum (Kuklenyik et al. 2004, 2005). In both methods, we used tandem mass spectrometry with $^{18}O_2$-PFOS, $^{13}C_2$-PFOA, and $^{18}O_2$-PFOSA (only for NHANES 1999–2000) for quantification, the same multiple reaction monitoring transitions for quantification for PFOA (413/369) and PFOS (499/99), the same QC materials and analytical standards. $^{18}O_2$-PFOSA was not commercially available when the 2003–2004 NHANES samples were analyzed. Except for PFNA and PFOA, for which the LODs were the same regardless of the method, the method used for NHANES 1999–2000 (Kuklenyik et al. 2005) had slightly lower LODs than the method used for NHANES 2003–2004 (Kuklenyik et al. 2004) (Table 1). To estimate whether method differences could account for the differences in concentrations, we analyzed QC samples from low and high concentration pools and 124 split samples using both methods. The two methods showed good agreement from the results of the split sample analysis [presented for PFOA in Figures S1 and S2 in Supplemental

Table 6. Least-square geometric mean concentrations (μg/L) (95% confidence intervals) of PFOA, PFOS, PFHxS, and PFNA in various demographic groups.

Group	PFOA	PFOS	PFHxS	PFNA
Female		18.5 (17.1–20)		0.9 (0.7–1)
Male		23.6 (21.8–25.7)		1.1 (0.9–1.3)
Female: age P25	3.4 (3.1–3.7)		1.7 (1.5–1.9)	
Female: age P50	3.5 (3.3–3.8)		1.7 (1.5–1.9)	
Female: age P75	3.7 (3.4–4)		1.7 (1.5–2)	
Female :age P90	3.8 (3.4–4.2)		1.7 (1.5–2)	
Male: age P25	5.1 (4.7–5.5)		2.4 (2–2.8)	
Male: age P50	4.5 (4.2–4.9)		2.2 (1.9–2.6)	
Male: age P75	4.1 (3.7–4.5)		2.1 (1.8–2.4)	
Male: age P90	3.7 (3.2–4.2)		1.9 (1.6–2.3)	
MA			1.4 (1.1–1.7)	
NHB			1.9 (1.6–2.3)	
NHW			2.0 (1.8–2.3)	
Female, MA	2.6 (2.3–3)			
Female, NHB	2.8 (2.5–3.2)			
Female, NHW	3.8 (3.5–4.1)			
Male, MA	3.6 (3.3–3.9)			
Male, NHB	4.1 (3.5–4.8)			
Male, NHW	4.6 (4.2–5.1)			
MA: age P25		13.9 (12.5–15.5)		0.7 (0.6–0.8)
MA: age P50		15.1 (13.6–16.8)		0.7 (0.6–0.8)
MA: age P75		16.3 (14.4–18.4)		0.7 (0.5–0.8)
MA: age P90		17.7 (15.3–20.6)		0.6 (0.5–0.8)
NHW: age P25		20.1 (18.6–21.8)		1 (0.8–1.2)
NHW: age P50		21.2 (19.6–22.9)		1 (0.8–1.1)
NHW: age P75		22.3 (20.5–24.3)		0.9 (0.8–1.1)
NHW: age P90		23.5 (21.3–26)		0.9 (0.8–1)
NHB: age P25		19.9 (17.9–22.1)		1.1 (0.8–1.4)
NHB: age P50		22.6 (20.1–25.5)		1.2 (0.9–1.6)
NHB: age P75		25.5 (22.1–29.5)		1.3 (1–1.9)
NHB: age P90		29.0 (24.3–34.7)		1.5 (1–2.1)
NonSMK: age P25				1 (0.8–1.1)
NonSMK: age P50				1 (0.8–1.1)
NonSMK: age P75				1 (0.8–1.1)
NonSMK: age P90				1 (0.8–1.2)
SMK: age P25				1.1 (0.9–1.3)
SMK: age P50				1 (0.8–1.1)
SMK: age P75				0.9 (0.8–1)
SMK: age P90				0.8 (0.7–1)
< HS				0.7 (0.6–0.8)
= HS				1 (0.8–1.1)
> HS				1.2 (0.9–1.7)
< HS: age P25	3.7 (3.4–4.1)			
< HS: age P50	3.7 (3.4–4.1)			
< HS: age P75	3.7 (3.3–4.1)			
< HS: age P90	3.7 (3.3–4.2)			
= HS: age P25	4.4 (4.1–4.7)			
= HS: age P50	4 (3.7–4.3)			
= HS: age P75	3.7 (3.3–4.1)			
= HS: age P90	3.3 (2.8–4)			
> HS: age P25	4.2 (3.8–4.6)			
> HS: age P50	4.1 (3.7–4.5)			
> HS: age P75	4.1 (3.6–4.6)			
> HS: age P90	4 (3.4–4.7)			

Abbreviations: HS, high school; MA, Mexican American; NHB, non-Hispanic black; NHW, non-Hispanic white; NonSMK, nonsmoker; P25, 25th percentile of age = 26 years; P50, 50th percentile of age = 41 years; P75, 75th percentile of age = 55 years; P90, 90th percentile of age = 70 years; SMK, smoker.

Material (online at http://www.ehponline.org/docs/2007/10598/suppl.pdf)]. Results were similar for all other analytes (data not shown). In general, analysis of the QC pools showed mean concentrations and coefficients of variation which were similar between the two methods (Table 1).

Discussion

We detected PFOS, PFOA, PFHxS, and PFNA in > 98% of persons in this representative sample of the civilian, noninstitutionalized U.S. population, ≥ 12 years of age. These findings confirm that measurable serum concentrations of these compounds were prevalent in the United States in 2003–2004, even after 3M in 2002 discontinued its industrial production of PFOS and related compounds, including the ammonium salt of PFOA. Direct and indirect sources of PFOA still exist in the United States, although since 1999, global emissions of PFOA reportedly have decreased by more than half as of 2004 (Prevedouros et al. 2006), and current producers have committed to reducing manufacturing emissions of PFOA and its salts and precursors (U.S. EPA 2006).

Other PFCs, however, were detected infrequently. For example, PFBuS was detected in < 0.5% of the samples. PFBuS is a final degradation product of perfluorobutanesulfonyl fluoride, now used in the manufacture of materials as a replacement for POSF-related chemicals [C-6 (e.g., PFHxS) and C-8 (e.g., PFOS)] that were phased out beginning in 2000. Similarly, in a study involving 18 volunteer employees from 3M Company, PFBuS was detected only in workers with production-related duties, whereas PFOA, PFOS, and PFHxS were detected in most workers (Ehresman et al. 2007). The lower frequency of detection of PFBuS than PFOS, PFOA, and PFHxS suggests that human exposures to PFBuS are indeed lower, and/or that pharmacokinetic factors, which might include increased urinary elimination, are different.

PFOS showed the highest geometric mean and 95th percentile concentrations, followed by PFOA, PFHxS, and PFNA. For PFOS, PFOA, and PFNA, however—unlike lipophilic POPs whose serum concentrations increase with age (Needham et al. 2006)—concentrations were quite similar among the four age groups (Tables 2–5), a finding that agrees with previous data (Calafat et al. 2007; Olsen et al. 2003, 2004b, 2004c). By contrast, for PFHxS, the geometric mean and 95th percentile concentrations were higher for adolescents than for adults, as previously reported (Calafat et al. 2007; Olsen et al. 2004b). The higher concentrations of PFHxS in children and adolescents could be related to their increased contact with carpeted floors containing PFHxS, which is used for specific postmarket carpet-treatment applications (Olsen et al. 2004b).

In agreement with previous reports (Calafat et al. 2006a, 2007; Fromme et al. 2007; Harada et al. 2004; Midasch et al. 2006; Yeung et al. 2006), we observed sex and race/ethnicity differences. Females had significantly lower LSGM concentrations of PFOS than did males (Table 6). For PFOA and PFHxS, sex differences also existed but were not as pronounced for the elderly (Table 6). Mexican Americans had the lowest LSGM concentrations of PFHxS and non-Hispanic whites and non-Hispanic blacks had similar concentrations (Table 6). Racial differences for PFOS and PFNA were age dependent, whereas those for PFOA were sex dependent (Table 6). These sex and racial differences may reflect variability in exposure patterns as a result of differences in factors such as lifestyle, diet, and use of products containing PFCs that may contribute to the observed serum concentrations of PFCs.

To evaluate whether the discontinued production of PFOS and related compounds by 3M Company in 2002 and technologic changes implemented by other companies have led to a subsequent decrease in serum PFC concentrations in the general U.S. population (Olsen et al. 2007b), we compared NHANES data of 1999–2000 with NHANES data of 2003–2004. The distribution of serum concentrations of PFOS, PFOA, PFHxS, and PFNA by sex, race/ethnicity, and age in 2003–2004 (Tables 2–5) was similar to that for the general U.S. population in 1999–2000 (Calafat et al. 2007). However, the geometric mean concentrations for PFOS, PFOA, and PFHxS in 2003–2004 were lower than for 1999–2000. For PFNA, 2003–2004 levels were higher than those found in 1999–2000. These concentrations differed significantly for all demographic groups except for PFHxS in Mexican Americans (Table 7). Various concentration percentiles similarly decreased for PFOS, PFOA, and PFHxS. We analyzed the NHANES 1999–2000 and 2003–2004 samples by using two different methods; however, these approaches provided equivalent results [Table 1; Figures S1 and S2 in the Supplemental Material (online at http://www.ehponline.org/docs/2007/10598/suppl.pdf)], indicating that the differences cannot be attributed to changes in the analytical methodology. The decrease in serum concentrations of PFOS and PFOA during this time interval agreed with the reported reductions in PFOS and PFOA concentrations for a group of Red Cross blood donors in the United States (Olsen et al. 2007b) and in PFOS (temporal trends for PFOA were not examined) in Arctic ringed seals in the same time (Butt et al. 2007). These decreases in serum concentrations of PFOS and PFOA in humans and wildlife had been related to the phaseout of POSF-based materials in 2000–2002 (Butt et al. 2007; Olsen et al. 2007b).

For PFHxS, although the geometric mean concentrations were lower in 2003–2004 than in 1999–2000, the differences were less evident, and in some cases they reversed at the higher concentration percentiles for some demographic categories. These findings may be related to the lower concentrations of PFHxS than of PFOS or PFOA and to differences in the estimated geometric mean serum

Table 7. Geometric mean concentrations (95% confidence intervals) of PFOA, PFOS, PFHxS, and PFNA in NHANES 1999–2000 and NHANES 2003–2004 for the whole population and different demographic groups.[a]

	PFOS		PFOA		PFHxS		PFNA	
Variable	1999–2000	2003–2004	1999–2000	2003–2004	1999–2000	2003–2004	1999–2000	2003–2004
All	30.4 (27.1–33.9)	20.7 (19.2–22.3)	5.2 (4.7–5.7)	3.9 (3.6–4.3)	2.1 (1.9–2.4)	1.9 (1.7–2.2)	0.5 (0.5–0.7)	1.0 (0.8–1.1)
12–19 years	29.1 (26.2–32.4)	19.3 (17.5–21.4)	5.5 (5.0–6.0)	3.9 (3.5–4.4)	2.7 (2.1–3.4)	2.4 (2.1–2.9)	0.5 (0.4–0.5)	0.9 (0.7–1.0)
20–39 years	27.5 (24.9–30.2)	18.7 (17.3–20.1)	5.2 (4.7–5.7)	3.9 (3.6–4.2)	2.0 (1.7–2.3)	1.8 (1.6–2.0)	0.5 (0.4–0.6)	1.0 (0.8–1.1)
40–59 years	33.0 (28.0–38.8)	22.0 (19.7–24.5)	5.4 (4.7–6.2)	4.2 (3.8–4.8)	2.1 (1.8–2.3)	1.9 (1.6–2.2)	0.6 (0.4–0.7)	1.1 (0.9–1.4)
≥ 60 years	33.3 (28.5–38.8)	23.2 (20.8–25.9)	4.8 (4.3–5.5)	3.7 (3.3–4.1)	2.2 (1.9–2.5)	2.0 (1.7–2.4)	0.6 (0.5–0.8)	0.8 (0.7–1.0)
Female	28.0 (24.6–31.8)	18.4 (17.0–20.0)	4.8 (4.3–5.3)	3.5 (3.2–3.8)	1.8 (1.6–2.1)	1.7 (1.6–1.9)	0.5 (0.4–0.6)	0.9 (0.7–1.0)
Male	33.4 (29.6–37.6)	23.3 (21.1–25.6)	5.7 (5.2–6.3)	4.5 (4.1–4.9)	2.6 (2.3–3.0)	2.2 (1.9–2.5)	0.6 (0.5–0.7)	1.1 (0.9–1.3)
Mexican American	22.7 (19.8–25.9)	14.7 (13.0–16.6)	3.9 (3.6–4.2)	3.1 (2.8–3.4)	1.5 (1.1–1.9)	1.4 (1.2–1.7)	0.3 (0.3–0.4)	0.7 (0.6–0.8)
Non-Hispanic black	33.0 (26.2–41.6)	21.6 (19.1–24.4)	4.8 (4.1–5.6)	3.4 (3.0–3.8)	2.2 (1.6–2.9)	1.9 (1.6–2.3)	0.8 (0.6–1.0)	1.1 (0.8–1.5)
Non-Hispanic white	32.0 (29.1–35.2)	21.4 (19.9–23.1)	5.6 (5.0–6.2)	4.2 (3.9–4.5)	2.3 (2.0–2.5)	2.0 (1.8–2.3)	0.6 (0.5–0.7)	1.0 (0.8–1.1)

[a]For PFOS, PFOA, and PFNA, all differences between NHANES 1999–2000 (Calafat et al. 2007) and NHANES 2003–2004 geometric mean concentrations are statistically significant ($p < 0.001$). For PFHxS, except for Mexican Americans ($p = 0.209$), all other differences are also statistically significant with $p < 0.001$, except for females ($p = 0.037$), persons ≥ 60 years of age ($p = 0.016$), persons 12–19 years of age ($p = 0.004$), and non-Hispanic blacks ($p = 0.004$).

elimination half-life (PFHxS, 7.3 years; PFOA, 3.5 years; and PFOS, 4.8 years) (Olsen et al. 2007a). Furthermore, the correlation between the serum concentrations of PFOS and PFOA was higher than correlations of PFHxS and either PFOA or PFOS, suggesting potential common exposure pathway(s) for PFOA and PFOS, but probably not for PFHxS (mostly used in carpet-treatment applications (Olsen et al. 2004b). Pharmacokinetic factors may also contribute to these differences. The transformation of certain POFS-related sulfonamides to PFOS and potentially to PFOA in the atmosphere was suggested as a common mechanism for formation of both PFOS and PFOA, which would account at least partly for the high correlation in serum concentrations (Olsen et al. 2007b). On the other hand, PFOA and other perfluorocarboxylates (e.g., PFNA), but not PFOS, might be formed from the biodegradation of the volatile fluorotelomer alcohols (Ellis et al. 2004).

Current manufacturing practices exclusively use fluorotelomers for the synthesis of perfluorocarboxylates (Prevedouros et al. 2006). Perfluorocarboxylates, including PFNA, were present as reaction by-products in POSF-based materials (Prevedouros et al. 2006). Interestingly, our data suggest that PFNA geometric mean concentrations in 2003–2004 approximately doubled over those of 1999–2000. However, because human exposure data for PFNA are more limited than they are for PFOS, PFOA, and even PFHxS, these results must be interpreted with caution. In 2004, the estimated annual production of the ammonium salt of PFNA, primarily used as a processing aid in the manufacture of such fluoropolymers as polyvinylidene fluoride, was 15–75 tonnes (Prevedouros et al. 2006). Information about efforts to reduce manufacturing emissions for PFNA, estimated at about 10% of the amount produced, was not found (Prevedouros et al. 2006). As a comparison, global manufacturing emissions of PFOA were about 15 tonnes in 2004, down from about 45 tonnes in 1999 (Prevedouros et al. 2006).

For most PFCs, these NHANES 2003–2004 results are consistent with reduced population exposure because of recent efforts of industry and government. U.S. and worldwide efforts continue in attempts to reduce exposures to PFCs, including PFOS and PFOA, and many halogenated POPs, including polybrominated diphenyl ethers. We will continue to assess exposure to these and other chemicals in the U.S. population through NHANES, an effort that will provide unique information on trends of exposure to these chemicals over time. In addition, we are analyzing pooled serum samples from 3- to 11-year-old children to fill data gaps for mean PFC concentrations in this age range.

References

Alexander BH, Olsen GW, Burris JM, Mandel JH, Mandel JS. 2003. Mortality of employees of a perfluorooctanesulphonyl fluoride manufacturing facility. Occup Environ Med 60:722–729.

Apelberg BJ, Witter FR, Herbstman JB, Calafat AM, Halden RU, Needham LL et al. 2007. Cord serum concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in relation to weight and size at birth. Environ Health Perspect 115:1670–1676; doi:10.1289/ehp.10334 available via http://dx.doi.org/ [Online 31 July 2007].

Butenhoff JL, Kennedy GL, Frame SR, O'Connor JC, York RG. 2004. The reproductive toxicology of ammonium perfluorooctanoate (APFO) in the rat. Toxicology 196:95–116.

Butt CM, Muir DCG, Stirling I, Kwan M, Mabury SA. 2007. Rapid response of arctic ringed seals to changes in perfluoroalkyl production. Environ Sci Technol 41:42–49.

Calafat AM, Kuklenyik Z, Caudill SP, Reidy JA, Needham LL. 2006a. Perfluorochemicals in pooled serum samples from United States residents in 2001 and 2002. Environ Sci Technol 40:2128–2134.

Calafat AM, Kuklenyik Z, Reidy JA, Caudill SP, Tully JS, Needham LL. 2007. Serum concentrations of 11 polyfluoroalkyl compounds in the US population: data from the National Health and Nutrition Examination Survey (NHANES) 1999–2000. Environ Sci Technol 41:2237–2242.

Calafat AM, Needham LL, Kuklenyik Z, Reidy JA, Tully JS, Aguilar-Villalobos M, et al. 2006b. Perfluorinated chemicals in selected residents of the American continent. Chemosphere 63:490–496.

CDC (Centers for Disease Control and Prevention). 2003. National Health and Nutrition Examination Survey. National Center for Health Statistics. Available: http://www.cdc.gov/nchs/about/major/nhanes/intro_mec.htm [accessed 11 June 2007].

CDC (Centers for Disease Control and Prevention). 2005. NHANES 2003–2004 Public Data General Release File Documentation. Available: http://www.cdc.gov/nchs/data/nhanes/nhanes_03_04/general_data_release_doc_03-04.pdf [accessed 12 March 2007].

CDC (Centers for Disease Control and Prevention). 2006a. Analytic and Reporting Guidelines. The National Health and Nutrition Examination Survey (NHANES). Available: http://www.cdc.gov/nchs/data/nhanes/nhanes_03_04/nhanes_analytic_guidelines_dec_2005.pdf [accessed 12 March 2007].

CDC (Centers for Disease Control and Prevention). 2006b. General Documentation on Laboratory Data. General Information about the NHANES 2003-2004 Laboratory Methodology and Public Data Files. Available: http://www.cdc.gov/nchs/data/nhanes/nhanes_03_04/lab_c_generaldoc.pdf [accessed 30 July 2007].

Ehresman DJ, Froehlich JW, Olsen GW, Chang SC, Butenhoff JL. 2007. Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals. Environ Res 103:176–184.

Ellis DA, Martin JW, De Silva AO, Mabury SA, Hurley MD, Sulbaek Andersen MP, et al. 2004. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. Environ Sci Technol 38:3316–3321.

Emmett EA, Zhang H, Shofer FS, Freeman D, Rodway NV, Desai C, et al. 2006. Community exposure to perfluorooctanoate: Relationships between serum levels and certain health parameters. J Occup Environ Med 48:771–779.

Fromme H, Midasch O, Twardella D, Angerer J, Boehmer S, Liebl B. 2007. Occurrence of perfluorinated substances in an adult German population in southern Bavaria. Int Arch Occup Environ Health 80:313–319.

Gilliland FD, Mandel JS. 1993. Mortality among employees of a perfluorooctanoic acid production plant. J Occup Environ Med 35:950–954.

Grice MM, Alexander BH, Hoffbeck R, Kampa DM. 2007. Self-reported medical conditions in perfluorooctanesulfonyl fluoride manufacturing workers. J Occup Environ Med 49:722–729.

Guruge KS, Taniyasu S, Yamashita N, Wijeratna S, Mohotti KM, Seneviratne HR, et al. 2005. Perfluorinated organic compounds in human blood serum and seminal plasma: a study of urban and rural tea worker populations in Sri Lanka. J Environ Monit 7:371–377.

Hansen KJ, Clemen LA, Ellefson ME, Johnson HO. 2001. Compound-specific, quantitative characterization of organic: fluorochemicals in biological matrices. Environ Sci Technol 35:766–770.

Harada K, Koizumi A, Saito N, Inoue K, Yoshinaga T, Date C, et al. 2007. Historical and geographical aspects of the increasing perfluorooctanoate and perfluorooctane sulfonate contamination in human serum in Japan. Chemosphere 66:293–301.

Harada K, Saito N, Inoue K, Yoshinaga T, Watanabe T, Sasaki S, et al. 2004. The influence of time, sex and geographic factors on levels of perfluorooctane sulfonate and perfluorooctanoate in human serum over the last 25 years. J Occup Health 46:141–147.

Hornung RW, Reed LD. 1990. Estimation of average concentration in the presence of nondetectable values. Appl Occup Environ Hyg 5:46–51.

Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG. 2006. Biological monitoring of polyfluoroalkyl substances: a review. Environ Sci Technol 40:3463–3473.

Kannan K, Corsolini S, Falandysz J, Fillmann G, Kumar KS, Loganathan BG, et al. 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ Sci Technol 38:4489–4495.

Karrman A, Mueller JF, van Bavel B, Harden F, Toms LML, Lindstrom G. 2006. Levels of 12 perfluorinated chemicals in pooled Australian serum, collected 2002–2003, in relation to age, gender, and region. Environ Sci Technol 40:3742–3748.

Kennedy GL, Butenhoff JL, Olsen GW, O'Connor JC, Seacat AM, Perkins RG, et al. 2004. The toxicology of perfluorooctanoate. Crit Rev Toxicol 34:351–384.

Kuklenyik Z, Needham LL, Calafat AM. 2005. Measurement of 18 perfluorinated organic acids and amides in human serum using on-line solid-phase extraction. Anal Chem 77:6085–6091.

Kuklenyik Z, Reich JA, Tully JS, Needham LL, Calafat AM. 2004. Automated solid-phase extraction and measurement of perfluorinated organic acids and amides in human serum and milk. Environ Sci Technol 38:3698–3704.

Lau C, Butenhoff JL, Rogers JM. 2004. The developmental toxicity of perfluoroalkyl acids and their derivatives. Toxicol Appl Pharmacol 198:231–241.

Luebker DJ, York RG, Hansen KJ, Moore JA, Butenhoff JL. 2005. Neonatal mortality from in utero exposure to perfluorooctanesulfonate (PFOS) in Sprague-Dawley rats: Dose-response, and biochemical and pharamacokinetic parameters. Toxicology 215:149–169.

Midasch O, Schettgen T, Angerer J. 2006. Pilot study on the perfluorooctanesulfonate and perfluorooctanoate exposure of the German general population. Int J Hyg Environ Health 209:489–496.

Needham LL, Patterson DG Jr, Calafat AM, Sjodin A, Turner W, Kuklenyik Z. 2006. Distribution of halogenated environmental chemicals among people of different ages, races, and sexes in the United States. Organohalogen Compounds 68:484–487.

Olsen GW, Burlew MM, Marshall JC, Burris JM, Mandel JH. 2004a. Analysis of episodes of care in a perfluorooctanesulfonyl fluoride production facility. J Occup Environ Med 46:837–846.

Olsen GW, Burris JM, Ehresman DJ, Froehlich JW, Seacat AM, Butenhoff JL, et al. 2007a. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. Environ Health Perspect 115:1298–1305.

Olsen GW, Church TR, Hansen KJ, Burris JM, Butenhoff JL, Mandel JH, et al. 2004b. Quantitative evaluation of perfluorooctanesulfonate (PFOS) and other fluorochemicals in the serum of children. J Child Health 2:53–76.

Olsen GW, Church TR, Larson EB, van Belle G, Lundberg JK, Hansen KJ, et al. 2004c. Serum concentrations of perfluorooctanesulfonate and other fluorochemicals in an elderly population from Seattle, Washington. Chemosphere 54:1599–1611.

Olsen GW, Church TR, Miller JP, Burris JM, Hansen KJ, Lundberg JK, et al. 2003. Perfluorooctanesulfonate and other fluorochemicals in the serum of American Red Cross adult blood donors. Environ Health Perspect 111:1892–1901.

Olsen GW, Huang HY, Helzlsouer KJ, Hansen KJ, Butenhoff JL, Mandel JH. 2005. Historical comparison of perfluorooctanesulfonate, perfluorooctanoate, and other fluorochemicals in human blood. Environ Health Perspect 113:539–545.

Olsen GW, Mair DC, Reagen WK, Ellefson ME, Ehresman DJ,

Butenhoff JL, et al. 2007b. Preliminary evidence of a decline in perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) concentrations in American Red Cross blood donors. Chemosphere 68:105–111.

Organisation for Economic Co-operation and Development. 2002. Co-Operation on Existing Chemicals. Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and Its Salts. 1-362. Available: http://www.oecd.org/dataoecd/23/18/2382880.pdf [accessed 20 April 2007].

Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. 2006. Sources, fate and transport of perfluorocarboxylates. Environ Sci Technol 40:32–44.

Taniyasu S, Kannan K, Horii Y, Hanari N, Yamashita N. 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. Environ Sci Technol 37:2634–2639.

United Nations Environment Programme. 2004. Stockholm Convention on Persistent Organic Pollutants (POPs) [Press Release]. Available: http://www.pops.int/documents/press/pr2-04SC.pdf [accessed 20 April 2007].

U.S. EPA. 2006. 2010/15 PFOA Stewardship Program. Available: http://www.epa.gov/oppt/pfoa/pubs/pfoastewardship.htm [accessed 20 April 2007].

Yeung LWY, So MK, Jiang GB, Taniyasu S, Yamashita N, Song MY, et al. 2006. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. Environ Sci Technol 40:715–720.

CALIFORNIA ASSOCIATION of SANITATION AGENCIES

925 L Street, Suite 200 • Sacramento, CA 95814 • TEL: (916) 446-0388 • www.CASAweb.org

January 10, 2022

To: Sierra Club Headquarters

From: Greg Kester, Director of Renewable Resource Programs, and multiple partners from across the United States

Subject: Response to "Sludge in the Garden: Toxic PFAS in Home Fertilizers Made from Sewage Sludge"

To Whom it May Concern:

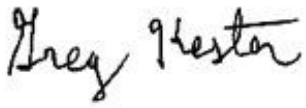
The public wastewater sector in the United States and across the globe appreciates the Sierra Club report highlighting a concerning public health issue of which we are all struggling to address. Specifically, per- and polyfluoroalkyl substances (PFAS) are synthetic compounds used in every-day products across the world for decades and are thus ubiquitous throughout our environment and bodies. While our scientific understanding of adverse effects is evolving, only recently have we become aware of the potential public health and environmental consequences of their continued use.

The public wastewater sector provides essential public health services by treating the wastewater generated in homes, commercial establishments, and industry. Such treatment of the water and solids allows its safe return to waters of the United States, for water recycling, and the production of carbon and nutrient rich biosolids which can be beneficially recycled to agricultural land as a soil amendment and fertilizer while simultaneously improving soil health and mitigating climate change, through carbon sequestration and minimizing the use of fossil fuel based inorganic fertilizer.

We agree that society needs to understand the consequences of using chemicals and the potential health and environmental issues they may pose. However, it is important to understand that wastewater systems receive these chemicals but neither produce nor use them. We are working hard to identify and eliminate those industrial discharges of PFAS which may be entering our systems and as a society we must reconsider our use of products utilizing them. It is of paramount importance that we identify the sources of PFAS and address them. We do take issue with some of the points made in the report and collectively hired toxicological experts to provide a critical review. It is attached and intended to help educate everyone on this issue.

The wastewater and biosolids community welcome the opportunity to collaborate with the Sierra Club on PFAS issues and to work to eliminate them from production and minimize their use. Please feel free to contact me with any questions or comments at gkester@casaweb.org or 916-844-5262 and I will be in touch within several weeks to determine a proactive path forward together as public health and environmental stewards and partners.

Sincerely,



Greg Kester
Director of Renewable Resource Programs

Collaborative Partners Include:

California Association of Sanitation Agencies
Irvine Ranch Water District
Orange County Sanitation District
San Francisco Public Utilities Commission
Union Sanitary District
Water Environment Federation
North East Biosolids and Residuals Association
North West Biosolids
Mid Atlantic Biosolids Association
National Association of Clean Water Agencies
Municipal Environmental Group (Wisconsin)
Oregon ACWA
Synagro Technologies
Denali Water
Merrell Brothers

GSI ENVIRONMENTAL

MEMORANDUM

TO: Greg Kester, CASA

FROM: Rob Scofield, GSI

RE: Comments on Sierra Club Report: Sludge in the Garden

GSI is pleased to submit our comments on the technical aspects of the Sierra Club Report, "Sludge in the Garden: Toxic PFAS in Home Fertilizers Made from Sewage Sludge". The Sierra Club report addresses a wide range of issues associated with the use of biosolids as a soil amendment. As discussed in greater detail below, the discussions of many of the issues are misleading and present a less favorable view of the safety of using biosolids than is supported by existing data and that credible scientific research supports.

Several of the more noteworthy issues with the Sierra Club report are identified below, along with our response to each issue.

Issue 1: The Sierra Club report (p. 2) acknowledges the value and importance of a circular economy and the role municipal biosolids can play in the circular economy.

Response: It is certainly true that responsibly applied biosolids can play an important role in a circular economy. For decades, the USEPA, states, and local governments have provided substantial guidance and regulation to advance the safe use of biosolids as a soil amendment. The USEPA succinctly summarized the benefits of the application of biosolids as a soil amendment in the following excerpt[1]:

> "Examples of beneficial use include application to agricultural land and reclamation sites (e.g., mining sites). When applied to land at the appropriate agronomic rate, biosolids provide several benefits including nutrient addition, improved soil structure, and water reuse. Land application of biosolids also have economic and waste management benefits (e.g., conservation of landfill space; reduced demand on non-renewable resources like phosphorus; and reduced demand for synthetic fertilizers)."

Biosolids can also be disposed of by incineration, landfilling, or surface disposal (monofilling). Such methods of disposing of biosolids carry substantial environmental disadvantages, however, and do not provide the benefit of net greenhouse gas emission reductions and the improvements to soil quality that are provided when biosolids are used as a soil amendment. Other disposal methods would also be inconsistent with the Zero Waste policy supported by the Sierra Club[2]

[1] USEPA, 2021. Basic Information About Biosolids. Accessed 10/13/2021 at https://www.epa.gov/biosolids/basic-information-about-biosolids

[2] Sierra Club Zero Waste Policy. 2019. The Sierra Club recognizes the following internationally peer-reviewed definition of Zero Waste: "Zero Waste is the conservation of all resources by means of responsible production, consumption, reuse, and recovery of products, packaging, and materials without burning, and with no discharges to land, water, or air that threaten the environment or human health." Accessed 10/17/2021 at

Issue 2: The Sierra Club report includes a statement that PFAS are "virtually unregulated" (p.2).

Response: This comment is internally inconsistent with the several references to federal and state regulations (e.g., pages 1,3,4, and 6) for PFAS chemicals included in the Sierra Club report. The regulation of PFAS is active and expanding, and has been so for several years at the state and local level as well as nationally and internationally. The USEPA PFAS Strategic Roadmap provides a good example of the kind of regulatory efforts planned for the future at the national level[3]. The Interstate Technology and Research Council (ITRC) Committee on PFAS has been monitoring and tracking the rapidly expanding regulation of PFAS and is a good first resource for anyone interested in an overview of the many regulations affecting this large group of chemicals[4].

Issue 3: Despite the many regulations and regulatory programs addressing PFAS, the Sierra Club report includes several calls for "urgent" action to reduce environmental releases and exposures to PFAS (e.g., pages 1, 2, 4, and 8).

Response: As mentioned above, and as discussed within the Sierra Club report, many local, state, federal, and international regulations and programs, such as the USEPA PFOA 2010/2015 Product Stewardship program[5], have reduced production, emissions, and exposures to many PFAS. Similarly, multiple public and private policies, practices (including halts in the production of specific PFAS) have contributed to the reduction in production and exposure to some PFAS. The effectiveness of results in reducing exposures is reflected in the reduction of the serum levels of PFOS and PFOA and other PFAS that have been documented by the National Health and Nutritional Examination Survey (NHANES). For the U.S. population, the geometric means of PFOS levels in human blood serum fell by approximately 84% between 1999 and 2015; and PFOA levels in human blood serum fell by approximately 70% over that same period[6]. Serum levels for PFHxS and PFDA are also falling over time, but serum levels for PFNA increased minimally from 1999-2000 to 2009-2010 and started to decline thereafter. (See Figure 5-3 below, which was copied from the 2021 ATSDR Toxicity Profile for Perfluoroalkyls).

https://www.sierraclub.org/sites/www.sierraclub.org/files/Sierra%20Club%20Zero%20Waste%20Policy%20December%202019.pdf

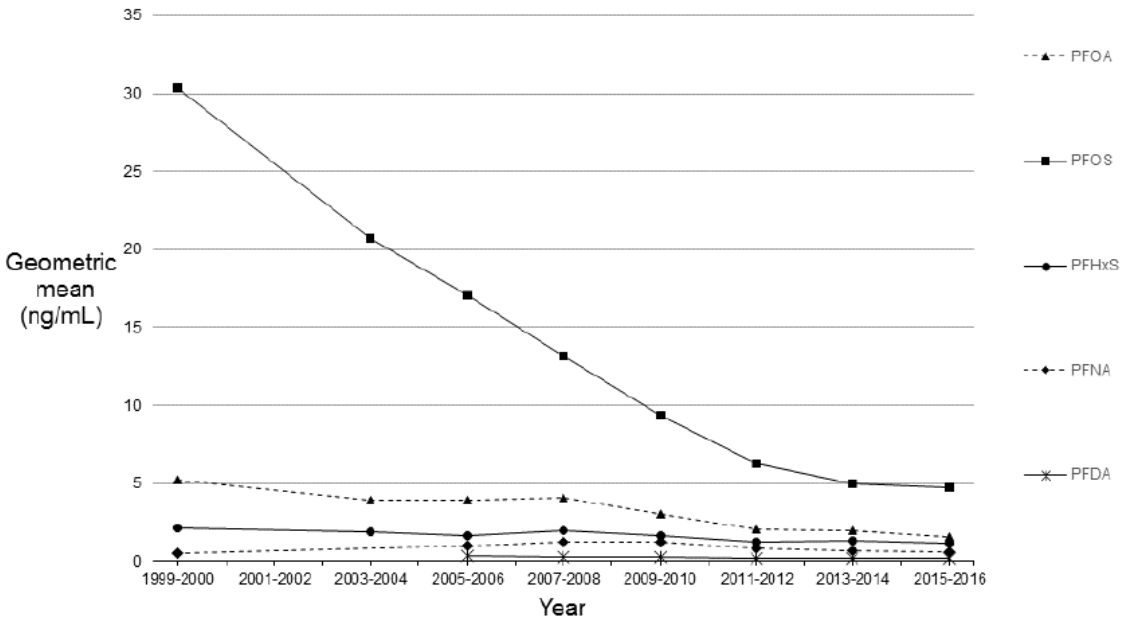
[3] https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024

[4] https://pfas-1.itrcweb.org/fact_sheets_page/PFAS_Fact_Sheet_Regulations_April2020.pdf

[5] https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program

[6] Agency for Toxic Substances and Disease Registry (ATSDR), 2021. Toxicological Profile for Perfluoroalkyls. U.S. Department of Health and Human Services. Released May.

Figure 5-3. Geometric Mean Concentrations of PFOA, PFOS, PFHxS, PFNA, and PFDA in U.S. Residents from 1999 to 2016



NHANES = National Health and Nutrition Examination Survey; PFDA = perfluorodecanoic acid; PFHxS = perfluorohexane sulfonic acid; PFNA = perfluorononanoic acid; PFOA = perfluorooctanoic acid; PFOS = perfluorooctane sulfonic acid

Source: CDC 2018

Issue 4: The Sierra Club report states that PFAS are "widely understood to pose a serious health risk to people, wildlife and the environment" (p.2); and that "[s]cientists and advocates have raised concerns that 'short-chain' PFAS are not safer than the PFOS and PFOA-type chemicals they are replacing" (p.6).

Response: Characterizing the toxicity of all PFAS as toxic to people and wildlife is not technically supportable. PFAS is a large and diverse group of chemicals, and it is factually incorrect to say that PFAS are "widely understood to pose a serious health risk to people, wildlife and the environment."

The Organization for Economic Cooperation and Development (OECD)[7] addressed a concern about the use of the term "PFAS" when the discussion only addressed or was based on a subset of the several thousand chemicals meeting the definition of PFAS, which include chemicals with a wide range of chemical and toxicological properties. PFAS do not all have the same plant uptake properties, the same soil migration properties, the same half-life in the environment, or the same toxicity, for example. To help prevent inaccurate and misleading representations, the OECD notes that the use of

[7] OECD (2021), *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance*, OECD Series on Risk Management, No. 61, OECD Publishing, Paris.

the term "PFAS" is overly broad and recommends the use of more precise and accurate subgroupings to avoid the "ambiguity and even factual error in the statements" that can be introduced by improper use of the term PFAS. The generalization that PFAS are "widely understood to pose a serious health risk to people, wildlife and the environment" is an example of the overly broad use of the term "PFAS" that leads to "ambiguity and "factual errors".

Some non-polymer PFAS share some toxicological target organs (e.g., liver, developmental endpoints, thyroid). The exposure levels that cause adverse effects vary significantly, however, and not all non-polymer PFAS have the same toxicological profile. For example, the USEPA's high-throughput Tox 21 *in vitro* dataset for various perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), and fluorotelomer alcohols (FTOHs) show that different PFAS interact with very different molecular targets[8]. More specifically, short-chain perfluoroalkyl acids (PFAAs) demonstrate relatively low activity, interacting with 0–2 nuclear receptors with weaker binding affinity, while long-chain PFAAs can interact with as many as 6–16 different nuclear receptors. Notably, available data do not support the idea that "short-chain" PFAS are as toxic to humans and wildlife as the long-chain, non-polymer PFAS they have replaced. Rather, the science shows that short-chain PFAS have different toxicological profiles and are less toxic.

The Sierra Club report cites Kwiatkowski et al. (2020)[9] to support the assertion that, "[s]cientists and advocates have raised concerns that these 'short-chain' PFAS chemicals are not safer than the PFOA and PFOS-type chemicals they are replacing." The concern expressed by Kwiatkowski et al (2020) appears to be based on generalizations about the toxicity, mobility, and persistence of PFAS. Regarding the toxicity of short-chain PFAS Kwiatowski et al (2020) expressed the opinion (p. 534) that, …" a growing body of evidence suggests they are associated with similar adverse effects as long-chain PFAS." In addition, Kwiatowski (2020) et al express the opinion (p. 534) that "[r]esearch has demonstrated that short-chain PFAS can be equally environmentally persistent and are even more difficult to remove from drinking water than longer-chain PFAS."

Later in their article, Kwiatkowski et al. 2020 (p. 535) do state, "[n]otably, effects observed with other (short-chain) PFAA may occur at larger administered doses compared to the long-chain PFAA." This statement acknowledges the different threshold response levels for different PFAS compounds and that short-chain PFAS are generally less toxic than long-chain PFAS.

As was emphasized by the OECD in their recent guidance on the definition of PFAs and the need for more consistent terminology for referring to chemicals in the PFAS

[8] The USEPA ToxCast Chemical Inventory List (EPAPFASINV) was reviewed to identify all PFAS that have been tested for bioactivity in ToxCast/Tox21 high-throughput assays (Accessed August 06, 2020, at https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINVIVO). As of September 2019, ToxCast data were available for 21 unique CASRNs, including several PFSAs (e.g., PFBS, PFHxS, and PFOS), PFCAs (e.g., PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFUnDA), and fluorotelomers (e.g., 8:2 and 6:2 fluorotelomer alcohol (FTOH)).

[9] Kwiatkowski, C.F. et al, 2020. Scientific Basis for Managing PFAS as a Chemical Class. Env. Sci. & Tech. Letters. 7(8): 532-43. June 30

universe, discussing the chemical and toxic properties of “PFAS" without referring to more specific subgroupings can lead to “ambiguity and even factual error in the statements.”[10] The suggestion by Kwiatowski et al (2020) that PFAS can be managed as a chemical class clashes with the OECD warning about the communication hazards that one can encounter when discussing chemical and toxic properties of “PFAS” as a chemical class.

Singh and Papanastasiou (2021)[11] published a response to the Kwiatkowski et al. (2020) publication that discussed the wide differences in toxicity, chemistry, and uses between the many subgroups of chemicals comprising PFAS. They discussed the fact that the differences in chemistry and toxicity between chemicals that make up the PFAS class are much greater than the differences in other chemicals that are regulated as chemical classes. While the Sierra Club report does include discussion of the chemistry and toxicity of individual PFAS, it introduces ambiguity and is misleading in places where it extrapolates chemical and toxic properties of individual PFAS to all PFAS. More specifically, the statement on page 2 of the Sierra Club report that PFAS are, “widely understood to pose a serious health risk to people, wildlife and the environment” is an example of the overgeneralization that the OECD warned against in which use of the term “PFAS” introduces miscommunication and is misleading. The statement generalizes the chemical and toxicological characteristics of some PFAS that do not apply to all PFAS.

Issue 5: The Sierra Club report expresses a concern that biosolids may introduce PFAS into the food supply, stating on page 2 that, “[a]vailable evidence suggests that PFAS and related chemicals in sewage sludge could jeopardize the safety of the commercial food supply and home gardens.”

Response: This assertion is repeated many times (e.g., pp. 1,2,4,8,9) in a few different ways in the Sierra Club report, but no specific evidence of food uptake from biosolids used under USEPA or other best practices is cited. There are many research studies of plant uptake from crops treated with biosolids/treated wastewater (e.g., Blaine et al., 2013; Blaine et al., 2014; Gottschall et al.,2017; Pepper et al, 2021)[12]. As briefly noted in only one location in the Sierra Club report, however, the available studies largely demonstrate the uptake of PFAS into edible portions of plants is predominantly associated with only the short-chain PFAAs. Short-chain PFAAs are less toxic than long-chain PFAAs such as PFOA and PFOS. Moreover, there is no evidence of the widespread occurrence of any PFAS in food grown or produced in areas associated with

[10] OECD (2021), *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance*, OECD Series on Risk Management, No. 61, OECD Publishing, Paris.
[11] Singh, R.R., and D.K. Papanastasiou. 2021. "Comment on “Scientific Basis for Managing PFAS as a Chemical Class”." *Env. Sci. & Tech. Letters* 8(2): 192-194
[12] Blaine et al, 2013, Uptake of Perfluoroalkyl Acids into Edible Crops via Land Applied Biosolids: Field and Greenhouse Studies. Env. Sci. &Tech., 47(24): 14062-69; Blaine et al. 2014. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. Env. Sci. & Tech. 48(14):7858-65; Gottschall, et al, 2017. Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field.

environmental PFAS contamination, as indicated by a study by the US Food and Drug Administration (FDA). In this study the FDA conducted two separate rounds of sampling for numerous PFAS in grocery store food items throughout the U.S. No PFAS were detected in any of the more than 100 fruit and vegetable items (raw or processed)[13]. The FDA program collected samples from specific geographic areas with known PFAS contamination at the request of states. FDA explains these findings as follows,

> "As needed, the FDA conducts evaluations to determine the potential dietary exposure to PFAS from these foods. Previous analyses by the FDA have shown that PFAS contamination in the environment where food is grown does not necessarily mean the food itself will contain detectable PFAS. This is because the amount of PFAS taken up by crops depends on many factors, including the specific type of PFAS and characteristics of the food."

These findings are consistent with dietary exposure studies of PFAS in grocery store foods in Canada, the United Kingdom, and Germany, all of which demonstrate that PFAS are rarely, if ever, detected in fruits and vegetables.[14]

Data on PFAS uptake in plants are available from laboratory studies and field studies. Academic research has demonstrated some crop uptake in artificial laboratory studies and where industrially-impacted biosolids or sludge from industrial operations have caused high levels in soils, but nothing significant in field studies with typical biosolids (Blaine et al., 2013; Blaine et al., 2014; Gottschall et al.,2017)[15]. Limited testing of crops grown in real-world soils amended with biosolids in New England and Arizona showed no significant impacts on the quality of farm products following typical, multi-year applications of typical, non-industrially-impacted biosolids. Specifically, "some tests on New England farms have found no PFAS in high moisture corn, corn silage, and haylage grown on fields applied with biosolids or septage for many years. However, ongoing investigations in Maine are finding some uptake of PFOS in grass, resulting in measurable levels in hay that, when fed to animals, may lead to elevated levels in milk and beef,"[16] but these concerns are only where PFOS soil levels are very high because of industrial contamination.

The Sierra Club report repeatedly offers the speculation that biosolids may jeopardize the safety of food, even though the available data support the point that the agricultural use of municipal biosolids with typical levels of PFAS compounds, not affected by strong industrial sources, does not pose a threat to the food supply. The concerns regarding the

---

Sci. Tot. Env. 574:1345–59; Pepper, I.et al. 2021, Incidence of PFAS in soil following long-term application of class B biosolids. Sci. Tot. Env. Vol 793, 1 November

[13] FDA, June 30, 2021. Constituent Update: https://www.fda.gov/food/cfsan-constituent-updates/fda-issues-update-recent-activities-pertaining-pfas-food

[14] ATSDR. 2021. Toxicological Profile for Perfluoroalkyls. Released May 2021. U.S. Department of Health and Human Services.

[15] See footnote 13 above for citations

[16] North East Biosolids and Residuals Association (NEBRA), 2021. PFAS and Biosolids and Septage on Northeast Farms. May 19, 2020, updated December 28, 2021. (Available at https://www.nebiosolids.org/resources#/pfas-biosolids/)

presence of PFAS in foods grown in areas where biosolids have been applied are not substantiated by studies showing the absence of PFAS in the general food supply, including foods grown in soils with known PFAS contamination. For example, in Maine, there are a few farm fields, out of scores of biosolids-using farms, contaminated with PFAS likely from industrial inputs to biosolids and land-applied industrial residuals. While soils, waters, and milk at two farms had relatively high PFOS levels, those levels never impacted the overall safety of the food supply, according to extensive testing by the state agriculture department and highly conservative risk assessment by the Maine Center for Disease Control (ME CDC). Testing at other Maine farms that received biosolids for many years found no reason for concern about the safety of farm products.

Issue 6: The Sierra Club states that food is the primary source of PFAS exposure, contradicting data demonstrating that plant uptake is not likely to account for PFAS in the diet.

Response: As mentioned above, the results of dietary exposure studies by the US FDA indicate there is no widespread occurrence of non-polymer PFAS in the general U.S. supply of farm produce. While some have suggested that food is a predominant source of PFAS to the general public, there is insufficient recent data to demonstrate whether this is, indeed, a predominant source. In addition, the PFAS that are most likely to be detected in food are the long-chain PFAAs such as PFOS and PFNA that may accumulate in meat or fish – not in produce. Additionally, due to their hydrophilic, hydrophobic, and oleophobic properties, some specific types of PFAS have been used in food contact materials to impart oil, grease, and water repellency[17] Therefore, bioaccumulation of long-chain PFAAs and migration of some PFAS from food contact materials into food products represent a much more likely source of PFAS into the general population's diet than plant uptake from soils where biosolids have been applied.

Issue 7: The Sierra Club report mentions three "high profile" incidents of PFAS contamination of agricultural land and products: Decatur, Alabama; Stoneridge Farm in Arundel, Maine; and the Tozier Farm in Fairfield, Maine. The implication is that these are examples of problems that can arise from the application of typical municipal biosolids to agricultural soil.

Response: The three incidents highlighted by the Sierra Club do not stem from applications of typical municipal biosolids. Rather, these incidents stemmed from releases of high concentration industrial wastes for a prolonged period to public wastewater treatment plants and, likely, and in at least one of the cases, the direct application of residuals (sludges) from paper processing plants to agricultural land. While there are lessons to be learned from these case studies, they are not representative of typical applications of municipal biosolids as soil amendments. They stand in contrast to hundreds of biosolids use programs and many more studies demonstrating the safety of the application of municipal biosolids to agricultural land. Part of the confusion

[17] Trier, X., Granby, K. and Christensen, J.H., 2011. Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. *Environmental Science and Pollution Research*, *18*(7), pp.1108-1120.

associated with descriptions of these cases stems from the use of the term “biosolids” to refer to both municipal biosolids and as well as residuals from industrial operations, such as coated-paper manufacturing plants. Technically, the term biosolids, as used in the U. S., does not apply to any material except for municipal wastewater solids (sludge) treated to the standards for beneficial recycling to land. It is important to differentiate municipal biosolids from industrial sludges when discussing the environmental effects of applying these very different materials to agricultural soils.

Decatur, Alabama

The issues surrounding the application of biosolids from the Decatur Utilities Dry Creek Wastewater Treatment Plant were studied by the USEPA and the ATSDR. The studies were initiated in response to a manufacturer’s report that large volumes of PFCAs had been discharged from its factory to the Decatur Utilities wastewater treatment plant and the realization that biosolids from the wastewater treatment plant had been applied to about 5000 acres of agricultural land from 1996 to 2008. The USEPA sampled biosolids and soil in fields to which biosolids had been applied and found that PFAS in the tested agricultural fields were higher than background levels. They followed up by sampling surface water, groundwater, drinking water, and soil in areas near the treated fields. Based on the detection of PFAS in many of the samples, USEPA asked ATSDR to perform an exposure investigation for people in the vicinity of the treated fields.

Certain PFAS were detected in private wells near the treated fields and in a nearby public water supply. The ATSDR (2013)[18] reported that other industrial sources of PFAS emissions in the area and not the agricultural fields that received the biosolids were expected to be the source of the PFAS detected in the public water supply.

As part of their exposure investigation, the ATSDR tested serum levels of PFAS in 155 residents including people who lived on or near soils that received biosolids or were exposed to drinking water containing PFAS. The ATSDR reported that the geometric mean concentrations of three PFAS (PFOA, PFOS, and PFHxS) were higher in people that used the public water supply than in a national survey (NHANES). No link between serum level of PFAS and individual exposures to PFAS through biosolids or consumption of local cattle, fish, and vegetables was discerned. The Sierra Club report does not report the ATSDR’s finding and instead presents an alarmist characterization of the studies by these two agencies. The wastewater sector shares the Sierra Club concern for atypical situations such as in Decatur and increasingly is utilizing its pretreatment authority to eliminate potential discharges of PFAS from industrial sources into their treatment systems.

It should be noted that the Sierra Club report refers to the potential contamination of food resulting from the biosolids applied to agricultural fields, but it does not refer to the testing completed by the FDA and USDA and the resulting conclusion that "…this testing supports USDA's finding that there is no reason to believe there are human health

[18] ATSDR. 2013. Health Consultation. Exposure Investigation Report. Perfluorochemical Serum Sampling in the Vicinity of Decatur, Alabama, Morgan, Lawrence, and Limestone Counties. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Division of Community Health Investigations, Atlanta, Georgia. April 1.

concerns with consuming the meat processed from cattle grazed on lands receiving these biosolids." Two milk samples were also collected. No PFOA or PFOS was found in one sample of milk collected from a single cow. A PFOS detection of 0.16 ppb was detected in another milk sample collected from a bulk tank. The detection in the bulk milk sample was characterized by the ATSDR as being "very low"[19]. (It was also lower than the Maine CDC's screening level of 0.21 ppb for milk.[20])

While the ATSDR Exposure Investigation does mention the possibility of exposure by locally produced food, it does not refer to any testing of PFAS in food. The statement in the Sierra Club report that people are exposed to PFAS via food is not supported by test data. The fact that only people drinking water from the local public water supply had elevated serum levels of specific PFAS suggests that food did not contribute a significant exposure, if any.

The Decatur case study describes an unfortunate incident of a large and prolonged industrial discharge of PFAS to a wastewater treatment plant and illustrates how such an event can adversely affect biosolids from a treatment plant. This incident is not representative of typical PFAS levels in biosolids applied to agricultural soil, however. Moreover, with our increasing awareness of PFAS we can mitigate industrial discharges to our treatment plants.

Stoneridge Farm, Arundel, Maine

While municipal biosolids were applied at the Stoneridge Farm, the farm was also licensed by the State to accept paper mill residuals;[21] and paper mill residuals applied at the farm may have come from a mill known to have manufactured PFAS coated paper products[22]. The Maine DEP investigated the site and their investigation suggest municipal biosolids are not the source of the anomalously high PFOS levels found at the property. One finding is that the high levels of PFOS are on the western side of the property and not on the eastern side of the property where municipal biosolids had been applied. PFAS levels on the eastern side of the farm are similar to levels seen on other farms where the same municipal biosolids had been applied. The fact that the ongoing problems at the farm are limited to PFOS and not to the larger range of PFAS typically found in municipal biosolids also suggests a source other than municipal biosolids. In addition, long-term biosolids application sites in the area have not seen the same impacts to soils, surface water, or groundwater. There were no known large industrial dischargers of PFAS to the wastewater treatment plant that was the source of the municipal biosolids applied to the Stoneridge Farm[23].

---

[19] Ibid

[20] Maine Department of Health and Human Services. Maine Center for Disease Control and Prevention. 2020. Derivation of PFOS soil screening levels for a soil-to-fodder-to-cow's milk agronomic pathway. September 16.

[21] https://www.reuters.com/article/us-usa-dairy-chemicals/the-curious-case-of-tainted-milk-from-a-maine-dairy-farm-idUSKCN1R01AJ

[22] North East Biosolids & Residuals Association (NEBRA). 2019. PFAS Contamination at Stoneridge Farm, Arundel. Maine, March 26. Available at https://www.nebiosolids.org/pfas-biosolids

[23] Ibid

The past and ongoing situation at the Stoneridge Farm suggests that rigorous monitoring of industrial residuals applications is warranted, but it does not support a concern that typical municipal biosolids applications pose a significant environmental or public health risk.

Tozier Farm, Fairfield, Maine

As noted in the Sierra Club report, the Tozier farm also received a great deal of press attention because of PFOS detected in milk from the dairy. The sample with detected PFOS was one of 20 milk samples collected by the State in 2020 and was the only sample with a level of PFAS above the laboratory reporting limit[24]. Testing of 26 milk samples from stores across Maine in 2019 found no detections of PFAS.[25] In the third round of state-wide testing of milk conducted in January 2021, one milk sample had a detectable level of PFOS; but the sample did not come from a farm with a history of spreading biosolids.

Investigation of the source of the PFOS detected at the Tozier farm was undertaken. One newspaper reported that "[t]he cause of the contamination is now clear: sludge from paper mills or wastewater treatment plans that was applied as fertilizer."[26] The detection of PFOS and other PFAS at and around the Tozier farm may be from the application of paper mill residuals as well as one particular municipal biosolids that had a large industrial input of PFAS over many years. This finding reinforces the need to identify industrial sources of PFAS and mitigate the discharge to wastewater treatment plants, utilizing pretreatment protocols. Given the widespread application of municipal biosolids in the region, a much higher frequency of detection of PFAS in locally produced milk would be expected if even typical municipal biosolids were a significant source of PFAS in milk.

The sampling and investigation in Maine point to milk contamination as a rare event attributable to contamination likely from land application of certain paper mill wastes and one municipal biosolids affected by strong industrial input, rather than the result of the use of typical municipal biosolids.

Issue 8: The Sierra Club report includes results from the testing of several commercially available soil amendments using USEPA Method 537.1 "modified", total fluorine, and total inorganic fluorine. The report also highlights the point that eight of the nine products tested exceeded PFAS screening levels set by the State of Maine.

Response: While the Sierra Club report notes that the levels of PFOA and PFOS measured in eight of the nine tested soil amendments exceeded biosolids and soil screening levels adopted by the State of Maine, it failed to report that the PFOS and PFOA levels in all of the tested products were below the PFOS screening level adopted by the State of Michigan. The screening levels set by the State of Maine are based on

[24] News Center Maine. July 24, 2001. Available at https://www.newscentermaine.com/article/news/health/high-pfos-levels-detected-on-maine-farm-maine-milk-supply-deemed-safe/97-6612bb54-039f-4c9b-a6cc-45da4b0df520

[25] Maine Department of Agriculture, Conservation, and Forestry (DACF). Per- and Polyfluoroalkyl Substances (PFAS). Available at: https://www.maine.gov/dacf/ag/pfas/index.shtml Accessed October 12, 2021.

[26] Press Herald July 18, 2021. Trail of 'forever chemicals' leads to Maine paper mills

very conservative assumptions and the use of a transport model that does not provide valid estimates of the migration of PFAS. More specifically, the mathematical models used to predict the potential migration of PFAS in soil (i.e., vadose zone models) are intended for organic chemicals (e.g., pesticides) that have very different chemical structures and properties compared with PFOA and PFOS[27]. Maine's modeling was based on leakage of contaminants from a point source, like an underground storage tank, and not appropriate for modeling PFAS dispersion from biosolids land application.

The Sierra Club report suggests that finding concentrations of PFAS above screening levels should be interpreted as indicating an unsafe situation or product. That is an incorrect interpretation of a screening level. Rather, concentrations lower than screening levels are interpreted as posing no or negligible health risk. Concentrations that exceed a screening level warrant additional, usually more site-specific evaluation to better verify and quantify potential exposures and health risks.

The Maine screening levels are set very low and are intended to trigger site-specific evaluations that may require the use of chemical migration models and site-specific soil properties and site-specific exposure assumptions in place of the conservative default assumptions used in the derivation of the screening levels. The assumptions used in the derivation of screening levels are intentionally selected to assure that concentrations below the screening level would not pose a health risk, but the detection of levels above the screening levels does not provide a basis for concluding a soil or a soil amendment poses a health risk.

As noted above, the Sierra Club report states that PFOA or PFOS levels in eight of the nine tested products exceeded screening levels adopted by the Maine Department of Environmental Protection. Page 1 of their report includes the statement that "[t]he chemicals were measured at levels that would not be acceptable for the state's agricultural soils". That statement is an inaccurate characterization of the regulatory guidance for action to be taken when finding PFOA or PFOS levels above the State's screening levels. The detection of chemicals above the Maine screening levels triggers the need for performing loading rate calculations to determine if soil concentrations would be within concentration limits acceptable to the State[28]. Finding concentrations above the screening levels does not mean that the products would not be acceptable for the State's agricultural soil as was stated in the Sierra Club report.

In the discussion of the total fluorine results, the Sierra Club report refers to "mystery compounds" and notes that these are likely "fluorine-based polymers". Many PFAS polymers are not water-soluble and not mobile in the environment. The implication that the measurement of total fluorine reflects PFAS compounds ignores the fact that some pharmaceuticals, drugs, pesticides, toothpastes, and fragrances contain fluorine, and fluorine is naturally occurring in many soils and waters and is intentionally added to drinking water all over the United States. The Sierra Club testing should have included an analysis for these compounds to determine their contribution to the total fluorine

[27] Anderson, R.H. 2021. The case for direct measures of soil-to-groundwater contaminant mass discharge at AFFF-impacted sites." *Env. Sci. & Tech.* 55(10):6580-6583.

[28] Maine Department of Environmental Protection. 2019. Guidance for Facility Owners and Operators. Reviewing PFAS Data and Requesting Approval to Resume Distribution of Residuals for Agronomic Utilization. April 29.

measurements or at least should have acknowledged that total fluorine measurements would reflect many more chemicals than PFAS.

Issue 9: In support of their claim that PFAS chemicals are present in the biosolids products they tested at "concerning" levels (p.1), the Sierra Club report includes a comparison of concentrations detected in the soil amendments they tested to drinking water health advisory levels.

Response: This comparison of the two values is not a scientifically valid evaluation, and it is misleading to people who are not familiar with the basis of the drinking water health advisories. The comparison of health advisories to concentrations of chemicals in biosolids is misguided because health advisories are calculated to be protective for completely different exposure scenarios than apply to biosolids.

On page 2 of the report, concentrations of total PFAS measured in commercial compost are reported to range from 38 to 233 ppb. The Sierra Club report notes "for reference" that these concentrations in biosolids are "thousands of times higher than the amounts that are regulated in drinking water." This comparison presumably alludes to values such as 0.070 µg/L (ppb) – the current USEPA chronic drinking water health advisory for the sum of PFOA and PFOS. The report fails to note that it is quite common for health-based screening levels to vary by many orders of magnitude when compared across exposure media in this manner. For example, USEPA's current Rule 503 (§503.13, Table 1) risk based concentration limits for arsenic and lead in biosolids are 41 mg/kg (or 41,000 ppb) and 300 mg/kg (or 300,000 ppb)[29]. For reference, USEPA's risk-based regional screening levels (RSL) for arsenic and lead in residential tap water are 0.052 µg/L (ppb) and 15 µg/L (ppb), respectively[30]. Therefore, the concentration of arsenic in biosolids could be almost 800,000 times greater than the tap water RSL and still be well below the recommended risk-based limit for arsenic in biosolids[31]. Similarly, the concentration of lead in biosolids could be 20,000 times greater than the tap water RSL and still be well below the biosolids, risk-based limit for lead.

Issue 10: The Sierra Club reports results from Total Oxidizable Precursor (TOP) analyses and claims that these results reflect future levels of PFOA and PFOS in an analyzed sample.

Response: The Sierra Club report presents factually incorrect and misleading conclusions regarding the interpretation of results from the TOP Assay. The TOP Assay is used to determine the presence and estimated concentration of PFAS capable of degrading into PFCAs. In the TOP analysis, samples are treated with a highly basic persulfate solution and heated at a high temperature for several hours to oxidize any precursor compounds present in the sample. Importantly, the oxidation conditions do not represent real-world conditions. Therefore, the TOP assay does not predict the rate of transformation nor the types of transformations possible in the natural environment. At

[29] https://www.govinfo.gov/content/pkg/CFR-2018-title40-vol32/xml/CFR-2018-title40-vol32-part503.xml
[30] The ratio of biosolids ceiling level: tapwater RSL for arsenic is 41,000 / 0.052 = 788,462
[31] The ratio of biosolids ceiling level: tapwater RSL for lead is 300,000 / 15 = 20,000

best, the data generated from the TOP assay can be used as a screen that can guide the evaluation and significance of precursor PFAS.

Issue 12: The Sierra Club report includes a claim that USEPA sets standards for pathogens and some inorganic chemicals in biosolids but does not set limits for other chemicals (p.2).

Response: That statement is misleading because it ignores the substantial previous and ongoing efforts at USEPA to evaluate organic and other chemicals in biosolids to determine if additional numeric limits are needed. USEPA performed a large-scale risk assessment for the land application of biosolids before issuing the Part 503 rules in 1993.[32] That risk assessment began with an evaluation of over 400 chemicals of potential concern in biosolids. The initial phase of the risk assessment included an evaluation of the frequency with which each chemical was detected in biosolids, the concentrations of detected chemicals, and the toxicity of the detected chemicals. USEPA used this initial screening process to reduce the list of chemicals to a list of 24 chemicals that were subjected to a formal risk assessment. Scores of scientists inside and outside of the agency worked on and reviewed the risk assessment, which included an evaluation of 14 potential exposure pathways from land application of biosolids to humans and the environment. These exposure pathways included evaluations of small children eating biosolids every day for years, people eating only food grown from gardens fertilized with biosolids and cattle grazing or eating feed from pastures and farms using biosolids. Based on this evaluation, USEPA identified 10 metals and metalloids for which health-based numeric standards were set. Recognizing that new chemicals are being identified in biosolids and new information is being developed on the fate and transport and toxicity of chemicals, the USEPA is required under the Clean Water Act to undertake biennial reviews of the chemicals detected in biosolids and to consider additional regulations.

A focused review on the need for regulation of dioxins in biosolids was completed in the early 2000s, as was an evaluation of ten chemicals identified in USEPA's Targeted National Sewage Sludge Survey[33]. USEPA and others have examined many chemicals, including trace organic compounds, and these evaluations have supported a determination that land application of biosolids does not present unacceptable health risks warranting additional monitoring or land application restrictions under Part 503. USEPA is currently updating risk assessment screening models for chemicals of potential concern using the most current analytical and risk assessment tools. Once the model passes peer review – expected in 2022, modeling will include screening-level risk assessment for PFAS in biosolids[34].

While the USEPA has not seen the need to set numeric limits in biosolids for chemicals other than ten metals and PCBs, the identification of chemicals requiring numeric limits

[32] US Environmental Protection Agency (USEPA), 1994. A Plain English Guide to the EPA Part 503 Biosolids Rule. September. EPA/832/R-93-003.
[33] USEPA 2015. 2011 Biosolids Biennial Review. Office of Water. EPA 822-F-15-001. March.
[34] USEPA 2020. https://www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

is based on an extensive and ongoing evaluation of additional chemicals identified or suspected of being present in biosolids. Thus, it is incorrect for Sierra Club to say that other chemicals have been ignored.

Issue 13: The Sierra Club report cites concerns raised by the USEPA Inspector General (IG) in 2018 about gaps in the USEPA oversight of biosolids and gaps in the tools and data available to evaluate safety.

Response: The Sierra Club included alarming-sounding excerpts from the IG report, creating a narrative that the IG questioned the safety of biosolids. However, the Sierra Club did not report the counterbalancing statements that were also provided in the same IG document. Neither did they report contradictory conclusions on the topic from the USEPA Office of Water, the National Research Council (NRC), and the US Department of Agriculture (USDA).

Even though the IG report included a critically-important statement from the USEPA Office of Water that that "the occurrence of pollutants in biosolids does not necessarily mean that those pollutants pose a risk to public health and the environment", the Sierra Club report failed to include that excerpt in their summary of the IG report. The IG report also included the statement from the NRC, based on their evaluation of the use of biosolids, that, "[t]here is no documented scientific evidence that the [Biosolids Rule] has failed to protect public health. However, additional scientific work is needed to reduce persistent uncertainty about the potential for adverse human health effects from exposure to biosolids"[35] The Sierra Club report did not include that statement from the NRC either.

In response to concerns about the IG report expressed by the USEPA Office of Water and from practitioners in the field of biosolids regarding the inaccuracies in the IG report, a long-standing research committee convened by the US Department of Agriculture (USDA) was asked to review the concerns raised by the IG that the USEPA was unable to assess the impact of unregulated pollutants in land-applied biosolids on human health and the environment. This research group's report was co-authored by the National Institute of Food and Agriculture (NIFA) Research Committee W4170: Beneficial Use of Residuals to Improve Soil Health and Protect Public and Ecosystem Health. This research group has provided scientific support to the regulatory community responsible for the use of biosolids and other residuals for more than 45 years[36].

As stated in their report, the objective of the evaluation undertaken by the W4170 Committee was to provide a science-based review of claims in the IG's report about chemicals of concern. This review examined both: (i) chemicals of concern that are federally regulated by their placement on the National Institute of Occupational Health (NIOSH) hazardous drugs list, Priority Pollutant list, and/or the RCRA P-list (acutely toxic) and U-list (toxic); and (ii) the remaining "unlisted" chemicals that may be present in biosolids.

[35] National Research Council (NRC) 2002. Biosolids Applied to Land: Advancing Standards and Practices. Committee on Toxicants and Pathogens in Biosolids Applied to Land. National Academy Press.
[36] US Department of Agriculture (USDA). 2020. W4170 Multistate Research Committee. Response to USEPA OIG Report No. 19-P-002. June.

One of the key criticisms the Committee had of the IG evaluation was that it did not consider the concentration of chemicals in biosolids. After performing their own evaluation, the W4170 committee concluded that:

> "Overall, sufficient data and research are available to conclude that current biosolids regulations are protective of human health and the environment. Of course, as with any regulation intended to protect public health and the environment, they must always be dynamic and evolve with updated science. That fact does not imply that they are not protective while research is ongoing."

The Sierra Club report included alarmist excerpts from the IG report, and in so doing, implied that the IG reported that the public is not protected from health risks potentially associated with the use of biosolids as a soil amendment. Their report failed to report the contradictory statements that were also included in the IG report as well as the contradictory findings by the committees of independent scientists working on behalf of the NRC and the USDA. In short, the Sierra Club report presented a misleading characterization of the IG report.

Issue 14: The Sierra Club report claims that new technologies for the treatment of PFAS in wastewater are “desperately needed”. (p.11)

Response: There are currently millions of research dollars being spent in the U.S. on cost-effective and viable PFAS remediation technologies. The USEPA actively tracks treatment options for water in the “Drinking Water Treatability Database”[37] and provides current information on treatment options for PFOA, for example, that includes information on options such as adsorptive media, chemical treatment, granular activated carbon, ion exchange, membrane filtration, and membrane separation.[38] In 2020, the USEPA established the PFAS Innovative Treatment Team (PITT), which was a team focused full-time for six months on the disposal and/or destruction of PFAS-contaminated media and waste. This group published a series of research briefs that identified four promising destruction technologies warranting further evaluation.[39] Another example of ongoing treatment technology research can also be reviewed via the Department of Defense Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) research programs, which has spent many millions of dollars on treatment technology grants since 2011[40].

The discussion of treatment technology research presented in the Sierra Club report does not acknowledge the substantial effort being applied to the topic. This omission leaves the misleading impression that this topic is not the subject of substantial research and development.

---

[37] https://tdb.epa.gov/tdb/home/
[38] https://tdb.epa.gov/tdb/contaminant?id=10520
[39] https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt
[40] https://map.serdp-estcp.org/FeatHeured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/pfas_efforts.pdf

Science of the Total Environment 864 (2023) 161083

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Microplastics in biosolids: A review of ecological implications and methods for identification, enumeration, and characterization

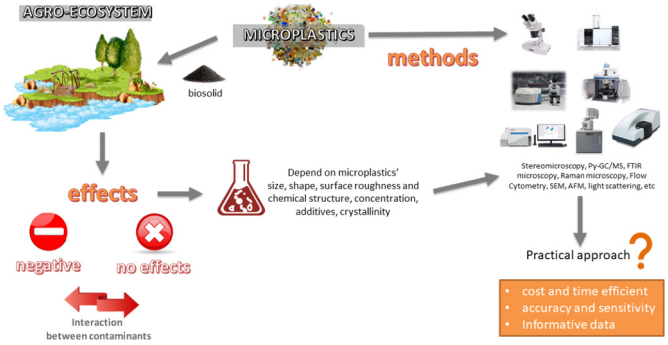
Anggelia Essi Christian, Ingo Köper *

Flinders Institute for Nanoscale Science and Technology, College of Science and Engineering, Flinders University, Bedford Park, SA 5042, Australia

HIGHLIGHTS

- Conflicting evidence of microplastics ecological impacts has been reported.
- Microplastics' characteristics, amount, and exposure time influence the effects.
- Each analytical technique has limitations and standardized method is required.
- Methods scaling approach is suggested for practical purposes.
- Continuous research is critical to monitor microplastics occurrence and impacts.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Qilin Wang

Keywords:
Microplastics
Soil
Wastewater treatment plant
Sludge
Biosolid
Analytical techniques

ABSTRACT

Biosolids, or treated sludge, are by-products of the wastewater treatment processes and are commonly used in agricultural applications to enrich soil nutrients. However, it contains microplastics, plastic particles with a diameter below 1 mm. Microplastics exist and accumulate in the environment, which can have major impacts on the ecosystem. Despite their abundance in the environment, there are to date no standardized methods for their enumeration and characterization.

A literature review was conducted focusing on the occurrence of microplastics at wastewater treatment plants, particularly in the solid waste stream, and their influence on the soil ecosystem where biosolids is applied. We found a conflicting evidence to which extent microplastics negatively impact the ecosystem. Some reported either a direct negative impact of microplastics or because of microplastic interaction with other soil contaminants. Meanwhile, other studies showed no effect or at certain amount of microplastics on the ecosystem.

We also found that microplastics size, shape, type, concentration, and exposure time play a critical role in their ecological impacts. However, currently, there is no unified approach for microplastics identification and characterization in solid waste resulting in a various and incomparable data. Therefore, utilizing standardized methods for microplastics analysis must be considered as the initial step to better understand the impact of microplastics onto the environment. We suggest a method's scaling comparison as a practical approach to select and develop techniques based on cost, time, data obtained, accuracy, and sensitivity criteria. Further research into the ecotoxicity of microplastics and continuous monitoring of biosolid applications are also necessary.

* Corresponding author.
E-mail address: ingo.koeper@flinders.edu.au (I. Köper).

http://dx.doi.org/10.1016/j.scitotenv.2022.161083
Received 14 September 2022; Received in revised form 15 December 2022; Accepted 16 December 2022
Available online 21 December 2022

Contents

1. Introduction

Microplastics (we will use the term microplastics when we talk about microplastic particles), are commonly defined as plastic particles with a size between 1 μm and 5 mm; they have become an emerging environmental issue over the past decade (Hartmann et al., 2019; Hidalgo-Ruz et al., 2012; Thompson, 2015).

Microplastics are considered an environmental contaminant because they can harm organisms in the ecosystems, and eventually disrupt the food chain (de Sá et al., 2018; Lambert et al., 2017; Ng et al., 2018; Oehlmann et al., 2009). They can enter the ecosystem through various pathways, one of them is through biosolid application for agricultural purposes. Although biosolid are rich in nutrients and minerals (Hopewell et al., 2020; Toffey and Brown, 2020), they are known as a sink for plastic particles from household and industrial activities (Ball H et al., 2019). Current wastewater treatments aim to remove plastic particles from the wastewater flow, but most of these particles (around 99 %) are transferred and retained in the sewage sludge, which then through some treatments, such as drying and lime stabilization, is converted into biosolids (Ball H et al., 2019; Bayo et al., 2016; Murphy et al., 2016; Okoffo et al., 2019).

Once biosolids are applied to the soil, the contained plastic particles tend to persist in the soil ecosystem (Alexander et al., 2016; Bayo et al., 2016; Bläsing and Amelung, 2018; Bretas Alvim et al., 2020; He et al., 2018; Toussaint et al., 2019). Consequently, the amount of microplastics in the soil increases over time. For example, Corradini et al. investigated agricultural fields in Chile that underwent sludge application for a period of ten years and observed an 800 % increase in the microplastics load in the soil (Corradini et al., 2019; Rolsky et al., 2020).

The amount of microplastics reported in sludge varies between countries and regions. For example, Mahon et al. found 4196 to 15,385 particles kg^{-1} (dry weight) in sludge from seven different WWTPs in Ireland (Mahon et al., 2016), whereas Li et al. (2018) reported 1600 to 56,400 particles kg^{-1} of dry sludge in 28 different wastewater treatments plants across 11 Chinese provinces.

There are several studies on microplastics analysis in the solid waste stream at the wastewater treatment plant, yet no standardized methods have been established. It leads to a highly variable in microplastics data. There are some challenges in developing the techniques for analyzing and tracing microplastics at the wastewater treatment plant. This including the ununified definition and classification of microplastics (Hartmann et al., 2019), the various possible pathways and sources of microplastics entering the wastewater treatment plant and into the ecosystem (Gatidou et al., 2019; Hurley and Nizzetto, 2018; Ziajahromi et al., 2017), and the numerous yet discrete studies reported on the implications of microplastics on the agroecosystems linked to solid waste i.e., sludge and biosolids (Boots et al., 2019; Bosker et al., 2019; Cartwright et al., 2000; de Souza Machado et al., 2019; de Souza Machado et al., 2018; Hamilton et al., 2020; Jacques and Prosser, 2021). As microplastics are mostly invisible by the naked eye, physical and chemical analysis is required in combination with some analytical instruments in order for accurate characterization and enumeration.

This article reviews the emerging issue of microplastics in sludge as a contaminant for land or agricultural applications. This includes the implications of plastic particles on the agroecosystem, the available analytical techniques and guidelines of plastics identification, enumeration, and characterization, as well as recommended approaches in selecting and developing the methods of analysis. This paper aims to show how the characteristics of plastic particles such as size, shape, and type are critical to discern their impacts on the ecosystem. For enumeration, a consistent measure, for example number of microplastics per unit mass is also important. Accurate and validated methods used for microplastics identification and enumeration are essential, yet largely missing.

2. Definition of microplastics

There is ambiguity in the definition of microplastics. When the term was introduced in 2004, Thompson et al. reported plastics fragments they found in the ocean around the UK of about 20 μm in size (Thompson et al., 2004). Since then, there is an increased interest to study microplastics in the environment, and the need for a standardized definition and category for plastic debris has been identified. In 2008, the first International Microplastics Workshop in Washington was hosted by the National Oceanic and Atmospheric Administration; it defined microplastics as plastic particles with a size <5 mm (Arthur et al., 2009; Thompson, 2015). The European Commission adopted the same definition in 2011 in their guideline for Monitoring of Marine Litter in European Sea (European Commission, 2011). In 2017, Ivelva et al., introduced a new submicrometer category for any plastic particle with a size between 100 nm and 1 μm (Ivleva et al., 2017).

In 2019, Nana B. Hartmann et al. recommended a framework for the definition and classification of plastic debris (Hartmann et al., 2019). They suggested four categories: (i) nanoplastics (1 to <1000 nm), with subdivisions for nanoplastics (1 to <100 nm) and submicron-plastics

(100 to <1000 nm); (ii) microplastics (1 to <1000 μm); (iii) mesoplastics (1 to 10 mm) and (iv) macroplastics (1 cm and larger). However, these categories leave plastic fragments sized 11 mm to 999 mm with no group.

In 2020, the International Organization for Standardization released ISO/TR 21960:2020, which defines any solid plastic particles insoluble in water with any dimensions ranging from 1 μm to 1000 μm (=1 mm) as microplastics, from 1 mm to 5 mm as large microplastics, and above 5 mm as macroplastics (The International Organization for Standardization, 2020).

In this paper, and for comparison of literature data, we will adopt the definition as shown in Fig. 1, which classifies plastic particles in six size-depending subcategories.

3. Pathways of microplastics into the agroecosystem

There are various pathways how microplastics enter the wastewater treatment plant and a detailed knowledge can inform effective removal treatments and control strategies (Arthur et al., 2009; European Commission, 2011; Hartmann et al., 2019; He et al., 2019; Hidalgo-Ruz et al., 2012). Microplastics reach the wastewater from a wide range of sources including households (e.g. laundry washing, toilet, showering or bathing) and industries such as textile, food and beverage, and cosmetic and personal care (Fig. 2) (Environment Protection Authority, 2020).

During the treatment processes in the wastewater treatment plant, sewage sludges are generated in sedimentation and settling tanks after the aeration or floatation process. Ninety-nine percent of the plastic material in the wastewater is retained in the sludge (Australian and New Zealand Biosolids Partnership, 2020; Kerstin and Norén, 2014; Liu et al., 2019; Lusher et al., 2017). The sewage sludges undergo additional treatments such as digestion, lime stabilization, composting, and heat treatment with the aim of pathogen inactivation, dewatering, nutrient management, and stabilization (Australian and New Zealand Biosolids Partnership, 2020).

The removal efficacy of microplastics during wastewater treatments depends on the treatment techniques used, and there is currently no approach that can remove all plastic materials in sewage sludge (Australian and New Zealand Biosolids Partnership, 2020; Lusher et al., 2019; Rolsky et al., 2020). For example, a study by Mahon et al. analysed sludge that had been treated with different processes i.e. thermal drying, anaerobic digestion, and lime stabilization and found 4196 to 15,385 microplastics particles per kg (d.w.) of sludge (Mahon et al., 2016). Despite the plastic content, the resulting biosolids are typically used for applications such as landfilling, landscaping, composting, or disposal through incineration (Fig. 3). Such applications transfer the microplastics into the environment; the incineration process can also produce harmful contaminants such as dioxins and polychlorinated biphenyls emitted to the air (Lambert et al., 2017).

Biosolids from wastewater treatment plants are not the only source for microplastics entering the environment, especially the land ecosystem. Agricultural practices, such as plastic mulching, compost from bio-wastes, irrigation pipe, and cleaned sewage or groundwater for irrigation, are other sources of plastic debris in the soils. It is also likely that external inputs from street littering, road and urban areas runoff, flooding in the riparian zone, and wind which could blow out the debris from other surface areas, are potential suppliers of microplastics (Bläsing and Amelung, 2018; Hopewell et al., 2020; Hurley and Nizzetto, 2018). Biosolids for landfill applications are also a source of microplastics in the ocean due to leaching and transport through surface run-off (He et al., 2019).

4. Impact of microplastics on the ecosystem

There is an emerging debate about the impact of microplastics on the ecosystems and human health. This includes the role of microplastics in biosolids, either as plastic material, or as a transporter of other contaminants. Concentration, size, and shape of microplastics as well as exposure time are factors that influence potentially negative effects on the ecosystem. In terms of type, a pristine, weathered, and commercial microplastics shown different impact on the ecosystem (Qi et al., 2020; Renner et al., 2018). Table 1 summaries recent studies about the impact of microplastics and it seems that there is contradicting evidence. Some studies found direct adverse effect of microplastics, while other studies reported no effects. Additionally, there are studies shown the effect of microplastics only at certain concentration. Variation in parameters used in the reported studies making it incomparable and difficult to isolate the impact of the microplastics alone.

Microplastics can significantly affect the structure of soil and microorganisms within the soil (Ng et al., 2018). One example showed that after intentionally exposing earthworms with polystyrene microplastics, their growth slowed and their mortality increased (Cao et al., 2017). A different study exposed soil to different types of microplastics, and a decrease in soil bulk density and microbial activity was observed. Changes in the water retention capacity, soil structure and function were observed as well. Especially the internal soil structure in terms of macroaggregates was significantly modified (Boots et al., 2019; de Souza Machado et al., 2018).

Similar results were obtained by Zhu et al. in their study using springtails (Collembola, *Folsomia candida*), organism that contribute to the fragmentation of organic materials and the control of soil microbial communities. After exposing Collembola to PVC microplastics, changes in the collembolan gut structure were observed as well as an inhibition in organism growth and reproduction (Zhu et al., 2018).

The effect of microplastics on plants was reported by Boots et al. (2019). They showed that microplastics (HDPE, PLA, and synthetic fibres) decreased the number of germinated grass seeds and reduced the shoot height (*Lolium perenne*). de Souza Machado et al. (2019) reported a significant change in plant biomass, tissue elemental composition, and root traits of *Allium fistulosum* (spring onion) after they were exposed to six different microplastics types (PA, HDPE, PES, PET, PP, and PS). However, the degree of impacts was varied depending on the type of plastic. Degraded plastic mulch (LDPE and starch-based) also showed negative effects on vegetative and reproductive growth of wheat (*Triticum aestivum*) (Qi et al., 2018).

Not all studies of microplastics have shown a negative impact on organisms. Kolkalj et al. reported that microplastics did not affect the feeding behavior and energy reserve of terrestrial isopods, *Porcellio scaber*, which play an important role in breaking down organic materials. After intentionally exposing the isopods for 14 days with derived

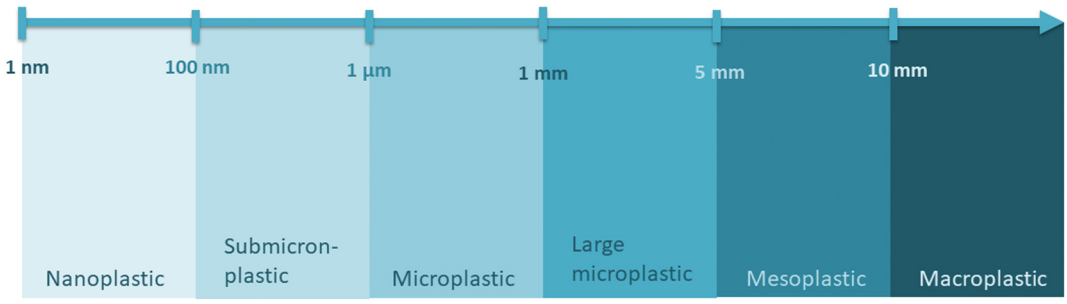


Fig. 1. Suggested definition and classification of plastic particles adopted in this manuscript.

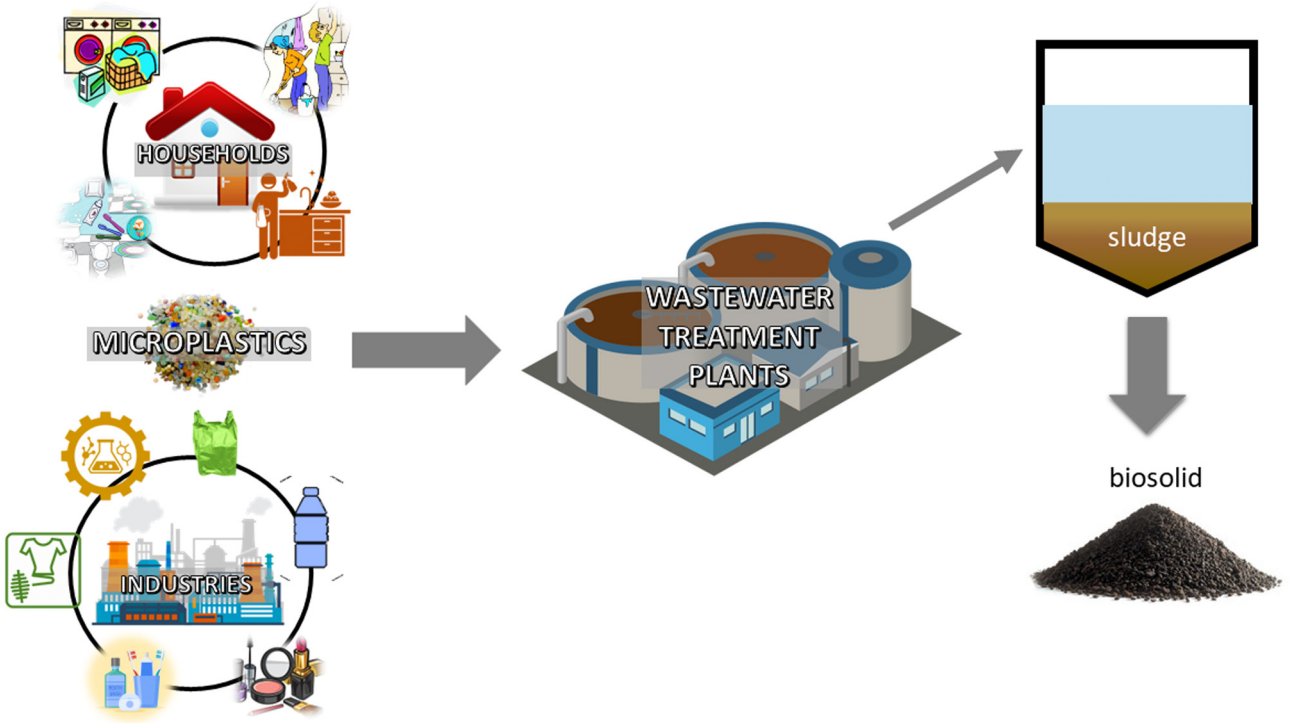


Fig. 2. Illustration on the pathways of microplastics from sources to biosolids.

microplastics from plastic bags and facial cleanser, the isopods did not show any significant change in body mass, food ingestion rate, food assimilation rate, defecation rate, mortality, and energy reserve (Jemec Kokalj et al., 2018).

A similar result was seen by Rodriguez et al. in their study of microplastics effects on earthworms, *Eisenia Andrei*. After exposing the earthworms for 28 days to polyethylene microplastics, no significant changes were seen in the earthworms' survival, number of juveniles, and final weight of adult earthworms (Rodriguez-Seijo et al., 2017).

Another study investigating plants and soil biota also reported no significant effect of HDPE, PET, and PVC microplastics on wheat seedling growth and biomass production, as well as on earthworm mortality, growth, or avoidance behavior after nine months. Microplastics were intentionally added into compost-like output and no clear trends on microbial community growth and diversity were observed (Judy et al., 2019).

Most studies reporting negative effects of microplastics on invertebrates used concentrations well above any realistic values that might result from the application of biosolid to land or soil (Hopewell et al., 2020).

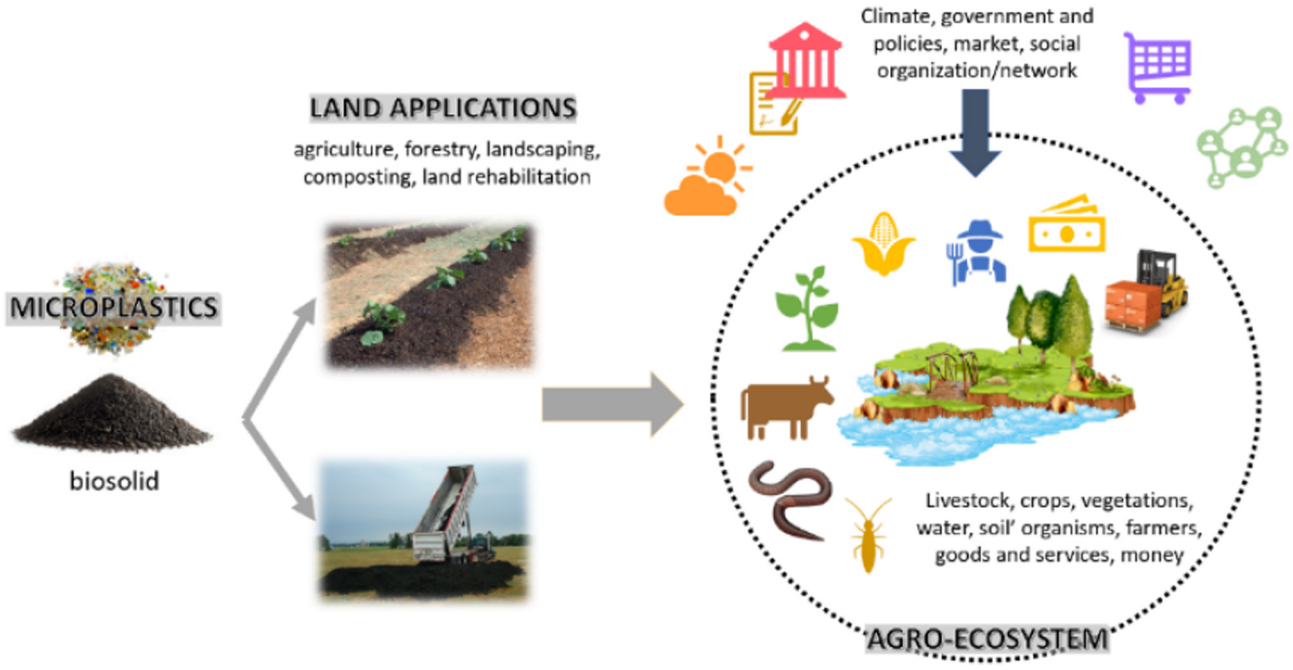


Fig. 3. Illustration on microplastics pathways from biosolids to agroecosystem.

Table 1
Various effects of different type, size, concentration, and exposure time of microplastics on organisms and ecosystem.

Effect	Affected organisms or ecosystem	Type of plastics[b]	Size	Amount	Exposure duration	Impacts	Reference
Negative	Earthworms	Polystyrene[a]	58 μm	1–2 %	30 days	Growth slowed, mortality increased	(Cao et al., 2017)
	Soil	Polyacrylic fibres[c]	1540–6300 μm	Up to 2 %	35 days	Microbial activity decreased, Water holding capacity, structure, and function changed	(de Souza Machado et al., 2018)
		Polyamide beads[a]	>10 μm				
		Polyester fibres[c]	>10 μm				
		Polyethylene fragments[a]	160–1200 μm				
	Soil	HDPE[a]	102.6 μm	0.1 %	30 days	pH, water-stable aggregate profile, macro-aggregates altered significantly	(Boots et al., 2019)
		PLA[a]	65.6 μm	0.1 %			
		Synthetic fibres[a]	<2 mm; 2–7 mm; >7 mm	0.0001 %			
	Lolium perenne	HDPE[a]	102.6 μm	0.1 %	30 days	Germinated grass seeds decreased; the shoot height reduced	(Boots et al., 2019)
		PLA[a]	65.6 μm	0.1 %			
		Synthetic fibres[a]	<2 mm; 2–7 mm; >7 mm	0.0001 %			
	Collembola	PVC[c]	80–250 μm	0.1 %	56 days	Growth and reproduction inhibited	(Zhu et al., 2018)
	Spring onions	PA[a]	15–20 μm	2 %	60 days	Change in plant biomass, tissue elemental composition, and root traits; effects depended on plastic types	(de Souza Machado et al., 2019)
		HDPE[a]	643 μm	2 %			
		PES[c]	5000 μm	2 %			
		PET[a]	222–258 μm	2 %			
		PP[a]	647–754 μm	2 %			
		PS[a]	555–647 μm	0.2 %			
	Wheat	Degraded plastic mulch[c] (LDPE and starch-based)	50 μm – 1 mm	1 %	120 days	Vegetative and reproductive growth disturbed	(Qi et al., 2018)
No effect	Isopods	Plastic bag films[c]	183 nm	0.4 %	14 days	Did not show any change in body mass, food ingestion rate, food assimilation rate, defecation rate, mortality, and energy reserve	(Jemec Kokalj et al., 2018)
		Beads from facial cleanser[c]	137 nm				
	Earthworms	Polyethylene[a]	250–1000 μm	0–0.1 %	28 days	No significant changes in survival, number of juvenile, and final weight of adult earthworms	(Rodriguez-Seijo et al., 2017)
	Wheat and mixed-waste organic output	HDPE[c]	<2 mm	0.01–1 %	270 days	No significant effect, and no clear trend observed on microbial community growth and diversity	(Judy et al., 2019)
		PET[c]					
		PVC[c]					
At certain level	Earthworms	Polystyrene[a]	58 μm	1–2 %	30 days	Little effects on the fitness at lower concentration (<0.5 %), while it was significantly increased at higher concentration (>1 %)	(Cao et al., 2017)
	Earthworms	Polyethylene[a]	<150 μm	7–60 %	60 days	Growth rate and weight decreased at higher concentration (28–60 %), but no effect was observed on reproduction even though at higher concentration	(Huerta Lwanga et al., 2016)
	Garden cress	Polystyrene[a]	50–4800 nm	103–107 particles/mL	24 h	Reduction in germination rate after 8 h, but no effect at 24 h; no difference in germination rate regardless the microplastics size, yet different in the root growth	(Bosker et al., 2019)

[a] Pristine plastics.
[b] Weathered plastics. This type of plastics was not used among the above studies.
[c] Commercial plastics.

Additionally, concentrations used often vary in number and units, resulting in inconclusive and incomparable results.

There are few studies that investigated the concentration and particle-size dependence on the observed effects. For example, earthworm fitness was hardly affected at lower concentrations of polystyrene microplastics (≤0.5 % w/w), while the effect was significantly increased at higher concentrations (>1 % w/w) (Cao et al., 2017).

Similarly, 7 % w/w of polyethylene microplastics (size <150 μm) after 60 days did not affect the fitness of earthworms *Lumbricus terrestris*, whereas higher concentrations (28–60 %) led to a decrease in the earthworms' growth and weight. However, no effect was observed on their reproduction (Huerta Lwanga et al., 2016).

In addition to the concentration of microplastics, other parameters such as size, shape, type, surface character, and exposure time also can play in important role, however relevant studies are still very limited (Lambert et al., 2017). For example, PE particles with sizes <150 μm (0–60 % for 60 days) led to a decreased growth rate and weight in earthworms, while larger particles (250–1000 μm, 0–0.1 % for 28 days) showed no significant effects (Huerta Lwanga et al., 2016; Rodriguez-Seijo et al., 2017). In a study investigating different exposure times, a short exposure (8 h) of garden cress (*Lepidium sativum*) to polystyrene microplastics (size 50–4800 nm; concentration 103–107 particles/mL) showed a reduction in germination rate. For longer exposure times (24 h), the germination rate was not affected, however a decrease root growth rate has been observed (Bosker et al., 2019).

Further implications of microplastics on a higher level of the ecosystem, particularly on humans, are still unknown. Such investigations are challenging as factors such as diversity in food intake, soil condition, animal activities and metabolisms have to be taken into account (Ng et al., 2018; Prata et al., 2021).

5. Microplastics analysis

Microplastics analysis is significantly impeded by the lack of standardized methods. In the following we review current guidelines and methods to then discuss a systematic approach to analyzing microplastics. Most of the current work is focused on marine samples such as seawater and

sediment. Techniques used include Fourier-transform Infrared (FTIR) and Raman microspectroscopy, Py-GC/MS, and Flow Cytometry.

To date, three guidelines have been published about microplastics analysis for solid samples (Table 2). Two of them, the guidelines from the European Commission in 2013 and from the National Oceanographic and Atmospheric Agency in 2015, are for sediments in the marine environments, and only the guideline from the UK Water Industry Research refers to solid waste, i.e. sludge and biosolids (Ball H et al., 2019; Galgani et al., 2013; Masura et al., 2015).

Additionally, the three guidelines lead to very different outcomes, mainly focusing on the enumeration of plastic particles, and much less on their identification.

5.1. Analytical techniques

Microplastics analysis is basically divided into three stages: (1) sample collection, (2) sample processing or pre-treatment, and (3) sample analysis that includes identification, characterization, and quantification. Among the techniques that can be used for sample analysis, the following methods are the most common ones.

5.1.1. Light or optical microscopy

This is a visual identification method usually combined with dyes such as Nile Red and Rose Bengal to differentiate between synthetic and natural polymer or other organic and inorganic particles. Image processing software, e.g. ImageJ or MP-VAT, can be used for automatic particles counting, size estimation, and shape characterization (Bayo et al., 2020; Corradini et al., 2019; Lv et al., 2019; Maes et al., 2017; Prata et al., 2019a, 2019b).

5.1.2. FTIR and Raman spectroscopy

FTIR and Raman are the most used spectroscopic techniques for microplastics analysis (Lares et al., 2019), however they are limited by the particles size that can be analysed. The FTIR or micro-FTIR technique is able to detect microplastics down to a size of 20 μm, while Raman or micro-Raman can be used for plastic particles down to 1 μm (Hidalgo-Ruz et al., 2012; Schwaferts et al., 2019; Sun et al., 2019). Software such as ParticleFinder and siMPle is commonly applied to assist in particles counting, size measurement, and shape characterization (Frère L et al., 2016; Primpke et al., 2020b). Although the sample analysis can be time consuming (several hours or even days could be needed to obtain final data), these methods are still recommended for microplastics analysis due to their accuracy and sensitivity. Some adjustments may be necessary depending on the type of sample. For example, in Raman spectroscopy, because of its sensitivity to fluorescence particles, choosing a suitable substrate or filter material of membrane filter is recommended to avoid background interference (Oßmann et al., 2017).

5.1.3. Py-GC/MS or TED-GC/MS

Pyrolysis (Py) and Thermal Extraction Desorption (TED) in combination with gas chromatography and mass spectrometry (GC/MS) is a thermo-analytical approach that is more time-efficient compared with spectroscopic methods. The techniques can give insights into polymer concentration and type. Particle count, size, and shape characteristics cannot be generated, due to the destructive nature of the method where particles are intentionally thermo-degraded (Hermabessiere et al., 2018; Okoffo et al., 2020).

5.1.4. Others: Flow cytometry, Dynamic Light Scattering, Nanoparticle Tracking Analysis, Electron and Force microscopy

Less common methods used for microplastics analysis are Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). They can give access to detailed information on size, shape, and surface characteristics of the plastic particles. Flow cytometry/imaging, Dynamic Light Scattering (DLS), and Nanoparticle Tracking Analysis (NTA) are mainly utilized to characterize size distribution, particle count, and surface charge (Braun et al., 2018; Gallego-Urrea et al., 2010; Primpke et al., 2020a; Ter Halle et al., 2017).

5.2. Selection and development of methods

There is no single technique, that will provide a complete analysis of a microplastics sample. The large number of different analytic techniques, each with different requirements and outcomes, makes it difficult to identify a preferred one. We rather recommend a purpose-fit approach to design an appropriate analytical approach: (1) determine the desired approach, e.g. routine monitoring, mapping, treatment efficacy monitoring; (2) choose the evidence or parameters required, e.g. size, type, shape, amount (3) select the methods that generate the required data.

5.2.1. Strategy and criteria

Method selection and development are study dependent. While there are some commonly used techniques for microplastics analysis in

Table 2
Published guidelines of microplastics analysis for solid samples.

Guideline/by/year	Samples	Sampling tools/methods	Identification methods	Reports
Guidance on Monitoring of Marine Litter in European Seas/Joint Research Center of the European Commission, Marine Strategy Framework Directive (MSDF)/2013 (Galgani et al., 2013)	Beach Intertidal and Subtidal Sediments	Veen grab, multi corer, or box cores/Samples are fractioned into two classes (20 μm – 1 mm and 1–5 mm) using metal sieves, followed by the density separation with concentrated saline NaCl solution	Binocular microscope (50× magnifying), and FTIR or Raman spectroscopy	Items/ml of sediment in size bins of 100 μm i.e., 20–100 μm, 101–200 μm and so on. The characters of plastic particles are reported based on the main colors, shapes, and polymer types
Laboratory Methods for the Analysis of Microplastics in the Marine Environment: Recommendations for quantifying synthetic particles in waters and sediments/National Oceanic and Atmospheric Administration, Marine Debris Division, US Department of Commerce/2015 (Masura et al., 2015)	Beach and Bed Sediments	Shovel, spade, corer, or grab sampler e.g., Ponar sampler/Samples are dried overnight, and potassium metaphosphate is added, followed by lithium metatungstate for density separation. Fenton's reagent is used to remove organic matters, then NaCl solution is added for further isolate microplastics particles.	Dissecting microscope (40× magnification) and gravimetric analysis	Mass of all microplastics in the size range of 0.3–5 mm
Sink to River – River to Tap: A Review of Potential Risks from Nanoparticles and Microplastics/UK Water Industry Research/2019 (Ball H et al., 2019)	Sludges	Trowel/Samples are dried at 50 °C for around one week prior to analysis. Sub-sampling is recommended i.e., 1 g dry mass sludge sampled from the sieved material (1 mm size pore mesh), followed by Fenton's reaction to remove organic materials, flotation using $ZnCl_2$ solution for density separation, and cellulase enzyme digestion. Plastic particles then are separated into “coarse” (>178 μm) and “fine” (<178 μm) fractions	FTIR spectrometer analysis combined with MPhunter software for data analysis.	Number of particles with size >25 μm complemented by their polymer type

Table 3
The scale number for method comparison.

Scale	Time	Cost	Accuracy	Sensitivity	Data-types
1	Most time-consuming (weeks)	Most expensive	Least accurate	Least sensitive	One
2	Days	Expensive	Low accuracy	Low	Two
3	1 day	Average	Average	Average	Three
4	Hours (<1 day)	Cheap	Less accurate	Less sensitive	Four
5	Fastest (minutes)	Cheapest	High accuracy	High sensitivity	Five

sludge and biosolid samples, often a combination of methods is necessary, depending on the research goal. For examples, in order to understand the morphology of plastic particles such as surface roughness and size, electron microscopy is the suitable method, yet will not yield the chemical nature of the particles. On the other hand, the combination between light microscopy and FTIR spectroscopy is the most common technique to gain data on the amount, size, shape, and type of the plastic particles (Schwaferts et al., 2019; Sun et al., 2019). Further exploration on the possible novel insight in the microplastics analysis could be done by enabling the online or direct analysis of some available techniques which could reduce the risks of cross contamination (Schwaferts et al., 2020). Also, the synthesis of nanoparticles is a recent approach to trace or tag the nanoplastics in the environment matrices (Frehland et al., 2020; Mitrano et al., 2019).

When selecting a method, additional parameters such as costs, working time, data obtained, accuracy, and sensitivity have to be taken into account. These factors are considered as the critical ones in determining the method for commercial or industrial purposes.

5.2.2. Scaling comparison

A scaling approach is using a number or scale to compare available analytical techniques. The approach should help choosing a specific (or combination of) technique(s) depending on circumstances of the study and desired outcomes. This approach is more practical for industrial purposes than listing the benefits and limitations of each technique or instrument, which are endless as their development is still ongoing.

The following tables are the scaling comparison of different analytical methods for microplastics evaluated based on some referred resources. The higher of the scale number represents the preferable methods that implied less working time and costs as well as more accurate and sensitive method (Table 3). This scale comparison can be adjusted depending on the aims of the research and type of samples.

For pre-treatment and separation methods, Fenton reagent and Floatation using salt share the same total scale number. They are considered as the best as it is the fastest with average costs, and a quite high accuracy as well as sensitivity. Both techniques are commonly used subsequently to gain higher organic matter removal efficiency of the matrices (Al-Azzawi et al., 2020; Hurley et al., 2018; Prata et al., 2019a, 2019b; Steinmetz et al., 2020; Ziajahromi et al., 2021). Although Field Flow Fractionation (FFF) has high accuracy, the cost is more expensive and may require a trained analyst (Table 4).

For identification, quantification, and characterization methods, Py-GC/MS is preferred because of its high accuracy and sensitivity for mass quantification. This method is not limited to certain size and shape of the plastic particles but depends on the purpose of the study because the generated data is limited to total mass and type of polymers. Therefore, Py-GC/MS is recommended to be employed in complement of FTIR or Raman microspectroscopy as these techniques produce information on size and shape of the particles. As an alternative, DLS or NTA are suggested as their working time is the fastest although they are not as accurate and sensitive compared with FTIR, Raman, and Py-GC/MS (Table 5). However, there is a possibility to modify the DLS or NTA method by combination with Py-GC/MS as explained in the following paragraph.

Combination of Pressurized Liquid Extraction (PLE) and Py-GC/MS (combination D), and ultrafiltration, DLS, and Py-GC/MS (combination F) placed the highest scale number because their time, cost, and sensitivity are outnumbered the others. However, combination D is limited to total mass and type of polymer (Table 6). Such downsides can be covered by either FTIR or Raman spectroscopy techniques or using combination F. However, combination F method has not been validated for sludge or biosolid sample as well as other solid environmental samples.

6. Final thoughts and future studies

6.1. How many microplastics to be considered as contaminants

Browne et al. suggested using hypothetical links to assess the likely impacts of plastic debris for the unknown ecological linkages. Using the known toxicological consequences for the individual organism, the identified variables can be utilized to develop a guideline for risk assessment and management. Such guidelines, then, can provide early warning for ecological impacts and assist to monitor the contaminated systems toward recovery. The authors also pointed out on considering the population impacts instead of individuals because responses to debris vary among individuals. Nevertheless, experimentally testing relevant hypotheses impacts is necessary to demonstrate causalities and direct effects (Browne et al., 2015; Jiang et al., 2020).

Developing the hypothetical links for impacts of sludge and biosolid containing microplastics on the ecosystem needs a systematic literature review, which is not the aim of this study. However, the research reports,

Table 4
Scaling of commonly used methods for pre-treatment and separation.

Method	Time	Cost[a]	Accuracy[b]	Sensitivity[c]	SUM	Average
Field Flow Fractionation (Schwaferts et al., 2019; Schwaferts et al., 2020)	4	2	3	5	14	3.5
Fenton reagent (Al-Azzawi et al., 2020; Ball H et al., 2019; Hurley et al., 2018)	5	4	4	4	17	4.25
Trichlorobenzene (TCB) (Steinmetz et al., 2020)	5	4	3	3	15	3.75
Floatation with salt e.g. NaI, $ZnCl_2$ (Ball H et al., 2019; Hurley et al., 2018)	4	5	4	4	17	4.25
Flocculation with $KAl(SO_4)_2$ (Steinmetz et al., 2020)	5	4	3	3	15	3.75

[a] Cost is in USD, estimated based on commercial prices and/or Primpke et al. (2020a).
[b] Validation by Recovery/Spike rates = false positive and blanks/controls = false negative tested or potential used for soil, sediment, sludge, or biosolid samples.
[c] Verification and Calibration with LOD (Limit of Detection) and LOQ (Limit of Quantification).

Table 5
Scaling of commonly used methods for identification, quantification, and characterization

Method	Time	Cost[a]	Accuracy[b]	Sensitivity[c]		Data obtained	SUM	Average
Light microscopy (Bayo et al., 2020)	3	5	1	1	4	Size, shape, type, counts	14	2.8
FTIR microspectroscopy (Lares et al., 2019)	3	2	5	3	4	Size, shape, type, mass	17	3.4
Raman microspectroscopy (Lares et al., 2019)	3	1	5	4	4	Size, shape, type, mass	17	3.4
Py-GC/MS (Okoffo et al., 2020)	4	2	5	5	2	Type, mass	18	3.6
DLS/NTA[d] (Gallego-Urrea et al., 2010; Ter Halle et al., 2017)	4	3	3	4	3	Size, shape, counts	17	3.4
Flow cytometry/imaging (Braun et al., 2018; Primpke et al., 2020a)	3	2	3	4	4	Size, shape, counts, type	16	3.2

[a] Cost (in USD): Light microscopy $2–3 k; FTIR/μFTIR $200-250 k; Raman/μRaman $200–400 k; Py-GC/MS $ > $215 k; DLS/NTA $60-120 k; Flow Cytometry/imaging $ > 130 k. It is estimated based on commercial prices and/or Primpke et al. (2020a).
[b] Validation by Recovery/Spike rates = false positive and blanks/controls = false negative tested or potential used for soil, sediment, sludge, or biosolid samples.
[c] Verification and Calibration with LOD (Limit of Detection) and LOQ (Limit of Quantification).
[d] DLS: Dynamic Light Scattering; NTA: Nanoparticle Tracking Analysis.

so far, on microplastics effect on the ecosystems, have shown that concentration, size, type of microplastics, and time exposed significantly influence the degree of effects. In fact, all these factors vary widely for each research report. In terms of concentration, it is difficult to determine the lethal limit of microplastics presence in the ecosystem because its effects vary for each organism's behavior and soil biophysical composition.

Since microplastics are contaminants, they have poisonous impacts on the ecosystem. Evidence proves that microplastics cause disruption and death of the organisms, but it does at a certain level, size, type, and is varied for each organism. Then, the problem is on determining the limits of microplastics' amount, which needs a long-term study and monitoring. At present, risk assessment and management as well as developing the

Table 6
Scaling of combination methods for microplastics analysis in solid environmental matrices.

Method	Time	Cost[a]	Accuracy[b]	Sensitivity[c]		Data obtained	SUM	Average
A (FFF-UV-MALS-RT[d]) (Schwaferts et al., 2020)	3	1	3	5	4	Size, shape, type, mass	16	3.2
B (Fenton-Density-Visual-FTIR) (Ziajahromi et al., 2021)	3	2	4	4	4	Size, shape, type, mass	17	3.4
C (Nile Red + automated software MP-VAT) (Prata et al., 2019a,b)	3	4	4	3	3	Size, shape, counts	17	3.4
D (Pressurized Liquid Extraction + Py-GC/MS) (Okoffo et al., 2020)	3	3	5	5	2	Type, mass	18	3.6
E (micro-Raman + software "Particle Finder") (Oßmann et al., 2017)	3	2	4	4	4	Size, shape, type, mass	17	3.4
F (ultrafiltration + DLS + Py-GC/MS) (Ter Halle et al., 2017)	3	3	3	5	4	Size, type, counts, mass	18	3.6
G (Fenton + $KAl(SO_4)_2$ + TCB + Py-GC/MS) (Steinmetz et al., 2020)	4	1	4	4	2	Type, mass	15	3
H (Metal-doped nanoplastics) (Frehland et al., 2020; Mitrano et al., 2019)	2	3	5	5	2	Counts, mass	17	3.4

[a] Cost is in USD, estimated based on commercial prices and/or Primpke et al. (2020a).
[b] Validation by Recovery/Spike rates = false positive and blanks/controls = false negative tested or potential used for soil, sediment, sludge, or biosolid samples.
[c] Verification and Calibration with LOD (Limit of Detection) and LOQ (Limit of Quantification).
[d] FFF: Field Flow Fractionation; MALS: Multi Angle Light Scattering; RT: Raman Tweezers.

guidelines for microplastics removal treatment and recovery are steps that can be taken while continuing with experiments to collect the data and assemble the ecotoxicological effects.

6.2. A field evaluation is crucial

Field evidence is a crucial factor in determining ecological linkage (Browne et al., 2015). Using other countries' data for plastic loads estimation is unreliable due to variation in the field condition between regions and countries. Spatial and temporal conditions influence the plastic loads greatly.

Rolsky et al. suggested that data coverage in geographical conditions is essential to obtain a better understanding of how microplastics are likely to occur and accumulate in the ecosystem. This includes seasonality and sociality or urbanization. For example, a study in South Korea by Lee and Kim showed that increasing precipitation positively correlated with the number of microplastics in sludge (Lee and Kim, 2018). In China, increasing infrastructure and industrial activities as well as smaller areas of afforested land also showed a positive correlation with a higher concentration of microplastics in sludge (Li et al., 2018). These factors also reflect the population size and their behavior.

6.3. Continuous studies

Microplastics in biosolids should be considered as a contaminant for agricultural applications, yet their presence is unavoidable. To what level should they be limited or rejected for land applications?

Plastic debris disrupts the ecosystem, and more experiments are necessary to determine the magnitude of sublethal and lethal impacts from plastics exposures. This includes detailed information on plastic-type, size, shape, dimensions, volume, and mass. Thus, accurate and precise microplastics' quantification and characterization methods are urgently needed.

Incorporation with the identification techniques development, continuous monitoring of biosolids application i.e. frequency or period, and the amount of application are necessary as well. The reason is plastic debris tends to accumulate and its degradation needs days, months, even years, so does the ecosystem that is evolving. Also, the interactions of microplastics with other contaminants, such as additives and persistent organic pollutants, could worsen the effects on the ecosystem. It is arguable that the only source of microplastics in agricultural soils is from biosolids applications. There is a possibility of other sources such as plastic mulch, twine, rope, and irrigation pipe (Hopewell et al., 2020).

Achieving zero plastic debris in biosolids sounds very unlikely considering the current usage of plastic materials in diverse applications from households to industries. However, if we do not start to increase our awareness of how it could vastly and unnoticedly increase for the years to come, such invisible threats could be a silent killer for the next generation.

Author contributions

Both authors contributed equally to the manuscript.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

Acknowledgements

This on-going project is supported by South Australia Water (SA Water) corporation. The authors acknowledge Alexandra Keegan, Milena Fernandes, Clos Ilda, and Melody Lau (SA Water) for their continuous support and advice on this project; to Professor Paul Kirkbride (Flinders University) for his assistance on analytical techniques; and Shima Ziajahromi (Griffith University) for her advice in this study.

References

Al-Azzawi, M.S.M., Kefer, S., Weißer, J., Reichel, J., Schwaller, C., Glas, K., Knoop, O., Drewes, J.E., 2020. Validation of sample preparation methods for microplastic analysis in wastewater Matrices—Reproducibility and standardization. Water 12 (9), 2445. https://www.mdpi.com/2073-4441/12/9/2445.

Alexander, J., Barregard, L., Bignami, M., Ceccatelli, S., Cottrill, B., Dinovi, M., Edler, L., Grasl-Kraupp, B., Hogstrand, C., Hoogenboom, L., Knutsen, H.K., Nebbia, C.S., Oswald, I., Petersen, A., Rogiers, V.M., Rose, M., Roudot, A.-C., Schwerdtle, T., Vleminckx, C., Chain, E.P.C.F., 2016. Presence of microplastics and nanoplastics in food, with particular focus on seafood. Efsa Journal 14 (6). https://doi.org/10.2903/j.efsa.2016.4501 Article Unsp 4501.

Arthur, C., Baker, J.E., Bamford, H.A., 2009. Proceedings of the international research workshop on the occurrence, effects, and fate of microplastic marine debris, september 9–11, 2008. University of Washington Tacoma, Tacoma, WA, USA.

Australian, New Zealand Biosolids Partnership, 2020. Biosolids. Retrieved 10 September from https://www.biosolids.com.au/info/what-are-biosolids/#:~:text=Sewage%20sludge%20is%20regarded%20as,15%25%20to%2090%25%20solids.

Ball H, C.R., Grove, E., Horton, A., Johnson, A., Jürgens, M., Read, D., Svendsen, C., 2019. Sink To River - River To Tap. A Review of Potential Risks From Nanoparticles and Microplastics. EQ 01 A 231UK Water Industry Research Limited. https://ukwir.org/view/$NvDnwfm!.

Bayo, J., Olmos, S., López-Castellanos, J., Alcolea, A., 2016. Microplastics and microfibers in the sludge of a municipal wastewater treatment plant. International Journal of Sustainable Development and Planning 11 (5), 812–821. https://doi.org/10.2495/SDP-V11-N5-812-821.

Bayo, J., Olmos, S., López-Castellanos, J., 2020. Removal of microplastics from wastewater. Handbook of Microplastics in the Environment, pp. 1–20.

Bläsing, M., Amelung, W., 2018. Plastics in soil: analytical methods and possible sources. Sci. Total Environ. 612, 422–435. https://doi.org/10.1016/j.scitotenv.2017.08.086.

Boots, B., Russell, C.W., Green, D.S., 2019. Effects of microplastics in soil ecosystems: above and below ground. Environ. Sci. Technol. 53 (19), 11496–11506. https://doi.org/10.1021/acs.est.9b03304.

Bosker, T., Bouwman, L.J., Brun, N.R., Behrens, P., Vijver, M.G., 2019. Microplastics accumulate on pores in seed capsule and delay germination and root growth of the terrestrial vascular plant Lepidium sativum. Chemosphere 226, 774–781. https://doi.org/10.1016/j.chemosphere.2019.03.163.

Braun, U., Jekel, I.M., Gerdts, G., Ivleva, N.P., Reiber, J., 2018. Microplastics analytics: sampling. Preparation and Detection Methods. https://bmbf-plastik.de/sites/default/files/2019-02/Discussion%20Paper%20Mikroplastics%20Analytics%20Nov%202018.pdf.

Bretas Alvim, C., Mendoza-Roca, J.A., Bes-Piá, A., 2020. Wastewater treatment plant as microplastics release source – quantification and identification techniques. J. Environ. Manag. 255, 109739. https://doi.org/10.1016/j.jenvman.2019.109739.

Browne, M.A., Underwood, A.J., Chapman, M.G., Williams, R., Thompson, R.C., van Franeker, J.A., 2015. Linking effects of anthropogenic debris to ecological impacts. Proc. Biol. Sci. 282 (1807). https://doi.org/10.1098/rspb.2014.2929 20142929-20142929.

Cao, D., Wang, X., Luo, X., Liu, G., Zheng, H., 2017. Effects of polystyrene microplastics on the fitness of earthworms in an agricultural soil. IOP Conf. Ser.: Earth Environ. Sci. 61, 012148. https://doi.org/10.1088/1755-1315/61/1/012148.

Cartwright, C.D., Thompson, I.P., Burns, R.G., 2000. Degradation and impact of phthalate plasticizers on soil microbial communities. Environ. Toxicol. Chem. 19 (5), 1253–1261. https://doi.org/10.1002/etc.5620190506.

Commission, European, 2011. Commission recommendation of 18 october 2011 on the definition of nanomaterial. Off. J. Eur. Union 275, 38.

Corradini, F., Meza, P., Eguiluz, R., Casado, F., Huerta-Lwanga, E., Geissen, V., 2019. Evidence of microplastic accumulation in agricultural soils from sewage sludge disposal. Sci. Total Environ. 671, 411–420. https://doi.org/10.1016/j.scitotenv.2019.03.368.

de Sá, L.C., Oliveira, M., Ribeiro, F., Rocha, T.L., Futter, M.N., 2018. Studies of the effects of microplastics on aquatic organisms: what do we know and where should we focus our efforts in the future? Sci. Total Environ. 645, 1029–1039. https://doi.org/10.1016/j.scitotenv.2018.07.207.

de Souza Machado, A.A., Lau, C.W., Till, J., Kloas, W., Lehmann, A., Becker, R., Rillig, M.C., 2018. Impacts of microplastics on the soil biophysical environment. Environ. Sci. Technol. 52 (17), 9656–9665. https://doi.org/10.1021/acs.est.8b02212.

de Souza Machado, A.A., Lau, C.W., Kloas, W., Bergmann, J., Bachelier, J.B., Faltin, E., Becker, R., Görlich, A.S., Rillig, M.C., 2019. Microplastics can change soil properties and affect plant performance. Environ. Sci. Technol. 53 (10), 6044–6052. https://doi.org/10.1021/acs.est.9b01339.

Environment Protection Authority, 2020. Guidelinesfor the Safe Handling and Reuse of Biosolids in South Australia Adelaide, South Australia.

Frehland, S., Kaegi, R., Hufenus, R., Mitrano, D.M., 2020. Long-term assessment of nanoplastic particle and microplastic fiber flux through a pilot wastewater treatment plant using metal-doped plastics. Water Res. 182. https://doi.org/10.1016/j.watres.2020.115860 115860-115860.

Frère L, P.P.I., Moreau, J., Soudant, P., Lambert, C., Huvet, A., Rinnert, E., 2016. A semi-automated Raman micro-spectroscopy method for morphological and chemical characterizations of microplastic litter. Marine Pollution Bulletin 113 (1), 461–468. https://doi.org/10.1016/j.marpolbul.2016.10.051.

Galgani, F., Hanke, G., Werner, S., Oosterbaan, L., Nilsson, P., Fleet, D., Kinsey, S., Thompson, R.C., Vlachogianni, T., Scoullos, M., Viega, J.M., Palatinus, A., Matiddi, M., Maes, T., Korpinen, S., Budziak, A., Leslie, H., Gago, J., Liebezeit, G., Franeker, J.V., 2013.

Guidance on Monitoring of Marine Litter in European Seas. 128. Publication Office of the European Union.
Gallego-Urrea, J., Aacute, N.A., Tuoriniemi, J., Pallander, T., Hassell, Ouml, V.M., 2010. Measurements of nanoparticle number concentrations and size distributions in contrasting aquatic environments using nanoparticle tracking analysis. Environmental Chemistry 7 (1), 67–81. https://doi.org/10.1071/EN09114.
Gatidou, G., Arvaniti, O.S., Stasinakis, A.S., 2019. Review on the occurrence and fate of microplastics in sewage treatment plants. J. Hazard. Mater. 367, 504–512. https://doi.org/10.1016/j.jhazmat.2018.12.081.
Hamilton, K.A., Ahmed, W., Rauh, E., Rock, C., McLain, J., Muenich, R.L., 2020. Comparing microbial risks from multiple sustainable waste streams applied for agricultural use: biosolids, manure, and diverted urine. Curr. Opin. Environ. Sci. Health 14, 37–50. https://doi.org/10.1016/j.coesh.2020.01.003.
Hartmann, N.B., Hüffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A.E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M.P., Hess, M.C., Ivleva, N.P., Lusher, A.L., Wagner, M., 2019. Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. Environ. Sci. Technol. 53 (3), 1039–1047. https://doi.org/10.1021/acs.est.8b05297.
He, D., Luo, Y., Lu, S., Liu, M., Song, Y., Lei, L., 2018. Microplastics in soils: analytical methods, pollution characteristics and ecological risks. TrAC Trends Anal. Chem. 109, 163–172. https://doi.org/10.1016/j.trac.2018.10.006.
He, P., Chen, L., Shao, L., Zhang, H., Lu, F., 2019. Municipal solid waste (MSW) landfill: a source of microplastics?-evidence of microplastics in landfill leachate. Water Res. 159, 38–45. https://doi.org/10.1016/j.watres.2019.04.060.
Hermabessiere, L., Himber, C., Boricaud, B., Kazour, M., Amara, R., Cassone, A.-L., Laurentie, M., Paul-Pont, I., Soudant, P., Dehaut, A., Duflos, G., 2018. Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics. Anal. Bioanal. Chem. 410 (25), 6663–6676. https://doi.org/10.1007/s00216-018-1279-0.
Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ. Sci. Technol. 46 (6), 3060–3075. https://doi.org/10.1021/es2031505.
Hopewell, K., Batstone, D., Dale, G., Keegan, A., Lee, E., Randall, L., Tao, E., 2020. ANZBP Preliminary Report on Microplastics Risk for the Australian and New Zealand Biosolids Industry July 2020.
Huerta Lwanga, E., Gertsen, H., Gooren, H., Peters, P., Salánki, T., van der Ploeg, M., Besseling, E., Koelmans, A.A., Geissen, V., 2016. Microplastics in the terrestrial ecosystem: implications for lumbricus terrestris (Oligochaeta, Lumbricidae). Environ. Sci. Technol. 50 (5), 2685–2691. https://doi.org/10.1021/acs.est.5b05478.
Hurley, R.R., Nizzetto, L., 2018. Fate and occurrence of micro(nano)plastics in soils: knowledge gaps and possible risks. Curr. Opin. Environ. Sci. Health 1, 6–11. https://doi.org/10.1016/j.coesh.2017.10.006.
Hurley, R.R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. Environmental Science & Technology 52 (13), 7409–7417. https://doi.org/10.1021/acs.est.8b01517.
Ivleva, N.P., Wiesheu, A.C., Niessner, R., 2017. Microplastic in aquatic ecosystems. Angew. Chem. Int. Ed. 56 (7), 1720–1739. https://doi.org/10.1002/anie.201606957.
Jacques, O., Prosser, R.S., 2021. A probabilistic risk assessment of microplastics in soil ecosystems [Article]. Science of the Total Environment 757, 143987. https://doi.org/10.1016/j.scitotenv.2020.143987.
Jemec Kokalj, A., Horvat, P., Skalar, T., Kržan, A., 2018. Plastic bag and facial cleanser derived microplastic do not affect feeding behaviour and energy reserves of terrestrial isopods. Sci. Total Environ. 615, 761–766. https://doi.org/10.1016/j.scitotenv.2017.10.020.
Jiang, B., Kauffman, A.E., Li, L., McFee, W., Cai, B., Weinstein, J., Lead, J.R., Chatterjee, S., Scott, G.I., Xiao, S., 2020. Health impacts of environmental contamination of micro- and nanoplastics: a review. Environ. Health Prev. Med. 25 (1), 29. https://doi.org/10.1186/s12199-020-00870-9.
Judy, J.D., Williams, M., Gregg, A., Oliver, D., Kumar, A., Kookana, R., Kirby, J.K., 2019. Microplastics in municipal mixed-waste organic outputs induce minimal short to long-term toxicity in key terrestrial biota. Environ. Pollut. 252, 522–531. https://doi.org/10.1016/j.envpol.2019.05.027.
Kerstin, M., Norén, F., 2014. Screening of microplastic particles in and downstream a wastewater treatment plant. Swedish Environmental Research Institute, Report.
Lambert, S., Scherer, C., Wagner, M., 2017. Ecotoxicity testing of microplastics: considering the heterogeneity of physicochemical properties. Integr. Environ. Assess. Manag. 13 (3), 470–475. https://doi.org/10.1002/ieam.1901.
Lares, M., Mohamed Chaker, N., Sillanpää, M., Sillanpää, M., 2019. Intercomparison study on commonly used methods to determine microplastics in wastewater and sludge samples. Environ. Sci. Pollut. Res. Int. 26 (12), 12109–12122. https://doi.org/10.1007/s11356-019-04584-6.
Lee, H., Kim, Y., 2018. Treatment characteristics of microplastics at biological sewage treatment facilities in Korea. Mar. Pollut. Bull. 137, 1–8. https://doi.org/10.1016/j.marpolbul.2018.09.050.
Li, X., Chen, L., Mei, Q., Dong, B., Dai, X., Ding, G., Zeng, E.Y., 2018. Microplastics in sewage sludge from the wastewater treatment plants in China. Water Res. 142, 75–85. https://doi.org/10.1016/j.watres.2018.05.034.
Liu, X., Yuan, W., Di, M., Li, Z., Wang, J., 2019. Transfer and fate of microplastics during the conventional activated sludge process in one wastewater treatment plant of China. Chem. Eng. J. 362, 176–182. https://doi.org/10.1016/j.cej.2019.01.033.
Lusher, A., Hurley, R., Vogelsang, C., 2019. Microplastics in sewage sludge: captured but released? In: Karapanagioti, Hrissi K., Kalavrouziotis, Ioannis K. (Eds.), Microplastics in Water and Wastewater Download citation file: Ris (Zotero) Reference Manager EasyBib Bookends Mendeley Papers EndNote RefWorks BibTex Close Search
Lusher, A.L., Hurley, R., Vogelsang, C., Nizzetto, L., Olsen, M., 2017. Mapping Microplastics in Sludge (8257769509).
Lv, L., Qu, J., Yu, Z., Chen, D., Zhou, C., Hong, P., Sun, S., Li, C., 2019. A simple method for detecting and quantifying microplastics utilizing fluorescent dyes - safranine T, fluorescein isophosphate, Nile red based on thermal expansion and contraction property. Environ. Pollut. 255, 113283. https://doi.org/10.1016/j.envpol.2019.113283.
Maes, T., Jessop, R., Wellner, N., Haupt, K., Mayes, A.G., 2017. A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile red. Sci. Rep. 7 (1), 44501. https://doi.org/10.1038/srep44501.
Mahon, A.M., Connell, B., Healy, M., O'Connor, I., Officer, R., Nash, R., Morrison, L., 2016. Microplastics in sewage sludge: effects of treatment. Environ. Sci. Technol. 51. https://doi.org/10.1021/acs.est.6b04048.
Masura, J., Baker, J.E., Foster, G.D., Arthur, C., Herring, C., 2015. Laboratory methods for the analysis of microplastics in the marine environment : recommendations for quantifying synthetic particles in waters and sediments. Technical Memorandum NOAA technical memorandum NOS-OR&R ; 48. https://repository.library.noaa.gov/view/noaa/10296.
Mitrano, D.M., Beltzung, A., Frehland, S., Schmiedgruber, M., Cingolani, A., Schmidt, F., 2019. Synthesis of metal-doped nanoplastics and their utility to investigate fate and behaviour in complex environmental systems. Nat. Nanotechnol. 14 (4), 362-+. https://doi.org/10.1038/s41565-018-0360-3.
Murphy, F., Ewins, C., Carbonnier, F., Quinn, B., 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environ. Sci. Technol. 50 (11), 5800–5808. https://doi.org/10.1021/acs.est.5b05416.
Ng, E.-L., Huerta Lwanga, E., Eldridge, S.M., Johnston, P., Hu, H.-W., Geissen, V., Chen, D., 2018. An overview of microplastic and nanoplastic pollution in agroecosystems. Sci. Total Environ. 627, 1377–1388. https://doi.org/10.1016/j.scitotenv.2018.01.341.
Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K.O., Wollenberger, L., Santos, E.M., Paull, G.C., Van Look, K.J.W., Tyler, C.R., 2009. A critical analysis of the biological impacts of plasticizers on wildlife. Philos. Trans.: Biol. Sci. 364 (1526), 2047–2062. http://www.jstor.org.ezproxy.flinders.edu.au/stable/40485981.
Okoffo, E.D., O'Brien, S., O'Brien, J.W., Tscharke, B.J., Thomas, K.V., 2019. Wastewater treatment plants as a source of plastics in the environment: a review of occurrence, methods for identification, quantification and fate [10.1039/C9EW00428A]. Environ. Sci. Water res. Technol. 5 (11), 1908–1931. https://doi.org/10.1039/C9EW00428A.
Okoffo, E.D., Ribeiro, F., O'Brien, J.W., O'Brien, S., Tscharke, B.J., Gallen, M., Samanipour, S., Mueller, J.F., Thomas, K.V., 2020. Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography–mass spectrometry. Sci. Total Environ. 715. https://doi.org/10.1016/j.scitotenv.2020.136924.
Oßmann, B.E., Sarau, G., Schmitt, S.W., Holtmannspötter, H., Christiansen, S.H., Dicke, W., 2017. Development of an optimal filter substrate for the identification of small microplastic particles in food by micro-raman spectroscopy. Anal. Bioanal. Chem. 409 (16), 4099–4109. https://doi.org/10.1007/s00216-017-0358-y.
Prata, J.C., da Costa, J.P., Duarte, A.C., Rocha-Santos, T., 2019. Methods for sampling and detection of microplastics in water and sediment: a critical review. TrAC Trends Anal. Chem. 110, 150–159. https://doi.org/10.1016/j.trac.2018.10.029.
Prata, J.C., Reis, V., Matos, J.T.V., da Costa, J.P., Duarte, A.C., Rocha-Santos, T., 2019. A new approach for routine quantification of microplastics using Nile red and automated software (MP-VAT). Sci. Total Environ. 690, 1277–1283. https://doi.org/10.1016/j.scitotenv.2019.07.060.
Prata, J.C., da Costa, J.P., Lopes, I., Andrady, A.L., Duarte, A.C., Rocha-Santos, T., 2021. A one health perspective of the impacts of microplastics on animal, human and environmental health [Review]. Sci. Total Environ. 777, 146094. https://doi.org/10.1016/j.scitotenv.2021.146094.
Primpke, S., Christiansen, S.H., Cowger, W., De Frond, H., Deshpande, A., Fischer, M., Holland, E., Meyns, M., O'Donnell, B.A., Ossmann, B., 2020. Critical assessment of analytical methods for the harmonized and cost efficient analysis of microplastics. Appl. Spectrosc. 74 (9), 1012–1047.
Primpke, S., Cross, R.K., Mintenig, S.M., Simon, M., Vianello, A., Gerdts, G., Vollertsen, J., 2020. Toward the systematic identification of microplastics in the environment: evaluation of a new independent software tool (siMPle) for spectroscopic analysis. Appl. Spectrosc. 74 (9), 1127–1138. https://doi.org/10.1177/0003702820917760.
Qi, R., Jones, D.L., Li, Z., Liu, Q., Yan, C., 2020. Behavior of microplastics and plastic film residues in the soil environment: a critical review. Sci. Total Environ. 703, 134722. https://doi.org/10.1016/j.scitotenv.2019.134722.
Qi, Y., Yang, X., Pelaez, A.M., Huerta Lwanga, E., Beriot, N., Gertsen, H., Garbeva, P., Geissen, V., 2018. Macro- and micro- plastics in soil-plant system: effects of plastic mulch film residues on wheat (Triticum aestivum) growth. Sci. Total Environ. 645, 1048–1056. https://doi.org/10.1016/j.scitotenv.2018.07.229.
Renner, G., Schmidt, T.C., Schram, J., 2018. Analytical methodologies for monitoring micro (nano)plastics: which are fit for purpose? Curr. Opin. Environ. Sci. Health 1, 55–61. https://doi.org/10.1016/j.coesh.2017.11.001.
Rodriguez-Seijo, A., Lourenço, J., Rocha-Santos, T.A.P., da Costa, J., Duarte, A.C., Vala, H., Pereira, R., 2017. Histopathological and molecular effects of microplastics in Eisenia andrei Bouché. Environ. Pollut. 220, 495–503. https://doi.org/10.1016/j.envpol.2016.09.092.
Rolsky, C., Kelkar, V., Driver, E., Halden, R.U., 2020. Municipal sewage sludge as a source of microplastics in the environment. Curr. Opin. Environ. Sci. Health 14, 16–22. https://doi.org/10.1016/j.coesh.2019.12.001.
Schwaferts, C., Niessner, R., Elsner, M., Ivleva, N.P., 2019. Methods for the analysis of submicrometer- and nanoplastic particles in the environment. TrAC Trends Anal. Chem. 112, 52–65. https://doi.org/10.1016/j.trac.2018.12.014.
Schwaferts, C., Sogne, V., Welz, R., Meier, F., Klein, T., Niessner, R., Elsner, M., Ivleva, N.P., 2020. Nanoplastic analysis by online coupling of raman microscopy and field-flow fractionation enabled by optical tweezers. Anal. Chem. 92 (8), 5813–5820. https://doi.org/10.1021/acs.analchem.9b05336.
Steinmetz, Z., Kintzi, A., Munoz, K., Schaumann, G.E., 2020. A simple method for the selective quantification of polyethylene, polypropylene, and polystyrene plastic debris in soil by pyrolysis-gas chromatography/mass spectrometry. J. Anal. Appl. Pyrolysis 147 (104803). https://doi.org/10.1016/j.jaap.2020.104803.

Sun, J., Dai, X., Wang, Q., van Loosdrecht, M.C.M., Ni, B.-J., 2019. Microplastics in wastewater treatment plants: detection, occurrence and removal. Water Res. 152, 21–37. https://doi.org/10.1016/j.watres.2018.12.050.

Ter Halle, A., Jeanneau, L., Martignac, M., Jardé, E., Pedrono, B., Brach, L., Gigault, J., 2017. Nanoplastic in the North Atlantic subtropical gyre. Environ. Sci. Technol. 51 (23), 13689–13697. https://doi.org/10.1021/acs.est.7b03667.

The International Organization for Standardization, 2020. ISO/TR 21960:2020 Plastics - Environmental Aspects - State of knowledge and Methodologies.

Thompson, R.C., 2015. Microplastics in the marine environment: Sources, consequences and solutions. Marine Anthropogenic Litter. Springer, Cham, pp. 185–200.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic? Science (New York, N.Y.) 304 (5672), 838. https://doi.org/10.1126/science.1094559.

Toffey, W., Brown, S., 2020. Biosolids and ecosystem services: making the connection explicit. Curr. Opin. Environ. Sci. Health 14, 51–55. https://doi.org/10.1016/j.coesh.2020.02.002.

Toussaint, B., Raffael, B., Angers-Loustau, A., Gilliland, D., Kestens, V., Petrillo, M., Rio-Echevarria, I.M., Van den Eede, G., 2019. Review of micro- and nanoplastic contamination in the food chain. Food Addit. Contam. Part A 36 (5), 639–673. https://doi.org/10.1080/19440049.2019.1583381.

Zhu, D., Chen, Q.-L., An, X.-L., Yang, X.-R., Christie, P., Ke, X., Wu, L.-H., Zhu, Y.-G., 2018. Exposure of soil collembolans to microplastics perturbs their gut microbiota and alters their isotopic composition. Soil Biol. Biochem. 116, 302–310. https://doi.org/10.1016/j.soilbio.2017.10.027.

Ziajahromi, S., Neale, P.A., Rintoul, L., Leusch, F.D.L., 2017. Wastewater treatment plants as a pathway for microplastics: development of a new approach to sample wastewater-based microplastics. Water Res. 112, 93–99. https://doi.org/10.1016/j.watres.2017.01.042.

Ziajahromi, S., Neale, P.A., Telles Silveira, I., Chua, A., Leusch, F.D.L., 2021. An audit of microplastic abundance throughout three australian wastewater treatment plants. Chemosphere 263, 128294. https://doi.org/10.1016/j.chemosphere.2020.128294.

Environmental Science & Technology

Article

pubs.acs.org/est

Polybrominated Diphenyl Ethers in U.S. Sewage Sludges and Biosolids: Temporal and Geographical Trends and Uptake by Corn Following Land Application

Robert C. Hale,* Mark J. La Guardia, Ellen Harvey, Da Chen, Thomas M. Mainor, and Drew R. Luellen

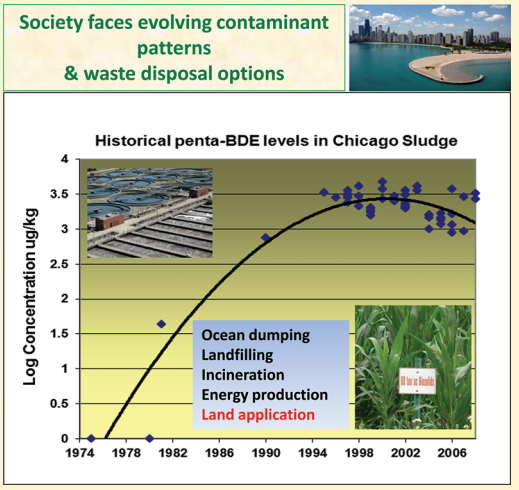
Department of Environmental and Aquatic Animal Health, Virginia Institute of Marine Science, Gloucester Point, Virginia 23062, United States

Lakhwinder S. Hundal

Metropolitan Water Reclamation District of Greater Chicago, R&D Department, Section 123, 6001 West Pershing Road, Cicero, Illinois 60804-4112, United States

Supporting Information

ABSTRACT: Polybrominated diphenyl ethers (PBDEs) have been used extensively to flame-retard polymers and textiles. These persistent chemicals enter wastewater streams following manufacture, use, and disposal, concentrating in the settled solids during treatment. Land application of stabilized sewage sludge (known as biosolids) can contribute PBDEs to terrestrial systems. Monitoring sludge/biosolids contaminant burdens may be valuable in revealing trends in societal chemical usage and environmental release. In archived Chicago area sludges/biosolids from 1975 to 2008, penta-BDE concentrations increased and then plateaued after about 2000. Penta-BDE manufacture in the United States ended in December 2004. Deca-BDE concentrations in biosolids rose from 1995 to 2008, doubling on a 5-year interval. Evaluation of U.S. Environmental Protection Agency Targeted National Sewage Sludge Survey data from 2006 to 2007 revealed highest penta-BDE biosolids levels from western and lowest from northeastern wastewater treatment plants (2120 and 1530 μg/kg, respectively), consistent with patterns reported in some recent indoor dust and human blood studies. No significant regional trends were observed for deca-BDE concentrations. Congener patterns in contemporary Chicago biosolids support the contention that BDE-209 can be dehalogenated to less brominated congeners. Biosolids application on agricultural fields increased PBDE soil concentrations. However, corn grown thereon did not exhibit measurable PBDE uptake; perhaps due to low bioavailability of the biosolids-associated flame retardants.



INTRODUCTION

For centuries society has used water to transport wastes from human population centers. Initially, untreated wastes were dispersed directly into surface waters, often with negative environmental consequences. Alternatively, wastewater may be directed to wastewater treatment plants (WWTPs). In addition to degradative processes, WWTPs separate hydrophobic pollutants by partitioning to solids and subsequent sedimentation. In the United States, 75% of citizens are served by centralized wastewater treatment, producing 29 kg/person dry sludge annually.[1] Using current U.S. census figures of 310 million people leads to an estimated annual sludge production of 6.8 million metric tons (MT) per annum. This is comparable to the 7.8 million MT estimated for the European Union (EU) for 2000.[1] To reduce putrefiable materials and pathogen content, sludges may be further subjected to anaerobic digestion, liming, composting, or high-temperature treatments. The term "biosolids" has been coined to denote such stabilized solids. Biosolids contain substantial nitrogen, phosphorus, and organic carbon, making them attractive soil amendments and crop fertilizers. Bans on ocean dumping of sewage sludges and escalating landfilling and incineration costs have further incentivized land application. Today, about 60% of biosolids produced in the United States are land-applied.[2] Recipients include environmentally compromised industrial sites (i.e., "brownfields"), as well as farmland, forests, and public lands. In the European Union, the extent of land application varies

Received: September 8, 2011
Revised: January 24, 2012
Accepted: January 26, 2012
Published: January 26, 2012

dx.doi.org/10.1021/es203149g | Environ. Sci. Technol. 2012, 46, 2055–2063

greatly, ranging from zero in The Netherlands to 62% in the United Kingdom.[1]

Pollutants in land-applied biosolids, particularly chemicals resistant to degradation, are an environmental concern. While thousands of chemicals may enter wastewater, the U.S. Environmental Protection Agency (U.S. EPA) examined only 411 in its 1988 National Sewage Sludge Survey.[2] Those results were used in the development of an initial risk assessment in support of the 1993 Title 40 Code of Federal Regulations Part 503 rule governing land application. That assessment assumed that use of persistent organic pollutants (POPs) in the United States had ceased, that existing sludge concentrations were not toxicologically significant, and that levels would decrease further over time. However, since the 1990s, several new POPs in wastewaters have been discovered, for example, brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs). Commercial PBDE use is thought to have begun in the 1970s and one product, deca-BDE, remains a high production volume chemical. Originally presumed to be retained within treated plastics and textiles, it was later observed that PBDEs may volatilize from or be released following fragmentation of finished products[3−5] and contribute to the milligram per kilogram levels observed in indoor dust and sewage sludge. The status of the PBDEs within the sludge, that is, contained within small plastic fragments or sorbed to the surface of organic-rich particles, will influence their subsequent bioavailability. To date, limited research has examined the fate and bioavailability of PBDEs in biosolids-amended soils. Duarte-Davidson and Jones[6] prioritized chemicals therein with the greatest potential for transfer into the food chain. Factors of concern included chemical persistence, groundwater leachability, plant root retention, translocation within the plant, and foliar uptake from the air. Ironically, these authors noted that brominated aromatics were not evaluated in their model as they had not yet been reported in sewage sludges.

Elucidation of temporal patterns of PBDE usage and environmental release has been hampered by the lack of publicly available production data. This has been a particular issue in the United States, where such statistics have been shielded from public scrutiny by confidentiality provisions. However, some North American BFR demand data were released for 2001. Corresponding penta- and deca-BDE demands were 95% and 44% of the global total, respectively.[7] However, U.S. penta-BDE production ended after 2004. Recent data indicated that deca-BDE usage in the European Union has remained fairly constant over the past decade,[8] but the trajectory of U.S. usage is uncertain. Deca-BDE use in the United States is, however, scheduled to cease after 2012. Nonetheless, large BFR reservoirs will remain in in-use and discarded products. These will continue to release PBDEs into wastewater streams and the environment for an extended period.

While determination of levels of persistent contaminants in sewage sludge/biosolids may be valuable for assessing societal chemical usage patterns and predicting environmental release trends, this approach has seldom been exploited. PBDEs were not included in the U.S. EPA national sludge surveys conducted in 1982, 1988, or 2001. However, the 2006−2007 EPA Targeted National Sewage Sludge Survey (TNSSS) included 11 PBDE congeners present in the commercial penta-BDE (BDEs 28, 47, 66, 85, 99, 100, 138, 153, and 154), octa-BDE (BDE-183), and deca-BDE (BDE-209) mixtures.[9] Sludges/biosolids were collected from 74 WWTPs in 35 U.S. states. While contaminant data and treatment strategies could not be linked to specific WWTPs in the report, the regions of the contributing facilities were identified.

The goals of the current research were to (1) assess temporal trends of PBDE concentrations in municipal wastewater sludge/biosolids from a major U.S. city, Chicago, over a 30+ year period; (2) compare PBDE concentrations in contemporary Chicago biosolids to those reported in the 2006−2007 U.S. EPA TNSSS; (3) examine geographical trends in PBDE concentrations by use of available EPA TNSSS data; (4) evaluate PBDE congener profiles in contemporary biosolids and biosolids-amended soils for evidence of degradation; and (5) assess the accumulation of PBDEs in corn grown on biosolids-amended soils.

EXPERIMENTAL SECTION

Historical Trends of PBDEs in Chicago Sewage Sludge/Biosolids. Forty-eight historical and recent sludge/biosolids samples, including those from the farmland application study described below, were provided by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). These were generated by several publicly owned WWTPs operating in the Chicago area between 1975 and 2008, using different wastewater treatment and solids stabilization approaches. Samples preceding in time the field application study had been air-dried and stored at room temperature in the dark. These storage conditions are consistent with those recommended by the National Institute of Standards and Technology for its freeze-dried Standard Reference Materials certified for semivolatile contaminants, including PBDEs (e.g., SRM 1944 sediment). All samples were examined for a range of PBDE congeners and the polybrominated biphenyl (PBB) congener PBB-153.

PBDEs in Agricultural Soils Amended with Contemporary Chicago Biosolids and in Corn Grown Thereon. Biosolids used in the farmland application study were generated at the MWRDGC Stickney WWTP between 2004 and 2007. This WWTP serves 2.4 million people and has a treatment capacity of 4.5 billion L/day, making it one of the largest in the world. Class B biosolids were generated by an activated sludge process, followed by anaerobic mesophilic digestion and dewatering by centrifugation. Mean moisture content of the biosolids received was 73.6% (standard deviation, SD, 3.7%). Biosolids were applied via common agricultural practices to two Illinois farm fields possessing heavy textured clay soil in Will County and a light-textured sandy soil in Kankakee County. Initially, biosolids were applied with a spreader and incorporated to a depth of 15−20 cm by plowing and discing. Plots at both sites received different rates of biosolids application (clay soil, 0, 2.1, 3.2, 4.3, 5.3, and 8.5 dry MT/hectare; sandy soil, 0, 1.1, 2.1, 3.2, 4.3, and 6.4 dry MT/hectare biosolids per year) for three consecutive years. Additional descriptions of the soils are available elsewhere.[10]

Aliquots of the biosolids applied at the two sites were analyzed for PBDEs (six samples, one per year and site). Surface soil samples were collected after the third annual biosolids application in the summer of 2007, by compositing five subsamples (taken with an auger from 0 to 15 cm depth) from each of the treatment plots. Corn (*Zea mays*) was grown in the soils by conventional agricultural practices. Corn stover (leaves and stalks) from the two highest biosolids rate plots and the nonamended plot (3 treatments × 2 replicates × 2 sites =

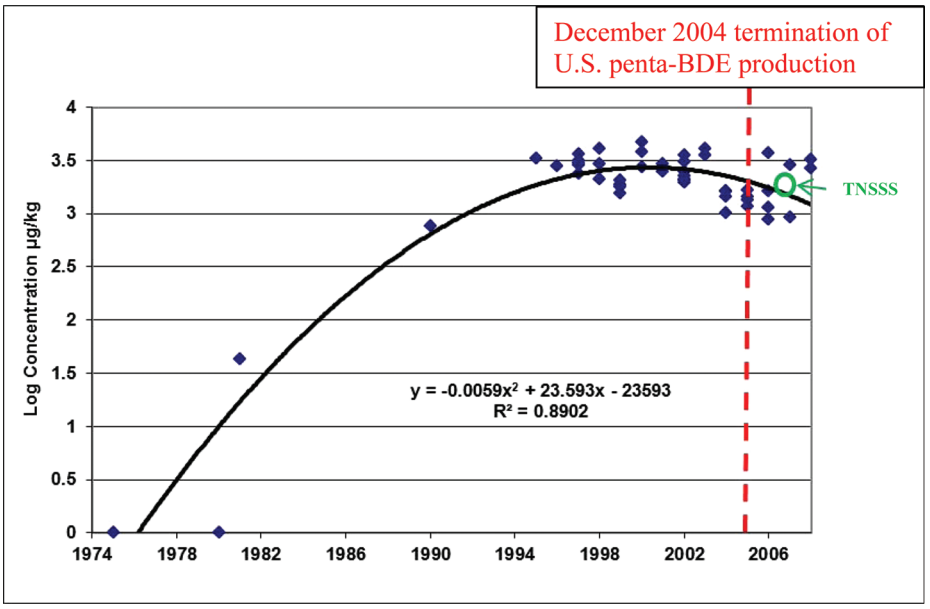


Figure 1. ∑Penta-BDE concentrations in Chicago WWTP sludge/biosolids generated between 1975 and 2008. For comparison, the mean ∑penta-BDE concentration from the 2006−2007 U.S. EPA TNSSS was 1760 μg/kg, consistent with values observed in contemporaneous Chicago sludge/biosolids.

12 samples) were collected to assess PBDE uptake. Grain was collected from all five biosolids-applied plots and the nonamended plot (6 treatments × 2 replicates × 2 sites = 24 samples). Roots, to a depth of 15 cm, were sampled from the five biosolids-applied plots only (5 treatments × 2 sites = 10 samples).

PBDE Analysis Methods. Details of the PBDE analytical methods are provided in the Supporting Information. Briefly, samples were lyophilized, spiked with a surrogate standard (BDE-166), and subjected to accelerated solvent extraction. Extracts were purified by size exclusion and silica gel liquid chromatography. An internal standard (decachlorodiphenyl ether) was added and the final extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) with electron-capture negative chemical ionization (EC-NCI). Quantitation was accomplished by use of five-point quantification curves and authentic standards. The following PBDE congeners were determined: BDEs 17, 28, 47, 49/71, 66, 85, 99, 100, 153, 154, 183, 196, 197, 201, 202, 203, 206, 207, 208, and 209. PBB-153 was analyzed separately by GC/MS in the electron impact ionization mode.

Study Quality Control. Sodium sulfate lab blanks were analyzed with each sample set to monitor for potential laboratory contamination. No PBDEs were detected in the blanks. Method quantitation limits varied by matrix type, as a function of their densities and the amounts extracted. These limits were 1−2 μg/kg for soil, 2−10 μg/kg for biosolids, and 1−5 μg/kg for corn samples (less brominated congeners and BDE-209, respectively). BDE-166 surrogate recoveries from the samples were as follows: biosolids 86.8% (SD 14.0%), sandy soil 102% (SD 4.5%), clay soil 99.6% (SD 15.4%), corn roots 93.5% (SD 14.2%), stover 104% (SD 10.6%), and grain 109% (SD 19.2%). PBDE concentrations in replicate samples agreed well. Three biosolids were also spiked with ^{13}C-labeled BDE-209 and BDE-166. Mean recoveries of these surrogates were similar, 108% and 106%, respectively.

RESULTS AND DISCUSSION

Environmental media such as sediments and archived biological samples (e.g., human sera and wildlife) have been widely utilized[11−14] to establish contaminant temporal trends. However, sediments must be dated by ancillary techniques and can be disturbed by physical and biological perturbations. Contaminant burdens in organisms may be influenced by gender, age, biotransformation, and migratory behaviors. Sediments and wildlife sampled are often distant from sources. Thus, contaminant burdens therein may be low and slow to respond to changes in societal chemical releases. Analysis of rapidly responding WWTP sludge/biosolids provides an avenue for early detection of the release of problematic chemicals. This provides an opportunity to implement pre-emptive strategies to stem further environmental dissemination. However, it should be noted that, over time, treatment strategies at WWTPs may change and this could alter POP sequestration in sludges/biosolids. Also, in general, sludge/biosolids must be collected at the time produced; although examination of POPs in sludge-only landfill samples has been suggested.[15]

Temporal Trends in Legacy POPs and PBDEs in Chicago Biosolids. The utility of sludge/biosolids analysis as a tool for identifying contaminant temporal trends is illustrated by examining burdens of PBBs, PBDEs, and polychlorinated biphenyls (PCBs). PBBs became notorious after their accidental introduction into livestock feed in Michigan in 1974. This led to a ban on U.S. production of the hexa-PBB product, in which PBB-153 was the major constituent congener. While this event is well-known, it is noteworthy that the total U.S. PBB production for the period 1970−1976 was only 6000 MT.[16] This is less than the North American penta-BDE demand for 2001 alone, that is, 7100 MT. Our analysis of archived Chicago WWTP sludges revealed PBB-153 levels in the 1975, 1980, and 1990 samples of 177, 41, and 67 μg/kg, respectively. PBB-153 was not quantifiable in later sludge samples. Zhu and Hites[14] noted a 1980 peak in

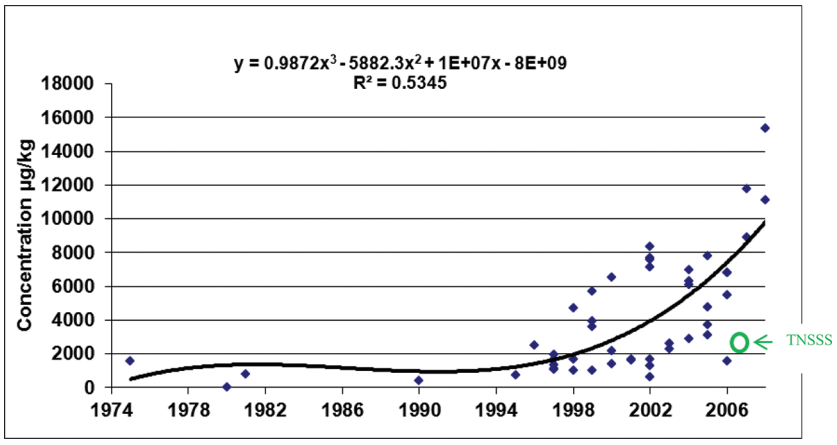


Figure 2. Concentrations of BDE-209 in Chicago sludges/biosolids from 1975 to 2008. The mean concentration in the EPA 2006−2007 TNSSS was 2310 μg/kg (standard deviation 3110).

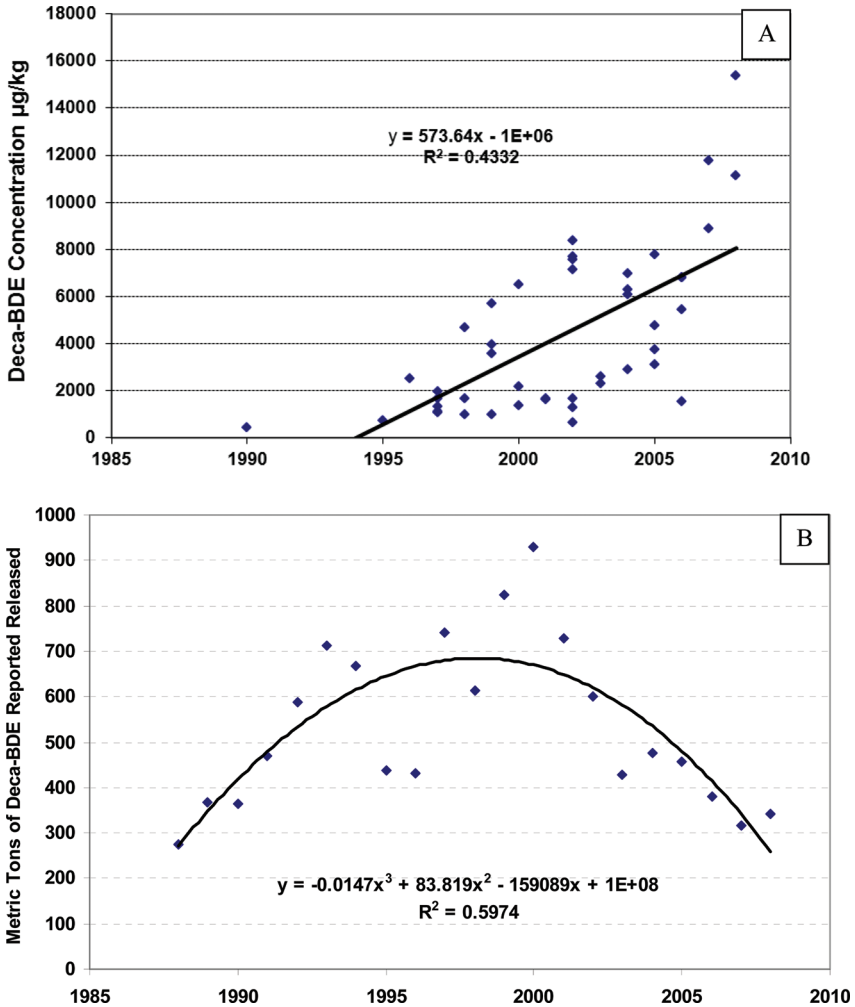


Figure 3. (A) Concentrations of deca-BDE (micrograms per kilogram) detected in Chicago wastewater sludges/biosolids (this study) from 1990 to 2008. (B) Amounts (MT) of deca-BDE reported released by U.S. industries via the U.S. EPA Toxics Reduction Inventory database from 1998 to 2008.

PBB-153 concentrations in Laurentian Great Lakes sediments, lagging the U.S. regulatory restriction on new PBB uses by 5 years. Due to their chemical similarity, PBDEs may have been marketed as a direct replacement for PBBs in many commercial applications. A mid-1970s date is also consistent with the appearance of PBDEs in dated environmental media. However, years passed between the presumed period of first usage and the initial 1981 report of PBDEs in wildlife.[17] Sludge/biosolids analysis may also reveal the reappearance of legacy chemicals in contemporary wastewater streams. For example, in 2007 substantial PCB levels were detected in samples of Milwaukee's biosolid product Milorganite.[18] The origin of the PCBs was

later identified as a shuttered metal die-cast facility. From there the PCBs are believed to have entered a sewer line and later traveled to a WWTP following pipe cleaning. Unfortunately, the chemical analysis was completed after the biosolids were applied on several city parks, triggering a soil remediation effort.

The PBDE congener profiles in the Chicago area historical sludges/biosolids we analyzed were similar to those of the penta- and deca-BDE commercial mixtures.[19] Time-trend analysis of ∑penta-BDE related congener (∑BDE 17, 28, 47, 49/71, 66, 85, 99, 100, 153, and 154) concentrations in these sludges suggest an exponential increase from the mid-1970s, peaking in the mid-1990s (Figure 1). Concentrations appeared to have leveled off ca. 2000 and may be decreasing thereafter. Octa-BDE-related congeners (mainly BDE-183) exhibited a similar temporal pattern but contributed only 2% of the total PBDEs in the sludges. Estimation of the octa-BDE contribution was confounded by overlap of congeners between the other two, more dominant commercial mixtures (e.g., BDE-207 in deca-BDE and BDE-153 in penta-BDE).[19]

Alcock et al.[20] suggested that the North American penta-BDE use may have peaked in the mid-1990s. The temporal trends we observed in sewage sludge/biosolids PBDE burdens are consistent with this. Kohler et al.[21] observed a peak in penta- and octa-BDE concentrations in Swiss lake sediments dated to the mid-1990s, while deca-BDE continued to increase. Hassanin et al.[22] reported a decrease in PBDE levels (BDE-209 was not assayed) in archived U.K. vegetation samples collected primarily between 1961 and 2004. Despite cessation of commercial penta- and octa-BDE production and efforts to restrict deca-BDE production and use, the bulk of PBDEs remain in in-service or discarded polymer products, wherein they routinely were added at percent levels. If escape from such products is a major release pathway, as has been suggested,[23] trends in environmental levels might be expected to lag changes in production.

Chicago Stickney WWTP biosolids generated between 2004 and 2007, and later applied to agricultural soils, contained mean ∑penta-BDE, ∑deca-BDE (∑BDEs 206, 207, 208, and 209), and ∑PBDE concentrations of 1080, 6630, and 7800 μg/kg, respectively. In biosolids from a mid-Atlantic U.S. WWTP, Andrade et al.[24] observed lower ∑penta-BDE (∑BDEs 28, 47, 99, 100, 153, and 154), BDE-209, and ∑PBDEs (∑BDEs 28, 47, 99, 100, 153, 154, 183, and 209) concentrations, that is, 574, 920, and 1500 μg/kg, respectively. They perceived no significant PBDE concentration changes over the short interval sampled, 2005−2008. The 2006−2007 EPA TNSSS data returned a higher mean for ∑penta-related congeners (∑BDEs 28, 66, 47, 85, 99, 100, 138, 153, and 154) for samples collected from across the United States, that is, 1760 μg/kg (SD 1510).[9] Maximum TNSSS-reported ∑penta-BDE and BDE-209 concentrations for the continental United States were 11 000 and 17 000 μg/kg, respectively. The mean BDE-209 level in the EPA TNSSS was lower than the 2004−2007 Chicago biosolids, that is, 2310 μg/kg (SD 3110). Unfortunately, BDEs 206, 207, and 208 were not determined in the TNSSS. These congeners are valuable for gauging the extent of degradation via dehalogenation. Some problems were reported during the TNSSS BDE-209 analysis that might have compromised its accurate determination.[9] Ricklund et al.[25] reported a mean BDE-209 concentration of 5240 μg/kg in five samples from U.S. WWTPs obtained from 1999 to 2000.

The trajectory of BDE-209 concentrations in the Chicago sludges/biosolids was relatively flat from 1974 to 1994 but increased thereafter (Figure 2). Log transformation of concentrations did not improve the overall trend line fit. The mean BDE-209 level in 2006−2007 Chicago biosolids was 6870 μg/kg (SD 3410), exceeding both the EPA 2006−2007 TNSSS mean and that reported in a multistate U.S. biosolids study[26] from 1999 to 2000 (mean 1010 μg/kg; SD 1400). Given that BDE-209 levels in Chicago biosolids were increasing rapidly from 1995 to 2006 (Figures 2 and 3A), the latter observation is understandable. The substantial between-sample variability observed may reflect intermittent releases or the distribution of major BFR sources, for example, textile operations. Differing industrial practices and levels of industrial product stewardship during plastics and textile manufacturing may also contribute. For example, incomplete emptying of BFR delivery containers by plastics and textile manufacturers prior to disposal was recently identified as a path for substantial releases to landfills.[8] Also, while the textile industry represents less than a third of total deca-BDE demand, it may contribute disproportionately to releases to WWTPs and surface waters.[8] Better management of aqueous waste streams could reduce that contribution.

While the temporal trajectory of BDE-209 concentrations in Chicago sludges/biosolids since 1990 (Figure 3A) was positive (doubling time 5 years), the nationwide industry-reported release of deca-BDE (based on the U.S. EPA Toxics Reduction Inventory (TRI) database)[27] peaked around 2001 (Figure 3B), coincident with rising concerns regarding PBDEs in the U.S. environment. This release estimate (to all compartments, including landfills) represented about 3% of the total reported 2001 North American deca-BDE demand of 24 500 MT. In contrast, the EU Voluntary Emissions Control Action Programme[8] reported an environmental release of only 0.1% of the total used by participating members in 2009.

Geographical Patterns of PBDEs in Sewage Sludges/Biosolids. California has the strictest flame retardancy standards in the United States. Hence, it has been postulated that PBDE usage might be more intensive in the West. Accordingly, we investigated the influence of WWTP location on sludge/biosolids ∑penta-BDE and BDE-209 concentrations by mining the EPA 2006−2007 TNSSS data.[9] The PBDE data were log-transformed to approximate normal distributions (confirmed by Shapiro Wilks tests) and then subjected to analysis of variance (ANOVA) ($p < 0.01$). Regional concentration relationships for ∑penta-BDE and BDE-209 showed different trends (see Supporting Information, Figure S1). For BDE-209, the ANOVA of regional differences was not statistically significant. However, differences might have been obscured by BDE-209 quantitation problems, as mentioned above. In contrast, ∑penta-BDE concentrations in sludges/biosolids differed statistically by region ($F_{3,74}$) = 3.46 (p 0.02). A posthoc comparison test (Newman−Keuls) indicated that ∑penta-BDE concentrations in northeastern biosolids were lower than midwestern (p 0.042) and western (p 0.01) biosolids but not southern WWTP solids (p 0.08). See Supporting Information for further details. Zota et al.[28] recently reported a similar regional ∑penta-BDE (∑BDEs 47, 99, and 100) concentration pattern (west > south > midwest > northeast) in human blood sera and higher indoor dust levels in California than other U.S. regions.

PBDEs in Chicago Biosolids Applied to Illinois Agricultural Plots. Mean ∑PBDEs in the 2004−2007 Chicago (Stickney WWTP) biosolids applied to the sandy soil (Kankakee County; biosolids collected in the spring) and clay soil (Will County; biosolids collected in the fall) were

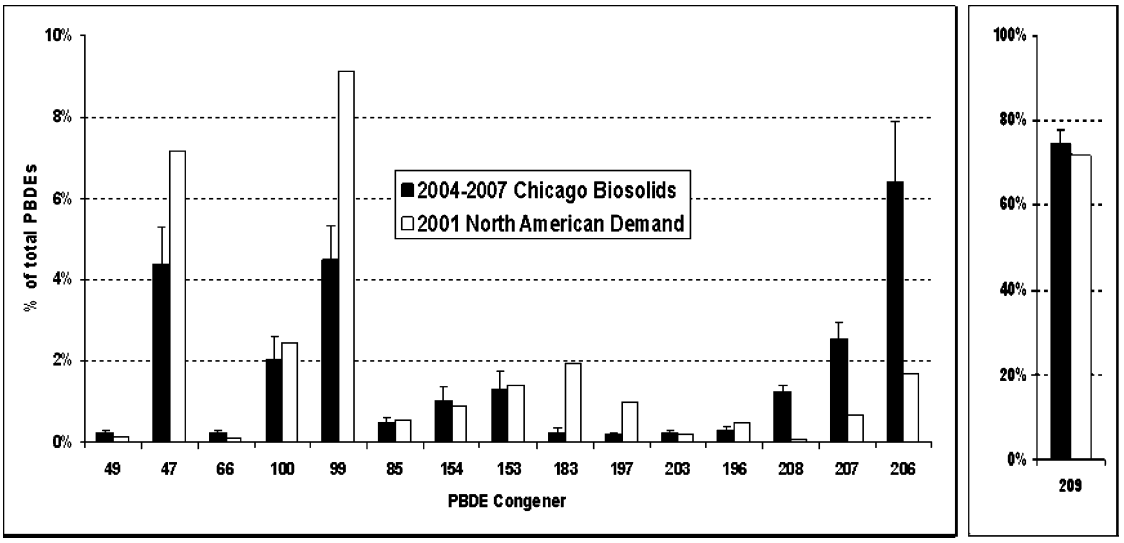


Figure 4. PBDE congener contributions in 2004−2007 Chicago-derived biosolids versus their predicted distribution based on 2001 North American PBDE demand and published commercial mixture compositions.[19] BDE-209 (right inset) is shown separately due to its large contribution.

significantly different (ANOVA, $p < 0.05$): 9060 μg/kg (SD 929) and 6530 μg/kg (SD 597), respectively. BDE-209 dominated in these biosolids, constituting on average 74% of the total PBDEs, and ranged from 4250 to 7840 μg/kg.

The congener profiles, as a percent of total PBDEs, were consistent between samples. We compared these profiles to predicted congener distributions (Figure 4) generated from the industry-reported 2001 North American market demands for the three commercial mixtures (penta-BDE, DE-71; octa-BDE, DE-79; and deca-BDE, Saytex 102E), weighted by their respective congener compositions.[19] BDE-209 (constituting 97% of the deca-BDE product Saytex 102E) dominated in these contemporary Chicago biosolids. Predicted and measured BDE-209 biosolid contributions matched well (Figure 4). Interestingly, BDE-206 was the next most abundant congener, and the levels of both BDE-206 and BDE-207 were 4-fold higher than predicted. In the Chicago biosolids, BDE-208 was 23-fold higher than we predicted. We hypothesize that these three nonabrominated congeners arise from BDE-209 degradation. Following a 238-day lab incubation, Gerecke et al.[29] reported anaerobic, microbially mediated dehalogenation of BDE-209 in sludge obtained from a mesophilic digester. A mixture of nona- and octa-BDEs was generated, with the level of BDE-208 being particularly increased. These authors commented that the presence of brominated primers enhanced the BDE-209 degradation rate by 2-fold. They noted that congener patterns in grab samples from a Swiss WWTP anerobic digestor, with a 28-day residence time, also supported BDE-209 degradation.

In the contemporary land-applied Chicago biosolids, BDEs 49, 66, 100, 85, 153, 154, 203, and 196 approximated our predicted contributions (Figure 4). In contrast, BDEs 47 and 99 (major penta-BDE congeners), as well as BDEs 183 and 197 (major octa-BDE constituents) were quantified at less than predicted levels. This might relate to decreasing releases following the December 2004 termination of U.S. penta- and octa-BDE manufacture, degradation to other constituents, or lower local usage of these products. Andrade et al.[24] also reported low contributions of BDE-183 to ∑PBDEs in mid-Atlantic U.S. biosolids collected from 2005 to 2008. This congener is often reported to be low in environmental samples. This relates to modest market demand but also perhaps to its use in electrical wiring and thermoplastics rather than in polyurethane foam (penta-BDE) and textiles (deca-BDE).

Stapleton and Dodder[30] suggested that the observation in environmental samples of BDE-202 (below detection in commercial deca-BDE mixtures) or a low BDE-197/BDE-201 ratio (these two octa-BDEs were not reported present in the deca-BDE product Saytex 102E and with a ratio >20 in the commercial octa-BDE) might indicate BDE-209 degradation. Debromination may occur via abiotic (e.g., photodegradation) or biologically mediated processes. In our 2004−2007 Chicago biosolids, we detected low concentrations of BDE-202 (mean concentration of 4.2 μg/kg; SD 1.17) and a BDE-197/BDE-201 ratio of 1.7. Dehalogenation is a concern as BDE-209 is now the most abundant PBDE congener in many abiotic media (such as soils, sediments, and sludge/biosolids), substantial amounts continue to enter the environment and the less brominated congeners exhibit higher bioaccumulation potentials.

PBDE Levels and Profiles in Biosolids-Applied Soil. Biosolids land-application rates are based on the nitrogen needs of crops. They typically are not reapplied annually, as a substantial fraction of nutrients are released gradually. However, in the current project, biosolids were applied for three consecutive years to two Midwest U.S. agricultural fields (clay soil and sandy soil) below, above, and at the agronomic rate. Soils amended with biosolids exhibited increased PBDE burdens versus nonapplied control plots. Concentrations of PBDEs increased linearly with the amounts of biosolids applied for the high clay soil ($r^2 = 0.866$; Figure 5) and sandy soil plots ($r^2 = 0.785$; see Supporting Information, Figure S2). Maximum soil ∑PBDE concentrations detected were 565 and 1810 μg/kg, respectively. The ∑PBDE concentrations measured in the biosolids-amended clay soil approximated the predicted values, based on the nominal amounts applied and measured levels in representative biosolids samples. However, the PBDE values determined in the sandy soils exceeded predictions. Soil densities of 1.3 and 1.6 g/cm^3 (high clay and sandy soil) and a biosolids incorporation depth of 15 cm were used to calculate expected soil PBDE concentrations. This apparent over-application might be due to loss of traction by the biosolids

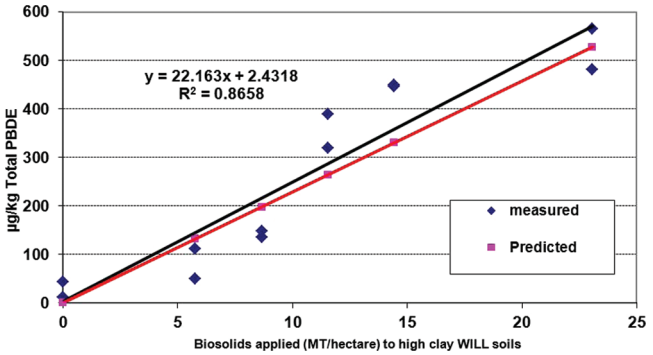


Figure 5. Measured PBDE concentrations in clay soil from the Will County site, in good agreement with predicted values, calculated from the expected biosolids application rates and PBDE concentrations determined in biosolids subsamples. This indicates PBDEs are relatively persistent and will accumulate in soils following repeated biosolids application.

spreading apparatus on the sandy soil. Indeed, Higgins et al.,[10] examining samples from the same plots, reported deviations from expected triclosan and triclocarban soil concentrations for the sandy soil plots.

As in the case of the biosolids themselves, the major congener detected in the soils was BDE-209, constituting 67−100% of the total PBDEs detected. The maximum soil ∑penta-BDE detected was 93.5 μg/kg. Low PBDE levels, mostly BDE-209, were also detected in the non-biosolids-applied clay soil control plots (replicates: 12.3 and 43.4 μg/kg).

BDE-209 was also the major congener detected in the sandy soil plots, constituting 66−87% of the total PBDEs detected. The maximum ∑penta-BDE detected in the sandy soil was 232 μg/kg. The congener distribution of the less brominated congeners (i.e., BDEs 47, 99, and 100) in both soils was similar to that reported in DE-71,[19] the dominant commercial penta-BDE product used in North America. While higher soil levels for electronic waste site soils have been reported, our PBDE concentrations were comparable to those reported by Wang et al.[31] for soil contaminated by burning of electronics waste in China.

Limited published data on PBDEs in agricultural soils following application of biosolids are available. Eljarrat et al.[32] examined soil PBDE levels after application of 15−25 dry MT of biosolids/hectare for 2 or 3 years at several agricultural sites in Spain, comparable to our higher application scenarios. The ∑PBDEs in the biosolids applied there ranged from 197 to 1185 μg/kg (dry weight). Observed soil levels ranged from 30 to 689 μg/kg. As expected, BDE-209 was the dominant congener. Spanish soil that received no intentional biosolids application exhibited a ∑PBDE concentration of 20.7 μg/kg, 71.0% of which was BDE-209. The authors concluded that PBDEs, including BDE-209, were persistent due to their continued presence in soils years after biosolids application. Andrade et al.[24] examined PBDEs in soils from 30 mid-Atlantic U.S. fields that had received varying amounts of biosolids from different WWTPs. PBDE soil burdens increased with the number of biosolids applications. They noted a lesser dominance of BDE-209 in biosolids-applied soils than in the biosolids that were applied, relative to BDEs 47 and 99. This was postulated to be due to BDE-209 degradation or higher penta-BDE burdens in the older biosolids. Likewise, Xia et al.[33] observed increasing ∑penta-BDE concentrations in U.S. soils receiving biosolids applications for 33 years. They also noted substantial accumulation of PBDEs in surface soils and minimal apparent degradation.

The relative contributions of BDE-206, BDE-207, and BDE-208 compared to BDE-209 in both the biosolids-amended clay and sandy soils were higher than in the commercial deca-BDE mixture[19] but did not exceed the ratios we observed in the biosolids that were applied. This is consistent with a lack of anaerobic conditions in the soil required for microbially mediated dehalogenation.

PBDE Concentrations in Corn. Several plant uptake pathways for PBDEs exist, but few studies, especially via land-applied biosolids, have been undertaken. Semivolatiles, such as PBDEs, may volatilize from soils and later sorb to the waxy outer surfaces of leaves or bark.[34] In the case of direct soil uptake, contaminants are believed to be first solubilized into soil interstitial water and then enter the roots and pass up the xylem to the remainder of the plant. Hence, plant uptake of hydrophobic compounds is expected to be limited.[35]

The extent of association between the PBDEs and the soil or biosolids matrix will influence their bioavailability. Uptake of PBDEs by Italian ryegrass (*Lolium multiflorum*), pumpkin (*Cucurbita pepo*), and maize (*Zea mays*) from weathered electronic waste recycling site soils in China[36] was recently examined. The authors reported preferential accumulation of the less brominated congeners, consistent with their greater water solubility and mobility. Decreasing PBDE levels were observed as one progressed from roots to stems and leaves. They noted planting reduced soil PBDE concentrations but attributed this predominantly to enhanced soil degradation and volatilization, rather than accumulation by the plant. Uptake of hydrophobic contaminants may be greater when soil amendment occurs via spiking with neat compounds rather than delivered via organic-rich media such as biosolids. For example, Huang et al.[37] observed substantial BDE-209 root/soil dry weight concentration ratios, ranging from 14% to 57% in various plants. Lipid content of the plant tissue was reported to be a strong determinant of dry weight PBDE content. Mueller et al.[38] harvested radishes (*Raphanus sativus*) and zucchini (*Cucurbita pepo*), grown for 10 weeks from seeds, on soils amended with penta-BDE at 75 μg/kg. However, these plants exhibited low PBDE levels, about 1 and 4 μg/kg, respectively. Interestingly, they reported that the organic solvent extractability of soil-amended penta-BDE increased 8-fold in the presence of a mixed consortium of plant species, compared to single species or in the absence of plants. They hypothesized that this might be due to plant exudates. Nevertheless, PBDE uptake in plants was not higher in mixed than monoculture plantings. Concentrations in zucchini shoots exceeded those in roots, and BDE-100 levels exceeded those of BDEs 47 and 99.

In the only published sludge/biosolids-related plant PBDE uptake study we located, Vrkoslavová et al.[39] grew nightshade (*Solanum nigrum*) and tobacco (*Nicotiana tabacum*) directly in undiluted biosolids (∑penta-BDE, 568 μg/kg; BDE-209, 400 μg/kg) over a 6 month period. These plants accumulated up to 15.4 and 76.6 μg/kg ∑penta-BDE, respectively, with highest levels in the stems versus the roots or leaves. Tobacco leaves accumulated 68.4 μg/kg ∑penta-BDE and 117 μg/kg BDE-209. No BDE-209 was detected in the tobacco leaves or roots. Beck et al.[40] noted that uptake of semivolatiles at high levels in sludge might be mediated by soil to air versus soil to root transfer due to the hydrophobicity of these compounds and strong sorption to soil organic matter. They also noted that biosolids have higher percentages of lipoidal materials that may

bind such contaminants more strongly than natural soil organic matter.

In our study we did not detect PBDEs in any of 46 corn grain, stover, or root samples examined (except for a single, apparently compromised stover control sample; see Supporting Information). Quantitation limits for BDE-209 were 5 μg/kg (dry weight basis) and 1−2 μg/kg for non-BDE-209 congeners. Lipophilic PBDEs associate with soil organic matter.[24,36] Total organic carbon content of our biosolids was 18−20%, about 10-fold higher than typical agricultural soils. Application of dewatered biosolids cake by agricultural spreaders disperses small organic-rich conglomerates rather than a homogeneous layer of material on the soil surface. The existence of such aggregates in soil may delay plant uptake of entrained PBDEs compared to other exposure scenarios, most notably organic solvent-based lab amendment. Indeed, Andrade et al.[24] hypothesized increasing PBDE persistence with increasing soil organic matter in biosolids-applied fields. Also, if PBDEs remain associated with small fragments of the original polymer as commercially produced, their bioavailability may be low, at least in the short term.[41] Teuten et al.[42] reported that equilibrium partition coefficients for hydrophobic contaminants and polymers, such as polyethylene, are orders of magnitude greater than for these contaminants and natural organic matter. These same authors also noted that addition of clean plastic to sediments reduced the availability of hydrophobic contaminants to aquatic invertebrates.

The referenced studies and our results indicate that physicochemical factors related to the soil/chemical compartment, as well as physiological and ecological aspects of the plants themselves, may influence uptake of PBDEs. Thus, additional research on the long-term fate and bioavailability of contaminants associated with land-applied biosolids is indicated.

■ ASSOCIATED CONTENT

Supporting Information

Additional text, two tables, and two figures with more detailed descriptions of analytical methodology and results. This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hale@vims.edu; phone: 804-684-7228.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Sample collection and partial funding were provided by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). Richard Stevens, U.S. EPA, provided access to a spreadsheet version of the TNSSS data. This is contribution 3209 from the Virginia Institute of Marine Science.

■ REFERENCES

(1) Kalogo, Y.; Monteith, H. State of the science report: Energy and resource recovery from sludge. Global Water Research Coalition, London, U.K., 2008.

(2) Biosolids applied to land: Advancing standards and practices. National Research Council. Committee on Toxicants and Pathogens in Biosolids Applied to Land, National Research Council, The National Academies Press, Washington, DC, 2002; http://www.nap.edu/catalog/10426.html

(3) Zubris, K. A. V.; Richards., B. K. Synthetic fibers as an indicator of land application of sludge. *Environ. Pollut.* **2005**, *138*, 201−211.

(4) Hale, R. C.; La Guardia, M. J.; Harvey, E.; Gaylor, M. O.; Mainor, T. M. Brominated flame retardant concentrations and trends in abiotic media. *Chemosphere* **2006**, *64*, 181−186.

(5) Webster, T. F.; Harrad, S.; Millette, J. R.; Holbrook, R. D.; Davis, J. M.; Stapleton, H. M.; Allen, J. G.; McClean, M. D.; Ibarra, C.; Abdallah, M.; Covaci, A. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. *Environ. Sci. Technol.* **2009**, *43*, 3067−3072.

(6) Duarte-Davidson, R. E.; Jones, K. C. Screening the environmental fate of organic contaminants in sewage sludges applied to agricultural soils: II: the potential for transfers to plants and grazing animals. *Sci. Total Environ.* **1996**, *185*, 59−70.

(7) Hale, R. C.; Alaee, M.; Manchester-Neesvig, J. B.; Stapleton, H. M.; Ikonomou., M. G. Polybrominated diphenyl ether (PBDE) flame retardants in the North American environment. *Environ. Int.* **2003**, *29*, 771−779.

(8) The Voluntary Emissions Control Action Programme: Annual Progress Report 2010. European Flame Retardants Association/ Bromine Science and Environmental Forum. http://www.vecap.info/uploads/VECAP_2011_light.pdf.

(9) Targeted National Sewage Sludge Survey Sampling and Analysis Technical Report, EPA-822-R-08-016. Office of Water, U.S. Environmental Protection Agency, Washington, DC, 2009; http://water.epa.gov/scitech/wastetech/biosolids/tnsss-overview.cfm.

(10) Higgins, C. P.; Paesani, Z. J.; Talia, E.; Chalew, A.; Halden, R. U.; Hundal, L.S.. Persistence of triclocarban and triclosan in soils after land application of biosolids and bioaccumulation in *Eisenia foetida*. *Environ. Toxicol. Chem.* **2011**, *30*, 556−563.

(11) Chernyak, S. M.; Batterman, S. A.; Gwynn, E. A.; Cantonwine, D.; Jia, C.; Begnoche, L. J.; Hickey, J. Trends of brominated diphenyl ethers in fresh and archived Great Lake fish (1979−2005). *Chemosphere* **2007**, *69*, 444−457.

(12) Sjodin, A.; Jones, R. S.; Focant, J. F.; Lapeza, C.; Wang, R. Y.; McGahee, E. E.; Zhang, Y. L.; Turner, W. E.; Slazyk, B.; Needham, L. L.; Patterson, D. G. Retrospective time-trend study of polybrominated diphenyl ether and polybrominated and polychlorinated biphenyl levels in human serum from the United States. *Environ. Health Perspect.* **2004**, *112*, 654−658.

(13) Park, J. S.; Holden, A.; Chu, V.; Choi, G.; Kim, M.; Shi, Y.; Chin, T; Chun, C.; Linthicum, J.; Walton, B. J.; McKeown, K.; Jewell, N. P.; Petreas, M.; Hooper, K. Time-trends and congener profiles of PBDEs and PCBs in California peregrine falcons (*Falcoperegrinus*). *Environ. Sci. Technol.* **2009**, *43*, 8744−8751.

(14) Zhu, L.; Hites, R. A. Brominated flame retardants in sediment cores from lakes Michigan and Erie. *Environ. Sci. Technol.* **2005**, *39*, 3488−3494.

(15) Capel, P. D.; Lichtensteiger, Th.; Brunner, P. H. The use of sludge-only landfills as historical records of persistent organic chemicals and heavy metals in sewage sludge. *Water Res.* **1989**, *23*, 525−527.

(16) Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers (PBBs and PBDEs). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services. Atlanta, GA, 1995. http://www.atsdr.cdc.gov/toxprofiles/tp68.pdf

(17) Andersson, Ö.; Blomkvist, G. Polybrominated aromatic pollutants found in fish in Sweden. *Chemosphere* **1981**, *10*, 1051−1060.

(18) Health Risks from Polychlorinated Biphenyls in Fertilizer Applied to Soil in Recreation Areas. Wisconsin Department of Health Services, June 23, 2009. http://www.atsdr.cdc.gov/hac/pha/MilwaukeePCBinMilorganite/HealthRisksfromPCBinFertilizerAppliedtoSoilinRecreationAreas6-23-09.pdf.

(19) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDEs technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40*, 6247−6254.
(20) Alcock, R. E.; Sweetman, A. J.; Prevedouros, K.; Jones, K. C. Understanding levels and trends of BDE-47 in the U.K. and North America: an assessment of principal reservoirs and source inputs. *Environ. Int.* **2003**, *29*, 691−698.
(21) Kohler, M.; Zennegg, M.; Bogdal, C.; Gerecke, A. C.; Schmid, P.; Heeb, N. V.; Sturm, M.; Vonmont, H.; Kohler, H.-P. E.; Giger, W. Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss lake sediments. *Environ. Sci. Technol.* **2008**, *42*, 6378−6384.
(22) Hassanin, A.; Johnston, A. E.; Thomas, G. O.; Jones, K. C. Time trends of atmospheric PBDEs inferred from archieved U.K. herbage. *Environ. Sci. Technol.* **2005**, *39*, 2436−2441.
(23) Hale, R. C.; Kim, S. L.; Harvey, E.; La Guardia, M. J.; Mainor, T. M.; Bush, E. O.; Jacobs, E. M. Antarctic research bases: local sources of polybrominated diphenyl ether (PBDE) flame retardants. *Environ. Sci. Technol.* **2008**, *42*, 1452−1457.
(24) Andrade, N. A.; McConnell, L. L.; Torrents, A.; Ramirez, M. Persistence of polybrominated diphenyl ethers in agricultural soils after biosolids applications. *J. Agric. Food Chem.* **2010**, *58*, 3077−3084.
(25) Ricklund, N.; Kierkegaard, A.; McLachlan, M. S. An international survey of decabromodiphenyl ethane (deBDethane) and decabromodiphenyl ether (decaBDE) in sewage sludge samples. *Chemosphere* **2008**, *73*, 1799−1804.
(26) Hale, R. C.; La Guardia, M. J.; Harvey, E. P.; Gaylor, M. O.; Mainor, T. M.; Duff, W. H. Flame retardants: Persistent pollutants in land-applied sludges. *Nature* **2001**, *412*, 140−141.
(27) U.S. EPA Toxics Reduction Inventory website. http://www.epa.gov/tri/.
(28) Zota, A. R.; Rudel, R. A.; Morello-Frosch, R. A.; Brody, J. G. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards? *Environ. Sci. Technol.* **2008**, *42*, 8158−8164.
(29) Gerecke, A. C.; Giger, W.; Hartmann, P. C.; Heeb, N. V.; Kohler, H. E.; Schmid, P.; Zenneg, M.; Kohler, M. Anaerobic degradation of brominated flame retardants in sewage sludge. *Chemosphere* **2006**, *64*, 311−317.
(30) Stapleton, H. M.; Dodder, N. G. Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. *Environ. Toxicol. Chem.* **2008**, *27*, 306−312.
(31) Wang, Y.; Luo, C.; Li, J.; Yin, H.; Li, X.; Zhang, G. Characterization of PBDEs in soils and vegetations near an e-waste recycling site in South China. *Environ. Pollut.* **2011**, *159*, 2443−2448.
(32) Eljarrat, E.; Marsh, G.; Labandeira, A.; Barcelo, D. Effect of sewage sludges contaminated with polybrominated diphenyl ethers on agricultural soils. *Chemosphere* **2008**, *71*, 1079−1086.
(33) Xia, K.; Hundal, L. S.; Kumar, K.; Armbrust, K.; Cox, A. E.; Granato, T. C. Triclocarban, triclosan, polybrominated diphenyl ethers, and 4-nonylphenol in biosolids and in soil receiving 33-year biosolids application. *Environ. Toxicol. Chem.* **2010**, *29*, 597−605.
(34) St-Amand, A.; Mayer, P. M.; Blais, J. M. Modeling atmospheric vegetation uptake of PBDEs using field measurements. *Environ. Sci. Technol.* **2007**, *41*, 4234−4239.
(35) Simonich, S. L.; Hites, R. A. Organic pollutant accumulation in vegetation. *Environ. Sci. Technol.* **1995**, *29*, 2905−2914.
(36) Huang, H.; Zhang, S.; Christie, P. Plant uptake and dissipation of PBDEs in the soils of electronic waste recycling sites. *Environ. Pollut.* **2011**, *159*, 238−243.
(37) Huang, H.; Zhang, S.; Christie, P.; Wang, S.; Xie, M. Behavior of decabromodiphenyl ether (BDE-209) in the soil-plant system: Uptake, translocation, and metabolism in plants and dissipation in soil. *Environ. Sci. Technol.* **2010**, *44*, 663−667.
(38) Mueller, K. E.; Mueller-Spitz, S. R.; Henry, H. F.; Vonderheide, A. P.; Soman, R. S.; Kinkle, B. K.; Shann, J. R. Fate of pentabrominated diphenyl ethers in soil: Abiotic sorption, plant uptake, and the impact of interspecific plant interactions. *Environ. Sci. Technol.* **2006**, *40*, 6662−6667.
(39) Vrkoslavová, J.; Demnerová, K.; Macková, M.; Zemanová, T.; Macek, T.; Hajšlová, J.; Pulkrabová, J.; Hrádková, P.; Stiborová, H. Absorption and translocation of polybrominated diphenyl ethers (PBDEs) by plants from contaminated sewage sludge. *Chemosphere* **2010**, *81*, 381−386.
(40) Beck, A. J.; Johnson, D. L.; Jones, K. C. The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils. *Sci. Total Environ.* **1996**, *185*, 125−149.
(41) Gaylor, M. O.; Harvey, E.; Hale, R. C. House crickets can accumulate polybrominated diphenyl ethers (PBDEs) directly from polyurethane foam common in consumer products. *Chemosphere* **2012**, *86*, 500−505.
(42) Teuten, E. L.; Rowland, S. J.; Galloway, T. S.; Thompson, R. C. Potential for plastics to transport hydrophobic contaminants. *Environ. Sci. Technol.* **2007**, *41*, 7759−7764.

Concentrations of Polybrominated Diphenyl Ethers in Air and Soil on a Rural−Urban Transect Across a Major UK Conurbation

STUART HARRAD* AND STUART HUNTER

Division of Environmental Health and Risk Management, Public Health Building, School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, United Kingdom

Polybrominated diphenyl ethers (PBDEs) were measured in air (using PUF disk passive samplers) and soil samples taken at approximately monthly intervals over 1 year at 10 locations on a transect across the West Midlands of the UK. Concentrations in air are consistent with those detected elsewhere in Europe and the Great Lakes basin. Concentrations in soil fall within the range reported for rural woodland and grassland soils in the UK and Norway. In both air and soil, concentrations clearly decrease with increasing distance from the city center, supporting the existence of an urban "pulse", indicating the West Midlands conurbation to be a source of PBDEs to the wider environment. Examination of seasonal trends revealed no evidence of a "spring pulse" in concentrations in air, with no summer peak in concentrations in air observed for 70% of sites. The PBDE congener pattern in air differs from that in soil, with ratios of congeners 47:99 higher in air than in soil. It is hypothesized that PBDEs volatilize from treated products indoors, before ventilating outdoors, where congener 99 undergoes preferential atmospheric deposition and accumulation in soil.

Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated compounds widely used as flame retardants. In recent years, production and use of PBDEs has been in the guise of three formulations: penta (consisting primarily of BDEs 47 and 99 (37% each), alongside smaller amounts of other tetra-, penta-, and hexa-BDEs); octa (a mixture of hexa (10−12%), hepta- (44−46%), octa- (33−35%), and nona- (10−11%); and deca (98% decabromodiphenyl ether (BDE 209) and 2% various nona-BDEs) (*1*, *2*). Worldwide, PBDE production is dominated by the deca commercial formulation, with global demand in 2001 an estimated 56 100 t (*3*). This is similar to the 1999 estimate of 54 800 t (*4*). By comparison, 2001 global demand for the penta product was 7500 t (*3*), down slightly from 8500 t in 1999 (*4*). Production and use of commercial PBDE formulations in Europe was considerably less than that in North America; for example, in 2001, 7100 t of penta product was used in North America, compared to just 150 t in Europe (*3*). The uses for these commercial formulations are myriad: the penta product was employed principally to flame-retard polyurethane foams in carpet underlay, furniture, and bedding; the octa formulation was used to flame-retard thermoplastics such as high-impact polystyrene, and the deca product is used principally in plastic housings for electrical goods such as TVs and computers, as well as in textiles (*1*). As a result of concerns surrounding these contaminants owing to their presence in the diet and indoor air and dust (*5*−*7*), and human tissues (*8*), coupled with evidence relating to their potential adverse effects on human health (*2*, *9*), several jurisdictions have banned the marketing and use of penta- and octa-BDEs. Furthermore, the main United States producer and the U.S. EPA, have reached a voluntary agreement to discontinue production of the penta- and octa-BDE mixtures. Despite this, there remain comparatively few data relating to their presence in outdoor air, with information relating to their concentrations in soil also restricted. With respect to outdoor air, while the limited ($n = 6$) data reported by our group for Birmingham, U.K. (*5*), suggested concentrations to be in line with those reported for Chicago (*10*), other—again limited ($n = 7$)—data from a Europe-wide study suggest the UK to be the focus of the most contaminated locations, with the highest contamination detected in major urban centers such as Manchester, Middlesborough, and London (*11*). There is only one substantial survey reporting concentrations of PBDEs in surface soils, revealing concentrations in UK grassland ($n = 16$), and both UK ($n = 17$) and Norwegian ($n = 21$) woodland (i.e., rural) soils to be similar in magnitude to those detected for PCBs (*12*). Given this, we set out to study the atmospheric and edaphic behavior of PBDEs within the West Midlands conurbation (population 2.5 million), at the heart of which is Birmingham (population 1 million), the second most populous UK city.

This study reports concentrations of a number of PBDE congeners in outdoor air (using PUF disk passive air samplers) and surface soil taken from 10 locations on a 79 km transect across the West Midlands. The direction of the transect corresponds with the prevailing wind direction (i.e., from the southwest (upwind) to the northeast (downwind) of the West Midlands) thereby affording a potential insight into the role of the heavily urbanized center as a source of PBDEs to the wider environment. By covering distances from Birmingham city center of 48 km southwest to 31 km northeast with intersite distances of 3−17 km, spatial variation between a range of rural, sururban, and urban locations could be studied. Samples of both air and soil were taken on an approximately monthly basis at each location, thereby facilitating elucidation of seasonal trends.

While recognizing that other PBDE congeners such as BDE 49, 66, 75, and 85 etc. may be present in measurable quantities in air, we focused on BDEs 28, 47, 99, 100, 153, and 154. These congeners were selected for two principal reasons, specifically: (i) they have been identified as the most abundant in air (*11*) and soil (*12*), and (ii) they are the principal congeners monitored in previous comparable studies (*10*). Although decabromodiphenyl ether is being increasingly reported, it was not included in this study owing to the difficulties in achieving its reliable determination at the outset of the study (*13*).

Our principal objectives were the following: (1) to significantly augment the worldwide database on concentrations of PBDEs in both outdoor air and topsoil; (2) to assess the spatial and seasonal variation of concentrations and congener profiles of PBDEs in outdoor air and topsoil within

* Corresponding author e-mail: S.J.Harrad@bham.ac.uk; phone: +44 121 414 7298; fax: +44 121 414 3078.

10.1021/es0606879 CCC: $33.50
Published on Web 06/21/2006

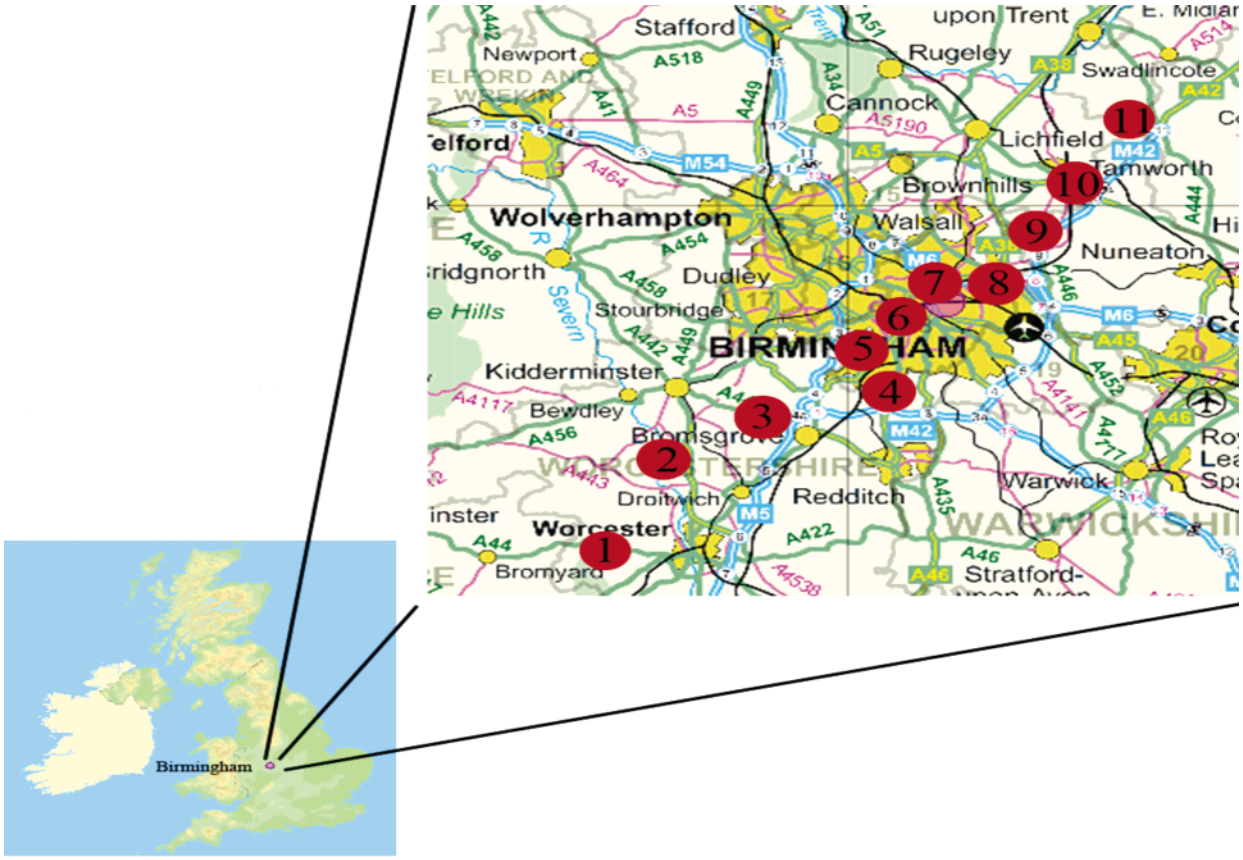


FIGURE 1. Sampling locations.

TABLE 1. Sampling Site Information

site	distance from city center (km)	site classification	site name
1	48	rural	Whitbourne
2	31	rural	Bishops Wood
3	21	rural	Chaddesley Wood
4	11	suburban	West Heath
5	6	suburban	Weoley Castle
6	3	urban	EROS
7	0	urban (city center)	Centenary Square
8	6	urban	Hodge Hill
9	18	rural	Kingsbury Water Park
10	23	suburban	Tamworth
11	31	rural	Newton Regis

TABLE 2. Sampling Periods at All Sites and Air Temperatures at Site 6 Averaged over Each Sampling Period

sample	period date	mean air temp. (°C)
1	16/08/2003 – 06/10/2003	10.8
2	06/10/2003 – 07/11/2003	9.4
3	07/11/2003 – 10/12/2003	10.1
4	10/12/2003 – 19/01/2004	6.6
5	19/01/2004 – 19/02/2004	4.1
6	19/02/2004 – 26/03/2004	5.8
7	26/03/2004 – 23/04/2004	9.2
8	23/04/2004 – 17/06/2004	13.2
9	17/06/2004 – 30/07/2004	14.7
10	30/07/2004 – 01/09/2004	17.4
11	01/09/2004 – 15/10/2004	11.9

the West Midlands; and (3) to use these data to further understanding of the environmental sources and fate of PBDEs, in particular the significance of urban areas as source regions.

Experimental Section

Sampling Strategy. Outdoor air and soil samples were collected from 10 sites within the West Midlands conurbation. Sampling sites were located on a southwest (upwind) to northeast (downwind) transect at intervals of between 3 and 17 km across the conurbation. Hence, a mix of rural, suburban, and urban sampling locations was studied. Figure 1 shows the location of each outdoor sampling location, with each number relating to a specific location for which relevant data are given in Table 1. Table 2 provides information on the average air temperature recorded at site 6 (meteorological information was not available for the other sites) and the dates of each sampling period (these were identical for all sites). For operational reasons, sampling at location 10 ceased after 2 months and no data are reported for this site. At each location, 11 paired air and soil samples were taken.

Air Sampling. Passive air samplers (i.e., PUF disks) were employed to provide a time-integrated sample over each sampling period. These have been used successfully in other studies (*11*, *14*). To provide sufficient contaminant mass, four PUF disk samplers (each comprising one shelter each fitted with one PUF disk) were simultaneously deployed approximately 20 cm apart at a height of 1.5 m above the surface at each site and combined after sampling to provide 1 sample for analysis. Each PUF disk measured 14 cm in diameter and 1.2 cm in thickness, giving a surface area of 360 cm^2, and density 0.01685 g cm^{-3}. Disks were sheltered by two different size stainless steel housings (18 cm diameter, 1 L bottom housing and 23 cm diameter, 2 L top housing, respectively). Prior to deployment, disks were washed thoroughly in tap and distilled water sequentially to remove loose material, then extracted in hexane using a Soxhlet apparatus for 48 h to remove any target or interfering

TABLE 3. Average[a] (σ_{n-1}) Concentrations (pg m^{-3}) of PBDEs in Air Samples in This and Other Studies Employing PUF Disk Samplers

site/reference	28	47	99	100	153	154	ΣBDE	47:99 ratio
1	0.50 (0.52)	2.78 (1.17)	0.97 (0.45)	0.39 (0.11)	0.15 (0.16)	0.12 (0.12)	4.92 (2.02)	2.95 (0.96)
2	0.32 (0.31)	1.63 (0.94)	0.49 (0.27)	0.23 (0.12)	0.11 (0.15)	0.07 (0.10)	2.84 (1.61)	3.49 (1.23)
3	0.55 (0.35)	2.31 (0.72)	0.76 (0.27)	0.40 (0.13)	0.11 (0.05)	0.12 (0.18)	4.25 (1.45)	3.19 (0.79)
4	0.87 (0.50)	5.89 (1.86)	1.98 (0.69)	0.89 (0.40)	0.40 (0.36)	0.26 (0.14)	10.3 (3.39)	3.04 (0.59)
5	1.15 (0.89)	8.22 (2.20)	2.64 (0.85)	1.23 (0.48)	0.51 (0.54)	0.29 (0.14)	14.0 (4.17)	3.22 (0.75)
6	1.65 (0.60)	10.4 (1.78)	3.25 (0.98)	1.56 (0.49)	0.48 (0.19)	0.43 (0.13)	17.8 (3.2)	3.62 (1.79)
7	2.04 (0.77)	13.73 (2.72)	4.26 (1.13)	2.08 (0.60)	0.63 (0.22)	0.53 (0.08)	23.3 (4.23)	3.45 (1.26)
8	1.44 (0.63)	6.64 (2.15)	2.22 (0.90)	0.95 (0.35)	0.29 (0.13)	<0.1	11.5 (3.79)	3.16 (3.37)
9	0.87 (0.41)	4.95 (1.73)	1.55 (0.62)	0.73 (0.31)	0.20 (0.07)	0.17 (0.10)	8.47 (3.04)	3.37 (1.07)
11	0.55 (0.32)	3.90 (0.78)	1.28 (0.32)	0.60 (0.19)	0.17 (0.08)	0.16 (0.05)	6.67 (1.41)	3.15 (0.74)
EROS (*5*)[c]	na[b]	9.4 (5.5)	5.0 (2.4)	1.4 (0.96)	2.9 (1.8)	1.8 (0.46)	21 (8.7)	3.57
Europe-wide (*11*)	<0.5−30	<8−80	<10−120	<2−20	<0.7−15	<0.8−10	0.5−250[d]	
Ottawa (*15*)	0.095 (0.089)	0.87 (0.11)	1.1 (0.78)	0.11 (0.15)	na	na	2.2 (1.7)	
Great Lakes Basin[e] (*16*)	0.2−2.0	2.5−25	1.5−10	0.6−2.2	0.4−0.9	0.4−0.8	<3−37	
Asia (*27*)	<0.13−130	<0.13−78	<0.13−50	<0.13−5.5	Na	na	<0.13−340[f]	
Toronto (*14*)	0.11−2.19	1.50−15.7	0.53−7.34	0.17−2.36	0.00−0.61	0.03−0.46	2.7−30.0[g]	

[a] Where congener was not detected, concentration assumed to equal zero for purposes of calculating averages and standard deviations. [b] Not analyzed. [c] Obtained using high-volume air samplers; same as site 6 in this study. [d] Sum of PBDEs 28, 47, 49, 75, 99, 100, 153, and 154. [e] Concentrations given as the range of annual averages for 15 sites covering a range of urban and rural locations. [f] Sum of PBDEs 17, 28, 32, 47, 49, 75, 99, and 100. [g] Sum of PBDEs 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 138, 153, 154, and 183.

compounds. Following extraction, disks were desiccated to remove solvent, spiked with known quantities of PCBs 19 and 147 as QA/QC standards to provide a measure of contaminant loss during sampling, and stored in pre-cleaned foil in airtight solvent-cleaned glass jars. On deployment, disks were removed from the jars on site and transferred into the shelters. At the end of each sampling period, disks were removed from shelters and stored in solvent-cleaned aluminum foil in airtight glass jars at 4 °C until extraction.

Conversion of contaminant masses per sample into concentrations in air requires knowledge of the air sampling rate of the PUF disk samplers employed and the sampler deployment time. Examination of the literature relating to sampling rates of similar PUF disk sampler configurations employed outdoors led us to select a sampling rate of 4 m^3 day^{-1} for PBDEs (*11*). It must be acknowledged that there is a degree of uncertainty associated with extrapolation of sampling rates derived for one sampler configuration to another, and the use of a uniform rate independent of sampling temperature and congener. However, the close correlation between concentrations derived at site 6 via both active high-volume samplers (*5*) and in this study (Table 3), gives confidence that the selected sampling rate is appropriate for the configuration employed here, and that the concentrations reported are sufficiently accurate to facilitate comparison of spatial and seasonal trends.

Soil Sampling. Soil samples were collected at the same locations as the air samples, at the end of each air sampling period. At each sampling event, 3 subsamples were taken using a soil corer to 5 cm from the same 10 m × 10 m area immediately adjacent to the air sampler. Samples were pooled, transported back to the laboratory, immediately transferred to clean, solvent-rinsed, amber glass storage bottles, sealed, and stored at −18 °C until analysis. Before extraction, soil samples were homogenized, an accurately weighed 50 g subsample was mixed with anhydrous sodium sulfate (20 g), and transferred to a clean Soxhlet apparatus.

Determination of Soil Organic Carbon Content. Aliquots of soil sampled at each site during sampling period 7 (March−April 2004), were subjected to determination of their organic carbon content using a Leco RC-412 instrument.

Analytical Protocols. Samples were treated with known quantities of internal standards ($^{13}C_{12}$−BDEs 28, 47, 99, and 153), prior to Soxhlet extraction for 12 h with hexane (air samples), and hexane/acetone (2:3 v/v) (soil samples). Concentrated crude extracts were washed with water (soil samples only), then concentrated H_2SO_4, prior to further purification via the following: elution through a florisil column (10 g) with dichloromethane (50 mL) (soil samples only), solvent exchange to hexane followed by lipid removal via solvent exchange between dimethyl sulfoxide and hexane, and florisil chromatography (2 g, eluted with 20 mL hexane). After concentration and solvent exchange to nonane, GC/MS analysis was conducted on a Fisons MD-800 instrument fitted with a Varian Factor 4 VF-5ms column (60 m × 0.25 mm i.d., 0.25 μm film thickness). A 1-μL aliquot of sample extract was injected in splitless mode at an injector temperature of 280 °C. The oven temperature program was as follows: 140 °C for 2 min; 5 °C/min to 200 °C; 2 °C/min to 300 °C; and held for 10 min. Twenty ions (for BDE-28 and $^{13}C_{12}$−BDE-28: 405.8, 407.8, 417.8, and 419.8; BDE-47 and $^{13}C_{12}$−BDE-47: 485.8, 487.8, 495.8, 497.8; BDEs 99 and 100, and $^{13}C_{12}$−BDE-99: 403.8, 405.8, 415.8, 417.8; and BDEs 153, 154, and $^{13}C_{12}$−BDE-153: 481.7, 483.7, 493.7, 495.7; plus for QA/QC PCB standards 19 and 147: 255.95, 257.95, 359.9, and 361.9) were monitored in 5 acquisition groups in EI selected ion monitoring mode (ionization voltage, 70 eV; ion source temperature = 250 °C).

Peaks were accepted only if the following criteria were met: signal-to-noise ratios for the least abundant ion exceeded 3:1; peaks eluted within 5 s of standards run in the same batch as the samples; and isotope ratios for peaks were within 20% of those obtained for standards run in the same batch as the samples.

Field blanks consisting of a PUF disk (treated identically to those used for sampling, except that no air was aspirated through them) for air samples (n = 11), and method blanks (i.e., as field blanks but PUF disks were not transported to/from sampling site) (n = 5) were analyzed and found to contain concentrations of target PBDEs no greater than 6% of the concentrations found in the corresponding samples. Our data are thus not corrected for blank concentrations. Average recoveries of internal standards for all samples ranged from 45% ($^{13}C_{12}$−BDE-153) to 67% ($^{13}C_{12}$−BDE-47). Similarly, average recoveries of the QA/QC standards (PCBs 19 and 147) added to the PUF disks prior to sampling to provide an indication of measure of contaminant loss during sampling *and* analysis combined, were 95 and 75%, respectively. Air sample concentrations were not corrected for such losses. The repeatability of our passive sampling and analytical procedures combined was evaluated by simultaneously deploying 4 passive samplers at the same location.

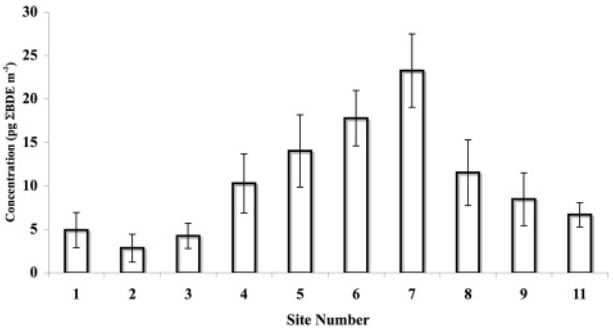


FIGURE 2. Spatial variation of average concentrations (pg m^{-3}) of ΣBDE in air samples (error bars are ±1 σ).

The low relative standard deviations observed for concentrations of the target PBDE congeners (average 3.8%; range 0.9−6.0%) demonstrate good repeatability for our sampling and analytical method. Method detection limits for individual BDEs were typically 0.05 pg m^{-3} and 0.5 pg g^{-1} dry weight for air and soil samples, respectively. The accuracy of our methods is indicated by our satisfactory performance in the 2002 BSEF/QUASIMEME interlaboratory comparison on brominated flame retardants (*5*).

Results and Discussion

PBDE Concentrations in Air. Table 3 summarizes the concentrations of target PBDEs in air samples taken in this study. A full dataset containing concentrations in each sample is provided as Supporting Information (Table S1). The concentrations recorded in this study are compared with others of relevance. Particularly relevant are those recorded for Site 6, as this is identical to the location for which PBDE concentrations have been recorded previously (*5*). Given that the sample sets were taken 2−3 years apart, using different sampling equipment and sampling durations (the earlier study used high-volume active air samplers over 48 h periods), there is a remarkably strong similarity between the two data sets. The one noticeable discrepancy is that the earlier study reported higher concentrations of BDEs 153 and 154. It seems likely that this reflects the fact that passive PUF disk samplers sample primarily the gas phase, which represents a relatively small proportion of the total airborne concentrations of these congeners (*5*). Compared to the other studies summarized in Table 3—all of which used similar PUF disk passive samplers—concentrations in this study are noticeably higher than those recorded in outdoor air in Ottawa (*15*), but well within the ranges reported for larger studies covering sites within Europe (*11*), the Great Lakes basin (*16*), and along an urban−rural transect in Toronto (*14*). Although to date based on a limited dataset, the similarity in concentrations of PBDEs in European and North American outdoor air and diet (*5*), is not inconsistent with recent claims that intercontinental differences in indoor contamination are the explanation for the higher body burdens in North Americans compared to Europeans (*6*, *17*).

Figure 2 reveals a clear "urban pulse", whereby concentrations are highest at Birmingham city center (site 7) and decrease with distance from the center. We have expressed the magnitude of this pulse as the ratio of the average concentration detected at the city center to the average concentration for all sites. For air samples, it is 2.2. Furthermore, the higher concentrations to the northeast of the city center (sites 9 and 11) cf. those to the southwest (sites 2 and 3) are not inconsistent with the city center being a source of PBDEs to upwind locations. These findings are in line with those recently reported for an urban−rural transect in Toronto (8 locations, simultaneously sampled over 3 periods), that showed downtown concentrations to be about a factor of 2 higher than those at rural sites (*14*).

Seasonal Variation and Temperature-Dependence of Concentrations of PBDEs in Air. A "spring pulse", whereby atmospheric concentrations of semivolatile organic contaminants (SOCs) are at a maximum in the spring has been reported (*18*). Our data showed no evidence of such a phenomenon (concentrations for sampling periods 7 and 8 in Table S1 are not noticeably elevated above those for other sampling periods), suggesting that such a spring pulse—hypothesized to arise due to increased surface−air exchange of SOCs that have accumulated in the surface layer during the winter—does not occur in temperate climates such as the West Midlands. There is a well-established positive linear relationship between atmospheric concentrations of PCBs and air temperature (*19*, *20*), which has more recently been observed for PBDEs (*21*). Although our dataset was not designed to study such relationships (being limited with respect to the numbers of samples taken at each site (*22*), unable to capture short-term responses in concentrations to temperature fluctuations, and temperature data was available only for site 6), we examined the relationship between concentrations of BDE 47 (as the most prevalent congener constituting ∼57% of ΣBDE) and air temperature averaged over each sampling period. Interestingly, while there were significant positive relationships for the city center (site 7; $p < 0.01$), site 9 ($p < 0.05$), and site 4 ($p = 0.1$); no such significant relationships ($p > 0.1$) were observed for any of the other sites. Notwithstanding the aforementioned caveats that preclude overinterpretation of this apparent lack of temperature-dependence, it is still surprising that at 70% of the sites monitored, no "summer peak" in concentrations was detected. As this implies that volatilization of PBDEs from environmental surfaces such as soil is not the dominant source to the atmosphere at many sites in this study, this aspect clearly warrants further attention.

PBDE Concentrations in Soil. Table 4 summarizes concentrations (pg g^{-1} dry weight) of target PBDEs in soil samples taken in this study. Comparison with concentrations reported previously for rural woodland and grassland UK and Norwegian soil samples, shows our data to fall within these previously reported ranges. As concentrations of POPs in soil are strongly influenced by the organic carbon/matter content of the soil, Table 5 summarizes the concentrations of PBDEs in soils when normalized for soil organic carbon content. A full dataset containing concentrations (both dry weight and organic carbon basis) in each sample is provided as Supporting Information (Table S2). As for air samples, a marked "urban pulse" is apparent (Figure 3), whereby organic carbon-normalized concentrations are highest at Birmingham city center (site 7). This pulse is expressed as the ratio of the average concentration detected at the city center to the average concentration for all sites. This urban pulse is greater for soil (4.89) than for the corresponding air samples (2.2). As for the corresponding air samples, there is clearly a strong decline in organic carbon-normalized concentrations of ΣBDE and the distance from the city center (Figure 3). Similar declines in concentration with distance from city center exist for all individual target congeners.

Sources of PBDEs. In line with previous indications (*10*, *14*, *16*, *21*, *23*), the existence of the "urban pulse" observed in this study is strong evidence that urban areas act as sources of PBDEs. Given the lack of temperature-dependence of PBDE concentrations in air samples in most locations in this study, which implies that volatilization from environmental surfaces such as soil is not a significant source to the atmosphere; we hypothesize that the high density of indoor environments contaminated with PBDEs due to usage of, e.g., furnishings and electronic goods (*5*) in urban areas, results in significant emissions when these environments exchange air with outdoors.

TABLE 4. Average (σ_{n-1}) Concentrations (pg g^{-1} DW) of PBDEs in Soil Samples in this Study and Elsewhere (*12*)

site/description	28	47	99	100	153	154	ΣBDE	47:99 ratio
1	11.9 (6.3)	67.8 (8.0)	102 (51.9)	20.5 (11.1)	19.1 (11.1)	14.1 (10.3)	235 (58.4)	0.85 (0.43)
2	4.3 (4.1)	34.6 (6.2)	int[a]	17.1 (13.5)	13.6 (5.7)	6.6 (7.1)	73.2 (16.7)	
3	10.8 (5.9)	62.7 (6.6)	88.1 (59.8)	18.5 (12.5)	21.9 (12.0)	15.0 (13.3)	217 (70.1)	0.65 (0.23)
4	10.6 (5.0)	59.9 (5.9)	102 (54.9)	24.8 (19.9)	25.6 (4.3)	17.5 (9.5)	241 (70.4)	0.88 (0.72)
5	13.0 (4.0)	101 (36.9)	177 (64.0)	38.3 (13.9)	41.8 (5.0)	29.7 (12.7)	401 (51.0)	0.73 (0.52)
6	17.2 (4.7)	114 (32.9)	227 (79.6)	60.6 (11.2)	64.0 (9.8)	65.4 (44.4)	538 (82.2)	0.61 (0.34)
7	116 (20.2)	909 (34.1)	1710 (110)	392 (17.0)	410 (24.3)	357 (41.6)	3890 (139)	0.53 (0.04)
8	27.2 (4.3)	190 (7.1)	382 (63.6)	79.2 (14.0)	96.6 (8.6)	66.2 (44.2)	841 (46.4)	0.51 (0.11)
9	10.1 (6.2)	69.0 (7.2)	131 (53.2)	25.2 (12.3)	29.6 (10.9)	19.9 (9.5)	285 (63.1)	0.63 (0.30)
11	9.4 (5.6)	65.2 (7.4)	130 (52.6)	21.1 (14.6)	27.5 (6.1)	19.8 (8.7)	273 (59.8)	0.60 (0.27)
UK grassland soils[b]	17 (12−21)	61 (7−520)	280 (78−3200)	36 (8−470)	72 (19−600)	22 (8−240)	440[c] (15−5000)	
UK woodland soils	21 (8−200)	490 (50−1400)	900 (190−3200)	110 (11−360)	210 (38−1200)	100 (14−420)	1800[c] (75−5600)	
Norwegian woodland soils	29 (8−49)	250 (12−860)	360 (63−1400)	58 (18−230)	51 (11−270)	46 (13−310)	710[c] (90−2600)	

[a] Int = interference prevented quantification of BDE 99 in all samples from this site. [b] Median − average not given (range in parentheses). [c] Sum of PBDEs 47, 99, 100, 153, and 154.

TABLE 5. Average (σ_{n-1}) Concentrations (pg g^{-1} OC) of PBDEs in Soil Samples in This Study

site	28	47	99	100	153	154	ΣBDE
1	230.4 (121.1)	1309 (153.6)	1968 (1001)	395.9 (213.8)	368.4 (213.8)	273.1 (199.1)	4545 (1128)
2	177.7 (167.6)	1429 (257.9)	int[a]	708.5 (559.8)	560.7 (234.4)	272.2 (293.0)	3023 (689.4)
3	332.3 (180.8)	1928 (201.5)	2709 (1841)	569.5 (383.6)	674.4 (369.9)	462.7 (408.8)	6676 (2158)
4	513.0 (240.4)	2892 (283.6)	4947 (2650)	1197 (959.7)	1235 (207.1)	846.3 (459.5)	11630 (3399)
5	463.3 (144.5)	3616 (1318)	6336 (2284)	1368 (494.9)	1492 (178.4)	1062 (452.3)	14340 (1822)
6	582.3 (160.3)	3849 (1112)	7657 (2691)	2048 (377.1)	2163 (330.7)	2209 (1500)	18160 (2778)
7	3301 (574.7)	25880 (970.3)	48740 (3123)	11160 (485.0)	11680 (693.3)	10180 (1185)	110900 (3970)
8	1043 (162.9)	7284 (272.4)	14620 (2437)	3035 (534.8)	3703 (331.1)	2536 (1694)	32220 (1779)
9	214.9 (132.8)	1467 (152.8)	2787 (1132)	535.4 (261.2)	628.8 (232.1)	422.8 (203.0)	6056 (1342)
11	672.1 (400.1)	4660 (526.8)	9260 (3759)	1505 (1040)	1962 (433.1)	1413 (617.9)	19473 (4273)

[a] Int = interference prevented quantification of BDE 99 in all samples from this site.

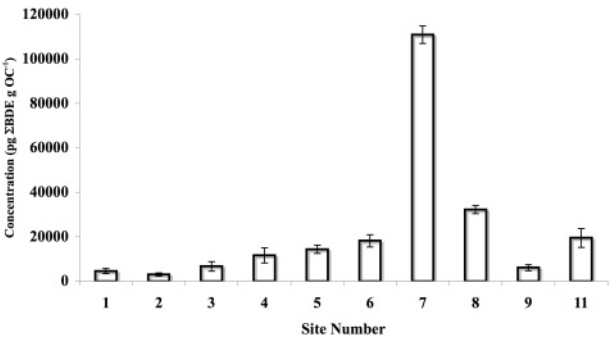


FIGURE 3. Spatial variation of average concentrations (pg g^{-1} OC) of ΣBDE in soil samples (error bars are ±1 σ).

As previously reported (*12*), the PBDE congener pattern in air is markedly different from that in soil. To illustrate, average 47:99 ratios in this study range between 2.95 and 3.62 in outdoor air but from 0.53 to 0.88 in soil (the average value cited in ref 12 was ∼0.5). It has been reported that preferential volatile emissions of the lower brominated 47 cf. 99 from household items favor higher ratios in air compared to those detected in the treated material itself (*24*), which for the penta-BDE DE-71 and Bromkal 70-5DE formulations employed in the UK are ∼0.7 and ∼1.0 respectively (*21, 25*). Such volatilization is a likely source of the elevated concentrations of PBDEs detected in indoor air (*5*). Once emitted from indoor to outdoor air, it is reasonable to hypothesize that the higher K_{OA} of BDE 99 (*26*) leads both to its greater atmospheric deposition, and greater retention by soil postdeposition relative to BDE 47, with consequent lower 47:99 ratios in soils.

This study significantly augments our knowledge of the environmental fate and behavior of PBDEs in urban areas. On the evidence presented here, urban centers are not only contaminated with PBDEs, but constitute important sources of these pollutants to the wider environment.

Acknowledgments

The authors gratefully acknowledge the provision of a studentship to Stuart Hunter from the UK Natural Environment Research Council (ref. NER/S/A/2001/05985).

Supporting Information Available

Tables listing concentrations of individual PBDE congeners in each air (Table S1) and soil sample (Table S2, both (a) dry weight and (b) normalized to organic carbon content). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Alcock, R. E.; Sweetman, A. J.; Prevedouros, K.; Jones, K. C. Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. *Environ. Int.* **2003**, *29*, 691−698.

(2) McDonald, T. A. A perspective on the potential health risks of PBDEs. *Chemosphere* **2002**, *46*, 745−755.

(3) Bromine Science Environmental Forum. http://www.bsef.com (accessed January 2004).

(4) Renner, R. Increasing levels of flame retardants found in North American environment. *Environ. Sci. Technol.* **2000**, *34*, 452A−453A.

(5) Harrad, S.; Wijesekera, R.; Hunter, S.; Halliwell, C.; Baker, R. A preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers. *Environ. Sci. Technol.* **2004**, *38*, 2345−2350.

(6) Jones-Otazo, H.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B. Is house dust the missing exposure pathway for PBDEs? an analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* **2005**, *39*, 5121−5130.
(7) Stapleton, H. M.; Dodder, N. G.; Offenberg, J. H.; Schantz, M. M.; Wise, S. A. Polybrominated diphenyl ethers in house dust and clothes dryer lint. *Environ. Sci. Technol.* **2005**, *39*, 925−931.
(8) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945−956.
(9) Darnerud, P. O.; Eriksen, G. S.; Jóhannesson, T.; Larsen, P. B.; Viluksela, M. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ. Health Perspect.* **2001**, *109* (Suppl 1), 49−68.
(10) Strandberg, B.; Dodder, N. G.; Basu, I.; Hites, R. A. Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environ. Sci. Technol.* **2001**, *35*, 1078−1083.
(11) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* **2004**, *38*, 34−41.
(12) Hassanin, A.; Breivik, K.; Meijer, S. N.; Steinnes, E.; Thomas, G. O.; Jones, K. C. PBDEs in European background soils: levels and factors controlling their distribution. *Environ. Sci. Technol.* **2004**, *38*, 738−745.
(13) Covaci, A.; Voorspoels, S.; de Boer, J. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples − a review. *Environ. Int.* **2003**, *29*, 735−756.
(14) Harner, T.; Shoeib, M.; Diamond, M.; Ikonomou, M.; Stern, G. Passive sampler derived air concentrations of PBDEs along an urban-rural transect: spatial and temporal trends. *Chemosphere* **2006**, *64*, 262−267.
(15) Wilford, B. H.; Harner, T.; Zhu, J.; Shoeib, M.; Jones, K. C. A passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada. *Environ. Sci. Technol.* **2004**, *38*, 5312−5318.
(16) Gouin, T.; Harner, T.; Blanchard, P.; Mackay, D. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin. *Environ. Sci. Technol.* **2005**, *39*, 9115−9122.
(17) Harrad, S.; Diamond, M. Exposure to PBDEs and PCBs: current and future scenarios. *Atmos. Environ.* **2006**, *40*, 1187−1188.
(18) Motelay-Massei, A.; Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs and organochlorine pesticides. *Environ. Sci. Technol.* **2005**, *39*, 5763−5773.
(19) Currado, G. M.; Harrad, S. Factors influencing atmospheric concentrations of polychlorinated biphenyls in Birmingham, U.K. *Environ. Sci. Technol.* **2000**, *34*, 78−82.
(20) Harrad, S.; Mao, H. Atmospheric PCBs and organochlorine pesticides in Birmingham, UK: concentrations, sources, temporal and seasonal trends. *Atmos. Environ.* **2004**, *38*, 1437−1445.
(21) Hoh, E.; Hites, R. A. Brominated flame retardants in the atmosphere of the East-Central United States. *Environ. Sci. Technol.* **2005**, *39*, 7794−7802.
(22) Carlson, D. L.; Hites, R. A. Temperature dependence of atmospheric PCB concentrations. *Environ. Sci. Technol.* **2005**, *39*, 740−747.
(23) Butt, C. M.; Diamond, M. L.; Truong, J.; Ikonomou, M. G.; Ter Schure, A. F. H. Spatial distribution of polybrominated diphenyl ethers in Southern Ontario as measured in indoor and outdoor window organic films. *Environ. Sci. Technol.* **2004**, *38*, 724−731.
(24) Kemmelein, S.; Hahn, O.; Jann, O. Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials. *Atmos. Environ.* **2003**, *37*, 5485−5493.
(25) Sjödin, A.; Jakobsson, E.; Kierkegaard, A.; Marsh, G.; Sellström, U. Gas chromatographic identification and quantification of polybrominated diphenyl ethers in a commercial product, Bromkal 70-5DE. *J. Chromatogr. A* **1998**, *822*, 83−89.
(26) Harner, T.; Shoeib, M. Measurements of octanol-air partition coefficients (K_{OA}) for polybrominated diphenyl ethers (PBDEs): predicting partitioning in the environment. *J. Chem. Eng. Data* **2002**, *47*, 228−232.
(27) Jaward, F. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* **2005**, *39*, 8638−8645.

Received for review March 22, 2006. Revised manuscript received May 8, 2006. Accepted May 19, 2006.

ES0606879

Sally Schlichting
Alaska Department of Environmental Conservation
P.O. Box 111800
Juneau, AK 99811-1800

Delivered by email to sally.schlichting@alaska.gov

November 2, 2018

Re: Proposed ADEC Amendments to 18 AAC 75 – Setting Cleanup Levels for PFAS

Dear Review Board,

We represent water quality professionals who treat the wastewater from homes and businesses and organics recyclers who compost residential and commercial green wastes – with the ultimate goal of recycling nutrients and organic matter from biosolids and other organic residuals back to farmland, gardens, and soils. We are writing as a collective to commend the Alaska Department of Environmental Conservation (ADEC) for your continued work on protecting and cleaning up Alaska's soils.

We are concerned about the proposed ADEC Amendments to 18 AAC 75 – Setting Cleanup Levels for PFAS. Our members and stakeholders are involved in soil health and management through recycling of organic residuals (i.e. biosolids, composts, septage, and manures) and wastewaters. We work with farmers, gardeners, and other landowners to sustainably improve land and grow crops (feed, food, turf, trees, and native ecosystems).

We appreciate this opportunity to offer the following comments for consideration.

While we appreciate ADEC's interest in establishing soil cleanup standards, in particular for industrially contaminated sites, we are concerned about the potential for unintended consequences that will significantly impact our members in Alaska and other municipalities and businesses. In particular, ADEC's proposed (and current) migration to groundwater soil cleanup standard for five of the six PFAS are inappropriate and indefensible based on current scientific knowledge and are unmeasurable, and, thus, untenable. We recommend that ADEC eliminate the migration to groundwater pathway soil cleanup values for the five PFAS chemicals other

than PFBS, including the current values already in place for PFOA and PFOS in Table B1 of 18 AAC 75.[1]

Current knowledge and understanding of PFAS dictate a more careful, targeted approach to regulation. Most states are taking this targeted approach, recognizing that the high levels of uncertainty and the ubiquitous dispersion of several PFAS chemicals in the environment in many matrices and their unusual chemical characteristics make the regulation of these chemicals particularly challenging. Most states are properly focused on:

- Investigating and mitigating drinking water impacts;
- Investigating and mitigating industrial, military, and fire-fighting sites where levels of PFOA and PFOS in particular are very high in soils, groundwaters, and surface water due to historical contamination (these sites pose the greatest potential risks); and/or
- Reducing uses and discharges of PFOA and PFOS in particular; the phase-out of these two PFAS has already resulted in significant reduction of any potential risk in the general population.

A few states have set soil cleanup standards based on direct exposures by ingestion and dermal contact. And U.S. EPA also set direct exposure standards as part of their 2009 residential soil screening guidance values for PFOS at 6mg/kg and PFOA at 16 mg/kg. We support ADEC for the proposed direct exposure standards in the proposed regulation.

However, very few states have begun attempts to set migration to groundwater soil or materials standards, and they have already retreated, recognizing the challenges, uncertainties, and potential unintended consequences:

- In 2017, New York DEC began testing soils and organic residuals (e.g. biosolids and paper mill residuals) applied to soils, to see if they could establish screening levels for PFOA and PFOS in those matrices. After conducting some leaching experiments, they backed away from the project and have not set any clear standards, because of the difficulties presented by these unique chemicals.[2]
- In 2017, Maine DEP initiated rulemaking that included setting a screening value for PFOA and PFOS in materials that are placed on soils for non-agronomic purposes (e.g. dredgings, fill). The proposed values were obtained by running routine models using default values, similar to how ADEC came up with its migration to groundwater soil cleanup values. Maine DEP's initial proposed values were untenably low, and, after receiving comments, they landed on the still-somewhat-arbitrary and indefensible screening levels of 2.5 ppb for PFOA and 5.2 ppb for PFOS. And Maine DEP has clarified

[1] Perfluoroheptanoic Acid (PFHpA): proposed migration to groundwater = .00024 mg/kg
Perfluorohexane Sulfonic Acid (PFHxS): - 0.00029 mg/kg
Perfluorononanoic Acid (PFNA): 0.00041 mg/kg
Perfluorooctane Sulfonic Acid (PFOS): 0.00053 mg/kg Currently 0.0030 mg/kg
Perfluorooctanoic Acid (PFOA): 0.00029 mg/kg Currently 0.0017 mg/kg

[2] In the end, NY DEC did apply their evaluation of leaching to one particular permit for a composting facility that accepts paper mill residuals. For that one permit, the permittee is required to screen paper mill residuals against a screening value of 72 ug/kg (ppb) for PFOA & PFOS.

that these are only initial screening values, not compliance standards. If they are exceeded, it only triggers further risk analysis. Maine DEP is stating that they will not apply them to agronomic residuals, such as biosolids, manures, and other residuals.

We are now concerned that ADEC is making a similar mistake. We recommend that ADEC eliminate the migration to groundwater pathway soil cleanup values for the five PFAS chemicals other than PFBS.

Here's why:

1. PFAS are so ubiquitous and much remains unknown about them. When setting standards, there is a tendency to over-apply uncertainty factors, resulting in unintended impacts, including impacts on municipalities and their materials management (waste management, wastewater management) programs.

Sampling data from several states[3] have found PFAS in soils and groundwaters around numerous landfills and other waste management sites. Even the smallest and least-impacted of these sites would require extensive cleanup if the ADEC proposed migration to groundwater standards were enforced on them.

Looking more specifically at the residuals our members deal with: many municipalities, including several in Alaska, such as Fairbanks, recycle wastewater solids – biosolids to soils in environmentally sound and publicly supported programs that benefit soils, landowners, the public, and the municipal facility ratepayers. Recent data from testing typical biosolids, composts, and other residuals around the nation – materials that are not impacted by industrial sources – show concentrations of PFAS that would preclude their use on soils if the proposed cleanup levels were adopted. The source of PFAS in these products is almost certainly household dust.

Here's a back-of-the-envelope calculation that would be of concern, for example, for the highly-successful and long-standing Fairbanks biosolids composting program. There are no data of which we are aware regarding the PFAS levels in Fairbanks compost, but we can use typical recent biosolids compost data for this illustration:

A NH biosolids compost (ug/kg or ppb):

PFOA 13
PFOS 8.7
PFNA 3.4
PFHxS 0.48
PFHpA 2.8
Total ~28 ppb of the five PFAS with untenably low migration to groundwater soil cleanup levels proposed by ADEC

[3] We know of data publicly available – much of it online – from MN, NH, and VT in particular.

Taking the highest level, which is for PFOA, and assuming a typical application rate of compost to soil of 10 dry tons/acre, which is tilled into the top 6" of soil and thus diluted by 200 times, will result in 0.65 ppb in the compost-amended soil. The proposed ADEC clean-up level is 0.41 ppb for PFOA.

Of course, the reality is that the leaching potential from this biosolids compost is not accurately estimated by the proposed ADEC value, and even multiple agronomic applications of Fairbanks or any other biosolids compost do not pose significant risk to groundwater - as we discuss below.

We have found that those calculating such PFAS standards in other states (e.g. Maine) are unaware of the real-world meaning of the results of their calculations. We surmise that the same is true for ADEC.

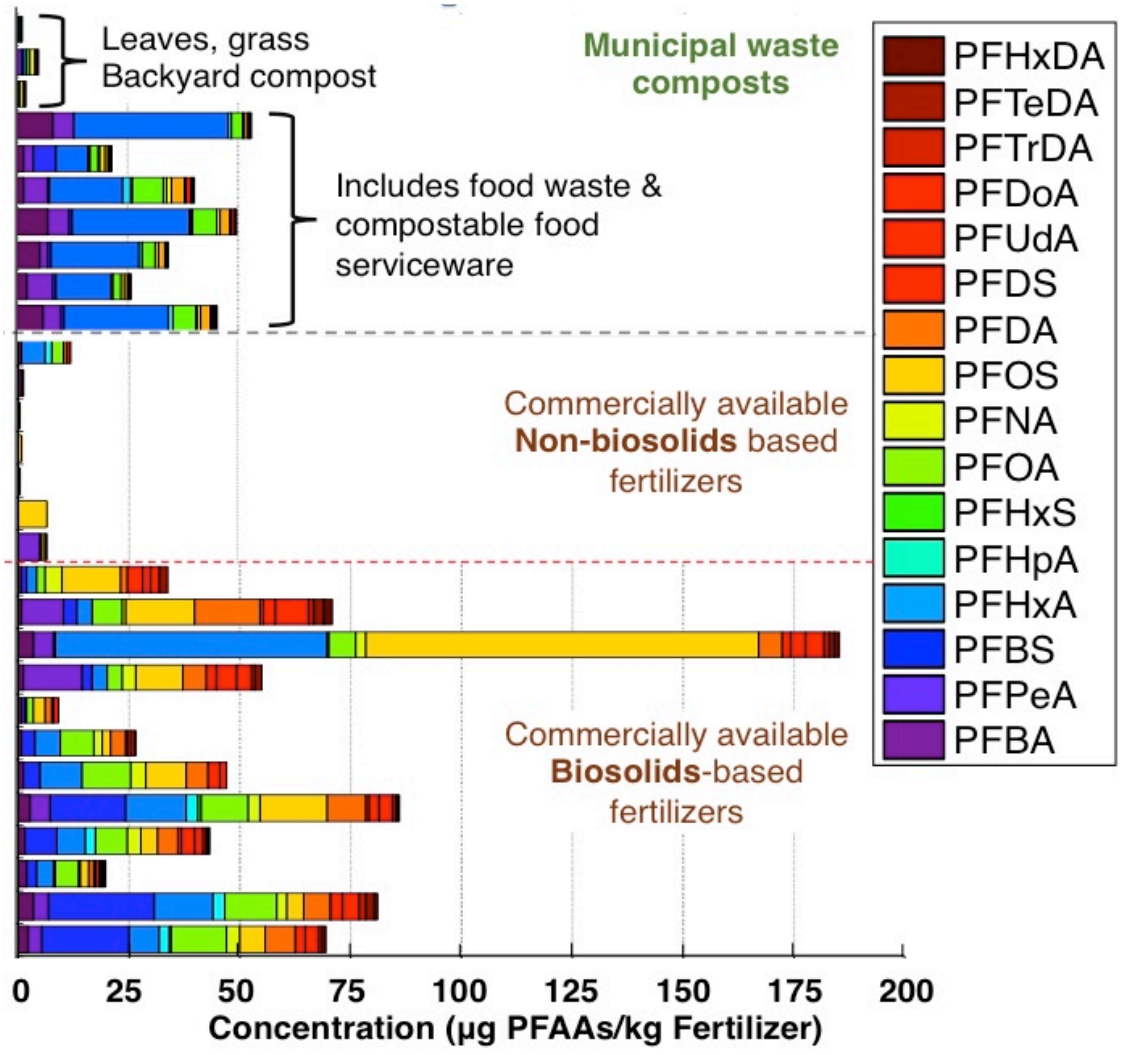


Figure 1

Kim Lazcano, R. and Lee, L. 2018. Data in publication, Purdue University.

Biosolids products are not the only soil amendments containing PFAS (see Figure 1). But biosolids products tend to convey higher levels of PFAS, because domestic wastewater carries PFAS from our homes and businesses. Recent data compiled by NEBRA show that levels in biosolids reflect the common uses of PFAS in our daily lives, where our human exposure is greatest. Back in the early 2000s, when PFOA and PFOS were in much greater use, levels of PFOS were in the hundreds of parts per billion (ppb) in a national survey of 2001 biosolids. Now they are at least an order of magnitude lower, because of the phase out of PFOS and PFOA.[4] The best way to mitigate exposures and impacts of those PFAS considered most concerning for public health and the environment is to phase them out of use. This also works to protect the quality of soils and the soil amendments, like biosolids, that are applied to soils.

2. Impacts could be significant to recycling and municipalities and businesses managing waste, wastewater, and biosolids.

Consider:

- As illustrated above, waste streams handled by municipalities will undoubtedly contain levels of PFAS above the proposed migration to groundwater soil cleanup levels – even wastes from purely domestic sources – because these chemicals have been ubiquitous in common products, some for decades.

- The change to "section 330, Interim Removal Actions, which allows the department to require a responsible party to provide alternative water if groundwater contamination exceeds cleanup levels," raises the question of whether or not ADEC will charge a municipal wastewater treatment facility or biosolids composting program as a responsible party. This could be a significant financial burden on Alaska's towns and cities. It would also result in the loss of a valuable resource for homeowners, businesses, and farmers who rely on biosolids and composts to help their farms and gardens.

- The fiscal evaluation included in the proposed regulation public notice is inadequate. Municipalities will be significantly impacted if the proposed values – or even values an order of magnitude higher – are finalized. For example, there is ample experience indicating that a treatment system for PFAS reduction in drinking water in a private residence costs on the order of $2,000. Installing a treatment system for a public drinking water well in Maine cost the public water system nearly $2 million. The state of New Hampshire reports that $40 million has been spent on PFAS investigation and mitigation over the past 2 years, both by the state and by responsible parties – major industrial facilities. Identified responsible parties will bear considerable costs in Alaska too. Understanding the ubiquitous nature of these contaminants, many states are

[4] Venkatesan, K., and Halden, R., 2013. National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. Journal of Hazardous Materials, 252-253, (2013), 413-418. NEBRA has ongoing data compilation of PFAS levels in recent biosolids and other residuals, available on request (info@nebiosolids.org).

properly focused only on charging responsible parties that are involved with the larger, more significant, direct industrial and military and fire-fighting related PFAS contaminated sites. ADEC will need to clarify how it intends to identify and categorize responsible parties. The brief statement in the ADEC proposal regarding potential municipal liability is insufficient: "Specifically, when a municipality is considered an RP or when there is a presence of PFAS above the adopted cleanup levels on municipal property. Facilities such as fire stations and water systems are more likely to be affected due to the nature of PFAS contamination."

3. The proposed soil cleanup standards are unmeasurable.

- There is no EPA approved method for PFAS in any matrix other than the Method 537 rev. 1.1 for drinking water. The Department of Defense specifies a particular isotope dilution method, but our understanding is that commercial laboratories are using their own modified Methods 537. And test results show considerable variation between different labs. The situation has improved over the past two years, but we believe that any test data for PFAS in any matrices other than drinking water, current or past, should be evaluated with some skepticism and should only be used for screening purposes and improving general understanding.

- Some commercial laboratories are claiming they can measure PFAS in solids (e.g. sediments, soils, residuals) at reporting limits as low as 0.2 ug/kg (ppb). These claims are highly suspect. Actual lab results often show detection limits in the 2 – 5 ppb range. In addition, the various methods being used by laboratories widely diverge. For example, Vermont DEC[5] conducted split sample tests comparing a DOD-preferred isotope dilution method (MLA 110) with one of the many "modified Method 537" methods (each lab has developed their own). When analyzing wastewater (a complex matrix, but not as complex as biosolids or soil), they found differences in the results from the two methods ranging from 10% - 200%. When analyzing wastewater solids, the range of difference between the methods went higher than 300%.

Thus, the proposed ADEC soil cleanup values for migration to groundwater are currently unmeasurable and unenforceable.

4. Data on PFAS are insufficient for modeling.

We applaud ADEC for relying on the U. S. EPA public health advisory screening level as the target drinking water and groundwater value for its risk evaluations of PFOA and PFOS. While there is ongoing debate amongst toxicologists about the appropriateness of that EPA number, it is the most thoroughly vetted number and incorporates a large amount of uncertainty about potential health impacts from PFAS. In comparison to the U. S. approach to PFAS, an expert

[5] Weston & Sampson, 2018. Wastewater Treatment Facility and Landfill Leachate PFAS Sampling Various Locations, Northern Vermont, Report to J. Schmelzer, VT DEC, May 3, 2018.

health panel in Australia stated that the "the Panel's advice to the Minister on this public health issue is that the evidence does not support any specific health or disease screening or other health interventions for highly exposed groups in Australia, except for research purposes.[6] This is obviously quite different from EPA's approach and that of the CDC's Agency for Toxic Substances & Disease Registry (ATSDR), whose 2018 report has been interpreted by some to mean that the drinking water standard should an order of magnitude lower than EPA's current 70 ppt.

We urge ADEC to consider the following:

- Summing the levels of 5 PFAS to meet the 70 ppt public health advisory (PHA) drinking water screening level is arbitrary. We know that other states are doing this for regulatory simplicity, tilting toward over-protection. But it is not based on good science[7].

- Any references in the ADEC documentation about this proposed regulation should not include anything about the toxicology or health impacts of PFOA and PFOS (and the other PFAS too). ADEC has chosen to use the EPA PHA value as an endpoint for modeling its soil cleanup standards. That PHA value has embedded in it all of the uncertainties and assumptions regarding health impacts and toxicology.

- Using the standard ADEC calculator and default values is inappropriate for PFAS chemicals.

    - The modeling and calculations used to derive the proposed migration to groundwater screening values have not been field-verified for any of the PFAS chemicals, and there is insufficient published research on soil leaching of PFAS to allow for robust understanding of the potential leaching risks.

---

[6] Expert Health Panel for PFAS Report, 2018: http://www.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-expert-panel.htm

[7] U. S. EPA has not included PFOA, PFOS, PFNA, PFHxS, and PFHpA in their RSL Composite Tables for good reason: robust data are not yet available. However, ADEC proposes numerous assumptions (ADEC Contaminated Sites Program - Procedures for Calculating Cleanup Levels, p. 19). While the molecular structures of the compounds are similar and somewhat similar biological activities can be assumed, other assumptions are not supported by evidence:

- The half-lives of the compounds vary in humans and often considerably between humans and test animals;
- Toxicities, while still the subject of debate, also vary considerably, and all necessary assumptions and conservative protective factors have already been integrated into the EPA RfDs and drinking water public health advisory level. ADEC should not add any additional uncertainty factors for toxicity when using EPA-established endpoints that have already included such uncertainty factors!
- There is little to no evidence of additive or synergistic health effects.

In short, the assumptions made by ADEC are not supported and the additive approach is for regulatory efficiency with a highly conservative tilt.

- Example: foc, the fraction of organic matter in soil, is assumed to be .1%. This does not apply to most soils (and thus is highly conservative and protective), and it is especially inappropriate when organic residuals (e.g. biosolids, composts, manures) are applied, as they contain high percentages of organic matter.

- Example: (Koc). As noted in the National Groundwater Association (NGWA) report: "Koc values for these PFAS may vary over several orders of magnitude depending on the site-specific geochemistry" (NGWT, 2017, *Groundwater and PFAS: State of Knowledge and Practice*, p. 4.6)[8]. ADEC used the default, EPA Koc values for PFOA and PFOS, which are at the low end of values reported in the literature.

We ran ADEC's online calculator, using alternative values for foc and Koc. The results are significantly different, with only these two changes:

PFAS Chemical	ADEC proposed M2G soil cleanup standard (ppb)	Alternative foc	Alternative Koc[9]	Resulting alternative M2G soil cleanup standard (ppb)
PFOA	0.291	2 %	316	35
PFOS	0.528	2 %	3470	370

These two factors – foc and Koc – are not the only ones that could reasonably be changed, resulting in higher, more reasonable and measurable migration to groundwater soil cleanup levels.

[8] For Koc, the Department used U. S. EPA figures for PFOA and PFOS of 114.8 L/kg (2.06 log Koc) and 371.5 L/kg (2.57 log Koc), respectively. In comparison, Zareitabalad et al. (2013) noted lab sorption experiments that show "an average log K(oc) of approximately 2.8 for PFOA [631 L/kg] and 3.0 [1,000 L/kg] for PFOS." They found higher values in field experiments and noted: "Applying lab-based log K(oc) distribution coefficients can therefore result in a serious overestimation of PFC concentrations in water and in turn to an underestimation of the residence time of PFOA and PFOS in contaminated soils" (Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater - A review on concentrations and distribution coefficients *Chemosphere:* 91(6):725-32). Most recently, in 2017, a paper cites ranges of Koc values of 83 – 389 L/kg (1.92 – 2.59 log Koc) for PFOA and 250 – 50,100 (2.4 – 4.7 log Koc) for PFOS (U. S. National Library of Medicine, 2017, Hazardous substances data bank). The fact is, knowledge regarding this one key modeling parameter is conflicted at this point. What seems to be known suggests that PFAS in biosolids and residuals may not leach as much as in other matrices, because:

- the Kocs depend on site-specific conditions,
- longer-chain PFAS (such as PFOA and PFOS) have higher sorption (an estimated 0.5 log Koc increase for each CF_2 group (Higgins and Luthy, 2006, *Env. Sci. & Tech*)),
- sludge has a higher Koc than sediments (Chen et al., 2012), and
- "organic rich soils retard movement of PFAS" (E. Houtz, 2017, Arcadis presentation to NEWMOA, May 8 – 10, 2017).

[9] Koc for sludges, as reported in Chen et al., 2012.

In addition, the rote model is arguably not appropriate for PFAS compounds because such models do not assess the ionic nature of PFAS in soil solution and the additional binding effects thus created.

In summary…

We strongly recommend removal from the proposed regulations of the five migration to groundwater soil cleanup standards for PFAS (leaving only PFBS, for which EPA has more appropriate data). And we recommend the removal of the current values already in place for PFOA and PFOS in Table B1 of 18 AAC 75. There is insufficient scientific understanding to model these five chemicals' leaching potential. Including screening levels here at this time could dramatically – and perhaps unintentionally – disrupt the agronomic utilization of biosolids and other residuals, a highly-valuable and successful recycling program. Every biosolids and most composts – even some certified organic composts – will exceed the proposed values. What does that mean for recycling of these materials?

If ADEC proceeds with including the six UCMR 3 PFAS chemicals in soil cleanup standards based on migration to groundwater, a clear exemption should be stated: "The soil cleanup screening values for migration to groundwater for PFAS chemicals are not appropriate for and shall not be applied to organic residuals and soil amendments added to soils, including composts, manures, and biosolids. PFAS contained in these organic residuals and soil amendments are affected by factors that were not assumed in the calculations from which were derived the migration to groundwater soil cleanup values listed here. Organic residuals and soil amendments – and any levels of organic matter greater than the .1% assumed in risk calculations – change the behavior of PFAS in the soil, significantly reducing their migration to groundwater."

PFOA and PFOS are already legacy issue compounds. These two most concerning and ubiquitous PFAS have been mostly phased out of use, and human blood serum levels are already down 60% or more.[10] How much Alaskans will spend on addressing small amounts in various matrices is an important policy issue. We urge ADEC to avoid disrupting other important environmental programs and policies with inadvertent impacts. The best way to address compounds used ubiquitously that become of concern is to phase them out of use. Over the years, our organizations and our members have assisted in promoting source reductions and phase-outs of other trace contaminants (e.g. triclosan, microbeads), because it is in our interest to ensure quality biosolids and residuals products.

Wastewater, biosolids, and other organic residuals are not sources of PFAS; they convey them from our daily lives. Municipalities and businesses that manage these resources can be affected by regulations of this family of chemicals, and we need to act judiciously in setting those regulations.

[10]Centers for Disease Control, National Health and Nutrition Examination Survey (NHANES), 2015

Thank you for your time and consideration of our concerns. We look forward to a continued dialogue with Alaska. Please feel free to contact us if you have any questions.

Yours truly,

Maile Lono-Batura, Executive Director

Northwest Biosolids

Northwest Biosolids is a 501(c)(6) non-profit professional association that works to advance wastewater management and environmental sustainability through the beneficial use of biosolids in the Pacific Northwest. Our member utilities manage biosolids for nearly eleven million residents and ratepayers across six states and provinces. Together, our membership continues to dedicate half of our annual budget to research biosolids end use options that include returning nutrient-rich biosolids back to soils. For the past 31 years, our biosolids network has leveraged our collective to ensure quality biosolids programs across the region. Please visit our website for more information on who we are and what we do: http://www.nwbiosolids.org

Ned Beecher, Executive Director

North East Biosolids & Residuals

NEBRA is a 501(c)(3) non-profit professional association advancing the environmentally sound and publicly supported recycling of biosolids and other organic residuals in New England, New York, and eastern Canada. NEBRA membership includes the environmental professionals and organizations that produce, treat, test, consult on, and manage most of the region's biosolids and other large volume recyclable organic residuals. NEBRA is funded by membership fees, donations, and project grants. Its Board of Directors are from CT, MA, ME, NH, VT, and Nova Scotia. NEBRA's financial statements and other information are open for public inspection during normal business hours. For more information: http://www.nebiosolids.org. Since January 2017, NEBRA has led efforts in the biosolids and wastewater management profession to understand the implications of PFAS contamination and regulation on municipal and private wastewater, biosolids, and residuals management programs.

Frank Franciosi, Executive Director

U.S. Composting Council

Established in 1990, the **US Composting Council (USCC)** is the only national organization in the United States dedicated to the development, expansion and promotion of the composting industry. The USCC achieves this mission by encouraging, supporting and performing compost related research, promoting best management practices, establishing standards, educating professionals and the public about the benefits of composting and compost utilization, enhancing compost product quality, and developing training materials for compost manufacturers and markets for compost products. USCC members include compost manufacturers, compost marketers, equipment manufacturers, product suppliers, academic institutions, public agencies, nonprofit groups and consulting/engineering firms. For more information: https://compostingcouncil.org/

Michele Riggs, President

Washington Organics Recycling Council

The **Washington Organics Recycling Council (WORC)** is a nonprofit 501(c)6 trade organization formed in response to demands for increased recycling of organic materials. Since 1991, WORC has been recognized as the statewide organization representing organic recyclers, and facilitates communication between the private and public sectors. WORC provides a unified statewide voice on many issues: research, education (through Operator Training, conferences, and other programs), product safety and standards, government regulations, environmental planning, trade, marketing, and public education and involvement. Its members are a diverse group that includes organic waste processors, government officials, vendors, consultants, educators, students, researchers, and private citizens. All firmly believe in and work to support the organic recycling industry in Washington State. The Council works closely with state and regional organizations, such as the Washington State Recycling Association and the Northwest Biosolids Management Association, to promote and encourage recycling of organic materials. WORC's Soils for Salmon initiative is changing building practices to protect and restore soil. Nationally, WORC coordinates with other state composting organizations and the US Composting Council. For more information: https://www.compostwashington.org/

Science of the Total Environment 863 (2023) 160956

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Temporal trends in concentrations of brominated flame retardants in UK foodstuffs suggest active impacts of global phase-out of PBDEs and HBCDD

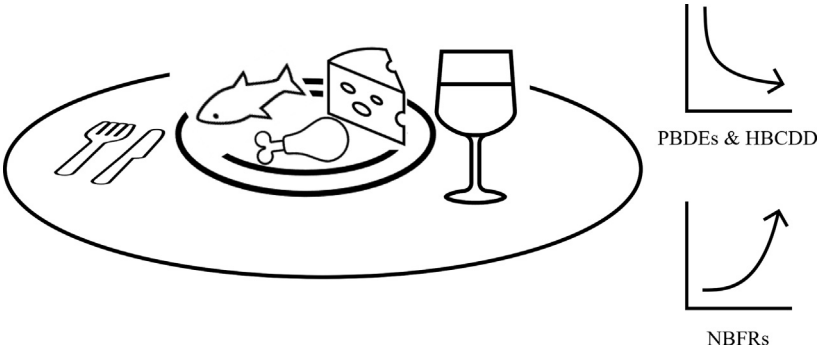
Yulong Ma [a,*], William A. Stubbings [a], Mohamed Abou-Elwafa Abdallah [a], Reginald Cline-Cole [b], Stuart Harrad [a]

[a] School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK
[b] Department of African Studies & Anthropology, School of History and Cultures, University of Birmingham, Birmingham B15 2TT, UK

HIGHLIGHTS

- NBFRs were the predominant BFRs in UK foodstuffs.
- Levels of legacy BFRs dropped significantly in UK foodstuffs.
- Levels of BTBPE and BEH-TEBP increased considerably in UK foodstuffs.
- Significant decrease in DBDPE levels was observed in UK foodstuffs.
- Dietary exposure to BFRs decreased significantly for children with increasing age.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Paromita Chakraborty

Keywords:
Dietary exposure
NBFRs
BTBPE
BEH-TEBP
DBDPE

ABSTRACT

Global restrictions on use of legacy brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have generated demand for novel BFRs (NBFRs) as substitutes. Our research group has previously reported decreased concentrations of PBDEs and HBCDD and increased concentrations of NBFRs in UK indoor environments, suggesting that restrictions on PBDEs and HBCDD are exerting an impact. In this study, we analysed UK foodstuffs collected in 2020–21 and compared the BFR concentrations found with those found in similar samples collected in 2015 to investigate whether similar trends in BFR concentrations would be observed. Concentrations of PBDEs and HBCDD isomers detected in our samples had declined by 78–92 % and 59–97 % since the 2015 study, respectively. Moreover, concentrations of NBFRs (dominated by 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE), and bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH)) in UK foodstuffs increased significantly (28–1400 %) between 2015 and 2020–21. Combined, these findings suggest that restrictions on use of PBDEs and HBCDD have had a discernible impact on concentrations of these legacy BFRs and their NBFR replacements in UK foodstuffs. Interestingly, given recent reports of a significant increase in concentrations of decabromodiphenyl ethane (DBDPE) in UK house dust between 2014 and 2019, a significant decline (70–84 %) in concentrations of DBDPE was observed in UK foodstuffs.

1. Introduction

Brominated flame retardants (BFRs) have been widely used in commercial products to help meet fire safety regulations. Owing to their extensive use, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDDs) have been detected in all aspects of the environment and biotas including humans (Jiang et al., 2019; Klincic et al., 2020; Ma et al., 2021; Ma et al., 2022). This ubiquitous presence is compounded by concerns about their adverse effects on humans and the environment, including genetic toxicity, endocrine disruption, neurotoxicity, behavioural disorders, cancer, etc. (McDonald, 2002; Schrenk et al., 2021; Yu et al., 2015). Combined with

* Corresponding author.
E-mail address: yxm901@student.bham.ac.uk (Y. Ma).

http://dx.doi.org/10.1016/j.scitotenv.2022.160956
Received 19 October 2022; Received in revised form 29 November 2022; Accepted 12 December 2022
Available online 16 December 2022

their persistence in the environment and capacity for bioaccumulation (Fernandes et al., 2016; Łabunska et al., 2015; Tao et al., 2017; Wang et al., 2019; Zacs et al., 2021), such evidence has led to restrictions on their production and use. In Europe, commercial penta- and octa-BDE were banned in 2004, with deca-BDE products heavily restricted in 2008 (Ma et al., 2022). These actions were followed by their listing under the Stockholm Convention on Persistent Organic Pollutants (POPs) of the United Nations Environment Programme (UNEP) in 2009 and 2017, respectively, resulting in a global phase-out of PBDEs (Sharkey et al., 2020). HBCDD was also listed under the Stockholm Convention in 2014, leading to global phase-out of their production and applications (Sharkey et al., 2020) – albeit with some exemptions. As a result of these restrictions, global demand for alternative FRs has increased sharply, with novel BFRs (NBFRs) being an important option (Ma et al., 2022).

Current understanding is that continuous consumption of BFRs should generate higher BFR concentrations in the environment, while environmental contamination with and human exposure to BFRs should decline in response to measures designed to restrict/prohibit their use. This is supported by temporal changes in concentrations of BFRs in indoor and outdoor environments (Drage et al., 2020; Hale et al., 2006; Li et al., 2015; Tanabe, 2008; Tao et al., 2016), biota (Johansson et al., 2011; Shi et al., 2018; Tanabe, 2008), and humans (Fangstrom et al., 2008; Koizumi et al., 2005; Ma et al., 2013; Ma et al., 2017; Shi et al., 2018; Toms et al., 2012). Following restrictions on use of PBDEs and HBCDD in Europe, we reported contaminations of legacy and novel BFRs in UK foodstuffs and indoor environments (Drage et al., 2020; Tao et al., 2016; Tao et al., 2017). Interestingly, while temporal changes in concentrations of BFRs in UK indoor environments appeared consistent with the restrictions in Europe (Drage et al., 2020; Tao et al., 2016), we did not observe any significant changes in BFR concentrations in UK foodstuffs, suggesting slow response of UK foodstuffs to restrictions on use of PBDEs and HBCDD (Tao et al., 2017).

Therefore, following the same sampling, extraction, and clean-up protocols as those employed by Tao et al. (2017), UK foodstuffs were collected and analysed in the present study. Our target BFRs were: 8 PBDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, -209), 9 NBFRs (pentabromobenzene (PBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), hexabromobenzene (HBBz), 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate (EH-TBB or TBB), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE), bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH), decabromodiphenyl ethane (DBDPE)), and 3 HBCDD isomers (α-, β-, γ-HBCDD). The aims of the current study were to: 1) characterise current concentrations and relative abundance of legacy and novel BFRs in UK foodstuffs; 2) establish whether there have been any significant temporal changes in concentrations of these BFRs in UK foodstuffs since the study of Tao et al. (2017); and 3) estimate dietary exposure to these BFRs for UK citizens and evaluate any potential health risks.

2. Materials and methods

2.1. Sampling methodology

UK food samples were collected and processed in accordance with a previously reported strategy (Tao et al., 2017). This enables temporal changes in BFR concentrations in UK food items to be characterised. During December 2020 and October 2021, a total of 108 individual food samples (covering 15 food categories) were collected from 3 supermarkets in Birmingham representing national retail chains. Specifically, only animal-derived foodstuffs were sampled and analysed because BFRs are lipophilic and bioaccumulative compounds. Three samples of each food category were purchased from each supermarket (except for cheese and chicken eggs, for which more samples were collected and analysed), and homogenised into a composite sample. Detailed information on the food samples collected is summarised in Table S6. All composite samples (n = 36) were freeze-dried and then stored at −20 °C prior to analysis.

2.2. Analytical protocols

Information on the chemicals and reagents used in this study was given in Section 1.1 in Supplementary Materials. Extraction and clean-up of food samples and determination of lipid content were conducted following a previously reported protocol (Tao et al., 2017), with detailed information given in Section 1.2 in Supplementary Materials. Briefly, approximately 0.5 g of freeze-dried food samples were accurately weighed and spiked with internal (or surrogate) standards (BDE-77, BDE-128, ^{13}C-BDE-209, ^{13}C-HBBz, ^{13}C-EH-TBB, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, ^{13}C-α-HBCDD, ^{13}C-β-HBCDD, and ^{13}C-γ-HBCDD) before extraction. Hexane/acetone (3:1, *v*/v) was used to extract the samples in an accelerated solvent extractor (Dionex ASE 350). The ASE cells (34 mL) were filled from bottom to top with: pre-cleaned hydromatrix, 2 g florisil, 3 g alumina, samples, and pre-cleaned hydromatrix. The extracts were collected and concentrated to 5 mL before shaking with 5 mL sulfuric acid (95 %) to remove lipids and proteins. The purified extracts were then reconstituted into 50 μL toluene containing 200 pg/μL ^{13}C-BDE-100 and d_{18}-γ-HBCDD as recovery determination (or syringe) standards before GC–MS and LC-MS/MS analysis.

Analysis of PBDEs and NBFRs was conducted on a Trace 1310 GC coupled to an ISQ™ single quadrupole mass spectrometer (Thermo Scientific, TX, USA) operated in EI mode. Analysis of HBCDD diastereomers was conducted on a Shimadzu LC-20AB HPLC (Shimadzu, Kyoto, Japan) coupled to a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) operated in electrospray negative ionisation (ESI^-) mode. Detailed information was given in Section 1.3 in Supplementary Materials.

2.3. Estimation of daily dietary intake of BFRs

The equation below was adopted to estimate daily dietary intake of BFRs in this study:

$$DI = \sum_{i=1}^{n} \frac{C_i \times CR_i}{BW}$$

where C_i is the concentration (ng/g ww) of BFRs in a particular food item i (Tables S6-S9); CR_i is the daily food consumption (g/day) of a particular food item i (Tables S14-S16); BW is the average body weight (kg) of UK citizens from all age groups (Table S13).

2.4. QA/QC

A full 5-point calibration was conducted for all the target compounds. The relative standard deviation (RSD) of relative response factors (RRFs) for each analyte was below 10 %, with the corresponding R^2 values of 0.9890–0.9999, indicating excellent linearity of the calibration plots. The limit of detection (LOD) and limit of quantification (LOQ) for each analyte were calculated based on signal/noise ratios of 3 and 10, respectively. One method blank was processed for each batch of 5 samples. None of the target compounds were detected in the method blanks except for BDE-47, which was detected at concentrations below the LOQ. As a result, concentrations were not blank-corrected. Five replicates of an egg sample were conducted to evaluate the precision of the method. The RSD of the concentrations of each analyte was below 10 % except for BDE-99, for which the RSD was 12 %. More information on QA/QC is provided in Section 1.4 and Tables S1-S5 in Supplementary Materials.

2.5. Statistical analysis

Statistical analysis was conducted using Microsoft Office 365 and IBM SPSS Statistics 28.0 (Chicago, IL, USA). Paired samples *t*-test was used to identify any changes in BFR concentrations in UK foodstuffs between 2015 and 2020–21. For statistical purposes, concentrations below LOD (or LOQ) were assumed to be 0.5 × LOD (or 0.5 × LOQ) when the detection frequency (DF) exceeded 50 % for a specific analyte, while

concentrations below LOD (or LOQ) were assumed to be DF × LOD (or DF × LOQ) when DF < 50 % (Tao et al., 2017).

3. Results and discussion

3.1. Concentrations and relative abundance of BFRs in UK foodstuffs

Table 1 presents descriptive statistics for all the target BFRs in UK foodstuffs. Mean concentrations of BFRs in different food items are shown in Fig. 1, with detailed data provided in Tables S6 – S9. The relative contributions of NBFRs, PBDEs, and HBCDD isomers to total BFRs are shown in Fig. 2 and Fig. S2.

3.1.1. Concentrations and relative abundance of NBFRs in UK foodstuffs

Concentrations of Σ_9NBFRs ranged from <0.42 ng/g lw (<110 pg/g ww) to 170 ng/g lw (5600 pg/g ww) in UK foodstuffs, with mean and median concentrations of 29 ng/g lw (910 pg/g ww) and 9.9 ng/g lw (460 pg/g ww), respectively. BTBPE (mean: 15 ng/g lw or 480 pg/g ww) and BEH-TEBP (mean: 11 ng/g lw or 360 pg/g ww) were the most abundant and most frequently detected NBFRs, contributing 52 % and 38 % of ΣNBFRs, respectively. EH-TBB, DBDPE, and DPTE were detected in <50 % of samples. Mean concentrations of these three NBFRs were 1.5 ng/g lw (21 pg/g ww), 0.63 ng/g lw (26 pg/g ww), and 0.97 ng/g lw (27 pg/g ww), respectively. PBBz was only detected in one composite food sample at 0.29 ng/g lw (14 pg/g ww), while concentrations of PBT, PBEB, and HBBz were below LOD in all samples.

Table S10 summarises literature data on concentrations of NBFRs in foodstuffs from different countries. Surprisingly, BTBPE and BEH-TEBP concentrations reported in this study were broadly comparable to the concentrations reported in foodstuffs collected from several e-waste recycling sites in China (Labunska et al., 2015; Zeng et al., 2016; Zheng et al., 2016), and were generally one order of magnitude higher than the concentrations reported in foodstuffs collected from France (Venisseau et al., 2018), Belgium (Poma et al., 2018), Tanzania (Polder et al., 2016), and China (non-e-waste recycling areas) (Shi et al., 2016). Comparable concentrations to this study were reported for DPTE in foodstuffs from China (Shi et al., 2016), as well as for DBDPE in foodstuffs from China (Labunska et al., 2015; Shi et al., 2018) and Spain (Trabalon et al., 2017). EH-TBB was detected in UK foodstuffs at concentrations broadly comparable to those in French food samples (Venisseau et al., 2018), but concentrations in our study were 1–2 orders of magnitude lower than the concentrations reported in foodstuffs collected from an e-waste recycling site in China (Labunska et al., 2015).

3.1.2. Concentrations and relative abundance of PBDEs in UK foodstuffs

Concentrations of Σ_8PBDEs ranged from 0.13 ng/g lw (13 pg/g ww) to 36 ng/g lw (760 pg/g ww) in UK foodstuffs, with mean and median concentrations of 4.2 ng/g lw (190 pg/g ww) and 2.3 ng/g lw (120 pg/g ww), respectively. BDE-183 and BDE-47 were the only PBDE congeners with detection frequencies higher than 50 %. This was followed by BDE-209, which was detected in 44 % of the samples. Compared to previous studies conducted in other countries (Table S11), PBDE concentrations reported in this study were generally at the same level with the concentrations reported in foodstuffs from Latvia (Zacs et al., 2021), Netherlands (Gebbink et al., 2019), France (Riviere et al., 2014; Venisseau et al., 2018), Belgium (Covaci et al., 2009; Poma et al., 2018), and Japan (Kakimoto et al., 2012), but were considerably lower than the concentrations reported in foodstuffs from Tanzania (Polder et al., 2016), Spain (Trabalon et al., 2017), Ireland (Garcia Lopez et al., 2018), China (Wang et al., 2019; Zeng et al., 2016), and the US (Hites et al., 2004; Schecter et al., 2010).

At least one PBDE congener was detected in all UK food samples. This could reflect the wide use of PBDEs. However, the average contribution of PBDEs to total BFRs was only 13 %, strongly outweighed by the average contribution of 86 % of NBFRs to total BFRs. Following global restrictions on PBDE production and consumption, our findings may provide evidence of the replacement of PBDEs by NBFRs in consumer products.

3.1.3. Concentrations and relative abundance of HBCDDs in UK foodstuffs

Σ_3HBCDDs made only a very small contribution (1.2 %) to total BFR concentrations in UK foodstuffs. Concentrations of Σ_3HBCDDs ranged from <0.056 ng/g lw (<4.0 pg/g ww) to 3.5 ng/g lw (420 pg/g ww), with mean and median concentrations of 0.41 ng/g lw (33 pg/g ww) and 0.13 ng/g lw (6.9 pg/g ww), respectively. All 3 diastereomers of HBCDDs targeted in this study were detected in <50 % of our samples. With an average contribution of 50 % to Σ_3HBCDDs concentrations, α-HBCDD was most abundant, followed by β-HBCDD and γ-HBCDD, which account for 37 % and 13 % of Σ_3HBCDDs concentrations, respectively.

Table S12 summarises concentrations of HBCDD in foodstuffs from different countries. HBCDD concentrations in chicken eggs reported in this study were comparable to those reported in Latvia (Zacs et al., 2021),

Table 1
Descriptive statistics for BFR concentrations (pg/g ww in parentheses) in UK foodstuffs (ng/g lw).

BFRs	DF [a]	Minimum	5th percentile	25th percentile	Median	75th percentile	95th percentile	Maximum	Mean
BDE-28	0 %	<0.019 (<1.6)	<0.020 (<2.2)	<0.026 (<2.6)	<0.044 (<3.2)	<0.096 (<4.2)	<0.75 (<6.6)	<1.1 (<7.1)	<0.16 (<3.7)
BDE-47	58 %	<0.0069 (<0.59)	<0.016 (<0.85)	<0.055 (<1.0)	0.13 (13)	0.37 (24)	2.3 (300)	3.3 (500)	0.48 (52)
BDE-99	28 %	<0.0050 (<0.42)	<0.0054 (<0.56)	<0.0082 (<0.73)	<0.026 (<1.0)	0.3 (47)	5.4 (340)	10 (490)	0.87 (62)
BDE-100	36 %	<0.0058 (<0.51)	<0.0063 (<0.68)	<0.0099 (<0.91)	<0.029 (<1.4)	0.19 (29)	1.0 (55)	2.9 (94)	0.26 (14)
BDE-153	25 %	<0.0038 (<0.33)	<0.0046 (<0.44)	<0.0065 (<0.54)	<0.017 (<0.78)	0.060 (2.5)	0.46 (23)	4.6 (24)	0.18 (4.5)
BDE-154	19 %	<0.0048 (<0.41)	<0.0056 (<0.55)	<0.0082 (<0.66)	<0.021 (<0.82)	<0.16 (<1.6)	0.36 (64)	13 (93)	0.41 (10)
BDE-183	61 %	<0.024 (<2.6)	<0.029 (<2.8)	<0.087 (<4.6)	0.16 (12)	0.45 (23)	2.2 (42)	2.7 (61)	0.42 (15)
BDE-209	44 %	<0.026 (<3.0)	<0.031 (<3.3)	<0.044 (<4.0)	<0.53 (<8.7)	0.85 (50)	6.7 (100)	23 (150)	1.6 (30)
Σ_8PBDEs	**–**	**0.13 (13)**	**0.27 (18)**	**1.0 (38)**	**2.3 (120)**	**3.8 (290)**	**16 (570)**	**36 (760)**	**4.2 (190)**
PBBz	3 %	<0.010 (<0.92)	<0.011 (<1.2)	<0.015 (<1.5)	<0.025 (<1.8)	<0.069 (<2.4)	<0.19 (<3.8)	0.29 (14)	0.010 (0.44)
PBT	0 %	<0.017 (<1.5)	<0.018 (<2.0)	<0.024 (<2.3)	<0.039 (<2.9)	<0.085 (<3.7)	<0.67 (<5.8)	<0.98 (<6.4)	<0.14 (<3.3)
PBEB	0 %	<0.0069 (<0.60)	<0.0074 (<0.80)	<0.0096 (<0.96)	<0.016 (<1.2)	<0.035 (<1.5)	<0.27 (<2.4)	<0.40 (<2.6)	<0.057 (<1.3)
DPTE	19 %	<0.061 (<5.3)	<0.065 (<7.6)	<0.092 (<9.1)	<0.18 (<13)	<2.4 (<21)	5.6 (180)	9.1 (190)	0.97 (27)
HBBz	0 %	<0.0076 (<0.66)	<0.0081 (<0.88)	<0.011 (<1.1)	<0.018 (<1.3)	<0.038 (<1.7)	<0.30 (<2.6)	<0.44 (<2.9)	<0.062 (<1.5)
EH-TBB	11 %	<0.051 (<4.4)	<0.057 (<6.2)	<0.077 (<7.3)	<0.12 (<9.5)	<0.52 (<15)	7.2 (150)	35 (290)	1.5 (21)
BTBPE	83 %	<0.29 (<44)	<0.44 (<70)	0.67 (72)	3.0 (120)	13 (390)	83 (1800)	110 (5500)	15 (480)
BEH-TEBP	61 %	<0.33 (<37)	<0.44 (<40)	<0.77 (<60)	1.1 (110)	9.8 (300)	56 (1100)	65 (4700)	11 (360)
DBDPE	22 %	<0.15 (<13)	<0.17 (<18)	<0.24 (<23)	<0.45 (<32)	<2.5 (<54)	2.8 (104)	4.8 (440)	0.63 (26)
Σ_9NBFRs	**–**	**<0.42 (<110)**	**0.58 (120)**	**2.3 (270)**	**9.9 (460)**	**29 (830)**	**120 (3800)**	**170 (5600)**	**29 (910)**
α-HBCDD	39 %	<0.029 (<2.5)	<0.035 (<3.3)	<0.055 (<4.1)	<0.13 (<5.2)	0.72 (9.6)	0.78 (160)	3.1 (370)	0.20 (25)
β-HBCDD	22 %	<0.054 (<4.7)	<0.067 (<5.3)	<0.093 (<5.9)	<0.21 (<6.5)	<0.49 (<9.1)	0.55 (9.4)	1.6 (50)	0.15 (4.7)
γ-HBCDD	31 %	<0.021 (<1.5)	<0.022 (<2.0)	<0.042 (<2.4)	<0.071 (<3.1)	0.076 (3.6)	0.21 (14)	0.30 (23)	0.055 (3.1)
Σ_3HBCDDs	**–**	**<0.056 (<4.0)**	**<0.063 (<5.3)**	**<0.12 (<6.8)**	**0.13 (6.9)**	**0.40 (15)**	**1.5 (170)**	**3.5 (420)**	**0.41 (33)**
Σ_{20}BFRs	**–**	**1.7 (90)**	**2.3 (140)**	**3.7 (460)**	**13 (620)**	**32 (1200)**	**130 (4000)**	**210 (5900)**	**33 (1100)**

[a] DF = detection frequency.

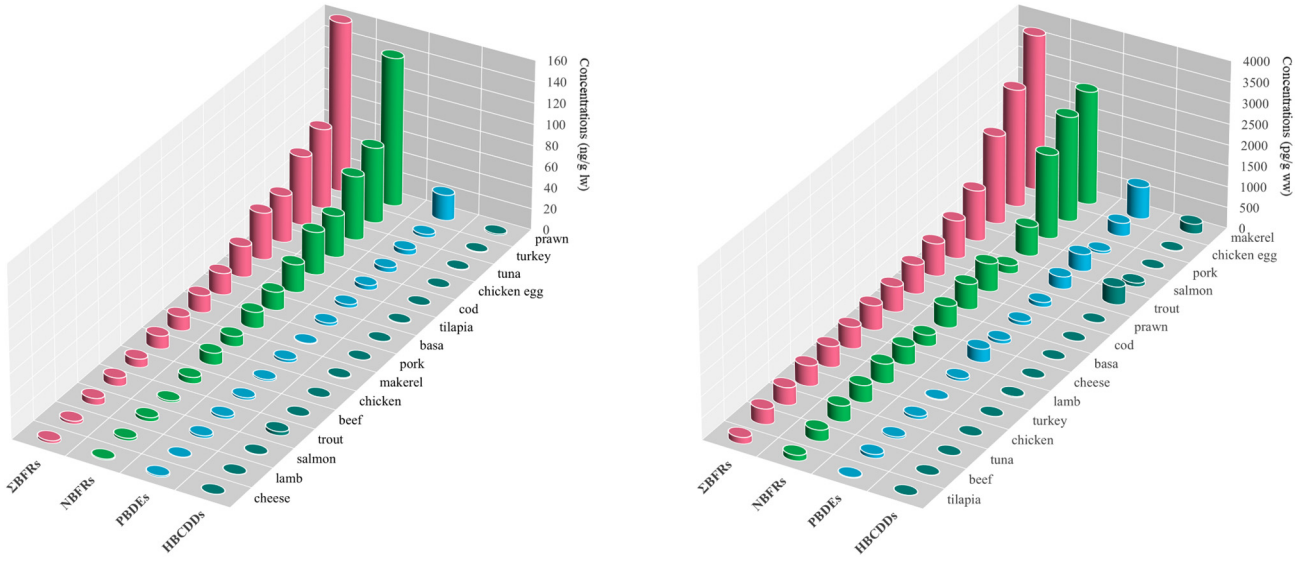


Fig. 1. Mean concentrations of BFRs in UK foodstuffs (left: data based on lipid weight; right: data based on wet weight).

France (Riviere et al., 2014), Ireland (Garcia Lopez et al., 2018), and the US (Schecter et al., 2010), but were considerably lower than HBCDD concentrations in chicken eggs from China (Labunska et al., 2015; Wang et al., 2019; Zeng et al., 2016), Belgium (Covaci et al., 2009; Poma et al., 2018), Sweden (Remberger et al., 2004), and Tanzania (Polder et al., 2016). In the meantime, HBCDD concentrations in meat, fish, and cheese samples collected from the UK were generally lower than reported previously elsewhere (Garcia Lopez et al., 2018; Kakimoto et al., 2012; Labunska et al., 2015; Poma et al., 2018; Remberger et al., 2004; Riviere et al., 2014; Schecter et al., 2010; Venisseau et al., 2018; Wang et al., 2019; Zacs et al., 2021). The extent to which the lower concentrations in our study reflect recent restrictions on use of HBCDD is unclear.

3.2. Temporal changes in BFR concentrations in UK foodstuffs between 2015 and 2020–21

We have previously reported concentrations of NBFRs, PBDEs, and HBCDD in UK foodstuff samples collected in 2015 (Tao et al., 2017). In the current study, we employed a similar sampling strategy as well as identical sample extraction and clean-up protocols for BFR analysis in UK foodstuffs. Combined, this facilitates assessment of temporal changes in BFR concentrations in UK foodstuffs. Specifically, the percentage changes in concentrations of 6 PBDE congeners (BDE-47, -99, -100, -153, -154, and -209), 4 NBFRs (EH-TBB, BTBPE, BEH-TEBP, and DBDPE), and 3 HBCDD diastereomers (α-, β-, and γ-HBCDD) in UK foodstuffs between 2015 and 2020–21 were calculated (Fig. 3 and Figs. S3a-S5b).

3.2.1. Temporal changes in NBFR concentrations in UK foodstuffs

3.2.1.1. Σ_4NBFRs. Arithmetic mean concentrations of Σ_4NBFRs in meat, fish, cheese, and eggs have increased by 110 %, 320 %, 28 %, and 1400 % between 2015 and 2020–21, respectively. Paired-Samples *t*-test revealed such increases were statistically significant ($p = 0.047$). This suggests that increased use of NBFRs due to restrictions on PBDE and HBCDD production and consumption is now impacting food supplies in the UK. Although recent data on consumption volumes of NBFRs in Europe (especially in the UK) remains limited, global production of DBDPE was estimated to increase from 4540 to 22,700 t in 2006 to 22,700–45,400 t in 2012

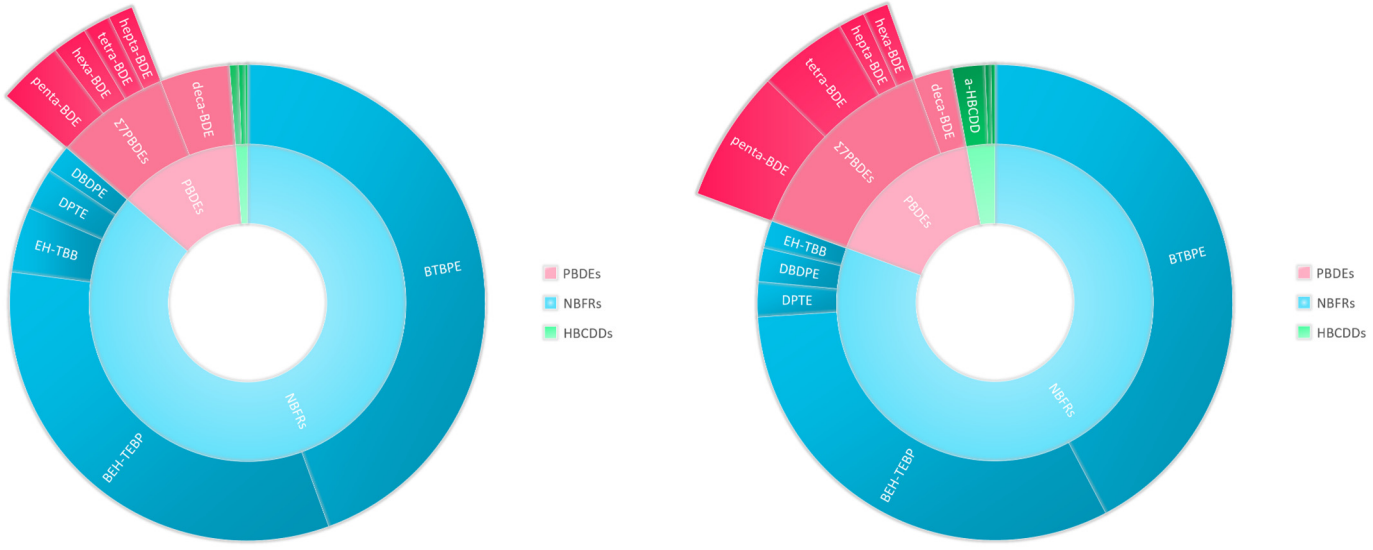


Fig. 2. Relative abundance of NBFRs, PBDEs, and HBCDDs in UK foodstuffs (left: data based on lipid weight; right: data based on wet weight).

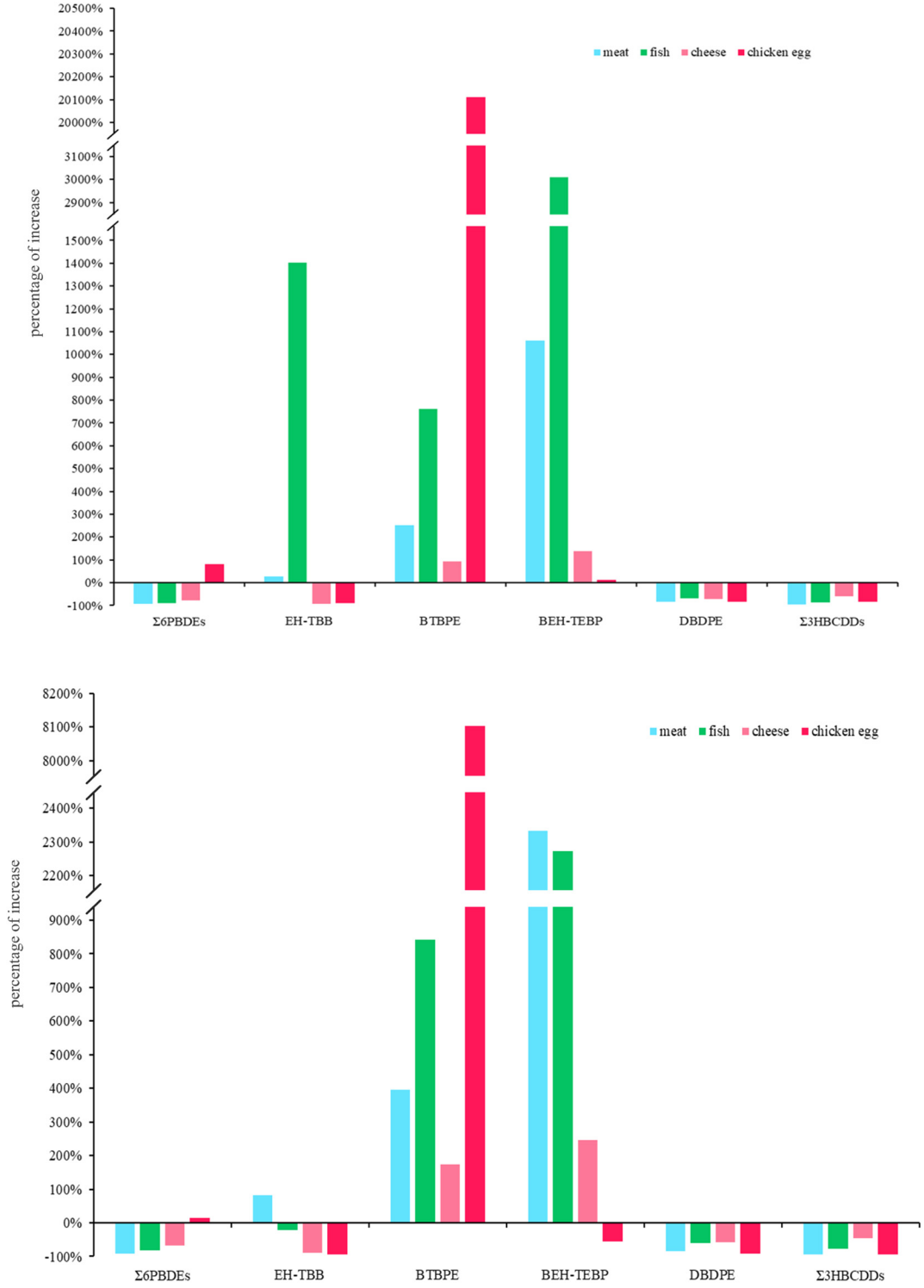


Fig. 3. Increase in BFR concentrations in UK foodstuffs between 2015 and 2020/2021 (up: data based on lipid-weight concentrations; down: data based on wet-weight concentrations).

(Hong et al., 2015), and global production of BTBPE also climbed sharply from ~5000 t to 16,710 t between 1997 and 2001 (Covaci et al., 2011; de Jourdan et al., 2013). BEH-TEBP was listed as a high production volume chemical by the US EPA (Xiong et al., 2019), and its annual production volumes in the US were 450–4500 t (Covaci et al., 2011). EH-TBB was also listed as a high production volume chemical by the US EPA in 2006 (Ma et al., 2012), but it was removed from the US EPA High Production Volume Information System in 2015, implying a production and import volume of <450 t in the US (Knudsen et al., 2016; Xiong et al., 2019).

3.2.1.2. BTBPE. Mean concentrations of BTBPE (the predominant NBFR) in meat, fish, and cheese have increased by 250 %, 760 %, and 94 % between 2015 and 2020–21, respectively, with another surprising 200-fold increase in chicken eggs. Paired samples *t*-test suggested that the increase in BTBPE concentrations in UK foodstuffs was close to statistical significance ($p = 0.070$). As inter alia a replacement for Octa-BDE, use of BTBPE is projected to rise (Covaci et al., 2011; Ezechias et al., 2014; Hou et al., 2021; Ma et al., 2022), which might explain the considerable increase in BTBPE concentrations in UK foodstuffs. Additionally, lab-based and

field-based studies have identified strong bioaccumulation and biomagnification abilities of BTBPE in a variety of species, evidenced by calculated bioaccumulation factors (BAFs) of 57–1,200,000 (La Guardia et al., 2012; Lee et al., 2019; Wu et al., 2011) and biomagnification factors (BMFs) of 1.9–3.6 (Mo et al., 2012; Tomy et al., 2007), respectively. Such propensity for bioaccumulation/biomagnification is a plausible contributory factor to the increased concentrations of BTBPE observed in the current study, coupled with the relatively long half-life (43–1900 days) of BTBPE in biota (Lee et al., 2019; Tomy et al., 2007; Zheng et al., 2018). However, the relatively small sample sizes in the two studies are a limitation, as only 5 composite egg samples were analysed in the current study and only one composite egg sample was analysed in our previous study (Tao et al., 2017). Further investigation is recommended to evaluate temporal changes in BTBPE concentrations in chicken eggs from the UK.

3.2.1.3. BEH-TEBP. A statistically significant increase ($p = 0.049$) in BEH-TEBP concentrations (the second most predominant NBFR in this study) was also identified in UK foodstuffs. Between 2015 and 2020–21, increases of 1100 %, 3000 %, 140 %, and 11 % were determined for BEH-TEBP concentrations in meat, fish, cheese, and chicken eggs, respectively. Unfortunately, there is no information on the production of BEH-TEBP in recent years, but restrictions on use of the penta-BDE formulation are likely to increase global demand for BEH-TEBP. The significant increase in concentrations of BEH-TEBP in UK foodstuffs could also be explained by its strong ability to bioaccumulate in various species (BAFs = 510–100,000) (Ezechias et al., 2014; Hou et al., 2022; La Guardia et al., 2012), as well as its long half-life in biota (36–690 days) (Bearr et al., 2012; Zheng et al., 2018).

3.2.1.4. EH-TBB. Despite the significant increase observed in concentrations of BTBPE and BEH-TEBP, concentrations of EH-TBB reported in this study were not significantly different ($p = 0.25$) from those reported previously (Tao et al., 2017). Arithmetic mean concentrations in meat of EH-TBB have increased by 26 % between 2015 and 2020–21, while those in cheese and eggs dropped by 93 % and 88 % respectively. Interestingly, while a 14-fold increase in lipid-based concentrations of EH-TBB was observed in fish samples, the corresponding wet-weight concentrations dropped by 22 %. Such a seeming contradiction stems from a lower lipid content (0.36 %) and thus a much higher lipid-based concentration of EH-TBB (35 ng/g lw) in one tuna sample. Exclusion of this sample as an outlier resulted in a 94 % decrease in concentrations of EH-TBB in fish samples. However, previous studies reported BAFs (16–8900) (Hou et al., 2022; La Guardia et al., 2012; Lee et al., 2019) and half-lives (29–1000 days) (Bearr et al., 2012; Lee et al., 2019) of EH-TBB to be similar to those of BTBPE and BEH-TEBP, suggesting similar bioaccumulation abilities. Hence, our observed discrepancy between temporal trends in these 3 NBFRs in UK foods may instead reflect reduced use of EH-TBB.

3.2.1.5. DBDPE. A decline in DBDPE concentrations was also identified in UK foodstuffs between 2015 and 2020–21. Arithmetic mean concentrations of DBDPE have decreased by 84 %, 70 %, 71 %, and 83 %, respectively, in meat, fish, cheese, and egg samples. A paired samples *t*-test suggested such changes in DBDPE concentrations were statistically significant ($p = 0.0078$). DBDPE is now primarily used as a replacement for Deca-BDE (Covaci et al., 2011), and has been frequently detected in UK and Irish indoor dust and indoor air samples at elevated concentrations, suggesting its increased use over the last few years (Drage et al., 2020; Tao et al., 2016; Wemken et al., 2019). However, DBDPE was barely detected in human breast milk from UK and Ireland (Tao et al., 2017; Wemken et al., 2020). Together with the decline in DBDPE concentrations in UK foodstuffs observed in this study, these results probably reflect very low bioavailability of DBDPE. Although high BAFs (77–13,000,000) and BMFs (1.6–9.2) were reported for DBDPE in various aquatic organisms from different ecosystems (He et al., 2012; Hou et al., 2022; Law et al., 2006), BMFs <1 were also reported for fish-kingfisher from Pearl River (China) (Mo et al., 2012), an aquatic food web from Taihu Lake (China) (Zheng et al., 2018), and white fish-emerald shiner from Winnipeg Lake (Canada) (Law et al., 2006). These results indicated that bioaccumulation and biomagnification abilities of DBDPE were strongly species-dependent. Moreover, much shorter half-lives have been reported for DBDPE (2.5–17 days) than for other NBFRs (Hou et al., 2021; McKinney et al., 2011; Wang et al., 2020; Zheng et al., 2018), which could provide a rationale for the different temporal trends in DBDPE concentrations in UK foodstuffs compared to indoor dust.

3.2.2. Temporal changes in PBDE concentrations in UK foodstuffs

Significantly lower concentrations were observed in UK foodstuffs for both Σ_6PBDEs ($p < 0.001$) and individual PBDE congeners ($p = 0.0011$–0.065). Concentrations of Σ_6PBDEs have decreased by 92 %, 90 %, and 78 %, respectively, in meat, fish, and cheese samples during 2015 and 2020–21. This is very likely due to the global phase-out of PBDEs. In contrast however, concentrations of Σ_6PBDEs showed an unexpected increase by 81 % in chicken eggs over the same period, due to increased concentrations of lower-brominated BDEs, as concentrations of BDE-209 declined in egg samples (Figs. S4a and S4b). A possible explanation for this was debromination of BDE-209 to lower-brominated BDEs, as chicken eggs had higher ratios of $\Sigma_{\text{tri-hepta}}$PBDEs/BDE-209 (12) than did meat (1.6), fish (1.2), and cheese (7.0) in the current study.

We have previously reported temporal declines in PBDE concentrations in UK indoor environments (Tao et al., 2016), but did not identify any temporal declines in PBDE concentrations in UK foodstuffs, concluding that food responded relatively slowly to global restrictions on PBDE production and consumption (Tao et al., 2017). In the current study, however, we observed significantly declined concentrations of PBDEs in UK foodstuffs between 2015 and 2020–21. Combined with our observation of higher contributions of NBFRs than PBDEs to BFRs (Section 3.1.2), this study suggests restrictions on PBDEs are now reducing their presence in UK foodstuffs.

3.2.3. Temporal changes in HBCDD concentrations in UK foodstuffs

Similar to PBDEs, concentrations of Σ_3HBCDDs in UK foodstuffs also declined significantly ($p = 0.003$). Σ_3HBCDD concentrations in meat, fish, cheese, and chicken eggs fell by 97 %, 87 %, 59 %, and 85 % between 2015 and 2020–21, respectively. Our previous study reported comparable HBCDD concentrations in UK foodstuffs in 2015 to those in 2004 (Driffield et al., 2008) and 2006 (Food Standards Agency, 2006), suggesting slow response of UK foodstuffs to restrictions on use of HBCDD. The significantly lower concentrations of HBCDD observed in the present study indicate restrictions on HBCDD use have had a discernible impact on UK dietary contamination.

3.3. Estimation of daily dietary intake of BFRs for UK citizens

Daily dietary intakes of BFRs for UK citizens were estimated using the equation described in Section 2.3. Body weight data for UK citizens was obtained from NHS Digital (2019) (Table S13). Daily consumption of various food items for UK citizens from different age groups was obtained from University of Cambridge, MRC Epidemiology Unit, NatCen Social Research (2022), and is summarised in Tables S14-S16.

Estimates of daily dietary intake of BFRs for UK citizens are shown in Table 2 and Figs. 4, S6a, and S6b. Both average intake (where average consumption of food contaminated at the average concentration was assumed) and high-end intake (assuming food contaminated at the average concentrations consumed at the mean rate + 2 standard deviations) were estimated for UK citizens from all age groups. Daily dietary intake of BFRs was estimated to range from 2.7 ng/kg bw/day to 9.9 ng/kg bw/day under an average food intake scenario, and from 18 ng/kg bw/day to 62 ng/kg bw/day under a high food intake scenario, respectively. NBFRs constituted 85 % of total BFR intake, with the remaining 13 % and 2 % attributed to PBDEs and HBCDD, respectively. Consumption of meat and chicken eggs contributed most to dietary intake of BFRs, accounting for 48 % and 31 %, respectively. This was followed by consumption of fish/prawns (17 %) and cheese (4 %).

Table 2
Estimated average and high-end[a] dietary intake of BFRs (ng/kg bw/day) for UK citizens.

BFRs	Dietary intake	0–1 years	2–4 years	5–7 years	8–10 years	11–12 years	13–15 years	16–24 years	25–34 years	35–44 years	45–54 years	55–64 years	65–74 years	75+ years
DPTE	Average	0.25	0.15	0.12	0.10	0.087	0.071	0.076	0.084	0.081	0.076	0.072	0.068	0.070
	High-end	1.5	0.94	0.76	0.62	0.50	0.45	0.45	0.50	0.47	0.46	0.45	0.40	0.44
EH-TBB	Average	0.19	0.12	0.092	0.078	0.067	0.055	0.059	0.065	0.063	0.059	0.056	0.053	0.054
	High-end	1.2	0.73	0.59	0.48	0.39	0.35	0.35	0.39	0.37	0.35	0.35	0.31	0.34
BTBPE	Average	4.4	2.7	2.1	1.8	1.5	1.3	1.4	1.5	1.4	1.3	1.3	1.2	1.2
	High-end	27	17	13	11	9.0	8.0	8.0	9.0	8.4	8.1	7.9	7.1	7.8
BEH-TEBP	Average	3.3	2.0	1.6	1.3	1.2	0.95	1.0	1.1	1.1	1.0	0.96	0.91	0.93
	High-end	20	13	10	8.3	6.7	6.0	6.0	6.7	6.3	6.1	6.0	5.3	5.9
DBDPE	Average	0.24	0.15	0.11	0.097	0.083	0.069	0.074	0.081	0.078	0.073	0.069	0.066	0.067
	High-end	1.5	0.91	0.73	0.60	0.49	0.43	0.44	0.49	0.45	0.44	0.43	0.39	0.42
ΣNBFRs	Average	8.4	5.1	4.0	3.4	2.9	2.4	2.6	2.8	2.7	2.6	2.4	2.3	2.3
	High-end	51	32	26	21	17	15	15	17	16	15	15	13	15
BDE-209	Average	0.20	0.11	0.089	0.071	0.061	0.046	0.046	0.062	0.058	0.056	0.058	0.059	0.059
	High-end	1.4	0.81	0.67	0.52	0.44	0.37	0.35	0.44	0.41	0.39	0.39	0.36	0.39
ΣPBDEs	Average	1.3	0.73	0.56	0.45	0.39	0.29	0.29	0.39	0.37	0.36	0.37	0.38	0.38
	High-end	8.8	5.1	4.3	3.3	2.8	2.3	2.2	2.8	2.6	2.5	2.5	2.3	2.4
α-HBCDD	Average	0.13	0.054	0.048	0.043	0.034	0.028	0.027	0.043	0.040	0.041	0.044	0.051	0.054
	High-end	1.2	0.58	0.57	0.45	0.35	0.34	0.29	0.41	0.37	0.35	0.37	0.36	0.39
β-HBCDD	Average	0.025	0.010	0.0091	0.0080	0.0064	0.0052	0.0050	0.0082	0.0075	0.0078	0.0083	0.0095	0.010
	High-end	0.23	0.11	0.11	0.085	0.066	0.064	0.055	0.076	0.069	0.066	0.069	0.067	0.074
γ-HBCDD	Average	0.017	0.0067	0.0060	0.0053	0.0042	0.0034	0.0033	0.0054	0.0050	0.0051	0.0055	0.0063	0.0067
	High-end	0.15	0.072	0.070	0.056	0.043	0.042	0.036	0.050	0.046	0.043	0.046	0.044	0.049
ΣHBCDDs	Average	0.18	0.071	0.064	0.056	0.045	0.037	0.035	0.057	0.053	0.055	0.058	0.067	0.071
	High-end	1.6	0.77	0.75	0.59	0.46	0.45	0.39	0.54	0.48	0.46	0.48	0.47	0.52

[a] High-end estimations were made assuming high-end food intakes of mean + 2SD (Table S14), because statistically this equals to 95th percentile values.

Comparison with dietary intake estimates from our previous research (Tao et al., 2017) revealed a considerable decrease in the dietary intake of PBDEs and HBCDD of UK citizens between 2015 and 2020–21 (Table S17). Dietary intake of PBDEs decreased by 62 %–83 % and 65 %–84 % for UK toddlers (≤ 3 years old) and adults (≥ 18 years old) from 2015 to 2020–21, while intake of HBCDD decreased by 70 %–92 % and

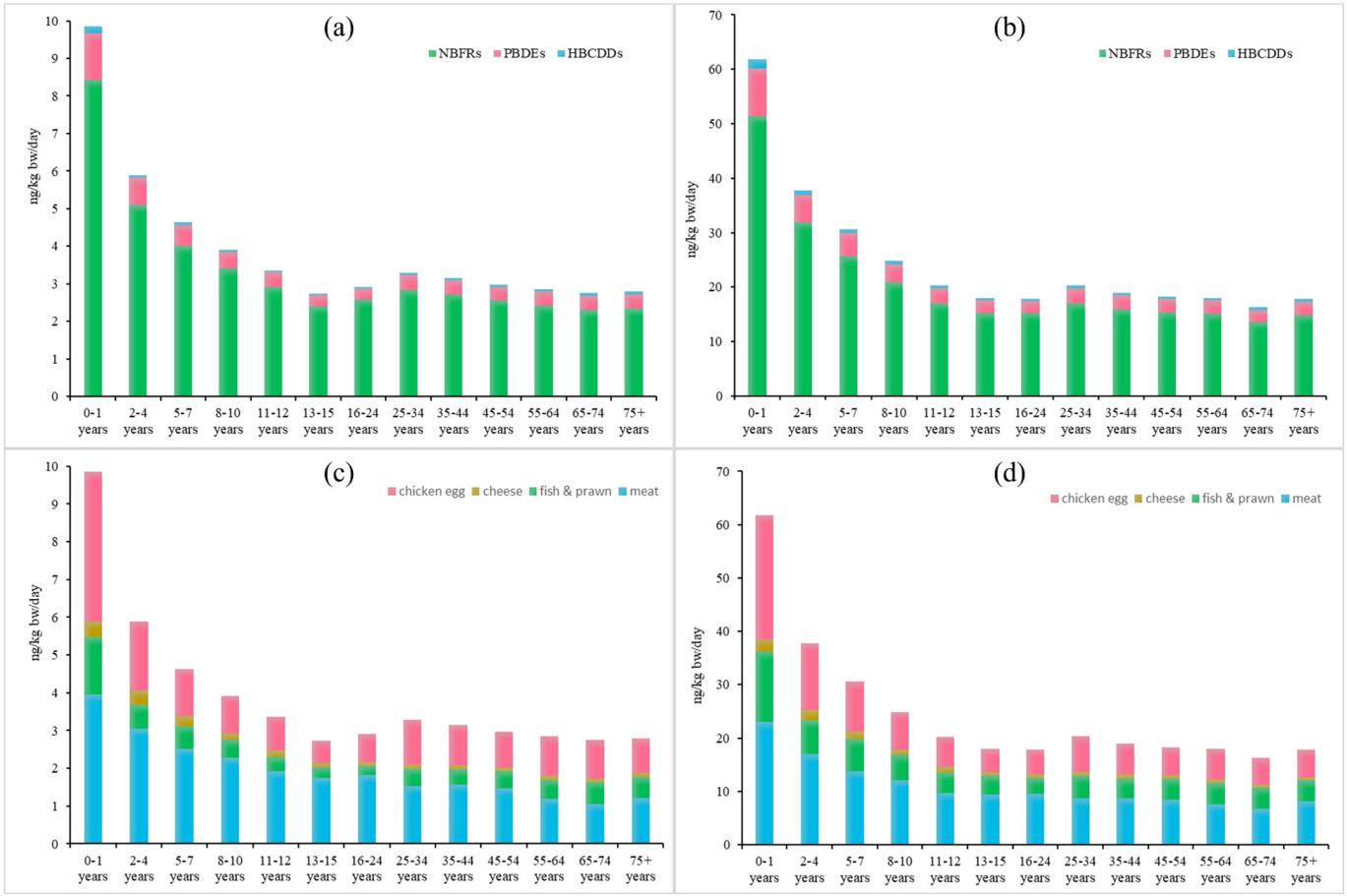


Fig. 4. Estimated dietary intake of BFRs for UK citizens from different age groups ((a) and (c): average estimations where average food intakes were assumed; (b) and (d): high-end estimations where high-end food intakes of average + 2SD were assumed).

74 %–92 %, respectively. Conversely, estimated UK dietary intake of NBFRs in this study was 2–3 times higher than our previous estimates. However, despite such increased intakes, it is noteworthy that dietary intake of NBFRs for UK citizens was generally 3 to 5 orders of magnitude lower than corresponding health-based reference doses (Table S18).

As is shown in Fig. 4, we observed significantly decreased dietary intake (body weight normalised) of BFRs with increasing age for children (p = 0.014), while for adults no considerable difference in intake of BFRs was observed between different age groups. These results raise concerns about possible adverse health effects of BFRs on toddlers because of their higher exposure doses and less developed immune system. Moreover, in addition to the relatively higher exposure doses estimated for toddlers than for other age groups based on our dietary data, this study still very likely underestimates dietary intake of BFRs for toddlers, as human milk and baby food (which were not sampled in this study) constitute important parts of their diet. Additionally, the margin of safety will be lower once other exposure pathways (e.g., dust ingestion, dermal uptake, etc.) are taken into account.

4. Conclusions

This study reported considerably increased concentrations of BTBPE and BEH-TEBP along with significantly lower concentrations of PBDEs and HBCDDs in UK foodstuffs from 2015 to 2020–21. Compared to our previous study where PBDEs were the predominant BFRs in UK foodstuffs in 2015 (Tao et al., 2017), the contribution of PBDEs to total BFRs was substantially outweighed by NBFRs in UK foodstuffs in 2020–21. These results likely reflect the global phase-out of use of PBDEs and HBCDD and their consequent replacement by NBFRs. In contrast, concentrations of EH-TBB and DBDPE in UK foodstuffs fell between 2015 and 2020–21. While reduced consumption of EH-TBB is a plausible explanation, the decrease in concentrations of DBDPE cannot be explained in the same way, and instead probably reflect the very low bioavailability of this high molecular weight chemical. Overall, estimates of UK dietary intake of BFRs show considerably decreased exposure to PBDEs and HBCDD but increased exposure to NBFRs. Significantly decreased dietary intakes of BFRs with increasing age was observed for children, while for adults no considerable difference in BFR exposure was observed between different age groups. This is of concern for toddlers, given their higher exposure and less developed immune system.

CRediT authorship contribution statement

Yulong Ma: Methodology, Validation, Formal analysis, Investigation, Visualization, Writing – original draft. **William A. Stubbings:** Writing – review & editing. **Mohamed Abou-Elwafa Abdallah:** Writing – review & editing. **Reginald Cline-Cole:** Supervision, Writing – review & editing. **Stuart Harrad:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is supported by the Global Challenges PhD Scholarship granted to Yulong Ma by the University of Birmingham. We acknowledge Dr. Joseph Shavila from Food Standards Agency gratefully for our access to the data on daily food consumption for UK citizens. We also acknowledge Dr. Muideen Remilekun Gbadamosi from the University of Birmingham gratefully for collaborative sampling of UK foodstuffs.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.160956.

References

Bearr, J.S., Mitchelmore, C.L., Roberts, S.C., Stapleton, H.M., 2012. Species specific differences in the in vitro metabolism of the flame retardant mixture, Firemaster® BZ-54. Aquat. Toxicol. 124–125, 41–47.
Covaci, A., Roosens, L., Dirtu, A.C., Waegeneers, N., Van Overmeire, I., Neels, H., et al., 2009. Brominated flame retardants in Belgian home-produced eggs: levels and contamination sources. Sci. Total Environ. 407, 4387–4396.
Covaci, A., Harrad, S., Abdallah, M.A.E., Ali, N., Law, R.J., Herzke, D., et al., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ. Int. 37, 532–556.
de Jourdan, B.P., Hanson, M.L., Muir, D.C., Solomon, K.R., 2013. Environmental fate of three novel brominated flame retardants in aquatic mesocosms. Environ. Toxicol. Chem. 32, 1060–1068.
Drage, D.S., Waiyarat, S., Harrad, S., Abou-Elwafa, A.M., Boontanon, S.K., 2020. Temporal trends in concentrations of legacy and novel brominated flame retardants in house dust from Birmingham in the United Kingdom. Emerg. Contam. 6, 323–329.
Driffield, M., Harmer, N., Bradley, E., Fernandes, A.R., Rose, M., Mortimer, D., et al., 2008. Determination of brominated flame retardants in food by LC–MS/MS: diastereoisomer-specific hexabromocyclododecane and tetrabromobisphenol A. Food Addit. Contam. 25, 895–903.
Ezechias, M., Covino, S., Cajthaml, T., 2014. Ecotoxicity and biodegradability of new brominated flame retardants: a review. Ecotoxicol. Environ. Saf. 110, 153–167.
Fangstrom, B., Athanassiadis, I., Odsjo, T., Noren, K., Bergman, A., 2008. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980–2004. Mol. Nutr. Food Res. 52, 187–193.
Fernandes, A.R., Mortimer, D., Rose, M., Smith, F., Panton, S., Garcia-Lopez, M., 2016. Bromine content and brominated flame retardants in food and animal feed from the UK. Chemosphere 150, 472–478.
Food Standards Agency, 2006. Brominated chemicals: UK dietary intakes. available at https://webarchive.nationalarchives.gov.uk/ukgwa/20120403220652/http://www.food.gov.uk/multimedia/pdfs/fsis1006.pdf. (Accessed 24 April 2022).
Garcia Lopez, M., Driffield, M., Fernandes, A.R., Smith, F., Tarbin, J., Lloyd, A.S., et al., 2018. Occurrence of polybrominated diphenylethers, hexabromocyclododecanes, bromophenols and tetrabromobisphenols A and S in Irish foods. Chemosphere 197, 709–715.
Gebbink, W.A., van der Lee, M.K., Peters, R.J.B., Traag, W.A., Dam, G.T., Hoogenboom, R., et al., 2019. Brominated flame retardants in animal derived foods in the Netherlands between 2009 and 2014. Chemosphere 234, 171–178.
Hale, R.C., La Guardia, M.J., Harvey, E., Gaylor, M.O., Mainor, T.M., 2006. Brominated flame retardant concentrations and trends in abiotic media. Chemosphere 64, 181–186.
He, M.J., Luo, X.J., Chen, M.Y., Sun, Y.X., Chen, S.J., Mai, B.X., 2012. Bioaccumulation of polybrominated diphenyl ethers and decabromodiphenyl ethane in fish from a river system in a highly industrialized area, South China. Sci. Total Environ. 419, 109–115.
Hites, R.A., Foran, J.A., Schwager, S.J., Knuth, B.A., Hamilton, M.C., Carpenter, D.O., 2004. Global assessment of polybrominated diphenyl ethers in farmed and wild Salmon. Environ. Sci. Technol. 38, 4945–4949.
Hong, B., Wu, T., Zhao, G., Sun, Y., Wang, X., Zhao, J., et al., 2015. Occurrence of decabromodiphenyl ethane in captive Chinese alligators (Alligator sinensis) from China. Bull. Environ. Contam. Toxicol. 94, 12–16.
Hou, R., Lin, L., Li, H., Liu, S., Xu, X., Xu, Y., et al., 2021. Occurrence, bioaccumulation, fate, and risk assessment of novel brominated flame retardants (NBFRs) in aquatic environments - a critical review. Water Res. 198, 117168.
Hou, R., Huang, Q., Pan, Y., Lin, L., Liu, S., Li, H., et al., 2022. Novel brominated flame retardants (NBFRs) in a tropical marine food web from the South China Sea: the influence of hydrophobicity and biotransformation on structure-related trophodynamics. Environ. Sci. Technol. 56, 3147–3158.
Jiang, Y., Yuan, L., Lin, Q., Ma, S., Yu, Y., 2019. Polybrominated diphenyl ethers in the environment and human external and internal exposure in China: a review. Sci. Total Environ. 696, 133902.
Johansson, A.K., Sellstrom, U., Lindberg, P., Bignert, A., de Wit, C.A., 2011. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in Swedish Peregrine falcon (Falco peregrinus peregrinus) eggs. Environ. Int. 37, 678–686.
Kakimoto, K., Nagayoshi, H., Yoshida, J., Akutsu, K., Konishi, Y., Toriba, A., et al., 2012. Detection of dechlorane plus and brominated flame retardants in marketed fish in Japan. Chemosphere 89, 416–419.
Klincic, D., Dvorscak, M., Jagic, K., Mendas, G., Romanic, S.H., 2020. Levels and distribution of polybrominated diphenyl ethers in humans and environmental compartments: a comprehensive review of the last five years of research. Environ. Sci. Pollut. Res. 27, 5744–5758.
Knudsen, G.A., Sanders, J.M., Birnbaum, L.S., 2016. Disposition of the emerging brominated flame retardant, 2-ethylhexyl 2, 3, 4, 5-tetrabromobenzoate, in female SD rats and male B6C3F1 mice: effects of dose, route, and repeated administration. Toxicol. Sci. 154, 392–402.
Koizumi, A., Yoshinaga, T., Harada, K., Inoue, K., Morikawa, A., Muroi, J., et al., 2005. Assessment of human exposure to polychlorinated biphenyls and polybrominated diphenyl ethers in Japan using archived samples from the early 1980s and mid-1990s. Environ. Res. 99, 31–39.

La Guardia, M.J., Hale, R.C., Harvey, E., Mainor, T.M., Ciparis, S., 2012. In situ accumulation of HBCD, PBDEs, and several alternative flame-retardants in the bivalve (Corbicula fluminea) and gastropod (Elimia proxima). Environ. Sci. Technol. 46, 5798–5805.

Labunska, I., Abdallah, M.A.E., Eulaers, I., Covaci, A., Tao, F., Wang, M., et al., 2015. Human dietary intake of organohalogen contaminants at e-waste recycling sites in Eastern China. Environ. Int. 74, 209–220.

Law, K., Halldorson, T., Danell, R., Stern, G., Gewurtz, S., Alaee, M., et al., 2006. Bioaccumulation and trophic transfer of some brominated flame retardants in a Lake Winnipeg (Canada) food web. Environ. Toxicol. Chem. 25, 2177–2186.

Lee, H., Jung, J., Kwon, J., 2019. Evaluation of the bioaccumulation potential of selected alternative brominated flame retardants in marine fish using in vitro metabolic transformation rates. Sci. Total Environ. 653, 1333–1342.

Li, W., Qi, H., Ma, W., Liu, L., Zhang, Z., Mohammed, M.O.A., et al., 2015. Brominated flame retardants in Chinese air before and after the phase out of polybrominated diphenyl ethers. Atmos. Environ. 117, 156–161.

Ma, Y., Venier, M., Hites, R.A., 2012. 2-Ethylhexyl tetrabromobenzoate and bis (2-ethylhexyl) tetrabromophthalate flame retardants in the Great Lakes atmosphere. Environ. Sci. Technol. 46, 204–208.

Ma, W.L., Yun, S., Bell, E.M., Druschel, C.M., Caggana, M., Aldous, K.M., et al., 2013. Temporal trends of polybrominated diphenyl ethers (PBDEs) in the blood of newborns from New York state during 1997 through 2011: analysis of dried blood spots from the newborn screening program. Environ. Sci. Technol. 47, 8015–8021.

Ma, Y., Li, P., Jin, J., Wang, Y., Wang, Q., 2017. Current halogenated flame retardant concentrations in serum from residents of Shandong Province, China, and temporal changes in the concentrations. Environ. Res. 155, 116–122.

Ma, Y., Stubbings, W.A., Cline-Cole, R., Harrad, S., 2021. Human exposure to halogenated and organophosphate flame retardants through informal e-waste handling activities - a critical review. Environ. Pollut. 268, 115727.

Ma, Y., Stubbings, W.A., Abdallah, M.A.E., Cline-Cole, R., Harrad, S., 2022. Formal waste treatment facilities as a source of halogenated flame retardants and organophosphate esters to the environment: a critical review with particular focus on outdoor air and soil. Sci. Total Environ. 807, 150747.

McDonald, T.A., 2002. A perspective on the potential health risks of PBDEs. Chemosphere 46, 745–755.

McKinney, M.A., Dietz, R., Sonne, C., De Guise, S., Skirnisson, K., Karlsson, K., et al., 2011. Comparative hepatic microsomal biotransformation of selected PBDEs, including decabromodiphenyl ether, and decabromodiphenyl ethane flame retardants in Arctic marine-feeding mammals. Environ. Toxicol. Chem. 30, 1506–1514.

Mo, L., Wu, J.P., Luo, X.J., Zou, F.S., Mai, B.X., 2012. Bioaccumulation of polybrominated diphenyl ethers, decabromodiphenyl ethane, and 1,2-bis(2,4,6-tribromophenoxy) ethane flame retardants in kingfishers (Alcedo atthis) from an electronic waste-recycling site in South China. Environ. Toxicol. Chem. 31, 2153–2158.

NHS Digital, 2019. Health Survey for England, 2019: data tables. available at https://digital.nhs.uk/data-and-information/publications/statistical/health-survey-for-england/2019/health-survey-for-england-2019-data-tables. (Accessed 17 October 2021).

Polder, A., Muller, M.B., Brynildsrud, O.B., de Boer, J., Hamers, T., Kamstra, J.H., et al., 2016. Dioxins, PCBs, chlorinated pesticides and brominated flame retardants in free-range chicken eggs from peri-urban areas in Arusha, Tanzania: levels and implications for human health. Sci. Total Environ. 551–552, 656–667.

Poma, G., Malysheva, S.V., Goscinny, S., Malarvannan, G., Voorspoels, S., Covaci, A., et al., 2018. Occurrence of selected halogenated flame retardants in Belgian foodstuff. Chemosphere 194, 256–265.

Remberger, M., Sternbeck, J., Palm, A., Kaj, L., Strömberg, K., Brorström-Lundén, E., 2004. The environmental occurrence of hexabromocyclododecane in Sweden. Chemosphere 54, 9–21.

Riviere, G., Sirot, V., Tard, A., Jean, J., Marchand, P., Veyrand, B., et al., 2014. Food risk assessment for perfluoroalkyl acids and brominated flame retardants in the French population: results from the second French total diet study. Sci. Total Environ. 491–492, 176–183.

Schecter, A., Haffner, D., Colacino, J., Patel, K., Papke, O., Opel, M., et al., 2010. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclodecane (HBCD) in composite U.S. food samples. Environ. Health Perspect. 118, 357–362.

Schrenk, D., Bignami, M., Bodin, L., Chipman, J.K., del Mazo, J., Grasl-Kraupp, B., et al., 2021. Update of the risk assessment of hexabromocyclododecanes (HBCDD s) in food. EFSA J. 19, e06421.

Sharkey, M., Harrad, S., Abdallah, M.A.E., Drage, D.S., Berresheim, H., 2020. Phasing-out of legacy brominated flame retardants: the UNEP Stockholm Convention and other legislative action worldwide. Environ. Int. 144, 106041.

Shi, Z., Zhang, L., Li, J., Zhao, Y., Sun, Z., Zhou, X., et al., 2016. Novel brominated flame retardants in food composites and human milk from the Chinese Total Diet Study in 2011: concentrations and a dietary exposure assessment. Environ. Int. 96, 82–90.

Shi, Z., Zhang, L., Li, J., Wu, Y., 2018. Legacy and emerging brominated flame retardants in China: a review on food and human milk contamination, human dietary exposure and risk assessment. Chemosphere 198, 522–536.

Tanabe, S., 2008. Temporal trends of brominated flame retardants in coastal waters of Japan and South China: retrospective monitoring study using archived samples from es-Bank, Ehime University,Japan. Mar. Pollut. Bull. 57, 267–274.

Tao, F., Abdallah, M.A.E., Harrad, S., 2016. Emerging and legacy flame retardants in UK indoor air and dust: evidence for replacement of PBDEs by emerging flame retardants? Environ. Sci. Technol. 50, 13052–13061.

Tao, F., Abdallah, M.A.E., Ashworth, D.C., Douglas, P., Toledano, M.B., Harrad, S., 2017. Emerging and legacy flame retardants in UK human milk and food suggest slow response to restrictions on use of PBDEs and HBCDD. Environ. Int. 105, 95–104.

Toms, L.M., Guerra, P., Eljarrat, E., Barcelo, D., Harden, F.A., Hobson, P., et al., 2012. Brominated flame retardants in the Australian population: 1993–2009. Chemosphere 89, 398–403.

Tomy, G.T., Palace, V.P., Pleskach, K., Ismail, N., Oswald, T., Danell, R., et al., 2007. Dietary exposure of juvenile rainbow trout (Oncorhynchus mykiss) to 1, 2-bis (2, 4, 6-tribromophenoxy) ethane: bioaccumulation parameters, biochemical effects, and metabolism. Environ. Sci. Technol. 41, 4913–4918.

Trabalon, L., Vilavert, L., Domingo, J.L., Pocurull, E., Borrull, F., Nadal, M., 2017. Human exposure to brominated flame retardants through the consumption of fish and shellfish in Tarragona County (Catalonia, Spain). Food Chem. Toxicol. 104, 48–56.

University of Cambridge, MRC Epidemiology Unit, NatCen Social Research, 2022. National Diet And Nutrition Survey Years 1-11, 2008-2019. UK Data Service. SN: 653319th edition. https://doi.org/10.5255/UKDA-SN-6533-19 [available at: https://beta.ukdataservice.ac.uk/datacatalogue/studies/study?id=6533; accessed 24 Apr. 2022].

Venisseau, A., Bichon, E., Brosseaud, A., Vaccher, V., Lesquin, E., Larvor, F., et al., 2018. Occurence of legacy and novel brominated flame retardants in food and feed in France for the period 2014 to 2016. Chemosphere 207, 497–506.

Wang, J., Zhao, X., Wang, Y., Shi, Z., 2019. Tetrabromobisphenol A, hexabromocyclododecane isomers and polybrominated diphenyl ethers in foodstuffs from Beijing, China: contamination levels, dietary exposure and risk assessment. Sci. Total Environ. 666, 812–820.

Wang, Y., Ling, S., Lu, C., Jiang, L., Zhou, S., Fu, M., et al., 2020. Exploring the environmental fate of novel brominated flame retardants in a sediment-water-mudsnail system: enrichment, removal, metabolism and structural damage. Environ. Pollut. 265, 114924.

Wemken, N., Drage, D.S., Abdallah, M.A.E., Harrad, S., Coggins, M.A., 2019. Concentrations of brominated flame retardants in indoor air and dust from Ireland reveal elevated exposure to decabromodiphenyl ethane. Environ. Sci. Technol. 53, 9826–9836.

Wemken, N., Drage, D.S., Cellarius, C., Cleere, K., Morrison, J.J., Daly, S., et al., 2020. Emerging and legacy brominated flame retardants in the breast milk of first time Irish mothers suggest positive response to restrictions on use of HBCDD and penta- and octa-BDE formulations. Environ. Res. 180, 108805.

Wu, J., Guan, Y., Zhang, Y., Luo, X., Zhi, H., Chen, S., et al., 2011. Several current-use, non-PBDE brominated flame retardants are highly bioaccumulative: evidence from field determined bioaccumulation factors. Environ. Int. 37, 210–215.

Xiong, P., Yan, X., Zhu, Q., Qu, G., Shi, J., Liao, C., et al., 2019. A review of environmental occurrence, fate, and toxicity of novel brominated flame retardants. Environ. Sci. Technol. 53, 13551–13569.

Yu, L., Han, Z., Liu, C., 2015. A review on the effects of PBDEs on thyroid and reproduction systems in fish. Gen. Comp. Endocrinol. 219, 64–73.

Zacs, D., Perkons, I., Abdulajeva, E., Pasecnaja, E., Bartkiene, E., Bartkevics, V., 2021. Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDD), dechlorane-related compounds (DRCs), and emerging brominated flame retardants (EBFRs) in foods: the levels, profiles, and dietary intake in Latvia. Sci. Total Environ. 752, 141996.

Zeng, Y., Luo, X., Tang, B., Mai, B., 2016. Habitat- and species-dependent accumulation of organohalogen pollutants in home-produced eggs from an electronic waste recycling site in South China: levels, profiles, and human dietary exposure. Environ. Pollut. 216, 64–70.

Zheng, X., Xu, F., Luo, X., Mai, B., Covaci, A., 2016. Phosphate flame retardants and novel brominated flame retardants in home-produced eggs from an e-waste recycling region in China. Chemosphere 150, 545–550.

Zheng, G., Wan, Y., Shi, S., Zhao, H., Gao, S., Zhang, S., et al., 2018. Trophodynamics of emerging brominated flame retardants in the aquatic food web of Lake Taihu: relationship with organism metabolism across trophic levels. Environ. Sci. Technol. 52, 4632–4640.