APPENDIX B: 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 B contains the full text of the following references:

Meng, T., Cheng, J, Tang, Z., Yin, H. & Zhang, M. (2021). Global distribution and trends of polybrominated diphenyl ethers in human blood and breast milk: A quantitative meta-analysis of studies published in the period 2000–2019. Journal of Environmental Management, 280(2021). https://doi.org/10.1016/j.jenvman.2020.111696

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Research article

Global distribution and trends of polybrominated diphenyl ethers in human blood and breast milk: A quantitative meta-analysis of studies published in the period 2000–2019

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are a class of flame-retardants that are found throughout the human body. However, global trends and diversity of the concentrations in human body and the potential risks remain largely unresolved. Based on published data during 2000–2019, we conducted a systematic meta-analysis to understand the burden and risks of PBDEs in humans and their spatiotemporal variations. The report provides a global picture of PBDE concentrations in human blood and breast milk. We found the levels of body PBDE burden in the North American population were higher than those from Asia and Europe. However, high concentrations of blood PBDEs in occupational population from Asia were observed, largely because of poorly controlled e-waste recycling operations. Penta- and deca-BDE were the main contributors in North America and Asia, respectively, reflecting the difference in the production and use of these chemicals. On a global scale, no substantial decreases in the concentrations of PBDEs in the blood and breast milk were observed, although most of the chemicals have been phased out. The results suggested that humans will be exposed to PBDEs with relatively high concentrations in a certain period because of the legacy in products and the environmental media. And the potential health risks necessitate careful study in the future. Our results also remind that the uses of degradation-resistant chemicals should be attached great importance to their safety.

1. Introduction

Multiclass flame retardants including organic and inorganic chemicals have been used to delay or prevent flaming worldwide. Polybrominated diphenyl ethers (PBDEs) have been used extensively as flame retardants in a variety of products, including electronics, plastics and synthetic building materials, because of their excellent fire-resistant properties (Rahman et al., 2001). Since the 1970s, large amounts of PBDEs have been produced worldwide as commercial penta-, octa- and deca-BDE formulations (Darnerud et al., 2001). The historically cumulative total global productions of commercial penta- and octa-BDEs were estimated to be 175,000-tons and 130,000-tons, respectively (Abbasi et al., 2019; UNEP, 2006). The historical production of the commercial deca-BDE was estimated to be around 1,100,000-tons by 2005, and deca-BDE accounted for 100% of all PBDE production after 2005 (Abbasi et al., 2019; UNEP, 2017). The largest manufacturer and supplier of deca-BDE mixture in 2006 was China producing about 15,000 tons; however, production capacity in China has declined sharply since 2009 (Shen et al., 2019).

Most of commercial PBDEs are used as additives that are not chemically bound to the product matrix, and therefore can easily migrate and enter the ambient environment. Meanwhile, these chemicals readily accumulate in organisms because of their strong lipophilicity and high resistance to degradation (Siddiqi et al., 2003). As a result, PBDEs can easily enter humans via multiple external exposures including dietary intake, environmental exposure and dermal contact with products (Costa et al., 2016; Fromme et al., 2009). Subsequently, various organs will be exposed to PBDEs in the blood, a typical internal exposure, causing various adverse effects on human health.

PBDEs in humans can disrupt endocrine and thyroid hormones,

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change behavior, impair memory, delay neurodevelopment and increase the risk of gestational diabetes mellitus (Fitzgerald et al., 2012; Hoppe and Carey, 2007; Huang et al., 2014; Liu et al., 2018). In addition, PBDEs in the maternal body can impact children through maternal-neonatal transfer or breastfeeding. Prenatal and early childhood exposures have negative effects on children, including neurodevelopment, reproductive development and thyroid hormone levels (Eskenazi et al., 2013; Herbstman et al., 2008; Luan et al., 2019). Thus, human exposure to PBDEs and the associated health hazards have attracted worldwide attention.

Because of the health hazard posed by PBDEs, the production and use of these chemicals have been reduced or prohibited worldwide. In the European Union (EU), the production and use of penta- and octa-BDE in electrical and electronic equipment have been restricted since 2004 (EU, 2003). Commercial penta- and octa-PBDE mixtures were also banned in Australia, Canada and the United States (US) (NICNAS, 2007; USEPA, 2006). The tetra- to hepta-BDEs and deca-BDE have been classified as persistent organic pollutants by the Stockholm Convention. These measures aimed to reduce and eliminate PBDEs worldwide, and thus human PBDE burden might decrease correspondingly. Nonetheless, the legacy of PBDEs in many products have and will continue to be released into environment (ATSDR, 2017). Human exposure to these chemicals may increase over a short period with the surge of obsolete products being discarded and recycled that contain PBDEs (Bi et al., 2007).

The concentrations and compositions of serum PBDEs in various populations differed among different regions (Kalantzi et al., 2011; Stapleton et al., 2008a; Uemura et al., 2010). Moreover, the PBDEs in placenta, cord blood and breast milk have also been investigated widely in an effort to understand the effects of maternal PBDEs on infants (Chen et al., 2014; Gascon et al., 2012). PBDEs in the serum of children have been investigated to understand the potential impact on the growth and development of children (Chen et al., 2010; Knudsen et al., 2017; Perez-Maldonado et al., 2009). These results provided important information about human exposure to PBDEs. However, most of these studies focused on PBDEs in human blood or milk on a regional scale, and some only within specific local industrial areas. Currently, there is a paucity of available information detailing PBDEs in human blood and milk on a global scale. The difference in the contamination and risks of the chemicals in humans between regions remains unclear.

The trends of human levels of PBDEs have been reported in several previous studies. Generally, serum levels of BDE-47, -99 and BDE-100 in Swedish mothers decreased significantly between 1996 and 2010 (Darnerud et al., 2015). In the US, plasma penta-BDE concentrations were also found to decrease from 1998 to 2013 (Cowell et al., 2018). The concentrations of tri-to hepta-BDEs in human milk in Beijing decreased significantly between 2005 and 2014 (Chen et al., 2019). However, the concentrations of total PBDEs in Canadian human milk between 2002 and 2005 were significantly higher than those in the 1980s and 1990s (Ryan and Rawn, 2014). To date, nearly all previous studies have focused on the trend of PBDE contamination of limited geographical areas. The changes in the concentrations and risks of PBDEs in humans at a global scale have still not been understood.

In this study, we analyzed the worldwide distribution of PBDEs in human blood and breast milk, to enable a reliable understanding of the global distribution and potential effects of these chemicals on human health. Further, the difference in the contamination patterns and possible sources of PBDEs among different regions were examined, providing information on development of regionally specific management measures. We assessed the global trends in human PBDE concentrations and the health risks between 2000 and 2016, and our results will help to evaluate the effectiveness of current global policies on the restriction, elimination and risk control of PBDEs and further develop relevant strategies. In addition, a variety of other alternative organic flame retardants have been used widely worldwide, which will inevitably lead to human exposure. Our results also provide a good reference for understanding the long-term effects and health risks from the global use of these new chemicals, facilitating to plan risk management measures in time.

2. Research methodology

2.1. Data collection

We searched databases including the Web of Science, Scopus and Chinese National Knowledge using the keywords “polybrominated diphenyl ethers” (or PBDEs) combined with “human blood”, “human plasma”, “human serum” or “breast milk” and/or “cord blood/serum/plasma”. In this study, a total of 814 relevant studies published between January 2000 and May 2019 were found. The valid data from each study included: (1) reported concentrations of PBDE in human blood or breast milk; and (2) the detection method must be described clearly and the measurements were done by taking individual human samples rather than pooled samples. Selected PBDE concentrations were excluded from the study if they were only presented in the abstract, in the validation of analytical methods, or as a predicted concentration. Totally, 107 studies were selected for data extraction. A diagram representing the screening strategy of the available literature used in this meta-analysis is depicted in Fig. S1, Appendix A, Supporting information.

Concentrations of PBDEs reported as ng/g or ng/mL without lipid standardizations were excluded. In this study, the concentrations of BDE-28, -47, −99, −100, −153, −154, −183 and BDE-209 were selected, because most of their concentrations were reported separately in the available literature. Basic information taken from our selected literature are described in Appendix B, Supporting information. Moreover, the specific compositions of PBDEs in human blood and breast milk are also provided in Appendix B, Supporting information.

2.2. Data treatment, specification and analysis

The extracted data was divided into different groups according to geographical area (Asia, Europe and North America), matrices (PBDEs in human blood and breast milk) and population subgroups (general population, occupational population). In this study, the “general population” included all people other than “occupational population”, whereas the “occupational population” included residents and workers living around the recycling plants. We summed the cord blood, children’s blood and pregnant women’s blood to “general population”. Moreover, PBDE concentrations in breast milk were assumed to be independent of the sampling time during the lactation period (Hooper et al., 2007; Lee et al., 2013).

Some information in the literature has been simplified. For the convenience of temporal trend assessment, the sampling period in each previous study was simplified to a single point (i.e., year), and the details are shown in Section S1, Appendix A, Supporting information. The units of PBDE concentrations reported in different studies were unified or converted to ng/g lipid weight (lw). The median of PBDE concentrations reported in literature was preferred, and if not available the geometric mean was taken. The PBDE concentrations reported in studies as below the limit of quantitation (LOQ) or not detected was defined as half the LOQ for our data analysis. Total PBDE concentrations were the sum of median concentrations of BDE-28, -47, −99, −100, −153, −154, −183 and BDE-209.

2.3. Statistical analysis

All statistical analysis was conducted using SPSS 18.0 (IBM SPSS, Armonk, NY, USA). The Kolmogorov-Smirnov test was applied to examine whether data followed normal distributions. When the data were not normally distributed, the median and range were reported; and the Mann-Whitney test and the Kruskal-Wallis test were used in the comparison of two groups and multiple sets of data comparing, respectively. The reported individual PBDE congeners in the available studies differed. To ensure the reliability of the results, only studies that reported the concentrations of BDE-47, -99, −100, −153, −154 and BDE-209 in blood, and BDE-47, -99, −100, −153 and BDE-209 in milk were selected for principal component analysis (PCA). The logarithmic transformation was used to ensure the data conformed or approximately conformed to the normal distribution. And the Kaiser-Meyer-Olkin test and Bartlett's test of sphericity were conducted to diagnose the data suitability for PCA. In this study, the statistical significance was defined at $p < 0.05$.

3. Results and discussion

3.1. PBDEs in blood and breast milk

In our collected data, PBDE concentrations in blood were reported in 63 studies, which included approximately 14,000 participants from 15 countries, whereas those in breast milk were reported in 44 studies, which included about 3300 participants from 19 countries. Summary statistics of PBDE concentrations in blood and breast milk worldwide are presented in Tables 1 and 2. On a global scale, total concentrations of PBDEs ranged from 0.79 to 613 (median, 31.6) ng/g lw in blood and between 0.38 and 85.6 (median, 3.22) ng/g lw in breast milk. The PBDE concentrations both in blood and breast milk had non-normal distributions ($p < 0.05$), likely due to many local contamination caused by the manufacturing and/or use of PBDEs.

The concentrations of blood PBDEs in different population subgroups varied. Total concentration of PBDEs in the occupational populations was 2.39 times higher than that in the general populations ($p < 0.05$). In the selected literature, the occupational population mainly included workers engaged in the recycling and/or disposal of e-waste, or residents living in and around the e-waste recycling sites. High concentrations of PBDEs were usually reported in e-waste, and locally severe and regionally significant environmental contaminations posed by poorly controlled e-waste recycling operations have been reported in many areas (Eguchi et al., 2013; Leung et al., 2007; Zhou et al., 2019). Total concentration of blood PBDEs in children was highest, approximately 8.31 and 7.30 times higher than that in pregnant women and umbilical cords, respectively. Because of extended periods of playing, mouthing behavior and frequent hand-to-mouth contact, children are more likely to be exposed to indoor dust and specific products that contain high concentrations of PBDEs (Darrow et al., 2017; Ionas et al., 2016; Lunder et al., 2010; Stapleton et al., 2008b). More importantly, children may have much lower metabolic capacity to catabolize/remove these chemicals relative to adults (Toms et al., 2009).

Concentrations of the eight PBDEs in blood differed (Table 1). Overall, the median concentration of BDE-47 was highest, followed by BDE-153 and BDE-209, which were all significantly higher than the concentrations of the other five congeners (all at $p < 0.05$). BDE-47 is a main component of penta-BDE products (La Guardia et al., 2006). The wide use of penta-BDEs can cause high human exposure to BDE-47. Additionally, BDE-209 and BDE-99 can be converted to BDE-47 in organisms (Feng et al., 2015; Stapleton et al., 2004). BDE-153, a component of commercial penta- and octa-BDEs, has been used worldwide, resulting in the wide distribution of this BDE in the environment and organisms (Li et al., 2012; Widelka et al., 2016). Moreover, the relatively high abundance of BDE-153 found in this study could attribute to the metabolism of BDE-209, in addition to its longer half-life in human serum (Stapleton et al., 2006; Thuresson et al., 2006). BDE-209 is the major congener (50%–97%) of commercial deca-BDE products (La Guardia et al., 2006). The massive use of deca-BDE has resulted in relatively high concentrations of this chemical in dust, soils, sediments and fish (Coakley et al., 2013; Leung et al., 2007; Luo et al., 2007). However, BDE-209 has a short half-life (11–18 days) in the human body and is readily metabolized/debrominated to low-brominated compounds, likely resulting in a relatively low abundance in humans (Feng et al., 2015; Thuresson et al., 2006). In addition, relative to BDE-47, BDE-99 is more likely to be degraded to hydroxylated PBDEs, although BDE-99 is the most abundant congener of some penta-BDE products (La Guardia et al., 2006; Qiu et al., 2008). This might result in relatively low concentrations of blood BDE-99 in humans.

The concentrations of individual PBDEs in different populations also varied. The concentrations of BDE-153, -154, −183 and BDE-209 in the blood of the occupational population were significantly higher than those of the general population ($p < 0.05$). The higher concentrations of BDE-153, -154 and BDE-183 in blood might attribute to the debromination of BDE-209 (Du et al., 2013; Lee and He, 2010; Söderström et al., 2004). The concentrations of BDE-47 and BDE-153 in blood were significantly higher in children than those found in pregnant women and the umbilical cord samples (all at $p < 0.05$), further reflecting the exposure of PBDEs to children through multiple routes and the low eliminating capacity of PBDEs by children (Chen et al., 2009; Toms et al., 2009).

The homologue profiles of PBDEs in blood from different subgroups were further identified (Fig. S2). In general, BDE-47, -209 and BDE-153 represented 35.0%, 20.4% and 18.5% of the total concentrations of PBDEs, respectively. However, BDE-209 was found to be the main PBDE

Table 1
Median and range of PBDE concentrations (ng/g lipid weight) in human blood.

Groups	Σ_8PBDEs[a]	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
People in Asia	29.0 (0.79–613)	0.77 (0.01–29.2)	1.82 (0.01–78.2)	0.71 (0.01–23.4)	0.21 (<MDL–14.8)[b]	2.67 (0.29–35.0)	0.38 (<MDL–41.8)[b]	0.78 (0.01–46.9)	17.2 (<MDL–521)[b]
People in Europe	7.25 (1.23–37.1)	0.04 (0.01–0.71)	1.52 (<MDL–7.00)[b]	0.69 (0.03–7.43)	0.25 (0.06–4.5)	0.86 (0.32–3.7)	0.12 (0.02–1.91)	0.12 (0.03–1.30)	1.50 (<MDL–27.1)[b]
People in North America	58.5 (19.0–187)	1.46 (0.42–3.11)	29.2 (7.90–82.2)	5.98 (1.40–40.9)	5.81 (1.20–29.8)	10.2 (2.95–29.4)	0.66 (0.025–1.43)	0.38 (<MDL–0.76)	2.95 (0.02–24.0)
The whole population	31.6 (0.79–613)	0.82 (0.01–29.2)	3.30 (<MDL–82.2)[b]	1.94 (0.01–40.9)	1.43 (<MDL–29.8)[b]	2.96 (0.29–35.0)	0.34 (<MDL–41.8)[b]	0.42 (<MDL–46.9)[b]	2.81 (<MDL–521)[b]
General population, worldwide	26.7 (0.79–613)	0.802 (0.01–29.2)	3.25 (<MDL–82.2)[b]	2.30 (0.01–40.9)	1.60 (0.01–29.8)	2.92 (0.29–32.5)	0.25 (<MDL–41.8)[b]	0.34 (<MDL–46.9)[b]	2.63 (<MDL–403)[b]
Occupational population, worldwide	90.3 (2.11–554)	1.14 (0.01–21.1)	3.52 (0.16–78.2)	1.12 (0.09–6.00)	0.70 (<MDL–5.00)[b]	5.00 (0.51–35.0)	0.54 (0.02–25.0)	3.77 (0.03–33.0)	66.8 (0.46–521)
Pregnant women, worldwide	8.23 (0.79–31.6)	0.18 (0.01–1.43)	1.60 (<MDL–11.0)[b]	0.57 (0.01–3.17)	0.18 (0.01–1.90)	1.55 (0.31–5.73)	0.15 (0.01–1.91)	0.21 (0.01–1.65)	2.12 (<MDL–16.0)[b]
Children, worldwide	76.6 (2.96–187)	1.65 (0.33–9.90)	39.6 (0.55–82.2)	8.21 (0.05–40.9)	7.19 (0.05–29.8)	12.3 (0.43–29.4)	0.70 (0.04–3.99)	0.60 (<MDL–6.04)[b]	2.67 (1.21–146)
Cord blood, worldwide	9.23 (3.31–119)	0.33 (0.02–3.32)	1.95 (0.40–18.0)	1.24 (0.06–11.0)	0.33 (0.05–7.60)	0.94 (0.29–20.3)	0.17 (0.04–6.00)	0.59 (0.13–6.50)	2.45 (<MDL–101)[b]

[a] The concentrations of Σ_8PBDEs represent the sum of concentrations of BDE-28, -47, −99, −100, −153, −154, −183, and BDE-209.

[b] MDL, the method detection limit in individual literature that we collected.

Table 2
Median and range of PBDE concentrations (ng/g lipid weight) in human breast milk.

Regions	Σ_8PBDEs[a]	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
Asia	2.39	0.12	0.52	0.14	0.16	0.56	0.05	0.10	0.48
	(0.38–85.6)	(<MDL–6.10)[b]	(0.02–21.0)	(<MDL–17.0)[b]	(<MDL–4.70)[b]	(0.03–8.90)	(<MDL–4.10)[b]	(<MDL–7.00)[b]	(<MDL–45.6)[b]
Europe	4.38	0.04	0.99	0.50	0.39	0.54	0.05	0.05	0.34
	(1.13–7.98)	(<MDL–0.33)[b]	(0.16–3.12)	(0.06–1.04)	(0.06–0.64)	(0.10–2.51)	(0.01–0.52)	(<MDL–0.38)[b]	(<MDL–5.81)[b]
North America	28.9	1.20	16.2	4.13	2.65	2.52	0.27	0.07	1.16
	(20.3–51.3)	(0.93–1.72)	(5.60–31.3)	(2.42–6.48)	(1.40–5.52)	(1.20–6.31)	(0.17–0.40)	(0.07–0.20)	(0.25–13.0)
The whole world	3.23	0.09	0.72	0.26	0.20	0.63	0.05	0.07	0.50
	(0.38–85.6)	(<MDL–6.10)[b]	(0.021–31.3)	(<MDL–17.0)[b]	(<MDL–5.52)[b]	(0.03–8.90)[b]	(<MDL–4.10)[b]	(<MDL–7.00)[b]	(<MDL–45.6)[b]

[a] The concentrations of Σ_8PBDEs represent the sum of concentrations of BDE-28, -47, −99, −100, −153, −154, −183, and BDE-209.

[b] MDL, the method detection limit in individual literature that we collected.

congener in the occupational population. BDE-47, -99 and BDE-153 were the most abundant congeners in the blood taken from children, whereas BDE-47, -153 and BDE-209 were predominant in the blood of pregnant women. Cord blood was composed mainly of BDE-47, -99 and BDE-209. The contamination patterns could reflect the difference in exposure and metabolism of PBDEs in different populations.

The concentrations of selected individual congeners in breast milk varied significantly ($p = 0.000$) (Table 2). BDE-47, -153 and BDE-209 were the dominant congeners, representing 29.5%, 21.9% and 21.9% of the total PBDEs, respectively (Fig. S3), implying different sources and metabolism pathways of milk PBDEs.

We found that the total concentrations of PBDEs in blood were significantly higher than those in breast milk ($p < 0.05$). The median of total PBDE concentrations in blood was 8.78 times higher when compared with that of breast milk, suggesting that accumulation differs between human blood and breast milk. For individual congeners, the concentrations of BDE-47, -153 and BDE-209 were also significantly higher (all at $p = 0.000$) in blood, which were about 3.55, 3.70 and 4.59 times higher than those in breast milk, respectively. Many factors have been considered to affect the partitioning of PBDEs between maternal serum and breast milk, including molecular weight, molecular size, steric hindrance, lipophilicity and halogenation, in addition to higher lipid content in blood relative to milk (Needham et al., 2011; Schecter et al., 2010). Mannetje et al. (2012) found a clear trend between the increasing mean serum/milk ratio and increasing molar volume, hydrophobicity, molecular weight and number of halogen substitutes in PBDEs. Less brominated congeners move more easily from blood to milk, and the position of the halogen substitutes determines the rigidity of the molecular structure and consequently its ability to pass from blood to breast milk (Mannetje et al., 2012). Similar results were also observed in the serum/milk ratios for PCDD/Fs and PCBs (Inoue et al., 2006; Mannetje et al., 2012). In addition, the roles of other factors besides the molecular size and structure cannot be excluded, including differential debromination in serum and milk, or differential binding to proteins in serum and milk. In addition, the excretion of BDE-209 in milk was lower than that of BDE-47 and BDE-153 (Inoue et al., 2006). In addition, the concentrations of BDE-153 and BDE-209 in the transition from colostrum to mature milk were substantially reduced, whereas no differences were observed in maternal serum (Jakobsson et al., 2012).

3.2. Geographical distribution of PBDEs in human

Total concentrations of PBDEs in human blood taken from Asia, Europe and North America are presented in Table 1. The highest PBDE concentration was observed in North America, one-fold and 7-fold higher when compared with that in Asia and Europe, respectively, indicating that the North American population has been exposed to the highest levels of PBDEs. Over half of the total global production of PBDEs has been consumed in North America (Hale et al., 2003). In particular, up to 98% of the global demand for technical penta-BDE mixtures was estimated to come from North America before 2004 (Hale et al., 2003). As a result, higher concentrations of PBDEs in various environmental media and food from North America have been confirmed in many previous studies (Harrad et al., 2008; Hites, 2004).

We also compared the concentrations of individual PBDEs and the homologue profiles of blood PBDEs in North America, Asia and Europe. The concentrations of most of the selected congeners were highest in North America, whereas the maximum concentrations of BDE-183 and BDE-209 were present in Asia (Table 1). BDE-47, -153 and BDE-99 were main contributors in blood sampled from North America, representing 53.2%, 16.4% and 10.8% of the total PBDE concentrations, respectively (Fig. S2). The majority (>97%) of globally produced penta-BDE formulations (containing BDE-47, -99 and BDE-153) were used in North America before being phased-out in the US in 2005 (UNEP, 2006). In Asia, BDE-209 contributed highest (about 59.4%) to the total concentration of blood PBDEs (Fig. S2). This is consistent with Asia being the main producer and consumer of deca-BDE mixtures. Crude recycling of e-waste has been practiced intensively in Asia (Zhang et al., 2019). In particular, the phasing out of penta- and octa-BDE in China resulted in deca-BDE to be the only PBDE manufactured and used in the past few years (UNEP, 2014).

Total concentrations of PBDEs in breast milk differed significantly ($p < 0.05$) among North America, Asia and Europe (Table 2). Although the maximum concentrations of several congeners were present in Asia, the median concentrations of all selected congeners, excluding BDE-183 and -209, were significantly higher in North America (all at $p < 0.05$). Similar to the composition profiles in blood PBDEs, BDE-47, -99, −100 and BDE-153 were the main contributors to breast milk PBDEs in North America, representing 60.6%, 12.4%, 10.0% and 9.20% of the total concentration, respectively (Fig. S3). However, in Asia and Europe, BDE-47, BDE-153 and BDE-209 were the main PBDEs found in breast milk.

Principal component analysis (PCA) was applied to further understand the contamination patterns of blood and milk PBDEs in Asia, Europe and North America. Fig. 1 (A) shows the PCA plots by the blood samples from different areas. Overall, the plots were clustered into three groups based on PC1 and PC2 scores, further indicating region-specific differences in PBDE profiles. The first group was formed by most of the samples from North America, with similar loading for the two principal components, except for site N_1. In these samples, the summed concentrations of BDE-47 and BDE-99 contributed a median of 64.0% of the total blood PBDE concentrations (Fig. S2), thus contributing a much higher value when compared with those values from Asia and Europe. Site N_1, the blood samples from the US, had a high negative load in PC2; in these samples, BDE-47 and -99 contributed 71.2% of the concentration of total PBDEs, and the blood PBDEs were considered to be related to the release of chemicals from polyurethane and fabrics of pillows and automotive seats (Imm et al., 2009). Therefore, PBDEs in blood samples from North America might reflect the relatively high contribution of technical penta-BDEs relative to Asia and Europe.

Blood samples from Asia were clustered into the second group, showing similar scores in PC2. This can be explained by commercial deca-BDEs accounting for most of the PBDE uses in many Asian countries, especially in China, Japan and India. In the group, site A_1 had the highest loading in PC1; in the samples, BDE-209 was reported to be

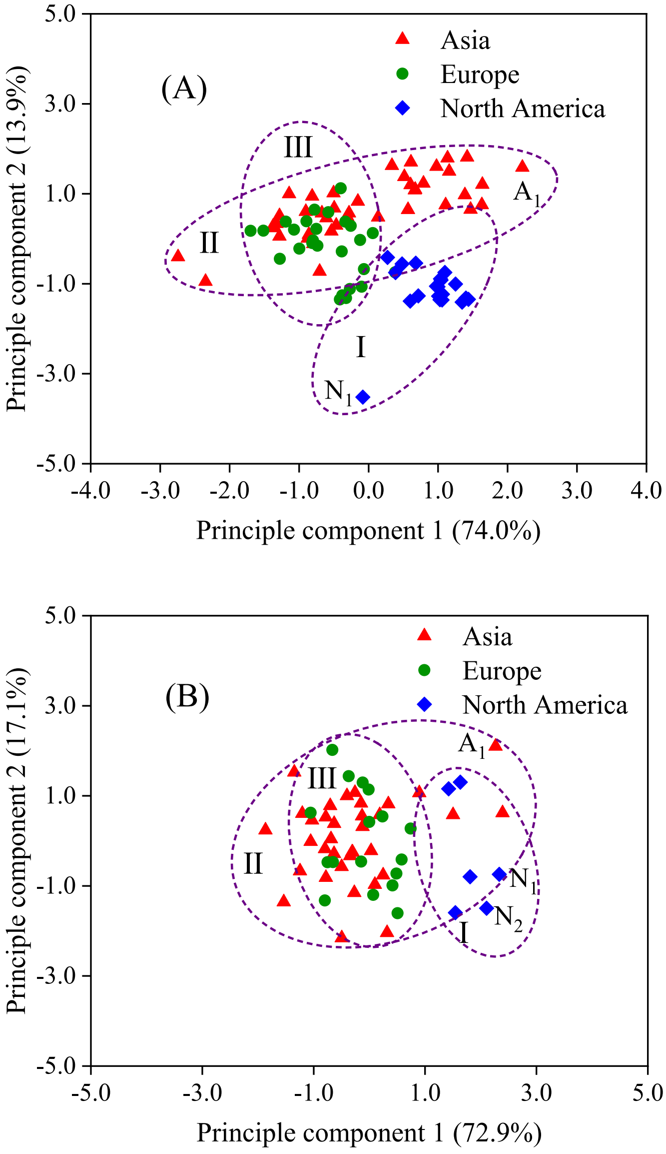

Fig. 1. Plot of PC1 versus PC2 from the principal components analyses of (A) human blood and (B) breast milk samples worldwide.

mainly from inhalation and dietary intake, and contributed to 65.7% of the total blood PBDEs (Jin et al., 2009). Results presented in Fig. 1 (A) show that samples from Europe formed the third group, and this group overlaps partly with the first and second groups, suggesting that the use of PBDEs in European countries may have similar characteristics to the above two clusters.

All milk samples also clustered into three groups based on the PCA scores (Fig. 1 (B)). The milk samples from North America formed the first group, in which BDE-47 and BDE-99 commonly contributed 73.0% of the total PBDE concentrations and the contributions were higher when compared with those from Asia and Europe. In the group, sites N_1 and N_2, samples from the US and Canada, respectively, had the highest loading in PC1; BDE-47 and BDE-99 commonly represented 73.6%, and 72.2% of the total PBDEs in the samples, respectively. Asian milk samples, with a high contribution of BDE-209 to the total PBDE concentrations, formed the second group. Fig. 1 (B) showed, however, that some samples in the second group were scattered, suggesting that their contamination pattern and possible sources of PBDEs differed from most samples from Asia. In some e-waste recycling areas, BDE-47 and BDE-99 were observed to be present in relatively high abundance in milk samples (Devanathan et al., 2012; Tue et al., 2010), attributing to the contribution of the release of penta-BDEs in crude recycling processes. Milk samples from Europe formed the third group with similar scores for the two principal components. The summed contributions of BDE-47 and BDE-99 were higher than those in Asia but lower than those in North America (Fig. S2), suggesting that PBDEs in milk from Europe may have characteristics reminiscent of both Asia and North America.

3.3. Temporal trend of PBDEs in human

In order to understand changes in human burdens, worldwide trends of total PBDE concentrations in blood during the period 2000–2016 were examined. Given the gap between sampling time and publication time, there were no relative data sampled in 2017–2019. In this study, no obvious trend of blood PBDEs was observed (Fig. 2 (A)). Our results may be affected to some extent by the non-uniformity of sampling times for the collected literature. In 2009, tetra-to hepta-PBDEs were listed as controlled chemicals, likely resulting in some changes in PBDEs in humans after 2009 (UNEP, 2009). We compared the difference of blood PBDE concentrations before and after 2009 to further explore changes. No significant difference in PBDE concentrations was found between 2000–2009 and 2010–2016. Blood PBDE concentrations were expected to decrease because of the restriction or prohibition of the manufacture and use of PBDE-based chemicals in the past decade. However, our findings indicated that there was no substantial decline of PBDE burden in blood on a global scale, although some uncertainty are present in this study.

On the other hand, the trends of blood PBDE burden among different regions differed. In Europe, the total concentrations of blood PBDEs varied significantly between the two periods ($p < 0.05$), with the median concentrations decreasing from 8.38 ng/g lw in 2000–2009 to 3.43 ng/g lw in 2010–2016 (Fig. 2 (A)). The concentrations of PBDEs were also observed to decrease in European environments (Olofsson et al., 2012;

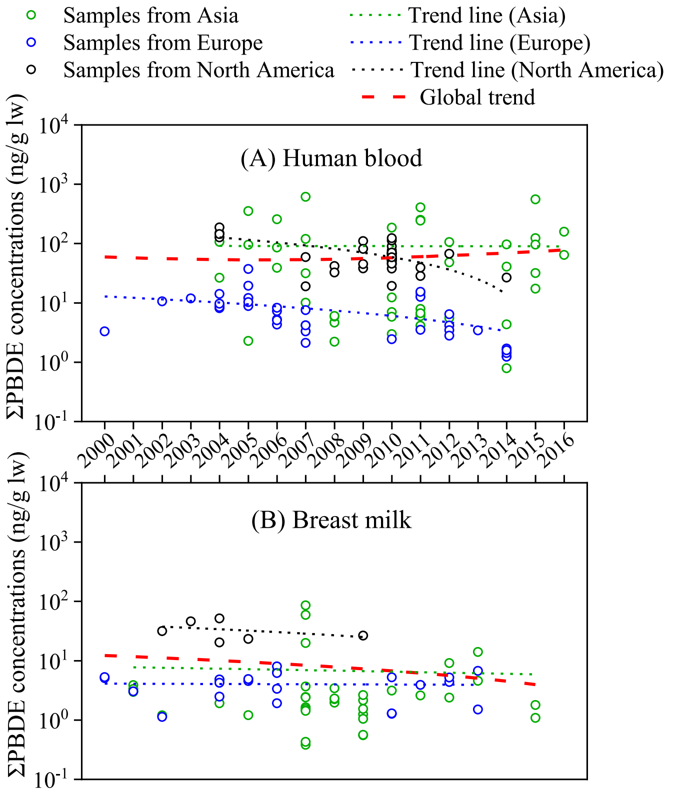

Fig. 2. Temporal trends of ΣPBDE concentrations in (A) human blood and (B) breast milk samples from the Asia, Europe and North America. ΣPBDE concentrations, summed concentrations of the median concentrations of eight PBDE congeners.

Schuster et al., 2011). Typically, the burden PBDEs in European background soils were found to decrease between 1998 and 2008 (Schuster et al., 2011). This may reflect a substantial decline in contamination by chemicals in Europe, leading to a reduction in human exposure to PBDEs. However, no significant decrease in PBDE blood burden was observed in Asia and North America. In the US, the observed trends in PBDE contaminations in different environmental media were inconsistent (Liu et al., 2016; Sutton et al., 2014). Currently, no substantial decline in PBDE environmental pollution on a national scale has been observed in China, although soil PBDE concentrations in some e-waste dismantling areas exhibit a slight decrease since 2007 (Li et al., 2016; Wang et al., 2013). Our results indicate that the blood PBDE burden might be influenced by many factors including time-lapsed effects following restrictions or bans on the production and use of PBDEs.

On a global scale, the contribution of BDE-47, the most abundant congener, to total concentration of blood PBDEs was lower in 2010–2016 than that in 2000–2009, although the difference was not statistically significant ($p > 0.05$) (Fig. S4 (A)). This suggests that the low-brominated BDEs in blood have decreased to some extent. Production and use of penta-BDEs have been gradually banned since 2004, whereas deca-BDE is still widely used since 2009, especially in Asia (UNEP, 2007; 2009). In our study, the contribution of BDE-209 to the total concentration of blood PBDEs increased from 37.4% in 2000–2009 to 51.4% in 2010–2016; however, the increase was also not statistically significant ($p > 0.05$), presumably partly due to the debromination/degradation of BDE-209 in humans (Stapleton et al., 2006).

The total concentrations of milk PBDEs worldwide seemed to have decreased from 2000 to 2015 (Fig. 2 (B)). However, there was no significant difference in the median concentrations of total PBDEs between 2000–2009 and 2010–2015, which was consistent with the temporal trend in PBDE concentrations in pregnant women serum. In the two periods, slight decreases in milk PBDE concentrations were observed for Asia, Europe and North American regions (Fig. 2 (B)), which follows the global trends. The trends of composition profiles of PBDEs in milk were similar to those in blood (Fig. S4 (B)), suggesting that blood PBDEs contaminate human milk.

4. Conclusions

The report provides a global picture of PBDEs in human blood and breast milk and describes the temporal trend of these chemicals in human. We found that the concentrations of blood PBDEs in different groups differed. Typically, the concentration of PBDEs in blood of the occupational population engaged in e-waste recycling was higher than that of the general population, and higher concentration was observed in children relative to pregnant women, suggesting that more attention to specific populations that suffered from higher exposure to PBDEs are needed. We also found that the concentrations and contamination patterns of PBDEs in blood and milk samples from Asia, Europe and North America differed clearly, reflecting that the exposure to PBDEs varied among the three regions because of the difference in the production and use of these chemicals. In general, the population from North America has been exposed to the highest levels of PBDEs. In this study, we did not find clear trends showing a decrease in concentrations of PBDEs in human blood and milk following the phasing out of these chemicals, suggesting that humans will continue to be exposed to PBDEs in the coming period and the associated health risks still need great attention.

On the other hand, this study is a pilot survey and some limitations should be noted. Some reports on human PBDEs may not have been collected in this study. The sample sizes varied widely among the areas, times and populations examined, and likely posed bias in the data obtained and might yield some uncertainty in our results, although the available data have been carefully screened. Inconsistencies in the methods used to analyze the PBDEs between studies might also lead to some uncertainty in the selected total concentrations. In this study, only statistical values obtained from literature were analyzed because detailed data in previous studies was difficult to obtain, which also generated an element of uncertainty in our findings.

Currently, the human PBDE burden is far from being well studied and available information is still limited. There have been few systematic investigations of human PBDE contamination at the national scale. The information on human PBDEs in Africa and South America are scarce. The data gap makes it difficult to assess the effectiveness of existing policies and to further develop risk management measures. Moreover, our understanding of the potential hazards caused by human PBDEs is still preliminary. To date, there has no benchmarks for the risk estimation of individual and total PBDEs in human blood and breast milk. In addition, little information is available regarding the occurrence, distribution, and potential risks of some metabolites of PBDEs in human body, including methoxylated and hydroxylated PBDEs. Similar big knowledge gap also exists in other degradation-resistant chemicals that have been and/or are widely using, including some alternative organic flame retardants. More research is required to investigate the human burden of these chemicals and the associated with health risks, providing information for developing risk management measures.

Credit author statement

Tong Meng: Resources, Data curation, Formal analysis, Investigation, Software, Writing – original draft. Jiali Cheng: Methodology, Investigation, Funding acquisition, Writing – review & editing. Zhenwu Tang: Conceptualization, Methodology, Project administration, Funding acquisition, Writing – review & editing. Hongmin Yin: Investigation, Data curation, Formal analysis. Minna Zhang: Investigation, Formal analysis.

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 article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2020.111696.

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Incidence of Pfas in soil following long-term application of class B biosolids

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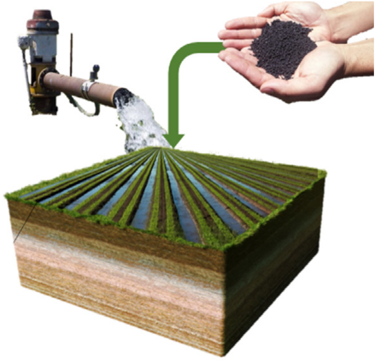
HIGHLIGHTS

- Long-term land application of biosolids resulted in low incidence of soil PFAS analytes.
- PFAS soil concentrations in irrigated agricultural plots with or without land application of biosolids were similar.
- Biosolids and irrigation water were sources of PFAS.
- >70% attenuation of total PFAS occurred within the surface 180 cm of soil.

GRAPHICAL ABSTRACT



PFAS Accumulation and Leaching in Agricultural Soils

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ABSTRACT

This field study investigated the impact of long-term land application of biosolids on PFAS presence in soils that received annual repetitive land application of Class B biosolids from 1984 to 2019. Soil samples were collected from three depths of 30.5, 91 and 183 cm below land surface. Biosolid and groundwater samples used for irrigation were also collected. Concentrations measured for 18 PFAS compounds were evaluated to assess incidence rates and potential impact on groundwater. No PFAS analytes were detected at the three sampling depths for soil samples collected from undisturbed sites with no history of agriculture, irrigation, or biosolids application (background control sites). Relatively low mean concentrations of PFAS ranging from non-detect to 1.9 μg/kg were measured in soil samples collected from sites that were used for agriculture and that received irrigation with groundwater, but never received biosolids. PFAS concentrations in soils amended with biosolids were similarly low, ranging from non-detect to a mean concentration of 4.1 μg/kg. PFOS was observed at the highest concentrations, followed by PFOA for all locations. PFAS detected in the irrigation water were also present in the soil. These results indicate that biosolids and irrigation water are both important sources of PFAS present in the soils for all of the study sites. Not all PFAS detected in the biosolids were detected in the soil. Very long chain PFAS present in the biosolids were not detected or were detected at very low levels for soil, suggesting potential preferential retention within the biosolids. The precursor NMeFOSAA was present at the second highest concentrations in the biosolids but not detected in soil, indicating possible occurrence of transformation reactions. The total PFAS soil concentrations exhibited significant attenuation with depth, with a mean attenuation of 73% at the 183 cm depth. Monotonically decreasing concentrations with depth were observed for the longer-chain PFAS.

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1. Introduction

Per and polyfluoroalkyl substances (PFAS) are fluorinated compounds that comprise a family of anthropogenic chemicals that have been used for decades to make products resistant to heat, oil stains, grease, and water (e.g., Buck et al., 2011; Kotthoff et al., 2015). PFAS are emerging contaminants of concern due to their persistence, widespread distribution in the environment, and potential for adverse human-health effects (e.g., Ahrens, 2011; Washington et al., 2019; Brusseau et al., 2020). Studies have found associations between PFAS exposure and a range of health outcomes including immunotoxicity in children, dyslipidemia, and possible carcinogenic effects (Sunderland et al., 2019).

Exposure to PFAS can result from a variety of anthropogenic uses and products including aqueous-film forming foams (AFFFs) for firefighting, textiles, carpets, paper products, and food packaging (e.g., Bečanovā et al., 2016; Schaider et al., 2017). Household dust has also been shown to be a significant source of exposure to PFAS (Fraser et al., 2013). Due to their ubiquitous usage, PFAS are also found in wastewater, biosolids, and soil.

Perfluorooctanoate (PFOA) and perfluorosulfonate (PFOS) are two PFAS that have raised particular concern, and as a result have been a focus of mitigation efforts. PFOS was phased out of production in the early 2000s in the U.S., and PFOA by 2015. This has resulted in biosolids concentrations of PFOS and PFOA decreasing over time (CDC, 2019). In addition, blood levels of PFAS in the U.S. have also declined significantly (ATSDR, 2017). However, products containing PFAS can still be imported into the U.S., and legacy effects also warrant attention. More recently, attention has switched to shorter-chain PFAS and precursor PFAS that can break down into more recalcitrant PFAS, including perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs) (Buck et al., 2011). Such shorter-chain and other replacements for PFOA and PFOS include hexafluoropropylene oxide-dimer acid (GenX) and other perfluoroalkyl ether acids (PFEAs) (Brandsma et al., 2019; Munoz et al., 2019).

It has become clear that PFAS are ubiquitous in the environment, in both the U.S. and globally (e.g., Ahrens, 2011; Kraft and Riess, 2015; Washington et al., 2019; Brusseau et al., 2020). In particular, several studies have now documented the global importance of soil as a long-term reservoir of PFAS that can potentially adversely impact surface water, groundwater, and even the atmosphere (Brusseau et al., 2020; Washington et al., 2019; Rankin et al., 2016; Strynar et al., 2012). In most instances, industrial sites and military bases are where the highest levels of contamination have been reported, but even remote areas with no obvious source of PFAS have been documented as having low levels of PFAS (Rankin et al., 2016; Brusseau et al., 2020).

Given the widespread consumer use of products that contain PFAS, it is not surprising that PFAS can be found in wastewater and sewage sludges within wastewater treatment plants, and ultimately in biosolids and effluent that result from wastewater treatment (e.g., Gallen et al., 2018; Chen et al., 2012; Loganathan et al., 2007). Studies also show that treatment plants receiving sewage from PFAS industrial dischargers have higher concentrations of PFAS in their sludge than plants not receiving industrial inputs (Clarke and Smith, 2011; Lindstrom et al., 2011). However, the fact that PFAS have been found in sludge from municipal facilities without industrial inputs puts into perspective the importance of domestic sources of PFAS (Venkatesan and Halden, 2013).

Due to the multiple routes of exposure to PFAS, PFOA and PFOS have been reported in the blood serum and breast milk of almost all humans throughout the world (Poothong et al., 2020; Jian et al., 2018). This in turn has led to increased concern regarding exposure to PFAS via potable water (Boone et al., 2018). In response to this, EPA adopted a drinking water health advisory of 70 ng/L (ppt) for the combined concentrations of PFOS and PFOA in May 2016 (EPA, 2016). Standards set by several U.S. states are more stringent. Massachusetts and Vermont have adopted drinking water standards of 20 ng/L for the sum of the concentrations of six and five individual PFAS compounds, respectively, while California has set drinking water notification levels at 5.1 and 6.5 ng/L for PFOA and PFOS.

The presence of PFAS in biosolids has generated concern over the environmental impacts and potential human-health risks associated with land application of biosolids. One particular concern is transfer of PFAS from biosolids to soil, and subsequent leaching to groundwater. These concerns have led to various restrictions placed on land application across the U.S. For example, a moratorium was imposed on land application of biosolids in Pima County, Arizona on January 1, 2020 (Pima County, 2020) due to concerns over PFAS. This action, enacted by the Pima County Board of Supervisors, doubled management costs for biosolids.

The goal of this study was to evaluate the potential impact of land application of biosolids on PFAS incidence in soil, and the potential for groundwater contamination by PFAS. A field study was implemented in the Arizona agricultural communities of Pima and Pinal County, involving multiple agricultural plots receiving repetitive annual land application of Class B biosolids from 1984 to 2019. Depth-discrete soil samples were collected from the plots. Biosolids samples and samples of groundwater used for irrigation were also collected. PFAS concentrations measured for the samples were evaluated to assess incidence rates and potential impact on groundwater.

2. Materials and methods

2.1. Approach

This study was conducted at long-term biosolids land application sites in Pima and Pinal County, Arizona. Annual land application of Class B biosolids was initiated in 1984, and continued through 2019. Land application in Arizona is allowed on permitted lands registered with the Arizona Department of Environmental Quality, and requires annual documentation of loading rates and biosolids quality. Since biosolids are known to contain PFAS, loading rates allowed for the incidence of accumulated PFAS in soil to be determined following long-term application of known amounts of biosolids. Until 2014, thickened biosolids contained 3 to 7% solids and the material was applied via surface spraying or soil injection to a depth of 30 cm. From 2014 through 2019, cake biosolids with 14% solids were applied and disked into the soil to a depth of 1 f. (30 cm). Sample site selection was carefully considered to reflect biosolids application rates, crop diversity, seasonal crop rotations, groundwater hydrology, and possible sources of PFAS influence. For example, agricultural sites located near a small regional airport were excluded from this study as soil and irrigation water sources could potentially contain PFAS originating from fire training exercises at the airport.

The agricultural sites are comprised of approximately 809 ha spread out over a 277 km area including northern Pima County and Southern Pinal County, AZ. Two primary known sources of PFAS in the Tucson area are represented by the Davis Monthan Air Force Base and Tucson International Airport, which are located approximately 34 km south of agricultural application sites selected for this study. While both of these entities discharge domestic sewage to metropolitan wastewater treatment facilities, it is not believed that prior usage of aqueous film forming foams (AFFF) were discharged to sewers. Because the Santa Cruz River receives effluent from both the Tres Rios and Agua Nueva wastewater treatment facilities, samples sites were distributed throughout the valley in order to minimize the impacts of the Santa Cruz River as a potential source of contamination.

2.2. Soil samples

A total of 72 soil samples were collected at depths of 30.5, 91 and 183 cm below the surface using hand operated soil augers. Soil was collected from five field types with different management histories:

i) undisturbed desert soil (no agriculture); ii) irrigated agricultural soils that have never received biosolids; and iii) irrigated agricultural soils receiving biosolids at three different cumulative loading rate ranges per hectare: ≤44,834 (20 tons); 47,075–67,251 kg (21–30 tons); and >67,251 kg (30 tons) (Table 1). The Tres Rios WRF was the source of biosolids for all application sites. The primary crop for this area is cotton, with occasional double-cropping with barley or wheat. Four soil-boring locations were chosen for each field type. Additional surface soil samples were collected at a site located 0.8 km from agricultural parcels receiving the highest loading of biosolids to assess possible airborne dust deposition of PFAS generated during farming operations on nearby properties.

Each soil sample was collected from a single 8 cm borehole at the designated soil depths. Field blanks and equipment blanks were collected. Strict precautions were taken to avoid extraneous PFAS contamination during sampling. Specifically, protocols from the Michigan Department of Environmental Quality Soil PFAS Sampling Guidance (11/2018) were followed. PFAS-free sampling equipment, field clothing, hygiene, personal protective equipment (PPE), and equipment decontamination procedures were critical to the collection of representative samples. Sampling equipment was constructed primarily of stainless steel and sample containers were high-density polyethylene (HDPE). Samplers did not use equipment containing Teflon materials or low-density polyethylene (LDPE). Clothing consisted of cotton uniforms, well laundered without fabric softener, and polyvinyl chloride waders in lieu of water repellent boots. Samplers did not shower on the morning of sampling events and avoided the use of cosmetics, perfumes, deodorants, and skin crèmes. Sampling equipment was decontaminated in the field between sample depths and at the laboratory after each sample event. PFAS free deionized water and pesticide grade methanol were used to rinse the equipment after each decontamination.

All soil samples were immediately transported to the University of Arizona Water and Energy Sustainable Technology Center (WEST), where they were air-dried prior to sieving (2 mm). The processed samples were then packaged for shipment to the commercial lab for analysis.

2.3. Biosolid samples

The Tres Rios Wastewater Reclamation Facility (WRF) is one of two large municipal sewage treatment facilities located in Tucson, AZ and provides 121,133 $m^3$of sewage treatment daily serving a population of approximately 367,000 people. The sewage is predominantly domestic in composition with very few industrial sources. Class B biosolids samples were taken from the Pima County Tres Rios WRF. Dewatered biosolids samples were collected four times in July of 2020 representative of four different digester contents at the Tres Rios WRF. No additional sampling equipment was necessary for sample collection. All samples were transported to the Pima County CRAO Laboratory and stored at 4 °C prior to shipment to Eurofins for subsequent PFAS.

2.4. Groundwater samples

Groundwater samples were collected from nine irrigation wells associated with the sampled agricultural sites. Water samples were collected from the discharge pipes immediately prior to entering the irrigation canals. HDPE sample bottles were provided by the contract lab. No additional sampling equipment was necessary for sample collection. All samples were transported to the Pima County CRAO Laboratory and stored at 4 °C prior to shipment to Eurofins for subsequent PFAS analysis.

2.5. Analytical methods

Samples of soil, groundwater, and biosolids were analyzed for a suite of PFAS compounds. The analyses were conducted by an international certified analytical laboratory, Eurofins TestAmerica, specializing in PFAS analyses of soil and water. Eurofins TA Sacramento analyzed all project samples using their SOP for *Method 537* (*Modified*), *Method PFAS by LCMSMS Compliant with QSM Table B-15, Revision 5.1 and higher*. This is in line with Department of Defense (DoD) minimum QC requirements. Although some information in the SOP is confidential and proprietary, the following is a summary of the extraction procedure for soils and waters. 250 mL water samples were extracted using a solid phase extraction (SPE) cartridge. PFAS were eluted from the cartridge. For soils and biosolids, 5 g of well homogenized samples were extracted with a KOH/methanol solution using an orbital shaker for 3 h followed by sonication for 12 h. The mixture was centrifuged and the solvent filtered.

The final 80:20 methanol/water extracts were analyzed by LC/MS/MS. PFAS were separated from other components on a C18 column with a solvent gradient program. The mass spectrometer detector was operated in the electrospray (ESI) negative ion mode for the analysis of PFAS.

An isotope dilution technique was employed for the compounds of interest. The isotope dilution analytes (IDA) consisted of carbon-13 labeled analogs, oxygen-18 labeled analytes, or deuterated analogs of the compounds of interest, and were spiked into the samples at the time of extraction with every analyte having its own labeled isotope analogue, otherwise it was calculated with a closely related compound (1 carbon chain difference, etc.) This technique allowed for the correction for analytical bias encountered when analyzing more chemically complex environmental samples. Quantitation by the internal standard method is employed for the IDA analytes/recoveries. IDA recoveries were to meet 25–150% recovery, however for any outside recoveries, it was assured that the data quality was not affected as long as the IDA signal-to-noise ratio was greater than 10:1, which was achieved in all samples reported.

Each sampling batch included a field sample duplicate, field blank, and equipment blanks were first submitted with three initial sampling events to ensure that the sampling procedures were being performed to eliminate cross contamination to the greatest extent possible. During analyses, Eurofins included a Laboratory Control Sample (LCS), and a Matrix Spike/Matrix Spike duplicate per preparatory batch. Matrix Spike and Matrix Spike Duplicates were included with each analytical batch. Although there were a few instances where the Matrix Spike was unacceptably higher than the laboratory specified limits, the associated Laboratory control Sample (LCS) recovery was acceptable and the

Table 1
Project sample plan criteria.

Field type	Agriculture	Irrigated[a]	Cumulative biosolids applied	Duration of application (years)
Undisturbed	No	No	–	–
Agricultural	Yes	Yes	–	–
Group 1	Yes	Yes	≤20 (tons/acre) (44,834 kg/ha)	4–9
Group 2	Yes	Yes	21–30 (tons/acre) (47075–67,251 kg/ha)	12–20
Group 3	Yes	Yes	>30 (tons/acre) (67,251 kg/ha)	6–9

[a] Irrigation with groundwater.

data result, if detected would have been slightly biased high and therefore remained included in the study. On two occasions the Matrix Spike was unacceptably lower than the laboratory specified limits, however the LCS recovery was acceptable and all samples reported for the affected PFA, which was PFTriA, was ND (below the method detection limit) for all samples analyzed in the study. All % RPDs were within the SOP's criteria of <30% RPD between spike duplicates. Data for field blanks, equipment blanks and % recoveries for matrix spikes are presented in Supplemental Information.

3. Results

3.1. PFAS concentrations in biosolids

When land application of biosolids began in Pima County in 1984, PFAS had not been identified as an emerging contaminant. Consequently, Pima County biosolids samples were not analyzed for PFAS during most of the early land application period. PFAS analyte data for biosolids analyzed in this current (2020) study are shown in Table 2. Data show that current concentrations of PFAS in the biosolids are in the low ppb range, with PFOS concentrations ranging from 14 to 36 μg/kg and <1.2 μg/kg for PFOA. This contrasts with data from the 2001 National Sewage Sludge Survey, where mean values of PFOS and PFOA in biosolids were reported to be 403 and 34 μg/kg respectively.

3.2. PFAS concentrations in irrigation water

Concentrations of PFAS in groundwater samples collected from the irrigation sources are presented in Table 3. Overall, 8 out of 18 PFAS compounds were detected in one or more irrigation sources with concentrations exhibiting considerable variation amongst the irrigation sources. The two irrigation sources containing the highest concentrations of PFOS and PFOA also had elevated concentrations of PFHxS and PFHxA. The source of these PFAS is unclear as irrigation sources at this location were also the furthest removed from any potential sources of PFAS such as an airport, fire-fighting activities, or the Santa Cruz River.

The amount of irrigation water applied to individual sites varies widely depending on the selected crops being grown. For example, a typical cotton crop receives approximately 4934 m^3 per ha of water each season whereas a seasonal rotation with cotton and wheat may receive >8364 m^3 per ha annually. While pasture crops such as alfalfa receive up to 7400 m^3 per ha of water annually, these are typically year-round crops and therefor receive less frequent biosolids applications.

3.3. Individual PFAS concentrations in soil

The incidence of PFAS in the five different field types comprising over 809 ha are shown in Tables 4–8. Data on individual soil borings are presented in Supplemental Information. The analysis of soil samples collected from undisturbed plots with no history of agriculture, irrigation, or land application of biosolids showed that no PFAS analytes were detected at any of the three sampling depths. In contrast, soil samples collected from locations with a history of irrigated agriculture but no land application of biosolids showed detectable amounts of eight PFAS, including PFOS and PFOA (Table 4). Tables 5, 6, and 7 provide PFAS data for soil samples from locations with a history of irrigated agriculture with land application of biosolids at different cumulative loading rates. The same PFAS analytes were detected in the soil samples receiving any of the three different biosolid-loading rates.

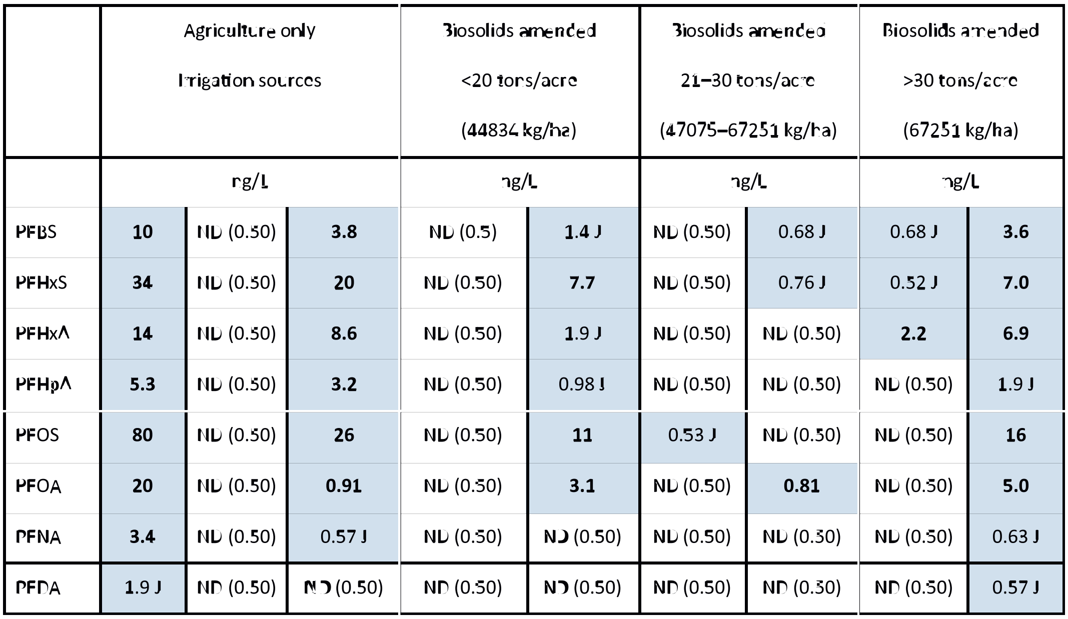
Overall, PFAS soil concentrations are relatively low for the biosolids-amended fields, with mean values ranging from non-detect to 4 μg/kg. PFOS and PFOA were detected at the highest concentrations for all plots. The maximum mean concentrations for PFOS are: 1.6 (±1.7) μg/kg (≤44,813 kg biosolids/ha); 3.1 (±2.0) μg/kg (44,813–110,688 kg biosolids/ha); and 4.1 (±1.9) μg/kg (>110,688 kg/ha). The mean PFOS soil concentrations increase with increasing cumulative loading rate of biosolids. However, the concentrations for PFOS and other PFAS vary across each plot type and, as a result, the standard-deviation ranges of the concentrations overlap for all three loading rates. For comparison, the maximum mean PFOS concentration is 1.9 (±1.2) μg/kg for the soil samples collected from the plots that received irrigation but no biosolids applications. The PFAS concentrations in irrigated agricultural soils

Table 2
PFAS analyte data for dewatered biosolids samples collected on 4 occasions at Tres Rios WRF (Pima County Arizona).

Location	**TRES RIOS WRF**			
Sample date	**7/16/2020**	**7/16/2020**	**7/27/2020**	**7/27/2020**
PFAS	**Units = µg/kg (ppb)**			
PFBS	**1.9**	**1.4**	**6.5**	ND (0.13)
PFHxS	**3.7**	**3.5**	**15**	ND (0.16)
PFHxA	**4.2**	**4**	**4.1**	**2**
PFHpA	ND (1.4)	ND (1.4)	ND (0.15)	0.15 J
NEtFOSAA	ND (19)	ND (19)	ND (1.9)	**11**
NMeFOSAA	**21**	**22**	**23**	**18**
PFOS	**34**	**36**	**27**	**14**
PFOA	ND (4.3)	ND (4.3)	ND (0.44)	**1.2**
PFNA	ND (1.8)	**2**	**2**	**1.1**
PFDA	**12**	**13**	**12**	**12**
PFUnA	**2.3**	**2.1**	**2.4**	**1.8**
PFDoA	**8**	**7.3**	**7.4**	**6.5**
PFTriA	ND (2.5)	ND (2.5)	ND (0.26)	ND (2.5)
PFTeA	**3.2**	**3.3**	ND (1.0)	ND (1.0)

Notes: μg/kg = micrograms of contaminant per kilogram of dry weight of biosolids, equivalent to parts per billion (ppb).
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects on all dates: DONA; F-53B (Major); F-53B (Minor); GenX.

Table 3
PFAS in groundwater used for irrigation.



	Agriculture only Irrigation sources			Biosolids amended <20 tons/acre (44834 kg/ha)		Biosolids amended 21–30 tons/acre (47075–67251 kg/ha)		Biosolids amended >30 tons/acre (67251 kg/ha)	
	ng/L			ng/L		ng/L		ng/L	
PFBS	**10**	ND (0.50)	**3.8**	ND (0.5)	**1.4 J**	ND (0.50)	0.68 J	0.68 J	**3.6**
PFHxS	**34**	ND (0.50)	**20**	ND (0.50)	**7.7**	ND (0.50)	0.76 J	0.52 J	**7.0**
PFHxA	**14**	ND (0.50)	**8.6**	ND (0.50)	**1.9 J**	ND (0.50)	ND (0.50)	**2.2**	**6.9**
PFHpA	**5.3**	ND (0.50)	**3.2**	ND (0.50)	0.98 J	ND (0.50)	ND (0.50)	ND (0.50)	**1.9 J**
PFOS	**80**	ND (0.50)	**26**	ND (0.50)	**11**	0.53 J	ND (0.50)	ND (0.50)	**16**
PFOA	**20**	ND (0.50)	**0.91**	ND (0.50)	**3.1**	ND (0.50)	**0.81**	ND (0.50)	**5.0**
PFNA	**3.4**	ND (0.50)	0.57 J	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	0.63 J
PFDA	1.9 J	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	0.57 J

Multiple irrigation sources are depicted for each soil group.
ND indicates not-detected.
ng/L = ppt.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects for all irrigation waters: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFDoA, PFUnA.

without any history of biosolids application are in the similar low-ppb range as those measured for the soils with land application of biosolids.

The highest soil concentrations for some of the PFAS are associated with the shallowest sampling interval. Additionally, the concentrations decline monotonically with depth for these PFAS. This is illustrated in Fig. 1, which presents the concentration distribution of PFOS. The concentration distributions for PFBS, PFHxS, PFHpA, and PFOA deviate from this trend. For these four PFAS, the highest measured soil concentrations are associated with the intermediate or deepest sampling intervals. Hence, the concentrations do not decline monotonically with

Table 4
PFAS soil concentrations in agricultural soils without land application of biosolids. Agricultural parcels represent historically farmed locations receiving groundwater irrigation, but without land applied biosolids.

Depth	**30 cm**	**91 cm**	**183 cm**	**Irrigation source Presence**
Contaminant	**µg/kg (ppb)**			
PFBS	0.03 J	ND (0.3)	ND (0.3)	√
PFDA	0.05 J	ND (0.2)	ND (0.02)	√
PFHpA	0.05 J	0.03 J	0.04 J	√
PFHxS	0.07 J	0.06 J	0.09 J	√
PFHxA	0.09 J	0.06 J	0.05 J	√
PFNA	0.08 J	ND (0.04)	ND (0.04)	√
PFOS	**1.9 ± 1.2**	**0.59 ± 0.36**	0.25 ± 0.16 J	√
PFOA	**0.26 ± 0.14**	0.18 ± 0.12 J	**0.22 ± 0.09**	√
PFOS attenuation	N/A	69%	87%	

N/A: not applicable.
ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).

Table 5
PFAS soil concentrations in agricultural soils that received <20 tons of biosolids/acre. Data represent the mean of four soil-boring locations at the three depths. These land parcels have been farmed, received irrigation, and received biosolid applications of <20 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	**30 cm**	**91 cm**	**183 cm**	**PFAS present**	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation source**
PFBS	ND (0.03)	0.08 J	0.04 J	√	√
PFDA	0.10 J	ND (0.03)	ND (0.03)	√	
PFHpA	0.08 J	0.06 J	ND (0.03)	√	√
PFHxS	0.10 J	0.17 J	0.04 J	√	√
PFHxA	0.14 J	0.11 J	ND (0.05)	√	√
PFNA	0.06 J	ND (0.04)	ND (0.04)	√	√
PFOS	**1.6 ± 1.7**	0.29 ± 0.20 J	ND (0.22)	√	√
PFOA	**0.32 ± 0.33**	**0.26 ± 0.25**	ND (0.1)	√	√
PFOS attenuation	**N/A**	**82%**	**93%**		

ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFDoA, PFUnA.

Table 6
PFAS soil concentrations in agricultural soils that received 21–30 tons of biosolids per acre. Data represent the mean of four soil-boring locations at the three depths. These land parcels have been farmed, received irrigation, and received biosolid applications of 21–30 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	**30 cm**	**91 cm**	**183 cm**	**PFAS present**	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation source**
PFBS	0.17 J	0.10 J	0.12 J	√	√
PFDA	**0.56 ± 0.42**	0.06 J	0.05 J	√	
PFDoA	0.04 J	ND (0.08)	ND (0.08)	√	
PFHpA	0.09 J	0.09 J	0.06 J	√	√
PFHxS	ND (0.04)	0.04 J	0.05 J	√	√
PFHxA	0.13 J	0.09 J	0.09 J	√	
PFNA	**0.43 ± 0.09**	0.12 J	ND (0.04)	√	
PFOS	**3.1 ± 2.0**	**0.64 ± 0.30**	0.22 ± 0.09 J	√	√
PFOA	**0.47 ± 0.28**	**0.49 ± 0.18**	**1.7 ± 2.3**	√	√
PFOS attenuation	**N/A**	**79%**	**93%**		

ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFUnA.

Table 7
PFAS soil concentrations in agricultural soils that received >30 tons of biosolids per acre. Data represent the mean of four soil-boring locations at the three depths. These land parcels have been farmed, received irrigation and have received biosolid applications of greater than 30 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	**30 cm**	**91 cm**	**183 cm**	**PFAS present**	
PFAS	**μg/kg (ppb)**			**Biosolids**	**Irrigation wells**
PFBS	**0.37 ± 0.47**	0.20 J	0.14 J	√	√
PFDA	**0.98 ± 0.41**	0.11 J	0.15 J	√	√
PFDoA	**0.24 ± 0.17**	ND (0.08)	0.08 J	√	
PFHpA	0.19 J	0.16 J	**0.24 ± 0.29**	√	√
PFHxS	0.12 J	0.15 J	0.16 J	√	√
PFHxA	**0.51 ± 0.51**	**0.22 ± 0.21**	0.13 J	√	√
PFNA	**0.43 ± 0.17**	0.15 J	0.05 J	√	√
PFOS	**4.1 ± 1.9**	**1.2 ± 1.4**	0.46 ± 0.46 J	√	√
PFOA	**0.84 ± 0.48**	**1.3 ± 1.4**	**0.51 ± 0.61**	√	√
PFTeA	0.09 J	ND (0.06)	ND (0.06)	√	
PFUnA	0.10 (0.04)	ND (0.04)	ND (0.04)	√	
PFOS attenuation	**N/A**	**71%**	**89%**		

ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTriA.

depth. This behavior is illustrated in Fig. 2 for PFOA. This non-monotonic distribution generally results from higher concentrations reported for just one or two of the plots rather than all plots. An extreme example of this variability is reflected in the observation that the standard deviation for PFOA concentrations at the deepest interval is larger than the mean value for the Group 2 fields (Table 6).

3.4. Total PFAS concentrations in soil

Total mean concentrations of PFAS in soil samples for the different field types are presented in Table 8. The concentrations for the sites receiving the lowest biosolids application are very similar to those receiving no biosolids. The total concentrations are approximately twice and three-times as large for the field receiving the intermediate and highest biosolids application, respectively. However, as noted previously, the concentrations of individual PFAS range greatly across the plots for each field type, and the concentration ranges overlap between field types.

The mean concentrations of short-chain versus long-chain PFAS are also presented in Table 8. The magnitudes of the concentrations are similar for the no-biosolids and lowest-application fields, and higher for the intermediate and highest biosolids application fields, similar to the total PFAS concentrations. Overall, the short-chain PFAS comprise a small fraction of the total.

The total PFAS concentrations are highest in the shallowest sampling interval for all four field types. In addition, the highest concentrations of the total short-chain and long-chain PFAS are also highest in the shallowest intervals. Monotonic declines in total concentrations with depth are observed for all field types except for Group 2 biosolids-amended fields. For example, the values decrease from 2.5 to 0.9 to 0.6 μg/kg with depth for the sites that received irrigation but no biosolids. The mass-fraction of short-chain PFAS is observed to increase with depth. These results are consistent with prior field-sampling studies examining PFAS concentration distributions in soil cores (e.g., Washington et al., 2010; Sepulvado et al., 2011; Brusseau et al., 2020).

4. Discussion

The goal of this study was to evaluate the potential impact of land application of biosolids on PFAS incidence in soil, and the subsequent potential for impacts to groundwater. Soils were sampled from five types of sites, which varied with respect to history of irrigated agricultural activity, and extent of land application of biosolids. Soils that received land applied biosolids were typical of arid land soils with respect to pH, which were routinely around pH 8, and soil organic matter levels, which were low and routinely less than 1%. The textures of the land applied soils varied widely from sandy loams to loams to clay loams and even a clay. This variability in soil texture was present in each of the five types of sites.

4.1. Biosolids PFAS concentrations

Current biosolids PFAS concentrations from Tres Rios WRF were at a low ppb level, with several of the PFAS not detected (Table 2). PFOS is present at the highest concentrations, up to 36 ppb. This finding is consistent with other reports where PFOS is the dominant PFAS found in biosolids (Gallen et al., 2018; Clarke and Smith, 2011). In addition, the

Table 8
Mean total PFAS concentrations in biosolids, soil, and groundwater.

Biosolids	Concentration (μg/kg)	Undisturbed soil (no agriculture)	Concentration (μg/kg)
Total PFAS	87.6	Total PFAS	ND[b]
Total short-chain[a]	6.3	Total short-chain[a]	ND
Fraction SC	0.07	Fraction SC	–
Total long-chain	81.3	Total long-chain	ND
Fraction LC	0.93	Fraction LC	–

Soil: agricultural sites (irrigation, no biosolids)				
Concentration (μg/kg)	30 cm	91 cm	183 cm	Groundwater (μg/L)
Total PFAS	2.5	0.9	0.6	0.081
Total short-chain[a]	0.2	0.1	0.1	0.015
Fraction SC	0.07	0.10	0.14	0.19
Total long-chain	2.3	0.8	0.6	0.066
Fraction LC	0.93	0.90	0.86	0.81
Soil: Group 1 (biosolids amended, <20 tons/acre) (44,834 kg/ha)				
Total PFAS	2.5	1.0	0.08	0.015
Total short-chain[a]	0.3	0.2	0.04	0.003
Fraction SC	0.10	0.26	0.47	0.18
Total long-chain	2.2	0.7	0.04	0.012
Fraction LC	0.90	0.74	0.53	0.82
Soil: Group 2 (biosolids amended, 21–30 tons/acre) (47075–67,251 kg/ha)				
Total PFAS	5.0	1.6	2.2	0.004
Total short-chain[a]	0.4	0.3	0.3	0.001
Fraction SC	0.08	0.17	0.12	0.35
Total long-chain	4.6	1.3	2.0	0.002
Fraction LC	0.92	0.83	0.88	0.65
Soil: Group 3 (biosolids amended, >30 tons/acre) (>67,251 kg/ha)				
Total PFAS	8.6	4.0	1.9	0.024
Total short-chain[a]	1.1	0.6	0.5	0.008
Fraction SC	0.12	0.15	0.26	0.33
Total long-chain	7.6	3.4	1.4	0.016
Fraction LC	0.88	0.85	0.74	0.67

[a] Short-chain is defined by convention as those perfluoroalkyl carboxylic acids and others with <7 perfluorinated carbons and perfluoroalkane sulfonates with <6 perfluorinated carbons (Buck et al., 2011).

[b] ND = non-detect.

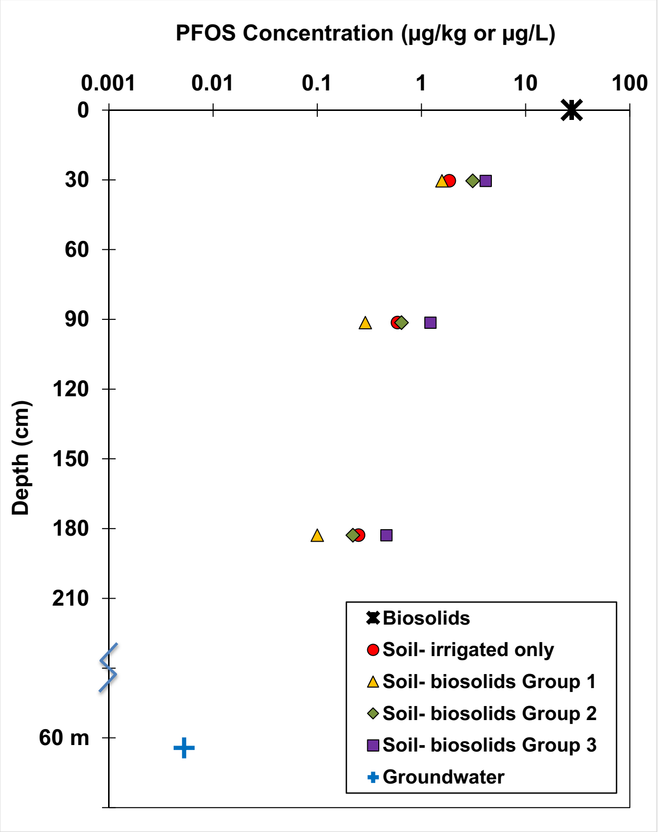


Fig. 1. Mean concentrations of PFOS in biosolids, soil, and groundwater. Note that the geometric mean concentration for all field types is used for groundwater.

concentrations of PFHpA, PFOA, PFNA, PFDA, PFUnA, and PFDoA in the Tres Rios biosolids are very similar to those reported by Gallen et al. (2018). A primary observed difference is the presence of PFHxA and PFHxS at single-digit ppb concentrations in the Tres Rios biosolids versus <1 ppb levels for the Gallen et al. study.

The Pima County biosolids PFAS concentrations are lower than values reported in earlier studies (Venkatesan and Halden, 2013). For example, concentrations of PFOS and PFOA in biosolids samples collected in a 2001 National Sewage Sludge survey averaged 403 and 34 ppb respectively (Venkatesan and Halden, 2013). Lower concentrations of PFAS from more recent studies most likely reflects the fact that PFOS and PFOA were phased out of production in the early 2000s, such that the current source of these compounds are from legacy products. Note also that the levels of PFAS in the Pima County biosolids are much lower than those reported for biosolids receiving industrial inputs of PFAS (Sepulvado et al., 2011).

4.2. PFAS concentrations in soils

Field and equipment blanks were all negative for PFAS analytes except PFHxS blanks taken during sampling of undisturbed soil samples. However, the actual undisturbed soil samples were found to be negative for PFHxS.

No PFAS analytes were detected at any of the three sampling depths for the soil samples collected from undisturbed sites with no history of agriculture, irrigation, or biosolids application. This is in contrast to prior studies wherein PFAS have been detected in soils at the great majority of locations tested, including agricultural fields (Brusseau et al., 2020; Rankin et al., 2016). The Method Detection Limits (MDL) for PFOS and PFOA were 0.2 and 0.085 μg/kg respectively. This provides some indication that ambient levels of PFAS in soils in the study area are very low. An additional surface soil sample was collected approximately 0.8 km from agricultural soils receiving the highest loads of biosolids, and analyzed for PFAS. However, no PFAS analytes were detected (data not shown), illustrating that airborne dust deposition of PFAS generated during farming operations had not occurred at measurable levels. The observation of non-detectable PFAS concentrations in the undisturbed soils is likely due at least in part to the absence of industrial sources of PFAS in the region.

Analysis of soils from locations with a history of irrigated agriculture but no land application of biosolids revealed low-ppb levels of PFOS and PFOA, and multiple detectable amounts of other PFAS analytes (Table 4). The likely source of the PFAS is the groundwater used for irrigation that has been applied over the years. First, no biosolids have ever been applied to these sites. Second, PFAS are present at moderately high concentrations in the groundwater used at the sites for irrigation (Table 3). Third, the PFAS present in the soils are the same compounds detected in the irrigation water (Tables 3 and 4). The possible source of PFAS in groundwater is unclear.

The concentrations of PFAS in the irrigation water were significantly lower than the soil concentrations measured for the shallowest (30-cm) sampling interval. The soil:groundwater concentration ratios range from approximately 4 to 58, with a geometric mean of 20. These ratios are considerably larger than the magnitudes of sorption equilibrium coefficients expected for these PFAS. For example, the ratio for PFOS is roughly an order of magnitude larger than the sorption coefficients measured for PFOS sorption by soils similar to those present at the field sites (Brusseau et al., 2019). The large soil:groundwater

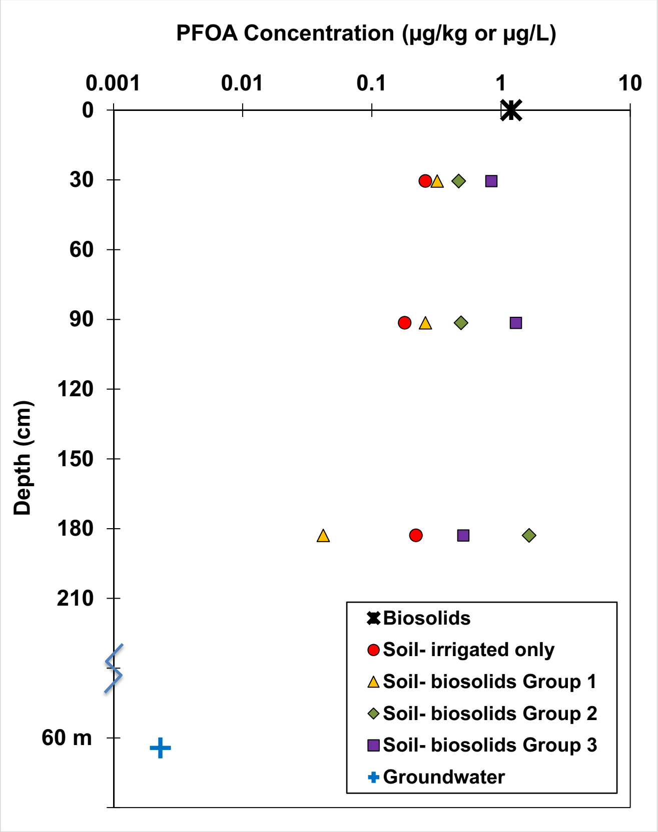


Fig. 2. Mean concentrations of PFOA in biosolids, soil, and groundwater. Note that the geometric mean concentration for all field types is used for groundwater.

concentration ratios are likely the result of the long-term application of irrigation water to the fields.

PFAS concentrations in soils sampled from locations with a history of irrigated agriculture plus land application of biosolids were also in the low-ppb range (Tables 5, 6, and 7). The mean soil concentrations of PFOS, PFOA, and some other PFAS were larger for the soils receiving higher biosolids application rates, but the values are within the range of variability exhibited for all field types. For the highest maximum cumulative biosolids loading rate, the mean concentrations of the two highest analytes detected were 4.1 and 0.84 μg/kg for PFOS and PFOA, respectively.

Thirteen out of the 18 PFAS analyzed were detected in the biosolids samples. Eight of these 13 were detected in all three of the biosolids-amended soil groups. In addition, low levels of PFDoA were present for Group 2 soils and low levels of PFDoA, PFUnA, and PFTeA were present for Group 3 soils. Notably, these longer-chain PFAS were not detected for the Group 1 soils, those with the lowest rate of biosolids amendment. In addition, PFNA and PFDA were detected at very low levels for only the shallowest sampling interval for these soils. These results suggest that the longer-chain PFAS may be retained within the biosolids to a greater degree than the shorter-chain PFAS.

Interestingly, the precursors NEtFOSAA and NMeFOSAA were present in the biosolids but were not detected in any of the soils. In fact, the concentrations of NMeFOSAA (~20 μg/kg) are the second highest of all PFAS in the biosolids, and are just slightly lower than those of PFOS (~27 μg/kg). The absence of detectable levels of NEtFOSAA and NMeFOSAA in the soils indicates that transformation processes likely occurred after application of the biosolids to the soil. Transformation of these precursors would contribute to the total mass of PFOS present in the soils. Given the relatively high concentrations of NMeFOSAA in the biosolids, precursor transformation may be one reason why the mean PFOS soil concentrations are larger in the higher-rate biosolids-amended fields than the non-amended fields.

One way in which to evaluate the relative significance of the measured concentrations in soil is to compare them to concentrations measured for other secondary-source sites reported in a recent meta-analysis of PFAS in soil (Brusseau et al., 2020). Secondary-source sites are those that represent for example locations at which biosolids and other amendments were applied to the ground surface, and/or sites at which surface water, groundwater, or treated wastewater was used for irrigation. The medians of the maximum PFOS and PFOA soil concentrations reported for these sites are 680 and 38 μg/kg, respectively. These levels are approximately two orders-of-magnitude higher than the concentrations measured in the present study. The soil concentrations observed in the present study can also be compared to values reported for prior specific studies of biosolids-amended field sites. Washington et al. (2010) and Sepulvado et al. (2011) both reported PFOS concentrations ranging up to >400 μg/kg in surface soil samples collected from fields that received biosolids applications. These concentrations are approximately two orders-of-magnitude greater than the PFOS soil concentrations reported in the present study.

Another way to evaluate the relative significance of the measured soil concentrations is to compare them to soil screening levels. For example, the US EPA provides risk-based soil screening levels (SSLs) for Superfund sites. It is important to note that these SSLs are not cleanup standards, and that they were developed specifically for use at Superfund sites. Specific SSLs are provided for PFBS in the EPA Regional Screening Levels tables (EPA, 2020). The resident soil value for noncancer direct child exposure is 1300 mg/kg, whereas the industrial soil value for noncancer direct exposure is 13,000 mg/kg. Values for other PFAS are not listed in the EPA tables. The Interstate Technology & Regulatory Council reported resident-soil SSLs generated using the EPA risk calculator for PFOS (1260 μg/kg) and PFOA (1260 μg/kg) (ITRC, 2020). The maximum PFOS, PFOA, and PFBS soil concentrations measured for the present study are orders of magnitude below these SSLs. These SSLs are for exposure via direct contact (ingestion, inhalation, dermal contact) with soil. Another set of SSLs are determined for protection of drinking-water sources (e.g., groundwater). These represent screening levels for soil that would be protective of groundwater that is used for drinking water (i.e., the exposure route is via ingestion of water). The EPA tables list a value of 130 μg/kg for PFBS, which is much higher than values observed in the present study. Again, no values are listed for PFOS or PFOA; however, the ITRC lists values of 0.378 and 0.172 μg/kg for PFOS and PFOA, respectively, based on application of the EPA risk calculator. These values are lower than the highest concentrations reported for the study. It is unclear if the assumptions and simplifications made in application of the risk calculator are applicable for the conditions present at the study site. For example, the groundwater-protection SSLs are determined based on the assumption of aqueous-phase leaching of contaminants from the ground surface to groundwater. Given the arid climate and the use of managed irrigation, the magnitude of leaching is likely to be small. A robust determination of leaching rates would require a full-scale mathematical modeling analysis, which is beyond the scope of this study.

It is important to note that PFAS concentrations in the soils that received biosolids were similar to the levels found in agricultural soils that received irrigation water but no biosolids. It should also be noted that the groundwater irrigation source containing the highest PFAS concentrations had no previous history of biosolids application. Comparison of the data sets is complicated by the variability in PFAS concentrations in the irrigation water observed across the sites. However, the similarity of soil concentrations for the sites with and without biosolids application indicates that both irrigation water and biosolids are important sources of the PFAS present in the soils. However, the relative inputs of PFAS from these two sources are unclear. A full-scale examination of the relative impact of irrigation water versus biosolids on PFAS concentrations in the soil profile would require detailed consideration of irrigation rates, annual crop conditions, biosolids loading rates, biosolids and irrigation-water PFAS concentrations, and other factors.

The total PFAS concentrations are highest in the shallowest sampling interval for all four field types. Individual PFAS concentrations in soil generally decreased monotonically with depth. Exceptions were observed for some plots for PFBS, PFHxS, PFHpA, and PFOA. In addition, with one exception (Group 2 fields), the total mean PFAS concentrations decreased monotonically with depth. The mean magnitude of attenuation was 73% at the 183 cm soil depth. This significant amount of apparent attenuation occurred despite the use of the flooded-furrow method of irrigation, which may maximize the potential for irrigation-induced leaching. The fraction of total PFAS comprised of short-chain compounds increased with depth. This may indicate preferential leaching of the short-chain versus the long-chain PFAS. This is consistent with the expected differential retention of PFAS as a function of chain length, or molecular size. The potential presence of PFAS at depths below the sampling domain was not investigated. Determining the potential for migration of PFAS beyond the sampling interval would require mathematical modeling analysis, which as noted previously is beyond the scope of this study.

It is possible that a fraction of PFAS present in the soil may have been removed via phytoaccumulation. Uptake of PFAS into crops was demonstrated for example by Blaine et al. (2013). Specifically shorter chain PFAS were preferentially taken up over longer chain PFAS. However, much remains to be learned about the effects of multiple variables on plant uptake including soil properties, crop type, and biosolids PFAS concentration and application rate.

5. Conclusion

The presence of PFAS in biosolids has generated concern over the environmental impacts and potential human-health risks associated with land application of biosolids. One particular concern is transfer of PFAS from biosolids to soil, and subsequent leaching to groundwater. A field study was implemented in Pima and Pinal County, AZ, involving multiple agricultural plots comprising 809 ha distributed over a 445 km^2 area that have received land application of Class B biosolids from 1984 to 2019. Depth-discrete soil samples were collected from the plots. Biosolids samples and samples of groundwater used for irrigation were also collected. PFAS concentrations measured for the samples were evaluated to assess incidence rates and potential risks to groundwater.

Even after decades of land application, the concentration and accumulation of PFAS in soils receiving the biosolids was comparatively low. In addition, it was observed that ~73% attenuation of PFAS occurred within 183 cm of the soil surface. These results suggest that the potential for groundwater contamination is relatively small, particularly considering the significant depth to groundwater (~61 m below ground surface), the low rates of precipitation, and the high rates of evapotranspiration in the region. The potential for leaching of PFAS is enhanced with irrigated agriculture in arid regions, where 3700–6167 m^3 of irrigation water are routinely applied during a crop growing season. Despite this, minimal apparent migration of the analytes was observed. Such magnitudes of attenuation and the associated retention processes have been discussed in other studies (Washington et al., 2010; Sepulvado et al., 2011; Brusseau, 2018, 2019, 2020; Guo et al., 2020).

Overall, the results of this study suggest that contamination of groundwater at the study sites by leaching of biosolids-associated PFAS is unlikely due to a number of factors. One is the relatively low levels of PFAS present in the Pima County biosolids, likely reflecting the absence of significant industrial inputs to the wastewater system. Another important factor is the climatic and associated conditions, including the great depth to groundwater and the high evapotranspiration rates. The significance of this study is shown by the fact that following publication of the data in a report (Pima County, 2020), the moratorium on land application of biosolids in Pima County was rescinded in November of 2020 with a resumption in land application of biosolids in February of 2021.

CRediT authorship contribution statement

Ian L. Pepper: Writing – review & editing. **Mark L. Brusseau:** Writing – review & editing. **Frank J. Prevatt:** Writing – review & editing, Supervision. **Barbara A. Escobar:** Writing – review & editing, Resources.

Declaration of competing interest

None of the authors have competing or conflict of interests in the subject material of this study, or the manuscript. Two of the authors are employees of Pima County Wastewater Reclamation Department.

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Supplementary data

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Measured physicochemical characteristics and biosolids-borne concentrations of the antimicrobial Triclocarban (TCC)

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ABSTRACT

Triclocarban (TCC) is an active ingredient in antibacterial bar soaps, a common constituent of domestic wastewater, and the subject of recent criticism by consumer advocate groups and academic researchers alike. Activated sludge treatment readily removes TCC from the liquid waste stream and concentrates the antimicrobial in the solid fraction, which is often processed to produce biosolids intended for land application. Greater than half of the biosolids generated in the US are land-applied, resulting in a systematic release of biosolids-borne TCC into the terrestrial and, potentially, the aquatic environment. Multiple data gaps in the TCC literature (including basic physicochemical properties and biosolids concentrations) prevent an accurate, quantitative risk assessment of biosolids-borne TCC. We utilized the USEPA Office of Prevention, Pesticides, and Toxic Substances (OPPTS) harmonized test guidelines to measure TCC solubility and log K_{ow} values as 0.045 mg L^{-1} and 3.5, respectively. The measured physicochemical 2 properties differed from computer model predictions. The mean concentration of TCC in 23 biosolids representative of multiple sludge processing methods was 19 ± 11 mg kg^{-1}.

1. Introduction

Triclocarban (TCC; Fig. 1) is an active ingredient in antibacterial bar soaps and the subject of recent criticism by consumer advocate groups and academic researchers alike. Concerns primarily center on uncertainties regarding TCC environmental concentrations and fate (Heidler et al., 2006), persistence (Ying et al., 2007; Miller et al., 2008), toxicity (Heidler et al., 2006), bioaccumulation potential (Daughton and Ternes, 1999; Darbre, 2006; Coogan et al., 2007), endocrine effects (Chen et al., 2008), and potential for antibacterial resistance development (Suller and Russell, 1999; Walsh et al., 2003). Triclocarban is monitored under the USEPA High Production Volume (HPV) chemical (i.e. 227–454 Mg produced/imported $year^{-1}$) program, but a recent report identifies TCC as a Moderate Production Volume (MPV) chemical (i.e. <227 Mg produced/imported $year^{-1}$) (USEPA, 2009a). Following typical use in personal care products, TCC is washed down the drain and commonly becomes a constituent of domestic wastewater at documented concentrations of 0.4–50 μg L^{-1} (TCC Consortium, 2002a; Halden and Paull, 2004; Heidler et al., 2006).

Activated sludge wastewater treatment readily removes TCC from the liquid waste stream (88–97% removal; TCC Consortium, 2002a; Heidler et al., 2006) and concentrates the antimicrobial in the solid fraction (e.g. 76 ± 30% sorbed; Heidler et al., 2006). The sludge accumulated within wastewater treatment plants (WWTPs) is often processed to produce biosolids intended for land application that meet USEPA pathogen, metals, and vector control standards. About half of the biosolids generated in the US are land-applied (NRC, 2002), resulting in a systematic release of biosolids-borne TCC into the terrestrial environment. Despite widespread use of antimicrobial personal care products, the propensity of TCC to partition to sludge during wastewater treatment, and potential adverse health effects of TCC, human and ecological health risk assessments for TCC in land-applied biosolids have not been conducted.

The USEPA has collected screening-level health and environmental effects data (TCC Consortium, 2002a,b) voluntarily submitted by TCC sponsor companies under the High Production Volume (HPV) Challenge Program, and performed a screening-level TCC hazard characterization (USEPA, 2008a). The hazard characterization was subsequently coupled with Inventory Update Reporting (IUR) exposure potential data for a screening-level exposure characterization, risk characterization, and risk-based prioritization in the document entitled Initial Risk-Based Prioritization of HPV Chemicals, Triclocarban (USEPA, 2009a). The USEPA listed TCC as a “High Priority” HPV chemical for further assessment and risk management activities, and requested additional source and exposure data from

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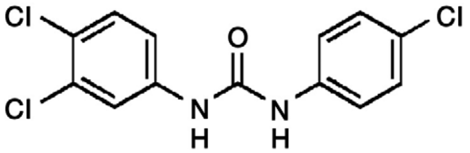

Fig. 1. Chemical structure of Triclocarban (TCC; N-(4-chlorophenyl)-N′-(3,4-dichlorophenyl) urea).

HPV sponsor companies on a voluntary and non-confidential basis (USEPA, 2009a).

Although considerable effort was expended in compiling the HPV reports, very little attention was given to the potential risks associated with biosolids-borne TCC related exposures. Multiple components of biosolids-borne TCC human and ecological risk assessments are incomplete, and much of the available data originate from studies that are unavailable for further review and/or are inadequately described (TCC Consortium, 2002a,b). As of 2005 (i.e. the time of initiation of the project described herein), data gaps included conclusive TCC solubility and partitioning measurements, TCC concentrations in nationally representative biosolids, and biosolids-borne TCC environmental transport, persistence, and soil organism impacts following land application.

Water solubility and K_{ow} are key risk assessment input parameters, and greatly affect environmental concentrations, exposure pathways, susceptible populations, and the potential for subsequent human/ecological health outcomes. The two factors critically influence the extent to which a compound leaches through the soil profile or moves laterally with surface runoff, and the amount of compound available for microbial degradation, plant uptake, and bioaccumulation. Triclocarban can bioaccumulate in snails [*Helisoma trivolvis* (Say)] (Coogan and La Point, 2008) and algae (*Cladophora* spp.) (Coogan et al., 2007), and might also be expected to accumulate in terrestrial organisms.

The literature contains conflicting measured and estimated values for the water solubility and octanol–water partitioning coefficients (K_{ow}) of TCC, which were determined using a variety of methods (TCC Consortium, 2002a; Halden and Paull, 2005; Sapkota et al., 2007; Ying et al., 2007). Triclocarban solubility data are limited to early measurements (0.11 mg L^{-1}; Roman et al., 1957), inadequately described methods (0.11 or 11 mg L^{-1}; TCC Consortium, 2002b), or are estimated using QSAR analyses ($0.65–1.55 \text{ mg L}^{-1}$; Halden and Paull, 2005; Sapkota et al., 2007; Ying et al., 2007). Commonly reported log K_{ow} values range from 4.2 to 6.0 (TCC Consortium, 2002a; Halden and Paull, 2005; Sapkota et al., 2007; Ying et al., 2007).

The behavior and effects of biosolids-borne TCC in the environment have been hypothesized based on mathematical estimates of physicochemical properties (e.g. non-validated predictions using computer models such as those packaged in EPI Suite) (USEPA, 2008b), but an accurate quantitative risk assessment requires definitive measurements (preferably utilizing standardized laboratory methods). Standardized experimental design and analytical methods for characterizing physicochemical properties and behavior in biosolids systems would also facilitate valid cross-comparisons of data collected in different laboratories.

The USEPA Office of Prevention, Pesticides, and Toxic Substances (OPPTS) harmonized test guidelines (particularly the Product Properties; Fate, Transport, and Transformation; Ecological Effects; and Health Effects Guidelines) are tools that could facilitate the development of a consistent and uniform biosolids-borne contaminant database. The OPPTS Guidelines are the result of blending test guidance from the USEPA Office of Pollution Prevention and Toxics (OPPT), the USEPA Office of Pesticide Programs (OPP), and the Organization for Economic Cooperation and Development (OECD). Harmonization of multiple guidelines reduces inconsistencies in testing methodology and helps standardize data required under the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) (7 U.S.C. 136 et seq.). The Product Properties OPPTS Guidelines simplify the process of measuring organic contaminant physicochemical characteristics, and determinations can be quick and inexpensive. Other guidelines pertinent to the study of biosolids-borne contaminants (e.g. Fate, Transport, and Transformation; Ecological Effects; and Health Effects), however, require some simple adaptations to account for the unique effects of the biosolids matrix.

Equally important to a biosolids-borne TCC risk assessment as basic physicochemical properties is the typical range of TCC concentrations in biosolids. Prior to project initiation, results of a single study that measured TCC concentrations in WWTP sludge (mean: 40 mg kg^{-1}; range: $<1–283 \text{ mg kg}^{-1}$, $n = 10$) was available in the published literature (TCC Consortium, 2002a), and no information was available for biosolids-borne TCC concentrations. Multiple researchers have since quantified TCC concentrations in a variety of biosolids and sludges (hereafter collectively referred to as "WWTP products") (Heidler et al., 2006; Chu and Metcalfe, 2007; Halden, 2007; Sapkota et al., 2007; USEPA, 2009b,c).

The largest study of TCC concentrations in WWTP products to date was performed as a component of the Targeted National Sewage Sludge Survey (TNSSS) (USEPA, 2009b,c), in which WWTP products from WWTPs in 35 states were analyzed for a host of organic and inorganic contaminants. Seventy-four WWTPs were statistically selected to represent the distribution of plants receiving 1–10, 10–100, and >100 MGD (million gallons of wastewater day^{-1}). Triclocarban was detected in all of the 84 WWTPs product samples tested in the TNSSS (including duplicate samples from, or two sampling sites within, 10 WWTPs). The range of TCC concentrations in the WWTP products was $0.187–441 \text{ mg kg}^{-1}$, with a mean and 95th percentile concentration of $39 \pm 60 \text{ mg kg}^{-1}$ and 131 mg kg^{-1}, respectively (USEPA, 2009c). The two greatest TCC concentrations measured in the TNSSS (441 and 189 mg kg^{-1}) were flagged as measurements corrected for low labeled compound recovery, and are likely biased high. The next greatest TCC concentration was 123 mg kg^{-1}. Unfortunately, the published TNSSS data are not stratified to allow correlations between treatment methods and resulting TCC concentrations, nor did the TNSSS report distinguish between sewage sludge and processed biosolids intended for land application. Nevertheless, the TNSSS data are useful for characterizing the range of potential biosolids-borne TCC concentrations.

The relatively small fraction of WWTPs (there are >16,000 treatment facilities in the US; USEPA, 2008c) sampled for biosolids-borne TCC concentration determinations (as opposed to sludge-borne TCC concentrations), and variability in the level of detail reported regarding WWTP biosolids processing methods makes it difficult to confirm a mean or typical range for biosolids-borne TCC concentrations, or to identify treatment processes that most effectively reduce TCC concentrations in sludge.

The purpose of the study presented herein was to fill some of the most basic TCC data gaps and contribute to the body of knowledge required for a quantitative biosolids-borne TCC risk assessment. We applied the OPPTS water solubility and octanol–water partitioning coefficient guidelines to TCC analyses, and measured TCC concentrations in 23 biosolids (and one sludge) representative of multiple wastewater treatment processes.

2. Methods and materials

2.1. Chemicals

Solvents of HPLC-grade or greater were purchased from Aldrich, JT Baker, or Fisher Scientific. Water used in the solubility and K_{ow} determinations was collected from a Milli-Q System (Millipore; Milford, MA USA). Analytical-grade n-octanol was purchased from Aldrich. Ammonium acetate was purchased from JT Baker.

Triclocarban (CAS no. 101-20-2) was obtained from United States Pharmacopeia (99.9% purity) and the Procter & Gamble Company (98+% purity). Deuterated TCC (TCC-d_7) and ^{14}C-TCC (specific activity: 75 mCi/mmol) were also supplied by the Procter & Gamble Company.

2.2. Biosolids-borne TCC extraction efficiency validation

Heidler et al. (2006) reported 91 ± 8% and 93 ± 17% recoveries from a single digested sludge that was spiked with 50% and 100% of indigenous TCC content, respectively, and extracted with acetone by accelerated solvent extraction (ASE). Similar percent recoveries were obtained by extracting with 50/50 methanol:acetone on a mechanical shaker overnight. Uniformly labeled ^{14}C-TCC was used in the present study to validate the published extraction method. One gram (dry wt. equivalent) subsamples of biosolids collected from three different WWTPs were transferred in triplicate to 35 mL glass, round-bottom centrifuge tubes and wetted to ~95% water content (by weight) to promote even distribution of the ^{14}C-TCC spike (~100,000 dpm or 0.189 µg ^{14}C-TCC). Each spiked sample was vortexed for 60 s and equilibrated 24 h. Following equilibration, samples were lyophilized and extracted by ASE (Dionex ASE 200; Bannockburn, IL) (100% acetone), or shake-flask (50/50 methanol:acetone; 18 h) followed by sonication (50/50 methanol:acetone; 2 h). The tubes were subsequently centrifuged at 800 × *g* for 1 h (Sorvall RC 5B "Plus," Thermo Fisher Scientific, Waltham, MA). The supernatants were dried under nitrogen, reconstituted in methanol, and aliquots were analyzed by liquid scintillation counting (LSC) (Beckman LS 6500; GMI, Inc., Ramsey, MN).

2.3. Biosolids-borne TCC concentration determination

Twenty-three biosolids and one sludge collected by the authors or supplied via the USEPA TNSSS or the USEPA "50 City Survey" of publicly owned treatment works (POTWs), were analyzed in two batches. Nine of the biosolids were part of split samples from the TNSSS study, thus allowing direct WWTP-specific comparisons of data analyzed in different labs without concerns about sampling time differences. Although not known at the time of collection or receipt, all tested materials were the products of activated sludge treatment, and all USEPA-supplied biosolids were products of anaerobic digestion.

One gram (dry wt. equivalent) triplicates of Batch 1 materials ($n = 9$) were lyophilized and extracted (2 × 20 mL 50/50 methanol: acetone) by shake-flask (18 h) followed by sonication (2 h). Extracts were dried under nitrogen, reconstituted in 50/50 methanol:Milli-Q water, and fortified with TCC-d_7 internal standard prior to analysis. Triclocarban concentrations in Batch 1 materials were corrected for extraction efficiency by applying the average percent recovery calculated from the ^{14}C-TCC extraction recovery experiment.

Triclocarban analysis was improved for Batch 2 ($n = 15$) by applying the isotope dilution technique (Heidler et al., 2006) to correct for percent recovery. One gram (dry wt. equivalent) triplicates of Batch 2 biosolids were wetted to ~95% water content and spiked with 1 µg TCC-d_7 as the surrogate standard. Following mixing (60 s) and equilibration (24 h), the biosolids were processed identically to Batch 1 materials. Triclocarban concentrations in Batch 2 extracts were automatically corrected for percent recovery of the surrogate standard.

2.4. Water solubility determination

The water solubility of TCC was determined according to the EPA Product Properties Test Guideline OPPTS 830.7840 Water Solubility; Column Elution Method (USEPA, 1996a). The column elution method is prescribed for compounds with expected water solubilities below 10 mg L^{-1}. Briefly, an excess of TCC was dissolved in acetone, poured onto glass beads (100/120 mesh), and dried by Rotavap. Two grams of the TCC-coated beads were loaded into a glass column (185 mm × 10 mm) plugged with 10 mm of glass wool. The glass

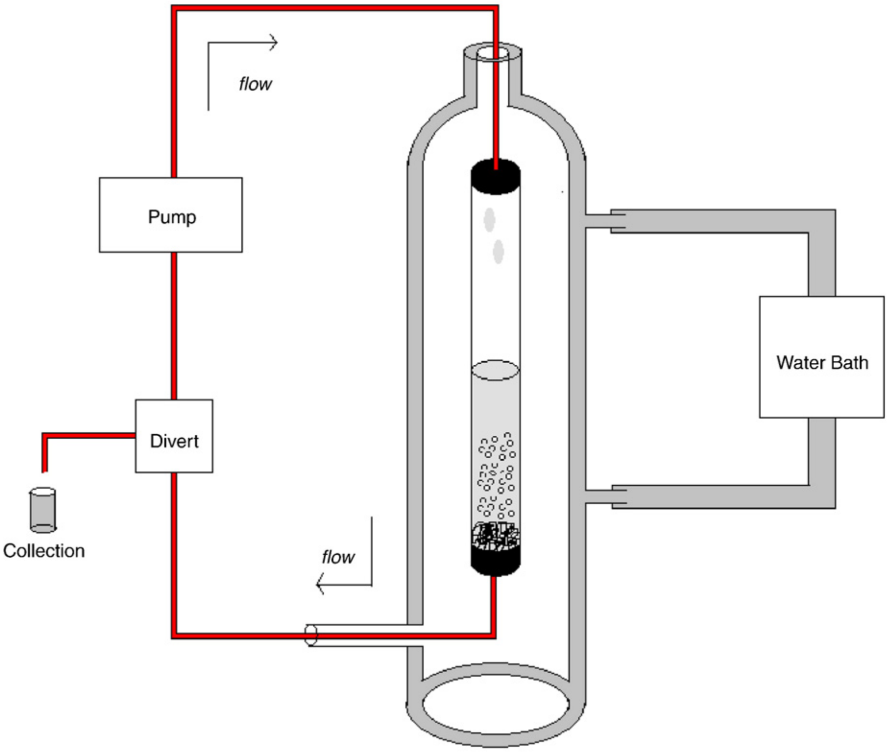

Fig. 2. Triclocarban (TCC) solubility determination: column elution diagram.

beads occupied approximately 1.5 cm^3 (one bed-volume). The loaded column was filled with eight bed-volumes of Milli-Q water, inserted into a water jacket (25 °C), and allowed to equilibrate for 2 h. Following equilibration, the column was connected to a circulating pump via HPLC tubing (Fig. 2) and five bed-volumes of water were diverted to remove potential impurities. The divert valve was then switched off and water was allowed to circulate through the column at a rate of ~10 bed-volumes per hour. Approximately 500 µL was diverted and collected at 1-hour intervals, and spiked with TCC-d_7 internal standard prior to analysis. The OPPTS guideline defines equilibrium as five successive samples whose concentrations do not differ by more than 30% in random fashion. In the second of two runs, water flow was allowed to continue overnight and a final sample was taken after a 14-hour interval to confirm saturation.

2.5. Octanol–water partition coefficient (K_{ow}) determination

The TCC K_{ow} was determined according to the EPA Product Properties Test Guideline OPPTS 830.7550 partition coefficient (n-octanol/water); Shake Flask Method (USEPA, 1996b). A standard solution was created by dissolving 6.75 mg TCC in 135 mL of n-octanol saturated with Milli-Q water. The following proportions of standard solution and Milli-Q water (saturated with n-octanol) were combined, in duplicate, in 35 mL glass centrifuge tubes: 15 mL standard solution/15 mL water (samples A and B), 7.5 mL standard solution/15 mL water (samples C and D), and 30 mL standard solution/15 mL water (samples E and F). The centrifuge tubes were placed on a wrist-action shaker (Burrell Model 75; Burrell Scientific, Pittsburg, PA) for 5 min and then centrifuged at 800 × g to separate the phases. One mL aliquots of the aqueous phase and the diluted n-octanol phase were prepared with TCC-d_7 internal standard prior to analysis.

2.6. HPLC/MS analyses

Water solubility and K_{ow} samples, and "cold" (i.e. non-radiolabeled) biosolids extracts, were analyzed by HPLC/MS at Procter & Gamble (P&G) laboratories on a Waters Alliance 2795 LC system (Waters Corporation, Milford, MA) coupled to a Micromass ZMD single quadrupole MS detector controlled by MassLynx 4.0 software. Analytical methodology was developed according to TCC research previously conducted at Procter & Gamble and guidance provided in Halden and Paull (2005) and Chu and Metcalfe (2007). Liquid chromatography was performed on a Phenomenex Luna C_{18} column (3 µm particle size, 2 × 100 mm; Phenomenex, Inc., Torrance, CA), using a 25 µL sample injection volume. Analyte separation was achieved at a flow rate of 300 µL min^{-1} using an elution gradient of water/methanol with 1 mM ammonium acetate: 25:75 water/methanol (held 1 min), increasing to 0:100 water/methanol (over 5 min, and held 3 min), and decreasing back to 25:75 water/methanol (over 0.5 min). Mass spectrometry was performed in negative ion mode with select ion recording (SIR). Precursor and product ions monitored were m/z 313, 315 (TCC), 320 (TCC-d_7) and m/z 160 (TCC), 163 (TCC-d_7), respectively, with a 100 ms dwell time for each transition. A linear calibration curve using the response ratios of TCC to the TCC-d_7 internal standard, and comprised of ≥7 standard levels spanning expected sample analyte concentrations, was used for quantification ($R^2 \geq 0.999$). The calculated limit of quantitation (LOQs) by HPLC/MS was 10 ng TCC mL $extract^{-1}$ or, in the case of biosolids extracts, 0.4 mg TCC kg $biosolids^{-1}$ (dry wt.).

3. Results and discussion

3.1. TCC extraction method validation

The average ^{14}C-TCC percent recovery from the three biosolids was 84 ± 7%, which is 7–9% less than the average TCC recoveries reported by Heidler et al. (2006), but well within the authors' reported standard deviations. The discrepancy in average recoveries could be due to the relatively small ^{14}C-TCC spike mass (~0.75–1.35% of indigenous TCC content), natural variation in individual biosolids, and differences in spike equilibration times.

Table 1
Triclocarban (TCC) concentrations in Batch 1 WWTP materials.

Batch 1 materials	Treatment process	Region (U.S. census)	TCC concentration (mg kg^{-1}) $n = 3$
DYSK[a]	Compost (mixed with mulch)	South	6 ± 1
GRBC[a]	Aerobic digestion	South	7 ± 1
DYMK[a]	Mixed compost (mixed with food waste and mulch)	South	8 ± 2
OSBC[a]	Anaerobic digestion	South	14 ± 2
ORBC-AL[ab]	Lime stabilization (immediately following lime addition)	South	18 ± 1
ORBC-BL[c]	Untreated (before lime stabilization)	South	25 ± 1
GEPZ[a]	Anaerobic digestion (pelletized)	South	29 ± 3
CFBC[a]	Anaerobic digestion	Midwest	40 ± 2
RCKF[a]	Anaerobic digestion	Unknown	21 ± 3

[a] Biosolids.
[b] Immediately following lime addition.
[c] Sludge immediately prior to lime addition.

3.2. Biosolids-borne TCC concentrations

The mean TCC concentration, which incorporated the average of one set of quality control duplicate samples (UNKJ and UNKL) from a single WWTP in the TNSSS, for the 23 assessed biosolids was 19 ± 11 mg kg^{-1} (Tables 1 and 2), and fell within the range of previously reported TCC concentrations in WWTP products (Fig. 3). Mean TCC concentrations in the US regions from which multiple plants were sampled ranged from 16.4 to 25.6 mg kg^{-1}. The differences between TCC concentrations in the nine TNSSS split samples (UNKD-UNKL), as measured at the P&G laboratories and TNSSS contract labs, were ≤15%.

The aerobically digested biosolids (GRBC) and the aerobically composted biosolids (DYSK and DYMK) contained some of the lowest measured concentrations of TCC (6–8 mg kg^{-1}), suggesting enhanced TCC biodegradation under aerobic conditions, as compared to anaerobic conditions (7–43 mg kg^{-1}). However, similarly low TCC concentrations were also measured in the anaerobically digested biosolids UNKE, UNKI, CHCM-CC, and CHCM-AD. Further, the low TCC concentrations in the aerobically treated DYSK and DYMK materials likely reflect a "dilution" of initial TCC concentrations due to the addition of food waste and/or mulch (neither of which is expected to

Table 2
Triclocarban (TCC) concentrations in Batch 2 WWTP materials.

Batch 2 materials	Treatment process	Region (U.S. census)	TCC concentration (mg kg^{-1}) $n = 3$
UNKL[a]	Anaerobic digestion	South	12 ± 0.5
UNKJ[a]	Anaerobic digestion	South	31 ± 0.4
UNKD[a]	Anaerobic digestion	South	43 ± 3
UNKI[a]	Anaerobic digestion	Northeast	8 ± 0.4
UNKF[a]	Anaerobic digestion	Northeast	23 ± 0.3
UNKH[a]	Anaerobic digestion	Northeast	31 ± 0.7
UNKK[a]	Anaerobic digestion	Northeast	31 ± 1
UNKG[a]	Anaerobic digestion	Northeast	35 ± 1
CHCM-CC[ab]	Anaerobic digestion	Midwest	7 ± 0.9
CHCM-AD[ac]	Anaerobic digestion	Midwest	8 ± 0.8
CHST-CC[ab]	Anaerobic digestion	Midwest	13 ± 0.9
CHST-AD[ac]	Anaerobic digestion	Midwest	14 ± 0.8
UNKE[a]	Anaerobic digestion	West	10 ± 0.3
UNKC[a]	Anaerobic digestion	Unknown	24 ± 1
UNKB[a]	Anaerobic digestion	Unknown	25 ± 1

[a] Biosolids.
[b] Centrifuged cake.
[c] Air-dried.

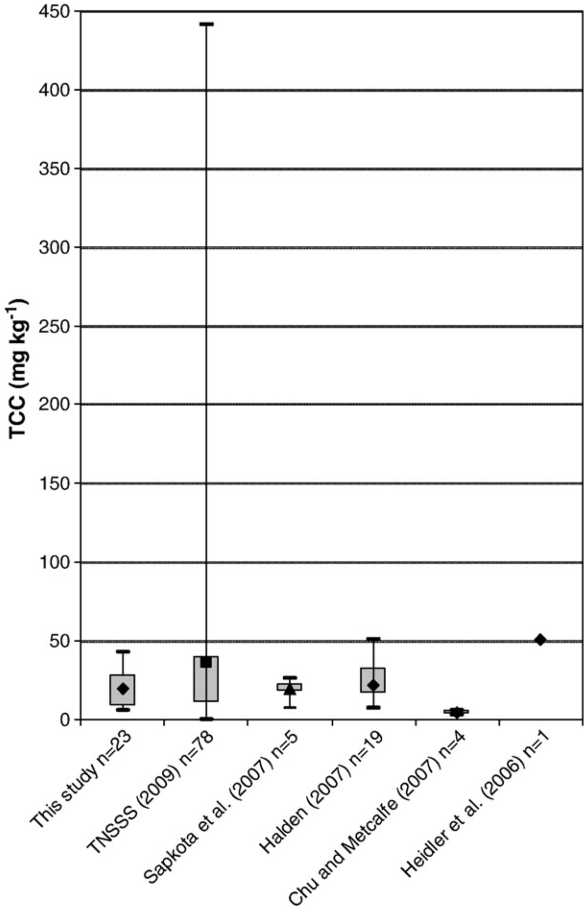

Fig. 3. Reported Triclocarban (TCC) concentration distributions in WWTP products (◆: biosolids, ▲: sludge; ■: biosolids/sludge).

contain TCC). Additional aerobically treated biosolids should be analyzed before a correlation between aerobic conditions and enhanced TCC degradation in biosolids can be established. No other TCC concentrations in biosolids characterized as products of aerobic treatment processes were identified in the current literature.

Anaerobically digested biosolids ($n=19$) exhibited a wide TCC concentration range (7–43 mg kg^{-1}), but the greatest TCC concentration was 8 mg kg^{-1} less than the greatest known biosolids-borne TCC value (51 mg kg^{-1}) reported by Heidler et al. (2006), and 80 mg kg^{-1} less than the greatest WWTP product concentration reported in the TNSSS. The ORBC-BL material (activated sludge prior to lime addition; not approved for land application) contained a moderate TCC concentration (25 mg kg^{-1}), which decreased following lime addition to 18 mg kg^{-1} (sample ORBC-AL). Differences in TCC concentrations across biosolids could be due to several factors, including: varying influent TCC concentrations, differing digestion periods and methods, adding of other materials, or other treatment conditions unique to particular WWTPs. For example, extended anaerobic digestion periods often improve total solids reduction, and could concentrate TCC in the final biosolids product.

Of the factors that might influence biosolids-borne TCC concentrations, WWTP designers and operators have the greatest control over the wastewater treatment method and the product form. Understanding the effects that sludge treatment processes and product form have on TCC concentrations (or other organic contaminants) in biosolids could contribute to better informed waste management decisions that reduce environmental contamination and human/ecological exposures. For example, lime stabilization of biosolids might impact biosolids-borne TCC concentrations or environmental behavior, as elevated pH levels (11 or 12) could result in ionization and a subsequent increase in solubility (estimated p$K_a=12.8$; Sapkota et al., 2007), and/or changes in the hydrolysis half-life predicted at circumneutral pH levels (>1 year; EPI Suite; USEPA, 2008b). Processes and forms that significantly reduce TCC concentrations could then be preferentially selected for biosolids intended for land application.

3.3. TCC water solubility and K_{ow}

Triclocarban solubility, as measured in duplicate determinations (according to OPPTS guidelines), was 0.044 ± 0.001 mg L^{-1} ($n=5$) and 0.046 ± 0.004 mg L^{-1} ($n=5$), averaging 0.045 mg L^{-1} (Table 3). The average measured solubility, 0.045 mg L^{-1}, is less than commonly reported measured and estimated values.

In light of a measured TCC water solubility less than previously published values, we expected the measured TCC log K_{ow} to be equal to, or greater than, the commonly reported log K_{ow} values (4.2–6.0; TCC Consortium, 2002a; Halden and Paull, 2005). However, the measured log K_{ow} of TCC was 3.5 ± 0.06 (Table 4). Mass balance of TCC in the octanol and water fractions was 101 ± 1.8%, indicating no loss of TCC during the partitioning test.

Our measured TCC water solubility and log K_{ow} values (0.045 mg L^{-1} and 3.5, respectively) suggest less bioavailability and bioaccumulation potential than earlier predictions based on physicochemical estimates, and the unexpected relationship between the two physicochemical parameters highlights the importance of measured data collected by standardized methodology. Chemical property estimation tools such as linear free-energy relationships (LFERs) and EPI Suite are often utilized without considering whether the training dataset is appropriate for the compound of interest, and prediction output requires substantiation. Free-energy relationships equations usually assume a negative linear relationship between two chemical parameters (e.g. solubility and K_{ow}), and are derived using a group of compounds for which the two parameters are known. Multiple K_{ow}/solubility relationships are available in the literature (Lyman et al., 1982), but few are appropriate for assessing TCC solubility or K_{ow}. An ideal LFER is one developed using multiple compounds similar to the compound of interest and characterized by a large R^2 value (i.e. the regression coefficient), indicating good parameter predictability for the compounds on which the LFER is based. In some publications, the data on which a LFER is based are only described by the r^2 value (i.e. the coefficient of determination), which simply relates the strength of association between the independent and dependent variables. The LFER developed by Hansch et al. (1968) incorporates 156 mixed-class compounds with an R^2 value of 0.874:

$$\log(1/S) = (1.339^{*}\log K_{ow}) - 0.978 + 0.0095(t_m - 25) \quad (1)$$

where S is measured in mol L^{-1} and t_m is the TCC melting point (250 °C). Using the measured log K_{ow} value (3.5), Eq. (1) estimates TCC solubility as 0.45 mg L^{-1}, ten-fold greater than the value measured herein. Using

Table 3
Triclocarban (TCC) solubility measurements.

Sampling interval	Run 1 (mg TCC L^{-1})	Run 2 (mg TCC L^{-1})
1	0.038	0.039
2	0.041	0.049
3	0.042	0.049
4	0.045	0.053
5	0.044	0.045
6	0.043	0.043
7	0.045	0.045
8	0.045	0.044
Mean of last 5 intervals	*0.044 ± 0.001*	*0.046 ± 0.004*
Mean of duplicate runs	*0.045*	

Table 4
TCC K_{ow} measurements.

n-Octanol/water ratio	Log K_{ow}
1:1	3.6
1:1	3.5
1:2	3.4
1:2	3.6
2:1	3.4
2:1	3.5
Average	*3.5 ± 0.06*

the measured TCC solubility value (0.045 mg L^{-1}), Eq. (1) overestimates the TCC log K_{ow} as 4.2.

Various estimation programs within EPI Suite (i.e. ECOSAR, KOWWIN, WATERNT, and WSKOWWIN) (USEPA, 2008b) can also erroneously predict TCC solubility and log K_{ow}. When none of the three physicochemical parameters utilized in ECOSAR (i.e. solubility, K_{ow}, and melting point) are manually entered, the predicted TCC solubility and log K_{ow} values are 1.55 mg L^{-1} and 4.9, respectively (Halden and Paull, 2005). Solubility is estimated in ECOSAR using LFERs developed by Meylan and Howard (1994a,b) and Meylan et al. (1996), and the K_{ow} is copied from output of KOWWIN:

$$\log(S) = -0.312–1.02(\log K_{ow}) \tag{2}$$

where S is measured in mol L^{-1}, n equals 1450 mixed-class compounds, and the r^2 is 0.786, and

$$\log(S) = 0.2236–1.009(\log K_{ow})-0.00956(t_m–25) \tag{3}$$

where S is measured in mol L^{-1}, t_m is the TCC melting point (250 °C), n equals 1450 mixed-class compounds, and the r^2 was not available.

The KOWWIN program estimates K_{ow} using the Atom/Fragment Contribution (AFC) method, by which the structure of a compound is divided into fragments that are each given coefficient values derived by multiple regression of >2400 measured log K_{ow} values. The fragment coefficients are summed to estimate the log K_{ow}. Regardless of the solubility and melting point entered into ECOSAR, the log K_{ow} remains 4.9.

The ECOSAR program does not allow back-calculation of the log K_{ow} using the LFERs employed in estimating solubility, but the calculations can be performed independently. Eqs. (2) and (3) predict TCC log K_{ow} values of 6.4 and 4.9, respectively (when using 0.045 mg L^{-1} solubility).

When the measured TCC log K_{ow} is entered into ECOSAR as a known parameter (and solubility and the melting point are not entered), the model over-predicts TCC solubility as 41.41 mg L^{-1}. However, the predicted TCC solubility (0.04242 mg L^{-1}) is similar to the measured solubility when only the measured melting point (250 °C; TCC Consortium, 2002a) is manually entered. A host of other solubility values are predicted when various combinations of measured and estimated parameters are entered into ECOSAR, and range from 0.20 to 5.1 mg L^{-1}.

The WATERNT program in EPI Suite estimates solubility by utilizing a "fragment constant" method similar to that used in KOWWIN. Unlike most predictions by ECOSAR that overestimate TCC solubility , WATERNT underestimates TCC solubility as 0.024 mg L^{-1}.

Unlike WATERNT, which does not integrate the melting point and log K_{ow} into solubility estimates, WSKOWWIN allows manual entry of the physicochemical parameters. Like ECOSAR, WSKOWWIN utilizes LFERS (Eqs. (4) and (5) (Meylan and Howard, 1994a,b, Meylan et al., 1996)) modified from those used by ECOSAR, and the log K_{ow} predicted by KOWWIN. The WSKOWWIN program predicts TCC solubility as 0.59 and 0.23 mg L^{-1} with and without manual entry of the measured log K_{ow}, respectively, and a melting point of 250 °C. Predicted TCC solubility values range from 0.12 to 10.2 mg L^{-1} when a variety of additional measured and estimated parameter combinations are entered into WSKOWWIN. Back-calculation of the log K_{ow} using the measured TCC solubility in Eqs. (2)–(4) and (2)–(5) result in predicted values of 6.3 and 4.7 ($t_m = 250$ °C), respectively.

$$\log(S) = 0.796-0.854(\log K_{ow})-0.00728(MW) \tag{4}$$

where S is measured in mol L^{-1}, MW is the molecular weight of TCC (313 g mol^{-1}), n equals 1450 mixed-class compounds, and r^2 is 0.934, and

$$\log(S) = 0.693-0.96(\log K_{ow})-0.0092(t_m-25)-0.00314(MW) \tag{5}$$

where S is measured in mol L^{-1}, t_m is the TCC melting point (250 °C), MW is the molecular weight of TCC (313 g mol^{-1}), n equals 1450 mixed-class compounds, and r^2 is 0.970.

4. Conclusions

The mean TCC concentration measured in the 23 biosolids described herein fell within the range of previously reported TCC concentrations in WWTP products, but was less than the mean concentration reported in the TNSSS. Further, the greatest biosolids-borne TCC concentration measured herein was significantly less than the two greatest TNSSS concentrations.

The differences in predicted TCC solubilities and log K_{ow} values as a function of estimation program and use of measured/estimated values underscores the importance of confirmed physicochemical parameters. Chemical solubility and partitioning behavior are key input parameters in most organic contaminant environmental fate and transport models used to screen chemicals for human and environmental health risks. Use of inaccurate physicochemical data such as those predicted by the aforementioned LFER and ECOSAR program could contribute to erroneous predictions of fate, toxicity, and risk, or direct focus to inappropriate environmental compartments. Measured values of TCC solubility and K_{ow} are expected to yield more accurate predictions of bioavailability, toxicity, persistence, and environmental transport.

It should be noted however, discrepancies can also occur between measured physicochemical parameters when inconsistent or inappropriate determination methodologies are applied. For example, the solubility of hydrophobic compounds (i.e. $<10^{-2}$ g L^{-1}; USEPA, 1996b) should not be measured using a shake-flask method (as opposed to the column elution method herein, or the generator column method), as relative errors in weighing solute mass prior to dissolution can be large. Similarly, the log K_{ow} can be inaccurately measured if the water and n-octanol are not mutually saturated prior to addition of the compound of interest, as emulsions that exaggerate solubility can develop.

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Review

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

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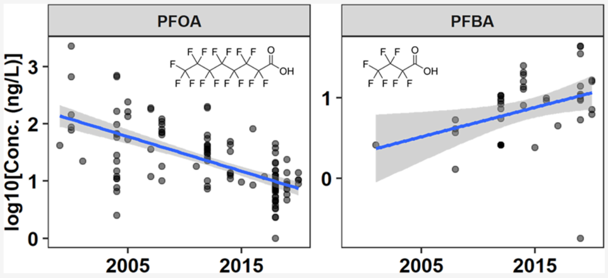

ABSTRACT: This paper presents an up-to-date meta-analysis assessing per- and polyfluoroalkyl substance (PFAS) concentrations at wastewater treatment plants (WWTPs) as well as changes over time. PFAS concentrations were compiled for WWTPs in the United States from peer-reviewed studies, technical reports, and original data. Perfluorooctanoic acid (PFOA) increased by an average of 6.0 ± 1.6 ng/L from the influents to the effluents of WWTPs, but perfluorosulfonic acid (PFOS) did not significantly change, indicating sorption to sludge is offset by biotransformation of precursor compounds. The occurrence of individual PFAS may vary temporally; for example, perfluoropentanoic acid correlated weakly with seasonal temperatures at a site in Virginia. Wastewater effluent PFOA concentrations decreased at a site in Nevada from 2012 to February 2020 but appeared to increase during the COVID-19 pandemic. Effluent PFOA also declined nationally from 1999 to 2020 by ∼13% per year. Nevertheless, the national mean PFOA concentration was 8.4 ± 0.4 ng/L in data collected from 2013 to 2020 with outliers omitted, indicating persisting low-level occurrence. This would equate to 383 ± 20 kg of PFOA per year continuing to enter the environment via WWTP effluents.

1. INTRODUCTION

Poly- and perfluoroalkyl substances (PFAS) are ubiquitous in municipal wastewater and biosolids. Major point sources include PFAS-producing or -using industrial sites, such as papermaking, textile mills, and electroplating.[1−4] However, PFAS have been detected in wastewater even without direct industrial sources, such as in septic tanks and office buildings.[5,6] Similarly, PFAS have been detected in the biosolids of small municipal wastewater treatment plants (WWTPs) without known direct industrial sources.[7] PFAS detected in wastewater and biosolids include not only the two most studied PFAS, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), but also short-chain PFAS and polyfluorinated compounds.[5,8−10] It is suspected that PFAS in non-industrial wastewater may occur in part due to environmental degradation of polyfluorinated microfibers released by water-resistant clothing during laundry.[11] Another plausible non-industrial source of PFAS in municipal wastewater is human excretion after oral exposure.[12,13] Often, a portion of the PFAS in wastewater effluent can be ascribed to PFAS in the community's tap water.[14,15]

Certain PFAS have been under increasing regulatory scrutiny due to their persistence, bioaccumulation, and toxicity. PFOA has probable links with several toxicological end points, including kidney cancer, testicular cancer, and high cholesterol.[16] PFOS has been linked with reproductive toxicity, immune effects, and kidney toxicity in laboratory animals.[17,18] Biomarker studies have indicated similar effects in humans.[18] PFOA and PFOS have been phased out in the United States under the 2010/2015 PFOA Environmental Protection Agency (EPA) Stewardship Program and replaced with short-chain PFAS, polyfluorinated compounds, and perfluoroethers.[19,20] Shorter-chain alternatives have been utilized due to their shorter half-lives in the human body [e.g., 2.9 years for PFOS but 0.12 year for perfluorobutanesulfonic acid (PFBS)].[21] Less is known about the toxicity of short-chain PFAS, but precaution is warranted on the basis of the similarity of their persistence to that of PFOA and PFOS.[19] PFAS in wastewater effluent may also pose a hazard to aquatic ecosystems. The Australian PFAS National Environmental Management Plan recommends a guideline of 0.23 ng/L PFOS for 99% species protection in aquatic ecosystems.[1022]

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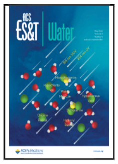

PFAS are poorly removed by WWTPs and conventional drinking water treatment plants.[8,23] In many cases, the concentrations of perfluoroalkyl acids (PFAAs) increase due to the biotransformation or oxidation of polyfluoroalkyl precursor compounds.[23,24] Without appropriate mitigation methods, human exposure could occur from wastewater through de facto and planned potable reuse, or through bioaccumulation into food or leaching into groundwater from biosolid application sites.[2,25−28]

Many studies have quantified PFAS in wastewater effluent[8,23,29,30] or biosolids.[7,31,32] Venkatesan and Halden[9] measured PFAS in five composites of 110 biosolid samples collected from 94 WWTPs in the United States in 2001. However, because of the way the samples were composited, distributions could not be analyzed and sources could not be identified. Furthermore, the types of PFAS observed in biosolids have changed since 2001 due to shifts in manufacturing toward short-chain PFAS.

Armstrong et al.[31] found no significant decline in PFAAs in biosolids at a WWTP in the mid-Atlantic region of the United States from 2005 to 2013.[33] However, because PFOS and PFOA were gradually phased out by different producers from 2002 to 2015, these two studies may have occurred too soon to observe any resulting changes in PFAS in biosolids.[34,35] Houtz et al.[36] found two short-chain PFAS, perfluorobutanoic acid (PFBA) and perfluorohexanoic acid (PFHxA), increased in the effluent of WWTPs in the San Francisco Bay Area between 2009 and 2014, but the sample size was limited (n = 6).[37] Arvaniti and Stasinakis[38] thoroughly reviewed occurrence studies for PFAS in wastewater and biosolids in 2015, but new data have emerged in the six years since.[1,25,39−48]

A comprehensive estimate of national average PFAS concentrations in WWTPs would have several uses and benefits. For one, WWTPs could compare their influent PFAS concentrations to the average to determine whether they are representative of baseline residential wastewater concentrations, or likely coming from an industrial source. PFAS WWTP effluent occurrence data could be compared with de facto reuse data to estimate PFAS exposure via drinking water due to PFAS in effluent.[49] PFAS biosolid concentrations could be used as inputs to models to estimate human exposure through agricultural products from land application sites.[50,51] The historical rate at which PFAS concentrations have changed at WWTPs should be quantified, so older PFAS data can be appropriately omitted or adjusted when conducting literature reviews or meta-analyses. Whether PFAS concentrations in wastewater effluent vary seasonally should also be investigated. This would inform the sample size and sampling frequency in future PFAS monitoring campaigns.

The goal of this meta-analysis was to generate an updated, comprehensive estimate of PFAS in U.S. WWTP influent, effluent, and biosolids. For effluent, which had the most data and over the widest time range, long-term trends were also examined. Seasonal patterns were also investigated at an individual WWTP with a relatively large sample size. To explore the impact of industrial wastewater on the overall average, outliers or WWTPs with stated industrial sources were sometimes omitted.

2. METHODS

2.1. Long-Term Trends (a single WWTP). Wastewater effluent concentrations of perfluoropentanoic acid (PFPeA), PFHxA, perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorohexanesulfonic acid (PFHxS), and PFOS were compiled from a WWTP in Nevada from 2012 to 2021 (n = 36 total, n = 22 from 2012 to February 2020). Details about the Nevada WWTP and its sample locations are provided in Text S1 and Figure S1. Some of the PFAS data evaluated for the Nevada site have been published previously,[1,52,53] while some have been collected for ongoing research projects using published methods.[54,55] Linear modeling was conducted in R with the lm() function. To investigate whether the PFOA phaseout was causing on overall trend toward shorter-chain PFAS in effluent, the average PFCA chain length was calculated as

$$L_{\mathrm{av}} = \frac{5[\mathrm{PFPeA}] + 6[\mathrm{PFHxA}] + 7[\mathrm{PFHpA}] + 8[\mathrm{PFOA}] + 9[\mathrm{PFNA}] + 10[\mathrm{PFDA}]}{[\mathrm{PFPeA}] + [\mathrm{PFHxA}] + [\mathrm{PFHpA}] + [\mathrm{PFOA}] + [\mathrm{PFNA}] + [\mathrm{PFDA}]} \tag{1}$$

where square brackets denote concentrations in nanomolar.

2.2. Seasonal Patterns. Twenty-seven PFAS were monitored every 2 weeks from May 2019 to May 2020 in the secondary effluent of a WWTP in Virginia using published methods (n = 24).[48,55] This WWTP has a design flow of 110000 m^3/day (30 MGD) with a five-stage Bardenpho process, and its sewershed has a landfill as a known PFAS source.

Certain PFAS such as PFPeA, PFHxA, PFHpA, and PFOA biotransform from polyfluorinated precursors, such as n:2 fluorotelomer alcohols and 6:2 fluorotelomer sulfonic acid (FTSA), which have been observed in wastewater.[39,48,56,57] 6:2 FTSA is known to biotransform from polyfluorinated substances in aqueous film forming foam (AFFF).[38,55,58] The Virginia WWTP has a zero discharge policy toward AFFF, and discharges of AFFF to sewers in general would be unlikely. Nevertheless, it was suspected that 6:2 FTSA might biodegrade from related higher-molecular weight polyfluorinated substances in wastewater. PFBA can also biotransform from the same polyfluorinated precursors as PFPeA and PFHxA[57] but was not evaluated due to the low detection frequency at the WWTP (12.5%). The impact of temperature on polyfluorinated precursor biotransformation rates has not been studied in controlled wastewater microcosms to the best of our knowledge. However, it is well-known that higher temperatures generally facilitate biological activity in WWTPs. Higher summer temperatures have been shown to increase the removal of acesulfame[59] and pharmaceuticals.[60] Tavasoli et al. found higher total measured PFAS concentrations in July than in March.[46]

Thus, it was hypothesized that these five PFAS would have a seasonal pattern caused by variables such as temperature accelerating biotransformation during certain times of year. Single-factor analysis of variance (ANOVA) was conducted with data points categorized into four seasons (winter, spring, summer, and fall). The normality of the PFAS concentrations at the Virginia WWTP was tested using normal probability plots, histograms, skewness, and kurtosis. Single and multiple

Table 1. Slopes of PFAAs and Average PFCA Chain Lengths over Time (2012 to February 2020) in Wastewater Effluent at a WWTP in Nevada

parameter	*n*	predicted concentration in 2012 (ng/L)	slope (ng L^{-1} $year^{-1}$)	SE[a] (ng L^{-1} $year^{-1}$)	R^2	*p* value
PFPeA	22	17	0.15	0.44	0.006	0.73
PFHxA	22	8.8	0.19	0.22	0.034	0.41
PFHpA	22	2.2	−0.10	0.033	0.30	0.0084
PFOA	22	9.4	−0.73	0.079	0.81	1.2×10^{-8}
PFNA	22	2.7	−0.30	0.041	0.73	4.6×10^{-7}
PFDA	22	1.8	−0.14	0.022	0.65	5.4×10^{-6}
PFHxS	22	1.5	0.033	0.13	0.0033	0.80
PFOS	22	5.4	−0.52	0.37	0.088	0.18
average PFCA length[b]	22	6.2	−0.064	0.0094	0.70	1.4×10^{-6}

[a] SE is the standard error of the slope. [b] The units for average PFCA length are numbers of carbons.

linear correlations between PFAS concentrations and temperature, aerobic solid retention time, and percentage of flow from landfill leachate were investigated in R with the lm() function.

2.3. National Estimates. PFAS wastewater influent, effluent, and biosolid data were compiled from peer-reviewed articles searched using Web of Science. Statistical analyses were limited to studies sampling WWTPs in the United States to control for different PFAS practices among countries and so the data could be used for national PFAS emission estimates. Analyses were also limited to studies that reported data for individual WWTPs. Otherwise, (1) WWTPs within studies that reported averages only would be underweighted and (2) the distribution of PFAS concentrations would appear to be narrower than the true distribution. Three studies for wastewater influent or effluent and one study for biosolids were omitted on the basis of this criterion.[5,61−63] If multiple stages of wastewater treatment were sampled, only the final, most treated sample (e.g., disinfected tertiary effluent but not the preceding secondary effluent) was included to avoid double-counting WWTPs.

Sludge, digested sludge, and biosolids were analyzed as a group due to the relatively small sample size and because studies indicate that current full-scale solid handling practices have little impact on PFAS concentrations except for dilution or incineration.[32,64] The protocols if multiple solid samples were collected from different locations in the same WWTP or if the same solid samples were analyzed in multiple studies are described in Text S2.[65−67]

On the basis of this scope, aqueous data were analyzed from 20 peer-reviewed articles,[7,8,25,30,39−41,43−48,68−74] one Water Research Foundation (WRF) technical report,[1] one 3M report,[75] and one state government report.[42] Original data were also included for six WWTPs managed by a single utility in Virginia. The data for biosolids were analyzed from 10 peer-reviewed articles and one 3M report. The combined data set is provided in the second Supporting Information file. Concentrations below the method detection limit (MDL) were assumed to be half of the MDL. Alternatively, concentrations were assumed to be half of the method reporting limit (MRL) or limit of quantitation (LOQ) if the MDL was not reported. The half-MDL approach is considered adequate for summary statistics with <70% censoring and group comparisons with <25% censoring.[76,77] Statistical analyses were conducted for each PFAS for which the sample size was ≥30 and the detection frequency was ≥30% under each set of assumptions. Results for PFOA are shown in the text, and results for other PFAS with sufficient sample size are shown in the Supporting Information. Total U.S. wastewater flow was assumed to be 4.6×10^{13} L/year.[78] The total mass of biosolids was assumed to be 6.51×10^{9} kg/year, of which approximately 55% is land applied for agriculture.[79]

Juxtaposing the mean PFAS concentrations with and without major point sources would indicate the relative importance of such sources. This would in turn reveal the limit to which industrial source control could reduce PFAS in wastewater effluent. PFAS concentrations in WWTPs without major point sources were investigated through two approaches. First, WWTPs that were clearly and specifically stated in the cited studies to have industrial PFAS sources were omitted. Due to the limited information available about WWTPs' sewersheds in published studies, industrial PFAS sources were not strictly defined on the basis of industrial categories or confirmed PFAS usage. Rather, the cited references' criteria for defining and reporting industrial PFAS sources to the WWTPs were taken at face value. However, studies might not consistently and clearly report on point sources to the WWTPs, and point sources might be highly dilute or emit PFAS other than the analyte in question. Therefore, a second, data-driven approach was also explored for omitting WWTPs with major industrial point sources. Using Tukey's outlier test (values greater than the 75th percentile plus 1.5 times the interquartile range), the highest outlier was iteratively omitted and the percentiles were recalculated until no high outliers remained.[80−82]

The simplest approach for estimating the mean of concentrations in wastewater or biosolids would be to treat all of the literature data as a simple random sample (SRS). The mean and standard error of the sample would then be treated as a direct estimate of the likely range of the mean of the population (i.e., all U.S. WWTPs). However, this approach would ignore the possibility that certain subpopulations of WWTPs—most critically, those with or without major PFAS point sources—might be over- or underrepresented in the literature data.

Stratified sampling is a statistical method for correcting for differences between the sample and the population in terms of the relative frequency of key subpopulations. For stratified samples, the mean is calculated as

$$\bar{x}_{st} = \sum_{i=1}^{j} w_i \bar{x}_i \qquad (2)$$

where $\bar{x}_{st}$ is the mean of the stratified sample, $\bar{x}_i$ is the mean within each stratum, w_i is the weight of each stratum, j is the number of strata, and w_i is the weight assigned to each stratum.

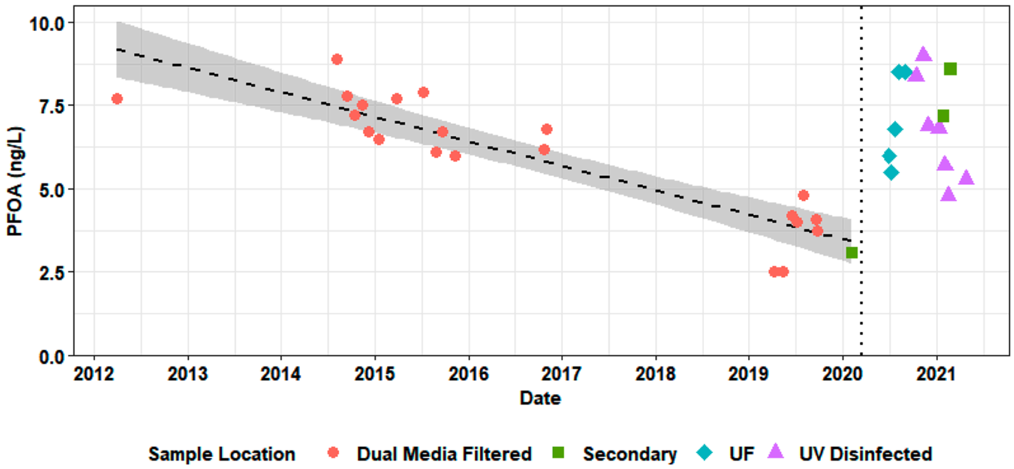

Figure 1. Concentrations of PFOA from 2012 to 2021 at the Nevada WWTP (n =36). The dashed line represents the line of best fit of the correlation with time from 2012 to February 2020 (n = 22). The shaded gray area is its 95% confidence band. The dotted vertical line indicates March 17th, 2020, the day closures of non-essential business went into effect in Nevada due to the COVID-19 pandemic. UF is ultrafiltration.

The standard error of the mean of stratified samples is calculated as

$$\mathrm{SE} = \left(\sum_{i=1}^{j} \frac{w_i^{\,2} \times \mathrm{Var}_i}{n_i} \right)^{1/2} \tag{3}$$

where Var_i is the variance within each stratum.[83] However, a limitation of this approach is that it requires knowledge of the proportion of each subpopulation within both the sample and the population. Such information is not always consistently available when conducting meta-analyses.

3. RESULTS AND DISCUSSION

3.1. Long-Term Trends (a single WWTP). From 2012 to February 2020, PFOA concentrations in wastewater effluent at the Nevadan WWTP significantly declined at a rate of −0.73 ± 0.079 ng L^{-1} year^{-1} (n = 22; $p = 7.8 \times 10^{-8}$) (Table 1 and Figure 1). PFHpA, PFNA, and PFDA significantly declined, as well (Table 1 and Figure S2). The average PFCA chain length decreased by −0.064 ± 0.0094 carbon/year (n = 22; $p = 1.4 \times 10^{-6}$) (Figure S3). PFOS would have been significantly decreasing if not for a high outlier in late 2014 (Figure S4).

However, PFOA concentrations at this WWTP increased during 2020 and then returned closer to 2019 levels by early 2021. This spike in PFOA concentrations coincided with the early stages of the societal response to the COVID-19 pandemic in the United States. The maximum PFOA concentration, 9 ng/L, was measured in November 2020, more than double the expected value of ∼4 ng/L based on the 2012−2019 trendline. PFOS (Figure S2) and PFDA (Figure S3) also approximately doubled in 2020 before returning to values similar to those of 2019 by 2021. Flow at this WWTP decreased by 17% in March 2020 due to reduced flow from the hospitality industry,[85] which would not be expected to contribute substantially to PFAS loads. Therefore, the 2-fold increase in long-chain PFAS could be explained partially, but not fully, by reduced dilution from that sector. Changes in consumer product use (e.g., more usage of home cookware, more take-out or drive-through instead of dine-in restaurant experiences, and more washing of informal clothing) may also have contributed to the divergence from the previous trend. Effluent at this WWTP was sampled at different locations within its tertiary treatment after 2019, which could appear to confound this observation. However, the processes between these sample points are known to have a negligible effect on PFAS based on studies at this WWTP (Text S1).[1]

3.2. Seasonal Patterns (a single WWTP). Visually, PFPeA had the most plausible seasonal pattern among the PFAS evaluated, with the highest concentrations in the summer (Figure S5). PFPeA correlated with raw influent temperature with a significant p value of 7.97×10^{-3} but a low R^2 of 0.28 (Figure 2 and Table S1). A single-factor ANOVA was conducted to test whether the mean PFPeA concentration likely differed among the seasons. However, the p value of this ANOVA was not quite significant (p = 0.0501). Histograms and normal probability plots indicated PFPeA concentrations were somewhat right-skewed (Figures S6 and S7). However, the kurtosis and skewness of PFPeA had absolute values of <2, indicating acceptable normality for ANOVA.[86] Further testing

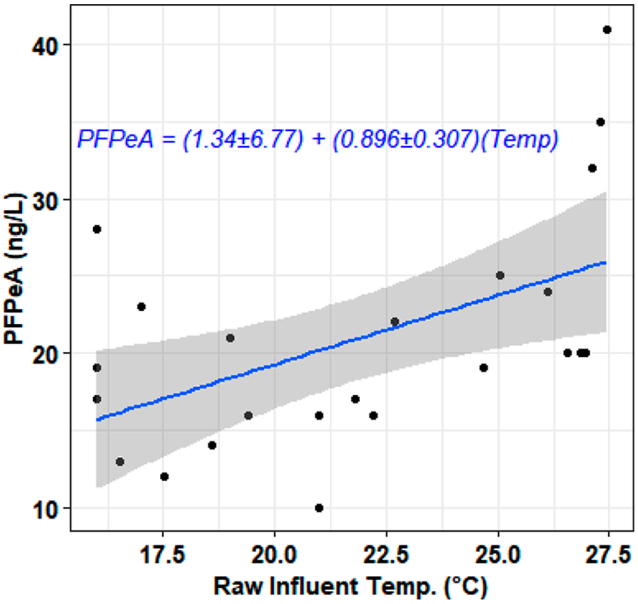

Figure 2. Correlation between effluent PFPeA concentration and raw influent temperature at the Virginia WWTP.

Table 2. Estimates of PFOA Concentrations and National Emissions in Wastewater Effluent[a]

method	n	mean concentration (ng/L)	mean concentration SE (ng/L)	estimated emissions (kg/year)	estimated emissions SE (kg/year)
SRS, all studies	129	68.9	19.7	3141	899
SRS, no stated industrial source	112	50.5	10.7	2303	486
SRS, no outliers	70	8.6	0.401	391	18.3
SRS, 2013−2020	68	12.8	1.58	585	72.0
SRS, 2013−2020, no outliers	58	8.41	0.444	383	20.2
stratified, 0.1% stated industrial source	129	50.7	10.7	2309	486
stratified, 20% stated industrial source	129	78.4	27.7	3575	1263

[a] SE is the standard error. SRS is a simple random sample. See Tables S2−S14 for similar tables of other PFAS. The sample year range is 1998−2020 unless otherwise noted.

at monthly or greater frequencies at other WWTPs is needed to conclude whether the temperature correlation observed here is generalizable, not site-specific or coincidental.

3.3. National Estimates.

3.3.1. Wastewater Effluent.

3.3.1.1. All Data. Considering all literature data, the mean PFOA concentration was 69 ± 20 ng/L (Table 2). This concentration corresponds to total emissions of 3141 ± 899 kg/year, which is within reason compared to the estimated range of 5000−40000 kg/year of total PFOA emissions to water in the United States, Japan, and western Europe prior to 2003 according to Wang et al.[89] However, the PFOA data were not normally distributed, with an extreme right skew and an outlier 165 times higher than the median (Figure S8A). This non-normality indicates a confidence interval might not reflect the true likely range of the mean concentration. Furthermore, the outliers are presumably from WWTPs with major industrial PFAS sources.

3.3.1.2. Stated Industrial Point Sources Omitted. Omitting WWTPs with stated industrial sources decreased the mean PFOA concentration to 51 ± 11 ng/L. However, the PFOA concentration distribution remained right skewed with multiple outliers (Figure S8B). This was at least partly because this data subset still contained some WWTPs with major industrial sources. For example, EGLE[42] stated six of 42 sampled WWTPs had industrial PFAS sources but did not state which six.

3.3.1.3. Tukey Outliers Omitted. After Tukey outliers had been omitted, the mean PFOA concentration was only 8.6 ± 0.4 ng/L, 6 times lower than the mean relying on references to state industrial influence accurately. Thus, it is apparent that industrially impacted WWTPs are not consistently identified in the literature. After outliers had been omitted, the remaining PFOA data appeared to be normally distributed (Figure S8C). However, this was not the case for PFBS, or PFDA, possibly due to a greater proportion of the data for these analytes being below their MDLs (Figure S11).

3.3.1.4. Long-Term Trends and Recent Data. When all WWTPs were included, the PFOA concentration significantly correlated with sample year with a slope of −14 ± 3 ng L^{-1} $year^{-1}$ ($p = 1.2 \times 10^{-5}$) (Figure S14A). PFOS (−18 ± 6 ng L^{-1} $year^{-1}$; $p = 0.0060$) and FOSA (−0.75 ± 0.30 ng L^{-1} $year^{-1}$; $p = 0.016$) also showed significant negative trends (Figure S15). In contrast, PFBA, a short-chain PFAS, was significantly increasing at a rate of 0.98 ± 0.33 ng L^{-1} $year^{-1}$. However, the true long-term trends could be confounded if industrially impacted WWTPs were more likely to be sampled in older or more recent years. When WWTPs with stated industrial sources were omitted, only PFOA had a significant downward trend, declining at a rate of −8.7 ± 1.7 ng L^{-1} $year^{-1}$ ($p = 1.1 \times 10^{-6}$) (Figures S14C and S16). Data subsets with outliers omitted were not analyzed for long-term trends because a data point could plausibly be an outlier due to being relatively old rather than being industrially impacted.

Because the concentration of PFOA in U.S. wastewater effluent is decreasing over time, older studies may no longer be representative of current emissions. Considering the confidence band of the correlation between PFOA and sample year, 2013 was selected as the most distant past year in which mean PFOA concentrations would be expected to be like 2020 (Figure S14C). Therefore, "recent" studies were herein defined as those sampling wastewater effluent in 2013−2020. When the data set was restricted to only recent studies, the mean PFOA concentration was only 13 ± 2 ng/L (Table 2). PFOA and PFNA were significantly decreasing over this more limited time frame (Figure S17).

When Tukey outliers were omitted from the recent data, the mean PFOA concentration was 8.4 ± 0.4 ng/L, significantly lower than with outliers (Table 2). This indicates PFOA industrial sources were still important after 2013. The maximum PFOA concentration during 2013−2020 after omitting outliers was 15 ng/L. Therefore, PFOA concentrations above this level would be considered atypical for recent samples from WWTPs without major PFAS point sources.

Linear regression on log-transformed concentrations showed PFOA significantly declined at an annual rate of 13% (i.e., half-life of 5.0 years) when all data were analyzed and 12% (i.e., half-life of 5.3 years) when WWTPs with stated industrial sources were omitted (Figure S14B and Figure 3). Using the log-transformed correlation without stated industrial sources, the mean PFOA concentration would reach the Illinois drinking water health advisory level of 2 ng/L around 2030.[91]

3.3.1.5. Stratified Analyses for Industrially Impacted WWTPs. It would be useful to conduct a stratified analysis to correct for differences in the proportion of industrially impacted WWTPs between the sample and the true population. However, this would require knowledge of the percentage of WWTPs in the United States that are substantially impacted by PFAS-producing or -using industries. Unfortunately, this is difficult to estimate. EGLE[42] sampled PFAS at 42 WWTPs in Michigan, of which six (14%) were industrially impacted. However, that study took place in a relatively industrial state and intentionally focused on larger WWTPs that are simultaneously more likely to contain industrial point sources yet also have a high degree of dilution for any point sources. Hu et al.[2] identified 16 PFAS-producing

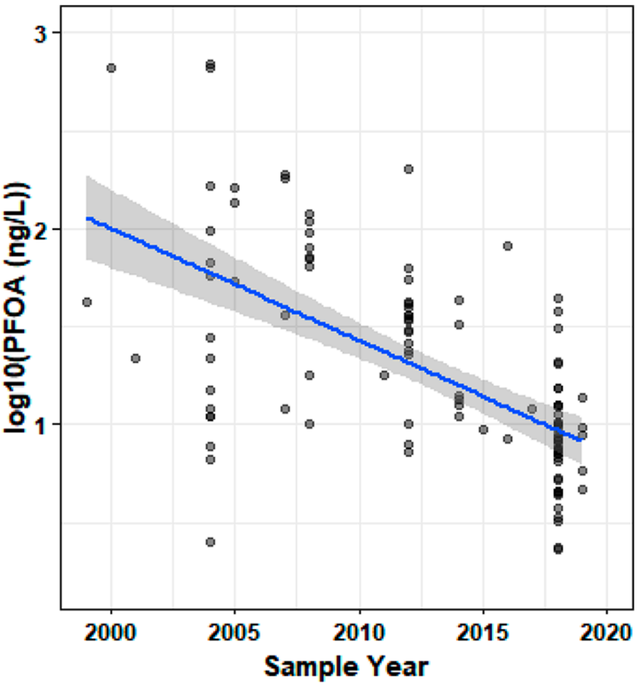

Figure 3. Correlations between log-transformed wastewater effluent PFOA concentration and sample year in the United States without stated industrial sources. The blue line represents the line of best fit, and the shaded gray area represents its 95% confidence band.

facilities in the United States, but it is unclear which, if any, of these facilities discharge PFAS to municipal sewers. Hu et al.[2] also identified 533 AFFF-certified airports, which may emit AFFF to the sewer intermittently if at all. The Environmental Working Group (EWG) identified 2444 facilities suspected of using PFAS based on their industrial categories.[92] However, this is likely an overestimate because, for example, not all textile-manufacturing facilities may produce water- or stain-resistant fabric. Furthermore, it is unclear how many of these industrial sites discharge to municipal sewers or directly to the aquatic environment, or how many clusters of sites discharge to the same few sewer systems. The U.S. EPA Chemical Data Reporting Rule lists 28 facilities known to produce or use large amounts of PFAS, but this may be an underestimate because it is based on voluntary reporting.[92]

There were at least 2600 active municipal landfills in the United States in 2020 according to the U.S. EPA.[93] With a few exceptions in arid regions, the leachate from these landfills is discharged to municipal sewers. The total PFOA emission from landfills in the United States in 2013 was estimated to be 52 kg/year.[94] This would be <2% compared to the wastewater effluent estimate using all data (3141 ± 899 kg/year) or <10% compared to the estimate for 2013−2020 (585 ± 72 kg/year) (Table 2). Estimated emissions of other PFAAs from landfills in the same study would also be ≤10% compared to estimated wastewater effluent emissions (Tables S2−S13). The measured PFAS with the highest landfill emission was the polyfluorinated compound 5:3 fluorotelomer carboxylic acid.[94] However, few data were available for this analyte in U.S. wastewater effluent. Thus, landfill leachate is likely a minor contributor to total, national wastewater PFAS emissions. Nonetheless, landfills could cause high PFAS concentrations in site-specific situations, particularly considering landfills may discharge to small WWTPs because they tend to be located outside city centers. An example of a small WWTP with PFAS concentrations meaningfully impacted by landfill leachate was documented by Tavasoli et al.[46]

On the basis of the considerations mentioned above, a sensitivity analysis was conducted assuming the true proportion of the 16000 WWTPs in the United States with substantial industrial impact was as low as 0.1% or as high as 20%. The literature data were treated as a stratified sample with two strata: stated industrial PFAS source(s) or no stated industrial PFAS source. WWTPs with industrial PFAS sources were defined as those clearly stated to be so in the references (i.e., the same assumption as the second row of Table 2). On the basis of these assumptions and weights, the mean PFOA concentration in wastewater effluent would be as low as 51 ± 11 ng/L or as high as 78 ± 28 ng/L (Table 2). These end cases are not put forth as best estimates of the true, current mean PFOA concentration in U.S. wastewater effluent, considering they incorporate data collected before 2013 and the true proportion of industrially impacted WWTPs is likely somewhere in the middle. Rather, these extreme possibilities demonstrated the necessity of better data on the use and disposal of PFAS by industries, such as including some PFAS in the federal Toxic Release Inventory.

3.3.1.6. Relative Concentrations. Which PFAA had the highest mean concentration depended on the set of assumptions. PFPeA was the highest including all data at 87 ± 51 ng/L (Table S3). PFOA was the highest omitting known industrial sources at 51 ± 11 ng/L (Table 2). PFHxA was the highest when omitting suspected industrial outliers at 23 ± 2 ng/L (Table S4). PFHxA was also highest when limiting to 2013−2020 data at 48 ± 11 ng/L.

Knowing the typical relative proportions of different PFAS analytes in effluent would have multiple benefits. For one, effluents that significantly deviate from these proportions could be identified as likely industrially impacted. For another, surface waters that match these proportions with equal or lower total concentrations could be identified as likely impacted by de facto reuse. To this end, data were filtered to only WWTPs at which all of the following common PFAAs were analyzed: PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS (n = 23). Proportions were calculated on a molar basis and are shown in Figure 4. PFPeA, PFHxA, and PFOA each accounted for ∼25% of the commonly measured PFAAs in wastewater effluent without stated industrial sources.

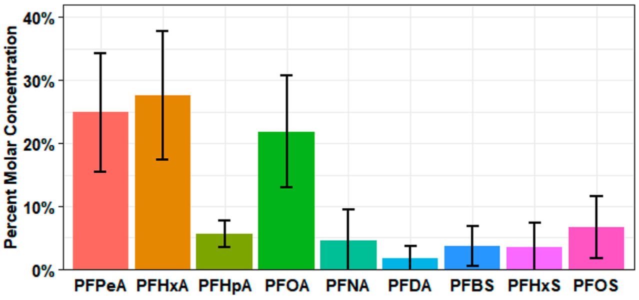

Figure 4. Mean molar proportions of PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS in wastewater effluents without stated industrial sources (n = 23). Error bars are standard deviations.

3.3.1.7. Downstream Surface Water Implications. For context, PFOA and PFOS concentrations were divided by their Michigan surface water standards, or water quality values (WQVs) (Table S14). Michigan has set lower WQVs for water bodies used for drinking water and higher WQVs for water bodies not used for drinking water. For PFOA, the drinking water and nondrinking water WQVs are 420 and 12000 ng/L, respectively. For PFOS, the drinking water and nondrinking water WQVs are 11 and 12 ng/L, respectively. Under none of the sets of assumptions explored in this study would the mean effluent PFOA concentration exceed its drinking water WQV (Figure 5 and Figure S18). In contrast, mean effluent PFOS would exceed its WQVs by a factor of ≥2 considering all data, data without stated industrial sources, and data for 2013−2020 (Figure 5 and Figure S18). Without Tukey outliers, mean PFOS is 10.0 ± 0.7 ng/L, indicating some non-industrially impacted WWTPs could have effluent PFOS above these WQVs. However, de facto reuse of >50% is rare in the United States.[49] Therefore, considering dilution, it is unlikely municipal wastewater effluent would cause an exceedance of these WQVs without an industrial source.

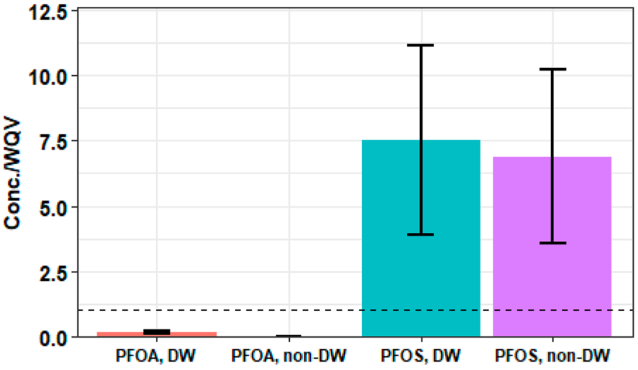

Figure 5. Mean concentration divided by Michigan water quality values (WQVs) for drinking water (DW) and nondrinking water (non-DW) water bodies considering all literature data. Error bars are standard errors of the mean. The dashed horizontal line represents 1 or a concentration equal to the WQV.

3.3.2. Wastewater Influent. A smaller sample size was available in the literature for PFAS in U.S. wastewater influent, with only PFOA and PFOS having $n \geq 30$ (Table S16). Furthermore, a majority of these PFOA and PFOS data were from a single study in Michigan, so it may not be nationally representative.[42] When all data were included, the mean PFOS influent concentration was 35 ± 14 ng/L, which corresponded to a loading of 1596 ± 638 kg/year ($n = 67$). When all data were included, the mean PFOA influent concentration was 11 ± 2 ng/L, which corresponded to a loading of 495 ± 101 kg/year ($n = 62$). This mean influent PFOA concentration was ~7 times lower than the effluent concentration when all data were included.

The lower mean PFAS in influent may have been partly due to the influent data set having fewer industrially impacted WWTPs and a more recent average sampling year, but it could also be partly from PFOA precursor transformation. The increase in average PFOA in WWTPs with both influent and effluent data was 6.0 ± 1.6 ng/L ($n = 62$). The increases in PFOA were not normally distributed (Figure S19A), but both a t test ($p = 0.00019$) and a Wilcoxon signed rank test ($p = 1.5 \times 10^{-7}$) indicated the mean difference was greater than zero. The true PFOA formation could be somewhat greater considering ~14% of influent PFOA is expected to sorb to sludge.[98] In WWTPs with both influent and effluent data available, PFOS did not significantly increase or decrease from influent to effluent (t test $p = 0.73$, and Wilcoxon $p = 0.94$). Considering ~50% of influent PFOS would be expected to sorb to sludge,[98] it could be PFOS formation and sorption roughly offset each other. Alternatively, the true trend in PFOS concentrations changes through WWTPs may have been obscured by extreme outliers in both directions (Figure S19B).

3.3.3. Biosolids and Sludge. Within the scope of this meta-analysis, only PFOS ($n = 36$) and PFOA ($n = 36$) had $n \geq 30$ in sludge and biosolids. Due to this smaller sample size, data for solids were not subsetted by industrial impact or sample year like was done for WWTP effluent. However, data were stratified assuming 0.1% or 20% of the known industrial sources, as was done with influent and effluent. Assuming 20% of WWTPs nationwide were industrially impacted increased the estimated mean concentration in influent and effluent. However, for solids, this assumption resulted in a similar estimated mean concentration as treating the data as a simple random sample (Table 3). This was because samples of industrially impacted solids were overrepresented in the database at 22%.

3.3.4. Limitations. Differences in analytical methods among the cited studies may have contributed to uncertainty in the estimates of long-term trends and national averages. For example, most studies employed solid phase extraction[8,96] but some used direct injection.[30] Isotope dilution with internal mass-labeled standards is an effective method for correcting for extraction efficiency. One study used external calibration only;[96] some studies used mass-labeled internal standards for a subset of PFAS analyzed,[69] while others used mass-labeled standards for all PFAS.[8] Overall method recoveries varied among studies.[8,96] Generally, sources of imprecision like these would tend to obscure a true correlation rather cause a false positive.[97]

Studies differed in terms of whether they censored data based on MDL,[71] MRL,[8] or LOQ.[69] MRLs and LOQs also differed within and among studies.[8,44,69] Less than 1% of WWTP effluent samples included in this meta-analysis had PFOA below the censored level, so nondetections and different

Table 3. Estimates of PFOA Concentrations and National Emissions in Biosolids and Sludge[a]

method	n	mean concentration (ng/g)	mean concentration SE (ng/g)	estimated load (kg/year)	estimated load SE (kg/year)
SRS, all studies	36	23.8	6.84	155	44.5
stratified, 0.1% stated industrial source	36	15.3	4.30	99.7	28.0
stratified, 20% stated industrial source	36	22.9	6.12	149	39.8

[a] SE is the standard error. SRS is the simple random sample. See Table S17 for a similar table of PFOS.

censored levels would have little impact on the PFOA statistics discussed in the text. However, nondetections may have increased the uncertainty for other PFAS featured in the Supporting Information; e.g., 25% of PFNA data points were below their censored level.

Insufficient data were available for emerging PFAS [e.g., perfluoroethers and polyfluorinated substances except for N-ethyl perfluorooctane sulfonamido acetic acid (EtFOSAA) or 6:2 FTSA] to make statistically sound inferences about long-term trends, seasonal patterns, or national average concentrations in the United States. Furthermore, none of the cited studies stated whether the sampled WWTPs had combined sewers or sanitary sewers only. Therefore, the impact of intentional urban runoff mixing on PFAS concentrations could not be investigated with the literature data.[84,87,88,90,95]

4. CONCLUSIONS

Concentrations of long-chain PFAS, particularly PFOA, declined over time in wastewater effluent. Concentrations of short-chain PFAAs, such as PFBA, may be increasing. The long-term trend for PFOA was observed both nationally and at a specific WWTP in Nevada with a relatively high sample size from 2012 to February 2020. However, the COVID-19 pandemic may have caused a divergence from the prior long-term trend at the Nevadan WWTP. Seasonal analysis of PFPeA at a WWTP in Virginia showed a weak correlation with temperature. Mean PFAS concentrations in the literature are dominated by industrially impacted outliers. Historically, industrial discharges to sewers likely caused the majority of the PFAS emissions from WWTPs; more recently, it appears PFAS from domestic wastewater accounts for most of the load. A precise, confident estimate of the total WWTP PFAS emissions, including industrial contributions, would require more information about the location, number, and emissions of PFAS users. PFOA and PFOS may be formed from transformation of precursors and partition to solids within WWTPs. For PFOS, these processes roughly offset each other, while PFOA had a mean net increase of 6.0 ± 1.6 ng/L.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00377.

Additional meta-analysis methodological details as well as tables and figures particularly for PFAS other than PFOA (PDF)

Data for cited and original wastewater influent, effluent, and biosolids used for this meta-analysis (XLS)

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Notes

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SCIENCE ADVISORY BOARD
A Federal Advisory Committee to the U.S. Environmental Protection Agency

October 12, 2023

EPA-SAB-24-001

The Honorable Michael S. Regan
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20460

Subject: Transmittal of the Science Advisory Board report titled "SAB review of EPA's Standardized Framework for Sewage Sludge Chemical Risk Assessment (External Peer Review Draft)"

Dear Administrator Regan,

Please find enclosed the final report from the Scientific Advisory Board (SAB). The EPA's Office of Water requested that the SAB review the Agency's draft Standardized Framework for Sewage Sludge Chemical Risk Assessment. In response to the EPA's request, the SAB assembled the SAB Biosolids Panel with subject matter experts to conduct the review.

The SAB Biosolids Panel held three meetings on April 5, 2023, May 2-3, 2023, and July 5, 2023, to discuss the EPA's request and deliberate on the charge questions. The full SAB discussed and approved the report with revisions in a public meeting held September 21-22, 2023. Oral and written public comments were considered throughout the advisory process. This final report conveys the consensus advice of the SAB.

With regard to the entire draft for a standardized framework, the SAB wishes to commend the EPA for the overall high level of work and for its responsiveness to a broad array of community concerns. The SAB found the framework's approach to be sound and the accompanying documentation generally accessible to stakeholders. The scenarios offered within the framework reflect current biosolids managements including common, beneficial uses in agriculture.

In reviewing framework components, the SAB identified some potential pitfalls and limitations, mostly associated with adapting existing tools, processes and models to biosolids risk assessment. While the SAB includes several recommendations within this report, we would like to highlight the following:

- PICS bias: An explicit and transparent evaluation step in the framework focused on the output from the PICS process is needed. This modification would allow decision-makers to rapidly determine the scientific necessity of having to evaluate chemicals for which there is known insignificant public health and/or ecological risk.
- Appropriate consideration of the biosolids and biosolids-soil matrix: The SAB is concerned that the approach may be insufficiently nuanced to account for the unique characteristics of the biosolids matrix and for the potential modifications to chemical availability/toxicity when applied to soil. Sources of data for baseline information may conflate concentrations in biosolids with those in industrial waste streams. Concentrations must also be considered in the context of those that occur naturally and/or can be sourced to other factors common to human environments. Further, the aspects of chemical fate and transport that may be markedly different from that expected in an aqueous matrix and their controlling factors are not well-represented in the selected models. Overall, the SAB recommends a more explicit consideration of the municipal biosolids-soil matrix to ensure scientifically defensible application of the framework.
- Compounded conservatism and high-end assumptions: The SAB is concerned that assumptions made within the framework align with those expected for a Maximally Exposed Individual rather than for Reasonable Maximum Exposure. For example, farm family exposures assume subsistence farming and patterns and durations of occupancy, farming activities, and consumptions of farm-sourced food and water, that are well outside the norm of present-day family farms. The SAB notes that the vast majority of biosolids applications are made to lands that are not used for producing foods directly consumed by humans but rather to lands used for producing animal feed, fiber and/or fuel. Further, for ubiquitous compounds, consideration is needed for how high-end assumptions compare to prevailing environmental concentrations and whether risk simulations reflect our current understanding of these contaminants. For these reasons, the SAB makes numerous recommendations intended to support a more reasonable estimate of exposures without curtailing the framework’s ability to identify chemicals of risk to human and ecological receptors.
- Ecological risk assessment: The SAB finds that the farm pond and agricultural field are not appropriate ecosystems for the ecological risk assessment. For ecological receptors, the general practice of environmental risk assessment focuses on populations and communities greater than an individual (family farm) pond or field and on the attributes that are important to protect. The SAB recommends the EPA reconsider its problem formulation to be consistent with its own, previously published Guidelines for Ecological Risk Assessment.
- Software ease-of-use and longevity: The SAB encountered some challenges associated with installing the software and it is not agnostic with respect to operating systems. Further, the SAB noted the BST is superimposed on a Microsoft Access database using an outdated file type, Microsoft’s commitment to supporting Access is uncertain, and combined these factors suggest the software may be difficult to maintain. The SAB recommends that for the BST and all other software development efforts, the EPA carefully consider the issues of stakeholder accessibility and software obsolescence to ensure tools are aligned with their inclusivity goals and incorporate state-of-the-art technologies.

As the EPA finalizes its draft assessment, the SAB encourages the EPA to address the concerns raised in the enclosed report and consider the recommendations provided. The SAB appreciates this opportunity to review the draft assessment and looks forward to the EPA's response to these recommendations.

Sincerely,

/s/	/s/
Alison C. Cullen, Sc.D. Immediate Past Chair EPA Science Advisory Board	Sylvie M. Brouder, Ph.D. Chair EPA Science Advisory Board Biosolids Panel

Enclosure

NOTICE

This report has been written as part of the activities of the EPA Science Advisory Board, a public advisory committee providing extramural scientific information and advice to the Administrator and other officials of the Environmental Protection Agency. The Board is structured to provide balanced, expert assessment of scientific matters related to problems facing the Agency. This report has not been reviewed for approval by the Agency and, hence, the contents of this report do not represent the views and policies of the Environmental Protection Agency, nor of other agencies in the Executive Branch of the Federal government, nor does mention of trade names or commercial products constitute a recommendation for use. Reports of the EPA Science Advisory Board are posted on the EPA website at https://sab.epa.gov.

The SAB is a chartered federal advisory committee, operating under the Federal Advisory Committee Act (FACA; 5 U.S.C. 10). The committee provides advice to the Administrator of the U.S. Environmental Protection Agency on the scientific and technical underpinnings of the EPA's decisions. The findings and recommendations of the Committee do not represent the views of the Agency, and this document does not represent information approved or disseminated by EPA.

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SAB review of EPA's
"Standardized Framework for Sewage Sludge Chemical Risk Assessment (External Peer Review Draft)"

TABLE OF CONTENTS

ACRONYMS AND ABBREVIATIONS

3MRA	Multimedia, Multi-Pathway, Multi-Receptor Exposure and Risk Assessment
Al	Aluminum
B[a]P	Benzo[a]pyrene
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BER	bioactivity to exposure ratios
BST	Biosolids Tool
CFR	Code of Federal Regulations
DAF	Dilution Attenuation Factor
DOC	Department of Commerce
DOE	Department of Energy
EPACMPT	EPA's Composite Model for Leachate Migration
EPI Suite	Estimation Program Interface Suite
ExpoFIRST	EPA's Exposure Factors Interactive Resource for Scenarios Tool
HER	hazard to exposure ratio
IAM	Information Availability Metric
K_{oc}	OC-normalized sorption coefficient
K_{ow}	n-Octanol/Water Partition Coefficient
MEI	Maximally Exposed Individual
MRA	Multimedia, Multipathway, Multireceptor
MT	Metric Ton
NACWA	National Association of Clean Water Agencies
OC	Organic Carbon
PCB	Polychlorinated biphenyl
PFAS	Per-and Polyfluoroalkyl Substances
PICS	Public Information Curation and Synthesis
RAIDAR	Risk Assessment IDentification and Ranking
RME	Reasonable Maximum Exposure
SAB	Science Advisory Board
SDM	Scientific Domain Matric
TER	Toxicological Concern to Exposure Ratios
TNSSS	Targeted National Sewage Sludge Survey
U.S. EPA	U.S. Environmental Protection Agency
USDA	U.S. Department of Agriculture
VOC	Volatile Organic Compounds
WBAN	Weather Bureau Army Navy
WW	Wet Weight

1. INTRODUCTION

The Environmental Protection Agency (EPA) Office of Water requested that the Science Advisory Board (SAB) conduct a peer review of its draft "Standardized Framework for Sewage Sludge Chemical Risk Assessment". The framework includes a prioritization process, deterministic screening-level risk assessment, and a refined, probabilistic risk assessment (probabilistic risk assessment). The purpose of the framework is to support the EPA's efforts to assess human health and ecological risk from pollutants found in biosolids. Specifically, EPA's goal is to identify pollutants, pathways, and receptors of greatest interest to inform decisions on whether to perform a more refined biosolids risk assessment.

In response to the EPA's request, the SAB convened a panel of subject matter experts to conduct the review. The Science Advisory Board Biosolids Panel convened three public meetings to conduct a peer review of the EPA's assessment framework. Meetings were held on April 5, 2023, May 2-3, 2023, and July 5, 2023. Oral and written public comments were considered throughout the advisory process.

Charge questions were specified by the Office of Water. Recommendations are prioritized to indicate relative importance during EPA's revisions. Priorities are defined as follows:

- Tier 1: Key Revisions – Actions that are necessary to improve the critical scientific concepts, issues, and/or narrative within the assessment/document/model/guidelines.

- Tier 2: Suggestions – Actions that are encouraged to strengthen the scientific concepts, issues, and/or narrative within the assessment/document/model/guidelines, but other factors (e.g., EPA need) should be considered by the EPA before undertaking these revisions.

- Tier 3: Future Considerations – Useful and informative scientific exploration that may inform future evaluations of key science issues and/or the development of future assessments/documents/models/guidelines. These recommendations are likely outside the immediate scope and/or needs of the current review.

All materials and comments related to this report are available at: https://sab.epa.gov/ords/sab/f?p=114:18:9587163122946:::RP,18:P18_ID:2610.

2. RESPONSE TO CHARGE QUESTIONS

2.1. Prioritization

2.1.1. Application of the PICS process:

> *Does the SAB find that the application of the PICS process to the chemicals found in biosolids is sufficient to identify the chemicals that should move to a deterministic screening-level risk assessment?*

Over 700 chemicals have been identified in sewage sludge during three national sewage sludge surveys covering the years 1988, 2001, and 2006 (U.S. EPA, 2022) and in peer-reviewed literature available publicly. Prior to now, the EPA has had no framework for risk assessment of chemicals within the complex mixture of a biosolids. The Public Information Curation and Synthesis (PICS) was originally developed to support chemical prioritization under the Toxic Substances Control Act and underwent external peer review (U.S. EPA, 2023). PICS integrates publicly available information on these chemicals to establish occurrence, fate, and transport in the environment, human health and ecological effects, and other relevant information for these chemicals found in biosolids. Synthesis of this information is used to understand the overall degree of potential concern related to human health and the environment. The PICS process utilizes two matrices to identify whether or not each chemical that has been identified in biosolids is a high- or low-priority candidate for further study and analysis. The Information Availability Metric (IAM) utilizes information and data from relevant studies and databases such as the National Sewage Sludge Surveys and published literature. The Scientific Domain Matric (SDM) groups the information into seven scientific domains affecting human or environmental health (Table 1). Chemicals with large amounts of information and a high potential risk of adverse health effects are identified as strong candidates for further risk assessment.

Table 1. Scientific Domain Matric Groups (see page 13, U.S.EPA, 2023).

Human hazard to exposure ratio
Ecological hazard
Carcinogenicity
Genotoxicity
Susceptible populations
Persistence and bioaccumulation
Skin sensitization and skin/eye irritation

Overall, the SAB supports the PICS process and sees it as a scientifically-defensible and technically sound approach for identifying and prioritizing chemicals found within biosolids that should undergo a screening-level risk assessment evaluation. Although we applaud the EPA's basic approach, the following concerns and questions have been identified.

Overall concerns:

> Has the information needed for prioritization in both the IAM and SDM itself been evaluated and prioritized? This is important because some parameters for either the IAM or SDM, are critical. For example, (1) dose response data on a given chemical is vital since without dose response data, no risk assessment can be undertaken; (2) if multiple routes of exposure to a given chemical are possible, which of the routes is the most important to consider; (3) if a chemical is highly soluble, contaminated groundwater ingestion would be important, whereas if it is highly volatile, inhalation could be more important; and (4) with respect to incidence, bioavailable concentrations are far more important than total concentrations, particularly for metals. Further

the extent to which evaluations of the IAM and SDM data would be quantitative versus subjective was unclear as was the overall weight of the IAM relative to the SDM. We encourage the EPA to provide a clear and unambiguous description of the process by which IAM values will be utilized relative to SDM values in supporting its chemical prioritization decisions.

- Has a full-scale, exhaustive literature search of peer-reviewed, and non-peer-reviewed reports been conducted to glean the vast majority of available published information on metals and trace organics? If not, we encourage the EPA to conduct one.

IAM concerns:

- Are concentrations derived only from municipal biosolids and not industrially contaminated biosolids? This is a critical consideration since industrially contaminated biosolids have atypical levels of per- and polyfluoralkyl substances (PFAS). The SAB is concerned that the prioritization process may be initiated using data overly influenced by concentrations found only in industrial biosolids/waste-streams.

- Are total or bioavailable concentrations utilized? Only bioavailable concentrations should be used – total values do not provide useful information. For example, total metal concentrations are known to be greater than the bioavailable concentrations that are reflective of plant uptake (Smith et al., 2014).

- Are stated biosolid chemical concentrations current? For example, biosolid PFAS concentrations may be lower now versus twenty years ago, due to Perfluorooctane sulfonic acid and Perfluorooctanoic acid being phased out of production in the early 2000s.

- Is the biosolid matrix properly considered in modeling the fate and transport of chemicals? This is important since chemicals including metals, trace organics, and microbial pathogens are known to behave differently when contained within the biosolid matrix as opposed to being in aqueous solution. For example, there is a general consensus in the literature that metals are strongly bound to organic material due to complexation that limits their solubility and potential bioavailability in soil (Smith, 2009). An additional example is the leaching of viruses from biosolids. Chetochine et al (2006) showed that leaching from biosolids was significantly reduced by sorption within the biosolid matrix, which significantly reduced the potential for subsequent leaching through soil.

SDM concerns

Of the seven scientific domains identified as affecting human or environmental health, only the human hazard to exposure ratio (HER) and the ecological hazard domain are quantitative. The other five scientific domain matrices are qualitative in nature and can only be evaluated subjectively, which represents a potential weakness in the chemical prioritization process. Specifically, will the EPA recognize that, for some data, significant uncertainty may exist that is not captured within the SDM estimation process? For example, there is considerable variability among n-Octanol/Water Partition Coefficient (K_{ow}) values for many compounds of concern including polychlorinated biphenyl (PCB). This can result in significant differences in estimated human health or ecological risks (Linkov et al., 2005). Inherent data quality differences associated with HERs, bioactivity to exposure ratios (BER), and threshold of toxicological concern to exposure ratios (TER) should be fully described and explained within the SDM estimation process. Finally, the SAB suggests that sorption be included in the SDM.

The following recommendations are noted:

Tier 1

- The EPA should examine the data and information found within the IAM and SDM to identify the maximum concentrations of chemicals of concern in biosolids that are allowable if the material is to be land applied. Biosolids with concentrations of chemicals higher than the maximum allowable level would not be eligible for land application until the industrial source of the chemicals of concern had been identified and removed from the municipal waste stream. This was the process that was implemented for metals, and the pre-treatment programs have been very successful in removing metals as an issue of concern for land application. A stringent monitoring and reporting program would be needed for implementation and compliance of this new program. A peer review panel of expert stakeholders could then review EPA's findings.[1]

Tier 2

- The SAB recommends that all data required for prioritization in the IAM and SDM should be prioritized using a quantitative approach, when possible, for critical aspects of chemical categories and their predominant exposure pathways, prior to the evaluation of the chemicals.
- The SAB recommends that EPA provide a clear and unambiguous description of how the IAM and SDM data will be utilized in the prioritization process.

Tier 3

- The SAB recommends that a full-scale literature search for information on all 700 chemicals identified in biosolids be conducted and utilized in both the IAM and SDM.

2.1.2. Implementation consideration:

Are there additional steps EPA should consider for implementation during the prioritization process?

The EPA should examine the appropriateness and scientific relevance of the PICS process in the prioritization of the list of chemicals for screening-level risk assessment. The SAB applauds the EPA's acknowledgement of biases within the PICS process including the potential for testing and publication bias and the statement that "a lack of available data does not indicate a lack of toxicity." However, given the expectation of data gaps and/or other limitations in the PICS approach's fit-for-purpose, the SAB also anticipates the potential for chemicals being spuriously identified as high risk or low risk. Given the Agency's limited financial resources, the SAB is cognizant of the need for efficiency in identifying those chemicals of greatest public health and environmental concern from among the over 700 already identified in land applied biosolids. To achieve greater efficiency, the SAB recommends implementation of a more formalized evaluation step for generating outputs from the PICS process. This evaluation step would consider important process nuances such as:

- Eliminating outcomes identified as artifacts due to their inherent and known biases inadvertently captured by the PICS process. These artifacts generate improbable weighting

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[1] The SAB also acknowledges that a biosolid could have a chemical at concentrations that disallow land application without any comingling of sources; the EPA should also consider forwarding proposed solutions for this situation to expert stakeholders for peer review.

factors that are not germane to known biosolids exposure pathways and/or to the biosolids-soil matrix (examples previously described in 2.1.1).

- Modifying outcomes that identify human health and/or environmental risks associated with chemicals found in biosolids at concentrations that are well below the currently prevailing background levels (natural and anthropogenic) or substantially lower than levels of other, common exposure pathways. Potential examples include metals or metalloids with known occurrences of toxic geochemical background levels (Hettick et al., 2015; Kot, 2020), chemical concentrations that are on par with general dietary requirements, and/or chemicals at concentrations that are significantly lower than the intentional levels found in commercially available foodstuffs and/or other health, beauty, or personal care products. The SAB notes that currently prevailing background concentrations may attenuate over time as a result of measures that have been taken to address their anthropogenic release into the environment.

Other process nuances that could be relevant in chemical prioritization include the explicit parsing out of the chemical hazard to humans versus the ecological risks (see charge questions 2.2.1 for further discussion and recommendations).

Furthermore, the SAB encourages the EPA to provide additional clarity on how it intends to mitigate the potential elimination of those chemicals from the prioritization process for which published scientific literature may be sparse. The SAB fully recognizes that many high-risk, biosolids-associated chemicals may fall into this category, and a method to ensure their appropriate evaluation is needed. Moreover, chemicals that are known to have high toxicity and/or high exposure may be eliminated from the final list of those identified for risk evaluation if their scores were disadvantaged by the unweighted summing process employed by the SDM. While the draft framework explicitly states that the EPA "will begin by evaluating a set of chemicals from both the highest ranked chemicals by PICS for screening and a set of chemicals that were amongst the lower ranked chemicals," the SAB found that the scientific justification for this plan was vague and, therefore, wholly inadequate given the number of potential missteps that could ultimately undermine the credibility of reported outcomes. An additional, well-described, and transparent review and evaluation step would enhance the scientific credibility of the PICS process by reducing its inherent uncertainty. Ultimately, the decision framework may benefit from a geographic and state regulation component. For example, if a contaminate is only identified in a specific state and that state has regulations permitting applications resulting in concentrations higher than that identified by EPA as the level of concern, then the subsequent Risk Screening toward a Reasonable Maximum Exposure could be modified accordingly.

The SAB applauds the EPA's intention to improve future chemical prioritizations using the PICS process by identifying and implementing more conservative exposure parameters. The SAB supports establishment of a weighted (versus a summed) approach to rank chemicals within the SDM process. Establishing a scientifically defensible and transparent framework for developing and assigning weighting factors to specific chemical characteristics would advance this chemical ranking process objective.

The following recommendations are noted:

Tier 1

- The SAB recommends that the EPA develop an explicit and transparent evaluation step in the framework focused on the output from the PICS process. This modification would allow decision-makers to rapidly determine the scientific necessity of having to evaluate chemicals for

which there is known insignificant public health and/or ecological risk. This step creates an immediate and necessary off-ramp for spuriously identified chemicals and potentially strengthens the focus for understudied, yet potentially high-risk chemicals. Inclusion of this step also permits consideration of state-specific regulations and parameters important for efficient screening toward Reasonable Maximum Exposure.
- The SAB recommends that the EPA develop weighting factors for specific chemical characteristics to be employed in the PICS process. Specifically, assigning chemical weighting factors that consider the biosolids-soil matrix conditions would result in a more efficient prioritization process.

Tier 2
- The SAB has no specific recommendations for this tier.

Tier 3
- The SAB has no specific recommendations for this tier.

2.2. Deterministic Screening-level Risk Assessment

2.2.1. Selection process:

Does the SAB find the selection process for models within the BST to be appropriate for the exposure pathways for a screening-level risk assessment? If not, indicate why and provide recommendations for alternative model selection criteria.

EPA has developed a deterministic Biosolids Tool (BST) to evaluate if chemicals found in biosolids need a more refined risk assessment. To develop the BST, EPA found available, modifiable models to predict the exposure pathways, that could integrate with other models in the BST. The four major transport mechanisms of interest are: (1) air transport (dispersion and deposition of vapor phase and dust); (2) runoff and erosion to surface water; (3) leaching to groundwater; and (4) plant uptake. For chemicals that are deemed of potential concern, a more refined assessment will be conducted using a probabilistic modeling framework.

The SAB appreciates the clarity provided in the EPA's framework document (U.S. EPA, 2023) on the individual pathway model selection process. In general, the models selected are reasonable for a 'screening'-level risk assessment given the prevailing conceptual model, and the exposure pathways that need to be considered are appropriate. Some shortcomings were noted as summarized below. While there are many other models available that could have been evaluated, the process for selecting models is largely fit-for-purpose.

The models evaluated for use in the BST are largely single-media models for which the outputs are knitted together. EPA may want to consider exploring some of the many multimedia fate models that can estimate concentrations in particular media at a broader scale. Moreover, the scale at which risks to human receptors and ecological receptors are typically evaluated are often not the same. It is common practice for human health risk assessment to focus on evaluating (and protecting) individuals while ecological risk assessment often focuses on communities and populations. Given the latter, a larger-scale conceptual model for agricultural land application of biosolids may be more appropriate. If EPA were to evaluate potential ecological exposures and risks at a larger scale, the SAB suggests the Risk

Assessment IDentification and Ranking (RAIDAR) model (Arnot Research & Consulting, n.d.)[2] as a potential tool.

Aspects of the models that were lacking included algorithms that address: 1) pH-impacted availability and transport that are relevant for ionizable organic chemicals and speciation of inorganic compounds, which greatly impacts bioavailability-related parameters; and 2) air-water interfacial sorption, which is known to substantially retard PFAS transport in the vadose zone (Constanza et al., 2019; Brusseau and Guo, 2023). For the ionizability issue, the User Guide notes the limitation of ionizable compounds with a focus on organic compounds and indicates the need to conduct separate runs with updated parameters specific to the conditions of interest. However, this alone may not suffice when attempting to apply an organic carbon (OC)-normalized sorption coefficient (K_{oc}) concept when OC is not the driver, e.g., organic cation sorption, transport, and bioavailability can be controlled by the soil cation exchange capacity rather than OC (Sigmund et al., 2022). In most cases, assuming OC as the driver when it is not will overpredict transport and bio-uptake. In the case of some metals such as aluminum, failure to consider the role of soil pH will lead to over-predicting Al transport and adverse impacts on crops, etc.

Artificial drainage enhancements of agricultural fields are not accounted for in any models despite their prevalence, especially in the US Midwest (USDA, 2019). Subsurface, tile drainage involves placement of a perforated tile approximately 1-m below the soil surface to improve field drainage, thus reducing runoff, but allowing for direct transport from immediately below the rooting zone to streams. Therefore, the role of runoff in these cases will be overpredicted, thus impacting exposure estimates of more highly retained compounds of interest, but possibly underestimating the impact to streams of more mobile/soluble chemicals. For addressing tile-drain networks, it could be plausible to use the Multimedia, Multi-Pathway, Multi-Receptor Exposure and Risk Assessment (3MRA) to 1 meter (vs 2 m) and then direct discharge to stream coupled with the Variable Volume Water Model versus the dilution-attenuation factor (DAF).

The EPA clarified during the peer review public meetings that biotransformation is considered in the BST transport modeling within the top 2-m of soil; this point may need clarification in the User Guide. However, as pointed out in the User Guide, the risk evaluation does not include the transformation products (U.S. EPA, 2023a). The latter must be dealt with in individual model simulations with the addition of a new chemical, which is reasonable given the complexities of trying to simultaneously address the variety of degradation products that may occur on the way to mineralization.

EPA also noted a need to consider the IAM/human health concern bias (i.e., chemicals for which there is already a greater volume of available information and therefore a higher IAM tend to have a higher health and/or environmental impact concern (U.S. EPA, 2023)) specifically for chemicals found in biosolids and the potential that data availability, or lack thereof, may bias the deterministic/screening level analysis. It is not clear how this bias will be addressed in the process to ensure that a chemical is not inappropriately listed.

The following recommendations are noted:

Tier 1

- The SAB strongly recommends that the evaluation of the BST include corroboration, sensitivity analysis, and uncertainty analysis for a given chemical run consistent with EPA guidance (U.S. EPA, 2009). While EPA did conduct a Validation and Sensitivity Analyses of the model inputs

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[2] American Chemistry Council has provided funding to support Arnot Research and Consulting to further develop the RAIDAR model and other models through the ACC Long-Range Research Initiative.

(Appendix E of the Biosolids Tool (BST) User's Guide, U.S. EPA, 2023a), there is no step proposed to do a reality check for a chemical-specific output.

- Prior to the time-intensive probabilistic modeling, the SAB recommends that EPA conduct additional confirmatory evaluation of chemicals for which the BST estimates excess risk, such as reevaluating "background" levels, reviewing literature regarding key variables such as bioaccumulation or bioconcentration factors and/or data regarding the presence of the chemical in various exposure media/foodstuffs or ecological receptors. This would serve as a good "reality" cross-check of model results. Also, this may aid in addressing concerns regarding how significantly the IAM influences the results of the deterministic/screening level analysis. It was noted that the chemicals with a higher IAM tend to have a higher health/environmental impact concern specifically for chemicals found in biosolids.
- Likewise, many chemicals at concentrations found in biosolids could only be a risk concern to ecological receptors (e.g., aquatic communities) and not human health, which includes pharmaceuticals and other chemicals intentionally integrated into food and consumer products. Therefore, the SAB recommends reviewing concentrations acceptable to humans on this basis.
- For chemicals deemed a potential concern through the deterministic screening level assessment using the BST, the SAB recommends that EPA consider literature and/or a measurement approach to evaluate the chemical bioavailability specifically in relation to the biosolids matrix before deciding if the chemical needs to move forward to the refined risk assessment.

Tier 2

- The role of pH on chemical fate is not explicitly considered in the current models, which is acknowledged indirectly in noting the limitations for ionizable compounds. However, the SAB notes this may not be sufficient and urges EPA to consider how this may be best addressed.
- While the role of air-water interfacial sorption may not impact most of the chemicals on the list to be evaluated, PFAS transport to groundwater is known to be greatly impacted by this process in the vadose zone. Given the significance of PFAS in the current regulatory framework, the SAB urges EPA to consider how to address this transport process.

Tier 3

- EPA may want to consider exploring some of the many multimedia fate models that are able to estimate concentrations in particular media at a broader scale, particularly regarding ecological community effects.
- EPA should ensure clarity for what is and is not stated in the User Guide concerning biotransformation, hydrolysis, and sorption are considered in the model. This would benefit the public who directly requested the information during the peer review process.

2.2.2. BST receptors:

Are the receptors contained in the BST appropriate for a screening-level risk assessment for 1) human health and 2) aquatic and terrestrial wildlife? If not, please indicate why and provide recommendations for alternatives.

The use of the subsistence farm family for the crop and pasture scenarios generally represents an upper bound/high-end setting, receptor, and exposure scenario. Conceptually, the SAB consensus is that this is sensible for a screening step, assuming the purpose of this step is to simply "screen in" or "screen out" constituents and pathways to be carried forward in a more robust, probabilistic (to the extent feasible), refined risk assessment. However, as described in more detail below, it may be useful to consider modifications to the use of such a large number of exposure pathways/routes and upper bound exposure assumptions for some of the key variables such that a "compounding conservatism" with respect to the exposure setting and the intensity of exposures does not result in a "maximally exposed individual" (MEI) versus a reasonable maximum exposure (RME). It is current practice and recommended per EPA guidance for risk assessment (U.S. EPA, 1989), that an RME receptor should be used, combining both average and upper-bound values for various exposure parameters, to simulate an upper-bound exposure that could "reasonably be expected to occur." Because of the intertwined nature of the receptor scenarios selected, and the exposure pathways and assumptions, some of the comments presented below overlap with and are reiterated in the responses to charge questions 2.2.3. and 2.2.5.

The two land application scenarios, i.e., the "crop" and "pasture" scenarios, involve the greatest number of pathways and assumptions, and represent a very common, beneficial use for biosolids and hence are the focus of many of the SAB comments here and below in the related Charge Questions 2.2.3. and 2.2.5. The SAB finds the receptors, pathways, and settings for the other two scenarios included in the BST (reclamation and sewage sludge landfills) are generally appropriate and representative with one exception noted (below). In addition, the ecological receptors used in the BST are reasonable and appropriate, representing typical indicator species for various trophic levels and habitats. One SAB panelist expressed concern that it appeared EPA was seeking to protect organisms in individual family farm ponds and suggested that it may be more appropriate to look instead at ecological receptors on a population and/or community level at a greater scale (e.g., watershed scale, regional scale (U.S. EPA 1998 and 2003). This issue is further addressed in charge question 2.2.5. However, the approach taken for the specific receptor selection for the ecological screening does not appear inconsistent with the EPA guidelines for ecological risk assessment.

According to information available from the U.S. Department of Agriculture (USDA) (USDA, 2019) and similar sources such as the American Farm Bureau Federation (American Farm Bureau Foundation, 2021), it appears that (roughly) less than 2% of the U.S. population is comprised of farm and ranch families. Of that, only about 3% grow crops for human consumption, while the remaining families raise livestock for meat and/or dairy or to grow feedstock for animals or ethanol production. Also of note, less than 1% of all agricultural land receives biosolids (U.S. EPA, 2003) and almost none of that land is used for human consumption crops. For those farms growing crops, only a portion of them is used for subsistence agriculture, which is more prevalent on smaller, "family" type farms. It is reasonable that, due to the inferred rural nature of farmland areas, the farm family may rely on a private water supply well for potable water use including ingestion, showering, etc. The setting used in the BST, however, assumes that the surface water body "farm pond" receives runoff of the biosolids into pond water and sediment (which may be reduced/mitigated by biosolid land application and soil conservation requirements in some areas) and then assumes uptake into fish/shellfish upon which the farm family is assumed to rely for all of their fish intake[3]. The combination of all these factors for this population may lead to a characterization of potential risks above and beyond an RME, which is the intent of the EPA deterministic risk assessment process.

Also, we note that the farm family (adult and child) may not represent a reasonable maximum exposure to chemicals in biosolids with respect to fish consumption if a regional watershed was evaluated. As discussed later in sections 2.2.3 and 2.2.5, EPA should consider providing additional information regarding the potential for regional watershed exposures to the freshwater recreational angler and/or the Native American freshwater subsistence fishing receptors.

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[3] This seems to be somewhat in conflict with the fishing scenario described on page 39 of the Framework which indicates that the farm pond is assumed to be used for "recreational fishing".

There was substantial discussion by the SAB regarding the expected low probability of the same individuals in a "family farm" simultaneously experiencing all possible exposure pathways. The BST has the same receptors not only doing all land management practices (i.e., application/tilling of biosolids and associated planting/harvesting) with the associated inhalation and incidental ingestion exposures, but also incurring additional exposures from soil via field runoff, from relying on their total annual consumption of meat, dairy, crops and fish exclusively from the farm property, and from drinking and showering in impacted water from a private well. The farmer exposure scenario recommended by EPA (U.S. EPA, 2005) has several differences from the scenario used in the BST, some of which could support a protective but more realistic evaluation of exposures and risks from application of biosolids. Specifically, the default exposure pathways listed in this 2005 document do not include the ingestion of fish for the farmer exposure scenario. Furthermore, the consumption rates used for relevant ingestion pathways (such as ingestion of homegrown beef and milk or ingestion of homegrown produce) do not assume 100% is derived from the farm, but rather, only a portion of the farmer's diet. A related discussion point concerned the need to differentiate among individuals who provide and apply biosolids versus those who work in croplands or pastures and rely on that for an income stream versus those who may reside on essentially subsistence farms. Some of these workers may also have Occupational Safety and Health Administration regulations that apply. The SAB recommends that EPA consider two separate and distinct risk assessments: one for the farm family and, if deemed necessary, one for dedicated workers (e.g., contract applicators) who may have occupational exposures to chemicals in biosolids.

The same concern regarding bundling of multiple pathways applies to the farm family for the pasture scenario, except that the consumption of all meat and milk is derived from the farm instead of the crops. Both of these land application scenarios and receptors are assumed to engage in all of these activities, behaviors, and uses at or on the same farm property year after year, for a period of 61 years (13 years as a child and 48 as an adult). The vast majority of exposure parameters used for these subsistence scenarios were "upper bound," typically at or above the 90th percentile of the distributions described in the Exposure Factors Handbook (U.S. EPA, 2011). These specific parameters are discussed in more detail in Charge Question 2.2.3, below. Therefore, to ensure that the receptor scenarios remain protective but plausible, the SAB recommends that the EPA consider re-evaluating the current combination of conservative receptors/exposure scenarios/routes in the context of both the typical workflows, activities, and methods for the applicators of biosolids as well as the farmers who own/reside on both croplands and pastures. The logic for the selected receptor scenarios/pathways/routes could be described more robustly and be used to support the Conceptual Site Model. The basis for this recommendation is the potential for compounding conservatism beyond the RME and recent data from the USDA and other sources regarding US farm demographics and the use of biosolids.

Concerning the sewage sludge disposal scenario, it seems as if the abutter receptor scenario/pathways evaluated (inhalation of air, use of groundwater for private potable well, and inhalation of shower air) are more consistent with a "Local Child/Adult Resident" who may be living in proximity to the sewage sludge landfill, versus the current nomenclature of "Child/Adult Farmer." This receptor name change suggestion would likely also be perceived as more generically representative of residents who may live proximate to such sludge disposal landfills.

Another approach which may help maintain an RME (versus an "MEI") assessment and output for the screening tool would be to consider using the midpoint of the EPA target risk range (i.e., 1×10^{-5}) versus 1×10^{-6}. This could help counter the potential for an overestimation bias through the use of these settings and scenarios. For comparison, the EPA has used 1 x 10^{-6} as a “point of departure” for calculation of risk-based cleanup levels at Comprehensive Environmental Response, Compensation, and Liability Act Sites and has permitted the use of alternative target risk limits in certain settings or to take potential population impacts into account. For example, in the original development of Standards for the Use or Disposal of Sewage Sludge (40 CFR part 503), EPA used a risk target of 1 x 10^{-4}, largely because the aggregate risk assessment found little risk from biosolids even in the absence of regulation (U.S. EPA, 1993).

Lastly, the SAB recommends that EPA incorporate a model evaluation step of the BST consistent with EPA guidance (U.S. EPA, 2009). While EPA conducted some sensitivity and uncertainty analyses, a *model corroboration* for “evaluating the degree to which [the BST] corresponds to reality”, should also be conducted. For example, in cases where the model exposure results indicate the potential for significant risk for an analyte based on the screening scenarios, an assessment of consistency with existing observational data should be done. As noted previously in response to charge questions 2.1.2 and 2.2.1, additional factors that may warrant consideration may include typical “background” levels of the analyte, and a review of literature documenting levels of the analyte in environmental media, ecological receptors and/or food items, etc.

The following recommendations are noted:

Tier 1

- The SAB recommends that the current receptor/exposure pathways/routes for the Land Applications Scenarios be reviewed and modified as appropriate to confirm consistency with an RME evaluation and additional information be provided to support the Conceptual Site Model in the Framework document.
- The SAB recommends that the evaluation of the BST include corroboration, sensitivity analysis, and uncertainty analysis consistent with EPA guidance (U.S. EPA, 2009). The SAB recommends that EPA conduct an additional confirmatory evaluation of chemicals for which the BST estimates excess risk, such as evaluating “background” levels, reviewing literature regarding key variables such as bioaccumulation or bioconcentration factors and/or data regarding the presence of the chemical in various exposure media/foodstuffs or ecological receptors. This could be a good “reality” cross-check of model results.

Tier 2

- The abutter receptor and exposure setting evaluated for the sewage sludge disposal scenario is more consistent with a “child/adult local resident” versus a “child/adult farmer.” The pathways evaluated for this abutting receptor are appropriately limited to airborne exposures and potable water use exposures, including ingestion of tap water and inhalation of shower air. Accordingly, the SAB recommends revising the nomenclature for this receptor.
- The SAB recommends that EPA consider occupational exposures to chemicals in biosolids for dedicated workers who may be responsible for their application.

Tier 3

- The SAB has no specific recommendations for this tier.

2.2.3. Screening parameters:

Several screening parameters are set to health-protective, high-end values (e.g., concentration of chemical in biosolids, drinking water ingestion rates), but others are set near the central *tendency for that parameter (e.g., bioaccumulation factor). Does the SAB agree that these metrics generate reasonable high-end exposure estimates appropriate for screening for 1) human health and 2) aquatic and terrestrial wildlife? If not, please indicate why and provide recommendations for alternatives.*

The SAB finds that the compounded conservatism resulting from the selection of the screening level parameters may result in exposure estimates that are greater than the RME. Moreover, the approach for selecting whether a central tendency or high-end value is used appears arbitrary. While the overall approach may be linked to how the EPA's Office of Water intends to interpret "…any reasonably anticipated adverse effects…" (U.S. EPA, 2023), the rationale is not transparent. A consistent approach for selecting central tendency or high-end values should be articulated and applied. In addition, what constitutes "high-end" should also be clearly articulated and consistently applied.

The SAB recommends that EPA conduct a sensitivity analysis of human exposure factors and other parameters (such as Bioaccumulation factors (BAFs) and Bioconcentration factors (BCFs)) used in the BST so that it is understood how variability in the parameters may affect results from simulations, as well as which parameters exert the greatest influence on the model results so that these parameters can be considered carefully.

The SAB finds that the farm pond and agricultural field are not appropriate ecosystems for the ecological risk assessment. The SAB recommends that EPA reconsider its problem formulation for the ecological risk assessment of land applied biosolids consistent with the Guidelines for Ecological Risk Assessment (U.S. EPA, 1998). For the ecosystem of concern or other ecological entities, it is necessary to identify attributes that are important to protect. For ecological receptors, the general practice of environmental risk assessment focuses on populations and communities. Therefore, a reasonable high-end exposure estimate should not be overly conservative. That is, the environmental exposure level should estimate conditions that might occur at a reasonable high-end across ecosystems of concern such that they are ecologically relevant for the appropriate ecological endpoint.

Several specific examples where overly conservative assumptions may lead to unreasonably high screening level exposure estimates are discussed below.

1. **Subsistence Farming Family:** A subsistence farming family is an extremely small subset of the general U.S. population and even the U.S. farming population. As such, using high-end values for parameters in exposure modeling will result in overly conservative estimates. The SAB recommends central tendency parameters (e.g., concentration of chemicals in biosolids, drinking water ingestion rates) be used for the exposure scenarios associated with a subsistence farm family.

2. **Fish Consumption:**
    a. Adult Farmer: The consumption rate for the adult farmer is listed in the BST as 22 g WW/day which is the 90th percentile consumption at the 95% confidence interval for fresh and estuarine finfish and shellfish (raw weight) by consumers (based on U.S. EPA, 2014, Table E-7). However, the Users' Guide (Appendix A, Attachment A.1.6) states that the equations used to calculate the concentration in fish filet considers trophic levels 3 and 4 only (which have higher bioconcentration factors relative to lower trophic levels). The combined 90th percentile for fish consumption of trophic levels 3 and 4 fish is 13.7 g/day (see U.S. EPA, 2014 Tables 17 and 18). Furthermore, the use of 90th percentile

consumption rates at the 95% confidence interval for a scenario where a small farm pond is used for "recreational" purposes is overly conservative. Also, the generalization of higher BCFs (or BAFs) for trophic levels 3 and 4 fish may not apply to all contaminants. For example, the BCFs for PFAS (which are not lipophilic, but rather accumulate in fish through binding to proteins) may be higher in some lower trophic level fish than in higher trophic levels (Munoz et al., 2022).

   b. Recreational Freshwater Anglers and Native American Fishers: The "family farm" scenario may not represent a reasonable high-end exposure estimate for fish consumption. EPA may want to consider a high fish consumption scenario separate from the family farm model such as a recreational freshwater angler or a Native American subsistence freshwater fisher, especially in relation to Executive Orders 13985 (86 FR 7009) and 14008 (86 FR 7619) regarding equity for underserved communities and communities with environmental justice concerns. The 2014 Fish Consumption Report (U.S. EPA, 2014) does not appear to include recreational freshwater anglers or Native American fishers among its subpopulations for usual fish consumption rates. However, the EPA Exposure Factors Handbook (U.S. EPA, 2011) has summaries of relevant studies for Freshwater Recreational Fish Intake (Table 10-5) and Native American Fish Intake (Table 10-6). Additionally, EPA may want to consider how its target analytes for fish advisories (U.S. EPA, 2000) compare to those chemicals detected in the Targeted National Sewage Sludge Survey (TNSSS).

3. **Residential mobility:** Regarding residential mobility (and associated tenure for living in the same home), the BST assumes a total duration for a child and adult farmer is 61 years (13 years for children and 48 years for adults). Focusing on adult tenure, the Exposure Factors Handbook (U.S. EPA, 2011) indicates that the tenth percentile for mobility for farmers is 48 years. The 25th percentile for adult farmer mobility is much lower, or 26.7 years, which is close to the 10th percentile mobility for the more general "owners" population (32 years). The median length of home ownership is roughly 15 years. When looking at residential occupancy periods for the U.S. population (U.S. EPA, 2011, Table 16-108), the 90th percentile rate for "living in the same home" is 26 years, the 95th is 33 years, the 99th is 47 years and the 99.9th is 59 years (this is for total combined, regardless of age). It may be useful to consider these residential tenure durations as they relate to the assumptions in the BST.

4. **Air pathway:** It appears that a 24-hour per day exposure duration (350 days per year) is assumed for the (outdoor) dust and/or vapor inhalation pathway. Since no traditional volatile organic compounds (VOCs) were included among the BST example chemicals, it is difficult to evaluate the appropriateness of these parameters. One would expect that the off-gassing of VOCs that may be present in biosolids would persist for only a few days following application. Concerning fugitive dust/particulate exposures, although they are likely elevated during the application of biosolids and tilling, that same level of airborne particulate would not persist throughout the exposure period. Once the biosolids are applied, the potential for airborne emission of VOCs decreases over time. In addition, moisture and crop growth would further reduce the potential emission of VOCs and their inhalation.

5. **Beef and milk consumption**: The results from BST using defaults for the pasture scenario for Benzo[a]pyrene (B[a]P) indicated an unusually high level of risk. For a farm child, consumption of milk and beef associated with the default biosolids concentration of 2.19 ppm B[a]P resulted in risk estimates of 1.1×10^{-3} and 5.1×10^{-4}, respectively, for the cancer endpoint and a non-

cancer hazard index of 27 and 83, respectively. A soil concentration of 2.19 ppm B[a]P is generally consistent with an anthropogenic background in soils in the United States, such as those reported in a large study of both "natural" and "fill" soils in Massachusetts (MassDEP, 2002). These estimated risks seem very high and potentially could imply that background levels of select chemicals are posing an unacceptable risk to certain populations or, potentially, general consumers even without biosolids application. These elevated risks appear to be largely associated with the BAFs used for estimating exposure concentrations in beef and milk. The SAB recommends that EPA conduct a more in-depth evaluation of the assumptions and equations used to evaluate these two pathways, in particular, the approach used to estimate or calculate BAFs. The EPA Office of Water has issued recent documents regarding the development of "National" BAFs and BCFs (U.S. EPA, 2016), and there is also a plethora of literature regarding field measurements of BCFs and BAFs for many of the chemicals that have been identified in biosolids. Accordingly, it is recommended that a clearer explanation of the approach used to develop the BAFs and BCFs integrated into the BST equations be provided and that an emphasis be placed on using the most up-to-date literature and/or recommended methods to derive these values.

6. **Human exposure factors**: EPA should consider including both inhalation rate and dermal exposure factors among the human exposure factors included in the BST (see page 36, U.S. EPA, 2023).

The following recommendations are noted:

Tier 1

- The SAB recommends central tendency parameters should be applied when evaluating the example *subsistence farm family* including concentration of chemicals in biosolids, drinking water ingestion rates and tenure on a farm.
- The SAB recommends EPA review the data regarding fish consumption rates for an adult farmer to confirm the correct values are used corresponding with trophic level 3 and 4 fish consumption.
- The SAB recommends that EPA provide clarification on the approach used to develop BAFs and BCFs used in the BST equations and that empirical measurements and/or the most up-to-date approaches for estimation/modeling are used for these parameters.
- For common, ubiquitous contaminants (e.g., benzo(a)pyrene), the SAB recommends EPA consider how high-end assumptions compare to background concentrations and whether risk results from such a simulation reflect our current understanding of those contaminants.
- The SAB recommends EPA use inhalation rate and dermal exposure factors among the human exposure factors included in the BST.
- The SAB finds that the farm pond and agricultural field are not appropriate ecosystems for the ecological risk assessment. The SAB recommends that EPA reconsider its problem formulation for the ecological risk assessment of land-applied biosolids consistent with the Guidelines for Ecological Risk Assessment (U.S. EPA, 1998).
- The SAB recommends that site-specific, high-end values *not* be used in the ecological exposure assessment. The SAB recommends screening parameters for ecological exposure and risk assessment represent values that are more consistent across a broader geographic range than the family farm though they could be at the high-end of the distribution for that broad geographic area.
- The SAB recommends EPA review all the parameters used to configure the BST and cite in detail the source of the information. For example:

  - In the BST, under "Configure Model," in the "Inputs" tab and "Human Exposure" subtab, adult body weight is listed as 79 kg and EPA's 2011 Exposure Factors Handbook is cited. However, Table 8-1 lists the Recommended Values for Body Weight for Adults as 80.0 kg. If the BST is using data from a different source, that source should be cited.
  - In the BST, under "Configure Model," in the "Inputs" tab and "Chemicals" subtab, Reference body weight (bird) [Ref_BW_Bird] is listed as 191 kg (clearly an error).

Tier 2

- The SAB recommends EPA consider using the adult farmer fish consumption exposure scenario for fish consumption of trophic levels 3 and 4 fish at a central tendency consumption rate (e.g., 50th percentile consumption rate).
- The SAB recommends EPA evaluate the appropriateness of the 24-hour per day exposure duration (350 days per year) for the (outdoor) dust and/or vapor inhalation pathway.

Tier 3

- The SAB recommends EPA study the appropriateness of a high fish consumption scenario separate from the family farm model such as for a recreational freshwater angler or a Native American subsistence freshwater fisher.
- The SAB recommends that EPA study the alignment between the list of chemicals detected in the TNSSS and the list of target analytes for fish advisories (U.S. EPA, 2000).

2.2.4. Geographic exposure:

EPA proposes to evaluate three locations that have different meteorological characteristics (wet, median, dry). Are these three geographic exposure scenarios appropriate for this screening-level risk assessments? If not, please provide recommendations for an alternative set of locations and a rationale for selecting the locations.

The three representative locations selected by EPA are Charleston, South Carolina (Wet), Chicago, Illinois (Average), and Boulder, Colorado (Dry). The average annual precipitation for each location is 48, 37, and 21 inches respectively. These different meteorological characteristics only impact atmospheric transport and leaching to groundwater. Subsurface properties for each site were modeled probabilistically based on their hydrogeological properties as follow: Charleston (coastal beaches), Chicago (limestone), and Boulder (bedded sedimentary rocks). Based on the sensitivity analysis conducted for each site, climate was a relatively insensitive parameter. The results were impacted most by chemical and pathway selections rather than the climatic conditions. For example, the Boulder site had significantly greater DAF values or a reduction in chemical concentration at the well site when compared to the Chicago and Charleston sites. For the crop and pasture scenarios, the air pathway was the most sensitive. However, the reclamation scenario appeared the most impacted by climate with 4-Chloroaniline yielding results of 1×10^{-7} for the dry climate (Boulder) versus 1×10^{-3} for the average climate (Chicago) condition.

The SAB initially discussed the possibility of replacing Chicago with Kansas City, Missouri to represent the average condition. However, subsequent research has found Kansas City to have only marginally less rainfall than Chicago. The SAB instead recommends replacing Chicago with Omaha, Nebraska. Omaha has an annual average precipitation volume of roughly 30 inches, which is the national average for the Continental United States. Omaha has similar hydrogeological properties (Miller, 1964) as Chicago (Bretz, 1955) with limestone being the dominant parent soil material. Both features support recommending this change. There had been discussion of selecting an alternative site to represent the dry condition at a location where irrigation is the norm. However, the SAB concluded that this could be dealt with better and in greater detail in the refined risk assessment. The SAB also agrees with the EPA recommendation to utilize 41 climatic regions in the probabilistic refined risk assessment.

With respect to the overall impacts of precipitation on runoff and erosion, it was very difficult to parse out how such information was utilized in the model. Moreover, a description of chemical transport in the vadose zone is lacking. Since the intent is to make this model transparent and user-friendly, it is recommended that more explicit information be provided on how climate and soil type are utilized in the model formulations. It is not clear if runoff and erosion were considered in the BST or the probabilistic comparison of the three locations. This appears to be critical information based on rainfall and rainfall intensity. Short duration/intense storms would likely cause more runoff but how these parameters are considered is not clear.

The following recommendations are noted:

Tier 1

- The SAB recommends that EPA replace Chicago with Omaha as the average meteorological location in the BST assessment as Omaha is much closer to the national average for annual precipitation than Chicago.
- The SAB recommends that EPA provide a clear explanation of how the different meteorological locations are evaluated in the BST. This should include impacts from rainfall frequency, duration, and intensity as well as how the different soil types impact results.

Tier 2

- The SAB does not offer a recommendation in this tier.

Tier 3

- The SAB does not offer a recommendation in this tier.

2.2.5. Exposure pathways:

EPA has developed four scenarios for the screening-level risk assessment, including specific pathways. Are the pathways for exposure simulated in the BST appropriate for a national screening-level risk assessment? If not, provide recommendations on pathways of exposure EPA should consider for the screening-level risk assessment.

The four scenarios for the screening-level risk assessment of land-applied biosolids available in the BST described in Section 6.4 of the Standardized Framework for Sewage Sludge Chemical Risk Assessment are:

1. Agricultural land application – crop
2. Agricultural land application – pasture
3. Land reclamation
4. Disposal in a surface impoundment or lagoon

The four scenarios for the screening-level risk assessment of land-applied biosolids are appropriate for assessing human exposures as they represent potential high emissions to the environment and exposures to individual human receptors. However, the SAB finds that the current approach may not be sufficient as a national screening-level human health risk assessment. Several specific examples of enhancements to the existing human exposure scenarios or additional scenarios to complement the BST are discussed below.

1. **Dermal Exposure:** For those pathways where there is human contact with contaminated media (soil, groundwater, surface water), dermal exposures should be evaluated. It appears those pathways might include Pathways 3, 12 & 15 of the conceptual model of human exposure (see Figure 5, U.S. EPA, 2023).

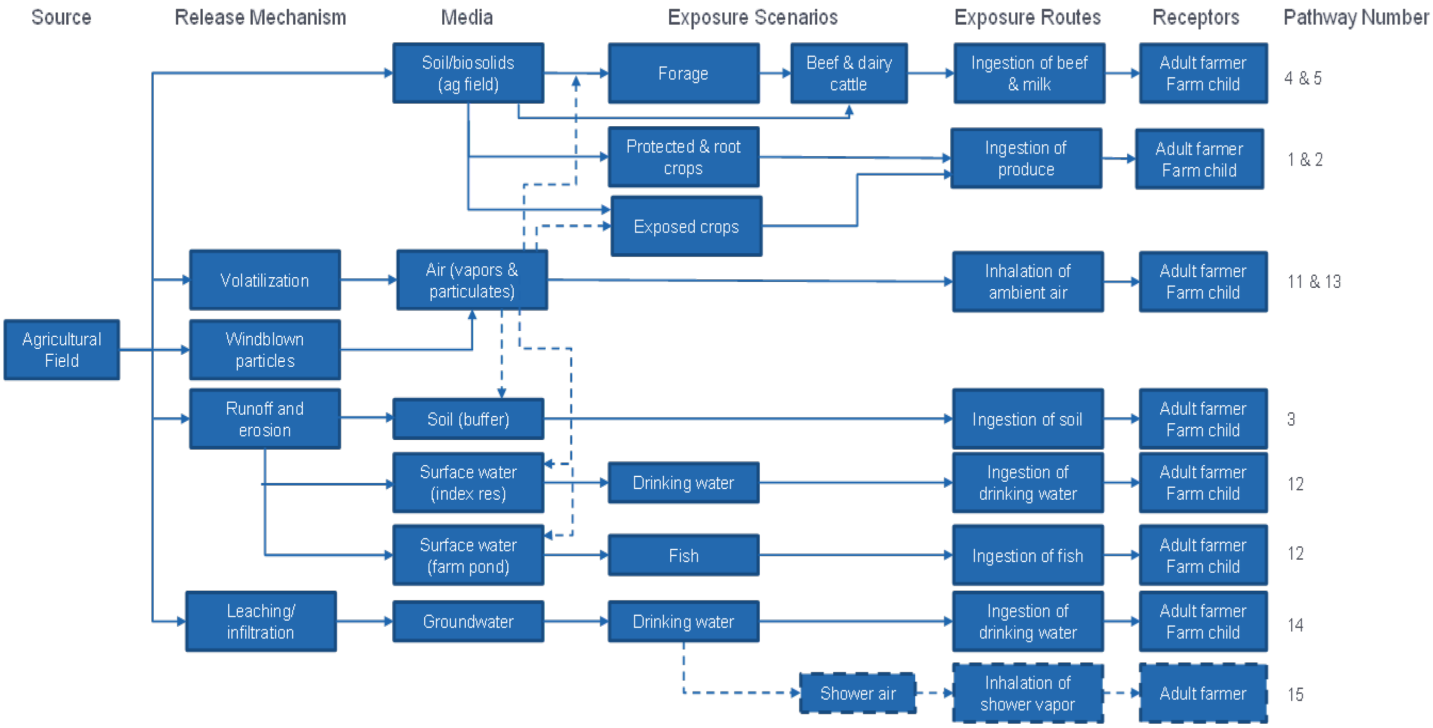

Figure 5. Conceptual model for the agricultural land application scenario and land reclamation scenario for human exposures. Dashed arrows and box outlines indicate a pathway or route that has been added since 1993 (when risk assessments that supported the Part 503 rule were completed) (U.S. EPA, 2023).

Many of the chemicals regulated under 40 CFR part 503 are metals that could present a dermal exposure opportunity through direct transfer to the skin. Studies have measured the potential for the dermal transfer from a source directly to the skin for arsenic (Hemond and Solo-Gabriele, 2004; Barraj et al., 2007; Gorman et al., 2011), iron (Avissar et al., 2004), zinc (Hughson and Cherrie, 2005), beryllium (Day et al., 2007), nickel (Lidén et al., 2008; Hughson et al., 2010; Gorman et al., 2011), cobalt (Klasson et al., 2017; Kettelarij et al., 2018 and 2018a), chromium (Lidén et al., 2008; Day et al., 2009; Julander et al., 2010; Gorman et al., 2011), lead (Enander et al., 2004; Sahmel et al., 2021, 2022) and cadmium (Gorman et al., 2011). Based on recent research, such metals or other substances may also be able to transfer to other surfaces such as general and/or personal protective equipment, and then present a dermal exposure opportunity even if there is no direct skin contact with the biosolids (Sahmel et al., 2021; Christopher et al., 2007).

Additionally, a number of the other chemical classes related to biosolids (anions, metals, polycyclic aromatic hydrocarbons, semi-volatiles, flame retardants, pharmaceuticals; see page 24, U.S. EPA, 2023) have quantitative dermal transfer data in the published literature (Vaananen et al., 2005; Api et al., 2007; Fransman et al., 2007; Henriks-Eckerman et al., 2007; Boeniger et al., 2008; Stapleton et al., 2008; Watkins et al., 2011; Keller et al., 2014; Fent et al., 2017).

It should be noted that the transfer and adherence to the skin of both soils generally and pesticides have also been measured (Holmes et al., 1999; Lu et al., 2000; Shoaf et al., 2005; Choate et al., 2006; Yamamoto et al., 2006; Aprea et al., 2009; Gorman et al., 2011). We also note that studies quantifying these values have different methodologies (e.g., mechanistic studies of soil ingestion e.g., by quantifying finger to mouth frequency, size of finger in mouth *etc.* versus by measuring soil tracers in diapers on toddlers) and the different methodologies can yield different results.

2. **Fish Consumption**: As noted above (Charge Question 2.2.3), the "family farm" scenario may not represent a reasonable high-end exposure estimate for fish consumption. EPA may want to consider a high fish consumption scenario separate from the family farm model such as a recreational freshwater angler or a Native American subsistence freshwater fisher, especially in relation to Executive Orders 13985 (2021) and 14008 (2021) regarding equity for underserved communities and communities with environmental justice concerns The 2014 Fish Consumption Report (U.S. EPA, 2014) does not appear to include recreational freshwater anglers or Native American fishers among its subpopulations for usual fish consumption rates. However, the EPA Exposure Factors Handbook (U.S. EPA, 2011) has summaries of relevant studies for Freshwater Recreational Fish Intake (Table 10-5) and Native American Fish Intake (Table 10-6). Additionally, EPA may want to consider how its target analytes for fish advisories (U.S. EPA, 2000) compare to those chemicals detected in the TNSSS.

3. **Family Farm**: The BST conceptual model assumes a 2.5-acre farm pond is immediately adjacent to the field where the farm family fish and where all aquatic ecological exposures occur (see page A-1, U.S. EPA 2023a). The Guide states that the farm pond would not in most cases be considered a "water of the United States" under the Clean Water Act (see 40 CFR 230.3(t)(5)(ii), which specifically states that "Artificial lakes or ponds created by excavating and/or diking dry land and used exclusively for such purposes as stock watering, irrigation, settling basins, or rice growing" are not "waters of the United States."). Therefore, no buffer is modeled for the farm pond. Notwithstanding this policy position, the SAB finds this assumption to be overly conservative and recommends that a 10-meter buffer be included between the farm pond and agricultural field receiving biosolids.

The four scenarios and associated ecological exposure pathways simulated in the BST *are not* appropriate for a national screening-level ecological risk assessment. The SAB finds that the farm pond and agricultural field are not appropriate ecosystems for the ecological risk assessment. The SAB recommends that EPA reconsider its problem formulation for the ecological risk assessment of land applied biosolids consistent with the Guidelines for Ecological Risk Assessment (U.S. EPA, 1998 and U.S. EPA, 2003a). For the ecosystem of concern or other ecological entities, it is necessary to identify attributes that are important to protect. For ecological receptors, the general practice of environmental risk assessment focuses on populations and communities at a scale greater than an individual (family farm) pond. Therefore, a reasonable high-end exposure estimate should not be overly conservative. That is, the environmental exposure level should estimate conditions that might occur at a reasonable high-end across ecosystems of concern such that they are ecologically relevant for the appropriate ecological endpoint (e.g., watershed scale, regional scale, national scale). Land application and surface disposal are appropriate uses of biosolids that should be evaluated but not at the scale of an individual family farm.

The BST is designed as a series of single media models the output of which are knitted together. The SAB notes that multimedia fate models estimate chemical concentrations in several environmental media simultaneously and at a broad scale. The SAB recommends that a larger-scale conceptual model for agricultural land application of biosolids be utilized. The SAB recommends that EPA evaluate the PROduction-To-EXposure framework as a potential tool for evaluating the multimedia fate of chemicals found in biosolids that are land-applied (Li et al., 2021).

The following recommendations are noted:

Tier 1

- The SAB recommends that EPA enhance the existing human exposure scenarios by including dermal exposure screening where appropriate.
- The SAB finds that the farm pond and agricultural field are not appropriate ecosystems for the ecological risk assessment.
    - The SAB recommends that EPA reconsider its problem formulation for the ecological risk assessment of land-applied biosolids consistent with the Guidelines for Ecological Risk Assessment (U.S. EPA, 1998).
    - The SAB recommends that EPA revise the scenarios and pathways for the screening-level ecological risk assessment such that they reflect an appropriate scale at which population or community-level effects may be observed.
- The SAB recommends that EPA update the family farm scenario to include a 10-meter buffer between the farm pond and the agricultural field receiving biosolids.

Tier 2

- The SAB does not offer a recommendation in this tier.

Tier 3

- The SAB recommends that EPA explore the use of multimedia fate models for the screening-level ecological risk assessment.
- The SAB recommends EPA study the appropriateness of a high fish consumption scenario separate from the family farm model such as a recreational freshwater angler or a Native American subsistence freshwater fisher.
- The SAB recommends that EPA study the alignment between the list of chemicals detected in the TNSSS and the list of target analytes for fish advisories (U.S. EPA, 2000).

2.2.6. User guide:

Does the User Guide describe how to use the BST for screening at an appropriate level of detail? If not, what additional information does the SAB recommend EPA add to the User Guide?

When evaluating written documents for clarity, accuracy, and usefulness it is important to keep the context in mind. While the user's manual alludes to the model being perhaps solely used by EPA it does not explicitly state who the intended target audience is or who the intended users will be. It would be helpful for EPA to articulate more clearly who the intended audience is.

The SAB raised several questions regarding the use of sets or ranges of percentages for some inputs and the absence of evaluation pathways (dermal). Questions about the mechanisms of the model are likely to be somewhat universal. It is recommended that EPA consider inserting brief explanations as to why the inputs are limited the way they are or why certain numbers were chosen over others.

Clarity is important to any user's manual and the SAB noted inconsistencies with the term "biosolids." Different definitions were presented in sections 3 and 4 of the draft framework and while not inconsistent, they could be confusing for the reader. Additionally, there are missing figure references in section 6.1 of the framework (page 17).

The User Guide should be amended to include additional guidance on the installation process. The guide currently states "The Tool will be installed in [*your_folder*]\BST. *Please note that the length of this install folder path cannot exceed 48 characters; if it does, the Tool will generate all zero results when run.*" At least one panelist experienced installation issues with a folder path shorter than 48 characters. The SAB recommends adding specific suggestions for naming the file pathway during installation, e.g., C:\Users**username**\BST with the 'username 'being something simple, e.g., initials, etc. The EPA could also consider adding a note for security issues. For example, the user could be instructed to install the BST in their download folder to ensure they are not downloading to a network drive.

Currently, the User Guide provides details on chemical limitations on pages 44-45. The SAB recommends placing this information upfront in the User Guide when first mentioned since the details are limited. Several questions are noted for specific compounds.

1. It is not clear why the model would not work for dioxin-like and PCB compounds since there seems to be no difference from the relevant model attributes that apply to PAHs, etc. in regard to a biota-sediment accumulation factor, especially for the PAHs with more than 4 aromatic rings as well as for highly brominated organics.

2. For ionizable compounds, the guide just says, "EPA encourages you to update these estimated parameter values with reported data from peer-reviewed literature when available to reduce uncertainties." However, the biggest parameter affecting ionizable behavior is pH, which also affects some of the inorganic compounds, e.g., aluminum as one obvious example but this applies to other metals of potential concern as well. Further, whether a compound is acidic or basic also affects the sorption mechanism and the significant soil properties, e.g., cation exchange capacity in the case of basic compounds like chloroaniline that forms organic cations in environmentally relevant conditions, which then affects all the bioaccumulation-related parameters.

3. Mercury compounds were noted early on as also not appropriately addressed by the BST, but no additional details are provided on pages 44-45 clarifying the limitation.

To aid the usability, the SAB recommends adding a Table of Contents to the front of each appendix and defining all acronyms included in the appendices. Finally, there are a few places where additional text could be added for clarification instead of referring the user to the appendices (e.g., the guide is not clear that tilling referred to the 'depth of waste incorporation', etc.).

The following recommendations are noted:

Tier 1

- The SAB recommends that EPA provide clarifications for the inclusion or exclusion of pathways and why specific concentrations values are set. EPA should also consider including brief explanations as to why some of the parameters were set the way they were. This would help make the guide more user-friendly.

- The SAB recommends that EPA clarify the software limitations (i.e., Apple is not supported).

Tier 2

- The SAB recommends that additional clarifying language be used in the User's Guide document as described in the comments above. Specifically, the guide would be improved with the inclusion of an acronyms list and definitions. For example, the term sludge and biosolids seem to be used interchangeably. In reality, both require different land application procedures and are not the same media type. Land application of sludge is a process requiring a permit that is currently covered under regulation.

Tier 3

- The SAB recommends that EPA continue to provide public access to the BST and that the revisions to the software and user guide be user-friendly.

2.3. Refined Risk Assessment

2.3.1. Data sources:

The whitepaper describes data sources EPA intends to search to support conducting a refined risk assessment (section 7.1). Are there any additional existing data sources on exposure that can be used as model inputs for Monte Carlo simulations? This could include data related to distributions describing biosolids land application rate, timing, number of applications per year, and operating life of the farm. Please provide references for these data sources.

While the SAB doesn't have any specific new data sources, several recommendations are provided for input parameters used in the refined assessment probabilistic model simulations.

The main difference between the screening BST and the refined risk assessment probabilistic tool is that BST is a single-parameter assessment tool while the refined assessment tool uses a distribution for several of the input parameters in a Monte Carlo model simulation. The input parameters identified by the EPA that require input distributions are biosolids chemical concentrations, biosolids application rate, operating life of biosolids application, location of the family farm (meteorological, hydrological), farm size, nearby water bodies, drinking well placement, human consumption (crops, animals, and drinking water), body weight of individuals, and exposure duration of the contaminants. The EPA uses a variety of data sources for these input parameters that have previously undergone extensive review.

When there are insufficient data available to develop input parameter distribution values for the probabilistic model, the EPA uses single values based on the best available data. Input parameters that currently have single input values include chemical-specific parameters (e.g., physical-chemical properties, degradation rates, human toxicity, and ecological benchmarks) and ecological exposure factors (i.e., diet fractions, consumption rates, body weights, and exposure durations). These input parameters currently do not have distribution information for the probabilistic model and selected input values are used that represent a reasonable conservative value.

For biosolids chemical concentrations, the EPA uses distributions from the TNSSS (U.S. EPA, 2009a and 2009b) and for chemicals not in the TNSSS the data are obtained from the literature to estimate distribution concentrations. While the SAB agrees with this approach, the SAB recommends that a literature review be conducted for the highest priority chemicals to supplement the TNSSS database since that data is now approximately 15 years old, and chemical use may have changed.

For the biosolids application rate, a single value of 10 metric tons (MT) dry weight/ha applied once per year for 40 years (crop and pasture) and a single value of 40 MT dry weight/ha applied one time (reclamation) is used. While EPA mentions that a distribution may be developed and applied for the crop and pasture scenarios, it appears there is currently no distribution available for the land application rate (U.S. EPA, 2023). The SAB recommends that the U.S. EPA develop biosolid rate distributions from the agronomic rates from different geographical regions. Such information could be requested from State Agencies or regional EPA offices.

The operating life of biosolids application to the family farm is assumed to occur once a year for 40 years (crop and pasture). Although EPA states that there are distributions for the crop and pasture scenarios (U.S. EPA, 2023), there was no reference to the source of these distributions. The SAB recommends that the EPA provide more detail on which input parameters have distribution values and the source of the distributions.

For locations of the family farms, meteorological and hydrologic data are needed. Meteorological data is used in the air model and hydrologic data is used for assessing the fate and transport of chemicals in the soil, groundwater, and surface water body due to runoff. EPA states that the meteorological data for probabilistic simulations represent 41 climate regions (U.S. EPA, 2023), but no specific reference was provided for the source of these data. The User's Guide (Appendix B, page B-5) (U.S. EPA, 2023a) provides input parameters for air temperature, meteorological WBAN (Weather Bureau Army Navy) station number, site latitude (degrees), mean annual wind speed, and water body temperature, which was obtained from Samson (U.S. DOC and U.S. DOE, 1993). The User's Guide also states that the meteorological inputs were obtained from U.S. EPA (2015). Since the User's Guide is for the BST, it is not clear which input parameters have distributions for use in the probabilistic model. The SAB recommends that the EPA provide more detail on which input parameters have distributions and the source of the distributions.

The agricultural field sizes were obtained from the 2012 Census of Agriculture (USDA, 2014). An 80-acre farm corresponds to the national median farm size. Probabilistic simulations are sampled from this dataset for farms up to 180 acres. The SAB agrees with this approach for assessing field sizes.

The size of nearby water bodies remains constant for all probabilistic model scenarios; thus, no distributions are currently applied. The standard farm pond size is assumed to be 1 hectare in area and 2 meters deep (U.S. EPA, 2019a) and the index reservoir is represented by Shipman City Lake in Shipman, Indiana (area of 13 acres and depth of 9 ft, and watershed area of 427 acres). The SAB recommends that the EPA develop a distribution for nearby water bodies for the probabilistic refined assessment simulations.

Drinking water exposure is assessed either via the index reservoir or from the groundwater near the family farm. Placement of the drinking water well could significantly impact the exposure concentration. The EPA Framework (U.S. EPA, 2023) states that the farm well may be located further downgradient and at varying depths in the refined assessment. However, there was no reference to the distributions used in the probabilistic refined assessment. The SAB recommends that the EPA provide more detail on the distribution of well placements and the source of the distributions.

The input parameters related to human exposure factors (consumption rates, body weight, and exposure duration) are also considered for use in the refined probabilistic simulations. The distributions for these input parameters were obtained from the Exposure Factors Handbook (U.S. EPA, 2011 and 2017). The SAB agrees that these distributions are appropriate for use in the probabilistic refined risk assessment, although distributions for factors such as inhalation rates and dermal exposures (i.e., the dermal surface area of contact, duration of dermal contact, dermal absorption rate in mass per square surface area of skin over time, etc.) may need to be added at the refined assessment stage.

There are empirically derived and estimated BCF and BAF values available for some pathways and chemicals. In particular, the SAB recommends that the EPA develop BAF input parameter distributions for the ingestion of beef and dairy.

The EPA should provide sources for the hazard values used in the probabilistic risk assessment model and clearly state that the hazard values are either chronic (NOEC, LOEC, NOAEL, LOAEL) or acute (LD50, EC50, LC50) values. In addition, more discussion is needed on how allometric scaling is combined with available test data to estimate terrestrial/avian hazard values. Moreover, a better explanation is needed for how the Pesticide Ecotoxicity Database was used for assessing the hazard of similar compounds. Perhaps a better source for determining ecological benchmarks is the Risk Assessment Information System Ecological Benchmark Tool.

In summary, while the SAB does not specifically provide any recommendations on additional data sources for conducting a probabilistic risk assessment, the SAB recommends that the EPA conduct additional data searches for determining appropriate distributions for several of the input parameters used in the probabilistic risk assessment model. In addition, the SAB recommends that a sensitivity analysis be performed to determine the most influential factors for conducting the data searches.

The following recommendations are noted:

Tier 1

- The SAB recommends that the EPA conduct additional data searches for determining appropriate distributions for several of the input parameters used in the probabilistic risk assessment model. These distributions should include biosolids concentrations for the highest priority chemicals, biosolids land application rates, nearby bodies of water, and BAF values for the ingestion of beef and dairy.

Tier 2

- The SAB recommends that the EPA provide more detail on which input parameters have distributions and the source of the distributions.

Tier 3

- To guide the prioritization of searches for additional data, the SAB recommends that a sensitivity analysis be performed to determine the most influential factors.

2.3.2. Transport models:

Are there alternative transport models that EPA should consider for the refined biosolids risk assessment? Please explain the basis for your recommendations and provide references.

The deterministic screening and probabilistic modeling largely rely on the same models, as noted in Table 3 of EPA's Framework (U.S. EPA, 2023). In the probabilistic modeling, probabilistic distributions of certain parameters are used. Below, the SAB suggests additional consideration be given to other models. For the refined assessments, the SAB recommends that a model or models which address background levels of common substances/contaminants be considered.

The SAB finds that there is a need for defining the difference between the RME, which is the goal of the assessment process per EPA, versus an MEI, particularly for the refined risk assessments, and the SAB recommends that the EPA clarify the goal of the assessment process and employ models that address the appropriate endpoint.

At the refined risk assessment stage, the SAB recommends that EPA consider models that can differentiate between the total concentration and bioavailable concentration of substances in biosolids (i.e., the biosolids matrix).

The SAB has the following observations and comments regarding the refined assessment step for specific pathways and parameters used or recommended for use in the BST:

1. The SAB finds that EPA should consider improving the descriptions of the transport models being used to represent the leaching of contaminants through the till zone and the unsaturated zone to the groundwater table. It is not clear if the current approach takes the pore water concentration in the till zone and uses the DAF method to estimate the groundwater concentration or if there is an additional modeling step that estimates the transport down to two meters in the unsaturated zone. Also, it is not clear if biodegradation is taken into account in the unsaturated zone (the guidance document for the DAF determination states that biodegradation was not considered). The SAB recommends that biodegradation and sorption should be considered in any refined risk assessments. The SAB agrees with the written comments submitted by National Association of Clean Water Agencies (NACWA) (2023) that the screening risk assessment assumptions in the BST associated with DAF are too conservative for the refined risk assessment step, and in certain instances will also be unrealistic for the screening risk assessment step. Depending on the soil type, chemical composition, and amount of rainfall (or irrigation); it is suggested that a better representation of the transport from the till zone to the groundwater could be simulated. It is not clear that the current refined risk assessment method simulates chemical transport in the unsaturated zone. The SAB recommends that EPA consider compound biotransformation and sorption of ionizable compounds in ionization, particularly at the refined risk assessment step.

   The SAB also finds that EPA should clarify how attenuation is being addressed in the BST, again, particularly at the refined risk assessment stop. The screening model currently uses the EPA's Composite Model for Leachate Mitigation model to define the DAFs, while the refined risk assessment step uses the Hydrus model. The SAB recommends that EPA consider using the Hydrus tool for both the screening and refined assessments and eliminate the use of the DAF. The SAB also recommends that EPA investigate how soil and groundwater transport is modeled in the European Union System for the Evaluation of Substances model (ECHA, 2019) and incorporate aspects of this approach as appropriate.

   The SAB recommends that evaluation of the air-water interface - be included for unsaturated zones and groundwater modeling using tools such as Hydrus or Predictive Integrated

Stratigraphic Modeling. This recommendation is also consistent with NACWA's written comments (2023).

2. The EPA DAF model assumes that sorption of a contaminant occurs only in a neutral (no charge) species state and sorption is determined by a K_{oc}. Many compounds are charged under agricultural soil pH conditions. The SAB recommends that EPA consider developing a model for compounds that ionize. This could be done using the Dow approach where the pH and pKa are used when appropriate.

   Additionally, the SAB finds that for PFAS, an assumption of sorption to soil solids may not be appropriate for modeling purposes (Brusseau and Guo, 2023). It has been reported that many PFAS analytes function as surfactants that sorb significantly at air/soil pore-water interfaces, particularly longer chain PFAS analytes (Costanza et al., 2019; Silva et al., 2021). Since the EPA DAF soil screening model for PFAS does not consider the air-water interface sorption, the SAB recommends that EPA consider the Brusseau and Guo (2023) analysis, which recently revised the EPA model. In addition, Guo et al. (2020) published a model for the retention of PFAS in the vadose zone. Specifically, this model evaluates surfactant-induced flow and solid-phase air/water interfacial adsorption and its effects on PFAS leaching potential. A simplified version of this model was recently published (Guo et al., 2022), and the SAB recommends that EPA also consider this model for use in BST.

3. The SAB finds that for certain substances, it could be important for the EPA to consider adding a dermal pathway model in the refined assessment step and that the EPA should also consider updating the human exposure pathways and routes considered in order to make the BST more internally consistent. For example, it seems inconsistent that inhalation exposure is considered during showering but not dermal exposure to the water. Additionally, it seems inconsistent to assume that a high percentage of fish consumption could occur directly from a farm pond, but that there would be no dermal exposure to the water in this pond or the solids around the pond. The EPA's 3MRA model, which is listed in the BST Framework, does not directly address dermal exposures, and so the SAB recommends that other models should be added/considered at the refined risk assessment step. Several other EPA documents include recommendations and guidance for performing dermal exposure and risk assessments, including the EPA's 2019 Guidelines for Human Exposure Assessment (U.S. EPA, 2019), the 2007 document entitled Dermal Exposure Assessment: A Summary of EPA Approaches (U.S. EPA, 2007), and the 2004 document on dermal exposure assessment that is part of the Risk Assessment Guidance for Superfund Volume I, entitled Human Health Evaluation Manual: Part E, Supplemental Guidance for Dermal Risk Assessment (U.S. EPA, 2004). The EPA's ExpoFIRST, Exposure Factors Handbook, and EPI Suite^{TM} tools may also be useful resources (U.S. EPA, 2011; U.S. EPA, 2012; U.S. EPA, 2016a).

4. Currently, use of field or lab BCFs and BAFs are recommended by EPA as part of the framework for selecting methods to derive National BAFs (U.S. EPA, Development of National Bioaccumulation Factors: Supplemental Information for EPA's 2015 Human Health Criteria Update, Jan. 2016). If plant uptake is based primarily on soil concentration and the K_{ow} in the screening-level model, the SAB recommends that a more advanced pathway model(s) be considered at the refined risk assessment step.

5. The SAB recommends that EPA clarify how saturated hydraulic conductivity and silt content are used in the model. It is not clear when soil biodegradation is used and when it is not used. According to the BST documentation, biodegradation was not used in the DAF assessment. As previously noted, the SAB recommends that the EPA consider using a fate and transport model for saturated and unsaturated zones in the BST at both the screening and the refined risk assessment steps.

The following recommendations are noted:

Tier 1:

- The SAB recommends that at the refined risk assessment stage, EPA consider models that can differentiate between the total chemical concentration and bioavailable concentration in biosolids (i.e., the biosolids matrix).
- The SAB recommends that EPA revisit the current approaches in BST for modeling of contaminant leaching through the till zone to groundwater and the current models used for sorption pathways that include ionization, attenuation, and fate and transport models in the saturated and unsaturated zones.
- The SAB recommends that EPA define and consider background levels for common substances/contaminants evaluated in the BST model.
- The SAB recommends that EPA examine the internal consistency of the human exposure pathways and routes used in the BST and the refined assessment. Currently, the SAB finds that evaluation of inhalation exposure potential but not dermal exposure potential in scenarios such as showering is not an appropriate application of risk assessment principles, particularly at the refined risk assessment step.

Tier 2:

- The SAB recommends that EPA consider compound biotransformation and sorption of ionizable compounds in the refined risk assessment step.

Tier 3:

- The SAB does not offer a recommendation in this tier.

2.3.3. Additional scenarios:

Are there additional scenarios for biosolids management that the EPA should consider for refined assessments? Please explain the basis for your recommendations.

The SAB applauds the EPA for identifying the most important biosolids management scenarios to evaluate in both the screening-level and refined risk assessments. These scenarios include 1) agricultural land application on cropland, 2) agricultural land application on pastureland, 3) reclamation of disturbed/marginal land, and 4) surface disposal in a liquid biosolids-only lagoon. While the SAB Panel acknowledges that these scenarios represent biosolids management practices with significant potential human and ecological health risks, some members have expressed concern over the EPA's decision to ignore the potential human health risks specifically associated with the biosolids land applier activities.

Given EPA's decision to focus on conducting high-end chemical risk screening and considering the field activities with which a "typical" biosolids land applier would be engaged, the SAB agrees with the EPA's conclusion that the "farm family" represents a significantly greater chemical exposure risk scenario than the potential risk confronting a biosolids land applier. The SAB further acknowledges that the physical distance established between the biosolids product and the biosolids land applier significantly reduces the potential human health risks associated with this scenario. For example, if liquid biosolids (< 10% solids) were land applied, they would have been initially transferred from the generation point (i.e., water reclamation facility) to an enclosed tanker truck using a pressurized conveyance system (e.g., flexible hoses or pipes). Once filled, the tanker truck would be driven across the agricultural field where the liquid product would be surface applied or subsurface injected. In either case, the biosolids land applier would remain in the truck cab during the land application event minimizing chemical exposure.

Similarly, if a dewatered or dried biosolids product (> 10% solids) were land applied, the biosolids product would have been transferred from its generation point to a staging area using a solids conveyance system (e.g., dump truck, front-end loader, conveyor belt or similar equipment). From the staging area, the biosolids material would be mechanically transferred to a land application vehicle (e.g., spreader truck, tractor-pulled manure spreader or similar land application vehicle) that would slowly drive across the agricultural field. Since the biosolids land applier would remain in the truck, front-end loader, and/or tractor cab through the entire duration of the biosolids land application event, potential chemical exposure would be relatively minor compared to the farm family that would experience daily and prolonged exposure to the biosolids product.

Before specifically addressing the question of additional biosolids recycling and/or disposal scenarios suitable for the refined risk assessment, the SAB strongly encourages the EPA to consider a number of cross-cutting scientific issues that could potentially affect the interpretation of the refined risk assessment results.

An important cross-cutting scientific issue that has been ignored in the EPA's refined risk assessment model formulation is the fate and transport of ionizable compounds. Specifically, the model should consider how the mobility and bioavailability of these compounds is influenced by various soil types as well as soil pH. The refined risk assessment model relationships established between K_{ow} and bio-uptake factors were developed for hydrophobic organic chemicals. These relationships are inappropriate for ionizable compounds, which often do not exhibit hydrophobic behavior. Various mathematical relationships exist to predict K_{oc} and the soil adsorption coefficient from K_{ow} values, but these relationships also assume that hydrophobicity dominates the chemical fate and transport behavior. Ionizable compounds do not follow the traditional hydrophobic organic compound paradigm because they exist in an ionic form under typical field pH conditions. To enhance the robustness of the refined risk assessment, the SAB strongly encourages the EPA to explicitly account for the effects of soil type and pH on the behavior of ionizable compounds associated with land applied biosolids.

Beyond the effective modeling of potentially ionizable compounds, the SAB recommends that EPA modify its refined risk assessment model formulation to account for the irreversible chemical sorption that typically occurs within the biosolids-soil matrix. Within this unique physico-chemical matrix many organic compounds become unavailable to human and/or ecological receptors through irreversible adsorption. Utilizing the total chemical concentration found in biosolids within the refined assessment model may result in significantly overestimating the true human health and/or ecological risks. The SAB encourages EPA to account for irreversible chemical adsorption as well as other relevant mechanisms that attenuate chemical risk exposure within the refined assessment. The remaining discussion summarizes additional land application and surface disposal scenarios that EPA may consider in future, more refined risk assessments.

Land Application (Beneficial Use) Scenarios:
In terms of a general approach to identifying additional scenarios beneficial to the Reasonable Maximum Exposure and the Risk Screening step, the SAB recommends utilizing the data reporting required in part 503 for appliers of sewage sludge (Process Design Manual Land Application of Sewage Sludge and Domestic Septage 15.6.3 EPA/625/R-95/001). Agronomically surface applied nutrients tend to stratify toward the soil surface impacting crop access to them. The most reasonable scenario for the agricultural land application crop scenario is that biosolids would either be injected or at a minimum eventually incorporated. Data from the data reporting may provide valuable insight into developing these scenarios. Additional scenario parameters that should be considered resulting in a more reasonable exposure screening include setbacks, application methods, food crops vs. commodity crops, soil pH, timing of applications, and number of subsequent applications. The SAB also recommends the following four, high-rate land application scenarios be considered for future refined assessments:

1. Given the absence of federal limits on the amount of biosolids that may be land applied under the land reclamation scenario, evaluation of beneficial use of biosolids under large, yet realistic land application rates, would allow the EPA to gauge the potential impact of this practice on ecological and human health chemical exposure. Mining site restoration, which has successfully employed biosolids land application rates in excess of 100 dry tons per acre, would represent an ideal worst-case scenario in which to evaluate ecological receptor exposure to biosolids contaminants as well as establish any potential correlation between emerging pollutant levels found in land applied biosolids and those reported in human foodstuffs (Pepper et al., 2013).

   To reduce human health and ecological exposure to current and emerging contaminants in biosolids, the establishment of chemical concentration limits are necessary, particularly in cases where large amounts of biosolids are land applied to reclaim disturbed and/or marginal lands used for animal grazing. The results of a refined risk assessment of land reclamation employing large one-time application rates will generate important technical guidance to those states and jurisdictions where land reclamation remains an important biosolids management option.

2. Within the currently available scenarios for refined assessments, the land reclamation scenario is limited to the restoration of mining sites. While restoration of mining sites is required as part of the federally mandated site closure plan, there are a number of other potential land reclamation scenarios where biosolids could be utilized to restore highly disturbed and/or marginal land. Biosolids land application has been employed to restore vegetation on wildfire-damaged land, sand dunes, construction sites, and over-grazed rangelands (McFarland et al., 2009).

   Each of these land reclamation scenarios has a unique set of requirements and potential human health and ecological chemical exposure pathways. For example, on over-grazed rangelands, ranchers are typically interested in maximizing the animal density on their property. Land application of large amounts of biosolids on over-grazed rangelands allows ranching operations to increase the animal stocking rate (animal units/acre) resulting in greater financial profits. However, the potential exposure of grazing animals to current and emerging biosolids pollutants increases with larger application rates. The economic benefits of an increased animal stocking rate must be considered and balanced against the potential adverse effects that increased soil pollutant loading have on grazing animal health and human food quality.

3. Within the current federal biosolids regulations (40 CFR Part 503), biosolids may be legally land-applied on certain permitted sites at annual rates that are significantly greater than the nutrient-

based agronomic rate. While these dedicated, beneficial use sites cannot be utilized to grow food for human or animal consumption, they may be employed to grow biomass for energy production (e.g., biofuels). The SAB encourages the EPA to consider the potential human health and ecological chemical exposure risks that may be associated with these highly-regulated agricultural operations.

4. The potential contribution of domestic septage land application on human health and ecological chemical exposure within the model farm scenario should be considered in the refined risk assessments given its inclusion within the current biosolids federal regulation (40 CFR Part 503, Subpart B). Approximately twenty percent (20%) of US households utilize on-site septic systems. The residual solids removed from septic tanks (i.e., domestic septage) can be land applied as a crop fertilizer and/or soil amendment. While domestic septage applied to non-public contact sites (i.e., private farms, ranches) do not have to meet specific numerical pollutant limits, domestic septage applied to public contact sites (i.e., parks, cemeteries, home gardens, etc.) must meet the same numerical pollutant limits as land applied sewage sludge.

Surface Disposal Scenarios:
Only the surface disposal of thickened biosolids (solids content ≤ 10%) in a liquid biosolids-only lagoon is evaluated under the refined assessment framework. While liquid biosolids-only lagoons are technically and financially feasible when located short distances from the water reclamation facility, in most cases, biosolids surface disposal sites are located in remote areas at considerable distances from the biosolids generation site. Given the increasing costs associated with biosolids transport, biosolids generation facilities normally reduce the biosolid's moisture content through physical dewatering and/or drying operations.

While the SAB acknowledges that the final moisture content of surface disposed biosolids will have a minimal impact on chemical transport, the selection of surface disposal systems that permit the installation of liners will significantly limit the potential leaching of chemicals to groundwater. For example, narrow surface disposal trenches (≤ 10 feet wide) can accept liquid or dewatered biosolids but are constructed without liners. However, other types of biosolids surface disposal systems such as area-filled mounds and wide surface disposal trenches (> 10 feet wide) are typically constructed with liners. The SAB encourages the EPA to provide a scientifically-defensible explanation for its decision to include only the liquid biosolids-only lagoon scenario in the refined assessment. Unless they are demonstrated to pose an insignificant public health and ecological risk, explicit consideration of the full range of available biosolids surface disposal options are warranted within the refined assessment.

The following recommendations are noted:

Tier 1

- The SAB recommends that EPA conduct effective modeling of the fate and transport of ionizable compounds with specific consideration of how various soil types and pH may affect their behavior.
- The SAB recommends that EPA incorporate the irreversible adsorption behavior of organic contaminants within the biosolids-soil matrix.
- The SAB recommends that EPA model land reclamation scenarios that reflect the use of large one-time biosolids application rates (i.e., > 100 dry tons/acre) and its potential impact on public health and ecological risks (Pepper et al., 2013).

Tier 2

- The SAB recommends that EPA consider the potential human health and ecological chemical exposure risks that are associated with dedicated biosolids beneficial use sites.
- The SAB recommends that EPA compare the potential human health and ecological risks associated with the disposal of sewage sludge in liquid-only lagoons to that associated with the disposal of liquid biosolids in unlined narrow trenches as well as disposal of dewatered biosolids cake in area-filled mounds, narrow and wide-area trenches (with and without liners).

Tier 3

- The SAB recommends that EPA consider the following to inform future evaluations/revisions of the refined assessment.
    - Land reclamation is currently limited within the refined assessment to the restoration of mining sites. There are several other potential land reclamation scenarios where biosolids could be utilized including being employed to restore vegetation on wildfire-damaged land, sand dunes, construction sites, and over-grazed rangelands (McFarland et al., 2009).
    - The potential contribution of domestic septage land application on human health and ecological chemical exposure within the model farm scenario should be considered. While domestic septage applied to non-public contact sites (i.e., private farms or ranches) does not have numerical pollutant limits, domestic septage applied to public contact sites (i.e., parks, cemeteries, home gardens, etc.) must meet the same numerical pollutant limits as land-applied sewage sludge.

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APPENDIX A

The following comments are noted for the EPA review documents.

Biosolids Tool (BST) User's Guide (U.S. EPA 2023a):

1. The User Guide states that scientists and staff at Research Triangle Institute (RTI), who developed this tool and associated User's Guide. (EPA Contract NO. 68HERC20D0019 Task Order: PR-OW- 20-00582. However, EPA Contract NO. 68HERC20D0019 was awarded to the Great Lakes Environmental Center, not RTI.

   EPA should clarify the developer of the BST or the contract number; which ever is applicable.

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National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey

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HIGHLIGHTS

- First study to report nationwide occurrence and concentrations of perfluoroalkyl substances (PFAS) in U.S. biosolids.
- Ten out of thirteen PFAS analyzed were consistently detected in all biosolids samples.
- PFOS was the most abundant PFAS in biosolids, followed by PFOA.
- Mean load of $\sum$PFASs in U.S. biosolids was estimated at 2749–3450 kg/year.
- PFASs in biosolids show no significant difference between pre- and post-phase out period.

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ABSTRACT

Using liquid chromatography tandem mass spectrometry, we determined the first nationwide inventories of 13 perfluoroalkyl substances (PFASs) in U.S. biosolids via analysis of samples collected by the U.S. Environmental Protection Agency in the 2001 National Sewage Sludge Survey. Perfluorooctane sulfonate [PFOS; 403 ± 127 ng/g dry weight (dw)] was the most abundant PFAS detected in biosolids composites representing 32 U.S. states and the District of Columbia, followed by perfluorooctanoate [PFOA; 34 ± 22 ng/g dw] and perfluorodecanoate [PFDA; 26 ± 20 ng/g dw]. Mean concentrations in U.S. biosolids of the remaining ten PFASs ranged between 2 and 21 ng/g dw. Interestingly, concentrations of PFOS determined here in biosolids collected prior to the phase-out period (2002) were similar to levels reported in the literature for recent years. The mean load of $\sum$PFASs in U.S. biosolids was estimated at 2749–3450 kg/year, of which about 1375–2070 kg is applied on agricultural land and 467–587 kg goes to landfills as an alternative disposal route. This study informs the risk assessment of PFASs by furnishing national inventories of PFASs occurrence and environmental release via biosolids application on land.

1. Introduction

Perfluoroalkyl substances (PFASs) are anthropogenic chemicals that have been widely used in commercial products since the 1950s [1]. Due to their unique properties of repelling both water and oil, PFASs are extensively used in the manufacture of surfactants, lubricants, polishes, textile coatings, and fire-retarding foams [1]. As a result PFASs are released into the environment at significant quantities and have been detected in surface water, fish, birds, mammals, and humans worldwide [2–6]. Although the production of two major PFASs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), has been phased out in several major U.S. companies, continued environmental contamination of PFASs results from the use of precursors such as fluorotelomer alcohols and polyfluoroalkyl phosphates [7]. PFASs are emerging contaminants of increasing interest to the scientific community, due to their widespread occurrence in the environment and evidence of potential or known adverse human health effects. PFASs have been shown to persist in the environment, to bioaccumulate in animals and to occur at significant levels even in remote regions like the Arctic [3,5,8,9]. PFOS is the predominant PFAS detected in all wildlife species worldwide [7]. One study reported bioaccumulation of PFOS in polar bears at concentrations even greater than polychlorinated biphenyls (PCBs) [10]. Results from animal studies have associated PFOS and PFOA with developmental and reproductive toxicity [11,12], as well as cancer [13]. In humans, both PFOS and PFOA are shown to cross the placenta readily [14,15],

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and epidemiological studies on fetal exposure have associated high levels of PFOS with reduced growth metrics of newborns [16]. Additionally, both PFASs have been associated with elevated total cholesterol levels in humans [17].

PFASs are considered to be highly resistant to biodegradation due to their extremely strong carbon–fluorine bonds [18]. They are not efficiently removed in municipal wastewater treatment plants (WWTPs), and the presence of PFASs in wastewater effluents and biosolids is of increasing concern [19]. Concentrations of PFOS and PFOA have been reported of up to 990 and 241 ng/g of biosolids, respectively [20–22]. Studies have also shown that several PFASs increase in concentration during the WWTP process train, suggesting the presence of precursor compounds that degrade and release persistent perfluorinated carboxylic acids and sulfonates (PFCAs and PFSAs) [20,23]. Land application of biosolids contaminated with PFASs was shown to contaminate soil, groundwater, and surface waters [19,22]. Soil concentrations of PFOS as high as 483 ng/g were reported at a land reclamation site in Illinois after 32 years of consecutive applications of biosolids at the rate of 69 Mg biosolids ha^{-1} yr^{-1} [22]. In Decatur, AL, about 22% of samples collected from surface and well water near fields with a history of PFASs contaminated biosolids application exceeded the health advisory level of the U.S. Environmental Protection Agency (U.S. EPA) of 400 ng/L for PFOA [19]. Multiple studies have shown that PFASs of shorter chain length tend to become mobilized from soil readily to contribute to contamination of surface water and groundwater [19,22]. The widespread occurrence of PFASs at significant concentrations in the environment necessitates a better understanding of environmental occurrence and transport processes in order to inform both human health risk assessments and regulatory requirements for these recalcitrant, mobile chemicals.

The U.S. EPA has performed several National Sewage Sludge Surveys (NSSS) to evaluate the need for regulating trace contaminants [24]. The present study was performed to extend this effort to other emerging contaminants that were excluded from past U.S. EPA studies. In a research collaboration, unused samples from EPA's 2001 survey were acquired and are being archived in the Biodesign Institute at Arizona State University as part of the U.S. National Biosolids Repository maintained there. The approach of analyzing archived composite biosolids had been validated previously in studies of pharmaceuticals and personal care products (PPCPs) and alkylphenol surfactants performed to evaluate their nationwide occurrence in biosolids [25–27]. The present work employed a similar methodology to analyze for PFASs to enable risk assessment and to determine baseline concentrations and national inventory for these chemicals in treated municipal sludge fit for land application.

2. Materials and methods

2.1. Sample description

Biosolids samples, originally collected by the EPA from 94 WWTPs in 32 states and the District of Columbia as part of the 2001 National Sewage Sludge Survey by U.S. EPA, were retrieved from the U.S. National Biosolids Repository at the Biodesign Institute at Arizona State University. Information on sampling locations is available in supplementary material. The facilities were selected by the U.S. EPA to obtain unbiased national estimates of chemical contaminants in U.S. sewage sludges that are disposed of primarily by land application. The samples were collected between February and March 2001 according to an established protocol, only from facilities that included secondary treatment [28,29]. All samples were collected in 500 mL glass or polyethylene jars, and to the best of our knowledge no Teflon containing tools were used during sampling of sludge; thus eliminating possible contamination during sampling of sludge samples by PFASs [29]. Samples were collected from only processed sewage sludges intended for disposal. The biosolids composites analyzed in this study constitute a representative sample (94 facilities) of the more than 16,000 U.S. WWTPs. The purpose of EPA's survey was to estimate levels of dioxins, dibenzofurans, and coplanar polychlorinated biphenyls in biosolids. After completion of 2001 NSSS, the samples were acquired by our laboratory and stored in amber glass jars (500 mL) at −20 °C for further analysis. Samples were stored initially at Johns Hopkins University, and later transferred to Arizona State University for long-term maintenance. Of the 94 WWTPs, 89 had single system (either aerobic or anaerobic digestion) and five of them had two systems for sludge treatment (both aerobic and anaerobic digestion). Samples were collected from each treatment systems amounting to a total of 113 biosolids samples. Three of these samples were excluded from analysis due to broken containers. The rest of the 110 biosolids samples were randomly grouped into five composite samples, each containing solids from between 21 and 24 individual samples. Sampling procedure and preparation of composites are described in detail elsewhere [27]. A duplicate of composite sample #1 was prepared to serve as a blind duplicate. Composite samples were prepared to establish national baseline levels for these compounds; the validity of the present approach has been demonstrated previously [25–27].

Supplementary material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.03.016.

2.2. Sample analysis

Biosolids composites were analyzed for PFASs by a commercial lab (AXYS Analytical Services Ltd., Sydney, British Columbia, Canada) that developed EPA Method 1694 for pharmaceuticals and personal care products, and that specializes in the analysis of traditional and emerging contaminants. AXYS is a nationally accredited commercial lab in Canada and also is accredited by the National Environmental Laboratory Accreditation Program (NELAC) in Florida and New Jersey for PFAS analysis. The analytical method used had been employed previously in peer-reviewed studies on the level of PFASs in various environmental matrices [30,31]. Analyte concentrations were determined using the isotope dilution technique for all compounds. About 5 g of dried homogenized (<4 mm) biosolids samples were spiked with isotope-labeled surrogates and analytes were extracted once with dilute acetic acid solution and then twice with a mixture of 0.3% ammonium hydroxide and 99% methanol solution, each time by shaking the slurries and collecting the supernatants. Supernatants were combined and treated with ultra pure carbon powder. The resulting solution was diluted with water and cleaned up by solid phase extraction (SPE; Oasis WAX, Waters, Milford, MA, USA). The eluate was then spiked with recovery standards prior to analysis. Sample extracts were separated by high performance liquid chromatography using a reversed-phase column (X terra C_{18} 3.5 μm, 2.1 mm × 100 mm; Waters, Milford, MA) as described previously [30,31]. Analyses were performed using a Micromass Quattro Ultima triple quadrupole tandem mass spectrometer (Waters, Milford, MA) in Selected Reaction Monitoring (SRM) mode (Table 1).

Quality assurance and quality control procedures included method blanks and matrix spikes to evaluate recovery rates in percent. Analysis of duplicate samples was performed by the lab for each batch with greater than six samples. Positive identification of target analytes, surrogate standard and recovery standards required the compound retention time to fall within 0.4 min of the predicted retention times from the mean determined from

Table 1
PFASs target analytes and their respective detection and quantification parameters.

Target analyte	Retention time (min)	Precursor ion *m*/*z*	Product ion *m*/*z*	Quantified against
Perfluorobutanoate (PFBA)	5	213	169	$^{13}C_4$-PFBA
Perfluoropentanoate (PFPeA)	5.8	263	219	$^{13}C_2$-PFHxA
Perfluorohexanoate (PFHxA)	6.2	313	269	$^{13}C_2$-PFHxA
Perfluoroheptanoate (PFHpA)	6.6	363	319	$^{13}C_2$-PFHxA
Perfluorooctanoate (PFOA)	7	413	369 (169)[a]	$^{13}C_2$-PFOA
Perfluorononanoate (PFNA)	7.4	463	419	$^{13}C_5$-PFNA
Perfluorodecanoate (PFDA)	7.9	513	469	$^{13}C_2$-PFDA
Perfluoroundecanoate (PFUnDA)	8.5	563	519	$^{13}C_2$-PFDA
Perfluorododecanoate (PFDoDA)	9	613	569	$^{13}C_2$-PFDoA
Perfluorobutane sulfonate (PFBS)	6.3	299	80 (99)[a]	$^{18}O_2$-PFHxS
Perfluorohexane sulfonate (PFHxS)	7.2	399	80 (99/119)[a]	$^{18}O_2$-PFHxS
Perfluorooctane sulfonate (PFOS)	8.2	499	80	$^{13}C_4$-PFOS
Perfluorooctane sulfonamide (PFOSA)	9.9	498	78	$^{13}C_4$-PFOS
Surrogate standard				
$^{13}C_4$-PFBA	5.0	217	172	$^{13}C_2$-PFOUEA
$^{13}C_2$-PFHxA	6.2	315	270	$^{13}C_2$-PFOUEA
$^{13}C_2$-PFOA	7.0	415	370	$^{13}C_4$-PFOA
$^{13}C_5$-PFNA	7.4	468	423	$^{13}C_2$-PFOUEA
$^{13}C_2$-PFDA	7.9	515	470	$^{13}C_2$-PFOUEA
$^{13}C_2$-PFDoDA	9.0	615	570	$^{13}C_2$-PFOUEA
$^{18}O_2$-PFHxS	7.2	403	84 (103)[a]	$^{13}C_2$-PFOUEA
$^{13}C_4$-PFOS	8.2	503	80 (99)[a]	$^{13}C_2$-PFOUEA
Recovery standard				
$^{13}C_2$–^{2}H-perfluoro-2-decenoic acid (PFOUEA)	7.3	459	394	–
$^{13}C_4$-perfluorooctanoic acid	6.9	417	372	–

[a] Alternate transition were used if necessary to avoid interference.

the initial calibration. Native compounds with labeled surrogate standards had to elute within 0.1 min of the associated labeled surrogates. All concentrations are reported on a dry weight (dw) basis. Precision between samples and duplicates was expressed as relative percent difference (RPD), which was calculated using the following expression:

$$\mathrm{RPD}\quad[\%] = \frac{|C_{\mathrm{sample}} - C_{\mathrm{duplicate}}| \times 100}{(C_{\mathrm{sample}} + C_{\mathrm{duplicate}})/2} \tag{1}$$

where C_{sample} and $C_{\mathrm{duplicate}}$ are the concentration detected in the original sample and in its duplicate, respectively.

2.3. *Estimation of annual loading of PFASs to agricultural soil*

The annual loading of PFASs in biosolids was calculated based on the annual biosolids production of 5.1–6.4 million metric dry tonnes (5.6–7 million dry U.S. tonnes) in the U.S. [32–34].

$$\begin{aligned}&\text{Annual load in biosolids} = [\text{minimum/maximum PFAS}\\&\quad\text{concentration detected in composites}\quad(\mu\text{g/kg})]\\&\times(10^{-9}\ \text{kg}/\mu\text{g}) \times (5.1\text{–}6.4 \times 10^{9}\ \text{kg of biosolids/year})\end{aligned} \tag{2}$$

The estimated percentage of total biosolids use and disposal (50–60% to land application; 17% to landfills; 20% to incineration) were used to calculate the load of PFASs to the various end use components from Eq. (2).

3. Results and discussion

3.1. *Method performance*

The method detection limits (MDL) for the various PFASs ranged between 0.03 and 0.14 ng/g dry weight (dw) of biosolids. Recoveries from matrix spike experiments for the various analytes ranged between 75 and 110% in biosolids (Table 2). Analysis precision, expressed as relative percent difference (RPD), was within 20% for most of the analytes in blinded duplicates for biosolids analysis except for PFBA (52%), PFPeA (24%), and PFBS (21%). The RPD for non-blinded duplicates of biosolids was within 9% for all analytes. No laboratory contamination was observed in method blanks.

3.2. *Study limitations*

A large number of biosolids samples were combined to form five composites in this study in order to reduce the number of samples to be analyzed and still provide with a defensible mean baseline concentration for the analytes. However, the mixing of samples is not well suited to capture the variation in concentrations of the individual analytes as a function of geographic location, treatment processes, population served etc. It is also possible for minor contaminants to become diluted during mixing. Hence the reported PFASs concentrations and detection frequencies are conservative. While this approach cannot determine the variability of concentrations between the large numbers of WWTPs studied, it is suitable for identifying major PFASs contaminants and determining their average concentrations in U.S. biosolids. Extrapolation of these average concentrations to total sewage sludge production in the U.S. carries potential risks. For example, if the plants selected by the U.S. EPA are not representative of all plants across the nation, estimates for the annual load or each PFAS could be skewed. However, the National Sewage Sludge Survey conducted by U.S. EPA is by far the most comprehensive survey on U.S. sewage sludges, as it contains 94 samples from 32 U.S. States and the District of Columbia. Given the large number of samples analyzed and their selection by the government agency on the basis of providing good representation of the more than 16,000 WWTPs in the U.S. nationwide, the obtained estimates are expected to carry only a small and acceptable level of uncertainty. The fact that a survey of these compounds has never taken place before at this scale in the U.S. or any other country in the world, makes the analytical results and loading estimates reported here a valuable contribution to the current understanding of the occurrence and fate of PFASs in the built environment of the United States.

Table 2
Concentrations and estimated annual loads of perfluoroalkyl substances in biosolids collected in 2001.

Compounds	CAS #	Matrix spike recovery (%)	Biosolids concentration (ng/g) Avg. (Min, Max)	RPD (%)		Frequency detected (%)	Estimated annual PFCs load (kg/year) (Min–Max)[a]			
				Blind duplicates	Non-blinded duplicates		Biosolids	To land application	To landfills	To incineration
Perfluorobutanoate (PFBA)	375-22-4	99.7	2 (1.2, 3.2)	51.6	–	80	10–12.5	5–7.5	1.7–2.1	2–2.5
Perfluoropentanoate (PFPeA)	2706-90-3	99.1	3.5 (1.8, 6.7)	23.6	2.3	100	17.7–22.2	8.8–13.3	3–3.8	3.5–4.4
Perfluorohexanoate (PFHxA)	307-24-4	107	6.2 (2.5, 11.7)	4.2	16.7	100	31.8–39.9	15.9–23.9	5.4–6.8	6.4–8
Perfluoroheptanoate (PFHpA)	375-85-9	104	3.4 (1.2, 5.4)	8.3	–	80	17.4–21.8	8.7–13.1	3–3.7	3.5–4.4
Perfluorooctanoate (PFOA)	335-67-1	103	34 (11.8, 70.3)	13.4	12.2	100	172–215	85.8–129	29.3–36.6	34.3–43.1
Perfluorononanoate (PFNA)	375-95-1	92.4	9.2 (3.2, 21.1)	7.9	14.3	100	47.2–59.1	23.5–35.5	8–10	9.4–11.8
Perfluorodecanoate (PFDA)	335-76-2	98.9	26.1 (6.9, 59.1)	6.6	12.6	100	133–167	66.6–100	22.7–28.4	26.7–33.4
Perfluoroundecanoate (PFUnDA)	2058-94-8	74.6	11.7 (2.8, 38.7)	6.6	2.4	100	59.9–69.7	29.9–45.1	10.2–12.8	12–15
Perfluorododecanoate (PFDoDA)	307-55-1	95.4	10.9 (4.5, 26)	6.7	6.4	100	55.6–69.7	27.8–41.8	9.4–11.9	11.1–13.9
Perfluorobutanesulfonate (PFBS)	45187-15-3	110	3.4 (2.5, 4.8)	20.8	–	60	17.6–22	8.8–13.2	3–3.7	3.5–4.4
Perfluorohexanesulfonate (PFHxS)	108427-53-8	97.8	5.9 (5.3, 6.6)	7.4	5.4	100	29.9–37.5	15–22.5	5.1–6.4	6–7.5
Perfluorooctanesulfonate (PFOS)	45298-90-6	96.9	403 (308, 618)	11.9	15.7	100	2052–2575	1026–1545	349–438	410–515
Perfluorooctane sulfonamide (PFOSA)	754-91-6	75.3	20.7 (2.2, 68.1)	19.2	20.2	100	105–132	52.7–79.3	17.9–22.5	21.1–26.4

– Represent non-detects in samples.

[a] These values were calculated based on the estimated percentage of total biosolids use and disposal (50–60% to land application; 17% to landfills; 20% to incineration) [32–34].

3.3. Nationwide occurrence of PFASs in U.S. biosolids

Ten out of thirteen PFASs analyzed were consistently detected in all composite biosolids samples except for PFBA, PFHpA, and PFBS (Table 2). The most abundant PFAS in biosolids was PFOS, detected at a concentration of 403 ± 127 ng/g dw, followed by PFOA (34 ± 22 ng/g dw). The remaining eleven PFASs ranged between 2 and 26 ng/g dw (Table 2) and the mean total concentration of PFASs ($\sum$PFAS) detected in the five composite samples was 539 ± 224 ng/g dw. The levels detected in U.S. biosolids are more than an order of magnitude higher than levels detected in sewage sludge samples collected from Spain and Germany [35]. For comparison purposes, the national baseline levels of PFASs detected in this study were plotted with levels reported in other studies for sludge samples collected from U.S. WWTPs (Fig. 1). It must be noted that the concentrations reported in the present study represent samples collected at 94 WWTPs from across the U.S., whereas previously reported values were limited to specific study locations and a maximum of 11 WWTPs. The levels of PFASs from other studies plotted in Fig. 1 are for sludge samples collected in the U.S. between 2004 and 2007 (except for one in 1998). Whereas, the biosolids samples analyzed in this study were collected by U.S. EPA between February and March 2001, which was during the phase out period of PFOS and perfluorooctanesulfonyl fluoride (POSF) related products by the 3M Company between 2000 and 2002. PFAS emission during manufacturing process has reduced since then in the U.S. [36] and hence their current concentrations in biosolids are expected to be lower. However, interestingly the mean concentration of PFASs detected in this study were not significantly different ($p > 0.05$) to concentrations reported in sludge samples collected between 2004 and 2007 (except for one collected in 1998) in U.S., years after 3M discontinued its industrial production of PFOS and related compounds. A similar observation was also reported for PFAS levels in human serum samples during the 2003–2004 NHANES survey [2]. The survey reported the prevalence of PFASs in more than 98% of the people analyzed even after the phase-out in production by 3M. Even though the current producers are committed to reducing emissions of PFASs, it is suggested that there still exist other direct and indirect sources of PFASs in the U.S. [2].

3.4. Annual loading of PFASs to U.S. biosolids and agricultural land

Based on the estimated biosolids production of 5.1–6.4 million metric tonnes (5.6–7 million U.S. tonnes) in the year 2001 [32–34], the nationwide annual loading rates to biosolids for various PFASs were calculated (Table 2). The estimated mean loading rate of $\sum$PFAS was 2749–3450 kg/year, with the most abundant compound being PFOS with a rate of 2052–2575 kg/year, followed by PFOA and PFDA at 172–215 and 133–167 kg/year, respectively. However, these loadings are significantly lower when compared to other major contaminants in biosolids, such as antimicrobials (triclocarban and triclosan) and non-ionic surfactants (nonylphenol and their ethoxylates), whose loading in biosolids had been determined in previous studies [25,27] (Fig. 2). The higher loading for the antimicrobials and surfactants may be explained by their high production volumes of greater than 1 million pounds per year in the U.S. and their disposal, which differs from $\sum$PFAS in that, they are almost exclusively discharged into wastewater by design.

Based on the estimated percentage of total biosolids applied on land (50–60%) [32–34], the mean loading rate of $\sum$PFAS to agricultural soil was found to be 1375–2070 kg/year. A significant amount of $\sum$PFAS (467–587 kg/year) was also estimated to go to landfills as an alternative disposal route for unwanted biosolids (Table 2). In many instances the leachate collected from landfills is sent back to the local WWTP and is thus re-incorporated into the sludge/liquid

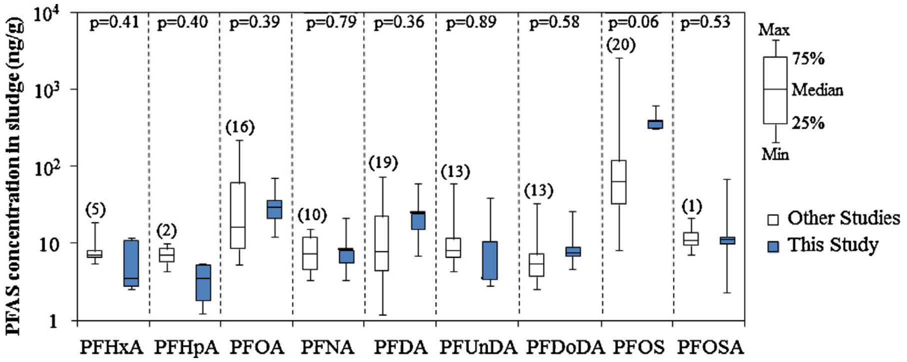

Fig. 1. Comparison of PFASs concentrations in U.S. sludge reported in other studies with levels detected in the present work. Values in parentheses represent the total number of wastewater treatment plants sampled for the particular analyte in other studies [20–22,37,38]. The *p*-values indicate lack of statistically significant differences between the paired datasets evaluated.

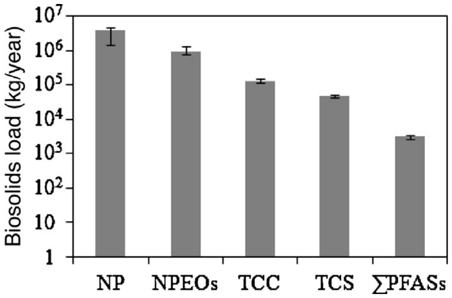

Fig. 2. Comparison of 2001 annual loads of emerging contaminants in U.S. biosolids. NP – nonylphenol; NPEOs – nonylphenol mono- and di-ethoxylates; TCC – triclocarban; TCS – triclosan; ∑PFASs – total perfluoroalkyl substances detected in this study. Error bars represent minima and maxima.

waste stream. As shown in the previous section, there is no significant change in PFASs levels in biosolids samples collected in the year 2001 and years 2004–2007. Hence one can expect a similar annual loading to soils in the following years, resulting in a net accumulation of these compounds in U.S. soils. These numbers should be viewed as conservative estimates, since only a selected number of PFASs were included in this study.

4. Conclusion

The nationwide concentrations of PFASs in U.S. biosolids provided in this study serves to inform both human exposure risk assessments and regulatory requirements for these recalcitrant chemicals. Although there were efforts in phasing out PFOS and related compounds from production beginning in the year 2002, a comparison of concentrations detected in samples collected in 2001 (this study) and in years 2004–2007 showed no noticeable differences. This suggests that the U.S. may have to consider regulations similar to those instituted in European countries, where PFOS and related compounds were banned from several uses. The significant loading to U.S. soils estimated in the present study further increases concern about groundwater and surface water contamination, as reported in previous investigations by others [19,22]. This study further demonstrated the use of mega composite samples for determining national and regional mean concentrations of major contaminants in sewage sludge in a scientifically sounds, yet economically attractive fashion.

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