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

Washington, J. W., Yoo, H., Ellington, J. J., Jenkins, T. M., & Libelo, E. L. (2010). Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA. Environmental Science & Technology, 44, 8390–8396. https://doi.org/10.1021/es1003846

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Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA

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Sludges generated at a wastewater treatment plant (WWTP) in Decatur, Alabama have been applied to agricultural fields for more than a decade. Waste-stream sources to this WWTP during this period included industries that work with fluorotelomer compounds, and sludges from this facility have been found to be elevated in perfluoroalkylates (PFAs). With this knowledge, the U.S. Environmental Protection Agency collected soil samples from sludge-applied fields as well as nearby "background" fields for PFA analysis. Samples from the sludge-applied fields had PFAs at much higher concentrations than in the background fields; generally the highest concentrations were perfluorodecanoic acid (≤990 ng/g), perfluorododecanoic acid (≤530 ng/g), perfluorooctanoic acid (≤320 ng/g), and perfluorooctane sulfonate (≤410 ng/g). Contrasts in PFA concentration between surface and deeper soil samples tended to be more pronounced in long-chain congeners than shorter chains, perhaps reflecting relatively lower environmental mobilities for longer chains. Several PFAs were correlated with secondary fluorotelomer alcohols (*sec*-FTOHs) suggesting that PFAs are being formed by degradation of *sec*-FTOHs. Calculated PFA disappearance half-lives for C6 through C11 alkylates ranged from about 1 to 3 years and increase with increasing chain-length, again perhaps reflecting lower mobility of the longer-chained compounds.

Introduction

For a little over a decade, a wastewater treatment plant (WWTP) in Decatur, AL has been permitted to apply sludge it generated on about 2000 ha of local agricultural land. Waste streams to this WWTP varied during this time, but are known to have included effluents from industries that conducted electrochemical fluorination and fluorotelomerization, as well as industries that worked with a variety of fluorotelomer compounds (FTCs) and perfluoroalkylates (PFAs). When sludges from this WWTP were analyzed for FTCs and PFAs they were found to be elevated relative to other sludges (see Supporting Information (SI); *1, 2)*. These elevated levels generated concern that the Decatur sludge applications might constitute an exposure route because application of sludges having high PFAs to soil has been documented to contaminate surface and drinking waters (*3*). Consequently, these elevated concentrations in the Decatur sludges spurred prudent efforts to decrease PFA loads to the WWTP, and sludge PFOA concentrations generated at the facility have fallen off dramatically since 2006 (Figure SI1). With this as background, in an effort to evaluate the impact of the sludges that had been applied to the Decatur fields, in late 2007 the U.S. Environmental Protection Agency (USEPA) collected and analyzed a small number of sludge and soil samples from fields that had received some of the highest sludge loads. These results documented the presence of high concentrations of several fluorotelomer alcohols (FTOHs) and PFAs in soils of the land-application areas.

The USEPA subsequently collected (November 2008) and analyzed water samples from a few Decatur, AL public drinking-water supplies. No levels of the perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS) were observed above the Provisional Health Advisories of 0.4 μg/L for PFOA and 0.2 μg/L for PFOS (*4*) in these municipal drinking-water samples. In February 2009, the USEPA collected additional water samples from selected private wells, agricultural ponds, and other surface waters located in and immediately around the land-application fields (*5*). Some of these samples were found to have PFA levels exceeding the Provisional Health Advisories.

An expanded set of surface and subsurface soil samples was collected in March 2009 to characterize the extent and magnitude of the PFA contamination in the land-application area. The general results of these efforts have garnered considerable attention in the lay press (*6, 7*), but the actual data have yet to be reported before now. In this paper, we report the analytical methodologies employed, the analytical results for both the 2007 and the 2009 surveys, and examine these data for patterns that illuminate the fate of these compounds. In a companion paper (*8*), we report analytical results for FTOHs, which have been shown to degrade to form some of the perfluorocarboxylates (PFCAs) we report here.

Materials and Methods

Sample Collection. Decatur, AL region soil samples were collected by USEPA regional scientists from (i) 2 sludge-applied fields and 1 sludge-free background field in September 2007; and (ii) 6 sludge-applied fields and 1 sludge-free background field in March 2009. One of the sludge-applied fields, 09H, received only one sludge application in the distant past. All sampled fields were in pasture; we plan to report upon analysis of grasses from these fields in a future paper. Table SI1 in the SI lists the sampled fields, documented sludge-application history, sample-identification numbers, and descriptions for the soil samples, and Figure 1 depicts the sampling locations.

The sampling equipment, composed of stainless steel, was washed three times with Optima-grade methanol (MeOH) prior to use. The samples were stored in certified-

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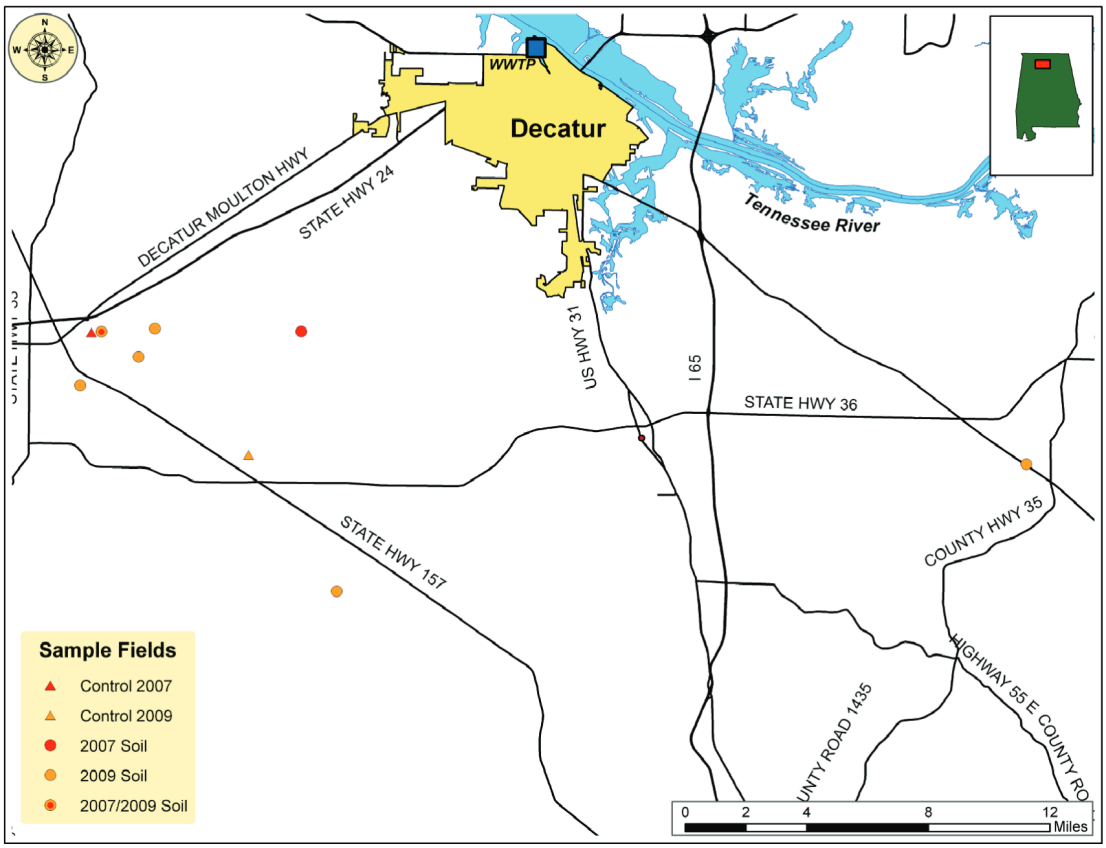

FIGURE 1. Sample locations for this study are south, and within an approximately 20-mile radius, of Decatur. Field numbers are not designated in the interest of preserving confidentiality regarding PFA concentrations of individual properties.

clean 500-mL, wide-mouth high-density polyethylene (HDPE) containers. The sampling equipment and containers were determined to be free of contamination for the intended analytes before the sampling trip by rinsing a representative of each item type with 60/40 (volume/volume) acetonitrile/water (ACN/H_2O) and analyzing the rinses. Surface-soil samples were collected from the 0- to 10-cm interval using sampling spoons, hand augers, and pans. Subsurface-soil samples were collected by Geo-probe from intervals bounded between the 23- to 56-cm and the 152- to 165-cm depths (Table SI1).

Quality-control samples taken to the field included Ottawa sand that has been shown to bear low concentrations of target analytes and a commercial top soil, the Cowart soil, for which the general range of concentrations of a variety of analytes has been documented to be low as well (*9, 10*). Also, duplicate field samples were collected from selected locations in the sludge-applied fields.

Chemicals. All chemicals used in this study were of the highest purity offered by the suppliers, uniformly ≥97% purity. We identify the chemicals we used in the Supporting Information.

Sample Preparation and Extractions. Field-moist samples from the 2007 sampling round were sieved through a MeOH-washed, 2-mm, stainless-steel sieve and extracted in triplicate. Because these samples yielded a high degree of variability in [FTOHs] between aliquots drawn from the same sieved sample (*9*), the 2009 sampling-round samples were homogenized by repeatedly passing them through 2-mm, stainless-steel sieves, coning and quartering until the sample was reduced to four approximately 1-g aliquots. Each of the four aliquots was transferred to a precleaned, labeled 16-mL polycarbonate (PPCO) centrifuge tube and sealed with a PPCO press-on cap; two of these aliquots were extracted for the PFA analyses reported herein and the remaining two were extracted for FTOH analyses which are reported in our accompanying paper (*8*). In addition, aliquots were removed from all samples to measure moisture content, by drying, which was used to calculate the concentrations reported herein on a dry-weight (dw) basis from the extractions which were performed on moist soils.

We extracted the 2007 and 2009 samples using different methods, but each was optimized for these sludge-applied soils as described below. For the 2007 samples, we performed an extraction designed to recover both PFAs and FTOHs from the same aliquot (*11*). We optimized this method for sludge-applied soils by extracting one sample seven times with MTBE to determine the number of steps necessary to balance satisfactory recoveries against diminishing returns with additional extraction steps. Based on this, we extracted the 2007 soils with four MTBE extractions in sequence, which we pooled for analysis, followed by an ACN extraction in accordance with the procedure described in our earlier paper (*11*). For the 2009 surface-soil samples we extracted the PFAs and FTOHs from separate aliquots drawn from each sample. For the PFAs, we used a modification of an ACN/H_2O extraction we reported upon earlier (*10*). Based upon exploratory efforts with a few sludge-applied samples from our 2007 survey, we deviated from our published ACN/H_2O extraction method for uncontaminated soils (*10*) by extracting these sludge-applied soils four times with 60/40 ACN/H_2O, which we pooled for analysis, but otherwise following our published method (*10*). Although we modified our extractions of these surface-soil samples as described above to accommodate their PFA-contaminated nature, we retained all other practices from our published methods (*10, 11*) including (i) spiking samples prior to extraction with $^{13}C_8$–PFOA as a recovery internal standard; (ii) subjecting extracts to ion-pairing cleanup to decrease analytical noise from natural organic matter that normally is concentrated in surface soils; (iii) reconstituting extracts in 60/40 ACN/H_2O with a suite of mass-labeled PFAs (Table SI3) present at 84 pg/g as matrix

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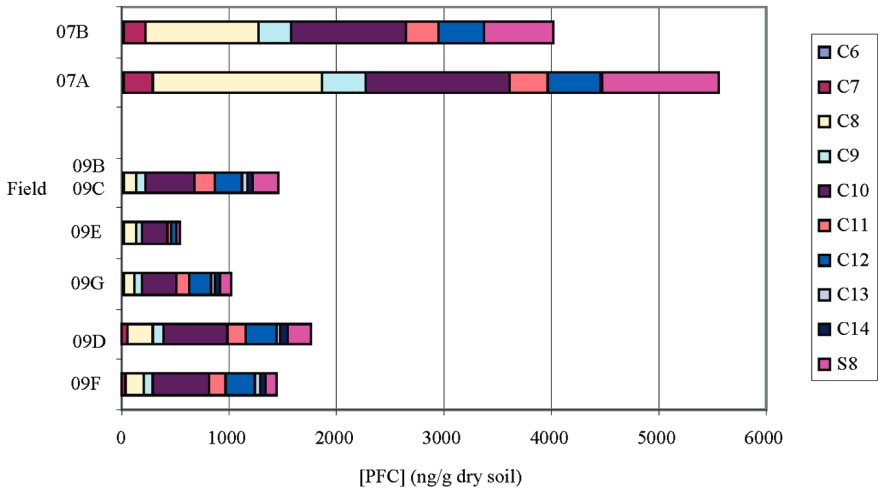

FIGURE 2. Geometric-mean surface-soil concentrations of analyzed PFAs within sampled fields. Results for the top two fields, 07A and 07B, are from the 2007 sampling campaign (n = 4 for 07B, n = 3 for 07A). The lower five fields are from the 2009 sampling campaign; fields 09B and 09C are contiguous and grouped together for this figure because they have similar sludge-application histories and only 3 samples between them (n = 5 for all other 09 fields).

internal standards; and (iv) running procedural blanks in which the extraction process was carried out on otherwise-empty extraction tubes. Additionally, we fortified selected samples from the 2009 campaign as a check of our analyte identification and quantitation.

Upon extraction of the 2009 samples, we discovered that all the subsurface soils exhibited poor returns of our mass-labeled recovery standard, $^{13}C_8$−PFOA, in contrast to satisfactory recoveries for all the surface soils. With exploration, we discovered that the relatively clay-rich subsurface samples tended to cohere into poorly permeable pellets when shaken on the Eberbach shaker table. When we performed the extraction again on the subsurface samples, replacing the shaker-table step with end-over-end rotation on a Labquake rotisserie, the subsurface soils did not pelletize and the $^{13}C_8$−PFOA recoveries fell in the satisfactory range as reported in the Results section. Because the subsurface soils were relatively low in natural organic matter, we found we could exclude the ion-pairing cleanup step on these samples with no deleterious effect.

Liquid Chromatograph, Tandem Mass-Spectrometer Analyses. Acetonitrile/water extracts were analyzed on a Waters Acquity ultraperformance liquid chromatograph (UPLC) interfaced with a Waters Quattro Premier XE tandem mass spectrometer operated in negative electrospray-ionization mode. Analytical methods are detailed in the Supporting Information along with an example of analytical results for an extract of a sludge-applied surface soil (Figure SI2).

Results

Data-Quality Metrics. In the Supporting Information, we report quality data reflecting on the field aspects of this study including (1) blanks and reference soil taken to the fields; (2) background-field samples; and (3) duplicate samples collected in the field. There were no anomalies among these metrics, except for the subsurface samples from the background fields (SI). These background subsurface samples returned detections for C6, C7, C8, and PFOS of about 4 orders of magnitude greater than their corresponding surface samples suggesting the possibility of low-level contamination of the subsurface sampling equipment for these analytes. For C6, C7, and C8, these detections still were an order of magnitude less than the detections in the sludge-applied fields, but PFOS was present in the background subsurface sample at about the same level as for the sludge-applied subsurface samples.

Quality data reflecting laboratory aspects of this study include (1) method blanks in which the extraction procedure was carried out in otherwise-empty tubes; (2) standard-curve back prediction; (3) recovery internal standards; and (4) standard additions to selected samples. All of these metrics indicate that the data in this study are of high quality (SI).

Results of Sampling in Sludge-Applied Fields. Analytical results for the samples from sludge-applied fields are tabulated in Tables SI9 for the 2007 survey and SI10 for the 2009 survey, and the average results for each field are depicted in Figure 2. For the 2007 survey, in fields 07A and 07B, the mass concentrations of analyzed PFAs sum to about 4−6 μg/g dry soil (Figure 2). In contrast, for the fields sampled in 2009, except for field 09H, mass concentrations of analyzed PFAs sum to only about 0.5−2 μg/g (Figure 2). Field 09H, which received only one sludge application in the distant past, had even lower PFAs, summing to <10 ng/g (Table SI10). Surface soils were sampled twice in each survey for one field, field B; while the number of samples is small, these data also show lower values in 2009 than 2007 (Figure SI3).

Considering all the data in whole, the dominant analyzed PFAs generally include PFDA (C10), PFOA (C8), and PFOS (S8), followed by PFDoA (C12), then PFUnA (C11), and PFNA (C9) (Figure 2). With the exception of PFOS, the analyzed perfluorosulfonates mostly were not detected. None of the unsaturated fluorotelomer acids were detected in either the 2007 or the 2009 survey. For the 2007 survey, the maximum analyzed concentrations (ng/g) of these dominant species were [C10] = 2100, [C8] = 2500, [S8] = 1400, [C12] = 1200, [C11] = 690, and [C9] = 650 (Table SI9). For the 2009 survey, however, the maximum analyzed concentrations (ng/g) of these dominant species were lower: [C10] = 140, [C8] = 320, [S8] = 410, [C12] = 530, [C11] = 310, and [C9] = 140 (Table SI10).

Discussion

These analytical results document that the majority of the Decatur soils in the sludge-application areas have concentrations of numerous PFAs well above background levels. Here we examine these data for patterns with respect to time, space, and precursors.

Sources of Variation in the Data: Sludge-Application Rate and Time Since Application. A simple visual-scan comparison of the 2007 and 2009 surface-soil data (Tables SI9 and SI10) reveals large general differences in PFA levels

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TABLE 1. First-Order Disappearance Constants and Half-Lives Modeled from Surface-Soil Data

	PFA F statistics[a]		disappearance rate constant, half life			
	sludge app. rate	time since app.	supported[b]		unsupported[c]	
PFA homologue length (C no.)			k (yr^{-1})	$T_{1/2}$ (yr)	k (yr^{-1})	$T_{1/2}$ (yr)
6	**12.26**	**31.56**	1.04 ± 0.32	0.7		
7	**29.16**	**70.00**	0.81 ± 0.25	0.9		
8	**23.83**	**64.09**	0.71 ± 0.30	1.0	0.78	0.89
9	**21.72**	**26.96**	0.44 ± 0.25	1.6		
10	**19.86**	**14.76**	0.37 ± 0.14	1.9	0.53	1.31
11	**36.34**	*4.48*	0.25 ± 0.21	2.7		
12	**28.56**	2.57				
13	**48.01**	1.84				
14	**20.35**	1.17				
8 (PFOS)	**73.50**	**26.97**	0.57 ± 0.15	1.2		
Crit. F (0.05)	*4.26*	*4.21*				
Crit. F (0.01)	**7.82**	**7.68**				

[a] F statistics from analysis of variance to test whether variation among sample (n = 31) sludge application rates (7 application rates) or a linear-functional model through time (4 time increments) explains a significant component of variation relative to among samples sharing a common sludge-application rate or time since sludge application. Bolded F values are significant at p = 0.01 and italicized values are significant at p = 0.05. See text for details. [b] Supported values characterize disappearance rates of PFAs that likely are being generated by degradation of their precursors, e.g., sec-FTOHs. [c] Unsupported values are estimates of disappearance rates in the absence of being generated by precursors. See text for details.

between the two surveys, with analytes being generally higher in the 2007 survey than the 2009. There are numerous possible causes for these differences including variation of PFA concentrations between batches of sludge applied to the fields, variation in sludge-application rates between fields, elapsed time between sludge application to the fields and soil sampling, and variation of soil physical or chemical properties among fields.

Evaluation of the contribution of temporal variation in sludge [PFA]s to data set variance is limited because we have analyses of only a few Decatur sludge samples (Figure SI1); however, all the sampled fields received sludge during the years in which the anomalously high sludge [PFOA] values were recorded, specifically 2002 through 2006 (SI discussion, Figure SI1 and Table SI1).

The effect of "sludge-application rate" and "elapsed time between sludge application and soil sampling" on the data variance can be evaluated independently so long as these two variables are not correlated; Figure SI4 illustrates the absence of a statistically significant relationship between these variables, so the effect of each on soil [PFA]s can be evaluated. "Elapsed time between sludge application and soil sampling" might factor in data variance because increasing time offers the opportunity for numerous processes to act on the PFAs in the sludge-applied soils, potentially including: (1) uptake into plants; (2) erosive overland flow with precipitation events; (3) leaching through the soil column; (4) ingrowth from FTOH, and perhaps higher-order, precursors; and (5) degradation. If one or more of these processes controls a large part of the total variation in these data, then plots of PFA concentration vs time elapsed between sludge application and soil sampling might exhibit temporal trends. Homologous [PFCA]s are plotted in Figure SI5, and [PFOS] are plotted in Figure SI6, as a function of both "sludge-application rate" and "elapsed time between sludge application and soil sampling". Because these data are not bivariate-normally distributed, they cannot be statistically evaluated with simple correlation coefficients so we used an analysis of variance for unequal repeated measures (*12*). Table 1 presents a statistical summary of these plots. Figure SI5 and Table 1 reveal an interesting pattern wherein surface-soil [PFCA]s have a stronger statistical relationship (i.e., greater F statistic) with (1) sludge-application rate than elapsed time for the long-chain homologues; and (2) elapsed time between sludge application and soil sampling than for sludge-application rate for the short-chain homologues. Among possible causes for this pattern is that environmental mobility decreases and/or recalcitrance increases with increasing homologue length.

Given these data as well as those of our accompanying paper (*8*), we can inspect the data for evidence of whether leaching through the soil column and/or ingrowth from precursors might play a role in the temporal variability of the short-chain PFAs observed in these soils.

Depth Profiles. Soil samples were collected from up to three depths, i.e., the surface, ~50 cm, and ~150 cm, at each of three locations in two contiguous sludge-applied fields, 09B and 09C (Table SI10) and the background field, 09Bgd (Table SI6). Numerous PFAs were detected in the subsurface samples at all three sludge-applied sample locations (Table SI10), albeit, generally at lower concentrations in the deep soils than at the surface (Figure 3). When the concentration ratios of the mid-depth (~50 cm) to the surface and deep (~150 cm) to the surface are plotted as a function of chain length, a regular pattern emerges for all three sample locations wherein the subsurface/shallow ratios increase with decreasing chain length (Figure 4a and b). This pattern suggests that at least part of the reason that short-chains exhibit statistical decreases through time but long-chains do not (Table 1; Figure SI5) is preferential leaching of the short-chain congeners.

[PFCA] as a Function of [FTOH]. Wang et al. (*13*) has shown the 7:2 *sec*-fluorotelomer alcohol (7:2*s*FTOH; $CF_3(CF_2)_6CH(CH_3)OH$) to be a degradation product of the 8:2 primary fluorotelomer alcohol (8:2*n*FTOH; $CF_3(CF_2)_7$-CH_2CH_2OH) and proposed the degradation sequence of 8:2*n*FTOH → 8:2 fluorotelomer aldehyde → 8:2 fluorotelomer acid → 8:2 fluorotelomer unsaturated acid → 7:2*s*FTOH → PFOA. Following this logic, Ellington et al. (*9*), detected homologues of 7:2*s*FTOH, i.e., 9:2*s*, 11:2*s*, and 13:2*s*FTOHs, in a limited survey of Decatur sludge-amended soils. In our accompanying paper (*8*), we show a statistically significant functional dependence of the *s*-FTOHs on their *n*-FTOH precursors, suggesting that the longevity of the *s*-FTOHs is supported by degradation of their *n*-FTOH precursors. In Figure 5, we plot [PFCAs] as a function of both their *n*- and *s*-FTOHs. The PFCAs are significantly related to their *s*-FTOH precursors for PFOA, PFDA, and PFDoA, but not PFTeA. In

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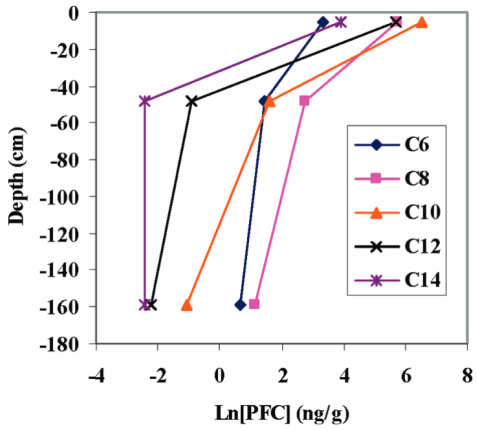

FIGURE 3. [PFA] (ng/g dry soil) vs depth for samples 09B3-1, 09B3-2, And 09B3-3. [PFA]s are transformed to the natural logarithms to facilitate depicting the wide concentration ranges among homologues and depths; nondetects are depicted at their limits of quantitation, also to ease depiction. With a few exceptions (Table SI10), analyte concentrations generally decrease or remain about the same with increasing depth. While only even-numbered PFCAs are depicted here, this relationship generally holds for odd-numbered PFCAs as well as PFOS (Table SI10).

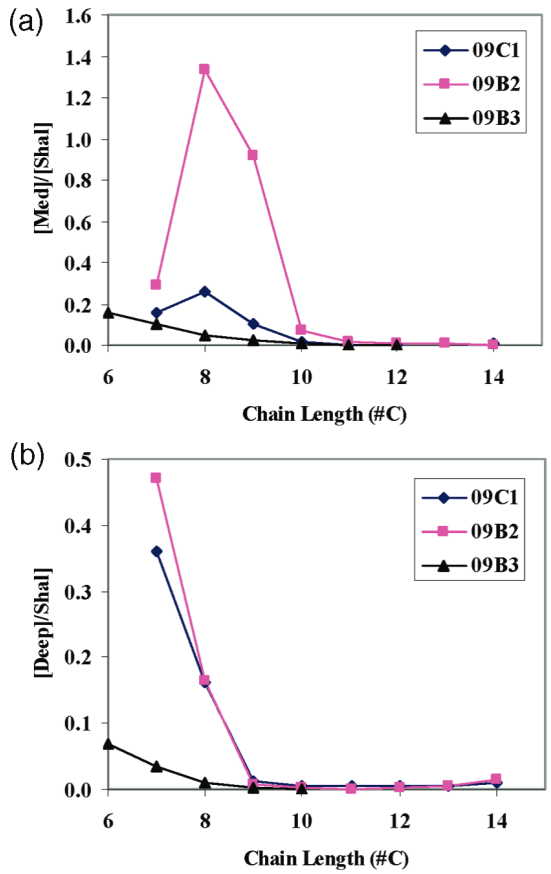

FIGURE 4. (a) [PFA] ratio (mid-depth/surface) at three sample locations. (b) [PFA] ratio (deep/shallow) at three sample locations. See text for discussion.

contrast, the PFCAs are correlated to their more remotely related *n*-FTOH precursors only for PFOA and PFTeA. The α oxidation of *n*-FTOHs to form odd-numbered PFCAs also has been identified as a minor biotransformation pathway (*14*); for this process, only 8:2*n*FTOH → PFNA exhibits a statistically significant relationship (Figure SI7). Taken as a group, these observations of significant relationships between some PFCAs and FTOHs supports the idea that part of their persistence in the sludge-applied soils is due to ingrowth from FTOH degradation.

Disappearance Half-Lives. Based on the observations presented above, at least part of the declines in short-chain [PFA]s through time (Figures SI5 and SI6) reflect a balance between losses from leaching (Figure 3), and perhaps other depletion processes, that are offset by ingrowth from *s*-FTOHs (Figure 5). While these processes commonly are modeled as first-order in the reactant (*15*), other more complicated factors might be at play as well. In the absence of evidence supporting such scenarios, however, we have modeled these losses as simple first-order. Nevertheless, it is important to realize that this modeling approach could significantly understate the persistence of these compounds in soil should more complex processes be active.

Supported Disappearance Half-Lives. The simplest first-order characterization of [PFA] loss through time reflects the effect of *support* by ingrowth from the chemical precursors, *s*-FTOHs, and the slope of linear regressions in ln[PFA]−time space yields estimates of supported first-order disappearance constants (k^s_{PFA}):

$$\ln[PFA] = \ln[PFA]_0 - k^s_{PFA}t \quad (1)$$

where $[PFA]_0$ equates to a statistical estimate of the PFA initial concentration when the sludge just has been applied. In turn, supported disappearance half-lives ($T^s_{1/2}$) for these compounds in the fields that have received applications of sludge containing these compounds can be calculated according to

$$T^s_{1/2} = \frac{\ln 0.5}{-k^s_{PFA}} \quad (2)$$

Supported first-order disappearance constants and half-lives of our analytes are tabulated in Table 1. These values of supported disappearance half-lives generally fall in the scale of years and increase with increasing chain length (Figure 6). This observation of half-life increasing with chain length is consistent with the observation that the ratio of subsurface- to surface-soil PFAs generally decreases with increasing chain length (Figure 4), possibly reflecting a stronger sorption affinity for soil of the long-chained homologues than the short-chains or a similar phenomenon.

The absence of unsaturated fluorotelomer acids in any sample (Tables SI9 and SI10) is noteworthy given their role as intermediates in the degradation of *n*-FTOHs to *sec*-FTOHs (*13*), both of which were in most sludge-applied surface-soil samples of our study (*8*). Assuming the unsaturated fluorotelomer acids are intermediates in the sludge-applied soils of this study, these nondetections suggest their disappearance half-lives are less than those we calculate for the perfluorocarboxylic acids (Table 1) or the FTOHs (*8*). Estimating the upper limit on half-lives of these acids using our detection limits (Table SI10), and eq 1 and the surface-soil 8:2*n*FTOH data of our accompanying paper (*8*), we estimate the disappearance half-life for the 8:2 unsaturated acid is <0.3 yr and the 10:2 unsaturated acid is <0.2 yr.

Estimated Unsupported Disappearance Half-Lives. Because supported PFA-fate properties evidently include the effect of ongoing ingrowth from degradation of *s*-FTOHs (Figure 5), these values (Table 1) likely overstate the persistence of these compounds when they are present in soil without any precursors. The persistence in soil of these compounds, in the absence of precursors, can be estimated according to the following (see SI for derivation):

$$[PFA] = \frac{k^u_{sFTOH}[sFTOH](1 - e^{-k^u_{PFA}t})}{k^u_{PFA}} + [PFA]_0 e^{-k^u_{PFA}t} \quad (3)$$

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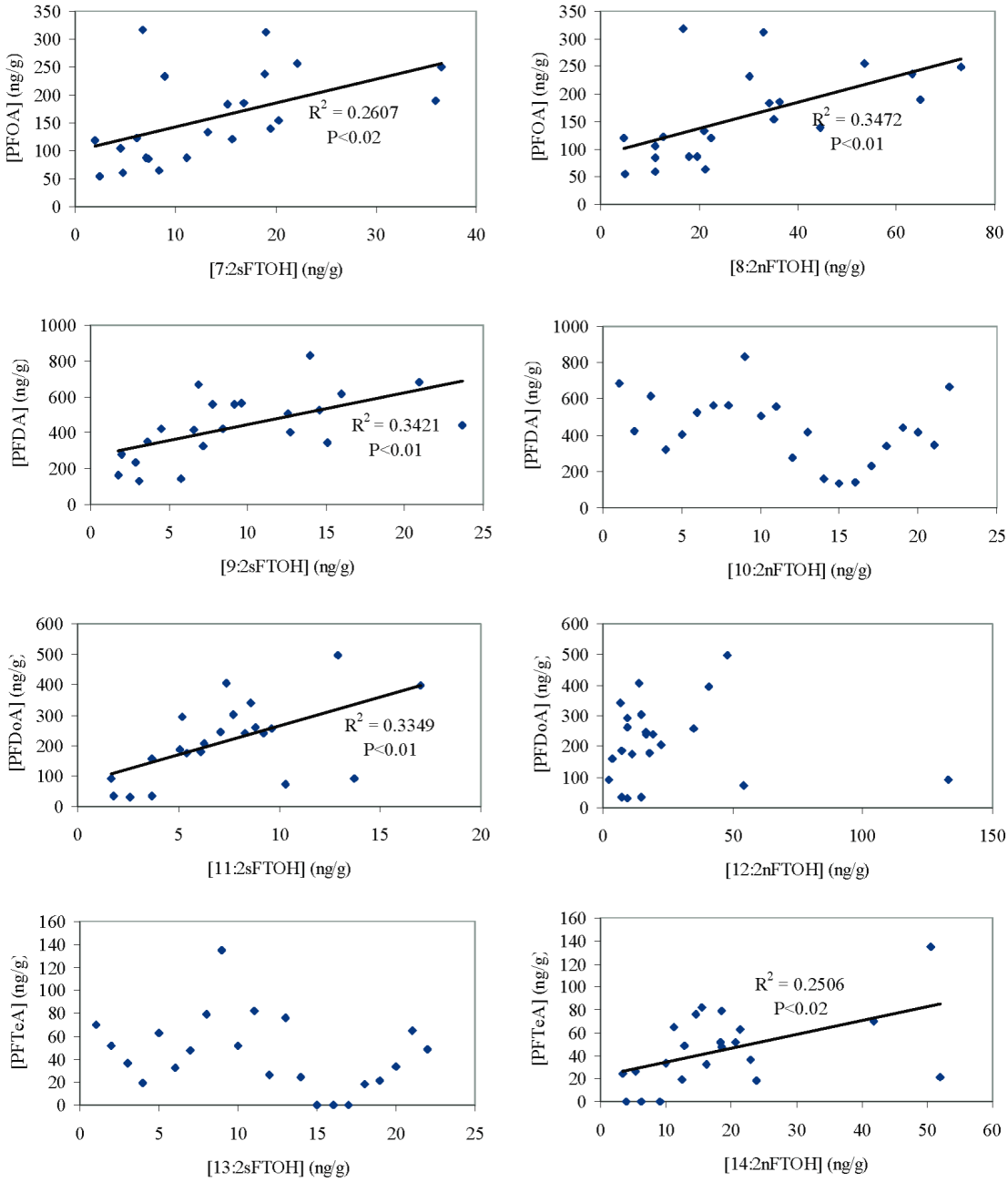

FIGURE 5. PFCAs in surface-soil samples (n = 23) as a function of FTOH precursors (ng/g dry soil). Acids generally are more strongly correlated with the *sec*-FTOHs than the *n*-FTOHs, presumably at least partly because the *s*-FTOHs are immediate precursors whereas the *n*-FTOHs are more remote precursors.

where k^u_{sFTOH} and k^u_{PFA} are the unsupported degradation constants of the PFA's precursor *sec*-FTOH and PFA, respectively. Equation 3 can be used to estimate the unsupported degradation constants of PFAs, given knowledge of the concentrations and unsupported degradation constant for the *s*-FTOH as reported in our accompanying paper (*8*), by taking the maximum [PFA] measured at 1.2 yr (Table SI1) to approximate $[PFA]_0$, and by minimizing the sums of squared errors between the estimated and observed values of [PFA]s as a function of k^u_{PFA} estimates. Estimates of unsupported degradation constants and half-lives are provided for PFOA and PFDA in Table 1. The estimated unsupported half-life for PFOA is 90% of the supported, and the unsupported half-life of PFDA is only 70% of its supported value.

Values derived from eq 3 are only as good as those of the input independent values. The values we used for unsup-

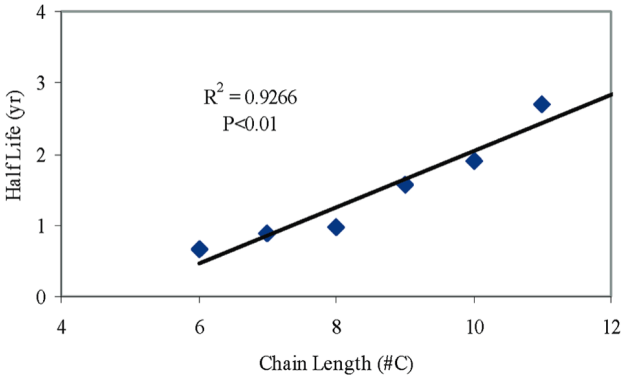

FIGURE 6. Calculated supported disappearance half-lives as a function of chain length (n = 5).

ported k^{u}_{sFTOH} were estimated from the concentrations of the *s*-FTOHs, their *n*-FTOH precursors, and calculated disappearance constants for the *n*-FTOHs (*8*). To the extent that the *n*-FTOHs were supported by precursor compounds, the resulting values for k^{u}_{sFTOH} and k^{u}_{PFA}, might be underestimated. In turn, the corresponding values for $T^{u}_{1/2}$ might be overestimates. We have no data on the presence or absence of *n*-FTOH precursor compounds, but polyfluoroalkylphosphoric acids (PAPs) (*16*) and fluorotelomer-based polymers (*11*) both are potential sludge constituents that have been shown to degrade to *n*-FTOHs. Considering all of this, our estimates of unsupported disappearance half-lives for PFAs in soils might best be considered upper-limiting values.

Perspective. In the sludge-applied surface soils we studied, PFA analytes summed to as high as ~5 μg/g and short-chain concentrations generally fell with increasing time since last sludge application. At least part of this decrease is from leaching losses to deeper soil. This loss evidently is offset by degradation of precursor compounds to form these analytes. Modeling the net losses of these PFA analytes from the surface soil as an analyte-first-order process, we get half-lives ranging from 1 to 3 years depending on chain length. These rough field-disappearance half-life estimates contribute to development of a useful perspective for environmental persistence of these compounds when cleanup and other options are being considered.

The relevance of the soil [PFA] data we report here to the general practice of application of sludge to land is unclear because much of the sludge that was applied to the fields in this study had substantially higher concentrations of PFOA, and likely other PFAs, than other sludges that have been reported in peer-reviewed literature (Figure SI1 and accompanying discussion).

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Supporting Information Available

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Field study on the uptake and translocation of perfluoroalkyl acids (PFAAs) by wheat (*Triticum aestivum* L.) grown in biosolids-amended soils

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ABSTRACT

Field experiments were performed to evaluate the uptake and translocation of perfluoroalkyl acids (PFAAs) in wheat (*Triticum aestivum* L.) grown in soils amended with biosolids at different rates. Nine perfluorocarboxylic acids (PFCAs) and three perfluorosulfonic acids (PFSAs) were detected in the soils and wheat tissues. Total concentrations of PFAAs in the soils and wheat root, straw, husk and grain increased with increasing application of biosolids. PFCA concentrations in grain increased logarithmically with increasing PFCA concentrations in soils ($P < 0.01$) while PFSAs in grain were correlated linearly with PFSA concentrations in soils ($P < 0.01$), indicating that PFCAs and PFSAs may have different transport pathways from soil to grain. While no significant correlation was found between the root concentration factors (C_{root}/C_{soil}) and PFAA carbon chain length, the transfer factors from roots to straws (C_{straw}/C_{root}) and from straws to grains (C_{grain}/C_{straw}) correlated negatively with PFAA carbon chain length ($P < 0.01$).
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1. Introduction

Land application of biosolids (treated sewage sludges) from municipal, agricultural and industrial waste water treatment plants is becoming an increasingly important global practice. It is considered a useful approach for the final disposition and an important recycling and resource recovery option (Clarke and Smith, 2011; Farrell and Jones, 2009). Biosolids constitute a valuable source of essential nutrients for agricultural cultivation. Organic matter from biosolids improves physical and chemical properties of soil. However this practice possesses potential risks associated with contaminant accumulation in surface soils. Previous studies focus on the phytoavailability and toxicity of metals in soils extensively in order to conduct risk assessment of biosolids application (Li et al., 2012; McLaughlin et al., 2006). Besides metals, biosolids are known to contain significant levels of organic contaminants. Particular attention has been given to the selected priority groups of persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and chlorinated dioxins/furans (PCDD/Fs) (Clarke and Smith, 2011; Farrell and Jones, 2009; Harrison et al., 2006). These POPs are highly persistent in the environment, leading to an accumulation in the terrestrial environment.

Perfluoroalkyl acids (PFAAs) have been employed in materials such as wetting agents, lubricants, corrosion inhibitors, stain-resistant treatments, and foam fire extinguishers. They have received great scientific concerns due to their wide occurrence in atmosphere (Li et al., 2011; Ahrens et al., 2011), soil (Yoo et al., 2010), surface water (Eschauzier et al., 2010), sediment (Kwadijk et al., 2010) and biota (Houde et al., 2011), and due to their toxicity as well (Olsen et al., 2009). One of the prevalent PFAAs, perfluorooctane sulfonate (PFOS), is recognized as an emerging persistent organic pollutant (Stockholm Convention, 2009).

Sewage sludge is widely recognized as a major sink of some PFAAs (Sun et al., 2011; Guo et al., 2010; Higgins et al., 2005). Higgins et al. (2005) reported that the concentrations of PFAAs in domestic sludge ranged from 5 to 152 ng/g for total perfluorocarboxylates and 55–3370 ng/g for total perfluoroalkyl sulfonyl-based chemicals. The use of biosolids as fertilizers in agriculture may present an exposure route of PFAAs into the soils. Sepulvado et al. (2011) found that concentrations of PFOS ranged 2–483 ng/g in biosolids-amended soils. In Decatur, Alabama, PFAAs

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and their precursors were notably accumulated in soils as a result of land use of industrially-contaminated biosolids (Yoo et al., 2010; Washington et al., 2010). Clarke and Smith (2011) pointed out that PFAAs are one of the main priority groups of compounds in biosolids requiring additional research.

Perfluoroalkyl acids in contaminated soils may be transferred to the food chain by plant uptake and exert a potential health risk. It is therefore necessary to understand the behavior of PFAAs in the soil-plant system as a result of biosolids application. So far very few studies have dealt with this issue in the soil-plant system. Pot studies by Zhao et al. (2013), Felizeter et al. (2012), Lechner and Knapp (2011) and Stahl et al. (2009) showed that PFAAs could be taken up, for example, by maize, oats, wheat, potatoes, lettuce, cucumbers and carrots. Plant accumulation of PFAAs was dose-dependent and varied with plant species. However, most of these studies only focused on two PFAAs, perfluorooctanoic acid (PFOA) and PFOS in pot experiments. The physical properties and molecular structures of different PFAA congeners may have different effects on their accumulation in plants. Moreover, greenhouse pot experiments and artificially polluted soils do not present the actual behavior of weathered PFAAs in field soils. Stahl et al. (2013) described a long-term lysimeter experiment that demonstrated the carry-over of PFAAs from spiked soil to plant under field conditions. Evidence for accumulation of PFAA congeners and fluorotelomer alcohols in the above-ground part of grasses grown in sludge contaminated soils was provided by Yoo et al. (2011). However, the unknown distribution pattern of PFAAs in grasses limits the understanding of PFAA congener uptake and translocation mechanisms in plant.

The aim of this study was to investigate the uptake of PFAAs from biosolids-applied field soils by wheat (*Triticum aestivum* L.) roots and their translocation to wheat above-ground tissues. Wheat was chosen as a model plant because it is widely cultivated and is an important dietary staple. PFAAs-contaminated wheat grains may present a threat to human health. Also, wheat straw is widely used as cattle feed and may pose another pathway for PFAAs to enter into the food chain. To our knowledge, this is the first report on the enrichment and distribution patterns of PFAAs in wheat grown in biosolids-amended agricultural fields.

2. Materials and methods

2.1. Materials

A standard solution of PFAAs containing eleven perfluorocarboxylic acids (PFCAs) and five perfluorosulfonic acids (PFSAs), and solutions of $^{13}C_4$-PFOA and $^{13}C_4$-PFOS were purchased from Wellington Laboratories (Guelph, Canada) and were used as-received. HPLC-grade methyl tert-butyl ether (MTBE, >99.98%), methanol (MeOH, >99.9%), dichloromethane (DCM, >99.9%) and acetonitrile (>99.9%) were purchased from Fisher Chemical (Firlawn, NJ, USA). Tetrabutylammonium hydrogen sulfate (TBAHS, >99%), sodium carbonate (>99%), sodium hydroxide (>95%), and ammonium acetate (≥99%) were purchased from Sigma Aldrich Chemical (Milwaukee, WI, USA). Milli-Q water was used throughout the experimental work.

2.2. Sample collection

Soils and plants were collected from Research Stations of Fertility and Fertilizer Effects in Fluvo-Aquic Soil in Changping, Beijing (40° 13′ N, 116° 15′ E). Air-dried biosolids from Beijing Sludge Disposal Plant have been applied as the basic fertilizer before wheat sowing (November) at the station once a year since 2006 (Li et al., 2012). There were five biosolids application rates in soils with the wheat-maize cropping system (Control and Plots 1–4, Table 1). Each application rate had three replications. The 15 plots (5 m × 8 m each plot) were arranged in a randomized complete block design. Soil and wheat plants were collected after wheat harvest in June, 2012. Soil samples of the plots were taken at 0–20 cm depth for chemical analysis. Five soil samples were taken from each plot and mixed into one composite sample. Visible stones and roots were taken away from soil samples. Ten wheat plants from each replication were randomly sampled. Each plant sample was divided into roots, straws, husks and grains. The subsamples of wheat were washed carefully with tap water and distilled water sequentially. The plant and soil samples were freeze-dried at the temperature of −50 °C for 48 h in a lyophilizer (FD-1, Beijing Boyikang Instrument Ltd, Beijing, China), ground, and weighed. The dried samples were then stored separately at −20 °C before analysis.

The soil samples were passed through a 2-mm sieve. Total nitrogen (TN), phosphorus (TP), and potassium (TK) in the soils were determined (Li et al., 2012). Soil pH, soil organic matter (SOM), and heavy metal concentrations, including Zn, Cu, Cr, Ni, Cd and Pb, were measured according to the methods of Fang et al. (2007). The chemical properties of soils are presented in Table 1. Root lipid content was determined following the same procedure that we previously employed (Huang et al., 2010), which was detailed in the Supplementary materials.

2.3. Selection of extractants for PFAAs in soil and plant samples

Studies have shown MTBE-NaOH (Felizeter et al., 2012) and MeOH-DCM (Yoo et al., 2010) to be efficient for the extraction of PFAAs from plant tissues. To evaluate the capability of different solvents, PFCAs and PFSAs in soils and wheat roots and straws collected from Plot 4 were extracted with MTBE-NaOH and MeOH-DCM according to the methods reported with some modifications, and cleaned up according to the method of Shi et al. (2012). Before extraction, recovery internal standards, 2 ng of $^{13}C_4$-PFOA and 2 ng of $^{13}C_4$-PFOS were spiked into 1 g soil or wheat tissues and aged for 24 h. The two extraction methods were detailed in the Supplementary materials. There were four replicates per treatment.

2.4. LC/MS/MS analysis and quantitation

An ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) was used to determine the concentrations of PFAAs. The UPLC system (ACQUITY, Waters Corp., USA) was equipped with a UPLC BEH C18 column (2.1 × 150 mm, 1.7 μm, Waters Corp., USA) that was maintained at 40 °C in column oven. The Quattro Premier XE tandem quadrupole mass spectrometer (Waters Corp., USA) was equipped with an electrospray ionization source. The mixture of acetonitrile/10 mmol/L ammonium acetate (50/50, v/v) was used as mobile phase at a flow rate of 0.2 mL/min. The MS/MS was operated in electrospray negative ionization mode. The collision energies, cone voltages, and MS/MS parameters for the instrument were optimized for individual analytes (Table S1).

2.5. Quality assurance and quality control measures

Quality control was done by regular analyses of procedural blanks, blind duplicate samples, and random injection of solvent blanks and standards. Uncontaminated soil and plant samples without biosolids applied were collected 5 miles away from the station. Matrix calibration curves using spiked uncontaminated

Table 1
Biosolids amendment rates and the chemical properties of the soils.

	Control	Plot 1	Plot 2	Plot 3	Plot 4
Biosolids applied (dry weight, t ha^{-1} y^{-1})	0	4.5	9.0	18.0	36.0
pH (Soil:$CaCl_2$ = 1:5)	8.11 (0.05)[a]	8.21 (0.06)	8.43 (0.10)	8.15 (0.08)	8.20 (0.10)
Soil Organic matter (%)	0.78 (0.04)	1.42 (0.03)	2.29 (0.06)	2.53 (0.08)	2.76 (0.07)
Total N (g kg^{-1})	0.83 (0.04)	0.98 (0.08)	1.92 (0.15)	2.30 (0.17)	2.64 (0.21)
Total P (g kg^{-1})	0.68 (0.08)	0.79 (0.06)	0.98 (0.10)	1.36 (0.12)	2.61 (0.44)
Total K (g kg^{-1})	23.7 (1.5)	25.4 (2.1)	24.6 (2.4)	25.6(2.0)	28.5 (0.16)
Zn (mg kg^{-1})	43.9 (3.3)	48.6 (3.1)	58.7 (3.4)	64.6 (4.8)	78.6 (4.4)
Cu (mg kg^{-1})	18.4 (0.9)	19.6 (1.9)	20.5 (1.6)	21.5(1.3)	21.9 (0.8)
Cr (mg kg^{-1})	55.6 (1.8)	58.8 (4.2)	54.6 (4.8)	59.4 (2.3)	59.7 (2.1)
Ni (mg kg^{-1})	33.6 (2.8)	34.6 (1.9)	33.8 (2.9)	34.8 (1.9)	36.7 (2.9)
Cd (mg kg^{-1})	0.114 (0.010)	0.111 (0.009)	0.113 (0.005)	0.112 (0.004)	0.117 (0.004)
Pb (mg kg^{-1})	16.7 (1.8)	17.2 (1.9)	17.8 (0.9)	18.8 (0.8)	19.8 (0.7)

[a] Standard deviation (σ).

samples that were extracted in analogy to the samples were applied for quantification. An eighteen-point calibration line was used for quantification. The fitted lines had r^2 values of at least 0.99 for all analytes. The method-detection limits (MDLs) were defined as the lowest concentration that could be distinguished from a sample containing no analyte and calculated with the mean peak area plus three standard deviations, MDLs = $y_0 + 3\sigma(y_0$, average of measured values for the blank matrix; σ, standard deviation of the measured values for the blank matrix). The limit of quantitation (LOQ) was calculated with the formula LOQ = $y_0 + 10\sigma$ (Lechner and Knapp, 2011). MDLs and LOQs were measured for each matrix on replicate analyses ($n = 6$) of blank samples (Table S1). Mean sample concentrations less than the calculated MDLs or LOQs were reported as <MDL and <LOQ, respectively. For the calculation of total concentrations, PFAA values <MDL were treated as zero and <LOQ values were assigned 1/2 LOQ. PFAA values <LOQ were not involved in the modeling. All samples were extracted and injected in triplicate. The accuracy of the determination was assessed by testing the recoveries of $^{13}C_4$-PFOA and $^{13}C_4$-PFOS from the spiked blank matrix in comparison to matrix-matched standards. The recoveries of $^{13}C_4$-PFOA and $^{13}C_4$-PFOS were found to be 91–108% with standard deviations ranging from 2 to 7% for all soil and plant samples. Because these two internal standards may not represent all PFAAs studied, the recoveries of PFAAs with different carbon chain length were determined by spiking a certain amount of nonlabeled PFAA standards in uncontaminated samples using the chosen extractant, i.e., MTBE-NaOH. The recoveries of PFAAs were 76–105, 73–110 and 76–105% for soil, root and straw, respectively (Table S2). The only exception is PFBA, in which recoveries were much lower (38–47%) than other PFAAs. Similar relatively low recoveries of PFBA were reported by Felizeter et al. (2012). Thus, it is assumed that the concentrations of PFBA may be underestimated when only two isotope-labeled internal standards were used. The results of PFBA were included due to its consistent recoveries.

2.6. Data analysis

All statistical analyses were conducted with the software SPSS 11.5 for Windows (SPSS Inc., Chicago, IL). One-way ANOVA was used to assess the significance of the difference between groups, and linear and nonlinear regression analyses were conducted by the least and least-squares methods, respectively. Statements of significant differences are based on $P < 0.05$.

3. Results and discussion

3.1. Section of extractant for PFAAs

The results of soil and plant tissue powder extraction by two solvents, MTBE-NaOH and MeOH-DCM are shown in Fig. S1. The extraction recoveries of $^{13}C_4$-PFOA and $^{13}C_4$-PFOS were 93–102% and 94–103% for MTBE-NaOH and MeOH-DCM, respectively (data not shown). No significant difference of recoveries between soils and plant tissues was found. The extractabilities of MTBE-NaOH were 1.4–2.0 times those of MeOH-DCM for short carbon chain PFCAs (C4–C6). No significant difference between the two extractants for most PFCAs (C7–C11) and PFSAs (C4–C8) was found. The extractabilities of MeOH-DCM were about 1.4 times those of MTBE-NaOH for PFTeA. Total concentrations of PFAAs extracted by MTBE-NaOH were higher than those of MeOH-DCM. Thus MTBE-NaOH was used in the following study.

3.2. Concentrations of PFAAs in soils

Concentrations of all PFAAs in the biosolids-amended soils are presented in Table 2. Nine PFCAs and three PFSAs have been detected in the soils, which ranged from 18.0 to 113 ng/g for PFCAs and from 23.4 to 107 ng/g for PFSAs, respectively. PFDoA, PFTrA, PFHpS and PFDS have not been found in soil samples. The total concentrations of PFAAs in biosolids-amended soils (Plots 1–4) are in the range of 41.4–220 ng/g. Only low contents of PFOA (0.6 ng/g) and PFOS (0.6 ng/g) were detected in the control soil, accounting for <5% of the corresponding PFAA concentrations in Plot 1 with the lowest biosolids application rate. Total PFAA concentrations in the soils positively correlated with the amount of biosolids applied ($P < 0.01$, Fig. S2), suggesting that biosolids application is the main source of PFAAs in the soils. Based on the Chinese sewage sludge regulation (GB4284-84) (Department of Rural and Urban Construction and Environmental Protection, China, 1984), a maximum level of 30 tons (dry matter) per hectare per year was tolerated, accumulation of PFAAs in soils would be more than 200 ng/g after seven-year application at this maximum level according to the regression line.

3.3. Distribution patterns of PFAAs in wheat

PFAAs have been detected in different parts of wheat: roots, straws, husks and grains, indicating that wheat has the ability not only to take up PFAAs from soils by roots, but also to translocate PFAAs to the above-ground parts (Table 3). Nine PFCAs and three PFSAs have been quantified in the roots and straws, but only seven PFCAs and two PFSAs have been detected quantitatively in the husks and grains. PFBS has not been detected in husks and grains, while the concentrations of PFUnA and PFTeA in husks and grains are below the LOQs. The total concentrations of PFAAs in roots, straws, husks and grains are in the range of 140–472, 36.2–178, 6.15–37.8 and 7.32–35.6 ng/g, respectively. The distribution of PFAAs followed the order of roots > straws > grains ≥ husks. This order was also verified by another study (Stahl et al., 2009).

Organic contaminants reach aerial plant organs in two ways: from the air and with the transpiration stream (Huang et al., 2010; Tao et al., 2009). It is possible that PFAAs in the soils evaporate into the ambient air and enter plants via gaseous uptake, contributing to their accumulation in the above-ground part of wheat, because PFAAs can be detected in the atmosphere (Li et al., 2011; Ahrens

Table 2
Total PFAA concentrations in soils (ng/g dry weight).

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFTeA	PFBS	PFHxS	PFOS	ΣPFAAs[a]
Control													
Mean	<MDL	<MDL	<MDL	<MDL	0.61	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.61	1.22
SD					0.04							0.02	0.06
Plot 1													
Mean	1.19	<LOQ	5.43	1.21	4.33	2.01	<MDL	0.17	0.28	<MDL	13.0	10.4	41.4
SD	0.09		0.56	0.07	0.45	0.18		0.01	0.03		1.1	1.0	3.5
Plot 2													
Mean	1.52	6.68	10.2	1.81	12.6	3.36	0.70	0.76	0.37	<MDL	25.8	15.4	79.1
SD	0.15	0.63	1.3	0.15	2.3	0.12	0.05	0.04	0.03		2.1	1.2	8.1
Plot 3													
Mean	5.91	10.1	22.8	7.33	19.8	12.5	4.50	0.62	0.39	19.4	31.1	28.3	163
SD	0.32	0.5	1.5	0.74	2.1	1.3	0.47	0.05	0.04	2.0	2.5	2.5	14.0
Plot 4													
Mean	13.5	12.4	15.2	12.9	26.1	22.0	7.82	0.89	1.89	31.2	34.9	40.8	220
SD	1.3	0.9	1.3	1.2	0.4	2.1	0.80	0.09	0.22	1.7	2.9	2.9	15.8

[a] PFAA value <MDL was treated as zero and <LOQ was assigned as 1/2 LOQ.

Table 3
Distribution of PFAA concentrations in the different part of wheat (ng/g dry weight).

		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFTeA	PFBS	PFHxS	PFOS	ΣPFAAs[a]
Control														
Roots	Mean	<MDL	<MDL	<MDL	<MDL	1.09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.93	2.02
	SD					0.11							0.07	0.18
Straws	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
	SD													
Husks	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
	SD													
Grains	Mean	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
	SD													
Plot 1														
Roots	Mean	5.28	10.3	24.8	5.79	21.4	8.34	<MDL	0.88	1.05	<LOQ	35.8	16.8	140
	SD	0.47	1.0	1.8	0.41	2.3	0.77		0.02	0.12		2.1	0.3	
Straws	Mean	3.05	<LOQ	6.59	1.95	6.67	2.45	<MDL	<LOQ	<LOQ	<MDL	8.66	3.45	36.2
	SD	0.14		0.44	0.08	0.68	0.17					0.93	0.41	
Husks	Mean	0.96	<MDL	1.45	<MDL	1.33	<LOQ	<MDL	<MDL	<LOQ	<MDL	1.96	<LOQ	6.15
	SD	0.08		0.09		0.09						0.21		
Grains	Mean	1.09	<MDL	1.58	<MDL	1.01	0.51	<MDL	<MDL	<LOQ	<MDL	2.45	0.80	7.32
	SD	0.11		0.12		0.10	0.05					0.11	0.02	
Plot 2														
Roots	Mean	6.21	28.2	31.6	6.42	31.6	9.10	1.85	2.08	1.06	21.9	54.1	18.3	212
	SD	0.66	2.5	1.2	0.65	1.7	0.72	0.18	0.20	0.08	1.7	3.6	1.5	
Straws	Mean	3.78	12.6	12.8	2.95	9.63	3.91	0.45	0.42	0.30	<MDL	12.0	3.66	62.5
	SD	0.27	0.9	1.01	0.17	0.66	0.22	0.01	0.01	0.03		1.3	0.34	
Husks	Mean	1.30	<MDL	4.02	<MDL	1.18	0.55	<MDL	<MDL	<MDL	<MDL	3.78	<LOQ	11.3
	SD	0.07		0.24		0.14	0.04					0.19		
Grains	Mean	1.52	<MDL	3.59	<MDL	2.01	1.09	<MDL	<LOQ	<MDL	<MDL	3.42	0.95	12.6
	SD	0.11		0.05		0.21	0.09					0.23	0.09	
Plot 3														
Roots	Mean	14.6	34.7	60.2	17.7	38.4	35.6	9.62	2.51	1.10	32.0	65.6	37.5	350
	SD	1.2	4.0	3.4	1.3	3.1	3.2	0.66	0.26	0.12	1.2	5.4	3.6	
Straws	Mean	12.2	18.0	25.3	7.25	14.8	8.11	3.02	0.71	0.34	<LOQ	13.7	7.25	121
	SD	0.9	1.3	1.7	0.58	0.98	0.79	0.33	0.03	0.02		1.4	0.79	
Husks	Mean	3.10	<LOQ	6.88	0.99	2.56	3.08	<MDL	<LOQ	<MDL	<MDL	3.98	1.89	25.9
	SD	0.22		0.41	0.10	0.21	0.19					0.43	0.08	
Grains	Mean	4.39	4.74	6.21	1.61	2.64	2.22	0.51	<MDL	<LOQ	<MDL	3.92	1.72	26.7
	SD	0.33	0.25	0.41	0.16	0.21	0.19	0.05				0.23	0.08	
Plot 4														
Roots	Mean	36.5	44.6	43.0	34.6	45.1	62.9	15.6	2.86	3.91	59.6	67.6	55.3	472
	SD	3.1	3.8	4.6	2.7	4.1	5.3	1.7	0.31	0.30	4.1	5.6	5.1	
Straws	Mean	22.2	20.2	20.5	15.9	22.1	21.4	6.28	0.80	0.95	21.8	14.9	11.0	178
	SD	1.1	1.5	1.8	0.4	1.7	1.8	0.43	0.05	0.10	2.0	1.2	1.2	
Husks	Mean	5.77	6.26	6.51	2.59	4.19	4.72	1.41	<LOQ	<LOQ	<MDL	3.86	2.20	37.8
	SD	0.54	0.32	0.41	0.23	0.38	0.50	0.11				0.31	0.12	
Grains	Mean	6.49	6.58	5.02	3.33	2.90	3.05	0.95	<LOQ	<LOQ	<MDL	4.37	2.53	35.6
	SD	0.24	0.23	0.49	0.17	0.20	0.23	0.08				0.22	0.21	

et al., 2011), though they do not readily volatize (Giesy et al., 2010). An alternative pathway for PFAAs transport is via aerial transport of volatile PFAA precursors with subsequent oxidation of the plant-bound PFAA precursors, such as fluorotelomer alcohols (FTOHs) or 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA), to form PFAAs (Yoo et al., 2011). In order to identify the contribution of acropetal transport of PFAAs to their accumulation in aerial plant organs, PFAA concentrations in the control plants were determined and considered to be due to their gaseous uptake, on the assumption that PFAAs evenly diffuse in the ambient air and equally absorb onto aerial plant organs of biosolids-treated plants and their nearby blank control plants (Tao et al., 2009). The results showed that PFAA concentrations in wheat straws, husks and grains of control are lower than MLD (Table 3), suggesting that the effect of aerial transport of PFAAs and the oxidation of absorbed PFAA precursors on PFAA accumulation is negligible.

3.4. Uptake of PFAAs by wheat roots

The concentrations of PFAAs in the wheat roots were significantly influenced by biosolids application rate. Total concentrations of PFAAs in roots grown in different plots followed the order: Plot 1 < Plot 2 < Plot 3 < Plot 4, which was consistent with the same order of PFAAs in the soils. Single correlation analysis was performed to assess the relationships between concentrations of PFAAs in soils and uptake by roots. The correlation coefficients obtained are listed in Table S3. Consistently positive correlations existed between the contents of PFAAs in the soils and in wheat roots (R^2 = 0.981–0.999) for all PFAAs detected in the soils and wheat with the sole exception of PFPeA. Root concentration factors (RCFs) were calculated based on the ratio of PFAA levels in wheat roots to those in the soils (C_{root}/C_{soil}, (ng/g_{root})/(ng/g_{soil})). The RCFs of PFCAs and PFSAs were 1.73–5.18 and 1.19–2.75, respectively (Table S4). Among four plots studied, the RCFs of Plot 1 were the largest (1.62–5.18), which may be due to the lowest soil organic matter (SOM) content of Plot 1 (Table 1). Hydrophobic organic compounds (HOCs) in soil tend to be sorbed by SOM, and their uptake by plant roots is essentially controlled by SOM rather than by HOC concentration in the whole soil (Huang et al., 2010; Li et al., 2005; Chiou et al., 2001). Though PFAAs are expected to behave differently from traditional HOCs because of their both hydrophobic and hydrophilic functionalities, the importance of SOM on the sorption of PFAAs was reported (Higgins and Luthy, 2006). Thus, wheat root/organic matter concentration factors (ROMCFs, (ng/

g_{root})/(ng/g_{SOM})) based on the ratio of PFAA concentrations in roots to those in SOM (C_{root}/(C_{soil}/C_{SOM})) were further calculated (Table S4). The average ROMCFs were 0.023–0.099, with the relative standard derivations (RSD) of 6.13–21.3%. The RSD of ROMCFs were lower than those of RCFs (9.04–46.1%), which indicated that SOM is one of the important factors limiting the uptake of PFAAs by wheat roots. It is suggested that the uptake of HOCs by plant roots is mainly characterized by lipid dominating partition processes and might be expected to be similar to their accumulation by lipid containing passive samplers (Huang et al., 2010; Tao et al., 2009). The root lipid/organic matter accumulation factors (RLOMCFs, (ng/$g_{root\ lipid}$)/(ng/g_{SOM})) on the basis of root lipid and SOM ((C_{root}/C_{lipid})/(C_{soil}/C_{SOM})) were calculated (Table S4) in order to make a comparison, though it is reported that lipid is not the main compartment of PFAAs in animals and fish (Peng et al., 2010; Hoff et al., 2003). The lipid concentration of wheat roots was found to be 2.18%. The RLOMAFs ranged from 1.05 to 4.55, which were higher than those of polybrominated diphenyl ethers (PBDEs, 0.02–0.71, Huang et al., 2011), but was similar to 4-ring polycyclic aromatic hydrocarbons (PAHs, 1.59–2.66, Tao et al., 2009). Yoo et al. (2011) suggested that the transfer potential of long-chain PFCAs from soils to plants was lower than that of short-chain PFCAs. However no significant correlations were found between the RCFs of PFCAs or PFSAs and their chain length in this study (Fig. S3).

3.5. Accumulation of PFAAs in straws

Concentrations of PFAAs in straws are shown in Table 3. A positive correlation existed between all PFAAs in straws and in soils ($P < 0.05$), with correlation coefficients (R^2) of 0.939–0.999, except for PFPeA, PFUnA, and PFDA (Table S3). The straw/soil concentration factors based on the ratio of PFAA concentrations in straws to those in soils (SCFs, (ng/g_{straw})/(ng/g_{soil})) and the wheat straw/organic matter concentration factors (SOMCFs, (ng/g_{straw})/(ng/g_{SOM})) based on the ratio of PFAA concentrations in straws to those in SOM (C_{straw}/(C_{soil}/C_{SOM})) were calculated (Table S5). The SOMCFs ranged from 0.00471 to 0.0569. Yoo et al. (2010) also calculated the grass/organic-matter accumulation factors (GOMAFs), which is the ratio of PFAA concentrations in above-ground portion of grasses to those in SOM, and reported that the values were 0.001–0.61. Our values were in the range of theirs. Concentrations of PFAAs in wheat straws were also found to correlate well with the corresponding concentrations in roots for PFBA, PFHxA, PFHpA, PFOA, PFNA, PFTeA, PFHxS, and PFOS ($P < 0.05$, Table S6), indicating that root uptake of PFAAs and subsequent translocation from roots to straws may make significant contribution to their accumulation in straws. The transfer factors from roots to straws were defined as the ratio of the PFAA concentrations in straws to those in roots on a dry weight basis ($TF_{r-s} = C_{straw}/C_{root}$, (ng/$g_{straw}$)/(ng/$g_{root}$), Table S7). The TF_{r-s} values calculated were 0.202–0.836 for PFCAs, which was higher than TF_{r-s} values for PFSAs (0.193–0.366). The TF_{r-s} values of short carbon chain PFAAs were higher than those of long carbon chain PFAAs. For example, the average TF_{r-s} of PFBA was 2.4 times that of PFTeA. An inverse relationship exists between TF_{r-s} and carbon chain length of PFCAs ($n = 32$, $R^2 = 0.504$, $P < 0.01$, Fig. 1a). Similar inverse correlation was found between TF_{r-s} and carbon chain length of PFSAs ($n = 9$, $R^2 = 0.700$, $P < 0.01$, Fig. 1b). Similar results of foliage/root concentration factors decrease with increasing carbon chain length for both PFCAs and PFSAs were reported by Felizeter et al. (2012). The inverse relationship indicated that the acropetal transfer potential from roots to straws for short-chain PFAAs was higher than that for long-chain PFAAs, which may be due to the relatively large molecule and/or high lipophilicity of long-chain PFAAs when compared with short-chain PFAAs. It is suggested that the transport of POPs from roots to stems was

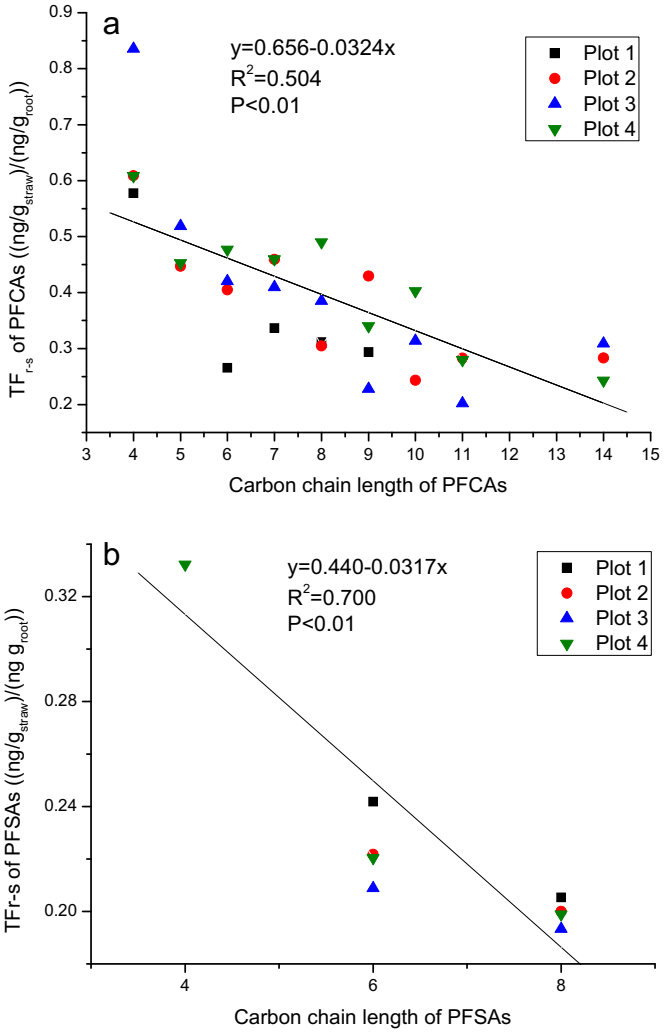

Fig. 1. Linear regression between transfer factors from roots to straws (TF_{r-s}) of PFCAs (a), PFSAs (b) and their carbon chain length.

mainly through transpiration (Murano et al., 2010; Collins et al., 2006; Burken and Schnoor, 1998). POPs with smaller size and lower lipophilicity are more easily translocated from root to shoot (Zhao et al., 2012; Satchivi et al., 2006).

3.6. Accumulation of PFAAs in grains

The PFAA concentrations in wheat grain are presented in Table 3. The grain concentrations increased with an increase of PFAA concentrations in soils, which suggests that soil PFAA accumulation could cause contamination to grain. The grain/soil concentration factors based on the ratio of PFAA concentrations in grains to those in soils (GCFs, (ng/g_{grain})/(ng/g_{soil})) and the grain/organic matter concentration factors (GOMCFs, (ng/g_{grain})/(ng/g_{SOM})) based on the ratio of PFAA concentrations in grains to PFAA concentrations in SOM (C_{grain}/(C_{soil}/C_{SOM})) were calculated (Table S8). The GCFs ranged from 0.0608 to 1.00. Grain PFAAs must be derived from either direct xylem transport from roots or remobilization of straw PFAA pools through phloem during grain filling. Different relationships between PFAAs in grains and in soils between PFCAs and PFSAs were found (Fig. 2). The concentrations of PFSAs in grains increased linearly with those in soils for PFHxS and PFOS ($R^2 = 0.997$–0.998, $P < 0.01$); whereas for PFCAs, there appears to

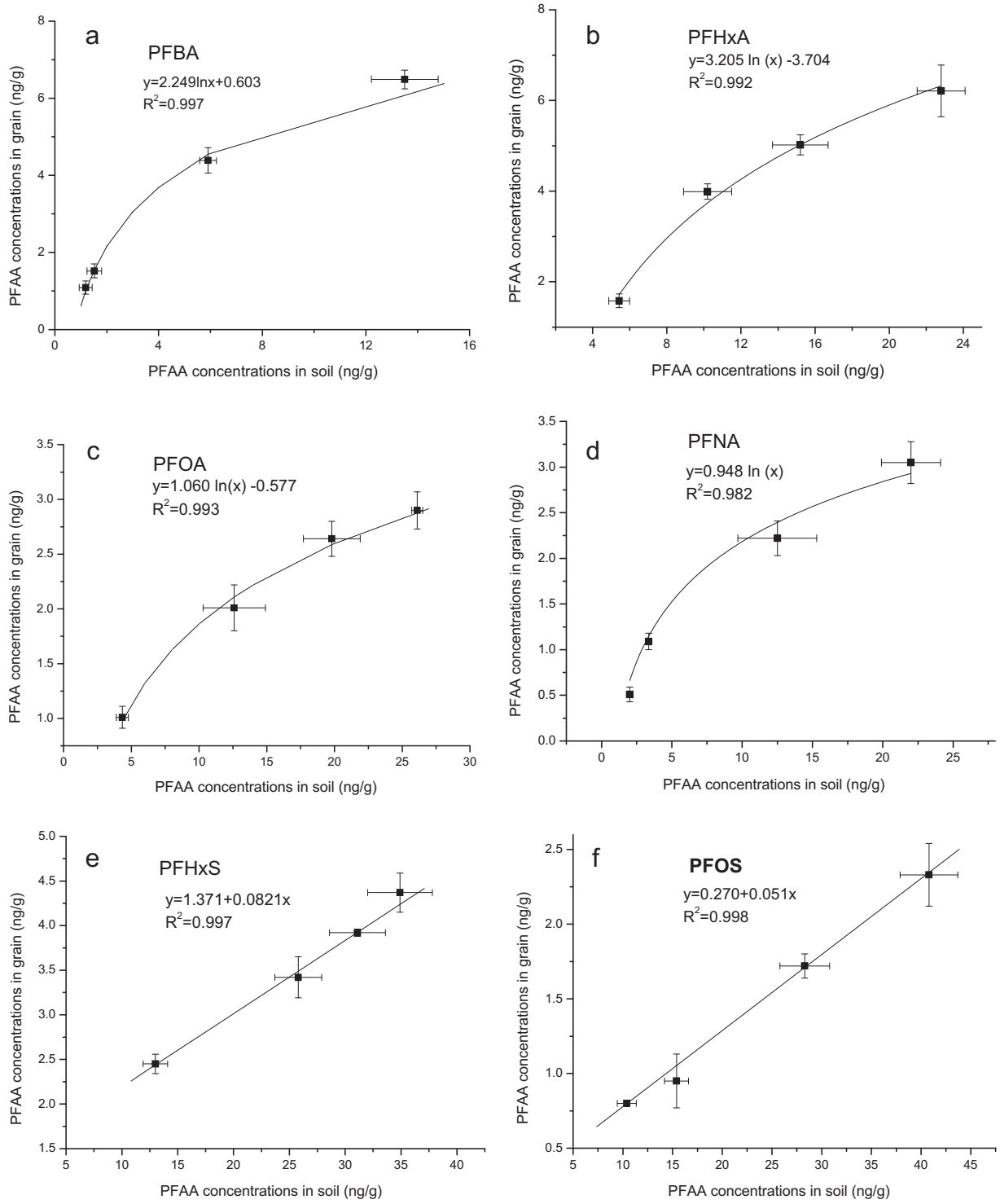

Fig. 2. Relationship between PFAA concentrations in grains and soils.

be a plateau effect. PFCA concentrations in grains increased logarithmically with increasing PFCAs in soils for PFBA, PFHxA, PFOA and PFNA (R^2 = 0.982–0.997). This difference indicated that the transport mechanisms from soils to grains between PFCAs and PFSAs may be different. The transport of PFAAs from soils to grains includes the uptake by roots, the translocation from roots to straws and the translocation from straws to grains. In order to understand the translocation of PFAAs from straws to grains, a straw-to-grain translocation factor defined as the ratio of PFAA concentrations in grains to those in straws on a dry weight basis was calculated ($TF_{s-g} = C_{grain}/C_{straw}$, $(ng/g_{grain})/(ng/g_{straw})$). The TF_{s-g} for PFCAs and PFSAs were in the range of 0.131–0.402 and 0.230–0.293, respectively (Table S7). For PFCAs and PFSAs with the same carbon chain length, the TF_{s-g} values of PFSAs were higher than those of PFCAs, which was opposite to TF_{r-s}. For example, the TF_{r-s} of PFOA (0.373 ± 0.086) was higher than that of PFOS (0.199 ± 0.005) while

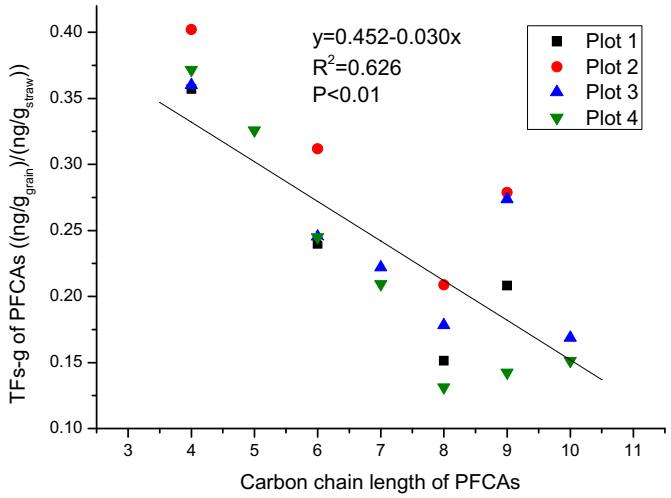

Fig. 3. Linear regression between transfer factors from straws to grains (TF_{s-g}) of PFCAs and their carbon chain length.

TF_{s-g} of PFOS (0.240 ± 0.013) was higher than that of PFOA (0.167 ± 0.034). Stahl et al. (2009) detailed the concentrations of PFOA and PFOS in wheat straws and ears. Based on their results, the C_{ear}/C_{straw} value calculated for PFOS (0.040 ± 0.018) was higher than that of PFOA (0.025 ± 0.007). This result revealed that PFCAs are easier than PFSAs to be translocated from roots to straws, while PFSAs are easier than PFCAs to be translocated from straws to grains. The TF_{s-g} values of short carbon-chain length were higher than that of long-chain length. For example, the average TF_{s-g} of PFBA was 2.2 times that of PFDA, and the TF_{r-s} of PFHxS was higher than PFOS. Inverse relationship existed between the translocation factors and carbon chain length of PFCAs ($n = 22$, $R^2 = 0.626$, $P < 0.01$, Fig. 3). These results indicated that the transfer potential for PFAAs from straws to grains of short-chain PFAAs was higher than that of long-chain PFAAs.

4. Conclusion

The results from this study demonstrated that the land application of biosolids could lead to the contamination of PFAAs in soils and crops in field circumstances. Contact of plants with PFAA contaminated soils could be a primary route of PFAAs transport via the roots into different plant tissues. Thus the application of biosolids provides an avenue for input of PFAAs into the food chain by following exposure pathways: contaminated soils → plants → human and/or contaminated soils → plants → livestock → human. The finding that the transfer potential for PFAAs from roots to straws and further to the grains for short-chain PFAAs was higher than that of long-chain PFAAs and that PFCAs and PFSAs may have different transport behaviors from soils to grains may help to understand the accumulation mechanisms of PFAAs in wheat, although an exact explanation for the observation remains to be provided from plant physiology.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.09.040.

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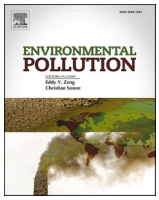

Bio-accumulation and health risk assessments of per- and polyfluoroalkyl substances in wheat grains☆

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) have been widely detected in various food, which has attracted worldwide concern. However, the factors influencing the transfer and bio-accumulation of PFASs from soils to wheat in normal farmland, is still ambiguous. We investigated the PFASs accumulation in agricultural soils and grains from 10 cites, China, and evaluated the health risks of PFASs via wheat consumption. Our results show that ∑PFASs in soils range from 0.34 μg/kg to 1.59 μg/kg with PFOA and PFOS dominating, whilst ∑PFASs in wheats range from 2.74 to 6.01 μg/kg with PFOA, PFBA and PFHxS dominating. The lower pH conditions and high total organic carbon (TOC) could result in the higher accumulation of PFASs in soils and subsequently in wheat grains, whilst the bioaccumulation factors of PFASs increase with increasing pH conditions but not with TOC. The estimated daily intake (EDI) values of PFBA, PFOA, and PFHxS are relatively high, but data supports that ingesting wheat grains does not result in any potential risk to the human beings. Our studies provided more information about PFASs accumulation in wheat grains, and help us understand the current potential risks of PFASs in food.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are recognized as a type of anthropogenic persistent organic pollutants (POPs) in which hydrogen atoms are completely replaced by fluorine atoms (Prevedouros et al., 2006). Because of their numerous excellent physical and chemical properties (Yu et al., 2018), PFASs have been widely used in chemical, industrial and consumer productions (Nickerson et al., 2021), including flooring, leather, packaging, cosmetics, lubricants, surfactants, pesticides and aqueous film-forming foams (AFFFs) (Hao et al., 2021).

Currently, PFASs are ubiquitous in variety of mediums of the global environment (Casal et al., 2017), like air (Lin et al., 2020), water (Neuwald et al., 2022; Song et al., 2020), soil (Brusseau et al., 2019) and sediment (Benskin et al., 2012). These PFASs released into environment could be transferred into plants like vegetables (Zabaleta et al., 2018) and cereals (Krippner et al., 2015), which could further be accumulated in animals (Smithwick et al., 2006) and human bodies (Zhou et al., 2014) through food chain. Human exposure to PFASs would increase the risk of suffering from diabetes (Duan et al., 2020) and cancer (Wang et al., 2021a). As such, many countries have put the legacy PFASs like perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid (PFHxS) in the constrain lists. Therefore, the study about the transfer and accumulation of PFASs in soils and plants is key to predicting and estimating the potential risks of PFASs.

Soils can act as an important sink of PFASs in terrestrial systems, and PFASs have been reported to accumulate in various kinds of soils, like airport (Liu et al., 2022) or firefighter training areas (FTAs) (Munoz et al., 2021), fluorine manufacturing parks (FMPs) (Chen et al., 2018;

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Wang et al., 2018b) and residential soils(Li et al., 2020). In agricultural soils, PFASs contamination is also reported in eastern coastal regions of China (Cheng et al., 2023) and China Mainland (Wang et al., 2024), such as Tianjin city (1.00–17.78 μg/kg) (Lan et al., 2020), Shanghai (0.141–0.225 μg/kg) (Li et al., 2010). In these agricultural soils, the legacy PFASs like PFOA and PFOS are the dominating compounds.

On the other hand, soils, particularly the agricultural soils, may also act as a potential source for the PFASs accumulation in plants. In agricultural food, the legacy PFASs like PFOA are also dominating PFASs contamination in crops(Lechner and Knapp, 2011). The laboratory experiment results show that PFASs could be accumulated in wheat grains, like PFBA at 13.5 μg/kg, PFBS at 31.2 μg/kg, PFOA at 21.6 μg/kg, PFOS at 40.5 μg/kg (Wen et al., 2014). The wheat in farmland near perfluorinated compounds were also reported to enrich PFOA up to 580 μg/kg, and total concentration of PFASs up to 2597 μg/kg (Liu et al., 2019b). However, these researches only focus on wheat from contaminated regions or soils but cannot reveal the actual accumulation level of PFASs in our daily-intake wheat grains, and thus there is a compelling need to investigate and identify the typical PFASs in wheat from normal farmland.

The typical factors influencing the transfer of PFASs from soils to plants include PFASs properties and soil properties. The generally trend is that the perfluoroalkyl carboxylic acids (PFCAs) are easier to be transferred and enriched in plants than perfluoroalkyl sulfonic acids (PFSAs), whilst bioaccumulation factors (BAFs) of each PFASs series generally decreased as the carbon chains lengthen (Xu et al., 2021). As for the soil properties, there is a debate about influences of pH conditions and soil organic matter (SOM) on the PFASs accumulation in plants. For instance, PFOS tend to enrich in wheat plants at around neutral pH (6–8) conditions than pH 4 or 10 (Zhao et al., 2013), but pH conditions seems have no influences on PFOS accumulation in maize plants (Krippner et al., 2014). Similarly, soil organic matter appears to decrease the accumulation of uptake of 8:2 perfluoroalkyl phosphate diester in lettuce (Bizkarguenaga et al., 2016), but the presence of fulvic acid probably accumulate the accumulation of F53B in wheat plant (Guo et al., 2022). Previous studies mainly focused on individual PFAS in the labotary experiment but not identify the typical PFAS compounds in normal wheat and investigate factors controlling PFAS accumulation in wheat grains. At present, it is still ambiguous whether PFASs accumulation in wheat grains follow the same trend with other plants or not, and how soil properties (especially pH and TOC) influence the bio-accumulation of various PFASs in grains planted in the normal farmland.

In this study, we investigated the occurrence and bioaccumulation of 30 PFASs in wheat soils and grains in 10 cities from China, and estimated the potential risks of PFASs in wheat grains. The aims of this study are to (i) observe the accumulation level of PFASs in the normal agricultural soils; (ii) to identify the typical PFASs compounds accumulated in wheat grains; (iii) to investigate the influences of PFASs and soil properties on the PFASs accumulation in wheat grains; (iv) to assess the risk levels of PFASs to human health.

2. Materials and methods

2.1. Sample collection and preparation

The soils and wheat samples were collected at 10 sites from different cities from May to July of 2022. The agricultural soil samples were collected from the surface layer (0–20 cm) of farmland during the wheat harvest season with stainless-steel trowel and polypropylene (PP) bags, and the corresponding unpeeled wheat grains were also collected at the same time with cloth sample bags. All selected sites were situated far away from known industrial facilities. After being transported to the laboratory, all samples were promptly stored at −20 °C upon arrival.

2.2. Chemical standards and reagents

A set of 30 target PFASs compounds were analyzed in this study, including 10 legacy, 10 emerging PFASs, 6 PFASs precursors and 4 perfluoroalkyl ether carboxylic/sulfonic acids (PFEC/S) (Table 1). All standards were purchased from the company Wellington Laboratory, Canada. The main reagents used in the experimental processes include methanol (chromatographically pure), ammonia ($NH_3{\cdot}H_2O$, Guaranteed reagent, GR), and ethanol (Guaranteed reagent, GR) were purchased from Thermo Fisher (Fisher Chemical).

2.3. Extraction experiment of PFASs

2.3.1. Soil samples preparation

Extraction of target compounds from soil samples was performed by referring to the previous method with minor modifications (Mejia-Avendano et al., 2017). The sample is air-dried at room temperature, and the soil sample is homogenized with a ceramic mortar and pestle, and sieved through a 1 mm sieve for further processing. Methanol and 0.1% $NH_3{\cdot}H_2O$ were mixed as the extraction solvent during the extraction process. Around 5 g of each soil sample were placed in a 15 mL polypropylene centrifuge tube (cleaned twice with HPLC grade methanol before use), and then 10 ng of mass-labeled internal standard was added, after which the mixture was shaken for 1 h to achieve equilibrium. Subsequently, the soil was mixed with 6.25 mL of extraction solvent and subjected to 30 min of ultrasonic treatment, followed by 60 min of oscillation on a rotary vibrator at 50 rpm. After centrifugation for 10 min, the supernatant was retrieved. The extraction process was repeated three times. The obtained extracts were concentrated to 1 mL under mild nitrogen flow. Then ENVI graphite powder (Sigma Aldrich) were added into the extracts to purify the solution. After centrifuging at 10000 rpm for 10 min, the supernatant was recovered, and another 1 ml of methanol were added to recover the remaining PFASs. After the purification, the solution was concentrated, filtered and stored at −20 °C for analysis within 3 days.

2.3.2. Wheat samples preparation

The extraction of PFASs from wheat grains were appropriately modified based on the experimental method by Guo et al. (2022). The air-dried whole wheat grains were cracked and homogenized with an electronic crusher. Around 5 g grain powder was added into 50 mL polypropylene (PP) centrifuge tube, with 10 ng of mass-labeled internal standard substance added to correct recovery losses during the extraction, after which the tubes were shaken at 50 rpm for 1 h. Then 20 mL of 0.25 M sodium carbonate solution and 10 mL of methyl tert-butyl ether (MTBE) were added, and then 10 mL of 0.5 M tetra butylammonium bisulfate (TBAS) were added into mixture. After ultrasonic extraction for 30 min, tubes were shaken evenly, flipped and shaken at 50 rpm for 30 min. After centrifuging at 6000 rpm for 20 min, the organic supernatant was retrieved in a new tube. The extraction process was repeated twice more. The combined supernatant was concentrated under a gentle nitrogen flow until almost dry, and 1 ml of methanol were added to re-dissolve the PFASs under ultrasound conditions. Then ENVI graphite powder were added into the suspension, after which the suspension was vigorously shaken for 1 min and centrifuged at 10000 rpm for 10 min, and the supernatant was collected in a new tube. Another 1 mL methanol were mixed with graphite powder to retrieve the remained PFASs. Finally, the purified supernatant was concentrated under the gentle flow of nitrogen, filtered with 0.2 μm membrane, and stored at −20 °C for analysis. The final concentration of the internal standard is 10 ng/ml. The 30 target PFAS were analyzed using Ultra High Performance Liquid Chromatography (UPLC) coupled with the Xevo TQ-XS triple quadrupole mass spectrometry (Waters ACQUITY UPLC I-Class).

Table 1
The detection efficiency, concentrations, and proportions of individual PFASs in soils.

	Compound	Detection efficiency (%)	Range	Mean ± SD	Median	Proportions of total PFASs
Legacy PFASs	PFHxS	50.00%	0–0.142	0.050 ± 0.651	0.001	5.24%
	PFHpS	30.00%	0–0.082	0.002 ± 0.003	0	0.19%
	PFOS	90.00%	0–0.622	0.150 ± 0.185	0.120	15.56%
	PFOA	100.00%	0.114-0.401	0.222 ± 0.082	0.215	23.06%
	PFNA	100.00%	0.043-0.102	0.072 ± 0.015	0.074	7.43%
	PFDA	100.00%	0.018-0.092	0.031 ± 0.022	0.025	3.18%
	PFUdA	100.00%	0.030-0.114	0.052 ± 0.025	0.046	5.41%
	PFDoA	50.00%	0–0.025	0.005 ± 0.008	2.0×10^{-4}	0.53%
	PFTeDA	n.d.	n.d.	n.d.	0	0.00%
	PFODA	10.00%	0–0.234	0.023 ± 0.074	0	2.43%
Emerging PFASs	PFBS	70.00%	0–0.196	0.075 ± 0.064	0.076	7.77%
	PFPeS	40.00%	0–0.030	0.106 ± 0.014	0	1.10%
	PFBA	100.00%	0.021-0.178	0.072 ± 0.047	0.067	7.49%
	PFPeA	70.00%	0–0.019	0.009 ± 0.007	0.011	0.95%
	PFHxA	100.00%	0.089-0.052	0.298 ± 0.015	0.033	3.10%
	PFHpA	100.00%	0.009-0.161	0.093 ± 0.049	0.106	9.70%
	HFPO-DA	100.00%	0.004-0.118	0.049 ± 0.039	0.041	5.09%
	9Cl-PF3ONS	50.00%	0–0.017	0.003 ± 0.005	5.0×10^{-4}	0.28%
	11Cl-PF3OUdS	20.00%	0–0.002	0.0003 ± 0.0007	0	0.04%
	ADONA	n.d.	n.d.	n.d.	0	0.00%
Precursors	4:2FTS	n.d.	n.d.	n.d.	0	0.00%
	6:2FTS	10.00%	0–0.005	0.0005 ± 0.002	0	0.05%
	8:2FTS	10.00%	0–0.006	0.0006 ± 0.002	0	0.06%
	FOSA	20.00%	0–0.020	0.004 ± 0.008	0	0.42%
	N-MeFOSA	10.00%	0–0.033	0.003 ± 0.010	0	0.34%
	N-EtFOSA	10.00%	0–0.037	0.004 ± 0.012	0	0.39%
PFEC/S	3,6-OPFHpA	20.00%	0–0.0001	0.00002 ± 0.000004	0	0.00%
	PF4OPeA	10.00%	0–0.009	0.0009 ± 0.003	0	0.09%
	PF5OHxA	10.00%	0–0.005	0.0005 ± 0.002	0	0.05%
	PFEESA	10.00%	0–0.005	0.0005 ± 0.002	0	0.06%

2.4. Quality assurance and quality control

All materials containing polytetrafluoroethylene and other fluoropolymers were avoided during the whole treatment and analysis processes. All containers underwent preliminary washing using Milli-Q water and HPLC-grade methanol. A series of nine calibration curve pints (0.05, 0.125, 0.25, 0.5, 1, 2.5, 5, 10 and 50 ng/mL) were prepared employing internal standards to quantify the individual PFASs, with correlation coefficients (r^2) for each calibration curve exceeding 0.95. Matrix recoveries were conducted at dose of 5, 10 and 20 μg/kg, and the mean recovery ranged from 57.2 ± 2.75% to 103 ± 5.37% (Tables S3 and S4). After every 10 sample injections, a solvent blank of HPLC-grade methanol and 10 ng/mL PFASs calibration standard were analyzed to check the carryover and background contamination as well as the instrument stability. No target PFASs were detected in blanks with concentrations higher than their detection limits. The concentrations of PFASs in samples were not corrected with the recovery efficiency as the recovery efficiency for most PFASs species are pretty good, but corrected with the calibration standard which were measured every 10 samples. The method detection limit (MDL) was defined as the lowest concentration of target compounds resulting in a signal-to-noise (S/N) ratio of 3, whilst method quantification limit was defined using an S/N ratio of 10.

2.5. Data representation and analysis

In this study, statistical tests, graphing and data processing were conducted using IBM SPSS statistics 22.0, Origin 2021 and Excel 2016 software, respectively. Correlations were analyzed and determined based on correlation coefficients (where $R > 0$ is positive correlation and $R < 0$ is negative correlation) and significance coefficients (p, $p < 0.0l$ and $p < 0.05$).

2.6. Bioaccumulation factors of PFASs and daily intake estimation of human

Bioaccumulation factors (BAFs) are defined as ratios between the chemical concentrations determined on a dry weight basis in the plant leaves and their corresponding concentrations in soil. BAFs were calculated using the equation as following:

$$\mathrm{BAF} = \frac{\text{PFASs concentration in wheat grains } (\mu g/\text{kg dw})}{\text{PFASs concentration in wheat soil } (\mu g/\text{kg dw})}$$

If BAF is > 1, the content of a compound is greater in the wheat than in the soil, indicating the compound is more readily transported and accumulated in the wheat.

2.7. Calculations of estimated dietary intake of PFASs

Consumption of wheat is one of the important pathways for human exposure to PFASs. In order to calculate the total dietary intake of PFASs from wheat, we invested local population number, which were divided into three age groups with the average age as the final calculation parameter. The following equation is the estimated daily intake (EDI) of PFASs influenced by body weight with three age groups:

$$\mathrm{EDI} = \frac{\mathrm{DC} \times \mathrm{C}}{\mathrm{BW}}$$

where C represents the mean concentrations of individual PFASs (μg/kg), DC is the mean daily consumption rate of wheat, and BW is the average body weight according to previous studies.

As for the EDI calculation for residents with different radiu, the average concentrations of PFASs in wheat grain collected in this study were used. The parameters for the estimation of EDI were cited from Highlight of Chinese Children's Exposure Factors Handbook, (China Environment Press. 2016 in Chinese), United States Environmental Protection Agency, A Review of The Reference Dose and Reference Concentration Processes (Rice, 2003) and Risk Assessment Forum.

The risk quotient (RQ) was calculated using the following formula.

$$RQ = \frac{EDI}{RfD}$$

The RfD (oral reference dose) values for PFBA, PFBS, PFOA, PFOS, PFHxA and HFPO-DA were respectively set as 1000 ng/kg/day, 300 ng/kg/day, 3 ng/kg/day, 2 ng/kg/day (Chen et al., 2023b), 320 ng/kg/day and 3 ng/kg/day based on USEPA. Values of RQ higher than 1 indicate a high risk from PFASs intake exposure, whereas RQ values lower than 1 represent a low risk.

2.8. Data collection of estimate daily intake of PFASs

The literature published between 2010 and 2023 were investigated to summarize the assessed daily intake of PFASs in foods (like grains, vegetables, fish, meat, and eggs), and the average EDI data for different age groups (Tables S5-6). These data published were compared with our results to deepen our understanding of the potential risks from PFASs in the wheat.

3. Results and discussion

3.1. Concentration and composition of PFASs in soil and wheat samples

3.1.1. Concentration and composition of PFASs in soils

The targeted PFASs were categorized in four main groups, namely, legacy PFASs, emerging PFASs, precursors and perfluoroalkyl ether carboxylic/sulphonic acids (PFEC/S). The detection efficiency, concentrations, and proportions of individual PFASs are shown in Table 1. The total concentrations of PFASs ranged from 0.34 μg/kg to 1.59 μg/kg with median values at 1.04 μg/kg, which is at similar level with ΣPFASs in the farmland soil from TianJin (0.4–5.2 μg/kg), from east coastal provinces in China (0.018–1.950 μg/kg), but lower than the farmland soil across China Mainland (0.074–24.88 μg/kg) (Cheng et al., 2023; Wang et al., 2021a). By contrast, the concentration level is far lower than the concentration of ΣPFASs in the Chinese residents soil (0.24–13.56 μg/kg) (Li et al., 2020), global residential soil (0.029–14.30 μg/kg), yam soil (4200–5300 μg/kg) and maize surface layer soil (3000–7900 μg/kg) in Uganda (Dalahmeh et al., 2018). As expected, the concentration of PFASs in wheat soil was generally lower than that in other soil types, probably because farmland is often located far away from fluorine chemical factories, and the long transport distance limits the PFASs accumulated in agricultural soils.

As shown in Fig. 1 and Table 1, the legacy PFASs are the dominating category of PFASs in soils, contributing to 62 % of total PFASs, followed by emerging PFASs, contributing to 36 % of total PFASs. Among legacy PFASs, PFOA, PFOS and PFNA were the main compounds, with median values at 0.22 μg/kg, 0.12 μg/kg, and 0.074 μg/kg, respectively. Our observation is consistent with previous studies that PFOA and PFOS were identified as the main PFASs compounds in agricultural soils (Cheng et al., 2023; Wang et al., 2024), natural forest soils across China (Wang et al., 2018a), sediments from five lake regions of China (Qi et al., 2016). In addition, our study demonstrated that the PFHxS (mean: 0.050 μg/kg, median: 0.0012 μg/kg, contribution to ΣPFASs: 5.24 %) is also the primary PFASs in agricultural soils.

Regarding the emerging PFASs, PFBA, PFHxA, PFHpA and HFPO-DA are the primary PFASs with detection efficiency >90% in agricultural soils, of which the average concentrations are 0.072 μg/kg, 0.030 μg/kg, 0.093 μg/kg, 0.050 μg/kg, respectively. Compared with legacy PFASs, emerging PFASs in agricultural soils appear to be much lower, but still contribute to ~30% of total PFASs contamination. It is also reported that emerging PFASs increased up to 30.0% over the past ten years in the eastern coastal regions of China (Cheng et al., 2023). As such the risks caused by the emerging PFASs increased with the accumulation in soils over time.

3.1.2. Concentration and composition of PFASs in wheats

As shown in Fig. 2 and Table 2, the total concentration of PFASs in wheat grains ranged from 2.75 μg/kg to 6.01 μg/kg, with mean and median values being 3.96 μg/kg and 3.29 μg/kg, respectively. Details about the detection efficiency, concentrations, and proportions of individual PFASs are shown in Table 2. Compared with other edible food, PFASs in wheat grains are much lower than that in the food collected from contaminated regions, like corn grains (ranging from 1.36 to 58.83 μg/kg; from the fluorochemical industrial park (FIP) field) (Liu et al., 2019b), maize grains (ranging from 0.7 to 58.8 μg/kg; median: 2.33 μg/kg; mean: 5.87 μg/kg; from a mega FIP) (Liu et al., 2017), vegetable leaves (cabbage, camphor and cephalotaxus; ranging from 11.88 to 115.14 μg/kg; median:31.78 μg/kg; mean:39.00 μg/kg; from the landfill) (Xu et al., 2021). In addition, PFASs in wheat grains are also much lower than that in meat (like beef with range of 11–16 μg/kg, median at 15 μg/kg and mean at 26 μg/kg; and like chicken with range of 6.2–33 μg/kg, median at 16 μg/kg, and mean at 15 μg/kg) (Wang et al., 2021b), eggs (range: 17–39 μg/kg; median: 31 μg/kg; mean: 29 μg/kg; purchased from supermarkets) (Wang et al., 2021c), shellfish (range: 0.061–178.259 μg/kg; median: 3.737; mean: 13.015 μg/kg) (Zhang et al., 2023), and marine products along the coastal regions of the Yellow-Bohai Sea (range: 1600–82990 μg/kg; mean: 2570 μg/kg) (Guo et al., 2023). In addition, PFASs in wheat grains from normal

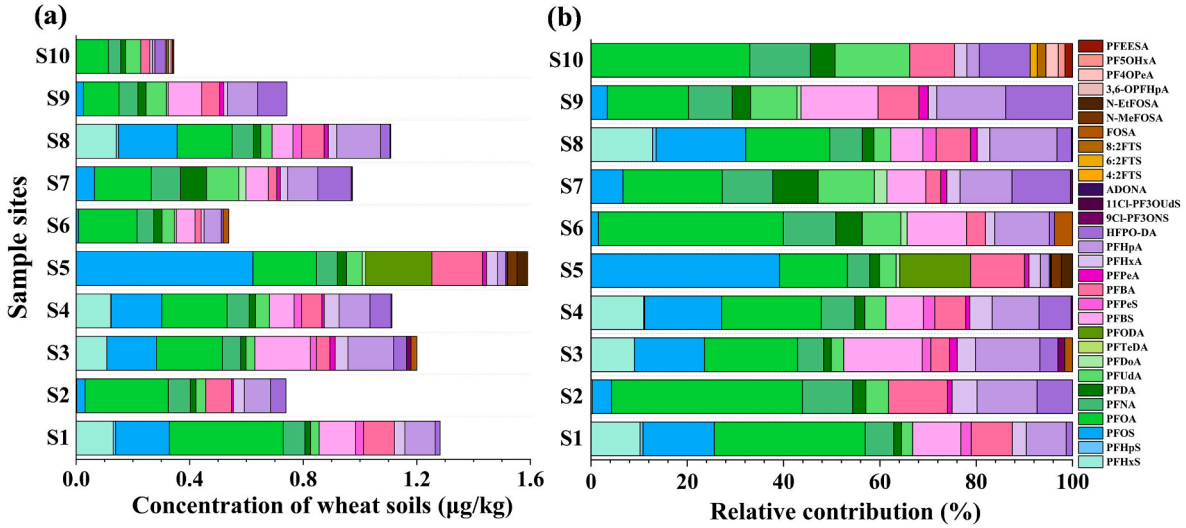

Fig. 1. Concentration and relative contribution of PFASs in wheat soils. a): sum of all PFASs concentrations and b): allocation of various PFASs.

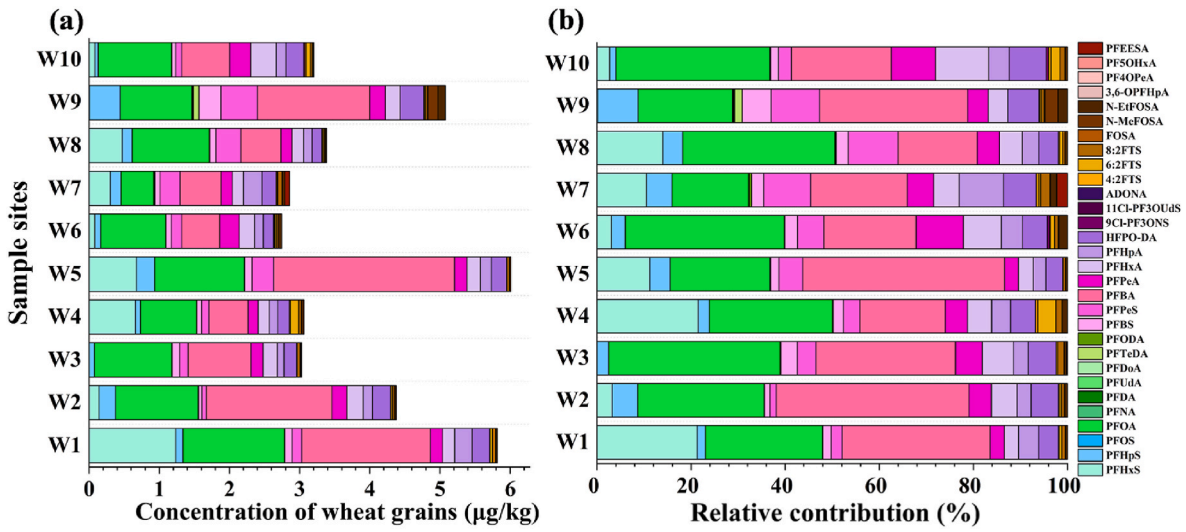

Fig. 2. Concentration and relative contribution of PFASs in wheat grains. a): sum of all PFASs concentrations and b): allocation of various PFASs.

Table 2
The detection efficiency, concentrations, and proportions of individual PFASs in wheat grains.

	Compound	Detection efficiency (%)	Range	Mean ± SD	Median	Proportions of total PFASs
Legacy PFASs	PFHxS	90.00%	0–1.236	0.365 ± 0.398	0.220	9.24%
	PFHpS	100.00%	0.041-0.436	0.160 ± 0.121	0.123	4.05%
	PFOS	n.d.	n.d.	n.d.	0	0.00%
	PFOA	100.00%	0.465-1.446	1.036 ± 0.268	1.072	26.20%
	PFNA	100.00%	0.001-0.006	0.003 ± 0.001	0.004	0.09%
	PFDA	100.00%	0.001-0.005	0.003 ± 0.001	0.002	0.07%
	PFUdA	20.00%	0–0.0056	0.0006 ± 0.002	0	0.02%
	PFDoA	10.00%	0–0.008	0.0008 ± 0.003	0	0.02%
	PFTeDA	20.00%	0–0.0785	0.008 ± 0.025	0	0.20%
	PFODA	30.00%	0–0.0131	0.002 ± 0.004	0	0.04%
Emerging PFASs	PFBS	100.00%	0.049-0.314	0.104 ± 0.077	0.081	2.62%
	PFPeS	100.00%	0.059-0.523	0.213 ± 0.149	0.145	5.39%
	PFBA	100.00%	0.539-2.580	1.163 ± 0.729	0.789	29.41%
	PFPeA	100.00%	0.144-0.301	0.200 ± 0.053	0.174	5.05%
	PFHxA	100.00%	0.155-0.363	0.207 ± 0.061	0.196	5.24%
	PFHpA	100.00%	0–0.270	0.141 ± 0.076	0.128	3.57%
	HFPO-DA	100.00%	0.142-0.337	0.213 ± 0.061	0.206	5.38%
	9Cl-PF3ONS	20.00%	0–0.015	0.003 ± 0.006	0	0.07%
	11Cl-PF3OUdS	10.00%	0–0.003	0.0003 ± 0.0009	0	0.01%
	ADONA	n.d.	n.d.	n.d.	0	0.00%
Precursors	4:2FTS	90.00%	0–0.017	0.008 ± 0.006	0.007	0.21%
	6:2FTS	100.00%	0.005-0.118	0.032 ± 0.034	0.020	0.81%
	8:2FTS	100.00%	0.016-0.057	0.035 ± 0.012	0.032	0.87%
	FOSA	90.00%	0–0.008	0.002 ± 0.002	5.0 × 10-4	0.04%
	N-MeFOSA	60.00%	0–0.014	0.015 ± 0.044	0.002	0.38%
	N-EtFOSA	100.00%	0.015-0.104	0.035 ± 0.027	0.025	0.87%
PFEC/S	3,6-OPFHpA	n.d.	n.d.	n.d.	0	0.00%
	PF4OPeA	10.00%	0–0.006	0.0006 ± 0.002	0	0.02%
	PF5OHxA	n.d.	n.d.	n.d.	0	0.00%
	PFEESA	10.00%	0–0.066	0.007 ± 0.021	0	0.17%

agricultural soils are much lower than that planted near fluorochemical industrial park, like wheat grains with PFASs concentration at 54.99 μg/kg near a fluorochemical industrial park (Dong et al., 2023). The concentrations of PFASs in grains are controlled by the distance between FIP and farmland soil. For instance, the concentration of PFASs in wheat grains reachs 407 μg/kg at 0.3 km, whilst the PFASs concentration decreased to 1.91 μg/kg at 10 km (Liu et al., 2019b). The low level of PFASs contamination in our wheat grains indicate that there no point source of PFAS pollution near the sampling sites.

Regarding the PFASs constituents in wheat grains, the main compounds of PFASs in wheat grains are legacy PFASs like PFHxS and PFOA, and emerging PFASs like PFBA and HFPO-DA. The mean concentrations of PFOA and PFHxS are 1.07 μg/kg and 0.22 μg/kg, contributing to 24.2% and 9.24% of total PFASs, respectively. The average concentrations of PFBA and HFPO-DA are 1.16 μg/kg and 0.21 μg/kg, contributing to 29.41% and 5.38% of total PFASs, respectively. As such PFBA and PFOA are the main PFASs compounds in wheat grains from normal farmland soils. It is also reported that for wheat planted near FIP, PFBA at 341.75 ng/g contributes to 85% of PFASs contamination in grains (Liu et al., 2019b), whilst PFBA (0.39–342 μg/kg, mean: 52.41 μg/kg) and PFOA (0.25–39.30 μg/kg, mean: 3.25 μg/kg) contribute to 72.65% and 4.5% of PFASs contamination, respectively, in wheat grains (Liu et al., 2017). In addition, previous studies have shown that PFBA and PFOA are also the main PFASs compounds in food like maize grains (PFBA: 0.5–37.37 μg/kg, mean: 4.57 μg/kg, contribution: 58.42 %; PFOA: 0.05–0.70 μg/kg, mean: 0.16 μg/kg, contribution: 2.65 %) (Liu et al.,

2017), tomato (PFBA: 28–87 μg/kg, mean: 53.8 μg/kg, contribution: 83.54%; and PFOA:0.35–1.70 μg/kg, mean: 0.93 μg/kg, contribution: 1.45%) and cucumber (PFBA: 17–63 μg/kg, mean: 39.60 μg/kg, contribution: 77.65% and PFOA:0.47–2.60 μg/kg, mean: 1.37 μg/kg, contribution: 2.69%) (Bao et al., 2020). Despite PFBA and PFOA, our study also reveals that PFHxS might be the main PFASs contaminants, whilst HFPO-DA is also the primary PFASs compounds in wheat grains.

Compared with the complex pattern of PFASs constituents in soils with various PFASs compounds, PFASs constituents appear to be simple with several dominating PFASs, namely PFHxS, PFOA, PFBA and HFPO-DA. In soils, concentration and proportions of PFOS are much higher than PFHxS, but in wheat, the trend appears to be reverse. For C8–C14 PFCAs, all compounds were observed in soils with discernible proportions contributing to the total PFASs, while only PFOA were observed in wheat grains. Interestingly, PFBA only contributed to ~8% of total PFASs in soils, but shared ~30% of total PFASs in wheat grains. Other short chain PFCAs (C4–C7) in crops account for a larger proportion of total PFASs, indicating a preference for bioaccumulation of these homologous compounds (Wen et al., 2014). Similarly, the proportions of HFPO-DA in wheat grains were much higher than that in soils. All of these suggest the different mobility from soils to wheat grains, as well as the different bioaccumulation factors for different compounds.

3.2. Bioaccumulation of PFASs

3.2.1. Influences of PFASs properties on bioaccumulation of PFASs in wheat

The bioaccumulation factors for different PFASs compounds were shown in Fig. 3, where the BAF values higher than 1 indicate that PFASs are easily transferred into organisms from soil. Here it is observed that BAFs for PFHxS (15.64 ± 22.39), C4–C8 PFCAs (PFBA: 17.67 ± 6.00; PFPeA:15.11 ± 6.43; PFHxA: 11.37 ± 11.41; PFHpA: 3.22 ± 4.47; PFOA: 5.14 ± 2.03) and HFPO-DA (12.30 ± 16.27) were much higher than 1, suggesting the easier accumulation of these compounds in wheat grains. As mentioned above, PFBA and PFOA are the main PFASs compounds in wheat grains from normal farmland soils (Fig. 2), and thus their BAF are compared with previous studies here. The BAF values of PFBA ranged from 7.2 to 25 with mean values at 17.67 ± 6.00, which are at same levels with the BAF values reported in wheat grains like 2.68–181.96(mean:31.81 ± 37.39) (Liu et al., 2017) and 5.2–71.80 (Liu et al., 2019b), but higher than 0.48–1.00 (mean:0.79 ± 0.23) (Wen et al., 2014). The BAF values of PFOA ranged from 2.32 to 9.23 with mean values at 5.14 ± 2.03, which are much higher than the reported values like 0.11–0.23 (mean:0.16 ± 0.05) (Wen et al., 2014), 0.01–0.42 (mean:0.12 ± 0.10) (Liu et al., 2017), 0.11–0.23 (Wen et al., 2014), and 0.08–0.12 (Liu et al., 2019b).

The bioaccumulation of different PFASs compounds were controlled by the properties of PFASs like different carbon chain length and different functional groups. For C4–C8 PFCAs in our study (Fig. 3), BAFs appear to decrease with increasing carbon chain length, which are consistent with the bioaccumulation trend in corn grains, fruit, fishes and egges etc.(Liu et al., 2024). When PFASs moves from soils to wheat grains, PFASs passing Casparian strip and moving up via transpiration are two of key processes controlling the transfer of PFASs in plant (Liu et al., 2019a). Research has shown that highly hydrophobic PFASs are more likely to overcome electrostatic repulsion and adsorb to crop roots with hydrophobic interaction (Qian et al., 2023). The PFASs with shorter carbon-chain tend to easier pass through Casparian strip (Zhang et al., 2019) and thus move to the shoot via vascular bundle tube. These short PFASs also have lower distribution coefficient (Kd) values (Nguyen et al., 2020), suggesting the higher mobility during the transpiration processes. As such, the shorter PFASs are easier transferred from roots to wheat grains.

The head functional group of PFASs is another key factor influencing the bioaccumulation of PFASs in wheat grains, where BAFs for PFSAs seems lower than that for PFCAs. Taking PFOS and PFOA as examples for

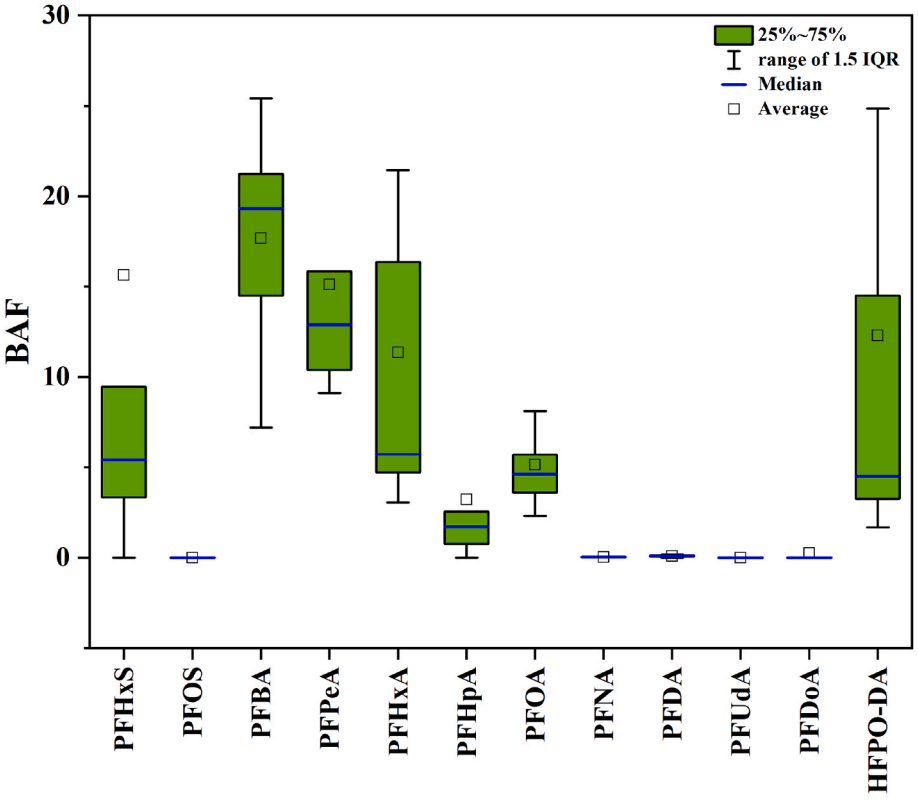

Fig. 3. BAFs of PFASs in wheat grains. The Box and whisker chart display the BAF values of a single PFASs, with boxes representing the 25th to 75th percentile lines. The solid blue line inside the box represents the median, and the black hollow box represents the average value.

comparison, both them are commonly detected PFASs contaminants in soils. The concentration of PFOA ranged from 0.47 μg/kg to 1.45 μg/kg and average value was 1.04 μg/kg, while PFOS were not detected in any wheat samples. The BAFs for PFOS is also much lower than PFOA as shown in Fig. 3. This could be derived from the different Kd values, where Kd of PFOS were much higher than that for PFOA, corresponding to the higher polarity. Previous studies documented that PFOS tend to be enriched in root issues (Liu et al., 2023), while PFOA is easier transferred up along the plant issues. As such, PFCAs are easier than PFSAs transferred up and finally accumulated in wheat grains. In addition, PFOA as the dominating legacy PFAS accumulates in the gas (251 pg/m^3), particle phases (1074 pg/m^3), and dust samples (994.5 ng/g) (Dong et al., 2023), which indicates PFOA may be preferential to pass through leaves spiracles during air exposure and finally accumulate in grains.

In this study, the bioaccumulation of HFPO-DA is also observed in wheat grains, which is usually utilized as substitutes for PFOA. Whereas, the different behaviors for PFOA and HFPO-DA, especially the transfer into plants, are seldomly studied. Our study revealed that BAFs for HFPO-DA (1.68–56.66; mean: 12.30; median: 4.49) seems to be higher than that for PFOA (2.32–9.23, mean: 5.14; median: 4.62). As such, HFPO-DA probably has higher mobility in wheat issues, and finally easier accumulates in wheat grains. The different mobility between PFOA and HFPO-DA were also observed in lettuce, where HFPO-DA were easier transported from soils to shoots than PFOA (Chen et al., 2023a), supporting our hypothesis that HFPO-DA has higher mobility in plant issues. In addition, HFPO-DA is more easily enriched in mouse liver than PFOA and probably has similar or higher biological toxicity (Gomis et al., 2018). Therefore, HFPO-DA may lead to higher human health risks through food chain transmission and biomagnification (Qian et al., 2023).

3.2.2. *Influences of soil properties on transfer and bioaccumulation of PFASs*

Soil properties like pH and total organic carbon are key factors, influencing the transferring process from soils to wheat grains. As shown in Fig. 4a, the total PFASs in soils and wheat grains generally decrease with increasing pH conditions, while BAF increase with increasing pH conditions. Specifically, the main compounds in soils like PFOA and PFOS, clearly shows a negative correlation with pH conditions of soils, whilst the main compounds in wheat grains like PFOA and PFBA also follow this trend (Fig. 4b). As previous studies reported, the lower pH conditions could facilitate the adsorption and fixation of PFASs onto minerals (Campos-Pereira et al., 2020; Tang et al., 2010), because the positive surface charge of soil minerals at lower pH could favor the adsorption of PFASs through electrostatic attraction. Our results also supported this that lower pH favor the accumulation of PFASs in agricultural soils, and the corresponding wheat grains also tend to enrich more PFASs at lower pH conditions, probably because more PFASs in soils could be accessed by wheat during the growth. Whereas, BAF of total PFASs tend to increase with increasing pH conditions, suggesting the higher mobility of PFASs at higher pH conditions. Typically, BAF of PFOA generally increased with increasing pH conditions ($r = 0.41$, $p = 0.27$). At higher pH conditions, these mobile PFASs like PFOA readily migrate from soils to be accessed by plant roots and finally accumulate in wheat grains. Generally speaking, the lower pH conditions could result in the higher concentrations of PFASs in soils and wheat grains, but the BAF at lower pH are lower than that at higher pH conditions.

Regarding the influences of soil organic carbon, TOC has weak positive relationship with total PFASs in soils, but present obviously positive relationship with PFASs in wheat grains (Fig. 5a). For each PFAS individual, the main compounds in soils like PFOS and PFBA present a strong positive correlation with TOC, although PFOA has the reverse trend, which combined together result in a weak positive relationship between ∑PFASs and TOC in soils (Fig. 5b). In wheats, the main compounds like PFOA and PFBA clearly show a positive correlation with TOC in soils (Fig. 5b). It has been documented that TOC could facilitate the adsorption of PFOS in soils through hydrophobic reactions, whilst the SOM account for around 30% of PFOS adsorption in soils because of

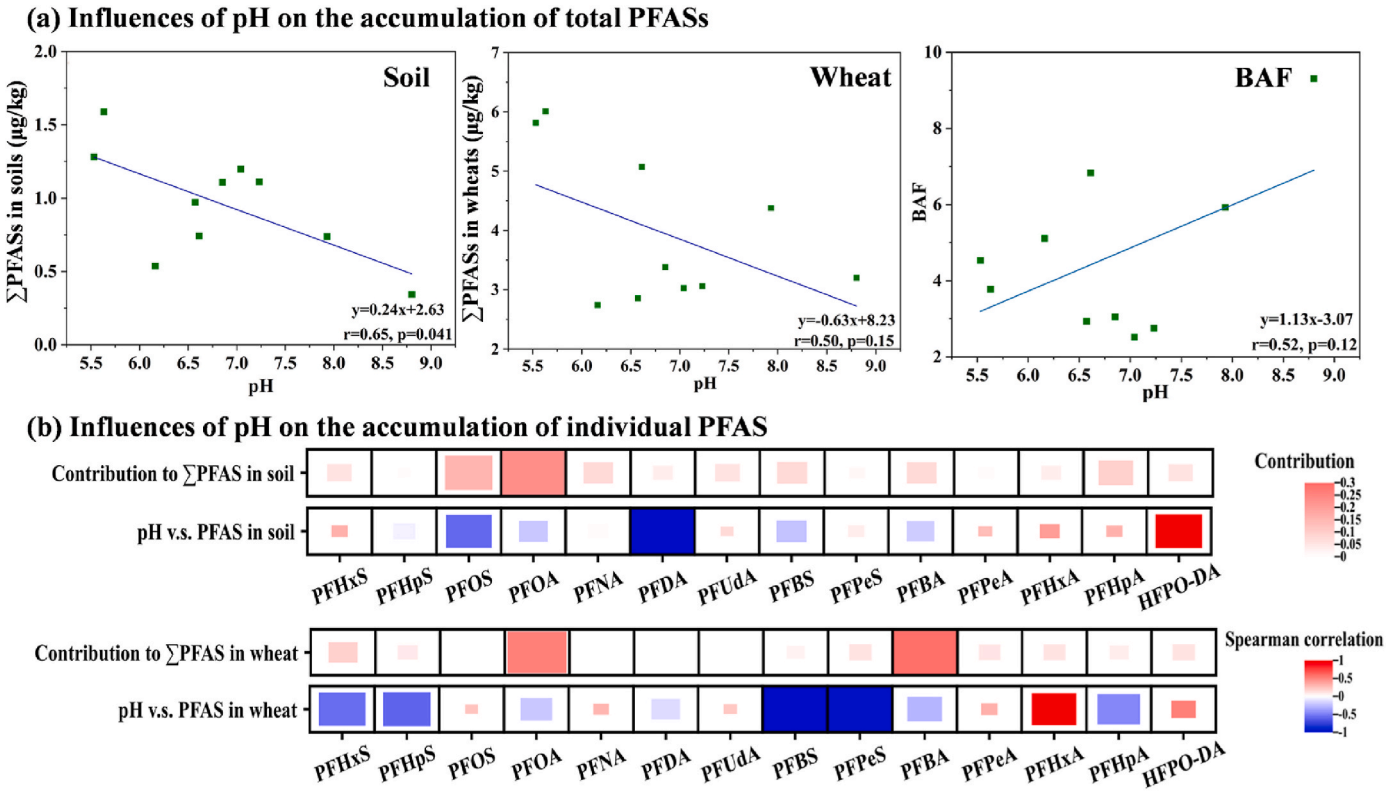

Fig. 4. Influences of pH on the PFASs accumulation in soils, wheat grains and bioaccumulation factors of PFASs.

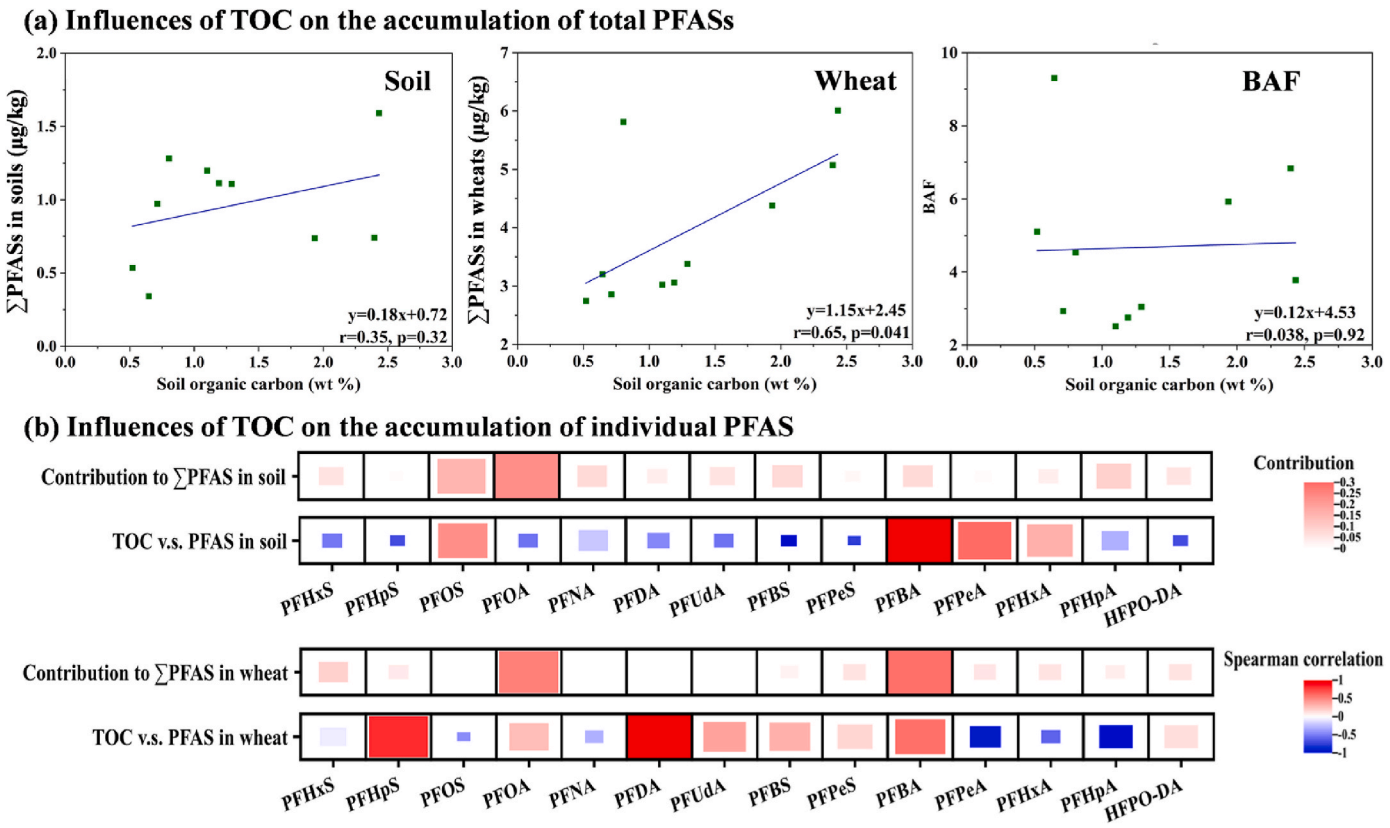

Fig. 5. Influences of soil organic carbon on the PFASs accumulation in soils, wheat grains and bioaccumulation factors of PFASs.

complexity of soil properties, like different soil minerals (Umeh et al., 2021). This observation is consistent with our results that TOC present a weak correlation with total PFASs. Generally, soils with higher TOC could enrich more PFASs in soils, and then more PFASs could be accessed and transferred into plants. However, BAF shows no relationship with TOC in soils, suggesting the mobility of PFASs have no relationship with TOC. Specifically, BAF of PFOA shows a positive relationship with TOC ($r = 0.69$, $p = 0.03$), while BAF of PFBA shows no relationship with TOC ($r = 0.04$, $p = 0.90$). This is inconsistent with our expectation that higher TOC probably result in lower mobility of PFASs and thus lower BAF (Zabaleta et al., 2018). The previous study reported that TOC facilitate the higher accumulation of PFBA, PFPeA and PFBS at 2%wt SOC than at 0.4 or 6% (Gomis et al., 2018). As such two different mechanisms of SOC influencing PFASs accumulation may exist. Soil organic carbon may facilitate the fixation of PFASs in soils through hydrophobic reactions, limiting the mobility of PFASs, whilst TOC may

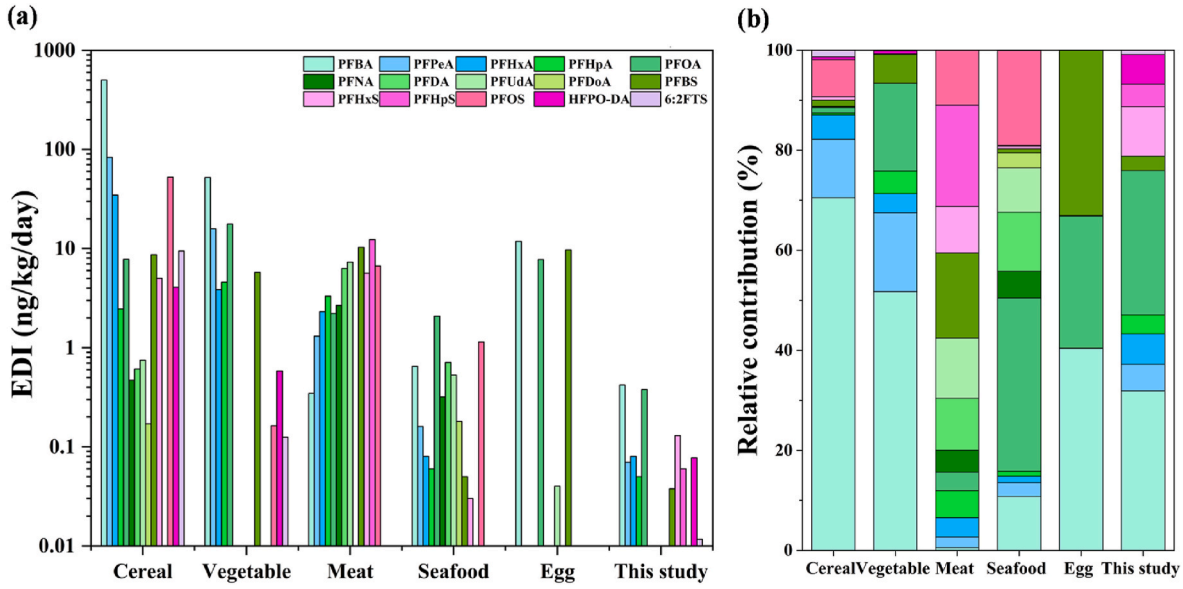

Fig. 6. The estimated daily intakes (EDIs) of main individual PFASs via consumption of wheat grains (ng/kg/day) (a) and the relative contribution of PFASs to dietary intake (b).

compete with PFASs for adsorption sites of soil minerals, resulting in higher mobility of PFASs (Qi et al., 2022). They combined together result in the plausible non-relationship BAF with SOC. Overall, the high TOC in soils facilitate the accumulation of PFASs in soils and subsequently in wheats, but not influence the BAF of PFASs.

3.3. Estimation daily intake and human health risk assessment of PFASs

PFASs accumulate in wheat grains and may eventually enter the human body through the food chain, probably causing adverse effects on human health (Blaine et al., 2014). Wheat is common carbohydrate for people living along the Yangtze River, which has been known as an important pathway of PFAS exposure to human (Liu et al., 2019b). As such, it is important to estimate the human exposure to PFASs via wheat consumption. The estimated daily intake (EDI) for major PFAS components has been calculated and shown in Fig. 6.

The values of EDI for average concentration of major PFASs ranged from 9×10^{-5}–0.42 ng/kg/day. The PFAS individual compounds with highest EDI values was PFBA at 1.26 ng/kg/d, followed by PFOA at 0.38 ng/kg/d, and by PFHxS at 0.15 ng/kg/d. EDI for other long-chain legacy PFASs in constrain list (PFOS, PFNA, PFDA, PFUdA, PFDoA) are much lower than PFOA and PFBA. In our study, EDI values for PFBA and PFOA are much higher than that for PFBS and PFOS, respectively, suggesting the carboxylic perfluorinated compounds are more likely to be transferred into food chains and finally enter human bodies. This trend reflects the mobility and accumulation of PFASs compounds in wheat grains, where PFCAs are easier transferred from soils to wheat and finally accumulate in grains. In addition, we also observed that EDI values of PFOA is higher than that for HFPO-DA. HFPO-DA is a common alternative of PFOA, but rare studies compare their environment behavior. Our results document that PFOA still have higher potential risks to human beings, although HFPO-DA is accumulated in soils very fast in recent years and is also observed to contribute to the daily intake of PFASs. The RQ values for PFBS (0.0013), PFOS (0), PFBA (0.00042), PFHxA (0.0024), PFOA (0.13), HFPO-DA (0.026), respectively, are much lower than 1, indicating that humans have a low risk from these PFASs through ingestion of wheat grains.

The daily intake of total PFASs in various food such as grains, vegetables, eggs, meat, and fishes are compared here. As shown in Fig. 6b, the main contaminants in food are PFBA, PFOA, PFHxS, PFOS and HFPO-DA. The proportions of PFBA and PFOA to daily intake are at similar levels in wheat grians, while PFBA dominates in vegetables and cereals, and PFOA/PFNA dominates in seafood and eggs. It is worth noting that the daily intake of HFPO-DA for wheat grains is observed here, and the proportion is much higher in grains than in other food. Previous studies suggest that EDI values of PFASs via grains are the highest, hundreds of times higher than those via eggs and meat (Liu et al., 2017). However, results from our study suggest that EDI from PFASs in wheat grains is lower by several magnitudes than that for other foods. The possible reason is that some data in literature were collected from the vicinity of the pollution source area, where the PFASs accumulation in food is much higher. As such, our data could suitably reflect the EDI of PFASs for wheat grains, which are at very low levels, suggesting the extremely low potential risks to human beings.

4. Conclusions

In this study, we collected soils and wheat grains from normal framland, investigated the accumulation of 30 PFASs in wheat soils and grains, and further evaluated their potential health risks to humans. The concentrations of PFCAs are typically higher than PFSAs in soils, where PFOA and PFOS are the main substances. In wheat grains, PFBA, PFOA and PFHxS are the major compounds. The lower pH conditions could result in the higher concentrations of PFASs in soils and then in wheat grains, while the BAF at lower pH are lower than that at higher pH conditions. The high TOC in soils facilitate the accumulation of PFASs in both soils and wheats but not influence the BAF of PFASs. Legacy PFASs (especially C4–C8 PFCAs) show a trend of decreasing BAF values as carbon chains increase, whilst PFCAs have a stronger bioaccumulation ability than PFSAs. The EDI values of PFBA, PFOA, and PFHxS are relatively at high levels, but data shows that ingesting wheat grains does not result in any potential risk to the human beings.

CRediT authorship contribution statement

Huan Yang: Writing – original draft, Methodology. **Yao Zhao:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Conceptualization. **LiNa Chai:** Formal analysis. **FuJun Ma:** Investigation. **JianLong Yu:** Formal analysis, Data curation. **KeQing Xiao:** Methodology, Funding acquisition, Conceptualization. **QingBao Gu:** Visualization, Supervision, Resources, Investigation.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124351.

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Review

The geological cycle of plastics and their use as a stratigraphic indicator of the Anthropocene

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ABSTRACT

The rise of plastics since the mid-20th century, both as a material element of modern life and as a growing environmental pollutant, has been widely described. Their distribution in both the terrestrial and marine realms suggests that they are a key geological indicator of the Anthropocene, as a distinctive stratal component. Most immediately evident in terrestrial deposits, they are clearly becoming widespread in marine sedimentary deposits in both shallow- and deep-water settings. They are abundant and widespread as macroscopic fragments and virtually ubiquitous as microplastic particles; these are dispersed by both physical and biological processes, not least via the food chain and the 'faecal express' route from surface to sea floor. Plastics are already widely dispersed in sedimentary deposits, and their amount seems likely to grow several-fold over the next few decades. They will continue to be input into the sedimentary cycle over coming millennia as temporary stores – landfill sites – are eroded. Plastics already enable fine time resolution within Anthropocene deposits via the development of their different types and via the artefacts ('technofossils') they are moulded into, and many of these may have long-term preservation potential when buried in strata.

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1. Introduction

The concept of the Anthropocene, an epoch of time in which humans have come to dominate many surface geological processes, has been widely discussed since it was first proposed by Crutzen and Stoermer (2000) and Crutzen (2002). Sufficient evidence exists to suggest that the Anthropocene is a real geological phenomenon, with potential to be formalized within the Geological Time Scale (Zalasiewicz et al., 2008; Williams et al., 2011; Waters et al., 2014). Although many suggestions have been put forward regarding the timing of the Anthropocene, there is growing consensus that a starting time around the mid-20th century and the post-WWII 'Great Acceleration' of population, industry and resource use (Steffen et al., 2007, 2015) is optimal. This is partly a result of the increase in scale of human impacts on the Earth system, such as the ~120 ppm rise in CO_2 above pre-industrial levels, while the "Great Acceleration" interval is also marked by key, near-synchronous stratigraphic markers that enable the strata of a putative Anthropocene Epoch to be identified (Waters et al., 2016). These markers include artificial radionuclides (Hancock et al., 2014; Zalasiewicz et al., 2015; Waters et al., 2015), aluminium metal (Zalasiewicz et al., 2014), fly ash particles (Rose, 2015; Swindles et al., 2015), persistent organic pollutants (Muir and Rose, 2007) and a variety of biological indicators (Barnosky, 2014; Wilkinson et al., 2014).

One further potential indicator is plastic, as this material has been manufactured in abundance since the mid-20th century. Plastics are key to the momentum of the technological revolution from the start of the 'Great Acceleration', because of their remarkable utility and versatility. They are fundamental to contemporary hygiene, as wrapping for foodstuffs and other materials, as disposable gloves, coats and medicine encapsulations used in hospitals, and in providing inexpensive clean water systems via water bottles and pipelines. Plastics are also components of many of our buildings, tools and machines.

Although now indispensible, plastics are easily disposable. Discarded in various ways after use, we see them widely around us as litter. The scope and range of plastic contamination has become increasingly apparent over the last few decades, and it is now regarded as a major, and growing, environmental hazard (see below). A corollary of this dispersal is that plastics might be used as markers of the age and character of the sedimentary deposits that they are buried in, much in the way that geologists use fossils to characterize and date strata. It is this potential that we explore in this paper.

Plastics are relatively easily recognizable, without the need for sophisticated analytical equipment, as is the case for the detection of radionuclides. They may, therefore, be widely effective stratigraphic markers for Anthropocene strata. However, appreciation of their utility requires consideration of their behaviour as a *geological* material, rather than as a product of material science, or as an environmental pollutant. This idea of plastics as a significant component of the present-day sedimentary cycle is growing, although clear and detailed global characterization of this concept has only just begun (e.g. Reed, 2015; Corcoran 2015).

This paper thus places current knowledge about the environmental behaviour of plastics into a general geological perspective. We consider the extent to which plastics may provide a pragmatic stratigraphic marker, not just in soils and other terrestrial deposits, but also far into the marine realm. We develop this analysis to provide the first predictive model of the transport, distribution and burial of plastics as sedimentary particles in a representative array of global sedimentological settings, both terrestrial and marine. We also consider the factors affecting the long-term preservation of plastics once buried in geological strata. Plastics, seen through this prism, may range more widely through time and space than can be seen by the casual eye.

2. The nature and production of plastics

Plastics are malleable solids made of high molecular weight organic polymers. Most are entirely synthetic – primarily made from petrochemicals – although some are cellulose-based. The first plastics to become commonly used were permanently hard and brittle, such as shellac, for gramophone records from the late 19th century, and bakelite, produced widely from the 1920s to the 1940s and still in minor use today (Albus et al., 2006). Viscose silk and rayon, made from a cellulose base, have been manufactured since the early 20th century, and remain in production. Nylon, polystyrene (PS), polyvinyl chloride (PVC), polyethylene (PE) and polytetrafluoroethylene (PTFE) began to be produced in the late 1930s and 1940s, polypropylene (PP) and expanded polystyrene foam in the 1950s, and polyethylene terephthalate (PET), from which most containers and bottles are now made, was patented in 1973 (Fig. 1). Development continues to this day, with some 15–20 main groups of plastic (Shah et al., 2008).

The extraordinary global expansion of this now indispensible material (Andrady and Neal, 2009) can be seen in the dramatic rise of produced plastics, from the less than 2 million tonnes manufactured in 1950 to the 300 million tonnes made annually today (Fig. 2). The cumulative amount produced as of 2015 is of the order of 5 billion tons, which is enough to wrap the Earth in a layer of cling film, or plastic wrap. The current global annual production represents ~40 kg of plastics produced annually for each of the 7 billion humans on the planet, approximating the total human biomass (Zettler et al., 2013). The amount projected by 2050, on current trends, is about 40 billion tons (Rochman et al., 2013), which is enough to wrap 6 layers of cling film around the planet. It is an enormous industry, currently using approximately 8% of global oil extraction for its manufacture (Thompson et al., 2009). Approximately 4% is used as a source material for the plastics, and 4% is used to provide the energy to produce the plastics: http://www.wastewatch.org.uk/data/files/resources/13/Plastics-information-sheet-FINAL-Oct-08.pdf.

Most of the global plastics that have been produced are still present in the environment. Of the plastics produced in Europe, about half are accounted for by recycling, energy recovery (i.e. incineration) and landfill, with the proportions incinerated and put into landfill varying greatly from country to country (PlasticsEurope, 2013, 2015). The proportion recycled, within the half that is

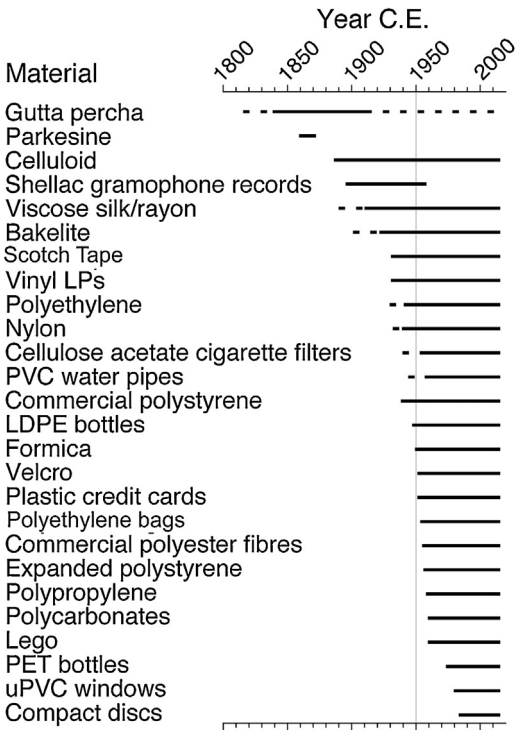

Fig. 1. Stratigraphic appearance of some major types of plastics and plastic artefacts. Gutta-percha, the hardened sap of any of eight tree species from southeast Asia, is not strictly a plastic. Nevertheless, it features in some early histories of this material. Between 1850 and 1899, some 27,000 tons were laid on the seafloor to serve as insulation for telegraph cables due to its resistance to saltwater corrosion (Tully, 2009). Adapted from information mostly in http://www.bpf.co.uk/Plastipedia/Plastics_History/Default.aspx.

accounted for, is typically 15–25% in Europe (op. cit.), but figures provided by Barnes et al. (2009) for the USA suggest recycling rates there are below 5%. The half of plastics production that is not accounted for (see also Rochman et al., 2013) presumably stays in the environment, either as components of some 'permanent' object or is disposed of otherwise, including casually as litter.

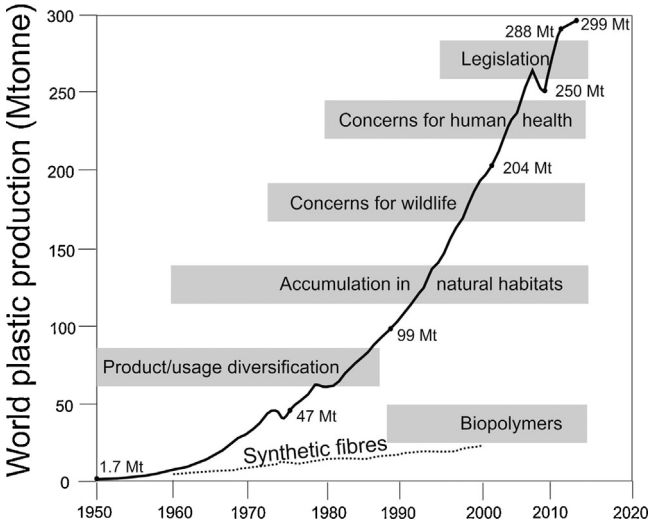

Fig. 2. Growth of plastics production: from PlasticsEurope (2013, 2015). Synthetic fibres production (million tons per year) from Thompson et al. (2004) and historical stages in plastics development, in grey boxes, from Thompson et al. (2009).

3. Plastics in the environment

Plastics are useful to humans because they are light, strong, flexible and relatively inert. They are insoluble in water, and resistant to biological decay and much chemical attack, over decades to centuries at least. They are easily transported by wind (Gasperi et al., 2015) and water through the environment, where they may accumulate. Plastics are proving to be much more mobile than other human-made materials such as ceramics or glass. It took ceramics thousands of years to achieve anything resembling a global distribution, and they are distributed mainly in terrestrial deposits, with very little incursion into marine environments (Edgeworth et al., 2015). From being a local 'litter' problem a few decades ago, plastics are increasingly recognized as a major environmental problem on land and in the sea. In response, there has been a rapidly expanding body of literature on the subject within the last few years (e.g. Ivar do Sul and Costa, 2014).

Plastics in the environment are divided broadly into macroplastics and microplastics. Macroplastics are >5 mm, and include everything that we would recognize as litter, such as plastic bags and bottles, discarded fishing nets, plastic toys, and sections of plastic piping (Fig. 3). In some surveys, for instance by cameras on remotely operated submarine vehicles, macroplastics are the only plastics that can be observed (Watters et al., 2010; Richards and Beger, 2011).

Microplastics (<5 mm) are commonly invisible to the naked eye, particularly when mixed into sediment. Some microplastics are of their original size, such as the 10–1000 μm plastic microbeads (polyethylene microspheres that are put into certain cosmetics, facial scrubs and toothpaste) as well as lentil-sized resin pellets ("nurdles") that are the raw materials for plastic products. Other microplastics have been physically or physico-chemically degraded. A microplastic category recently recognized as important is plastic fibres (~0.1 mm across and usually up to 2–3 mm long), detached from synthetic fabrics during washing. A single synthetic garment, for instance, can release over a thousand fibres in a single wash cycle (Fig. 4). Too small to be filtered out either by machine or sewage plant, these can travel far by river and sea current, and become deposited in sediment layers (Browne et al., 2010, 2011; Woodall et al., 2014).

Plastics can be considered sedimentary components in both terrestrial and marine environments; however, their distribution on land appears to have had much less study than that in the sea (Thompson et al., 2009; Rillig, 2012). This may be a result of the greater heterogeneity of landscape, both natural and anthropogenic, which makes analysis difficult. Nevertheless, it is clear even by casual observation that macroplastic debris may be found in

Fig. 3. Plastic debris on Kamilo Beach, Hawaii (item on right of photo is plastiglomerate); field of view is 20 cm across.

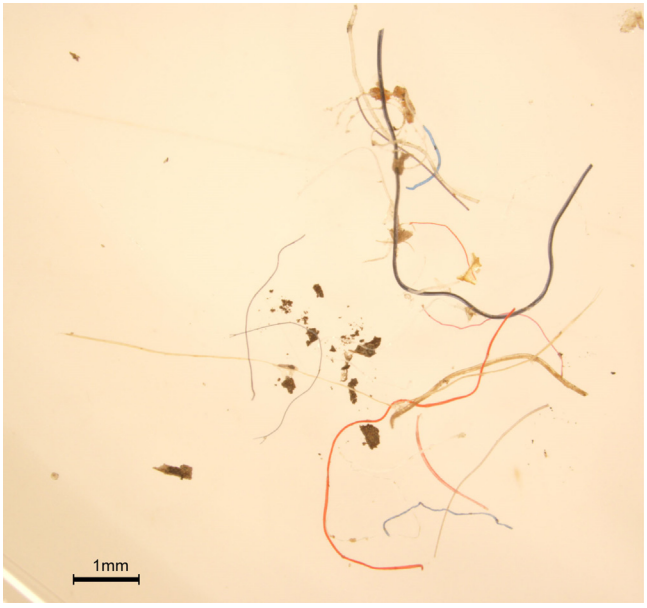

Fig. 4. Microplastic fibres found in bottom sediments of Lake Ontario—sampled by glew corer (photo: Anika Ballent).

most inhabited environments. Microplastics are not easily visible, but methods for their analysis in the environment have been developed. They can be extracted from water by filtering, and separated from sediment via sieving or density separation using centrifuge and salt solutions (Nuelle et al., 2014; Woodall et al., 2014; Corcoran et al., 2015).

Nanoplastics are particles that are typically tens of nanometres in diameter. These may be produced intentionally, for example for drug delivery, detergents or cosmetic use, or they may result from fragmentation of larger plastic particles. Studies of nanoplastics have indicated their large surface-to-volume ratio, which increases their capacity to adsorb organic compounds, potentially gives an ability to penetrate cell walls, and they have been shown to affect the growth and reproduction of at least some aquatic invertebrates (e.g. Besseling et al., 2014; Della Torre et al., 2014; Velzboer et al., 2014). The distribution of nanoplastic particles in the natural environment is very poorly known because of the technical difficulty of isolating them from water or sediments, but they are almost certainly becoming increasingly commonly dispersed.

3.1. Land

On land and away from shorelines, plastic litter is widely distributed in the surface environment, most clearly in and around urban areas via casual littering. However, its distribution seems to have had little detailed study (Thompson et al., 2009; Rillig, 2012). The use of plastics in agriculture has grown since the 1960s, and Hussain and Hamid (2003) noted that global agricultural consumption of plastics is ~2.5 million tons per year. They are used in transplant and bedding plant production, as irrigation tape, trays and pots, tunnels, hay bale wraps, and in greenhouse construction. Plastics may become incorporated into cultivated soils, where they become thoroughly mixed with other materials to the full depth of ploughing.

The stratigraphic distribution of plastics below the ground surface correlates strongly with the distribution of landfill sites, where plastics in the last few decades have come to make up approximately 10% by weight of the waste buried (Thompson et al., 2009). Where landfill sites have been mapped out and their operation dated, sedimentary deposits up to several tens of metres thick with concentrations of plastics may be delineated (Figs. 5 and 6). In 1967, in the UK, plastics formed about 3% of municipal landfill waste (Bridgewater, 1986). However, increasing production of plastics in the 1960s coincided with increased casual disposal of single-use goods rather than re-use and repair. This contributed to the rapid increase in the proportion of plastics in landfill in the 1970s (Fig. 11 in Ford et al., 2014). Subsequent legislation across many parts of the world has stimulated increasing reuse and recycling of plastic goods, such as supermarket plastic bags, but at best this has restricted rather than reversed the relentless growth of plastic disposal. The problem is greater in some developing

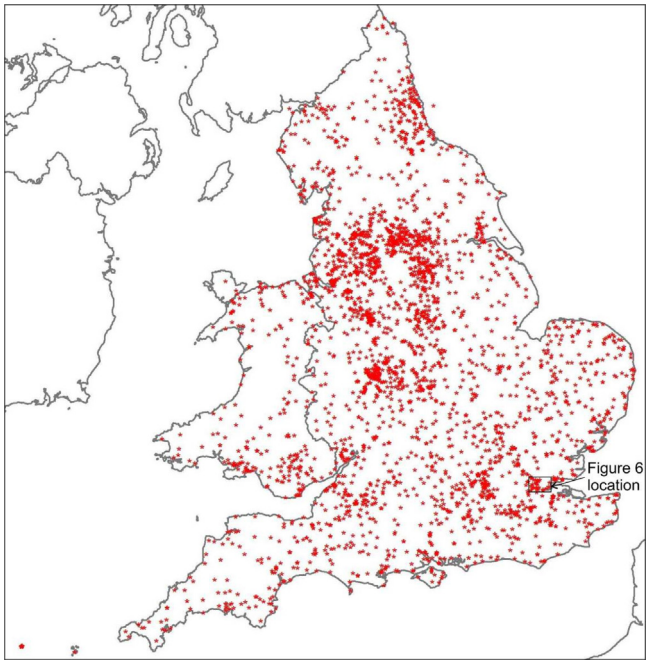

Fig. 5. Distribution of 3055 waste disposal sites across England and Wales active during the period 1971 – 3.
Source: British Geological Survey database, held on behalf of Department of Environment). Box shows location of Fig. 6. BGS ©NERC 2015. All rights reserved.

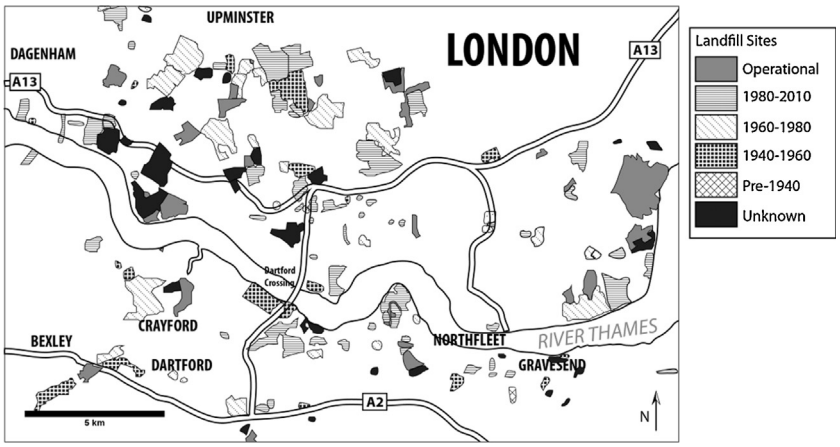

Fig. 6. Landfill locations in part of east London, showing operational history; post-1960 sites generally include significant plastics content (from Environment Agency data).

countries where the arrival of abundant packaged goods is associated with inefficient waste disposal.

The distribution of landfill sites commonly coincides with the (former) outcrop of bulk minerals, such as quarries for aggregate and for brick clay. Landfill sites, especially modern ones with leak-proof seals, tend to mummify material – even paper and foodstuffs – rather than encourage it to decay (Rathje and Murphy, 1992). Hence, plastics may be expected to survive even longer in landfills than at the surface (cf. Tansel and Yildiz, 2011), with the potential to become fossilized or reworked by future erosion (see Section 5).

Road networks have increasingly become corridors of plastic deposition, partly through surface deposition of discarded material, where plastics are likely to degrade or be dispersed relatively quickly and not accumulate as substantial deposits. Nevertheless, these are likely to be zones of microplastics production through degradation and fragmentation. Plastics are also widely used in the laying of cables and pipes for services and communications, which are deliberately buried in backfilled trenches, often under or along roads.

Plastics are starting to be used as stratigraphic markers in field archaeological practice - as indicators of modern or recently disturbed deposits (Fig. 7). Even small amounts of plastic found as inclusions within a layer can be used as evidence of date of deposition. This can provide precise constraints on the age of the specific deposit within which it is found, and also confers relative dating information on layers that are stratigraphically above ('later than') and below ('earlier than') the plastics-bearing layer.

3.2. Lakes and rivers

Plastics have been found in freshwater ecosystems (Eerkes-Medrano et al., 2015), such as lakes (e.g. Eriksen et al., 2013; Imhof et al., 2013; Free et al., 2014; Zbyszewski et al., 2014), and rivers, such as the Thames (Morritt et al., 2014), Danube (Lechner et al., 2014) and Yangtze (Zhao et al., 2014). Plastics are likely to be at least as widely distributed in lakes as they are in the oceans (see below). Although their distribution on shorelines and as floating debris on water has locally been determined, as in the Great Lakes of North America, their distribution in lake bottom sediments has only recently been investigated (Corcoran et al., 2015).

Microplastics are introduced to rivers via wind, storm sewers, and wastewater treatment plants; they also host distinct microbial communities (McCormick et al., 2014). However, the low density of the most commonly produced plastics, polyethylene and polypropylene, means that a significant proportion stays within or upon the water column and is transported farther downstream or out to lakes and seas (Sadri and Thompson, 2014). The majority of plastic debris is sourced from land. Thus, rivers are conduits for plastics to enter their final sink: the marine or lake realms. For example, in South Wales about 80% of litter on estuarine beaches comes from rivers (Williams and Simmons, 1996), and near Toronto, Canada, plastic pellets were observed travelling down the Humber River into Lake Ontario (Corcoran et al., 2015).

Plastics often act as sediment baffles in rivers, as does vegetation and wood debris. Along lake shorelines and river banks, plastics tend to become trapped in organic debris brought in by waves and currents (Zbyszewski et al., 2014; Corcoran et al., 2015). In addition, high-density plastics may accumulate within channel bedload, where mobile plastic elements in the traction carpet may be abraded rapidly (Williams and Simmons, 1996) and reduced to microplastic particles. Between rivers and the sea, mangrove stands can trap plastics (Ivar do Sul et al., 2014).

3.3. Nearshore marine

That macro- and microplastics were entering the seas, and were likely to cause significant environmental impact, was observed

Fig. 7. 1980s plastic bags in the upper fill of an ornamental moat in Tudor gardens from evaluation at Cedars Park, Broxbourne, Herts by Museum of London Archaeology, 2010 (image reproduced courtesy of MOLA). The plastic in this case has been in the ground for 30 years. It is well preserved, providing a visual and colourful marker in the profile of an archaeological deposit or anthrosol (a completely or nearly complete human-made soil). As a dateable horizon within a stratigraphic sequence, the plastic-bearing layer here provides relative dating for all layers above (1980s or later) and all layers below (1980s or earlier). Its utility as a stratigraphic marker extends to the whole sequence.

from the 1960s in seabird populations (Kenyon and Kridler, 1969; Harper and Fowler, 1987) and from the 1970s on the sea surface (Carpenter and Smith, 1972). Since then, both the phenomenon itself and study into it have grown markedly, particularly in the last decade (Ivar do Sul and Costa, 2014; Leinfelder, 2016). Attention has focused on the impact of ingestion and entanglement on biota, on their distribution within both water and sediments, and on possible toxic effects. Although plastics are generally inert, they can accumulate toxins such as PCBs on their surfaces or release harmful constituents such as bisphenol A as they weather.

The sea is the final resting place for a range of different types of human litter, from glass to metals to building waste, though plastics form the most striking component. Making up some 10% of all human refuse by weight, plastics are then selectively transported by wind and water to make up >50% of marine litter, and locally considerably more (Barnes et al., 2009). A similar selective concentration of certain natural resistant rock types, such as flint and vein quartz, occurs within sedimentary deposits. There have been some studies of physical sorting of plastics, particularly in coastal areas. For instance, Browne et al. (2010) examined the sorting of microplastics within the Tamar estuary near Plymouth, UK, and noted segregation of lighter and more dense microplastics, although no relationship between microplastics and clay particle distribution was observed. Isobe et al. (2014) noted selective transport of mesoplastics (~5 mm) towards the shore and microplastics towards offshore in the Seto Sea of Japan.

Plastics enter the sea via rivers, from point and diffuse sources along the shoreline and from ships, though such dumping is now in theory banned by international shipping regulation (Ryan et al., 2009). Estimates of plastics currently entering the sea each year range from 6 million tons (UNEP 2009 in Pham et al., 2014) to between 4.8 and 12.7 million tons (Jambeck et al., 2015), with the amount predicted to increase by an order of magnitude by 2025 (Jambeck et al., 2015). Differences in source are evident, for example around the UK coastline, with various proportions derived from rivers, fly-tipping, sewage outfalls, ship discharges (Williams and Simmons, 1996) and coastal tourism.

Significant microplastics (38–234 particles per cubic metre), have been found frozen in Arctic sea ice, having seemingly been derived from the Pacific Ocean (Obbard et al., 2014). The Arctic is thus a major global sink for these tiny plastic particles. However, melting at current rates could unlock over one trillion pieces of microplastics over the next decade. Rayon was the most common material, much of it from cigarette filters (one cigarette filter tip comprises ~10 000 fibres) and hygiene products. Other materials included polyester, nylon, polypropylene (PP), polystyrene (PS), acrylic and polyethylene (PE).

Once within the sea, low-density plastics such as polyethylene (PE) and polypropylene (PP) – that together comprise ~55% of output in Europe (PlasticsEurope, 2015) – float in seawater. These low-density plastics can be moved by wind stress and by surface currents, and in this way they encircle the Earth, becoming concentrated in mid-ocean gyres such as the 'Great Pacific Garbage Patch', some thousand kilometres in diameter (Moore et al., 2001; Ryan et al., 2009; Law et al., 2014). There have been widely reported examples of spilled cargoes of such distinctive objects as plastic ducks tracked to reveal marine pathways (e.g. Ebbesmeyer and Scigliano, 2009; Hohn, 2011). Ultimately, plastics may be washed up on far-distant beaches. On Korean beaches, Jang et al. (2014) found that more than half of the plastic material beached had come from the ocean, via long-distance travel, and not from nearby land.

Plastic fragments with densities >1 gm/cm^3, including PVC, sink in seawater. They can then be moved by tidal and storm-driven currents in shallow water, and by various gravity-driven currents (e.g. turbidity and contour currents) in deep water before finally being deposited. However, low-density plastics have also been found in lake-bottom sediments, having been deposited as a result of density increase by mineral fillers during production, or mineral adsorption while in the water column (Corcoran et al., 2015; Corcoran, 2015). It is also being increasingly realized that the transport of plastics through the water column is often mediated biologically (see below) because microbial films rapidly develop on submerged microplastics and change their buoyancy (Lobelle and Cunliffe, 2011).

Studies of plastics in sediment to date have typically focused on the amount and type of plastics present and on their geographical distribution. However, very few investigations include data on the vertical distribution of plastics within the sediment (exceptions include Kusui and Noda, 2003; Ng and Obbard, 2006; Turra et al., 2014; Corcoran et al., 2015). Inferences on such distribution must be made using general sedimentary facies considerations.

Coastlines and beaches have understandably attracted much attention, given their sensitive status in human society and the high visibility of plastic litter deposited there. The monitoring of

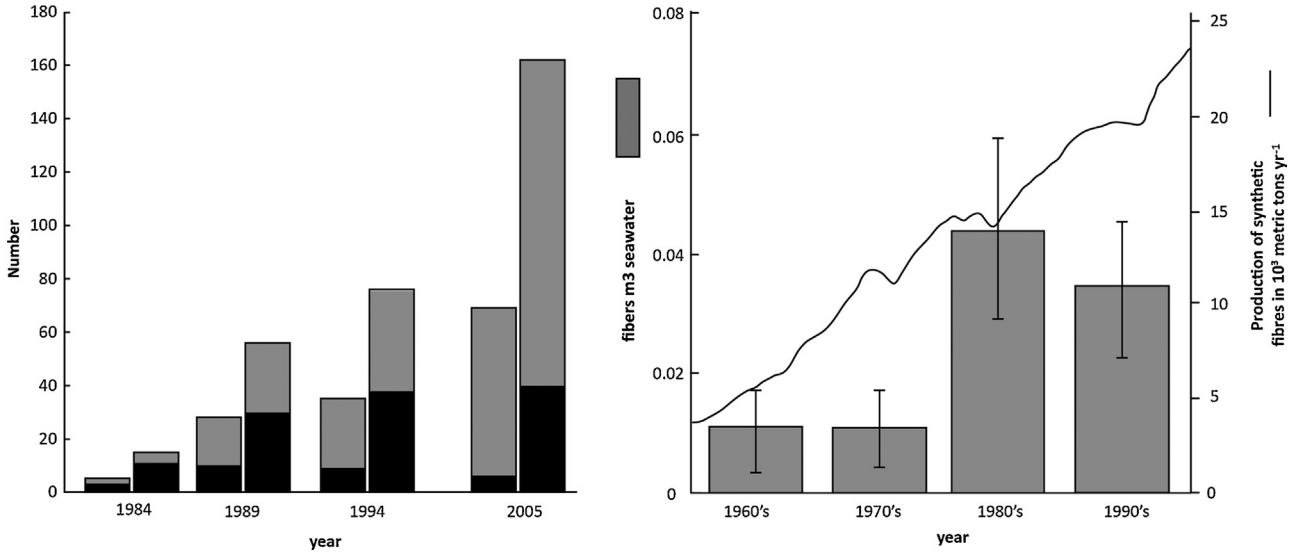

Fig. 8. (Left) increase in number of plastic bottles (left bar) and lids (right bar) on beaches with regular cleaning programmes (in black) or no formal cleaning (in grey), redrawn from Ryan et al. (2009). (Right) microplastic time series data from Thompson et al. (2004).

beach litter, mostly macroplastic, is typically done by counting items at the surface per unit length (e.g., per 100 m) of coastline, and noting such aspects as type, composition, weight and volume. A recent study of Korean beaches (Hong et al., 2014) found 300–1000 items/100 m, including polystyrene fishing buoys, and plastic bags and bottles. Cigarette filter tips are generally the single most common item found in studies of such sort and in beach cleanups. Of the ~6 trillion cigarettes smoked annually, the filter-bearing tips of over 4 trillion end up as litter each year (Carlozo, 2008).

Plastics are virtually omnipresent in the coastal zone globally, not only in densely populated regions, but also because of long-distance transport to remote areas. Barnes (2005) noted substantial amounts of macroplastics on remote islands. On some islands such as Diego Garcia, hermit crabs have taken to using plastic bottle tops as homes (see also Reed, 2015 p. 32). He also noted a diminishing trend of plastics from equator to pole in the Southern Ocean, although noticeable amounts still reach Antarctic coasts. In Hawaii, accumulations of plastic debris have formed what Corcoran et al. (2014) referred to as 'plastiglomerates' in which melted plastic associated with campfires (Fig. 3) has bonded beach pebbles and sand to form a rock (theoretically the activity of wildfires and volcanic activity could also cause melting). These dense hybrid plastic-sediment materials have good potential for burial and long-term preservation.

Successive surveys have shown that amounts of plastics in coastal sediment have increased through time, broadly mirroring the rise in global production (Ryan et al., 2009; Fig. 8 herein; Claessens et al., 2011). This trend continues: British beaches in 2009 saw record levels of litter, with an average of 2195 items/km in a survey of 374 beaches nationwide, compared with 1045 items/km in 1994 (Adam, 2009). This trend occurs despite strenuous clean-up efforts by local authorities and volunteer groups, and the activities of beachcombers. Peak levels can be much greater, exceeding 30 000 items/km or 'much higher' in beaches in Europe, Asia and South America (Pham et al., 2014 and references therein).

In the dynamic beach environment, objects can be buried and exhumed many times (Smith and Markic, 2013). Overall, the few studies (e.g. Turra et al., 2014) involving depth profiles of beaches suggest that plastic items may locally extend downwards for as much as 2 m, with there being an order of magnitude more buried plastic than surface plastic. Hence, there is a sediment body forming in the coastal zone that, if seen in cross-section, could contain sufficient macroplastic material to be recognizable to the field geologist as a post-mid-20th century deposit (Fig. 9). In some instances, these macroplastic fragments are already visible in beachrock deposits, as in the Basque coast (Irabien et al., 2015).

Such distribution of macroplastics, particularly in remote areas, may be sufficiently sporadic to prevent consistent identification of Anthropocene deposits. An additional complication occurs where winter storms sweep sandy beach deposits out to sea, replenishing them in the spring and summer.

Microplastic particles are more abundant, and more widely and evenly distributed, than are macroplastics, and can be recognized even in samples as small as 50 g of coastal sediment (Browne et al., 2010, 2011). This can include relatively large particles such as resin pellets, that are near-ubiquitous in some beach sediments. Around São Paulo in Brazil, pellets are commonly present at levels of up to 10 000/m^3 in sediment, and locally of up to 25 000/m^3 (Turra et al., 2014).

Small microplastics are particularly abundant. Largely composed of microfibres (Fig. 4) detached from machine-washed artificial fabrics (Browne et al., 2011) and transported via sewage outfalls to rivers and dumped sewage sludge, these have become very widely dispersed. Browne et al. (2011) suggested that fibres have become incorporated in, and routinely extractable from, shoreline sediments throughout the world, in quantities that range from tens to hundreds of fibres per litre of sediment (Fig. 10) (Browne et al., 2011; Ivar do Sul and Costa, 2014). For example, Dekiff et al. (2014) reported ~5–25 microplastic particles (mostly microfibres) per kilogram of sediment for Norderney (North Sea), whereas Reis (2014) found an average of 66/kg on the Baltic island of Fehmarn. This potentially provides a near-ubiquitous signature of the Anthropocene in coastal settings.

Fig. 9. Plastic fragment in carbonate-cemented beach rock on Gorrondatxe-Azkorri beach, Basque region, Spain (photo: H. Astibia).

3.4. Offshore marine

This encompasses shelf, slope and abyssal sediments, where the extent and stratigraphy of anthropogenic litter has been made clearer by an array of recent studies. Most attention has been gained by the visible plastic debris now floating in the water, following the discovery by Moore et al. (2001) of 'the Great Pacific Garbage Patch'. Plastics concentrate in the slowly circulating waters of the North Pacific gyre, with similar concentrations now known to be present in the other great gyres of the world (Law et al., 2014; Fig. 11). The global assessment by Eriksen et al. (2014) showed the scale of the phenomenon: 5 trillion plastic pieces weighing some 250 000 tons are now afloat at any one time. They noted one unexpected result—macroplastics made up the great majority of this by weight (ca 85%). The proportion of microplastics was far less than had been expected (see also Cozar et al., 2014). The ocean gyres show modelled concentrations of surface plastic debris within the mid-latitudes of all oceans (Fig. 11) that mimic atmospheric circulation patterns of radiogenic fallout (e.g. Waters et al., 2015), thus providing a potential dual signature in marine sediments for recognition of the Anthropocene.

Zettler et al. (2013) found that most fragments collected from the marine water were of polyethylene and polypropylene, two plastics commonly used in packaging and other single-use applications. This plastic marine debris is colonized by a complex microbial community referred to as the "Plastisphere". Plastisphere communities are distinct from those of surrounding surface water, implying that plastics serve as novel ecological habitats in the open ocean. Microbes may be taking part in the degradation of plastics via physical or metabolic means. Bacteria and fungi are well known to degrade highly refractory compounds, including plastic, but this has not yet been demonstrated in the open ocean.

The likely sink for the 'missing surface microplastics' noted above seems be the deep sea. Fischer et al. (2015) discovered

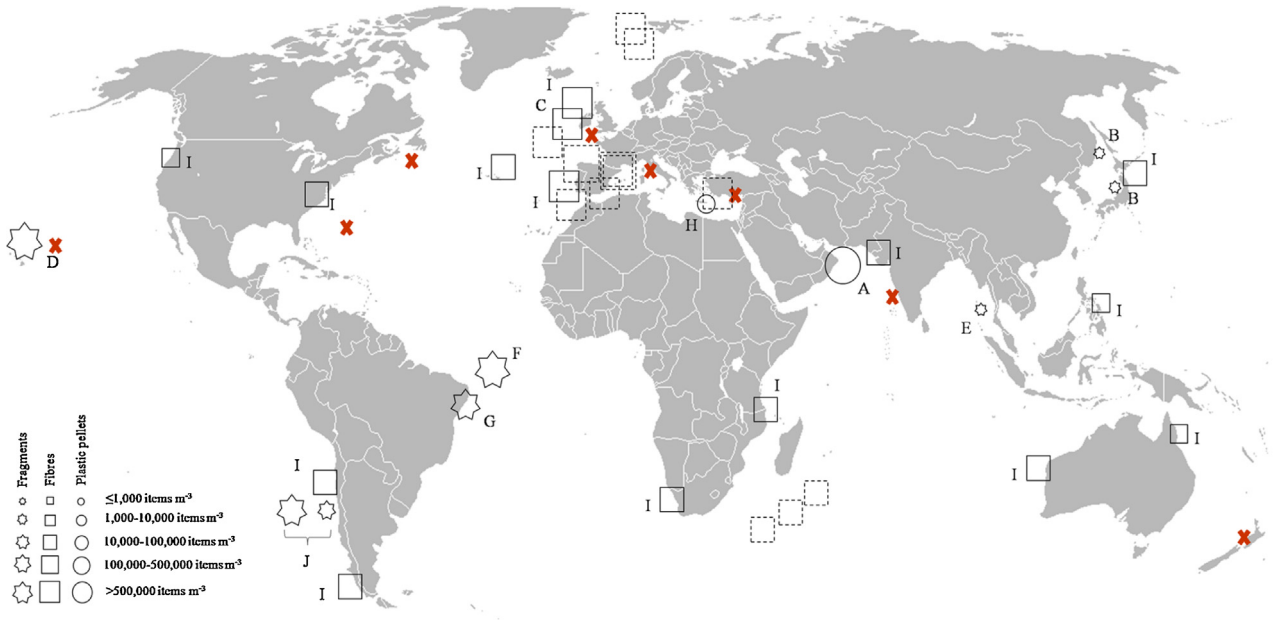

Fig. 10. Reports on the amounts and distribution of microplastics in marine sediment samples. Stars, squares and circles represent the average number of items per cubic metre of sediment available and/or estimated. (A) Khordagui and Abu-Hilal, 1994; (B) Kusui and Noda, 2003; (C) Thompson et al., 2004; (D) McDermid and McMullen, 2004; (E) Ng and Obbard, 2006; (F) Ivar do Sul et al., 2009; (G) Costa et al., 2010; (H) Turner and Holmes, 2011; (I) Browne et al., 2011; (J) Hidalgo-Ruz and Thiel, 2013; (K) Woodall et al., 2014. Dashed squares represent deep-sea sediment core samples. Red crosses represent works that registered microplastics in sediments but did not allow estimation within the scale used here. Extracted and modified from Ivar do Sul and Costa (2014). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

microplastics, mainly fibres, at depths of 4869–5766 m in the Kuril-Kamchatka Trench and adjacent abyssal plain. Even at these great depths, concentrations were as high as 2000/m^2. Woodall et al. (2014) (see also Goldberg, 1997; and Van Cauwenberghe et al., 2013 for earlier records) examined deep-sea sediment core samples from the sub-polar North Atlantic and North-east Atlantic, the Mediterranean, and seamounts on the SW Indian Ocean. All contained microplastics, mainly as fibres, in abundances ranging from 1.4 to 40 fibres (average 13.4) per 50 ml of sediment (Fig. 10). That was some 4 orders of magnitude more abundant than in the contaminated surface waters above. Even the Indian Ocean seamounts, which showed the lowest abundances, were conservatively calculated to have 4 billion fibres per square kilometre, or 4000/m^2 (Woodall et al., 2014).

How did the plastics get to these ocean floors, far distant from land? The fibres were mostly composed of acrylic and polyester, which are denser than seawater. These, it was suggested, may have behaved like fine clay particles, slowly drifting in storm- or turbidity current-generated nepheloid plumes, or carried by thermohaline currents. There were low-density microplastics, too, that had sunk to the ocean floor. These could have been ingested by zooplankton and ejected as faecal pellets, or sank with the plankton when they died, or travelled within the faeces or bodies of fish that ate the zooplankton (Boerger et al., 2010; Cole et al., 2013; Setälä et al., 2014). The microplastics could also have been caught up in gelatinous marine snow. In this respect, microplastics behave in a similar way to other microplanktonic taxa preserved in the geological record (e.g. coccoliths in deep-sea oozes), and represent a primary tool of biostratigraphical correlation in the geological record because of a widespread distribution within strata that are likely preservable long into the future.

Other surveys have shown the spread of larger plastic fragments, by dredging or by remotely operated underwater vehicle (ROV) cameras. Bottles, plastic bags and abandoned fishing nets are abundant (Watters et al., 2010; Richards and Beger, 2011; Tubau et al., 2015; Corcoran, 2015 and references therein), and are often concentrated by topography or currents into submarine lows, such as the bottoms of submarine canyons (Schlining et al., 2013; Tubau et al., 2015). The study by Tubau et al. (2015), of the seabed at 24 of 26 ROV dive sites in the submarine canyons of the NW Mediterranean at depths of 140–1731 m, showed that plastics were the dominant component of litter (72%). Most of the litter was observed on canyon floors at depths over 1000 m, and may have been carried there by down-slope flows originating near shore. Litter density ranged up to 11.8 items per 100 m survey line, and averaged between 8000 and 15,000 items/km^2, reaching a maximum of 167,540 litter items/km^2 at one site (Tubau et al., 2015). Pham et al. (2014) considered that the relative scarcity of macroplastic objects on shelves was because they were being current-swept into deep water, particularly via submarine canyons. Such deeper water and submarine canyon environments, being less disturbed by bottom trawling than are shelf sediments, may provide a good record of the history of plastics influx associated with the Anthropocene. This new plastic-dominated debris layer overlies the debris of previous centuries. Overall, this earlier material is sparser, but a notable component is clinker from the old coal-fired steamships, thrown overboard en route and hence forming 'pavements' below the sailing routes (Ramirez-Llodra et al., 2011).

Thus, in both shoreline and offshore sediments, there is a near-ubiquitous distribution of microplastic fibres, invisible to the naked eye though sufficiently abundant to be extractable from most sediment samples, together with scattered macroplastics. The number of items vary, but, for example, Pham et al. (2014) used submersible cameras to analyse visible debris (mostly plastic) in the north-east Atlantic off Europe. Debris was found everywhere, as far as the Mid-Atlantic Ridge, with densities ranging from ~100 to 300 objects/km^2 in continental shelf areas, to 200–600 objects/km^2 on continental slopes and ocean ridges, to 400–700 objects/km^2 on submarine banks and mounds, to 600–1200 objects/km^2 in submarine canyons. In addition, the Argo profiling

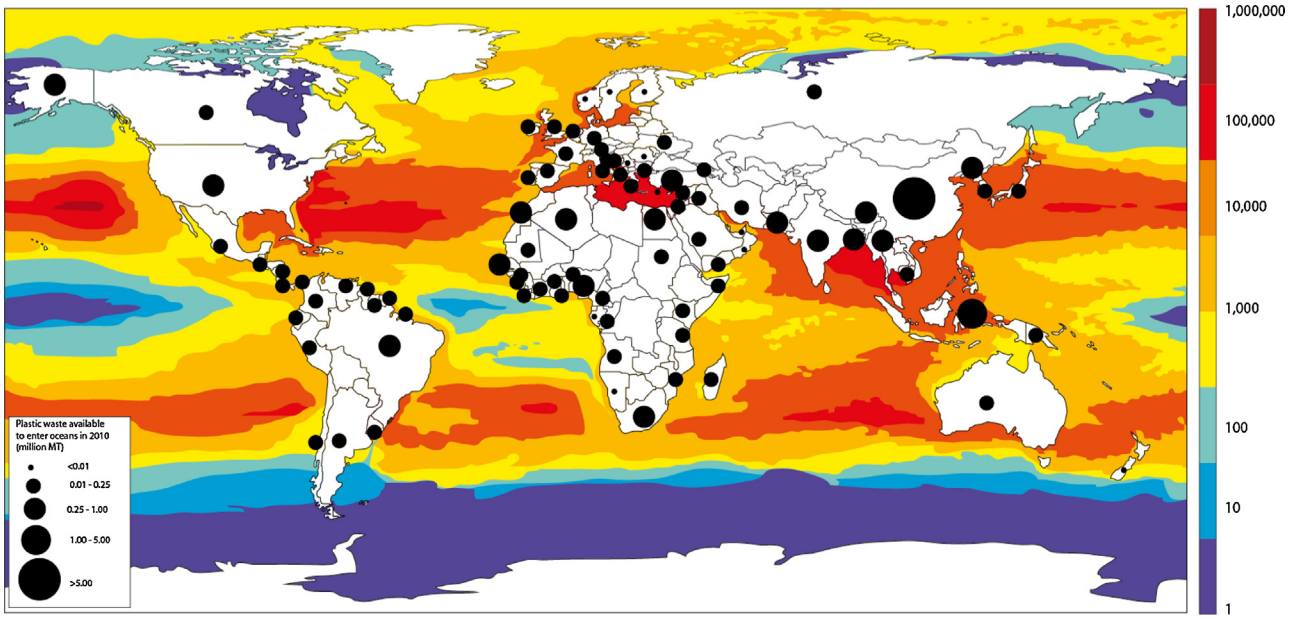

Fig. 11. Modelled distribution of microplastics in ocean surfaces shown by Eriksen et al. (2014, Fig. 2) (1 mm ≤ 4.75 mm). Onshore estimated mass of mismanaged plastic waste is in millions of metric tons, generated by 2010 within 50 km of the coast (Jambeck et al., 2015).

float programme was developed to sow the ocean with 3000 floats to record the temperature and salinity of the ocean down to depths of 2000 m. The programme is intended to operate indefinitely, and will provide further 'scientific litter' comprising the metre-long plastic housings of the floats when they sink to the ocean bed after their batteries die at the end of an approximately 4-year lifetime (www.argo.ucsd.edu/; http://en.wikipedia.org/wiki/Argo_(oceanography)).

4. Preservation potential of plastics in the geological record

The geological longevity of plastic polymers is poorly known, mainly because these are novel materials that have been in the environment for only decades. Will such plastics still be recognizable over geological timescales? Degradation of plastics may take place chemically, by modification of the molecular structure, or physically or biologically (Kay and Blond, 2005; Shah et al., 2008). Chemical degradation can result from alteration of molecular bonds through chemical reactions driven by heat or solar radiation, or via hydrolysis at very high or very low pH. Physical degradation includes partial or total extraction of additives (e.g. pigments, plasticizers and fillers), the action of solvents and environmental stress-cracking. Biological degradation by bacteria and fungi occurs following depolymerization of plastic by other physical or chemical processes.

Plastics are clearly long-lived on human time-scales, especially when buried and beyond the reach of the ultra-violet light present in sunlight that can break bonds in their chemical structure, causing the plastics to become brittle and then fragment (photodegradation) (Shah et al., 2008). Most fragmentation occurs through photodegradation, mainly in beach environments.

Plastics as a whole are resistant to microbial attack, and this underlies a good deal of their practical utility and of their longevity in the environment. Nevertheless, some evidence of digestion by microbes has locally been observed (Harshvardhan and Jha, 2013; Yang et al., 2014; see also Kasirajan and Ngouajio, 2012), and plastics may host microbial communities different to the generally ambient ones (McCormick et al., 2014). The sudden appearance of plastics as a widespread new addition to the surface environment, together with the rapid evolutionary rates observed in microbes subject to strong selective pressures, suggests that microbial degradation may become more common over time, not least because any microbes that can use plastics as a food source will be selectively advantaged. Nevertheless, this is currently a minor factor—and it must be noted that many eminently digestible and decomposable organic tissues (shell because of its organic matrix; bone; wood) may be commonly fossilized once buried. However, in common with shells, plastic items may be fossilized in 'cast' and 'imprint' form even if all the original material is lost through biodegradation. Thus the outlines of biros, plastic bottles or compact disks (CDs) may be found as fossils in sedimentary rock in the future even if the plastic itself has degraded or been replaced by other materials.

Colder temperatures within the deep ocean, associated with a lack of UV light, make plastics on the sea-bed more likely to be preserved. In these conditions, they are said to last for 'centuries to millennia' (Gregory and Andrady, 2003), mostly via inference from short-period laboratory studies. Over longer timescales, their diagenesis and fossilization potential once buried in strata is a topic of considerable academic interest, although of no analytical study yet, as far as we are aware. The nearest comparison is with the long-chain polymers in recalcitrant organic fossils such as wood, spores and graptolites. These fossilize by the loss of part of the material, expelled as hydrocarbon liquid or gas, to leave a carbonized husk and, depending on the size and rigidity of the fossil and the nature of the enclosing fossil, also an impression (an external mould). On preliminary consideration, it seems that many plastics will behave similarly over geological timescales. The hydrocarbons released during diagenesis might contribute to future oil and gas deposits.

5. Discussion

Plastic debris is widely distributed on land and in the sea. On the land surface, the locally abundant but highly heterogeneous distribution of plastics seems imprecisely described by scientific

study. There is, though, considerable potential for plastics to be recorded in archaeological excavations, by a minor adjustment of existing methodologies. And, in developed countries where landfill sites have been categorized, mapped and dated, as in the UK, concentrations of plastic-rich (i.e. ~10%) anthropogenic deposits, metres to tens of metres thick, may be delineated.

In the coastal realm, the accessibility and relative ease of study of environments such as beaches has encouraged more systematic study, and plastic debris has been found to be common along shorelines. It is clear, too, that plastics are widely distributed, both as macroplastics and as microplastics, across the sea floor in most parts of the world (Browne et al., 2011; Woodall et al., 2014; Corcoran, 2015). Overall, therefore, plastics, and particularly microplastics, seem to provide an effective signal for recognizing terrestrial and marine sediments deposited since the mid-20th century.

There is a need, though, for more precise study of the use of plastics as stratigraphic indicators. We note that the distribution of plastics is unlike that of artificial radionuclides, where the test bomb-related signal has an abrupt base in about 1952 (Hancock et al., 2014; Zalasiewicz et al., 2015; Waters et al., 2015), reaches peaks in the mid-1960s, then tails off. In contrast, the plastics signal grows more gradually through time and is less evenly distributed across space. We envisage sporadic appearances in the stratigraphic record of some early forms of plastic, notably bakelite and rayon, from the early 20th century, mostly confined close to urban areas in Europe and North America. This putative, localized fore-runner plastics signal (still to be constrained by stratigraphic study) then gives way in the mid-20th century to a more widespread signal of plastics dispersal, increasing from scarcely perceptible to clearly obvious over little more than half a century (cf. Fig. 2). For instance, a significant presence of plastics within landfill sites on land was not apparent until the early 1970s in developed countries, and displayed some regional diachroneity over the subsequent decade or so as plastics became a global commodity.

In the marine environment, recognition of plastics as an environmental problem did not surface until the late 1960s. Over subsequent decades, the evidence base has become larger while the volume of plastics entering the marine environment has grown exponentially. Thus, the transport of plastics by organisms (and vice versa, in considering floating plastic as vectors for encrusting species) has been well studied, including the ingestion/entanglement (often fatal) by fish and larger vertebrates (e.g. Gregory, 2009). Such specific studies have led to more general relations between filter-feeding plankton, benthic organisms and microplastics (Browne et al., 2008; Cole et al., 2013) being analysed (Ivar do Sul and Costa, 2014).

Little research has been carried out to recognize the extent of the marine plastic signature in the 1940s and 1950s during the early years of its usage and before its environmental impact was realized. That slow beginning makes defining (or precisely locating) the base of the Anthropocene on the basis of plastic materials sensu lato impractical, although plastics are clearly an effective identifier of Anthropocene strata. However, the many forms of plastic developed at different times may be used as time-specific species indicators (Albus et al., 2006) (Fig. 2). For example, acrylic fibres were first created by DuPont in 1941, but not produced in large quantities until the 1950s. This is similar to the stratigraphic use of artificial radionuclides, the onset of signatures for different isotopes being at different times (Waters et al., 2015).

Over geological timescales, the plastics buried in landfill sites may be in part a 'time-bomb' of plastic release. Some landfills, in low ground in tectonically subsiding areas, will simply be buried by more strata, to be fossilized as palaeontological middens. Where landfills are eroded, though, they will begin releasing their debris, including plastic, into the sedimentary cycle (see below).

Virtually all plastics are moulded into artefacts of many different kinds, each of which in this context may be regarded as a technofossil (Zalasiewicz et al., 2014), which is a trace fossil produced by humans. Technofossils show extremely rapid evolution, entirely detached from the evolution of the trace-making organism (i.e. of humans), and hence the appearance of the different artefacts can mark a fine chronology—even to the day, as seen in the date-stamping of plastic food wrapping. This character of litter has been used to precisely date extreme flood events affecting the Oman coast (Hoffmann and Reicherter, 2014). Although it is important to recognize the distinction between production date and the timing of accumulation, which may be

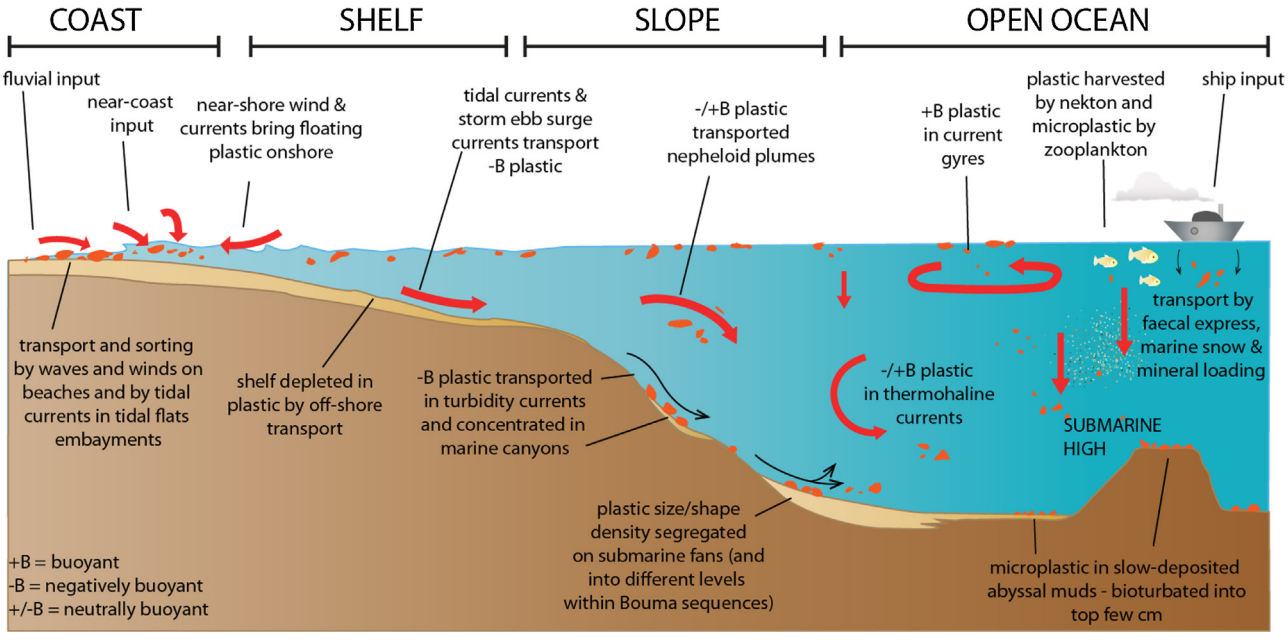

Fig. 12. Conceptual model of plastics transport through and accumulation in the marine realm.

months or years later, this is still a resolution of dating rarely available to geologists.

Spatially, plastics need to be considered as sedimentary particles contained within 3-dimensional sedimentary bodies (sometimes termed 'lithosomes') that have been shaped by a variety of physical and chemical processes. In the Anthropocene, of course, these sedimentary bodies are still accumulating. Such factors as sedimentation rate, transport paths, sedimentary sorting and biological influence become important. Foci of anthropogenically-influenced sediment input, such as large-river delta-front estuaries, already identified as sensitive recorders of other kinds of human-driven perturbation (Bianchi and Allison, 2009), would merit particular study. In drawing up some preliminary patterns of plastic distribution in the context of sedimentology, one might suggest the following as components of a predictive model to be tested and further developed (Fig. 12).

The dynamic coastal zone will often have a relatively thick (metres-scale) plastic-bearing sediment body. Plastic levels can be very high in populated areas and lower, but often still measurable, in uninhabited areas because of long-distance transport. In zones of wave/current reworking, such as beaches, the plastics-bearing sediment body may be locally sharp-based and show internal variations reflecting selective transport and sedimentary sorting, with attrition and enhanced photodegradation of plastic particles prior to burial. In depositional areas, such as deltas and estuaries, where sediment buildup dominates, plastics have preservation potential and may show a stratigraphic pattern of upward increase in relative abundance, reflecting historic increase in plastic production and release. Individual high energy-events, such as storms (Hoffmann and Reicherter, 2014) and tsunamis, may sweep plastic debris far inland. In carbonate-producing environments, plastics have been observed in beach rock (Cara Lauria, pers. comm.; Irabien et al., 2015) and may provide nucleation points for microbial carbonate precipitation.

On continental shelves, there may be continuously current-swept areas such as parts of the tidal North Sea, where sediment is swept along in shelly sand dunes. Only the denser plastic fragments might be incorporated there, while lighter or smaller, but still negatively buoyant particles such as fibres might be winnowed out to travel further. On quieter or more distal shelves, plastics may travel with debris in storm ebb surges (or the ebb currents from tsunamis) to be deposited as tempestite layers.

Along continental slopes, plastics will be funneled together with sediment through submarine canyons, as already observed (e.g. Pham et al., 2014). Within canyons, there is likely to be size/shape/density sorting of the plastic debris, as there is of the accompanying sediment. Much of the plastic, especially the microplastic, will be transported through the canyons to end up deposited within turbidite layers covering the surface of submarine fans that extend seawards from the canyons. These turbidite layers will show size/shape density sorting of plastic fragments, comparable to that seen in different fossils in ancient turbidites (for example, robust shell fragments typically end up in the bottom, Bouma A-B divisions of turbidite layers while the less dense fossils are typically concentrated a little higher, in the ripple-laminated Bouma C division: Davies et al., 1997). We expect plastic fragments to behave similarly, and to be concentrated in the upper, C-E divisions, depending on their size, shape and density. Over the course of the Anthropocene, these turbidites, and the tempestite layers noted above, are likely to be of thin (centimetres to decimetres) but of wide extent. Plastics content will reflect the density and behavior of human populations (hence littering potential) along the terrestrial rivers and coast upstream of the canyon. Plastics are likely to show good preservation potential in these settings.

Beyond the turbidite fans there are the pelagic realms of the ocean floor, in part analysed by Woodall et al. (2014). There, sedimentation rates are low and the Anthropocene will be represented by millimetres in stratigraphic thickness, if that, and so the plastics may represent a significant part of the input. Most of the sea floor is oxygenated and burrowed (bioturbated) by benthic organisms. Therefore, the plastics, over depths of (normally) a few centimetres will, like the rest of the sediment, be mixed in with older deposits, and separated from them by a diffuse gradational boundary. This is one of the practical problems of applying chronostratigraphy over very short time intervals (Zalasiewicz et al., 2007). Bioturbation will in effect blur the boundary; but, for practicality's sake, the whole plastic-bearing bioturbated unit might be regarded as Anthropocene.

The preservation potential for the plastic material, as for any other organic compound, will probably increase strongly under dysaerobic or anaerobic conditions. "Dead zones" of coastal and open marine bottom waters will likely become more frequent and more widespread in the Anthropocene, owing to increasing land-derived anthropogenic nutrient runoff, as well as more frequent surface water stratification caused by warming seas (cf. Gruber, 2011; Keeling et al., 2010). In such settings, plastic material might remain preserved in poorly oxygenated sediments over geological timescales. In contrast, in the more aerated, carbonate-supersaturated marine settings of tropical lagoons, plastics are likely to become initially incorporated within early cemented sediment layers. If the plastic fragments then degrade or become fragmented after a few hundred years, there would result a new type of highly porous, vuggy limestone with voids or pseudomorphs mirroring the shape of leached plastic technofossils.

Some contemporary sedimentary units may still remain effectively plastic-free. Whereas beaches in Antarctica have become polluted with plastic, the fringing deeper-water sediments derived from the melting of rock debris-laden glaciers should be pristine, as should remote land-based ice-masses. Perhaps similarly, the contourite drifts that mantle the base of the eastern North American continental slope, derived from deep south-flowing currents from the Arctic Circle, may be largely plastic-free. In volcanic settings, hot primary pyroclastic flows are unlikely to preserve plastics, but the low-temperature lahar deposits derived from them, if they flow through populated areas, will pick up and entomb plastics on the way.

Tsunamis, too, will generate an unsorted mass of materials that, if sourced from urban areas, can entrain a significant amount of plastics. Large amounts of plastic transported in this way may be carried inland along coastal zones, to form perched deposits. Alternatively, these materials may be carried back out to the ocean as a chaotic backflow of poorly-sorted plastic-bearing sediment. Once identified, such tsunami deposits could also be used as time-specific stratigraphic indicators. In the case of the Boxing Day 2004 tsunami, existing wastes in landfill sites were also transported out to sea, (e.g. in Banda Aceh http://www.gdrc.org/uem/disasters/disenvi/tsunami.html).

6. Conclusions

There is a growing abundance of plastics in the surface environment. These materials may be considered not only as environmental pollutants, but also as contributors to the character of recent (generally post mid-20th century) and contemporary strata.

Plastics are now widely enough distributed to characterize such strata over large parts of the world, even in remote environments such as that of the deep sea floor and the polar regions. Especially in marine sediments, microplastics form superficially invisible, but

potentially widespread markers, directly akin to microfossils in more conventional palaeontology.

It can be reasonably assumed, from the few studies carried out to date, that the patterns of distribution of plastics as both large and small particles provide a means of characterizing global sedimentary systems by age. Once accumulated within sedimentary strata, plastic particles are likely to have a variable but generally good preservation potential, comparable to that of recalcitrant organic fossils. Plastics are already present in sufficient numbers to be considered as one of the most important types of 'technofossil' that will form a permanent record of human presence on Earth.

Stratigraphically, plastics within sediments comprise a good practical indicator of Anthropocene strata, using a mid-20th century beginning for this postulated epoch. Recognizing the exponential growth of plastics production since WWII, the onset of this marker of the Anthropocene is likely to be diffuse and not perfectly isochronous in stratigraphic successions. For instance, a significant presence of plastics in the marine and terrestrial environments was not recorded until the late 1960s to early 1970s. Therefore, despite their utility for practical stratigraphy – namely recogition and characterization of Anthropocene deposits – plastics cannot be expected to act as a primary marker for precisely defining the start of the Anthropocene. Their correlation potential, though, now stretches out into space, as they have now been carried across the solar system by spacecraft, and placed in orbit around the Earth and on the surface of the Moon and Mars.

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Critical Review

A Review of Microplastics in Table Salt, Drinking Water, and Air: Direct Human Exposure

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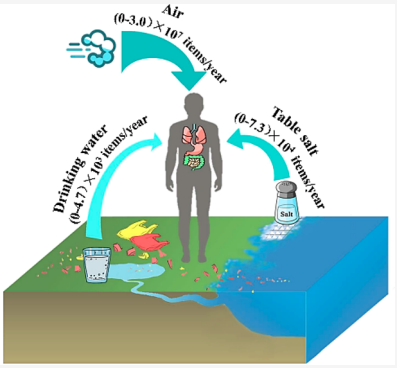
ABSTRACT: The ubiquity of microplastics in aquatic and terrestrial environments and related ecological impacts have gained global attention. Microplastics have been detected in table salt, drinking water, and air, posing inevitable human exposure risk. However, rigorous analytical methods for detection and characterization of microplastics remain scarce. Knowledge about the potential adverse effects on human health via dietary and respiratory exposures is also limited. To address these issues, we reviewed 46 publications concerning abundances, potential sources, and analytical methods of microplastics in table salt, drinking water, and air. We also summarized probable translocation and accumulation pathways of microplastics within human body. Human body burdens of microplastics through table salt, drinking water, and inhalation were estimated to be $(0–7.3)\times10^4$, $(0–4.7)\times10^3$, and $(0–3.0)\times10^7$ items per person per year, respectively. The intake of microplastics via inhalation, especially via indoor air, was much higher than those via other exposure routes. Moreover, microplastics in the air impose threats to both respiratory and digestive systems through breathing and ingestion. Given the lifetime inevitable exposure to microplastics, we urgently call for a better understanding of the potential hazards of microplastics to human health.



INTRODUCTION

Plastic production and use have been growing rapidly since the 1950s, due to the superb properties of plastics such as low cost, versatility, and durability. The widespread use of plastic products has generated large amounts of plastic wastes. Recent modeling results predicted that global plastic waste will triple to 270 million tons from 2015 to 2060.[1] Plastic wastes have undoubtedly aggravated environmental pollution.[2,3] Upon entering the environment, plastic wastes will continuously break down to small fragments and particles.[4] Our current knowledge on environmental behavior and ecological impacts of small plastic fragments and particles is limited, which further complicates the issue of plastic pollution. For example, elimination of micro- and nanosized plastics from the environment is more challenging than bigger plastic debris.

Since the concept of "microplastic" was introduced in 2004,[5] microplastics (MPs) have been found in various environmental compartments and organisms globally.[6−10] Until now, more than 690 marine species have been reported to be contaminated by MPs.[11,12] Numerous experiments have demonstrated toxic effects of MPs, such as growth inhibition, oxidative damage, and immune stress.[13,14] A recent study suggested that high concentration of MPs may have caused direct life history responses in algae and *Daphnia* populations.[15] Microplastic particles can also accumulate in marine organisms and transfer through the food chain to higher trophic levels including humans.[9]

More recently, potential threats of MPs to human health have attracted intense attention because of the widespread detection of MPs in human-related food and environments, such as honey,[16] milk,[17] beer,[18] seafood,[19] table salt,[20,21] drinking water,[22] and air.[23] Consumption of some food products such as seafood, honey, and beer can be intentionally minimized or avoided, but exposure to MP-contaminated table salt, drinking water, and air is inevitable.[24] Despite the small daily intake of salt compared with the other exposure routes presented, salt MP contamination is significant in some regions, for example, in Croatia $(1.4–2.0)\times10^4$ items·kg^{-1} salt and Italy $(1.6–8.2)\times10^3$ items·kg^{-1} salt.[25] Besides, the actual salt intake can be much higher (e.g., 10 g·d^{-1} worldwide and 18 g·d^{-1} in Turkey) than the recommended intake threshold of 5 g·d^{-1} by the World Health Organization.[26,27] Microplastics in table salt and drinking water can enter human body through the digestive tract, whereas MPs in the air can cause exposure of both digestive and respiratory systems. Suspended MPs can be inhaled and deposited MPs can be ingested through hand-to-mouth contact, especially for children.[23,28] Although based on a relatively small sample size, the first evidence of MPs found in human stools suggests that humans are being exposed to MPs.[29]

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Table 1. Summary of Microplastics in Table Salt

country	extraction	separation	pore size (μm)	abundances (item·kg^{-1})			size (μm)	references
				sea salt	lake salt	rock salt		
Australia	UW[a]	NaI	149	0−9	-[b]	-	160−980	37
	17% H_2O_2	-	2.7	46	-	-	100−5000	36
Belarus	17% H_2O_2	-	2.7	-	-	8	100−5000	36
Brazil	17% H_2O_2	-	2.7	2.0×10^2	-	-	100−5000	36
Bulgaria	17% H_2O_2	-	2.7	12	-	-	100−4000	36
China	30% H_2O_2	-	5	$(5.5-6.8)\times10^2$	43−364	7−204	45−4300	20
	17% H_2O_2	-	2.7	$0-1.7 \times 10^3$	28	0−14	100−4000	36
	UW	-	5	9.8	-	-	1−1500	34
Croatia	UW	-	0.45	$(1.4-2.0)\times10^4$	-	-	15−4628	25
	UW	-	0.2	$(0.7-2)\times10^2$	-	-	10−150	33
	17% H_2O_2	-	2.7	58	-	-	100−5000	36
France	UW	NaI	149	0−2	-	-	160−980	37
	17% H_2O_2	-	2.7	0	-	-	-	36
Germany	17% H_2O_2	-	2.7	-	-	2	100	36
Hungary	17% H_2O_2	-	2.7	-	-	12	100−4000	36
India	30% H_2O_2	-	0.45	$(0.6-1.0)\times10^2$	-	-	500−2000	30
	17% H_2O_2	-	2.7	$(0.3-3.7)\times10^2$	-	-	1000−5000	36
Indonesia	17% H_2O_2	-	2.7	1.4×10^4	-	-	-	36
	UW	-	0.45	6.7−53.5	-	-	390−9360	35
Iran	UW	NaI	149	-	1	-	160−980	37
Italy	UW	-	0.45	$(1.6-8.2)\times10^3$	-	-	4−2100	25
	17% H_2O_2	-	2.7	4−30	-	80	100−5000	36
	UW	-	0.2	$(1.7-3.2)\times10^2$	-	-	10−150	33
Japan	UW	NaI	149	0	-	-	-	37
Korea	17% H_2O_2	-	2.7	$(1.0-2.3)\times10^2$	-	-	100−3000	36
Malaysia	UW	NaI	149	1	-	-	160−980	37
New Zealand	UW	NaI	149	0−1	-	-	160−980	37
Pakistan	17% H_2O_2	-	2.7	-	-	100	100−5000	32
Philippines	17% H_2O_2	-	2.7	-	-	120	100−5000	36
Portugal	UW	NaI	149	0−10	-	-	160−980	37
Senegal	17% H_2O_2	-	2.7	48	800	-	100−3000	36
South Africa	UW	NaI	149	1−3	-	-	160−980	37
	UW	NaI	0.2	-	-	-	0−2000	39
Spain	UW	-	5	$(0.5-2.8)\times10^2$	-	115−185	30−3500	32
Thailand	17% H_2O_2	-	2.7	$(0.7-4.0)\times10^2$	-	-	100−5000	36
Turkey	30% H_2O_2	NaI	0.2	16−84	8−102	9−16	20−5000	31
U.S.A.	UW	-	11	$(0.5-8.0)\times10^2$	-	113−367	100−5000	18
	17% H_2O_2	-	2.7	32	-	5	100−1000	36
U.K.	17% H_2O_2	-	2.7	1.4×10^2	-	-	100−2000	36
Vietnam	17% H_2O_2	-	2.7	76−88	-	-	100−5000	36

[a]Ultrapure Water. [b]No data.

Assessing human health risk of MPs remains in its infancy with limited information on exposure routes, biological fates, and health effects. This review aims to survey our current knowledge on direct human exposure to MPs via the three main exposure pathways: table salt, drinking water, and air. It also provides an overview of potential health effects associated with different potential exposure routes. Data from peer-reviewed papers, books, and reports related to MPs in table salt, drinking water, and air published by the end of January 2020 were collected and summarized. The keywords used in iterative literature search were microplastics, table salt, drinking water, air, atmospheric, dust, ingestion, intake, toxicology, risk, and human health. The searched resources included Science Direct, Web of Science, Directory of Open Access Journals (DOAJ), EBSCOhost, Spring Link, Wiley Online Library, BioMed Central, and PubMed Central. In total, 46 publications focusing on the occurrence of MPs in table salt, drinking water, and air were analyzed. The abundances and analytical methods of MPs were summarized and classified in tables and figures. All raw data extracted from the literature were presented in mean values or range values and expressed in unified units. Other literatures concerning ecological hazards, health risk, toxicology, and seafood were also selected and discussed after the initial screening.

MICROPLASTICS IN TABLE SALT

Occurrence and Abundance. Microplastics have been widely detected in table salt of > 100 brands all over the world (Table 1).[30−35] The abundances of MPs in table salt varied widely. The highest abundance was reported in Croatia (1.4×10^4−2.0×10^4 items·kg^{-1}),[25] followed by Indonesia (1.4×10^4 items·kg^{-1}),[36] Italy (1.6×10^3−8.2×10^3 items·kg^{-1}),[25] the United States (0.5×10^2−8.0×10^2 items·kg^{-1}),[18] and China (5.5×10^2−6.8×10^2 items·kg^{-1}).[20] However, MP pollution in

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Table 2. Number of Different Analytical Methods Applied for Microplastics Analysis in Table Salt, Drinking Water, and Air

	table salt	drinking water			air		
analytical method	sea/lake/well salt	DWTP[a] water	tap water	bottled water	wet and dry deposition	dust	air sampler
dissolution	12[b]	0	0	0	0	0	0
digestion	5	3	0	0	3	6	0
flotation							
NaCl[c]	9	0	0	0	0	0	0
NaI	3	0	0	0	0	0	0
$ZnCl_2$	0	1	0	0	1	3	0
filtration	(pore size)						
<1 μm	6	2	1	1	3	2	2
1−5 μm	3	2	2	2	4	3	7
>5 μm	3	0	0	0	1	2	1
identification	Methods						
μ-FTIR	9	3	2	1	5	5	8
μ-Raman	2	2	0	2	2	0	0
others[d]	1	1	1	2	0	3	2

[a]Indicates drinking water treatment plant. [b]Indicates the number of studies that have applied the corresponding analytical processes. [c]Indicates no additional flotation agent (i.e., filtration of supernatant alone, filtration of all salty solution including deposited sediment, or filtration of supernatant and deposited sediment separately). [d]Includes dyeing, SEM-EDX, and fluorescence.

different regions cannot be directly compared with each other due to different analytical methods used. A recent study compared the MP abundances in table salts collected from different regions, using sea salt as a seawater MP pollution indicator, and found a significantly higher MP abundance in Asia than in other continents.[36] Relatively low abundances of MPs were reported in table salts from Australia, France, Iran, Japan, Malaysia, Zealand, Portugal, and Africa.[37] This was probably caused by the usage of filters with a large pore size (149 μm), allowing smaller-sized MPs to escape in the filtration process and resulting in underestimated MP abundances.[37]

Source Diagnostics. Table salts can be sourced from seas, rocks, or salt lakes. Several studies found that the abundance of MPs was higher in sea salt than in rock salt or lake salt,[20] which could be explained by higher level of MP pollution in coastal zones. However, such a source-specific difference was not found by Iniguez et al.[32] The presence of MPs in rock/well salts suggests that MPs may be introduced during collection, transportation, drying, or packaging processes.[20] Therefore, the general public should pay particular attention to food production, because other commercial foods may also be produced and packed in a similar manner as that for table salt.[38] In contrast, another study found that the origin of MPs in table salt was irrelevant to the packaging or grinding process,[32] implicating for other potential sources of MP contamination during concentration, crystallization, or refinement, such as airborne MPs.

Analytical Methods. The various analytical methods used for MPs in table salt, drinking water, and air are summarized in Table 2. The common analytical method for determining MPs in table salt includes sample collection, dilution, extraction, observation, and identification. However, the differences in experimental instrument, extraction reagent, and filter pore size lead to low comparability of the results among different studies, which urgently call for a standard analytical method. The first step of establishing a standard analytical method is to consider sample quantity as well as brand or type of salts. Three types of salts (sea, lake, and rock salts) and three or more brands are recommended so as to prevent either overestimation or underestimation of MP abundances in salt from a region. Sufficient amount of salt is needed to achieve reasonable detection sensitivity. Based on the results of our group[20] and other groups,[25,32] 100−250 g of salts per sample are suggested. It should be noted that the sample amount is empirical. Reducing the salt quantity would reduce the detection frequency. Conversely, the filter membrane is likely to be clogged by excessive impurities such as soil and organic matter with larger salt sample amount.[31,37] The recommended sample amount is expected to be decreased with the development of identification technologies in future. H_2O_2 has been used to digest organic matter in 40% of the studies,[36] while some investigators believe such digestion is not necessary due to small amounts of organic matter in table salts.[25] Additional flotation agent is commonly excluded, and only three studies used saturated NaI solution as flotation agent to isolate MPs (Table 2).[31,37,39] Although NaI saturated solution (1.8 $g \cdot cm^{-3}$) can enhance MP separation, its use is not recommended for the following reasons: (1) The color of NaI would interfere with MP identification; (2) NaI solution reacts with H_2O_2; and (3) NaI is also an environmental pollutant. Generally, the number of other particles and impurities in table salt is relatively low. Thus, the priority option is to filter all solutions after salt sample dissolution. In the case of large numbers of impurities in table salt, saturated NaCl solution is suggested to be used as a flotation agent. NaCl solution has been proven efficient for separating MPs, including PS, PA, PP, PVA, and PE with recovery rates of 85−95%.[40,41] Other flotation agents (e.g., $ZnBr_2$, $ZnCl_2$, and NaBr) were reported to produce high recovery rates, but all factors including cost, practicability, and environmental friendliness must be taken into consideration.[40,42,43] Filtration is a critical step for MP extraction. The use of different filter membranes with diverse pore sizes ranging from 0.2 to 149 μm impedes the standardization of analytical methods. A 5 μm pore size is recommended for filtration, followed by identification using μ-

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Table 3. Summary of Microplastics in Drinking Water

sampling and locations	pore size (μm)	abundances (item·L^{-1})	size (μm)	references
Drinking Water Treatment Plants				
Germany	3	0−7 × 10^{-3} (raw water)	50−150	45
	3	7 × 10^{-4} (drinking water)	50−150	45
Czech	0.2	(1.5−3.6)×10^{3} (raw water)	1−10	46
	0.2	(3.4−6.3)×10^{2} (drinking water)	1−10	46
Norway	1.2	0	-[b]	47
China	0.22	6.7 × 10^{3} (raw water)	1−100	48
	0.22	9.3 × 10^{2} (drinking water)	1−100	48
Tap Water				
U.K.	2.5	7.7 (3.7−13.0)	100−5000	18
Germany	2.5	0.9 (0−1.8)	100−5000	18
Ireland	2.5	1.8	100−5000	18
Italy	2.5	0	100−5000	18
Slovakia	2.5	3.8 (0−10.9)	100−5000	18
Switzerland	2.5	2.7 (0−5.5)	100−5000	18
U.S.A.	2.5	9.2 (0−60.9)	100−5000	18
Denmark	0.2	0	-	50
India	2.5	6.2 (0−20)	100−5000	18
Indonesia	2.5	3.2 (0−10.8)	100−5000	18
Lebanon	2.5	6.6 (0−23.3)	100−5000	18
Uganda	2.5	3.9 (0−12.7)	100−5000	18
Cuba	2.5	7.2	100−5000	18
Tap Water				
Ecuador	2.5	4.0 (0−9.0)	100−5000	18
Ecuador	2.5	-	-	49
Bottled Water				
Germany	0.4	2.6 × 10^{3} (PET[a] bottle)	0−5	51
	0.4	4.9 × 10^{3} (reusable PET bottle)	0−5	51
	0.4	6.3 × 10^{3} (glass bottle)	0−10	51
Germany	3	11 (beverage carton)	5−100	52
	3	50 (glass bottle)	5−100	52
	3	118 (returnable plastic bottle)	5−100	52
	3	14 (single-use plastic bottle)	5−100	52
Italy	-	5.4 × 10^{7}	0−10	53
U.S.A.	1.5	58−1.4 × 10^{3}	6.5−5000	22
Mexico	1.5	(0.2−6.9)×10^{2}	6.5−5000	22
Brazil	1.5	(0.1−1.5)×10^{2}	6.5−5000	22
Lebanon	1.5	49.3	6.5−5000	22
Thailand	1.5	4.7 × 10^{2}	6.5−5000	22
China	1.5	(0.7−1.6)×10^{2}	6.5−5000	22
Indonesia	1.5	(0.4−7.1)×10^{2}	6.5−5000	22
India	1.5	0−39	6.5−5000	22
Kenya	1.5	74.6	6.5−5000	22

[a]PET = Polyethylene terephthalate. [b]No data.

FTIR, which is a reliable approach for determining the chemical composition of MPs.[44]

MICROPLASTICS IN DRINKING WATER

Occurrence and Abundance. Only 10 studies have investigated on MP contamination in drinking water (Table 3), covering raw and treated water from drinking water treatment plants (DWTPs),[45−48] tap water,[18,49,50] and bottled water[22,51−53] from 22 countries. These data suggested that particles larger than 50 μm can be removed from raw water by traditional drinking water treatments with removal rates in the range of 25−90%, depending on local treatment technologies.[46] The lowest abundance of MPs in tap water was observed in Italy and Denmark (0 items·L^{-1}), while the highest abundance was found in the United States (9.2 items·L^{-1}).[20] The abundance of MPs in bottled water varied from 0 to 5.4 × 10^{7} items·L^{-1}.[22,50−52] Water in returnable-used plastic bottles contained significantly more MPs compared with that in single-used bottles.[51] Similar to table salt, a direct comparison of MP abundances in drinking water samples from different studies is difficult due to the use of filter membranes with different pore sizes and different identification methods.

Source Diagnostics. Surface water and groundwater are important drinking water sources.[54,55] Given that macroplastics and MPs have been widely identified in freshwater bodies,[56] MPs in drinking water are usually believed to originate from polluted freshwater resources, such as lakes, rivers, canals, and groundwater.[45] However, some freshwater bodies are less polluted by MPs compared with tap water and bottled water.[57] As summarized by Koelmans et al.,[57] groundwater (1 × 10^{-2} items·L^{-1}) has the lowest MP abundance in all types of fresh water. Therefore, it is possible that MPs found in drinking water are derived from water supply chain or product packages such as caps and bottle walls.[51] Schymanski et al.[47] showed that the majority types of MPs in bottled water were polyethylene terephthalate and polyester which may be derived from the materials of the bottles. Unexpectedly, large amounts of MPs were also found in glass bottled water (6.3 × 10^{3} ± 1.1 × 10^{4} items·L^{-1}) and the potential source is the abrasion of plastic bottle cap against the glass bottle body.[47] Thus, we consider the packaging process as an important source of MPs for bottled water.

Detection Methods. The analytical methods used for MP detection in drinking water are simple and they share more common steps. Sampling and treatment methods, as well as

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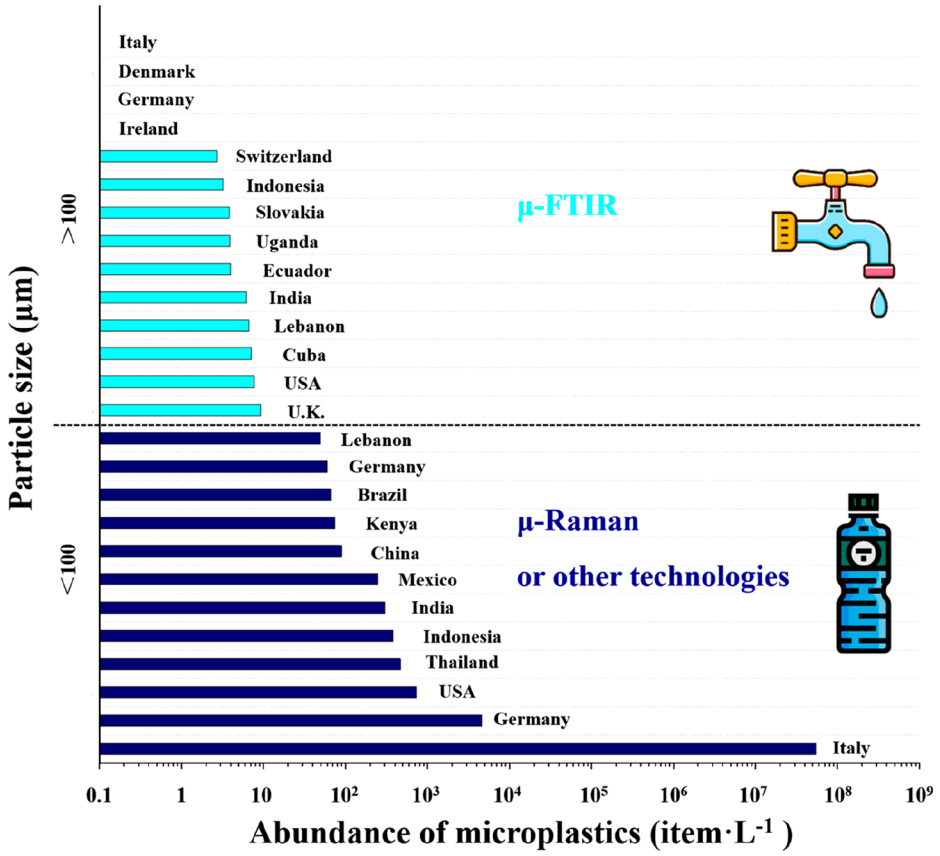

Figure 1. Abundance of microplastics in tap water and bottled water. To show the influence of identification methods on the existing data (size and abundance), the results were classified into two categories according to their identification methods, that is, (1) μ-FTIR and (2) μ-Raman or other technologies (dyeing, SEM-EDX). The microplastics >100 μm with <5% in abundance in bottled water were ignored for clearer comparison.

precautions, have been elaborated by Koelmans et al.[57] The present review only focuses on the methods for filtration and identification of MPs in drinking water. Surprisingly, the abundance of MPs has an up to 11 orders of magnitude difference among samples (Table 3). One of the main factors may be the pore size of filter membrane. For example, MP abundances obtained with 0.4 μm pore size filters[51] were much higher (2.6×10^3–6.3×10^3 items·L^{-1}) than those (0.1×10^2-1.2×10^2 items·L^{-1}) using 3 μm pore size filters,[52] both in bottled water from Germany. As approximately 50% of MPs were smaller than 1.5 μm,[51] most small MPs may be lost if the solution is filtered with 3 μm pore size filters. Therefore, unified membrane pore sizes are necessary for meaningful assessment of MP abundances.

In addition to pore size of filter membrane, the difference in identification methods is another crucial factor affecting the size ranges and abundances of detected MPs. For instance, MPs in tap water were often analyzed by μ-FTIR with a size of > 20 μm captured, whereas MPs in bottled water were normally processed by μ-Raman or other technologies (e.g., dyeing and SEM-EDX) capable of detecting smaller MPs (<10 μm). The results of MPs in drinking water, therefore, can be classified into two groups based on identification methods, that is, 1) μ-FTIR method and 2) μ-Raman or other technologies. Microplastics in tap water are larger in size and lower in abundance, whereas they are smaller in size but higher in abundance in bottled water (Figure 1). It is critical to point out that the reported higher MP abundance in bottled water than that in tap water is likely due to the use of identification method with lower size detection limit. In other words, the reported MP abundance in tap water or other type of samples where only μ-FTIR was used can be underestimated due to the instrumental incapability of detecting MPs smaller than 10 μm. This notion is corroborated by Pivokonsky et al.[46] who obtained high abundances (3.4×10^2 to 3.6×10^3 items·L^{-1}) of small-sized MPs (1–10 μm) in DWTPs using a μ-Raman approach.

MICROPLASTICS IN THE AIR

Occurrence and Abundance. Occurrence of MPs in the air has attracted increasing attention since 2015. Three different sampling methods have been used to collect atmospheric MPs, that is, wet and dry deposition,[23,58–62] atmospheric sampling,[63–69] and dust collection,[43,70–74] which makes a direct comparison of studies employing different sampling approaches not feasible. The size of fibers (the largest dimension of a MP fiber is defined as its size[75]) in the air is in the range of 100–5000 μm,[43,58,59] but much smaller particles can be detected using air samplers.[64,76] The width of MP fibers is small, about a few micrometers to tens of micrometers.[77,78] Some general trends can be found in Table 4. For example, the MP abundance in the air was higher in an urban area than in a suburban area in Paris.[59] Meteorological factors largely determine the dispersion and levels of MPs in the air. For instance, the lowest level of MPs was observed during dry weather periods, whereas the highest level occurred during rainy seasons.[23] In rainy days, rainfalls wash out fibers, inflating the amounts of MPs collected by wet and dry deposition

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Table 4. Summary of Microplastics in the Air

sampling and location	types of samples	pore size (μm)	abundance	size (μm)	references
Wet and Dry Deposition (item·m^{-2}·day^{-1})					
China (Dongguan)	outdoor	1	36	0−5000	58
France (Paris)	outdoor	1.6	1.2×10^2	100−5000	23
	urban	1.6	1.1×10^2	0−5000	59
	suburban	1.6	53	0−5000	59
	indoor	1.6	$(0.2-1.1)\times10^4$	0−5000	63
Germany (Hamburg)	outdoor	5−13	2.8×10^2	0−5000	60
China (Yantai)	outdoor	5	4.0×10^2	50−1000	61
U.K. (London)	outdoor	0.2	7.7×10^2	0−3000	62
France (Pyrenees mountains)	outdoor	0.45	3.7×10^2	0−750	79
Air Sampler (item·m^{-3})					
France (Paris)	indoor	1.6	0.8−6.0 (location 1)	0−3250	63
		1.6	1.3−19.6 (location 2)	0−3250	63
		1.6	0.4−5.4 (location 3)	0−3250	63
Denmark (Aarhus)	indoor	0.8	14.0 ± 2.2 (location 1)	11−105	65
		0.8	10.6 ± 5.9 (location 2)	11−105	65
		0.8	3.4 ± 2.6 (location 3)	11−105	65
France (Paris)	outdoor	1.6	0.01−0.5	0−1650	63
Iran (Asaluyeh)	outdoor	2	1 (0.3−1.1)	2−100	64
China (Shanghai)	outdoor	1.6	0.4 (0−2)	12−2191	66
West Pacific Ocean	outdoor	1.6	0.06 (0−1.4)	16.14−2086	67
Indonesia (Surabaya)	outdoor	1.6	$(1.3-1.8)\times10^4$	0−5000	68
Pearl River Estuary	outdoor	1.6	4.2×10^{-2}	59−2252	69
South China Sea	outdoor	1.6	$(0.8-1.3)\times10^{-2}$	59−2252	69
East Indian Ocean	outdoor	1.6	$(4-6)\times10^{-3}$	59−2252	69
Turkey (Sakarya)	outdoor	50	0.3−12.9	50−500	74
China (Shanghai)	outdoor	1.6	1.42 (0−4.18)	23−9955	76
China (Beijing)	outdoor	0.8	5.7×10^3 (location 1)	5−200	78
		0.8	5.6×10^3 (location 2)	5−200	78
Sweeping Operation[a]					
Iran (Tehran) (item·g^{-1})	outdoor dust	2	2.7−20	0−5000	43
Iran (Asaluyeh) (item·g^{-1})	outdoor dust	2	60 (3.3−67)	1000−5000	64
China (39 cities) (mg·g^{-1})	indoor dust	-[b]	27 (PET); 4.6×10^{-3} (PC)	50−2000	70
	outdoor dust	-	2.8 (PET); 2.0×10^{-3} (PC)	50−2000	70
12 countries (mg·g^{-1})	indoor dust	-	2.9×10^{-2}−1.1×10^2 (PET)	-	71
		-	1.1×10^{-4}−0.8 (PC)	-	71
Forni Glacier (item·g^{-1})	cryoconite	0.45	7.1×10^{-2}	100−5000	72
Japan (item·m^{-2})	outdoor dust	100	2.0 ± 1.6	100−5000	73
Vietnam (item·m^{-2})	outdoor dust	100	19.7 ± 13.7	100−5000	73
Nepal (item·m^{-2})	outdoor dust	100	12.5 ± 10.1	100−5000	73
Turkey (item·g^{-1})	outdoor dust	50	18−29	50−500	74
Arctic Fram Strait (item·L^{-1})	snow	-	$0-1.4 \times 10^4$ (Arctic snow)	11−475	77
		-	1.9×10^2−1.5×10^5 (European snow)	11−475	77

[a]The data units of sweeping operation were inconsistent due to the differences in identification methods or sample quantification; the data of Iran (Tehran and Asaluyeh) and Turkey were selected for intake calculation. [b]No data.

method.[59] In addition to larger populations, weaker airflows in urban areas also greatly contribute to higher atmospheric levels (and therefore stronger deposition) of MPs compared to rural areas.[59] More suspended MPs have been found in indoor environments than in outdoor environments.[63] Road dusts have also been recognized as an important source of MPs in urban areas.[43,64] Moreover, children may directly ingest large amounts of deposited dust through mouthing toys and hands. Abbasi et al.[64] calculated that more than 900 MP particles may be ingested by a child per year through dust ingestion (200 mg·day^{-1}) in a normal exposure scenario.

Source Diagnostics. Synthetic textiles (e.g., plastic fibers or fragments from clothes), rubber tire erosion, and road dust are considered as the major sources of primary atmospheric MPs, which can be transferred to other environmental compartments by winds.[79] Other sources of MPs in the air may be household furniture products, building materials, rubbish incineration, landfills, industrial discharge, and particulates emitted by vehicles.[23,59,63] In addition, the horticulture field also releases MPs through synthetic particles used in soils as well as sewage sludge used as fertilizers.[80]

Analytical Methods. Different sampling methods can be selected based on specific objectives (Figure 2). Wet and dry

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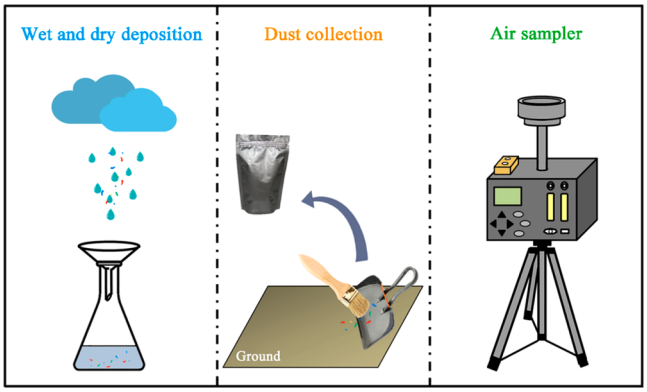

Figure 2. Sampling methods for microplastics in the air.

deposition, for instance, is simple and suitable for monitoring total MPs,[23,58,59] whereas atmospheric sampling within a breathing zone is more appropriate for estimating human inhalation.[64,76] Dust ingestion usually occurs in children or construction workers; therefore, sampling deposited dust is of significance.[70]

Subsequent treatment procedures depend on the type of samples (Table 2). Generally, aqueous samples obtained by wet and dry deposition require filtration.[58] For air samplers, the filters can be detached from inside of the device for direct observation.[64,76] MPs on air sampler filters can also be washed off and filtered again for further analysis.[64,70] Subsequent digestion (e.g., 30% H_2O_2) and flotation (e.g., saturated NaCl solution) are necessary for dust samples.[55] μ-FTIR is commonly used for identifying MPs in air samples, and other methods including SEM-EDX,[43] fluorescence microscopy,[64] and μ-Raman,[79] are also used.

EXPOSURE PATHWAYS AND HUMAN HEALTH RISK OF MICROPLASTICS

Human Body Burden. The most common routes for MPs to penetrate into the human body are ingestion and inhalation. Contaminated food (e.g., table salt, drinking water, and seafood, etc.) and dust containing deposited MPs from air are the sources of gastrointestinal exposure, and suspended MPs in the air may enter the respiratory system. An estimate on the body burdens of MPs was made based on the abundances of MPs detected in table salt, drinking water, and air and the average exposure rate of each route (Figure 3). The abundances of MPs were extracted from the "abundance" column in Tables 1, 3, and 4. Mean value was used if there was one, and maximum and minimum were used when range values were available. Although not the focus of the present review, the ingestion of MPs via seafood consumption was also compared with the other three media amid the availability of numerous data on MPs in seafood (Figure 3). For statistical analysis of the MP intake comparison, normality of the data was tested with Shapiro-Wilk's test. The Kruskal−Wallis test was then used followed by the Mann−Whitney U test using Bonferroni correction to adjust the probability (SPSS 22.0).

We first estimated the intake of MPs through gastrointestinal exposure. The abundance of MPs in table salt ranges widely from 0 to 2.0 × 10^4 items·kg^{-1} (Table 1). When global mean value (10 g·day^{-1}) is selected as salt exposure rate,[81] the intake of MPs from salt is estimated to range from 0 to 200 items per day, equivalent to 0−7.3 × 10^4 items per year (Figure 3). With consumption of 1.4 L water per day,[36,82] the annual MP intake

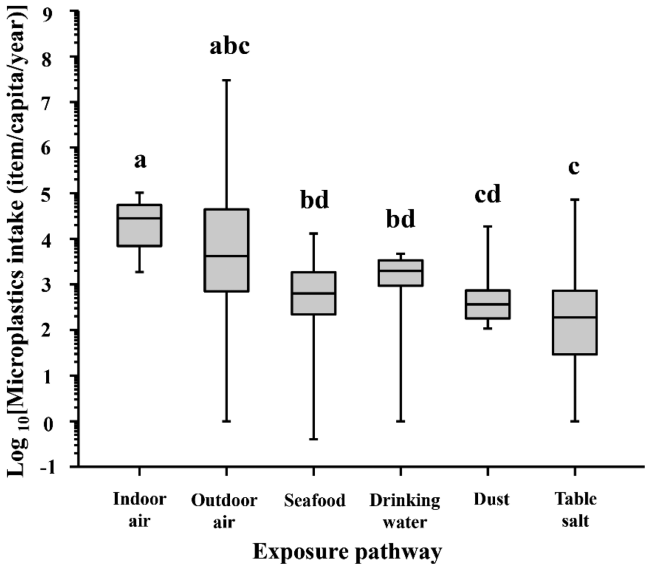

Figure 3. Human intake of microplastics through different exposure pathways. Maximum, minimum, and mean values obtained from literatures were plotted. The upper and lower boundaries of each box represent the 75th and 25th percentiles, respectively. The horizontal line inside the box represents the median value. The whisker represents the maximum or minimum value. The minimum values of MP intake through outdoor air, drinking water, and table salt were zero, which were not suitable for logarithmic representation and were not shown. The general ratio of the soft tissue mass to the total mass of shellfish (0.4) reported in previous surveys was used for microplastic intake calculation via seafood consumption.

through tap water and bottled water, is estimated to be 0−2.8 × 10^{10} items. The worst scenario can be calculated based on the abundance of MPs in bottled water of Italy (5.4 × 10^7 items·L^{-1}).[51] However, no detailed procedures for sample preparation and detection was provided in this study.[48] Because MPs detected in bottled water showed very different size fractions (<10 μm) from those detected in other samples (i.e., tap water, air, and table salt), we only calculated human MP intake through drinking water (0−4.7 × 10^3 items per year; Figure 3) using the tap water data, without considering the bottled water data.

Another gastrointestinal exposure pathway of MPs is dust ingestion, especially through mouthing dirty toys and hands by children.[83] After excluding the data of cryoconite,[72] only three studies have been conducted on MPs in dust with the unit of item·g^{-1}, and the abundance ranges are too limit for calculating human MP intake.[43,74,84] Therefore, we used the original abundance data of each sampling site from these articles. The range of MP intake through dust ingestion is estimated to be 1 × 10^2 to 1.9 × 10^4 items per year for adults, based on the average dust exposure of 100 mg·day^{-1} (Figure 3).[43] It needs to be acknowledged that the actual individual intake may be influenced by "activity", for example, the portions of outdoor and indoor activities. Among various food items, the presence of MPs in seafood has been widely recognized.[85−87] We extracted the MP abundances in seafood from Hantoro et al.[88] and Li et al.[10] as well as some more recent studies (SI Table S1). Only shellfish data but not fish data were used for calculation. It is because MPs in fish are mostly found in the gastrointestinal tract, which is usually discarded. The global shellfish consumption rates reported by the Food and Agriculture Organization (FAO) are 1.79 kg·capita^{-1}·year^{-1}

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for Crustacean and 2.5 kg·capita^{-1}·year^{-1} for Molluscs.[89] It should be noted that the consumption rates were calculated based on whole tissue including shell and soft tissue, while MP abundance of shellfish is often expressed as item·g^{-1} wet soft tissue. Considering the general ratio of the soft tissue mass to the total mass of shellfish reported in previous surveys (0.4),[90−94] MP intake via shellfish consumption ranges from 0 to 1.3 × 10^4 particles per person (Figure 3).

The respiratory tract exposure of MPs was also considered. Only abundance data of atmospheric MPs with unit of item·m^{-3} were used for calculation. Extremely high levels (1.3 × 10^4−1.7 × 10^4 items·m^{-3}) of MPs in outdoor air samples from a heavily trafficked roads[68] and low levels (0−1.37 items·m^{-3}) of atmospheric MPs from oceans[67,69] were excluded because neither site is the main place for human activities. The inhalation rate is 14.3 m^3·day^{-1}.[95] The abundance of inhalable MPs was reported to range from 0 to 5.7 × 10^3 items·m^{-3}.[66,78] As MP abundance in indoor environments is generally higher than that in outdoor settings, human MP intakes through indoor and outdoor air inhalation were calculated separately. An adult is expected to annually inhale 1.9 × 10^3−1.0 × 10^5 and 0−3.0 × 10^7 MPs through indoor and outdoor air, respectively (Figure 3).

Overall, the human MP intakes were calculated based on the abundance of MPs with similar size range, making data comparison more reasonable. Among the different exposure pathways, inhalation of indoor and outdoor air contributes the most to human exposure to MPs (Figure 3), suggesting a long-term monitoring of airborne MPs in the future. In our estimation, the amount of MP inhalation presents the MPs entering human body through nose. It is still unknown for the exact quantity of MPs entering the trachea, bronchus, and lung. Besides, up to date, the abundance of smaller MPs (e.g., <5 μm) and nanoplastics has not been documented due to the limitations of analytical methods. As we know, however, small particles are more likely to enter the lower respiratory system. Therefore, more efforts are highly needed to overcome these difficulties. In the current stage, it is still hard to compare human intake and health risks of MP inhalation with other inhalable pollutants such as PM 2.5. First of all, PM 2.5 is often expressed as μg·m^{-3}, whereas suspended MPs are often expressed as item·m^{-3}. Besides, due to the special characteristics of plastic material and the additives it contains, the toxicological mechanism of MPs may also differ from that of PM 2.5 or other pollutants.

Table salt, drinking water, and air not only represent direct MP exposure routes of humans, but also cause indirect MPs exposure during human food consumption. Salt is used as a preservation agent in many processed food items. Water is also commonly used throughout the entire food consumption process. Air contact is almost inevitable from food acquisition to human ingestion. The indirect consumption routes complicate the assessment of human exposure to MPs through food intake. The quantity of salt or water added into various foods and ingestion rates of processed food vary largely among people, making it difficult to incoporate indirect exposure pathways into estimation of MP intake. In addition, the discovery of more MP exposure routes suggests MPs are entering human body in imperceptible ways, such as the MPs released from tea bags.[38]

In a recent review, Cox et al.[96] estimated the human intake of MPs, with a focus on the recommended intakes for Americans (e.g., salt, honey, sugar, seafood, bottled water, tap water, and alcohol) and air inhalation. The authors indicated that the total intake of MPs ranged from 7.4 × 10^4 to 1.2 × 10^5 items per year, which is within the range reported in the present review. Different to their study, we emphasized on up-to-date global data and reviewed different analytical methods, and more importantly, we provided original and novel insights on the MP intake. Cox et al.[96] suggested that an effective way to reduce MP intake is to abandon bottled water. However, it might be inappropriate to draw that conclusion based on the current knowledge because of the large differences in pore size of the filters used as well as instrumental limitations, which has been often ignored. High concentrations of small-sized MPs (<10 μm) have only been reported in bottled water but not in any other media (tap water, table salt, and air), which may be because μ-Raman used for bottled water has higher particle size sensitivity. Thus, comparison of MP abundance should be conducted within a similar particle size range. Additionally, actual MP intake varies among individuals and is greatly influenced by regional pollution levels. In the future, unified protocols and large-scale surveys will allow for more comparable and accurate estimation of MP intake.

Translocation and Accumulation in Human Body. Upon ingestion or inhalation, MPs are capable of translocating and accumulating in different organs and tissues. Microplastics have been found to be internalized in the gastrointestinal tract, and the unabsorbed portion is excreted with human feces.[29] Some MPs may enter the respiratory tract. The depth of settlement depends on their aerodynamic equivalent diameter, which is used to measure the settling velocities of particles with different densities and shapes.[97] Particles with smaller aerodynamic equivalent diameters are likely to reach the lower airway. Plastic fibers have been detected in lung tissue, confirming that fibers can penetrate into the deep lung.[98] An in vitro study showed that polypropylene and polyethylene fibers exhibited no dissolution and changes after 180 days in synthetic lung fluid, suggesting high potential persistence of MPs in the respiratory tract.[99] Other nanosized plastic particles were shown to penetrate across the blood-brain barrier and placenta, and even cell membranes.[100] However, no direct evidence shows the distribution and accumulation of MPs in human organs. The only mouse-model-based experiment has shown that MPs can accumulate in liver, kidney, and gut.[101]

Human Health Risk. Current knowledge on whether MPs would reach human organs and cause adverse health impacts remains poor. The available animal testing results may have some implications for human health effects of MPs. Ingestion of MPs can cause inflammatory responses in the digestive system in *Mytilus*.[102] The immune system of fish is also the target of MP attack.[103] Exposure of the innate immune system of fathead minnow to nanoplastics significantly increased degranulation of primary granules and neutrophil extracellular trap release.[103] Inflammations including chemokine expression and pulmonary hypertension were induced by intrajugular injection of polystyrene microspheres in rats, probably due to increased blood coagulability or vascular occlusions.[104] *In vivo* experiments showed that polystyrene could be internalized in macrophages, erythrocytes, and rat alveolar epithelial cells, damaging intracellular structures.[105] Moreover, persistent organic pollutants, metals, and pathogenic microorganisms can sorb on MPs, and the leaching of chemical additives can also aggravate the toxic effects of MPs.[106,107] Potential harmful effects of MPs on human health remain debatable. Some researchers emphasized the dangers posed by food chain

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transfer, while others claimed no adverse effect caused by MPs or MP additives.[107] The controversies mostly lie in the uncertainty of MP intake estimates, and therefore more efforts on MP intake measurements and modeling are desirable.

Even though MP toxicology is in its infancy, occupational diseases have been associated with inhalation of MP particles.[97] Flock workers exposed to polypropylene may have an increased risk of 3.6 (odds ratio of 3.6) for respiratory symptoms compared to nonexposed individuals.[97] Gene mutation may also result from chronic inhalation exposure to low concentrations of fine particles.[108] A higher cancer incidence rate was observed in synthetic textile workers after 10−20 years of exposure to polypropylene fibers.[97] Polyvinyl chloride workers suffered increased lung cancer risk, with age, working years, and exposure duration at the factories.[97] More investigations are needed to quantify the atmospheric and tissue concentrations of MPs and understand the mechanical toxicity of MPs.

PERSPECTIVES

Microplastics were first discovered in oceanic water and sediment that are considered as the sinks of plastic debris. Only until recent years have researchers began to recognize the association of MPs with human health through food consumption. This may explain the relatively small number of literature reviewed here when comparing with the marine MP counterpart. More surveys and studies, therefore, are required to assess the occurrence of MPs in human exposure pathways and related health impacts. It is reasonable to consider table salt, drinking water, and air as the three major human exposure pathways of MPs. Among the different pathways leading to human body burdens of MPs, the intake of atmospheric MPs through inhalation is estimated to be the most significant (1.9×10^3 to 1.0×10^5 items·year^{-1} indoor air; 0−3.0×10^7 items·year^{-1} outdoor air).

So far, many important questions on MPs remain unanswered. The exact routes of MP cellular intake, the tissue accumulation of MPs, and the potential adverse effects after long-term MP exposure in human are unknown. The fate and transport of MPs upon entering an organism through absorption and excretion is unclear. The changes at cellular level or even molecular level and specific mechanisms have not been studied. The potential health risks to human body are only speculated by referring to animal testing results, and this knowledge gap needs to be filled. To move forward, high vertebrate human homologue *in vivo* models such as mice complemented with *in vitro* human cell bioassays can be employed to reveal the toxicity mechanisms at molecular, cellular, and individual levels. Researchers can also learn from epidemiology and occupational studies for other environmental particle pollutants. Also, similar to other hazards, generalization in human health risk assessment of MPs should be highly cautious when the research objectives are occupational or vulnerable populations (e.g., the elderly and children).

ASSOCIATED CONTENT

Supporting Information

This information is available free of charge via the Internet at . The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b04535.

Data on microplastics in shellfish species (Table S1) and geographical distribution of microplastic pollution in table salt (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

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