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Source apportionment of perfluoroalkyl substances in surface sediments from lakes in Jiangsu Province, China: Comparison of three receptor models

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ABSTRACT

Receptor models have been proved as useful tools to identify source categories and quantitatively calculate the contributions of extracted sources. In this study, sixty surface sediment samples were collected from fourteen lakes in Jiangsu Province, China. The total concentrations of C₄–C₁₄-perfluoroalkyl carboxylic acids and perfluorooctane sulfonic acid (Σ_{12} PFASs) in sediments ranged from 0.264 to 4.44 ng/g dw (dry weight), with an average of 1.76 ng/g dw. Three commonly-applied receptor models, namely principal component analysis-multiple linear regression (PCA-MLR), positive matrix factorization (PMF) and Unmix models, were employed to apportion PFAS sources in sediments. Overall, these three models all could well track the Σ_{12} PFASs concentrations as well as the concentrations explained in sediments. These three models identified consistently four PFAS sources: the textile treatment sources, the fluoropolymer processing aid/fluororesin coating sources, the textile treatment/metal plating sources and the precious metal sources, contributing 28.1%, 37.0%, 29.7% and 5.3% by PCA-MLR model, 30.60%, 39.3%, 22.4% and 7.7% by PMF model, and 20.6%, 52.4%, 20.2% and 6.8% by Unmix model to the Σ_{12} PFASs, respectively. Comparative statistics of multiple analytical methods could minimize individual-method weaknesses and provide convergent results to enhance the persuasiveness of the conclusions. The findings could give us a better knowledge of PFAS sources in aquatic environments.

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Introduction

The mass production and widespread usage of perfluoroalkyl substances (PFASs) have begun since the late 1940s (Kim et al., 2012). PFASs are ubiquitous in various environmental media, such as water, soils, sediments, sewage sludge, biota and human bodies (Wang et al., 2015; Zhao et al., 2012). It was inferred that a large proportion of PFASs would be released to the surface waters, and sediments, as the natural

environment of benthic organisms, are considered as one of the most important environmental sinks of PFASs (Prevedouros et al., 2006). PFASs have been found in sediments from several countries and regions, and PFAS concentrations have reached up to 800 ng/g dry weight (dw) (Ahrens et al., 2015; Campo et al., 2015; Zhou et al., 2013). Source apportionment of PFASs in sediments is of great significance for pollution control and ecological protection of aquatic environments.

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Qualitative and semiquantitative methods have been widely employed to identify PFAS sources. Xiao et al. (2012) adopted cluster analysis, correlation analysis, ANOVA and per capita discharge to distinguish different PFAS patterns in influent samples from thirty-seven wastewater treatment plants in a multi-city survey. Murakami et al. (2009) used ratio methods to evaluate PFAS contributions from street runoff and wastewater to the aquatic environments. A few methods, e.g., principal component analysis (PCA), multiple linear regression model (MLR), positive matrix factorization (PMF) and Unmix models, have been applied to quantitative source apportionment of PFASs. However, only one or two of these models are usually applied to source apportionment of PFASs, and it is not enough to provide comprehensive information for PFAS sources (Kuroda et al., 2014; Qi et al., 2016).

Jiangsu Province, located in the lower reaches of the Yangtze River and Huaihe River, is traversed by the Beijing-Hangzhou Grand Canal from north to south. It forms part of the Yangtze River Delta urban agglomeration, which is one of the six world-class city clusters. As one of the most intensively industrialized provinces in China, Jiangsu Province contributed the largest portion of perfluorooctane sulfonic acid (PFOS) emissions in China (Xie et al., 2013). PFOS concentrations in Taihu Lake in Jiangsu Province even exceeded US EPA standards of 0.2 $\mu\text{g/L}$ for PFOS in drinking water (US EPA, 2009; Yang et al., 2011). Our published work showed that lake sediments from Jiangsu Province have also suffered the heaviest PFAS pollution (mean 1.76 ng/g dw) among all provinces studied (Qi et al., 2016). In this study, PCA-MLR, PMF and Unmix models were applied to identify source categories and quantitatively calculate source contributions of PFASs in lake sediments from Jiangsu Province. Results from three models were evaluated and compared in order to improve source apportionment of PFASs. Comparative statistics could enhance the persuasiveness of the conclusions and offer us a better knowledge of PFAS sources in lake sediments.

1. Materials and methods

1.1. Standards and reagents

Seventeen PFASs including C_4 – C_{14} -perfluoroalkyl carboxylic acids (PFCAs) and C_4 , C_6 , C_8 and C_{10} -perfluoroalkane sulfonic acids were targeted. A mixture of seventeen native PFASs and nine stable isotope-labeled surrogate internal standards in 2 $\mu\text{g/mL}$ solution mixtures were both purchased from Wellington Laboratories (Guelph, ON, Canada). Perfluoro-1-[1,2,3,4,5,6,7,8- $^{13}\text{C}_8$]octanesulfonate and perfluoro-n-[1,2,3,4,5,6,7,8- $^{13}\text{C}_8$]octanoic acid (50 $\mu\text{g/mL}$, 99%) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Detail information is shown in Appendix A.

1.2. Sample collection

The sampling campaign was carried out in 2013. In total, sixty surface sediment samples from fourteen lakes of China were analyzed (Fig. 1). Geographic and limnological features of fourteen lakes are listed in Appendix A Table S1. Details on sample collection are displayed in Appendix A.

1.3. Sample extraction and instrumental analysis

The samples were pretreated as previously published procedures with minor modifications and optimizations, using methanol extraction and cleanup by Oasis WAX-SPE cartridges (Zhou et al., 2013). PFAS analysis was accomplished using an ultra-high performance liquid chromatography coupled to a negative electrospray ionization tandem mass spectrometer (UPLC-ESI-MS/MS, Xevo TQD, Waters Corp., Milford, MA, USA) operated in the quantitative multiple reaction monitoring mode. Detail information on sample extraction, instrument analysis and quality assurance/quality control is shown in Appendix A.

1.4. Statistical analysis

PFAS concentrations are reported on a dry weight basis. Twelve PFASs, including C_4 – C_{14} -PFCAs and PFOS, were further analyzed, with high detection frequencies of 87%–100%. At least 93% of concentrations were quantifiable for each PFAS. In further analysis, all concentrations lower than the limits of detection (LODs) and limits of quantification (LOQs) were reported as half of the LODs and LOQs, respectively. The total concentrations of C_4 – C_{14} -PFCAs and PFOS were represented by the $\sum_{12}\text{PFASs}$. Raw data were obtained from the MassLynx V4.1 workstation (Waters Corp., Milford, MA, USA) and processed in the Microsoft Office 2010 software (Microsoft Inc., Redmond, WA, USA). Pearson correlation analysis was conducted with the SPSS 22.0 software (SPSS Inc., Chicago, IL, USA). Data for Pearson correlation analysis conform to a normal distribution. PCA-MLR, PMF and Unmix models were run with the Matlab R2014b software (MathWorks Incor., Natick, MA, USA), US EPA PMF 5.0 and Unmix 6.0 software packages, respectively.

1.5. Receptor models

PCA-MLR, PMF and Unmix models are three multivariate factor analysis receptor models, and none of them need source categories of pollutants in advance. In source appointment, it was assumed that PFAS compositions of each source did not change as they moved from source to receptor and did not react with each other, as described in the previous study, and so forth (Watson, 1984). Generally, they can be described by the following Eq. (1):

$$c_{ij} = \sum_{k=1}^n x_{in} f_{nj} + e_{ij} \quad (1)$$

where, c_{ij} is the concentration of i th species for the j th sample; x_{in} is the i th species concentration from the n th source; f_{nj} is the contribution of the n th source to the j th sample; e_{ij} is the error or uncertainty (Yang et al., 2013). Details regarding these three receptor models were given in their respective user manuals.

PCA-MLR model explains data variables by fewer independent factors. Prior to statistical analysis, all data were transformed into a dimensionless standardized form as Eq. (2). Factors with eigenvalues >1 were evaluated, and the variables were considered to identify source categories if their factor loadings were >0.5 (absolute value). The model was carried out using

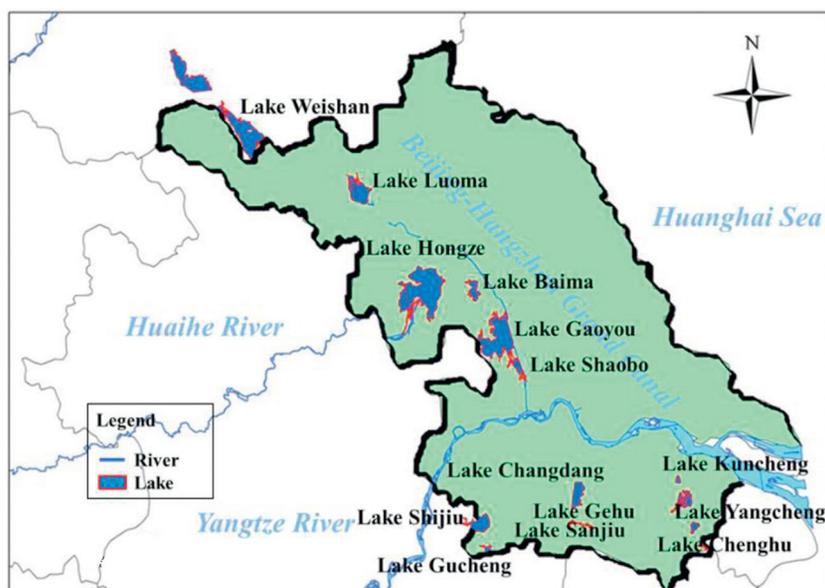


Fig. 1 – Location of the sampling sites in Jiangsu Province, China.

Varimax rotation with Kaiser normalization. Detail description of PCA-MLR model could be found in the study of Thurston and Spengler (1985).

$$Z_{ij} = \frac{(c_{ij} - \bar{c}_i)}{\sigma_i} \quad (2)$$

where Z_{ij} is the standardized concentration of i th species for the j th sample and often termed the Z-score; \bar{c}_i is the average concentration of i th species over all sampling sites; and σ_i is the standard deviation of the concentration of i th species.

PMF model runs with non-negative constraints on variables. It retains missing and below detection values with the associated uncertainties and considers their uncertainties in the assessment of the quality and reliability of each data point. The matrix of measured uncertainties was calculated by the LOD for each species and the error. If the concentration \leq the LOD, uncertainty = $5/6 \times \text{LOD}$ (Polissar et al., 1998), otherwise, uncertainty = $\sqrt{(\text{error} \times \text{concentration})^2 + \text{LOD}^2}$ (Yang et al., 2013). Roughly based on the relative standard deviations, the errors of all species were set to 0.05. The extra modeling uncertainty was set to a value of 5%.

The robust Q is the goodness-of-fit parameter calculated excluding points not fit by the model, defined as samples for which the uncertainty-scaled residual is greater than 4, while the true Q is calculated including all points. Different runs were carried out to improve results by down weighting the species with low signal-to-noise (S/N) from “strong” to “weak”. In this way, twelve variables were all included by considering them “strong”. The \sum_{12} PFASs as the total variable was considered as “weak”. The factor number (P) was gradually adapted from 3 to 5. Increasing P is supported only if the decrease of Q is significant. Consequently, PMF model was run with four factors. All runs converged to find a similar global minimum. The robust Q was 4073.5 and the true Q was 5976.3. After a reasonable solution was obtained, the uncertainties in

the modeled solution were further estimated by performing a total of 300 bootstrap runs (Henry and Christensen, 2010). All runs converged with a minimum r-value of 0.6 for base-boot factor mapping. Residuals were checked to be between -3 and 3 for all species and at least 96% of the observations. $F_{\text{peak}} = 0.1$ was adopted in the model fitting.

Unmix model is also based on nonnegative constrains. It reduces the dimensionality of data by the Singular Value Decomposition method to estimate the number of sources. Source apportionment results obtained from Unmix model mainly depend on the minimum R^2 (Min. R^2) and minimum signal-to-noise (Min. S/N). It was suggested that perfluoropentanoic acid (PFPeA) should be excluded, because PFPeA presented more than 50% of the variance and might be detrimental to the model due to error. It would be better to keep consistent in PFAS species for three models. Additionally, PFPeA had only a little more than 50% error, thus it was not excluded from the modeling process. Scatter plots of all species versus the total species were used to identify these species with well-defined edges, which would be applied in the analysis. The model was set to consider the \sum_{12} PFASs as the total species. Four sources were identified by Unmix model for 12 PFAS species with Min. R^2 value of 0.81 and Min. S/N value of 2.48.

2. Results and discussion

2.1. PFAS concentrations in sediments

PFASs were detected in all sediment samples. The \sum_{12} PFASs concentrations ranged from 0.264 to 4.44 ng/g dw, with an average of 1.76 ng/g dw. 87%–100% of sediment samples had concentrations higher than LODs for twelve individual PFAS species. PFOS was the predominant compound, with an average of 0.384 ng/g dw, followed by perfluoroundecanoic acid

(PFUnDA) and perfluorooctanoate acid (PFOA) with averages of 0.337 and 0.320 ng/g dw, respectively. Average concentrations of the long-chained PFCAs (C₉–C₁₄) showed about three times greater than those of the short-chained PFCAs (C₄–C₇). These composition characteristics were consistent with previous studies (Ahrens et al., 2009; Yeung et al., 2013; Zhao et al., 2015).

Average concentrations of PFASs from fourteen lakes in Jiangsu Province were 2.17 ng/g dw, with the highest at Yangcheng Lake (4.28 ng/g dw) and the lowest at Luoma Lake (0.929 ng/g dw). In general, PFAS levels in sediments from fourteen lakes in Jiangsu Province of China reached the low end of the worldwide levels (Appendix A Fig. S1). PFOS and PFOA ranked at low levels compared with those in sediments from other regions, while PFUnDA levels were in the middle.

2.2. Source apportionment

A 12 × 60 dataset (twelve individual PFASs and sixty sampling sites) was introduced into PCA-MLR, PMF and Unmix models to identify source categories and quantify the contributions of extracted sources to the \sum_{12} PFASs.

2.2.1. Source apportionment by PCA-MLR model

Four principal components (PC1, PC2, PC3 and PC4) were extracted with the eigenvalues > 1 by PCA-MLR model, accounting for 83.4% of the total variances. PC1 explained 51.3% of the total variances and was characterized by high loading of the long-chained PFCAs, specifically perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTTrDA) and perfluorotetradecanoic acid (PFTeDA), and moderate loadings of PFPeA and perfluoroheptanoic acid (PFHpA) (Table 1). Long-chained PFCAs (C₁₀–C₁₆) were usually used for textile impregnation spray for car interior, thus PC1 was interpreted to reflect the contributions of PFASs from textile treatments (Cai et al., 2012). PC2 explained 14.4% of the total variances and was dominated by PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and PFUnDA (Table 1). It was reported that PFOA was the most predominant PFAS compound in water samples near Daikin Industries Ltd. in Jiangsu Hi-Tech Fluorochemical Industry Park, contributing at least 88% to the \sum PFASs (Cui et al., 2013). Daikin Industries Ltd. is one of eight international manufacturers of fluorine chemical industry and fluoro-resin coatings are the featured products of the chemicals division. The salts of PFOA and PFNA have been also used for many decades as an essential “processing aid” in the manufacture of fluoropolymers (Buck et al., 2011). The production of PFUnDA and PFDA was limited, so they were considered to be the degradation products of precursors (Young et al., 2007).

Consequently, PC2 was identified as the fluoropolymer processing aid/fluoro-resin coating sources. PC3 contributed 9.0% of the total variances and was characterized by high loadings of perfluorohexanoic acid (PFHxA) and PFOS (Table 1). PFOS emissions (tones/year) in Jiangsu Provinces came mainly from textile treatments and metal platings, accounting 54% and 43% of the total emissions, respectively (Xie et al., 2013). Thus, PC3 was selected to represent the joint contributions of textile treatments and metal platings. PC4 explained 8.7% of the total variances and was dominated by perfluorobutyric acid (PFBA), which was mainly applied to the flotation agent in the synthesis of precious metals (Campo et al., 2015) (Table 1). Therefore, PC4 was the indicator of the precious metal sources.

The MLR analysis yielded excellent coefficients for the four component scores at a stipulated minimum 95% confidence. The absolute factor scores matrix for PFAS contributions of the four factors obtained from PCA-MLR model were expressed using Eq. (3):

$$Z_{\text{PFASs}} = 0.4946T_1 + 0.6527T_2 + 0.5230T_3 + 0.0927T_4 - 1.87065 \quad (3)$$

The coefficients were set as t_i , and the contributions of each factor were calculated using Eq. (4):

$$\text{Percentage} = (t_i / \sum t_i) \times 100\% \quad (4)$$

The results showed that the textile treatment sources contributed 28.1% to the \sum_{12} PFASs, followed by the fluoropolymer processing aid/fluoro-resin coating sources (37.0%), the textile treatment/metal plating sources (29.7%) and the precious metal sources (5.3%) (Table 2). The 100% (1.76 ng/g dw) of the observed \sum_{12} PFASs was explained by PCA-MLR model. These four sources represented the average concentration contributions of 0.493, 0.650, 0.521 and 0.092 ng/g dw to the \sum_{12} PFASs, respectively (Table 2).

2.2.2. Source apportionment by PMF model

A total of four sources were chosen as the optimal number for PMF model. Source profiles for PFASs obtained from PMF model are displayed in Table 1. The first source had high concentrations for PFAS species including PFUnDA, PFDoDA, PFTTrDA and PFTeDA, identified as the textile treatment sources. For the second source, PFPeA, PFHpA, PFOA, PFNA and PFDA got high weighting. Thus, the second source represented the joint contributions of fluoropolymer processing aids and fluoro-resin coatings. The third source was predominated by PFBA, interpreted as the precious metal sources. The fourth source was highly related to PFHxA and PFOS, which were the indicators of textile treatments and metal platings.

Table 1 – PFAS species in each extracted source by PCA-MLR, PMF and Unmix models.

Models	Textile treatments	Fluoropolymer processing aids/ fluoro-resin coatings	Textile treatments/ metal platings	Precious metals
PCA-MLR	PFPeA, PFHpA, PFDoDA, PFTTrDA, PFTeDA	PFOA, PFNA, PFDA, PFUnDA	PFHxA, PFOS	PFBA
PMF	PFUnDA, PFDoDA, PFTTrDA, PFTeDA	PFPeA, PFHpA, PFOA, PFNA, PFDA	PFHxA, PFOS	PFBA
Unmix	PFPeA, PFDoDA, PFTTrDA, PFTeDA	PFHpA, PFOA, PFNA, PFDA, PFUnDA	PFHxA, PFOS	PFBA

PFAS: perfluoroalkyl substances; PCA-MLR: principal component analysis-multiple linear regression; PMF: positive matrix factorization.

Table 2 – Estimated profile contributions and source contributions for PFASs by PCA-MLR, PMF and Unmix models.

Sources	Profile contributions			Source contributions		
	PCA-MLR (ng/g dw)	PMF (ng/g dw)	Unmix (ng/g dw)	PCA-MLR	PMF	Unmix
Textile treatments	0.493	0.464	0.365	28.1%	30.6%	20.6%
Fluoropolymer processing aids/fluororesin coatings	0.650	0.612	0.931	37.0%	39.3%	52.4%
Textile treatments/metal platings	0.521	0.380	0.360	29.7%	22.4%	20.2%
Precious metals	0.092	0.121	0.120	5.3%	7.7%	6.8%
Modeled	1.76 (100.0%)	1.70 (96.7%)	1.77 (101.0%)			

The contributions to the Σ_{12} PFASs of the four sources were also estimated by PMF model (Table 2). 96.7% (1.70 ng/g dw) of the observed Σ_{12} PFASs was explained according to this model, while 3.3% of the Σ_{12} PFASs (0.058 ng/g dw) was not identified. The highest contributions to the Σ_{12} PFASs in sediments were the fluoropolymer processing aid/fluororesin coating sources with a contribution of 39.3%, followed by the textile treatment sources (30.6%), the textile treatment/metal plating sources (22.4%) and the precious metal sources (7.7%). These sources constituted on average 0.668, 0.519, 0.381 and 0.131 ng/g dw of the Σ_{12} PFASs, respectively.

2.2.3. Source apportionment by Unmix model

Four sources for identifying source categories of PFASs were extracted by Unmix model. These sources were comparable to those identified by PCA-MLR and PMF models with minor differences (Table 1). The first source was dominated by PFBA, which were the same as PC4 of PCA-MLR and the third source of PMF. PFHxA and PFOS were prominent in the second source, agreeing to PC3 of PCA-MLR and the fourth source of PMF. PFPeA, PFDODA, PFTTrDA and PFTeDA got high weighting in the third source, in keeping with PC1 of PCA-MLR and the first source of PMF. The fourth source had high concentrations for PFHpA, PFOA, PFNA, PFDA and PFUnDA, which is in accordance with PC2 of PCA-MLR and the second source of PMF. Four sources obtained from Unmix model were identified as the precious metal sources, the textile treatment/metal plating sources, the textile treatment sources and the fluoropolymer processing aid/fluororesin coating sources, respectively.

Estimated profile contributions and source contributions for PFASs by Unmix model are shown in Table 2. The estimated source contributions were also similar to those assigned by PCA-MLR and PMF models, with the order of 52.4%, 20.6%, 20.2% and 6.8%. These sources represented the average concentration contributions of 0.930, 0.365, 0.359 and 0.120 ng/g dw to the Σ_{12} PFASs, respectively. This model slightly overestimated the Σ_{12} PFAS concentrations, with a modeled value of 1.77 ng/g dw.

2.3. Comparison of PCA-MLR, PMF and Unmix results

To better understand PFAS sources, results obtained from three receptor models were compared and estimated. When comparing these three models, it is proposed that the following four conditions must be fully considered: the fitting degree between the modeled and observed Σ_{12} PFASs

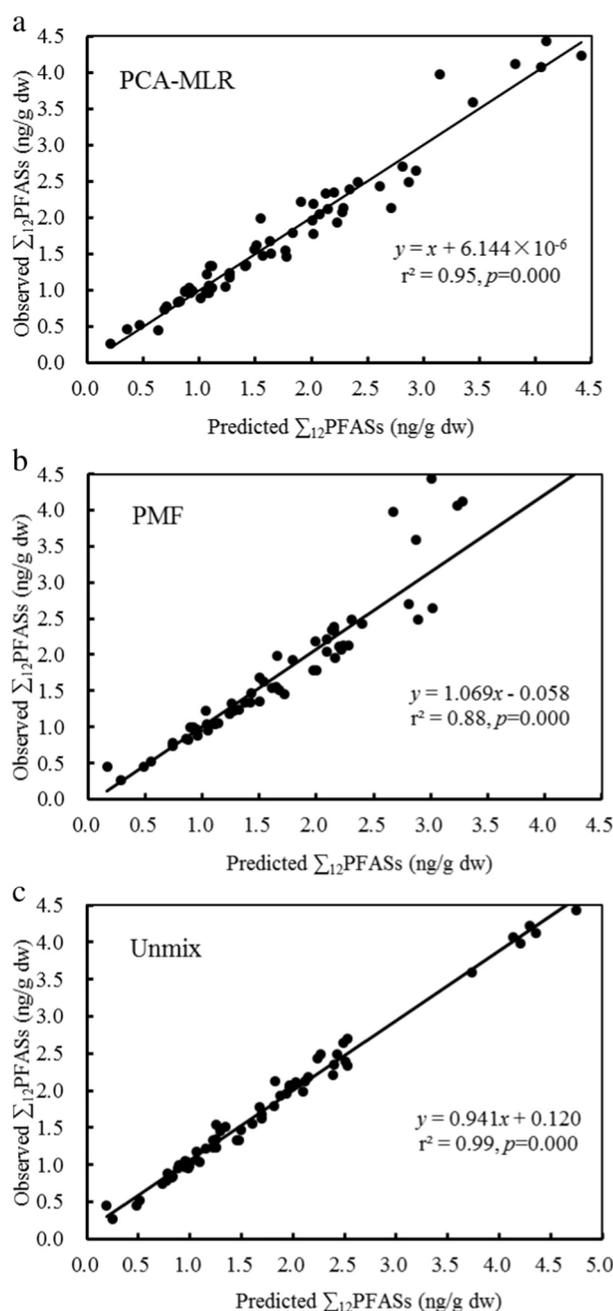


Fig. 2 – Fitting plots between the modeled and observed perfluorooctane sulfonic acid (Σ_{12} PFASs) concentrations for all sediment samples.

concentrations in a certain model, the fitting degree between the modeled Σ_{12} PFASs concentrations among different models, the number and characteristics of identified sources as well as the contributions of each extracted source to the Σ_{12} PFASs.

An intra-comparison was conducted by performing linear regression between the observed concentrations of PFAS species against those modeled by a certain model. The fitting plots displayed that these three models all provided good correlations between the observed and modeled Σ_{12} PFASs concentrations (r^2 ranged from 0.88 to 0.99, $p = 0.000$) (Fig. 2). Similar slopes were measured in all cases, especially PCA-MLR model showed a slope equal to unity, with a high correlation coefficient ($r^2 = 0.95$, $p = 0.000$). The intercepts varied greatly with the lowest value found for PMF model. The correlation coefficients as well as the error percentages between the modeled and observed concentrations of individual PFAS species were also used to evaluate these three models' performance (Table 3). Generally, the r^2 were quite high ($p = 0.000$), suggesting that these three models reproduced well the spatial evolution of individual PFAS species. As for the errors, these three models all generated the acceptable values in most cases. Especially, PCA-MLR model consistently produced almost the identical modeled values of individual PFAS concentrations as the observed ones. PMF model generated consistently the modeled values less than or equal to the observed ones, with the absolute errors in the range of 0–10% (except for PFBA of 32%, PFPeA of 16%, PFUnDA of 11% and PFOS 18%). The opposite was the case for Unmix, with the positive errors of 0–10%, and there are exceptions to PFPeA, PFOA, PFHxA and PFNA, with the negative errors of –4%, –3%, –7% and –7%, respectively.

Good correlations were also observed in an inter-comparison of the modeled Σ_{12} PFASs concentrations. As shown in Fig. 3, r^2 varied from 0.83 to 0.94 ($p = 0.000$), with the intercepts ranging from –0.126 to 0.171. The regression between PCA-MLR and Unmix models displayed an optimal slope very close to unity, with the lowest absolute intercept. Regarding the Σ_{12} PFASs explained by each model, similar percentages of

the observed Σ_{12} PFASs were explained by these three models (Table 2). In terms of the explained concentrations, PCA-MLR model explained perfectly 100% of the Σ_{12} PFASs concentrations. PMF model slightly underestimated the Σ_{12} PFASs concentrations with a percentage of 96.7%, and Unmix model slightly overestimated the Σ_{12} PFASs concentrations with a percentage of 101.0%. In regard to the experimental evidence on source apportionment, four sources were identified by these three models (Table 4). The textile treatments/metal plating sources were identified with high correlation coefficients among these three models ($r = 0.861$ – 0.953 , $p = 0.000$). For other sources, perfect correlations only occurred between PMF and Unmix models, with r ranging from 0.905–0.930 ($p = 0.001$). These differences might be caused by the considerations of the models themselves (e.g. the uncertainties and non-negativity constraints) or the species selected as variables (Callén et al., 2009; Yang et al., 2013). It suggested that the identified sources by PMF and Unmix models were more reliable than those by PCA-MLR model.

Results from both the intra- and inter-comparisons of the observed and modeled Σ_{12} PFASs by these three models indicated that they all could well track the Σ_{12} PFASs as well as the concentrations explained in sediments. In contrast, the fitting degree between the modeled and observed Σ_{12} PFASs concentrations, the correlation coefficients as well as the error percentages between the modeled and observed concentrations of individual PFAS species in Unmix model were better than PCA-MLR and PMF models. Thus, Unmix model was the preferred receptor model in source apportionment of PFASs in sediments, without considering the slightly overestimation. PMF model was more reliable than PCA-MLR model, because four sources were all identified with strong positive correlations between PMF model and Unmix model. Divergent source profiles were closely related to the models themselves and the datasets (Yang et al., 2013). In future studies, it is suggested that source apportionment should be conducted through multiple methods to mitigate the weaknesses of individual methods to get more convincing conclusions.

Table 3 – Information of individual PFAS concentrations obtained from PCA-MLR, PMF and Unmix models.

	Observed (ng/g dw)	PCA-MLR			PMF			Unmix		
		Modeled (ng/g dw)	r^2	%Error ^a	Modeled (ng/g dw)	r^2	%Error	Modeled (ng/g dw)	r^2	%Error
PFBA	0.091	0.091	0.73	0	0.062	0.23	–32	0.092	0.98	1
PFPeA	0.036	0.036	0.58	0	0.030	0.42	–16	0.034	0.46	–4
PFHxA	0.039	0.039	0.87	0	0.036	0.86	–9	0.037	0.84	–7
PFHpA	0.029	0.029	0.71	0	0.026	0.54	–10	0.029	0.63	0
PFOA	0.320	0.320	0.88	0	0.310	0.82	–3	0.310	0.77	–3
PFNA	0.136	0.136	0.86	0	0.136	0.95	0	0.127	0.52	–7
PFDA	0.188	0.188	0.95	0	0.174	0.79	–7	0.193	0.91	3
PFUnDA	0.337	0.337	0.84	0	0.301	0.64	–11	0.348	0.76	3
PFDoDA	0.069	0.069	0.95	0	0.067	0.95	–4	0.072	0.90	4
PFTTrDA	0.105	0.105	0.91	0	0.103	0.95	–2	0.105	0.90	0
PFTeDA	0.021	0.021	0.86	0	0.019	0.77	–10	0.021	0.87	1
PFOS	0.384	0.384	0.87	0	0.316	0.72	–18	0.407	0.90	6
Σ_{12} PFASs	1.76	1.76	0.95	0	1.70	0.88	–3	1.77	0.99	1

^a %Error = (modeled concentration – observed concentration) × 100 / observed concentration.

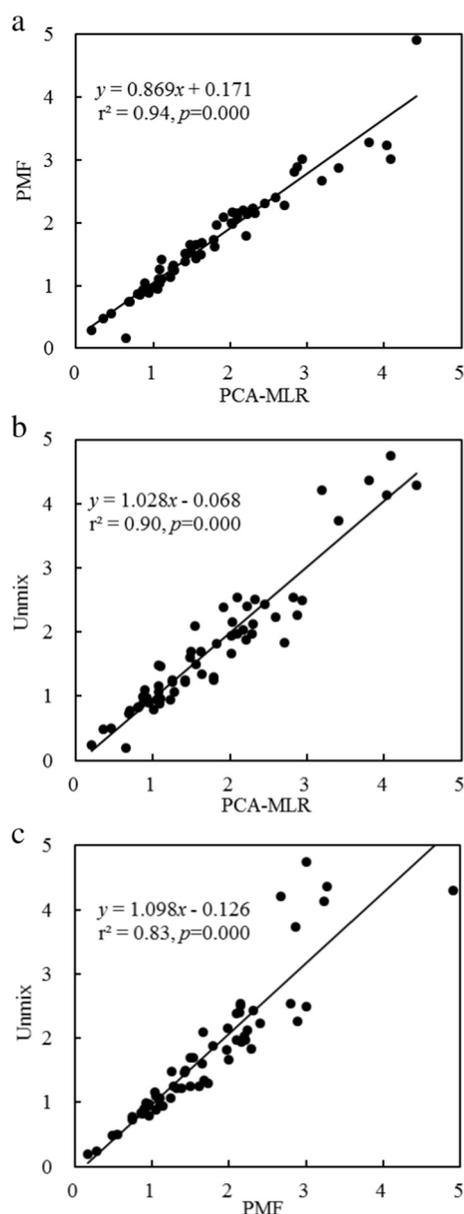


Fig. 3 – Fitting plots among the modeled Σ_{12} PFAS concentrations in all sediment samples by three receptor models.

3. Conclusions

In this study, sixty sediment samples were collected from fourteen lakes in Jiangsu Province of China. Concentrations of the Σ_{12} PFASs ranged from 0.264 to 4.44 ng/g dw, with an average of 1.76 ng/g dw. All targeted PFASs were quantifiable and PFOS was the most abundant compound. Source apportionment of PFASs in sediments was conducted by three multivariate factor analysis receptor models: PCA-MLR, PMF and Unmix. Four sources were identified consistently by three models: textile treatments, fluoropolymer processing aids/fluororesin coatings, textile treatments/metal platings and precious metals, contributing 28.1%, 37.0%, 29.7% and 5.3% by PCA-MLR model, 30.60%, 39.3%, 22.4% and 7.7% by PMF model, and 20.6%, 52.4%, 20.2%

Table 4 – Pearson correlation coefficients among the identified sources by PCA-MLR, PMF and Unmix models.

Source	Models	Pearson coefficient
Textile treatments	PCA-PMF	-0.745**
	PCA-Unmix	-0.609*
	PMF-Unmix	0.905**
Fluororesin coatings	PCA-PMF	0.024
	PCA-Unmix	-0.230
	PMF-Unmix	0.905**
Textile treatments/metal platings	PCA-PMF	0.872**
	PCA-Unmix	0.861**
	PMF-Unmix	0.953**
Precious metals	PCA-PMF	0.033
	PCA-Unmix	-0.127
	PMF-Unmix	0.930**

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

and 6.8% by Unmix model to the Σ_{12} PFASs, respectively. The similarities showed that these three models were all useful tools for source apportionment of PFASs in sediments. Unmix model was recommended as the preferred receptor model in this work, and PMF model was more reliable than PCA-MLR model. The combination of various methods could provide more information for source apportionment than individual methods. The overlapping conclusions from convergent results of multiple methods were more persuasive.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2016.12.007>.

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