Q1 Perspective

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 C_4–C_{14}-perfluoroalkyl carboxylic acids and perfluorooctane sulfonic acid ($\sum_{12}$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 $\sum_{12}$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 $\sum_{12}$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

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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.

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 μg/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 μg/mL solution mixtures were both purchased from Wellington Laboratories (Guelph, ON, Canada). Perfluoro-1-[1,2,3,4,5,6,7,8-$^{13}C_8$]octanesulfonate and perfluoro-n-[1,2,3,4,5,6,7,8-$^{13}C_8$]octanoic acid (50 μg/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 a 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 $\sum_{12}$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):

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

where, c_{ij} is the concentration of ith species for the jth sample; x_{in} is the ith species concentration from the nth source; f_{nj} is the contribution of the nth source to the jth 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