



Short communication

Chromatographic fingerprint similarity analysis for pollutant source identification

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ABSTRACT

In the present study, a similarity analysis method was proposed to evaluate the source-sink relationships among environmental media for polybrominated diphenyl ethers (PBDEs), which were taken as the representative contaminants. Chromatographic fingerprint analysis has been widely used in the fields of natural products chemistry and forensic chemistry, but its application to environmental science has been limited. We established a library of various sources of media containing contaminants (e.g., plastics), recognizing that the establishment of a more comprehensive library allows for a better understanding of the sources of contamination. We then compared an environmental complex mixture (e.g., sediment, soil) with the profiles in the library. These comparisons could be used as the first step in source tracking. The cosine similarities between plastic and soil or sediment ranged from 0.53 to 0.68, suggesting that plastic in electronic waste is an important source of PBDEs in the environment, but it is not the only source. A similarity analysis between soil and sediment indicated that they have a source-sink relationship. Generally, the similarity analysis method can encompass more relevant information of complex mixtures in the environment than a profile-based approach that only focuses on target pollutants. There is an inherent advantage to creating a data matrix containing all peaks and their relative levels after matching the peaks based on retention times and peak areas. This data matrix can be used for source identification via a similarity analysis without quantitative or qualitative analysis of all chemicals in a sample.

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1. Introduction

Contaminant source identification is essential to the investigation of the environmental process of pollutants. Early multivariate methods, such as chemical mass balance models, used the profiles of target pollutants from suspected sources as input. This type of approach is biased on a priori assumptions of the number and nature of the potential sources (Galarneau, 2008). Factor analysis methods, such as principal component analysis, address this concern based on a posteriori estimation. However, the aforementioned methods assume that the profiles of the target pollutants associated with each source are unique. In reality, the relative proportions of the species for a suspected source are typically not unique or constant. In addition to the transformation of target pollutants that occurs in the environment, sample collection,

instrumental analysis, the environmental process (e.g., the transport of pollutants), and spatial and temporal variation also have a substantial effect on the affected profiles. Therefore, the source-sink relationship of environmental pollutants is extremely difficult to identify because many variable processes may be involved. Isotopic measurements can be used to trace the source and behavior of environmental contaminants (Sturchio et al., 2012). However, real-world applications require additional chemical and site evaluation information, as well as an understanding of how and when isotopes fractionate (Cipro et al., 2012; Mechlińska et al., 2010; Sturchio et al., 2012; Wilson et al., 2012). Because of their simplicity and ease of application, profile-based methods continue to be used in the current literature, despite their limitations (Galarneau, 2008). Thus, improvement in the effectiveness of profile-based methods is crucial.

Environmental media, such as soil and sediment, always contain various chemicals other than pollutants that concern environmental scientists. This complex composition is similar to traditional Chinese herbal medicine (TCHM), which often contains multiple

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botanicals. The analysis and quality control of TCHM are becoming more integrative and comprehensive to better address the inherent holistic nature of TCHM (Xie et al., 2006). For example, chromatographic fingerprint analysis has been used to determine the identity, stability, and consistency of TCHM, as well as to identify adulterants. This method can potentially characterize the marker components (i.e., target pollutants) and the unknown components (i.e., non-target chemicals) in a complex system (i.e., a certain environment medium) (Li et al., 2015). Interestingly, we may be able to use chromatographic fingerprint analysis for source identification, especially for the identification of the source-sink relationships among different environmental media.

To our knowledge, there is no report regarding the application of fingerprint analysis for the source identification of environmental pollution. The objective of this study was to establish a simple and efficient similarity analysis method for the examination of the source-sink relationships among different environmental media. In the present study, polybrominated diphenyl ethers (PBDEs) were selected as the target pollutants for the development of this similarity analysis method to improve the profile-based method for source identification.

2. Methodology

Two hundred three topsoil samples (0–10 cm) and 114 surface sediment samples were collected from different sampling sites in Shenzhen, China. Fourteen PBDE congeners (BDE28, 47, 49, 85, 99, 100, 138, 153, 154, 183, 196, 206, 208, and 209) were selected for quantitative analysis. Detailed procedures for sample collection, analysis and quality control are provided in previous studies (Ni et al., 2012; Sun et al., 2013) and are summarized in the Supporting Information (SI). Moreover, five commonly used plastics in electronic waste (polystyrene (PS), propene polymer (PP), acrylonitrile butadiene styrene (ABS), polyethylene (PE) and polyvinyl chloride (PVC)) in which flame-retardants were used as additives to protect the electronic equipment against ignition were also collected for analysis. For each plastic, five types of electronic products were selected as samples, and each 5 g plastic sample was cut into small pieces and extracted using a Soxhlet extraction (dichloromethane and n-hexane, 3:1, v:v). Then, a glass column packed with silica gel/alumina was used for sample cleanup (Sun et al., 2013).

The pollution profiles of the extracted mixtures were analyzed using a Shimadzu Model 2010 gas chromatograph coupled with a Model QP2010 plus mass spectrometer (Shimadzu, Japan) using negative chemical ionization in selected ion monitoring mode. A 15 m DB-5MS capillary column (0.25 mm i.d., 0.10 μm film thickness) was used to separate the PBDE congeners. The column temperature was programmed from 110 °C (held for 5 min), then from 110 to 200 °C at 20 °C/min (held for 5 min) and, finally, from 200 to 310 °C at 10 °C/min (held for 15 min). The interface and ion source temperatures were set to 280 and 200 °C, respectively. All samples were automatically injected (2 μL) at 290 °C in the splitless mode, with the split mode turned on 1 min after injection. Ion fragments of *m/z* 79 and 81 were used to monitor for mono- to nona-BDEs; *m/z* 79, 81, 486.7 and 487.6 were used to monitor for BDE209. BDE-209 (0.1 ng/g) was found in only one procedural blank of sediment with a concentration close to the lowest level of the calibration curve. More information on the quality control of the PBDE measurements in plastics is presented in the SI. The median, minimum, and maximum concentrations of PBDEs in soil, sediment, and plastic samples are summarized in the SI, Table S1.

Based on the comparison of the fingerprint chromatograms of the compounds in different environmental media, including target pollutants and non-target compounds, a source identification

model evaluated by calculating the similarity using the angle cosine method was proposed in the present study. First, using the median concentration from all of the chromatograms of common compounds (compounds that appeared in more than two samples) in each environmental compartment, their unique fingerprint chromatograms were developed. Then, the similarity index of these chromatograms in different media was calculated using Formula (1) (Ye, 2011):

$$\text{similarity index} = \frac{\sum_{i=1}^n a_i b_i}{\sqrt{\sum_{i=1}^n a_i^2} \cdot \sqrt{\sum_{i=1}^n b_i^2}} \quad (1)$$

where a_i and b_i are the peak areas of the i th peaks in the chromatograms of common compounds in two environmental media of interest. In contrast to the chromatographic fingerprint analysis used in TCHM, there is no reference fingerprint for the intercomparison of fingerprint chromatograms of soil, sediment, and plastic in electronic waste. Note that there are differences among the fingerprint chromatograms of soil or sediment samples from different locations. Even for the same matrix, slight differences remain between the fingerprint chromatograms. Therefore, we developed their fingerprint chromatograms using the median concentration from all of the chromatograms of the target pollutants in each environmental compartment.

3. Results and discussion

Using retention time and the mass spectrum information, 14 to 22 peaks were detected in the extracts of all the samples. According to the concept of common compounds defined above, the number of common compounds in all the samples was greater than 43. Most peak areas (absolute intensity) of the common compounds were greater than 10^5 , indicating that the common compounds in the samples were present at relatively high concentrations. These results indicate that the pollution profiles of chemicals (with PBDEs as the major target pollutants) in soil, sediment, and plastic in electronic waste are wide variable.

The mass spectra and the retention times were used to determine whether the same compound was represented by the same identification number in all samples. We then evaluated the similarity between spectra based on two criteria: (1) a signal-to-noise ratio of 10 was employed to avoid disturbances caused by low noise information, and (2) a higher (from zero to one) similarity index indicates a higher similarity between spectra. There were 17 common peaks (14 individual PBDEs and 3 non-target compounds) in the three types of environmental media, and the area sum of these peaks accounted for more than 90% of the overall peak area (Fig. 1). The 14 individual PBDEs were identified by a comparison with their corresponding chemical references under the same conditions (Fig. 1), and three unidentified non-target compound peaks were also present. These 17 common peaks were used to calculate the cosine correlation for the similarity analysis.

According to Formula (1), the cosine correlations between plastic and soil or sediment and between soil and sediment were acquired. As shown in Fig. 2, the cosine correlation ranged from 0.53 to 0.68, suggesting that plastic in electronic waste is an important source of PBDEs in the environment. This has already been shown in many studies (Labunska et al., 2014; Li et al., 2014; Needhidasan et al., 2014; Ni et al., 2010; Park et al., 2014; Peeters et al., 2014). Furthermore, the cosine correlations between plastic and soil or sediment are much less than one, indicating that there are sources other than plastics for PBDEs in soil or sediment. A cosine value less than one also indicates that the physicochemical transformation of PBDEs can occur during the transfer and diffusion

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