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GAS CHROMATOGRAPHY

Screening and Quantification of Organic Pollutants in Soil Using Comprehensive Two-dimensional Gas Chromatography with Time-of-flight Mass Spectrometry

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ABSTRACT

The identification and quantification of organic compounds in leaching basin soil is important for the evaluation of soil pollution. In this study, a non-target screening strategy and a quantitative analytical method were developed based on the accelerated solvent extraction method followed by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. First, a screening method for potential risk compounds in soil samples was established, and the major compounds were screened under the conditions such as matching similarity, signal-to-noise ratio, and relative area ratio. Second, a quantitative method was further developed by internal calibration curves for 50 main organic pollutants in the soil samples, including 27 polycyclic aromatic hydrocarbons and their derivatives (PAHs), 10 phthalic acid esters, eight phenolic compounds, and five benzene derivatives. The quantitative procedure exhibited good selectivity, accuracy, precision, low limits of detection (0.03–1.02 ng/g), and quantification (0.1–3.0 ng/g) for all target compounds. Finally, the proposed strategy was applied to the soil samples that were collected from a leaching basin and polluted by electroplating wastewater. Abundant PAHs and phenolic compounds were detected in the topsoil sample, which were mainly released from the electroplating wastewater. The application of this multi-dimensional strategy in leaching basin soil samples can also be used for the assessment of organic pollution in other complex soil samples.

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KEYWORDS
Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry; organic pollutants; quantification; screening; soil

Introduction

A leaching basin generally installed in the remote regions of rainy weather is an artificial catch basin that permits the infiltration of runoff into the ground. The bottom and sides of the leaching basin are perforated so that the water entering the basin can enter the surrounding stone fill and infiltrate into the ground. Some small factories use this simple drainage system to discharge incompletely treated industrial wastewater into the ground, evading environmental regulations (Li and Zhu 1981; Zhou 2012; Pandey et al. 2016). When the wastewater enters the ground through leaching basins, pollutants will migrate along with the soil seepage flow or the surface runoff into the soil, posing potential risk

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to the surrounding surface water, groundwater, air, and food chain, thus threatening the surrounding ecosystem and inhabitants (Plagellat et al. 2006; Naidoo and Olaniran 2014).

Wastewater is a major route for the release of organic contaminants to the environment (Ternes, Joss, and Siegrist 2004; Gómez et al. 2011). The effluents released from the electroplating industry not only contain a large number of heavy metals, but also high levels of organic pollutants (Liu et al. 2011; Zhao et al. 2013). However, their numbers and types of organic pollutants are still limited to the emission standard for electroplating wastewater (Ministry of Environmental Protection of the People's Republic of China 2008). Many contaminants outside the criteria can be freely discharged into the environment because of a lack of environmental concern, especially when the sewage enters into the ground through leaching basins, and may seriously contaminate the surrounding terrestrial and aquatic ecosystems (Liu et al. 2011). Therefore, an effective method offering rapid and reliable screening of all compounds in a sample is urgently required. A non-target screening analysis combining a target analysis is feasible to assess the comprehensive pollution, where the screening analysis provides a primary evaluation of the organic composition in the soil sample, and the target analysis provides further quantitative information of the major pollutants in the sample.

At present, multi-residue analysis is the main method for the identification of organic compounds in environmental samples (Kasprzyk-Hordern, Dinsdale, and Guwy 2008; Huntscha et al. 2012; Robles-Molina et al. 2013). The residue analysis of semi-volatile organic compounds in soil is usually accomplished by gas chromatography–mass spectrometry (GC–MS) or tandem mass spectrometry (Gómez et al. 2009; Guitart and Readman 2010). Both methods need to limit the number of analytes for accurate quantification by single ion monitoring (SIM) or the multi-reaction monitoring (MRM) mode. In fact, as the detector, mass spectrometry can be operated in the full scan mode as an untargeted approach, overcoming the restrictions of the target analysis to screen all the components in a sample. Nevertheless, conventional one-dimensional (1D) chromatography is hard to deal with a large number of target compounds in a complex matrix in a single analysis and often shows co-elution (Mostafa and Gorecki 2013). Therefore, mass spectrometer is usually operated in the SIM or MRM mode to focus on a certain mass range, but in this way, a comprehensive analysis requires multiple and complementary approaches.

Comprehensive two-dimensional gas chromatography (GC × GC) is a multi-dimensional chromatographic technique, which has significantly enhanced the chromatographic separation using two different GC columns with different retention mechanisms; therefore, its separation capability is much higher than one-dimensional GC. Moreover, GC × GC provides more information by structured chromatograms, making the technique more suitable for sample screening than one-dimensional GC. Besides, the total run time of GC × GC is comparable to that in one-dimensional method because the modulator collects analytes eluted from the first column and injects them into the second column in a series of very short pulses, simultaneously generating both retention times for each peak. Furthermore, GC × GC can also reduce the sample clean-up procedures as the high separation capability of the technique allows reducing matrix interferences on the target compounds (Dalluge, Beens, and Brinkman 2003).

In this study, GC × GC was connected to a time-of-flight mass spectrometer. As a fast detector, time-of-flight mass spectrometry (TOF-MS) is the only mass spectrometric

technique that can acquire more than 50 mass spectra per second, allowing proper reconstruction of GC × GC chromatograms by providing enough identification points per peak (Dalluge, Beens, and Brinkman 2003). In recent years, the use of comprehensive GC × GC with TOF-MS is rapidly becoming prevalent in petrochemicals (Sfetsas et al. 2011; Weng et al. 2015), food industries (Dasgupta et al. 2010; Zhang et al. 2013), as well as in medical science (Rocha et al. 2012) and environmental samples (Matamoros, Jover, and Bayona 2010).

Non-target screening aims to obtain an overview of the sample constituents and identifies all eligible peaks in the sample. The soil samples contaminated by electroplating wastewater usually contain a large amount of organic pollutants with high matrix interferences (Zhao et al. 2013). To choose an effective sample extraction method, three commonly used extraction methods including accelerated solvent extraction (ASE), Soxhlet extraction, and microwave-assisted extraction (MAE) have been compared based on the previous reports (Wang et al. 2007; Rodriguez-Solana et al. 2015; Jurado-Sanchez, Ballesteros, and Gallego 2013). Among these methods, ASE provides the best extraction efficiency for the isolation of most semi-volatile organic compounds in soil samples with a short extraction time and low solvent consumption (Wang et al. 2007). Soxhlet extraction also provides good recovery and reproducibility; however, it consumes more time and solvent. MAE is easy to operate and consumes less time and solvent; however, it suffers from lower recoveries for some compounds (Wang et al. 2007; Jurado-Sanchez, Ballesteros, and Gallego 2013). Therefore, ASE based on the method of Wang et al. (2007) was chosen as the extraction method in this study.

The main purpose of this study was to develop, optimize, and validate both non-target screening and quantification methods for organic pollutants in complicated soil samples based on ASE and GC × GC-TOF-MS, which would contribute to the assessment of organic pollution in complex soil samples. To the best of our knowledge, only very limited reports have been published on the analysis of soil organic pollution in leaching basins. In this study, soil samples were collected from a polluted leaching basin that mainly used for electroplating wastewater discharge. First, a non-target screening method was developed for primary evaluation of overall organic compositions of the samples. Second, a quantitative analysis for 50 major contaminants was further developed by the internal standard method and applied to the soil samples.

Materials and methods

Chemicals and standards

Analytical standards of high purity including 27 polycyclic aromatic hydrocarbons (PAHs), 10 phthalic acid esters (PAEs), eight phenolic compounds, and five benzene derivatives subjected to analysis are listed in Table 1 and were purchased from AccuStandard (New Haven, Connecticut, USA). Stock solutions were prepared in isooctane, and then diluted into seven concentration levels, from 1 to 500 μg/L. The stock solution was kept at −18°C until use.

The internal standard solution with a concentration of 10 mg/L was diluted from an Internal Standard Mix purchased from AccuStandard (New Haven, Connecticut, USA) and used to determine the concentration of target compounds, noting that the selected deuterated internal standards were stable and would not interfere with the sample

Table 1. Validation data for 50 target compounds and their concentrations in the investigated soil samples.

Peak number	Compound	Quantitative. ion (m/z)	Determination coefficient	Limit of detection (ng/g)	Limit of quantification (ng/g)	Recovery (%)	Precision as the relative standard deviation (%)		Concentration (ng/g) ± standard deviation		
							Intra-day	Inter-day	Sample #1	Sample #2	Sample #3
1	Aniline	93	0.9987	1.02	3.0	71.2	8.3	15.2	105 ± 3.5	–	–
2	Phenol	94	0.9989	0.15	0.7	74.9	7.2	9.6	20653 ± 5.8	734 ± 3.4	–
3	Phenol, 2-chloro-	128	0.9976	0.32	0.9	76.2	9.6	11.0	26.8 ± 1.4	–	–
4	2,3-Benzofuran	118	0.9960	0.25	1.0	85.6	7.1	13.8	820 ± 5.6	6.10 ± 12	–
5	*o*-Cresol	108	0.9906	0.35	1.0	72.8	7.5	10.9	2113 ± 3.3	12.8 ± 2.7	–
6	*p*-Cresol	107	0.9980	0.20	1.0	76.1	7.5	10.1	4774 ± 2.8	15.6 ± 6.3	–
7	Phenol, 2,4-dimethyl-	122	0.9912	0.80	2.5	91.6	8.3	12.5	6683 ± 15	50.6 ± 11	–
8	Phenol, 2,4-dichloro-	162	0.9955	0.20	0.6	84.0	3.9	8.4	10248 ± 3.3	345 ± 1.1	–
9	Naphthalene	128	0.9979	0.45	2.0	89.1	3.4	6.8	25810 ± 5.9	61.2 ± 6.3	2.70 ± 6.1
10	Phenol, 2,6-dichloro-	162	0.9982	0.12	0.5	86.0	7.7	10.3	3426 ± 2.8	11.4 ± 5.3	–
11	Naphthalene, 2-methyl-	142	0.9974	0.33	0.8	96.4	3.8	6.0	581 ± 1.5	–	–
12	Naphthalene, 1-methyl-	142	0.9955	0.40	1.3	89.5	4.6	5.1	6819 ± 4.3	4.90 ± 1.8	–
13	Phenol, 2,4,6-trichloro-	196	0.9985	0.32	1.0	88.4	6.5	9.0	14396 ± 4.1	44.7 ± 7.4	–
14	Benzene, 1,2,3,4-tetrachloro-	216	0.9994	0.03	0.1	68.3	1.9	5.3	29.0 ± 6.2	–	–
15	2-Chloronaphthalene	162	0.9996	0.80	2.0	92.9	5.7	6.9	10.8 ± 1.6	–	–
16	Naphthalene, 1,3-dimethyl-	156	0.9986	0.04	0.1	78.1	5.6	9.5	5511 ± 8.4	6.50 ± 5.4	–
17	Dimethyl phthalate	163	0.9961	0.03	0.1	104	7.7	10.3	168 ± 10	4.60 ± 5.5	2.30 ± 3.9
18	Naphthalene, 1,4-dimethyl-	156	0.9951	0.18	0.8	79.7	5.2	8.2	185 ± 1.5	–	–
19	Acenaphthylene	152	0.9927	0.04	0.2	76.4	2.2	7.3	171 ± 9.7	–	0.60 ± 10
20	Acenaphthene	153	0.9936	0.05	0.2	95.6	6.5	9.8	7949 ± 5.1	8.20 ± 3.6	–
21	1-Naphthalenamine	143	0.9969	0.09	0.3	74.8	5.9	6.3	9.8 ± 3.8	–	–
22	2-Naphthalenamine	143	0.9941	0.10	0.4	80.4	6.7	8.1	12.3 ± 4.2	–	–
23	Naphthalene, 1,4-dichloro-	196	0.9992	0.04	0.2	75.2	2.2	4.3	56.9 ± 3.2	–	–
24	Naphthalene, 2,6-dichloro-	196	0.9995	0.33	1.0	80.3	4.7	6.7	48.2 ± 8.9	–	–
25	Diethyl phthalate	149	0.9982	0.09	0.4	76.5	6.5	8.9	502 ± 6.5	105 ± 10	7.8 ± 6.5
26	Fluorene	166	0.9975	0.10	0.3	75.5	7.9	9.4	9054 ± 2.0	11.0 ± 2.8	1.60 ± 4.1
27	Benzene, 1-chloro-4-phenoxy	204	0.9956	0.05	0.8	80.4	5.2	6.9	542 ± 4.4	8.9 ± 5.0	–

28	Naphthalene, 1,4,5-trimethyl-	155	0.9947	0.05	0.2	88.6	8.9	11.2	404 ± 7.5	–	–
29	Benzene, pentachloronitro-	237	0.9933	0.18	0.8	101	5.8	6.0	15.2 ± 9.3	–	–
30	Phenanthrene	178	0.9992	0.45	1.8	85.7	6.8	8.0	584 ± 9.2	28.2 ± 9.3	3.90 ± 2.7
31	Anthracene	178	0.9985	0.33	1.0	81.4	4.7	5.8	6744 ± 2.1	5.80 ± 5.4	–
32	Diisobutyl phthalate	149	0.9981	0.15	0.6	105.5	5.6	10.7	503 ± 9.3	10.2 ± 2.5	2.60 ± 3.4
33	Dibutyl phthalate	149	0.9995	0.06	0.3	104.5	8.1	10.3	2329 ± 3.1	203 ± 1.3	5.50 ± 15
34	1,2,3,4-Tetrachloro-naphthalene	266	0.9993	0.10	0.4	92.0	3.5	6.0	20.8 ± 8.7	–	–
35	Bis(2-methoxyethyl) phthalate	149	0.9984	0.29	1.3	76.4	4.0	5.8	108 ± 9.2	–	–
36	Fluoranthene	202	0.9970	0.33	1.0	88.4	5.2	6.7	14733 ± 4.1	18.0 ± 2.8	1.70 ± 4.1
37	Dihexyl phthalate	149	0.9991	0.15	1.9	101.5	6.9	9.2	309 ± 1.5	11.0 ± 6.6	3.20 ± 9.2
38	Bis(2-ethoxyethyl) phthalate	149	0.9987	0.06	0.3	105.7	5.1	8.4	81.6 ± 8.7	–	–
39	Diamyl phthalate	149	0.9975	0.16	0.8	76.8	3.6	7.7	589 ± 2.5	11.0 ± 7.7	–
40	Pyrene	202	0.9959	0.12	0.4	92.5	5.3	5.8	13940 ± 1.0	15.8 ± 1.6	–
41	Benzyl butyl phthalate	149	0.9953	0.25	1.0	92.6	2.6	3.9	51.1 ± 6.5	2.90 ± 10	–
42	Benz[*a*]anthracene	228	0.9989	0.30	1.2	98.5	4.0	6.9	3133 ± 8.1	30.3 ± 3.8	–
43	Chrysene	228	0.9959	0.35	1.0	99.3	5.3	6.5	9446 ± 0.7	24.4 ± 1.3	–
44	Benzo[*b*]fluoranthene	252	0.9940	0.25	1.0	91.5	4.8	5.6	7165 ± 1.8	61.2 ± 0.9	–
45	Benzo[*k*]fluoranthene	252	0.9938	0.14	0.6	92.9	3.7	5.3	–	–	–
46	Benzo[*a*]pyrene	252	0.9927	0.48	1.5	107	3.5	6.8	2013 ± 1.2	9.40 ± 3.2	–
47	Dinonyl phthalate	149	0.9916	0.60	1.9	102	5.2	7.3	20.5 ± 9.2	–	–
48	Indeno[1,2,3-*cd*]pyrene	276	0.9947	0.34	1.2	110	2.3	5.4	699 ± 4.7	–	–
49	Dibenz[*a,h*]anthracene	278	0.9907	0.25	1.0	102	2.2	5.9	187 ± 1.9	–	–
50	Benzo[*g,h,i*]perylene	276	0.9976	0.35	1.5	104	3.4	7.6	917 ± 5.1	–	–

components. The surrogate standard solution was prepared at 10 mg/L for 2-fluorophenol and *p*-terphenyl-d_{14} for performing the quality control function, since its recovery was used to evaluate the efficiency of the analytical method. The organic solvents, of analytical grade, were purchased from J&K Scientific (Beijing, China).

Sample information and sample preparation

In this study, three soil samples were chosen for the analysis and to provide the explanation of the whole workflow. Two soil samples were collected from a leaching basin (Boxing, Shandong Province, China), surrounded by two small electroplating factories and polluted by electroplating wastewater. Sample #1 and Sample #2 were taken from the top layer soil (0–20 cm) and middle layer soil (20–50 cm) of the leaching basin bottom using a soil auger of 5 cm diameter, respectively. Sample #3, collected from the top layer soil (0–20 cm) of a hill 200 m away from the leaching basin, was relatively clean and uncontaminated.

Soil samples were air-dried at room temperature, sieved through a 50-mesh sieve after removing stones, and then stored in desiccators prior to analysis. Dionex ASE 200 from Thermo Scientific (Waltham, MA, USA) was used for ASE of soil samples. A 10.0 g soil sample, spiked with surrogate solution (10 µL, 10 mg/L), was placed in a 22-mL stainless steel vessel. 3.0 g of diatomite was added to the vessel for more complete homogenization. The extraction was performed with dichloromethane at 80°C, 1500 psi and repeated for 2 cycles. Each cycle contains a 6-min heat-up followed by a 5-min static extraction. The extracted fractions were combined and evaporated to 1–2 mL using a rotary evaporator.

The concentrated extracts were transferred to the top of a chromatography column ($30 \times 1\ cm^2$) filled with 10 g silica gel and 2 g anhydrous sodium sulfate for removing interfering compounds. The column was then eluted with 15 mL *n*-hexane and 15 mL dichloromethane. The eluted fractions were concentrated to approximately 1 mL under a gentle stream of nitrogen, and the final volume of the extract was adjusted to 1 mL with *n*-hexane after adding 10 µL internal standard solution (10 mg/L). To ensure the testing results are meaningful and reliable, a duplicate sample was made and measured for each soil sample by the same analytical procedures.

Instrumentation

The GC × GC analytical system was an Agilent 7890A GC (Agilent Technologies, Santa Clara, CA, USA) equipped with a multi-purpose autosampler (Gerstel, Mülheim, Germany) connected to a Pegasus 4D time-of-flight mass spectrometer (Leco Corp., St Joseph, MI, USA). Liquid nitrogen was used to cool down the nitrogen gas for cold pulses and automatically filled from a Dewar by a liquid meter. Instrument control and data processing were carried out by ChromaTOF software, version V4.51 (Leco Corp., St Joseph, MI, USA).

Chromatographic separation was performed using a nonpolar capillary column Rtx-5 (30 m × 0.25 mm × 0.25 µm, Agilent Technologies) in the first dimension and a medium-polar capillary column Rxi-17MS (1.0 m × 0.10 mm × 0.10 µm, Restek) in the second dimension. The injection temperature was 250°C with 1 µL injection in the splitless mode. Helium (purity, 99.999%) was used as the carrier gas at a constant flow of 1.2 mL/min. The column temperature program for the primary oven was optimized as follows: initial at 50°C, held for 2 min; ramped to 300°C at 10°C/min, then held for

8 min. The secondary oven was programmed 5°C ahead of the primary GC oven gradient. The modulation temperature offset was 20°C to the primary oven temperature program. The modulation period (P_M) was set to 3.0 s with a 0.6 s hot pulse.

The TOF-MS was operated in the electron ionization mode at an acquisition rate of 100 spectra/s. Mass spectra were collected in the full-scan mode in the m/z range 50–500. Ion source and transfer line temperatures were set at 250 and 280°C, respectively. The detector voltage was 1.70 kV. A solvent delay of 7 min was used to prevent the damage of the ion source filament.

Non-target screening analysis

In this study, the National Institute of Standards and Technology (NIST) library was used for searching and identifying the possible compounds in soil samples. Automatic peak detection and mass spectrum deconvolution were performed based on the peak width set to 0.1 s, signal-to-noise (S/N) ratios >50, and spectral similarity >700. After setting the parameters, the entire workflow ran automatically, and the obtained data were submitted to a following data processing. The searching results including first and second retention times, similarity, signal-to-noise ratio, and characteristic ions, were presented in the peak table. Next, group type classification was performed by drawing borderlines in the contour plot to highlight the major groups in the samples. Finally, another filtration condition was added to isolate the most abundant pollutants in the samples by setting a criterion for the minimum relative peak area.

Quantitative analysis

The quantification was carried out by the internal calibration method. The calibration curves for 50 target compounds in the range 1–500 μg/L were used to calculate the concentration of analytes in the soil samples. For each of the 50 compounds, the linearity of calibration curve was assessed by plotting the peak area against the theoretical concentration and expressed by the determination coefficient (R^2). The limit of detection and quantification of each compound were calculated by progressively decreasing the analyte concentration in a spiked sample until yielding 3 and 10 times the signal-to-noise ratio, respectively. The accuracy of the method was tested by recovery studies of blank soil samples spiked with the known amounts of target compounds (5 μg/L) in triplicate. The precision of the method was evaluated by the repeatability and reproducibility through analyzing five solutions of the same standard concentration (5 μg/L) on the same day (intra-day precision) and daily for three times over 1 week (inter-day precision).

Results and discussion

Optimization of GC × GC-TOF-MS

For complex matrix, to obtain a satisfactory separation of most compounds in the samples with adequate sensitivity and resolution, the separation conditions of GC × GC-TOF-MS should be chosen.

The column set is an important parameter for target separation; however, it is difficult to predict the potential compounds in the soil samples. Thus, a common column set combining a nonpolar column (Rtx-5) and a mid-polar column (Rxi-17MS) was selected in this

study. Based on a previous study (Gómez et al. 2011) and the authors' experience, the column set Rtx-5 × Rxi-17MS has been used for the determination of PAHs, organochlorine pesticides, and some personal care products in environmental samples, and provided good results for both selectivity and sensitivity. Although it was not completely orthogonal, it improved the separation of almost all the compounds because of significant difference in the polarity between the two columns. Figure 1 shows the GC × GC-TOF-MS contour plot of the identified compounds in Sample #1, where more than 700 analytes are separated by volatility (on the *x*-axis) and polarity (on the *y*-axis), and their concentrations are plotted on the *z*-axis by peak height.

Then, a standard solution of 50 μg/L was used for the following method development and optimization. GC oven temperature is an important parameter that affects the extent of the analyte resolution; therefore, the GC oven temperature program was optimized. The second oven was situated in the first oven in our GC × GC system, so the second oven was 5°C ahead of the primary GC oven gradient. The separation was evaluated by three heating rates ($X = 5$, 10, and 15°C/min) in the main oven temperature program. The temperature program was as follows: 50°C, held for 2 min, then increased to 300°C at *X*°C/min, held for 8 min. The heating rate of 5 and 10°C/min both provided good separation for all target compounds. 10°C/min was better because of shorter analysis time (35 min), providing a more efficient laboratory output and reducing the liquid nitrogen consumption. When the heating rate increased to 15°C/min, the resolution between some peaks decreased and lead to some co-elution of peaks, so it was abandoned. Thus, 10°C/min was selected as the heating rate. Under this condition, the oven temperature program was achieved with an initial temperature of 50°C held for 2 min; then ramped to 300°C at 10°C/min and held for 8 min.

The modulation period (P_M) is a key step in GC × GC separation, as it needs to preserve the first-dimension separation and make all analytes elute from the two columns with good

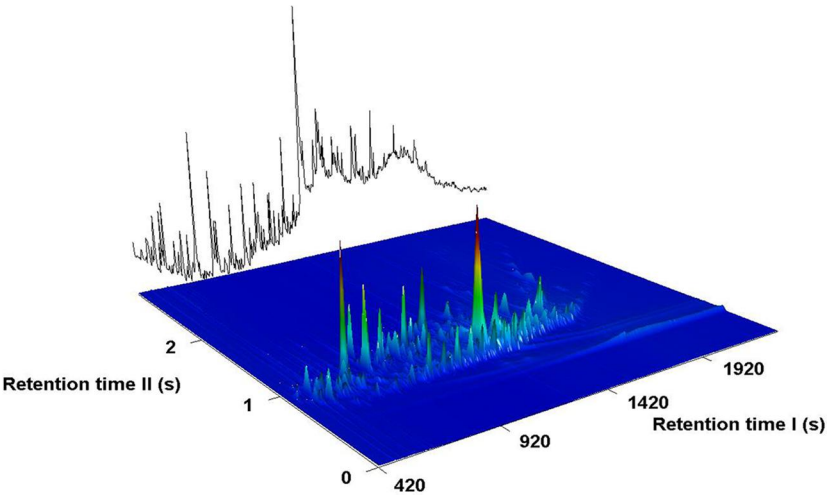

Figure 1. Contour plot of soil Sample #1 analyzed by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. The analytes were separated by volatility in the first dimension (on the *x*-axis) and by polarity in the second dimension (on the *y*-axis), and their concentration is presented on the *z*-axis as the peak height.

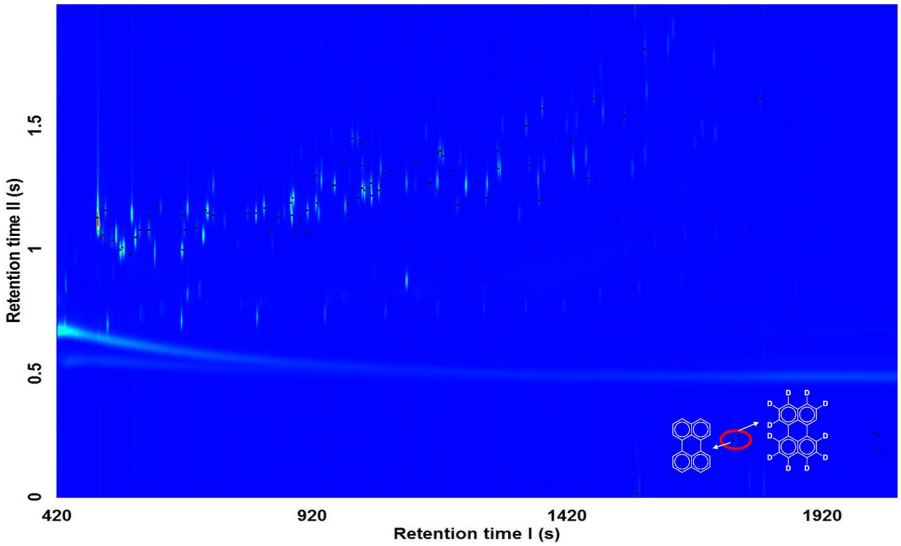

Figure 2. Two-dimensional chromatogram of a standard solution obtained at modulation period = 2.0 s.

peak shapes. In this experiment, modulation periods of 2.0, 2.5, and 3.0 s with a 20% hot pulse duration were investigated to obtain the best sensitivity. When the modulation period was 2.0 and 2.5 s, the peaks had good shape, but wraparound was observed for less-volatile PAHs such as perylene and perylene-d_{12} (Figures 2 and 3). This shortcoming previously reported (Pena-Abaurrea et al. 2012) was reduced by increasing the modulation period. When the modulation period was extended to 3.0 s (Figure 4), all target compounds were

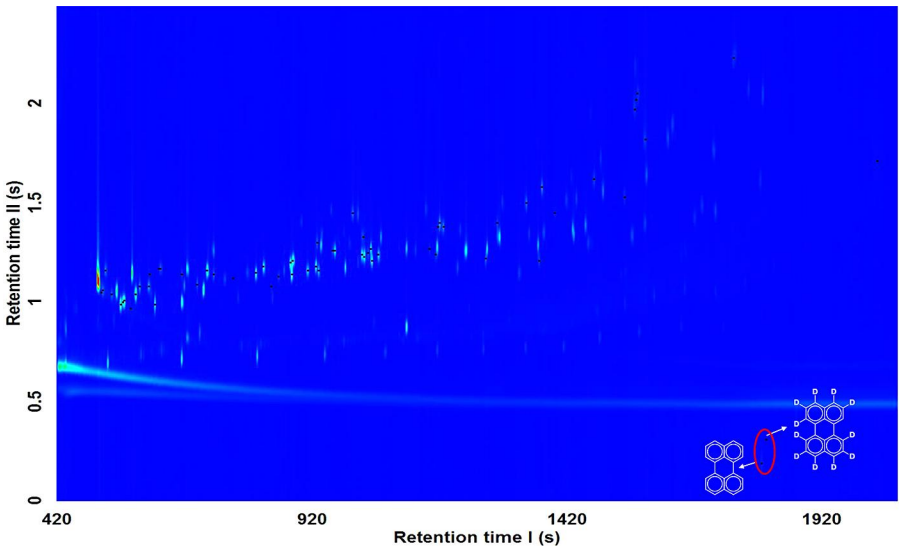

Figure 3. Two-dimensional chromatogram of a standard solution obtained at modulation periods = 2.5 s.

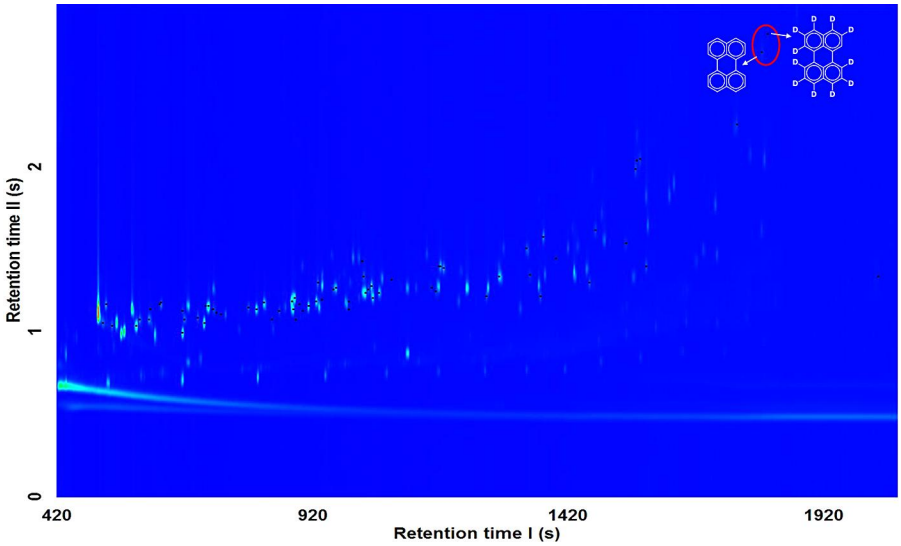

Figure 4. Two-dimensional chromatogram of a standard solution obtained at modulation periods = 3.0 s.

eluted in one period with good peak shapes. With further increasing the modulation period, the separation achieved on the first column decreased, exacerbating the mixing effect and may lead to co-elution in some cases. Therefore, the modulation period was set to 3.0 s as the optimum value.

Finally, the detector voltages were optimized to obtain the best sensitivity for target compounds. Here, the signal-to-noise ratio was used to measure the effect of detector voltage on the sensitivity because both the peak signal and noise signal increase with detector voltage. The effect of detector voltages (1.65, 1.70, and 1.75 kV) on several representative compounds is shown in Figure 5. With increasing voltage, the trends of signal-to-noise ratio for different

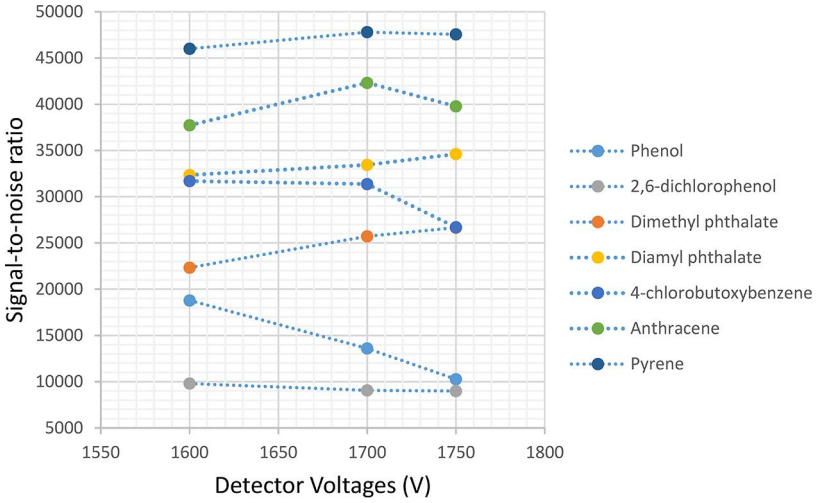

Figure 5. Effect of detector voltages on peak signal of seven representative compounds.

compounds are different, but that of each class is basically the same. Overall, nearly half of the compounds decreased in sensitivity with increasing voltages, and considering the higher voltage accelerates the aging of the detector, 1.70 kV was chosen in this study.

Screening of potential risk compounds

In this study, an efficient non-target screening strategy was carried out to find potential risk compounds in our soil samples. The matching similarity is an indication of how well the acquired mass spectrum matches the reference mass spectra in the NIST library, where a higher value means a better fit. Therefore, the minimum required matching similarity was set to 700 (maximum 999). In addition, to ensure the accuracy and avoid the false positives from the complex matrix, the signal-to-noise ratio was set to exceed 50 (Gómez et al. 2011; Michailof et al. 2014). Although lower thresholds increased the number of detected peaks in the chromatogram, this may lead to increased false identification, especially for complex matrix.

Under these conditions, more than 700 and 200 peaks were detected for Samples #1 and #2, respectively, but only few compounds were detected in Sample #3. The results of peak identification including the compound names, retention times, characteristic ions, and similarities are listed in the peak table. The compounds confirmation was performed by the examination and comparison with the mass spectra in the NIST library as well as the retention times and elution order described in the literature. It is worth noting that GC × GC-TOF-MS uses the full mass range spectrum for identification rather than three to four characteristic ions, thus improving its detectability compared to the conventional GC–MS.

The group classification of components was then performed by the facilities of ChromaTOF software to draw borderlines in the contour plot, better assisting overview and comparison of different samples. The analytes in Sample #1 were roughly classified into six different groups (Figure 6): (1) PAHs, (2) PAEs, (3) phenolic compounds,

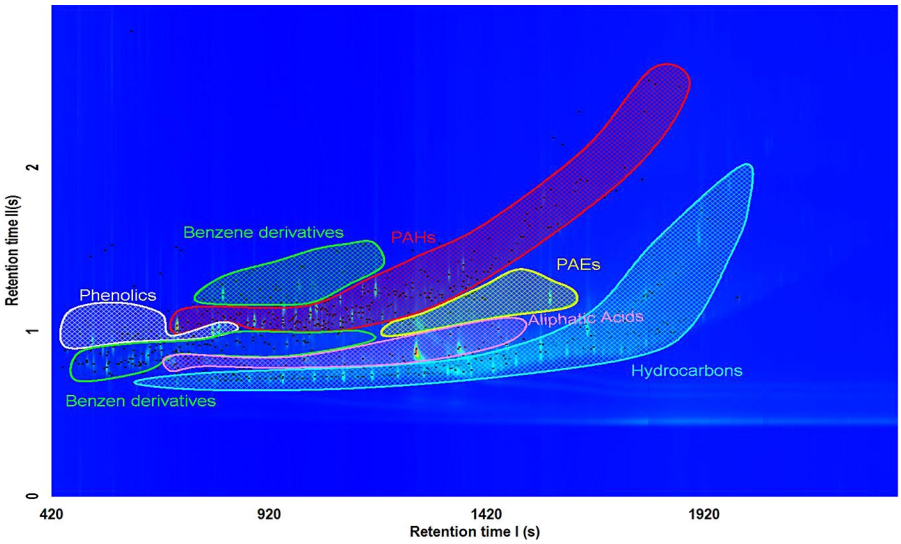

Figure 6. Group designation of Sample #1 by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry.

(4) hydrocarbons, (5) benzene derivatives, and (6) aliphatic acids. The outliers are compounds such as nitrogen-containing compounds, which do not belong to the specified groups. It is worth noting that in several cases, some compounds belonging to different groups of elute in the neighboring retention times, and thus the borderlines are not exactly correct, especially when hundreds of components are present in the chromatogram. The peak density of each of the assigned areas allows for a primary evaluation of the composition of each soil sample. It appears that Sample #1 has a diverse composition with higher concentration of hydrocarbons, aliphatic acids, and PAHs. This example confirms that the group classification is helpful to recognize the compound classes present in the sample in greater proportion and concentration.

Based on the overview of the sample's constituents, another filter condition was added to pick out the most abundant compounds in the soil samples. According to the previous studies (Marsman et al. 2008; Sfetsas et al. 2011; Michailof et al. 2014), a minimum relative peak area $> A\%$ ($A = 0.1$–0.5) was set as the selection criterion. First, the absolute peak areas of the solvent peak (dichloromethane), internal standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}), surrogate standards (nitrobenzene-d_5 and *p*-terphenyl-d_{14}), and siloxanes (column bleed) were removed. The residual peak areas of the remaining peaks were converted to their relative area contribution (100%). Next, the data in the peak table were transferred to Microsoft Excel and were shown in descending order of relative peak area. The selection results, including the number of selected peaks and their total relative area, are listed in Table 2.

By selection of components with a relative area >0.3%, 50 and 29 compounds were screened out in Samples #1 and #2, describing 72.0 and 86.0% of the total relative area, respectively, indicating that a few compounds can basically represent the composition of the sample. However, when the selection criterion changed to relative area >0.1 or >0.5%, the number of analytes increased or decreased considerably, resulting in too many or too few screened compounds, which no longer represented the sample's composition well. Therefore, when the list of target compounds for quantification mainly consulted the compounds selected by relative peak area >0.3%.

In all, non-target screening is useful in the primary estimation of organic composition for samples, but it cannot be directly correlated with its actual weight composition. Therefore, an accurate quantitative method was further developed and implemented for the analysis of samples.

Quantification of 50 target compounds

Based on the main pollutants in the soil samples obtained from the non-target screening and the standard substances in our laboratory, 50 compounds including 27 PAHs, 10 PAEs,

Table 2. Summary of the number of compounds detected in the soil samples. The selection criteria are described in the text.

	Number of peaks detected and their relative areas (in parentheses)	
Criteria for selection	Sample #1	Sample #2
1. Total numbers of peak	674 (100%)	186 (100%)
2. Peak area >0.5%	29 (63.9%)	18 (81.7%)
3. Peak area >0.3%	50 (72.0%)	29 (86.0%)
4. Peak area >0.1%	131 (85.8%)	86 (95.8%)

8 phenolic compounds, and 5 benzene derivatives were selected for quantitative analysis. Although some aliphatic acids and hydrocarbons were found to be abundant in Sample #1, they are less toxic and thus were not considered for quantification in this study. Quantification was carried out by internal calibration and the calibration curves were constructed in the range 1–500 μg/L for each target compound.

The details of the quantitative method, including quantitative ions, correlation coefficient (R^2), limit of detection, limit of quantification, mean recovery, and mean relative standard deviations are shown in Table 1. All the calibration curves showed good linearity over the concentration range, with the determination coefficient $R^2 > 0.9906$ for all the compounds. The limits of detection and quantification ranged from 0.03 to 1.02 ng/g, and from 0.1 to 3.0 ng/g, respectively. The obtained low limits of detection and quantification for most of the target compounds are comparable and even better than the previous reports (Pena-Abaurrea et al. 2012), guarantying accurate determination of the investigated compounds at low levels. Accuracy and precision of the 50 compounds were determined by a repeatability assay using blank samples spiked with the known amounts of target compounds (5 μg/L). All target compounds showed recovery values between 70 and 110% with relative standard deviations less than 15% for intra-day and less than 20% for inter-day precision. Compounds with hydroxyl (e.g., *o*-cresol) or amino groups (e.g., aniline) presented higher relative standard deviations, but were still within the acceptable range. The surrogate standards showed good recovery (92.0–108.3%) for all samples.

In conclusion, the feasibility of the developed quantitative method was demonstrated for quantifying 50 target compounds in three soil samples. Table 1 summarizes the concentrations of these compounds in the investigated soil samples and the measured concentration are shown as mean ± standard deviation because each sample was measured in duplicate. It appears that organic pollutants mainly concentrated in the surface soil (Sample #1) and decreased sharply with increasing soil depth (Sample #2), and this result is in accordance with the screening results. From the result of Sample #3, it can be seen that some plasticizers (e.g., dimethyl phthalate, diethyl phthalate) and PAHs (e.g., naphthalene, phenanthrene) were ubiquitous in the environment; however, the background values were far below the measured values in Samples #1 and #2. Considering no other artificial source closed to the leaching basin except two electroplating factories, we speculated that these pollutants mainly came from the electroplating effluent of the neighboring factories.

It is worth noting that the concentrations of three carcinogenic PAHs [benzo(a)pyrene, benzo(b)fluoranthene, and benz(a)anthracene] in Sample #1 exceeded the maximum permissible value of industrial soil (United States Environmental Protection Agency 2016; Ministry of Environmental Protection of the People's Republic of China 2007). Fortunately, these PAHs were less persistent as their concentrations in Sample #2 decreased to the permissible range, probably because of their higher affinity for microbial degradation. The concentrations of measured benzene derivatives were relatively low in all the samples, but their strong mobility may threaten the groundwater and thus should be given attention.

Conclusion

This study demonstrates the applicability of the GC × GC-TOF-MS for the effective non-target screening and quantitative analysis of various classes of organic compounds

in complex soil samples. The screening method allowed the automatic inspection of the constituents of samples, defined by the separation of compounds, identification, group type classification, and pick out the risk pollutants with a higher concentration. Based on the screening result, a quantitative analysis for 50 target pollutants was further developed by internal calibration, which exhibited good selectivity, accuracy, and precision with low limits of detection and quantification across a relative wide range. The proposed methods have been applied to the leaching basin soil samples that polluted by electroplating wastewater. Although the number of soil samples is limited, the result obtained by this strategy is reliable and meaningful has been submitted to the local environmental department, and may be useful for the forthcoming soil management. In all, we believe this work would contribute to the assessment of organic pollution in complex soil using GC × GC-TOF-MS.

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