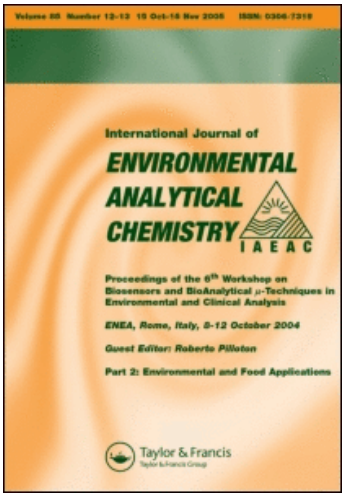

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Simultaneous analysis of organic pollutants in soils by gas chromatography and gas chromatography-mass spectrometry

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Simultaneous analysis of organic pollutants in soils by gas chromatography and gas chromatography–mass spectrometry

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An analytical method for the simultaneous determination of organochlorine pesticides (OCPs), phthalate esters (PAEs) and polycyclic aromatic hydrocarbons (PAHs) in soils is described. Soils were ultrasonically extracted with a mixture of acetone–petroleum ether (1:1, v/v). Two equal portions of combined extracts were fractionated with different polarity solvents via Florisil and silica gel chromatography, to determine OCPs and PAEs, and PAHs, respectively. Reliable recoveries were obtained, which were 92–121% for OCPs, 68–141% for PAEs, and 75–120% for PAHs. The limits of detection were 0.001–0.017 $ng\,g^{-1}$ for OCPs, 0.001–0.022 $\mu g\,g^{-1}$ for PAEs, and 0.002–0.042–$\mu g\,g^{-1}$ for PAHs. In order to check the method, soils collected from the Beijing region were analysed. The average concentrations were 39–91 $ng\,g^{-1}$ for OCPs, 1–2 $\mu g\,g^{-1}$ for PAEs, and 0.24–2.12 $\mu g\,g^{-1}$ for PAHs in urban and rural areas, respectively. Gas chromatography–mass spectrometry (GC–MS) was used to confirm the analyzed compounds by gas chromatography (GC).

Keywords: Organochlorine pesticides; Phthalate esters; Polycyclic aromatic hydrocarbons; Soil; GC/GC-MS

1. Introduction

A wide variety of chemicals such as some of the organochlorine pesticides (OCPs), phthalate esters (PAEs), and polycyclic aromatic hydrocarbons (PAHs) have been identified as endocrine disrupters, suggesting their potential harmfulness to human reproductive health [1]. It has been reported that increasing exposure to the pesticides and phthalates might be partially responsible for the decline in male:female ratio [2] and the premature breast development in young girls [3]. These organic

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compounds are common contaminants found in human diet [4], breast milk [5], and urine samples [6, 7].

Nine out of twelve persistent organic pollutants (POPs) listed in the Stockholm Convention are OCPs. PAHs were included in the POPs Long-range Transboundary Air Pollution Protocol developed by the United Nations Economic Commission for Europe (UNECE 1998, http://www.unece.org/env/lrtap/). The US EPA has promulgated 16 unsubstituted PAHs as 'Consent Decree' priority pollutants, which are monitored routinely for regulatory purposes. PAEs constitute another big group of man-made products that has been investigated regarding their suspected endocrine-disrupting potential. Some European Union Directives have limited the use of these substances, warning of their risks.

Soils are likely to be the main environmental sinks for these lipophilic substances. These contaminants are available for uptake by plants [8, 9] and may leach into ground water [10]. Therefore, their identification and quantification in soil is imperative. Analytical methodologies for OCPs [11, 12] and PAHs [13–15] in soils have been well documented. However, although some methods have been developed for quantitative determination of several phthalates in other matrices [16–18], relatively few methods are available for the analysis of phthalates in soils, and only covering selected phthalates [19]. Furthermore, procedures have been developed only for the analysis of OCPs, PAHs or PAEs separately. As far as we are aware there has been only one report about analysis for nine phthalates, along with PCBs and several OCPs, in environmental samples such as soil, sediment and landfill leachate, and the method reported used by fractionating the extract on a dual-column liquid chromatography [20]. In fact, comprehensive screening of the three groups of compounds in soils often requires the use of three or more methodologies.

The purpose of this study was to develop a convenient analytic method for the simultaneous determination of PAHs, OCPs, and PAEs in soils with minimal steps. We also investigated PAE residues in Beijing soils. Gas chromatography–mass spectrometry (GC–MS) was used to confirm the compounds analyzed by GC.

2. Experimental

2.1 *Chemicals and materials*

Reference standard solutions (1000 μg mL^{-1}) of 20 OCPs 16 PAEs, and 16 PAHs (listed in table 1) were purchased from Supelco (West Chester, PA, USA) individually. The surrogates 2-flurobiphenyl (2-FB), 2,4,5,6-tetrachloro-*m*-xylene (TCMX), and diphenyl phthalate (DPP) were purchased from Aldrich (WIS, USA). Two other pesticides (HCB and *o,p′*-DDT), each at 100 μg mL^{-1}, were obtained from the National Research Center for Certified Reference Materials of China. The standards were further diluted with isooctane (2,2,4-trimethylpentane) to prepare for working standard solutions of PAHs, OCPs, and PAEs. All solvents (Beijing Chemical Factory, China) were of analytical purity and re-distilled in an all-glass system before use. Silica gel (100–200 mesh; Qingdao Haiyang Chemical Company, China) was activated at 130°C for 12 h. Florisil (60–100 mesh; Supelco) was activated at 140°C for 16 h. Anhydrous sodium sulfate (Beijing Chemical Factory) was heated at 600°C for 12 h to destroy any organic contamination.

Table 1. Target compounds determined in the soils and the average spiked recoveries.

	Compound	Abbreviation	Recovery (%)	RSD (%)[b]
	OCPs			
1	α-HCH		117	4
2	HCB		98	6
3	β-HCH		112	8
4	γ-HCH		119	4
5	δ-HCH		102	7
6	Heptachor		109	7
7	Aldrin		109	4
8	Heptachor epoxide		118	3
9	γ-Chlordane		114	5
10	Endosulfan I		110	7
11	α-Chlordane		111	5
12	p,p'-DDE		113	7
13	Dieldrin		92	7
14	Endrin		105	8
15	Endosulfan II		0	3
16	p,p'-DDD		109	8
17	o,p'-DDT		121	5
18	Endrin aldehyde		27	13
19	Endosulfan sulfate		2	70
20	p,p'-DDT		115	7
21	Endrin ketone		34	24
22	Methoxychlor		20	18
	PAEs			
1	Dimethyl	DMP[a]	75	3
2	Diethyl	DEP[a]	89	2
3	Diisobutyl	DIBP	129	9
4	Di-n-butyl	DBP[a]	141	6
5	Bis-(2-methoxyethyl)	BMEP	4	18
6	Bis-(4-methyl-2-pentyl)	BMPP	68	7
7	Bis-(2-ethoxyethyl)	BEEP	1	47
8	Diamyl	DAP	106	1
9	Dihexyl	DHP	120	6
10	Butyl benzyl	BBP[a]	108	9
11	Hexyl 2-ethylhexyl	HEHP	105	5
12	Bis-(2-n-butoxyethyl)	BBEP	13	6
13	Dicyclohexyl	DCP	107	11
14	Bis-(2-ethylhexyl)	DEHP[a]	120	8
15	Di-n-octyl	DOP[a]	114	8
16	Dinonyl	DNP	109	8
	PAHs			
1	Naphthalene	Na	107	3
2	Acenaphthylene	Acy	98	4
3	Acenaphthene	Ace	101	2
4	Fluorene	Fl	89	7
5	Phenanthrene	Ph	110	3
6	Anthracene	An	105	4
7	Fluoranthene	Flu	103	3
8	Pyrene	Pyr	98	8
9	Benz[*a*]anthracene	BaA	90	6
10	Chrysene	Chy	106	2
11	Benzo[*b*]fluoranthene	BbF	101	4
12	Benzo[*k*]fluoranthene	BkF	120	8
13	Benzo[*a*]pyrene	BaP	96	3
14	Indeno[1,2,3-*cd*]pyrene	InP	75	6
15	Dibenz[*a,h*]anthracene	DBA	90	9
16	Benzo[*g,h,i*]perylene	BghiP	76	6

[a] Representing the PAEs listed as priority pollutants by US EPA.
[b] Relative standard deviation.

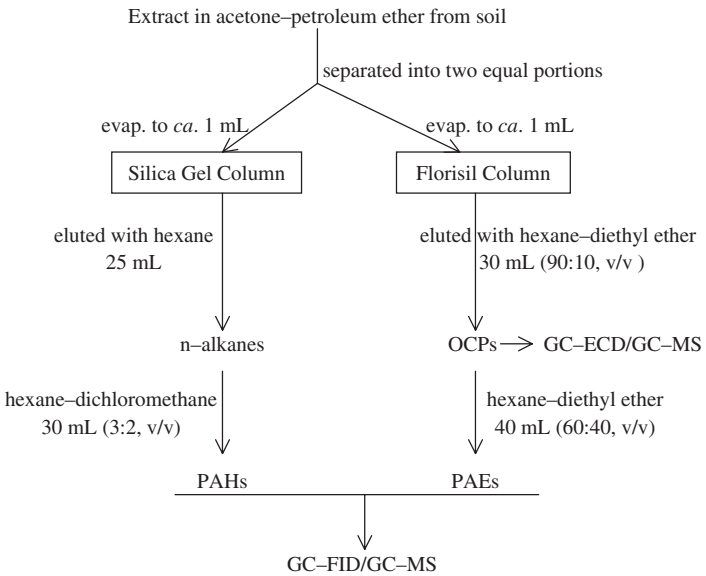

Figure 1. Liquid chromatographic separation of organic pollutants.

Since PAEs are widespread in the environment, great care must be taken to minimize contamination during the laboratory work-up. The glassware was prepared as follows: washed successively with acetone and water, heated at 450°C (5 h), and rinsed with acetone just before use.

2.2 *Sampling*

Six urban (U) and six rural samples (R) at depths of 0–5 cm to 0–30 cm were collected in the Beijing region. The urban area had heavy traffic and many residents, while the rural area was far from the city and free from evident industries. At each site, multiple cores were collected with a coring cylinder (2 cm I.D.) to obtain one representative sample. Deep soil (free of pollution) collected at depths of about 10 m was used as blank soil. The samples were air-dried in a fume hood at room temperature, fully mixed, ground in a mill to achieve particle diameters smaller than 1 mm, and stored in glass bottles at −4°C. The remaining water content in each sample of the soil was determined gravimetrically after drying of a subsample in an oven at 105°C for 12 h. All results were reported as dried weight basis.

2.3 *Ultrasonic extraction*

The samples were analysed according to the straightforward procedure shown in the flow chart (figure 1). Before extraction, 1.0 mL of TCMX at 0.4 μg mL^{-1}, DPP at 4.0 μg mL^{-1}, and 2-FB at 4.0 μg mL^{-1} were added as recovery surrogates to compensate for the losses of OCPs, PAEs, and PAHs, respectively. In each case approximately 10 g of soil were extracted in 30 mL of acetone–petroleum ether (1:1, v/v) thrice during 15 min. The combined extract was divided into two portions, one for pesticides and PAEs analysis, and the other for PAHs analysis. The solvent in each portion

was evapourated off on a Kuderna-Danish (K.-D.) apparatus and the volume was then reduced to about 1.0 mL by a gentle stream of nitrogen for further cleanup.

The efficiency of the extraction and cleanup procedure was checked by spiked recovery experiments ($n = 5$). We first analyzed the soil blank used as matrix for spiking. The result demonstrated that blanks were free of contamination, and showed only peaks at the same retention times corresponding to DIBP, DBP, and DEHP. No background subtraction was used to correct the results. Spiked soils were prepared by adding 1.0 mL of a standard mixture of OCPs at 0.4 $\mu g\,mL^{-1}$, 1 mL of a mixture of PAEs at 4.0 $\mu g\,mL^{-1}$, and 1.0 mL of a mixture of PAHs at 4.0 $\mu g\,mL^{-1}$ to 10 g of blank soil. Three surrogates were also added to the soils before extraction.

In order to test the method, it was used to analyse PAH-contaminated soil/sediment certified reference material CR912 (U.S. EPA). All the measurements fell within the given performance criteria.

2.4 *Chromatographic cleanup*

2.4.1. PAHs. One portion of the concentrated extract was cleaned up with a chromatographic column (30 cm × 10 mm I.D.) containing 10 g of silica gel. The column was pre-eluted with 40 mL of hexane and allowed to drain to bed level before loading of the raw extract. After the sample was transferred onto the column it was eluted with hexane–dichloromethane in different ratios. The silica gel column was first eluted with 25 mL of hexane, and followed by 30 mL of hexane–dichloromethane (3:2, v/v). The first fraction contained n-alkanes, and the second PAHs.

2.4.2. OCPs and PAEs. The other portion of the concentrated extract was cleaned up with a chromatographic column (30 cm × 10 mm I.D.) containing 5 g of Florisil. The groups of OCPs and phthalates were fractionated by hexane–diethyl ether in different ratios. The first fraction containing OCPs was eluted by 30 mL of hexane–diethyl ether (90:10, v/v). and the second fraction containing PAEs was eluted by 40 mL of hexane–diethyl ether (40:60, v/v).

The solvent in each fraction was evaporated on the K.-D. apparatus with a gentle stream of nitrogen, and then the volume was adjusted to 0.2 mL for GC injection.

2.5 *GC and GC-MS analysis*

Analysis of OCPs was performed on an Agilent 6890 GC equipped with a ^{63}Ni Electron Capture Detector (GC-ECD). Separations were performed on a DB-5 fused silica capillary column (30 m × 0.25 mm I.D.; 0.25 μm film thickness) with nitrogen as carrier and make-up gas. The oven temperature was programmed as follows: initial temperature of 100°C was held for 2 min, increased at a rate of 6°C min^{-1} to 280°C, then held for 2 min. The injector and detector temperature were 280°C and 300°C, respectively. Analysis of PAHs and PAEs was performed on an Agilent 6890N gas chromatograph equipped with DB-5 column and Flame Ionization Detector (GC-FID). Each temperature program was the same as follows: initial temperature of 50°C was held for 2 min, increased at a rate of 4°C min^{-1} to 280°C, then held for 20 min

for PAHs and 5 min for PAEs, respectively. The injector and detector temperatures were 280°C and 300°C, respectively.

An Agilent 6890 GC-5973 MSD system was used for confirmation of the samples and analytes. The electron-impact energy was 70 eV. The carrier gas was helium (99.999%) at a flow rate of 1 mL min^{-1}. PAHs were screened in full-scan mode (50–550 D). PAEs and OCPs were identified using selected-ion monitoring. The temperature programs were as described above. The major selected ions (m/z) were as follows: 181, 219 and 183 for α-, β-, γ-, and δ-HCH; 284, 286 and 282 for HCB; 246, 318, 316 and 248 for *p,p′*-DDE; 235, 237 and 165 for *p,p′*-DDD, *o,p′*-DDT and *p,p′*-DDT; 163, 149 for DMP; 149 for other PAEs.

Eluate identification was based on retention time and mass spectrum with appropriate individual standards. Comparing the peak areas of samples with the corresponding peaks of the standard mixture enabled a quantitative analysis to be carried out.

3. Results and discussion

3.1 *Chromatography*

The gas chromatograms showed a baseline separation of all target analytes for accurate quantification except for the pair endosulfan I/α-chlordane and the two-isomer mixture of BMPP.

3.2 *Elution profiles*

OCPs and PAEs were fractionated on Florisil columns by adjusting the ratios of hexane and diethyl ether. PAHs were fractionated on silica gel columns by adjusting the ratios of hexane and dichloromethane. The ratios of each elution solution were adjusted with each new batch of silica and Florisil.

3.3 *Recovery and limit of detection*

The average recoveries are listed in table 1. Surrogate recoveries were from 85–100%. The average recoveries were 92–121% for OCPs, 68–141% for PAEs, and 75–120% for PAHs. A good repeatability of the method was demonstrated by low relative standard deviations ($< 12\%$). The exceptions were endosulfan II, endrin aldehyde, endosulfan sulfate, endrin ketone, methoxychlor, BMEP, BEEP, and BBEP, with recoveries less than 35%. This may be attributed to their strong sorption on the adsorbent. The recoveries of DIBP and DBP were higher than 120%, which could be attributed to the presence of these compounds in the blanks as described above.

The limit of detection (LOD) for each compound was estimated as three times the response of the signal-to-noise ratio of 3:1 in soil blank samples. The LODs were calculated as 0.001 ng g^{-1} (β-HCH)–0.017 ng g^{-1} (γ-chlordane) for OCPs, 0.001 μg g^{-1} (BMPP)–0.022 μg g^{-1} (DEHP) for PAEs, and 0.002 μg g^{-1} (Chy)–0.042 μg g^{-1} (Na) for PAHs.

3.4 *Application to real samples*

The surface soils from rural (R) and urban (U) areas in Beijing region were analysed by the method described. To assure the quality of the proposed analytical method, the procedure blank, matrix spike, and sample were successively analysed. The results for OCPs, PAEs and PAHs in soils are shown in figure 2.

The average concentrations of OCPs were $39\,ng\,g^{-1}$ in the urban area, and $91\,ng\,g^{-1}$ in the rural area. The HCHs (rural: $14\,ng\,g^{-1}$; urban: $13\,ng\,g^{-1}$) and DDTs (rural: $75\,ng\,g^{-1}$; urban: $18\,ng\,g^{-1}$) were the most abundant compounds detected, accounting for 98 and 80% in soils, respectively. Aldrin was another relatively abundant compound in urban soil ($6\,ng\,g^{-1}$). HCB was detected in all samples, with a slightly higher concentration in the urban compared with the rural area. The abundance of HCHs, HCB and DDTs was confirmed by GC–MS. In all samples, DDE was the main contributor to the sum of DDTs, suggesting that most of the parent DDT had been transformed into its metabolites [21]. As for HCHs, the concentration of β-HCH accounted for about 81% of the urban and 85% of the rural soils HCHs, indicating an old HCH source [22]. The ratio of α-/γ-HCH ($\approx$2) [23] suggests the use of technical HCH and lindane for both agricultural and domestic pest control. In comparison with other areas, the HCHs level in this survey is lower than that in rural areas of the Jianghan plain in China ($455\,ng\,g^{-1}$) [24] but higher than those detected in the USA [21], Germany [25], and some European countries such as Belgium, Italy and Greece ($0.4–0.9\,ng\,g^{-1}$) [26].

The average total concentration of PAEs was $1\,\mu g\,g^{-1}$ in rural and $2\,\mu g\,g^{-1}$ in urban soils, respectively, which was in the same order as reported by Hu *et al.* [27]. DIBP, DBP, and DEHP were the most abundant compounds in these samples, accounting for about 85% in urban soils. The concentration of BBP, a potential estrogen, was $60\,\mu g\,g^{-1}$ in both areas. The high values for these compounds are consistent with their high production. The content of six priority phthalates listed by US EPA (DMP, DEP, DBP, BBP, DEHP, and DOP) together with DIBP accounted for up to 86% in urban samples and 56% in rural soils. DAP and DNP were another two abundant compounds in rural area. DMP and DEP were found at lower concentrations in soils.

It seems that PAH levels in the surface soils in Beijing's outskirts were obviously above the endogenous level ($0.001–0.010\,\mu g\,g^{-1}$) [28]. The total concentrations of the 16 priority PAHs in urban soils ($2.12\,\mu g\,g^{-1}$) was 8.8 times that in the rural area ($0.24\,\mu g\,g^{-1}$). The PAHs levels in the urban soils fell within the range of those of urban background ($1–3\,\mu g\,g^{-1}$) in highly industrialized countries [29]. The most abundant hydrocarbons were Flu and BkF. The high molecular weight PAHs (4–6 ring) known to be carcinogenic [30] represented 65% (urban) and 60% (rural soils) of the total PAHs studied. This indicates a combustion (pyrogenic) origin [31]. As one typical total-ion chromatogram of the soil sample by GC–MS shown in figure 3, the unsubstituted PAHs were the most abundant components, which also suggested that a combustion or pyrolysis process was a dominant source of the PAHs contamination in our studied samples. The quotient of the sum of major combustion-specific compounds (Flu, Pyr, BaA, Chr, BbF, BkF, BaP, InP and BghiP) to the sum of 16 PAHs averaged 0.6 in urban samples and 0.5 in rural samples, which further indicated that more extensive combustion activities such as motor vehicle use affected the PAH levels in urban soils in Beijing.

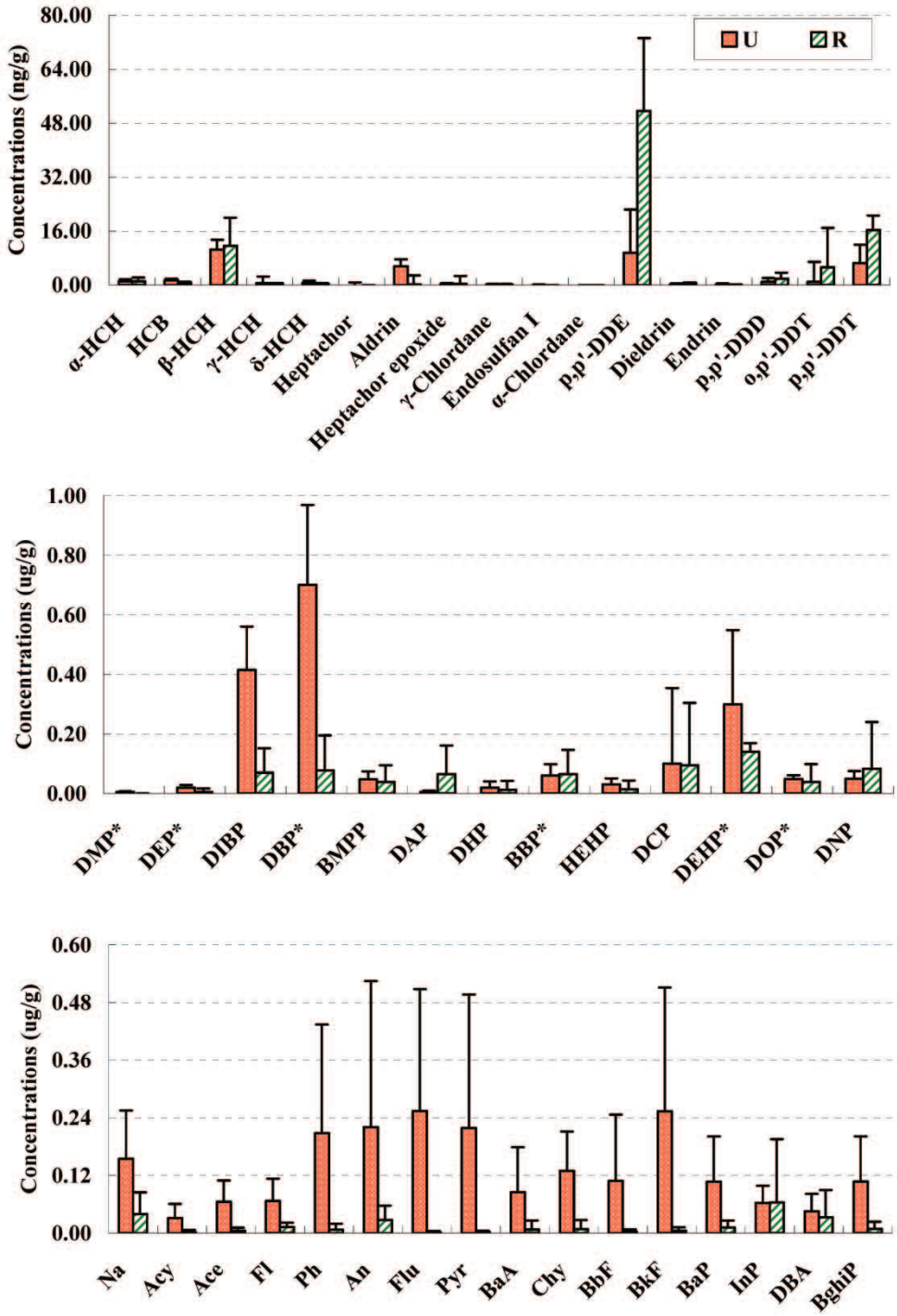

Figure 2. The concentrations of each compound in the surface soils from urban (U) and rural (R) areas in Beijing region.

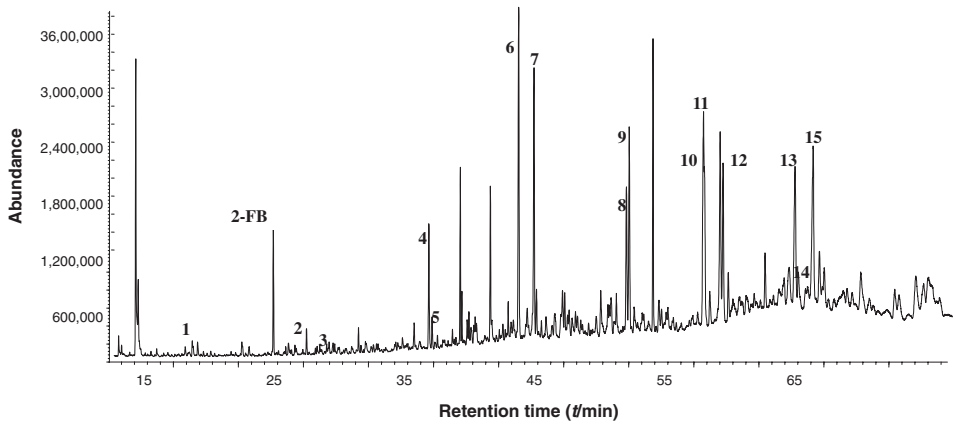

Figure 3. One total-ion chromatogram of PAHs in urban soil. 1. Na, 2. Acy, 3. Ace, 4. Ph, 5. An, 6. Flu, 7. Pyr, 8. BaA, 9. Chy, 10. BbF, 11. BkF, 12. BaP, 13. InP, 14. DBA, 15. BghiP.

4. Conclusions

Generally, the method described in this report provides a convenient alternative for the simultaneous determination of a large range of organic priority pollutants in soils, and would be especially applicable for use in routine monitoring studies. The use of this method may possibly be extended to other matrices, such as sediments.

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