Bull Environ Contam Toxicol (2010) 84:401–405
DOI 10.1007/s00128-010-9958-3

Determination of Endocrine Disrupting Chemicals in Surface Water and Industrial Wastewater from Beijing, China

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Received: 30 July 2009 / Accepted: 5 March 2010 / Published online: 30 March 2010

Abstract An analytical method was developed for determination of some endocrine-disrupting chemicals in water samples from Beijing, China. Fifty two surface water and 50 industrial wastewater samples were analyzed. The residue was detected in 26 industrial wastewater and 19 surface water samples. Atrazine was detected in 8 samples at different levels ranging from 0.12 to 5.16 μg L^{-1}, and phenolic compounds were detected in 19 samples ranging from 0.8 to 26.1 μg L^{-1}. The results show that the main pollutants of surface water samples were atrazine and octylphenol. In industrial wastewater samples, bisphenol A and octylphenol were most commonly found.

Keywords Water · Determination · EDCs · Beijing

Environment hormones namely endocrine-disrupting chemicals (EDCs) released by human use have become a major concern among the scientific field due to their potential threats to the health of human and wildlife in recent years. Since the normal functions of all organ systems are regulated by endocrine factors, small disturbances in endocrine function, especially during early stages of the life cycle such as development, pregnancy, and lactation, can lead to profound and lasting effects (Kavlock et al. 1996). EDCs widely exist in air, water and soil et al. Many pesticides and phenols are considered as the important sources of EDCs. Large-scale use of pesticides in agriculture is one of the major causes of pollutions in surface and ground water (García de Llasera and Bernal-González 2001). Recently phenolic compounds are also grouped as an important source of water pollutions because of their potential toxicity, even at low environmental concentrations (Faraji 2005). Monitoring of these environmental hormones in water will be of great importance for both human and environmental use of water resource. Whereas many newly developed methods have only been laboratory applications. Difficulties relating to the presence of metabolites produced environmentally and great variety of possible matrix effects can only be evaluated correctly by the analysis of considerable number of real samples (Fernandez-Alba et al. 1998). Consequently, there are strict programs to control and monitor the levels of these contaminants in water resources. In China, these programs have not been implemented, and only a few studies have been performed. Several methods for analyzing pesticides and phenols are available in the literature. Because of low concentrations of trace organic pollutants in water samples, pre-concentration steps such as liquid–liquid extraction (LLE) or solid phase extraction (SPE) are commonly applied prior to GLC, and GC–MS analysis (Azevedo et al. 2001; Bielicka-Daszkiewicz et al. 2006; Faraji 2005; García de Llasera and Bernal-González 2001; Vink and van der Poll 1996; Wang et al. 2007; Wissiack et al. 2000; Yokley et al. 2002). So far, analysis of phenols has mainly been accomplished by GC–MS or LC–MS, and LC with various detectors (Chang et al. 2005; Moral et al. 2005; Peng et al. 2006; Stuart et al. 2005).

The purpose of this work was to develop a method for determination of some important endocrine disrupting

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chemicals in environmental water samples utilizing off-line SPE extraction followed by GC/LC analysis.

Materials and Methods

The analytes monitored in this study included 11 pesticides, 4 phenolic compounds, as identified in Table 1. The standards used were 98.5%–100% pure. Fenvalerate, cypermethrin, deltamethrin, bifenthrin, parathion-methyl, malathion, parathion were from ICAMA (Beijing, China), atrazine, acetochlor, alachlor, metribuzin were from Riedel-de Haen (USA), Bisphenol A, octylphenol were from Sigma–Aldrich Company (USA), heptylphenol, nonylphenols were from Lancaster Company (UK). Stock solutions of 1,000 mg L^{-1} were prepared and then stored at −20°C.

Methanol (HPLC grade) was from Fisher Scientific, HPLC grade acetonitrile was from Tedia Company, and analytical reagent *n*-hexane, isopropyl alcohol were purchased from Beijing Chemical Reagents Company. All solutions were prepared on a volume/volume basis. Solid-Phase Extraction Columns, the 500 mg/6 mL capacity ODS C18 Bond II SPE columns were obtained from Agilent Company.

About 50 industrial wastewater samples were collected from 18 sampling sites in Beijing area and 52 surface water samples were collected from 52 sample sites of 5 main surface systems which were mainly used for agricultural irrigation and drinking water in Beijing area. Samples were collected in 1 L precleaned, amber glass bottles, filtered through 1.2 and 0.45 μm glass fiber filters to remove suspended particles and stored at 4°C in dark until analyzed.

The C-18 SPE column was conditioned with 2 × 1 mL acetonitrile and 2 × 1 mL methanol. Twenty gram Sodium chloride (NaCl) was added to a 1,000-mL aliquot portion of water sample (fortification at the appropriate concentration level could be done at this time, if desired, for procedural recovery purposes). The water sample was loaded onto the SPE column under low vacuum with a flow rate of about 3 mL min^{-1}. When all but 1 mL of the sample had entered the SPE column, the glass bottle previously containing the water sample was rinsed with 5 mL of redistilled water and was then added to the SPE column. After the sample had completely entered the sorbent bed of the SPE column, the column was dried under vacuum for a minimum of 10 min. The analytes were eluted with two 2-mL isopropanol and *n*-hexane, respectively and then the elute was subjected to rotary evaporation at 40°C to dryness then reconstituted to 1 mL with *n*-hexane for GC analysis or with acetonitrile for LC analysis.

Samples from different sources were analyzed by Agilent GC 4890 with electron capture detector (ECD) for determination of Pyrethroids, by Agilent GC 4890 with nitrogen phosphorus detector (NPD) for determination of organophosphorus and by HP 1100 LC with ultraviolet (UV) detection for phenols. The instrumental operating

Table 1 Correlation coefficient, recovery, RSD and LOQ of the compounds

Compounds	*tR* (min)	Calibration equation	R^2	Rec (%)	RSD (%)	LOQ (μg/L)	MCL/HAL (μg/L)
GC-NPD							
Atrazine	20.7	$y = 14694x - 3709$	0.994	87	13.3	0.05	3
Alachlor	23.3	$y = 2365.4x - 779$	0.997	82	17.2	0.15	2
Acetochlor	24	$y = 2242.4x - 386$	0.993	85	16.9	0.15	2
Metribuzin	24.9	$y = 5151.6x - 1122$	0.994	27	5.7	0.15	200[a]
Parathion-methyl	25.9	$y = 15044x - 11286$	0.988	84	23.0	0.08	2[a]
Malathion	26.7	$y = 12039x - 7725$	0.994	95	18.0	0.08	100[a]
Parathion	29	$y = 23592x - 12813$	0.991	90	16.4	0.07	2.3[a]
GC-ECD							
Bifenthrin	15.4	$y = 2E{+}06x - 24848$	0.992	96	9.7	0.01	–
Cypermethrin	22.3–23.1	$y = 2E{+}06x - 79221$	0.988	79	8.7	0.01	–
Fenvalerate	26.5, 27.5	$y = 1E{+}06x - 1E{+}06$	0.988	74	15.4	0.01	–
Deltamethrin	29.5, 30.8	$y = 78370x - 76411$	0.984	68	3.7	0.01	–
LC-UVD							
Bisphenol A	6.8	$y = 54.912x - 5.977$	0.998	72	12.9	0.5	5
Heptylphenol	17.4	$y = 41.173x + 7.0211$	0.939	77	10.3	0.8	–
Octylphenol	18.3	$y = 20.461x + 2.4602$	0.998	83	14.9	1	25
Nonylphenols	19.4	$y = 19.756x + 2.9594$	0.997	91	4.5	1	100

–, Not available

[a] HAL data

parameters were as follows: GC-ECD analyses were carried out with the use of a 0.25 mm × 30 m HP-5 capillary column (supplied by Agilent Company). Nitrogen was used as the carrier gas at a flow-rate of 1 mL min^{-1}. The column temperature was held at 120°C for 1 min, then ramped at 20°C min^{-1} to 230°C and held for 2 min, then at 20°C min^{-1} to 270°C held for 22 min. The injector and detector temperature were 280 and 300°C, respectively, the inject volume was 1 µL.

The analysis with GC-NPD was carried out with the use of a 0.25 mm × 30 m HP1701 capillary column (supplied by Agilent Company). Nitrogen was used as the carrier gas at a flow-rate of 1 mL min^{-1}. Hydrogen was at a flow rate of 3.5 mL min^{-1}. The column temperature was held at 80°C for 1 min, ramped at 10°C min^{-1} to 200°C, then at 3°C min^{-1} to 220°C held for 20 min, then at 10°C min^{-1} to 240°C and held 2 min. The injector and detector temperature were 240 and 260°C, respectively. The inject volume was 1 µL.

Phenolic compounds separation was performed on LC-UVD (HP series 1100), the column was Kromasil C_{18} (25 cm × 4.6 mm). Gradient elution was carried out with LC solvent acetonitrile and water according to the following program: 50%–100% acetonitrile in 14 min. After 11 min at 100% acetonitrile, mobile phase returned to initial conditions in 5 min and after more 5 min of stabilization, the next sample was injected. Flow rate was 1 mL min^{-1}; 10 µL was injected each time. The wavelength was 215 nm.

Redistilled water was used. Compounds were spiked in 1,000 mL water to give a final concentration of 1.0 or 5.0 µg L^{-1} for pesticides and 0.5 or 5 µg L^{-1} for phenols. Five replicates were carried out for each spiked level. The water sample was acidified, and then extracted with the C-18 SPE column.

Calibration plots were performed by solvent standard. Calibration equations for the different compounds were constructed and were linear over the range 0.5–5.0 mg L^{-1}. The LOQs were calculated using a signal-to-noise ratio of 10. Average recoveries and LOQs are shown in Table 1.

External standard calibration was used to quantify extracts. Calibration was by plotting peak area versus amount injected. Calibration curves were constructed with the aid of standard solutions. Linearity of the system was measured at 4–5 points for all compounds at concentrations: 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg L^{-1}. Calibration equations and R^2 values are in Table 1.

Results and Discussion

Recoveries of most of the basic/neutral pesticides and acidic/phenolic compounds followed the C-18 cartridge treatment were satisfied. Compounds with a low or high affinity to the C-18 material showed lower recoveries. An improvement may be achieved by using cartridge with more sorbent material or using larger volumes of eluents. Metribuzin shown in our study had very low recovery. Therefore we can use larger volumes of eluents or switch to other eluents with more similar polarity. Calibration curves were linear over the range of interest. Most of the correlation coefficients were >0.99, indicating good performance of the instruments.

Limit of quantitations of the proposed method were calculated using a signal-to-noise ratio of 10. For most of the compounds, the LOQs were well below their maximum contaminant levels (MCLs) or health advisory levels (HALs) as shown in Table 1.

Fifty industrial wastewater and 52 surface water samples collected from Beijing (China) areas were analyzed following the sample preparation procedures described above. The residue was detected in 45 out of 102 samples (44.2% of total samples). The residues were found in 26 industrial wastewater samples and 19 surface water samples. Residue levels in the 102 samples are shown in Tables 2 and 3. Atrazine was detected in a total of 8 samples at different levels ranging from 0.12 to 5.16 µg L^{-1} and 7 of them were from surface water samples. Potential water contamination due to atrazine has accelerated the issue of regulations aimed at restricting or prohibiting its use in agriculture. Pyrethroid (fenvalerate, cypermethrin, deltamethrin, bifenthrin) was detected mainly in industrial wastewater samples. Due to their instability under environmental conditions, only 4 surface water samples were detected to contain fenvalerate or cypermethrin. Deltamethrin and bifenthrin were not detected in surface water samples. Phenolic compounds were detected in 19 samples at different levels ranging from 0.8 to 26.1 µg L^{-1}. The most commonly found phenolic compounds were bisphenol A and octylphenol. Bisphenol A was mainly found in industrial wastewater samples because it is an important raw material for organic chemical manufactures. However, bisphenol A was also detected in some surface water samples, which indicated that surface water had been contaminated in some sites. Bisphenol A and octylphenol accounted for 17.6% (18/102) of analyzed samples. These findings indicate that, triazine herbicides and phenolic compounds have become the major water pollutants in these sites. Actions should be taken to solve the problem.

Residues of diverse classes of pesticide and phenol detected in this study show that the proposed method is rapid, simple, sensitive and more environmental friendly (less organic solvent is used). It properly should be applied for the rapid monitoring of water pollutants in areas with potential pesticide or phenol contaminations.

Table 2 Residues of compounds in wastewater samples and their concentrations

Sample ID	Pesticides found	Concentration (μg/L)	Detector
GD7	Acetochlor	0.96	NPD
GD8	Acetochlor	2.51	NPD
GD9	Acetochlor	4.02	NPD
GD10	Acetochlor	1.47	NPD
GD22	Parathion	1.81	NPD
GD23	Parathion	2.05	NPD
GD44	Malathion	0.11	NPD
GD47	Atrazine	0.34	NPD
GD2	Cypermethrin	0.099	ECD
	Fenvalerate	0.052	ECD
GD5	Cypermethrin	0.101	ECD
	Fenvalerate	0.216	ECD
GD6	Bifenthrin	0.279	ECD
	Cypermethrin	0.92	ECD
	Fenvalerate	0.352	ECD
	Deltamethrin	0.32	ECD
GD7	Bifenthrin	0.014	ECD
	Cypermethrin	0.073	ECD
	Fenvalerate	0.034	ECD
GD10	Bifenthrin	0.013	ECD
	Cypermethrin	0.438	ECD
	Fenvalerate	0.36	ECD
	Deltamethrin	0.632	ECD
GD11	Bifenthrin	0.013	ECD
	Cypermethrin	0.183	ECD
	Fenvalerate	0.349	ECD
	Deltamethrin	0.056	ECD
GD12	Fenvalerate	0.247	ECD
GD13	Fenvalerate	0.051	ECD
GD14	Fenvalerate	0.068	ECD
GD15	Cypermethrin	0.121	ECD
	Fenvalerate	0.28	ECD
GD22	Cypermethrin	0.969	ECD
GD24	Cypermethrin	0.658	ECD
	Fenvalerate	1.246	ECD
	Deltamethrin	0.587	ECD
GD1	Octylphenol	5.8	UVD
GD2	Octylphenol	5.1	UVD
GD3	Bisphenol A	1.9	UVD
	Octylphenol	5.4	UVD
GD4	Bisphenol A	21.3	UVD
	Octylphenol	5.6	UVD
GD5	Octylphenol	1.1	UVD
GD6	Octylphenol	1.4	UVD
GD17	Bisphenol A	1.1	UVD
GD18	Bisphenol A	1	UVD
GD20	Bisphenol A	15.2	UVD
	Octylphenol	6	UVD
GD21	Bisphenol A	26.1	UVD
	Octylphenol	11.4	UVD
GD22	Heptylphenol	5.5	UVD
GD35	Bisphenol A	18.2	UVD
	Heptylphenol	1.3	UVD
GD36	Bisphenol A	3.1	UVD

Table 3 Residues of compounds in surfacewater samples and their concentrations

Sample ID	Pesticides found	Concentration (μg/L)	Detector
ZH20	Atrazine	0.41	NPD
ZH23	Atrazine	0.21	NPD
ZH39	Parathion-methyl	0.54	NPD
ZH45	Atrazine	0.2	NPD
ZH47	Atrazine	0.16	NPD
ZH57	Metribuzin	35.09	NPD
ZH60	Atrazine	5.16	NPD
ZH62	Atrazine	0.12	NPD
ZH116	Atrazine	0.25	NPD
ZH5	Cypermethrin	0.325	ECD
ZH123	Fenvalerate	0.017	ECD
ZH126	Fenvalerate	0.021	ECD
ZH152	Cypermethrin	0.012	ECD
ZH52	Octylphenol	1.2	UVD
ZH53	Octylphenol	1.6	UVD
ZH55	Octylphenol	1.1	UVD
ZH131	Octylphenol	1	UVD
ZH149	Bisphenol A	0.8	UVD
ZH162	Octylphenol	1	UVD

A rapid, simple and sensitive method was developed for determination of some endocrine disrupting chemicals in aquatic environment using GC/LC. The target compounds were extracted simultaneously using solid phase extraction, and the method gave good recoveries for most target compounds. The analytical method was successfully applied to determination of these compounds in industrial wastewater samples and river water samples in Beijing, China. This paper shows that SPE treatment followed by GC/LC can be used in routine monitoring programs. The herbicides atrazine and phenolic compounds Bisphenol A and octylphenol were most commonly found pollutants in the water samples. Other pesticides such as parathion-methyl, fenvalerate and nonylphenols also appeared in some samples. This study will lay a foundation for establishing a monitoring program for some common pesticides and phenolic compounds in the region and its surroundings. The results will be helpful to the government in setting up relevant management policies. Further study on the distribution of compounds that are harmful to the environment and on the estimate of magnitude to which human is exposed is urgent.

Acknowledgments The authors appreciate Beijing Natural Science Foundation of China for the financial support of this study (No. 8000001).

References

Azevedo DA, Lacorte S, Viana P, Barceló D (2001) Analysis of priority pesticides and phenols in Portuguese river water by liquid chromatography–mass spectrometry. Chromatographia 53:113–118

Bielicka-Daszkiewicz K, Voelkel A, Szejner M, Osypiuk J (2006) Extraction properties of new polymeric sorbents in SPE/GC analysis of phenol and hydroquinone from water samples. Chemosphere 62:890–898

Chang CM, Chou CC, Lee MR (2005) Determining leaching of bisphenol A from plastic containers by solid-phase microextraction and gas chromatography–mass spectrometry. Anal Chim Acta 539:41–47

Faraji H (2005) β-Cyclodextrin-bonded silica particles as the solid-phase extraction medium for the determination of phenol compounds in water samples followed by gas chromatography with flame ionization and mass spectrometry detection. J Chromatogr A 1087:283–288

Fernandez-Alba AR, Agüera A, Contreras M, Peñuela G, Ferret I, Barceló D (1998) Comparison of various sample handling and analytical procedures for the monitoring of pesticides and metabolites in ground waters. J Chromatogr A 823:35–47

García de Llasera MP, Bernal-González M (2001) Presence of carbamate pesticides in environmental waters from the northwest of Mexico: determination by liquid chromatography. Water Res 35:1933–1940

Kavlock RJ, Daston GP, Creteal DeRosa (1996) Research needs for risk assessment of the USEPA-sponsored workshop. Environ Health Perspect 104:715–740

Moral A, Sicilia MD, Rubio S, Pérez-Bendito D (2005) Determination of bisphenols in sewage based on supramolecular solid-phase extraction/liquid chromatography/fluorimetry. J Chromatogr A 1100:8–14

Peng X, Wang Z, Yang C, Chen F, Mai B (2006) Simultaneous determination of endocrine-disrupting phenols and steroid estrogens in sediment by gas chromatography–mass spectrometry. J Chromatogr A 1116:51–56

Stuart JD, Capulong CP, Launer KD, Pan X (2005) Analyses of phenolic endocrine disrupting chemicals in marine samples by both gas and liquid chromatography–mass spectrometry. J Chromatogr A 1079:136–145

Vink M, van der Poll JM (1996) Gas chromatographic determination of acid herbicides in surface water samples with electron-capture detection and mass spectrometric confirmation. J Chromatogr A 733:361–366

Wang S, Zhao P, Min G, Fang GZ (2007) Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid-phase extraction and gas chromatography–mass spectrometry. J Chromatogr A 1165:166–171

Wissiack R, Rosenberg E, Grasserbauer M (2000) Comparison of different sorbent materials for on-line solid-phase extraction with liquid chromatography–atmospheric pressure chemical ionization mass spectrometry of phenols. J Chromatogr A 896:159–170

Yokley RA, Mayer LC, Huang SB, Vargo JD (2002) Analytical method for the determination of metolachlor, acetochlor, alachlor, dimethenamid, and their corresponding ethanesulfonic and oxanillic acid degradates in water using SPE and LC/ESI-MS/MS. Anal Chem 74:3754–3759