Comparison of Different Extraction Methods for Analysis of 10 Organochlorine Pesticides: Application of MAE–SPE Method in Soil from Beijing

Shanshan Di¹ · Shengchao Shi¹ · Peng Xu² · Jinling Diao¹ · Zhiqiang Zhou¹

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Abstract Four commonly applied extraction techniques for organochlorine pesticides, microwave-assisted extraction (MAE), accelerated solvent extraction (ASE), quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction and ultrasonic solvent extraction, were applied on soil samples in order to evaluate their performances. The extracts were analyzed by GC–ECD and confirmed by GC–MS/MS. The MAE and QuEChERS extraction methods generally yielded higher results compared to the ultrasonication and ASE methods, while the lowest recovery (56.8 %) for *o,p'*-DDD was obtained using the QuEChERS method. The MAE method was further applied to six different soils from Beijing. In the soil samples only α -endosulfan and β -endosulfan were not detected. The ratios of α -HCH/ γ -HCH and α -HCH/ β -HCH indicated HCH residues likely originated from historical use of HCHs, and that technical HCHs were not likely being currently applied in Beijing.

Keywords Organochlorine pesticides · Extraction methods · Purification methods · Methods comparison · Soils

Organochlorine pesticides (OCPs) are effective pest control chemicals that were used globally in agriculture from the 1950s to the mid-1980s (Chikuni et al. 1997). These

compounds are now avoided due to their high bioaccumulation potential, persistence in the environment, and high toxicity to non-target organisms (Jia et al. 2007; Loganathan and Kannan 1994). They are classified as typical persistent organic pollutants (POPs) (Zhao et al. 2012).

Although many OCPs have been banned in most countries for almost 40 years, high residue concentrations are still detected in almost all environmental media, including air (Pozo et al. 2008), soil (Tao et al. 2008), plant (Srivastava et al. 2006), animal (Gebbink et al. 2007), and even human tissues (Zietz et al. 2008). Soil is the principal reservoir of environmental pesticides and plays an important role in the global distribution and fate of OCPs. The OCPs retained in soils are bound to soil organic matter (OM) through covalent bonds, hydrophobic interactions and diffusion-controlled partitioning (Zhang et al. 2011b). The OCPs not only have a large retention capacity but also re-emit these old organic pollutants into the atmosphere, ground water and living organisms as a secondary source (Zhang et al. 2013).

The extraction of OCPs from soils is a critical sample preparation step. Microwave-assisted extraction (MAE) has been considered as a realistic and effective alternative to conventional solvent extraction methods. In recent years, the extraction of organic compounds by microwave irradiation, as originally proposed by Ganzler et al. (1986), has been used to analyze environmental contaminants, such as polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), and phenols, from various solid and liquid matrices (Pino et al. 2000; Parera et al. 2004; Zhang et al. 2012b). In general, all of these methods are effective, but they vary in their requirements for time and solvent volume.

In this study, the performance characteristics of different extraction techniques, including MAE, ASE, ultrasonic

✉ Zhiqiang Zhou
zqzhou@cau.edu.cn

¹ Department of Applied Chemistry, China Agricultural University, Yuanmingyuan West Road 2, Beijing 100193, People's Republic of China

² Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Shuangqing RD 18, Beijing 100085, People's Republic of China

solvent extraction and quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction were compared for determination of 10 OCPs in soil. Then, the MAE method was applied to real samples from Beijing, and the extracts were analyzed by GC–ECD and confirmed by GC–MS/MS.

Materials and Methods

For this study, 10 OCPs were analyzed: α -, β - and γ -HCH, *o,p'*-DDT, *o,p'*-DDD, *o,p'*-DDE, *cis*-chlordane, *trans*-chlordane, α -endosulfan, and β -endosulfan. Pesticide standards (purity > 99.0 %) were obtained from J&K Scientific Ltd (Beijing, CN). The recovery surrogate 2,4,5,6-tetrachloro-*m*-xylene (TCMX) and internal standard (IS) pentachloronitrobenzene were also purchased from J&K Scientific Ltd. Acetone, *n*-hexane, acetonitrile, and petroleum ether (60–90°C) were pesticide grade and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, CN).

The study area for this investigation was Beijing, located in the northern China. Soil was collected from 6 sampling sites, and the physicochemical properties of the soils are listed in Table 1. After the superficial layer of 1–2 cm was removed, the soil was collected to a depth of 10 cm and put into a plastic bag with a zip lock, then transported to the laboratory. After removing stones and residual roots, the samples were freeze-dried, thoroughly mixed, sieved through a 2 mm mesh sieve, and then stored at –20°C until analysis.

OCP analyses were carried out on an Agilent GC–ECD HP-7890A series system with a HP-5 column (30 m, 0.32 mm i.d., 0.25 μ m film; Agilent Technologies Inc. Palo Alto, CA, USA). High-purity N₂ (99.999 %) was used as the carrier gas, and the flow rate was 1.0 mL/min. The injector and detector temperatures were 270 and 290°C, respectively. The oven temperature program was as follows: initial temperature began at 90°C for 1 min, increased to 180°C at 15°C/min (5 min hold time), to 185°C at 5°C/min (11.5 min hold time), to 225°C at 35°C/min

(1 min hold time), and finally increased to 270°C at 20°C/min (3 min hold time). One μ L of sample was injected in splitless mode.

The identities of OCPs in the samples were confirmed using a Thermo Trace-Ultra gas chromatograph coupled to a triple quadrupole mass detector Thermo TSQ Quantum (Waltham, MA, USA). The separation was performed on a Thermo Scientific TRACE TR-35MS column (30 m, 0.25 mm i.d., 0.25 μ m film thickness). Helium was used as carrier gas at a constant flow rate of 1.0 mL/min. The ion source and MS transfer temperature was 250 and 280°C, respectively. GC conditions were as follows: initial column temperature 90°C (1 min), increased at 25°C/min to 210°C, held for 15 min, then 20°C/min to 218°C, and held for 5 min, then 20°C/min to 270°C, and held for 5 min.

Microwave-assisted extraction (MAE) was carried out with a Mars 6 Xpress laboratory microwave extraction system (CEM, Matthews, NC, USA). The instrument is able to concurrently extract 40 solid samples in PTFE extraction vessels in a single step. Soil samples (5 g) were accurately weighed out and transferred into the microwave extraction vessels. The solvent selected for the extraction was petroleum ether–acetone (1:1, v/v). This mixture is one of the most adequate solvents for the extraction of OCPs, because good recoveries are obtained when the mixture is used and the time consumed in the evaporation step is small. Thirty mL aliquots of petroleum ether–acetone were added to the vessels, and then the sample was manually shaken for 2 min for homogenization. The extraction conditions were as follows: the temperature was ramped to 100°C over 5 min and held for 10 min, then cooled down for 15 min. The microwave power was 800 W. After extraction, the extracts were filtered through 5 g of anhydrous sodium sulfate for dehydration, transferred to a pear-shaped flask, and concentrated to dryness using a RE-52A rotary vacuum evaporator in a water bath at 35°C.

Accelerated solvent extraction (ASE) was carried out with an ASE 350 extractor (Dionex, Sunnyvale, CA, USA). The extraction program for solid samples was as follows: 5 g soil was mixed with 2.5 g bergmeal in a 34 mL

Table 1 Physicochemical properties of the soil samples

Soil type	Xiaotangshan Sandy loam	Liulin Silt loam	Xixiaoying Loam	Shangzhuang reservoir Sandy loam	CAU Loam	Tiangongyuan Loam
Organic matter, g/100 g _{dwt}	42.0 $\pm$ 0.5	14.2 $\pm$ 0.4	14.5 $\pm$ 0.2	5.4 $\pm$ 0.1	8.6 $\pm$ 0.1	3.8 $\pm$ 0.1
Clay (<2 μ m), %	10.8 $\pm$ 0.1	26.8 $\pm$ 0.1	24.8 $\pm$ 2.8	16.8 $\pm$ 2.8	16.8 $\pm$ 2.8	16.8 $\pm$ 2.8
Silt (<20–2 μ m), %	20.0 $\pm$ 5.7	52.0 $\pm$ 0.1	44.0 $\pm$ 0.1	18.0 $\pm$ 8.5	40.0 $\pm$ 0.1	36.0 $\pm$ 5.7
Sand (2000–20 μ m), %	69.2 $\pm$ 5.7	21.2 $\pm$ 0.1	31.2 $\pm$ 2.8	65.2 $\pm$ 5.7	43.2 $\pm$ 2.8	47.2 $\pm$ 2.8
pH	8.34 $\pm$ 0.02	8.32 $\pm$ 0.01	8.21 $\pm$ 0.06	7.88 $\pm$ 0.03	8.35 $\pm$ 0.01	8.61 $\pm$ 0.03

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stainless steel vessel, then 10 g quartz sand was placed in the vessel. Acetone: petroleum ether (1:1, v/v) was used as the extraction solvent at 110°C under a pressure of 1500 psi with 6 min for heating. The extraction was carried out in two cycles with 5 min static extraction. In the end, the extraction cell was flushed with solvent (60 % of the cell volume) and purged with nitrogen (60 s). The extracts were concentrated to dryness by rotary evaporation.

Ultrasonication extraction was performed with a KQ 5200DB extractor (Kunshan, CN) over a period of 30 min using 20 mL of acetone: petroleum ether (1:1, v/v) as the solvent. Then the polypropylene centrifuge tubes were centrifuged at 3500 rpm for 3 min. The extraction was repeated twice using fresh solvent. The combined solvent phase was filtered through 5 g of anhydrous sodium sulfate and evaporated to dryness on a vacuumed rotary evaporator at 35°C.

A QuEChERS extraction procedure was also used to compare the extraction efficiency with the above-mentioned methods. The spiked soil (5 g) was accurately weighed and put into a 50 mL polypropylene centrifuge tube. Three mL of water and 7 mL of acetonitrile were added, and the mixture was vortex-mixed for 1 min. Afterwards, 6 g magnesium sulphate (MgSO_4), 1.5 g sodium chloride (NaCl), 0.75 g disodium citrate sesquihydrate ($\text{Na}_2\text{HCit}\cdot 1.5\text{H}_2\text{O}$) and 1.5 g sodium citrate dihydrate ($\text{Na}_3\text{Cit}\cdot 2\text{H}_2\text{O}$) were added and vortex-mixed to prevent salt agglomeration. Then the mixture was sonicated in an ultrasonic bath for 1 min and centrifuged at 4000 rpm for 10 min. The supernatant was transferred to a glass pear-shaped bottle and concentrated to dryness with a rotary vacuum evaporator (35°C).

After extraction, three purification methods were used to compare the purification capacity. The first method was solid phase extraction. A Florisil-SPE cartridge (1000 mg, 6 mL, Agilent SampliQ Products) was used to clean up interfering substances. The cartridge was preconditioned by rinsing with 10 mL of acetone followed by 5 mL of *n*-hexane and equilibrated with 5 mL leachate (acetone: *n*-hexane = 1:15, v/v). The elution was performed with 6 mL leachate. The eluate was concentrated to dryness under a gentle nitrogen flow, and diluted to 1.5 mL with *n*-hexane, and 100 μL internal standard was added.

The second method was as follows: after the extracts were concentrated to dryness, 10 mL *n*-hexane and 5 mL 98 % H_2SO_4 were added to the glass pear-shaped bottle. The same purification step was repeated twice, and then 2×10 mL of 2 % Na_2SO_4 aqueous solution was added for washing. The supernatant was filtered through 5 g of anhydrous sodium sulfate for dehydration and evaporated to near dryness on a vacuumed rotary apparatus. The residue was reconstituted in 1.5 mL of *n*-hexane, and 100 μL

internal standard was added prior to analysis by gas chromatography.

The third method was as follows: after the extracts were concentrated to dryness, 1.5 mL *n*-hexane and 100 μL internal standard were added to the glass pear-shaped bottle. One mL supernatant was removed and transferred to the clean-up tube containing 50 mg of PSA (primary secondary amine), 150 mg of MgSO_4 and 50 mg of C18. The tubes were capped tightly and shaken by the vortex for 1 min, followed by centrifugation. Prior to instrument analysis, the supernatant was filtered through a 0.45 μm filter.

Results and Discussion

Recovery efficiency is an important factor when the analytical method is evaluated. Table 2 shows the recoveries and RSD of 10 OCPs extracted from the spiked soil sample using different extraction methods. Ultrasonication and ASE extraction were found to yield lower recoveries. In most cases, the recoveries for these two methods were below 70 %, especially for β -endosulfan. The high volatility of β -endosulfan resulted in a greater loss for ASE when the sample was purged with nitrogen. For ultrasonication, the increased movement of the molecules of compound and the high volatility of β -endosulfan led to the very low result. These results indicated that ultrasonication and ASE were unsuitable methods to effectively extract the 10 OCPs under these experimental conditions. Several studies also reported that ASE had a lower extraction recovery than MAE when the OCPs were determined in vegetable samples (Barriada-Pereira et al. 2007). The MAE and QuEChERS extractions generally yielded higher results compared to the ultrasonication and ASE extractions. In most cases, the recoveries for MAE and QuEChERS were between 80 % and 120 %. However, the lowest recovery (56.8 %) for *o,p'*-DDD was obtained using QuEChERS method. Moreover, the recoveries of α -HCH and β -HCH with QuEChERS extraction were over 120 %. It may be attributed to several causes. The first might be the interferences of the matrix also known as “matrix induced chromatographic response enhancement” effect. Another reason could be the matrix effect on transfer of compounds from the injection port, because major components may compete for the active sites of the liner, enabling transfer of larger amounts of analytes into the column (Zhang et al. 2011c). In addition, QuEChERS yielded relatively higher RSD values compared to MAE, which indicated that MAE could provide more robust and repeatable results under the specified extraction conditions in this study. Thus, MAE was selected for further work based on a combination of

Table 2 Extraction efficiencies for MAE, QuEChERS, ultrasonification and ASE

	MAE		QuEChERS		Ultrasonification		ASE	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
α -HCH	102.8	1.9	123.4	6.0	91.4	4.3	89.8	4.1
β -HCH	100.3	4.1	124.1	8.5	88.9	6.3	76.4	4.0
γ -HCH	95.5	1.8	102.2	6.8	67.6	3.5	65.8	2.3
<i>trans</i> -Chlordane	96.4	3.7	98.8	6.9	58.9	3.2	52.9	2.2
<i>o,p'</i> -DDE	101.5	4.7	107.3	9.0	63.9	3.3	59.4	3.0
α -Endosulfan	100.6	4.1	107.1	9.5	63.7	3.4	57.3	2.5
<i>cis</i> -Chlordane	114.9	4.2	113.9	9.8	70.0	4.0	64.2	2.8
<i>o,p'</i> -DDD	104.1	4.9	56.8	11.2	127.9	7.4	117.9	6.0
β -Endosulfan	102.1	2.7	77.9	1.7	44.5	3.0	47.5	5.0
<i>o,p'</i> -DDT	108.8	2.4	86.9	12.1	63.7	4.2	53.0	1.4

factors, including relatively ideal recoveries, low organic solvent volumes and short time.

Owing to the complex soil matrix and high extraction efficiency of MAE, it was important to reduce the number of interferences before chromatographic analysis, which could damage the chromatographic column and result in matrix effects (Zhang et al. 2011c). Recoveries of all 10 OCPs for the Florisil SPE cartridge, sulfonation and sorbent methods were in the ranges of 95.5 %–114.9 %, 12.6 %–76.1 % and 31.5 %–87.3 %, respectively, and the RSD ranged from 1.8 % to 4.9 % for SPE, 0.9 %–3.7 % for sulfonation and 3.0 %–9.3 % for sorbent (Fig. 1). Very low purification recoveries of α -endosulfan (40.2 %) and β -endosulfan (12.6 %) were found when the sulfonation method was used. These low values could be attributed to the instability of endosulfan in sulfuric acid. We also found poor recoveries of β -HCH (31.5 %), β -endosulfan (45.1 %), and *o,p'*-DDT (37.0 %) for sorbent purification, which could be due to the higher adsorption of these pesticides to the sorbent. Therefore, the SPE purification method was selected to analyze the real soil samples.

To evaluate the MAE–SPE method, recoveries from soil samples spiked at low and high concentrations were 60.6 %–119.0 % and 55.3 %–109.0 %, respectively (Table 3). The overall reproducibility was evaluated and the relative standard derivation (RSD) values of OCPs were

Table 3 Recoveries of pesticides spiked into soil at two concentrations

	0.01 mg/kg		0.1 mg/kg	
	R (%)	RSD (%)	R (%)	RSD (%)
α -HCH	109.6	2.7	95.1	3.6
β -HCH	109.9	3.3	92.3	4.6
γ -HCH	92.3	8.7	70.2	2.0
<i>trans</i> -Chlordane	119.0	4.2	56.7	3.0
<i>o,p'</i> -DDE	93.0	12.0	64.8	3.5
α -Endosulfan	60.6	7.9	62.4	2.3
<i>cis</i> -Chlordane	90.7	5.9	66.7	3.3
<i>o,p'</i> -DDD	99.6	5.9	109.0	4.6
β -Endosulfan	89.5	7.8	55.3	2.7
<i>o,p'</i> -DDT	98.1	6.2	63.2	4.5

≤ 12.0 %. Therefore, the reproducibility of the measurements was satisfactory, and the MAE–SPE method was considered to be both accurate and precise.

Linear calibration curves for all pesticides over five calibration levels, from 0.005 to 0.5 mg/L were constructed using TCMX as an internal standard. The calibration curves were linear over the whole concentration range tested for all the OCPs with coefficients of determination (R^2) over 0.9905 (Table 4). Limits of detection (LOD) and limits of quantitation (LOQ) were defined to be the pesticide concentrations at which the signal-to-noise ratios (S/N) were equal to three and ten, respectively. The LOD and LOQ of the pesticides ranged from 0.33–1.08 to 1.09–3.61 $\mu\text{g/kg}$, respectively (Table 4).

The MAE–SPE method was applied to measure trace levels of the 10 OCPs in 6 soil samples from Beijing. The results are shown in Table 5. Only α -endosulfan and β -endosulfan (confirmed by GC–MS/MS) were not found in the 6 soil samples. *Trans*-chlordane was found in three

Fig. 1 Pesticide recoveries by three purification methods

Table 4 Matrix-matched calibration regression equations, coefficients of determination (R^2) and LOD and LOQ concentrations for 10 pesticides

Pesticides	Regression equation	R^2	LOD ($\mu\text{g/kg}$)	LOQ ($\mu\text{g/kg}$)
α -HCH	$y = 12.021x + 0.4464$	0.9956	0.35	1.17
β -HCH	$y = 8.171x + 1.133$	0.9905	0.82	2.73
γ -HCH	$y = 15.91x + 0.5256$	0.9960	0.46	1.53
<i>trans</i> -Chlordane	$y = 36.428x + 0.0416$	0.9999	0.33	1.09
<i>o,p'</i> -DDE	$y = 13.744x + 0.2954$	0.9972	0.71	2.36
α -Endosulfan	$y = 31.501x + 0.0702$	0.9998	0.38	1.28
<i>cis</i> -Chlordane	$y = 21.58x - 0.2574$	0.9983	0.43	1.42
<i>o,p'</i> -DDD	$y = 17.772x - 0.1389$	0.9990	0.53	1.78
β -Endosulfan	$y = 13.244x + 0.5134$	0.9911	1.08	3.61
<i>o,p'</i> -DDT	$y = 31.335x + 0.6502$	0.9964	1.03	3.43

Table 5 Trace levels of 10 OCPs in six soil samples from Beijing analyzed using the MAE–SPE procedure

Pesticides ($\mu\text{g/kg}$)	Xiaotangshan 1	Liulin 2	Xixiaoying 3	Shangzhuang reservoir 4	CAU 5	Tiangongyuan 6
α -HCH	0.019	0.031	0.046	0.648	0.083	0.067
β -HCH	0.015	0.041	0.01	0.181	0.053	0.061
γ -HCH	0.035	0.056	0.033	1.093	0.257	0.046
<i>trans</i> -Chlordane	–	–	–	0.014	0.007	0.003
<i>o,p'</i> -DDE	0.042	0.086	0.043	1.268	0.085	0.068
<i>cis</i> -Chlordane	–	–	–	–	0.005	0.006
α -Endosulfan	–	–	–	–	–	–
<i>o,p'</i> -DDD	–	0.059	–	2.54	0.206	0.084
<i>o,p'</i> -DDT	0.467	0.551	0.569	17.616	2.983	0.518
β -Endosulfan	–	–	–	–	–	–
HCHs	0.07	0.128	0.089	1.923	0.393	0.174
DDTs	0.508	0.695	0.613	21.424	3.274	0.67
α -HCH/ γ -HCH	0.554	0.553	1.377	0.592	0.323	1.455
α -HCH/ β -HCH	1.275	0.769	4.794	3.574	1.558	1.109

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samples and *cis*-chlordane was found in two samples, while α -HCH, β -HCH, γ -HCH, *o,p'*-DDT and *o,p'*-DDE were found in all six soil samples. The concentrations of total HCHs for all the sampling sites ranged from 0.07 to 1.92 $\mu\text{g/kg}$. The concentrations of HCHs in all soils were comparatively lower than DDTs. There were two possible reasons. The first possibility may be that HCHs have lower lipophilicity and higher volatility and water solubility than DDTs (Zhang et al. 2013), and thus could be more easily transferred from surrounding soils into rivers, atmosphere and other environmental media. On the other hand, it may be due to their different amounts of application and production over the past decades (Zhu et al. 2005). The residue levels of DDTs in soils in Beijing were lower than those reported in Tianjin (average of 80 $\mu\text{g/kg}$) (Tao et al. 2005), and Zhejiang (average of 86 $\mu\text{g/kg}$) in China (Zhang et al. 2012a). The concentration levels of HCHs in Beijing were

also much lower than those reported in other areas in China, such as Guangzhou (average of α -, β - and γ -HCH were 0.88, 2.31, and 0.76 $\mu\text{g/kg}$ respectively) (Zhang et al. 2002). Strong correlations among α -, γ -, and β -HCH ($R \geq 0.959$) suggested similar sources likely originated from historic use of technical HCHs.

The ratio of α -HCH/ γ -HCH was between 5 and 7 in the technical HCHs and nearly zero for α -HCH/lindane. The ratio of α -HCH/ γ -HCH could be used to evaluate whether the source was from technical HCHs or lindane (Zhang et al. 2011a). HCH isomer ratios in each soil sample were shown in Table 5. The ratios of α -HCH/ γ -HCH were all below 5.0 in this work, which indicated that HCH residues at these sites were most likely from historic use of technical HCHs. The ratio of α -HCH/ β -HCH was another useful indicator to assess if technical HCHs were recently applied in the region (Zhang et al. 2011a), as the ratio is

approximately 11.8 for technical HCHs. From Table 5, the ratios of α -HCH/ β -HCH in all samples were below that of technical HCHs. The results suggested that fresh application of technical HCHs in large quantities are not likely occurring in Beijing.

A procedure based on MAE–SPE had been developed for analysis of OCPs in soils. The high extraction efficiency of MAE combined with purification on Florisil–SPE column resulted in satisfactory recovery, clean chromatograms, and good selectivity and accuracy. Moreover, compared with other extraction methods, this method had advantages of shorter analysis time, lower solvent consumption, and greater automation. Therefore, it can be concluded that this is a promising method for the analysis of organochlorine pesticides as an alternative to traditional extraction techniques.

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