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Ultra trace analysis of 17 organochlorine pesticides in water samples from the Arctic based on the combination of solid-phase extraction and headspace solid-phase microextraction–gas chromatography-electron-capture detector

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ABSTRACT

Solid-phase extraction (SPE) was combined with headspace solid-phase microextraction (HS-SPME) for the highly effective enrichment of 17 ultra trace organochlorine pesticides in water samples. The target compounds were successfully transferred from water samples to a gas chromatography capillary column by means of four consecutive steps, namely SPE, solvent conversion, HS-SPME, and thermal desorption of the SPME fiber. Parameters, including elution volume and breakthrough volume in the SPE step, temperature in the solvent conversion step, and fiber type, ionic strength, extraction temperature, extraction time, and pH in the SPME step were optimized to improve the performance of the method through either single factor comparative experiment or the orthogonal experimental design approach. After optimization, the method gave high sensitivity with a method detection limit ranging from 0.0018 to 0.027 ng L^{-1}, good repeatability with a relative standard deviation less than 20% ($n = 4$) and acceptable recovery with a value mostly exceeding 60%. External standard calibration was employed for the quantification, and a wide linear range (from 0.0010 to 60 ng mL^{-1}) with R^2 values ranging from 0.9988 to 0.9999 were observed. In the end, the method was successfully applied to the Arctic samples, and the results showed that, among all the organochlorine pesticides, hexachlorocyclohexanes (HCHs) were the most predominant in the Arctic surface water body with sum of their concentrations ranging from 0.262 to 3.156 ng L^{-1}.

1. Introduction

Organochlorine pesticides (OCPs) were once used in great amount worldwide as an agricultural insecticide, and some of them, such as linden, DDT and endosulfan, were also used with great effort to control mosquitoes spreading malaria, acarus infesting animals and lice transmitting typhus. They were gradually banned (linden and endosulfan were banned only recently) in the agricultural use by increasing countries around the world after they were found to be persistent, estrogenic, carcinogenic [1,2], and able to bioaccumulate and biomagnify in higher trophic level animals through the food chain [3,4], however their use in vector control has not been banned in both developed and developing countries. In 2001, the UNEP published the initial list of 12 persistent organic pollutants (POPs), 9 of which were OCPs. Although most OCPs have been banned for decades, the residual problem is still serious due to their persistence and their huge historical usage. OCPs are regarded as semi-volatile organic pollutants with a normal boiling point usually less than 300 °C, so that they can be transferred not only through common ways such as groundwater and river, but also through long distance atmospheric transport [5], and thus distribute globally. OCPs can vaporize in tropical or subtropical areas and be transferred to polar areas, which have been demonstrated to be sinks for volatile and semi-volatile organic compounds due to the extremely low temperatures prevailing there [6,7]. The process is known as global distillation, and has become a hot spot in environmental science [8–12], especially, as the threat of global warming becomes more and more inevitable.

As mentioned before, OCPs are now distributed extensively in global environment. Once OCPs enter the aquatic environment, due to their lipophilicity, they tend to partition in either the suspended phase or the sediment phase, both of which are regarded to be richer in organic substances than the water phase. Therefore, most of the associated literature focuses on the matrices with a comparatively high concentration of the target compounds, such as sediment [13–15], the animal tissue [16–18], foodstuff [19], lake water [20,21], river water [22,23], and costal water [24,25], but only a limited number of papers can be found dealing with water

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samples featuring extremely low concentration, such as the Arctic water sample [26]. One possible reason lies in the difficulty involved in using modern enrichment techniques to enrich enough target compounds for the instrument analysis which follows.

So far, the most important techniques for the analysis of OCPs are liquid–liquid extraction (LLE), SPE and SPME. LLE, though classical and once widely used, is now seldom used because a large volume of hazardous organic solvent has to be used during the process. SPE is a more attractive technique in that only a small amount of organic solvent is needed and thus it is more environmentally friendly. Although many other striking advantages can be found in SPE, one inherent disadvantage is the low percentage of injection, because it often has to be coupled with the traditional liquid injection mode, in which only a fraction of the final extract is used (generally no more than 1% depending on the volume of the final extract and injection). SPME is such a novel technique that it has been widely used in environmental science [27–36] ever since its introduction. However, it is not easily applied to analyze water samples with extremely low concentration of target compounds due to its property of non-exhaustive extraction.

In the present paper, we have developed the concept of combining SPE and SPME to overcome the inherent shortcomings of both methods for the enrichment of ultra trace OCPs in seawater samples. The concept was first successfully applied in the determination of phenylurea herbicides in natural waters at concentrations below 1 ng L^{-1} [37]. Later, another successful case was reported, in which the combination of SPE and SPME was employed for the analysis of chlorobenzenes in air [38], but to our knowledge few papers were published dealing with the application of such combination to the enrichment of OCPs in the water sample. To achieve the combination of SPE and SPME, a method based on initial evaporation using a gentle nitrogen stream as well as stirring for a considerable time (60 h) was adopted in the former paper, while simply transferring the SPE sorbent into a headspace vial for the following HS-SPME was employed in the latter paper. The former method is time-consuming, while the latter one cannot be applied extensively due to the immobility of the commercial SPE sorbent, which is usually packed in a cartridge or a disk and supposed to be processed inside and hence cannot easily be removed to a SPME vial as was done in the latter paper mentioned above. In the present study, an alternative solvent conversion technique, based on a manual solvent conversion device assisted by low vacuum, heating and stirring, was developed to achieve the combination of SPE and SPME. To obtain high performance results each step of the method was carefully optimized before its *in situ* application in the Arctic.

2. Materials and methods

2.1. Chemical reagents and standards

Ultra pure water was prepared using a Milli-Q water purification system from Millipore (Bedford, MA, USA). The organic solvents were of pesticide residual grade, and purchased from Tedia (USA). Merchandized pH buffer solutions with four pH levels (4, 7, 9, and 10) were obtained from Riedel-de Haën (Germany). An analytical mixture standard solution of OCPs, containing α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide, α-endosulfan, dieldrin, endrin, β-endosulfan, p,p′-DDD, p,p′-DDE, endrin aldehyde, p,p′-DDT, methoxychlor and endosulfan sulfate, was purchased from the Doctor Ehrensdosfer Laboratory (Augsburg, Germany). The stock solution was prepared by diluting 1 mL original mixture standard solution (20 mg L^{-1}) to a 2 mg L^{-1} with methanol in a 10 mL volumetric flask and stored at −5 °C. Fresh working solutions were prepared by proper dilution of the stock solution with methanol every other day and stored at 5 °C.

2.2. Sample preparation

Standard water samples were prepared by spiking a certain amount of working solution into different volumes of Milli-Q water according to requirement in the QA/QC experiments and the optimization experiments for SPE step, while standard water samples in the optimization experiment for SPME step were prepared by spiking 30 μL working solution of 80 μg L^{-1} into 200 μL water matrix, of which both the ionic strength and pH were modified according to the orthogonal experimental design table, discussed in detail later. The *in situ* raw water samples were first filtered with a glass fiber filter (47 mm in diameter, 0.7 μm pore size, Millipore, USA; burned under 450 °C for 5 h before use) assisted by a vacuum pump before the experiments. All samples were contained in dark glass bottles, which had been carefully washed with surfactant, and rinsed in turn with tap water and Milli-Q water.

2.3. Sample enrichment

Both the standard water samples for QA/QC experiment and *in situ* filtered water samples were first drawn through conditioned SPE cartridges (ENVI-18, 500 mg, 3 mL, SUPELCO, USA) at about 15 mL/min. After sample loading, the SPE cartridge was air dried for 30 min under vacuum to remove as much residual water as possible. Further elution of the loaded and dried SPE cartridge was then done using 10 mL n-hexane.

Thereafter, the eluent from SPE was first concentrated through a manual solvent conversion device assisted by conditions of low vacuum, cold water circulation (5 °C), stirring and heating. This set of device (Fig. 1) was modified from a rotating vaporizer, of which the water bath was substituted by a magnetic stirring/heating machine. Through this device, the eluent was first concentrated to about 200 μL, and then the concentrated solution was transferred to a smaller headspace vial (1.5 mL), to which 200 μL pH buffer solution (pH 10) and a magnetic stirrer had been previously added. Then the vial was connected to the PTFE connecter and solvent conversion was carried out, until no visible layer of organic solvent could be seen in the vial.

After the solvent conversion step, the headspace vial (1.5 mL) was sealed with an aluminum cap furnished with a PTFE-faced septum for the following SPME step. The SPME step took 20 min at 50 °C under stirring in the headspace mode with a polydimethylsiloxane (PDMS) coated fiber (100 μm film thickness, conditioned before use) (SUPELCO, Bellafonte, PA, USA). In the end, the loaded SPME fiber was thermally desorpted for 8 min at 250 °C in the GC injection port.

2.4. Orthogonal experimental design

Orthogonal experimental design was employed to optimize the potential parameters, which may affect the performance of the SPME experiment. Five factors with five levels were studied in the orthogonal experiment, including fiber type (PDMS, PA, DVB–CAR–PDMS, CAR–PDMS and PDMS–DVB), extraction time (10, 20, 30, 40 and 50 min), extraction temperature (30, 50, 70, 85, and 95 °C), pH value (4, 6, 7, 9 and 10), and ionic strength (w/v) (0, 7, 11, 18 and 21%; modified by sodium chloride). The orthogonal table of $L_{25}(5^6)$ was selected accordingly to arrange all the five factors in the experiment. As shown in Table 1, by employing orthogonal experimental design, it was possible to accomplish the optimization experiment with only 25 trials in stark contrast to the 3125 trials theoretically needed when using the full factorial design. Moreover, unlike the optimization technique based on the single factor comparison experiment, the trials in orthogonal experiment design table are uniformly dispersed in the set of all possible cases and thus more representative [39].

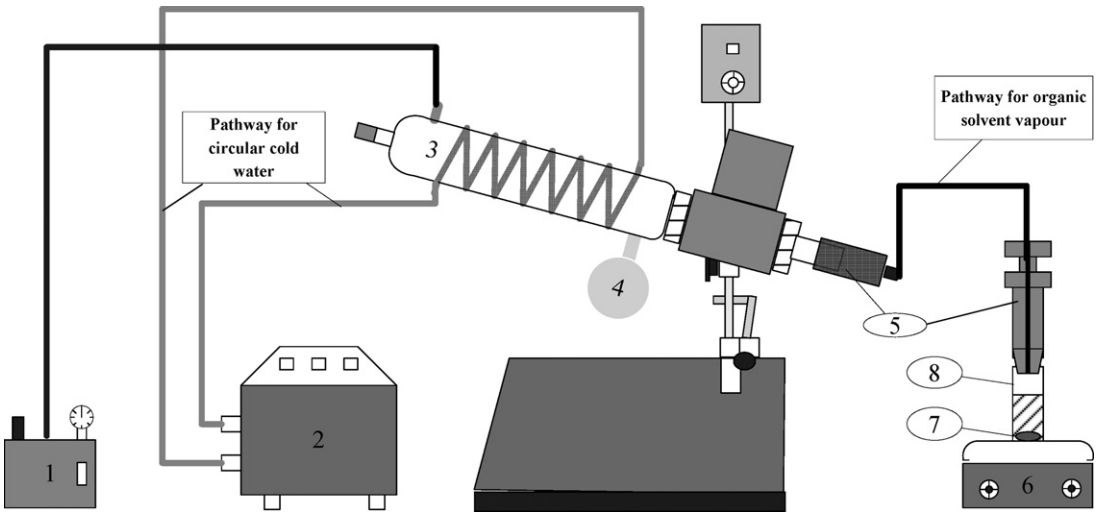

Fig. 1. Schematic diagram of solvent conversion device. (1) Vacuum pump, (2) cooling circulating pump, (3) condenser tube, (4) collecting bottle, (5) PTFE connector, (6) magnetic heating stirring machine, (7) magnetic stirrer, and (8) headspace vial.

Following the orthogonal experiment, the table of results was reordered five times in such a way that each time all the trials, featuring the same level of the factor considered, were lined as in a group, as representatively shown in Table 2. Each time the orthogonal experiment table was reordered, five trials with the same level for each factor under consideration would be lined together, while the levels of all the other factors were uniformly distributed in each five-trial group, namely covering all the five levels of each factor. Therefore, it was reasonable to regard the mean (named as the level influence value in the following discussion) of the results of each five-trial group, mentioned before, as a valuable index to evaluate the influence of the associated level of the factor considered on the performance of the experiment, since the influence of the other factors had been unified by calculating the average in each five-trial group. This allowed comparison among the five level influence values (LIVs) of each factor without having to consider the influence of the other factors. The higher the LIV, the higher was the chromatographic response expected to be at the associated level. To ensure the comparability of the different kinds of OCPs, the original LIVs were at first normalized following Eq. (1), where N is normalized LIV, D the original LIV, MI the minimum value of LIV for each associated factor of each individual target compound, and MA the maximum value of LIV for each associated factor of each individual target compound. The LIVs for the 17 OCPs are compiled in Table 3:

$$N = \frac{D - \mathrm{MI}}{\mathrm{MA} - \mathrm{MI}}. \quad (1)$$

2.5. Instruments and settings

A gas chromatograph (HP6890, Agilent, USA), equipped with split/splitless injector, a fused-silica capillary column (HP-5, 30 m × 0.25 mm i.d., 0.25 μm film thickness; J&W, Agilent, USA) and an electron-capture detector (^{63}Ni), were employed to separate and

Table 1
Orthogonal experimental design table.

Trial	Fiber[a]	Ionic strength	Extraction temp.	Extraction time	pH
1	PDMS	0%	30 °C	10 min	4
2	PDMS	7%	50 °C	20 min	6
3	PDMS	11%	70 °C	30 min	7
4	PDMS	18%	85 °C	40 min	9
5	PDMS	21%	95 °C	50 min	10
6	PA	0%	50 °C	30 min	9
7	PA	7%	70 °C	40 min	10
8	PA	11%	85 °C	50 min	4
9	PA	18%	95 °C	10 min	6
10	PA	21%	30 °C	20 min	7
11	DVB–CAR–PDMS	0%	70 °C	50 min	6
12	DVB–CAR–PDMS	7%	85 °C	10 min	7
13	DVB–CAR–PDMS	11%	95 °C	20 min	9
14	DVB–CAR–PDMS	18%	30 °C	30 min	10
15	DVB–CAR–PDMS	21%	50 °C	40 min	4
16	CAR–PDMS	0%	85 °C	20 min	10
17	CAR–PDMS	7%	95 °C	30 min	4
18	CAR–PDMS	11%	30 °C	40 min	6
19	CAR–PDMS	18%	50 °C	50 min	7
20	CAR–PDMS	21%	70 °C	10 min	9
21	PDMS–DVB	0%	95 °C	40 min	7
22	PDMS–DVB	7%	30 °C	50 min	9
23	PDMS–DVB	11%	50 °C	10 min	10
24	PDMS–DVB	18%	70 °C	20 min	4
25	PDMS–DVB	21%	85 °C	30 min	6

[a] PDMS: polydimethylsiloxane; PA: polyamide; CAR: carboxen; DVB: divinylbenzene.

Table 2
Results of orthogonal experiment after reordering orthogonal experiment table (taking fibers into consideration).

Trial	Fiber	Ionic strength	Extraction temp.	Extraction time	pH	Peak area for α-HCH	Level influence value of fiber
1	PDMS	0%	30 °C	10 min	4	11,498.2	34,454.74
2	PDMS	7%	50 °C	20 min	6	57,913.5	
3	PDMS	11%	70 °C	30 min	7	60,065.1	
4	PDMS	18%	85 °C	40 min	9	41,319.5	
5	PDMS	21%	95 °C	50 min	10	1477.4	
6	PA	0%	50 °C	30 min	9	27,480.3	30,098.12
7	PA	7%	70 °C	40 min	10	18,691.1	
8	PA	11%	85 °C	50 min	4	38,747.9	
9	PA	18%	95 °C	10 min	6	31,834.9	
10	PA	21%	30 °C	20 min	7	33,736.4	
11	DVB–CAR–PDMS	0%	70 °C	50 min	6	72,251.2	68,881.36
12	DVB–CAR–PDMS	7%	85 °C	10 min	7	68,915.2	
13	DVB–CAR–PDMS	11%	95 °C	20 min	9	60,776.7	
14	DVB–CAR–PDMS	18%	30 °C	30 min	10	49,432.8	
15	DVB–CAR–PDMS	21%	50 °C	40 min	4	93,030.9	
16	CAR–PDMS	0%	85 °C	20 min	10	4990.9	10,747.12
17	CAR–PDMS	7%	95 °C	30 min	4	10,365	
18	CAR–PDMS	11%	30 °C	40 min	6	11,400.5	
19	CAR–PDMS	18%	50 °C	50 min	7	13,946.5	
20	CAR–PDMS	21%	70 °C	10 min	9	13,032.7	
21	PDMS–DVB	0%	95 °C	40 min	7	73,609.6	69,351.12
22	PDMS–DVB	7%	30 °C	50 min	9	46,481.8	
23	PDMS–DVB	11%	50 °C	10 min	10	51,924	
24	PDMS–DVB	18%	70 °C	20 min	4	95,204.5	
25	PDMS–DVB	21%	85 °C	30 min	6	79,535.7	

Table 3
Normalized level influence values of each factor for the 17 OCPs.

Factors	Fiber					Extraction temperature (°C)					Extraction time (min)				
Levels	PDMS	PA	D–C–P[a]	C–P[a]	P–D[a]	30	50	75	85	95	10	20	30	40	50
α-HCH	0.38	0.33	0.98	0.00	1.00	0.08	0.75	1.00	0.00	0.65	0.00	1.00	0.25	0.89	0.70
β-HCH	0.43	1.00	0.31	0.00	0.80	0.00	1.00	0.13	0.48	0.48	0.00	0.72	0.70	0.08	1.00
γ-HCH	0.37	0.30	0.89	0.00	1.00	0.00	0.83	1.00	0.03	0.98	0.00	1.00	0.61	0.54	0.87
δ-HCH	0.20	0.02	0.35	0.00	1.00	0.24	0.00	0.43	0.56	1.00	0.16	1.00	0.00	0.41	0.91
Heptachlor	0.88	1.00	0.50	0.08	0.00	0.06	0.00	0.32	1.00	0.94	0.00	0.87	0.80	0.73	1.00
Aldrin	0.89	1.00	0.01	0.00	0.78	0.00	0.68	0.82	0.83	1.00	0.00	0.99	0.96	0.89	1.00
Heptachlor epoxide	0.87	1.00	0.08	0.00	0.57	0.00	1.00	0.53	0.81	0.91	0.00	1.00	0.94	0.82	0.98
α-Endosulfan	0.76	1.00	0.29	0.00	0.75	0.28	0.14	0.00	0.28	1.00	0.00	1.00	0.65	0.80	0.92
Dieldrin	1.00	0.98	0.00	0.33	0.40	0.00	1.00	0.26	0.82	0.89	0.00	1.00	0.96	0.71	1.00
Endrin	0.70	1.00	0.31	0.00	0.46	0.12	1.00	0.00	0.77	0.61	0.00	0.92	0.96	0.67	1.00
β-Endosulfan	0.53	1.00	0.00	0.37	0.49	0.19	1.00	0.00	0.77	0.78	0.00	1.00	0.95	0.62	1.00
p,p′-DDD	0.65	1.00	0.00	0.09	0.48	0.44	0.00	0.13	0.69	1.00	0.00	0.90	0.72	0.41	1.00
p,p′-DDE	1.00	0.53	0.19	0.00	0.30	0.00	1.00	0.12	0.90	0.68	0.00	0.75	0.94	0.41	1.00
Endrin aldehyde	1.00	0.03	0.06	0.00	0.25	0.00	1.00	0.13	0.36	0.62	0.00	0.43	0.48	0.13	1.00
p,p′-DDT	1.00	0.43	0.20	0.00	0.25	0.00	1.00	0.23	0.93	0.74	0.00	0.82	0.89	0.45	1.00
Methoxychlor	1.00	0.00	0.39	0.20	0.01	0.00	1.00	0.69	0.79	0.82	0.00	0.96	0.97	0.81	1.00
Endosulfan sulfate	1.00	0.59	0.09	0.00	0.17	0.25	0.92	0.00	1.00	0.39	0.00	0.48	0.86	0.08	1.00

Factors	pH					Ionic strength (w/v, %)				
Levels	4	6	7	9	10	0	7	11	18	21
α-HCH	1.00	0.00	0.45	0.97	0.96	0.00	0.39	0.97	1.00	0.81
β-HCH	0.73	0.00	0.17	0.47	1.00	0.00	0.08	1.00	0.91	0.03
γ-HCH	0.71	0.00	0.42	0.91	1.00	0.46	0.00	0.95	1.00	0.79
δ-HCH	0.47	0.00	0.30	0.45	1.00	0.00	0.79	0.85	0.29	1.00
Heptachlor	0.45	0.00	0.45	0.28	1.00	0.00	0.92	1.00	0.55	0.36
Aldrin	0.00	0.64	1.00	0.90	0.76	0.31	1.00	0.23	0.12	0.00
Heptachlor epoxide	0.00	0.87	0.77	0.51	1.00	0.00	1.00	0.90	0.97	0.49
α-Endosulfan	0.69	0.00	0.62	0.83	1.00	0.00	0.50	0.88	1.00	0.18
Dieldrin	0.00	1.00	0.79	0.32	0.90	0.00	0.78	0.72	1.00	0.30
Endrin	0.08	0.91	0.72	0.00	1.00	0.14	0.67	1.00	0.84	0.00
β-Endosulfan	0.33	1.00	0.17	0.00	0.65	0.00	0.50	0.51	1.00	0.16
p,p′-DDD	0.90	0.00	0.24	0.75	1.00	0.00	0.23	1.00	0.78	0.26
p,p′-DDE	0.00	0.94	1.00	0.58	0.76	0.00	0.32	0.87	1.00	0.68
Endrin aldehyde	0.00	0.06	1.00	0.37	0.28	0.00	0.01	0.41	1.00	0.50
p,p′-DDT	0.00	0.85	1.00	0.71	0.75	0.00	0.39	1.00	0.98	0.65
Methoxychlor	0.00	0.47	1.00	0.78	0.50	0.00	0.88	0.87	0.97	1.00
Endosulfan sulfate	0.10	0.88	1.00	0.00	0.33	0.00	0.12	0.72	1.00	0.60

[a] D–C–P, C–P, P–D represent DVB–CAR–PDMS, CAR–PDMS and PDMS–DVB respectively.

Table 4
Henry's Law constant (HC) and headspace-sample partition coefficient (K_{hs}) of the 17 organochlorine pesticides.

	α-HCH	β-HCH	γ-HCH	δ-HCH	Heptachlor	Aldrin	Heptachlor epoxide	α-Endosulfan	Dieldrin	Endrin	β-Endosulfan	p,p′-DDD	p,p′-DDE	Endrin aldehyde	p,p′-DDT	Methoxychlor	Endosulfan sulfate
HC at 25 °C atm m^3/mol ($\times 10^5$)[a]	1.22	0.044	0.51	-	29.40	4.40	2.10	6.50	1.00	0.64	0.039	0.66	4.16	-	0.83	0.020	1.22
K_{hs} at 25 °C dimensionless ($\times 10^5$)[b]	49.24	1.78	20.75	-	1186.65	177.59	84.76	262.35	40.36	25.67	1.58	26.64	167.91	-	33.58	0.82	49.24

[a] The HC of Dieldrin is cited from Ref. [47], and the HC of all the other target compounds are cited from Ref. [48].
[b] K_{hs} is a constant deduced from HC according to K_{hs} = HC × $10^5/RT$, where R is the thermodynamic constant with a value of 8.314 and T is the thermodynamic temperature with a value of 298 here.

detect the target compounds. The oven temperature of the GC was programmed as follows: initial temperature of 150 °C, increased to 200 °C at a rate of 2 °C/min, and continually increased to 260 °C at a rate of 3 °C/min. Nitrogen (99.999% purity) was used as carrier gas at a constant flow rate of 2 mL/min. The injector temperature was set to 250 °C, and the split/splitless switch was set open at 3 min with a split ratio of 50. The temperature of the detector was set to 300 °C with nitrogen makeup gas at a rate of 60 mL/min.

2.6. Quantification scheme and QA/QC experiments

External standard calibration was adopted for quantification, beginning from solvent conversion, to HS-SPME and finally to thermal desorption of the SPME fiber. To do this, different amounts of target compounds were previously spiked in 10 mL n-hexane to make five standard calibration samples with concentration levels of 0.0001, 0.003, 0.015, 0.3 and 1.5 ng mL^{-1}.

QA/QC experiments, including a blank sample test, recovery test, repeatability test, and method detection limit (MDL) experiment were performed to evaluate the feasibility of the method. 4 L Milli-Q water served as the water sample for the blank test, while the water samples for the recovery test and repeatability test were made by spiking 40 μL 20 ng mL^{-1} working solution into 4 L Milli-Q water. The MDL experiment was undertaken following the USEPA method. All test samples passed through the entire procedure including SPE, solvent conversion, HS-SPME and thermal desorption of the SPME fiber.

3. Results and discussion

3.1. Optimization in SPME step

3.1.1. Selection of extraction mode

SPME is a process of mass transfer. When equilibrium was achieved, the amount of target compounds being absorbed by the fiber could be theoretically calculated according to Eq. (2) (HS-SPME) [40] or Eq. (3) (direct immersion solid-phase microextraction, DI-SPME) [41]:

$$n^{\infty} = \frac{K_{fs}V_f}{K_{fs}V_f + K_{hs}V_h + V_s} n_0 \quad (2)$$

$$n^{\infty} = \frac{K_{fs}V_f}{K_{fs}V_f + V_s} n_0 \quad (3)$$

$$n^{\infty} = \frac{K_{fs}V_f}{K_{fs}V_f + V_h + V_s} n_0 \quad (4)$$

$$n^{\infty} = \frac{K_{fs}V_f}{K_{fs}V_f + K_{hs}V + (1 - K_{hs})V_s} n_0 \quad (5)$$

Here, n_0 is the initial amount of analyte in sample; K_{fs} and K_{hs} are the fiber-sample and headspace-sample partition coefficient; V_f, V_h and V_s are the volume of fiber coating, headspace and sample respectively.

For the volatile and semi-volatile target compounds, mass transfer is considerably more effective in the HS-SPME mode than in the DI-SPME mode, therefore the equilibrium time is much shorter using the HS-SPME mode compared with the DI-SPME mode. Another striking advantage of HS-SPME lies in the fact that it is possible for the SPME fiber to absorb target compounds without being in contact with the matrix solution, usually modified through salt addition or pH adjustment, and therefore can increase the lifetime of the SPME fiber. Furthermore, during DI-SPME coexisting high-molecular-mass compounds in the complex matrix are more likely to be absorbed irreversibly by the SPME fiber, thus changing the property of the SPME fiber and rendering it unusable. This disadvantage can be effectively avoided by applying the HS-SPME

mode, since high-molecular-mass compounds usually have such high boiling points that they tend not to partition in the headspace phase.

Apart from equilibrium time, the extraction amount (n^{∞} in Eqs. (2) and (3)) is another important index to evaluate the extraction efficiency under different extraction mode. To make comparable all of the parameters in Eqs. (2) and (3), transformation of Eq. (3) is necessary, since the volume of sample under DI-SPME (V_s in Eq. (3)) is equal to the volume of extraction vial, which comprises two parts under HS-SPME, namely volume of headspace (V_h in Eq. (2)) and volume of sample (V_s in Eq. (2)). So Eq. (3) was transformed as Eq. (4) by substituting V_s with "$V_s + V_h$". Based on the comparison between Eqs. (2) and (4), K_{hs} is found to be the final constant that determines the difference of extraction amount under two SPME modes. K_{hs} is a dimensionless constant, which can be deduced from the Henry's Law constant. Both K_{hs} and Henry's Law constant of each target compound were compiled as Table 4. Since K_{hs} of each target compound is far less than 1, the extraction amount under HS-SPME will be higher than that under DI-SPME. Therefore, considering the equilibrium time, SPME fiber lifetime and extraction efficiency, HS-SPME was finally chosen in the present study.

To make clear the relation between sample volume (V_s) and extraction amount (n^{∞}) under HS-SPME, Eq. (2) was further transformed to Eq. (5) by substituting V_h with "$V - V_s$", where V is the volume of extraction vial. According to Eq. (5), lower (K_{hs} is far less than 1 here) the sample volume (V_s) and the extraction vial volume (V), higher the extraction amount (n^{∞}) will be, since all the other parameters will be constant when the same conditions are maintained during each experiment. Therefore, a considerably small extraction vial, with a size of only 1.5 mL, as well as a sample matrix volume as low as 200 μL was selected here to achieve good extraction efficiency during HS-SPME.

3.1.2. Level analysis on the results of orthogonal experiment

After normalization, there were five LIVs ranging from 0 to 1 for each individual factor of each target compound (Table 3). After plotting the normalized LIVs of all 17 target compounds, we obtained level response diagrams for each of the five factors. As shown in Fig. 2, for most target compounds, the LIV of extraction time increased sharply from the lowest value at level 1 (10 min) to the first high peaks at level 2 (20 min), and then decreased slightly with level before reaching another high value at level 5 (50 min). The change indicated that the extraction was effective enough to approach equilibrium within 20 min. The response pattern for the ionic strength factor inferred that moderate ionic strength (11 and 18%) exhibited higher response than either the low level (0 and 7%) or the high level (21%), which probably resulted from the salting-out effect under low ionic strength and the competitive absorption effect under high ionic strength. In the case of extraction temperature, although the temperature increase could facilitate the mass transfer and thus improve the extraction efficiency, the positive effect would be offset to some extent due to the exothermic effect of absorption reaction between target compounds and the fiber phase [42], as shown in Fig. 2. In the case of pH, although the trends of response were unclear, two features could be roughly seen from Fig. 2, one at level 2 (pH 6) and level 3 (pH 7) featuring moderate pH values, in which case the pH exhibited a positive effect for several target compounds, and the other at level 5 (pH 10) featuring a high pH value, in which case the positive effect could be seen for almost every target compound. This trend might be due to the difference in molecular structure of each target compound. In terms of fiber factor, a comparatively high response value could be seen in three fibers (PDMS, PA, and PDMS–DVB), which could be further subdivided into two groups with one (PDMS) exhibiting a high response value generally, and the others (including PA and PDMS–DVB) exhibiting an extremely low response for two or three individual target compounds.

3.1.3. Range analysis on the results of orthogonal experiment

While level analysis was helpful in showing the response change with level for each single factor, range analysis was a robust manner to evaluate the comparative significance of different factors. The ranges for each factor were easily obtained by subtracting the associated minimum LIV from the associated maximum LIV, and then further normalized according to Eq. (6), where NR represents the normalized range, R the original range, and SUM the sum of all the original ranges of each target compound:

$$\mathrm{NR} = \frac{R}{\mathrm{SUM}} \tag{6}$$

After normalization, each range had a value greater than 0 but less than 1, and the sum of the five ranges for each individual target compound was unified to 1, so that it was possible to make a comparison of the ranges on the comparative weight of each range among individual target compounds. The comparative significance of each factor for all 17 target compounds is clearly shown in Fig. 3, and it can be seen that the major factors were fiber type and extraction time, the sum of which exceeded or approached 60%, while the minor factors included extraction temperature, ionic strength and pH, the values of each seldom exceeding 20%. It should be pointed out, in the case of the α-HCH, β-HCH, γ-HCH, δ-HCH, α-endosulfan and p,p′-DDD, comparatively higher pH ranges were found than the other target compounds, therefore pH was regarded as second major factor here.

3.1.4. Selection of factor levels

The objective of the orthogonal experiment was to find the optimum factors which would improve the performance of the experiment. For the major factors, the optimum factor level could be obtained through level analysis, while some compromise levels were chosen on practical grounds for the minor factors. Based on this level analysis, the optimum factor levels were as follows: a sample matrix pH of 10; ionic strength of 18%; solid-phase microextraction using the SPME fiber coated with PDMS; and an extraction temperature of 95 °C for 20 min. Since the extraction temperature and ionic strength were minor factors, based on the range analysis, compromise values for these two factors were selected as 50 °C and 0% (no ionic strength adjustment) respectively in order to save energy and resources.

3.2. Optimization in the SPE step

3.2.1. Selection of cartridge type for SPE

OCPs belong to the class of weak polarity organic compounds, therefore according to the rule of *like dissolves like*, an SPE sorbent with similar polarity will facilitate enrichment. At present, the most commonly used SPE sorbent for the enrichment of OCPs in water samples is reversed-phase carbon 18-bonded silica. Such SPE sorbent has been applied widely in the research of environmental pollutant chemistry [43–46]. Based on the theoretical principle as well as literature account, carbon 18, bonded to reversed-phase silica supporter, was selected as the SPE sorbent in this study.

3.2.2. Selection of elution solvent

The ideal elution solvent should be strong enough to elute all of the target compounds, and the elution strength of the organic solvent is dependent upon the type of sorbent used. For the reversed phase, an organic solvent with lower polarity will exhibit stronger elution. Since the reverse sorbent was used here, n-hexane was selected as the elution solvent due to its strong elution strength as well as its striking property of non-polarity and low vapor pressure,

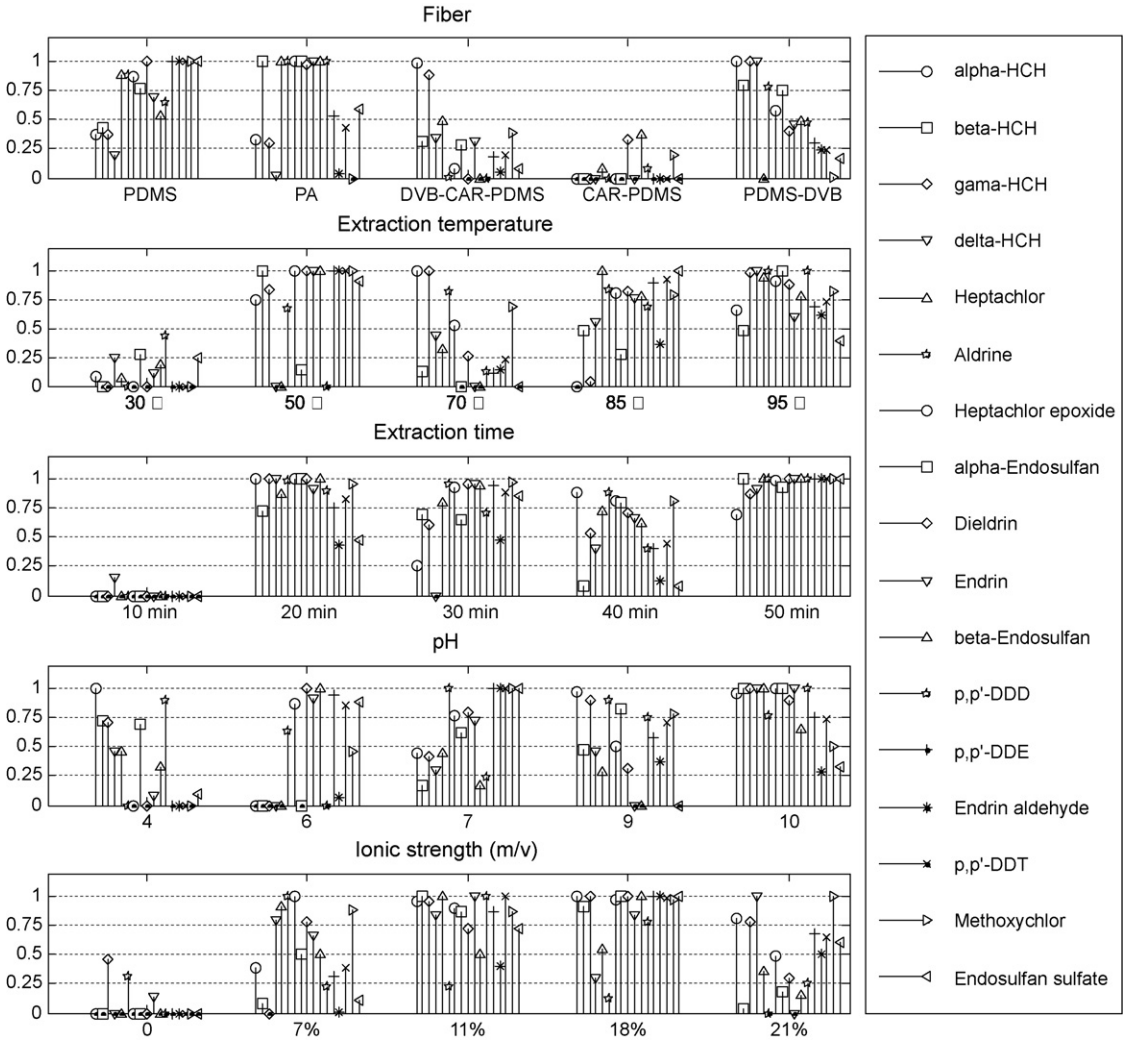

Fig. 2. Level analysis of each factor for 17 OCPs in the orthogonal experiment.

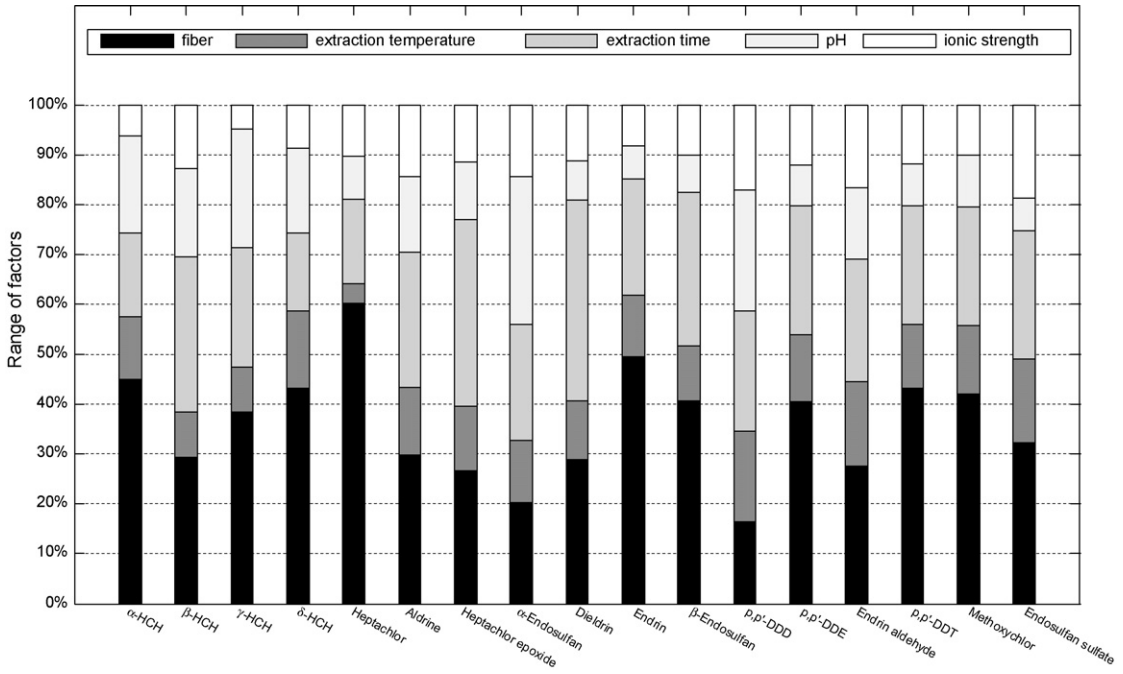

Fig. 3. Range analysis of each factor for 17 OCPs in the orthogonal experiment.

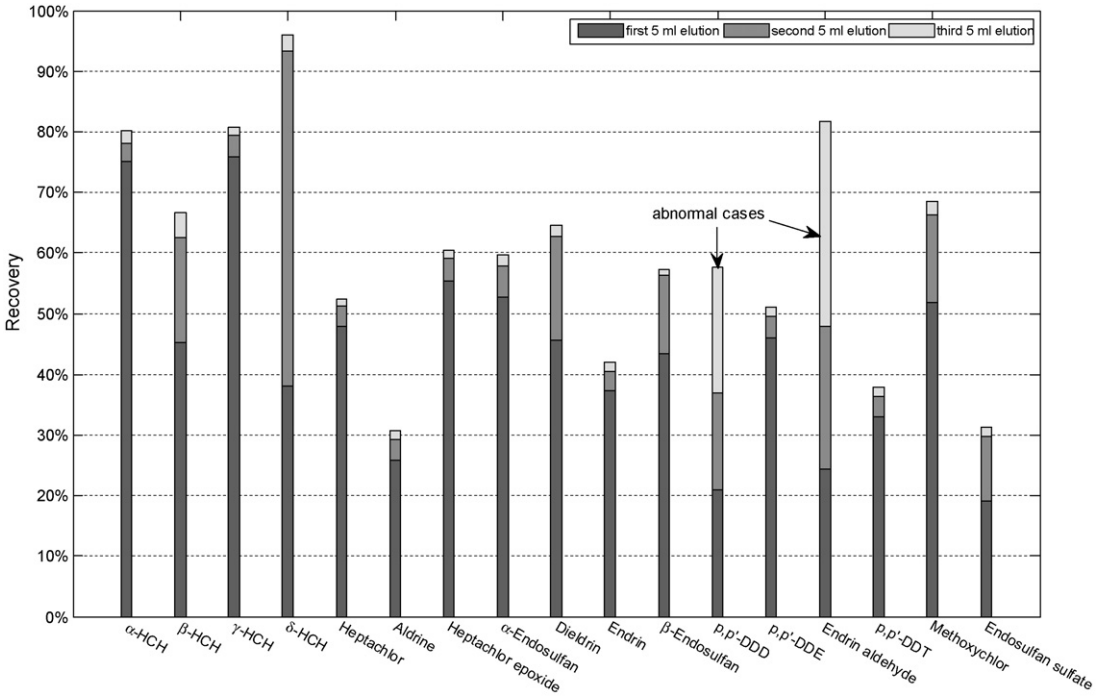

Fig. 4. Diagram of elution in the SPE step.

both of which is necessary to achieve effective solvent conversion from organic solution to aquatic solution, discussed in detail later.

3.2.3. Optimum amount of elution solvent

The optimum elution amount was evaluated through an elution experiment, in which a spiked SPE cartridge (30 μL 80 ng L^{-1} working solution spiked directly in a conditioned SPE column) was eluted three times successively with 5 mL n-hexane. Another 5 mL n-hexane, spiked with the same amount of target compounds, served as the control group. The test groups as well as the control group were separately processed through the same procedures, involving solvent conversion, HS-SPME and thermal desorption of the SPME fiber. The recovery rate of each individual target compound in each elution step was calculated by comparing the chromatographic responses of the test group with that of the control group. As clearly shown in Fig. 4, most of the target compounds could be eluted with an accumulated recovery exceeding or approaching 60% after the second elution, except for p,p′-DDD and endrin aldehyde, which exhibited a comparatively higher response even in the third 5 mL eluent. As a compromise, 10 mL n-hexane was chosen to elute the target compounds during consideration to the common case for most of the target compounds as well as the possibility of more severe environmental contamination posed by the extra usage of organic solvent.

3.2.4. Breakthrough experiment

The breakthrough volume here is regarded as the volume at which a particular target compound pumped continuously through the SPE column begins to elute. The breakthrough volume can vary with the concentration of the target compound, which is more likely to breakthrough at higher concentration. So the breakthrough volume should be evaluated at the conservatively highest predictive concentration of the target compound in the research area, and a higher or lower prediction will result in underestimation or overestimation accordingly. Since the method here aims for the trace analysis of OCPs in the open sea or polar areas, the conservative predictive concentration was 0.6 ng L^{-1}, which is slightly higher than the level reported in the Arctic [26].

Different volumes of Milli-Q water samples (1, 2, 4 and 6 L) were spiked appropriately to produce four test samples with a concentration of 0.6 ng L^{-1}. All the test samples then underwent four sequential steps, namely SPE, solvent conversion, HS-SPME, and thermal desorption of the SPME fiber. Four control samples, made by spiking the same amount of target compounds in 10 mL n-hexane, were processed in the same way as the test samples, from solvent conversion onwards. As seen in Fig. 5, there was no apparent decrease in recovery rate with water volume except for the four HCHs, especially the β-HCH and δ-HCH, where recovery fell by a comparatively greater extent from 4 to 6 L than in the other cases after discarding the abnormal results from the 1 L test sample. This meant the breakthrough volume of α-HCH, β-HCH, γ-HCH, δ-HCH was about 4 L. By contrast, the breakthrough volumes of the other OCPs in this study exceeded 6 L based on the change of recovery with volume illustrated in Fig. 5. Therefore, 4 L was safely selected as the optimal sampling volume, which might enable effective enrichment without the occurrence of breakthrough of the target compounds.

3.3. Solvent conversion to an aquatic matrix for SPME

According to Henry's Law, both the organic solvent and target compounds will partition between the headspace phase and the solution phase during solvent conversion. Obviously the temperature increase will facilitate the vaporization of organic solvent, but it may simultaneously be a problem, since the possibility of the target compounds becoming lost will increase under a higher temperature. Therefore, optimization of the temperature for heating during solvent conversion was carried out to obtain the optimum temperature for the organic solvent to vaporize quickly but with smaller amounts of target compounds being lost during the process. Four temperature levels, including 30, 35, 40, and 45 °C, were considered in the experiment. After the temperature was set to each level, the magnetic heating/stirring machine was kept on for another 1 h to achieve temperature equilibrium, readable using a digital thermometer. Then the solvent conversion experiment was carried out at each temperature level using a test sample made

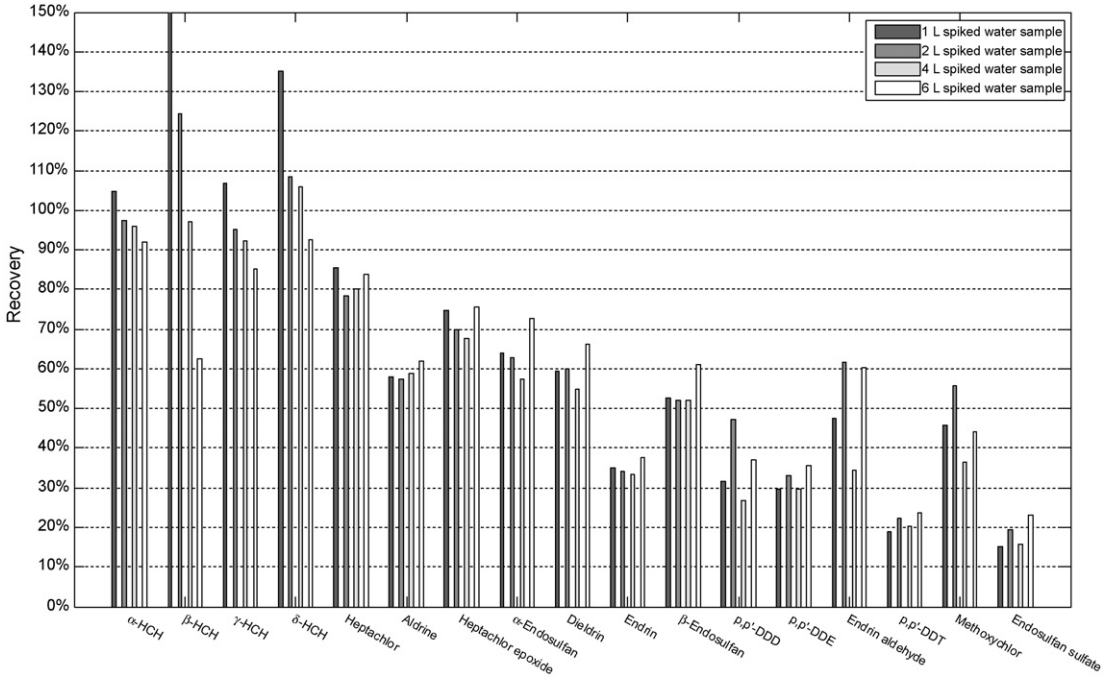

Fig. 5. Diagram of breakthrough in the SPE step.

previously by spiking 30 μL 80 ng mL^{-1} fresh working standard in 10 mL n-hexane. The results of chromatographic response were first normalized following Eq. (1) to make possible the comparison among individual target compounds. As shown by the normalized results in Fig. 6, the response was positive with temperature for most target compounds after excluding the abnormal results from the temperature level of 35 °C, seemingly contradicting the theoretical deduction mentioned above. However, this was regarded as reasonable, when we compared the time needed for the solvent conversion at each temperature level. The solvent conversion time was observed to fall sharply from 17 min at a temperature of 30 °C to only 6 min at a temperature of 45 °C, and this probably implied that a negative effect due to extension of the solvent conversion time extenuated to great extent the positive effect brought about by the decrease in temperature. Therefore, an optimum temperature of 45 °C was selected during solvent conversion.

3.4. Validation of the developed method

The performance of the whole method based on the combination of SPE and SPME was evaluated using the linear range and residual square value for the external quantification as well as QA/QC experiment indexes, including recovery rate, reproducibility, and MDL. The results, listed in Table 5, indicate wide linear ranges from 0.0040 to 60 ng mL^{-1} with residual square (R^2) values more than 0.998 were achieved. High performance was also

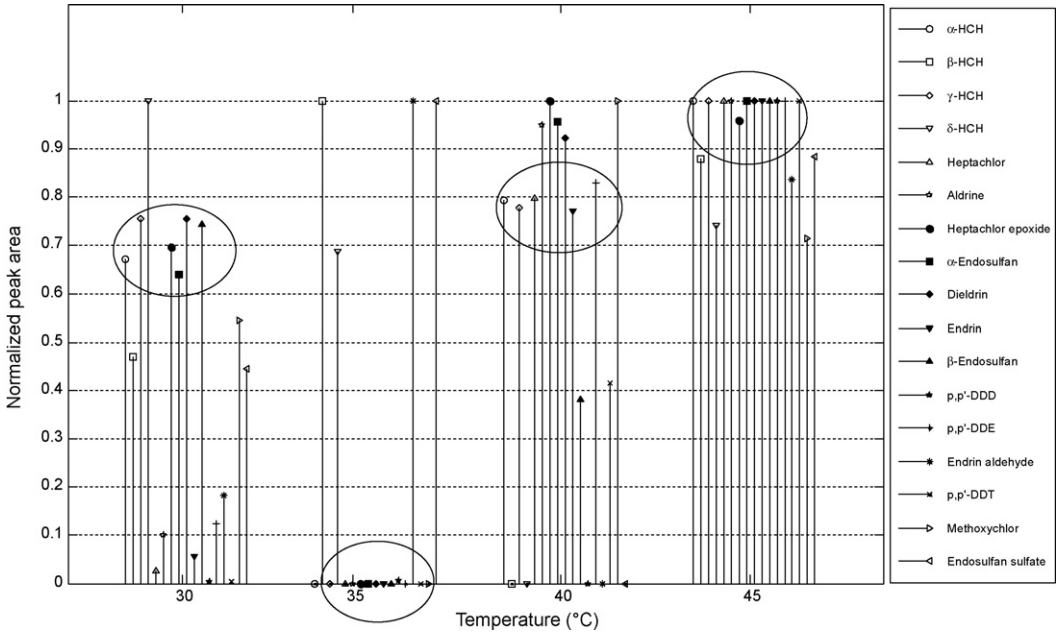

Fig. 6. Comparison of solvent conversion efficiency at different temperatures (the elliptic zones represent the common cases at each temperature level).

Table 5
Results of QA/QC experiment.

OCPs	Linear range (ng mL^{-1})	R^2	Recovery rate	RSD (n = 4)	MDL (ng L^{-1})
α-HCH	0.0040–60	0.9999	102.81%	3.24%	0.004
β-HCH	0.0040–60	0.9998	128.14%	17.85%	0.027
γ-HCH	0.0040–60	0.9999	99.17%	7.58%	0.002
δ-HCH	0.0040–60	0.9999	110.71%	11.38%	0.008
Heptachlor	0.0040–60	0.9999	90.38%	5.19%	0.003
Aldrin	0.0040–60	0.9999	65.24%	10.17%	0.005
Heptachlor epoxide	0.0040–60	0.9994	76.10%	4.92%	0.003
α-Endosulfan	0.0040–60	0.9993	65.80%	4.69%	0.004
Dieldrin	0.0040–60	0.9993	64.30%	5.53%	0.003
Endrin	0.0040–60	0.9997	44.67%	13.30%	0.008
β-Endosulfan	0.0040–60	0.9995	65.71%	3.92%	0.005
p,p′-DDD	0.0040–60	0.9997	37.38%	14.86%	0.005
p,p′-DDE	0.0040–60	0.9996	41.72%	13.67%	0.008
Endrin aldehyde	0.0040–60	0.9994	78.64%	16.33%	0.034
p,p′-DDT	0.0040–60	0.9999	38.20%	20.43%	0.015
Methoxychlor	0.0040–60	0.9988	44.39%	15.23%	0.018
Endosulfan sulfate	0.0040–60	0.9999	31.34%	19.35%	0.015

observed in terms of the MDL which ranged from 0.0018 to 0.027 ng L^{-1}, and the RSD with values less than 20% (n = 4), which met the USEPA standard. However, undesirable recovery rates (lower than 60%) were also observed for some target compounds (endrin; p,p′-DDD; p,p′-DDE; p,p′-DDT; methoxychlor and endosulfan sulfate), which probably resulted from the losses of target compounds induced by the absorption or adsorption during SPE by either the Si–OH group on the inside wall of the glass sample vial or the SPE tube made of PE material.

3.5. Comparison of sensitivity between SPE and SPE–SPME

The developed method based on the combination of SPE and SPME was compared in terms of chromatographic response with the traditional single SPE method using the liquid injection mode. Two 4 L spiked water samples with the same concentration (0.024 ng L^{-1}) were made in parallel. Both samples were first processed equally through SPE, n-hexane elution, and then the eluent was either concentrated to 200 μL prior to 1 μL liquid injection in the test of single SPE, or the solvent was converted to 200 μL aquatic matrix (pH 10) followed in turn by HS-SPME and thermal desorption of the SPME fiber in the test involving the combination of SPE and SPME. The results of the SPE and SPE–SPME test are compared in Fig. 7, and a considerably higher chromatographic response of each target compound was clearly observed in the SPE–SPME test, compared to the case in the single SPE test. This provided strong evidence of a distinguishing enrichment feature of the method based on the combination of SPE and SPME, due to its highly effective transition of target compounds to the capillary column in contrast to the extremely low sample acquisition in the traditional liquid injection mode.

3.6. Application of the method in the Arctic

The method developed was applied to the determination of OCPs in surface Arctic seawater samples during the third Chinese

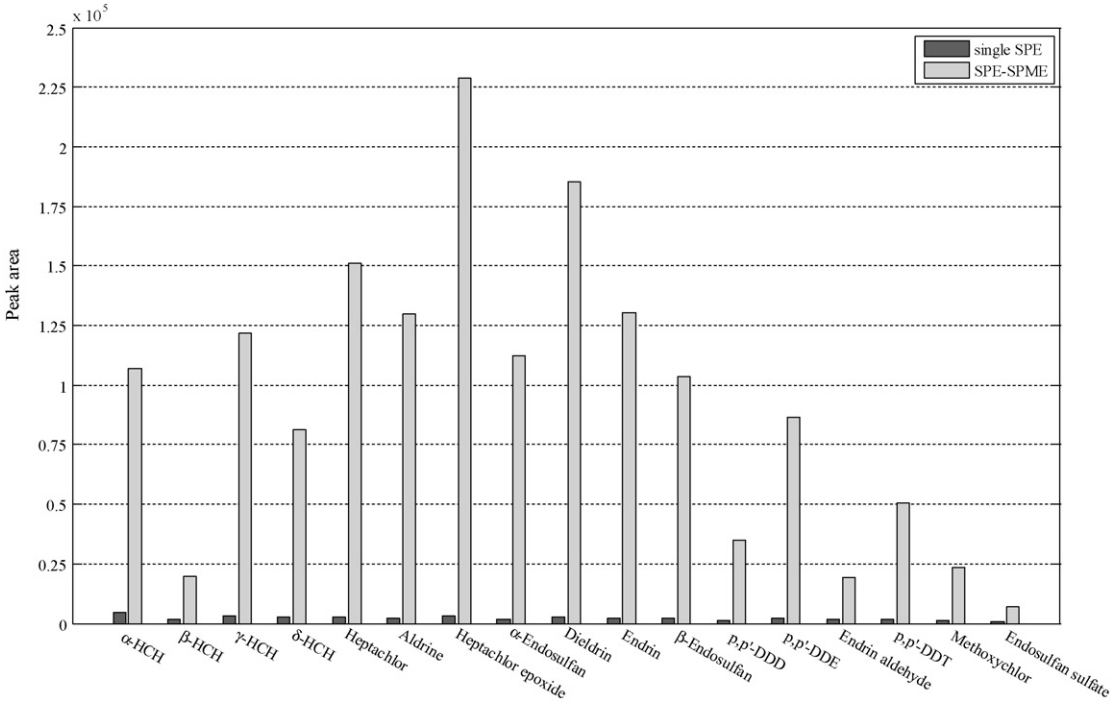

Fig. 7. Chromatographic response comparison between SPE and the combination of SPE and SPME.

Table 6
Concentrations of the 17 OCPs in the surface water samples from the Arctic (unit: ng L^{-1}).

OCPs	BR01	BR03	BR09	NB24#	ROO	C19	S13	C17	S15	B79	B81	B83	B85
α-HCH	0.321	0.065	0.128	0.267	0.086	0.389	0.393	0.117	0.118	0.553	0.755	0.644	0.169
β-HCH	0.332	0.788	0.100	ND[a]	0.160	0.118	2.324	0.574	ND	0.583	0.581	0.650	2.588
γ-HCH	0.137	0.073	0.718	ND	0.051	0.925	0.104	0.608	0.089	0.214	0.365	0.547	0.264
δ-HCH	0.126	0.055	0.053	0.083	ND	0.256	0.051	0.103	0.055	ND	ND	0.235	0.135
Heptachlor	0.192	0.058	ND	0.237	ND	0.215	ND	0.048	ND	0.042	0.042	0.830	0.423
Aldrin	0.084	0.038	0.045	0.028	0.295	0.047	0.178	0.065	0.734	0.500	0.056	0.922	0.101
Heptachlor epoxide	0.017	0.017	0.016	0.046	0.022	0.031	0.024	0.029	0.024	0.032	0.040	0.077	0.037
α-Endosulfan	0.087	0.020	0.021	0.020	0.019	0.061	0.035	0.054	0.098	0.019	0.029	0.096	0.053
Dieldrin	0.016	0.015	0.002	0.016	0.015	0.019	0.016	0.030	0.017	0.016	0.019	0.052	0.016
Endrin	0.040	0.028	0.035	0.034	0.025	0.053	0.026	0.057	0.028	0.027	0.027	0.084	0.030
β-Endosulfan	0.023	0.021	0.024	0.030	0.024	0.039	0.020	0.042	0.023	0.027	0.020	0.079	0.035
p,p′-DDD	0.037	0.038	0.024	0.026	0.028	0.045	0.021	0.063	0.029	0.032	0.038	0.071	0.022
p,p′-DDE	0.040	0.038	0.038	0.053	0.035	0.072	0.051	0.073	0.039	0.035	0.037	0.100	0.039
Endrin aldehyde	ND	0.475	0.007	ND	0.318	ND	0.490	0.587	0.199	ND	ND	ND	ND
p,p′-DDT	0.055	0.050	0.050	0.055	0.048	0.050	ND	0.098	0.050	0.049	0.055	0.143	0.050
Methoxychlor	0.034	0.040	0.040	0.079	0.035	0.067	ND	0.069	ND	0.039	0.033	0.087	0.035
Endosulfan sulfate	0.092	0.088	0.088	0.100	0.086	0.173	ND	0.088	ND	ND	0.086	0.100	0.123

[a] ND: under the method detection limit.

Arctic expedition cruise from October in 2008 to February in 2009. In the cruise 37 surface water samples were sampled. The filtration and SPE were undertaken on deck, while the steps which followed were carried out in the laboratory after the cruise. The loaded SPE cartridges were preserved at −20 °C prior to the laboratory processing. The results of 13 samples were representatively selected, as compiled in Table 6. As shown in Table 6, the predominant OCPs in the surface water of the Arctic were the HCHs (especially α-HCH and γ-HCH) with the sum of their concentrations ranging from 0.262 to 3.156 ng L^{-1}, while for the other OCPs the concentration was relatively low with the sum of their concentrations seldom exceeding 1.0 ng L^{-1}. Our results are in good agreement with those reported earlier [26]. A more detailed discussion concerning the horizontal distribution of OCPs in the Arctic is beyond the scope of this paper, and will be presented in another paper.

4. Conclusion

A novel enrichment technology based on the combination of SPE and SPME was developed for the trace analysis of dissolved OCPs in order to overcome the inherent problems of both the single SPE method and the single SPME method. Good results with high performance were achieved using the optimized method as follows: 4 L filtered water sample was first solid phase extracted using a conditioned ENVI-18 SPE cartridge, and then 10 mL n-hexane was used to elute the target compounds from the SPE cartridge. Thereafter, the eluent was solvent-converted to 200 μL aquatic matrix (pH 10) through a robust solvent conversion device assisted by conditions of low vacuum, stirring and heating. Finally, the target compounds were further enriched using a PDMS coated SPME fiber under headspace mode before they were transferred to a GC injection port through thermal desorption of the SPME fiber. The results of a validation experiment provided strong evidence on the method's reliability, which was further confirmed by its successful application in the Arctic. Even more effort should be made in the future to deal with the problems associated with absorption or adsorption-induced low recovery rates for some target compounds during SPE, before the method can be applied to the enrichment of other categories of semi-volatile or volatile organic pollutants.

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References

[1] U. Ahlborg, L. Lipworth, L. Titus-Ernstoff, C. Hsieh, A. Hanberg, J. Baron, D. Trichopoulos, H. Adami, Crit. Rev. Toxicol. 25 (1995) 463.
[2] C. Sonnenschein, A. Soto, M. Fernandez, N. Olea, M. Olea-Serrano, M. Ruiz-Lopez, Clin. Chem. 41 (1995) 1888.
[3] C. Halsall, R. Bailey, G. Stern, L. Barrie, P. Fellin, D. Muir, B. Rosenberg, F. Rovinsky, E. Kononov, B. Pastukhov, Environ. Pollut. 102 (1998) 51.
[4] D. Muir, C. Ford, B. Rosenberg, R. Norstrom, M. Simon, P. Beland, Environ. Pollut. 93 (1996) 219.
[5] E. Goldberg, W. Bourne, E. Boucher, A. Preston, Proc. Roy. Soc. Lond., B: Biol. Sci. 189 (1975) 277.
[6] T. Bidleman, L. Jantunen, P. Helm, E. Brorstrom-Lunden, S. Juntto, Environ. Sci. Technol. 36 (2002) 539.
[7] H. Hung, C. Halsall, P. Blanchard, H. Li, P. Fellin, G. Stern, B. Rosenbergs, Environ. Sci. Technol. 36 (2002) 862.
[8] P. Schmid, M. Kohler, E. Gujer, M. Zennegg, M. Lanfranchi, Chemosphere 67 (2007) 16.
[9] W. Wilcke, Geoderma 141 (2007) 157.
[10] M. Felipe-Sotelo, R. Tauler, I. Vives, J. Grimalt, Sci. Total Environ. 404 (2008) 148.
[11] S. Meijer, J. Grimalt, P. Fernandez, J. Dachs, Environ. Pollut. 157 (2009) 1815.
[12] G. Lammel, A. Sehili, T. Bond, J. Feichter, H. Grassl, Chemosphere 76 (2009) 98.
[13] Y. Kim, H. Eun, T. Katase, H. Fujiwara, Chemosphere 67 (2007) 456.
[14] Z. Zhao, L. Zhang, X. Yu, Z. Li, J. Lake Sci. 20 (2008) 579.
[15] S. Sarkar, A. Binelli, C. Riva, M. Parolini, M. Chatterjee, A. Bhattacharya, B. Bhattacharya, K. Satpathy, Arch. Environ. Contam. Toxicol. 55 (2008) 358.
[16] C. Henny, T. Anderson, J. Crayon, Hydrobiologia 604 (2008) 137.
[17] M. Kaur, J. Sharma, J. Gill, R. Aulakh, J. Bedi, B. Joia, Bull. Environ. Contam. Toxicol. 80 (2008) 154.
[18] A. Souza, J. Torres, R. Meire, R. Neves, M. Couri, C. Serejo, Chemosphere 73 (2008) 186.
[19] G. Darko, S. Acquaah, Chemosphere 71 (2008) 294.
[20] M. Abbassy, H. Ibrahim, H. Abdel-Kader, Bull. Environ. Contam. Toxicol. 70 (2003) 1158.
[21] X. Wang, S. Qi, J. Li, J. Environ. Sci. Eng. 2 (2008) 22.
[22] J. Gao, L. Liu, X. Liu, J. Lu, H. Zhou, S. Huang, Z. Wang, P. Spear, Environ. Int. 34 (2008) 1097.
[23] T. Poolpak, P. Pokethitiyook, M. Kruatrachue, U. Arjarasirikoon, N. Thanwaniwat, J. Hazard. Mater. 156 (2008) 230.
[24] I. Monirith, D. Ueno, S. Takahashi, H. Nakata, A. Sudaryanto, A. Subramanian, S. Karuppiah, A. Ismail, M. Muchtar, J. Zheng, Mar. Pollut. Bull. 46 (2003) 281.
[25] P. Carvalho, P. Rodrigues, M. Basto, M. Vasconcelos, Chemosphere 75 (2009) 595.
[26] Y. Zi-wei, J. Gui-bin, X. Heng-zhen, Environ. Pollut. 116 (2002) 49.
[27] C. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[28] M. Guidotti, M. Vitali, Ann. Chim. 87 (1997) 497.

[29] J. Poerschmann, F.D. Kopinke, J. Pawliszyn, Environ. Sci. Technol. 31 (1997) 3629.
[30] E.U. Ramos, S.N. Meijer, W.H.J. Vaes, H.J.M. Verhaar, J.L.M. Hermens, Environ. Sci. Technol. 32 (1998) 3430.
[31] P. Mayer, W.H.J. Vaes, F. Wijnker, K. Legierse, R.H. Kraaij, J. Tolls, J.L.M. Hermens, Environ. Sci. Technol. 34 (2000) 5177.
[32] J.A. Koziel, J. Noah, J. Pawliszyn, Environ. Sci. Technol. 35 (2001) 1481.
[33] B.I. Escher, J.L.M. Hermens, Environ. Sci. Technol. 36 (2002) 4201.
[34] M. Carballa, F. Omil, J.M. Lema, M. Llompart, C. Garcia-Jares, I. Rodriguez, M. Gomez, T. Ternes, Water Res. 38 (2004) 2918.
[35] T. Gorecki, J. Pawliszyn, Field Anal. Chem. 1 (1998) 277.
[36] Y.Z. Tang, W.H. Schroeder, D. Mackay, Q. Tran, M. Chai, H. VanOoijen, Development and evaluation of sampling and analytical techniques for investigating air–water exchange of chemicals, in: Symposium on Chemistry and Fate of Modern Pesticides, Paris, France, 1995.
[37] A. Gerecke, C. Tixier, T. Bartels, R. Schwarzenbach, S. Müller, J. Chromatogr. A 930 (2001) 9.
[38] R. Barro, S. Ares, C. Garcia-Jares, M. Llompart, R. Cela, J. Chromatogr. A 1045 (2004) 189.
[39] T. Ryan, Modern Experimental Design, Wiley–Interscience, 2007.
[40] M.T. Tena, J.D. Carrillo, Trends Anal. Chem. 26 (2007) 206.
[41] D. Louch, S. Motlagh, J. Pawliszyn, Anal. Chem. 64 (1992) 1187.
[42] A. Penalver, E. Pocurull, F. Borrull, R.M. Marce, Trends Anal. Chem. 18 (1999) 557.
[43] G. Shukla, A. Kumar, M. Bhanti, P. Joseph, A. Taneja, Environ. Int. 32 (2006) 244.
[44] Q. Huang, J. Li, J. Zhao, R. Xu, L. Xie, Chin. J. Geochem. 25 (2006) 181.
[45] M. Asi, A. Hussain, S. Muhmood, Int. J. Environ. Res. 2 (2008) 43.
[46] E. Concha-Grana, M. Turnes-Carou, S. Muniategui-Lorenzo, P. Lopez-Mahia, D. Prada-Rodriguez, E. Fernandez-Fernandez, Chemosphere 64 (2006) 588.
[47] C.P. Rice, S.M. Chernyak, Organohalogen Compd. 24 (1995) 439.
[48] J. Altschuh, R. Bruggemann, H. Santl, G. Eichinger, O.G. Piringer, Chemosphere 39 (1999) 1871.