

## Distribution characteristics of organochlorine pesticide in the water environment in Lanzhou section of Yellow River

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**Abstract.** Surface water, surface sediments and suspended particles in the Lanzhou section of Yellow River were collected. After the samples were lyophilised, extracted, concentrated, purified and separated, organochlorine pesticides in the samples were analysed by GC-MS. Results showed that organochlorine pesticide contents in surface water, surface sediments and suspended particles ranged from 28.63 ng/L to 123.2 ng/L, from 0.86 ng/g to 4.51 ng/g and from 23.29 ng/g to 126.14 ng/g, respectively. HCHs, DDTs and HCB were high; among these contents, HCH contents ranged from 1.49 ng/L to 18.1 ng/L, from 0.04ng/g to 1.53 ng/g and from 2.74ng/g to 25.64 ng/g, respectively. DDT contents ranged from 1.49 ng/L to 18.1 ng/L, from 0.04 ng/g to 1.53 ng/g and from 2.74 ng/g to 25.64 ng/g, respectively. Component analysis results showed that organochlorine pesticide in the Lanzhou section of Yellow River was mainly from early residues or soil after pesticides were applied and long-term weathering occurred. Correlation analysis results showed that total organic carbon was an important factor affecting the distribution of organochlorine pesticide in sediments. Moderate organochlorine pesticide contents were detected in surface water in Lanzhou section of Yellow River compared with other rivers in our country and in other countries. Furthermore, the ecological risk of organochlorine pesticide in surface sediments was low.

### 1.Introduction

As the second longest river in China, Yellow River flows through nine provinces in North China with a length of 5,464km, a basin of 795,000 km<sup>2</sup> and average sediment concentration of 2.83 kg/m<sup>3</sup>. Yellow River is one of the most important water sources of industrial and agricultural applications, as well as human consumption[1]. The Lanzhou section of Yellow River belongs to the upstream of Yellow River with a length of 219.7 km. Although the Lanzhou section is a source of water supply for local urban residents, as well as for industrial and agricultural production, this section is a pollutiondischarge-concentrated area. Approximately 40 km of the river is located in Lanzhou City. As a consequence of concentrated industrial and mining enterprises, as well as dense population, the Lanzhou section of Yellow River receives a large amount of production and household wastewater, which becomes one of the main pollution sources of Yellow River. Wastewater contains a large number of persistent organic pollutants, including organochlorine pesticide[2].

Organochlorine pesticide is a refractory toxic organic pollutant with stable physicochemical properties. With hydrophilic lipophilicity, organochlorine pesticide penetrating the environment easily accumulates in sediments, thereby damaging the ecosystem[3,4]. As such, China has gradually



prohibited the use of organochlorine pesticide since 1983. However, organochlorine pesticide can still be detected in several environmental media because of low biodegradability[5].

Further research has been conducted regarding organochlorine pesticide in rivers, estuaries and coastal water, but no report has been presented regarding the distribution of organochlorine pesticide in the Lanzhou section of Yellow River. In this study, contents, components and distribution characteristics of organochlorine pesticide were investigated in surface water, suspended particles and surface sediments of the Lanzhou section of Yellow River; possible sources of these substances were also analysed. Furthermore, the pollution level of organochlorine pesticide in water environment was evaluated. This study aimed to provide a scientific basis for the treatment of organochlorine pesticide in Yellow River.

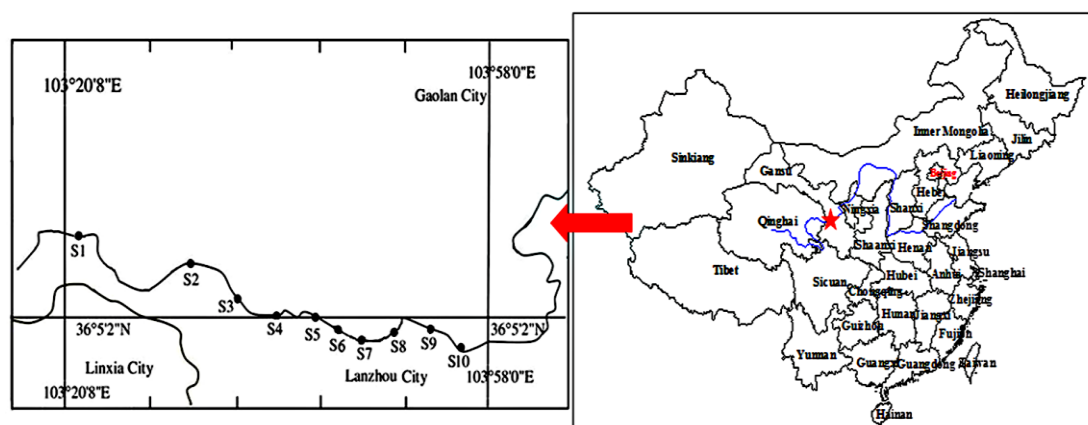
## 2. Materials and methods

### 2.1. Chemicals

The following chemicals were used: standard sample of organochlorine pesticide (Supelco Bellefonte, USA), *n*-hexane, dichloromethane, acetone (HPLC grade; J. T. Baker, USA), anhydrous sodium sulphate (heated at 450 °C for 8 h; Chenguang, Tianjin) and silica gel (heated at 150 °C for 4 h; Merck, USA).

### 2.2. Sample collection and study area

The samples were collected in October 2015. Sampling point distribution is shown in Fig.1 and latitudes and longitudes of the sampling points are listed in Table 1. Water sample (as surface water) was collected from 0.5 m below the surface and placed in 1 L sampling bottle. Surface sediment sample was collected using a grab sampler. Suspended particles were obtained by filtering a large volume of water sample through 0.45  $\mu\text{m}$  glass fibre filtration film[6]. After the sample was transported to the lab, surface water was stored at 4°C; surface sediments and suspended particles were stored at -20°C[7].



**Fig. 1** Spatial distributions of the 10 sampling sites in Lanzhou reach of the Yellow River in Northwest China

**Table 1** Description of sampling locations in detail

Station	Location					
S1	N36°	10'	10.6"	E103°	29'	07.8"
S2	N36°	08'	12.8"	E103°	36'	45.7"
S3	N36°	05'	58.9"	E103°	40'	39.1"
S4	N36°	05'	15.0"	E103°	43'	11.6"
S5	N36°	04'	57.7"	E103°	45'	56.5"
S6	N36°	04'	13.1"	E103°	47'	39.8"
S7	N36°	03'	47.9"	E103°	49'	08.4"

S8	N36°	04'	25.3"	E103°	51'	33.8"
S9	N36°	04'	07.3"	E103°	54'	10.4"
S10	N36°	03'	10.1"	E103°	56'	52.8"

### 2.3. Sample extraction

For surface water sampling, 1 L of water sample was placed in a separatory funnel and 30 mL of methylene chloride was added. The funnel was shaken for 2 min and left to stand to allow the mixture to separate into layers. The organic phase in the sublayer was dried with anhydrous sodium sulphate and then collected in a round-bottomed flask. This procedure was repeated twice. The extracting solutions were combined and purified through silica gel column chromatography. The solution was concentrated to 2 mL to 3 mL. n-Hexane (10 mL) was added to replace the solvent. The concentration of the solution was adjusted until the final volume was 1 mL. For surface sediment and suspended particle sampling, the samples were placed in a Soxhlet extractor. The mixture (200 mL) containing acetone and n-hexane with a volume ratio of 1:1 was added to the extractor and then subjected to extraction for 48 h. After extraction was completed, the extracted solution was purified by silica gel column chromatography; the concentration was adjusted to 2 mL to 3 mL. n-Hexane (10 mL) was added to replace the solvent. The concentration of the solution was further adjusted until the final volume reached 1 mL[8].

### 2.4. Analytical procedure

Samples were detected with an Agilent 6890N-5975B mass spectrometer coupled to a gas chromatograph. An HP-5MS capillary chromatograph column (60 m × 0.25 mm × 0.25 μm) was also used. The injection temperature was 250 °C with splitless injection mode. The flow rate of high-purity helium as carrier gas was 0.8 mL/min. The temperature of the transmission line was 280 °C. The temperature program of gas chromatography was set as follows: initial column temperature, 80 °C for 1 min; increase to 160 °C at a speed of 10 °C/min; increase to 250 °C at a speed of 2.0 °C/min; and final increase to 300 °C at a speed of 30.0 °C/min; temperature was then maintained at 300 °C for 5 min. No split injection of 2.0 μL was set for current flow. The temperature of ion source was 150 °C. The electron energy was 70 eV. The scanning quality scope was m/z 50–500[9,10]. The retention times of chromatogram peaks of standard samples were applied to qualitatively analyse organochlorine pesticide in actual samples[11].

The total organic carbon (TOC) of surface sediments was determined using a TOC-5000A analyser.

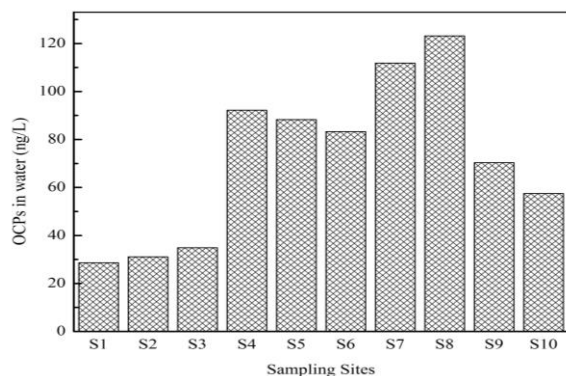
### 2.5. Quality control and assurance

The samples were monitored to determine recovery rate by using the following quality references and parameters: method blank, spike blank, duplicate and standard material; data were then corrected on the basis of recovery rate.

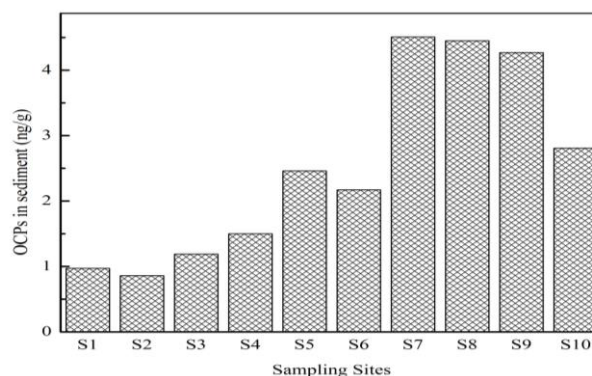
## 3. Results and discussion

### 3.1. Organochlorine Pesticide in Surface Water

Fig. 2 shows the total content distribution of organochlorine pesticide in surface water of 10 sampling points in the Lanzhou section of Yellow River. The organochlorine pesticide content ranged from 28.63 ng/L to 123.2 ng/L with an average of 72.13 ng/L. Furthermore, the maximum content was detected at S8 and the minimum content was found at S1 (Fig. 2). The organochlorine pesticide content at S4 to S8 was high possibly because these sections were close to the urban centre, where urban wastewater and industrial pollution were the main sources of high organochlorine pesticide contents.



**Fig.2** Concentration of OCPs in water in Lanzhou Reach of Yellow River



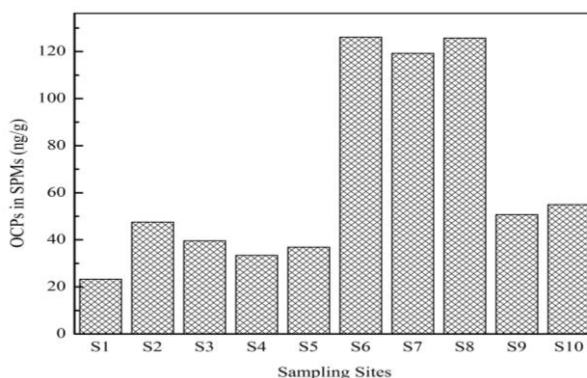
**Fig.3** Concentration of OCPs in sediment in Lanzhou Reach of Yellow River

### 3.2. Organochlorine Pesticide in Surface Sediments

Fig. 3 shows the total content distribution of organochlorine pesticide in surface sediments of 10 sampling points in the Lanzhou section of Yellow River. The organochlorine pesticide content ranged from 0.86 ng/L to 4.51 ng/L with an average of 2.52 ng/g. The maximum content was found at S7 and the minimum value was detected at S2. This result showed a gradual increasing trend from upstream to downstream. This observation occurred because a large amount of organochlorine pollutants flowed into Yellow River via industrial and urban wastewater.

### 3.3. Organochlorine Pesticide in Suspended Particles

Fig. 4 shows the total content distribution of organochlorine pesticide in suspended particles of 10 sampling points in the Lanzhou section of Yellow River. The organochlorine pesticide content ranged from 23.29 ng/L to 126.14 ng/L with an average of 65.76 ng/g. The maximum content was found at S6 and the minimum content was detected at S1. Overall, the content of organochlorine pesticide in suspended particles was similar to that in surface water but higher than that in surface sediments. This result was possible because suspended particles were characterised by a large surface area, high viscosity and high organic matter content; thus, organochlorine pesticide exhibits strong absorption ability[12].



**Fig.4** Concentration of OCPs in SPMs in Lanzhou Reach of Yellow River

### 3.4. Comparison of Organochlorine Pesticide in Yellow River with that in Other Rivers and Water Bodies

Table 2 lists the total HCH and DDT residues in surface water and surface sediments in the Lanzhou section of Yellow River were compared with those of other rivers in our country and in other countries. The HCH content in surface water in Yellow River was higher than that in Liao River but lower than that in Jiulong River; the HCH content in surface water in Yellow River was equal to that in Suzhou River. Likewise, the DDT content in surface water in Yellow River was higher than that in

Liao River but lower than that in Suzhou River and Jiulong River. HCH and DDT contents in rivers in our country were higher than those in rivers in other countries. The HCH content in surface sediments was lower than that in Parramata River, Kaveri River, Haihe River and Pearl River but almost equivalent to that in Huangpu River. Likewise, the DDT content was low. In general, organochlorine pesticide content in surface water in the Lanzhou section of Yellow River was moderate and that in surface sediments was low.

**Table 2** Comparisons of HCHs and DDTs in water and sediment from rivers in other areas

Medium	Location	HCHs	DDTs	Reference
Water (ng/L)	Ebro River, Spain	3.1	3.4	Fernandez et al. (1999)
	St. Lawrence River, Canada	0.06	0.9-22	Pham et al. (1993)
	Suzhou River, China	17-90	17-99	Hu et al. (2005)
	Liao River, China	7.6-31	0.1-4.2	Zhang et al. (2002)
	Jiulong River, China	32-130	19-97	Zhang et al. (2001)
	Lanzhou Reach of Yellow River, China	11-88	1.5-18	This study
Sediment (ng/g)	Parramata River, Australia	7.7	26	Iwata et al. (1994)
	Kaveri River, India	4.4-158	0.7-4.9	Rajen et al. (1999)
	Haihe River, China	7.8-11	9.5-12	Wu et al. (1999)
	Pearl River, China	1.4-3.8	2.2-5	Luo et al. (2005)
	Huangpu River, China	0.14-0.77	0.7-4.4	Hu et al. (2005)
	Lanzhou Reach of Yellow River, China	0.18-1.1	0.4-1.5	This study

### 3.5. Composition Characteristics of Organochlorine Pesticide

**3.5.1. Composition Characteristics of HCHs.** The HCH contents in surface water, surface sediments and suspended particles in the Lanzhou section of Yellow River ranged from 1.12 ng/L to 88.43 ng/L, from 0.18 ng/g to 1.1 ng/g and from 2.47 ng/g to 52.08 ng/g with averages of 42.55 ng/L, 0.54 and 20.26 ng/g, respectively. The average percentages of  $\alpha$ -HCH,  $\beta$ -HCH and  $\gamma$ -HCH in surface water were 40%, 27% and 33%, respectively. The average percentages of  $\alpha$ -HCH,  $\beta$ -HCH and  $\gamma$ -HCH in surface sediments were 14%, 46% and 40%, respectively. The average percentages of  $\alpha$ -HCH,  $\beta$ -HCH and  $\gamma$ -HCH in suspended particles were 5%, 19% and 76%, respectively. The ratios of  $\beta$ -HCH to  $\gamma$ -HCH at most sampling points of surface water were  $\leq 1$ ; by contrast, the ratios of all sampling points of suspended particles were  $< 1$ , indicating the presence of a new pollutant in the Lanzhou section of Yellow River or the application of lindane pesticide [13]. The ratios of  $\beta$ -HCH to  $\gamma$ -HCH in surface sediments were mostly between 1 and 2, indicating that HCHs in surface sediments was mainly from the residues of organochlorine pesticide after these substances undergo long-term degradation and lindane pesticide is applied [14]. The distribution characteristics of HCHs in surface water, surface sediments and suspended particles were compared. Our results showed that  $\alpha$ -HCH content in surface water was higher than that in surface sediments and suspended particles; likewise,  $\beta$ -HCH content in surface sediments was higher than that in surface water and suspended particles. Furthermore,  $\gamma$ -HCH content was the highest in suspended particles. This condition was observed because  $\alpha$ -HCH is highly volatile and easily present in water phase;  $\beta$ -HCH attaches to and accumulates in surface sediments with stable properties;  $\gamma$ -HCH easily attaches to microporous structures of suspended particles [15, 16].

**3.5.2. Component Characteristics of DDTs.** The DDT contents in surface water, surface sediments and suspended particles in the Lanzhou section of Yellow River ranged from 1.49 ng/L to 18.1 ng/L, from 0.04 ng/g to 1.53 ng/g and from 2.74 ng/g to 25.64 ng/g with averages of 6.38 ng/L, 0.7 ng/g and 14.33 ng/g, respectively. Under anaerobic condition, DDT is mainly degraded into DDD; under aerobic condition, DDT is mainly degraded into DDE. Therefore, DDT content is likely maintained at



a high level if DDT is continuously applied; without additional DDT, DDT content is possibly reduced, but the corresponding degradation product is likely increased in a continuous pattern. Thus, the ratios of DDT to DDD + DDE and DDD to DDE can be used to determine whether new DDT input is added and to trace the degrading environment of DDTs. At a DDT-to-DDD + DDE ratio of  $<2$ , early residues or long-term weathering residues are retained after pesticides are applied [17-19]. Table 3 shows the ratios of DDT to DDD + DDE of all sampling points in surface water and surface sediments. All of the ratios were  $<2$ , indicating that DDTs were mainly obtained from early residues or long-term weathering residues after pesticides were applied and no new DDTs were added. At the same time, the ratios of DDD to DDE in surface sediments were mostly  $<1$  and DDE was the main degradation product; this result indicated that DDTs in surface sediments underwent aerobic biodegradation, which was related to a large flow and great flow disturbance in this area.

**Table 3** The ratios of DDT / (DDD + DDE) in each sampling point of water and surface sediments

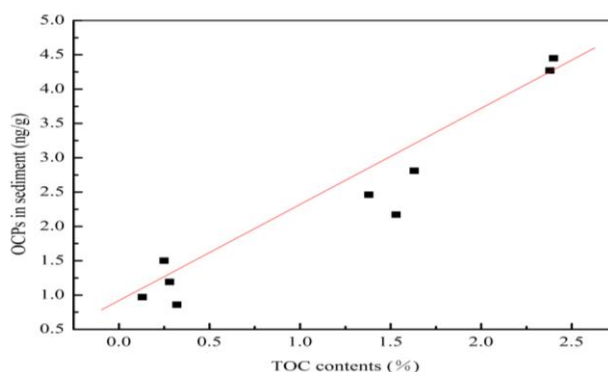
Locations	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
water	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$
sediment	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$	$<2$

**3.5.3. Ecological Risk Assessment on Organochlorine Pesticide.** No unified pollution assessment standard has been developed for the risk assessment of organic pollution. Long et al. [20] proposed the use of ERL and ERM to evaluate the risk degree of organic pollution in surface sediments. If pollutant concentration was smaller than ERL, negative ecological effects were rarely produced; if pollutant concentration was between ERL and ERM, negative ecological effects were occasionally produced; if pollutant concentration was greater than ERL, negative ecological effects were often produced. Based on the risk assessment value of surface sediments, the ecological risk of OCPs in surface sediments in the Lanzhou section of Yellow River was assessed (Table 4). The OCP contents at all sampling points were less than ERL, indicating that OCPs exhibited low risk in surface sediments in the Lanzhou section of Yellow River.

**Table 4** Effect range low (ERL) and effect range median (ERM) guideline values for OCPs in sediment

	ERL (ng/g)	ERM (ng/g)	Sites number		
			$<ERL$	ERL-ERM	$>ERM$
DDT	1	7	10	0	0
DDD	2	20	10	0	0
DDE	2.2	27	10	0	0
DDTs	1.58	46.1	10	0	0

**3.5.4. Correlation between Organochlorine Pesticide and TOC in Surface Sediments.** Fig. 5 shows the correlation between organochlorine pesticide content and TOC in surface sediments. Organochlorine pesticide content was significantly correlated with TOC in surface sediments ( $p = 0.05$ ); this result indicated that TOC was an important factor affecting organochlorine pesticide distribution in surface sediments. TOC corresponded to organic matter content in sediments. Organic matter content influences organochlorine pesticide in two mechanisms. On the one hand, organochlorine pesticide strongly affects the concentration of organic matter because of its low water solubility and high fat solubility; on the other hand, organic matter indicated high microbial content, which elicit biodegradation effects on organochlorine pesticide [21].



**Fig.5** Relation between concentrations of total OCPs and TOC contents in sediment in the Yellow River of Lanzhou

#### 4. Conclusions

In this study, organochlorine pesticide was analysed in surface water, surface sediments and suspended particles in the Lanzhou section of Yellow River. Based on the results, our conclusions are listed as follows: 1) Organochlorine pesticide content in surface water, surface sediments and suspended particles ranged from 28.63 ng/L to 123.2 ng/L, from 0.86 ng/g to 4.51 ng/g and from 23.29 ng/g to 126.14 ng/g with averages of 72.13 ng/L, 2.52 ng/g and 65.76 ng/g, respectively; HCH and DDT contents were high. 2)  $\alpha$ -HCH and  $\gamma$ -HCH were mainly present in surface sediments and suspended particles, respectively. The ratios of  $\beta$ -HCH to  $\gamma$ -HCH at most sampling points indicated that HCHs in the Lanzhou section of Yellow River were mainly residues of long-term organochlorine pesticide degradation and lindane pesticide application. 3) DDTs in the Lanzhou section of Yellow River were mainly from early residues or long-term weathering residues after pesticides were applied; DDTs in surface sediments were mainly produced by aerobic biodegradation. 4) Organochlorine pesticide content in surface water in the Lanzhou section of Yellow River was moderate compared with that in other rivers in our country and in other countries; organochlorine pesticide content in surface sediments was low, indicating an overall low ecological risk. 5) Organochlorine pesticide content in surface sediments was closely correlated with TOC. TOC was an important factor affecting organochlorine pesticide distribution in surface sediments.

#### Acknowledgment

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#### References

- [1] Gao H, Bao W Y, Zhang S G. Research on pollution chemistry and ecotoxicology in high sand content rivers. The Yellow River Water Conservancy Publisher, Zhengzhou, in Chinese, 2001.
- [2] Chen J, He D, Zhang N. Characteristics of and human influences on nitrogen contamination in Yellow River system, China, Environmental Monitoring and Assessment. 2004, 93: 125-138.
- [3] Szlinder-Richert J, Barska I, Mazerski J. Organochlorine pesticides in fish from the southern Baltic Sea: levels, bioaccumulation features and temporal trends during the 1995-2006 period, Marine Pollution Bulletin. 2008, 56: 927-940.
- [4] Zhang L F, Dong L, Shi S X. Organochlorine pesticides contamination in surface soils from two pesticide factories in Southeast China, Chemosphere 2009, 77: 628-633.
- [5] Wang F, Jiang X, Bian Y R. Organochlorine pesticides in soils under different land usage in the Taihu Lake region, Journal of Environmental Sciences-China, 2007, 19: 584-590.
- [6] Zhang L F, Dong L, Ren L J. Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, Journal of

- Environmental Sciences-China, 2012, 24: 335-342.
- [7] Montone R C, Taniguchi S, Weber R R. Polychlorinated biphenyls in marine sediments of Admiralty Bay, King George Island, Antarctica, *Marine Pollution Bulletin*, 2001, 42: 611-614.
- [8] Hu L M, Zhang G, Zheng B H. Occurrence and distribution of organochlorine pesticides (OCPs) in surface sediments of the Bohai Sea, China, *Chemosphere* 2009, 77(5): 663-672.
- [9] Li H P, Li G C, Jen J F. Determination of organochlorine pesticides in water using microwave assisted headspace solid-phase microextraction and gas chromatography, *Journal of Chromatography A*, 2003, 1012: 129-137.
- [9] Na T, Fang Z. The status of pesticide residues in the drinking water sources in Meiliangwan Bay, Taihu Lake of China, *Environmental Monitoring and Assessment*, 2006, 123: 351-370.
- [11] Vagi M C, Petsas A S. Determination of organochlorine pesticides in marine sediments samples using ultrasonic solvent extraction followed by GC/ECD, *Desalination* 2007, 210: 146-156.
- [12] Willett K L, Ulrich E M, Hites R A. Differential toxicity and environmental fates of hexachlorocyclohexane isomers, *Environmental Science and Technology*. 1998, 32: 2197-2207.
- [13] Carvalho P N, Rodrigues P N, Basto M C, Vasconcelos M T. Organochlorine pesticides levels in Portuguese coastal areas, *Chemosphere* 2009, 75: 595-600.
- [14] Yang H, Xue B, Yu P. Residues and enantiomeric profiling of organochlorine pesticides in sediments from Yueqing Bay and Sanmen Bay, East China Sea, *Chemosphere* 2010, 80: 652-659.
- [15] Walker K. Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment, *Environmental Science and Technology*. 1999, 33: 4373-4378.
- [16] Willett K L, Ulrich E M, Hites R A. Differential toxicity and environmental fates of hexachlorocyclohexane isomers, *Environmental Science and Technology*. 1998, 32: 2197-2207.
- [17] Mohn W M. Microbial reductive dechlorination, *Fems Microbiology Reviews* 1992, 56: 482-507.
- [18] Tan L, He M, Men B, Lin C. Distribution and sources of organochlorine pesticides in water and sediments from Daliao River estuary of Liaodong Bay, Bohai Sea (China), *Estuarine, Coastal and Shelf Science*. 2009, 84: 119-127.
- [19] Mohammed A, Peterman P, Echols K. Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in harbor sediments from Sea Lots, Port-of-Spain, Trinidad and Tobago, *Marine Pollution Bulletin* 2011, 62: 1324-1332.
- [20] Long E R, MacDonald D, S. L. Smith S L, Calder F D. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, *Journal of Environmental Management*. 1995, 19: 81-97.
- [21] Lee K T, Tanabe S, Koh C K H. Distribution of organochlorine pesticides in sediments from Kyeonggi Bay and nearby areas, Korea, *Environmental Pollution* 2001, 114: 207-213.