

Original Research

Historical Records and Source Apportionment of Organochlorine Pesticides (OCPs) in a Sediment Core from Songhua Lake, Northeast China

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Abstract

Organochlorine pesticides (OCPs) were quantified in a sediment core from Songhua Lake, a large artificial lake in Northeast China, to investigate their historical deposition behaviors and reconstruct their use history. The total OCPs concentrations ranged from 17.74 to 411.86 ng/g. Dichlorodiphenyltrichloroethane (DDTs) and hexachlorocyclohexanes (HCHs) were recorded as the dominant components. Historically, OCPs contaminations input were significant during the 1950s with also certainly deposition input in the mid-1960s and 1990s corresponding with historically intense anthropogenic activities with the development of industry and agriculture in the watershed. DDTs records showed that the deposition environment in Songhua Lake was inclined to the aerobic environment before the 1960s and after the mid-1980s. Principal component analysis (PCA) combined with the diagnostic ratios of OCPs and their metabolites indicated DDTs contamination was due to the input of industrial DDT, and HCHs pollution was from the mixture input of industrial HCHs and lindane source. The data analysis from sediment quality guidelines (SQGs) indicated that the ecological risk can be induced by the presence of DDTs, Lindane, and Dieldrin, which posed an adverse toxic ecological threat to benthic and aquatic organisms of relative regions and need to be taken seriously and managed.

Keywords: organochlorine pesticides (OCPs), sediment core, principal component analysis (PCA), Songhua Lake

Introduction

Organochlorine pesticides (OCPs) are a synthetic group of persistent harmful chemicals with highly toxic, refractory, long-distance migration and bioaccumulation and are extremely harmful to organisms [1]. They can accumulate in organisms through the process of the food chain and produce carcinogenic, teratogenic, and mutagenic effects on humans and wildlife [2]. The international community had recognized OCPs as the environmental priority control pollutants since the 1850s [3]. Among the 22 persistent organic pollutants (POPs), which were listed in the annexes of the convention targeted by the Stockholm Convention since 2004, there were as many as 15 OCPs [4]. OCPs are highly hydrophobic and lipophilic compounds. Entering the aquatic environment through dry and wet atmospheric deposition, attached to soil particles in water runoffs, or by wastewaters, they have a strong tendency to absorb suspended particulate matter and accumulate in aquatic (marine, river, lake) sediments as one of their main sinks [5]. Furthermore, they will be released to the water body again through the resuspension of sediments and the adsorption-desorption between water and sediment interface, resulting in secondary pollution [6]. Sediment core is an important information carrier in the field of environmental geochemistry, which can preserve a lot of environmental information in the past period [7]. Accordingly, the profile and mass fractions of persistent organochlorine pollutants preserved in layers of undisturbed lake sediment cores provide a historical record of pollutant input and enable one to track the long-term changes of environmental contamination [8].

Songhua Lake was located at the upper part of the second Songhua River, which is 24 km southeast of Jilin city, northeast China. The lake exhibits a long and narrow shape, with a total area of 550 km². The maximum width and depth of the lake reach 10 km and 75 m, respectively, and the mean depth varied from 30 to 40 m [9]. The Lake basin is an important agricultural production base in Jilin province, which involves power generation, flood control, irrigation,

aquaculture, and tourism. In the 30 years from 1952 to 1982 (the production and use of OCPs have been completely banned since 1983), the cumulative use of pesticides in Jilin Province was 284895 tons, with an average of 9496.5 tons per year. OCPs account for about 60% of the pesticides applied in these years [10]. These OCP compounds may enter the aquatic ecosystem through effluent release, atmospheric deposition, soil erosion, and surface runoff. Some previous studies on Songhua Lake mainly focused on the zooplankton community structure and water quality evaluation, including the occurrence and distribution of nutrients and toxic metals [9]. Yin et al. (2020) analyzed the sedimentary evolution history of n-alkanes in Songhua Lake sediments and draw a high concentration of n-alkanes, needing to be taken seriously and protected [11]. However, to the best of our knowledge, the study on the persistent organochlorine contaminants sedimentary evolution history in Songhua Lake is scarce.

Songhua Lake presents a sedimentation history of nearly 70 years as the Fengman hydropower station was completed in 1943. Over 60 cm thick of sediments were accumulated at the bottom of the lake and these undisturbed lake sediments may preserve the complete historical records for POPs inputs and their possible sources and enable one to track the long-term changes of environment contaminations [12]. Therefore, the objectives of the present study were to obtain a chronological overview of the contamination situation in respect of persistent OCPs vertical profiles from a dated sediment core, evaluate their potential ecological risks, and explore their possible sources for reconstructing the deposition and input history of OCPs in Songhua Lake basin and providing a scientific basis for the further environmental study and remediation of Songhua Lake.

Material and Methods

Sample Collection

The sediment core was collected at the water depth of approximate 10 m with a manual PVC tubular

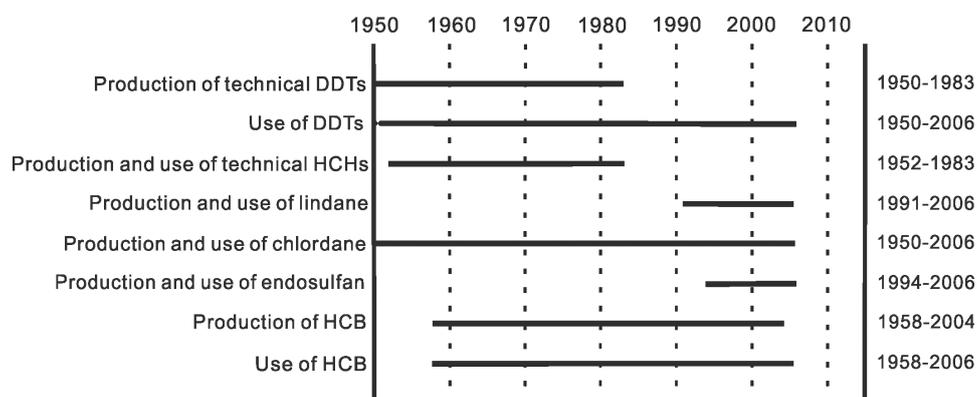


Fig. 1. Production and application history of individual OCPs in China (modified after reference [6])

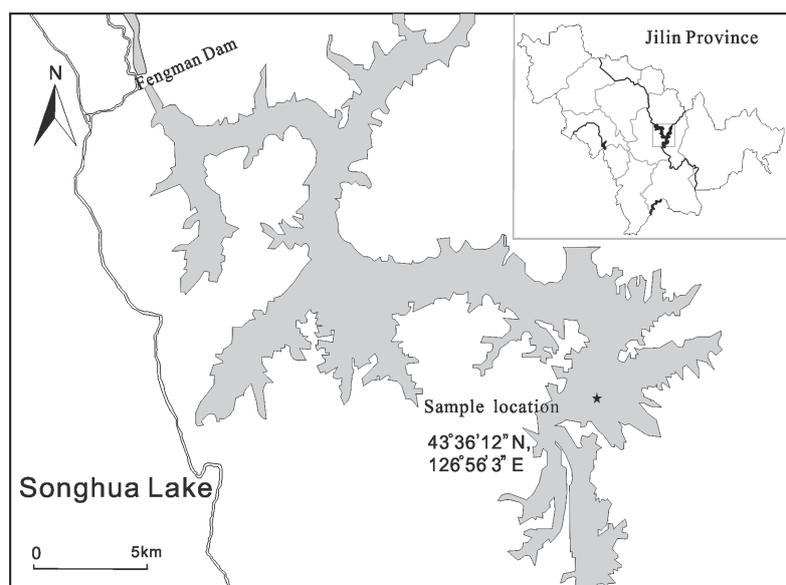


Fig. 2. Map of Songhua Lake in Jilin Province showing the sampling site of the sediment core (modified after reference [11]).

sampler in the southern Songhua Lake ($43^{\circ}36'12''\text{N}$, $126^{\circ}56'3''\text{E}$) on December 20, 2006 (Fig. 2). The sampling site was stable without the strong disturbance in the upper layer of the sediment core and the natural sedimentary characteristics were well preserved. The 65 cm-long sediment core consisted of a natural sedimentary sequence composed of silty clay throughout the upper 61 cm and weathered granite beyond 61 cm. The columnar sample 65 cm in length was divided into 33 subsamples (each 2 cm in length), the measured concentration of OCPs in each subsample represented a mean concentration of which historical time window. All samples were sealed and frozen immediately after collection until the laboratory analysis.

Dating of the Sedimentary Core

Radioactive isotope ^{137}Cs has been widely applied in the lake, estuarine and coastal sediments dating, which can provide a chronological basic for studying the lake sediment environment evolution. In the previous study, we had used the specific distribution characteristics of artificial nuclide ^{137}Cs to date this sediment core [9]. Results showed that there were three obvious ^{137}Cs accumulation peaks in the lake sediment core: the accumulation peak of 1964 at 37 cm, the 1971 peak at 27cm, and the 1975 peak at 23 cm, respectively. This study used the three confirmed accumulation peaks as the chronological time scales. Combining with the top of the sediment core of 2006 at 1cm and the dam impoundment time of 1943 at 61 cm, the sedimentation time was divided into four sections according to the five dating scales. Then the sedimentary years in each time section were achieved by linear interpolation.

Sample Pretreatment

OCPs in the sediment samples were pretreated according to the method described in the previous studies [11]. In brief, each sample was ground with the agate mortar, sieved through a 100-mesh sieve after freeze-drying, and weighted 30 g samples with 30 mL extractant of dichloromethane/methanol (93:7, v/v) into the Erlenmeyer flasks. Then, the mixture was extracted 3 times by an ultrasonic extractor, with 10 minutes for each time, and left overnight. Combined with anhydrous sodium sulfate and filtered for water removal, the extracts were concentrated to approximately 1 mL with a low-temperature vacuum rotary evaporator and purified via chromatography columns (1.5 cm inner diameter, 10 cm length, picked with chromatographic silica gel), eluent with n-hexane. Chromatography solutions were collected and constant volume with n-hexane to 2 mL for determination.

Analysis Determination and Quality Control

OCPs were qualitative and quantitative analyzed using Clarus 580/680 gas chromatograph -SQ8 mass spectrometry (ClarusSQ8 GC-MS, PerkinElmer, USA), equipped with a DB-5 elastic quartz capillary column ($30\text{m}\times 0.25\text{mm}\times 0.25\ \mu\text{m}$), using ultrapure helium (>99.999% pure) as the carrier gas. The sample extracts (each 1.0 μL) were injected in the splitless mode. The temperature at the SPL injector and Electron multiplier detector were 300°C and 320°C , respectively. The oven temperature programming was set to start at 50°C , holding for 3 min, increased to 300°C at a heating rate of $12^{\circ}\text{C}/\text{min}$, and holding to 45min. All laboratory materials, reagents, and glassware were purified for reducing background cross-contamination. The target

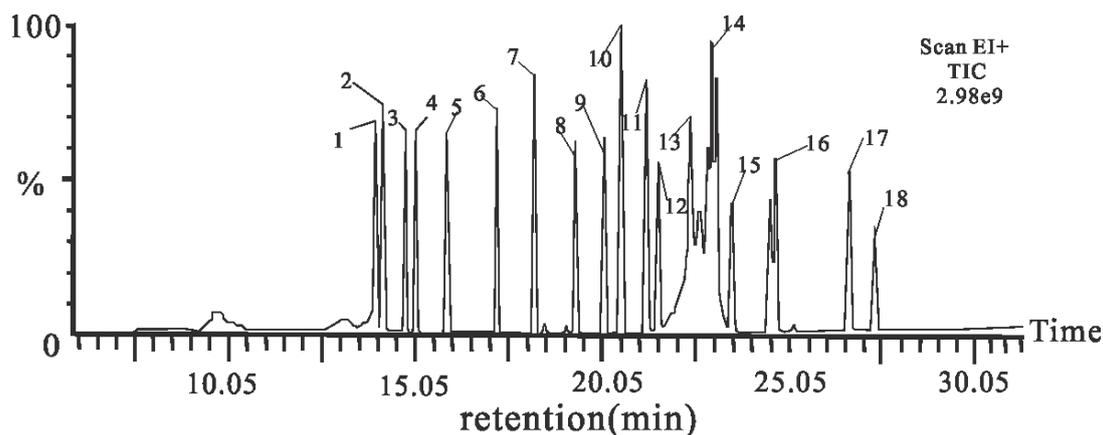


Fig. 3. The chromatogram of OCPs in standard solution: 1. α -HCH; 2. Hexachlorobenzene (HCB); 3. β -HCH; 4. γ -HCH; 5. δ -HCH; 6. Heptachlor; 7. Aldrin; 8. Heptachlor epoxide; 9. γ -Chlordane; 10. α -Endosulfan; 11. α -Chlordane; 12. p,p'-DDE; 13. Dieldrin; 14. Endrin; 15. β -Endosulfan; 16. p,p'-DDD; 17. o,p'-DDT; 18. p,p'-DDT.

compounds were identified based on their GC retention times and mass spectra. The quantitative results were determined using a suite of external standard mixture solutions containing 18 OCPs (Accustandard, USA). The chromatogram of the diluted standard solution of 18 OCPs standards is shown in Fig. 3.

Strict quality control procedures were applied to monitor the validity of data. The calculated calibration curves coefficient showed high-level linearity for all target analytes. Method detection limits (MDLs) for individual OCPs ranged from 0.04 to 0.20 ng/g, as described in detail in Table 1. Dibutylchloroendate was used as the surrogate standard, whereas pentachloronitrobenzene was used as the syringe standard to monitor the sensitivity and fluctuations of the FID detector. The recoveries of surrogate spiked in blank and matrix samples ranged from 90.25% to 110.49%. The standard deviation of individual OCPs in random duplicate samples was much lower than 35% ($SD < 35\%$). The analysis results of blank samples showed no or below the detection limit, peaks for the target analytes, which eliminated the possibility of cross-contamination from the field and glassware used [13].

Data Analyses Method

Principal component analysis (PCA) as a multivariate statistical method has been widely applied in environmental studies for identifying possible sources and degradation behavior of OCPs [14]. It is used to reduce a set of original variables and to extract a small number of latent factors for analyzing relationships among the observed variables [15]. For analyzing the correlation of individual OCPs, investigating their pattern distribution and degradation behavior, a 31×14 -correlation matrix was established without considering the low detection rate variables including Aldrin, γ -Chlordane, Heptachlor, and Heptachlor epoxide. Descriptive statistics and PCA were performed using IBM SPSS statistics 21.0, and data graphical plots

were conducted using Origin 8.0. Analysis data below the detection limit was set as half of the detection limits for statistics and analysis purposes.

Results and Discussion

Concentrations of OCPs in Sediment Core Samples

The results of 18 target OCP compounds in the sediment core of Songhua Lake are listed in Table 1, the average detection rate ranged from 58 to 100%. Based on the dry weight, the concentrations of total OCPs (Σ OCPs) in Songhua Lake sediment varied from 17.74 to 411.86 ng/g, average at 86.62 ng/g, which was higher than those exhibited in surface sediments of the Songhua mainstream in the north of Jilin city [16]. For individual OCPs, DDTs (including p,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT) and HCHs (including α -HCH, β -HCH, γ -HCH, δ -HCH) recorded the highest mean concentrations of 31.08 ng/g and 28.95 ng/g, respectively, followed by Σ DRINs (including Aldrin, Dieldrin, Endrin) and HCB with the average levels of 11.27 ng/g and 5.74 ng/g, the concentrations of Σ ENDs (including α -Endosulfan, β -Endosulfan) and Σ CHLOs (including α -Chlordane, γ -Chlordane, Heptachlor, Heptachlor epoxide) at 5.40 ng/g and 4.19 ng/g was the least in the sediment core of Songhua Lake. The high concentrations of DDTs and HCHs were detected in the sediment core, corresponding to the extensive use of DDTs and HCHs (the cumulative application amount reached 0.5 million tons) from the 1950s to 1983 in China [17]. Compared with other representative watersheds worldwide (Table 2), the concentrations of OCPs observed in the present study were higher than that deposited in some inland lakes in areas less affected by industrial and agricultural emissions, including Dianchi Lake and YamzhoYumco Lake, China, Plitvice Lakes, Croatia and Lake Brêt,

Switzerland. Compared to some open or semi-enclosed bays such as Gulf of Batabanó, Cuba, Venice Lagoon, Italy, Cua Dai Estuary, Vietnam, and Gwangyang Bay, Korea, St Lawrence Estuary, Canada, Narragansett Bay, USA, the input of OCPs in Songhua Lake was higher. This may be relevant to the relatively closed and stable lake basin as the barrier of the dam negatively reflected on the flow velocity after impoundment in Songhua Lake. While when it comes to compared with the large agricultural watershed in France and Germany, the OCPs residues in the sediment core of Songhua Lake were lower. This comparison further demonstrates that agricultural activities are still the key factor affecting OCPs residues in lake basins.

Temporal Trends of OCPs in Sediment Core Samples

Sediment core is an effective tool to evaluate and reconstruct the historical records of environmental pollutant input [12]. Lake sediment is the sink of a variety of organic pollutants, which can be used as the natural archives of past environmental conditions and may evaluate the impact of human activities on ecosystems. The specific evolution records of total and individual OCPs were exhibited in Fig. 4. There were four obvious accumulate peaks for Σ OCPs (Fig. 4a) during the deposition history of Songhua Lake. The first and second maximum peak concentrations

Table 1. Concentrations (ng/g, dry weight) of organochlorine pesticides (OCPs) in the sediment core samples of Songhua Lake, NE China

Compounds	Statistical parameters (ng/g)				CV ^c	DR ^d	MDL ^e (ng/g)	Correlation coefficient
	Min	Max	Mean	SD ^b				
α -HCH	N.D. ^a	57.27	5.80	13.77	1.71	82%	0.06	0.9991
β -HCH	N.D.	177.01	12.13	43.01	2.51	82%	0.06	0.9993
γ -HCH	N.D.	65.72	5.38	9.72	2.41	61%	0.06	0.9993
δ -HCH	N.D.	31.02	5.67	6.86	1.47	79%	0.06	0.9993
p,p'-DDE	1.22	22.27	6.20	3.68	0.82	100%	0.20	0.9982
p,p'-DDD	N.D.	48.65	7.49	11.5	1.17	97%	0.06	0.9986
o,p'-DDT	N.D.	20.91	3.16	1.12	1.34	82%	0.10	0.9985
p,p'-DDT	N.D.	151.22	14.24	36.66	1.89	82%	0.06	0.9949
Aldrin	N.D.	2.02	0.30	0.47	1.64	27%	0.10	0.9990
Dieldrin	N.D.	14.19	1.88	3.23	1.48	61%	0.04	0.9994
Endrin	N.D.	123.36	9.13	28.97	2.34	61%	0.08	0.9999
α -Endosulfan	N.D.	14.37	1.85	3.26	1.59	58%	0.08	0.9999
β -Endosulfan	N.D.	28.64	3.57	5.11	1.78	76%	0.06	0.9892
α -Chlordane	N.D.	19.3	3.06	2.26	1.63	94%	0.06	0.9960
γ -Chlordane	N.D.	1.71	0.17	0.04	2.25	15%	0.06	0.9999
Heptachlor	N.D.	9.67	0.57	0.14	3.81	9%	0.04	0.9982
Heptachlor epoxide	N.D.	6.28	0.45	1.62	2.86	15%	0.06	0.9988
Σ DDTs	2.99	215.28	31.08	37.9	1.22	90%	-	
Σ HCHs	N.D.	303.35	28.95	52.06	1.80	76%	-	
Σ DRINs	N.D.	137.55	11.27	23.68	2.10	50%	-	
HCB	0.04	36.54	5.74	9.07	1.58	91%	0.08	
Σ ENDs	N.D.	36.38	5.4	8.01	1.48	67%	-	
Σ CHLOs	N.D.	27.04	4.19	6.5	1.55	13%	-	
Σ OCPs	17.74	411.86	86.62	89.17	1.02	65%	-	

^aN.D.: not detected; ^bSD: standard Deviation; ^cCV: coefficient of variation; ^dDR: detection rate; ^eMDL: method detection limit, they were experimentally calculated as 3.143σ , where σ is the standard deviation of the response of 7 parallel analyses for the blank sample (quartz sand) containing the standard solution of 20 ng/g.

Table 2. Comparisons of OCPs concentrations (ng/g dry weight) in sediments from worldwide watersheds.

Sampling location	Concentration (range and mean (in parenthesis))			Reference
	OCPs	DDTs	HCHs	
Songhua Lake, China	17.74-411.86 (86.62)	2.99-215.28 (31.08)	N.D.-303.35 (28.95)	This study
Dianchi Lake, China	-	0.90-53.50	-	[37]
Yamzho Yumco Lake, China	-	0.14-1.05	0.01-0.38	[38]
Plitvice Lakes, Croatia	2.72-5.85	2.47-5.72	-	[39]
Lake Brêt, Switzerland	-	0.54-8.90	-	[8]
Gulf of Batabanó, Cuba	-	0.029-0.374	<0.006-0.05	[7]
Venice Lagoon, Italy	0.02-7.0 (0.665)	-	-	[40]
Cua Dai Estuary, Vietnam	-	0.7-3.7 (1.9)	0.9-3.2 (1.8)	[41]
Gwangyang Bay, Korea	0.13-0.27	-	-	[42]
St Lawrence Estuary, Canada	N.D.-6.0	-	-	[43]
Narrangasett Bay, USA	N.D.-10.0	-	-	[44]
Zayandehrud River, Iran	1.9-50.1 (15.7)	0.1-47.2	N.D.-12.5	[45]
Agricultural watershed, France	-	N.D.-90	90-1190 (380)	[46]
River Elbe, Germany	-	<5-3680	<2-475	[47]

-: not available

(411.86 ng/g and 375.10 ng/g) occurred in 1949 and 1953, respectively, corresponding to the large-scale production and use period of OCPs in the agricultural field in the early 1950s in China for controlling the pests and satisfying the increasing demands of the growing population for high food yields [18]. The first aggregation peak of Σ OCPs in 1949 was mainly caused by the sedimentary input of HCHs and HCB. The second aggregation peak of Σ OCPs in 1953 was mainly caused by the sedimentary input of the remaining four OCPs including DDTs, DRINs, ENDS, and CHLOs. Then the third and fourth peaks appeared in the mid-1960s and 1990s, suggesting that OCPs were used on a certain scale and transformed into Songhua Lake water bodies during the development process of agricultural production activities in the Songhua Lake basin in this period. OCPs can deposit into the water body through soil erosion, sediment transfer, and atmospheric deposition. Their yield and dosage, land development and application, and flood may affect the concentration of OCPs in the sediment core. It is recorded that the annual sediment amount of Songhua lake was 465000 m³ before 1958, while it increased to more than 30 million m³ in 1969 as the serious soil erosion in the basin [19]. Such a large amount of silting input could transport considerable OCPs and eventually load them on the lake bed causing the increase of OCPs concentration during this period.

Composition and Sources of OCPs in the Sediment Core

For OCPs, HCHs and DDTs made up the largest proportions of OCPs in the sediment core of Songhua Lake. Composition differences of HCH isomers or DDT and Chlordane congeners in the environment could reveal their different pollution sources [20]. HCHs in the environment mainly come from the use of industrial technical HCHs and lindane preparations. Typical technical HCHs contains α -HCH (60-70%), β -HCH (5-12%), γ -HCH (10-15%), and δ -HCH (6-10%) and some other HCHs isomers (3-4%), while γ -HCH is above 99% in lindane [21]. The environmental fates of the four HCH isomers were different as their different configurations and physicochemical properties, such as the stability of them is in the order of β -HCH > δ -HCH > α -HCH > γ -HCH [22]. In the natural environment, γ -HCH and α -HCH can be transformed into β -HCH under microbial decomposition and photosynthesis [23]. Therefore, if there is no fresh input of industrial HCH, β -HCH should be the main component of HCH in sediment samples. The composition pattern of HCHs in the sediment core of Songhua Lake was shown in Fig. 5(a), β -HCH was the predominant compound of HCHs in most sedimentary layers which indicated that there is no new HCHs contamination input. From 1980 to 2006, the concentration of δ -HCH increased significantly while that of γ -HCH approached 0, which may indicate that HCHs contaminants mainly derived from industrial technical HCH without the agricultural lindane after 1980 in Songhua Lake. The composition

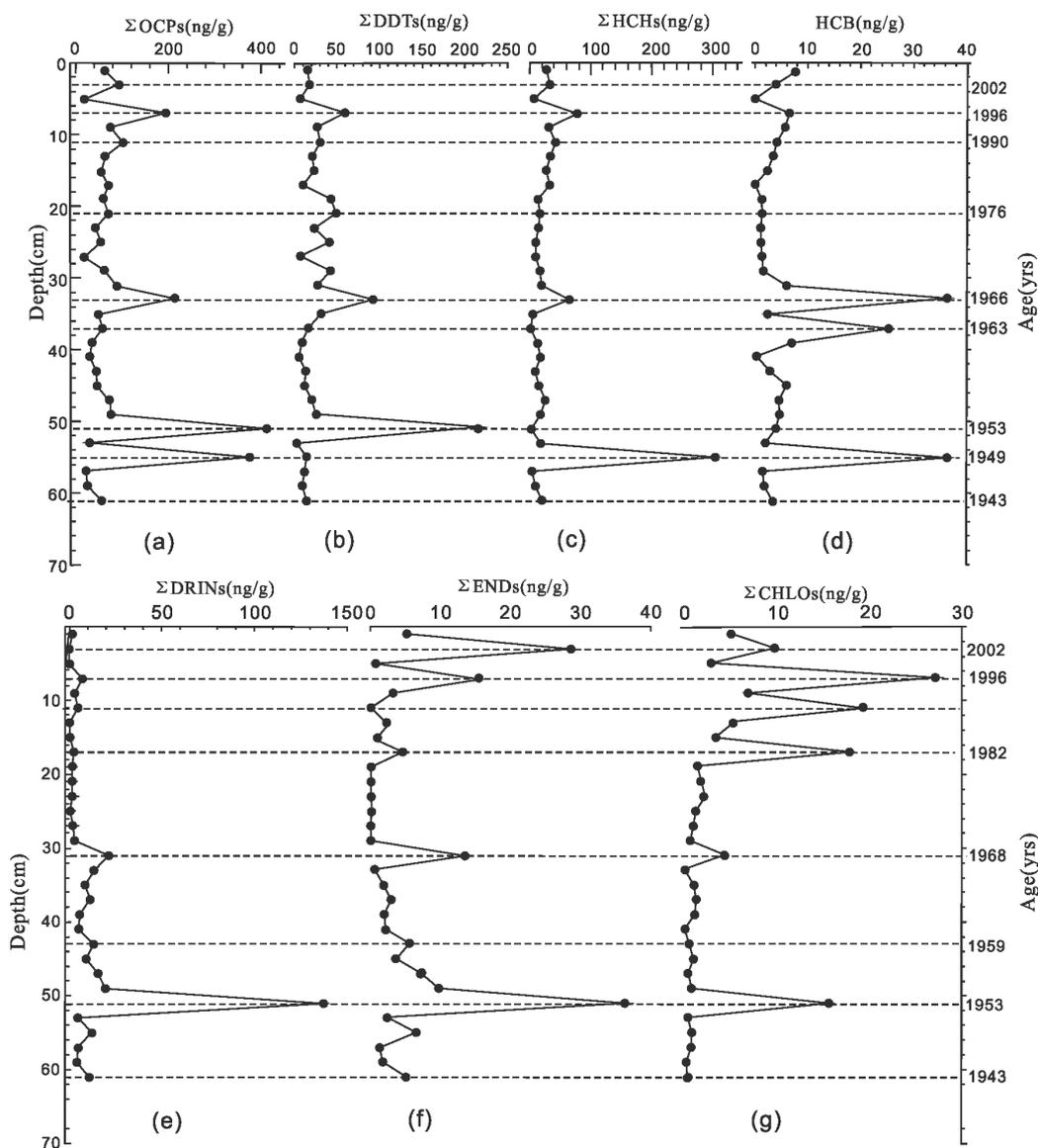


Fig. 4. Vertical distribution of organochlorine pesticides in the sediment core of Songhua Lake.

of HCH isomers can also identify the contamination sources. Generally, the ratio of α -HCH/ γ -HCH in the sediment samples ranged from 3 to 7 suggests the source of industrial HCH, while a lower ratio below 1 indicates lindane applications, and the ratio close to 0 suggests fresh input of lindane recently [24]. The values of α -HCH/ γ -HCH in the sediment core of Songhua Lake ranged from 0.35 to 2.24 (Fig. 5b), indicating that lindane is the main source of HCHs pesticides in the history of the Songhua Lake basin. While the ratio of α -HCH/ γ -HCH in the sample of 51 cm (1953) was much greater than 7, suggesting that the industrial HCHs have been used on a large scale in the Songhua lake basin and eventually entered the Songhua Lake through soil erosion or surface runoff.

The industrial DDTs are composed of p,p'-DDT (80-85%) and o,p'-DDT (15-20%), while p,p'-DDE and p,p'-DDD usually appear in the environment as the metabolites of p,p'-DDT. Commonly, p,p'-DDT can

be biodegraded into p,p'-DDD and p,p'-DDE under anaerobic and aerobic environments, respectively [25]. Therefore, the ratios of p,p'-DDD/p,p'-DDE can be used to distinguish the degradation conditions of DDTs and the ratios of (p,p'-DDD+p,p'-DDE)/p,p'-DDT can be used to judge the "new" or "old" DDTs pollution sources and estimate the degradation degree of DDTs. If p,p'-DDE+p,p'-DDD/p,p'-DDT > 1, suggesting that DDTs had undergone long-term degradation and transformation [26]. Research showed that dicofol was a kind of broad-spectrum acaricide with o,p'-DDT as the main components and applying dicofol in the environment will increase the ratio values of o,p'-DDT/p,p'-DDT [22]. Therefore, the ratios of o,p'-DDT/p,p'-DDT can be used to distinguish the pollution sources of DDT pesticides in the environment. Commonly, the ratios of o,p'-DDT/p,p'-DDT from industrial DDTs ranged from 0.2 to 0.3 and those from dicofol products ranged from 4.8 to 9.2 [27]. The composition of DDT isomers and their ratios in

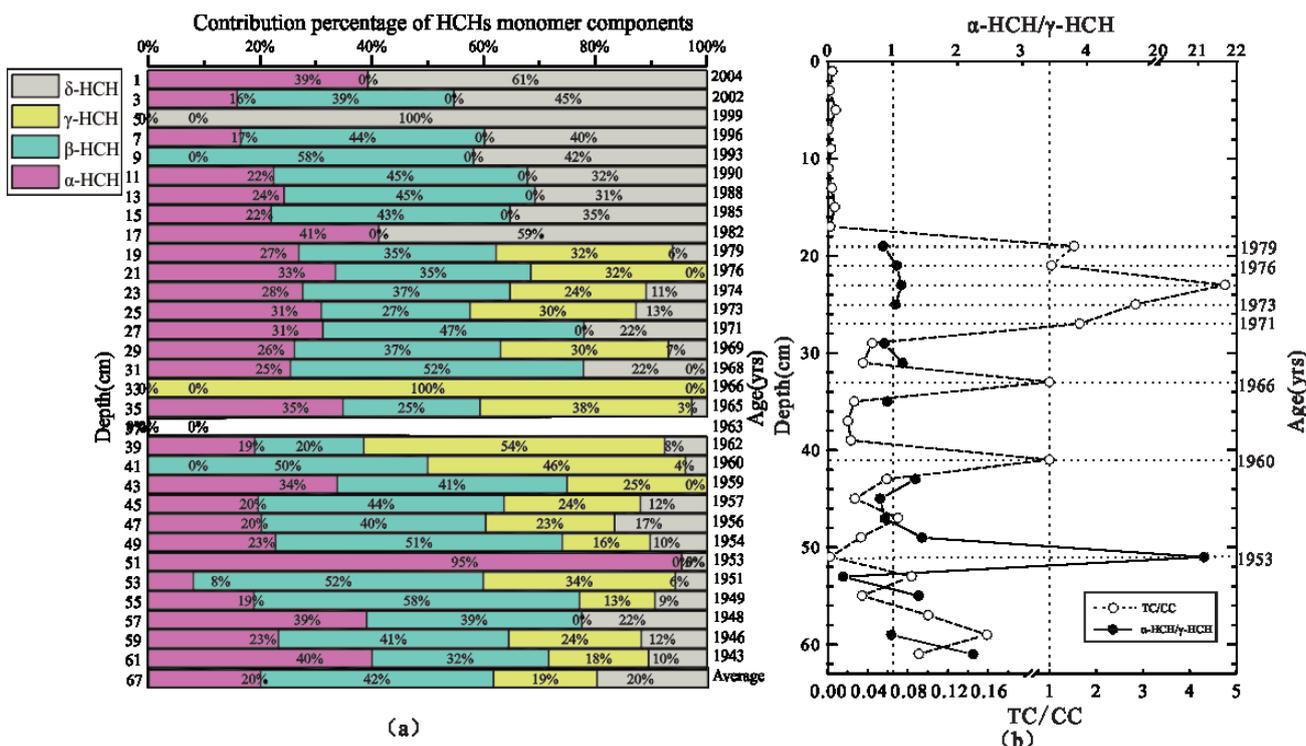


Fig. 5. Composition of HCHs a) and the ratios of the OCPs isomers b) in sediment core sample of Songhua Lake.

the sedimentary layers of Songhua Lake was shown in Fig. 6. At the first (from 1943 to 1962) and third (from 1985 to 2006) sedimentary stage, p,p'-DDT was the dominant component followed by p,p'-DDE. The ratio of p,p'-DDD/p,p'-DDE < 1 and the ratio of p,p'-DDE+p,p'-DDD/p,p'-DDT > 1 in these two stages, which indicated

DDTs pollution mainly came from "old" industrial DDTs and had undergone the process of slow anaerobic biodegradation in Songhua Lake sediments. At the second (from 1962 to 1985) sedimentary stage, p,p'-DDT was still the dominant component, but the concentration of p,p'-DDE residues significantly reduced. The ratio

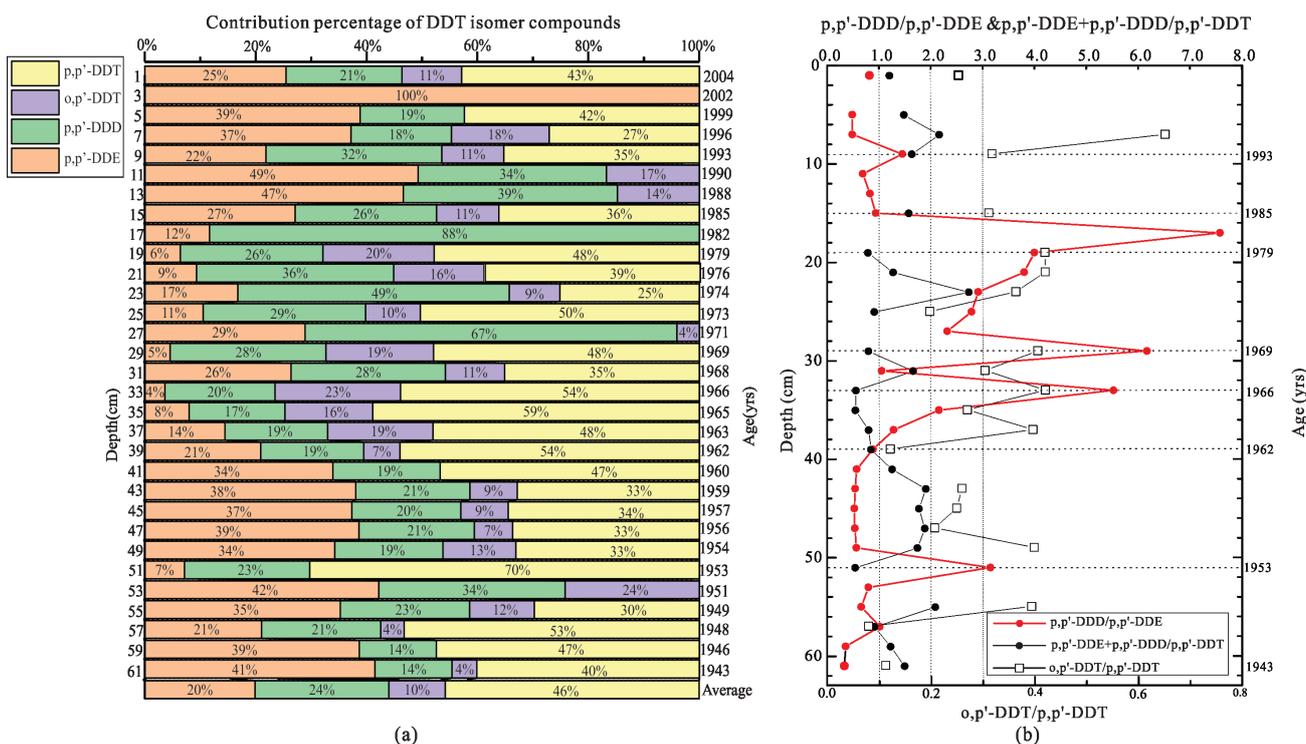


Fig. 6. Composition of DDTs a) and the ratios of the DDTs isomers b) in sediment core sample of Songhua Lake.

of p,p' -DDD/ p,p' -DDE >1 and p,p' -DDE+ p,p' -DDD/ p,p' -DDT <1 in this sedimentary stage, suggesting that DDTs contamination came from “new” industrial DDTs and the sedimentary environment of Songhua Lake from 1962 to 1985 inclined to the anaerobic environment. It is reported that Fengman Reservoir suffered floods in 1964 and 1975, resulting in serious soil erosion and a relatively large number of land-based input sediments [28]. This may be also the reason for the rapid increase of industrial DDTs during the second deposition stage with the anaerobic deposition environment. The ratio of o,p' -DDT/ p,p' -DDT varied from 0.04 to 0.65 in the whole sediment core samples, implying that DDT pollution in the Songhua Lake basin mainly came from the industrial DDTs.

Technology chlordane contains more than 140 compounds and the most abundant components are cis-chlordane (CC (α -), about 11%) and trans-chlordane (TC (γ -), about 13%). Chlordane was produced in the 1950s in China [29], which has been widely applied as agricultural insecticides against termites in China during the 1960s and 2009 [30]. Since TC is easier to degrade than CC in the environment, the ratio of TC/CC <1.0 usually indicates the aging of chlordane [31]. The concentration of CC in the sediment core samples ranged from ND to 18.77 ng/g, while TC was only detected in the 1970s, with the concentration ranging from ND to 1.71 ng/g. The ratio values of TC/CC were significantly higher than 1.0 in the 1970s

(Fig. 5b), which indicates that there may be fresh inputs of industrial chlordane in the Songhua lake basin in this period.

Principle Component Analysis

PCA was applied to estimate the source and degradation behavior of OCPs in this study. Four principal components with eigenvalues greater than 1 were extracted from all OCPs data, accounting for 88.34% of the total variance. The factor loadings obtained after varimax orthogonal rotation from OCPs data were given in Table 3 and the loading plot of the first three principal components (PC1, PC2, and PC3) which explained 73% variation in OCPs has been shown in Fig. 6. The respective loading factor for each component exhibited the association degree between each variable. PC1 explained 31.05% of the total variance with strong positive loading on p,p' -DDD (0.815), p,p' -DDT (0.923), Dieldrin (0.812), Endrin (0.988), α -Endosulfan (0.917). p,p' -DDT was the major component in industrial DDTs and it could be degraded into p,p' -DDD under the anaerobic environment. Meanwhile, the high factor loading of α -Endosulfan (0.917) was also can reflect the reduction environment in Songhua Lake sediments. Therefore, PC1 was mostly related to the degradation of industrial DDT under the anaerobic environment in the middle of the sediment core. PC2 explained 21.52% of the total variance correlated significantly with the contents

Table 3. Factor loadings (varimax normalized; marked loadings are >0.50) of four principal components (PCs) for Songhua lake sediment core.

OCP compounds	Principal components				Variance contribution
	PC1	PC2	PC3	PC4	
α -HCH	-0.027	0.145	0.949	0.028	6.60%
β -HCH	-0.027	0.081	0.959	0.07	6.66%
γ -HCH	0.083	-0.259	0.451	0.788	6.42%
δ -HCH	-0.25	0.708	0.587	0.014	6.49%
p,p' -DDE	0.273	0.879	0.063	-0.013	6.08%
p,p' -DDD	0.815	0.209	-0.168	0.305	5.91%
o,p' -DDT	-0.04	0.11	-0.132	0.948	6.64%
p,p' -DDT	0.923	0.098	-0.131	0.236	6.68%
HCB	0.098	-0.119	0.618	0.642	5.84%
Dieldrin	0.812	0.458	0.057	-0.093	6.29%
Endrin	0.988	0.058	-0.006	-0.049	7.01%
α -Endosulfan	0.917	-0.051	0.123	-0.207	6.44%
β -Endosulfan	0.442	0.671	0.072	-0.155	4.82%
α -Chlordane	0.047	0.948	-0.011	0.019	6.44%
Eigenvalue	4.346	3.013	2.843	2.165	-
Explained variance contribution	31.05%	21.52%	20.31%	15.47%	88.34%

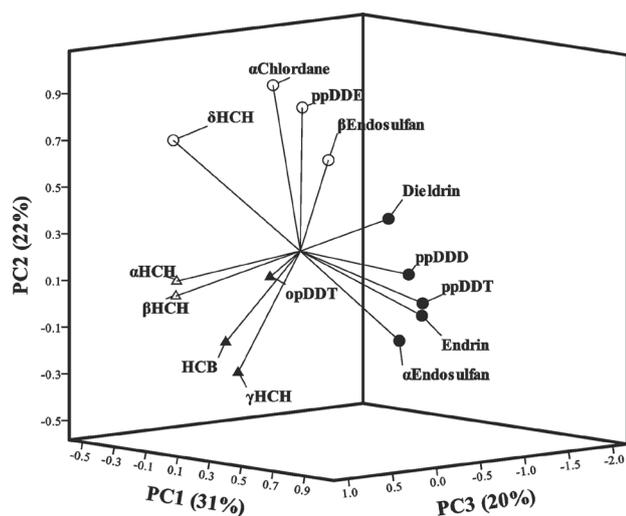


Fig.7. Loadings plot of the first three major principal components (PC1, PC2, and PC3) showing the distribution of individuals of OCPs.

of δ -HCH (0.708), p,p'-DDE (0.879), β -Endosulfan (0.671), and α -Chlordane (0.948). Combined with the temporal tendency analysis of OCPs in the sediment core, PC2 represented the oxidation environment in the upper member of the sedimentary core with the input of industrial HCHs, industrial Chlordane, and Endosulfan. PC3 accounting for 20.31% of the total variance was highly associated with α -HCH (0.949) and β -HCH (0.959), which indicated that PC3 was mostly related to the degradation of the historical industrial HCHs. PC4 represented 15.47% of the total variance with high positive loading on γ -HCH (0.788), o,p'-DDT (0.948), and HCB (0.642). γ -HCH and o,p'-DDT was the major impurity in lindane and dicofol, respectively. Therefore, PC4 can reflect the source of lindane and dicofol in the sediment core of Songhua Lake.

Ecotoxicological Concern of OCPs

in the Sediment Core

Ecotoxicological risk assessment refers to the effective prediction of the possible ecological effects caused by toxic pollutants in the environmental media and the method of assessing the probability of risk occurrence. Contaminated sediments can pose potential ecological risks to the aquatic ecosystem [32]. In this study, a level-screening ecotoxicological risk assessment was conducted using two international sediments quality guidelines (SQGs), the threshold effects level (TEL), probable effects level (PEL) guidelines proposed by Macdonald et al. (1996) [33], and the effects range-low value (ERL), effects range-median value (ERM) guidelines proposed by Long et al. (1995) [34]. ERL represents less than a 10% probability of adverse biological effects, while ERM means the probability less than 50%. The occurrence of residues below the TEL indicates that adverse biological effects may occur rarely, whereas the presence of residues above the PEL suggests that adverse effects may occur frequently [35].

According to the guidelines and the statistical results in Table 4, the levels of p,p'-DDT, p,p'-DDD, p,p'-DDE and Σ DDTs exceeded the TEL values in 82,91,88 and 97% of the sediment core samples, respectively. The concentrations of these compounds were also higher than ERL values in these samples. Significantly, the level of p,p'-DDT in more than half of the sediment core samples exceeded the ERM and PEL values, whereas the concentration of p,p'-DDD in 36% of the sediment core samples exceeded the PEL value, and p,p'-DDD concentration (48.65 ng/g, dw) in the sediment layer of 51 cm (corresponding to 1953) over the ERM value. Σ DDTs concentrations exceeded the ERM value in 15% of the sediment core samples and were over the PEL value in three samples (including 51 cm (1953a), 33 cm (1966a), and 7 cm (1996a)). These comparative results indicated that the possibility of adverse ecological effects for DDT metabolites may

Table 4. Assessments of potential ecotoxicological risks of selected OCPs in the sediment core of Songhua Lake using two sediment quality guidelines (SQGs) (unit: ng/g).

Selected OCPs	Range (Mean)	ERL ^a	Above ERL ^c	ERM ^b	Above ERM ^c	TEL ^c	Above TEL ^c	PEL ^d	Above PEL ^e
p,p'-DDT	N.D.-151.22(14.24)	1	82%	7	52%	1.19	82%	4.77	64%
p,p'-DDD	N.D.-48.65(7.49)	2	82%	20	0.03%	1.22	91%	7.81	36%
p,p'-DDE	1.22-22.27(6.20)	2.2	82%	27	0%	2.07	88%	374	0%
DDTs	2.99-215.28(31.08)	1.58	100%	46.1	15%	3.89	97%	51.7	0.09%
γ -HCH	N.D.-65.72(5.38)	-	-	-	-	0.32	58%	0.99	58%
Dieldrin	N.D.-14.19(1.88)	-	-	-	-	0.71	64%	4.3	12%
Endrin	N.D.-123.36(9.13)	0.02	70%	45	0.03%	-	-	-	-
Heptachlor	N.D.-6.28(0.45)	0.5	0.06%	6	0.06%	2.26	0.06%	4.79	0.06%

-: not available; a: Effects Range Low value; b: Effects Range Median value; c: Threshold Effects Level; d: Probable Effects Level; e: Percentage of samples above the corresponding levels. Guidelines data are from references (Liu et al. 2019; Wang 2017)

exposure to the neighboring benthic organisms in Songhua Lake. The concentrations of γ -HCH exceeded the TEL and PEL values in 58% of the sampling layers, which indicated that the input and accumulation of lindane corresponding to the coastal agricultural activities may cause certain adverse ecological effects in Songhua Lake sediments. Dieldrin concentrations exceeded the TEL and PEL values in 64% and 12% of samples, respectively, which suggests that it may cause some toxic biological effects to aquatic organisms. The Endrin and Heptachlor exhibited seldom possibility of adverse ecological effects compared with other compounds.

Conclusions

From the current work, it is sufficient to point out that DDTs and HCHs were always the dominant OCPs compounds in the sediment core of Songhua Lake and the content input of DDTs in the sediment core was the most continuous. Industrial HCHs have been continued input and experienced photolysis and microbial action during the whole sedimentary history of Songhua Lake. HCB mainly occurred in the midpieces of the sediment core corresponding to the 1960s when HCB was widely used in China's agricultural production. After the 1960s, CHLOs and ENDS had input with relatively low concentration and discontinuous input. Dieldrin and Endrin had a certain amount of sediment input in the lake with low concentrations by the 1970s. The diagnose ratio of characteristic compounds combined with PCA showed that DDT compounds mainly came from coastal industrial production HCHs compounds were contributed by technical HCHs and agricultural activities lindane, while other organochlorine pesticides were related to long-distance atmospheric transport. Before the 1960s and after the mid-1980s, the sedimentary conditions in Songhua Lake are inclined to an aerobic environment while the middle part tended to an aerobic environment. Overall, the tremendous efforts in banning the use of OCPs in the domain of agricultural and industrial production had a positive effect. However, in the late 1990s, the application of DDTs, Lindane, and their derivatives along the coast still needs to be a serious consideration. The results of this study can provide a reference for reconstructing the pollution records of organochlorine pesticides in the Songhua Lake basin and provide a basis for further study on ecological security and environmental restoration of Songhua Lake.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. BEHFAR A., NAZARI Z., RABIEE M.H., RAESI G., OVEISI M.R., SADEGHI N., JANNAT B. The Organochlorine Pesticides Residue Levels in Karun River Water. *Jundishapur Journal of Natural Pharmaceutical Products*, **8** (1), 41, **2013**.
2. JORFI S., ATASHI Z., AKHBARIZADEH R., KHORASGANI Z.N., AHMADI M. Distribution, and health risk assessment of organochlorine pesticides in agricultural soils of the Aghili plain, Southwest Iran. *Environmental Earth Sciences*, **78**, 603, **2019**.
3. PUČKO M., STERN G.A., BURT A.E., JANTUNEN L.M., BIDLEMAN T.F., MACDONALD R.W., BARBER D.G. Current use pesticide and legacy organochlorine pesticide dynamics at the ocean-sea ice-atmosphere interface in resolute passage, Canadian Arctic, during winter-summer transition. *Science of the Total Environment*, **580**, 1460, **2017**.
4. MUZYED S.K.I., KUCUKSEZGIN F., TUZMEN N. Persistent organochlorine residues in fish and sediments collected from Eastern Aegean coast: Levels, occurrence and ecological risk. *Marine Pollution Bulletin*, **119** (2), 247, **2017**.
5. BINELLI A., SARKER S.K., CHATTERJEE M., RIVA C., PAROLINI M., BHATTACHARYA B.D. A comparison of sediment quality guidelines for toxicity assessment in the Sunderban wetlands (Bay of Bengal, India). *Chemosphere*, **73**, 1129, **2008**.
6. LI P., WANG Y.H., HUANG W.Y., YAO H.M., XUE B.M., XU Y.Y. Sixty-year sedimentary record of DDTs, HCHs, CHLs and endosulfan from emerging development gulfs: a case study in the Beibu Gulf, South China Sea. *Bulletin of Environmental Contamination and Toxicology*, **92** (1), 23, **2014**.
7. ALONSON-HERNANDEZ C.M., TOLOSA I., MESA-ALBERNAS M. Historical trends of organochlorine pesticides in a sediment core from the Gulf of Batabano, Cuba. *Chemosphere*, **137**, 95, **2015**.
8. THEVENON F., DE ALENCASTRO L.F., LOIZEAU J.-L., ADATTE T., GRANDJEAN D., WILDI W. A high-resolution historical sediment record of nutrients, trace elements and organochlorines (DDT and PCB) deposition in a drinking water reservoir (Lake Brêt, Switzerland) points at local and regional pollutant sources. *Chemosphere*, **90**, 2444, **2013**.
9. HAO L.B., SUN L.J., ZHAO Y.Y., LU J.L. Sedimentary Records of Evolution of Heavy Metals in Songhua Lake, Northeast China. *CLEAN-Soil, Air, Water*, **41** (10), 1010, **2013**.
10. Annals of Jilin Province. Natural geography: the natural environment in the historical period. Available online: <http://was.jl.gov.cn/was5/web/search?channelid=248426&token=76.1496975281662.78&searchword=%E5%90%89%E6%9E%97%E7%9C%81%E5%BF%97%C2%B7%E8%87%AA>

- %E7%84%B6%E5%9C%B0%E7%90%86%E5%BF%97&noOther=1
11. YIN Y.C., HAO L.B., GU X., LU J.L., PAN Z.H. Source tracing of n-alkanes in Songhua Lake, based on correspondence analysis and geochemical index. *Environ Geochem Health* **42** (5), 1347, **2020**.
 12. LI C.C., HUO S.L., XI B.D., YU Z.Q., ZENG X.Y., ZHANG J.T., WU F.C., LIU H.L. Historical deposition behaviors of organochlorine pesticides (OCPs) in the sediments of a shallow eutrophic lake in Eastern China: Roles of the sources and sedimentological conditions. *Ecological Indicators* **53**, 1, **2015**.
 13. NDUNDA E.N., MADADI V.O., WANDIGA S.O. Organochlorine pesticide residues in sediment and water from Nairobi River, Kenya: levels, distribution, and ecological risk assessment. *Environmental Science and Pollution Research*, **25** (34), 34510, **2018**.
 14. DEVI N.L., YADAV I.C., RAHA P., QI S.H., DAN Y. Spatial distribution, source apportionment and ecological risk assessment of residual organochlorine pesticides (OCPs) in the Himalayas. *Environmental Science and Pollution Research*, **22** (24), 20154, **2015**.
 15. GOLOBOČANIN D.D., ŠKRBIĆ B.D., MILJEVIĆ N.R. Principal component analysis for soil contamination with PAHs. *Chemometrics and Intelligent Laboratory Systems*, **72** (2), 219, **2004**.
 16. WANG H.Z., HE M.C., LIN C.Y., QUAN X.C., GUO W. Distribution characteristics of organochlorine pesticides in river surface sediments in Song Liao Watershed. *Chinese Journal of Applied Ecology*, **18** (7), 1523, **2007** [in Chinese].
 17. DA C.N., WU K., JIN J., YU M.J. Levels and Sources of Organochlorine Pesticides in Surface Sediment from Anhui Reach of Huaihe River, China. *Bulletin Environmental Contamination and Toxicology* **98** (6), 784, **2017**.
 18. LIANG Y., XIAO H.Y., LIU X.Z. Distribution and source of organochlorine pesticides (OCPs) in the sediments of Poyang Lake. *Environmental Earth Science*, **76** (17), 622, **2017**.
 19. XU L.J., CHU J.Y., ZHOU Z.H., YAN J., YOU J.J. Analysis of water environmental quality features in Songhua River Basin. *Water Resources Protection*, **28** (6), 55, **2012** [in Chinese].
 20. WANH D., YANG S.K., WANG G., GAO L.C., WANG Y.N., JIANG Q.L., CHEN Y.Y. Residues and Distributions of Organochlorine Pesticides in China's Weihe River. *Polish Journal of Environmental Studies*, **25** (3), 1285, **2016**.
 21. GERESLASSIE T., WORKINEH A., ATIENO O.J., WANG J. Determination of Occurrences, Distribution, Health Impacts of Organochlorine Pesticides in Soils of Central China. *International Journal of Environmental Research and Public Health*, **16** (1), 146, **2019**.
 22. WEI H., HU D., LI K.B. Sediments contamination levels of organochlorine pesticides in Weihe River, Northwestern China. *Environmental Earth Sciences*, **75** (9), 797, **2016**.
 23. WALKER K., VALLERO D.A., LEWIS R.G. Factors Influencing the Distribution of Lindane and Other Hexachlorocyclohexanes in the Environment. *Environmental Science & Technology*, **33** (24), 4373, **1999**.
 24. KUMAR B., VERMA V.K., MISHRA M., GAUR R., KIMAR S., SHARMA C.S. DDT and HCH (Organochlorine Pesticides) in Residential Soils and Health Assessment for Human Populations in Korba, India. *Human and Ecological Risk Assessment*, **20** (6), 1538, **2014**.
 25. GOPALAN N.K., CHENICHERY S. Fate and distribution of organochlorine insecticides (OCIs) in Palakkad soil, India. *Sustainable Environment Research*, **28** (4), 179, **2018**.
 26. BARRON M.G., ASHUROVA Z.J., KUKANIEV M.A., AVLOEV H.K., KHAIDAROV K.K., JAMSHEDOV J.N. Residues of organochlorine pesticides in surface soil and raw foods from rural areas of the Republic of Tajikistan. *Environment Pollution*, **224**, 494, **2017**.
 27. LIU Q., TIAN S.Y., JIA R., LIU X.B. Pollution characteristics and ecological risk assessment of HCHs and DDTs in estuary wetland sediments from the Bohai Bay, North China. *Environmental Science and Pollution Research*, **24** (35), 26967, **2017**.
 28. LI C.L., LIAO W.H., ZHANG P.P., XUE Z.C., HUANG X.M. An Analysis of the Storm Flood Evolution Law in the Second Songhua River Basin. *China Rural Water and Hydropower*, **6** (12), 75, **2017** [In Chinese].
 29. LI P.Y., WANG Y.H., HUANG W.Y., YAO H.M., XUE B.M., XU Y.Y. Sixty-year sedimentary record of DDTs, HCHs, CHLs and Endosulfan from emerging development gulfs: a case study in the Beibu Gulf, South China Sea. *Bulletin of Environmental Contamination and Toxicology*, **92** (1), 23, **2014**.
 30. ZHOU S.S., TONG L., TANG Q.Z., GU X.T., XUE B., LIU W.P. Residues, sources and tissue distributions of organochlorine pesticides in dog sharks (*Mustelus griseus*) from Zhoushan Fishing Ground, China. *Marine Pollution Bulletin*, **73** (1), 374, **2013**.
 31. TANG J.F., FENG J.Y., LI G., LIANG M.Q., WANG R.J., CAI C. Occurrence and possible sources of organochlorine pesticides in soils of Ningbo, East China. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, **109** (3-4), 495, **2018**.
 32. AAMIR M., KHAN S., NIU L.L., ZHU S.Y., KHAN A. Occurrence, enantiomeric signature and ecotoxicological risk assessment of HCH isomers and DDT metabolites in the sediments of Kabul River, Pakistan. *Environmental Geochemistry and Health*, **39** (4), 779, **2017**.
 33. MACDONALD D.D., CARR R.S., CALDER F.D. LONG E.R., INGERSOLL C.G. Development and evaluation of sediment quality guidelines for Florida coastal water. *Ecotoxicology*, **5**, 253, **1996**.
 34. LONG E.R., MACDONALD D.D., SMITH S.L., CALDER F.D. Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments. *Environmental Management*, **19** (1), 81, **1995**.
 35. WANG W., BAI J.H., ZHANG G.L., WANG X., JIA J., CUI B.S., LIU X.H. Depth-distribution, possible sources, and toxic risk assessment of organochlorine pesticides (OCPs) in different river sediment cores affected by urbanization and reclamation in a Chinese delta. *Environmental Pollution*, **230**, 1062, **2017**.
 36. GUO J.Y., WU F.C., LIAO H.Q., ZHAO X.L., LI W., WANG J., WANG L.F. Sedimentary record of polycyclic aromatic hydrocarbons and DDTs in Dianchi Lake, an urban lake in Southwest China. *Environmental Science and Pollution Research*, **20** (8), 5471, **2013**.
 37. SUN Y., YUAN G.L., LI J., TANG J.H., WANG G.H. High-resolution sedimentary records of some organochlorine pesticides in Yamzho Yumco Lake of the Tibetan Plateau: Concentration and composition. *Science of the Total Environment*, **615** (1), 469, **2018**.

38. DVORŠČAK M., FINGLER S., MENDAŠ G., STIPIČEVIĆ S., VASILIC Ž., DREVENKAR V. Distribution of Organochlorine Pesticide and Polychlorinated Biphenyl Residues in Lake Sediment Cores from the Plitvice Lakes National Park (Croatia). *Archives of Environmental Contamination and Toxicology*, **77** (4), 537, **2019**.
39. SARAH P., ELISA M., ELENA G., MARCO V., FABIANA C., ROSSANO P., ANDREA G. Occurrence and source apportionment of organic pollutants in deep sediment cores of the Venice Lagoon. *Marine Pollution Bulletin*, **164**, 112053, **2021**.
40. THAM T.T., ANH H.Q., PHUONG B.T., TRINH L.T., THUY N.T.T., YEN N.T.H., TRI T.M., MINH T.B. Contamination status and temporal trends of persistent toxic substances in sediment cores from coastal areas of central Vietnam. *Marine Pollution Bulletin*, **156**, 111222, **2020**.
41. KIM Y.S., EUN H., CHO H.S., KIM K.S., SAKAMOTO T., WATANABE E., BABA K., KATASE T. Organochlorine pesticides in the sediment core of Gwangyang bay, South Korea. *Archives of Environmental Contamination and Toxicology*, **54** (3), 386, **2008**.
42. LEBEUF M., NUNES T. PCBs and OCPs in Sediment Cores from the Lower St. Lawrence Estuary, Canada: Evidence of Fluvial Inputs and Time Lag in Delivery to Coring Sites. *Environmental Science & Technology*, **39**, 1470, **2005**.
43. HARTMANN P.C., QUINN J.G., CAIRNS R.W., KING J.W. Depositional history of organic contaminants in Narragansett Bay, Rhode Island, USA. *Marine Pollution Bulletin*, **50** (4), 388, **2005**.
44. VARNOSFADERANY M.N., SOFFIANIAN A., MIRGHAFARI N., GU Z.Y., CHU G.Q. Occurrence and depositional history of organochlorine pesticides in the sediments of the Zayandehrud River in the arid region of Central Iran. *Chemosphere*, **225**, 126847, **2020**.
45. GARDES T., PORTET-KOLTALO F., DEBRET M., COPARD Y. Historical and post-ban releases of organochlorine pesticides recorded in sediment deposits in an agricultural watershed, France. *Environmental Pollution*, **288**, 117769, **2021**.
46. GÖTZ R., BAUER O-H., FRIESEL P., HERRMANN T., JANTZEN E., KUTZKE M., LAUER R., PAEPKE O., ROCH K., ROHWEDER U., SCHWARTZ R., SIEVERS S., STACHEL B. Vertical profile of PCDD/Fs, dioxin-like PCBs, other PCBs, PAHs, chlorobenzenes, DDX, HCHs, organotin compounds and chlorinated ethers in dated sediment/soil cores from flood-plains of the river Elbe, Germany. *Chemosphere*, **67** (3), 592, **2017**.