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Geochemical Indicators of Organo-Chloro Pesticides in Lake Sediments

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1. Introduction

The study area, Lake Liangzi is regarded as one of the least polluted lakes in Central China. This is because the local people have made great efforts to protect the lake from the use of all forms of chemicals for crop and fish farming activities. Besides this measure, other uses such as recreation, water supply and electricity production are also not permitted. In fact, it is noteworthy to mention that the lake supplies one of the most popular and delicious types of fish in Central China. It is called "Wuchang fish" and is very popular in most leading restaurants in Central China and quite expensive for its delicacy.

However, since modern technology has revealed that organic compounds such as Organo chloro-pesticides (OCPs) could be deposited into lakes and other water bodies from remote areas, far from the point of application, it will be worthwhile to undertake investigation to ascertain whether the lake is free from these contaminants. The path of investigation used dated sediment core since according to Venkatesan, et al, (1998), the history of chlorinated hydrocarbon contamination can be followed using contaminants from dated sediment cores, since sediments integrate and retain records of influx of recalcitrant organic contaminants. It should be mentioned that this volume of work is part of the author's PhD research and also one of the pioneering research works on pesticides in the lake.

OCPs are a group of common pollutants belonging to the class of pollutants called Persistent Organic Pollutants (POPs). One of the most important families of Persistent Organic Pollutants (POPs) that has a significant impact upon the environment are pesticides.

According to Sierra Club of Canada, (1998), pesticides are the only man-made toxic chemicals deliberately released over large areas. They are poisonous almost by definition. Pesticides poison the food chain, contaminate water supplies and are implicated in the declining populations of many biotic species.

In this study, a single drilled undisturbed sedimentary core extracted from Lake Liangzi in Central China was analyzed for target compounds using highly sophisticated instruments. Even though other organic compounds (such as Polycyclic Hydrocarbons; PAHs, Aliphatic Hydrocarbons; Ahs and heavy metals) were detected, they are not discussed in this article.. The focus of discussion are the organochloro-pesticides, including DDT, DDD and DDE and the geochemical relationship between them.

1.1 Brief background to DDT, DDD and DDE

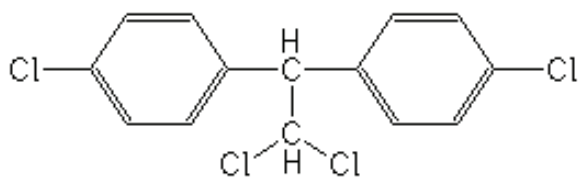
According to Environmental Protection Agency (EPA) of USA, (1989), the term DDT refers to the collection of all forms of DDT, DDE, and DDD.

The primary forms or isomers of DDT, DDE, and DDD are (namely *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD) (US EPA,1989). US EPA, (1989), also indicate that DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane) is a pesticide that was once widely used to control insects on agricultural crops and insects that carry diseases like malaria but is now used in only a few countries to control malaria. Technical-grade DDT is a mixture of three forms, *p,p'*-DDT (85%), *o,p'*-DDT (15%), and *o,o'*-DDT (trace amounts). All of these are white, crystalline, tasteless, and almost odorless solids. Technical grade DDT may also contain DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane) as contaminants. US EPA (1989), further indicate that both DDE and DDD are breakdown metabolites of DDT and that DDT does not occur naturally in the environment. They may occur in the atmosphere as a vapor or be attached to solids in air. Vapor phase DDT, DDE, and DDD may break down in the atmosphere due to reactions caused by the sun. DDT, DDE, and DDD last in the soil for a very long time, potentially for hundreds of years. Most DDT breaks down slowly into DDE and DDD, generally by the action of microorganisms. These chemicals may also evaporate into the air and be deposited in other places (EPA, 1989). These organic compounds, according to Agency for Toxic Substances and Disease Registry (ATSDR 2002), are easily broken down in air with a half-life of two days. Also according to ATSDR (2002), DDT and especially DDE build up in plants and in fatty tissues of fish, birds, and other animals.

DDT

Chemical formula: (C₁₄H₉Cl₅).

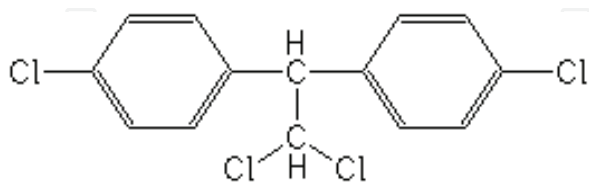
Structure:



DDD

Chemical formula, (C₁₄H₁₀Cl₄).

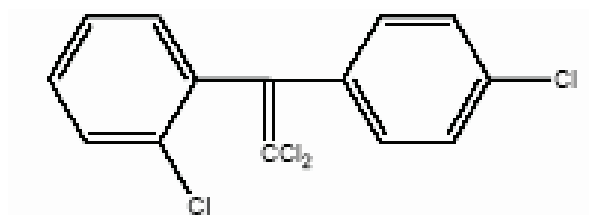
Structure:



DDE

Chemical formula (C₁₄H₈Cl₄)

Structure:



1.2 Study area



Fig. 1. Map of Wuhan and other major cities in Hubei Province (including the study area)
Source: LandingChina.com; "The Professional Travelling guide to China", 2004

1.2.1 The limnological data of the Lake Liangzi

The limnology according to Donyinah et al. (2007), is based on the information supplied by J. Xiangtan (1995). The lake which lies within the southeast area of the heavily industrialized city of Wuhan is the 13th largest freshwater lake in China and the second largest shallow lake of Hubei Province. It is a low-lying lake, which is located not far from the southern bank of the Yangtze River. In the 1950s, the actual surface area of the lake was 458.5km.² (177.0 mi²), but in the 1980s and 1990s, the area of the lake shrank to 227.15km² (87.70 mi²) because of reclamation of the lake for agricultural purposes. Also in the 1950s the lake was 2.25-2.8 m (7.38-9.18 ft) deep and the deepest area was 1.5 m (4.9 ft) during winter, when the water was lowest. In 1997 and 1998, the lake measured between 1.2 and 4.2 m (3.9 and 13.7 ft) and the average depth was 2.8 m (9.2 ft). The circumference of the lake totals more than 470 km (292 mi) and the shoreline is irregular. The vegetation around the lake is grass with a few trees. Except in the east, there are many small uplands and hills around the lake; the hills are, however, some distance away. Few croplands near the small hamlets around the extended edges of the lake. Rainfall is abundant, with the average rainfall range over several years being 1263.4mm/yr (49.7 in./yr). The average air temperature area the lake is about 17°C. The highest monthly air temperature is 28.6°C and the lowest is 3.3°C. The wind circulation pattern consists of cold winds from the north blowing in the winter and spring and northeast and east winds blowing in the summer and fall, respectively. The temperature

of the water in the lake is higher than the surrounding air. Whereas the average temperature of the surrounding air over several years is 17.5°C, the highest monthly average temperature of the lake is about 30°C and lowest is 4.7°C. Annually, there are 243 days when the temperature of the lake water is higher than 10°C. No significant difference exists between the temperatures of each layer of water in the lake; the difference between the upper layer and the bottom layer is not more than 1°C. The lake water is very clear, but the shallow water near the edges becomes turbid when there are stormy waves. The transparency changes between 0.3 and 1.4 m (1 and 4.5 ft) and the average is 0.8 m (2.6ft). Generally, the transparency in spring and winter is high, and the lake's water appears light green. The water is alkaline, and the pH is commonly about 8.1, with no distinct differences between the upper layer and the bottom layer. The main ions in the water are bicarbonate class. The iron content of the lake water is fairly high, and the average is 7 mg.

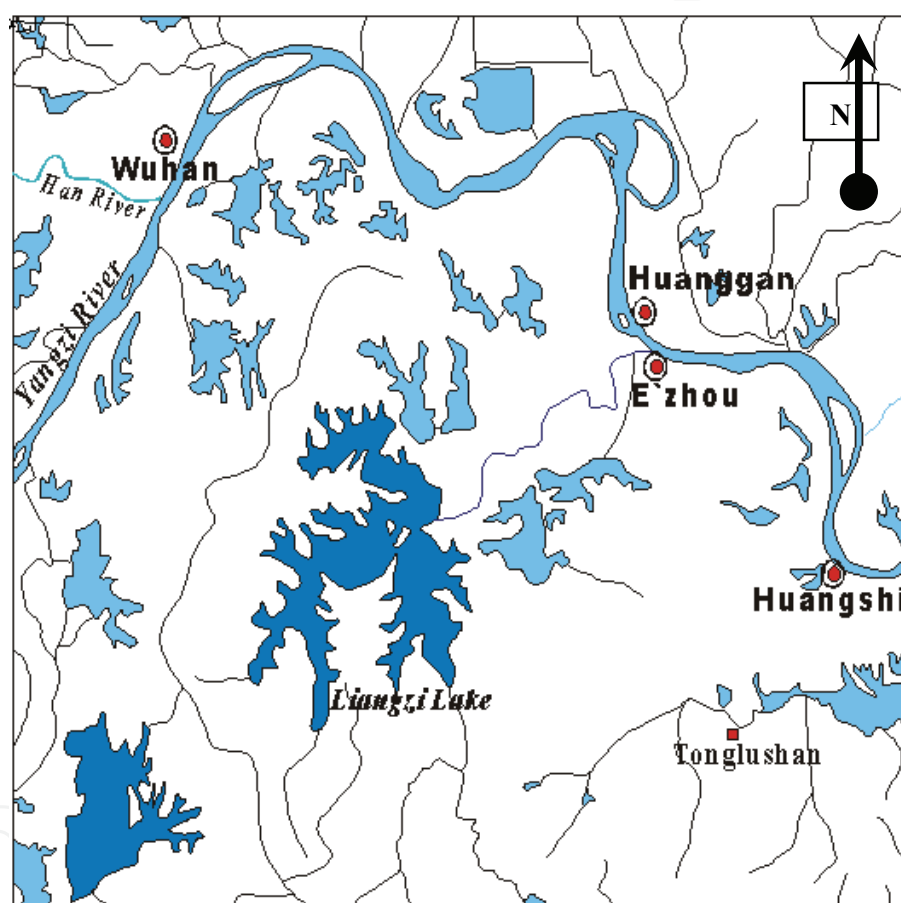


Fig. 2. A Map Showing the Location of Lake Liangzi

2. Sampling and sampling techniques

The location chosen for sampling was at the middle and the deepest part of the Lake, the sediment core samples will thus assumed to be a true representative of the Lake's sediments and therefore, reliable for all analyses.

Sampling was carried out from a small local motorized fishing boat, using a soft manual hand-driven core-drill (KC Kajak Sediment Core Sampler). Core samples were taking from a depth of 70~80cm in the lake's bed and each core sample was immediately sliced (from top to bottom) into fractions of (1cm thick), using a well polished and treated metallic soft-core

sediment cutter. The sliced samples were immediately put into fresh plastic sample bags and serially well labeled, using coloured felt pens. Maximum precaution was taken to avoid any contamination, such as skin exposure, especially the bare hands (since the touching with the bare hands could contaminate the samples from the possible lipids of the hands by touching with the bare hands) and thus sampling was carried out by wearing fresh plastic disposable gloves. In order to preserve the freshness of the samples, they were immediately stored in a freezer at -20°C until the time for the laboratory analysis. The handling and the transportation of the samples from the lake to the laboratory were carefully and cautiously handled to avoid any possible contamination.

2.1 Laboratory methods

For the purpose of instrumental analyses, the target compounds were extracted from the solid samples and transferred into liquid form. This initial extraction process is called the pretreatment of samples. The pre-treatment was performed at the Environmental Laboratory of the School of Environmental Studies, China University of Geosciences, Wuhan. Standard laboratory procedures were followed throughout the process.

The reagents used for the pretreatment were hexanes, dichloromethane, surrogate standards, silica gel, aluminum oxide and distilled water (for washing and rinsing of the apparatuses before usage).

A total of seventy-seven (77) samples were analyzed. One hundred milliliters of the initial solvent, dichloromethane, was poured into the sample for the extraction process. The surrogate standard was introduced into one selected sample in each set of batch samples. A set of six batches of samples were kept on hot water bath (Model HHS-6; temperature range 37°C - 100°C) and Soxhlet extractor at fixed temperature of 50°C and left for 48 hrs. The temperature fluctuation during the period was within an accuracy of $\pm 1^{\circ}\text{C}$. The extractor was then filtered into another round-bottomed flask and concentrated by rotation evaporation using a rotary evaporator (ZFQ-85A; speed range 0-200 rpm) and Auto Science vacuum and pressure (model AP-01; pressure range = 0- 30 mm Hg [0-4 kPa]). The pressure used for the evaporation was fixed at 20 mm Hg (2.6 kPa) for all the samples. The concentrate was carefully transferred into special 5 mL sample bottles using special pipettes and immediately stored in a freezer. After the transfer of each concentrate, the round-bottomed flask was thoroughly rinsed with dichloromethane. The process was repeated for all the 77 samples. The extracts were then left to evaporate naturally at room (ambient) temperature and then mixed with hexanes until all the dichloromethane totally evaporated.

These extracts were then column fractionated into the target compound (OCPs) using silica and aluminium oxide. The particle size of the aluminium oxide and the silica gel was 100-200 mesh. Care was taken to label each extracted solution. The column extraction was conducted through columns of aluminium oxide, and silica gel was placed in 100 mL burettes. The aluminium oxide formed the top column (5 mL), whereas the silica gel was the bottom column (15 mL). Prior to passing the samples through the columns; 30 mL of dichloromethane was initially passed through the columns to wash any possible contaminants in the column. Another 30 mL of the dichloromethane was passed through the columns after each sample was introduced into the column for the extraction of target organic compounds. These fractionated solutions were again concentrated by rotation evaporation using the Rotary evaporator (ZFQ-85A), and bottled in 8 milliliter cell bottles. They were then evaporated again, using a Nitrogen manifold setup with a gentle stream of nitrogen gas (99.9% purity) to about 5mL. The final extracted samples of analysis were analyzed by gas chromatography (GC) and GC-mass spectrometry (GC-MS).

2.2 Instrumental analyses

2.2.1 Gas chromatography and gas chromatography /mass spectrometry

2.2.1.1 Instrument

GC: HP 6890 GC/FID (flame ionization detector).

GC-MS: HP5890II GC equipped with HP5972 MSD.

2.2.1.2 GC parameters

Column: HP-5 fused silica capillary column (30m×0.25mm×0.25um i.d.), constant flow 1.5;

Inlet: splitless, temperature 290°C

Oven: initial 60°C keep 1 min, 6°C /m to 290°C keeps 20 min;

Detector: flame ionization detector (FID), temperature 300°C.

2.2.2 Qualitative analysis and quantitative analysis

2.2.2.1 The qualitative and quantitative analysis of PAH

The GC-MS was calibrated with standard compounds of known concentrations at eight different concentrations: 0.2 ppm¹, 0.4 ppm, 0.8 ppm, 1 ppm, 2 ppm, 4 ppm, 8 ppm, and 10 ppm. The calibration curves of 16 PAHs based on the average response factors were used for concentration determination. Target compounds were qualified using the internal standard technique. Their concentrations were reported as nanogram/gram (µg/g) based on dry sediment weight.

2.2.2.2 The qualitative and quantitative analysis of aliphatic compositions

The lack of standard compounds seems to bring difficulty to the qualitative and quantitative analysis of aliphatic composition, but the equally-spaced retention time makes it possible to determine the carbon number of aliphatic compositions properly once one of a series of samples was subject to GC-MS analysis. Because the response factors of aliphatic compositions with different carbon number are almost the same, the quantitative analysis was accomplished in accordance to the response factor of internal standard C₂₀d₄₂.

2.2.3 QC/QA

A strict Quality Control/Quality Assurance (QC/QA) measurement was followed throughout the process of analysis.

The recovery of the analytic procedure was determined by measuring the amounts of surrogate compounds added prior to sample extraction. The recoveries range from 44.2% to 118.3% (except Nap-d8 volatile even at room temperature), within the restrictive range of US EPA 610 method. Therefore, except Nap whose values can only serve as reference, other data satisfy the demand for quantitative analysis. All data have not been revised and all concentration values are according to the instrumental recoveries. All the PAH concentrations were reported on a dry weight sediment basis.

The relative standard derivation for duplicate samples ranged from 0 to 15%.

A method blank experiment was carried out for every 12 samples.

The solvent blanks were checked and none of the investigated substances were found in the blanks.

¹ ppm (parts per million)

2.3 Dating of sediments

The dating of the samples was carried out at the State Key Lab of Organic Geochemistry (SKLOG), Guangzhou Institute of Geochemistry, and Chinese Academy of Sciences.

Lead isotope 210 (²¹⁰Pb) was used for dating the samples and the results obtained showed that at a depth of 18 cm from the surface of the lake’s bed, the age of the samples was a little over 100 years, (precisely 101 years). A graph of depth age was plotted and indication showed that the age of the lake sediment at any depth could be found by simple extrapolation from the graph.

A regression graph was also plotted to indicate the accuracy of the technique of analysis. Both graphs are presented below.

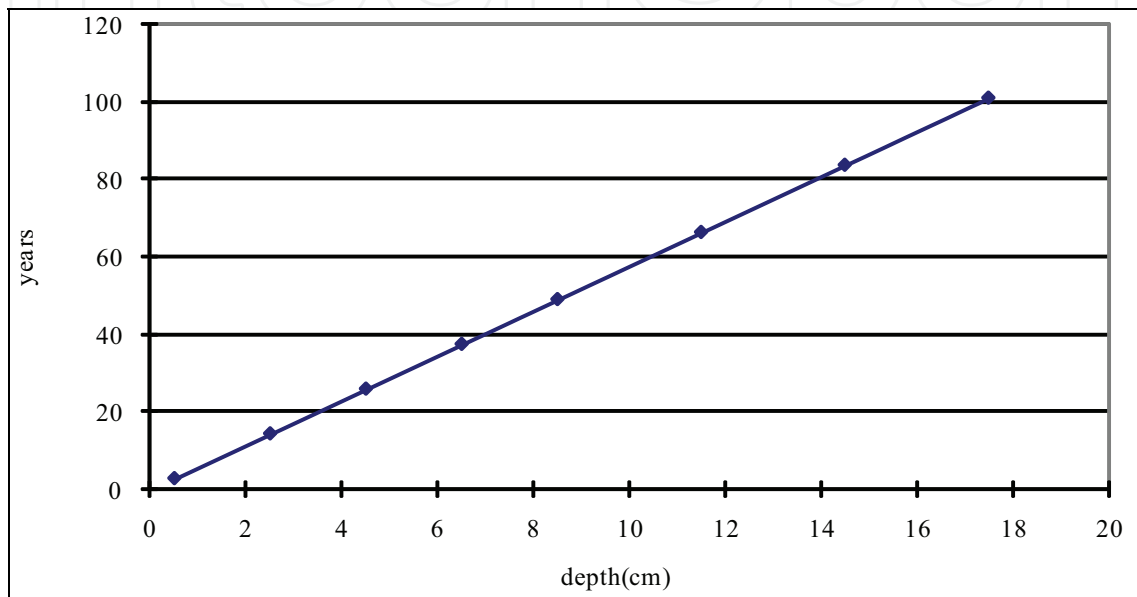


Fig. 3a. Graph of Dating (years) verses depth (cm)

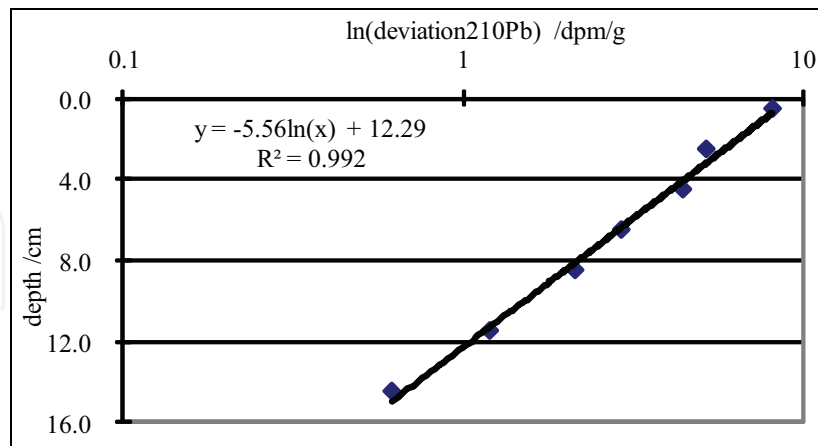


Fig. 3b. Regression Diagram of accuracy of Results of Dating by (²¹⁰Pb)

3. Results and discussions

The results derived from the instrumental analysis were processed using Excel and Original (Version b) and presented in a tabular form (tables 1 to 4 refer). Graphical illustrations are represented in figures 4 to 9.

Depth (cm)	TCMX	a-HCH	b-HCH	d-HCH	r-HCH	heptachlor	Aldrin
-3	0.30	0.28	1.42	1.36	0.80	0.09	0.07
-4	0.19	0.11	0.49	1.25	0.11	0.00	0.00
-5	0.12	0.10	0.80	0.45	0.35	0.00	0.00
-6	0.72	0.09	0.33	0.50	0.00	0.00	0.00
-7	0.05	0.08	1.99	0.23	0.10	0.00	0.00
-8	0.06	0.05	0.77	0.20	0.07	0.00	0.16
-9	0.05	0.04	0.29	0.42	0.10	0.00	0.01
-10	0.05	0.02	0.13	0.15	0.09	0.00	0.00
-11	0.05	0.01	0.11	0.12	0.07	0.00	0.00
-12	0.11	0.04	0.07	0.31	0.11	0.04	0.06
-13	0.00	0.01	0.08	0.09	0.08	0.00	0.04
-14	0.28	0.04	0.11	0.27	0.07	0.00	0.00
-15	0.12	0.04	0.10	0.13	0.03	0.00	0.03
-17	0.04	0.01	0.06	0.25	0.15	0.00	0.14
-18	0.08	0.00	0.07	0.18	0.06	0.00	0.03
-19	0.84	0.06	0.11	0.11	0.07	0.05	0.04
-20	0.54	0.07	0.07	0.10	0.08	0.00	0.00
-21	0.33	0.06	0.26	0.22	0.03	0.01	0.08
-22	0.40	0.08	0.10	0.56	0.06	0.01	0.06
-23	0.13	0.05	0.06	0.13	0.05	0.00	0.01
-24	0.28	0.08	0.05	0.26	0.11	0.03	0.00
-25	0.02	0.00	0.00	0.42	0.01	0.02	0.00
-26	0.03	0.01	0.06	0.13	0.07	0.04	0.02
-27	0.08	0.02	0.14	0.31	0.15	0.00	0.06
-28	0.07	0.03	0.06	0.18	0.08	0.00	0.00
-29	0.00	0.01	0.04	0.11	0.08	0.00	0.01
-30	0.05	0.03	0.07	0.54	0.13	0.03	0.00
-31	0.04	0.03	0.13	0.19	0.08	0.03	0.00
-32	0.02	0.02	0.16	0.20	0.18	0.04	0.00
-33	0.06	0.00	0.03	0.07	0.04	0.00	0.01
-34	0.04	0.06	0.08	0.11	0.02	0.00	0.00
-35	0.03	0.06	0.19	0.26	0.04	0.03	0.02
-36	0.04	0.04	0.07	0.10	0.09	0.00	0.00
-37	0.03	0.03	0.16	0.08	0.00	0.09	0.04
-39	0.03	0.02	0.03	0.09	0.05	0.00	0.00
-40	0.02	0.00	0.03	0.23	0.06	0.00	0.01
-41	0.05	0.03	0.09	0.17	0.07	0.00	0.00
-42	0.03	0.00	0.00	0.17	0.02	0.00	0.00
-43	0.03	0.01	0.06	0.06	0.05	0.01	0.00
-44	0.05	0.03	0.06	0.17	0.07	0.00	0.00
-45	0.04	0.03	0.06	0.32	0.07	0.01	0.00
-46	0.06	0.03	0.07	0.23	0.07	0.00	0.00
-47	0.01	0.00	0.00	0.11	0.02	0.00	0.00
-48	0.04	0.03	0.12	0.14	0.05	0.01	0.00
-49	0.03	0.01	0.05	0.14	0.03	0.00	0.00
-50	0.03	0.02	0.06	0.19	0.05	0.01	0.00
-51	0.03	0.02	0.05	0.18	0.05	0.01	0.00
-52	0.04	0.03	0.15	0.12	0.05	0.01	0.00
-53	0.06	0.01	0.05	0.24	0.10	0.02	0.00
-54	0.48	0.03	0.05	0.15	0.03	0.01	0.02
-55	0.00	0.03	0.03	0.14	0.01	0.01	0.01
-56	0.65	0.05	0.11	0.21	0.05	0.03	0.03
-57	0.00	0.04	0.03	0.06	0.00	0.00	0.01
-58	0.02	0.01	0.04	0.08	0.04	0.00	0.00
-59	0.00	0.03	0.00	0.10	0.05	0.01	0.02
-60	0.02	0.02	0.04	0.27	0.02	0.01	0.00

Table 1. Results of Organochloro-Pesticides (OCPs) (concentration in ng/g)

Depth (cm)	heptachlor epoxide	a-chlordane	endosulfan 1+r-chlordane	p,p'-DDE	Dieldrin	o,p'-DDE	Endrin
-3	0.19	0.28	0.38	7.56	0.27	2.25	0.44
-4	0.00	0.18	0.12	6.95	0.00	1.38	0.00
-5	0.00	0.09	0.15	7.55	0.00	1.29	0.00
-6	0.00	0.06	0.10	8.30	0.00	1.27	0.00
-7	0.00	0.08	0.07	9.36	0.00	1.42	0.00
-8	0.00	0.01	0.00	3.93	0.00	0.49	0.00
-9	0.00	0.02	0.00	2.01	0.00	0.27	0.00
-10	0.00	0.00	0.04	0.96	0.00	0.15	0.00
-11	0.00	0.00	0.03	0.79	0.00	0.12	0.00
-12	0.00	0.05	0.02	0.47	0.00	0.20	0.00
-13	0.00	0.07	0.05	0.27	0.00	0.21	0.00
-14	0.00	0.05	0.04	0.19	0.00	0.00	0.00
-15	0.00	0.00	0.03	0.31	0.00	0.14	0.00
-17	0.02	0.05	0.02	0.13	0.02	0.00	0.00
-18	0.00	0.10	0.05	0.15	0.00	0.00	0.00
-19	0.00	0.03	0.06	0.13	0.00	0.14	0.15
-20	0.00	0.00	0.00	0.12	0.00	0.00	0.00
-21	0.00	0.08	0.22	0.11	0.02	0.17	0.25
-22	0.00	0.07	0.02	0.13	0.00	0.06	0.09
-23	0.00	0.01	0.01	0.12	0.00	0.00	0.11
-24	0.00	0.00	0.02	0.07	0.00	0.14	0.81
-25	0.00	0.02	0.02	0.56	0.00	0.10	0.00
-26	0.00	0.01	0.02	0.06	0.00	0.13	0.00
-27	0.24	0.05	0.03	0.06	0.00	0.91	0.04
-28	0.00	0.05	0.04	0.10	0.00	0.00	0.00
-29	0.00	0.02	0.02	0.14	0.00	0.06	0.00
-30	0.00	0.19	0.09	0.09	0.00	0.13	0.00
-31	0.00	0.01	0.06	0.07	0.00	0.34	0.00
-32	0.00	0.12	0.21	0.10	0.00	1.93	0.00
-33	0.00	0.02	0.02	0.08	0.00	0.04	0.00
-34	0.00	0.02	0.02	0.07	0.00	0.00	0.00
-35	0.03	0.07	0.38	0.05	0.01	0.14	0.09
-36	0.00	0.03	0.02	0.05	0.00	0.06	0.00
-37	0.00	0.04	0.10	0.03	0.00	0.08	0.07
-39	0.00	0.01	0.01	0.03	0.00	0.00	0.00
-40	0.00	0.03	0.04	0.04	0.00	0.07	0.00
-41	0.00	0.01	0.07	0.03	0.00	0.22	0.00
-42	0.00	0.02	0.07	0.03	0.00	0.13	0.00
-43	0.00	0.00	0.02	0.03	0.00	0.13	0.00
-44	0.00	0.01	0.05	0.03	0.00	0.15	0.00
-45	0.00	0.09	0.06	0.02	0.00	0.09	0.00
-46	0.00	0.00	0.04	0.03	0.00	0.11	0.00
-47	0.00	0.01	0.01	0.02	0.00	0.02	0.00
-48	0.00	0.01	0.02	0.02	0.00	0.00	0.00
-49	0.00	0.01	0.03	0.03	0.00	0.09	0.00
-50	0.00	0.01	0.02	0.03	0.00	0.05	0.00
-51	0.00	0.01	0.02	0.03	0.00	0.08	0.00
-52	0.00	0.02	0.02	0.03	0.00	0.13	0.00
-53	0.00	0.05	0.03	0.03	0.00	0.07	0.00
-54	0.00	0.01	0.02	0.04	0.00	0.06	0.00

Table 2. Results of OCPs (concentration in ng/g) (Continue)

(cm)	Endosulfan 2	p,p'-DDD	o,p'-DDT	Endrin aldehyde	endosulfan sulfate	p,p'-DDT	Endrin ketone
-3	0.33	1.30	0.66	0.33	0.35	0.95	0.32
-4	0.12	0.73	0.32	0.05	0.07	0.44	0.20
-5	0.05	0.76	0.29	0.00	0.00	0.41	0.00
-6	0.00	0.84	0.13	0.00	0.00	0.24	0.35
-7	0.00	0.85	0.12	0.00	0.00	0.16	0.00
-8	0.01	0.24	0.15	0.00	0.00	0.23	0.02
-9	0.00	0.17	0.11	0.00	0.00	0.07	0.00
-10	0.06	0.11	0.51	0.00	0.00	0.00	0.00
-11	0.05	0.09	0.42	0.00	0.00	0.00	0.00
-12	0.05	0.06	0.41	0.00	0.00	0.04	0.03
-13	0.08	0.02	0.72	0.00	0.00	0.05	0.00
-14	0.01	0.02	0.06	0.00	0.00	0.03	0.01
-15	0.05	0.10	0.19	0.06	0.00	0.46	0.01
-17	0.08	0.01	0.81	0.00	0.00	0.08	0.03
-18	0.01	0.02	0.15	0.00	0.00	0.04	0.00
-19	0.08	0.05	0.31	0.00	0.11	0.37	0.02
-20	0.06	0.04	0.14	0.00	0.00	0.06	0.05
-21	0.10	0.07	0.34	0.06	0.04	0.22	0.12
-22	0.04	0.02	0.31	0.00	0.05	0.09	0.03
-23	0.01	0.02	0.07	0.00	0.00	0.03	0.00
-24	0.09	0.05	0.28	0.00	0.00	0.05	0.01
-25	0.01	0.05	0.12	0.00	0.00	0.14	0.11
-26	0.00	0.01	0.17	0.00	0.00	0.06	0.09
-27	0.16	0.04	0.20	0.10	0.12	0.32	0.20
-28	0.02	0.02	0.12	0.00	0.00	0.05	0.11
-29	0.02	0.01	0.23	0.00	0.00	0.03	0.11
-30	0.03	0.05	0.32	0.08	0.06	0.14	0.17
-31	0.05	0.02	0.10	0.00	0.00	0.09	0.11
-32	0.24	0.05	0.14	0.07	0.16	0.21	0.13
-33	0.01	0.01	0.10	0.00	0.00	0.06	0.08
-34	0.02	0.03	0.22	0.00	0.00	0.00	0.05
-35	0.08	0.06	0.17	0.08	0.11	0.33	0.07
-36	0.02	0.02	0.09	0.00	0.02	0.02	0.06
-37	0.10	0.05	0.16	0.04	0.15	0.16	0.12
-39	0.01	0.01	0.06	0.00	0.01	0.04	0.06
-40	0.02	0.02	0.12	0.00	0.00	0.06	0.13
-41	0.08	0.02	0.11	0.00	0.03	0.10	0.07
-42	0.05	0.02	0.10	0.00	0.00	0.04	0.08
-43	0.03	0.02	0.11	0.00	0.02	0.05	0.09
-44	0.05	0.02	0.13	0.00	0.00	0.09	0.10
-45	0.00	0.00	0.17	0.00	0.00	0.08	0.08
-46	0.05	0.02	0.12	0.00	0.00	0.08	0.07
-47	0.00	0.01	0.05	0.00	0.00	0.03	0.04
-48	0.00	0.00	0.20	0.00	0.00	0.09	0.08
-49	0.02	0.02	0.08	0.00	0.00	0.03	0.04
-50	0.01	0.01	0.13	0.00	0.00	0.05	0.11
-51	0.00	0.01	0.11	0.00	0.00	0.06	0.08

Table 3. Results of OCPs (concentration in ng/g) (Continue)

Depth (cm)	methoxychlor	PCB209	Totals without ISTD
-3	0.14	1.22	21.30
-4	0.48	0.42	13.61
-5	0.62	0.00	13.03
-6	0.52	1.81	15.27
-7	0.00	0.00	14.51
-8	0.04	0.00	6.44
-9	0.18	0.00	3.75
-10	0.09	0.00	2.35
-11	0.08	0.00	1.95
-12	0.04	0.61	2.71
-13	0.09	0.00	1.86
-14	0.03	0.00	1.22
-15	0.02	0.00	1.81
-17	0.10	0.00	2.00
-18	0.08	0.52	1.55
-19	0.05	0.00	2.76
-20	0.02	0.00	1.33
-21	0.64	0.00	3.43
-22	0.09	0.06	2.32
-23	0.13	0.00	0.93
-24	0.21	1.23	3.76
-25	0.07	0.00	1.67
-26	0.06	0.00	0.97
-27	0.11	0.00	3.33
-28	0.11	0.00	1.05
-29	0.05	0.00	0.92
-30	0.94	0.57	3.72
-31	0.11	0.00	1.45
-32	0.52	0.00	4.53
-33	0.18	0.00	0.81
-34	0.03	0.00	0.77
-35	0.22	0.00	2.52
-36	0.01	0.10	0.84
-37	0.01	0.00	1.55
-39	0.12	0.00	0.59
-40	0.08	0.04	1.01
-41	0.00	0.00	1.15
-42	0.00	0.24	1.01
-43	0.16	0.00	0.88
-44	0.03	0.00	1.03
-45	0.04	0.00	1.15
-46	0.00	0.00	0.99
-47	0.02	0.00	0.36
-48	0.02	0.00	0.84
-49	0.02	0.00	0.63
-50	0.06	0.05	0.89
-51	0.07	0.00	0.81
-52	0.02	0.00	0.99
-53	0.11	0.77	1.84
-54	0.12	0.00	1.22

Table 4. Results of OCPs (concentration in ng/g) (Continue)

A critical appraisal of the data indicated that concentration values were higher at the lake bed surface and near surface for all detected organic compounds. The shape of the graphs of concentration with depth as well as age-concentration values conformed to this general trend.

From activities around the lake, there was no indication of direct sources of supply of pesticide entry into the lake. This is due to a concerted effort by the local people who avoid the use and application of pesticides in and around the lake due to the importance of the local fishing industry. According to ATSDR (2002), one of the modes of transmission of these pesticides is through the atmosphere and therefore, it could be inferred that the only possible source of deposition into the lake is through atmospheric transfer.

The mode of transfer for pesticides into water bodies such as rivers, streams, lakes and estuaries can be either by direct point source or non-direct point source. The situation in Lake Liangzi involves non-point source, as there is no evidence of a direct point source within the lake's environs. The catchment area does not have any rivers or streams inflow into the lake (fig 2) and since the use of any pesticides for farming activities around the lake is prohibited, run-offs could not be a source of deposition.

According to Sierra Club, (1998), properties attributed to pesticides show that upon their release into the atmosphere they can travel far from the point of application. In view of this, it could be inferred that the possible source of these pesticides could only be from remote areas and through atmospheric transfer. A significant indication presented by the sediment core analysis and the presence of the organochloro-pesticides was that their concentration levels conform to the time of usage for chemical application in agriculture in China. According to Chiras (2000), the traditional Chinese pest control methods were the practice for farming until very recent times, when modern chemical application became popular. This practice was when the people dug trenches and directly confronted the pests by catching them. Furthermore, the correlation of the concentrations to the sediment dating is not a surprise as China only adopted modern chemical pesticides after 1949. Chen et al. (1996), mentioned the use of DDT in the 1960's, a peak period of use occurring during the 1970's and the chemical banned in the early 80's due to its toxic effect. It should therefore, be noted that the indication of DDT in the sediment core is from the residue of previous usage. Again, this should not be a surprise as these pesticides belong to POPs and can persist for years post deposition.

3.1 Geochemical degradation of DDT

The geochemical degradation of DDT was observed from the variable concentrations of its derivative compounds, DDD and DDE. According to ATSDR (2002), DDD and DDE enter the atmosphere as contaminants of toxic breakdown products of DDT. A critical examination of these three organochloro-pesticides reflects the organic processional relationships that exist between them. These organic compounds, according to ATSDR, are easily broken down in the atmosphere with a half-life of two days. DDT in soils breaks down slowly to DDD and DDE through micro-organism activity at a half-life of between two and fifteen days. This partially explains the presence of these compounds at variable concentrations at different levels of the sediment core, which did not conform to the trend indicated by the other pesticides (Compare figures 4 to 9).

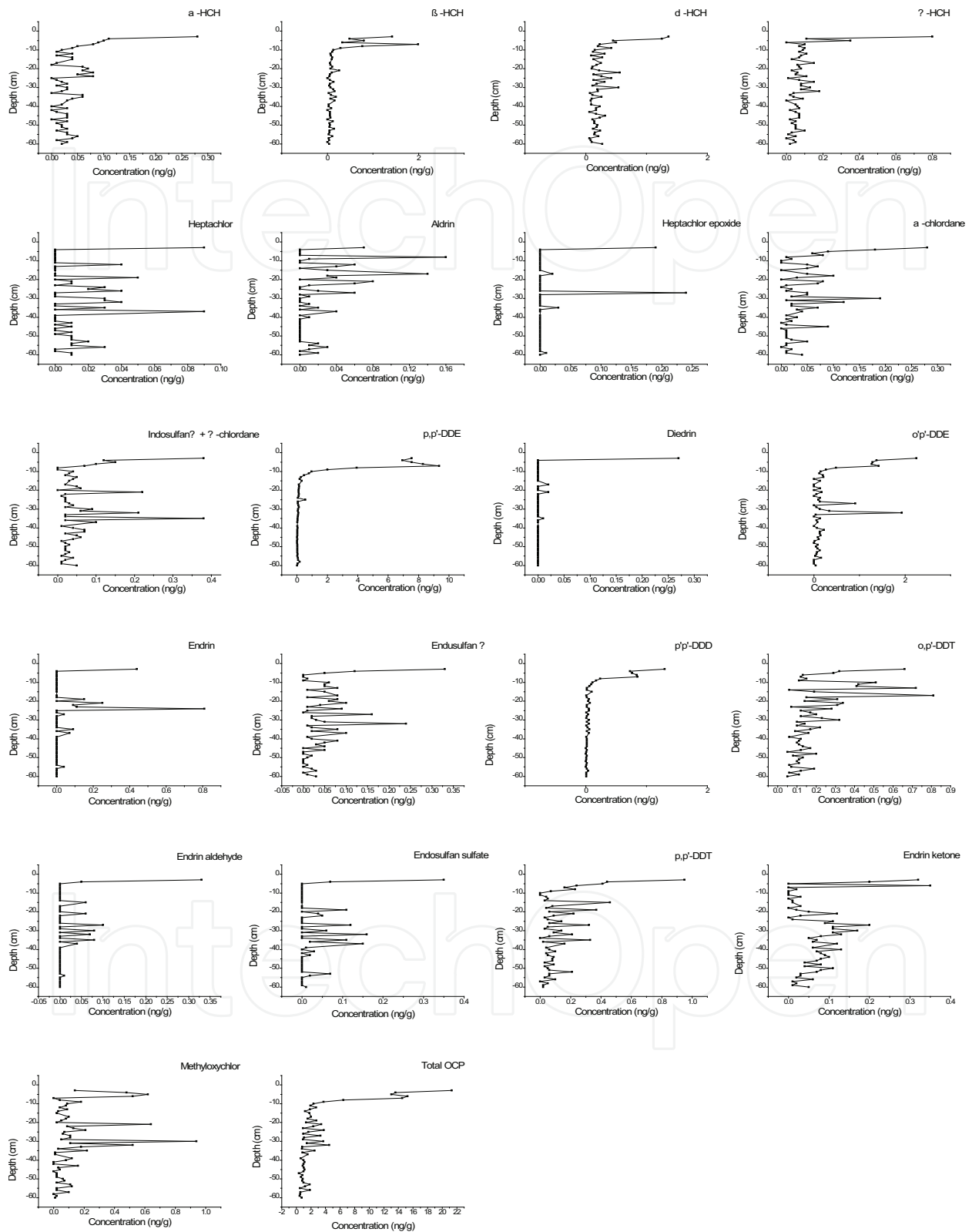


Fig. 4. Graphs of OCPs

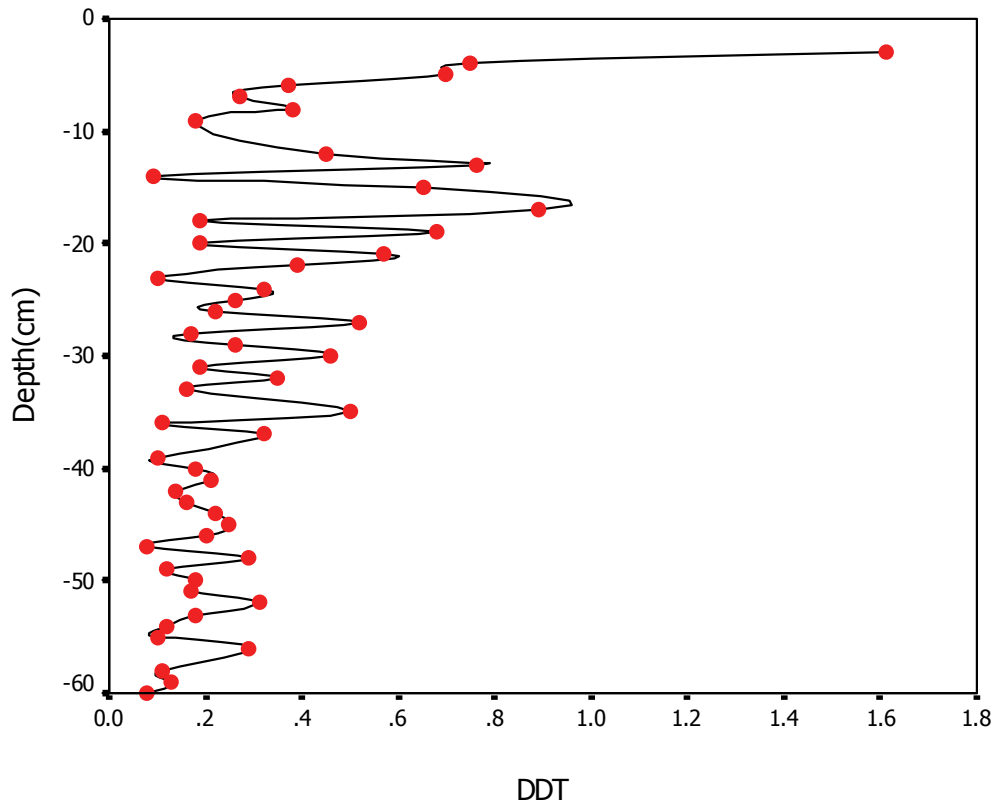


Fig. 5. Graph of Concentration (ng/g) of DDT versus Depth (cm)

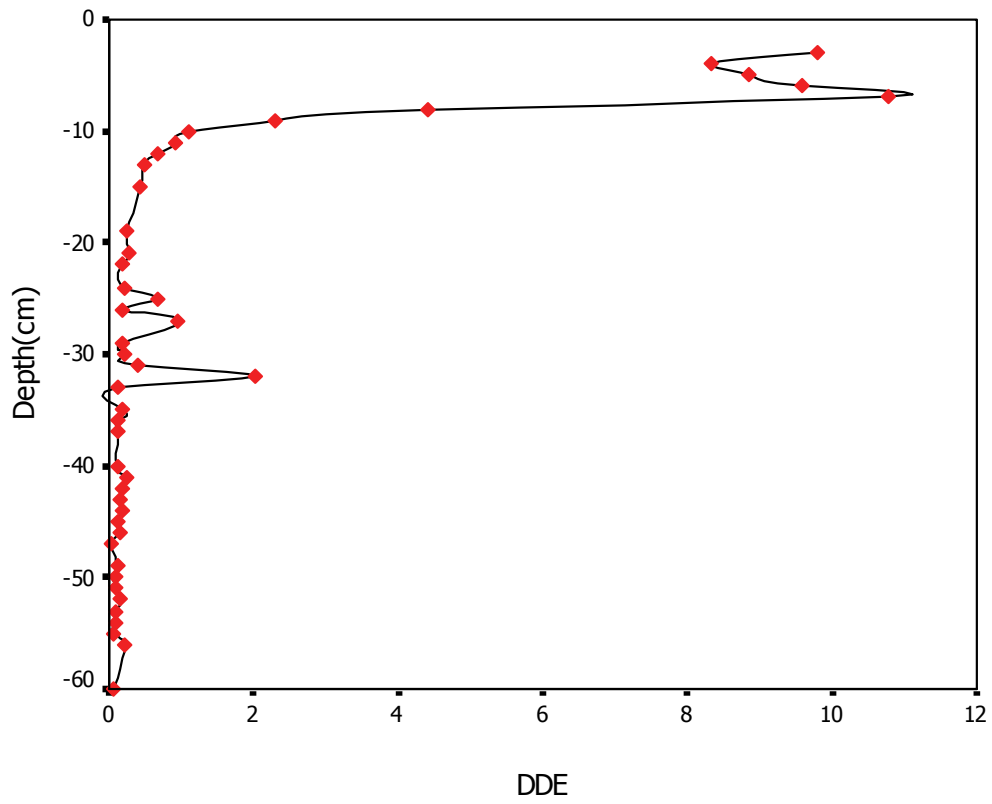


Fig. 6. Graph of Concentration (ng/g) of DDE versus Depth (cm)

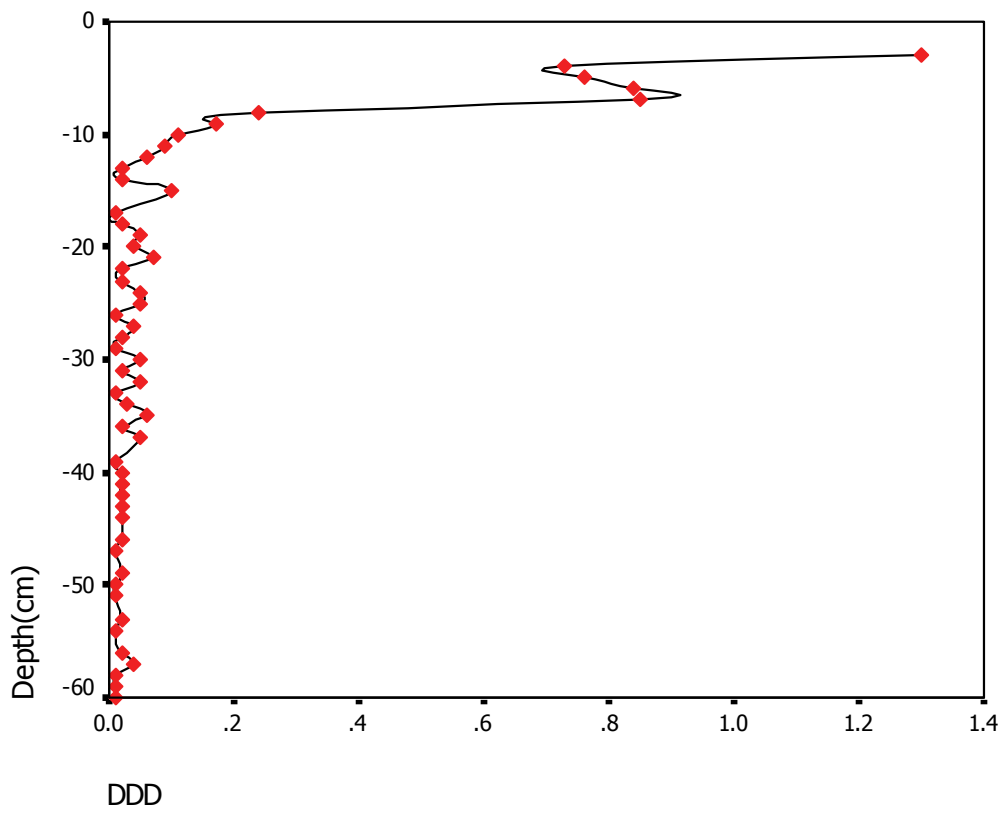


Fig. 7. Graph of Concentration (ng/g) of DDD verses Depth (cm)

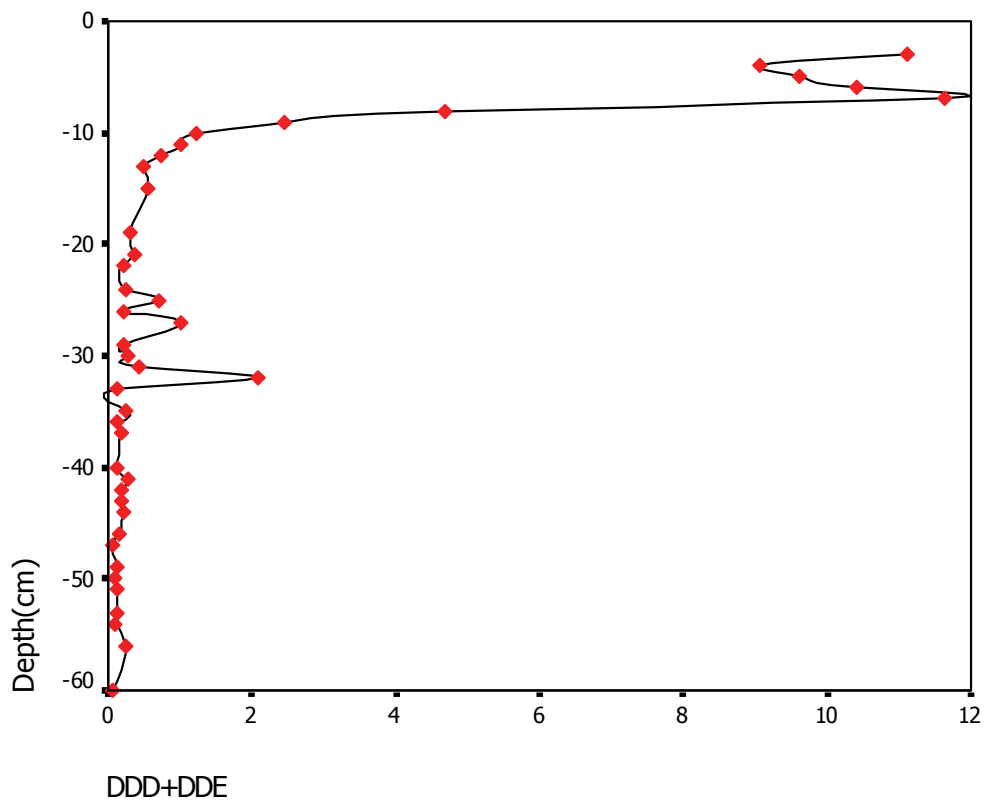


Fig. 8. Graph of Concentration (ng/g) of \sum DDD and DDE

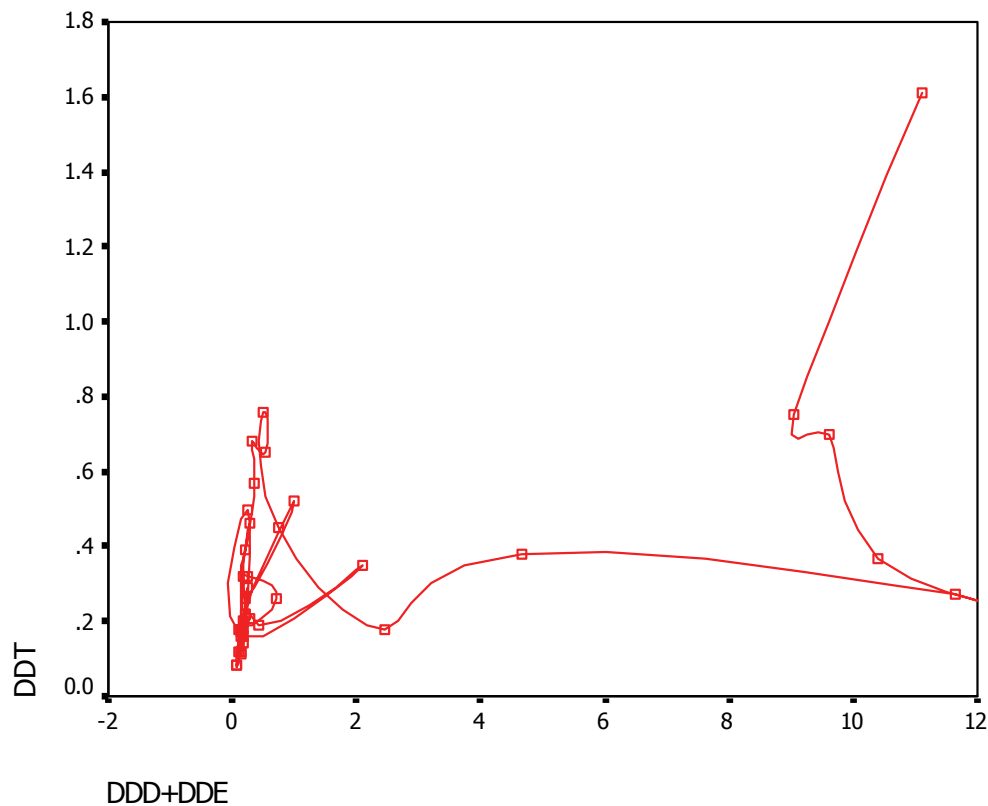


Fig. 9. Graph of ratio of DDT to \sum DDD and DDE

The most remarkable indication is the relatively higher concentrations of DDE over DDD. This is because DDE accumulates in plant and animal tissues. The extremely high concentration value for DDE at different levels is thus indicative of this phenomenon. It has been assumed that after the transformation from DDT or DDD the resultant DDE compound bio-accumulated in the fatty tissue of aquatic species (including micro-organisms) then decomposed and re-deposited in the lake sediments. The "apparent anomalous" indication of DDE and its predominance over other compounds detected is thus explained through this phenomenon of bioturbation. Also, according to Wedemeyer (1967), and Baxtor (1990), DDT undergoes slow degradation in comparison to DDD and DDE by chemical and biological processes in the natural environment. The degradation rate and degradation products are controlled by the parameters of environment conditions such as pH, redox condition and microbial activity. The ratio of various degradation products may, therefore, reflect some of the localized environmental conditions attributing to the degradation process.

An analysis of the general trend of the other detected organochloro-pesticides in the sediment core indicate that the variable concentrations may be attributed to leaching or post depositional geochemical processes within the sediment. In the analysis of sediment core, consideration will have to be given to the physical processes continually at work within sediments. This according to Sanders et al. (1992), could lead to a gradual alteration and possible disturbance of accumulating stratigraphy. Such mechanisms according to Sanders et al, eventually result in partial loss of temporal resolution within the core. Another issue to be considered according to Sanders et al. (1992), is the fate of a compound following deposition to a water surface, and the potential losses incurred during its passage through the water column and after incorporation into the sediment profile. They further indicate that biotic and abiotic degradation may serve to deplete certain susceptible compounds, and enhance levels of more recalcitrant components. It should be noted that a lake is an open

water body that is exposed to natural conditions such as the geochemical cycle, solar energy, atmospheric and aquatic effects. From the combination of these processes, and in view of the fact that these organochloro-pesticides are all of recent deposition into the lake, the equilibrium between deposition and maturity is yet to be reached. It should also be noted that the concentration levels of the pesticides detected are as a result of the recalcitrant nature of all the pesticides detected. It is suggested that the variability and distribution of the concentrations from high to low for most of the compounds detected throughout the sediment column could be attributed to these processes. Also sediment trap studies by Sanders (1993), suggest that fractions of organic pollutants entering the water column becomes incorporated into the bottom sediment and that large proportions of remainder is returned to the atmosphere, following outgassing across the water/air surface. Sanders indicate that it is important to acknowledge that historical sediment records do not quantifiably reflect inputs to a water body, but rather provide an over all qualitative time-trend assessment of the remaining resistant component.

4. Conclusion

Twenty one (21) different organo-chloro pesticides were detected from the single drilled sedimentary core from the bed of Lake Liangzi. All the 21 organochloro-pesticides detected indicated high values at the surface and decreased down in the sediment column. They all fall within the second generation of pesticides and the class of the organochloro-pesticides or organo-chlorines, commonly called OCPs. The organochloro-pesticides detected in the sediment core analysis included the most dangerous types; Dichloro Diphenyl Trichloro Ethane (DDT), Dichloro Diphenyl Dichloro Ethane (DDD) and Dichloro Diphenyl Dichloro Ethylene (DDE), which are among the ecological high risk class of organochloro-pesticides. The Organochloro detected were: Hexachlorocyclohexane (HCH, a,b,c), Heptachlor, Aldrin, Heptachlor Epoxide, Chlordane, Endosulfane 1 + r-Chlordane, Dieldrin, Endrin, Endosulfane II, Endrin Aldehyde, Endosulfane Sulfate, Endrin Ketone, Methoxychlor, p,p' DDE, o,p' DDE, p,p' DDD, o,p' DDT, and p,p' DDT

The general trend observed from the analysis indicated variable concentrations of the compounds throughout the column. Concentrations were relatively higher at the surface and near-surface of the column which is in conformity with dates during which pesticide use was prevalent in China. The geochemical degradation of DDT to DDD and DDE was also observed. The relatively higher concentration of DDE is due to the process of bioaccumulation. Most of the pesticides detected are from the residue of previous chemical composition, since DDT and other pesticides have been banned in China. The sources of deposition into the lake was atmospheric transfer, and their point source may be remote as there is no evidence of direct contamination for these organic compounds. The general trend observed indicated that the levels of concentration correlated with recent depositions for these organochloro-pesticides.

It could therefore, be inferred that Lake Liangzi has not been spared the menace of pollution, despite the attempts by the people to avoid the use and applications of any chemicals for farming activities.

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Pesticides in the Modern World - Risks and Benefits

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This book is a compilation of 29 chapters focused on: pesticides and food production, environmental effects of pesticides, and pesticides mobility, transport and fate. The first book section addresses the benefits of the pest control for crop protection and food supply increasing, and the associated risks of food contamination. The second book section is dedicated to the effects of pesticides on the non-target organisms and the environment such as: effects involving pollinators, effects on nutrient cycling in ecosystems, effects on soil erosion, structure and fertility, effects on water quality, and pesticides resistance development. The third book section furnishes numerous data contributing to the better understanding of the pesticides mobility, transport and fate. The addressed in this book issues should attract the public concern to support rational decisions to pesticides use.

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