Occurrence, Distribution and Sources of Organochlorine Pesticides (OCPs) in Karst Cave

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Abstract: Despite the numerous researches on Organochlorine pesticides (OCPs) in China and in the world, information regarding the distribution of OCPs in Karst caves is extremely limited. Karst area has much ecological vulnerability and it is so easy to be contaminated. This paper presents results of a monitoring program conducted in Dayan cave, Guilin, China that was designed to characterize levels, trends and sources of pesticides in soil samples. Thirteen soil samples were collected and OCPs were analysed. Inside the cave a total concentration of OCPs (∑OCPs) detected was 29.659 ng/g with a mean value of 3.295 ng/g and ∑OCPs detected outside the cave was 74.108 ng /g with a mean value of 18.527 ng/g. ∑OCPs outside the cave was higher than ∑OCPs outside the cave. The concentration of Chlordane in OCPs was highest among all the OCPs with range of 0.12─13.253 ng/g and mean value of 3.93 ng/g. The next compound with high level was Heptachlor wich ranged from Non-detected (ND) to 2.465 ng/g with a mean value of 1.4 ng/g. The pollution of OCPs in soil comparing with other countries and other areas in China was light. The analysis of Dichlorodiphenyltrichloroethane (DDT) and Hexachlorocyclohexane (HCH) isomers showed that there is a fresh input of Dicofol and Lindane in the area. By calculating the ratios of Dichlorodiphenyldichloroethane (DDD) to Dichlorodiphenyldichloroethylene (DDE) we found that the degradation of DDT outside the cave was aerobic and the degradation of DDT inside the cave was anaerobic. [Report and Opinion. 2009;1(1):6-16]. (ISSN: 1553-9873).

Key words: Organochlorine pesticides, Karst cave, Guilin, China

1.Introduction

Organochlorine pesticides are a group of persistent organic pollutants (POPs) which are to be eliminated or reduced on their release into the environment in many countries. Because of their persistence in the environment, and biological accumulation through the food web, OCPs can cause environmental damage, and affect human health (Colborn et al, 1996) .Due to their volatility and persistence in the air; OCPs are subjected to long-range atmospheric transport (LRAT). Therefore, OCPs released in the tropical and subtropical environments could be dispersed rapidly through air and water, and tend to be redistributed on a global scale (Tanabe, 1991) .The origin and fate of OCPs in soils with different land use have been extensively studied in many countries. Although the usage of OCPs was phased out for decades, the elevated concentrations were still observed in many agricultural soils (Harris et al., 2000) and the relationship between sites of greatest application and current residue levels was found strong (Shivaramaiah et al., 2002). The release of OCPs from soils continues to be a source to the environment (Meijer et al., 2001).

China is a large producer and consumer of Pesticides in the world (Rongbing et al., 2006). Large amount of OCPs were used in past decades to sustain over population in China. HCH and DDT were widely used in China from 1952-1983. Although their use had been discontinued in China since 1983, their persistence has left residual amounts in the soil in many areas (Zhao Ling

and Ma Yongjun, 2001). At present the use of DDT is still allowed to control mosquitoes, particularly in the malarial transmission zones in China (Zhang et al., 2005). Accordingly, China still produces a small amount of DDT and China is also allowed to export DDT to other countries for the same purpose. This paper presents the current status of OCPs residues in Dayan cave. The dataset generated will serve as a baseline for further studies.

2.Materials and Methods
2.1 Study Area

Region of research was in Guilin located in Guangxi Zhuang Autonomous Region in southeast China. Guangxi province (Southeast of China). The Geographical coordinates are 25° 40' 25" North, 108° 44' 0" East and has an altitude of 150m. It is bounded to the north-east by Hunan province, to the south-east by Hezhou town and it is next to Guangdong province. It has a surface area of 27, 800 square kilometers and a population of 4.76 million.

Dayan is an intermediate upper layer cave of Guilin Maomoatou cave system, located in the middle part of Guangming Mountain at right side of Taohua River in the north-west of Guilin. Guangming Mountain is a large peak cluster in Fenglin Plain, with an area of $0.92km^2$, the highest peak altitude of 404.4m and the plain altitude of 151m.The outcrop is a thick limestone layer of the Devonian system with a high intensity of Karst process. Dayan is a noncommercial cave located northeast to Ludiyan cave and southeast to Guangming Mountain. The map of Guangxi showing Guilin and plane diagram of Dayan cave are shown in Fig 1 and Fig 2 respectively.
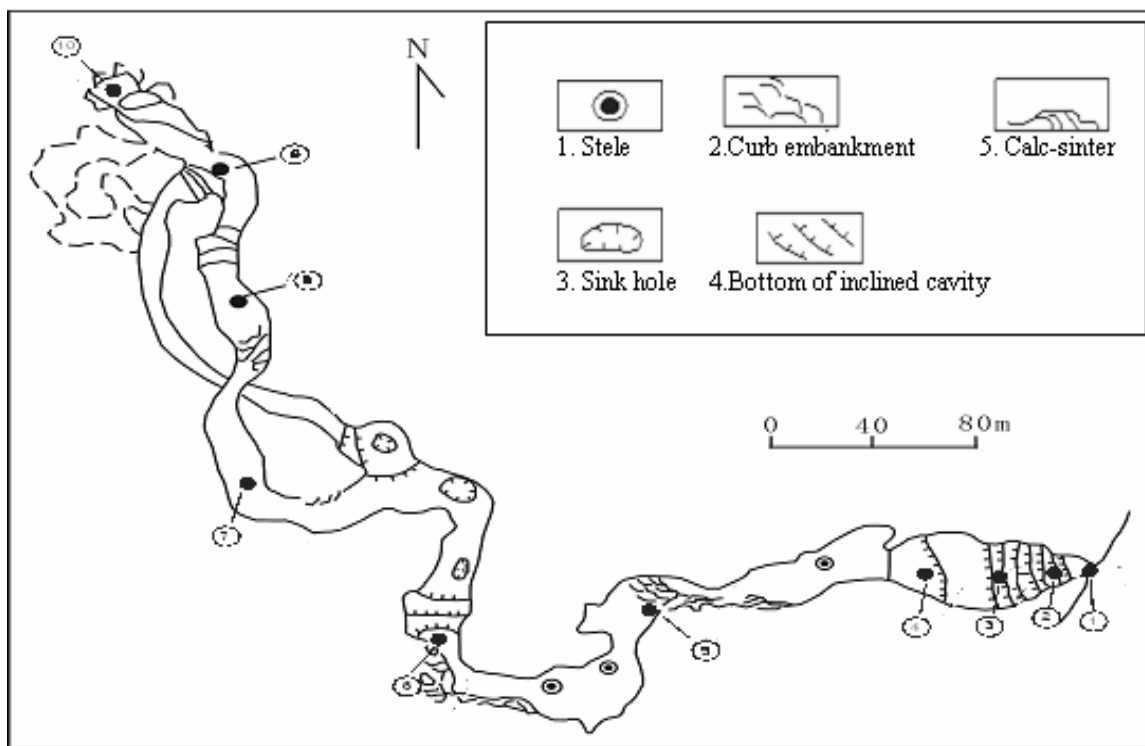

Fig 1: Map of Guangxi province showing Guilin

Fig 2: Map of Dayan Cave showing sampling locations (1─10) are sampling locations

2.2 Soil sampling

The collection of soil samples was done in September 2006 in the Dayan cave in Guilin. We placed 10 sampling locations inside the cave that followed the horizontal section from the east gate. (Sample number 1 was collected at the east gate) and the serial number was from 1-10 as shown in fig 2. Three samples (1 ', 2', 3') were also taken outside the east gate (downstream of the cave). Sampling was done with the use of a shovel and the samples were taken in a clean bag, and were well sealed and labeled. The weight of each sample was 500g. After the collection of samples, the samples were kept frozen in a refrigerator below -20°C prior to the commencement of the laboratory analysis.

2.3 Analysis
2.3.1 Experimental procedures

Before we began analyising the samples (before experiment) all glass wares were acid washed and cleansed with distilled water before they were dried in the oven at 200°C for about four hours. Reagents used for the experiment included: dichloromethane (DCM), hexane, acetone, sodium sulfate, alumina gel (100-200 mesh), silica gel (100-200 mesh), mesh hydrochloric acid and vitriol. Alumina and Silica gel were Soxhlet extracted for 24 hours in DCM solvent and then baked in the oven at 240°C and 180°C respectively for 12h. After cooling down, distilled water (3% of the reagent weight) was added to reduce the activity. Filter paper, aluminium foil, absorbent cotton and active copper were also used as materials.

A mixed standard sample of OCPs [2,4,5,6-tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (PCB 209)] were purchased as surrogate standards and were added to all the samples before the extraction. The whole process of pretreatment was based on US EPA SW-8080A method as reference. 20 g of the sample were weighed with electronic balance and injected with the surrogate (using a syringe) before the sample was Soxhlet-extracted for 48 hours with redistilled Dichloromethane (DCM). Active copper slices were added to the conical flask containing DCM to eliminate the influence of sulphur contained in the sample. After 48 hrs in the soxhlet extractor, the extracted samples were added with Sodium sulphate ($NaSO_4$) to remove unwanted water. After that, the solvents were concentrated to about 5 ml and then passed though a mixture of silica gel and alumina gel (10/3, V/V) for purification and it was rinsed by a mixture of DCM and hexane (2/3,V/V). The solvent was then condensed with high purity Nitrogen. 4 ml of the hexamethyl-benzene and PCNB (5ppb) were added as internal standards to help in quantifying the amount of OCPs present in the samples. Finally samples were stored and kept in the refrigerator until next analysis (Analysis by HP 6890 GC).

2.3.2 Analysis by HP 6890 GC

HP 6890 GC (Gas Chromatography) was equipped with a ^{63}Ni electron capture detector and a 30 m x 0.32 mm i.d (0.25 *lm* film thickness) DB-5 fused silica capillary column. Nitrogen was added as a carrier gas at 1.2ml/min. the oven temperature was kept at 40^oC for 5 minutes and increased to 290^oC at a rate of 4^oC/min. Injector and detector temperatures were maintained at 250 and 300^oC respectively. 2 Microliters (μl) of each sample was injected for analysis.

2.3.3 Quality control and Quality assurance (QC/QA)

Quality control and Quality assurance was made by the use of the USEPA method in the process of the experiment. The recovery rates and standard deviation of OCPs during separation and testing are within the limiting value of the US EPA 610 method. Recovery rates of TCMX and PCB209 are $69\pm6\%$ and $76\pm7\%$ respectively.

3.Results and Discussions
3.1 Concentration and distribution of OCPs

A summary of concentrations of OCPs detected in soil samples of Dayan cave is shown in Table 1.

Inside the cave ∑OCPs detected was 29.659 ng /g with a mean value of 3.295 ng /g and ∑OCPs detected outside the cave was 74.108 ng /g with a mean value of 18.527. ∑OCPs outside the cave is higher than the total concentration outside the cave (Fig 3). The levels of OCPs outside the cave compared to the levels inside indicate that despite the relatively closed environmental system of the cave and less human interference inside the cave, it still had OCPs contamination due to air transfer, rain water filtration and other processes, but the degree of contamination is not high.

Table1: Levels of OCPs in soil samples of Dayan Cave

	OCPs overall level range Min─Max(mean value）	OCPs level range inside the cave Min─Max(mean value) （2─10 samples）	OCPs level range outside the cave Min─Max(mean value) （1，1′，2′，3′samples）
α-HCH	0.014─0.170 (0.087)	0.014─0.126(0.043)	0.095─0.170(0.130)
β-HCH	0.026─0.219 (0.102)	0.026─0.219(0.087)	0.100─0.138(0.117)
γ-HCH	0.015─0.285 (0.092)	0.015-0.180(0.044)	0.075─0.285(0.140)
δ-HCH	0.009─0.072 (0.034)	0.009─0.045(0.024)	0.020─0.072(0.044)
TC	0.021─6.119 (1.841)	0.021─1.674(0.279)	3.226─6.119(3.403)
CC	0.085─7.134 (2.221)	0.101─3.111(0.849)	3.899─7.134(4.198)
Hep	ND─2.465 (1.399)	ND─1.087(0.139)	1.871─2.465(1.632)
Hep-Epo	ND─1.908 (0.911)	ND─1.022(0.379)	1.000─1.908(1.185)
EndoI	ND─0.230 (0.067)	ND─0.040(0.021)	0.103─0.230(0.122)
EndoII	ND─0.161 (0.046)	ND─0.057(0.021)	0.026─0.161(0.080)
Endosulfate	0.030─0.500 (0.175)	0.030─0.180(0.086)	0.200─0.500(0.294)
p,p'-DDE	0.011─0.342 (0.108)	0.011─0.109(0.041)	0.115─0.342(0.174)
p,p'-DDD	ND─0.121 (0.079)	ND─0.077(0.038)	0.011─0.121(0.059)
o,p'-DDT	0.049─0.467 (0.212)	0.049─0.226(0.113)	0.302─0.467(0.310)
p,p'-DDT	ND─0.090 (0.031)	ND─0.039(0.011)	0.046─0.090(0.050)
ΣDDTs[b]	0.094─0.875 (0.371)	0.094─0.384(0.162)	0.532─0.875(0.434)
ΣHCHs[a]	0.100─0.665(0.269)	0.100─0.453(0.197)	0.313─0.665 (0.430)
ΣOCPs[c]	1.159─23.625(10.911)	1.159─11.180(3.295)	13.250─23.625(18.527)

ND=Non- detected

ΣHCHs[a]= α-HCH + β-HCH + δ-HCH + γ-HCH.

ΣDDTs[b]= p, p'-DDE + p, p'-DDD + o, p'-DDT + p, p'-DDT.

ΣOCPs[c] =ΣHCHs+ΣDDsT+Σother OCPs.

Σother OCPs = Heptachlor (Hep) + Heptachlor epoxide (Hep-Epo) + TC (Trans-Chlordane) + CC (Cis-Chlordane) +EndoI (α-Endosulfan) +EndoII (β-Endosulfan) +Endosulfate.

The amount of Chlordane (TC+CC) in OCPs was highest among all the OCPs detected inside and outside the cave with a total concentration of 39.689ng/g and mean value of 9.92 ng /g inside the cave and a total concentration of 4.52 ng/g outside the cave with a mean value of 1.13 ng /g.

This is because South china have been using Chlordane to kill termites, so the high concentrations of Chlordane observed may be predominantly due to the use of technical Chlordane as a termiticide in this area in previous years . In China, technical chlordane is still being extensively used against termites in buildings, with an estimated amount of over 200 tons year^{-1} in recent years (Xu et al., 2004).

The next compounds with highest levels were Heptachlor (Hep) and Heptachlor epoxide (Hep-Epo.) Heptachlor (Hep) was also used and produced in large quantity in China. From 1967 to 1969 the amount of Heptachlor produced was 17 tons, to kill the termites and other insects in the soil. It is shown in Fig 4 that the majors parts of OCPs (HCHs and DDTs) at the cave's innermost sampling points 9 and 10 did not show the lowest values, but rather slightly greater than the values of sampling points 7 and 8 at the middle of the cave. This suggests that there may be a fracture pore near the north mouth that allows some air to come in.
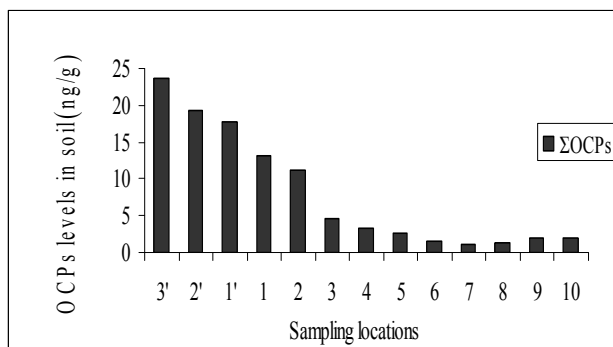
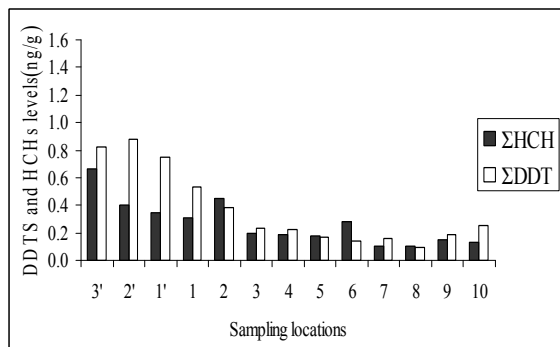Fig 3: Distribution of ΣOCPs in soil of Dayan cave

Fig 4: Distribution of ΣHCHs and ΣDDTs in soil of Dayan cave

Fig 4 shows that the total concentration DDTs (∑DDTs) in soil samples were higher than the total concentration of HCHs (ΣHCHs). This trend is consistent with the previous observations on the contamination of OCPs in soil in China (Zhou et al., 2001). A most likely explanation for the current low concentrations of HCHs in soil is due to the difference in the physicochemical and biochemical properties, wherein HCHs have higher water solubility, vapor pressure and biodegradability, and lower lipophicility and particle affinity compared to the DDTs (Rui et al., 2005). DDTs tend to remain in the particulate phase longer than HCHs. (Nhan et al., 2001).

In comparison with recent research reports, the concentrations of ∑DDTs and ∑HCHs measured in the study area was in the same low range with other pristine areas such as Tibet plateau where the concentration of ∑DDTs ranged from ND to 2.83 ng/g and ∑HCHs ranged from 0.18 to 5.38 ng/g (Fu et al., 2001), and European high altitude mountains that had ∑DDTs and ∑HCHs residual level in the range of 1.7-13 ng/g and 0.08-0.49 ng/g respectively (Grimalt et al., 2004). The average concentration outside the cave and inside the cave of∑ DDTs and∑ HCHs was lower than the average concentration of ∑DDTs and ∑HCHs which was 0.52 ng/g and 6.19ng/g respectively in Hong Kong soils (Zhang et al, 2006), and they were much lower than the average concentrations of ∑DDTs (37.6 ng/g) and ∑HCHs (12.2 ng/g) found in soils of Pearl River Delta Region (Fu et al., 2003). Some other studies reported around China, had higher residual levels of OCPs such as Beijing (Zhu et al, 2005), Tianjin (Tao et al., 2005), Nanjing (An et al., 2005). In Europe, DDTs and HCHs levels were in the range of 4.3-2400 and 0.36-110 ng/g in Poland soils (Falandysz et al., 2001). In comparison with similar research the levels of OCPs in Guilin were low and the reason is because there are mainly rice farms in the vicinity of Guilin city in which small amounts of OCPs were used with the rotary method of planting rice. The existence of alternating wet and dry conditions is beneficial to the aerobic and anaerobic degradation of OCPs, leading to a reduced amount of soil OCPs.

3.1.1 Distribution and degradation of HCH isomers

It has been widely recognized that HCH is available in two formulations: technical HCH and lindane. Technical HCH contains isomers in the following percentages: α, 55–80%; β, 5–14%; γ, 8–15%; δ, 2–16%; ε, 3–5% (Qiu et al., 2004), and Lindane contains > 90% of γ-HCH. The ratio of α- to γ-HCH has been used to identify the possible HCH source. If the source of HCH comes from fresh input of technical HCH, the ratio of α - to γ -HCH is between 3 and 7 (Yang et al., 2008). However, a lindane source will reduce the ratio to close or <1 (Willet et al., 1998). A higher ratio of α - to γ -HCH than 7 can be explained by long-range transport or re-cycling of technical HCH, because α -HCH has a longer atmospheric lifetime than γ isomer by about 25% (Willet et al., 1998). As shown in Fig 6, the ratios of α-HCH/γ-HCH in all soil sampling sites were lower than 3. Accordingly, the contamination of HCHs in this region probably came from local use of lindane and also indicated new Lindane inputs in the past several years.
By analyzing the individual HCH isomers (Fig 5) we found that β-HCH is the highest isomers detected, among all the samples it accounted from 20.03-79.13 %, especially in sample 3 to 7 where it accounted from 23-79% of the total HCHs detected. The β-HCH was higher because of its persistence in soil. The persistence of β-HCH in soils is mainly due to the higher K_{ow} (log K_{ow} =3.78) and lower vapor pressure value (3.6×10^{-7} mmHg, 20°C) (Zhang et al., 2006). These will make β-HCH easier to be absorbed to the soil organic matter and less evaporative loss from soils (Mackay et al., 1997). Furthermore, the spatial arrangement of Chlorine atoms in the molecular structure of β-HCH was supposed to be more resistant to microbial degradation in soils (Middeldorp et al., 1996).
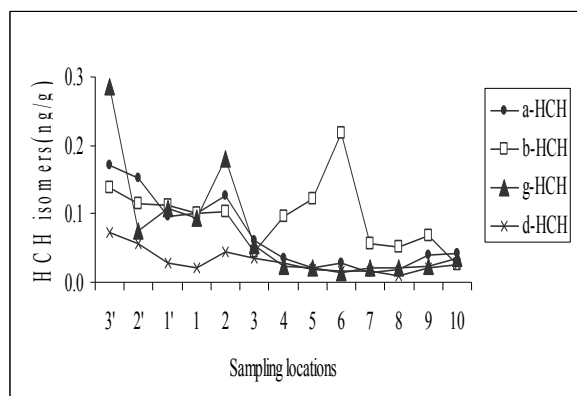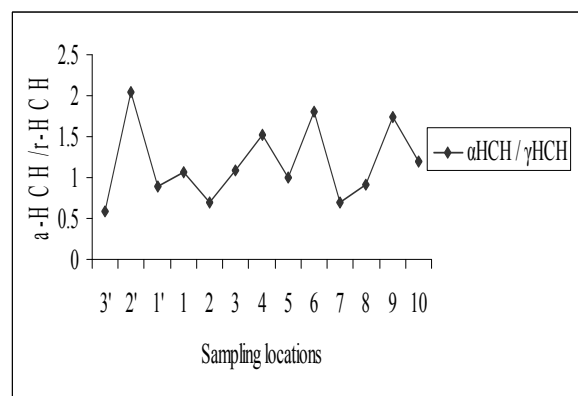

Fig 5: HCH isomers in soil of Dayan cave

Fig 6: Ratios of α-HCH to γ-HCH in soil of Dayan cave

3.1.2 Distribution and degradation of DDT isomers

Commercial DDT generally contains 75% *pp'*-DDT, 15% *o, p'*-DDT, 5%- *p, p'*-DDE, <0.5% *pp'*-DDD, <0.5 *op'*-DDE and <0.5% of unidentified compounds (WHO, 1979), but in Dicofol, the concentration of *o, p'*-DDT is more than *pp'*-DDT (Qiu et al., 2005). DDTs isomers have a long persistence in the environment and their levels in this study are shown in Fig. 7.

Since DDT can be biodegraded under aerobic condition to DDE and under anaerobic condition to DDD (Bossi et al., 1992). DDE and DDD Changes in the ratio of DDE and DDD to DDTs has been regarded as an indication of either no or decreasing inputs to the environment. The ratio of (DDE+DDD)/ ΣDDTs >0. 5 can be thought to be subjected to a long term weathering (Dong et al, 2002) and More *o*, *p′*-DDT than *p*, *p′*-DDT in the environment can demonstrate the dicofol-type DDT usage (Qiu et al., 2004).

The ratios of (DDE+DDD)/ ΣDDTs are shown in Fig 8. The ratios were in the range of 0.26-0.61 with most values being less than 0.5 (mean value is 0.4) and in Fig 7 we can see that the concentration of *o, p'* DDT is more than *p, p'* DDT as in Dicofol, this suggests that there is fresh input of Dicofol in the study area. Also, most values of DDD/DDE ratio (Fig 9) were greater than the unity inside the cave, indicating that the soil was dominated by *p, p'*-DDD, the product of anaerobic degradation of *p, p*'DDT (Zhou et al., 2006). DDD/DDE ratios ranged from 0.092 to 7 inside the cave with an average value of 2.31. Contrally outside the cave the ratios of DDD/DDE ranged from 0.052 to 0.53 with an average value of 0.35. The results obtained from the indices clearly indicated that DDTs in soil inside and outside of the Dayan cave may be derived from Dicofol and was retained under anaerobic conditions inside the cave and under aerobic condition outside the cave. The use of Dicofol in China is mainly in the southern and eastern provinces, mostly on litchi, longan, citrus crops and cotton (Yang et al., 2008).
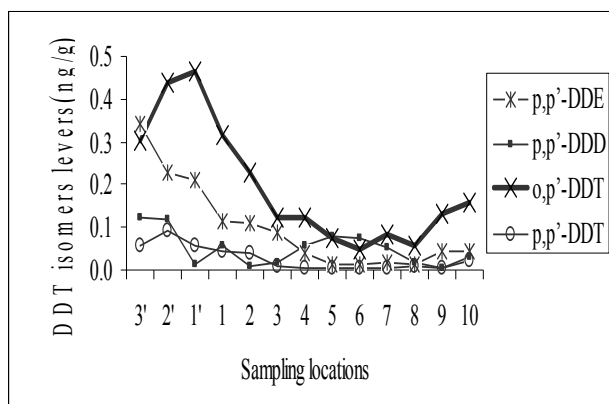

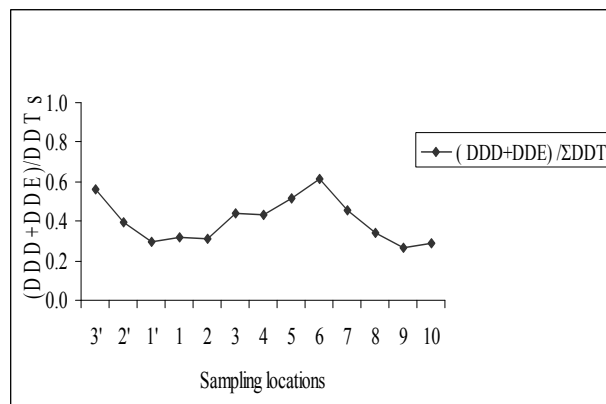Fig 7 Distribution of DDTs isomers in soil of Dayan Cave

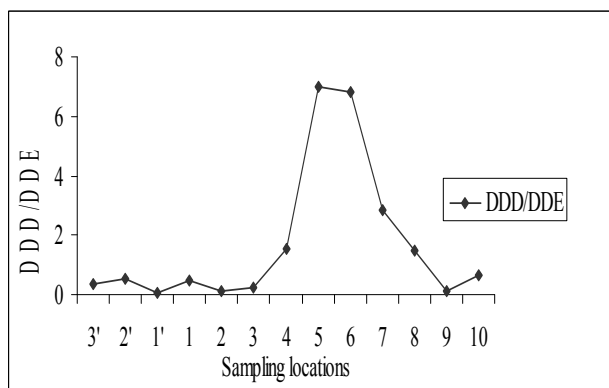Fig 8: Ratios of (DDD + DDE)/ ΣDDTs in soil of Dayan cave

Fig 9 Ratio of DDD/DDE in soil of Dayan Cave

4. Conclusion

The usage of HCHs and DDTs in China has been banned for 20 years and this sanction resulted in a tremendous decrease of OCPs concentrations in soils of Dayan cave. The residual levels of OCPs in soils outside Dayan cave were less than corresponding national values and among all the OCPs detected the concentration of chlordane and heptachlor were highest because they have been largely used in the study area. ΣDDTs and ΣHCHs in soil inside the cave were low in comparison with worldwide background mountains and polar regions. Summarily, the pollution of OCPs in the soils inside and outside Dayan cave was light. The analysis of isomers of DDTs and HCHs showed that there is fresh use of Dicofol and Lindane respectively in the study area. DDTs content in soil outside the cave was mainly aerobically degraded while anaerobic degradation occurred inside the cave.

Acknowledgement

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