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Organochlorine Pesticide Residue in Soils from Tibet, China

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Inexpensive and effective organochlorine pesticides, such as DDT and HCH used to be the most important pesticides after World War II, and they are intensively used even today to control vectors of disease such as malaria and yellow fever, or control forest pests in some countries. Although it is hard to estimate the total global consumption of DDT, it was reported that the production of DDT was 81,154 tones in 1963 in USA (WHO, 1979) and that of technical HCH in the world was estimated to be 40,000 tones in 1980 and 29,000 tones in 1990 (Li, 1996). DDT and HCH were also the main products of pesticides in China in 1970's. The production of DDT reached a maximum of 21,000 tones in 1973 and that of HCH was 14,497 tones in 1980. The production was banned in 1983 and only lindane (γ-HCH) is used in forest management to control pests in China. Although the use of organochlorine pesticides in agriculture has been banned for two or three decades in many countries, the behavior of the organochlorine pesticides in environmental system is even of more concern recently, because of their persistence in environmental system, toxicity to humans and animals, and their estrogenic effects in mammal and fish (Helm, 2000, Bidleman, 1995, Elkin, 1995, Willett, 1998).

Volatilization from reservoirs of accumulation, including soils, may be a significant source of these "old" pesticides to the atmosphere for decades after their usage have been banned. It was reported that cycles of volatilization, aerial transport, and deposition had led to a migration of organochlorine pesticides to lower temperature and polar regions (Mackay, 1996). Tibet is obviously a special area, not only because of its special geochemistry and geophysics characteristics, but also due to its special role in the recycling of persistent organic contaminates in the world. Situated at about 4,000 meters above sea level, Tibet is the highest plateau in the world and seems to be a receiving nexus for the deposition of trace contaminants coming from different long-range transports. Most parts of Tibet belong to remote area where influence of human activities is rare, and thus provide an ideal region to study the transportation of trace contaminants. However, up to now, there are very few researches on the organochlorine pesticides in Tibet. It is very important to investigate the environmental behaviors of organochlorine pesticides in this special area for appraising the environmental status. The purpose of this investigation is to study the distribution of HCH, DDT and its derivatives in the soils from Tibet.

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MATERIALS AND METHODS

Based on the preliminary investigation (Xie, 1997), eight basic stations were selected to collect soils for determination of organochlorine pesticides. The samples were collected from March 1993 to October 1994 by Institute of Geophysical and Geochemical Exploration. Some of them were the combined specimens which were collected from different sites near the sample location. The details are listed in Table 1. The sample locations are shown in Figure 1. The samples were ground to 60 mesh and stored in refrigerator until analysis.

2,4,5,6, -tetrachloro-m-xylene (97.00% purity) were purchased from Supelco Company. The reference standard mixture of organochlorine pesticides was obtained from National Research Center for Certified Reference Materials, China. All solvents were of analytical grade and redistilled in all glass system.

A modified method of EPA 608/8080 was used to analyze HCH and DDT in soil sample and is described as follows. Approximately 20-30 g of soil (wet wt.) was weighed accurately into beaker and 1 ml of 2,4,5,6-tetrachloro-m-xylene at the concentration of 1 μg/ml was added as internal standard. The sample was extracted with 50 ml acetone/ petroleum (1v/1v) by ultrasonication for 3 min. and then centrifuged at 3000 rpm to separate the extract from residue. This extraction was repeated three times. The combined extracts were reduced in volume by K.D. apparatus. After the solvent was changed to petroleum the sample solution was concentrated to about 1 ml under a gentle stream of nitrogen gas. A clean-up was performed by Florisil column chromatograph. The Florisil was activated for 16 h at 130 °C. Four grams of activated Florisil was packed in a 33 cm × 1 cm i. d. glass column with petroleum and covered with 1 g of anhydrous Na_2SO_4 on the top. After the sample solution was transferred onto the Florisil column, the column was eluted with diethylether/petroleum (1v/4v). 80 ml Eluate was collected and then reduced the volume to 1 ml for gas chromaotgraph analysis. HCHs and DDTs were analyzed by Varian 3700 gas chromatograph equipped with Ni^{63} electron capture detector (GC/ECD). A HP-17 column (25 m×0.30 mm) was used to analyze HCHs, DDTs with nitrogen as carrier gas. The injector temperature and detector temperature were 260° C and 270°C respectively. The oven temperature program was as follows: the initial oven temperature was 50°C for 2 min, then ramped to 260°C at 4°C /min and a final hold at 260°C for 10 min. All sample injectors were 1 μl in the splitless mode. Data acquisition was accomplished using a Shimadzu Chromatopac C-R3A. The reference standard mixture of eight organochlorine pesticides and metabolites (including α, β, γ, δ-HCH and op′-DDT, pp′-DDT, pp′-DDD pp′-DDE) was used for quantitative and qualitative analysis. The identification of organochlorine pesticides was based on retention time of analyte on chromatogram. Quantitative analysis was performed with internal standard. The detection limits of α,β,γ and δ-HCH were 0.08, 0.06, 0.40, 0.02 ng/g respectively, and those of op′-DDT, pp′-DDT, pp′-DDD and pp′-DDE were 0.17, 0.08, 0.06, 0.08 ng/g. The values below the detection limits were assigned as ND. The recoveries of HCHs ranged from

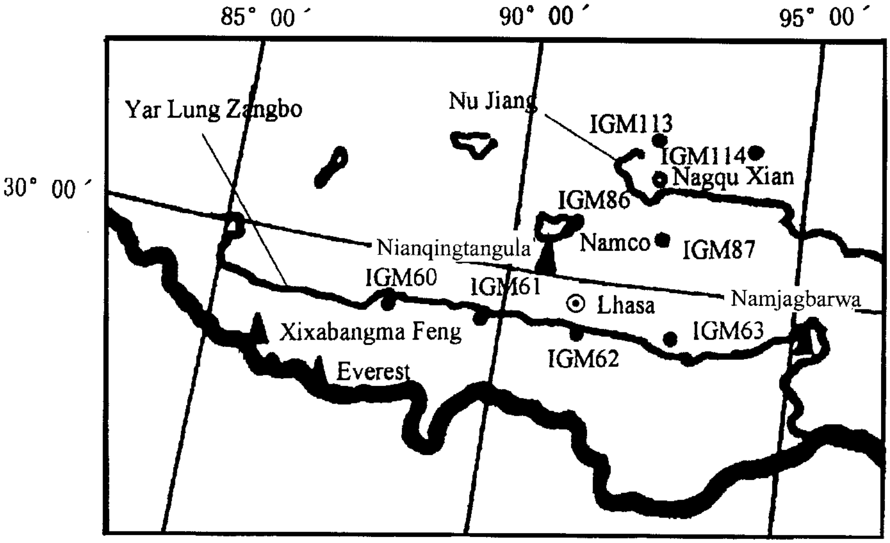

Figure 1. Study area and sampling stations

Table 1. The location of the sample stations

Location	Number of specimen	DATE	Longitude	Latitude
IGM 60	2	6/93	E88°0.8′	N29°15.0′
IGM 61	3	6/93	E89°37.7′	N29°15.0′
IGM 62	4	6/93	E91°14.6′	N29°15.0′
IGM 63	1	6/93	E92°51.5′	N29°15.0′
IGM 86	1	6/93	E90°52.3′	N30°45′
IGM 87	1	6/93	E92°30.5′	N30°45′
IGM 113	2	6/93	E92°12.8′	N32°15′
IGM 114	1	6/93	E93°52.5′	N32°15′

81.7% to 105.2%, and those of DDTs from 71.8% to 106.4%. A standard curve containing the pesticides and internal standard was freshly prepared and run daily.

Residual water was measured for each sample by heating subsample in oven at 105 °C for 12h and the concentration of the contaminates were calculated on dry weight (d. w.) basis.

RESULTS AND DISCUSSION

In this study, eight organochlorine pesticides were determined for the samples from different locations in Tibet. The concentration of DDTs and HCHs are listed in Table 2 and Table 3 respectively.

Table 2. Concentration of DDT in soil from Tibet (ng/g d. w.)

NUMBER	pp′-DDE	op′-DDT	pp′-DDD	pp′-DDT	ΣDDT
IGM 60	0.62	ND	ND	0.09	0.71
IGM61	0.50	ND	0.16	0.52	1.18
IGM62	0.58	ND	ND	ND	0.58
IGM63	1.06	0.34	0.36	0.26	2.02
IGM86	0.00	ND	ND	ND	ND
IGM87	2.83	ND	ND	ND	2.83
IGM113	0.94	0.21	ND	ND	1.15
IGM114	0.31	0.22	ND	ND	0.53

Table 3. Concentration of HCH in soil from Tibet (ng/g d. w.)

NUMBER	α-HCH	γ-HCH	β-HCH	δ-HCH	ΣHCH
IGM60	0.20	1.54	1.29	ND	3.03
IGM61	0.12	0.83	ND	ND	0.95
IGM62	0.13	0.05	ND	ND	0.18
IGM63	0.80	1.77	0.12	0.03	2.72
IGM86	2.55	1.12	1.71	ND	5.38
IGM87	0.13	0.53	1.08	ND	1.74
IGM113	0.13	0.92	ND	ND	1.05
IGM114	0.10	0.57	ND	ND	0.67

The concentration of ΣDDTs, including pp′-DDE, op′-DDT, pp′-DDD and pp′-DDT, ranged from ND to 2.83 ng/g. The highest concentration was found in sample IGM87 while those in sample IGM86 was below the detection limit. Although it seems that the two stations are nearby in the map, they are separated by a high mountain of Nianqingtangula (7,117 meter above sea level). Whether the mountain possibly interfered the distribution of DDTs in this area is an interesting question.

Many investigations reported the distribution of the organochlorine pesticides in China. Very little work, however, has been done on the contamination in soil from Tibet. There was only data reported by Sun and his co-operators in 1986. The DDT residue levels at the mountain of Namjagbarwa were 0.465-7.011ng/g (Sun, 1986). Comparing the previous data with those from this investigation, the contamination of DDTs in this area in 1993 was obviously lower than those of ten years ago, which may have resulted from China's banning the use of this insecticide in 1983. In 1982, an investigation showed that in Wu county, in the southeast of China, the concentration of DDT in soil ranged from 13 to 3669 ng/g, and the mean value was 306 ng/g(Ma, 1986). After ten years, in another investigation in 1992, it was reported that the pollution level of DDT in soils from the plain area of south of China was 0.12 μg/g (Yang, 1992). In 1990, Jing and his co-operators investigated the human exposure and body burden of organic chlorine compounds in Wuxi city, Jiangsu province, and reported that the contamination of DDTs in soil was 203 ng/g(Jiang, 1993). Based on these data and others investigations, the DDT pollution in Tibet area was much lower than those of other areas in China where DDT was directly used to control pest while the pollution in Tibet area resulted from snow, rain and long-range atmospheric transportation (Zhang, 1997).

In all samples analyzed, pp'-DDE, which is the main metabolite of pp'-DDT, was the compound that appeared at the highest concentration, ranging from ND to 2.83 ng/g. Generally, the parent/metabolite ratio decreases with time if there is no other pollution source and the ratio of concentration of ∑DDT versus those of DDE reflects the pollution resource (Dimond , 1996). In this investigation, the average ratio of ∑DDT vs. DDE was 1.48.

The concentrations of ΣHCH in the samples of soil ranges from 0.18 to 5.38 ng/g and the mean value is 1.97 ng/g. It was reported that the concentration of ΣHCH in soil in China ranged from 169-1065 ng/g in 1980, 740ng/g in 1981(Li, 1999). Zhang and his co-operators analyzed 350 paddy soil samples in China to determine HCH in 1983. The concentration ranged from 0.021 to 1.96 μg/g, and the mean value was 0.307 μg/g(Zhang, 1983). In Wu county the concentration was 0.035-3.669 μg/g and the mean value was 0.306 μg/g (Ma, 1986). In 1984, Liao investigated the HCH pollution in paddy field in the south of China and reported the concentration was 0.0017- 0.6793μg/g, while the mean value was 0.1462 μg/g (Liao, 1986). In these previous investigations, samples mostly collected from cultivated area. Considering the usage of technical HCH was 4464 kilo tons (Li, 1999) before 1983 in China, and most of them was used in the southeast, east, and northeast of China, the results are reasonable. The concentrations of HCH in samples from remote areas are much lower than those from cultivated soil samples. Xie and his co-operators determined the HCH in national area of Xiling snow capped mountains in 1994. The concentration of HCH ranged from ND to 0.004 μg/g (Xie, 1995). This concentration is closed to those results in our recent investigation in Tibet. It means that this range is the concentration of soil contaminated by HCH from long-range atmospheric transport.

Generally, technical HCH contains 55-80% α-HCH, 5-14% β-HCH and 8-15% γ-HCH. As α-HCH and γ-HCH are highly volatile compounds and tend to migrate faster than other isomer, the higher concentrations are generally found in arctic air and seawater or other remote area. In this investigation, α-HCH and γ-HCH were found in all the eight samples, and they were the predominant compounds of the eight determined organochlorine pesticides. It was reported that if technical HCH was the pollution source, the α-HCH/ γ-HCH should be from 5.3 to 6.67. As it can be seen in Table 3, the α-HCH/ γ-HCH ratio ranges from 0.13 to 2.6 and the average is 0.77, which is much lower than the values of 5.3. Based on these facts, the contamination of HCH in this area may mainly come from long-range transport.

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