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Chlorinated hydrocarbons in animal tissue samples from the Arctic Area

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Abstract This study presents our preliminary results of the concentrations of chlorinated hydrocarbon contaminants in muscle, liver of caribou and intestine tissues of seal collected from the Arctic Area by China Arctic Scientific Expedition in April 1995. Hexachlorocyclohexanes (α, β, γ and δ-HCH), DDT group (p,P′-DDE, o, P′-DDT, p,P′-DDD and p,P′-DDT) and polychlorinated biphenyls (PCBs) were analyzed. The concentrations of $\sum$HCH ranged from 3.13 ng/g to 7.02 ng/g and those of $\sum$DDT ranged from 0.16 ng/g to 1.28 ng/g. 14 individual PCB congeners, each in the range of 0.01 - 0.12 ng/g, were detected and the concentration of $\sum$PCB was from 0.14 ng/g to 0.60 ng/g. Also, the results were compared with the data reported previously.

Key words organic chlorinated pesticides, PCB, caribou, seal, Arctic.

1 Introduction

Existence and distribution of organic contaminants in the arctic biosphere bring on questions concerning the fate and temporal and spatial trends of contaminants in arctic marine, freshwater and terrestrial environments. The relatively simple food web structure and low biodiversity combined to offer an excellent investigative environment of the Arctic Area (Landers 1995). There are great gaps in our knowledge regarding their contamination of environmental compartments in polar region although former report has proved its presence(Elkin and Bethke 1995). It is very important for us to further our understanding of this topic. Caribou (*Rangifer tarandus*) are strict herbivores with a winter diet consisting primarily of lichens. Lichens have surfaces accumulating year round atmospheric contaminants nonselectively, resulting in a contaminant layer corresponding to atmospheric input through long-range transport. As a result, caribou exhibits a contaminant pattern very similar to that in the atmosphere. Its simple food chain and the pan-arctic distribution make caribou a good species for monitoring changes in arctic terrestrial ecosystem contamination (Elkin and Bethke 1995). Different from those of caribou, the principal food of seal (*Phoca hispida*) are fish, and the contaminants in their bodies are mainly from sea water. This study focuses on the concentrations and compositions of the organochlorine compounds in the animal samples.

2 Material and methods

2.1 Sampling

Samples of the liver and muscle of caribou and intestine of seal were collected on the Resolute Bay (74°N, 95°W) (Fig. 1) in April 1995. They were packaged with aluminum foil pre-cleaned with acetone and kept frozen until analyzed. The control sample, beef, was bought from a market in Beijing.

2.2 Analytical procedure

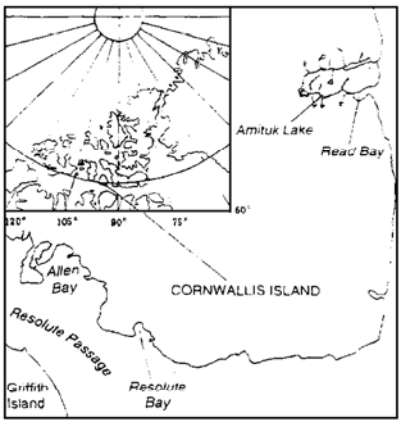

Fig. 1. Map of sampling location, Resolute Bay, N. W. T. Canada.

Liver, muscle and intestine samples were analysed for chlorinated pesticides and polychlorinated biphenyls separately and the methods are briefly introduced here. About 20 g tissue sample was homogenized with 40 g anhydrous Na_2SO_4 until free flowing powder was obtained. The powder was then extracted with 3 × 100 ml dichloromethane (DCM)/hexane (50:50, V/V) by ultrasonication and separated by centrifuging, then the extract was K. D. concentrated to about 5 ml. To clean up the sample the extract was washed with 5 ml concentrated H_2SO_4. This treatment should repeat several times until the organic phase was clear, then the organic solution was washed with distilled water and dried by anhydrous Na_2SO_4. The further separation was done by chromatography with Florisil column. Florisil (60 – 100 mesh from Floridin, US) was activated for 12 h at 130℃. 6 g of activated Florisil was packed in a 1 cm × 33 cm glass column with hexane and 1 g of anhydrous Na_2SO_4 on top. After the sample solution was concentrated to about 1 ml and the latter was transferred onto the Florisil column, two fractions F_1 and F_2 were prepared by eluting with 50 ml hexane and 50 ml DCM/hexane (85:15, V/V) successively. After concentrating the fractions to proper volume for GC analysis, F_1 was for p,P′-DDE and PCBs determination, while F_2 was for o,P′-DDT, p,P′-DDD, p,P′-DDT and HCH (Lazar *et al.* 1992).

The chlorinated hydrocarbons were analyzed with a Varian 3740A gas chromatograph equipped with ^{63}Ni electronic capture detector and the carrier gas was highly pure nitrogen. Two different kinds of quartz capillary columns were used to analyze the two fractions. SE-54 column (0.25 mm × 18 m) was used to analyze F_1 for PCBs and DDE, and HP-17 column was used to analyze F_2 for HCH and DDT group. The chromatographic conditions were as follows: when SE-54 column was used, injector temperature was 300℃ and detector temperature was 350℃. An initial oven temperature of 50℃ was maintained for 2 min, and increased at 4℃/min to a maximum of 280℃ for 20 min. When HP-17 column (0.32 mm × 25 m) was used, injector temperature was 280℃ and detector temperature was 300℃. An initial oven temperature of 50℃ was maintained for 2 min, and increased at 4℃/min to a maxi-

mum of 250℃ for 20 min. The sample was injected in splitless mode . Data acquisition was accomplished through a Shimadzu Chromatopac C-R3A.

In this report pesticides qualification was based on retention time and quantification on chromatographic peak area by external standard method excluding blanks with standard solution (including α, β, γ and δ-HCH and p, P′-DDE, o, P′-DDT, p, P′-DDD and p, P′-DDT, from National Standard Materials Research Center of China). PCB congeners qualification and quantification followed the methods suggested by Chu *et al.* (1996) and Capel *et al.* (1985) apiece with standard Aroclor 1254 (from Supelco, US) solution (Chu *et al.* 1996; Capel *et al.* 1985). The recoveries from spikes of 25 ng/g were 78.0% and 91.0% for HCH and DDT respectively and the relative deviation was less than 10%, for PCB-194, PCB-138, PCB-118 and PCB-52 the recoveries were 92.0%, 78.4%, 104.4% and 68.6% each from spikes of 1.06, 18.2, 23.0 and 6.68 ng/g respectively, and the relative deviation was less than 15%. The detection limits of α, β, γ and δ-HCH were 0.03, 0.04, 0.04 and 0.01 ng/g each while those of the total amounts of DDT and PCBs were 0.01 and 0.05 ng/g.

3 Result and discussion

Concentrations of organochlorines in three animal samples are listed in Table 1. ∑HCH is the sum of four HCH isomers and ∑DDT is the sum of four related DDT components. ∑HCH is 3.13 – 7.02 ng/g, and ∑DDT ranged from 0.16 ng/g to 1.29 ng/g. The eight pesticides were found almost in every sample except that p, P′-DDT was undetectable in caribou muscle. Although manufacture and usage of pesticides are far from the sampling site, the organic contaminants can be transported all over the world with atmosphere circulation, fish migration, etc.. In order to compare the contamination level a beef sample from the Beijing market was also analyzed. The concentrations of 20.9 ng/g ∑HCH and 33.9 ng/g ∑DDT obtained are nearly one and two orders of magnitude higher than those of the caribou muscle sample.

The values of ∑HCH/∑DDT in caribou muscle and liver are 19.6 and 14.3, close to the data from Lake Harbour (62°51′N, 69°53′W) 15.4 and Cape Dorset (64°14′N, 76°32′W) 15.6, and significantly different from the data of the Southampton Island (64°08′N, 83°10′W) 30.7 and Arviat (61°07′N, 94°04′W) 58.5.

Altogether 14 PCB congeners were detected and listed in Table 2. The sum concentration ∑PCB is 0.14 – 0.60 ng/g. The highest level was found in caribou liver followed by those in seal intestine and caribou muscle which is similar to that of

Table 1. Concentrations of chlorinated pesticides in samples of animals from the Arctic Area (ng/g wet weight)

Pesticides	Caribou muscle	Caribou liver	Seal intestine	Pesticides	Caribou muscle	Caribou liver	Seal intestine
α-HCH	1.01	3.32	2.47	p, P′-DDE	0.02	0.15	0.14
β-HCH	1.06	3.06	0.79	o, P′-DDT	0.11	0.13	0.12
γ-HCH	0.97	0.53	2.54	p, P′-DDD	0.03	0.01	0.10
δ-HCH	0.09	0.11	0.18	p, P′-DDT	–	0.20	0.93
∑HCH	3.13	7.02	5.98	∑DDT	0.16	0.49	1.29

HCH. It is reason-able to consider that detoxifying function and more fat consistence of liver tissue are the main reasons of its higher contaminants level. From the pattern of PCB congeners (Fig. 2), it can been seen that both the amount and number of congeners existing in liver are the highest. Some related analysis results of organochlorine contaminants in atmosphere of the Resolute Bay were reported as well. For example, Bidleman *et al.* (1995) informed that summation of α and γ-HCH was 124 pg/m^3 and p, P′-DDT was less than 0.3 pg/m^3. Oehme *et al.* (1995) obtained the conclusion that the concentrations of PCB-138 and PCB-153 changed with seasons. Although our preliminary data are very limited, it is shown that long range atmospheric transport is probablly the major source of chlorinated hydrocarbons contaminations.

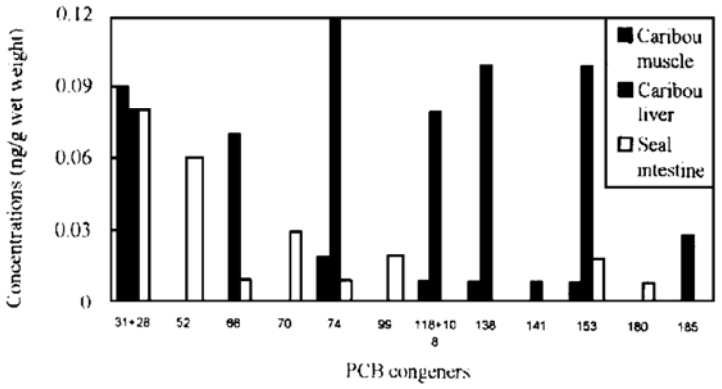

Fig. 2. Patterns of PCB congeners in the samples of animals from the Arctic Area.

Table 2. Concentrations of PCB congeners in samples of animals from the Arctic Area (ng/g wet weight)

IUPAC No.	Caribou muscle	Caribou liver	Seal intestine	IUPAC No.	Caribou muscle	Caribou liver	Seal intestine
31+28	0.09	0.08	0.08	138	0.01	0.10	
52			0.06	141	0.00	0.01	0.00
66		0.07	0.01	153	0.01	0.10	0.02
70			0.03	180			0.01
87			0.00	185		0.03	
99			0.02	194		0.00	
118+108	0.01	0.08		∑PCB	0.14	0.60	0.23

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