

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P300

Organic contaminants in natural surface soils from Svalbard

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Introduction

Long range transport of persistent organic pollutants (POP) to different parts of the Arctic environment has been extensively studied during the past years. A special focus has been on marine environments due to the special threat through biomagnification in a long and complex food web. There are considerably fewer available results from measurements of POP in terrestrial samples. However, to investigate deposition mechanisms, long-range air transport and the global fractionation theory it is necessary to study the POP concentrations in samples of vegetation, freshwater sediments or soil from remote areas. Soil samples taken in the Canadian and Russian Arctic (1) showed a background concentration of total PCB around 0.9 to 1.7 ng/g dry weight (dw). Samples in the vicinity of military radar stations showed concentrations up to 10000 ng/g dw. In this communication we report the concentration of PCB and HCB in natural surface soil taken on Svalbard (Spitsbergen archipelago).

Materials and Methods

During the summer seasons of 1990 and 1993 samples of natural surface soil were taken on Svalbard. The upper 2 – 3 cm of the humus layer were taken using a steel knife. The samples were stored in sealed aluminum boxes which were stored in cooling bags in the field. After return to the laboratory samples were stored at –20° C until analysis.

About 50 g soil sample was sifted through a 2 mm stainless steel sieve, weighed and transferred to a pre-cleaned cellulose extraction timble. Prior to extraction ¹³C-labelled PCB congeners and ¹³C-labelled HCB were added to the soil sample. The samples were first extracted with 300 ml acetone ((Merck, no 12) for 8 h and then with n-hexane (Merck, no 4371) for another 8 h. The extracts were combined and n-nonane was added as keeper. The combined extracts were concentrated to about 1 mL on a TurboVap 500 system (Zymark, Hopkinton, MA 01748). The concentrated extracts were treated with concentrated sulfuric acid. The organic phase was dried with sodium sulfate, transferred to a silica column and eluted with n-hexane/diethyl ether. After volume reduction to approximately 0.5 mL, 2 ng of tetrachloroaphtalene and 10 ng of octachloronaphtalene were added as recovery standards. The sample was further concentrated to 100 µL by applying a gentle stream of purified nitrogen.

Between 10 and 24 PCB and HCB congeners were determined by HRGC combined with high resolution mass spectrometry (HRMS) using a VG AutoSpec (Vg Analytical (now Micromass)) with a resolution > 10000. The separation was done on a 25 m x 0.22 mm x 0,11 µm Rtx-2330 GC column (Temperature program: 90 °C, 2 min, 20 °C/min to 170 °C, 1min isothermal, 3 °C/min to 210 °C, 20 °C/min to 270 °C, 4 min isothermal).

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Figure 1: Sampling stations of surface layer soil on Svalbard during summer seasons of 1990 and 1993. Results from sampling stations 605, 606, and 607, marked with brackets, are not shown in this report due to a very high sand content.

A rigorous quality control concept based on the requirements in the European quality norm EN 45001 was applied. Recently, the risk of PCB contamination of environmental samples were communicated (2) and a special focus was given to minimize contaminations and losses during the preparation steps in the laboratory environment. An extra set of laboratory blank samples were analyzed before starting the clean-up of the samples from Svalbard. In parallel as a part of NILUs quality control program, the laboratory air was analyzed for PCB and HCB.

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Results and Discussion

Table 1: Concentrations of PCB and HCB in soil samples from Svalbard determined in this project. Additionally, the mean values of PCB and HCB concentrations in soil from the Norwegian mainland and corresponding data for air sampled at Ny-Ålesund, Svalbard are given (3,4) together with the ratio Soil Svalbard/Soil Norway (SS/SN) and the ratio Air Svalbard/Soil Svalbard (AS/SS).

Sample ID	Soil Svalbard (pg/g dw)										Soil Norway		Air Svalbard	
	602	603	604	611	612	614	615	616	617	pg/g	SS/SN	pg/m ³	AS/SS	
HCB	1439	2577	447	252	2162	918	2644	1925	2577	7932	0.21	205	0.123	
PCB-18	-	-	16	54	41	50	90	116	52	-	-	-	-	
PCB-28	108	67	25	58	41	75	107	62	49	-	-	2.36	0.036	
PCB-31	107	66	16	59	41	76	91	61	46	988 ¹⁾	0.13	1.99	0.032	
PCB-47	-	-	8	17	13	21	27	27	18	-	-	-	-	
PCB-52	160	84	15	65	52	116	79	105	77	486	0.17	2.33	0.028	
PCB-66	-	-	13	64	56	163	96	61	66	-	-	-	-	
PCB-74	-	-	7	25	32	47	37	47	34	-	-	-	-	
PCB-99	-	-	7	21	29	30	57	73	42	-	-	-	-	
PCB-101	96	73	30	37	51	92	142	114	71	1204	0.065	1.87	0.024	
PCB-105	36	25	1	10	16	61	28	56	7	-	-	0.26	0.010	
PCB-114	-	-	<1	1	<1	2	2	2	2	-	-	-	-	
PCB-118	80	47	13	27	45	68	111	98	53	-	-	0.81	0.013	
PCB-123	-	-	22	<1	<1	154	58	164	38	-	-	-	-	
PCB-128	-	-	8	2	11	9	34	56	10	-	-	-	-	
PCB-138	37	64	13	35	39	84	79	141	110	2933	0.023	1.82	0.027	
PCB-149	-	-	19	17	35	52	85	93	77	-	-	-	-	
PCB-153	29	54	53	11	52	37	183	101	56	2096	0.031	0.99	0.015	
PCB-156	-	-	5	1	7	16	15	12	4	-	-	0.043	0.005	
PCB-157	-	-	1	0	2	4	4	3	1	-	-	-	-	
PCB-167	-	-	2	<1	6	2	8	4	1	-	-	-	-	
PCB-170	2	6	12	0	17	9	39	5	7	-	-	-	-	
PCB-180	5	21	26	2	41	12	84	38	13	2170	0.012	0.23	0.009	
PCB-187	-	-	20	1	31	12	85	18	25	-	-	-	-	
PCB-189	-	-	1	<1	<1	<1	2	<1	<1	-	-	-	-	
ΣPCB (6)	435	363	162	206	276	415	673	561	376	9876	-	9.60	0.025	

-: not analyzed; <: below detection limit; ΣPCB (6): Sum of PCB-28, 52, 101, 138, 153 and 180 (which makes up about 1/3 to 1/4 of total PCB); ¹⁾: Sum of PCB-28 and 31.

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The reported samples had an organic content in the range of 70 to 80%. Sample no 605, 606, and 607 with a much lower organic content (very high sand content) gave PCB concentrations not more than 10 times above method blank concentrations and were therefore removed from this report. The PCB air concentration in the laboratory building, where the soil samples were analysed, was $\Sigma\text{PCB}(6) \approx 350 \text{ pg/m}^3$ and thus in the same range as the background air concentration in Southern Norway. However, the air concentration in the laboratory building was higher than in Ny-Ålesund air samples $\Sigma\text{PCB}(6) \approx 10 \text{ pg/m}^3$.

In this project we determined between 10 and 24 PCB congeners. Comparison of different samples is often based on the sum of PCB-28, 52, 101, 138, 153 and 180 ($\Sigma\text{PCB}(6)$) which is estimated to make up between 1/4 and 1/3 of the sum of all detected congeners (total PCB). The PCB concentration given as $\Sigma\text{PCB}(6)$ ranges from 160 to 670 pg/g dw. This is in about the same concentration range as measured at remote stations in Canadian and Russian Arctic areas where concentration of between 0.89 to 1.7 ng/g dw given as total PCB have been reported (1).

The most remote station, nr 604 on Nordaustlandet, showed the lowest concentration for nearly all compounds with exception of the hexa- and heptachloro PCBs which exhibited at least comparable or slightly higher concentrations than in samples no. 611, 612 and 617.

For comparison with soil samples from the southern part of the Norwegian mainland, the mean of the results of 6 samples taken during 1990 were given in table 1 (2). The concentrations were in the same range as samples taken during 1993 and analyzed by Lead et al. (5). The soil concentration ratio Svalbard/Norwegian mainland (SS/SN in table 1) was 0.21 for HCB, 0.065 for PCB-101 and 0.012 for PCB-180. The air/soil concentration ratio on Svalbard (AS/SS in table 1) was 0.123 for HCB, 0.024 for PCB-101 and 0.009 for PCB-180. These findings support the global fractionation theory (6) which postulates that the more volatile compounds will travel more easily to remote polar regions. This explains the shift in the relative contribution of the different compounds towards a larger contribution of the volatile PCBs and HCB.

References

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