DISTRIBUTION OF ORGANOCHLORINE POLLUTANTS IN SOILS FROM THE ANTARCTIC EAST COAST

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Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are among the most prevalent contaminants and can be found in the environment even decades after being banned (1). Soil has been identified as a repository for these toxic chemicals from where they can be released into water or air. Recent analyses (2-4) have established that samples from Antarctica (water, biota, soil/ sediment), though far away from main pollution sources, are contaminated with persistent organic pollutants (POPs). However, the extent of this contamination with respect to the detected compounds, measured levels and geographic variation has not yet been comprehended. Possible sources are the long-range transport of pollutants produced by human activities on the neighbouring South America, Africa and Australia or the possible influence of the human activities near the Antarctic research stations.

In this work, we have measured concentrations of OCPs and PCBs in 11 soil and 1 lichen samples from East Antarctica. The coast territory, almost 6,000 km long (between Novolazarevskaya station, 70°46'S, 11°50'E, and Mirny station, 66°33' S; 93°01'E) was covered by T.G. Negoita from January until July 1998, as a participant in the 43rd Russian Expedition in Antarctica.

Methods

Samples

The soil samples of weathered rocks were collected near stations Novolazarevskaya (3 locations), Molodezhnaya (3 locations), Progress (3 locations) and Mirny (2 locations). Samples were conditioned on the spot, by a sieve of 2 mm, sealed in air-tight polyethylene containers for storage, transported and stored in frozen state until analysis. The depth of sampling was 1-10 cm, which was the maximum achievable. Before analysis, samples were dried at room temperature.

Analysis

The following PCB congeners (IUPAC numbering) were targeted for analysis: 18, 28, 31, 44, 52, 74, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 153, 156, 163, 167, 170, 177, 180, 183, 187, 194, 196 and 199. Additionally, hexachlorobenzene (HCB), α-, ß- and g-HCH hexachlorocyclohexane isomers (the sum expressed as HCHs), o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT (the sum expressed as DDTs) were included. The method used for the determination of selected POPs in soil has been previously described and validated (5) and briefly presented below. Approximately 20 g of soil were spiked with internal standards (ε-HCH, PCB 46 and 143) and extracted for 3h using hot Soxhlet manifold with 100 ml hexane:acetone=3:1, v/v. The extract was concentrated in the extractor and was further purified on a acidified silica cartridge. After elution with 30 ml hexane, the cleaned extract was concentrated to approximately 80 µl. A HP GC-µECD, equipped with a 50m x 0.22mm x 0.25µm HT-8 capillary column was used for the analysis of extracts. All

samples with high concentrations for PCBs or OCPs were confirmed by analysis on a HP GC/EI-MS, equipped with a 25m x 0.25mm x 0.25µm, DB-1 capillary column. Two ions of the molecular cluster (M^+ and $[M+2]^+$) were monitored for each analyte. Retention times, masses and relative abundance of confirmation ions with respect to quantification ions were used as identification criteria. Method limits of detection ranged between 0.01 and 0.03 ng/g soil, while recoveries of internal standards ranged between 70 and 85 %.

Results and discussion

All soil samples were previously chemically and biologically characterised (6). It was found that the organic carbon percent varied between 0.01 and 4.11% and that the highest quantities of organic matter were found at Mirny station. This is mostly due to the activity of the birds (droppings) which nestle, rest or sleep in the summer on the soil under the shelter of stones. However, the organic matter is restricted to the upper centimetres of the soil.

Concentrations of OCPs and PCBs in the analysed soil samples are given in Table 1. It is interesting to note that there was a high variability in the results obtained for different pollutants and between the sample locations. This is due to different pollution pathways and to the particular characteristics of the area from which samples were taken. Contaminants may be introduced to Antarctica by scientific support activities, ship operations, atmospheric fallout and disposal practices (7,8).

It was suggested that the values and the variability of the ratio between α-HCH and γ-HCH in space and time are strongly influenced by the relative usage of technical lindane (ratio 4-7) and lindane (ratio < 0.1). The ratio is also influenced by variable partitioning and persistence of the two HCH isomers. In our samples, a mean ratio of 0.13 (range 0.05-0.31) was found. This is in great accordance with values 0.08 (9) and 0.09 (10) found in the Antarctic air. Occasional higher values indicated that long-range transport contamination episodes from South America or Australia may occur (11). Moreover, a mean value of 0.44 (range 0.29 – 0.67) for the ratio between p,p'-DDT and sum DDTs shows that there is a recent input of DDT in the tropical level and that its transport occurs also atmospherically.

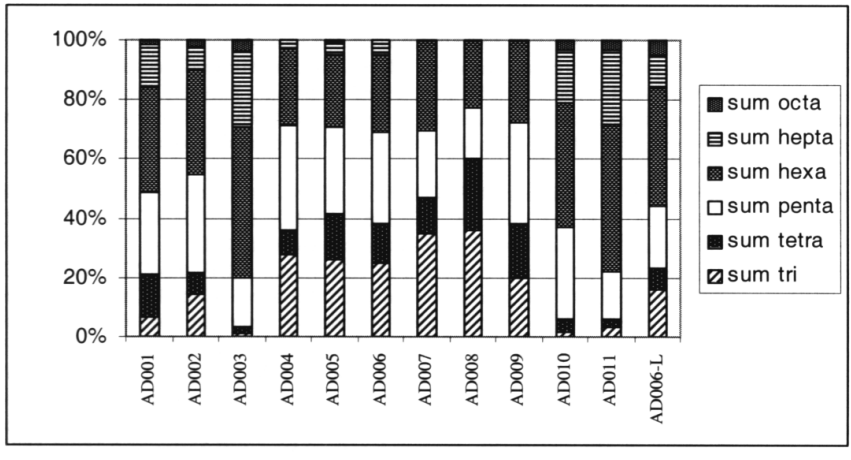

Figure 1. Percent contribution of PCB homologues in soil samples

For samples AD006, AD007, AD008 and AD009, containing low concentrations of PCBs (range 0.20 – 0.41 ng/g), organochlorine pesticides were the main contaminants. This is accordance with the predicted long-range atmospheric transport (11) and with the fact that in Antarctic air, pesticides are found in higher amounts than PCBs (10). In this case, the dominant compounds were γ-HCH, p,p'-DDT and p,p'-DDE. Furthermore, the PCB profile is dominated by the more volatile tri-, tetra- and penta-PCBs congeners (Figure 1). Concentrations of PCBs in these 4 soils samples are in agreement with values found by Fuoco et al. (12,13). Soils samples collected in 1991-1992 at Terra Nova Bay and Victoria Land showed concentrations between 0.06 and 0.12 ng/g for the sum of 9 PCB congeners.

One lichen sample (collected near Molodezhnaya station) presented measurable concentrations of POPs and similar ratios α-HCH/γ-HCH, γ-HCH/sum HCHs and p,p'-DDT/sum DDTs as in the neighbouring soil (AD006), showing that samples of plant origin might be used with success for the monitoring of pollutants.

Samples AD001, AD002, AD004 and AD005 contained moderate levels of PCBs (range 1.98 – 6.94 ng/g) and variable concentrations of pesticides. Beside the atmospheric deposition, an additional source of PCBs in these samples might be the presence (in reduced amounts) of droppings of birds. Moreover, samples AD002 and AD004 had a strong odour characteristic for high boiling aliphatic hydrocarbons as the collection area was used as combustible deposit.

Samples AD003, AD010 and AD011 contained extremely high concentrations of PCBs (range 90.3 – 157.5 ng/g) and low concentrations of pesticides (except for sample AD011). The presence in the contaminated samples of high molecular weight PCB congeners (such as 153, 180, 187 and others) strongly suggests a local source of PCBs rather than atmospheric transport. In these 3 samples, hexa- and hepta-PCB congeners were the major contributors to the sum PCBs (Figure 1). Except for sample AD003, collected near a old equipment deposit, the other 2 samples were collected from small areas where, during summer, Adélie penguins and to a lower extent skua birds nestle. It was already suggested (14) that on a local scale, biotic focusing of POPs can cause elevated contamination levels and become more significant than contaminant input via abiotic pathways. On a small scale, bird nests are areas of intense accumulation of faeces, and thus, it is likely that POPs accumulate in the vicinity of bird colonies, as there is a constant delivery of contaminants with the faeces.

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Table 1. Concentrations of organochlorine pesticides and PCBs (ng/g dry weight) in 11 soil and 1 lichens samples collected from 4 research stations situated on the East Antarctic coast.

ng/g Matrix	AD001	AD002	AD003	AD004	AD005	AD006 soil	AD007	AD008	AD009	AD010	AD011	AD006-L lichen
Location	*Novolazarevskaya*			*Molodezhnaya*			*Progress*			*Mirny*		*Molodezhnaya*
% organic carbon	0.1	0.1	0.2	0.39	0.95	0.21	0.02	0.04	0.08	4.11	3.31	-
sum tri (3 cong)	0.42	1.01	1.24	0.55	1.27	0.10	0.07	0.12	0.07	2.59	3.53	0.53
sum tetra (3 cong)	0.94	0.51	1.83	0.16	0.74	0.05	0.03	0.08	0.06	7.18	3.45	0.25
sum penta (6 cong)	1.77	2.36	15.71	0.71	1.41	0.12	0.05	0.06	0.12	49.77	18.75	0.70
sum hexa (8 cong)	2.28	2.47	47.03	0.51	1.18	0.11	0.06	0.07	0.10	68.19	56.80	1.34
sum hepta (5 cong)	0.91	0.55	23.67	0.05	0.22	0.02	0.00	0.00	0.00	28.78	28.53	0.37
sum octa (3 cong)	0.12	0.16	3.75	0.00	0.02	0.00	0.00	0.00	0.00	5.06	3.96	0.17
sum PCBs *(28 cong)*	**6.36**	**6.94**	**90.26**	**1.98**	**4.84**	**0.41**	**0.20**	**0.33**	**0.34**	**157.45**	**111.92**	**3.30**
HCB	0.25	1.07	0.09	0.41	1.16	0.02	0.02	0.03	0.02	3.78	25.28	0.30
α-HCH	0.32	0.79	0.17	0.79	2.69	0.24	0.15	0.09	0.11	0.91	2.01	3.93
γ-HCH	1.32	2.56	1.22	13.81	40.05	4.24	2.84	0.71	2.33	4.51	8.81	54.98
ß-HCH	0.13	0.12	0.07	0.24	0.32	0.11	0.10	0.05	0.05	0.03	0.23	0.23
δ-HCH	0.05	0.00	0.02	0.32	0.00	0.10	0.10	0.02	0.06	0.04	0.34	0.57
sum HCHs	1.83	3.48	1.49	15.16	43.06	4.69	3.20	0.86	2.56	5.50	11.40	59.70
γ-HCH/sum HCHs	0.72	0.74	0.82	0.91	0.93	0.90	0.89	0.82	0.91	0.82	0.77	0.92
α-HCH/ g-HCH	0.24	0.31	0.14	0.06	0.07	0.06	0.05	0.12	0.05	0.20	0.23	0.07
p,p'-DDE	0.32	0.51	0.38	1.46	3.19	0.19	0.14	0.03	0.16	2.13	1.53	0.40
o,p'-DDD	0.10	0.78	0.08	0.10	0.84	0.11	0.06	0.01	0.04	0.62	0.41	0.22
o,p'-DDT	0.27	0.36	0.00	2.70	6.27	0.25	0.20	0.00	0.23	0.00	0.94	0.00
p,p'-DDD	0.50	0.24	0.59	0.36	1.27	0.17	0.24	0.03	0.15	3.06	1.09	0.55
p,p'-DDT	1.24	0.92	2.13	4.52	14.89	0.50	0.52	0.04	0.59	2.33	2.26	0.71
sum DDTs	2.43	2.81	3.18	9.13	26.46	1.22	1.16	0.11	1.17	8.14	6.28	1.88
p,p'-DDT/sum DDT	0.51	0.33	0.67	0.49	0.56	0.41	0.45	0.36	0.50	0.29	0.36	0.38