Levels of PCDDs and PCDFs in Dated Lake Sediments in Subarctic Finland

T. Vartiainen[1], J. Mannio[2], M. Korhonen[2], K. Kinnunen[3] and T. Strandman[1]
[1]National Public Health Institute, Division of Environmental Health, P.O.Box 95, FIN-70701 Kuopio
[2]Finnish Environmental Agency. P.O.Box 140, FIN-00251 Helsinki, Finland
[3]Lapland Regional Environment Centre, P.O. Box 8060, FIN-96101 Rovaniemi, Finland

1. Introduction

Arctic Monitoring and Assessment Program[1] (AMAP) is one part of the Arctic Environmental Protection Strategy which is signed by all eight Arctic countries. The monitoring program will harmonize and expand existing international environment monitoring networks and activities (atmospheric, marine, terrestrial, freshwater and human health) to arctic areas. The priority pollutants are persistent organic compounds, heavy metals and radionuclides. There are currently insufficient data on sources, sinks and pathways and spatial and temporal trends of the contaminants in the arctic. The freshwater contaminant program of AMAP in Finland[1] is initially focused on lake sediments and fish. This paper present the results of polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) levels of two small subarctic headwater lakes in Lapland, the northern part of Finland.

2. Materials and Methods

Description of the Lakes

Two small subarctic headwater lakes were selected for PCDD/F sediment analysis. Lake Pahtajärvi (68°10' N 24°00'E) is a lake of 50,000 m^2 of area, nine meters deep, in Pallas-Ounas National Park, a fjeld area in northwestern Lapland. Lake "222" (69°27' N 29°10'E) is a 240,000 m^2 of area and 22 m deep lake in northeastern Lapland, ca. 40 km west from the nickel smelter area in Russia. Both lakes are situated near the tree line and are surrounded by rocky terrain with thin soil layers.

Determination of PCDD/Fs

Sediment cores were retrieved during winter 1994 using a 12.8 cm diameter gravity corer lowered through holes cut in the ice. Undisturbed cores were subsectioned immediately at one cm intervals from 0 to 10 cm and at 2 cm intervals from 10 to 20 cm. Sediments were stored cold and then freeze-dried before analysis. The sections were analyzed for dry weight and loss on ignition. About 10 g of freeze dried sediment samples was extracted in a Soxhlet apparatus for 24 h with toluene. Elemental sulfur was precipitated with copper and the extract was purified over a silica gel column, fractionated using activated carbon column containing Celite, and further cleaned with an activated alumina column. The analyses were performed with a high resolution mass spectrometry equipped with a fused silica capillary column (DB-DIOXIN) and a VG 70 SE mass spectrometry (resolution 10,000). Congeners present in the window of mass spectrometry having the right isotope ratio of the specific congener,

were analyzed. A total of 16 ^{13}C-PCDD/Fs congeners (100 pg/ sample, ED-998 tetra-octa chlorodioxin standard solution and EF-999 tetra-octa chlorofuran standard solution, Cambridge Isotope Laboratories) were used as internal standards.

Dating of Sediment Cores

The vertical distribution of ^{210}Pb within sediment cores was determined by the Environmental Research Center, University of Jyväskylä, Finland. Radon daughter nuclide ^{210}Pb was separated from the sediment samples by leaching with HNO_3-HCl. Pb-210 was deposited on a silver disc and the alpha- and gamma activities were determined. Age calculations according to the so-called "constant rate of supply" (CRS) model[3] were based on these measured activities.

3. Results and Discussion

Sedimentation rate in the Lake Pahtajärvi and Lake 222 in Northern Finland (Lapland)

Sedimentation rate in the both lakes showed to be low. The sampling time was in 1994 and at a depth of 18-20 cm the timing showed the years between 1864-1870 in Lake Pahtajärvi. So the sedimentation was on average only about 1.6 mm per year in Lake Pahtajärvi. In Lake 222, the sedimentation rate was even slower than in Lake Pahtajärvi, only 0.5 mm per year. The sedimentation of lake sediments in southern Finland is normally up to 10 mm per year.

Dioxin concentration in dated sediment cores

Dioxin concentration in the dated sediment cores are shown in Figure for Lake Pahtajärvi. The total level of PCDD/Fs in Lake Pahtajärvi was extremely low: in 1994 the total sum of all PCDD/Fs was 55 pg/g in dry weight but as international TEQs only 0.84 pg/g in dry weight. The total sum of PCDD/Fs concentration decreased to 2.29 pg/g in dry weight in 1890 corresponding to 0.14 pg/g as I-TEQ. A maximum value of the total sum of PCDD/Fs, 49 pg/g in dry weight and 2.69 pg/g I-TEQ, was found in 1978, almost as high as in 1994. The congener distribution of PCDD/Fs for both lakes are shown in Table.

Holoubek and co-workers[4] has presented a simple characterization for PCDD/F concentrations in sediment samples where <200 pg/g dry weight present background area, 200-1000 pg/g slightly polluted area, 1000-2000 pg/g polluted area, 2000-10,000 pg/g heavily polluted area and >10,000-100,000 pg/g very heavily polluted area. Rose and co-workers[5] mitigated the categorization by one step, where <200 pg/g dry weight present remote area, 200-1000 background area and so on. Using one or the other of these characterizations, the levels measured in this study, 20-60 pg/g on dry weight basis between 1965-1994, present "a real remote area". In Russia, in two top sediment samples from the northern part of Lake Ladoga, PCDD/F concentrations were at the depths of 0-1 cm 5.29 and 3.31 pg/g in dry weight as I-TEQs[6].

The level of PCDD/Fs showed to be extremely low between years 1880-1965 in Northern Finland, 2-20 pg/g on the dry weight basis. Between 1965-1994 the OCDD concentration dominate followed by hepta and then hexa chlorinated dioxins. The profile is similar also in the deep sediment cores.
The possible sources of dioxins in Finland are fallout mainly coming from south along with air flow, chemical industry, discharges of paper mill into water and air, and the widely use of the fungicide by name Ky 5 which contained high levels of dioxins as impurities[7]. In the Southern Finland, traces of

the profile of PCDD/Fs originated from Ky-5 are possible the find in the sediment cores[7] (Table) but sediment cores analyzed in this study did not show such a profile: in Southern Finland more than 50% of the total PCDD/Fs are furans but in Northern Finland 60-80% of the total PCDD/Fs are dioxins.

Table. PCDD/Fs in lake bottom sediments of Lake Pahtajärvi (Lake) and Lake 222 (222) at the depth of 1 to 2 cm compared with that in Lake Valkjärvi (C) in Southern Finland (Vartiainen et al., 1994) and the common fungicide synthesized and used in Finland between 1940 and 1988. Also percentage of various congeners is given for comparison.

PCDD/F congener	PCDD/F (pg/g dry weight)			percentage			
	Lake	222	C	Lake	222	C	KY-5
2,3,7,8-Cl_4DF	0.47	0.57	0.86	1.2 %	0.4 %	0.4%	<1%
other Cl_4DFs	0.65	4.63	6.10	1.7 %	3.2 %	2.7%	<1%
1,2,3,7,8-Cl_5DF	0.56	0.48	0.88	1.5 %	0.3 %	0.4%	<1%
2,3,4,7,8-Cl_5DF	0.29	0.54	0.86	0.8 %	0.4 %	0.4%	<1%
other Cl_5DFs	3.98	7.26	9.20	10.6 %	5.1 %	4.1%	2%
1,2,3,4,7,8-Cl_6DF	<0.01	0.62	0.07	<0.1 %	0.4 %	<0.1%	8%
1,2,3,6,7,8-Cl_6DF	0.29	0.77	0.90	0.8 %	0.5 %	0.4%	<1%
2,3,4,7,8,9-Cl_6DF	0.39	0.90	1.70	1.0 %	0.6 %	0.8%	<1%
1,2,3,7,8,9-Cl_6DF	<0.01	<0.01	<0.01	<0.1 %	<0.1%	<0.1%	<1%
other Cl_6DFs	<0.01	1.20	9.70	<0.1 %	0.8%	4.3%	<1%
1,2,3,4,6,7,8-Cl_7DF	3.12	4.18	42.3	8.3 %	2.9%	18.6%	42%
1,2,3,4,7,8,9-Cl_7DF	<0.01	<0.01	<0.01	<0.1 %	<0.1 %	<0.1%	<1%
other Cl_7DF	8.90	1.20	18.9	1.0 %	0.6%	8.3%	30%
OCDF	2.38	1.71	28.6	6.3 %	1.2 %	12.6%	5%
PCDFs	13.4	25.0	120	35.6 %	17.5 %	53%	87%
2,3,7,8-Cl_4DD	0.08	0.05	<0.5	<0.1 %	<0.1 %	<0.1%	<1%
other Cl_4DDs	<0.01	0.14	0.89	<0.1 %	2.0 %	0.4%	<1%
1,2,3,7,8-Cl_5DD	0.20	0.14	0.44	0.5 %	0.1%	0.2%	<1%
other Cl_5DDs	3.98	4.98	11.7	1.4 %	3.5 %	5.2%	1%
1,2,3,4,7,8-Cl_6DD	0.16	0.34	0.12	0.4 %	0.2 %	0.1%	<1%
1,2,3,6,7,8-Cl_6DD	0.43	0.19	1.39	1.1 %	0.1%	0.6%	1%
1,2,3,7,8,9-Cl_6DD	<0.01	0.37	0.18	<0.1 %	0.3 %	0.1%	<1%
other Cl_6DDs	5.29	5.65	24.3	14.0 %	4.0 %	10.7%	6%
1,2,3,4,6,7,9-Cl_7DD	2.62	30.2	10.4	7.0 %	31.6%	4.6%	3%
muut Cl_7DD	4.94	45.2	12.7	13.1 %	21.1 %	5.6%	1%
OCDD	10 .06	27.9	45.1	26.7 %	19.6 %	19.8%	<1%
PCDDs	24.3	117.8	107	64.4 %	82.5%	47%	13%
PCDD/Fs	37.71	143	227	100 %	100 %	100%	100%
TEQs	0.59	1.19	1.81				

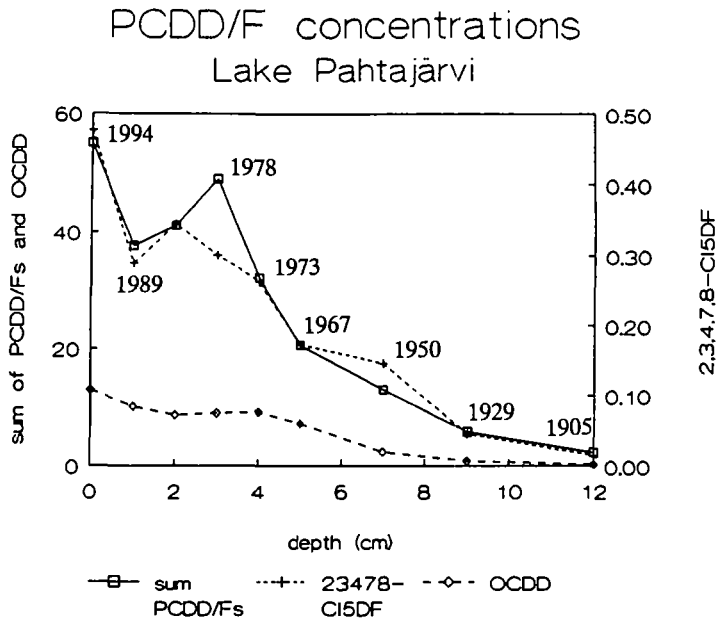

Figure. PCDD/F concentrations in dated sediment cores in Lake Pahtajärvi in Lapland, the arctic area of Finland. The upper line shows the total sum of PCDD/Fs, the second line 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-Cl_5DF), and the third line octachlorodibenzo-p-dioxin (OCDD) concentrations as pg/g on dry weight basis.

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