Atmospheric concentrations of chlorinated pesticides, PCDD/Fs and c-PCBs in West Greenland

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Introduction

Persistent organic pollutants (POPs) such as organochlorine pesticides (OCs), polychlorinated dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are globally distributed and have reached the remote regions, such as the Arctic. The major transport route of these compounds to remote regions is believed to be the atmosphere and to a minor extent the marine environment. OCs have been found in biota from west and east Greenland, with the highest concentrations in marine species from east Greenland, indicating a significant contribution from sources in the eurasiatic continent[1,2]. Very little information is available on the distribution of PCDD/Fs and coplanar PCBs (c-PCBs) in Greenland[2,3]. At present, no investigations are available on atmospheric concentrations of OCs, PCDD/Fs and c-PCBs in Greenland.

The aim of this study was to obtain data on the concentration levels of air pollutants in west Greenland that can be used for assessing seasonal variations and – in the longer term - trends. Long-range transport is the only source of atmospheric concentrations of chlorinated pesticides and trifluralin in Nuuk, since there are not any local sources of these compounds in Greenland. In contrast, PCDD/Fs may be formed locally by combustion processes such as garbage burning.

Materials and Methods

Sampling. Atmospheric samples of about 3500-4500 m^3 were collected bimonthly in the city of Nuuk, west Greenland (64 02N, 51 07W), each covering a period of half a month, from January to December 2004. The air sampling train consisted of a glass fiber filter (GFF) type A/E, 102 mm (Gelman), to collect particulate phase, followed by two cylindrical polyurethane foam (PUF) plugs, 6 cm diameter and 5 cm long with a density of 0,02 g/cm^3, positioned in series. For determination of OCs, each part of the sample unit was analyzed separately, in order to obtain information on the respective vapor and particle fraction and to monitor any possible breakthrough. For determination of PCDD/Fs and c-PCBs the whole sample was extracted, due to the low atmospheric concentrations expected for these compounds. The sampling method had been previously tested for breakthrough of PCDD/Fs[4]. No significant breakthrough was observed after sampling for one month. Half of the samples collected in 2004 were analyzed for pesticides and the other half was analyzed for PCDD/Fs and c-PCBs.

Analysis. The compounds included in the analytical program were a- HCH and g-HCH (lindane), endosulfan, heptachlor epoxide, dieldrin, p,p'-DDT, p,p'-DDE, o,p'-DDT, o,p'-DDE, cis- and trans-chlordane, trifluralin; dioxins (PCDDs): 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCCD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD; furans (PCDFs): 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF; non-*ortho* substituted PCB congeners (co-PCBs): CB77, CB126 and CB169. For analysis of OCs and trifluralin the samples were spike with deuterium labeled g-HCH, ^{13}C-HCB and ^{13}C-DDE and extracted by soxhlet with hexane/acetone (4:1, v/v) for 8 hours. The extract was evaporated, solvent exchanged to hexane and passed through a silica column (1 g). The analytes were eluted with 5 ml hexane followed by 5 ml hexane/dichloromethane (1:1, v/v). Both fractions were combined and evaporated to nearly dryness. The sample was reconstituted in isooctane and analyzed by GC-HRMS. The analysis of PCDD/Fs and c-PCBs was done as described[4], following a method adapted from European standard EN-1948 2-3 for analysis of PCDD/Fs in flue-gas [5]. The samples were spiked with eleven $^{13}C_{12}$-labelled PCDD/Fs congeners and three c-PCBs congeners, and soxhlet extracted for 20 hours with toluene. Clean up was performed by column chromatography using SiO_2/NaOH, SiO_2/H_2SO_4, acidic Al_2O_3, active C AX-21. The analysis of extracts was

performed by GC-HRMS. Field blank samples were analyzed with each analytical series and the amounts of the analytes found in the blank sample were subtracted from the amount found in the samples.

Results and Discussion

The results are summarized in Table 1. HCB was the most predominant compound in the atmosphere, followed by I-HCH, endosulfan and K-HCH. DDT was not found in any sample. Trifluralin was only sporadically found in samples collected in winter and autumn and never during the summer season. OCs concentrations did not show any seasonal variation (Figure 1), with the exception of lindane (Figure 2) which had maximum of 11.1 pg/m^3 in August. Lindane is still used in North America, particularly in the Canadian prairies for canola seed treatment. The air mass trajectories moving from the prairies to the Central Arctic latitudes have been found to contribute to the atmospheric load of contaminants by 30%[7]. The relative abundance of a- and g-HCH is expressed as a/g-HCH ratio. High a/g-HCH ratios (>4) are usually found in the Arctic regions, due to low g-HCH concentrations. The use of a-HCH is forbidden both in Europe and North America. Thus, the presence of a-HCH in the atmosphere is not determined by primary sources, but it is mostly the result of re-evaporation from terrestrial and aquatic surfaces previously contaminated by a-HCH. The a/g-HCH ratio found in Nuuk was >4 until March. The value decreased to 2.7-2.3 during the period April-September and increased again to values >4 after September. This indicates a contribution of long-range transport of g-HCH (Lindane) from the North American Continent during the period of use there and where the Continent is the predominant source of pollutants to the Nuuk area.

Table 1. Annual concentrations of OCs and trifluralin (pg/m^3), as well as PCDDs, PCDFs and c-PCBs (fg/m^3 WHO-TEQ) in Nuuk together with minimum and maximum values. The d/n column indicates number of detected concentrations above detection limit.

Compound	d/n	Unit	Mean	Median	Min	Max
alpha-Chlordane	13/13	pg/m³	0.4	0.4	0.2	0.9
gamma-Chlordane	13/13	pg/m³	0.5	0.5	0.3	0.7
4.4'-DDT	1/13	pg/m³	0.2	0.2	n.d.	0.2
2.4-DDT	0/13	pg/m³	n.d.	n.d.	n.d.	n.d.
p.p'-DDE	13/13	pg/m³	0.4	0.3	0.2	0.8
o.p'-DDE	11/13	pg/m³	1.1	0.2	0.0	5.0
Dieldrin	7/13	pg/m³	2.5	2.6	0.9	3.6
Endosulfan I + II	13/13	pg/m³	6.3	5.9	3.7	10.3
Heptachlor epoxide	13/13	pg/m³	0.8	0.7	0.3	1.2
Hexachlorobenzene	13/13	pg/m³	30.2	29.9	7.4	72.6
a-HCH	13/13	pg/m³	18.3	19.1	12.7	25.6
g-HCH (Lindane)	13/13	pg/m³	5.0	4.6	2.2	11.1
Trifluralin	4/13	pg/m³	0.2	0.2	0.0	0.6
PCDDs	3/6	fg/m³ WHO-TEQ	6.7	4.2	0.3	20.2
PCDFs	4/6	fg/m³ WHO-TEQ	12.4	10.5	0.5	31.5
c-PCBs	3/4	fg/m³ WHO-TEQ	0.6	0.6	0.2	1.0

The concentration unit for PCDD/Fs and c-PCBs is fg/m^3 WHO-TEQ. PCDFs are dominating, whereas the concentration of c-PCBs is very low. This is in contrast to what is found in biota, where c-PCBs are dominating. This observation indicates the existence of a complicated mechanism for the transport between abiotic and biotic matrixes.

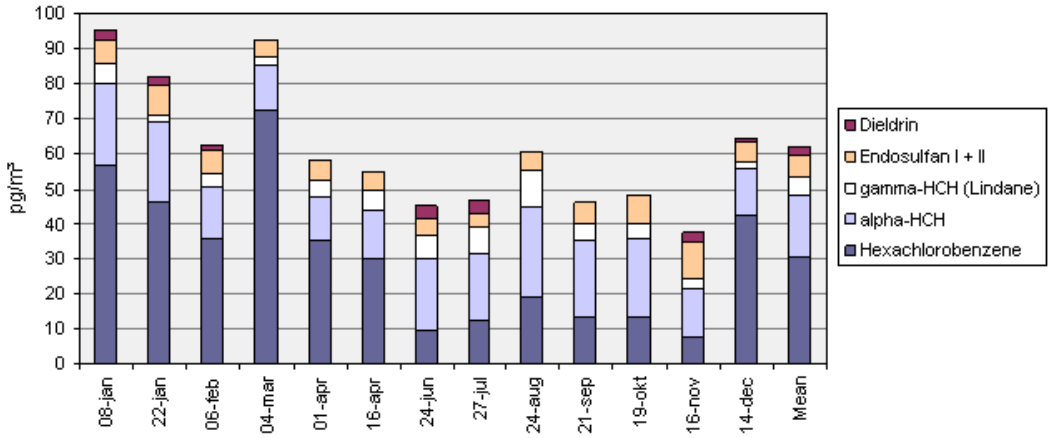

Fig. 1. Concentrations of most abundant OCs in air in Nuuk 2004 with half monthly sampling periods. The time indication is start time of the sampling.

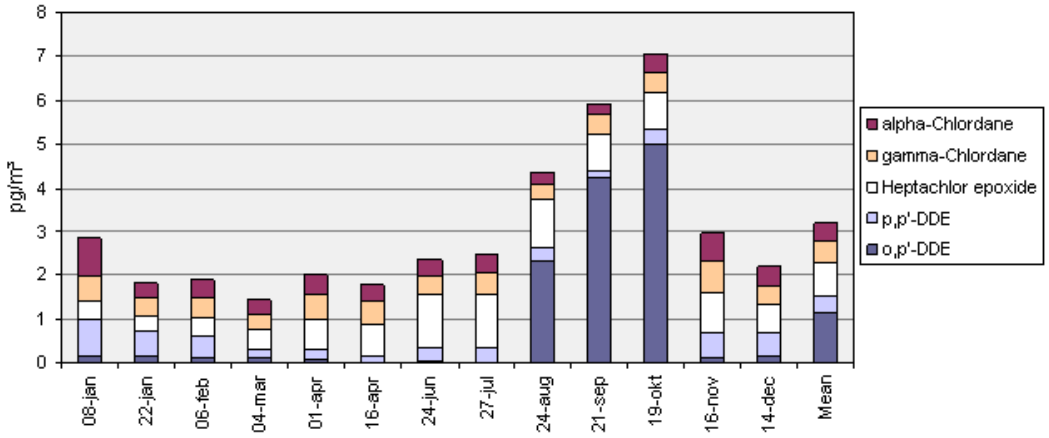

Fig. 2. Concentrations of OCs of least abundant compounds in air in Nuuk 2004 with half monthly sampling periods. The time indication is start time of the sampling. (Trifluralin has been left out).

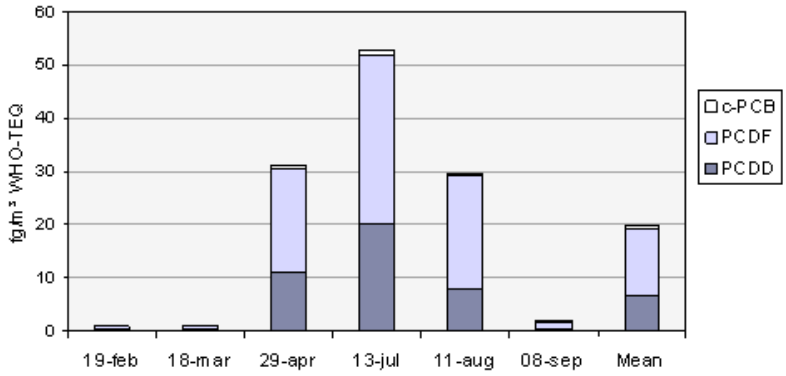

Fig. 3. Preliminary data for PCDDs, PCDFs and c-PCBs in air in Nuuk 2004. Half monthly sampling periods. The time indication is start time of the sampling

There is a very pronounced seasonal variation, characterized by a high abundance in the summer with maximum in July. Otherwise, the concentrations were close to the detection limit. This annual variation profile contrasts sharply with

the OC profiles above, and also with the Danish profile, which displays a sharp winter maximum[4]. The sharp variation indicates that emission originates from local sources, and since the maximum occurs in the summer, heating cannot be the cause. The prevailing heating method in Nuuk is oil firing, which does not give PCDD/Fs emissions. Probably, the emissions are due to industrial activities and/or garbage burning. A further noteworthy feature is the very low abundance of c-PCBs in the air, which, as mentioned above, is in contrast with observations in biota[2,7]. This indicates that other sources than atmospheric long-range transport is the primary c-PCBs source in the Arctic.

Acknowledgments

The Danish EPA financially supported the project. Hans Ahleson, Bjarne Jensen, Inga Jensen, Mary-Ann Chrillesen and Elsebeth Johansen are gratefully acknowledged for technical assistance.

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