Three years (2008–2010) of measurements of atmospheric concentrations of organochlorine pesticides (OCPs) at Station Nord, North-East Greenland†

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Atmospheric concentrations of organochlorine pesticides (OCPs) have been measured for the first time at Station Nord, North-East Greenland, from 2008 to 2010. The data obtained are reported here. Hexachlorobenzene (HCB), endosulfan I and hexachlorocyclohexanes (HCHs) were the predominant compounds detected in the atmosphere, followed by \( p,p'-\)DDE and dieldrin. Chlordane isomers and related compounds (\( \text{trans-} \) and \( \text{cis-} \)-chlordanes, heptachlor and heptachlor epoxide, \( \text{trans-} \) and \( \text{cis-} \)-nonachlor) were also detected. Atmospheric concentrations of the investigated compounds were correlated with temperature using the Clausius–Clapeyron equation in order to obtain information about their transport properties. The correlation between atmospheric concentrations and temperature was not significant for endosulfan I, \( \gamma\)-HCH and \( p,p'-\)DDT, which indicates that direct transport from direct sources is the dominating transport mechanism for these compounds. A significant correlation with temperature was found for all the other studied pesticides and pesticide degradation products, which indicates that re-emission of these compounds from previously contaminated surfaces is an important factor for the observed variation in concentrations. Pesticide concentrations were also correlated with sea ice cover. Concentrations of the compounds that have not been in use for decades correlated with temperature and ice cover, while concentrations of compounds still in use did not correlate with either of these parameters. These observations indicate that processes such as revolatilization from the open sea surface are important mediating factors in the dynamics of anthropogenic persistent pollutants in the Arctic environment under the expected influence of climate change processes.

Environmental impact

This paper reports for the first time atmospheric concentrations of organochlorine pesticides in a high Arctic region of Greenland. These data contribute to the general knowledge about transport and dynamics of persistent pollutants in Arctic regions.

Introduction

Legacy organochlorine pesticides (OCPs) have been used extensively since the late 1950s. After discovering their ubiquitous presence in the environment, their tendency to bioaccumulate in the food chain and their toxic and hazardous effects on top predators and humans, most OCPs have been banned or restricted in industrialized countries. Long range transport via the atmosphere and ocean currents has introduced measurable quantities of OCPs to pristine regions such as the Arctic. The highly lipophilic and persistent nature of these compounds causes them to bioaccumulate in the food web, reaching concentrations that can have toxic effects on top predators and humans.1,2 A number of OCPs – including chlordane, DDT, hexachlorocyclohexanes (HCHs), and more recently endosulfan – are regulated under the Stockholm Convention on Persistent Organic Pollutants (POPs).3 After reductions in primary emissions of OCPs as a result of control strategies, the re-emission from previously contaminated soils and oceans is considered to be the main source of atmospheric concentrations of OCPs. The repeated exchange of OCPs between atmosphere and soil and atmosphere and aqueous

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compartments leads to the process commonly known as the “grasshopper effect”, ending with the presence of OCPs in the environment of the cold Polar Regions. Another mechanism by which OCPs and other POPs are remobilized is the melting of the cryosphere, where POPs have been previously accumulated, and their consequent release to open ocean water and the atmosphere. Some OCPs are still in use as e.g. endosulfan or DDT, which are used in developing countries for disease vector control. Thus, primary emission of these compounds can still contribute to OCP concentrations in the atmosphere of remote regions.

OCPs have been detected in various compartments of the Greenlandic ecosystem with increasing concentrations in the marine food-web. OCPs have previously been measured in a two year study (2004–2005) in the atmosphere of Nuuk, South-West Greenland. Greenland is exposed to the long range atmospheric transport (LRT) of pollutants from both the North American and the Eurasian continents. However, the long range transport of air pollution in general has a much lower impact on the west coast than on the east coast of Greenland. Sources in Eurasia dominate the observed concentrations of anthropogenic pollutants at Station Nord, a monitoring station placed in North-East Greenland. Atmospheric measurements carried out at Station Nord in the periods 1990–2001 and 2006–2010 have shown that this region is burdened with considerable atmospheric pollutants, consisting of a wide variety of acidic and toxic compounds, which originate from mid-latitude industrial areas.

In the present study, atmospheric measurements of OCPs have been carried out at Station Nord, constituting the Danish atmospheric part of the Arctic Monitoring and Assessment Programme (AMAP). These data contribute to the AMAP long-term measurement of POPs, intended to facilitate assessment of their transport and presence in the Arctic atmosphere and evaluation of the consequences of international control measures. The results of atmospheric measurements of OCPs at Station Nord are reported here for the period 2008–2010. The aim of the study was to obtain measured concentrations of OCPs in North-East Greenland for use in assessing seasonal variations and – ultimately – long term trends, as well as to find indications of long range transport versus reemission from the local/regional area.

**Experimental**

**2.1 Air sampling**

Station Nord (81°36′ N latitude and 16°40′ W longitude; 24 m above sea level) is located in North-East Greenland (Fig. 1) and is only accessible courtesy of the Royal Danish Air Force. The general meteorological pattern at the site is described elsewhere. Weekly air samples of about 5000 m³ are collected once a month using a High Volume Sampler (Digitel, Hegnau, Switzerland) operating at a flow rate of 0.5 m³ min⁻¹. The sampler is placed in a hut and equipped with a heated sampling head (outside) for sampling total suspended particles. Via a stainless steel tube, sampled air is thereafter led into a PM₁₀ head that is located inside the hut before finally reaching a particle filter and a cartridge. The impactor surface in the PM₁₀ head is coated with silicone grease to avoid the bounce-off of larger particles. The grease is replaced 4 times a year during maintenance visits. A 15 cm diameter quartz fiber filter is used for particle collection, and a polyurethane foam/ XAD-2/polyurethane foam cartridge is used for vapor phase collection. The polyurethane foam and XAD-2 are cleaned before use by Soxhlet extraction for 8 hours using dichloromethane as the solvent. Quartz filters are baked at 450 °C for 24 hours. After sampling, cartridges and filters are kept at −20 °C. For the chemical analysis, it was decided that the filter and the PUF sandwich should be combined for each sample, as the temperature in the hut (±15 °C) could be up to 70 °C higher than ambient temperature and thus disturb the equilibrium between gas phase and particle bound phase.

**2.2 Analytical method**

Before extraction, each sample was spiked with a mixture of 13C-isotope labelled OCP standards (Cambridge Isotope Laboratories, Tewksbury, MA, USA). The samples were then Soxhlet extracted with n-hexane/acetone (4:1, v/v), and cleaned on silica columns. The extract was evaporated until nearly dry, and reconstituted in isooctane with 13C₆-PCB-53 (Cambridge Isotope Laboratories) added as a recovery standard. Identification and quantification of the target compounds were performed with a GC-HRMS (DFS, Thermo Scientific, Bremen, Germany). The HRMS was operated at a resolution of 10 000 in electron impact ionization mode (EI) at 45 eV. Two m/z values were monitored for each compound. The criteria for identification were based on the retention time of the analyte compared to that of a certified standard (±20%) and the isotope ratio of the two monitored m/z values (±20% of the theoretical value). The list of the analyzed compounds and the details of the analytical method are available in the ESI.

**2.3 Quality assurance and quality control (QA/QC)**

Laboratory and field blanks were extracted following the same procedure as the samples. Three laboratory blank and three
field blank samples were extracted for each sampling year. Concentrations of target analytes in samples were corrected for recovery of corresponding or similar labeled surrogate standards. Recoveries of the labeled surrogate standards are presented in Table 2 ESI. The uncertainty based on the results of interlaboratory comparison and calculated by the method described by Magnusson et al. was within 23 and 55% at 95% confidence interval.

Results and discussion

3.1 OCP concentrations and seasonal variations

Atmospheric concentrations (sum of gas and particulate phases) of the analyzed OCPs are summarized in Table 1. One weekly sample was available for each month from 2008 to 2010. The number of samples was reduced to seven in 2009 due to technical problems with the high volume sampler. No attempt to distinguish between gas phase and particulate bound compounds has been made since the sampler and part of the sampler inlet were kept at room temperature and thus the particle/gas phase distribution of the compounds in the sample does not reflect the distribution in the atmosphere, see Section 2.2.

In the present study, the highest recorded concentrations were for HCB, with an average of 79.5 pg m\(^{-3}\) and a range from 1.15 to 159 pg m\(^{-3}\). Atmospheric concentrations measured from 2000 to 2005 at Alert (Canadian Arctic) and Zeppelin (Svalbard) varied from a yearly average of 29 to 72 pg m\(^{-3}\), so the present dataset is at the high end for Arctic sites but comparable with values obtained at the two other high Arctic stations. HCB concentrations showed a weak seasonality at Station Nord, with slightly higher concentrations in summer. Su et al. observed that HCB concentrations at five Arctic stations were not influenced by variation of ambient temperature. Kallenborn et al. suggested that the expected high evaporation rates of HCB in the summer months are counterbalanced by increased photodegradation. However, the atmospheric lifetime of HCB determined by the reaction with OH radicals is 940 days.

Thus, photochemical degradation would probably not be a key mediating process for the observed variation in atmospheric concentrations of HCB.

The average annual concentrations of \(\alpha\)-HCH and \(\gamma\)-HCH measured at Station Nord were 8.9 and 1.27 pg m\(^{-3}\), respectively. The other isomers, \(\beta\)-HCH and \(\delta\)-HCH, were only sporadically detected at very low concentrations (average: 0.004 and 0.008 pg m\(^{-3}\)). After 2000, \(\alpha\)-HCH concentrations in the Arctic atmosphere have declined to about 20–30 pg m\(^{-3}\) and below, as the usage of technical HCH has constantly decreased since the 1980s and practically ceased worldwide. The global usage of lindane also declined significantly between the 1980s and 1990s. Canada and the European Union banned the use of lindane in 2004. \(\alpha\)-HCH and \(\gamma\)-HCH concentrations measured at Station Nord were at the lower end of the respective ranges reported for these compounds at other high Arctic stations over the period 2000–2006, but we believe that this reflects a continuous decrease in their atmospheric concentrations rather than to geographical differences.

The \(\alpha/\gamma\)-HCH ratio has previously been used to trace the sources of technical HCH and lindane. The higher water partition of \(\gamma\)-HCH and its shorter residence time in the atmosphere compared to that of \(\alpha\)-HCH result in relatively higher \(\alpha\)-HCH concentrations in the atmosphere when HCH has aged. The \(\alpha/\gamma\)-HCH ratios typically observed in the Arctic range were from 3.0 to 6.3. The highest annual average \(\alpha/\gamma\)-HCH ratio (8.0) was observed at Alert in 2004. The average annual \(\alpha/\gamma\)-HCH ratio observed in the present study was 12.8, which is higher than the ratios reported for the other Arctic stations. The size of the ratio measured at Station Nord implies that the present data are more recent and that re-volatilization of \(\alpha\)-HCH from secondary sources (e.g. contaminated sediments, soil and water surfaces) is the predominant process controlling \(\alpha\)-HCH concentrations.

Seasonal variations were observed at Station Nord for \(\alpha\)-HCH and \(\gamma\)-HCH (Fig. 2). Higher \(\alpha\)-HCH concentrations were observed from August to November, while \(\gamma\)-HCH concentrations were lower in the warm season (from May to August) and higher from September through the winter season. However, the bimodal seasonal cycle of \(\gamma\)-HCH observed at Alert, Zeppelin, Kinngait and Barrow, with a spring maximum event and relatively higher concentrations in September–October, was not observed at Station Nord. The spring and fall peak concentrations were attributed to pesticide application in spring and the tilling of soil in the fall in the last two cited studies.
Endosulfan-I was detected in all analysed samples (average: 3.8 pg m\(^{-3}\)), while endosulfan-II was only detected in 1/3 of the samples (average: 0.083 pg m\(^{-3}\)). Technical endosulfan, a pesticide that is still in use, is a mixture of 7:3 endosulfan-I and endosulfan II. In the atmosphere, the concentrations of endosulfan II are generally 1-100 times lower than those of endosulfan I, and concentrations of the corresponding degradation product endosulfan sulphate are even lower. Endosulfan sulphate was only sporadically detected, with an average concentration of 0.09 pg m\(^{-3}\). Comparable endosulfan I concentrations have been measured at Alert, with average values ranging from 3.3 (in 1993) to 5.4 (in 2003) pg m\(^{-3}\). These concentrations are in agreement with an average annual concentration of endosulfan I of 4.6 pg m\(^{-3}\) predicted by the model CliMoChem in the Arctic zones (70–90° N).\(^{23}\)

A seasonal pattern of endosulfan I in the atmosphere, characterized by elevated concentrations in October–November and to a lesser extent in April–May, has been observed at Alert and Kinngait.\(^{24,25}\) A similar pattern was observed in the present study, where concentrations peaked in April–May and rose again in September–October (Fig. 1 ESI†). A similar seasonal pattern is observed for a large number of compounds\(^{10,12}\) at Station Nord and has been explained by long range transport from mid-latitudes, mostly from Eurasia.

The two main components of technical chlordane, the stereoisomers trans-chlordane (TC) and cis-chlordane (CC), were detected in all samples from Station Nord, with average mean respective concentrations of 0.24 and 0.55 pg m\(^{-3}\) and an average TC/CC ratio of 0.43. These values are comparable to those measured at Alert and Zeppelin in 2000–2006.\(^{14}\) Technical chlordane also contains trace amounts of heptachlor, trans-nonachlor (TN) and cis-nonachlor (CN). Heptachlor has also been manufactured on its own as an insecticide. The degradation product of heptachlor, heptachlor epoxide, was detected in all samples with an average concentration of 0.64 pg m\(^{-3}\); a value close to the average concentration of CC (0.55 pg m\(^{-3}\)). Concentrations of heptachlor are usually below the detection limit in the Arctic atmosphere, since heptachlor is rapidly transformed to heptachlor epoxide.\(^{25}\) However, heptachlor was detected in 30 out of 32 samples in the present study. The average annual concentration of trans-nonachlor was 0.39 pg m\(^{-3}\), while cis-nonachlor concentrations were mostly close to the detection limit. Concentrations of all chlordane-related compounds showed seasonal variation, with relatively higher concentrations in the periods April–June and August–October (Fig. 2 ESI†).

Among DDTs and transformation products, \(p,p'\)-DDE (mean: 2.7 pg m\(^{-3}\)) was the most abundant compound, followed by \(o,p'\)-DDT and \(p,p'\)-DDT (mean: 0.30 and 0.51 pg m\(^{-3}\), respectively). The average annual ratio \(p,p'\)-DDT/\(p,p'\)-DDE was 0.40, which indicates that DDTs have aged when arriving at these latitudes.\(^{25}\) Unusually high concentrations of \(p,p'\)-DDE (range: 10.5–24.3 pg m\(^{-3}\)) were observed in August, September and December 2009 and again in June 2010, whilst the annual arithmetic mean concentration was 2.4 pg m\(^{-3}\) (Fig. 1 ESI†). Observed annual arithmetic mean \(p,p'\)-DDE concentrations at Zeppelin have been below 1 pg m\(^{-3}\) since the year 2000,\(^{26}\) with the exception of 2004 when the mean concentration was 2.32 pg m\(^{-3}\).

High \(p,p'\)-DDE concentrations were also observed at Zeppelin for the period June–December, reaching a maximum of 28 pg m\(^{-3}\) in August and September 2004. Elevated DDT concentrations were apparent in 2004 at both Canadian and Norwegian monitoring stations (Alert and Zeppelin). The high values may arise from transport episodes associated with regional sources or events such as boreal forest fires, which can release POPs previously deposited on the soil surface to the atmosphere.\(^{26}\) The seasonal profiles of \(p,p'\)-DDT measured at Station Nord showed a clear peak in June followed by a rapid decrease in July–August.

Dieldrin was detected in all samples with an average concentration of 1.69 pg m\(^{-3}\), while aldrin and endrin were detected in very few samples and were close to the detection limit. Atmospheric concentrations of dieldrin have decreased in the Arctic to approximately 50% between the 1990s and 2000 (ref. 14 and 25) after dieldrin and aldrin were banned in the USA and Europe in the late 1970s. The average concentration measured at Station Nord is closer to the average concentrations measured at Alert in the 1990s. The occurrence of dieldrin in the atmosphere is mainly due to re-emission from historically treated soils and the use of aldrin, which can be converted to dieldrin in the environment.\(^{27}\) In agreement with this statement, slightly higher dieldrin concentrations were observed between May and August (Fig. 1 ESI†).
3.2 Correlation with temperature and ice cover

The equilibrium between compounds adsorbed on surfaces and their concentrations in the atmosphere can be described by the Clausius–Clapeyron equation. Once in the atmosphere, the compounds will be distributed between gas phase and particle bound phase. We are measuring typically 1000 particles per cm$^3$ at Station Nord, with most being $<\text{PM}_{10}$ (unpublished results). The particle surface area concentration close to the earth’s surface can therefore be considered to be zero and ignored. The slope of the logarithm (log) of the concentration of a compound versus reciprocal temperature (1/T) can thus be used to interpret the relative importance of volatilization from local surfaces versus long-range transport.$^{6,28-30}$ A statistically significant relationship at the 95% confidence level between log C and 1/T with a negative slope indicates that the re-volatilisation surface is an important mediating factor for the atmospheric concentration of a compound. The statistical results of the linear correlation of the measured concentrations of OCPs with temperature, following the Clausius–Clapeyron equation, are listed in Table 2. The parameters used for calculating the $r^2$-values were obtained using the function LINEST in Excel.

Ice cover is also an important factor that may have an influence on atmospheric concentrations of persistent pollutants, and thus the measured concentrations were also tested against ice cover (Table 2). Monthly ice cover data were obtained from the NOAA website (http://www.arctic.noaa.gov/detect/ice-seaice.shtml).

HCB concentrations at Station Nord followed the Clausius–Clapeyron equation (Table 2) but were not correlated with ice cover. However, according to the $R^2$ value (0.17) only 17% of the variation in the Clausius–Clapeyron equation can be explained.

Measurements of atmospheric and surface water HCB concentrations carried out in the Arctic Ocean$^{31}$ have shown that HCB was closer to showing equilibrium between air and water compared to the other OCPs. The lack in seasonal variation, the weak correlation with temperature, and the absence of correlation with ice cover suggest that HCB concentrations are not substantially influenced by re-emission, and for a large part, HCB concentrations might still be controlled by primary sources (e.g. byproducts of chlorinated chemicals and incomplete combustion processes). This is further enforced by its very long atmospheric lifetime and high vapour pressure.

$\alpha$-HCH was found to follow the CC equation and was the compound with the strongest negative correlation with ice cover (Fig. 3).

According to Wania and Mackay,$^{32}$ about half of the global $\alpha$-HCH inventory remains in the Arctic Ocean. In fact, net re-evaporation of $\alpha$-HCH from sea to air has been found to be the prevailing process in the Arctic environment.$^{33,34}$ The lower volatility and higher water solubility of $\gamma$-HCH combined with the decreased use of this pesticide in almost all countries may explain the relatively lower concentrations of $\gamma$-HCH compared with $\alpha$-HCH concentrations observed at Station Nord from 2008 to 2010. $\gamma$-HCH concentrations did not follow the Clausius–Clapeyron equation, and were not correlated with ice cover either. The $\alpha$/$\gamma$-HCH ratio may further increase in the future due to increased remobilisation of the $\alpha$-HCH trapped in the Arctic Ocean following the retreat of sea ice, melt of glaciers and melt and erosion of permafrost areas together with a global decrease in the use of lindane. The lack of temperature dependency for $\gamma$-HCH concentrations was also observed by Hung et al.$^{35}$ in the Canadian Arctic, which indicates that the LRT input from source regions is still the dominating contributor to Arctic air.

No significant correlation was observed between temperature or ice cover and endosulfan I concentrations (Table 2), which agrees with the long range transport of endosulfan from remote source regions.

All the chlordane-related compounds followed the Clausius–Clapeyron equation, but only CC showed a negative correlation with ice cover (Table 2). The strongest correlation with temperature was found for heptachlor and heptachlor epoxide ($R^2 = 0.52$ and 0.35, respectively), indicating that re-volatilization from surfaces is the main factor governing the presence of these compounds in the atmosphere. The correlation between 1/T and the concentration for heptachlor is shown in Fig. 4.

Table 2 Temperature dependence of concentrations of OCPs obtained with the Clausius–Clapeyron (CC) equation and the significance of compound concentrations towards ice cover. The following parameters are shown: $N =$ degree of freedom; $R^2 =$ correlation coefficient; $p =$ significance at 0.05 level using Student’s $t$-test

<table>
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<tr>
<th>Compound</th>
<th>CC equation</th>
<th>Ice cover</th>
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<tr>
<td>$\alpha$-HCH</td>
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<tr>
<td>$\gamma$-HCH</td>
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Some direct input from source regions via air masses from the Asian continent cannot be excluded for the main components of technical chlordane (TC, CC and TN), as observed during the transport episode in August 2009 when high concentrations of γ-HCH (11.763 pg m\(^{-3}\)), dieldrin (16.970 pg m\(^{-3}\)), \(p,p’\)-DDE (15.710 pg m\(^{-3}\)) and \(p,p’\)-DDT (5.847 pg m\(^{-3}\)) were detected in the same sample. The higher \(p,p’\)-DDT concentrations measured in the summer period at Station Nord are consistent with the significant correlation with temperature and negative correlation with ice cover (Table 2). The \(R^2\) value (0.27) can only account for about 27% of DDT in the Clausius–Clapeyron equation, meaning that LRT sources may not be excluded. \(p,p’\)-DDE concentrations were not correlated with temperature, indicating a predominance of LRT rather than re-emission.

Dieldrin concentrations were significantly correlated with both ambient temperature and ice cover.

Conclusions

This study reports measurements of atmospheric OCPs at Station Nord, North-East Greenland for the period 2008–2010. The measured concentrations for most compounds are comparable to those found during the last decade at other high Arctic stations such as Alert and Zeppelin. The seasonal patterns of pesticide concentrations observed at Station Nord are also in agreement with those found in other circumpolar studies.

The correlation between atmospheric concentrations and temperature was not significant for endosulfan, γ-HCH and \(p,p’\)-DDT, which indicates the predominance of transport from primary sources rather than re-evaporation from contaminated surfaces for these compounds. This is in agreement with the fact that at least two of the compounds (endosulfan and DDT) are still in use. γ-HCH is nearly phased out worldwide, but some use of old stocks of lindane cannot be excluded.

The rest of the compounds followed the Clausius–Clapeyron equation, and most of them correlated negatively with ice cover. This finding is very important as it is expected that POPs trapped in or under sea ice will be released in the future when sea ice cover decreases. The result of this study may therefore represent a new problem with respect to the melt of sea ice.

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Notes and references