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Source: Arctic, Antarctic, and Alpine Research, 36(3) : 284-291

Published By: Institute of Arctic and Alpine Research (INSTAAR), University of Colorado

URL: https://doi.org/10.1657/1523-0430(2004)036[0284:TTIAHM]2.0.CO;2

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Arctic, Antarctic, and Alpine Research, Vol. 36, No. 3, 2004, pp. 284–291

Temporal Trends in Atmospheric Heavy Metal and Organochlorine Concentrations at Zeppelin, Svalbard

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Abstract

As a part of the national Norwegian monitoring program, long-term surveys of contaminants have been carried out at the Zeppelin atmospheric research station (Ny-Ålesund, Svalbard) since the early 1990s. In the present study, all obtained data have been summarized and analyzed in order to review possible temporal trends for selected atmospheric contaminants at Svalbard. The following heavy metals were determined in aerosols: Pb, Cd, Hg, Cu, Zn, Cr, Ni, Co, Mn, V, and As. Only Ni showed a decreasing trend in the concentrations over the past decade. Organochlorine compounds in combined gaseous phase and aerosol samples evaluated were the following: α-HCH (hexachlorocyclohexane), γ-HCH, HCB (hexachlorobenzene), and sum-DDT (dichlorodiphenyltrichloroethane). Only those organochlorines exhibiting significant statistically confirmed temporal trends were chosen for the present comparison. Thus, although polychlorinated biphenyls (PCBs) as well as chlordanes are routinely monitored at the Zeppelin station, they were not considered for the here presented report because no clear trends were determined. Therefore all, but sum-DDT showed significant decreasing trends, correlating well with the national and international governmental regulations.

Introduction

Air masses carry contaminant burdens over great distances into, from, and within arctic region. If these chemicals cannot be broken down or excreted as fast as they are accumulated, their concentration levels will increase in organisms' tissues. At a certain high enough level, many of these so-called persistent contaminants may even have adverse affects on wildlife and on human health (AMAP, 2002).

Long-term monitoring programs of contaminants in the Arctic are, thus, carried out with the following aims:

- To act as a control tool, with the focus on ascertaining whether the governmental regulations show an effect in the environment.
- To initiate in-depth control measures in cases when acute increases in contaminant levels are seen.
- To estimate and survey "natural" and ubiquitous background levels as an important basis for regulations.
- To act as an indicator and "early warning" tool. Even minimal changes in level and distribution may be a first signal for larger global changes expected at a later stage.

Today, the comprehensive analysis of state-of-the-environment observations plays a fundamental part in the scientific and political processes. The description of past temporal trends is important information in order to assist the sound evaluation of today's basic monitoring strategies to improve the condition of the environment in the future. In the present study, monitoring data have been summarized, evaluated, and analyzed in order to review the changing state of the atmospheric contaminant environment at Svalbard.

Experimental

THE SAMPLING STATION

Sampling was carried out at the monitoring station located at the Zeppelin Mountain, close to Ny-Ålesund, Svalbard (78°54′N, 11°53′E) (Fig. 1). The station is in an undisturbed arctic environment, away from major potential pollution sources. Situated at 474 m a.s.l. and above the inversion layer, minimal influence is expected from local pollution sources in the nearby small scientific community of Ny-Ålesund. The station is located on a mountain ridge, with steep slopes to the north and south and higher mountain peaks to the west and east (altitude 1000–1500 m). The first Zeppelin station was built in 1989–1990. After 10 yr of use, the old building was no longer adequate for operation of advanced equipment and the increasing activities. The old building was removed and replaced by a new modern station that was inaugurated in February 2000.

HEAVY METALS

The heavy metals were collected on filters (Whatman 41 paper) using a Norwegian Institute for Air Research (NILU) high volume sampler. To collect long-range transported heavy metals mainly of anthropogenic origin, an impactor (Sierra Anderson, US) in front discriminated against particles larger than 2 μm . The air flow was kept constant at 70 $m^3\ h^{-1}$. One 48-h sample was collected each week. Until 1994 the filters were digested with nitric acid (Merck suprapure) in closed PTFE-bombs at 150°C for 6 to 8 h. From 2000, the filters were digested with nitric acid in tetrafluorometaxil-bombs using a microwave oven (Milstone Srl, Ethos Plus, Italy). The metals (Pb, Cd, Cu, Zn, Cr, Ni, Co, Mn, V, and As) were analyzed using inductively coupled plasma mass spectrometry (VG Plasmaquad, VG Elemental, UK) (Berg et al., 1993). Quality control routines including use of standard reference material were used (Aas et al., 2003).

Until 2000, manual sampling of Hg was carried out; one 24-h sample of vapor phase mercury was collected each week with gold traps. Usually about 1000 L of air was sampled at a flow rate of about 0.7 L min^{-1}. Hg was analyzed by thermal desorption/AFS (thermal desorption: University of Umeå, Sweden/AFS:PS-Analytical, UK). The method has been described in detail in Berg et al. (2001). From 2000, a high resolution automatic system (Tekran 2537A) (Tekran Inc.,

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FIGURE 1. The location of Ny-Ålesund, Svalbard.

Canada) replaced the manual measurements. This method gave results of "gaseous elemental mercury" with 5-min time resolution. The automated system had a similar operational principle to the manual method. The method has been described in detail in Berg et al. (2003).

ORGANOCHLORINE COMPOUNDS

Organochlorine compounds (OC) (Table 1) were sampled using NILUs high volume air sampler with a glass fiber filter (GFF: collection of particulate matter) and two polyurethane foam plugs (PUF: collection of the gaseous phase). It consisted of an ELMO high volume pump (Siemens, Karlsruhe,Germany) with a filter holder connected to an air intake tube. The sample is passing through a particle filter (GFF: glass fiber Gelman Type AE) followed by two identical PUF foam plugs (diameter 100 mm, length 50 mm, density 25 kg m^{-3}) for sampling of gas phase components (Oehme and Stray, 1982). The sample flow is about 20 m^3h^{-1} and 48-h sampling resulted in 900- to 1200-m^3 air samples. One 48-h sample is collected weekly.

For OC analysis isotope labelled internal standards ($_{13}$C-standards) were added to the glass fiber filters and the polyurethane foam plugs before soxhlet extraction with n-hexane/diethyl-ether (9:1) for 8 h. After preconcentration the extract was repeatedly treated with concentrated sulphuric acid in order to remove interfering matrix compounds. The organic phase was dried using sodium sulphate and transferred to a column packed with sodium sulphate and silica. The sample was eluted with *n*-hexane/diethyl-ether (9:1, v:v) and preconcentrated to 0.5 ml on a Turbovap evaporator (Zymark, Hopkinton, CA). A recovery standard was added before analysis using gas chromatography combined with mass spectrometry (GC/MS). Negative ion chemical ionization (NICI) or electron impact ionisation (EI) was used as the ioniszation method for detection and quantification. The signal intensity of two ions per compound was monitored in "selected ion monitoring" (SIM) mode. More information on the method can be found in Oehme et al. (1996).

Methodology for Describing Trends

Full trend examination of changes in the atmospheric contaminant composition of the Arctic is a very long and exploratory process. Scientific approaches suitable for elaborating this type of comprehensive understanding usually emerge as the investigation strategy proceeds. The necessary first step, however, is simply to display and interpret observed pattern profiles. Subsequent statistical evaluation, and importantly multidisciplinary evaluation of all scientific results obtained, will then be based on a secure footing less prone to unexpected artefacts.

TABLE 1

Organochlorine compounds routinely monitored at the Zeppelin station

Chlorinated pesticides	Polychlortinated biphenyls (PCB)
α-hexachlorocyclohexane (HCH), γ-HCH, *trans*-, *cis*- chlordane, *trans*-nonachlor, *cis*-nonachlor, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT, hexachlorobenzene (HCB)	PCB-18, PCB-28, PCB-31, PCB-33, PCB-37, PCB-47, PCB-52, PCB-60, PCB-66, PCB-74, PCB-99, PCB-101, PCB-105, PCB-114, PCB-118, PCB-122, PCB-123, PCB-128, PCB-138, PCB-141, PCB-149, PCB-153, PCB-156, PCB-157, PCB-167, PCB-170, PCB-180, PCB-183, PCB-187, PCB-189, PCB-194, PCB-206, PCB-209

For the present study, in addition to a direct graphical presentation and evaluation, the nonparametric Mann-Kendall test has been used on annual means for detecting and estimating trends in heavy metal and POP concentrations at the Zeppelin station (Gilbert, 1997). Recently, the Mann-Kendall test has become a standard method when, as in the case here, missing values are evident, non-normality occurs, etc (Barrett et al., 2000). In parallel to this, the Sens slope estimator has been used to quantify the scale of potential trends. The Mann-Kendall test and Sens slope estimator have been carried out using the MAKESENS software (Salmi et al., 2002) which is today an important tool among the EMEP (European Monitoring and Assessment Programme) participants to analyze trends for atmospheric pollutants. In the Mann-Kendall test a nonparametric *S*-test is used when the dataset includes less than 10 data points. If the number of data points is at least 10, the normal approximation test is used. However, if there are several tied values (i.e. equal values) in the time series, it may reduce the validity of the normal approximation when the number of data values is close to 10.

Results

HEAVY METALS

Monitoring of heavy metals at Zeppelin were initiated as a part of the Arctic Monitoring and Assessment Programme (AMAP) in 1994 (Aas et al., 2003). Figure 2 shows annual averages for heavy metals and minimum and maximum (2-d sampling) in aerosols covering 9 yr. Table 2 presents results of trend analysis carried out on the data. Figure 3 shows the combined results for those compounds showing significant trends in the analysis. Only Ni showed a significant trend with a reduction of 58%. The annual averages have decreased from about 0.19 to 0.07 ng m^{-3} for this element. None of the other metals showed significant changes during the period. For Hg (gaseous elemental mercury) the annual means were in the range 1.50–1.79 ng m^{-3}. For Pb they varied between 0.48 and 0.83 ng m^{-3}. For Cd the annual averages were in the range 0.01–0.03 ng m^{-3}. For Cu the corresponding values were in the range 0.25–0.41 ng m^{-3}. For Zn they varied between 1.2 and 1.9 ng m^{-3}. Cr showed annual averages in the range 0.04–0.9 ng m^{-3}. Co concentration means were from 0.055 to 0.14 ng m^{-3}, and for Mn the corresponding values were in the range 0.24–0.57 ng m^{-3}. For V the annual averages were in the range 0.07–0.20 ng m^{-3}. Figure 4 displays indications for a seasonal pattern in the concentrations of Ni and Pb. More detailed information on the heavy metal data from Zeppelin are given in the AMAP Data Report (Berg, 2003).

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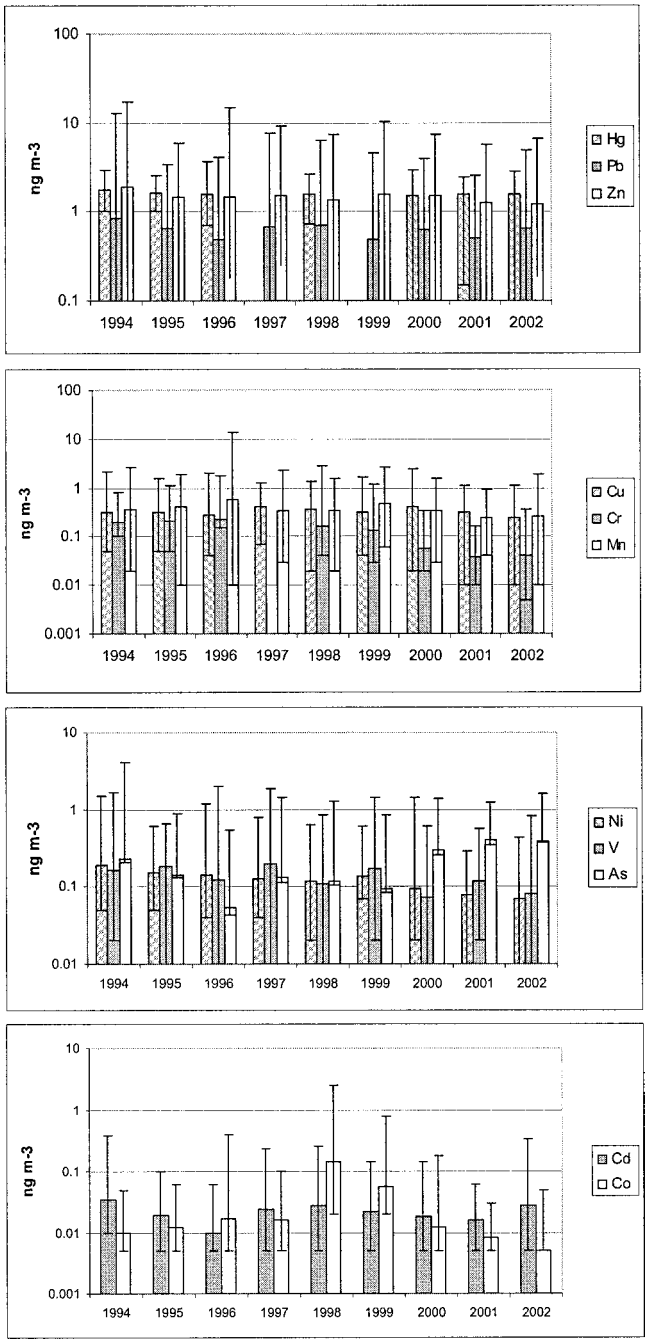


FIGURE 2. Annual means (columns) of heavy metals in aerosols and mercury in air (GEM) at Zeppelin. The bars show the minimum and maximum values measured for 52 samples each year.

TABLE 2

Trend analysis for heavy metals in aerosols at Zeppelin, Ny-Ålesund. Change is given as slope (best estimate of Sens' trend). The estimate of average change during the period is based on second-order polynomial regression. The slope is a part of Sens' trend estimator. "–" = reduction

Component	From	To	Trend-significance	Change ng m^{-3} yr^{-1} Slope median	Average change during the period (%)
Pb	1994	2002	no trend		
Hg	1994	2002	no trend		
Cd	1994	2002	no trend		
Cu	1994	2002	no trend		
Zn	1994	2002	no trend		
Cr	1994	2002	no trend		
Ni	1994	2002	99,9%	−0.012	−58
Co	1994	2002	no trend		
Mn	1994	2002	no trend		
V	1994	2002	no trend		
As	1994	2002	no trend		

temporal trends were determined for those compounds. However, in some cases, indications for seasonal trends were found and presented in the discussion of the paper. α-HCH showed a significant trend with a reduction of 81% over the past decade The annual averages has decreased from about 79 to 20 pg m^{-3} for this specific contaminant. γ-HCH showed a significant downward trend with a reduction of 65% over the past decade. The annual concentration averages has decreased from about 16 to 5 pg m^{-3}. HCB expresses a slightly significant trend with a reduction of 47% over the past 10 yr. The annual averages have decreased from about 115 to 55 pg m^{-3} . On the other hand, no significant trends were observed for sum-DDT (consisting of the concentration values for *p,p′*-, *o,p′*-DDT, dichlorodiphenyl dichloroethane: DDD, and dichlorodiphenyl dichloroethene: DDE). The annual average concentrations for this data set (starting 2 yr later than for the other OCs) have been found to be in the range 1- to 2.2 pg m^{-3}. Figure 7 displays indications for a seasonal pattern in the concentrations of cis-nonachlor, whereas Figure 8 shows p,p′-DDT/p,p′-DDE ratio derived from Zeppelin air. Detailed information on the data are given in the AMAP Data Report (Berg, 2003).

Discussion

HEAVY METALS

For all the heavy metals analyzed, only Ni showed a significant decreasing trend at Zeppelin for the period 1994–2003 (Fig. 3). Combustion of fossil fuels is assumed to be the main anthropogenic

ORGANOCHLORINE COMPOUNDS

Organochlorines have been subject to long-term circum-Arctic monitoring of atmospheric pollutants within the frame of AMAP (Kallenborn et al., 2002a, 2002b; Aas et al., 2003). Figure 5 shows annual averages for OCs at Zeppelin covering 8 to 10 yr. Table 3 presents results of trend analysis carried out on the data. Figure 6 shows results for those compounds showing significant trends in the analysis. Only those organochlorines exhibiting significant statistically confirmed temporal trends were chosen for the present comparison. Thus, although polychlorinated biphenyls (PCBs) as well as chlordanes are routinely monitored in atmospheric samples at the Zeppelin station, they were not considered for the here presented report because no clear

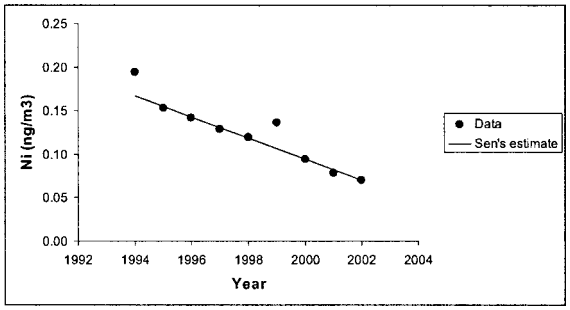


FIGURE 3. Time trend for Ni in aerosols at Zeppelin. In addition to data points (black dots) the figure also shows Sens trend estimate (line).

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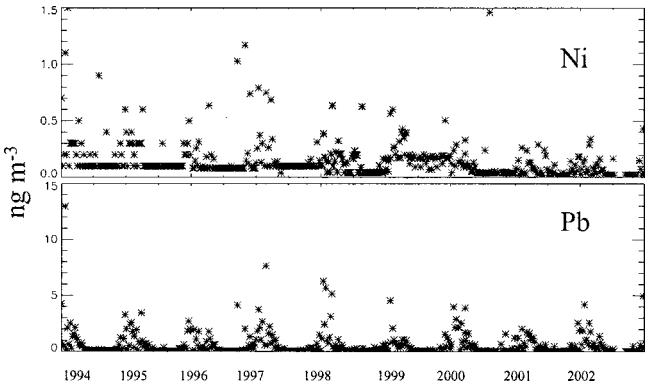


FIGURE 4. Ni and Pb as examples for seasonal variation in aerosols from the Zeppelin station.

source of Ni, but emissions from the smelters in Kola Peninsula will also be a significant source for atmospheric arctic contamination. However, today there exist practically no European or global emission data for Ni, but there is reason to believe that the decrease in Ni observed at Zeppelin are due to introduction of emission control systems in industrial processes and smelters. Ni is normally attached to particle sizes in the range 4–10 μm, but may also be attached to smaller particles. These small particles are not retained by standard industrial emission control systems and have the potential to be transported over long distances. Aerosol samples (winter data only) taken as a part of the Canadian Northern Contaminant program (Gong and Barrie, 2003) at Alert on Ellesmere Island during 1980–2000, showed a decreasing trend for Ni from 1982 to about 1990 and have since then been approximately constant.

The presented results indicate clearly that governmental regulations of Cd have not yet shown any effect in the Cd levels measured in the Zeppelin atmosphere (Fig. 2). Nevertheless, the lack of an expected downward trend may simply be caused by the fact that the atmospheric measurements at Zeppelin started in 1994 when most of the emission control systems already had been introduced. Campaign measurements at the old Ny-Ålesund station (located at the base of the Zeppelin mountain) in 1983–1984 (Pacyna et al., 1984; Pacyna and Ottar, 1985; Maenhaut et al., 1989), showed significantly higher concentrations than what have been measured during the last 9 yr. In the present study annual means in the range 0.01–0.03 ng m^{-3} were found. In the early 1980s a winter median of 0.08 (and a summer median of <0.11 ng m^{-3}) were measured. European Cd emissions to the atmosphere have decreased from about 900 t in 1990 (Pacyna, 1996) to about 360 t yr^{-1} in the second half of the 1990s (Pacyna and Pacyna, 2001). The global emissions have diminished from about 7500 t yr^{-1} in the 1980s to about 3000 t yr^{-1} in the second half of the 1990s (Pacyna and Pacyna, 2001). The major sources include nonferrous metal production, stationary fuel combustion and waste incineration. This decrease of Cd emissions is mostly related to the employment of highly

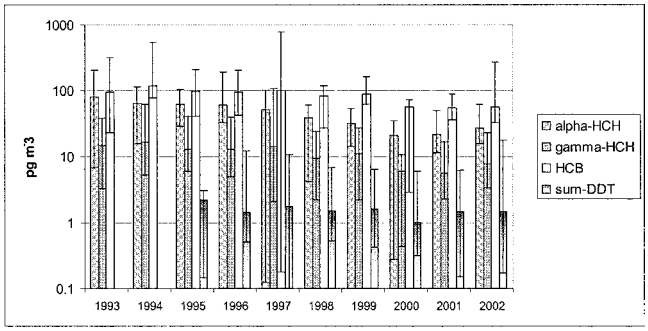


FIGURE 5. Annual means (columns) of OCs in air+aerosol at Zeppelin. The bars show the minimum and maximum values measured for 52 samples each year.

TABLE 3

Trend analysis for OCs in air+aerosol at Zeppelin, Ny-Ålesund. Change is given as slope (best estimate of Sens' trend) together with lower limit (Sens' trend estimate at –95% confidence interval) and higher limit (Sens' trend estimate at +95% confidence interval). The estimate of average change during the period is based on second-order polynomial regression. The slope is a part of Sens' trend estimator. "–" = reduction

Component	From	To	Trend-significance	Change ng m^{-3} yr^{-1} r Lower limit	Slope median	Higher limit	Average change during the period (%)
α-HCH	1993	2002	99.9%	−8.350	−6.855	−5.083	−81
γ-HCH	1993	2002	99%	−1.751	−1.137	−0.051	−65
HCB	1993	2002	95%	−9.124	−5.761	−1.226	−47
sum-DDT	1995	2002	no trend				

Sum_DDT include consentrations for *o,p′-/ p,p″*-DDE = dichlorodiphenyldichloroethene, *o,p″-/ p,p″*-DDT = dichlorodiphenyltrichloroethane and *o,p′-/ p,p″*-DDD = dichlorodiphenyldichloroethane.

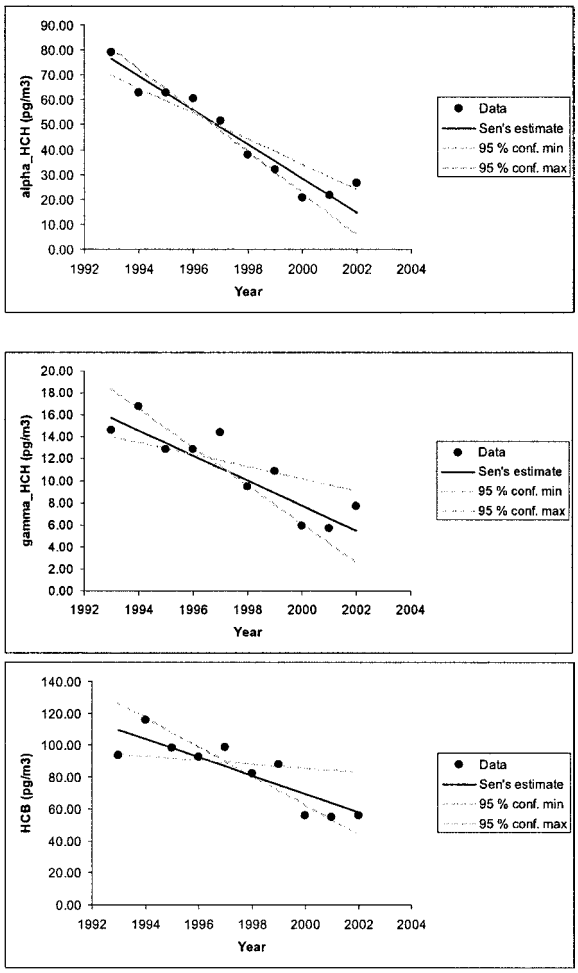


FIGURE 6. Time trend for OCs in air+aerosol at Zeppelin. In addition to data points (black dots) the figure also shows Sens trend estimate (line) and the lines for ±95% confidence interval (broken lines).

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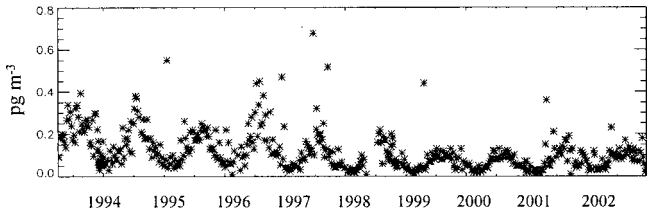


FIGURE 7. cis-nonachlor as typical example for seasonal variation in air from the Zeppelin station.

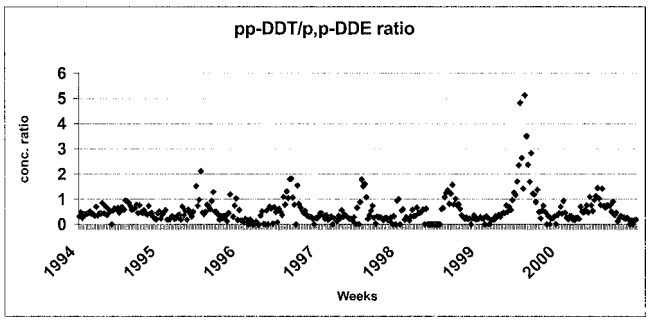


FIGURE 8. p,p′-DDT/p,p′-DDE ratio derived from Zeppelin atmospheric burdens in the period 1994–2000.

efficient emission control abatement in Europe to reduce the emissions of particles (Pacyna et al., 2002). Both in Europe and worldwide the emissions have been reduced with approx. 60% from mid 1980s to mid 1990s. The level of Cd in moss surveys carried out in Norway every 5 yr were in 2000 only 15% of that in 1977 (Berg and Steinnes, 1997; Steinnes et al., 2003).

As for Cd, the governmental initiatives on Pb have not shown any significant effect in the Pb concentrations measured in Zeppelin air (Fig. 2). The reason is probably the same as for Cd: The measurements started (1994) when most of the emission reductions had already been carried out. As for Cd, the campaign measurements in 1983–1984 (Pacyna et al., 1984; Pacyna and Ottar, 1985; Maenhaut et al., 1989) showed significantly higher concentrations than what have been measured during the last 9 yr. In the present study annual means in the range 0.48 and 0.83 ng m^{-3} were found. In the early 1980s a winter median of 3.0 (and a summer median of <0.7 ng m^{-3}) were measured. The European emission of lead has decreased continuously over the last decade from more than 58,000 t in 1990 to about 23,000 t in 2000 (Pacyna and Pacyna, 2000). These emissions have decreased worldwide from more than 330,000 t at the beginning of the 1980s to about 120 000 t in the mid 1990s (Pacyna and Pacyna, 2001). This decrease was mainly due to the decrease of lead additives to gasoline until its final phase-out. The European emissions have been reduced with about 70%. Aerosol samples taken at Alert during 1980–2000 (CACAR, 2003; Gong and Barrie, 2003), showed a decreasing trend from 1985 to 1993 and then increased (may be not statistically significant because of many data below the detection limit). When only winter data were studied from Alert a slight decreasing trend was observed. The concentrations of Pb in moss growing in Norway were in 2000 only 7% of that in 1977 (Berg and Steinnes, 1997; Steinnes et al., 2003).

Hg in air at Zeppelin has not dropped as expected from regional emission reduction (Fig. 2). European emissions of mercury from anthropogenic sources to the atmosphere have decreased from about 630 t in 1990 (Pacyna, 1996) through 340 t in 1995 (Pacyna et al., 2001) and to about 200 t in 2000 (EMEP MSC-W, 2002). The global anthropogenic emissions have changed from about 3600 t yr^{-1} in the 1980s to about 2000 t yr^{-1} in the second half of the 1990s (Pacyna and Pacyna, 2002; Pacyna et al., 2002). The main anthropogenic source of Hg is attributed to combustion of coal. Introduction of flue gas desulphurization in European power plants to remove sulphur dioxide, but also gaseous Hg has contributed mainly to the documented European emission decline of this element. It is rather difficult to compare directly changes in Hg emissions with measured concentrations, due to the fact that the natural sources of mercury are quite significant contributing to the atmospheric loads. It is estimated that between 200 and 250 t of Hg is emitted annually from these natural emission sources in Europe (Pacyna et al., 2001). Hg in air at Alert on Ellesmere Island measured during the period 1995–2000 has been approximately constant during the measurement period (Steffen et al., 2003). Hg observations at six sites in the Northern Hemisphere (including Zeppelin and Alert data), two sites in the Southern Hemisphere, and during eight ship cruises over the Atlantic Ocean provided a consistent picture suggestion that Hg concentration increased since the first measurements in 1977 to a maximum in 1980s and then decreased to a plateau in 1996–2001 (Slemr et al., 2003). Whereas the level of Hg in moss surveys carried out in Norway showed only small differences during 1985–1995, the 2000 data were approximately 30% lower (Steinnes et al., 2003).

Similar to Cd, Hg, and Pb, no decreasing trend were observed for Cu, Zn, Cr, Co, Mn, V, and As at Zeppelin during 1994–2002. At Alert, Zn and Cu showed a slight increase from 1980 to 1985 and then thereafter decreased. Al and Cu showed a slight decrease. (Gong and Barrie, 2003). The Canadians stated that the long-term trends observed at Alert for the anthropogenic components such as Cu, Pb, and Zn are governed by trends in the emission of the anthropogenic components surrounding the Arctic basin as well as transport/circulation patterns that influence the air masses that reach the Alert. This means that even a region with a constant emission could result in an oscillating contribution to the Arctic in a 4- to 14-yr cycle, which may either weaken or amplify contributions of the changes in the anthropogenic emissions to the observations. (Gong and Barrie, 2003).

The decreasing trends in the European emissions of the anthropogenic heavy metals are not only governed by employing emission control equipment. In Eastern Europe there was a clear decline of economy due to the change from centrally planned to market-oriented economy. This resulted in shutting down of several plants and consequently emission reduction. This fact should not be underestimated when discussing the emission changes in Europe in the 1990s (Pacyna and Pacyna, 2001).

Indications for seasonal dependent distribution patterns have been found for several heavy metals in Zeppelin aerosols as shown for Ni and V in Figure 4. Highest levels were found in winter whereas the lowest concentrations were reported for the summer period. A similar seasonal pattern were found for V, Mn, Cu, Zn, As, and Cd. This situation is mainly due to the character of major weather systems: In winter and spring, a high-pressure system over Siberia pushes the Arctic Front far to the south, so that important polluted areas are within the arctic air mass. During the arctic winter, emissions from the smelters in Kola Peninsula are a significant source for atmospheric arctic contamination. The aerosol residence times are also much longer in winter due to less deposition. Cr and Co showed higher concentrations during winter some years, whereas no seasonal pattern could be seen other years. These results are generally in line with findings at Alert where Na, Mg, K, Ti, Ni, Cu, Zn, V, and Pb showed a similar pattern (CACAR, 2003; Gong and Barrie, 2003). At Alert, no significant variations could be found for Ca, Al, Fe, Mn, and Ba. A completly different seasonal pattern has been found for gaseous elemental mercury at Zeppelin (Berg et al., 2003) and several other arctic and antarctic locations (Schroeder et al., 1998): Most of the year gaseous elemental mercury is at a background level of about 1.5 to

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1.6 ng m^{-3}. During a 3- to 4-mo period after polar sunrise, gaseous elemental mercury is disappearing from the air (concentrations below 0.1 ng m^{-3}) and is converted to more reactive species of mercury (known as mercury depletion events).

Summary: Heavy Metals

During the last 9 yr, a number of heavy metals has been monitored at the Zeppelin station. Only Ni showed a significant decreasing trend. The presented results indicate that governmental regulations have not yet shown any effect in the heavy metal levels measured in the Zeppelin atmosphere, but the lack of expected downward trends may probably also be caused by the fact that the atmospheric measurements at Zeppelin started in 1994 when most of the emission control systems already had been introduced. Campaign measurements from the early 1980s indicate that the concentrations levels at that time were considerably higher. However, at Alert where measurements have been carried out for 20 yr, some of the changes were consistent with the trends observed while others did not correlate at all. This were attributed to changes of the circulation patterns. Most of the heavy metals expressed seasonal distribution differences which is attributed to meteorology and deposition processes.

ORGANOCHLORINE COMPOUNDS

Most organochlorines (OCs) analyzed in the Zeppelin air monitoring programs are subject for strict governmental regulations which have been in place for a long time. The organochlorines routinely monitored at Zeppelin are listed in Table 1. However, due to the persistence of these compounds, significant downward temporal trends could just be confirmed for a selected number of compounds as already outlined above. Therefore, only those compounds for which clear trends/tendencies are confirmed are subject for further discussion.

Significant decreasing temporal trends were only found for the hexachlorocyclohexane-isomers (α- and γ-HCH) measured in Zeppelin air samples. The decrease was, however, much more pronounced for α-HCH than for γ-HCH. This is obviously due to restrictions in use of the technical product (where α-HCH with about 60% content is the main contributing component). Today, in western countries only the use of lindane (containing >95% γ-HCH) is allowed in agricultural application since the late 1970s. The relatively high concentrations of HCHs measured at Zeppelin are probably due to the high application volumes for technical HCH at high latitudes and, thus, the relatively high continuous environmental burdens in the northern environment. Almost 80% of the remaining use of technical HCH in Europe in 1996 (with α-HCH as major contributor) was attributed to the new states of the former Soviet Union (422 t of technical HCH according to Breivik et al., 1999). The other 20% was attributed to usage in some former Eastern European countries (Breivik et al., 1999). According to Centre International d'Etudes du Lindane (Breivik et al., 1999 and references therein), the average annual lindane consumption in Europe was 2130 t during the period from 1992 to 1997. France was the major user of lindane in Europe during this period, with an annual average consumption of 1600 t (Breivik et al., 1999 and references therein). Today reemission from sea surfaces is probably the most important source for α-HCH in arctic air. However, Li et al. (1998) identified two major reduction episodes for α-HCH. The first international ban for the use of α-HCH is clearly reflected in the strong atmospheric reduction in arctic atmosphere for the year 1982–1983. Also for the year 1990–1991, a strong reduction was found and has been attributed to the ban of the technical HCH as pesticide in China (Li et al., 1998, Li and Bidleman, 2003).

The hexachlorobenzene (HCB) levels have also been decreasing in Zeppelin air, but the trend is not as significant as demonstrated for the HCH-isomers. Many diffuse and varying sources make it more difficult to see significant results of regulative actions for HCB.

Indications for seasonal dependent distribution patterns have been found for several chlorinated compounds in Zeppelin air. As already published earlier (Oehme et al., 1996), concentration differences between winter and summer levels are confirmed for *cis*-nonachlor (Fig. 7) and transchlordane in Zeppelin air. Highest levels are found in summer, whereas the lowest concentrations are reported for the winter period. These seasonal pattern differences are confirmed for both cyclodiene pesticides. As major reason for this typical distribution pattern, microbial degradation is identified which is considerable reduced during wintertime. Oehme et al. (1996) stated that a weathered chlordane concentration mixture with *trans*-/ *cis*-chlordane ratios <1 are influencing the arctic atmosphere. This assumption is generally in line with the recent findings from the Zeppelin monitoring program. The same seasonal patterns found in Zeppelin air are also confirmed for atmospheric samples from Alert, Canada (Bidleman et al., 2003; MacDonald *et al.* 2003) and for Pallas, Northern Finland (Brorström-Lundén et al., 2003).

In addition to the cyclodienes, the distribution of DDT derivatives also seems to be seasonally dependent in Zeppelin air. The ratio between the parent compound *p,p′*-DDT and the main transformation product *p,p′*-DDE changes throughout the year (Fig. 8).

Probably due to diffences in degradation properties (microbial and photochemical), a seasonal shift in the ratios have been found with dominating *p,p′*-DDT (ratio >1) in the summer (1995–2000) and dominating *p,p′*-DDE (ratio <1) in winter periods (1995–2000). However, fresh transport of *p,p′*-DDT from Eastern European or Asian sources cannot be excluded as reason for the high *p,p′*-DDT proportions in Zeppelin air during winter.

The second Canadian Arctic Contaminant Assessment Report (CACAR) of the Canadian Northern Contaminant program (Bidleman et al., 2003) allows a first comparison between the most recent results of the Canadian and Norwegian atmospheric long-term monitoring programs. The CACAR 2003 report identified seasonal patterns as well as significant temporal reduction in the distribution of PCBs in Canadian Arctic Air (1993–1997). However, a comparable distribution was not seen in the Zeppelin air data. Since the Canadian data underwent digital filtration (DF) prior to the final statistical analysis, a comprehensive and detailed comparison with the Zeppelin data is currently very difficult. However, as a part of an ongoing interinstitutional cooperation between NILU and Meteorological Services, Canada, a detailed data comparison between the two monitoring programs is in progress and will be published when finished (Kallenborn et al. in preparation) as a joint publication. Therefore, only general tendencies will be described here. As outlined in the CACAR II report, OC levels in Alert seems, to be, in general, considerably lower than in the Zeppelin air samples. This is especially true for PCBs, These concentration differences are obviously caused by shorter transport routes and more frequent transport episodes from the main source regions in central and Eastern Europe. In Alert air samples, no seasonal changes in *p,p′*-DDT/*p,p′*-DDE ratios have been identified indicating different major sources for DDTs in the Canadian Arctic compared to the European Arctic.

Summary: Organochlorines

During the past decade, an array of persistent organochlorines has been monitored in Zeppelin air samples including polychlorinated biphenyls, cyclodiene pesticides, hexachlorobenzene, hexachlorocyclohexanes, DDT- derivatives. However, the fact, that just few of the monitored organochlorine compounds in Zeppelin air show significant downwards temporal trends over the past decade although regulatory measures and restrictions are in place shows that the high persistence of the chemicals make an immediate signal found during the monitoring programs very weak or even impossible to discover. A selected number

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of OCs express seasonal distribution differences assumed to be caused by a combination of long-range transport events and degration properties. In addition, due to changes in the equilibrium situation, secondary sources formerly serving as sinks may develop into new sources contributing to the atmospheric contaminant levels in the Northern environment. This has been shown for hexachlorocyclohexanes, where former sinks (surface waters) are today considered as major contributors for the atmospheric HCH loads in the Arctic (CACAR, 2003).

Conclusion

The here presented results, confirm that a 10-yr monitoring program is still not sufficient to evaluate temporal trends for most of the persistent contaminants present in the arctic atmosphere. Long-term continuous monitoring stretching over several decades is needed to evaluate the environmental fate for most of the contaminants.

Employment of emission-control equipment, application bans, and severe restriction of use are in place in western countries for many contaminants. However, atmospheric long-range transport is a regional/global process and integrates over potential sources far from the arctic deposition areas. Thus, uncontrolled emissions from Asian, South American, and African region are still contributing significantly to the contaminant levels in the arctic atmosphere. Thus, the here presented results should also be taken as additional argument to negotiate global regulations for persistent, bioaccumulative, and toxic chemicals (PBT) for the benefit of a global environment. Natural decadal variability in the meteorological transport patterns to the arctic also influence the concentrations measured.

Acknowledgments

For financial support we wish to acknowledge The Norwegian State Pollution Authority (SFT). We are grateful for technical support by the staff at Norwegian Polar Research Institute, Ny-Ålesund, and to Marit Vadset and Hans Gundersen, NILU for analysis.

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Ms submitted February 2004

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