Atmospheric transport of persistent organic pollutants (POPs) to Bjørnøya (Bear island)†

Roland Kallenborn,*[a] Guttorm Christensen,[b] Anita Evenset,[b] Martin Schlabach[a] and Andreas Stohl[a]

Received 22nd November 2006, Accepted 29th May 2007
First published as an Advance Article on the web 10th July 2007
DOI: 10.1039/b707757m

A first medium term monitoring of atmospheric transport and distribution for persistent organic pollutants (POPs) in Bjørnøya (Bear island) air samples has been performed in the period between week 51/1999 and week 28/2003. A total of 50 single compounds consisting of polychlorinated biphenyls (33 congeners), hexachlorobenzene (HCB), hexachlorocyclohexane isomers (α-, β-, γ-HCH), α-endosulfan, cyclodiene pesticides (chlordanes, nonachlor-isomers, oxy-chlordane, heptachlor and chlordane) as well as dichlorodiphenyltrichloroethane (DDT) derivatives were analysed and quantified. Atmospheric transport of POPs was identified as an important contamination source for the island. PCBs, HCB and HCH isomers were the predominant POP groups, contributing with 70–90% to the overall POP burden quantified in the Bjørnøya air samples. The highest concentration levels for a single compound were found for HCB (25–35 pg m^{-3}). However, the sum of 33 PCB congeners was found to be in the same concentration range (annual means between 15 and 30 pg m^{-3}). Cyclodiene pesticides, DDT derivatives and α-endosulfan were identified as minor contaminants. Several atmospheric long-range transport episodes were identified and characterised. Indications for industrial emissions as well as agricultural sources were found for the respective atmospheric transport episodes. A first simple statistical correlation assessment showed that for long-range transport of pollution, the local meteorological situation is not as important as the air mass properties integrated over the time period of the transport event. The local weather situation, on the other hand, is important when investigating deposition rates and up-take/accumulation properties in the local ecosystem. Based upon chemical data interpretation, valuable information about the influence of primary and secondary sources on the air mass contamination with chlorinated insecticides (*e.g.*, HCHs) was found and discussed. The interdisciplinary interpretation of contaminant data using statistical methods, chemical analysis, meteorological modelling and classical meteorological information for a comprehensive evaluation of atmospheric long range transport into the European Arctic (Bjørnøya) has proven to be a highly versatile tool not only for atmospheric scientists but also with strong potential for regulatory purposes.

Introduction

The recent published assessment report on persistent organic pollutants (POPs) in the Arctic confirmed the presence of POPs in practically all environmental compartments of the Arctic.[1] Although banned for decades in most of the industrialised countries, many legacy POPs are still found in considerable concentrations throughout the Arctic. Organochlorine pesticides like dichlorodiphenyltrichoroethane derivatives (DDT, DDE, DDD) and γ-hexachlorocyclohexane (γ-HCH, Lindane®) are still in use as pest control agents in many developing countries. Hexachlorobenzene (HCB) is known as a by-product in numerous industrial chemical processes and polychlorinated biphenyls (PCBs) are still released during decommissioning processes of PCB-containing products. Thus primary sources for this type of chemicals cannot be excluded even today, although the majority have been officially regulated by national and international agreements for decades.

Long-range transport through the atmosphere or *via* ocean currents is identified as a major source for POPs in the Arctic since only a few potential primary sources are identified in the region (*e.g.*, military installations, research stations and settlements). The pathways and processes of POP transport into the Arctic environments are highly complex and, today, considered as an global interactive distribution system depending on many environmental factors.[1–3]

Already in 1996 elevated levels of selected POPs were measured in sediment and fish from lake Ellasjøen, a lake located in the southern part of Bjørnøya (Bear island, 74°30′ N, 19°00′ E).[4] Also subsequent investigations proved

---

[a] *Norwegian Institute for Air Research, P.O. Box 100, NO-2027 Kjeller, Norway. E-mail: roland.kallenborn@nilu.no; Fax: +47 63 89 80 50; Tel: +47 63 89 80 00*
[b] *Akvaplan-niva, The Polar Environmental Centre, NO-9296 Tromsø, Norway. E-mail: akvaplan@akvaplan.niva.no; Fax: +47 77 75 03 01; Tel: +47 77 75 03 00*

† Electronic supplementary information (ESI) available: POPs in Bjørnøya atmospheric samples. See DOI: 10.1039/b707757m

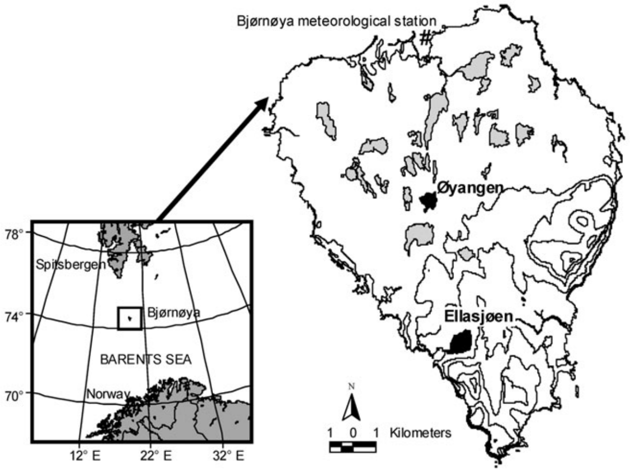

Fig. 1 Sampling location: Bjørnøya (Bear island).

that the lake Ellasjøen ecosystem is contaminated with a variety of POPs.[5,6,8,11] High concentrations of POPs have also been found in seabirds, marine fish and crustaceans from the marine environment around Bjørnøya.[12,13] Only a meteorological station is active all-year around at Bjørnøya. No other human activity besides campaign-based research projects have been reported from the island during recent years. Thus, no local source for POP pollution could be identified up to now. Based upon these findings, a comprehensive national research project was initiated in order to elucidate fate, distribution and origin of the POP contamination of the local Arctic ecosystem on the island. The study presented herein is a direct result of this national scientific endeavour. Bjørnøya is an Arctic island midway between the North Norwegian mainland and the Svalbard archipelago (Fig. 1). Additional information about Bear island has been published earlier.[11] Since no local contamination sources exist on the island, long-range transport of pollutants must be the major source for the presence of POPs in the Bjørnøya environment.

The main objective of the present study was to elucidate the contribution of atmospheric long range transport to the overall POP contamination of the Bjørnøya ecosystem.

Methods

Air samples were collected using a mobile electrical high volume air sampler developed by the Norwegian Institute for Air Research (NILU). Due to the need for an electric power supply, the air sampling device was installed in a sampling hut close to the meteorological station, located close to the shore at the northern tip of Bjørnøya (see Fig. 1). One high-volume air sample was collected per week by pumping air (flow rate 20 m^3 h^{-1}) subsequently through a glass fibre filter (GFF, particulate phase) and a polyurethane foam plug (PUF: gaseous phase). 72–96 h samples were collected with a continuous flow rate of 20 m^3 h^{-1} (average), resulting in sample volumes between 1800–3000 m^3 air. Air samples were collected by the engineer of the local staff at the meteorological station (Norwegian Meteorological Institute) during the 31 month sampling period, from December 1999 (week 51) until July 2003 (week 28).

The sampling scheme was divided into two separate schedules for every year:

October–April: 2–3 day sampling every second week
April–September: 2–3 day weekly sampling

A weekly sampling schedule was chosen for spring/summer instead of two weeks per sample in autumn/winter in order to investigate the influence of seasonal agricultural application of pesticides, including γ-HCH and DDT-derivatives, in middle latitude application regions on atmospheric long-range transport events at Bjørnøya. Samples were wrapped in aluminium foil and put into sealed ziplock bags and stored frozen until analyses. Target chemicals as well as sampling periods are listed in Table 1. Please note that cyclodiene pesticides (chlordanes, nonachlor, heptachlor, and transformation products) only were analysed during the sampling period from week 51, 1999 to week 36, 2001, and α-endosulfan even for a shorter period (week 51, 1999–week 45, 2000). After the analysis of the first sampling set, quantification of cyclodiene and α-endosulfan was omitted due to the overall low levels and small variability of the obtained data (see ESI†).

Daily meteorological information on average ambient temperature, humidity and precipitation rates were transformed into weekly average values and a Pearson correlation test was performed in order to evaluate the correlation between weekly atmospheric POP levels and the local meteorology at Bjørnøya.

Analytical methods

Sampling, clean-up procedures and quantification methods used at the laboratory of the Norwegian Institute for Air Research (NILU) are described in earlier publications.[7,8] Particulate phase (GFF) and gaseous phase (PUF) were

Table 1 Target chemicals and sampling period for the respective chemicals during the atmospheric survey conducted at Bjørnøya (Arctic Norway)

Persistent chlorinated contaminants selected for analysis in ambient air samples from Bjørnøya

Target compounds	Sampling period
Sum polychlorinated biphenyls (PCB): 18, 28, 31, 33, 37, 47, 52, 60, 66, 74, 99, 101, 105, 114, 118, 122, 123, 128, 138, 141, 149, 153, 156, 157, 167, 170, 183, 189, 194, 206, 209	Week 51/1999–week 28/2003
Hexachlorobenzene (HCB)	Week 51/1999–week 28/2003
Hexachlorocyclohexanes (HCH): α-HCH, β-HCH and γ-HCH	Week 51/1999–week 28/2003
Cyclodiene-pesticides:	
trans-chlordane (tr-CD), *cis*-CD, *trans*-nonachlor (tr-NO), *cis*-NO, chlordene, heptachlor, oxy-chlordane	Week 51/1999–week 36/2001
Dichlorodiphenyltrichloroethane (DDT)-derivatives: *o,p′-, p,p′*-DDT, *o,p′-, p,p′*-DDE, and *o,p′-, p,p′*-DDD	Week 51/1999–week 28/2003
α-endosulfan	Week 51/1999–week 45/2000

combined before extraction (Soxhlet extraction). Quantification was performed with capillary gas chromatography (Agilent 6890, Palo Alto, CA, USA) and high-resolution mass spectrometry (VG Autospec Ultima, Waters Inc., Elstree, UK). All solvents, chemicals and adsorbents used were of highest analytical quality and purchased from VWR (Oslo, Norway).

Quality control

Sampling and sample storage were an integrated part of the overall quality control program. The technician at the Bjørnøya meteorological stations followed detailed routines for sampling and sample storage developed by the Norwegian Institute for Air Research (NILU) in order to avoid unwanted contamination. A set of field blank samples were added to the field samples in order to control unintended contamination during storage and transport.

The analytical procedure was accompanied by a comprehensive quality control program based on the requirements of NILUs accreditation, according to EU standard EN 45001. The limit of detection (LOD) was determined by calculating the signal to noise ratio $(S/N) > 3$ for solvent blanks (using *n*-hexane). Extensive field and laboratory blank values were analysed in order to monitor and control possible contamination during transport and laboratory work. No evidence for contamination during sample processing was found (no elevated values in field and laboratory blanks). Based upon average blank concentrations (for both laboratory and field blanks) the limit of quantification (LOQ) was calculated for all compounds with a $\text{LOQ} > 10\times$ blank concentration.

All samples below the LOQ are considered with high uncertainties and, thus, were excluded from further statistical treatment and marked as below the LOQ (<LOQ).

Statistical methods

For statistical evaluations (Pearson correlation tests) the statistical software package WINSTAT® (R. Finch software, OH, USA) for Microsoft EXCEL® (Microsoft®, Lilleaker, Oslo, Norway) was used.

Back trajectories modeling

For the assessment of potential source regions of atmospheric POP contamination in Bjørnøya air, atmospheric back trajectory calculations were performed using the FLEXTRA trajectory model (NILU, Kjeller, Norway). A 3-dimensional 5 to 10 days back trajectory calculation was applied for potential source identification (http://www.nilu.no/trajectories/index.cfm). All 3-dimensional back trajectory calculations are based upon the meteorological data collected from the European Centre for Medium Range Weather Forecast (ECMWF, Reading, UK). The Lagrangian particle dispersion model FLEXPART[15] is a pure transport model and no removal processes were considered here. The only purpose of the model simulations was to identify the sources of the measured pollution.

FLEXPART was driven with analyses with 1° × 1° resolution. In addition to the analyses at 0, 6, 12 and 18 UTC, 3 h forecasts at 3, 9, 15 and 21 UTC (universal time coordinated) were used. FLEXPART calculates the trajectories of so-called tracer particles using the mean winds interpolated from the analysis fields plus random motions representing turbulence and a particle redistribution according to a convective mass flux scheme. In order to maintain high accuracy of transport near the poles, FLEXPART advects particles on a polar stereographic projection poleward of 75° but using the ECMWF winds on the latitude–longitude grid to avoid unnecessary interpolation.

A special feature of FLEXPART is the possibility to run it backward in time.[14] Backward simulations from Bjørnøya were made for 3 h time intervals in April and May 2006. For each such interval, 40 000 particles were released at the measurement point and followed backward in time for 20 days, forming what we call a retroplume, to calculate a so-called potential emission sensitivity (PES) function. The word "potential" indicates that this sensitivity is based on transport alone, ignoring removal processes that would reduce the sensitivity. The value of the PES function (in units of s kg^{-1}) in a grid cell is proportional to the particle residence time in that cell. It is a measure for the simulated mixing ratio at the receptor that a source of unit strength (1 kg s^{-1}) in the respective grid cell would produce. Here we only show the PES integrated over the entire atmospheric column (unit of ns m kg^{-1}). This quantity mainly serves to illustrate the pathway of the air during the 20 days before arriving at Bjørnøya. The main advantage over traditional back trajectory calculations is that the FLEXPART calculations also account for turbulence and convection and can be interpreted quantitatively. More FLEXPART products for Bjørnøya, also for times not shown here, as well as a more detailed description can be found at http://zardoz.nilu.no/~andreas/STATIONS/BJOERNOEYA/.

Results

In combination with the long-term monitoring program on atmospheric POP contaminants at the Zeppelin mountain research station (Ny-Ålesund, Svalbard) situated around 500 km north of Bjørnøya, the Bjørnøya atmospheric POP survey has been a unique scientific instrument for atmospheric monitoring in the European Arctic on a medium time scale. A first scientific comparison of the results from both stations is currently in progress and will be published at a later stage.

During the sampling period (see Table 1), 50 priority POPs were analysed and quantified in atmospheric high volume samples from the meteorological station at Bjørnøya (Bear island, Norway). Concentration distributions are summarised as arithmetic mean, minimum and maximum values in Table 2 for the respective sampling years. A more detailed information on the complete data set can be found in the ESI.†

In addition to contaminant concentrations, basic daily meteorological data (ambient air temperature, wind speed, precipitation rates and humidity) were provided for the entire sampling period from the Norwegian Meteorological Institute, Oslo. These data are publicly available, free of charge, from the institute's website (http://www.met.no).

Bjørnøya has a marine Arctic climate with relative high annual humidity (80–99%), low annual precipitation rates (around a total of 367 mm annually) and expressed

Table 2 Annual concentration range (arithmetic mean, minimum and maximum) for all target chemicals analysed during the atmospheric contaminant monitoring at Bjørnøya (Arctic Norway)[a]

(a) HCB and PCB congener distribution in Bjørnøya air (2000–2003)

	2000			2001			2002			2003 (until week 26)		
Compounds	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
HCB	6.70	68.63	33.37	7.23	45.18	21.49	9.36	39.70	20.37	15.51	47.50	29.81
18	1.14	22.20	7.94	1.09	3.35	1.94	0.71	5.69	2.90	1.86	4.13	2.92
28	0.76	11.85	4.41	0.84	2.56	1.45	0.37	3.74	1.71	1.18	2.75	1.84
31	0.73	11.43	4.19	0.80	2.20	1.31	0.41	3.30	1.51	1.06	2.17	1.57
33	0.59	9.19	3.37	0.54	1.80	1.01	0.32	2.56	1.17	0.58	1.48	1.08
37	0.11	1.82	0.63	0.07	0.50	0.22	0.01	0.49	0.19	0.12	0.35	0.23
47	0.52	10.05	3.50	0.38	3.43	1.27	0.27	3.72	1.21	0.72	4.00	1.56
52	0.55	9.55	3.53	0.82	2.45	1.32	0.35	2.26	1.18	0.94	1.90	1.37
60	0.04	0.77	0.26	0.03	0.36	0.11	0.01	0.20	0.08	0.05	0.11	0.07
66	0.18	3.50	1.25	0.01	1.76	0.59	0.15	0.75	0.33	0.26	0.61	0.36
74	0.09	1.80	0.64	0.01	0.85	0.30	0.01	0.45	0.21	0.16	0.45	0.27
99	0.07	1.57	0.53	0.15	3.76	0.43	0.01	0.42	0.19	0.13	0.48	0.26
101	0.20	5.78	1.57	0.38	1.13	0.65	0.18	1.10	0.56	0.39	1.05	0.65
105	0.04	0.58	0.18	0.03	1.20	0.19	0.01	0.15	0.05	0.04	0.19	0.07
114	0.01	0.05	0.02	0.01	0.21	0.02	0.01	0.01	0.01	0.01	0.02	0.01
118	0.10	1.73	0.54	0.11	4.67	0.58	0.01	0.43	0.22	0.13	0.65	0.27
122	0.01	0.12	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
123	0.01	0.22	0.03	0.01	0.10	0.02	0.01	0.01	0.01	0.01	0.01	0.01
128	0.01	0.24	0.09	0.02	0.53	0.09	0.01	0.02	0.01	0.02	0.11	0.04
138	0.06	1.85	0.52	0.11	1.68	0.39	0.01	0.38	0.19	0.15	1.01	0.29
141	0.03	0.36	0.14	0.02	0.21	0.07	0.01	0.12	0.04	0.03	0.20	0.07
149	0.13	1.97	0.77	0.15	0.76	0.37	0.10	0.49	0.28	0.21	0.59	0.34
153	0.19	2.25	0.79	0.13	1.77	0.42	0.01	0.42	0.26	0.21	1.64	0.46
156	0.01	0.10	0.04	0.01	0.44	0.06	0.01	0.01	0.01	0.01	0.06	0.02
157	0.00	0.02	0.01	0.01	0.06	0.01	0.01	0.01	0.01	0.01	0.01	0.01
167	0.01	0.05	0.02	0.01	0.33	0.03	0.01	0.01	0.01	0.01	0.04	0.01
170	0.01	0.18	0.06	0.01	0.50	0.06	0.01	0.08	0.03	0.01	0.10	0.03
180	0.03	0.77	0.25	0.02	1.95	0.19	0.01	0.18	0.07	0.04	0.43	0.12
183	0.01	0.28	0.09	0.01	0.83	0.07	0.01	0.03	0.01	0.02	0.14	0.04
187	0.03	0.55	0.20	0.02	1.23	0.13	0.01	0.13	0.05	0.04	0.28	0.10
189	0.00	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
194	0.01	0.06	0.02	0.01	0.07	0.01	0.01	0.01	0.01	0.01	0.01	0.01
206	0.01	0.11	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
209	0.01	1.51	0.09	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sum PCB	5.89	96.78	35.72	7.05	28.47	13.35	3.37	26.73	12.53	9.33	21.59	14.08

(b) Organochlorine pesticide (OCP) distribution in Bjørnøya air (2000–2003)

	2000			2001			2002			2003 (until week 14)		
Compounds	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
α-HCH	5.45	27.09	17.00	9.75	21.10	14.15	3.19	22.00	14.91	9.02	15.00	11.15
β-HCH	0.06	0.50	0.23	0.02	0.21	0.09	0.04	0.18	0.08	0.04	0.20	0.09
γ-HCH	1.79	17.10	7.79	2.64	10.81	5.07	1.20	8.97	4.88	2.79	5.48	3.89
Chlordene	0.01	0.10	0.03	0.01	0.13	0.03	na	na	na	na	na	na
Heptachlor	0.03	4.55	1.43	0.02	0.62	0.21	na	na	na	na	na	na
oxy-Chlordane	0.25	1.95	0.96	n.d.	n.d.	n.d.	na	na	na	na	na	na
trans-Chlordane	0.15	4.47	1.50	0.27	0.66	0.41	na	na	na	na	na	na
cis-Chlordane	0.27	3.42	1.45	0.46	1.28	0.84	na	na	na	na	na	na
trans-Nonachlor	0.26	3.48	1.42	0.38	1.32	0.81	na	na	na	na	na	na
cis-Nonachlor	0.04	0.23	0.13	0.02	0.25	0.08	na	na	na	na	na	na
o,p′-DDE	0.07	1.49	0.57	0.10	0.30	0.13	0.03	0.24	0.12	0.10	0.41	0.20
p,p′-DDE	0.53	12.44	3.89	0.40	10.20	1.43	0.29	1.28	0.85	0.60	5.64	1.87
o,p′-DDD	0.01	0.10	0.04	0.01	0.40	0.06	0.01	0.20	0.05	0.02	0.05	0.03
p,p′-DDD	0.01	0.16	0.04	0.01	0.50	0.09	0.01	0.06	0.03	0.01	0.37	0.07
o,p′-DDT	0.09	1.89	0.68	0.17	0.50	0.30	0.06	0.38	0.19	0.12	0.32	0.23
p,p′-DDT	0.18	2.99	0.99	0.10	1.00	0.42	0.05	0.46	0.20	0.07	0.61	0.24
Sum HCH	0.00	42.76	23.10	0.00	28.49	17.16	0.00	26.84	18.84	12.56	20.18	15.13
Sum CHL	0.00	17.49	6.33	0.00	3.83	1.86	na	na	na	na	na	na
Sum DDT	0.00	17.54	5.58	0.00	11.16	2.16	0.00	2.29	1.37	1.01	6.98	2.64

[a] Min = minimum concentration, max = maximum concentration, na = not analysed, CHL = chlordane derivatives.

seasonal patterns for wind velocity and ambient temperature (see Fig. 2).

A standard Pearson correlation test was performed for all 50 organohalogen target contaminants with regard to four

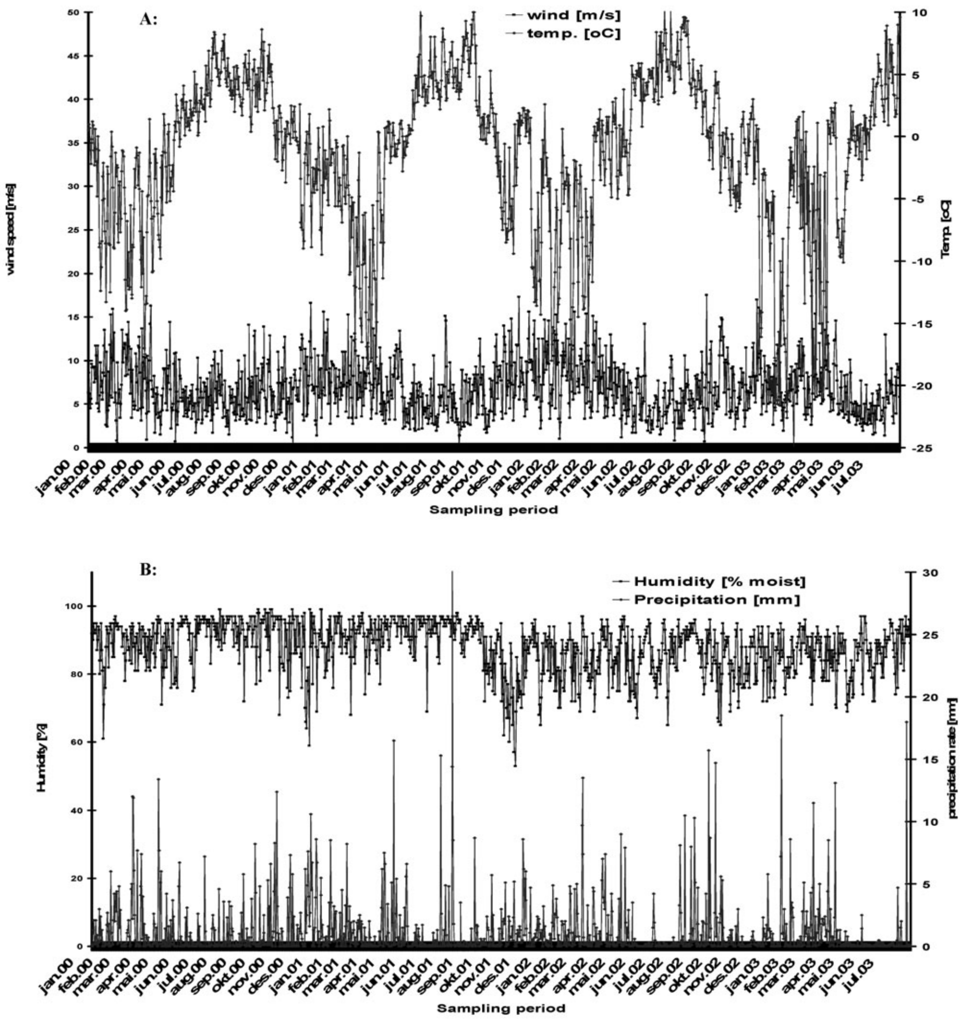

Fig. 2 Meteorological information for Bjørnøya: daily average wind speed and ambient temperature (A) as well as precipitation rates (mm month^{-1}) and humidity (B) for the sampling period January 2000–April 2003. *All information is freely available from the website of the Norwegian Meteorological institute.*

meteorological variables, namely ambient temperature, precipitation rate, wind speed and humidity measured at the station. The squared Pearson correlation coefficient is a measure of the covariance explained by a linear relation between the variables. Significant correlations for all four variables were found for *ca.* 30 compounds ($p < 0.1$). However only compounds expressing highly significant correlations ($p < 0.05$) are listed in Table 3.

Highly significant ambient temperature dependent distribution patterns were found for 12 semi-volatile halogenated contaminants. Concentration distribution of a total of 9 chemicals (including 8 PCB congeners and α-HCH) were

Table 3 Significant correlation ($p < 0.05$) confirmed between selected compounds and ambient temperature using "Pearson's correlation test"

Compounds with significant correlation to ambient temperature changes ($p < 0.05$)	Compounds with significant correlation to precipitation rates ($p < 0.05$)	Compounds with significant correlation to wind speed changes ($p < 0.05$)	Compounds with significant correlation to humidity changes ($p < 0.05$)
Polychlorinated biphenyls (PCB): PCB 18, 101, 122	Polychlorinated biphenyls (PCB): PCB 74, 105, 114, 123, 141, 167, 189, 209	Polychlorinated biphenyls (PCB): PCB 128	Polychlorinated biphenyls (PCB): PCB 74, 105, 114, 123, 141, 167, 189, 209
Hexachlorocyclohexane (HCH): β-HCH	Hexachlorocyclohexane (HCH): α-HCH	α-Endosulfan	Hexachlorocyclohexane (HCH): α-HCH
Cyclodiene-pesticides: Heptachlor, oxy-chlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor DDT-derivatives: *o,p′*-DDE, *o,p′*-DDT Hexachlorobenzene (HCB)		Hexachlorobenzene (HCB)	

significantly correlated with precipitation rate. Surprisingly, only three contaminants expressed a significant correlation to wind velocity changes during the sampling period. In addition, the level distribution of 9 contaminants (incl. 8 PCBs and α-HCH) were significantly correlated to humidity in air at the sampling site (*e.g.*, fog occurrence at Bjørnøya).

The concentration pattern of volatile low and medium chlorinated PCBs, cyclodiene pesticides and HCB in the Bjørnøya atmosphere seems mainly related to changes in ambient temperature and wind speed. Atmospheric levels of high chlorinated, less-volatile molecules like high chlorinated PCBs (octa- and nona-chloro congeners) and α-HCH are mainly associated with precipitation rate and changes in humidity over the island (Table 3).

Based upon this first statistical evaluation, indications were found that the influence of wind speed, humidity and precipitations plays an important role in the selective up-take and distribution processes of POPs in the local ecosystem on Bjørnøya.

At the first glance, indications for negative correlation between HCB levels and ambient temperature were found (Fig. 3). However, it is more likely that in this specific case average temperature should only be seen as an indicator parameter for seasonality in the Arctic environment at Bjørnøya (low temperature in Winter *versus* high temperature in summer) and that the HCB concentrations in the atmosphere above Bjørnøya are more influenced by light conditions and radiation intensity (*e.g.*, low HCB levels in summer due to effective photochemical degradation) throughout the Arctic year than temperature changes. The relatively high volatility of HCB would rather suggest high values in summer due to an increase in evaporation from the open sea surfaces. However, this increase in evaporation is obviously masked by the even stronger influence of photochemical degradation. This can also be assumed for low chlorinated PCBs and cyclodiene pesticides. Unfortunately no meteorological parameter was available for indication of radiation changes throughout the sampling period.

The concentration distribution for all POPs (annual arithmetic mean, minimum and maximum values) is presented in Table 2a and b. For all weekly data, please consult the ESI.†

The highest concentrations for a single compound in Bjørnøya air were found for HCB (25–35 pg m^{-3}). However, the sum of 33 PCB congeners was found to be in the same concentration range (annual means between 15 and 30 pg m^{-3}). The α-isomer of the three HCHs measured was the predominant compound for this sub-group of organohalogen pesticides in Bjørnøya air (11–17 pg m^{-3}). For all other contaminants analysed (DDT-derivatives, α-endosulfan, chlorinated cyclodiene pesticides) the concentrations values were in general relatively low and ranged from 0.1 to 3 pg m^{-3} (see Table 2). Thus, HCB, PCBs and HCHs usually represented 95–97% of the total POP burden identified in Bjørnøya air during the entire 134 weeks sampling period.

The PCB patterns were usually dominated by low-chlorinated congeners (tri- and tetra-chloro-PCB 18, 28, 31) which constituted more than 60% of the total PCB burden. Higher chlorinated PCBs contribute between 20–40% of the total PCB concentration. This pattern is consistent with previous findings from the Zeppelin mountain atmospheric research station and other atmospheric monitoring facilities.[1,11]

This pattern points towards a predominantly atmospheric transport, since the lower chlorinated compounds are more volatile than the higher chlorinated congeners.

During the first 21 weeks of the sampling period (week 51/1999–week 20/2000) several subsequent atmospheric transport episodes, with elevated levels of PCB, HCB, α-endosulfan, chlordanes and DDT, were found with no elevated levels for HCH isomers (sum POP distribution, see Fig. 4). The unusual distribution patterns point toward possible rapid atmospheric long-range transport episodes. This is confirmed by the FLEXPART results, which show frequent transport

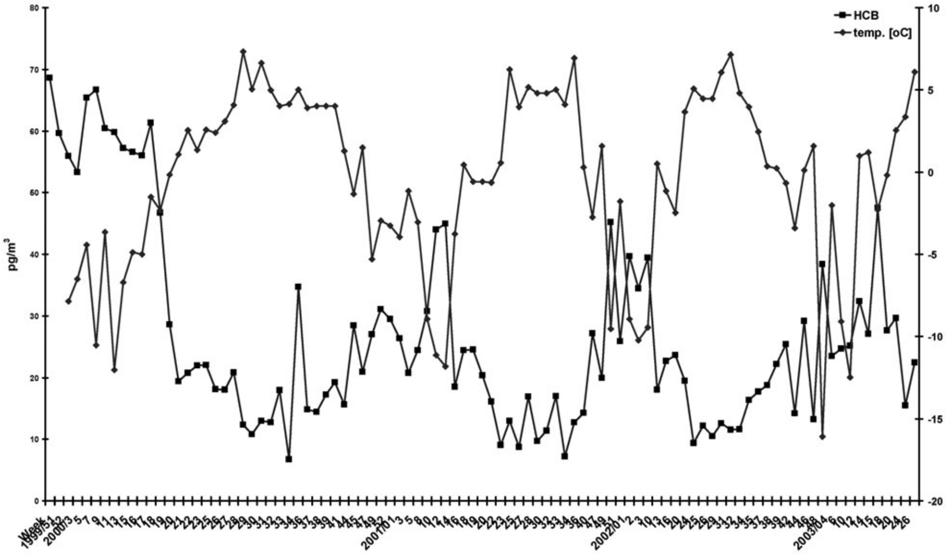

Fig. 3 Comparison of temperature distribution and HCB concentration in year-around ambient air samples from Bjørnøya (Bear island, Arctic Norway).

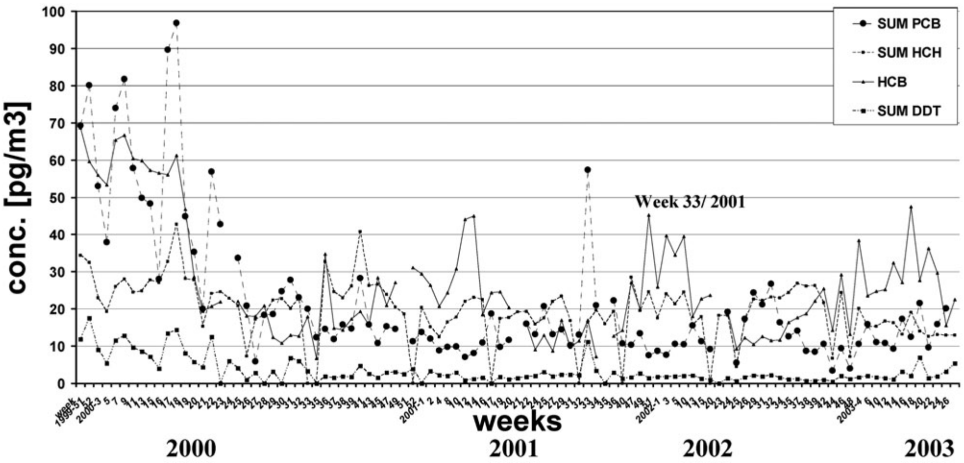

Fig. 4 Concentration distribution of sum 33 PCB congeners, 6 DDT derivatives, 3 HCH isomers and HCB in atmospheric samples from Bjørnøya (week 51/1999–week 28/2003). All congener specific weekly concentrations can be found in the ESI.†

episodes from eastern Europe/central Russian industrial areas during this time period. A representative map of the column-integrated PES for this period is presented in Fig. 5. An additional single atmospheric transport period was identified where elevated sum PCB levels were detected in Bjørnøya air (week 33, 2001: 12–18.08.2001). This transport episode is also reflected in the concentration data for PCB and DDT-derivatives (Fig. 4). FLEXPART calculations indicate that the emission sources are located in eastern Europe (Fig. 6).

For γ-HCH only, unusually high concentrations were found for week 41 in 2000. FLEXPART indicates an air mass transport episode from agricultural areas in central and eastern Europe and, thus, points towards lindane emissions from agricultural applications (Fig. 7). Indications for several other possible atmospheric transport episodes are found in the data material. However, identification and evaluation of potential atmospheric transport episodes will be the major focus of the subsequent discussion.

Discussions

Compared to the POP concentration distribution patterns found for the atmosphere at the Zeppelin mountain research station (Ny-Ålesund, Svalbard),[9] a significantly higher number of potential atmospheric long-range transport episodes was found for the Bjørnøya data set. These differences are obviously caused by different meteorological conditions (*e.g.*, influence of the polar and arctic front systems) and distance to potential source regions (including the Norwegian mainland). In addition, the Bjørnøya sampling site is located

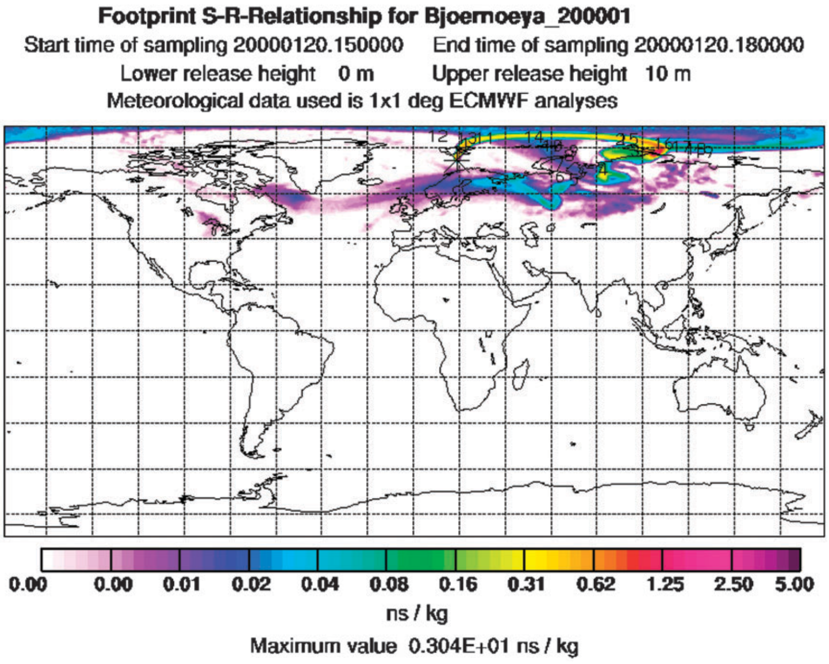

Fig. 5 Typical footprint potential emission sensitivity (PES) distribution derived from a 20 day FLEXPART backward simulation for the first part of the sampling period (20.01.2000).

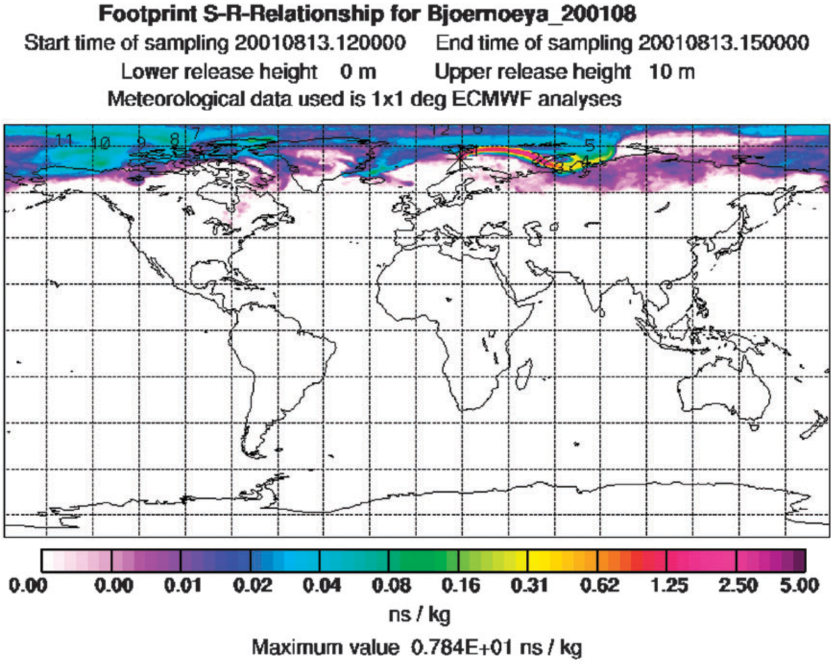

Fig. 6 The same as Fig. 5 except for a single transport episode for PCB and DDT-derivatives during week 33/2001 (13.08.2001).

near sea level and, thus, is directly exposed to re-evaporation of contaminants from the sea surface and the selective up-take on the sampling filters through aerosols (in particular sea salt). As a first measure for the identification of potential contamination sources, representative compounds for typical contaminant source can be plotted against each other.[10] In our case, γ-HCH (99% pure γ-HCH = lindane®), as a typical pesticide used in agricultural applications, is plotted against HCB, as representative for large scale industrial emissions (Fig. 8). The scatter plot reveals that during the period week 51/1999–21/2000 air masses with constantly elevated HCB (industrial sources) were arriving at Bjørnøya, with influences from agricultural contamination (elevated γ-HCH during week 51/1999, 52/1999 as well as 17/2000 and 18/2000) for a few samples. Concentrations of α-HCH (constitutes 60% of the technical HCH mixture) were not elevated during these respective time periods (see ESI†), indicating fresh γ-HCH emission only.

However, signals for predominant contamination from agricultural sources were confirmed for week 41/2000 and

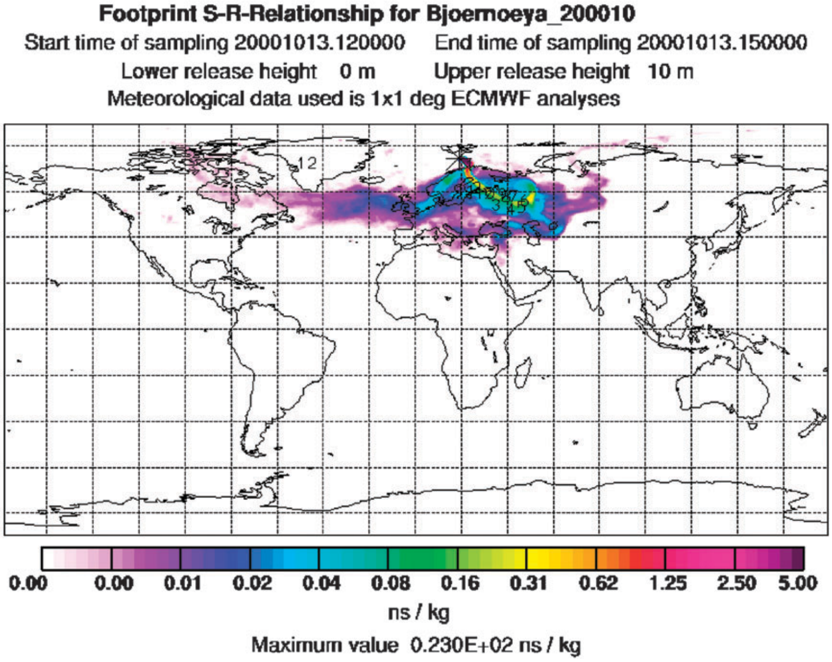

Fig. 7 The same as Fig. 5 except for a single transport episode for γ-HCH during week 41/2000 (13.10.2000).

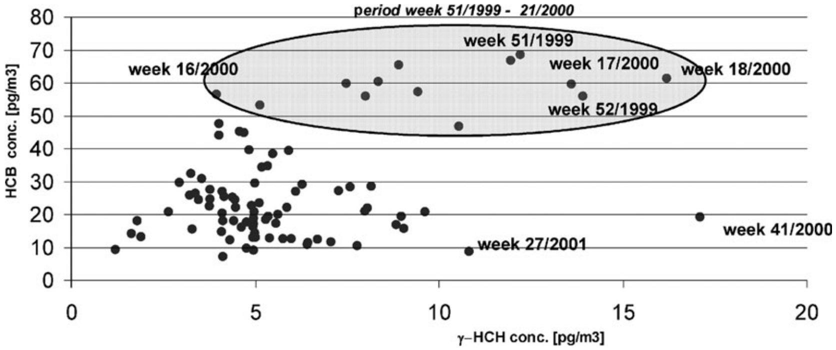

Fig. 8 Source identification in atmospheric long-range transport episodes using concentrations of typical chemicals representing potential emission sources. The concentrations of HCB (industrial emissions) are plotted against the levels of γ-HCH (agricultural emission sources, still in use in eastern European countries, Asia and central American nations).

27/2001 (Fig. 7). For HCH isomers, the concentration ratio of the predominant compounds, α-HCH and γ-HCH, can provide valuable information for the discrimination of primary and secondary sources for the HCH in air masses. The use of technical HCH (60% α-HCH) was banned in Europe and North America in the early 1980s whereas Lindane® (content >99% γ-HCH) is still a currently used pesticide in European countries and developing countries in Asia and Africa. The concentration ratio α-/γ-HCH in Bjørnøya air indicates fresh input from agricultural sources (unusually low ratio <2) or re-emission from secondary sources (contaminated sediment, sea and soil surface; ratio >4). The α-/γ-HCH concentration ratio confirms that for the identified atmospheric transport event (week 41/2000 and 27/2001) primary sources from agricultural application areas are the major HCH contribution (low α-/γ-HCH ratios: week 41/2000 = 1.4 and week 27/2001 = 1.0, respectively). In contrast to these findings, for week 16/2000 and 36/2000 secondary sources with elevated α-HCH were found to be the major contribution to the HCH burden in Bjørnøya air (week 16/2000 = 5.7, week 36/2000 = 5.0) during these sampling periods (Fig. 8).

The previously suggest PCB transport episode for week 33/2001 (Fig. 3 and 5) was neither reflected in the γ-HCH/HCB plot (Fig. 8) nor the α-/γ-HCH concentration ratio (Fig. 9). Thus, during 33/2001 only PCB and DDT emission sources contributed to the contamination of the air masses arriving at Bjørnøya during that sampling period whereas no elevated HCH and HCB levels were found.

Similar as described for PCBs, HCB and HCH-isomers, also for the cyclodiene pesticides, DDT derivatives and α-endosulfan elevated levels were found for the sampling period week 51/1999–week 21/2000 confirming the unusual long term stable air mass transport to the island during that time period. However, the concentration ranges were considerably lower than described for the predominating PCB congeners.

A first standard statistical correlation calculation (Pearson's correlation test) showed that only for a selected number of POP contaminants the concentrations values were influenced by the local weather situation (Table 3). Although precipitation type, as well as ambient temperature and wind situation on the sampling location influence the effectiveness of the deposition rates for most of these long-range transported chemicals, the meteorological and physical–chemical properties of the air masses (*e.g.*, velocity of the transport episode, aerosol content, temperature conditions *etc.*) are obviously of significant importance for the final contamination status.

Therefore a comprehensive characterisation of the air masses and the accompanying meteorological situation during the transport episode is of crucial importance when charactering contaminant profiles during atmospheric long-range transport, not only for the Bjørnøya data set. As shown in this study, a multi-disciplinary approach using quality controlled chemical analysis, statistically based data interpretation, meteorological modelling and classical meteorological information as interacting tools is mandatory for the comprehensive scientific evaluation of POP

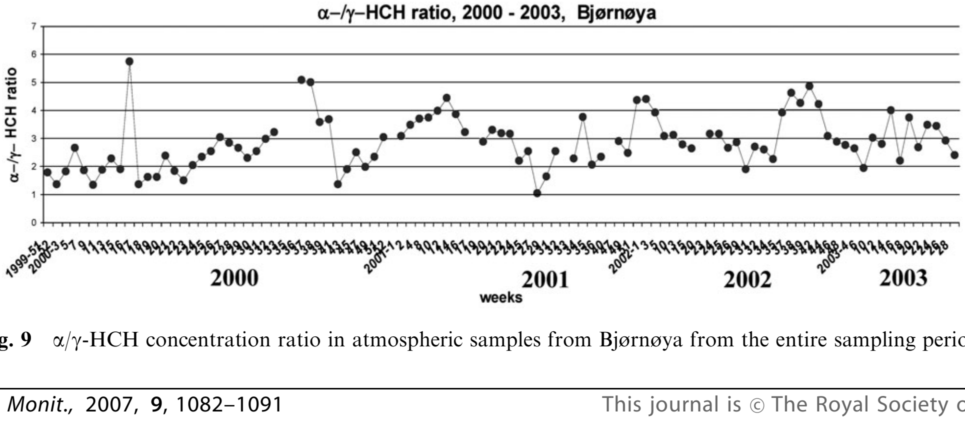

Fig. 9 α/γ-HCH concentration ratio in atmospheric samples from Bjørnøya from the entire sampling period.

distribution and fate during atmospheric transport into polar regions.

Conclusions

The first medium term study on atmospheric transport and fate of selected POPs in the Bjørnøya atmosphere showed that, also for this site, atmospheric transport is a significant source for persistent contaminants in the local ecosystem. The POP patterns found in the atmospheric samples reflect the complex interaction of emission sources, air mass properties, transport velocity and meteorological conditions during the transport events. In addition, transformation and degradation processes (*e.g.*, photochemistry) may also influence the POP concentration pattern found at the deposition site/sampling location. However, for rapid transport episodes (<10 days) the influence of degradation process is probably negligible. The first statistical evaluation using correlation calculations (Pearson's correlation test) showed, that only for selected POPs the local meteorological conditions appears to be significantly important for the concentrations found in the air masses over Bjørnøya. However, the local meteorology will have an important influence on deposition rates from the atmosphere to the ground. The concentration in the air masses, on the other hand, is mainly dependent on the air mass characteristics (*e.g.*, temperature/light conditions during transport, aerosol content, humidify, transport velocity *etc.*). Therefore, for the evaluation of atmospheric long-range transport, the air mass characterisation in combination with atmospheric chemistry methods is of major importance for both source characterisation, and assessment of the transport pathway.

Nevertheless, the local weather situation is an important scientific parameter, when the up-take efficiency and local distribution pathway of persistent pollutants is investigated.

Acknowledgements

The project has been jointly funded by the Research Council of Norway (Project Nos.: 135064/720, 135632/720) and the Norwegian State Pollution Control Authorities. In addition, the Norwegian Ministry of Environment funded part of the project through the Ecotoxicology Programme at the Polar Environmental Centre (Tromsø, Norway). The authors also wish to thank the Norwegian Coast Guard and the Norwegian Polar Institute (R/V Lance) for safe transport to and from Bjørnøya, as well as employees at Bjørnøya meteorological station for all their practical assistance and for accommodation.

We appreciate the commitment of the laboratory personnel at NILU and in particular Britt Teie, Gerd Staff Knudsen, Hans Gundersen and Ellen Katrin Enge who had the responsibility for sample preparation and quantification.

References

1 C. A. DeWit, A. T. Fisk, K. E. Hobbs, D. C. G. Muir, G. W. Gabrielsen, R. Kallenborn, M. M. Krahn, R. Norstrom and J. U. Skaare, *AMAP Assessment 2002: Persistent organic pollutants in the Arctic*, AMAP Secretariat, Oslo, Norway, 2004, p. 309.
2 R. W. Macdonald and J. M. Bewers, *ICES J. Mar. Sci.*, 1996, **53**, 537.
3 R. W. Macdonald, D. Mackay, Y. F. Li and B. Hickie, *Hum. Ecol. Risk Assess.*, 2003, **9**, 643.
4 T. Skotvold, E. Wartena, G. N. Christensen, E. Fjeld and M. Schlabach, *Statlig program for forurensningsovervakning, Norwegian Pollution Control Authority report 764/99. TA 1642-1999. Akvaplan-niva report 510.1443.1.*, 1999, p. 47.
5 R. Kallenborn, A. Evenset, D. Herzke, G. Christensen and M. Schlabach, *Organohalogen Compd.*, 2001, **52**, 387.
6 D. Herzke, G. W. Gabrielsen, A. Evenset and I. C. Burkow, *Environ. Pollut.*, 2003, **121**, 293.
7 M. Oehme, J. E. Haugen and M. Schlabach, *Sci. Total Environ.*, 1995, **161**, 139.
8 A. Evenset, G. N. Christensen, T. Skotvold, E. Fjeld, M. Schlabach, E. Wartena and D. Gregor, *Sci. Total Environ.*, 2004, **318**, 125.
9 T. Berg, R. Kallenborn and S. Manø, *Arct. Antarct. Alp. Res.*, 2004, **36**(3), 283.
10 R. Kallenborn, M. Oehme, D. D. Wynn-Williams, M. Schlabach and J. Harris, *Sci. Total Environ.*, 1998, **220**(2–3), 167.
11 A. Evenset, G. N. Christensen and R. Kallenborn, *Environ. Pollut.*, 2005, **136**, 419.
12 J. O. Bustnes, K. E. Erikstad, V. Bakken, F. Mehlum and J. U. Skaare, *Ecotoxicology*, 2000, **9**(3), 179–186.
13 J. Verreault, R. J. Letcher, D. c. G. Muir, S. G. Ch, W. A. Gebbink and G. W. Gabrielsen, *Environ. Toxicol. Chem.*, 2004, **24**(10), 2486–2499.
14 A. Stohl, C. Forster, S. Eckhardt, N. Spichtinger, H. Huntrieser, J. Heland, H. Schlager, S. Wilhelm, F. Arnold and O. Cooper, *J. Geophys. Res., [Atmos.]*, 2003, **108**, 4370.
15 A. Stohl, C. Forster, A. Frank, P. Seibert and G. Wotawa, *Atmos. Chem. Phys.*, 2005, **5**, 2461–2474.