STATISTICAL EVALUATION, METEORLOGICAL MODELLING AND MODERN TRACE ANALYSIS AS INTEGRATED TOOL FOR THE SOURCE ELUCIDATION OF ATMOSPHERIC LONG-RANGE TRANSPORT TO BJØRNØYA (BEAR ISLAND)

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Introduction

The recent published assessment report on persistent organic pollutants (POPs) in the Arctic confirmed the presence of POPs in practically all environmental compartment of the Arctic[1]. Although banned for decades, many legacy POPs are still found in considerable concentrations throughout the Arctic. Long-range transport through the atmosphere or via ocean currents is identified as major source for POPs in the Arctic. Bjørnøya is an Arctic islands midway between the North Norwegian mainland and the Svalbard archipelago (figure 1). Already in the 1990ties, elevated levels of selected POPs in Bjørnøya (Bear Island) was measured in sediments and biota from a lake (Lake Ellasjøen) on Bjørnøya[2]. 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.

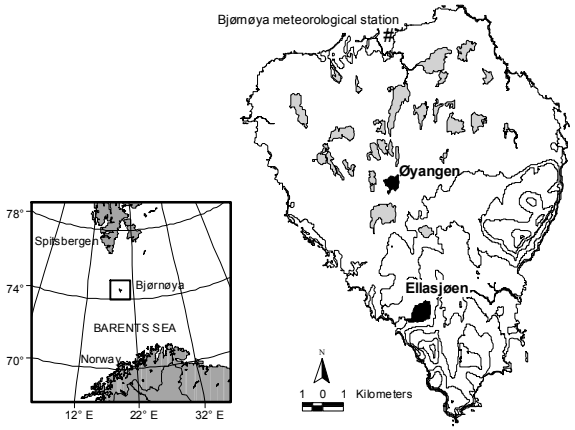

Figure 1: Location of the sampling site Bjørnøya (Bear Island)

An atmospheric monitoring program for POPs was initiated at Bjørnøya. Since no local contamination sources exist on the island, it is assumed that long-range transport of pollutants via atmosphere and/or ocean currents must be the major source for the presence of POPs.

Material and methods

A custom made high volume air sampler was installed in a hut close to the meteorological observatory on the northern shore of the island. One high-volume air sample was collected by pumping air through a glass-fiber filter (GFF, particulate phase) and polyurethane foam plugs (PUF: gaseous phase). 72 – 96 h samples were collected with a continuous flow rate of 20 m^3/h (average), resulting in sample volumes between 1800 – 3000 m^3. Air samples were collected during the 31-month sampling period, from December 1999 (week 51) until July 2003 (week 28). Due to economic reasons, 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. All samples were stored frozen (-18 °C) unil transport to the laboratory of the Norwegian Institute for Air Research (NILU), where the analysis were performed. Extraction, clean-up procedures and quantification methods used at NILU are described in earlier publications [3,4]. Hexachlorobenzene (HCB), 33 polychlorinated biphenyl congeners (PCB), α–, β–, γ–hexachlorocyclohexane isomers (HCH), α-endosulfan, as well as 6 dichlorodiphenyltrichloroethane-derivatives (DDT) were analysed and quantified. Particulate phase (GFF) and gaseous phase (PUF) were combined before extracting and quantified using Soxhlet extraction and capillary gas chromatography (Agilent 6890, Palo Alto, Cal., 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 form (VWR, Oslo, Norway).
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). As new advanced modelling technique for the interpretation of transport processes, a new quantitative dispersion model was applied which, also include full turbulence and convection parameterizations (FLEXPART, NILU, Norway).

Results and discussions
The POP sum concentration distribution in the Bjørnøya air samples are summarised as arithmetic mean, minimum and maximum values in table 2 for the respective sampling year.

Table 2: Arithmetic mean concentrations for POP groups analysed in Bjørnøya air samples in the period 2000 – 2003.

	2000			2001			2002			2003 (until week 28)		
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	28.55
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
SUM PCB	5.89	96.78	35.80	7.05	57.42	14.57	3.37	26.73	12.53	9.33	65.68	29.33

Na = not analysed

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). The α– isomer of the three HCHs measured were the predominant compound for this sub-group of organohalogen contaminants 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 between 0.1 and 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.
In addition to contaminant concentrations, basic meteorological data (ambient air temperature, wind speed, precipitation rates and humidity) were provided for the entire sampling period from the Norwegian Meteorological Institute (met.no, Oslo). The weather situation on Bjørnøya reflects a typical marine Arctic climate with rel. high annual humidity (80-99%), low annual precipitation rates (around a total of 370 mm annually) and expressed seasonal patterns for wind velocity and ambient temperature. A Pearson correlation test (WinSTAT® for Microsoft Excel®) was performed for all 50 organohalogen target contaminants with regard to four meteorological variables, namely ambient temperature, precipitation change, wind speed and humidity in the atmosphere. 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 significantly correlated with precipitation changes. 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 changes in humidity in air at the sampling site (eg., fog occurrence at Bjørnøya).
A typical back trajectory projection for the sampling periods is presented in figure 2. The subsequent high resolution atmospheric backward transport analysis (FLEXPART) confirm and indicate that mainly stable air mass transport from Eastern European and Scandinavian Source regions contribute significantly to the transport events and the elevated PCB and OCP contamination identified.

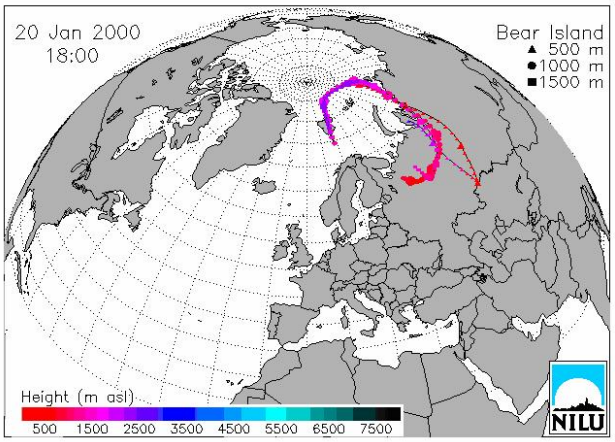

Figure 2: Typical 10 days 3-dimensional back trajectory (FLEXPART) for air masses arriving at Bjørnøya during January 2000.

Additional Indications for emission sources from Western Europe and Scandinavia are confirmed through trajectory calculations.
Compared to the POP concentration distribution patterns found for the atmosphere at the Zeppelin mountain research station (Ny-Ålesund, Svalbard)[5], located about 500 km North-West of Bjørnøya, a 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 Front systems) and distance to potential source regions (including the Norwegian mainland).
In order to reveal different contamination sources, 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 (figure 3). The concentration 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). Influences from agricultural emission sources were found for 4 -5 samples during that sampling period

Conclusion
A first standard statistical correlation calculation (Pearsons correlation test) showed, that only for a selected number of POP contaminants found in Bjørnøya air the concentrations values are influenced by the local weather situation. 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 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. As shown in

the here presented 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 distribution and fate during atmospheric transport into polar regions.

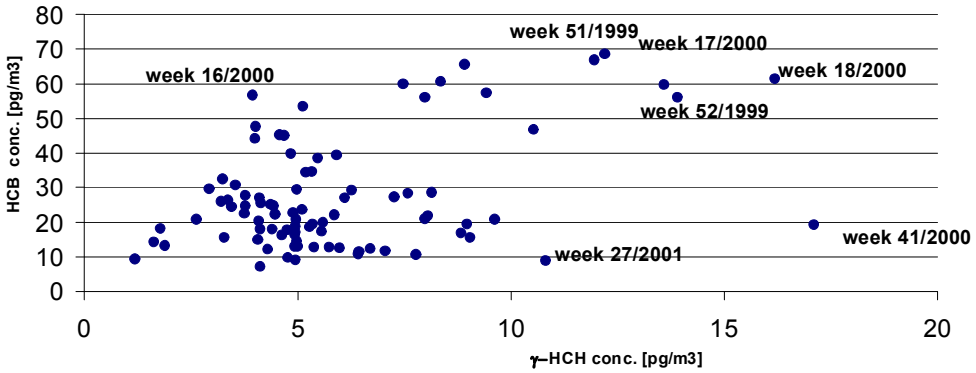

Figure 3: Source identification for atmospheric long-range transport episodes using typical concentration patterns of contaminants The concentrations of HCB (industrial emissions) are plotted against the levels of γ-HCH (agricultural emission sources).

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