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Twenty years of monitoring of persistent organic pollutants in Greenland biota. A review

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ABSTRACT

The Arctic Monitoring and Assessment Programme (AMAP) is a working group under the Arctic Council with the aim to monitor and assess temporal trends of contaminants in Arctic ecosystems. The Greenland AMAP Core programme was established to contribute to this effort. The Core programme includes three main components; routine monitoring, retrospective studies and new POP screening studies. The programme is based on an adaptive approach, which has led to changes throughout the years. An overview of the temporal trends during the last two to three decades is presently given together with selected examples of different characteristic trends of POPs. The results show how tissue banked samples and retrospective studies has helped in establishing time-series of compounds of emerging concern. Lastly, the statistical power of the Greenlandic time-series is discussed. The lesson learned is that trend monitoring improves with samples over time, and only pays off after decades of data are generated.

1. Introduction

Monitoring of persistent organic pollutants (POPs) in the Arctic has a number of advantages and the Greenland region is ideal to study long-range contaminant transport, because of the limited local use in the Arctic, bioaccumulation in long food chains and in some cases adverse effects. These are criteria that serve to define what is meant by "POPs" identified and listed under the Stockholm Convention on POPs (De Wit et al., 2004). Monitoring of contaminants in Greenland marine biota was initiated in 1994; a few years after the establishment of the Arctic Monitoring and Assessment programme (AMAP). AMAP is a working group under the Arctic Council with the task to implement the Arctic Environmental Protection Strategy (AEPS) and to support international processes that work to reduce the global threats from contaminants and climate change. Besides UNEP's Stockholm Convention on POPs, these include, for example, the UN Framework Convention on Climate Change, the Minamata Convention on Mercury, and the Convention on Long-Range Transboundary Air Pollution (LRTAP) of the United Nation's Economic Commission for Europe (UN ECE). The Stockholm Convention on POPs was adopted on 22 May 2001 and entered into force on 17 May 2004. Initially, 12 POPs ("dirty dozen") were listed with the intended goal of minimizing risk through measures to reduce and/or eliminate their emissions or discharges. In 2009 nine extra POPs were added to the list, which was further extended in 2011 and in 2013 with the addition of endosulfan and hexabromocyclododecane (HBCDD), respectively. The POPs that are listed are categorised as pesticides, industrial chemicals and/or by-products. Some of the POPs fit into more than one category e.g. hexachlorobenzene (HCB), which was used as a pesticide but also is a by-product in the manufacture of certain industrial chemicals.

POP monitoring in Greenland is organised via the Greenland AMAP Core programme, with the primary objective being to study temporal trends. Temporal trends are useful in showing whether POPs accumulate in Arctic species, which might make them candidates for control on grounds of long-range transport and bioaccumulation, and in assessing the effectiveness of international agreements. The AMAP Core programme is based on ongoing biannual sample collection except for polar bears (*Ursus maritimus*) from East Greenland which are sampled annually. All samples are stored in a tissue bank. Several persistent organochlorine compounds have been included from the start, while others have been

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added later. The brominated flame retardant known as polybrominated diphenyl ethers (PBDEs) as well as per-/poly-fluoroalkyl substances (PFASs), for example, were included in the programme 10–15 years ago as a consequence of retrospective studies performed on samples from the tissue bank (Bossi et al., 2005; Rigét et al., 2006; Dietz et al., 2008; Vorkamp et al., 2008).

In recent years, screening studies of compounds of emerging concern have been an integrated part of the AMAP Core programme. The selection of new compounds for a screening study can be based on the scientific literature (Vorkamp and Rigét, 2014). There can also be interest from policy makers in specific compounds for which Arctic data is considered useful, for example, in the context of an assessment of their long-range transport and bioaccumulation potential.

Statistical power is an important consideration in relation to temporal trend monitoring (Fryer and Nicholson, 1993; Bignert et al., 2004). It can be interpreted as the probability to discover a true change in contaminant levels over time. If, for example, the power of the time-series to detect a certain change is rather low, it will take a long time to detect a statistically significant change with some confidence and thereby prolong the time period before answers can be given on the effectiveness of regulations or the trends of currently unregulated compounds. Monitoring programmes should aim to increase the statistical power of the time-series through the sample collection, chemical analysis and statistical analysis.

The aim of this review is to present an overview of the results and the experiences obtained through the monitoring of POPs in Greenland biota. Examples will be given for legacy POPs and those regulated more recently as well as for screening results of currently unregulated compounds. Emphasis will also be placed on questions of statistical power.

2. The monitoring programme of POPs in biota from Greenland

2.1. Samples

Samples included in the Greenland AMAP Core monitoring programme of POPs are landlocked Arctic char (*Salvelinus alpinus*) from a small lake at Isortoq, Southwest Greenland, ringed seals (*Pusa hispida*) from Qeqertarsuaq, West Greenland and from Ittoqqortoormiit, East Greenland, black guillemot eggs (*Cepphus grylle*) and glaucous gulls (*Larus hyperboreus*) from East Greenland (Fig. 1). Polar bears from Ittoqqortoormiit, East Greenland and from Avanersuaq, Northwest Greenland were included in the regular programme in 2006, but the latter was withdrawn a few years later because of logistical challenges. Shorthorn sculpin (*Myoxocephalus scorpius)* from Qeqertarsuaq, West Greenland and from Ittoqqortoormiit were included in the programme from the mid-1990s to 2004 but was withdrawn from the programme because of rather low levels of POPs. Samples have mainly been collected by local hunters (Rigét et al., 2010a).

When the sampling programme was initiated in 1994 it covered more locations in Greenland than it does now. The sampling frequency was originally designed to be every five years. However, after the second sampling in 1999 it became obvious that the statistical power to detect trends was rather poor and that more frequent sampling would be required to be able to statistically detect trends within a reasonable period of time (Riget et al., 2000). Since 2004 the sampling frequency has been every second year but that also implied that the number of locations had to be reduced to balance the costs. However, polar bears (Ittoqqortoormiit, East Greenland) are sampled every year because of the relatively low number, which is possible to sample in one year and the relatively high variability from year to year. The presented time-series include data derived from related studies and therefore the number of years with data varies between species and areas.

The sampling is standardized as much as possible with respect to time of the year, age and sex (in case of glaucous gulls) and a similar length range for Arctic char. However, for ringed seals and polar bears standardized sampling is not fully consistent as ages were first determined at a later stage. POPs are known to occur at lower levels in juvenile marine mammals than in adults, and they are lower in adult females than in adult males (e.g. Bernhoft et al., 1997; Krahn et al., 1997). On reason for this is that female marine mammals transfer some of their POP body burden to their offspring (e.g. Greig et al., 2007; Bytingsvik et al., 2012). Therefore, temporal trends are presently evaluated separately for juveniles, and adult females and adult males for ringed seals and polar bears. All samples were stored in a tissue bank at −20 °C, which allows for retrospective time-series (e.g. Riget et al., 2006) and to screen for new contaminants of emerging concern (e.g. Vorkamp et al., 2015a).

2.2. Chemical analyses and determinations of supporting parameters

Different laboratories have been involved in the POPs analyses during the programme. The laboratories at the Department of Environmental Science, Aarhus University, Denmark (ENVS) have performed the majority of the chemical analyses. The Organic Contaminants Research Laboratory (OCRL, Environment Canada) at Carleton University, Ottawa, Canada has performed the analyses of legacy POPs and PBDEs in polar bear samples. A minor portion (i.e. arctic char sampled in 1999, shorthorn sculpin sampled in 1999 and 2000, ringed seal sampled in 1999) of the samples were analysed at the National Laboratory for Environmental Testing (NLET) of Environment Canada, and in 1994 arctic char samples were analysed by DLO-Netherlands Institute for Fisheries Research (RIVO-DLO). The time-series of arctic char, shorthorn sculpin and ringed seal therefore include data generated by more than one laboratory. Based on results from inter-comparison studies, Asmund et al. (2004) compared the performance of these laboratories and found a proportional error in the range of 6–24% dependent on the type of substance and laboratory with the tendency of a larger proportional error being from NLET rather than from ENVS. However, we considered the influence from different laboratories to be minor on these time-series as the few data points derived by NLET are surrounded by data derived by ENVIS. In case of the ringed seals $\sum_{10}$-PCB and $\sum$DDT time-series (12 time-series) no changes in the statistical evaluations based on a 5% significance level were found by omitting the NLET data from the analyses.

Detailed descriptions of the chemical analyses have been published previously, including analyses of legacy POPs in polar bears (Dietz et al., 2013a; Letcher et al., 2015; McKinney et al., 2011) and the remaining animals (Vorkamp et al., 2004a, 2011; Rigét et al., 2013a). Descriptions of chemical analyses of PBDEs and HBCDD of ringed seals and glaucous gull are found in Vorkamp et al. (2004b, 2011, 2012) and elsewhere for polar bears (Dietz et al., 2013b; Letcher et al., 2015; McKinney et al., 2011). Chemical analyses of PFASs are described in detail in Rigét et al. (2013b).

The quality assurance and quality control (QA/QC) measures of the chemical analyses in the programme were described by Asmund et al. (2004). The ENVS laboratory performing the majority of the chemical analyses has been accredited according to ISO 17025 for the analyses of polychlorinated biphenyls (PCBs) in biota since 2005 and for PBDEs in biota since 2008. The laboratory has participated in the relevant QUASIMEME proficiency testing schemes since 2001. POP and PBDE analysis in polar bear fat tissues