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Assessment of the spatial and temporal distribution of persistent organic pollutants (POPs) in the Nordic atmosphere

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HIGHLIGHTS

- The POP levels were generally higher in the south, closer to the original source areas, compared to the north.
- Elevated concentration levels of low-chlorinated PCBs, chlordanes and α-HCH were detected in the north.
- Most of the legacy POPs showed statistically significant decreasing trends varying from 2 to 6% per year.
- The projections suggest that the most long-lived compounds will persist in the atmospheric cycle beyond 2030.

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ABSTRACT

Long-term atmospheric monitoring data (1994–2011) of persistent organic pollutants (POPs) were assembled from a rural site in southern Sweden, Råö, and a remote, sub-Arctic site in Finland, Pallas. The concentration levels, congener profiles, seasonal and temporal trends, and projections were evaluated in order to assess the status of POPs in the Scandinavian atmosphere. Our data include atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), altogether comprising a selection of 27 different compounds.

The atmospheric POP levels were generally higher in the south, closer to the sources (primary emissions) of the pollutants. The levels of low-chlorinated PCBs and chlordanes were equal at the two sites, and one of the studied POPs, α-HCH, showed higher levels in the north than in the south.

Declining temporal trends in the atmospheric concentrations for the legacy POPs — PCBs (2–4% per year), HCHs (6–7% per year), chlordanes (3–4% per year) and DTTs (2–5% per year) — were identified both along Sweden's west coast and in the sub-Arctic area of northern Finland. Most of PAHs did not show any significant long-term trends.

The future projections for POP concentrations suggest that in Scandinavia, low-chlorinated PCBs and p,p′-DDE will remain in the atmospheric compartment the longest (beyond 2030). HCH's and PCB180 will be depleted from the Nordic atmosphere first, before 2020, whereas chlordanes and rest of the PCBs will be depleted between the years 2020 and 2025. PCBs tend to deplete sooner and chlordanes later from the sub-Arctic compared to the south of Sweden.

This study demonstrates that the international bans on legacy POPs have successfully reduced the concentrations of these particular substances in the Nordic atmosphere. However, the most long-lived compounds may continue in the atmospheric cycle for another couple of decades.

1. Introduction

Persistent organic pollutants, known as POPs, have a great potential for atmospheric long-range transport. Deposition from the atmosphere is an important pathway for these contaminants to environments both far from and close to their source areas, where

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they may have adverse effects both on ecosystems and humans (UNEP, 2014). That the atmosphere is an important pathway for POPs into the Nordic environment as well as the Arctic areas has been clearly demonstrated both via measurement activities and model exercises.

Many POPs are semi-volatile, and as such, they can be transported in the atmosphere either in the gas or particulate phases. Atmospheric transport, removal and degradation processes (e.g. precipitation scavenging, dry deposition, photolysis and atmospheric oxidation) act differently on gas and particle-bound substances, thereby affecting their potential for long-range transport (e.g. Bidleman, 1988; Lammel et al., 2009). The properties of atmospheric particles may also affect the gas/particle distribution of POPs, e.g. the organic matter contents of aerosols is an important factor affecting the partitioning between the two phases (e.g. Lohman and Lammel, 2004).

Due to their semi-volatility, several POPs are also characterised by an exchange between the atmosphere and environmental surfaces in a way that has been described as the 'grasshopper effect' (Wania and Mackay, 1996). Gas/surface partitioning is a temperature-driven process. Varying temperatures thus enable repeated surface-air exchanges, which can in turn lead to the migration of POPs by air from the warmer, mid-latitude, primary source areas to the cooler, high-latitude regions. During this 'global fractionation and condensation' process (e.g. Wania and Mackay, 1993, 1996; Lammel and Stemmler, 2012), POP mixtures become fractionated as more volatile substances undergo more frequent secondary releases and thus travel further.

Due to the lipophilic and bio-accumulative properties of POPs, they have a great affinity for organic material in soils and vegetation. Prior studies have demonstrated that global surface soils serve as an important reservoir for POPs (e.g. Meijer et al., 2003a; Ockenden et al., 2003; Dalla Valle et al., 2005; Cabrerizo et al., 2011). Thus remobilization of POPs is driven both by changes in temperature and soil organic matter (SOM) content (Cabrerizo et al., 2013).

Also, water surfaces are known to sequester atmospheric POPs by enhanced air–water diffusive fluxes driven by phytoplankton uptake and organic carbon settling fluxes (Berrojalbiz et al., 2011; Galbán-Malagón et al. 2012, 2013a, 2013b; Nizzetto et al. 2012).

Several of the substances included in the POP group have been used as industrial chemicals or as pesticides, but the majority of the direct production and use (primary emissions) are nowadays banned or have restricted use. However, as a result of their persistence they are still present in the environment and society and are emitted via various diffuse sources. Unintentional releases due to combustion (polycyclic aromatic hydrocarbons PAHs) and inappropriate waste management of decommissioned products (PCBs and organochlorine pesticides OCPs) still continue.

As emissions and atmospheric concentrations of the restricted POPs decline, reservoirs that have accumulated in oceans, on land and in snow/ice can become secondary sources of POPs released into the atmosphere (Bidleman et al., 1995; Stemmler and Lammel, 2009; Ma et al., 2011; Becker et al., 2012; Bidleman et al., 2015). The profile of POPs in the air at any given location is a combination of local and regional primary and secondary emissions and meteorological conditions coupled with transport from more distant regions, mainly through the air.

Long-term air monitoring is a powerful tool for following up on present levels and temporal trends and for assessing atmospheric transport processes and the pathways of POPs, e.g. to remote areas. Data from national monitoring programmes are reported and used within EMEP (Co-operative programme for monitoring and evaluating the long-range transmission of air pollutants in Europe) and AMAP (Arctic Monitoring Assessment Programme) to support international strategies and protocols. Long-term measurements are also used to identify source areas and to obtain information on developing follow-up policies to reduce emissions.

Here, the levels and time trends of POPs in the Nordic atmosphere are presented. Our data include selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), altogether comprising a selection of 27 different compounds that were measured between 1994 and 2011 at two Scandinavian air-quality monitoring stations, Råö and Pallas. Our methods include advanced time series analyses of this unique monitoring data, comparisons of seasonal variations and congener profiles as well as long-term trend analyses. Our goal is to define the status of POPs in the Scandinavian atmosphere with reference to the current distribution and possible sources.

2. Material and methods

2.1. Measurement sites

Råö (until 2002 Rörvik) (57.3937, 11.9142) is a background monitoring station for air pollutants within the EMEP network. It is located close to the shoreline along the west coast of southern Sweden, approximately 35 km south of Gothenburg (Fig. 1). The area has a mild coastal climate with an average monthly mean temperature in January-February of about 0 °C, in July 19 °C and a yearly mean of 9 °C (Gothenburg, SMHI Opendata, 2003–2012).

The Pallas area is located 170 km north of the Arctic Circle (Fig. 1). Pallas is actually an acronym for a collection of several research sites representing contrasting ecosystems. From the very beginning, in 1996, POP measurements have been carried out at the Matorova site (68.00, 24.23). Matorova lies at an elevation of 340 m a.s.l. and is on the top of a hill covered by coniferous forest (Lohila et al., 2015). The monthly mean temperature in January is about −14 °C, in July 14 °C and the yearly mean is −1 °C (Matorova/Kenttärova FMI, 2003–2012).

In terms of POPs, both sites serve as background sites, but Råö, which is located a thousand kilometres further south than Pallas, is more exposed to the potential on-going primary emissions from local and mid/low-latitude sources. Pallas is closer to the accumulated reservoirs of the Arctic ecosystems and potentially more influenced by the remobilised secondary emissions.

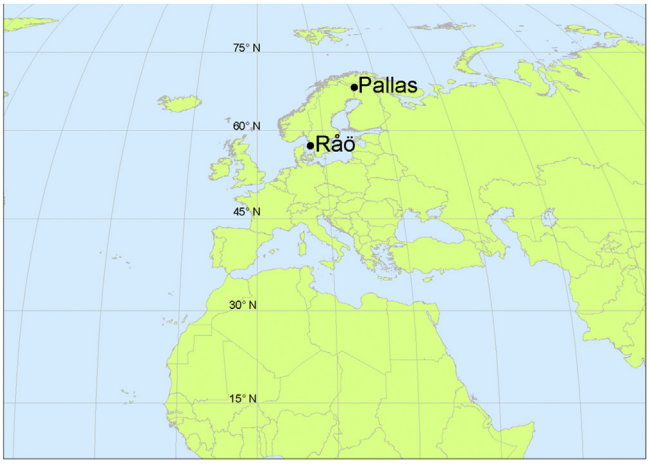

Fig. 1. Location of the sites.