1. EMEP MONITORING DATA FOR POPs IN AIR AND PRECIPITATION IN 2016

Persistent Organic Pollutants (POPs) were included in the EMEP’s monitoring program about two decades ago (1999). However, for a few compounds and stations, monitoring data extends back to the early 1990s [Tørseth et al., 2012]. These data provide vital information on observed spatial and temporal trends which, among other, are essential to help evaluate the modelling work carried out under the Convention. The chemical coordinating centre (CCC) supports EMEP with monitoring and analytical strategies and guidelines in order to gather quality data to assess regional scale air pollution across Europe. A long-term goal of CCC is to collect comparable monitoring data to facilitate consistent and comparable data sets for evaluation of spatial and temporal trends. To achieve this goal, CCC attempts to harmonize sampling methodologies and chemical analytical methodologies (EMEP/CCC 2014). Unlike many «classical» air pollutants, EMEP monitoring data on POPs still remain scarce and are only reported by some Parties, especially on other POPs than Polycyclic Aromatic Hydrocarbons (PAHs).

1.1. EMEP data and complementary monitoring activities

In 2016 there were in total 39 sites with POP measurements, from 17 Parties. Most of the sites only include PAHs, 12 sites from 7 Parties measure any of the other POPs, and these are mainly located in Northern- and Central Europe. The spatial distribution of the different sites and measurement program in air and precipitation (or deposition) is illustrated in Fig. 1.1.

![Fig. 1.1. Monitoring network of POPs in EMEP in 2016. Pesticides are either any DDTs or any of aldrin, dieldrin, endrin, heptachlor, oxychlorodane, heptachlorepoxide, mirex, endosulfan. POPs-F/Br means bromated or fluorinated POPs like BDEs, PFAS etc.](image)

In general terms, limited monitoring data mitigates opportunities for more comprehensive model evaluations within EMEP which, in turn, is required to fully evaluate if source-relationships for POPs are accurately predicted and understood. However, monitoring data on POPs in air and precipitation under EMEP are complemented by relevant research and national/regional monitoring activities
within Europe and beyond. Examples of such complementary monitoring activities using active air sampling are the UK TOMPs (Toxic Organic Micro Pollutants) Network performing long-term monitoring of POPs at six urban and rural sites in England and Scotland [Graf et al., 2016]. Over the last decade and beyond, active air monitoring have increasingly been complemented by various passive air sampling techniques [Shoebib et al., 2002]. Examples of passive air sampling studies at various scales include (i) the GAPS programme (Global Atmospheric Passive Sampling network), consisting of more than 50 sites world-wide [Pozo et al., 2006], (ii) different initiatives across or within parts of Europe [Jaward et al., 2004 and Pribylova et al., 2012], some of which often include a goal to complement the EMEP programme [Halse et al., 2011] and/or other national and international programmes and Conventions [Munoz-Arnanz et al. 2016 and Schuster et al., 2011]. While these passive air monitoring studies have gained valuable complementary information to the data within the EMEP programme, passive air sampling is still considered to be a semi-quantitative method. It is also incomplete in terms of total atmospheric occurrences for less volatile POPs as it is mainly designed to target the gaseous fraction in air. As a result, passive air sampling data are not fully comparable and consistent with the EMEP data based on active air sampling, although individual passive air sampling initiatives may at the same time offer data which are internally consistent.

In this year’s report, the main focus is on polychlorinated biphenyls and polycyclic aromatic hydrocarbons. These measurements will be discussed in some more detail to highlight the importance of long-term monitoring and issues which may merit further attention. For other POPs and more detailed information about the sites and the measurement methods, these are found in EMEP/CCC’s data report on heavy metals and POPs [Aas et al., 2018]. All the data are available from the EBAS database (http://ebas.nilu.no/).

1.2. Polychlorinated Biphenyls (PCBs)

Polychlorinated Biphenyls (PCBs) are a group of (mainly) industrial chemicals which were deliberately and extensively produced from ~1930 until the early 1990s. Production peaked around 1970, and was followed by various control measures on production and new use. PCBs are among the initial POPs included under the Aarhus protocol on POPs, and also among the compound groups for which monitoring data have been more extensively reported to EMEP. Data for selected PCBs in 2016 are included in Fig. 1.2.

PCBs represent an interesting class of POPs for a more in-depth discussion for several reasons. While most of the initial POPs regulated under CLRTAP were either pesticides (e.g. DDT, HCHs), or combustion by-products (e.g. PCDD/Fs, PAHs), PCBs are mainly an industrial chemical which was extensively used for various purposes and applications ranging from so-called open applications (e.g. carbonless copy paper) and closed systems (capacitors, transformers). Probably, the most extensive historical use in terms of tonnage was for electrical equipment.

While primary emissions are expected to have experienced a general decline over the last decade, as also seen in the EMEP monitoring data, primary emissions may still persist due to the long lifetime of
products and material containing PCBs. PCBs were also used in various building materials, such as paints, and many of these products may still remain in use, causing primary emissions to air and other environmental media even today. Emissions may also occur when material containing PCBs eventually are demolished (e.g. buildings from a certain period) or by accidental releases when old electrical equipment (e.g. containing capacitors) is not properly recycled and/or discarded. PCBs were produced as so-called technical mixtures (e.g. Aroclors), with different isomer (number of chlorines ranging from 1 to 10) and congeneric compositions (1 to 209).

Figure 1.2 shows the annual mean concentrations in 2016 at the EMEP sites for selected PCB congeners (28, 101, 153, 180). These four congeners are among the seven so-called indicator PCBs (or “Dutch PCBs”) which also were among the more abundant in various technical mixtures, and, among the congeners which are more frequently analyzed and reported. However, these and other PCBs represent a wide variety of environmental fate properties, reflecting differences in their temperature dependent physical-chemical properties [Li et al., 2003].

Fig. 1.2. Annual mean concentrations in 2016 for selected polychlorinated biphenyls (PCBs) in air, pg/m³.
Because of their semi-volatile properties, PCBs may be present in both the gaseous and particulate fractions in air. Depending on their partitioning between gas and particles, their mobility and persistence in air may hence vary widely, and hence are anticipated to show spatial and temporal variability in air across Europe. There are clues in Figure 1.2 that lighter and more volatile PCBs (e.g. PCB-28) remain relatively more abundant in air at remote sites at high latitudes, compared to the less volatile PCBs which appear more abundant in more densely populated areas which are suspected source regions within Europe.

The example of PCBs illustrates that more information on observed gas-particle partitioning for substances which may be present in both phases is desirable within EMEP for a more in-depth understanding of their atmospheric long-range transport potential and predictions thereof. Another feature associated with PCBs is their potential to undergo reversible atmospheric deposition, i.e. due to secondary emissions from environmental reservoirs as contaminated in the past. Hence, contemporary concentrations in air may in part be a result of primary emissions which occurred long time ago as well as secondary emissions [Nizzetto et al., 2010], which testifies the importance of long-time series of POPs and continued monitoring under the EMEP programme. These are temperature-dependent process, and it has been discussed if the relative significance of secondary emissions may increase as a result of climate change [Ma et al., 2011], e.g. from melting glaciers [Steinlin, 2016].

While this appears plausible, it has nevertheless been observed that PCBs and many other POPs often show decreasing time trends at monitoring sites within the EMEP domain, which testifies to the importance of long-time series of POPs and continued monitoring. Yet, long-term temporal trends of PCBs are rarely always consistent across sites. Nor are temporal trends of individual POP compounds, measured at individual sites, always showing continuous decline, an example being some PCB monitored at the Zeppelin station in Norway [Hung et al., 2016]. It is therefore interesting and important to sustain the long-term monitoring even long time after intentional PCB production has been banned.

There are still several important research questions, relevant for control strategies, which remain to be fully understood. One key example is the occurrence and potentially increasing significance of PCB congeners which were not typically associated with technical mixtures. PCBs may also be unintentionally formed and emitted as a result of de novo synthesis from the thermal processes, and PCB-118 has been proposed as a marker for such activities [Liu et al., 2013]. As emissions of PCBs from technical mixtures are expected to continue to decline, the role and possible magnitude of unintentionally produced PCB emissions from thermal processes in controlling contemporary and future PCB concentrations remains an open question.

Secondly, there are additional PCB congeners which may be unintentional by-products of manufacturing process, including those used to make certain pigments [Grossman, 2013]. Among these, PCB-11 has appeared to be a marker for non-legacy PCB contamination, but PCB-209, PCB-77, PCB-28, and PCB-52 are also implicated manufacturing by-products, according to a recent review [Vorkamp, 2016]. Hence, recent scientific literature suggest that the number of PCB congeners measured and reported under EMEP should ideally be expanded in order to obtain further knowledge
about these “new” PCBs, claimed to represent a possible largely overlooked environmental issue [Vorkamp, 2016].

Taken together, the examples may also serve to illustrate the importance of continued monitoring of PCBs in air under the EMEP program, even for substances for which production ceased decades ago. Continued efforts under EMEP to monitoring these relatively data-rich substances may also be to the benefit in terms of expanding sampling, analytical and modelling efforts towards less data-rich substances of more emerging concern, but with similar fate properties.

1.3. Polycyclic Aromatic Hydrocarbons (PAHs)

Unlike PCBs, PAHs are mainly considered as byproducts of incomplete combustion processes. Under EMEP, significant attention has recently been paid to these compounds, including discussions concerning apparent discrepancies between modelled and observed concentration in specific areas. Figure 1.3 summarizes the annual average concentrations of selected PAHs (Anthracene, Fluoranthene, Pyrene and Benzo[a]Pyrene) at EMEP sites in 2016. As seen from this Figure, the spatial variability across EMEP sites varies by more than an order of magnitude.

The spatial pattern for selected PAHs in background air may also be seen as different to many other POPs included in the EMEP program, with both relatively high and relatively low concentrations reported for stations in relative close proximity to each other (Fig. 1.3). The absence of a clear spatial pattern mirrors findings from Halse et al. [2011], who reported concentrations at 96 European background sites, and who attributed this to a more significant influence of local emission sources, rather than atmospheric long-range transport. Part of the explanation may thus be the relatively short atmospheric half-life of many PAHs in air, compared to e.g. other POPs as hexachlorobenzene (HCB). If this is reasonably correct, this then represents some additional challenges to accurately determine the spatial and temporal variability of emissions and testifies to the need for high temporal and spatial resolution in the models to improve the understanding of atmospheric source-receptor relationships.

Clearly, this also implies a need for a more dense network of monitoring stations to better capture some of the anticipated variability in background air, compared to POPs which are more “homogenously” distributed across the EMEP domain (e.g. HCB). Some PAHs are also, similar to the PCBs, compounds which may partition between the gas and particulate phases. Hence, more data on the observed partitioning between these two phases (i.e. by measuring and reporting both gaseous and particulate concentrations in air) may additionally help to increase confidence in model predictions.
Fig. 1.3. Annual mean concentrations in 2016 for selected polycyclic aromatic hydrocarbons (PAHs) in air and aerosols, ng/m$^3$. 

a) Anthracene
b) Fluoranthene
c) Pyrene
d) B[a]P