LONG-TERM TRENDS OF POPs UNDER THE EUROPEAN MONITORING AND EVALUATION PROGRAMME (EMEP) – CONTRIBUTION TO THE GLOBAL MONITORING PLAN

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Introduction

The European Monitoring and Evaluation Programme (EMEP) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP). The main objective of EMEP is to provide governments and subsidiary bodies under CLRTAP with qualified scientific information of the deposition and concentration of air pollutants, in order to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention[1]. The monitoring was initiated in the 1970s with focus on the trans-boundary transport of acidification and eutrophication but the scope was widened in 1999 to include persistent organic pollutants (POPs). Data for POPs have to some extent also been collected earlier, and the EMEP database thus includes older data, even back to 1991 for a few sites[2]. This allows for the development of time trends covering up to 20 years of monitoring. The data on POPs in air and precipitation from EMEP are publically available through a designated website where users may access and download the data (http://ebas.nilu.no/). The monitoring activities, including the EMEP database (EBAS), for POPs and other pollutants are coordinated by the Chemical Coordinating Centre of EMEP (EMEP-CCC) hosted by the Norwegian Institute for Air Research (NILU).

To date, a few studies have reported time trends of POPs in Europe[2-6]. It is both interesting and timely to further explore the EMEP measurements for POPs to study long-term temporal trends and seasonality of POPs. The goal of such trend analysis will be to evaluate the effectiveness of emissions reduction strategies under CLRTAP and the Stockholm Convention (SC) on POPs as well as analyze if the measured concentrations are results of primary emissions and long-range atmospheric transport, or other phenomena and processes (i.e. revolatilisation of POPs). Time trends from EMEP and other regional monitoring programs (such as HELCOM, AMAP, CAMP, IADN) will be included in the 2015 Global Monitoring Plan (GMP) Second Report for POPs under the SC.

Herein we present the EMEP network, and discuss how EMEP complements and contributes to the GMP for POPs. To illustrate some of the ongoing work, examples of preliminary long term temporal trends of polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs) from one EMEP site in Norway (i.e. the Birkenes observatory) are presented.

Materials and methods

Monitoring within EMEP takes place at carefully selected background monitoring sites. The Programme recommends the use of high-volume active air samplers (AAS) at all sites to determine the concentrations of POPs in air. Typically, a sampling duration of 24 to 48 hours are applied to balance the need for obtaining detectable amounts (i.e. sufficiently long sampling time) and to have the possibility to correlate the measurement results to air mass trajectories (i.e. sufficiently short sampling time). However, some stations use a longer sampling duration up to 14 days. The sampling frequency also varies from site to site and may typically be one sample per week or one sample per month.

To develop long-term temporal trends, the Digital Filtration (DF) Technique was used. DF is a statistical fitting technique that extracts seasonal cycles and inter-annual trends from time series. This technique has previously been applied to derive long-term trends of POPs monitored under the AMAP network[6-7]. In brief, an approximate long-term trend and an average seasonal cycle are determined by fitting a smoothing Reinsch-type cubic spline and Fourier components to the data, respectively, in an iterative manner until the fitted spline function becomes almost unchangeable. Outlier data, i.e. points that are more than 3 standard errors away from

the fitted curve, were successively rejected after each iterative fit. The percentage of data points rejected during this process is data set dependent. Long- and short-term variations of the trend and the seasonal cycle are then extracted using two Butterworth digital filters with two cutoff periods: a short-term cutoff period (4 months), and a long-term cutoff period (48 months). Variabilities longer than 4 months and shorter than 48 months are extracted to obtain the overall seasonal cycle, while variabilities longer than 48 months are extracted to obtain the final long-term trend. The cutoff periods, which produced the "best fit" to the specific data set, were chosen by trial-and-error based on visual inspection of the fitted seasonal cycle.

Results and discussion

Although the number of sites that monitor POPs in air have almost tripled during the last ten years (Figure 1) there is yet a limited spatial coverage of POP sampling sites and a predominance of sites located in north-western Europe within the EMEP network[8-9]. From the 23 EMEP stations reporting atmospheric POPs in 2011, 12 provide data on POPs relevant for GMP and the other 11 sites monitor solely PAHs. The high number of EMEP sites measuring PAHs is a result of requirements from the EUs air quality directive[10], and as a consequence, benzo(a)pyrene (B(a)P), which is the only POP/PAH compound included in the air quality directive, is the most frequently measured POP component in EMEP.

While the current spatial coverage may be considered reasonable for some POP compounds it may be insufficient for compounds for which a large spatial variability is expected[11]. A spatial coverage more adequate for all POPs may be obtained by complementing EMEP with other data sets on POPs, derived using passive air samplers (PAS). These include case-studies[11-13] and/or relevant monitoring networks within parts of Europe, such as the UK TOMPS, MONET CEEC, MONARPOP[5,14-15]. While enhancing the spatial coverage, these data are generally limited by uncertainties related to the ability of PAS to back-calculate air concentrations. Overall, this indicate a need for further evaluation of the number of sampling sites and the possibility to include new active air sampling sites within EMEP.

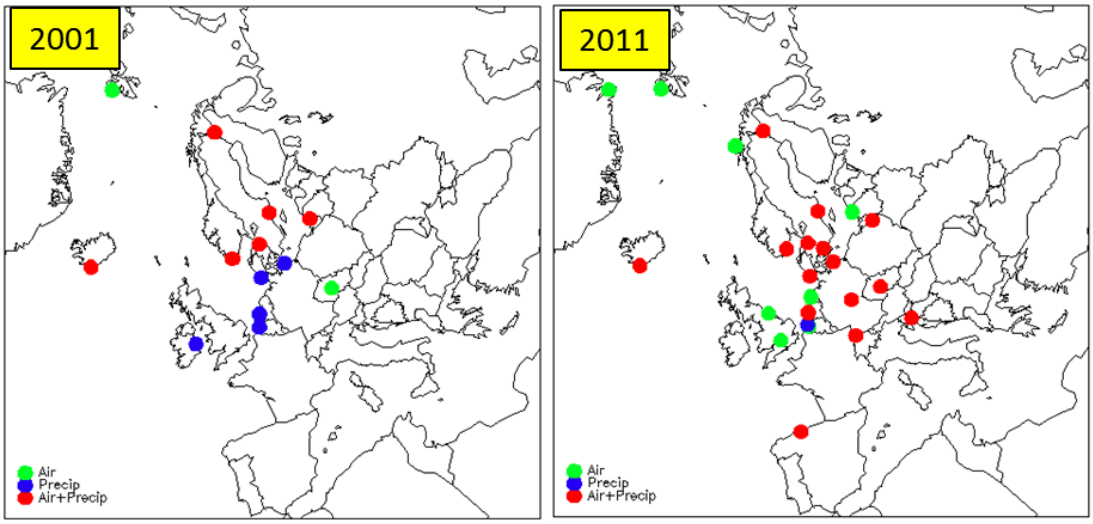

Figure 1. Sampling sites within EMEP where POPs in air and/or precipitation were monitored in 2001 and 2011.

A strength of the EMEP network is that all air measurements of POPs and PAHs are carried out using AAS techniques. This is essential as it: i) offers good temporal resolution which is encouraged by the EMEP, and ii) provides data to evaluate model predictions; assess potential source regions controlling specific long-range atmospheric transport events; and perform detailed trend analysis[16]. Some of which is lost when using PAS. In addition, a key advantage of the AAS approach, in contrast to most PAS strategies, is that it provides an actual quantitative measure of the air concentrations of POPs for a relatively short time-period and that they provide consistent data for particle-associated POPs. The use of PAS for POPs has so far not been recommended within EMEP, but is likely to be discussed and considered as a complementary sampling technique in future updates of

EMEP monitoring strategies. The data obtained from an AAS and PAS are yet difficult to compare in meaningful ways.

The presented temporal trends cover the period 2004-2011. They represent part of the work that will be included in the aforementioned 2015 GMP report.
Regarding PCBs and in particular the seven indicative PCB congeners; half lives ranged between 4.5 y and 8.0 y for PCB 118 and PCB 52, respectively, indicating a rather sharp decline. Interestingly, the decline in the PCB concentrations became sharper after 2008 (Figure 2). All seven PCB congeners followed a similar pattern over the studied period reflecting their common sources, similarly to what was reported by the TOMPs programme[5].

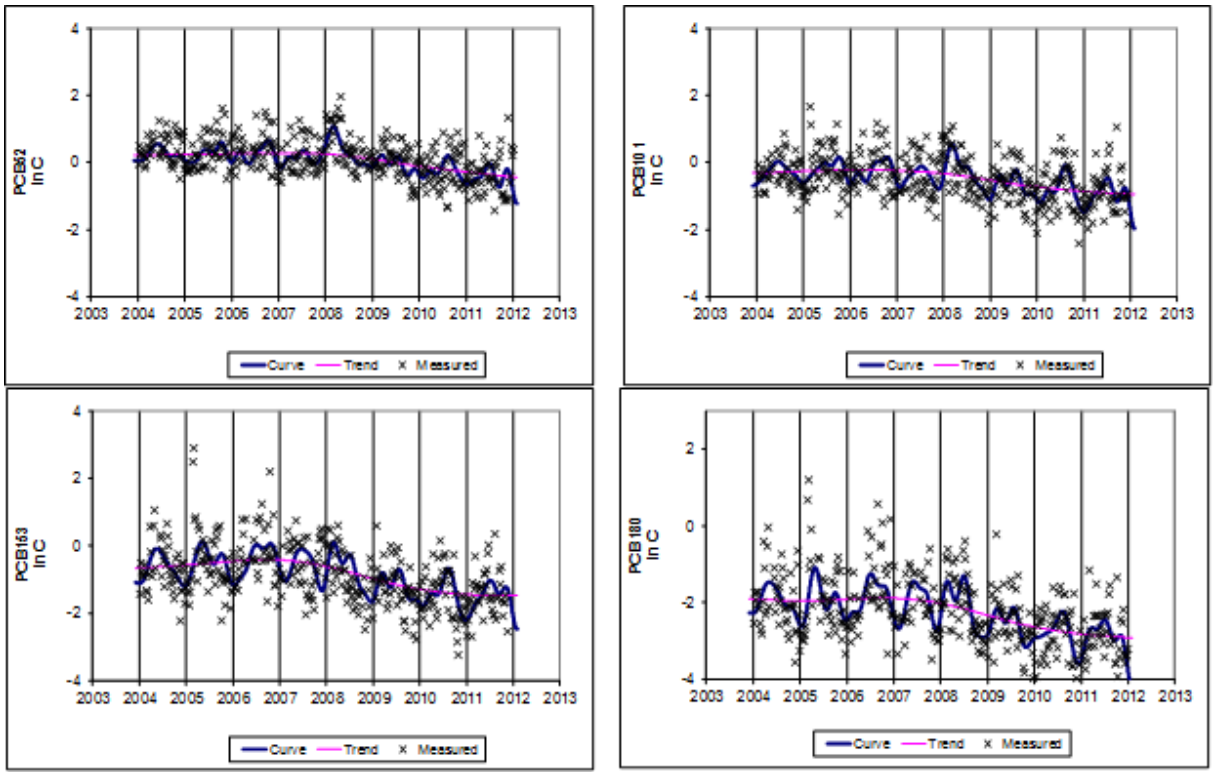

Figure 2: Long-term and seasonal trends of PCBs at Birkenes observatory.

Declining trends over the monitored period were also observed for HCHs (Figure 3) and HCB. HCB exhibits a halflife of 16.9 y, suggesting a slower decline, while α-HCH and γ-HCH show a more apparent decline and halflives of 5.2 y and 3.9 y respectively. The results for HCB are in contrast to the increased concentrations of HCB observed in the Arctic observatory Zeppelin, in Svalbard[7]. Apart from the apparent decline for HCHs, the analysis of the last decade's results, also suggest a repetitive seasonality of the HCH concentrations. In particular, the maximum concentrations are observed in the summer period during all years. This suggests that the more volatile POPs may be revolatilised from soil or other environmental surface media during warmer periods (i.e. secondary emission) but may also in part be due to remaining applications during summer months (i.e. primary emission)[17-19].

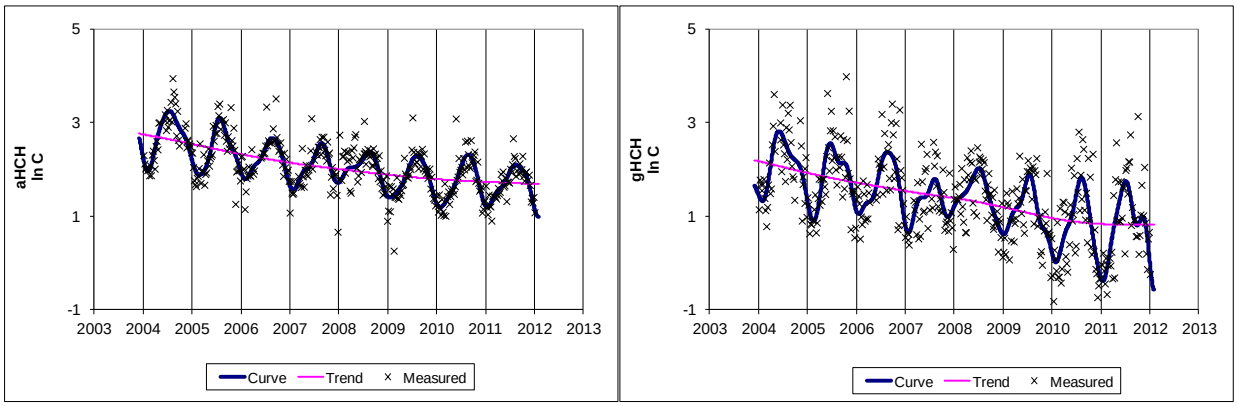

Figure 3. Long-term and seasonal trends of HCHs at Birkenes observatory.

The long-term trend analysis of POPs at Birkenes all show decreasing concentrations, albeit with different rates. It is well documented that this decline had started before the implementation of the SC, however the presented Birkenes results, show that this decrease continues after 2004, likely also reflecting the result that the SC have had on the environmental emissions and primary occurrence of POPs.

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