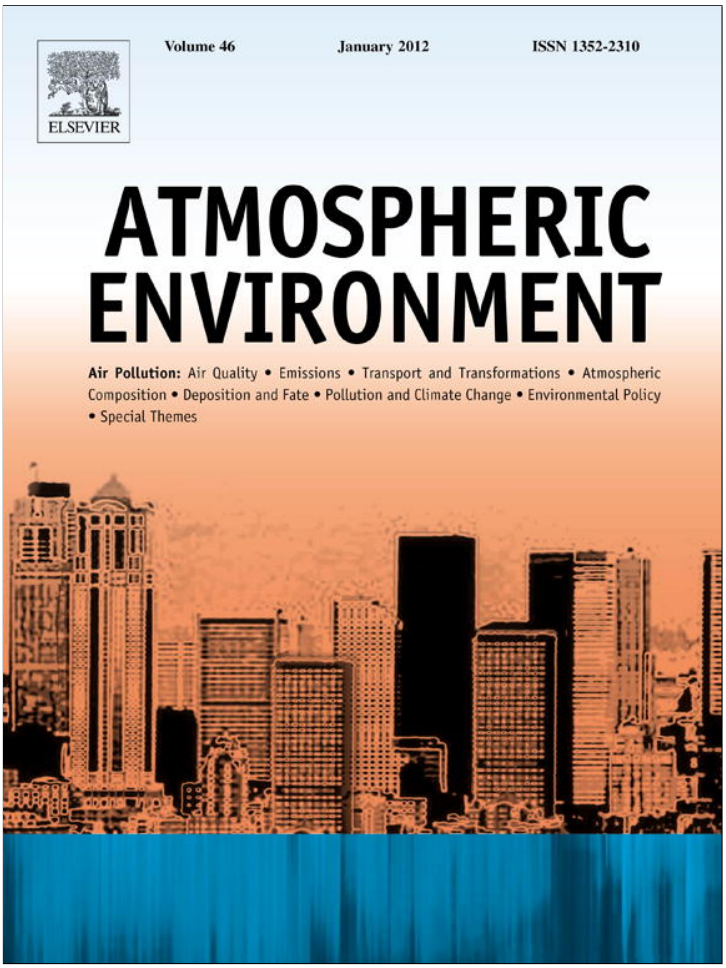

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Atmospheric Environment 71 (2013) 335–339

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Short communication

Forecasting long-range atmospheric transport episodes of polychlorinated biphenyls using FLEXPART

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HIGHLIGHTS

- Long-range atmospheric transport episodes of PCBs were studied at Birkenes, Norway.
- Potential episodes were initially forecasted using the FLEXPART model.
- Targeted samples collected during individual episodes were analyzed.
- Strong pollution episodes of PCBs were identified.
- A forecast system as presented could add value to relevant monitoring efforts.

ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form
4 February 2013
Accepted 11 February 2013

Keywords:
Persistent organic pollutants
Birkenes
FLEXPART
Forecast
Episodes
Polychlorinated biphenyls

ABSTRACT

The analysis of concentrations of persistent organic pollutants (POPs) in ambient air is costly and can only be done for a limited number of samples. It is thus beneficial to maximize the information content of the samples analyzed via a targeted observation strategy. Using polychlorinated biphenyls (PCBs) as an example, a forecasting system to predict and evaluate long-range atmospheric transport (LRAT) episodes of POPs at a remote site in southern Norway has been developed. The system uses the Lagrangian particle transport model FLEXPART, and can be used for triggering extra ("targeted") sampling when LRAT episodes are predicted to occur. The system was evaluated by comparing targeted samples collected over 12–25 h during individual LRAT episodes with monitoring samples regularly collected over one day per week throughout a year. Measured concentrations in all targeted samples were above the 75th percentile of the concentrations obtained from the regular monitoring program and included the highest measured values of all samples. This clearly demonstrates the success of the targeted sampling strategy.

1. Introduction

Background air measurements of persistent organic pollutants (POPs) within several existing monitoring programs (e.g. Tørseth et al., 2012; Wu et al., 2009) are typically conducted using active air sampling (AAS). However, the high cost associated with this type of sampling limits the spatial and temporal coverage of air measurements. Furthermore, sampling at many sites occurs only at fixed intervals (e.g. one day per week) without any *a priori* consideration of air mass transport (i.e., whether the air is likely to be polluted or not). While the current strategy is appropriate for the purpose of assessing long-term trends (years, decades), the intermittent sampling approach may not effectively capture key long-range atmospheric transport (LRAT) episodes (e.g. Yao et al., 2007), which are often associated with the highest POP concentrations (Eckhardt et al., 2007; Yao et al., 2007).

The objectives of this study were to (i) develop a forecast system using the FLEXPART model to predict long-range atmospheric transport episodes of POPs using PCB-28 as a model compound, (ii) to evaluate the capability of the forecast system to capture specific LRAT episodes at a background site in southern Norway (Birkenes) through targeted sampling (i.e. when LRAT episodes are predicted), (iii) to assess whether predicted LRAT episodes for PCB-28 coincide with elevated concentrations of additional PCBs, and (iv) to identify source regions of PCBs during individual episodes.

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http://dx.doi.org/10.1016/j.atmosenv.2013.02.022

2. Material and methods

2.1. The Birkenes observatory

Sampling was carried out at the Birkenes observatory, which has been in operation since 1981. The station is located in the southern part of Norway (N 58°23, E 08°15, 190 m.a.s.l), on top of a hill and is mainly surrounded by forest. We refer to Eckhardt et al. (2009) for further details.

2.2. Sampling

Air sampling was carried out by use of high volume air sampling devices (DHA-80, Digitel, Hegenau, CH), where both particulate and gas phase samples were collected. The samplers consist of a glass fiber filter (collecting particles), in combination with two polyurethane foam (PUF) plugs (7.5 cm × 4.5 cm), for collection of the gaseous compounds. The glass fiber filters (weight: 53 g m^{-2}, thickness: 260 μm, particle retention: 1.2 μm) were purchased from Whatman™ GF/C, GE Healthcare, Buckinghamshire, UK. Air was pumped through the sampling material. For regular monitoring samples collected once per week, the pump was set to sample ~770 m^3 (0.5 m^3 min^{-1}) of air for 24 h of sampling (Eckhardt et al., 2009). The targeted air samples were collected by use of a similar high-volume air sampling device (DHA-80, Digitel), using a different pump (SAH 155, Elmo Rietschle, Bad Neustadt, Germany). This included both an on-line control of the sampling system and the possibility to apply a higher flow rate to achieve shorter sampling periods, since LRAT episodes are often shorter than a day. The sampling volumes for the targeted LRAT samples ranged from 395 to 1443 m^3 (average 0.8, range 0.6–0.9 m^3 min^{-1}) and were collected over 12–25 h. After sampling was completed, the exposed PUF samples were sealed in a gas tight container and glass fiber filters were wrapped in alumina foil and sealed.

2.3. Clean-up and analysis

Prior to sampling, the glass fiber filters were heated to 450 °C for 8 h and wrapped in alumina foil. PUF plugs were pre-extracted with acetone and toluene for 8 h using a Soxhlet extraction system and dried under vacuum in desiccators (Eckhardt et al., 2009). After sampling was completed, a mixture of ^{13}C-isotope labeled internal standard of PCBs was added to the sample material (both filter and PUFs) prior to extraction. Samples were extracted via Soxhlet extraction using *n*-hexane/diethyl ether 9:1 as an extraction solvent (Eckhardt et al., 2009). All extracts were pre-concentrated to approximately 2 mL and treated with sulfuric acid to remove matrix related components. The organic phase was further cleaned up using a silica column and eluted with *n*-hexane/diethyl ether. The final extracts were reduced in volume to approximately 0.1 mL using nitrogen followed by the addition of a recovery standard (Eckhardt et al., 2009). An Agilent 6890 gas chromatograph coupled to a high resolution Waters AutoSpec mass spectrometer in an electron impact mode was used for quantification and identification of the target compounds. The gas chromatograph conditions are given elsewhere (e.g. Eckhardt et al., 2009).

2.4. FLEXPART model

The atmospheric transport of PCB-28 was simulated by use of the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005, 1998). The main purpose for FLEXPART model simulations was to calculate PCB-28 concentrations at the measurement station and identify the source regions of PCB-28. The model calculates the trajectories of so-called tracer particles and accounts for turbulence, convection, deposition and atmospheric reaction with hydroxyl (OH) radicals (Eckhardt et al., 2009).

FLEXPART was run in backward mode for this study in order to identify possible source regions influencing the measurement site during an air pollution episode (Eckhardt et al., 2007; Seibert and Frank, 2004). Following an earlier study for Birkenes (Eckhardt et al., 2009), PCB-28 was chosen as our model compound. We used the maximum emission scenario derived by Breivik et al. (2007) as model input. Physical–chemical properties for PCB-28 were adapted from Li et al. (2003) and the atmospheric reaction rate taken from Anderson and Hites (1996) as further detailed in Eckhardt et al. (2009).

FLEXPART was run daily using meteorological forecast data to predict airborne concentration of PCB-28 for the following day (further referred to as FLEXPART-forecast – *FLEXPART-f*). The FLEXPART run was initialized at the coordinates of the measurement site and at the future time and was then run backward in time incorporating first forecast meteorological data and, for past periods for which such data were already available at the time of the model calculations, analysis data. Predictions using *FLEXPART-f* began in December 2008. By the end of 2010, the upper 95% percentile for simulated concentrations of PCB-28 (5.7 pg m^{-3}) was determined and selected as a threshold limit for targeted sampling of predicted LRAT episodes. During 2011, upcoming LRAT episodes were identified one day ahead by *FLEXPART-f* as predicted concentrations exceeding the threshold of 5.7 pg m^{-3}.

After all targeted sampling was completed, FLEXPART was run again for dates in which sampling occurred but using meteorological analysis data (these runs will be referred to as FLEXPART-retrospective – *FLEXPART-r*). In *FLEXPART-f* 40 000 particles were released over a 24 h interval, and in *FLEXPART-r* 100 000 particles were released over the exact interval of the measurement, from the receptor site (Birkenes) and followed backwards in time for 20 days in order to calculate emission sensitivities (ES) (Seibert and Frank, 2004; Stohl et al., 2003, 2005). A larger number of particles were released for the *FLEXPART-r* runs for more accurate determination of source regions during the episodes which were sampled. The ES (unit nanoseconds) provides information about the residence time of an air mass within a grid cell and uptake of emissions was facilitated in the so-called footprint layer (0–100 m above ground) (Eckhardt et al., 2009). Multiplying the footprint ES value by emission fluxes from the PCB-28 emission inventory (Breivik et al., 2007) yields the geographical distribution of sources contributing to the simulated concentrations at the measurement site. Spatial integration of all contributions then gives the simulated concentration at the measurement site.

For the forecast system (*FLEXPART-f*), FLEXPART used meteorological forecast data taken every three hours (26 model levels and resolution of 1 × 1 globally) from the Global Forecast System (GFS) model of the National Centers for Environmental Prediction (NCEP) to predict the concentration of PCB-28 one day ahead. For the selected episodes which were subject to targeted sampling and analysis, FLEXPART (*FLEXPART-r*) was run for retrospective simulations driven by operational analysis from the European Centre for Medium-Range Weather Forecasts (ECMWF, 1995), with 1° × 1° resolution and 91 model levels. Analyzes at 00:00, 06:00, 12:00 and 18:00 UTC, and 3-h forecasts at 03:00, 09:00, 15:00 and 21:00 UTC were used.

3. Results and discussion

3.1. Annual averages and concentrations during the predicted episodes

Samples from targeted sampling (based on model results of *FLEXPART-f*) during three predicted LRAT episodes (E) in 2011,

Table 1
Sampling times for targeted samples collected during predicted episodes in 2011.

Episode	Start date	Start time	End date	End time
E1	06.01	11:50	07.01	23:49
E2	24.02	17:29	25.02	05:49
E3a	29.09	08:05	29.09	21:10
E3b	29.09	21:15	30.09	15:30
E3c	30.09	15:30	01.10	05:35
E3d	01.10	05:38	02.10	07:04
E3e	02.10	07:08	02.10	18:49

which occurred in January (E1), February (E2) and late September/early October (E3a, b, c, d, e), were analyzed (Table 1). An overview of predicted and measured concentrations is presented in Table A.1 in Appendix.

Fig. 1 compares the modeled *FLEXPART-r* concentrations of PCB-28, and selected PCBs measured during the individual episodes ($n = 7$, colored dots) with annual results obtained through the regular monitoring program ($n = 52$). We show results for *FLEXPART-r* modeled PCB-28 (a) and measured concentrations for seven PCBs (PCB-28, -52, -101, -118, -138, -153, -180) (b–h). In Fig. 1, the median and the percentiles were estimated based on annual results for the AAS sampler. To further facilitate interpretation of results, Table A.1 tabulates the predicted and measured concentrations (pg m^{-3}) during each sampled episode. Table A.2 presents the annual mean and standard deviation (SD) based on results from the regular monitoring program in 2011 ($n = 52$) and compares concentrations measured during each episode with the annual mean.

There are major uncertainties in the exact magnitude of PCB emissions with different emission scenarios varying by several orders of magnitude (Breivik et al., 2007 and references therein). Independent model evaluations using this data have therefore experienced difficulties in accurately reproducing the exact magnitude of observed concentrations (e.g. Gong et al., 2007; Macleod et al., 2005; Wania and Su, 2004). For all episodes, we start by noting that the model overestimated measured concentrations of PCB-28 during the episodes by a factor of 4.2 on average, ranging from 1.7 (E3e) to 7.7 (E2). This was anticipated based on past model evaluations using FLEXPART (Eckhardt et al., 2009; Halse et al., 2011) and mainly attributed to uncertainties in the maximum emission scenario used as model input (Breivik et al., 2007). Despite this uncertainty, the model was clearly successful in singling out LRAT episodes of PCB-28 as all targeted samples exceeded the 75 percentile of the regular monitoring program (Fig. 1b). The measurements were elevated, ranging from mean plus 0.8 standard deviations (E1) up to mean plus 6.4 standard deviations (E3e) (Table A.2), with two samples (E3e and E3c) exceeding the highest concentration of the 52 samples collected as part of the monitoring program. However, the ranking of predicted and observed concentrations of PCB-28 did not fully match, with predictions for PCB-28 decreasing from E3c > E2 > E3b > E3d > E3a ≈ E3e > E1 and observations declining from E3e > E3c > E3b > E3d > E3a > E2 > E1 (Table A.1). Nevertheless, the overall results indicate that there is a fairly good understanding of major source regions leading to elevated concentrations of PCB-28 at Birkenes.

An obvious question to follow is whether the model predictions may work as a suitable surrogate for PCBs other than PCB-28? For all other PCB congeners, each episodically collected sample was above the 75 percentile (Fig. 1c–h). Furthermore, the measurements of Σ_7PCBs were elevated by 0.7 (E1) to 6.9 (E3e) SDs (Table A.2) above the annual mean, with all congeners being elevated by more than two SDs for the five consecutive samples collected during autumn (E3). As the ranking of observed concentrations from high to low are identical for each PCB congener in all targeted samples (E3e > E3c > E3b > E3d > E3a > E2 > E1), we conclude that PCB-28 serves as a suitable surrogate to identify probable LRAT episodes for the other congeners included. This would imply that major source regions affecting concentrations of these PCBs are likely to be similar.

3.2. Source regions predicted using backwards simulation

Fig. 2a and b shows the corresponding *FLEXPART-r* emission contribution (EC) maps for the episodes with highest modeled (E3c) and measured (E3e) concentrations of PCB-28 in air at Birkenes, respectively. Similarly, Figs. A.6 and A.8 in the Appendix

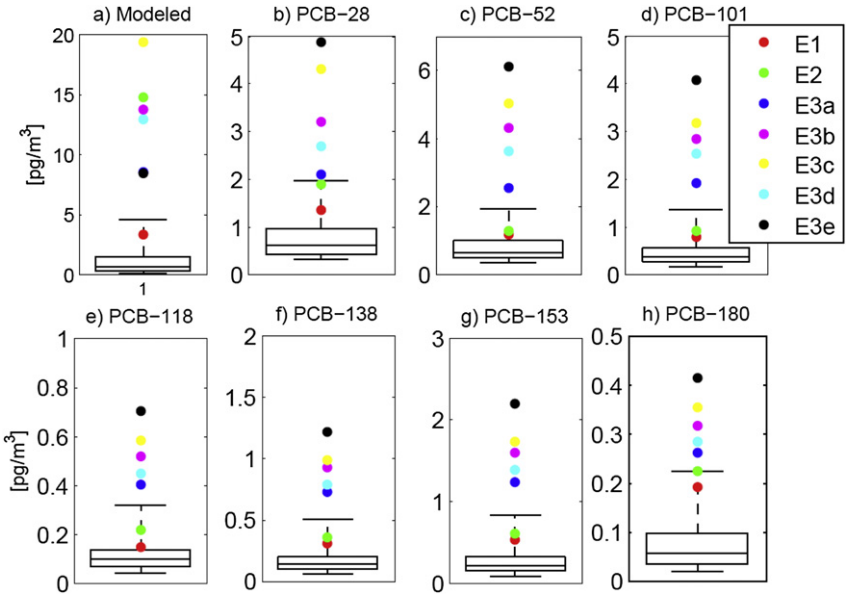

Fig. 1. Modeled (*FLEXPART-r*) PCB-28 (a) and measured PCB concentrations (b–h) in units of pg m^{-3}, for both the annual sampling program and the targeted samples. The box and whisker plots show the annual results (2011) for Birkenes, southern Norway based on weekly samples. The line shows the median, while the box and whiskers delineates the 25 and 75 percentiles and the 5 and 95 percentiles, respectively. Targeted samples are represented by colored dots.

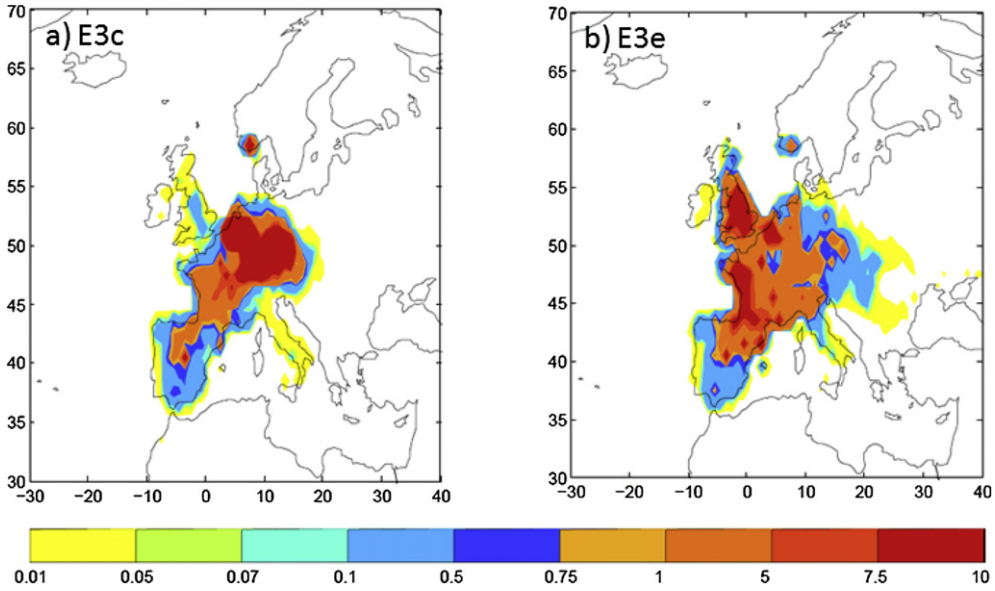

Fig. 2. Maps of *FLEXPART-r* EC (emission contributions, 1E-12 [pg m^{-3}]) for PCB-28 for the episodes with highest predicted (E3c) (a) and measured (E3e) (b) concentrations at Birkenes during 2011.

show the *FLEXPART-r* footprint emission sensitivity (ES) maps for these two episodes. Additional maps based on annual results as well as the other individual episodes are included in the Appendix (Figs. A.1–A.8).

While E3c had the highest modeled (*FLEXPART-r*) concentration of PCB-28, the highest measured concentration was found for E3e (Table A.1). This may reflect inaccuracies in the spatial emission pattern used as model input. In other words, the emissions in western parts of Europe highlighted in Fig. 2b (e.g. UK and/or France) might be underestimated in the emission inventory compared to those regions in more central parts of mainland Europe which are highlighted in Fig. 2a. A study done by Eckhardt et al. (2009) revealed that the dominating regions for PCB-28 affecting Birkenes were Eastern and Central Europe together with the UK and Ireland. Although the data set of targeted samples is too limited to infer any reliable conclusions (as e.g. atmospheric loss processes occurring en route could have been more efficient than predicted by the model in the case of E3c, relatively to E3e), it illustrates how a combined modeling and monitoring approach has the potential to better constrain our understanding of how major source regions are affecting concentrations of PCBs at a background site.

4. Conclusions

Trajectories have been widely used to interpret air measurement of various POPs and other pollutants. However, few studies have performed targeted air sampling of organic contaminants from suspected source regions as triggered by real-time meteorological forecast models (Yao et al., 2007). To the best of our knowledge, our study represents the first attempt to both (i) use model predictions driven by *a priori* information on emissions of POPs to trigger air sampling as well as (ii) retrospectively evaluate the source regions for measurements collected during predicted episodes. The *FLEXPART-f* model was clearly successful in identifying LRAT episodes for both PCB-28 and other PCBs as the measured concentration of PCB-28 in all seven targeted samples was above the 75 percentile with two samples exceeding concentrations measured in the 52 samples collected as part of the regular monitoring program. The *FLEXPART-r* model fails to accurately reproduce the magnitude of PCB-28 concentrations during individual episodes, but this can be mainly attributed to uncertainties in the absolute emission rates of PCB-28 used to drive simulations. We conclude that forecasting of pollution episodes has the potential to add value to relevant monitoring efforts which are normally collecting active air samples at fixed intervals in a non-continuous manner. Observations targeted at strong pollution episodes (as in this paper) or on transport from specific source regions with highly uncertain emissions (as could be done in a very similar forecasting framework) could significantly enhance our understanding of POP sources. However, in order to obtain more confidence in the forecast system and predicted source–receptor relationships (*FLEXPART-r*), the number of targeted samples which are collected and substances which are predicted and analyzed need to be increased.

Acknowledgments

This study was financed by the Research Council of Norway (183437/S30). We would also like to thank the Norwegian Climate and Pollution Agency for financing the POPs monitoring program at Birkenes, Olav Lien for support with the sampling, and Nick Warner for comments on this manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.02.022.

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