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

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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 to 25 hours 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.

2. Material and Methods

2.1.1 The Birkenes obervatory

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.

2.1.2 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 x 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/minute) of air for 24 hours 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/minute) and were collected over 12 to 25 hours. 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.

2.1.3 Clean-up and analysis

Prior to sampling, the glass fiber filters were heated to 450 °C for 8 hours and wrapped in alumina foil. PUF plugs were pre-extracted with acetone and toluene for 8 hours using a Soxhlet extraction system and

60   dried under vacuum in desiccators (Eckhardt et al., 2009). After sampling was completed, a mixture of

61   ^{13}C–isotope labeled internal standard of PCBs was added to the sample material (both filter and PUFs)

62   prior to extraction. Samples were extracted via Soxhlet extraction using *n*-hexane/diethyl ether 9:1 as an

63   extraction solvent (Eckhardt et al., 2009). All extracts were pre-concentrated to approximately 2 mL and

64   treated with sulfuric acid to remove matrix related components. The organic phase was further cleaned

65   up using a silica column and eluted with *n*-hexane/diethyl ether. The final extracts were reduced in volume

66   to approximately 0.1 mL using nitrogen followed by the addition of a recovery standard (Eckhardt et al.,

67   2009). An Agilent 6890 gas chromatograph coupled to a high resolution Waters AutoSpec mass

68   spectrometer in an electron impact mode was used for quantification and identification of the target

69   compounds. The gas chromatograph conditions are given elsewhere (e.g. Eckhardt et al., 2009).

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71   2.2 FLEXPART model

72   The atmospheric transport of PCB-28 was simulated by use of the Lagrangian particle dispersion model

73   FLEXPART (Stohl et al., 2005; Stohl et al., 1998). The main purpose for FLEXPART model simulations was

74   to calculate PCB-28 concentrations at the measurement station and identify the source regions of PCB-

75   28. The model calculates the trajectories of so-called tracer particles and accounts for turbulence,

76   convection, deposition and atmospheric reaction with hydroxyl (OH) radicals (Eckhardt et al., 2009).

77   FLEXPART was run in backward mode for this study in order to identify possible source regions influencing

78   the measurement site during an air pollution episode (Eckhardt et al., 2007; Seibert and Frank, 2004).

79   Following an earlier study for Birkenes (Eckhardt et al., 2009), PCB-28 was chosen as our model compound.

80   We used the maximum emission scenario derived by Breivik et al. (2007) as model input. Physical-chemical

81   properties for PCB-28 were adapted from Li et al. (2003) and the atmospheric reaction rate taken from

82   Anderson and Hites (1996) as further detailed in Eckhardt et al. (2009).

83   FLEXPART was run daily using meteorological forecast data to predict airborne concentration of PCB-28

84   for the following day (further referred to as FLEXPART-forecast – *FLEXPART-f*). The FLEXPART run was

85   initialized at the coordinates of the measurement site and at the future time and was then run backward

86   in time incorporating first forecast meteorological data and, for past periods for which such data were

87   already available at the time of the model calculations, analysis data. Predictions using *FLEXPART-f* began

88   in December 2008. By the end of 2010, the upper 95% percentile for simulated concentrations of PCB-28

89   (5.7 pg/m^3) was determined and selected as a threshold limit for targeted sampling of predicted LRAT

90   episodes. During 2011, upcoming LRAT episodes were identified one day ahead by *FLEXPART-f* as

91   predicted concentrations exceeding the threshold of 5.7 pg/m^3.

92 After all targeted sampling was completed, FLEXPART was run again for dates in which sampling occurred

93 but using meteorological analysis data (these runs will be referred to as FLEXPART-retrospective –

94 *FLEXPART-r*). In *FLEXPART-f* 40 000 particles were released over a 24 hour interval, and in *FLEXPART-r* 100

95 000 particles were released over the exact interval of the measurement, from the receptor site (Birkenes)

96 and followed backwards in time for 20 days in order to calculate emission sensitivities (ES) (Seibert and

97 Frank, 2004; Stohl et al., 2003; Stohl et al., 2005). A larger number of particles were released for the

98 *FLEXPART-r* runs for more accurate determination of source regions during the episodes which were

99 sampled. The ES (unit nanoseconds) provides information about the residence time of an air mass within

100 a grid cell and uptake of emissions was facilitated in the so-called footprint layer (0-100 m above ground)

101 (Eckhardt et al., 2009). Multiplying the footprint ES value by emission fluxes from the PCB-28 emission

102 inventory (Breivik et al., 2007) yields the geographical distribution of sources contributing to the simulated

103 concentrations at the measurement site. Spatial integration of all contributions then gives the simulated

104 concentration at the measurement site.

105 For the forecast system (*FLEXPART-f*), FLEXPART used meteorological forecast data taken every three

106 hours (26 model levels and resolution of 1×1 globally) from the Global Forecast System (GFS) model of the

107 National Centers for Environmental Prediction (NCEP) to predict the concentration of PCB-28 one day

108 ahead. For the selected episodes which were subject to targeted sampling and analysis, FLEXPART

109 (*FLEXPART-r*) was run for retrospective simulations driven by operational analysis from the European

110 Centre for Medium-Range Weather Forecasts (ECMWF, 1995), with 1°×1° resolution and 91 model levels.

111 Analyses 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

112 were used.

3. Results and Discussion

3.1. Annual averages and concentrations during the predicted episodes

115 Samples from targeted sampling (based on model results of *FLEXPART-f*) during three predicted LRAT

116 episodes (E) in 2011, which occurred in January (E1), February (E2) and late September/early October (E3a

117 ,b, c, d, e), were analyzed (Table 1). An overview of predicted and measured concentrations is presented

118 in Table A.1 in Appendix.

119 Figure 1 compares the modeled *FLEXPART-r* concentrations of PCB-28, and selected PCBs measured during

120 the individual episodes (n=7, colored dots) with annual results obtained through the regular monitoring

121 program (n=52). We show results for *FLEXPART-r* modeled PCB-28 (a) and measured concentrations for

122 seven PCBs (PCB-52,-101,-118,-138,-153,-180) (b-h). In Figure 1, the median and the percentiles were

123   estimated based on annual results for the AAS sampler. To further facilitate interpretation of results, Table

124   A.1 tabulates the predicted and measured concentrations (pg/m^3) during each sampled episode. Table

125   A.2 presents the annual mean and standard deviation (SD) based on results from the regular monitoring

126   program in 2011 (n=52) and compares concentrations measured during each episode with the annual

127   mean.

128   There are major uncertainties in the exact magnitude of PCB emissions with different emission scenarios

129   varying by several orders of magnitude (Breivik et al., 2007 and references therein). Independent model

130   evaluations using this data have therefore experienced difficulties in accurately reproducing the exact

131   magnitude of observed concentrations (e.g. Gong et al., 2007; Macleod et al., 2005; Wania and Su, 2004).

132   For all episodes, we start by noting that the model overestimated measured concentrations of PCB-28

133   during the episodes by a factor of 4.2 on average, ranging from 1.7 (E3e) to 7.7 (E2). This was anticipated

134   based on past model evaluations using FLEXPART (Eckhardt et al., 2009; Halse et al., 2011) and mainly

135   attributed to uncertainties in the maximum emission scenario used as model input (Breivik et al., 2007).

136   Despite this uncertainty, the model was clearly successful in singling out LRAT episodes of PCB-28 as all

137   targeted samples exceeded the 75 percentile of the regular monitoring program (Figure 1b). The

138   measurements were elevated, ranging from mean plus 0.8 standard deviations (E1) up to mean plus 6.4

139   standard deviations (E3e) (Table A.2), with two samples (E3e and E3c) containing the highest

140   concentrations of the 52 samples collected as part of the monitoring program. However, the ranking of

141   predicted and observed concentrations of PCB-28 did not fully match, with predictions for PCB-28

142   decreasing from E3c > E2 > E3b > E3d > E3a ≈ E3e > E1 and observations declining from E3e > E3c > E3b >

143   E3d > E3a > E2 > E1 (Table A.1). Nevertheless, the overall results indicate that there is a fairly good

144   understanding of major source regions leading to elevated concentrations of PCB-28 at Birkenes.

145   An obvious question to follow is whether the model predictions may work as a suitable surrogate for PCBs

146   other than PCB-28? For all other PCB congeners, each episodically collected sample was above the 75

147   percentile (Figure 1c-h). Furthermore, the measurements of Σ_7PCBs were elevated by 0.7 (E1) to 6.9 (E3e)

148   SDs (Table A.2) above the annual mean, with all congeners being elevated by more than two SDs for the

149   five consecutive samples collected during autumn (E3). As the ranking of observed concentrations from

150   high to low are identical for each PCB congener in all targeted samples (E3e > E3c > E3b > E3d > E3a > E2

151   > E1), we conclude that PCB-28 serves as a suitable surrogate to identify probable LRAT episodes for the

152   other congeners included. This would imply that major source regions affecting concentrations of these

153   PCBs are likely to be similar.

3.2. Source regions predicted using backwards simulation

Figures 2a and 2b 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, Figures A.6 and A.8 in the Appendix 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 (Figures 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 Figure 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 Figure 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-

185   continuous manner. Observations targeted at strong pollution episodes (as in this paper) or on transport

186   from specific source regions with highly uncertain emissions (as could be done in a very similar forecasting

187   framework) could significantly enhance our understanding of POP sources. However, in order to obtain

188   more confidence in the forecast system and predicted source-receptor relationships (*FLEXPART-r*), the

189   number of targeted samples which are collected and substances which are predicted and analyzed need

190   to be increased.

5. References

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242 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

243

244 **Figure Captions**:

245

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

251

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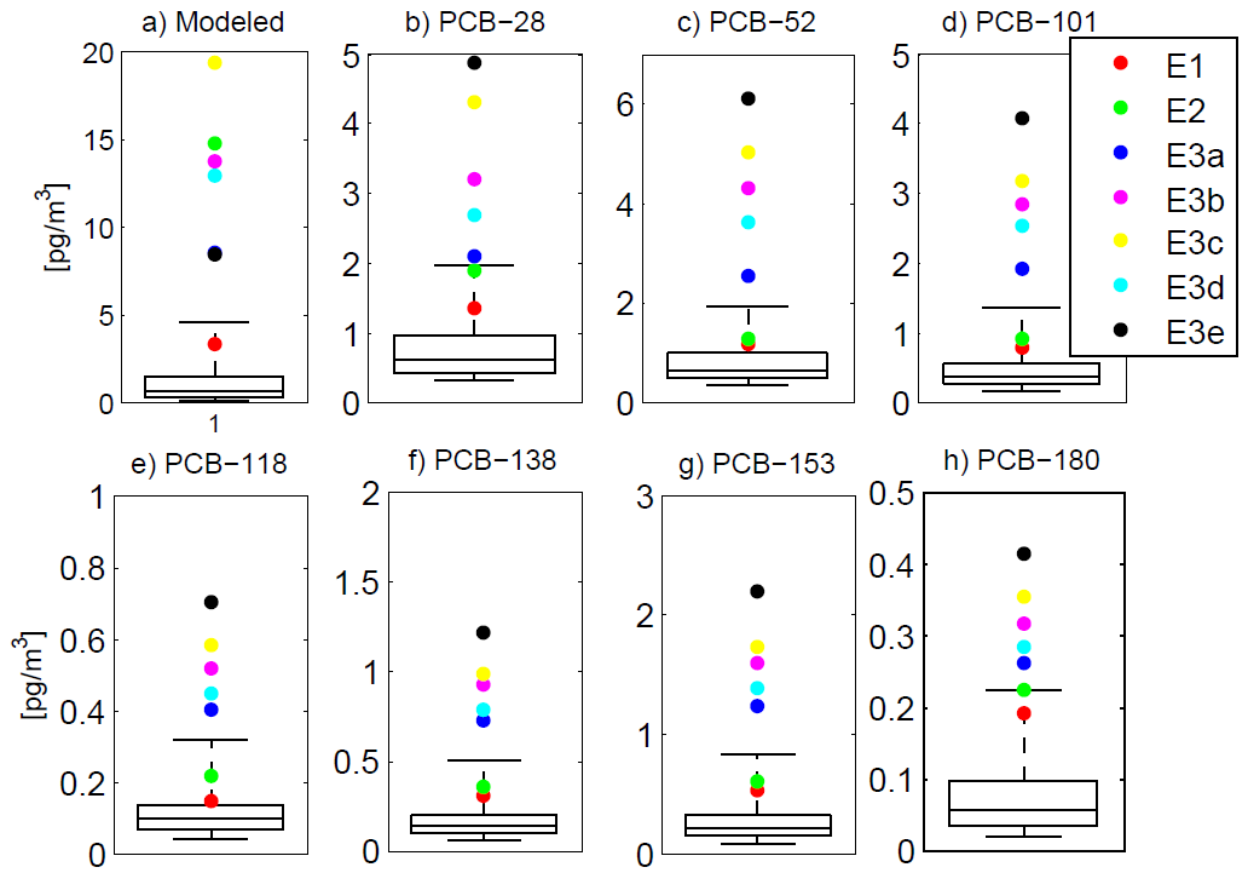253 with highest predicted (E3c) (a) and measured (E3e) (b) concentrations at Birkenes during 2011.
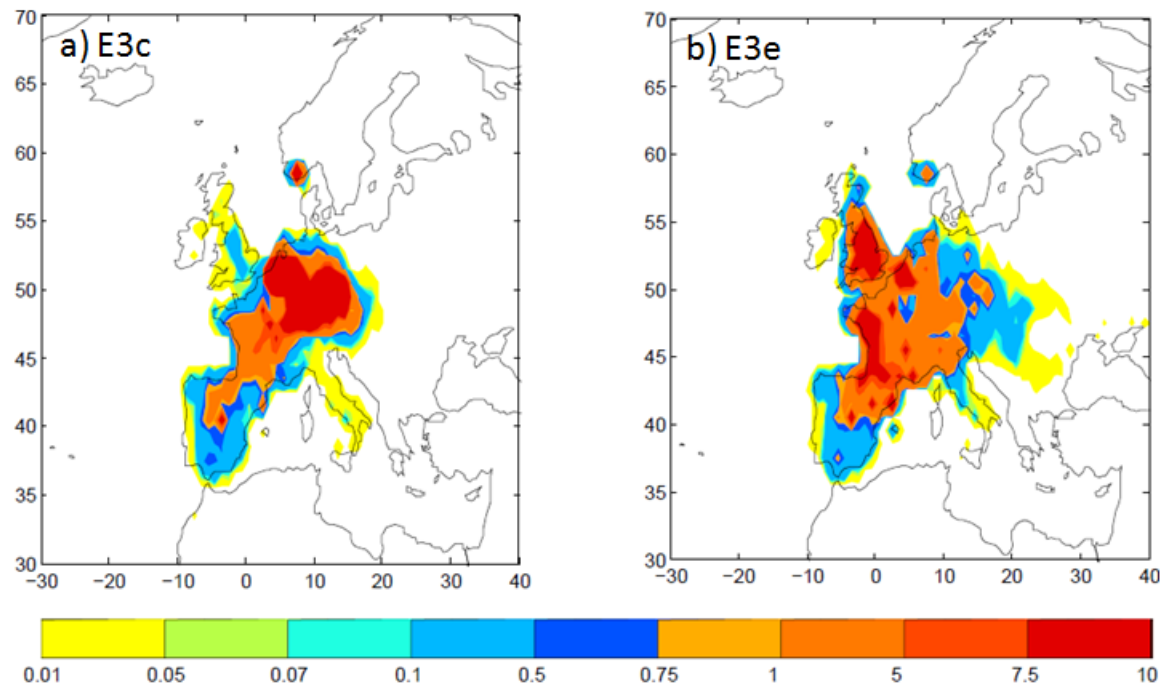
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Figure 1

Figure 2