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Primary source regions of polychlorinated biphenyls (PCBs) measured in the Arctic

Sandy Ubl [a], Martin Scheringer [a,*], Andreas Stohl [b], John F. Burkhart [b], Konrad Hungerbuhler [a]

[a] Institute for Chemical and Bioengineering, ETH Zurich, Switzerland
[b] Norwegian Institute for Air Research (NILU), Norway

HIGHLIGHTS

- Source regions of PCB concentrations measured in the Arctic are identified.
- PCB concentration peaks in the European Arctic are controlled by European emissions.
- Seasonal changes in PCB emissions and in atmospheric transport control PCB levels.

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ABSTRACT

We investigate the source regions of the three polychlorinated biphenyl congeners (PCBs) 28, 101, and 180 measured at the Arctic stations Alert and Zeppelin, and at Birkenes, which is located in southern Norway. Although the Arctic is remote from the main use areas of these chemicals, PCBs have been found in Arctic air, seawater and biota, which has caused concerns for human and environmental health. We used 20-day backward calculations of the Lagrangian Particle Dispersion Model FLEXPART to identify the origin of air masses associated with the 20% highest and lowest measured PCB concentrations. At Birkenes, high concentrations are clearly associated with air masses arriving from known source regions (primarily in Europe and Russia), whereas low concentrations are correlated with atmospheric transport from regions with low primary emissions. At Zeppelin, the influence from known source regions is also enhanced when high PCB-28 and PCB-101 concentrations were measured. At Alert, in contrast, there is no clear link between high/low PCB concentrations and atmospheric transport from source/non-source regions. Additionally, we combined the atmospheric transport patterns with PCB emission data to identify important source regions and their seasonal variability. For the Arctic stations, Western Russia is the dominant source region for PCB-28 and PCB-101. Central Europe is the most important source region for PCB-180, but sources in the US contribute up to 15% to PCB-180 measured at Alert.

1. Introduction

Polychlorinated biphenyls (PCBs) were widely used as dielectric and coolant fluids in transformers and capacitors. PCBs have been detected in Arctic regions (Harner et al., 1998; Hung et al., 2010) far from the areas of their production or use and it was found that they bioaccumulate in marine mammals, polar bears and humans (Kucklick and Baker, 1998; Halsall et al., 1998) causing health concerns for the indigenous Arctic population.

Because of the possible effects of PCBs on human health and the environment, PCBs are now regulated under the Stockholm convention on POPs (UNEP, 2001) and the 1998 Aarhus Protocol on POPs under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) (UNECE, 2009; Tuinstra et al., 2006).

PCBs can undergo reversible atmospheric deposition to terrestrial and aquatic environments. Based on the different physicochemical properties of lighter and heavier PCB congeners, a fractionation of PCB mixtures on a hemispheric scale was predicted by Wania and Mackay (1993). This fractionation has also been observed in the field (Meijer et al., 2003). However, it is still not clear whether environmental reservoirs act as sources or sinks and if primary or secondary sources are controlling the PCB levels in the environment (Meijer et al., 2003; Jaward et al., 2004; Sobek

* Corresponding author.
E-mail addresses: martin.scheringer@chem.ethz.ch, scheringer@chem.ethz.ch (M. Scheringer).

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and Gustafsson, 2004; Gioia et al., 2006; Semeena and Lammel, 2005).

The fate and atmospheric transport of PCBs have been analyzed with multimedia chemical fate models. These models include detailed descriptions of the partitioning of a chemical within and between the different environmental media (Mackay, 2001), but use only limited meteorological data. Alternatively, transport of PCBs has also been modeled with Chemistry Transport Models (CTM). These models have a detailed description of transport and chemistry in the atmosphere but only a very simple description of the other compartments (Gong et al., 2007). There are studies dealing with the comparison of these model types (Hollander et al., 2008).

Also Lagrangian Particle Dispersion Models (LPDMs) have been used to investigate the atmospheric transport of PCBs. Extraordinarily high PCB concentrations have been assigned to long-range transport of biomass burning emissions (Eckhardt et al., 2007) and source regions of PCB-28 measured at Birkenes in Norway (Eckhardt et al., 2009) have been identified by using the FLEXPART model (Stohl et al., 2003). FLEXPART was also used to calculate so-called emission contribution (EC) maps for PCB measurements taken in the West African Region (Gioia et al., 2011) and for European background sites (Halse et al., 2011). LPDMs have a detailed treatment of atmospheric transport including turbulence and convection and depending on the modeled chemical species, dry and wet deposition can be included. LPDMs can be run backward in time, which enables an identification of potential source regions of airborne chemicals. LPDM calculations can also be quantitative because the model output can be combined with the emission fluxes to derive modeled concentrations. In this study we used backward calculations of the FLEXPART LPDM to determine the source regions of three different PCB congeners for the two Arctic sites, Alert and Zeppelin, and a third station, Birkenes, located outside the Arctic in southern Norway.

2. Material and methods

2.1. Measurement data

We used measured PCB concentrations from the sites Birkenes, Zeppelin, and Alert (see Table A1 in the Supplemental Material (SM)). Birkenes is situated in Southern Norway and is an EMEP (European Monitoring and Evaluation Programme) monitoring site (e.g., Yttri et al., 2007) mainly surrounded by forest. The measurements were taken once a week with a sample volume of about 500 m^3 air taken over a 24-h period with a high volume sampler (years 2004–2009).

The research station Zeppelin is situated on a ridge of Zeppelin mountain on the west coast of Spitsbergen. At Zeppelin, by 48-h sampling 1000 m^3 of air were collected every week (years 1998–2009).

Alert is a baseline site in the World Meteorological Organization's Global Atmospheric Watch Network. It is located on the northeastern tip of Ellesmere Island in Nunavut. The samples at Alert represent approximately 13,000 m^3 of air and were sampled over seven days each week of the year (years 1998–2007).

Detailed descriptions of the sampling processes and analytical methods can be found in Hung et al. (2005); Bossi et al. (2008); Eckhardt et al. (2009), and on the UNECE–EMEP website: http://www.emep.int.

For our analysis, we selected PCB-28 (2,4,4′-trichlorobiphenyl) representing the less chlorinated congeners, PCB-101 (2,2′,4,5,5′-penta-chlorobiphenyl) representing the medium-weight PCBs, and PCB-180 (2,2′,3,4,4′,5,5′-heptachlorobiphenyl) representing the heavier congeners.

2.2. PCB emissions

We used annual primary emission fluxes for the three PCB congeners from an emission inventory created by Breivik et al. (2007) for the years 1998–2009. We used the maximum emission scenario, which is the most realistic one (Breivik et al., 2007). However, there are still large uncertainties of the actual emission estimates (Breivik et al., 2002, 2007). The main emission regions for all considered PCB congeners are eastern North America, Europe, Western Russia and Japan (Fig. B.1 in the SM). There are sub-categories of primary PCB emissions whose source strengths depend on the ambient air temperature (Breivik et al., 2002). This temperature dependence exists for all source categories where PCBs are in direct contact with ambient air and where there is no technical process such as incineration that determines the PCB flux. We assumed that primary PCB emissions from outdoor sources, such as outdoor paints, joint sealants, transformers, and also emissions from landfills and from PCB spills to soils are temperature dependent. Approximately 80%, 44%, and 5% of the primary emissions of PCB-28, PCB-101, and PCB-180, respectively, belong to these sub-categories. We used equation (1) (Lamon et al., 2009) to account for the temperature-dependent seasonal variability of the PCB emissions:

$$\frac{E_2}{E_1} = \exp\left[\frac{\Delta U_A}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \quad (1)$$

where E_2/E_1 is the ratio of the emission rates by volatilization at temperatures T_2 and T_1, ΔU_A (Schenker et al., 2005) is the internal energy of vaporization of the PCB congener, and R is the gas constant.

When PCBs travel through the atmosphere it has been suggested that they move in a sequence of deposition and re-volatilization, called grasshopper effect. Thus secondary emissions from soil and seawater may occur. However, an inventory of secondary PCB emissions is not yet available.

Secondary emissions from soil may occur in regions close to primary sources, where deposition from air has formed PCB reservoirs in soils and the direction of soil–air exchange is now from soil to air. In addition, PCBs can be released from soil back to air in warm regions and in regions with relatively low soil–air partition coefficients, i.e. regions with low soil Organic Matter (OM) content such as deserts (Li et al., 2010; Cabrerizo et al., 2011). Concerning the oceans, the available data indicate that in most parts of the oceans net deposition of PCBs takes place (Gioia et al., 2008a,b; Iwata et al., 1993). Gioia et al. (2008a) report results from PCB measurements in the North Atlantic and Arctic Ocean. In 74 pairs of samples in air and water for four PCB congeners, they found fugacities in air higher than in water in 71 cases, indicating net deposition from air to water. In the three other cases, the fugacities were very similar, indicating air/water equilibrium.

We conclude from the currently available studies on PCB re-emissions from soil and seawater that there is no evidence for strong secondary PCB emissions, at least not in regions without primary sources. We therefore do not include secondary PCB emissions from soil or oceans in our emission inventory.

2.3. Model calculations

The Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Stohl et al., 2005, 1998) calculates trajectories of so-called tracer particles. The particles move according to the mean wind field and turbulent fluctuations. The scheme of Emanuel and Zivkovic-Rothman (1999) is used for moist convective transport. It has been described and tested by Forster et al. (2007). FLEXPART was run backward in time with operational analysis data from the European Center for Medium Range Weather forecast (ECMWF) with $1^\circ \times 1^\circ$

resolution for the years 1998–2009. During every 3-h interval 60,000 so-called particles were released at the measurement point. The time interval of 3 h was adapted to the PCB sampling interval of each station. We considered backward runs for the measurement stations located at Birkenes, Zeppelin, and Alert. The particles were followed backward in time for 20 days. In backward mode, FLEXPART calculates an emission sensitivity function S, called source–receptor relationship (Stohl et al., 2003; Seibert and Frank, 2004). The S value, in units of s m^{-3}, in a particular grid cell is proportional to the particle residence time in that cell. The distribution of S close to the surface is of particular interest, as most emissions occur near the ground. Thus, S values are calculated near the ground, for the so-called footprint layer 0–100 m above the ground. The footprint indicates where the air has resided near the ground, and thus had the potential to take up pollutants before arriving at the measurement station. S can be combined with emission distributions of any chemical species to calculate receptor concentrations of that species, assuming that the species is not affected by chemical or other removal processes. In this study, we use S directly for our statistical analysis, but also in combination with emission distributions for PCB congeners, to identify source region contributions for the measured PCBs. We calculated average footprints (Hirdman et al., 2010) from the gridded footprint emission sensitivity field, $S(i,j,n)$, where i and j are the grid indexes of the model output grid, and $n = 1 \ldots N$ are the number of PCB observations available at the measurement site. The average footprint S_T is calculated as

$$S_T(i,j) = \frac{1}{N}\sum_{n=1}^{N} S(i,j,n) \tag{2}$$

We calculated average footprints for summer months (JJAS) and winter months (NDJFM). N (in Equation (2)) is the number of single footprints assigned to each season.

Next, we calculated average footprints for the 20% highest and lowest measured concentrations (after removing a linear trend from the data). We selected $L = N/5$ and calculated the average footprint emission sensitivity,

$$S_P(i,j) = \frac{1}{L}\sum_{l=1}^{L} S(i,j,l), \tag{3}$$

only for this data subset, where the percentile P is either 20 or 80. We then calculated the relative fraction R_P to remove the bias occurring due to decrease of emission sensitivity with distance from the measurement site.

$$R_P(i,j) = \frac{L}{N}\frac{S_P}{S_T} \tag{4}$$

If the measured PCB concentrations were completely unrelated to air mass transport patterns, $R_P(i,j) = 0.2$ would be expected for all i,j, because the full data set and the subset would look the same. The deviation from 0.2 contains information on sources and sinks (Hirdman et al., 2010). However, not all features of the R_P field are statistically significant. Regions with low S_T values indicate rare transport towards the receptor, even for the full data set, and are therefore not statistically significant for the R_P analysis. We used a threshold of $S_T < 10^{-9}$ s m^{-3} to remove spurious values of R_P (Hirdman et al., 2010).

3. Results and discussion

3.1. Variability of measured PCB concentrations

The trend and seasonal cycle for Zeppelin (ZEP) and Alert (ALT) are discussed by Hung et al. (2010) and for Birkenes (BIR) by Eckhardt et al. (2009). We calculated monthly median concentrations to compare the absolute values and the seasonal variability for the different PCB congeners at each station and between the stations (see Fig. 1). The different sampling times at the stations were considered in this calculation. Fig. 1 also shows the 80th and 20th percentiles.

There is no clear seasonal cycle for PCB-28 at Birkenes, monthly median values are between 1.2 pg m^{-3} and 1.5 pg m^{-3} throughout the year. At Zeppelin, PCB-28 concentrations are highest. Median values range from 2 pg m^{-3} in winter to 4 pg m^{-3} in summer. This seasonal cycle with higher values in summer than in winter is only visible at Zeppelin. At Alert PCB-28 concentrations range from 0.5 pg m^{-3} in summer to 0.8 pg m^{-3} in winter, which is just the opposite of the seasonal cycle at Zeppelin.

The concentrations measured for PCB-101 are highest at Birkenes, with slightly higher values in summer (0.8 pg m^{-3}) than in winter (0.6 pg m^{-3}). PCB-101 concentrations are between 0.3 pg m^{-3} and 0.5 pg m^{-3} at Zeppelin and Alert. At Zeppelin concentrations are slightly higher in winter than in summer.

PCB-180 has the lowest concentrations of the three considered PCBs. The concentrations are highest at Birkenes ranging from 0.07 pg m^{-3} in winter to 0.2 pg m^{-3} in summer. At Zeppelin, PCB-180 concentrations range from 0.04 pg m^{-3} to 0.06 pg m^{-3}. At Alert, PCB-180 concentrations are in the same range as for Zeppelin but with slightly higher values in summer than in winter.

For PCBs 101 and 180, higher concentrations at Birkenes can be explained by the station's relative proximity to source regions in Europe. However, there is no obvious explanation for the elevated PCB-28 concentrations at Zeppelin in comparison to Birkenes.

The variability of PCB concentrations may be caused by changing atmospheric transport patterns, by changing emissions and by loss processes acting on airborne PCBs. Among these factors, we focus on the influence of atmospheric transport patterns on the measured PCB concentrations.

3.2. Transport climatology of the measurement stations

The general transport climatology of Birkenes, Zeppelin, and Alert for summer and winter is given by the seasonal average footprint. The footprint indicates where the air has resided near the ground before arriving at the station, and therefore shows the potential source regions for this time. The footprints are shown for summer (JJAS) and winter (NDJFM) in Fig. C.2 in the SM.

The maximum S_T values are found in the vicinity of the measurement station and decrease with distance from the station. At Birkenes in summer, the decrease with distance is much stronger in the east of the station than in the west. In winter, the decrease is similar for both directions, indicating a stronger influence from the European continent in winter. The influence of Northwestern Europe for Birkenes is similar in summer and winter, but southern Europe is only important in winter. Transport from North-America to Birkenes is more important in winter than in summer. These results are in agreement with the source region description of Eckhardt et al. (2009).

The seasonal footprints for Zeppelin and Alert have been presented and discussed by Hirdman et al. (2010) and we just provide a brief overview here. In summer at Zeppelin high S_T values are found over the Arctic Ocean. The S_T values decrease sharply near the continental coasts, indicating that air arriving from the land masses is less likely to reach Zeppelin within the 20 days of transport. However, there is still influence from the northern parts of Europe, Asia and Canada. In winter high S_T values are found even in western and southern Europe and over Russia. This is consistent with the general understanding of atmospheric transport patterns to the Arctic in winter, when low-level transport occurs primarily

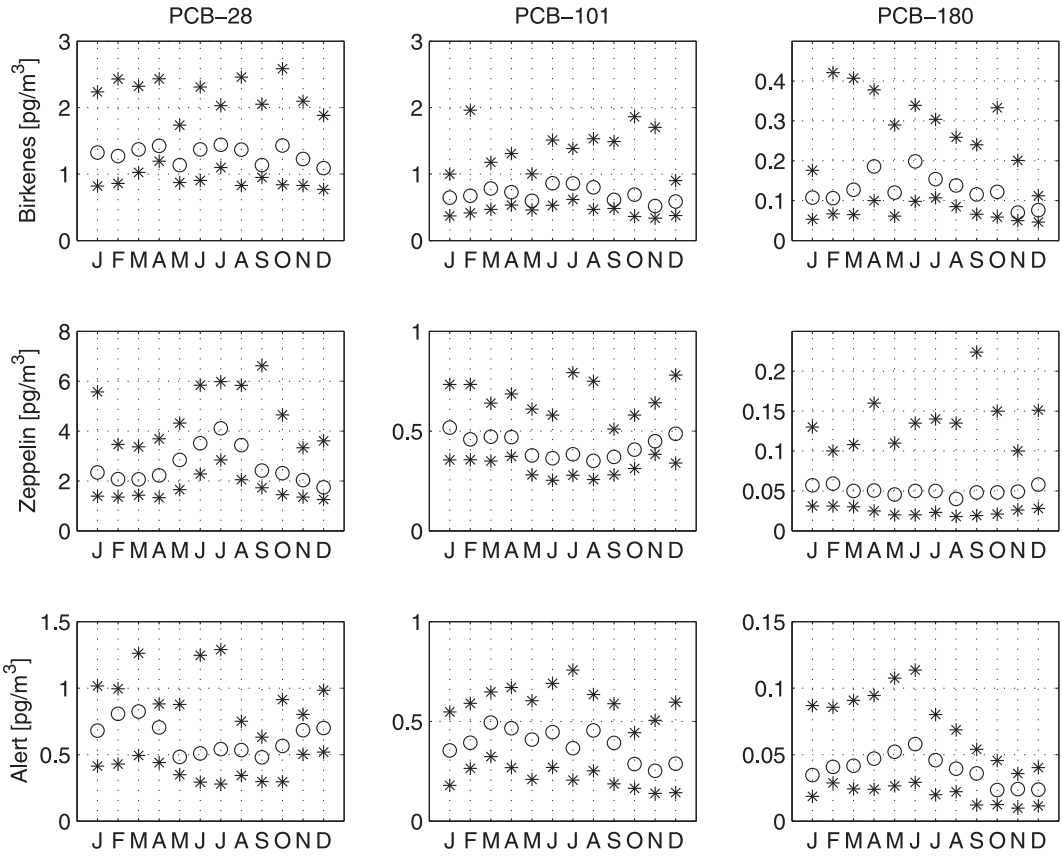

Fig. 1. Monthly PCB concentrations in pg m^{-3} measured at Birkenes (top), Zeppelin (middle), and Alert (bottom). The median concentrations are marked as circles, the 80th and 20th percentiles as stars.

from Eurasia (Barrie, 1986; Klonecki et al., 2003; Stohl, 2006; Law and Stohl, 2007; Shindell et al., 2008).

A similar distribution of S_T values is found for Alert. Generally, the influence of North America is more important for Alert than for Zeppelin. In winter, the high S_T values are more shifted to eastern Russia in comparison to Zeppelin. The S_T values over Central Europe are around two times lower for Alert in comparison to Zeppelin. Since PCB emissions are very high in this area, this is an important distinction and should lead to higher PCB concentrations at Zeppelin than at Alert (see Fig. 1).

3.3. Composite analysis

The general transport climatology of the three stations discussed in Section 3.2 is independent of the PCB measurements at the stations. To identify potential source regions of PCBs at Birkenes, Zeppelin, and Alert we coupled the transport calculations with the highest and lowest PCB measurements at the respective stations. We calculated the composite patterns, see Section 2.3, derived for the upper and lower 20% of the measured PCB-28, PCB-101, and PCB-180 concentrations for summer and winter at all stations (Figs. 2 and 3; composite patterns for PCB-180 are presented in the SM, Fig. D.3). Regions where R_P exceeds 0.2 (orange to red) are potential source regions. R_P values below 0.2 (blue) indicate that transport from these regions is less important for the considered concentrations.

3.3.1. PCB-28

At Birkenes (Fig. 2), high PCB-28 concentrations in summer are associated with transport from Central-, Eastern-Europe and Western Russia, and the US west coast, where R_P values exceed 0.2. In winter, transport from Central Europe is dominant. Episodes when the lowest 20% of the PCB concentrations were measured are associated with transport from the Arctic-, North Atlantic-, and Pacific-Ocean and from Eastern Russia. The composite patterns also indicate that there is no significant influence from Central Europe when PCB-28 concentrations are in the lower 20%.

The Zeppelin composite patterns are more noisy than the Birkenes composite patterns. However, for the upper 20% percentile in summer, a strong influence from Scandinavia and Eastern Europe is visible, where R_P values are above 0.2. In winter, the composite patterns indicate influence from the European continent and the US and Canada. The lower 20% of the PCB-28 concentrations in summer are associated with transport from the Arctic Ocean and from regions in Eastern Russia, where primary PCB emissions are low. Again, the influence from Europe is low.

At Alert, the composite patterns are not very pronounced. For elevated PCB-28 concentrations in summer, some influence from Scandinavia and Canada is visible. In winter, the composite patterns demonstrate influence from the European continent and Western Russia. Low PCB-28 concentrations in summer are neither related to transport from Europe and North America. In winter, low PCB-28 concentrations are related to transport from the North Atlantic Ocean and Eastern Russia.

3.3.2. PCB-101

The composite patterns of PCB-101 measured at Birkenes are similar to those of PCB-28. In summer, elevated PCB-101 concentrations are associated with transport from the US and Europe. In winter, high PCB-101 concentrations are associated with transport

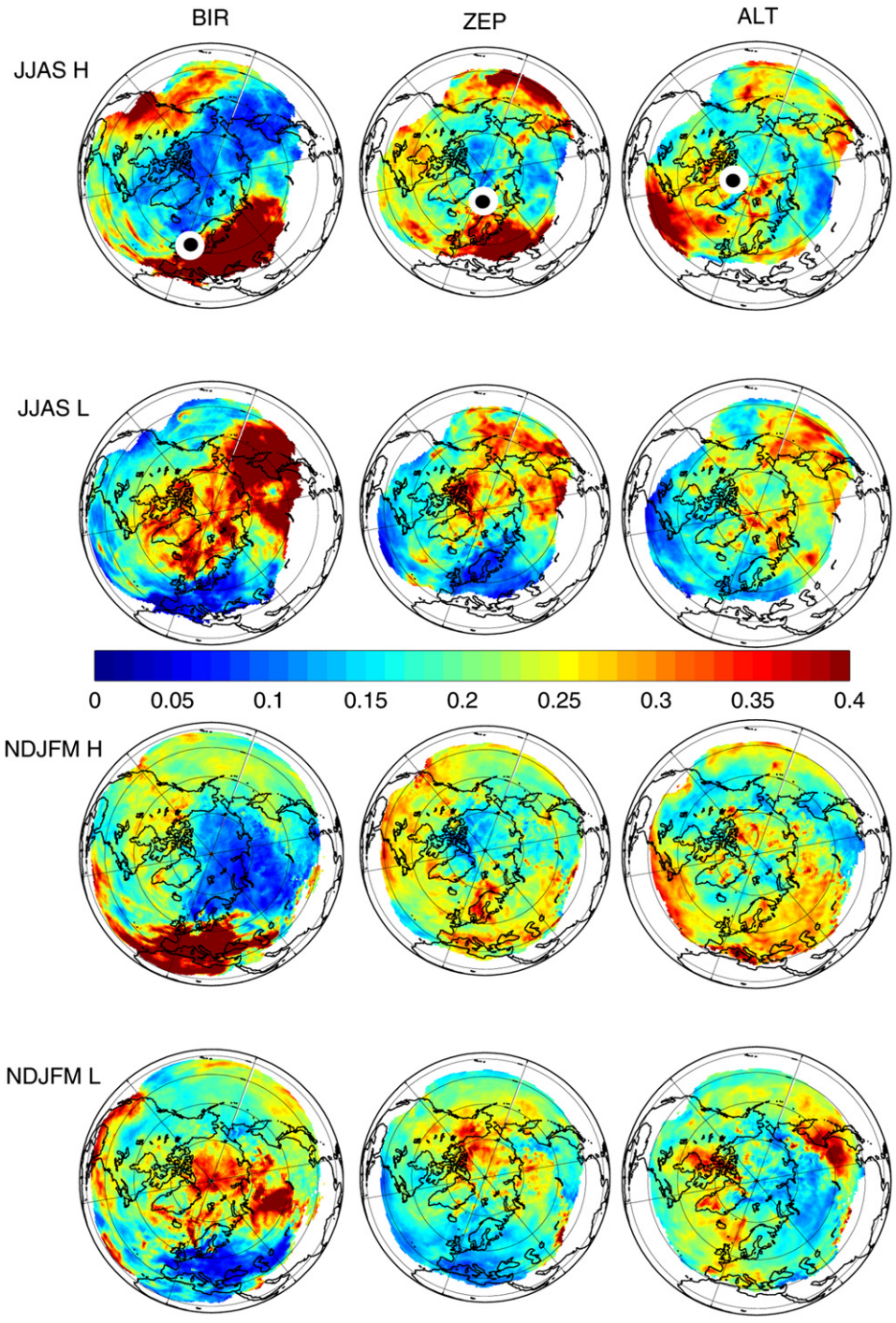

Fig. 2. Composite patterns (R_P) indicating the potential source regions for the highest (H) and lowest (L) 20% of PCB-28 concentrations measured at Birkenes, Zeppelin, and Alert for summer (JJAS) and winter (NDJFM). Areas where the average footprint (S_T) is too low (white) were excluded from the analysis. The stations are marked with black dots.

from Central Europe. PCB-101 concentrations for the lower 20% percentile are not related with transport from the main primary PCB emission regions over Europe (R_P values are below 0.2, see blue color in Fig. 3).

Also at Zeppelin, the composite patterns for PCB-101 are similar to those of PCB-28. In summer, the upper 20% percentile of PCB-101 is associated with transport from Europe, with R_P values exceeding 0.2. In winter, elevated PCB-101 values are related with transport from Europe and from the US.

High PCB-101 concentrations measured at Alert cannot be related to enhanced transport from the continents in summer. The composite patterns indicate transport from the Atlantic and Pacific Ocean. In winter, the composite patterns show large influence from Europe. For the lowest 20% of PCB-101, the composite patterns are rather inconclusive in summer and winter.

The interpretation of the Alert composite patterns is more complicated in comparison to Birkenes and Zeppelin, due to the low temporal resolution of the measurements (7 days), which makes it difficult to detect individual transport events. Additionally, Alert is the station most isolated from continental source regions, and especially in summer the Arctic front retreats far to the North limiting direct low-level transport from the surrounding continents.

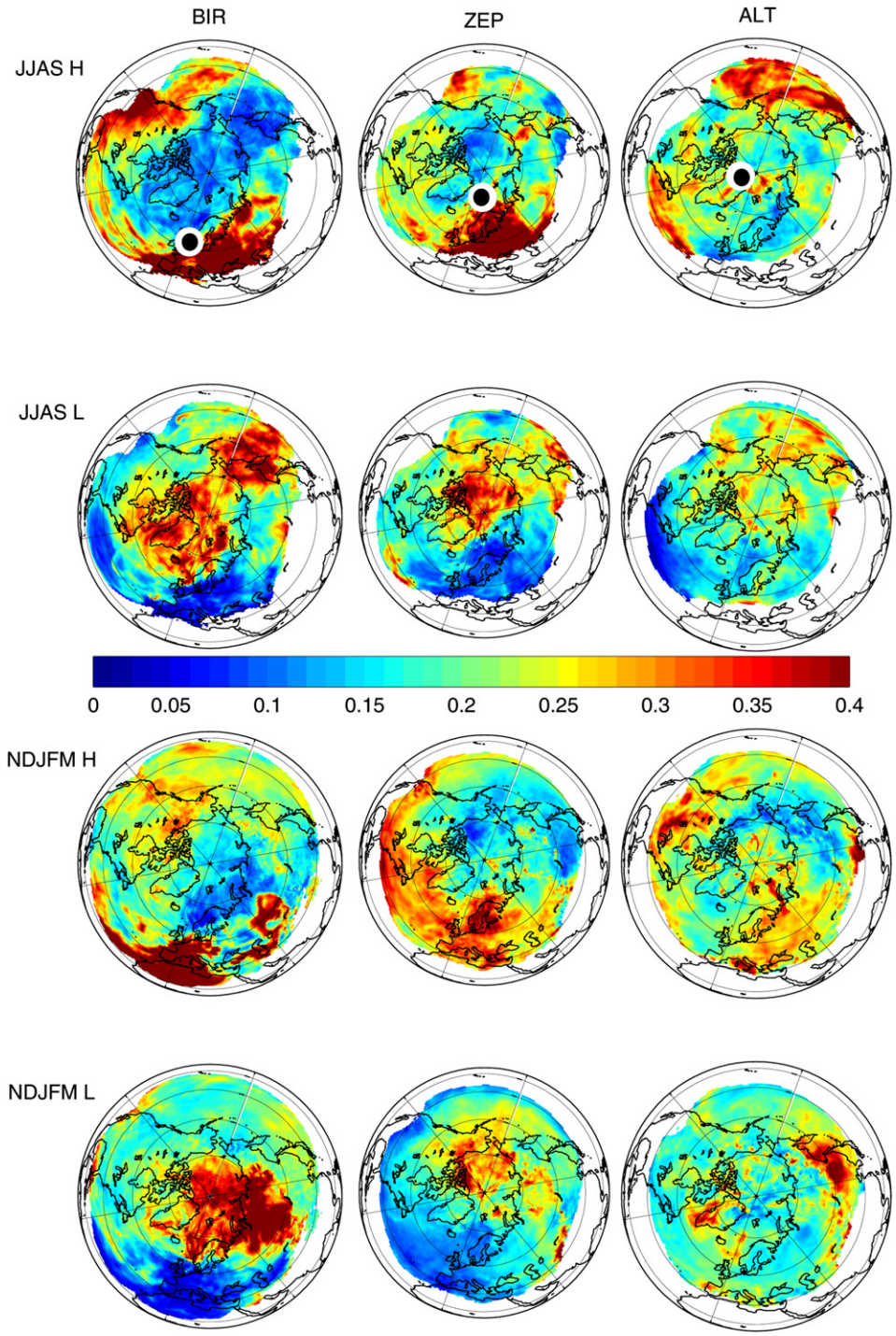

Fig. 3. Composite patterns (R_P) indicating the potential source regions for the highest (H) and lowest (L) 20% of PCB-101 concentrations measured at Birkenes, Zeppelin, and Alert for summer (JJAS) and winter (NDJFM). Areas where the average footprint (S_T) is too low (white) were excluded from the analysis. The stations are marked with black dots.

3.4. Primary source region contribution

The composite patterns discussed above provide information about the potential source regions influencing the measurement site for the highest and lowest measured PCB concentrations, but do not include PCB emission information. To determine the importance of PCB source regions, we combined the S_T fields with the primary emission inventory of each PCB congener, resulting in Emission Contribution (EC) maps. We integrated the results of the EC maps for ten selected primary PCB emission regions (see Fig. E.4 in the SM) to determine their relative contributions to the PCB concentrations measured in summer and winter (Fig. 4). To this end, we used all PCB measurements available for each season without separating them into high and low concentrations.

For PCB-28 at Birkenes in summer, around 30% is contributed by Central Europe and similar contributions (>10%) come from the UK, the US, Eastern Europe and Western Russia. In winter, Central Europe is the dominant source region, contributing 43% to the total

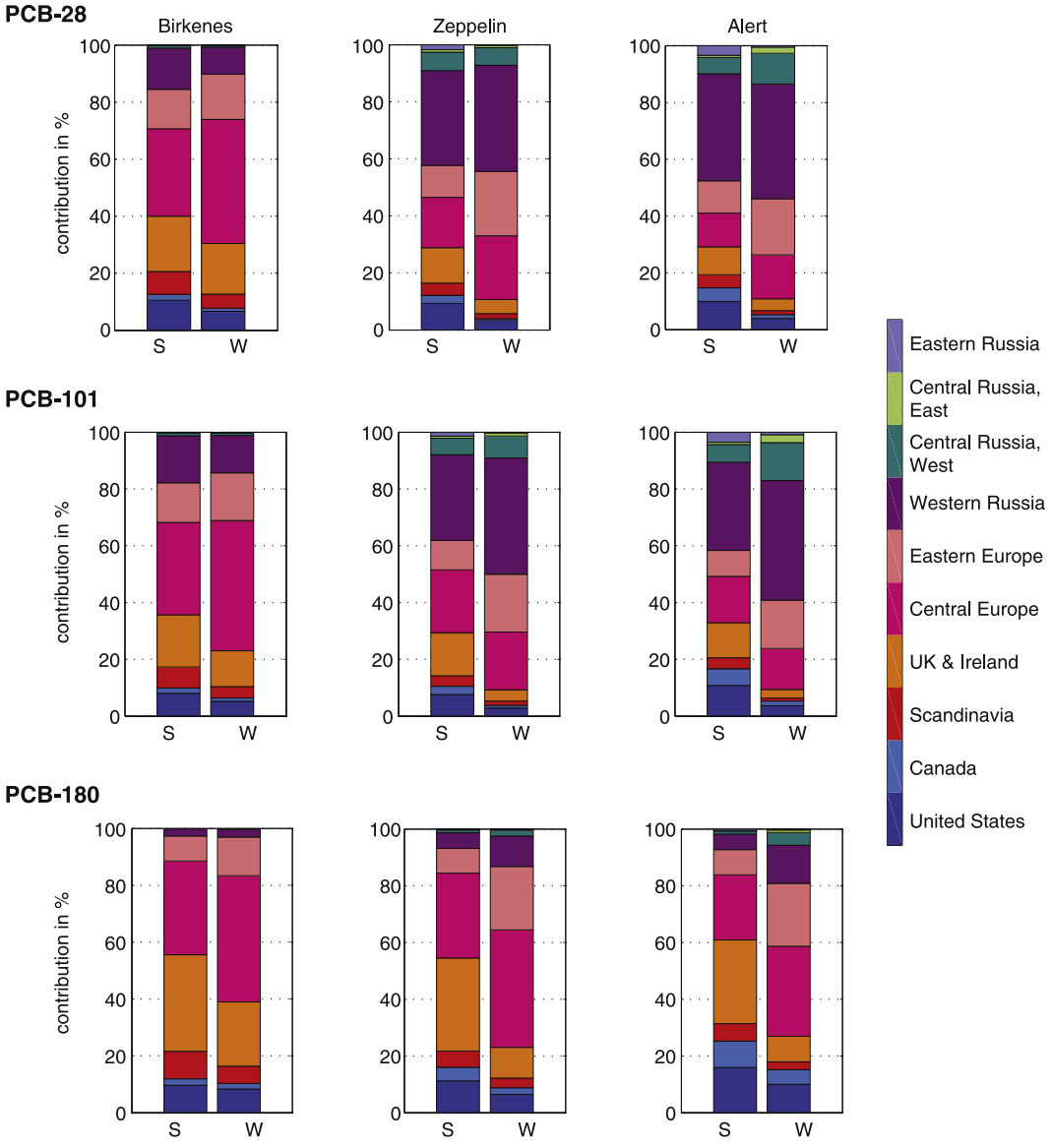

Fig. 4. Regional relative source contributions of PCB-28, PCB-101, and PCB-180 measured at Birkenes, Zeppelin, and Alert for JJAS (S) and NDJFM (W).

load of PCB-28 at Birkenes. The dominance of Central Europe in winter can be explained by high S_T values together with strong emissions in that area.

The emission contributions for PCB-28 are similar for Zeppelin and Alert. Western Russia is the most important source region in summer (35%) and winter (40%). High S_T values over Western Russia are responsible for the dominance of this sector in summer and winter. The dominance of Western Russia was also found by Malanichev et al. (2004).

Important contributions from the US for PCB-28 are only found in summer, when high PCB-28 emissions occur in this area.

For PCB-101, the emission contributions are similar to those of PCB-28 for all three measurement stations.

For PCB-180, the source contributions are similar for Birkenes, Zeppelin and Alert, and they are notably different from those of PCB-28 and PCB-101. In summer, around 30% is contributed by the UK and Central Europe. Central Europe dominates in winter, with contributions above 40% at Birkenes and Zeppelin, and 30% at Alert. At the Arctic stations in winter, contributions from Eastern Europe are higher than for Birkenes. Contributions from the US are higher in summer than in winter and are higher for Alert (16%) than for Birkenes and Zeppelin.

Because S_T is the same for each PCB, the similarity of the emission contributions for PCB-28 and PCB-101 (Fig. 4) indicates that their emissions are similarly distributed. On the other hand, the different emission contributions for PCB-180 and the lighter congeners can be explained by higher emissions of PCB-180 in the European region.

In addition to the above analysis, we also analyzed the emission contributions for the highest and lowest 20% of the PCB concentrations at all stations. Only at Birkenes the source region contributions are significantly different for high and low measured concentrations; this analysis is presented in the SM.

The finding that the source region contributions at the Arctic stations Zeppelin and Alert are similar for high and low PCB concentrations indicates that the meteorological transport pattern remains rather constant within the season, which leads to similar source region contributions, even for different PCB concentrations. Thus, the results obtained for Zeppelin and Alert reflect the constant transport pathways to the Arctic. During winter-time, low

level transport into the Arctic occurs primarily from Eurasia. A strong Arctic front in summer limits the transport from continental high-emission regions to the Arctic (Barrie, 1986; Klonecki et al., 2003; Stohl, 2006).

For the Arctic stations the actual contributions from Central and Eastern Europe are higher in winter than in summer, indicating that the seasonal change of atmospheric transport patterns is more important than the seasonal change of primary PCB emission source strength.

4. Uncertainty considerations

A major uncertainty is the potential contribution of secondary emissions to the measured PCB concentrations. Current data still indicate that it is unlikely that there are strong secondary emissions from soils in regions where there are not already primary sources (Li et al., 2010). In other words, it is unlikely that there are remote regions that have become significant new PCB sources just because of PCB revolatilization.

For the oceans, studies indicate that deposition dominates over volatilization (Gioia et al., 2008a,b). However, the range of fluxes estimated by Gioia et al. (2008a,b) also includes at the upper bound some positive fluxes from the ocean to the atmosphere. To calculate how much the oceans would contribute to the PCB burden at the Arctic measurement sites if they are a secondary source for PCBs, we took the maximum flux of 0.1 ng m^{-2} d^{-1} reported by Gioia et al. (2008a) and divided this value by four because the flux was given as the total for four PCBs. We thus assumed an emission of 0.025 ng m^{-2} d^{-1} from the entire seawater surface. In this scenario, at Zeppelin and in the summer, the oceans contribute 15% for PCB-28, 40% for PCB-101, and 74% for PCB-180. Contributions in winter are less than half of the summer contributions. The ocean contributions at Alert (19% for PCB-28, 59% for PCB-101, 86% for PCB-180) are higher than at Zeppelin, because Alert is even more influenced by the oceans. Currently, this scenario is highly unlikely, because Gioia et al. (2008a) report net deposition for the large majority of their measurement sites. However, this situation may change in the future when primary emissions further decrease and secondary emissions become more important (Nizzetto et al., 2010).

The choice of 20 days for the backward calculations together with exclusion of chemical-specific removal processes is another source of uncertainty. 20 days of backward calculations were also used in other studies (Halse et al., 2011) dealing with the transport of PCBs and were found to cover PCB transport from the important PCB source regions. Additionally, our footprint analysis (Section 3.2) showed that the main PCB emission regions located in Europe, Russia and the US, are covered within the 20 day of transport. Other studies (Hirdman et al., 2010) dealing with transport to the Arctic stations Zeppelin and Alert also showed in their footprint calculations that Europe and Russia are well covered.

Chemical-specific removal processes would have an influence on the absolute values of S_T, but as can be seen by the results of Eckhardt et al. (2009) the general location of the footprint is similar for model runs with and without removal processes. Because we use S_T and S_P relative to each other, exclusion of removal processes does probably not affect our main conclusions.

5. Conclusions

In this paper we combined PCB measurements from three measurement sites (Birkenes, Zeppelin, and Alert) with backward calculations from the Lagrangian Particle Dispersion Model FLEXPART to determine the source regions for times when the highest and lowest PCB concentrations were measured in summer and winter.

We analyzed average footprints (emission sensitivity) to assess the general atmospheric transport to each station. We found that the atmospheric transport from the continents is much stronger in winter than in summer. For Alert and Zeppelin, the emission sensitivity over the European continent is by a factor of ten higher in winter than in summer.

We calculated composite maps to link measured PCB concentrations with air mass transport patterns. The composite patterns for Birkenes are more pronounced than those for the Arctic stations. The pronounced composite patterns over Europe indicate that primary emission sources of PCBs are still important for the PCB levels measured at Birkenes and Zeppelin. At Alert, the composite patterns are generally less pronounced indicating that enhanced PCB concentrations are not primarily caused by changes in transport patterns.

Finally, we estimated emission contributions of ten primary source regions of the northern hemisphere to the measured PCB concentrations. Central Europe is the most important emission region for PCB-28, PCB-101, and PCB-180 measured at Birkenes, contributing around 44% in winter and 30% in summer to the total PCB load. For the Arctic stations, Western Russia is the most important source region for PCB-28 and PCB-101 with contributions above 30% in summer and winter.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.atmosenv.2012.07.061.

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