RECORD HIGH PEAKS IN PCB CONCENTRATIONS IN THE ARCTIC ATMOSPHERE DUE TO LONG-RANGE TRANSPORT OF BIOMASS BURNING EMISSIONS

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Abstract
Soils and forests in the boreal region of the northern hemisphere are recognised as having a large capacity for storing air-borne Persistent Organic Pollutants (POPs), such as the polychlorinated biphenyls (PCBs). Following reductions of primary emissions of various legacy POPs, there is an increasing interest and debate about the relative importance of secondary re-emissions on the atmospheric levels of POPs. In spring of 2006, biomass burning (BB) emissions from agricultural fires in Eastern Europe were transported to the Zeppelin station on Svalbard, where record-high levels of many air pollutants were recorded. Here we report on the extremely high concentrations of PCBs that were also measured during this period. 21 out of 32 PCB congeners were enhanced by more than two standard deviations above the long-term mean concentrations. In July 2004, about 5.8 million hectare of boreal forest burned in North America, emitting a pollution plume which reached the Zeppelin station after a travel time of 3-4 weeks. Again, 12 PCB congeners were elevated above the long-term mean by more than two standard deviations, with the less chlorinated congeners being most strongly affected. We propose that these abnormally high concentrations were caused by BB emissions. (More Information at: http://www.atmos-chem-phys-discuss.net/7/6229/2007/acpd-7-6229-2007.pdf)

Introduction
PCBs are intentionally produced organochlorine chemicals, assumed to have no signficant natural sources[1]. Primary emissions of PCBs into the atmosphere have been estimated to occur mainly in the industrialized regions of the middle latitudes. Following significant reductions in primary emissions over the last decades[2], the relative importance of secondary re-emissions is expected to increase[3]. Thus, it becomes important to investigate if there are processes that may have the potential to significantly enhance secondary re-emissions from major environmental storage reservoirs. Around 21 kt (1.6% of the cumulative production) of PCBs are stored in background soils, where the greatest reservoir is found between 45º- 60º N. [4]. Levels of PCBs in forest soils are typically elevated in comparison to grassland soils, because of the forest filter effect[5]. Thus, soils in the middle latitudes are playing a key role in the overall global fate of PCBs by both reducing the inflow of PCBs into the Arctic and acting as a significant reservoir of PCBs deposited in the past. BB is known to be a large source of many other air contaminants and BB plumes can be transported over intercontinental[6] and even hemispheric-scale[7] distances. It has been recognised that distinct chemical elements can be stored in the soils or biomass for a long time and, during a fire, can be re-injected into the atmosphere and subsequently transported over great distances. This has been documented, for instance, for mercury[8], and for radioactive cesium-137, which was produced by nuclear bomb testing in the last century and is still stored in forests[9]. However, we are not aware of a study that has documented an episode with enhanced atmospheric PCB concentrations as a result of BB. In this study, we show that PCB levels were greatly enhanced during two previously documented LRAT episodes[10,11] during which BB emissions were transported thousands of kilometres to a measurement station in the European Arctic.

Method
We present weekly measurements from the research station Zeppelin (11.9º E, 78.9º N, 478 m a.s.l.). The station is situated in an unperturbed Arctic environment on a ridge of the Zeppelin mountain on the western coast of Spitsbergen. For sampling of a variety of POPs, a combination of glass fiber filter and two polyurethane foam plugs was used. The isomer identification and quantification was done with GC/MS using a Hewlett-Packard 5890II (1990-2003) or 6890 (2003-2006) gas chromatograph coupled to an AutoSpec mass spectrometer.
Simulations of atmospheric transport were made using the Lagrangian particle dispersion model FLEXPART[12] (see http://zardoz.nilu.no/~andreas/flextra+flexpart.html). FLEXPART releases so-called tracer particles at emission sources and calculates their trajectories using the mean winds interpolated from the meteorological input fields plus random motions representing turbulence, and a deep convection scheme. FLEXPART was driven with operational analyses from the European Centre for Medium-Range Weather Forecasts with 1º x 1º spatial and 3 hourly temporal resolution. A special

feature of FLEXPART is the possibility to run it backward in time to produce information on the spatial distribution of sources contributing to a particular measurement [13,14]. Simulations with high time resolution were presented in the previous papers [10,11]. Here, backward simulations were made for the two two-day time periods over which the samples of main interest for this study were taken. 800000 particles were released from the location of the Zeppelin station for each of the two samples. The particles were followed backward in time for a couple of weeks, forming what we call a retroplume, to calculate a so-called potential emission sensitivity (PES) function [13,14]. The word potential here indicates that this sensitivity is based on transport alone, ignoring atmospheric removal processes that would reduce the sensitivity. The value of the PES function (in units of s/kg) in a particular grid cell is proportional to the particle residence time in that cell. It is a measure for the simulated mixing ratio at the receptor that a source of unit strength (1 kg/s) in the respective grid cell would produce. Of most interest is the PES in a so-called footprint layer (0-100 m above ground), where we assume that surface emissions of PCBs take place. The PES map informs us about where the sampled air mass was sensitive to emission input from a possible PCB source. We have clear evidence from a number of measurements and model results that the Zeppelin station was strongly influenced by BB emissions during two episodes in summer 2004 and spring 2006. These two episodes were presented in detail in two recent papers [10,11].

Results

In spring 2006 smoke from agricultural fires in Eastern Europe (mostly Russia, the Baltic countries, Belorussia and the Ukraine) intruded into the European Arctic and caused the most severe air pollution episodes ever recorded there, with significant reductions in visibility [11]. After a first short episode at the end of April, a stronger episode lasted from about 1 May until 5 May in the afternoon. Fortunately, a PCB sample was collected from May 1 at 10:14 UTC until May 3 at 08:38 UTC, a period that was heavily influenced by the BB emissions, except for the first few hours.

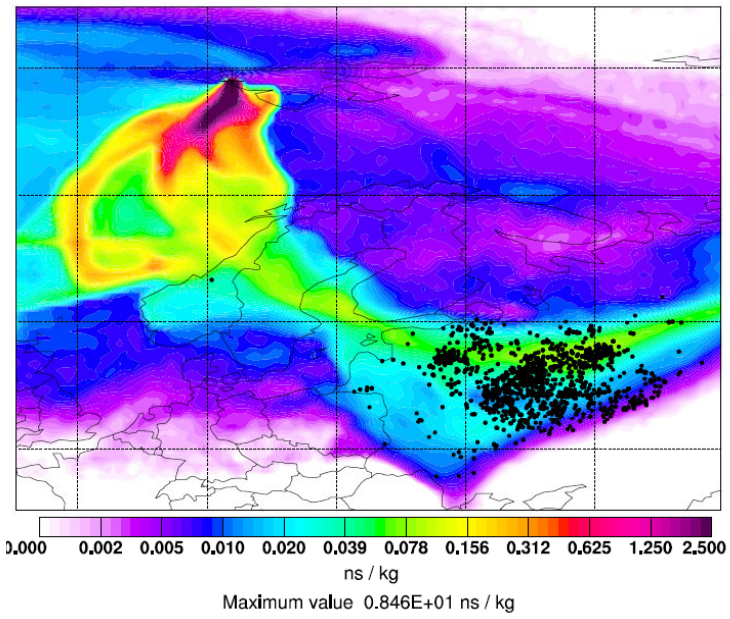

Fig.1: Transport pathway (backward in time) of the emission released during agricultural fires in Eastern Europe, the transport time up to the Zeppelin station in Spitsbergen was around 3 days. The contours show the potential emission sensitivity (PES) footprint map (0-100 m) for air arriving at Zeppelin between 1 May 2006 at 10:14 UTC and 3 May 2006 at 8:38 UTC 2006. Black dots show MODIS fire detections on days when the footprint emission sensitivity in the corresponding grid cell on that day exceeded 2 ps kg^{-1}.

Fig. 1 shows the footprint PES map from a retroplume simulation calculated 20 days back from the time period when the PCB sample was taken. Also shown are the locations of fires that were active on days when the retroplume passed over them. Over the two day measurement period the transport remained confined to a relatively narrow pathway that passed exactly over the region where the fires were burning in Eastern Europe. The transport from the fire region to the station took about 3-4 days.

During summer of 2004, about 2.7 million hectare of boreal forest burned in Alaska, the by far largest annual area burned on record, and another 3.1 million hectare burned in Canada. It was shown that smoke from these fires filled large parts of the Arctic [10]. Episodes of strongly enhanced concentrations of light absorbing aerosols were found at the stations Barrow (Alaska), Alert (Canada) and Summit (Greenland). At Zeppelin, the influence was relatively weak compared to Barrow and Summit, since the station is 4000 km away from where the fires burned and the air mass transport took about 3-4 weeks. To get an overview of how strong the enhancements were during the BB influenced periodes, long-term mean PCB concentrations and their variability at Zeppelin, data for 32 congeners from the period 1 January 2002 until 8 May 2006 were ananlysed. A box and whisker plot shows the statistics of all PCB-congeners (Fig. 2). Both BB episodes (26th to 28th of July 2004 (green dot), 1st to 3rd of May 2006 (orange dot)) clearly stand out.

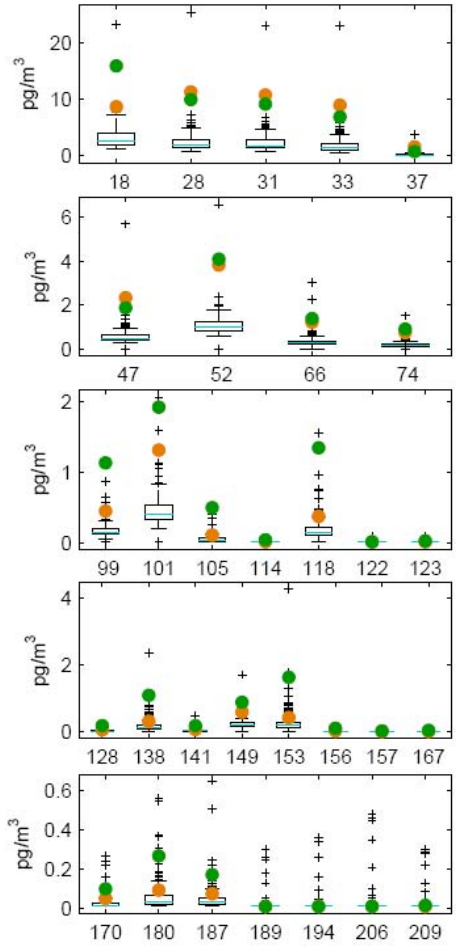

Fig 2: Box and whisker plots showing the frequency distributions of all PCB congeners [pg/m3] sampled at the Zeppelin station during the period from January 2002 to May 2006. The line shows the median, the box delineates the 25 and 75 percentiles, the whiskers are drawn at the 1.5 folded inter quartile range and the crosses mark outliers. The green dots indicate the sample from 26 to 28 July 2004, the orange dots indicate the sample from 1 to 3 May 2006.

For the lighter congeners (PCBs 28 and 52), the values are the second and third highest measured but even for the heavier congeners, the values are quite strongly enhanced. To compare the values measured during the BB episodes to the long-term record, we calculated for every congener how many times the standard deviation they are enhanced above the long-term mean. The forest fire episode during 2004 shows the clearest signal in the less chlorinated PCBs. For instance, for PCBs 52, 28 and 101, the values are 4.8, 4.3 and 3.4 times the standard deviation above the mean, respectively. In contrast, during the agricultural waste burning episode in 2006, the lighter as well as the heavier PCBs are significantly elevated (from 2.6 up to 6.6 times the standard deviation). The concentrations of most

congeners were strongly enhanced during the BB episodes. Of the 32 measured congeners the following eleven congeners were elevated by more than two standard deviations during both episodes: 18, 28, 31, 33, 47, 52, 66, 74, 99, 101, 149. In 2006, in addition the following ten congeners 105, 114, 118, 128, 138, 141, 153, 156, 167, 180 met the criterion. PCB 37 is the only congener which was high in 2004, but not in 2006. To summarize: During the episode in 2004, 12 out of 32 congeners, had extremely high concentrations outside the normal range of variability. The lighter chlorinated PCBs (i.e. all tri-CBs and tetra-CBs as well as 2 penta-CBs) were elevated more strongly than the heavier ones. In 2006, 21 out of 32 congeners were very high, with no systematic dependence on the level of chlorination.

Conclusion

Large-scale mass production of PCB ceased several decades ago. A significant fraction of the amounts produced in the past have now found their way into vegetation and surface soils of the boreal regions of the Northern hemisphere, which has a large capacity to retain various POPs. PCBs are still considered a serious threat to Arctic ecosystems, and the atmosphere has been shown to be a key pathway for these chemicals into the northernmost areas of the globe. So far, the perception has been that the occurrence of PCBs in Arctic air may be explained by transport of contaminated air masses from urban source regions and by repeated air-surface exchange (commonly termed grass-hopping). In this study, we argue that BB has the potential to boost re-emissions of POPs from terrestrial reservoirs, and that BB is a significant, yet overlooked, source of these chemicals into the atmosphere on a hemispherical scale. Moreover, our results illustrate that BB not only have the potential to re-release PCB that have been stored in soil and vegetation, but that this also results in significantly elevated levels in the Arctic, several thousands of kilometres away from the regions being subject to such fires. As the prevalence of BB events are expected to increase as a result of climate change, climate change may even mitigate the efficiency of contemporary control strategies for POPs that were motivated to protect vulnerable ecosystems of remote areas.

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