LEVELS OF PBDE IN AMBIENT AIR OF VIENNA

Gans O, Moche W, Thanner G and Uhl M

Federal Environment Agency Austria, Spittelauer Lände 5, Vienna, Austria

Abstract
In 2006 the Federal Environment Agency Austria carried out a sampling program for PBDE in ambient air at a sampling station in Vienna. The program consited of two sampling periods in winter and summer 2006, lasting 18 days each. The sampling of PBDE was carried out by a two stage high volume sampler Six samples have been collected consecutively during winter and summer period respectively, resulting in an overall sampling period of 18 days. Twenty-five PBDE congeners have been analysed in this study, but only eight congeners show a considerable contribution namely BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209. The total concentrations of the eight most abundant PBDE congeners lay in the range between 13 and 36 pg/Nm³ and are by a factor of ten lower than the total ambient air concentration of the 6 indicator PCB at the same sampling site in Vienna. During winter BDE-209 was the most abundant congener in the PBDE pattern, whereas in summer BDE-47 and BDE-209 were most abundant. The variations of the concentrations among the samples of one sampling period were twice as high in winter than in summer.

Introduction
In 2005 and 2006 the Federal Environment Agency Austria together with the Slovakian Hydrometrological Institute carried out the Project „Ballpop“, with the aim to get more information about the situation of POPs in the two very close conglomeration areas Vienna (Austria) and Bratislava (Slovakia). [1]. In each city an ambient air sampling site has been installed. At both sites the PM 10, PM 2.5 and PAH concentrations were measured whereas in Vienna Nitro-PAH and Nonylphenols have been investigated in those small particulates over a one year period. Additionally the ambient air concentrations of PBDE were measured in Vienna in two sampling periods in winter and summer 2006, lasting 18 days each. These PBDE measurements were the first exploration of these persistent pollutants in ambient air in Austria.

Materials and Methods
The sampling of PBDE was carried out by a two stage high volume sampler according to the German standard method VDI 3498/2. Ambient air has been sampled with a sampling rate of 14 m³/h for 72 hours resulting in a sample volume of about 1000 m³. The pollutants were collected on a glass fibre filter (GF 8, Schleicher & Schüll, Germany) and two PU-foam plugs. For the control of the sampling efficiency ^{13}C-labeled BDE-15 was spiked onto the GF-filter as a sampling standard prior to sampling.

Six samples have been collected consecutively resulting in an overall sampling period of 18 days. One sampling period was carried out during winter season in January 2006 and second one during summer season in June 2006. There was no rain or snowfall respectively during the sampling periods. The table 1 gives the sampling dates together with the average ambient temperature during sampling.

Table 1: Dates and average temperatures of three day sampling periods.

Date	Temperature (°C)	Date	Temperature (°C)
16.01.–19.01.2006	1,3	13.06.–16.06.2006	23,0
19.01.–22.01.2006	-1,1	16.06.–19.06.2006	24,7
22.01.–25.01.2006	-5,6	19.06.–22.06.2006	26,8
25.01.–28.01.2006	-9,2	22.06.–25.06.2006	24,4
28.01.–31.01.2006	-5,4	25.06.–28.06.2006	26,4
31.01.–03.02.2006	-2,4	28.06.–01.07.2006	21,0

Analysis

The analytic method used, published by W.Knoth et al.[2], includes soxhlet extraction by toluene, cleanup by 4 steps of column liquid chromatography and measurement with a GC/HRMS System. The quantification was done by isotope dilution with 10 ^{13}C-labeled standards, which were added prior to extraction. The detection limits were in the range between 0.002 and 0.9 pg/Nm³.

The following 25 PBDE congeners have been analysed: BDE-11, BDE-17, BDE-25, BDE-28, BDE-47, BDE-49, BDE-77, BDE-85, BDE-99, BDE-100, BDE-116, BDE-118, BDE-126, BDE-138, BDE-140, BDE-153, BDE-154, BDE-155, BDE-166, BDE-181, BDE-183, BDE-196, BDE-197, BDE-203 and BDE-209 .

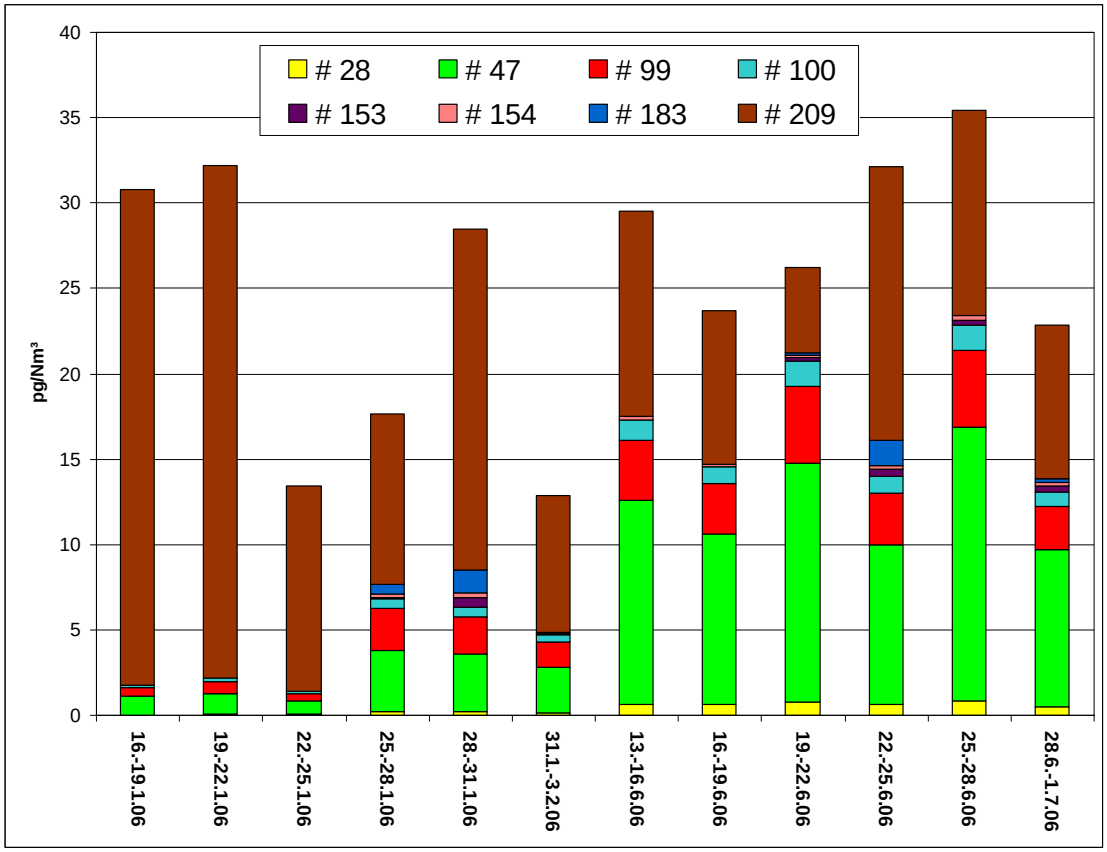
Results and discussion

Twenty-five PBDE congeners have been analysed in this study, but only eight congeners show a considerable contribution to the total concentrations. These eight congeners, which show a concentration of more than 0.5 pg/Nm³ in at least one of the 12 ambient air samples, are BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209. The total concentrations of these eight most abundant congeners are in the range of 12.8 pg/Nm³ and 35.4 pg/Nm³ (see picture 1).

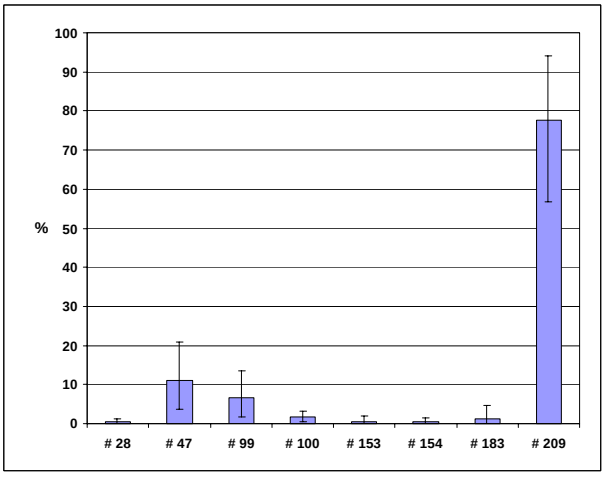
In the winter period BDE-209 (DecaBDE) was the most abundand congener with a contribution to the totals in the range of 57% to 94% (mean 77%). The concentrations of the individual congeners show very high variations during the six consecutive sampling periods.

In the summer period the situation was different, the contribution of the congeners BDE-47 and BDE-209 were nearly equal and together in a height of about 80 % of the totals. The third and fourth highest contributions, together about 20% of the totals, show the congeners BDE-99 and BDE-100. The concentrations of the individual congeners show much smaller variations during the six sampling periods in summer than found in the six winter periods. The reason could be that during summerly weather conditions especially the lower brominated congeners vaporize from ubiquitous sources giving a more homogenous distribution of the PBDE concentrations in ambient air. The pictures 2 and 3 show the average congener patterns of the winter and summer sampling periods.

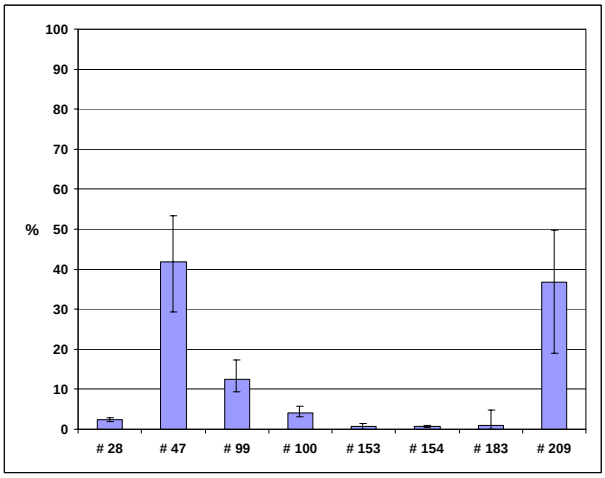
Picture 1: Total concentrations of the eight most abundant congeners



Picture 2: Average Congener pattern of the winter period including minimum and maximum contribution



Picture 3: Average Congener pattern of the summer period including minimum and maximum contribution



Conclusions

At the sampling site in Vienna the total concentrations of the eight most abundant PBDE congeners lay in the range between 13 and 36 pg/Nm³ and are by a factor of ten lower than the total ambient air concentration of the 6 indicator PCB at the same sampling site in Vienna [3]. During winter BDE-209 was the most abundant congener in the PBDE pattern, whereas in summer BDE-47 and BDE-209 were most abundant. The variations of the concentrations among the samples of one sampling period were twice as high in winter than in summer.

From a toxicological point of view the detected concentrations will cause no direct adverse affect to the citizens. Nevertheless the fate of these dangerous substances should be observed by ambient air monitoring programs in the same way as it is already done for other POPs like PCDD/F and PCB.

Acknowledgements

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