

CHANGES IN CONCENTRATIONS OF PAHs AND PCBs IN BRISBANE ATMOSPHERE BETWEEN SUMMER 1994/95 AND 2012/13

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Introduction

PAHs and PCBs are persistent organic pollutants (POPs) and priority pollutants and subject to international treaties to control their emission (i.e. the 1998 Protocol on POPs, the Stockholm Convention). As for many semivolatile organic chemicals, the atmosphere is an important route for human exposure either directly (e.g. PAHs) or via introducing them into the food chain (e.g. PCBs). One of the key tools for measuring the success in elimination of priority pollutants like PCBs and PAHs is through routine atmospheric monitoring programs such as The Integrated Atmospheric Deposition Network (IADN) in the Laurentian Great Lakes Region and The Toxic Organic Micropollutants Program (TOMPs) in the UK. However, with the exception of the Global Atmospheric Passive Sampling (GAPS) program (established in the last decade), to our knowledge, neither in Australia nor anywhere else in the Southern Hemisphere has long-term atmospheric monitoring programs for POPs been carried out. The GAPS program established some background monitoring sites in Australia and some other countries in the Southern Hemisphere in 2004¹. However, the use of passive samplers may limit the interpretation to chemicals that occur primarily in the gas phase. For PAHs, on the other hand, the main focus often is on higher molecular weight compounds that are more potent in terms of genotoxicity, such as benzo[a]pyrene.

One of the first studies on PAHs and PCBs in air in Australia commenced in the early 1990s on a sampling platform of Griffith University, a site which is essentially unchanged over the last twenty years and located about 8 km from the Brisbane City Centre in a forest reservoir². The few subsequent studies carried out on atmospheric PAHs and PCBs in and around Brisbane since 1990s have been more or less random with regard to space and time. This has limited any efforts in assessing whether PAH and PCB concentrations in the Brisbane atmosphere have changed.

The objective of this study is to revisit the 1994/95 study and repeat sampling and analysis with the aim to evaluate changes in PAH and PCB concentrations and compound profile in the Brisbane atmosphere between 1994/95 and 2012/13. The results will serve as a basis for further detailed studies to assess the contribution of sources to the concentrations of these priority pollutants. To our knowledge, this is the first study reporting the temporal trend of atmospheric PAHs and PCBs over almost two decades in Australia.

Materials and methods

For the purpose of this study we aimed to reproduce the sampling protocol that had been used to collect the samples in 1994/95. As mentioned above, the sampling was carried out at a sampling platform on a roof of a building in Griffith University at Nathan, Brisbane (27°33'12" S, 153°3'15" E). The filter-adsorbent type samplers were used with a sampling rate of approximate 4 m³/h (low_volume sampler) and 10 m³/h (medium_volume sampler). The sampling volume was calculated via recording the read of the gas meter before and after each sampling period. The 'particle associated fraction' of the samples were collected on glass fiber filters (GFFs) and XAD-2 cartridges were used to collect the 'gas phase' PAHs and PCBs. For the current work, three samples were collected from Nov 9th 2012 to Jan 11th 2013, Jan 17th 2013 to Jan 23rd 2013 and Jan 23rd 2013 to Jan 25th 2013, respectively. For comparison, data from Dec 15th 1994 to Jan 13th 1995 (for PAHs) and from Mar 3rd 1995 to Mar 10th 1995 (for PCBs) were selected. The temperature of each sampling duration was similar (25 °C in 94/95 during the sampling period for PAHs, 26 °C in 1995 during the sampling period for PCBs and 25°C in 12/13 during the sampling period for PAHs and PCBs) as well as the daily average rainfall (2 mm in

94/95 during the sampling period for PAHs, 2 mm in 1995 during the sampling period for PCBs and 3 mm in 12/13 during the sampling period for PAHs and PCBs)^{3,4}.

For the 2012/13 samples, the XAD cartridges and GFFs were extracted separately using an Accelerated Solvent Extractor (Dionex ASE 350) after being spiked with a solution containing 8 deuterated PAHs and 6 ¹³C₁₂-PCB congeners at different levels as the internal standards. Extracts from both XAD and GFFs were concentrated to 1 mL in hexane. A quarter of the extract was cleaned up by neutral alumina and neutral silica for PAHs and the remaining three quarters were cleaned up by neutral alumina and acid silica for PCBs. PAHs were eluted with 20 mL of the mixture of hexane: DCM 1:1 (v/v) and PCBs were eluted with 15 mL of hexane. The eluant was carefully blown down to almost dryness and recovery standard (50 ng of deuterated benzo[e]pyrene for PAHs and 200 pg of ¹³C₁₂-PCB 141 for PCBs) added before analysis by a Shimadzu GC-2010 gas chromatography coupled with QP-2010 mass spectrometer under EI-SIM mode.

A DB-5MS column (J&W Scientific) was used to separate the compounds (1 uL sample injection). The initial oven temperature was 80 °C held for 2 min, then raised to 180 °C at 20 °C min⁻¹, held for 0.5 min, and finally ramped to 290 °C at 10 °C min⁻¹ for 8 min. The injector, interface and EI source temperatures were 250 °C, 280 °C and 250 °C, respectively. Those peaks with a signal/noise ratio ≥ 3 were recognized and a total of 13 PAHs *viz.* phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IcdP), dibenzo[a,h]anthracene (DahA) and benzo[g,h,i]perylene (BghiP) and 6 PCB congeners *viz.* PCB 28, 52, 101, 153, 138 and 180 were quantified. The recovery of the internal standards ranged from 57% to 110%.

Results and discussion

PAHs. Figure 1 shows a comparison of concentrations of 13 PAHs (gas+particle-associated phases) between samples collected in Summer of 94/95² and Summer of 12/13 (this campaign). Depending on the specific PAH compound, concentrations decreased by 36% to 93% over this period. For BaP, which is classified as an IARC group 1 compound⁵, the level declined by 65% from 0.13 ng/m³ to 0.05 ng/m³. The concentration of \sum_{13} PAHs decreased by 85% over the last 18 years, whereas the contributions of different compounds to the summed PAH level remained relatively similar (Figure 2) where compounds with 3 rings dominated the profile of atmospheric PAHs.

We assume that the results are directly comparable (i.e. sampling and analysis did not contribute to the difference between 94/95 and 12/13). Hence the decrease reflects a combination of a) a decrease of PAHs from primary sources that may result from reduced emissions from combustion sources such as vehicles, including for example due to the introduction of the hybrid transmission systems in Brisbane in 1991⁶ and/or the Environmental Protection Act in 1994 which enforced the compliance to the particle release factor standard of the equipment for residential fuel-burning⁷ and/or b) a decrease in the release of PAH from 'reservoirs' such as soils that may act as the secondary sources.

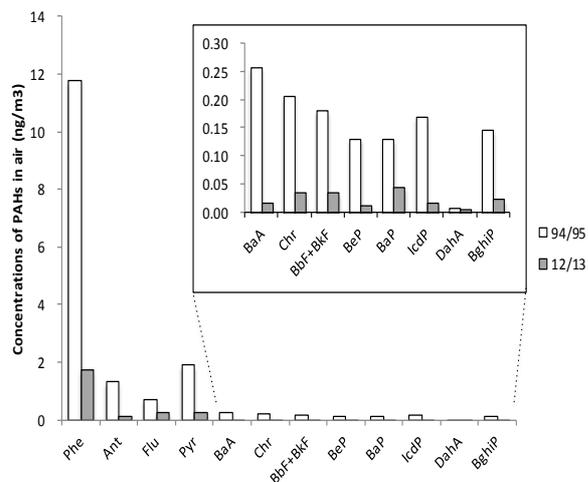


Fig. 1 Comparison of atmospheric concentrations of individual PAHs in Brisbane between 94/95 and 12/13

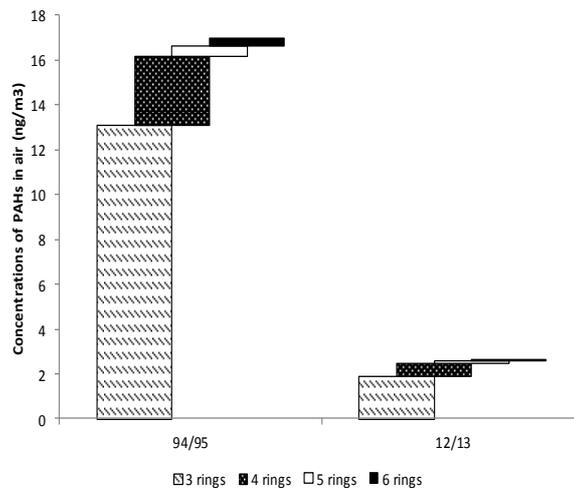


Fig. 2 Comparison of atmospheric concentration of and contributions of different compounds to Σ_{13} PAHs in Brisbane between 94/95 and 12/13

PCBs. None of the PCBs of interest were detected associated with particles either in the current campaign or in the study in 1995 so only the PCBs in the gas phase are presented. A comparison of concentrations of 6 PCB congeners between samples collected in 1995² and 12/13 is shown in Figure 3. Concentrations of each of the PCB congeners of interest were between 54% and 99% lower, except for PCB 52, which, interestingly, increased by 140% compared to 1995. Figure 4 shows the concentration of and the contributions of different compounds to Σ_6 indicator PCBs in 1995 and 12/13 respectively. On this basis, the concentration decreased by 22% compared with 1995 and the contributions of different compounds changed from tri-chlorinated congeners dominance to one where tetra-chlorinated congeners dominated due to the increase of PCB 52.

Again we assume that the results were directly comparable. Given this, the result may indicate that a) more PCB 28 was degraded during the long-range transport (LRT) since the rate constant for reaction of OH radicals with tri-chlorinated PCB congeners is 1.27 times that for tetra-chlorinated PCB congeners in gas phase⁸ and/or b) PCBs emitted from a 'reservoir' (e.g. soil) comprised more PCB 52 than 28 to the air since the half-life of PCB 52 in soil is about twice as long as PCB 28⁹. Overall, the results in this study indicate that the concentration of PCBs in the gas phase in Brisbane is currently dominated by historical PCB sources rather than the contemporary ones.

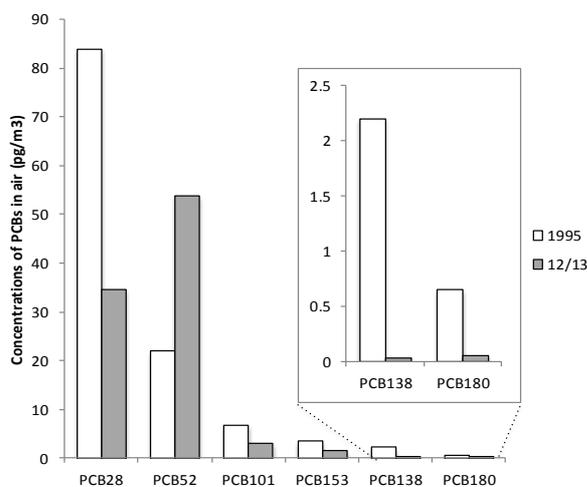


Fig. 3 Comparison of atmospheric concentrations of 6 indicator PCB congeners in Brisbane between 1995 and 12/13

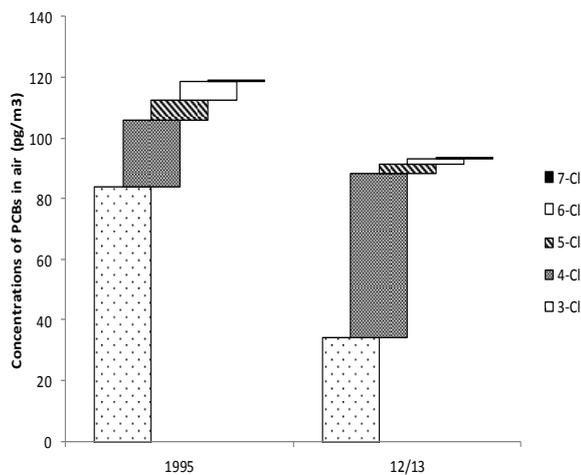


Fig. 4 Comparison of atmospheric concentrations of and contributions of different compounds to \sum_6 indicator PCBs in Brisbane between 1995 and 12/13

Although more samples are needed (especially the samples from a winter campaign) to further support the trend and to increase our confidence in their interpretation, the results show that atmospheric PAHs and PCBs in Brisbane over the last two decades have substantially been reduced, proving the success in reduction of priority pollutants like PAHs and indicating that historical PCB sources dominate the current concentration of PCBs in Brisbane air.

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