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Changes in Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls between the 1990s and 2010s in an Australian City and the Role of Bushfires as a Source

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Abstract
Over recent decades, efforts have been made to reduce human exposure to atmospheric pollutants including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) through emission control and abatement. Along with the potential changes in their concentrations resulting from these efforts, profiles of emission sources may have also changed over such extended timeframes. However relevant data are quite limited in the Southern Hemisphere. We revisited two sampling sites in an Australian city, where the concentration data in 1994/5 for atmospheric PAHs and PCBs were available. Monthly air samples from July 2013 to June 2014 at the two sites were collected and analysed for these compounds, using similar protocols to the original study. A prominent seasonal pattern was observed for PAHs with elevated concentrations in cooler months whereas PCB levels showed little seasonal variation. Compared to two decades ago, atmospheric concentrations of $\sum_{13}$ PAHs (gaseous + particle-associated) in this city have decreased by approximately one order of magnitude and the apparent halving time ($t_{1/2}$) was estimated as 6.2 ± 0.56 years. $\sum_{6}$ iPCBs concentrations (median value; gaseous + particle-associated) have decreased by 80% with an estimated $t_{1/2}$ of 11 ± 2.9 years. These trends and values are similar to those reported for comparable sites in the Northern Hemisphere. To characterise emission source profiles, samples were also collected from a bushfire event and within a vehicular tunnel. Emissions from bushfires are suggested to be an important contributor to the current atmospheric concentrations of PAHs in this city. This contribution is more important in cooler months, i.e. June, July and August, and its importance may have increased over the last two decades.

Capsule
PAH and PCB concentrations have decreased significantly compared to 2 decades ago and the contribution of bushfires to PAH concentrations has increased with time.

Key words
Polycyclic aromatic hydrocarbons; Polychlorinated biphenyls; Seasonal variation; Temporal change; Emission source profile.
1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are semi-volatile organic chemicals (SVOCs) and important pollutants because they are relatively persistent, toxic and have been associated with human health risks (IARC, 2015). Over recent decades, efforts have been made at eliminating or reducing release of and human exposure to these chemicals. Such efforts include banning manufacture and uses (of PCBs) and implementing controls of emissions from sources such as industries, combustion engines, automobile and fuels (for PAHs) (Dimashki et al., 2001; Sun et al., 2006).

The atmosphere is a major route for human exposure to these pollutants both via direct inhalation (e.g. PAHs) and also by introducing them into the food chain (e.g. PCBs). Monitoring levels of PAHs and PCBs and their long-term temporal trends in the air are key tools for assessing the effectiveness of pollutant emission regulations (Hung et al., 2013; Klánová and Harner, 2013; Melymuk et al., 2014; UNEP, 2007). Thus a range of programs have been established around the world for the purpose of monitoring such air pollutants, including the Integrated Atmospheric Deposition Network (IADN) in the Laurentian Great Lakes Region (Buehler and Hites, 2002), the Toxic Organic Micropollutants Program (TOMPs) in the UK (FRA, 1991; Meijer et al., 2008), the Arctic Monitoring and Assessment Programme (AMAP) (AMAP, 2010; Hung et al., 2010) and the European Monitoring and Evaluation Programme (EMEP) (EMEP, 1983; Halse et al., 2011).

However, to the best of our knowledge, limited data are available for systematically investigating long-term (i.e. decadal) changes in levels of atmospheric SVOCs in the Southern Hemisphere. Programs such as the Global Atmospheric Passive Sampling (GAPS) network (Environment Canada, 2004; Pozo et al., 2006) and Monitoring Network (MONET) in Africa (Holoubek et al., 2011; RECETOX, 2015) are valuable but rely mainly on passive sampling techniques. Available passive sampling devices are either limited to chemicals that occur primarily in the gas phase (e.g. XAD-based ones) or have uncertain applicability for particle-associated compounds (e.g. polyurethane foam (PUF)-based ones) (Melymuk et al., 2014). However for PAHs for example, the main focus is often on higher molecular weight compounds such as benzo[a]pyrene (BaP) that are more potent in terms of genotoxicity (IARC, 2015) and primarily associated with particles.

Along with the implementation of elimination/abatement strategies and thus potential changes in the concentrations of these chemicals over extended timeframes, emission source
profiles may have also changed. For example in Australia over the last few decades, efforts have been made at reducing PAH emissions from vehicles by setting emission standards for diesels and mandating the installation of catalytic converters on light petrol vehicles (DIRD, 2015). As a result, estimated annual emissions of $\Sigma_{16}$ PAHs from motor vehicles have decreased from 740 tons in 1990 to 100 tons in 2010 (Shen et al., 2011). Other initiatives include reducing emissions from residential biomass burning by regulating the use of stoves for such purposes since the 1990s (e.g. Environmental Protection Act 1994 (Australian Government, 2015)).

However, over the last 20 years, emissions from another important potential source for PAHs in Australia, namely large-scale wildfires (bushfires) (Freeman and Cattell, 1990), are likely to have remained relatively constant. One piece of evidence for this is that the annual estimated burning areas in Australia have changed relatively little within this timespan (AFPA, 2014). Provided that other sources have been successfully regulated, bushfires may have become a relatively more important source for PAH emissions. Indeed, it has been estimated that in 2007, 31% of PAH emissions could be attributed to contributions from wildfires in Oceania (Shen et al., 2013). However, direct evidence for this increasing contribution based on field data is scarce in Australia.

PCBs were never manufactured in Australia and importation ceased in 1975 (DoE, Australian Government, 2014). Analyses have subsequently shown concentrations in Australian air to be low by world standards (Gras et al., 2004). Bushfires have been estimated as one potentially important emission source of PCBs (Eckhardt et al., 2007), during which the temperature of on-site soil/plant can be elevated significantly and thus a strong re-volatilisation is supported. However, relevant data are few in Australia (Black et al., 2012; Meyer et al., 2004).

One of the first published studies on levels of PAHs and PCBs in Australian air was conducted in 1994 - 1995 at seven sites in Brisbane (Mueller, 1997; Mueller et al., 1998). Since then a limited numbers of other studies have been carried out (Bartkow et al., 2004; Gras et al., 2004; Kennedy et al., 2010; Lim et al., 2005). However no systematic effort has been made to assess long-term changes of levels of these SVOCs and changes of related source profiles in Australian air.

Therefore, this study aimed to address this gap by i) determining current monthly and seasonal variations in atmospheric concentrations of PAHs and PCBs in Brisbane, ii) evaluating the changes in their concentrations and profiles after two decades and iii)
assessing the current contribution of bushfire emissions to the atmospheric concentrations of PAHs and PCBs and whether this has changed over the last two decades.

2. Materials and methods

2.1 Sampling sites and protocol

Ambient air sample collection. Monthly air samples were collected from July 2013 to June 2014 by revisiting two sampling sites in the 1994/5 study (Mueller, 1997; Mueller et al., 1998) in Brisbane, which has a subtropical climate with hot summers and moderately warm winters.

As seen in Figure 1, one site (Site Gri, 27°33’12” S, 153°03’15” E) is approximately 100 m a.s.l. in a forest reserve at Griffith University, about 8 km from the city centre. A bus-only stop is located 100 m to the south of this site. A relatively small traffic volume of approximately 200 compressed natural gas powered buses per day on average was estimated during the sampling period (http://translink.com.au/). The closest busy roads are 600 m to the south and over 1000 m to the east. Therefore Site Gri may be characterised as a city background site with limited direct impacts from vehicle emissions. There are no known point sources for PCBs around Site Gri. The other site (Site WG, 27°29’50” S, 153°02’10” E) is located 10 m from an intersection with traffic lights on a busy multi-lane road and opposite a carpark near to the city centre in the suburb of Woolloongabba. A traffic volume of approximately 53,000 vehicles daily was recorded in 2014 (BCC, 2014) for the road. This ground-level site was chosen to reflect the direct impact from vehicular emissions for PAHs, enabling comparison with Site Gri.

Self-designed active air samplers were used with a sampling rate of approximate 4 m³ h⁻¹, similar to the one typically used during the 1994/5 study (Mueller, 1997). The sampling volume was recorded using a gas meter connected to the outflow of the pump. The particle-associated fraction of the samples was collected on a glass fibre filter (GFF) (Whatman™, 90 mm Ø, grade GF/A), followed by a cartridge containing 10 g of XAD-2 (styrene-divinylbenzene copolymer, Supelco®, 90 Å mean pore size) to collect chemicals in the gas phase.

Bushfire emission sample collection. To obtain the emission profiles of PAHs and PCBs from bushfires, a series of samples were collected during a controlled burn event in August 2013 in Brisbane. A sampling site was established within 20 m of the fire. Air samples were collected
at the site prior to and during the actual burn event as well as during subsequent smoldering
and when the fire was extinguished.

A high-volume air sampler (Kimoto Electric Co., LTD.) was used with a typical sampling
rate of 60 m$^3$ h$^{-1}$. Particle-associated and gaseous chemicals were collected on a GFF
(Whatman™, 203×254 mm, grade GF/A) and a subsequent PUF plug (90 mm diameter and
40 mm thickness) respectively. The sampler was calibrated using an orifice plate prior to the
sampling campaign and the sampling volume was calculated based on the calibrated sampling
rate and sampling duration. A bypass gas meter installed on the sampler was used to monitor
any anomalous fluctuation of the sampling rate during the collection.

Tunnel sample collection. An air sample was collected from a traffic tunnel in Brisbane to
obtain emission profiles for PAHs directly related to vehicle exhaust. The sample was taken
using a portable air sampler (SAICI Technology Co., LTD., LSAM-100) operating at 0.14 m$^3$
h$^{-1}$ in one of the ventilation outlets of the tunnel from 25th August to 2nd September 2014. An
average traffic volume of approximately 14,000 vehicles per day was estimated during the
sampling period (DSITI, 2015). An XAD-2 cartridge (1 g) was used to trap chemicals
(gaseous + particle-associated phases) and the flow rate was checked at the beginning and the
end of the sampling period to ensure its constancy.

Detailed information related to sample collection is provided as S1 in the supplementary
material (SM).
2.2 Chemical analysis

The collected GFFs, XAD and PUFs were extracted separately using an Accelerated Solvent Extractor (ASE, Thermo Scientific™ Dionex™ ASE™ 350) after being spiked with a solution containing 7 deuterated PAHs and 18 $^{13}$C$_{12}$-PCB congeners at different levels as internal standards for quantification purposes (Table S2). Concentrated extracts were divided into three portions. The first portion (40% v/v) was cleaned up by neutral alumina and neutral silica for PAH analysis, the second (40% v/v) was cleaned up by neutral alumina and acid silica for PCB analysis and the third (20% v/v) was archived for future analytical investigations. Eluants were carefully blown down to near dryness and refilled with 250 pg of $^{13}$C$_{12}$-PCB 141 (in 25 µL isoctane) employed as the recovery/instrument standard for estimating the recoveries of the spiked internal standards and monitoring the performance of the analytical instrument.

Samples were analysed using a Thermo Scientific™ TRACE™ 1310 gas chromatograph coupled to a Thermo Scientific™ DFS™ Magnetic Sector high resolution mass spectrometer (GC-HRMS). The HRMS was operated in electron impact-multiple ion detection (EI-MID) mode and resolution was set to $\geq$ 10,000 (10% valley definition). An isotopic dilution method, as also used in the 1994/5 study (Mueller, 1997), was used to quantify 13 PAH analytes and 18 PCB congeners comprising dioxin-like ($dI$-PCB) and indicator ($i$PCB) compounds (Table S2). Details are given as S2 in the SM.

2.3 Quality assurance and quality control (QA/QC)

Breakthrough test. Three cartridges containing half as much XAD as used in the actual sampling campaigns were connected in series and an air sample was collected at Site Gri during September 2013 for both of the self-designed active air samplers and LSAM-100 (Figure S2). The duration of the sampling period and flow rate of the pumps were the same as those employed during the actual sampling campaigns. The three cartridges were then extracted and analysed separately. Breakthrough percentages for individual compounds were calculated by dividing the mass of compound collected on the back layer by the summed mass from all three layers.

In addition, a solution of breakthrough standards containing 3 deuterated PAHs ($^2$D$_{10}$-Ant, $^2$D$_{10}$-Pyr and $^2$D$_{14}$-DahA; 100 ng each) was spiked onto PUF plugs (and XAD cartridges)
before each sampling event. These standards have vapour pressures (at 25 °C) ranging from 7.8×10^{-2} Pa (\textsuperscript{2}D\textsubscript{10}-Ant) (Odabasi et al., 2006) to 6.0×10^{-4} Pa (\textsuperscript{2}D\textsubscript{10}-Pyr) (Mackay et al., 1997) to 7.2×10^{-7} Pa (\textsuperscript{2}D\textsubscript{14}-DahA) (Odabasi et al., 2006), consistent with the vapour pressure range of the compounds targeted within this study. Recoveries of these compounds were used to estimate the breakthrough percentage (if any) for chemicals collected on the PUF plugs (and XAD cartridges). Any significant (i.e. ≥ 30%) loss of the breakthrough standards indicated the need to take this into account in the quantification of relevant target compounds.

**QC samples.** Known amounts of target compounds were spiked onto replicated clean matrices (GFFs, XAD and PUFs; n = 5 for each) and these spiked matrices were analysed as for the actual samples to estimate the reproducibility of the analytical protocols.

**Blank samples and method detection limits (MDLs).** Within each batch of samples analysed (typically 10 samples per batch), a solvent blank, a matrix blank and a field blank were incorporated to check for any contamination related to instruments, the sample preparation system and transportation and storage of samples. MDLs were defined as the average field blank plus three times the standard deviation. If the relevant compounds could not be detected within the field blank samples, MDLs were determined based on half the instrument detection limits (IDLs). MDLs for PAH and PCB analytes were mostly lower than 10 pg m\(^{-3}\) and 10 fg m\(^{-3}\) respectively (Table S3).

### 3. Results and discussion

#### 3.1 QA/QC results

**Breakthrough.** The breakthrough percentage of chemicals was typically negligible (Table S3). During each sampling event, loss of the breakthrough standards from PUF plugs and XAD cartridges was also minimal, with the highest percentage observed approximately 10% for \textsuperscript{2}D\textsubscript{10}-Ant during an event in the 2013/4 summer period.

**Reproducibility.** Within the replicated QC samples (n = 15 in total), relative standard deviation (RSD) of the analytical results was less than 15% for most (90%) analytes (Table S3).

**Blank levels.** Within the solvent and matrix blank samples, none of the target compounds could be detected at levels > 1% of the typical levels found in any of the samples. Within the
field blank samples, *dl*-PCB congeners could not be detected and for *i*PCB congeners and PAH compounds the levels were < 3% of the average level detected with actual samples. All the samples were nonetheless field blank corrected if data were available.

*Recoveries of internal standards.* Recoveries of the internal standards within the samples were between 32% - 150% and for 80% of the analytes ranged between 50% and 120% (Tables S4, S8 and S9).

### 3.2 Concentrations of PAHs and PCBs and monthly/seasonal variations in 2013/4

Concentrations (expressed as annual mean ± SD) of $\sum_{13}$ PAHs in the gaseous and particle-associated phases were 2,100 ± 560 and 180 ± 110 pg m$^{-3}$ respectively for Site Gri and 4,400 ± 770 and 770 ± 320 pg m$^{-3}$ respectively for Site WG (see Table S4 for details). 3- and 4-ring PAHs dominated the $\sum_{13}$ PAH concentration profiles in the gas phase samples, accounting for > 99% of those. In contrast, 5- and 6-ring PAHs contributed over 50% to the PAH levels measured in the particle-associated phase. In all the samples, Phe had the highest concentration among the gaseous PAHs, accounting for 51% - 72% of the summed concentration. Among the particle-associated PAHs, BeP had the highest concentration in most (> 80%) samples, accounting for 11% - 33% of the summed concentrations. Typically, levels of each compound (gaseous + particle-associated) showed a seasonal pattern with higher concentrations measured in cooler months/seasons. (As an example, the pattern for BaP is depicted in Figure 2(a)). A significant correlation (typically $P < 0.0001$) was observed between reciprocal temperature and concentration for all PAHs occurring predominantly in the particle phase (i.e. from BaA to BghiP) (data not shown).

Concentrations (gaseous + particle-associated, annual mean ± SD) of $\sum_{18}$ PCBs were 19,000 ± 4,400 and 22,000 ± 6,400 fg m$^{-3}$ at Sites Gri and WG respectively with the concentration of $\sum_{6}$ *i*PCBs at Site WG 20,000 ± 6,400 fg m$^{-3}$. The latter was similar to levels found in 2012 at the same site using XAD based passive air samplers (15,000 fg m$^{-3}$) (Wang et al., 2015). Overall, PCB analytes were mainly found in the gas phase (> 90% for all congeners except for some hexa- and heptachlorinated congeners at Site WG in the cooler months of the year). Unlike the trend observed for PAHs, concentrations of PCB congeners seemed to lack a clear seasonal variation (Figure 2(b) and Table S4). This was different to the typical seasonal trend in temperate climate zones where higher concentrations are found in warm seasons (e.g. (Diefenbacher et al., 2015)).
Figure 2. Monthly concentrations (gaseous + particle-associated) of (a) BaP and (b) $\sum_{18}$ PCBs at Sites Gri and WG and the monthly average temperature in Brisbane from July 2013 to June 2014.

### 3.3 Changes in concentrations of PAHs and PCBs in Brisbane air over two decades

Compared to two decades ago in 1994/5 (Mueller, 1997), median concentrations of $\sum_{13}$ PAHs (gaseous + particle-associated) at Site Gri in 2013/4 decreased by approximately one order of magnitude from 19,000 to 2,200 pg m$^{-3}$ (Figure 3(a)). This trend was also evident for individual PAHs, with levels decreasing by factors ranging from 3.7 (BaA) to 13 (I123cdP), (Table S5).

As shown in Figure 3(b), the median concentration of $\sum_6$ iPCBs at this site decreased by 80% (from 75,000 to 15,000 fg m$^{-3}$) over these two decades with the trichlorobiphenyl congener PCB 28 achieving the greatest reduction (81%) (Table S5). Additionally, the concentration of $\sum_{12}$ dl-PCBs at Site WG decreased by 81% compared to levels measured in 2002/3 at a nearby site (Gras et al., 2004).
Figure 3. Changes of atmospheric concentrations (gaseous + particle-associated) of (a) $\sum_{13}$ PAHs and (b) $\sum_{6}$ iPCBs between 1994/5 and 2013/4 at Site Gri. (‘+’ denotes the mean value).

The rate of decrease of PAH and PCB concentrations in air has previously been expressed as a halving time, estimated based on a model that assumes an exponential decrease in concentration with time (Meijer et al., 2008; Sun et al., 2006). In this work, the apparent halving time ($t_{1/2}$; y) of an SVOC analyte in air was calculated from applying a first order decay model using PAH and PCB data (gaseous + particle-associated) collated from studies carried out at Site Gri or WG (Table S6) over the last two decades. Besides the current study, concentrations of atmospheric PAHs at Site Gri were available for most months in 1994/5 (based on samples collected for several days in specific months) and PCB data were available for March, May and June 1995 (Mueller, 1997). For Site WG, PAH concentration data were available for June to August 1994 (Mueller, 1997), April 2002 (Bartkow et al., 2004), January to February and July to August 2007 (Kennedy et al., 2010).

Calculated $t_{1/2}$ values for $\sum_{13}$ PAHs and $\sum_{6}$ iPCBs as well as individual analytes are shown in Table S7. The halving time estimated for $\sum_{13}$ PAHs in ambient air of both Brisbane sites is just over 6 years, similar to those reported for some other urban areas such as London (approximately 5 years) (Meijer et al., 2008) and Chicago (approximately 9 years) (Sun et al., 2006). The halving time of $\sum_{6}$ iPCBs in Brisbane air at Site Gri is estimated to be $11 \pm 2.9$ years, similar to those reported for a range of sites across the Great Lakes (approximately 15 years) (Salamova et al., 2013; Venier and Hites, 2010).

### 3.4 Potential sources for PAHs and PCBs in Brisbane air

#### 3.4.1 Site comparison (2013/4)

PAHs. Mean concentrations (gaseous + particle-associated) of each compound were consistently higher at Site WG (paired $t$ test with $P < 0.01$). This is illustrated in Figure 2(a) for BaP. As mentioned, Site WG is located close to an intersection and a carpark where frequent acceleration, deceleration and cold-starts of vehicles may be expected. These operations have been considered to greatly increase PAH emissions (Baek et al., 1991). Therefore the significantly higher concentrations of PAHs at Site WG should reflect a major impact of traffic-related emission sources (Agudelo-Castañeda and Teixeira, 2014; Daisey et al., 1986; Gunawardena et al., 2012; Lim et al., 1999; Nielsen, 1996; Shen et al., 2013). Furthermore, it is generally considered that emitted gaseous PAHs from such sources tend to
firstly sorb onto pre-existing particles and then a considerable fraction of the relatively volatile compounds desorb from particles during their further transportation (Baek et al., 1991; Broddin et al., 1980; Thomas et al., 1968; Van Vaeck and Van Cauwenberghe, 1984). A higher particle-bound fraction of medium sized PAHs such as BaA and Chr was observed at Site WG (69% - 92%, as compared to 16% - 62% at Site Gri), which again indicated that PAH concentrations measured at Site WG were impacted by adjacent fresh sources, i.e. vehicle exhaust.

PCBs. Unlike PAHs, although levels of most PCB congeners were higher at Site WG, this difference was significant (paired t test, $P < 0.01$) only for a few congeners such as PCB 101, 118 and 138. It has been concluded that city centre areas are important source regions for PCBs due to the presence of urban-characterising sources such as emissions from old buildings and electrical capacitors (Gasic et al., 2009; Motelay-Massei et al., 2005; Wang et al., 2015). The similarity between the two sites suggested that emissions from the city centre area of Brisbane may not be the only source for atmospheric PCBs at Site Gri.

3.4.2 Seasonal variation (2013/4)

PAHs. To determine seasonal patterns, mean concentrations of each PAH analyte in cooler months (June, July and August) at Sites Gri and WG were compared to those in summer months (December, January and February). A higher ratio of $C_{\text{winter}}/C_{\text{summer}}$ was found for most compounds at Site Gri compared to WG (e.g. 9.1 vs 4.6 for BaP). Assuming that these two sites are subject to essentially the same meteorological conditions including seasonal variations, then this difference should result only from difference in source related contributions. As discussed previously, PAH levels measured at Site WG should be mainly related to emissions from vehicle exhaust and thus the seasonal variations may be attributed to factors such as an increased prevalence of cold starts of vehicle engines during cooler months. The consistently higher ratios of $C_{\text{winter}}/C_{\text{summer}}$ observed at Site Gri however suggests important contributions from sources other than traffic-related emissions that are also more important in winter.

Residential/commercial heating has been predicted to account for 50% of total PAH emissions in Oceania (Shen et al., 2013), but it is unlikely that this source is of significant relevance in Brisbane. Mild winter temperatures (e.g. a mean temperature of 17 °C was recorded for winter in 2013/4) show that domestic heating is rarely required. Furthermore, a dominant proportion of this limited activity is associated with electrical and natural gas
fuelled heating rather than wood combustion (ABS, 2012a, b), due to the regulation of the use of stoves for residential biomass burning (Australian Government, 2015).

Long-range atmospheric transport (LRAT) of contaminated air masses is another potential source for atmospheric PAHs. Daily back trajectory of air masses (Draxler and Rolph, 2014) were modelled and integrated for summer and cooler months respectively and shown in Figure 4. A larger proportion of air masses originated from inland areas during cooler months of the year, compared to warmer months when air masses typically originated from over the ocean. Throughout the whole year, a high frequency of bushfires typically occur in inland areas of Australia (see Figure S3 from 2013/4 as an example) where a limited population resides (ABS, 2001). Therefore the major sources for PAHs in inland areas would arguably be emissions from large-scale bushfires rather than anthropogenic sources such as domestic heating (if any) or vehicle exhaust. Thus, emissions from bushfires are suggested to be an important contributor to atmospheric concentrations of PAHs measured in Brisbane, particularly in cooler months. If the same back trajectories of air masses are applicable to both sites, but vehicle (cold starting) adds to PAH levels at Site WG, the contribution from bushfires would be more important at Site Gri compared to WG.

**Figure 4.** Monthly concentrations of BaP (gaseous + particle-associated, pg m\(^{-3}\)) at Site Gri and back trajectory frequency of air masses in summer (left) and during cooler months (right) in Brisbane in 2013/4.

*PCBs.* Apart from the possible emissions from legacy electricity equipment and old building materials, another major source of PCBs in the air may be re-volatilisation from contaminated terrestrial surfaces such as soil, a process that is temperature-mediated. During bushfires, the temperature of soil increases dramatically over a short period, which enhances re-volatilisation as a source for PCB and dioxin emissions during this process (Eckhardt et al., 2007; Meyer et al., 2009; Primbs et al., 2008). The lack of an apparent seasonal pattern for
PCBs at both sites in 2013/4 indicated that either the temperature variation between seasons in this subtropical area was not great enough and/or in the cooler months, other important emission sources of PCBs also existed. Such sources may include the re-volatilisation from reservoirs such as soils.

3.4.3 Temporal changes

*PAHs.* As seen in Table S7, for most PAHs, the average halving time estimated at Site WG was shorter than that for Site Gri. This result may reflect the efforts of reducing levels of exhaust gases from vehicles over the last two decades in Australia, meaning reductions in concentrations would be relatively greater at the traffic-dominated sampling site. On the other hand, the relatively longer halving times estimated at Site Gri confirmed that traffic-related emissions, as a source for PAHs, were not as dominant at Site Gri as compared to Site WG.

It was noted that the halving time of Ant was longer than Phe at Site Gri (Table S7). This was unexpected given that Ant is generally less stable in the air and has an estimated lifetime some 2 to 4 times shorter than its linear isomer (Phe) based on reaction with OH radicals (Biermann et al., 1985; Bunce and Dryfhout, 1992). However, this result was similar to that found in a rural site on Lake Superior where biomass burning was indicated as a constant contributor to freshly emitted atmospheric PAHs (Sun et al., 2006). Indeed it has been reported that wood combustion could emit a higher proportion of Ant compared to vehicle exhaust (Khalili et al., 1995). This observation is additional evidence that Site Gri was impacted to a greater extent by emission sources of biomass burning than Site WG.

*PCBs.* Overall, the estimated halving time for $\sum_6 \delta$PCBs (11 ± 2.9 years) in Brisbane air from Site Gri was comparable to that reported around the Great Lakes (approximately 15 years) within the IADN network based on observations from 1990 to 2010 (Salamova et al., 2013; Venier and Hites, 2010). In contrast, a shorter halving time (4.7 years) was reported in the UK within the TOMPS network from 1991 to 2008 (Schuster et al., 2010), where diffusive primary sources were indicated as being dominant. This may imply that primary sources such as emissions from old stock of electric equipment are of limited importance as contributors to concentrations of atmospheric PCBs at Site Gri.

Typically, larger congeners were found to have a longer halving time in this work, indicating the dominance of secondary sources over the twenty-year interval. PCB 101 for example had an observed halving time of 24 years, consistent with previous findings that secondary
emission sources are most important for penta- and hexachlorinated congeners (Lammel and Stemmler, 2012). It has also been estimated that the PCB congener fingerprint of soil between 90° S and 30° N showed the highest proportion of PCB 101 (4.0%) compared to 30 - 60° N (2.0%) and 60 - 90° N (2.3%) (Meijer et al., 2003).

Over the last two decades, the profile of indicator PCBs has shifted slightly towards a higher proportion of medium sized congeners. For example, the contribution of PCB 101 increased slightly from 3.6 ± 1.4% to 10 ± 7.0%, again indicating re-volatilisation from reservoirs such as soil have been acting as the main source for atmospheric PCBs in Brisbane.

### 3.5 Emission profile characteristics of key potential sources for PAHs and PCBs and their relevance to atmospheric burdens at the receptor sites

Source fingerprints were obtained for bushfires (for PAHs and PCBs) within a controlled burn event in 2013 and for vehicle exhaust (PAHs only) within a tunnel sampling event in 2014. As seen in Figures 5(a) and (b) and Tables S8 and S9, the PAH profiles from each type of event were dominated by Phe and generally the compound concentration decreased with increased molecular weight. This resulted in a significant correlation of the PAH profile between these samples ($r^2$ ranged from 0.946 to 0.999, $P < 0.001$). In spite of this similarity, the relevance of these key potential sources to atmospheric burdens of PAHs at the receptor sites (Sites Gri and WG) can still be estimated, as discussed later.

PCB profiles from Sites Gri and WG were dominated by PCB 28 and significantly correlated ($r^2 = 0.996, P < 0.001$) whereas the bushfire event presented a different PCB profile in which PCB 101 had the highest concentration (Figure 5 (c) and Table S8). This agrees with the previous discussion that soil is an important reservoir for PCB 101. While emissions from bushfires may contribute to the concentrations of PCBs in Brisbane air (resulting in a longer halving time for PCB 101), the weak correlation of PCB profiles between Sites Gri and WG and the bushfire event indicates that potentially other important sources may also contribute to the PCBs measured in air at these two receptor sites.
Figure 5. Source fingerprints of PAHs in (a) 1994/5 and (b) 2013/4 and of PCBs (c) in 2013/4. Data were normalized to the concentration of Phe for PAHs and PCB 28 for PCBs and for Sites Gri and WG data were from cooler months of the year.

A number of techniques have been employed to investigate the major sources of PAHs and PCBs in samples, and whether relative source contributions have changed over time. Diagnostic ratios of various PAHs have been used for example. In the current study, ratios were calculated from samples taken of the bushfire event, in the vehicular tunnel event and from Sites Gri and WG (both in 1994/5 and 2013/4). There is also some limited data on bushfire source profiles from the 1990s (Table S10). As seen in Figures 5, S4 and Table S10, compared to Pyr, Flu was relatively more enriched in the bushfire samples, leading to ratios of Flu/(Flu + Pyr) of 0.52 in the 2013/4 bushfire sampling campaign. Also shown in Figure S4 and Table S10, a ratio of 0.61 was obtained in a 1990 (published year; the sampling period was not stated in the publication) bushfire sampling event in Australia (Freeman and Cattell, 1990).
In contrast, a relatively higher concentration of Pyr was measured with the 2014 tunnel sample, resulting in a ratio of Flu/(Flu + Pyr) of 0.35. A ratio range of 0.36 - 0.43 (with an outlier of 0.51 in autumn) was observed at Site Gri in 1994/5 and this increased to 0.43 - 0.53 in 2013/4, indicating an increase of the contribution from wood combustion (bushfires) over this period. In the 2013/4 sampling campaign, this ratio was consistently and significantly (paired t test, \( P < 0.001 \)) higher at Site Gri (0.51 ± 0.025, ranging from 0.46 to 0.55) than at Site WG (0.44 ± 0.019, ranging from 0.42 to 0.47), again suggesting a greater contribution from wood combustion (bushfires) at Site Gri.

As shown in Figure S5, a clearly different pattern of benzopyrene isomers was observed for the samples from the bushfire event, where BaP dominated the pattern, compared with other types of samples in which BeP typically did. The BaP/(BaP+BeP) ratio of the bushfire event sample (close to 0.50; Table S10) is suggestive of freshly emitted particles (Oliveira et al., 2011). To a lesser extent this applied to the tunnel sample (close to 0.40; Table S10) as well. Furthermore, this diagnostic ratio was typically lower in 2013/4 (0.14 - 0.29) than in 1994/5 (0.29 - 0.51) at both sites (see Figure S5 as an example in the cooler season), indicating they have become more impacted by aged particles (presumably emitted from inland bushfires and transported via LRAT) with time.

Principal component analysis (PCA) was employed as another means of estimating the contribution of various potential sources to the PAH and PCB concentrations in air at the receptor sites. As seen in Figure S6, this revealed an association of bushfires with PAHs measured in cooler months in 2013/4 at Site Gri and also indicated vehicular emissions to be an important source for PAHs measured at Site WG. In addition, LRAT was identified as an important source of PCBs in air measured at Site Gri. This result, together with the previous discussion, implies that both LRAT and re-volatilisation of PCBs from reservoirs such as soils during bushfires are potentially important sources for PCBs in air measured at Site Gri.

Further details of the PCA analysis are provided in S10 in the SM.
Conclusions

Overall, atmospheric concentrations of PAHs and PCBs have significantly decreased compared to two decades ago in Brisbane area, at similar rates to those observed at comparable sites in the Northern Hemisphere. This result reflects the effectiveness of the related global treaties and pollutant emission regulations over this timespan. Our data also suggest that, compared to two decades ago, biomass burning including bushfires has become a more important emission source for atmospheric PAHs in the Brisbane area. For atmospheric PCBs, both LRAT and re-volatilisation of PCBs from reservoirs such as soils during bushfires are indicated as important sources.
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