Environmental Science Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Atmosphere is a key route for human exposure to persistent organic pollutants (POPs). Spatially resolved data in atmosphere are important for estimating their release from primary and secondary sources and their transport after they are emitted into the atmosphere. Compared to other continents, limited data are available for POPs in Australia's atmosphere. This study, by establishing a nation-wide PAS-based monitoring and archiving program, provides systematic data for atmospheric POPs in this world's sixth largest country by area and presents their spatial variations among sites with different land use.

Spatial Distribution of Selected Persistent Organic Pollutants (POPs) in Australia's Atmosphere

Xianyu Wang,[a] Karen Kennedy,[a] Jennifer Powell,[b] Melita Keywood,[b] Rob Gillett,[b] Phong Thai,[a] Phil Bridgen,[c] Sara Broomhall,[d] Chris Paxman,[a] Frank Wania[e] and Jochen Mueller[a]

[a]*National Research Centre for Environmental Toxicology, The University of Queensland, 39 Kessels Road, Coopers Plains, QLD, 4108, Australia*
[b]*CSIRO Oceans and Atmosphere Flagship, Aspendale laboratories, 107-121 Station Street, Aspendale, VIC, 3195, Australia*
[c]*AsureQuality Wellington Laboratory, 1c Quadrant Drive, Waiwhetu, Lower Hutt 5010, New Zealand*
[d]*Chemical Policy Section, Department of Sustainability, Environment, Water, Population and Communities, Australian Government, 787 Canberra ACT 2601, Australia*
[e]*Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4*

Abstract

A nation-wide passive air sampling campaign recorded concentrations of persistent organic pollutants in Australia's atmosphere in 2012. XAD-based passive air samplers were deployed for one year at 15 sampling sites located in remote/background, agricultural and semi-urban and urban areas across the continent. Concentrations of 47 polychlorinated biphenyls ranged from 0.73 to 72 pg/m^3 (median of 8.9 pg/m^3) and were consistently higher at urban sites. The toxic equivalent concentration for the sum of 12 dioxin-like PCBs was low, ranging from below detection limits to 0.24 fg/m^3 (median of 0.0086 fg/m^3). Overall, the levels of polychlorinated biphenyls in Australia were among the lowest reported globally to date. Among the organochlorine pesticides, hexachlorobenzene had the highest (median of 41 pg/m^3) and most uniform concentration (with a ratio between highest and lowest value ~5). Bushfires may be responsible for atmospheric hexachlorobenzene levels in Australia that exceeded Southern Hemispheric baseline levels by a factor of ~4. Organochlorine pesticides concentrations generally increased from remote/background and agricultural sites to urban sites, except for high concentrations of α-endosulfan and DDTs at specific agricultural sites. Concentrations of heptachlor (0.47-210 pg/m^3), dieldrin (ND-160 pg/m^3) and trans- and cis-chlordanes (0.83-180 pg/m^3, sum of) in Australian air were among the highest reported globally to date, whereas those of DDT and its metabolites (ND-160 pg/m^3, sum of), α-, β-, γ- and δ-hexachlorocyclohexane (ND-6.7 pg/m^3, sum of) and α-endosulfan (ND-27 pg/m^3) were among the lowest.

Key words

POPs; atmosphere; spatial distribution; Australia

1. Introduction

Persistent organic pollutants (POPs) include many semi-volatile organic chemicals (SVOCs) that can emit into the atmosphere from sources and transport away in large distances[1]. Subsequently they can be transferred into human and wildlife food chains[2] through terrestrial and aquatic ecosystem accumulation which makes the atmosphere-biological reservoirs-food (animal & plant origin) pathway a key exposure route for humans to POPs.

The systematic collection and analysis of POPs in samples from the ambient atmosphere has become an important tool for estimating their release from primary and secondary sources. Several atmospheric monitoring programs have been established to obtain spatially and/or temporally resolved data of atmospheric POPs on a regional scale. For instance, at the 17 sampling sites of the Integrated Atmospheric Deposition Network (IADN) in the Laurentian Great Lakes Region[3] more than 100 chemicals, including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), have been measured since 1990. Within the scope of the Toxic Organic Micropollutants Program (TOMPs) in the UK[4], over 100 chemicals including dioxins and PCBs have been analysed in samples collected at six sampling sites across England and Scotland since 1991. Similar activities are conducted elsewhere in Europe as part of the European Monitoring and Evaluation Programme (EMEP)[5].

In contrast, relatively few systematic data are available for POPs in the atmosphere of Australia, the world's sixth largest country by area. Data from two sampling sites established in Australia as part of the Global Atmospheric Passive Sampling (GAPS) network[1, 6, 7] suggest that the levels of atmospheric PCBs and OCPs at Australian sites are generally low compared to the sites in the Northern Hemisphere (NH). As part of Australia's National Dioxins Program (NDP)[8], data on dioxins levels from 10 sites across Australia indicated a clear increasing trend along a background-urban gradient as well as a strong seasonal cycle[9]. To date, these studies either had a limited number of sites or a limited number of target chemicals and thus do not amount to a systematic collection and analysis of atmospheric POPs in Australia.

Australia spans across several climate zones with a wide range of potential sources for POPs associated with different land uses. However, due to its large size and small population, a nation-wide continuous spatial and temporal air monitoring program requires cost-effective and innovative techniques. Passive air samplers (PAS), which meet these requirements, have been used widely for monitoring atmospheric POPs[7, 10, 11]. Therefore the aim of this study is to establish a PAS-based monitoring and archiving program for measuring the spatial variations in atmospheric concentrations of POPs in Australia. In this study we present and discuss the data for PCBs and OCPs for the year of 2012.

2. Materials and methods

2.1 Sampling protocol

XAD-resin based passive air samplers (XAD-PAS) were deployed for approximately one year at 15 sampling sites across all Australian states and territories, including five remote/background, five agricultural, one semi-urban and four urban sites (Figure 1). Since more than 85% of the population in Australia is concentrated within 50 km of the coastline[12] and thus most industrial and agricultural activities are concentrated along the coastal periphery, our sampling strategy aimed to cover different geographic and climate zones across Australia as well as to represent different population density and land-use areas. Design and dimensions of the XAD-PAS have been adapted from a previous study[13], using mesh cylinders 10 centimetres long and with a surface area of 62.5 cm^2 (i.e. half of the original design). Site-specific deployment details and an example photograph of sampler deployment at site UR3 (Homebush Bay, NSW) are presented in Table 1 and Figure S1 in the Supporting Information (SI) respectively. The XAD-PAS at UR4 (Adelaide) was duplicated.

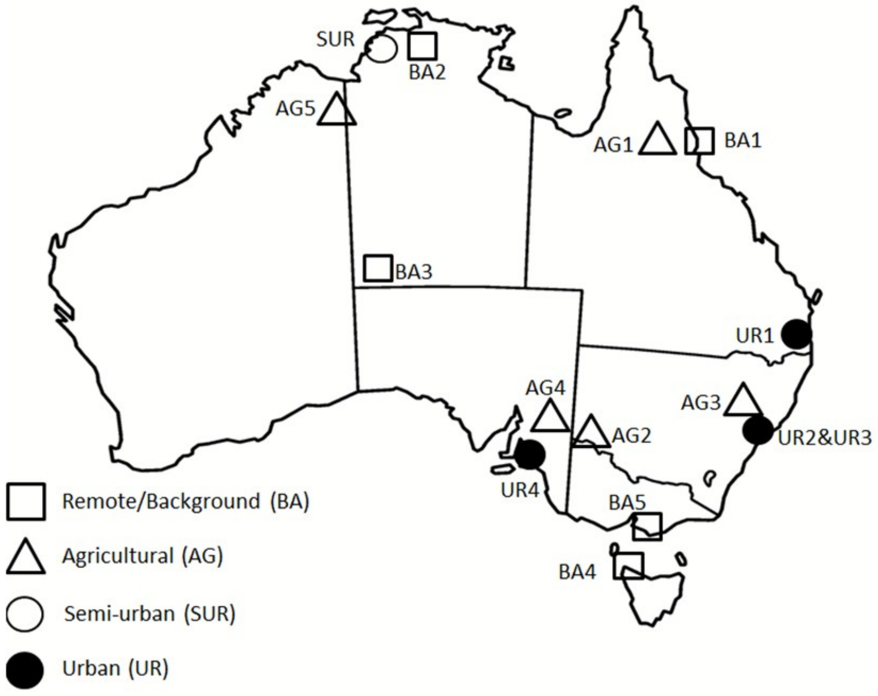

Figure 1. Map of sampling sites

During the PAS deployment period an active air sampler (AAS) operated by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) collected 12 monthly samples at site SUR (Darwin), by drawing ~12 m^3 of air per hour through a quartz fibre filter (QFF) and an XAD-polyurethane foam (PUF) sandwich cartridge. After sampling and retrieval, XAD cylinders, QFFs and XAD-PUF sandwich cartridges were stored at -20 °C until analysis.

Table 1. Site specific deployment details

Sampling site	Location*	Latitude	Longitude	Classification	Sampling period (from to)	Deployment duration (days)
BA1	Dunk Island QLD	17°56'07"S	146°08'34"E	Background	29/Feb/12 13/Mar/13	378
BA2	Kakadu NT	13°02'11"S	132°26'23"E	Background	25/Feb/12 15/Jan/13	325
BA3	Uluru NT	25°20'52"S	131°02'04"E	Background	08/Feb/12 28/Mar/13	414
BA4	Cape Grim TAS	40°40'60"S	144°40'60"E	Background	20/Jan/12 08/Jan/13	354
BA5	Phillip Island VIC	38°29'24"S	145°12'14"E	Background	18/Jan/12 06/Jan/13	354
AG1	Tully QLD	17°56'03"S	145°55'24"E	Agricultural	29/Feb/12 08/Mar/13	373
AG2	Mildura VIC	34°11'04"S	142°09'56"E	Agricultural	12/Jan/12 09/Jan/13	363
AG3	Gunnedah NSW	31°01'34"S	150°16'8"E	Agricultural	21/Feb/12 18/Jan/13	332
AG4	Barossa Valley SA	34°31'60"S	138°56'60"E	Agricultural	03/Feb/12 24/Jan/13	356
AG5	Kununurra WA	15°46'26"S	128°44'20"E	Agricultural	16/Jan/12 15/Feb/13	396
SUR	Darwin NT	12°27'41"S	130°50'31"E	Semi-urban	25/Jan/12 09/Jan/13	350
UR1	Brisbane QLD	27°29'51"S	153°02'06"E	Urban	13/Feb/12 06/Feb/13	359
UR2	Rozelle NSW	33°52'02"S	151°12'26"E	Urban	14/Feb/12 06/Mar/13	386
UR3	Homebush Bay NSW	33°49'21"S	151°05'02"E	Urban	15/Feb/12 06/Mar/13	385
UR4#	Adelaide SA	34°54'05"S	138°34'00"E	Urban	03/Feb/12 24/Jan/13	356

*** QLD-Queensland, NT-Northern Territory, TAS-Tasmania, VIC-Victoria, NSW-New South Wales, SA-South Australia, WA-Western Australia; # where duplicated samples are available**

2.2 Chemical analysis

Samples were analysed for 49 PCB congeners and 27 OCPs (listed in Table S1 in the SI) by AsureQuality Ltd. using USEPA Methods 1668A[14] and 1699[15] respectively. Briefly, samples were spiked with a range of ^{13}C-labelled PCB congeners and OCPs before Soxhlet extraction and cleanup. Sample analysis was then carried out by high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC-HRMS). The laboratory has ISO17025 accreditation for its test methods and reported results. Details on the chemical analysis are given in the SI.

2.3 Sampling rate (*R*) for XAD-PAS

The large sorption capacity of the XAD-PAS used in this study assures that uptake is linear for sampling periods in excess of one year for the chemicals of interest to this study[7, 16]. This allows the conversion of the amount of chemicals sequestered by the samplers during the deployment period (C_{PAS} in pg/sampler) into volumetric concentrations in air (C_{Air} in pg/m^3) using:

$$C_{Air} = \frac{C_{PAS}}{R \times t} \tag{1}$$

where R (m^3/sampler/day) is the compound-specific PAS sampling rate during the deployment period t (days). Sampling rates R for the target chemicals of this study were reviewed and collated from a range of outdoor studies (SI Table S2) and corrected for surface area, if they had been obtained with the longer sampler design. Briefly, an R of 0.55 m^3/sampler/day was used for all PCB congeners, whereas R for OCPs varied from 0.34 to 0.91 m^3/sampler/day. Since these sampling rates are collated from a range of different studies, involvements of uncertainty are expected and so are accordingly the volumetric concentrations converted from them.

3. Results and discussion

3.1 Quality assurance and quality control (QA/QC) results

Recoveries of internal standards (^{13}C-labelled analogues) spiked before extraction were 50%-120% for 95% of the samples (45-150% for PCBs and 24-144% for OCPs throughout all the samples), which were within the QC acceptance criteria of the USEPA methods[14, 15]. A few chemicals (including hexachlorobenzene (HCB), pentachlorobenzene (PeCB), PCB#1 and PCB#3) were detected in laboratory and field blank samples. The mass of HCB in blank samples was consistently less than 10% of the amounts in exposed samples and the reported values were not blank-corrected. Levels of PeCB and PCB#1 and #3 in the blanks were sometimes within the same order of magnitude as those in exposed samples and thus were excluded from further interpretation.

Reproducibility. Duplicated samplers deployed at sampling site UR4 agreed with an RSD of less than 15% for most analytes (SI Table S3), indicating good reproducibility with regard to sampler deployment and sample analysis.

Comparison between air concentrations obtained from this study and the ones from GAPS network. Within the GAPS network, XAD-PAS (using mesh cylinders 20 centimetres long and thus with a surface area of 125 cm^2) were deployed annually from 2005 to 2008 at site BA4 (Cape Grim) and SUR (Darwin) and were analysed for a range of OCPs[7]. The reported data are compared with the ones from this study (SI Figure S2, pg/sampler/day, normalised to a 10-cm length (62.5-cm^2 surface area) base). For frequently-detected OCPs, levels measured in this study are within the same order of magnitude as the reported data from 2005 to 2008 and agreed with an RSD of 2%-25% (between the levels measured in this study and the ones averaged from 2005 to 2008), indicating that no major bias is caused during sampler deployment and sample analysis in this study.

Comparison between air concentrations obtained from AAS and XAD-PAS. Monthly concentrations of atmospheric PCBs and OCPs derived from AAS throughout the year of 2012 at site SUR were averaged to obtain the annual mean concentrations and Figure 2 compares the logarithm of the annual mean concentrations of PCBs and OCPs at site SUR determined by XAD-PAS and AAS (data are also shown in SI Table S4). Although the concentrations derived from AAS were a combination of vapour phase and particle-associated phase, considering that XAD-PAS are not believed to sample particles to any significant extent and site SUR is a tropical background sampling site, where most of the interested chemicals in this study are assumed to be distributed mainly in the vapour phase[17], this concentration comparison suggests the absence of major bias.

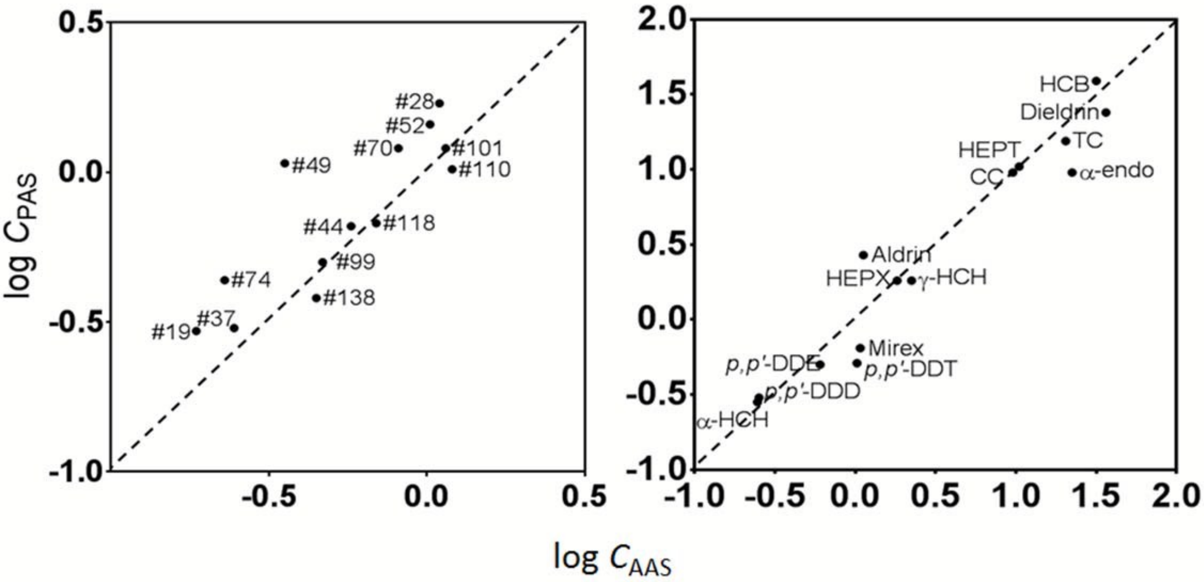

Figure 2. Comparison between annually averaged concentrations of PCBs (left panel) and OCPs (right panel) derived from the mean of 12 monthly active air samples (C_{AAS}, pg/m^3) and one annual passive air sample XAD-PAS (C_{PAS}, pg/m^3) at site SUR in Darwin, NT

C_{AAS} and C_{PAS} for the measured PCBs and OCPs (Figure 2 and SI Table S4) agreed with a mean RSD of 16%. Discrepancies between C_{PAS} and C_{AAS} for OCPs appeared to be random rather than systematic. The PCBs data may suggest that the R of 0.55 m^3/day resulted in C_{PAS} for the lower chlorinated congeners that were somewhat higher than the C_{AAS} (i.e. the R values might be slightly underestimated for these congeners). Overall this comparison supports the use of these sampling rates for estimation of PCB and OCP concentrations in this study.

3.2 Atmospheric concentrations and profiles and spatial distribution of PCBs in Australia

Concentrations of the ten PCB congeners that were detected in more than 50% of the samples are shown in Table 2; data for other congeners are presented in the SI (Table S5&6). Overall, the mean and median concentration of the sum of PCB congeners (∑PCBs, non-detectable ones excluded) in air was 21 and 8.9 pg/m^3. Similar atmospheric PCB level (20 pg/m^3, sum of congeners from di- to deca-) in Australia (at Cape Grim) was also reported by Genualdi et al. in a three-month period sampling campaign in 2009, using sorbent-impregnated polyurethane foam (SIP) disk PAS[18]. The concentrations varied by more than 2 orders of magnitude, from below 1.0 pg/m^3 at some of the background sites to between 39 and 72 pg/m^3 at the urban sites. The congeners measured at the highest median concentrations were #52 and #28 (1.5 and 1.2 pg/m^3 respectively) and in 13 out of 16 samples either of these two congeners had the highest concentration.

PCBs were consistently detected in higher concentrations at all urban sites (see Figure 3 and shaded values in Table 2 which represented values ≥3×median) with the highest concentration for most congeners and for ∑PCBs measured at UR3 (Homebush Bay, NSW), whereas PCBs at background and agricultural sites were consistently low with only very few random exceptions (i.e. lighter congeners at AG1 and PCB#70 at AG2). This trend is consistent with other studies reporting higher urban PCB levels, e.g. in Asia[19], North America[20] and the UK[21].

Congeners with 8 or more chlorines were not detected at any of the sites (SI Table S5&6) and the combined contribution of the hexa- and hepta-chlorinated congeners was never higher than 7.0% at any sites. However, a marginally higher contribution of hexa- and hepta- congeners was still observed at semi-urban and urban sites (3.0%-7.0%, mean 5.5%), compared to background (<5.0%, mean 2.6%) and agricultural (<6.0%, mean 2.2%) sites. These congeners have a lower potential of atmospheric transport, i.e. they are more likely to remain within, or in the vicinity of, source regions [22]. The above trend thus indicates that Australian urban areas are a source for atmospheric PCBs, as had previously been observed for urban areas in Switzerland[23], Asia[19], North America[24] and Argentina[25], most likely due to PCB emissions from existing and disposed electrical equipment[23].

Only a few dioxin-like PCBs (dl-PCBs) (3 out of 12 congeners including #118, #105 and #156) were detected and typically the concentrations were very low (SI Table S5&6). The sum of detectable dl-PCBs contributed at most 7.0% to ∑PCBs at each sampling site. This fraction also showed a slight remote/urban trend: <5.9% at background sites, <4.6% at agricultural sites and 1.5%-7.0% at semi-urban and urban sites, although the difference between each other was insignificant (t-test, P>0.05). WHO 2005 toxic equivalency factors (TEFs)[26] were used to calculate the dioxin toxic equivalent concentration (TEQ) for dl-PCBs at each sampling site. As shown in Table 2, a clear trend was again found with ∑dl-PCBs increasing from background (<0.0096 fg TEQ/m^3) to agricultural (<0.021 fg TEQ/m^3) and to semi-urban and urban sites (0.017-0.24 fg TEQ/m^3).

When compared with other countries (SI Table S9), the concentrations of atmospheric PCBs at Australian background sites were among the lowest. Similarly, concentrations at urban sites are consistently very low when compared to data from other industrialised nations in the NH (SI Table S10).

Table 2. Concentrations of atmospheric PCBs (pg/m^3), dl-PCB TEQ (fg/m^3), OCPs (pg/m^3) and isomer ratios for specific pesticides at each sampling site

Sampling site	BA1	BA2	BA3	BA4	BA5	AG1	AG2	AG3	AG4	AG5	SUR	UR1	UR2	UR3	UR4-1	UR4-2	Median
Location	Dunk Is	Kakadu	Uluru	Cape Grim	Phillip Island	Tully	Mildura	Gunnedah	Barossa Valley	Kununurra	Darwin	Brisbane	Rozelle	Homebush Bay	Adelaide	Adelaide	
State	QLD	NT	NT	TAS	VIC	QLD	VIC	NSW	SA	WA	NT	QLD	NSW	NSW	SA	SA	
PCB#4/10	0.43	ND	ND	ND	0.78	11	0.91	ND	0.73	ND	ND	7.4	4.3	6.1	8.9	7.8	0.76
PCB#28	ND	0.49	0.65	ND	1.1	4.1	1.3	ND	0.58	0.46	1.7	5.4	4.2	5.9	10	7.5	1.2
PCB#37	ND	ND	0.23	0.36	0.39	0.25	0.51	ND	ND	0.19	0.30	1.1	0.93	1.1	2.1	1.3	0.33
PCB#44	ND	ND	0.38	ND	0.48	0.72	1.5	0.26	ND	ND	0.65	2.9	2.7	6.6	3.9	3.2	0.57
PCB#49	ND	ND	0.60	ND	0.33	0.73	1.2	ND	0.54	0.29	1.1	2.1	2.2	6.7	3.2	2.7	0.67
PCB#52	0.34	ND	0.88	1.7	0.86	1.4	3.6	0.55	0.93	0.43	1.5	4.6	5.4	13	7.6	6.1	1.5
PCB#70	ND	ND	0.35	0.99	0.51	0.29	2.6	0.33	0.46	ND	1.2	3.2	4.4	5.7	4.7	4.1	0.75
PCB#101	0.15	0.13	ND	0.85	0.45	ND	1.3	0.31	0.40	0.26	1.2	2.6	2.6	6.7	3.5	3.0	0.65
PCB#110	ND	0.11	0.13	0.53	0.31	ND	0.62	0.20	ND	ND	1.0	2.2	1.8	4.7	2.8	2.5	0.42
PCB#153	ND	ND	0.11	0.25	0.19	ND	0.33	ND	ND	0.12	ND	1.3	1.2	2.0	1.8	1.7	0.16
∑PCBs	0.92	0.73	3.8	5.4	6.8	25	15	1.7	3.6	2.2	11	39	39	72	59	50	8.9
TEQ of ∑dl-PCBs	NA	NA	NA	0.0096	0.0076	NA	0.021	NA	NA	NA	0.020	0.017	0.24	0.11	0.081	0.055	0.0086
HCB	32	33	41	67	45	18	41	37	41	37	39	72	42	75	96	81	41
α-HCH	0.49	ND	ND	ND	0.34	ND	0.38	ND	0.28	ND	0.28	0.98	ND	0.74	0.52	0.43	0.28
γ-HCH	0.36	ND	ND	0.70	ND	ND	0.74	ND	4.0	ND	1.8	3.5	3.0	4.2	6.2	5.4	0.72
HEPT	4.4	1.2	0.65	0.79	1.8	2.0	180	6.9	4.6	0.47	10	62	210	160	130	120	5.7
HEPX	1.1	ND	ND	ND	0.92	0.26	1.9	2.2	0.54	ND	1.8	14	22	33	6.5	6.6	1.4
Dieldrin	6.8	ND	1.2	2.8	6.2	2.1	8.1	15	4.9	78	24	99	140	160	110	97	12
TC	2.0	1.1	0.54	0.63	2.4	0.65	9.6	14	5.3	0.94	15	35	110	130	120	110	7.5
CC	0.63	ND	0.29	0.54	1.6	0.23	2.5	2.8	1.8	0.96	9.6	11	35	43	59	51	2.2
α-endosulfan	3.6	4.3	5.7	8.8	ND	2.2	12	9.0	27	19	9.5	17	4.2	ND	20	20	8.9
o,p'-DDE	ND	ND	ND	ND	0.77	ND	0.55	0.28	0.30	19	ND	0.27	ND	1.8	0.45	0.45	0.28
p,p'-DDE	0.26	ND	0.15	0.59	2.8	0.31	3.9	3.9	7.5	120	0.50	5.4	4.2	18	7.1	6.2	3.9
p,p'-DDT	ND	ND	ND	ND	ND	0.19	0.55	0.47	0.70	7.0	0.52	5.3	2.9	3.3	ND	2.1	0.49
Mirex	ND	ND	0.11	0.091	0.77	0.10	0.058	0.073	ND	0.12	0.64	ND	0.43	0.31	ND	ND	0.082
TC/CC	3.1	NA	1.8	1.2	1.6	2.8	3.9	4.9	2.9	0.97	1.6	3.0	3.3	2.9	2.1	2.1	
p,p'-DDT/*p,p'*-DDE	NA	NA	NA	NA	NA	0.61	0.14	0.12	0.093	0.057	1.0	0.99	0.69	0.19	NA	0.34	
a-HCH/r-HCH	1.4	NA	NA	NA	NA	NA	0.51	NA	0.070	NA	0.15	0.28	NA	0.18	0.085	0.080	

The value with a shade means ≥3×median value and further with a border if ≥10×median value was measured

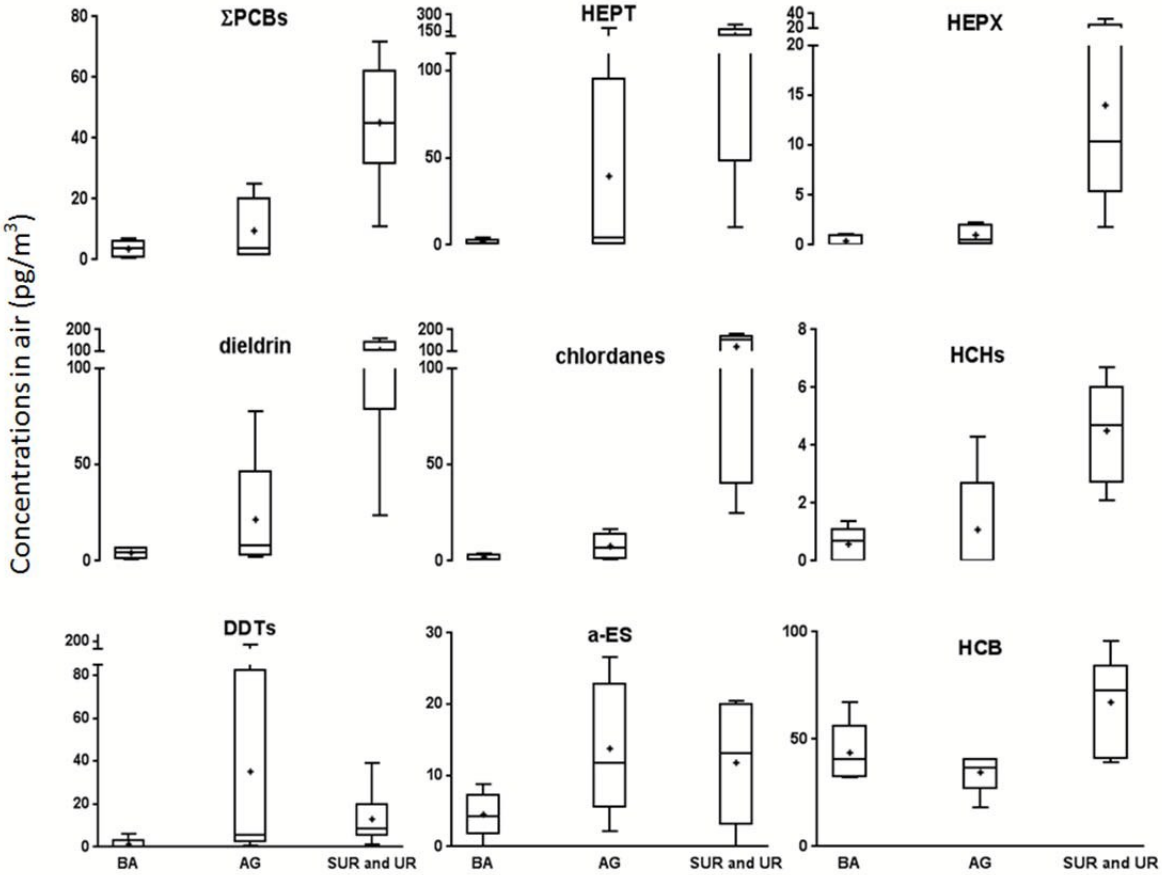

Figure 3. Box-and-whisker plot of concentrations of ∑PCBs and selected OCPs (pg/m^3) in air at sites with different land uses. The line and '+' within the box is plotted at the median and mean respectively and the top and bottom whiskers represent 99% and 1% of these data respectively

3.3 Atmospheric concentrations and spatial distribution of OCPs in Australia

Concentrations of the thirteen OCPs that were detected in more than 50% of the samples are shown in Table 2; data for other OCPs are presented in SI Table S7&8. Higher concentrations of OCPs were measured mostly at urban sites (Table 2 and Figure 3), although exceptions to this trend will be discussed below for DDTs and α-endosulfan (α-ES). HCB, heptachlor (HEPT) and trans-chlordane (TC) were detected in samples from all 15 sites. In terms of median values, HCB was the most abundant at 41 pg/m^3, followed by dieldrin (12 pg/m^3), α-ES (8.9 pg/m^3), TC (7.5 pg/m^3), HEPT (5.7 pg/m^3) and *p,p'*-DDE (3.9 pg/m^3) (Table 2). International comparison (SI Table S11-13) showed that concentrations of HEPT, chlordanes and dieldrin in Australian air are among the highest values (especially for the urban sites), whereas concentrations of DDTs, HCHs and endosulfans in Australian air are among the lowest, reflecting mainly different historical usage of these banned chemicals in Australia.

HCB. HCB was first introduced in 1930s as a fungicide and widely used afterwards. It has been banned in most application in Australia since 1972[27]. The median HCB concentration of 41 pg/m^3 (mean 50, range 18-96 pg/m^3) measured in this study is considerably higher than a median value for HCB in the atmosphere of the Southern Hemisphere (SH) of 11 pg/m^3, estimated from 228 data points from a range of studies conducted outside Australia between 1996 and 2008[28]. This discrepancy indicates the existence of potential sources of atmospheric HCB in Australia. Similar atmospheric HCB level (43 pg/m^3) in Australia (at Cape Grim) was also measured by Koblizkova et al. in a three-month period sampling campaign in 2009, using SIP disk PAS[29].

Pesticide applications, manufacturing and combustion were estimated to contribute 28 %, 41 % and 31 % of HCB to the atmosphere respectively in the mid-1990s[30]. Considering that application and manufacturing of HCB have been banned in most countries, combustion process (i.e. re-emission/formation from secondary sources during the thermal process) should now make the dominant contribution (although it can still be released as a by-product or impurity during the process of manufacturing chlorinated solvents, aromatics and pesticides[27]). Australia's mostly hot and dry climate favours frequent and wide-ranging bushfires. These fires are deemed to be the dominant emission sources for many pollutants in Australia, such as carbon monoxide (contribution to 80% of national level), nitrogen oxides (42%), VOCs (58%)[31] and dioxins[32, 33]. Although the correlation between bushfires and HCB emissions has to our best knowledge not yet been established in Australia, elevated concentrations of HCB in air have been measured during forest and/or agricultural fire events in the USA[34]. Therefore, bushfires may be one of the key contributors to the elevated concentrations (relative to the rest of the SH) of atmospheric HCB in Australia.

HCB was the most uniformly distributed compound among the OCPs (Figure 3), i.e. with the lowest coefficient of variation and the lowest ratio of highest to lowest concentration (H/L) at ~5. This result is consistent with a high degree of uniformity in HCB concentrations measured at the global scale[7] and at the continental scale in Europe[35], Asia with the exception of China[19, 36], North America[10] and some countries in the SH[11, 37]. This is the result of HCB's long atmospheric residence time and thus travel distance[38], which is due to inefficient precipitation scavenging (high K_{AW}), very limited association with atmospheric particles (relatively low K_{OA}[39]) and a long degradation half-life in the atmosphere[27].

HEPT, Chlordanes and Dieldrin. These compounds were mostly used to control termites in Australia until the mid-1990s[40, 41]. As seen in Table 2 and Figure 3, a clear increasing trend was found for them from background to agricultural and semi-urban and urban sites.

In environmental reservoirs such as soils, HEPT can be metabolised into heptachlor epoxide (HEPX), which is more stable, and both can be re-volatilised into atmosphere[42]. Whereas the concentration of

HEPX was typically higher than HEPT in air samples from Greenland[43], South Korea[44], France and North America[7], this was not the case in this study: at all sites, the concentration of HEPT in air was higher than HEPX (on average the concentration of HEPT was 10 times higher than that of HEPX). Possible explanations could be 1) that legacy HEPT in reservoirs such as soils had not deteriorated enough and HEPT could volatilise relatively easily compared to HEPX[42] and/or 2) recent/ongoing emissions of HEPT to the air, as also suggested by Tombesi et al.[25] in a case study in Argentina. Overall, however, the mean air concentration of HEPT in urban areas in this study was measured one order of magnitude lower compared to 1992/93[45], which reflected the effort of reducing/eliminating HEPT use over the last decades in Australia.

Technical chlordane contains the major components trans-chlordane (TC) and cis-chlordane (CC) at a ratio of about 1.2[46]. A value exceeding 1.2 is considered as an indication of close vicinity to source areas because TC has a higher vapour pressure than CC[39]. For instance, a higher ratio was found at some sites in India and Argentina, indicating proximity to potential sources[25, 47]. On the other hand, a lower ratio in air implies the impact from long-range atmospheric transport (LRAT) because TC is more likely to be photo-degraded during atmospheric transport[46]. A lower ratio has indeed been reported in polar regions[7, 48], where LRAT is believed to be the only source of chlordane. In this study, the TC/CC ratio was between 0.97 and 4.9 (Table 2) (averaged at 2.5). A low ratio (≤1.2) was found at sites BA4 and AG5, indicating the influence of weathered chlordane sources from LRAT. At the other sampling sites including all urban sites, on the other hand, local sources (most likely the evaporation from formerly contaminated soils[7]) influenced the air concentration of chlordanes.

The above trends and ratios indicate that the major use of these chemicals in Australia was population-related (i.e. termite control) and that local source(s) (presumably secondary ones) rather than LRAT dominate their concentrations in Australian air.

DDT and its metabolites. To our best knowledge, DDT has been banned for general use in Australia since 1987[40]. *p,p'*-DDE was detected in 15 out of 16 samples and *p,p'*-DDT and *o,p'*-DDE were detectable in 10 and 9 samples, respectively (Table 2). Other DDT-related compounds were detected in only a few samples.

With the exception of AG5 (Kununurra), where the concentration of *p,p'*-DDE was extremely high (120 pg/m^3) (and the concentration of *o,p'*-DDE, *p,p'*-DDT and *o,p'*-DDT was also the highest among all the sites respectively, as shown in SI Table S8) and thus suggested the presence of a local source, we found again a trend with low concentrations at background (<6.3 pg/m^3) and agricultural sites (0.50-9.2 pg/m^3) and consistently higher concentrations at semi-urban and urban sites (1.3-39 pg/m^3) (Figure 3).

In the environment, *p,p'*-DDT can be converted to *p,p'*-DDE and the ratio of DDT/DDE is used to distinguish fresh input (>1.0) from emission of aged residues (<1.0)[1]. In this study, the ratio of *p,p'*-DDT/*p,p'*-DDE was always lower than or equal to 1.0 (Table 2), indicating emissions from historical use.

HCHs. HCHs were widely used in Australia for agricultural purposes from the 1950s onwards and were deregistered in 1985-1987 (both for technical HCH and lindane)[49], although lindane was exempted to be used to treat symphylids in pineapples in Queensland until 7th June 2012 and was also available for use for the control of head lice and scabies as a human health pharmaceutical only and ceased in Australia several years ago. The α- and γ-isomers were detected in 9 of 16 and 10 of 16 samples respectively while the β- and δ-isomers were not detected in most samples. Whereas α- and γ-HCH were detected at all semi-urban and urban sites (the only exception was α-HCH at UR2), they were detected at only a few sites categorized as background or agricultural. The concentrations of ∑HCHs (sum of α-, β-, γ- and δ-) showed a gradient from background (<1.4 pg/m^3) to agricultural (<4.3 pg/m^3) and to semi-urban and urban sites (2.1-6.7 pg/m^3) (Figure 3), in agreement with what had been found in some other studies[25, 50, 51].

As shown in Table 2, the α-HCH/γ-HCH concentration ratio ranged from 0.070 to 1.4 at different sites, which is much lower than the ratio in technical HCH (5 to 7)[52], reflecting its insignificant use in Australia.

Endosulfans. Endosulfan has been widely used in Australia for the control of some insects and mites in crops[53], especially on cotton[40, 53]. However, transgenic Bt cotton, containing bacterium *Bacillus thuringiensis* which naturally produces chemicals harmful to selective insects, was commercially released in Australia in 1996/97 and 40% of total cotton area has been sown with Bt cotton by 2004/05. Furthermore, a removal of caps for BT cotton acreage helped to increase this number to 70%[54] from then. Therefore, although the registration of endosulfan in Australia was not cancelled until October 2010[55], the use of endosulfans in Australia was likely already reduced effectively between 1996/97 and 2004/05. Although Australian cotton production is mainly located in NSW (66%) and QLD (34%) [56], α-ES concentrations in air sampled at agricultural sites in these two states (AG1 and AG3) were lower than or equal to the overall median value. This result thus suggests that in 2012 primary sources were not the main contributing factor to the concentrations of endosulfan in Australian air, but rather historic use of endosulfan locally and/or LRAT, which will be further discussed below.

Technical grade endosulfan contains α- and β-isomers in the approximate ratio of 2.0~2.3. The higher ratio of α-ES/β-ES in the air samples could indicate LRAT of endosulfan to the sampling sites due to the significant loss of β-ES during atmospheric transport[7]. Unfortunately, due to the lack of detection for β-ES in this study, this ratio was mostly unavailable for these sampling sites. The only site where β-ES was detected was UR4-2 and the ratio of α-ES/β-ES was 6.7, supporting LRAT.

Mirex. Concentrations of mirex were consistently very low (Table 2). It is noteworthy that mirex was detected with higher concentration at site SUR (Darwin), where products containing mirex were used for control of giant termites under a specific agreement within the Stockholm treaty in Australia[57] until January 2007. However it was also found with relative higher concentration for example on site BA5 (Philip Island) and selected other sites, suggesting that low levels of mirex persist in air throughout Australia.

Acknowledgments

The authors thank Andrew Banks, Yan Li and Yiqin Chen (Entox) for their help in data process and all the volunteers for sampling assistance. The study is partly funded by the Commonwealth Department of Environment, Australian Government. Xianyu Wang is supported by International Postgraduate Research Scholarship (IPRS) granted by Australian Government and University of Queensland Centennial Scholarship (UQCent) granted by The University of Queensland. Phong Thai is supported by a UQ Postdoctoral Fellowship. Jochen Mueller is supported by an Australian Research Council (ARC) Future Fellowship. The National Research Centre for Environmental Toxicology (Entox) is a joint venture of the University of Queensland and Queensland Health Forensic and Scientific Services (QHFSS). Active sampling at Darwin was carried out under the National Monitoring of Hazardous Substances in Air project funded by the Commonwealth Department of Environment, Australian Government and CSIRO. The findings and conclusions in this paper are those of the authors and do not necessarily represent the views of the Australian Government Department of the Environment

References

1. K. Pozo, T. Harner, S. C. Lee, F. Wania, D. C. Muir and K. C. Jones, *Environmental science & technology*, 2009, 43, 796-803.
2. H. Hung, G. O. Thomas, K. C. Jones and D. Mackay, *Environmental science & technology*, 2001, 35, 4066-4073.
3. S. S. Buehler and R. A. Hites, *Environmental science & technology*, 2002, 36, 354A-359A.
4. D. f. E. Food and Rural Affairs, UK, Toxic Organic Micro Pollutants (TOMPs) Networks, http://uk-air.defra.gov.uk/networks/network-info?view=tomps.
5. EMEP, EMEP, http://www.emep.int/index.html.
6. K. Pozo, T. Harner, F. Wania, D. C. Muir, K. C. Jones and L. A. Barrie, *Environmental science & technology*, 2006, 40, 4867-4873.
7. C. Shunthirasingham, C. E. Oyiliagu, X. Cao, T. Gouin, F. Wania, S. C. Lee, K. Pozo, T. Harner and D. C. Muir, *Journal of environmental monitoring : JEM*, 2010, 12, 1650-1657.
8. A. G. Department of the Environment, National Dioxins Program, http://www.environment.gov.au/topics/environment-protection/chemicals-management/dioxins.
9. J. Gras, J. Müller, B. Graham, R. Symons, J. Carras and G. Cook, *Dioxins in Ambient Air in Australia, National Dioxins Program Technical Report No. 4*, Australian Government Department of the Environment and Heritage, Canberra, 2004.
10. L. Shen, F. Wania, Y. D. Lei, C. Teixeira, D. C. Muir and T. F. Bidleman, *Environmental science & technology*, 2005, 39, 409-420.

11. C. Shunthirasingham, B. T. Mmereki, W. Masamba, C. E. Oyiliagu, Y. D. Lei and F. Wania, *Environmental science & technology*, 2010, 44, 8082-8088.
12. A. B. o. Statistics, Population living within 50 Kilometres of the coast. , http://www.abs.gov.au/Ausstats/abs@.nsf/Previousproducts/1301.0Feature%20Article32004.
13. F. Wania, L. Shen, Y. D. Lei, C. Teixeira and D. C. G. Muir, *Environmental science & technology*, 2003, 37, 1352-1359.
14. US-EPA, *Method 1668, Revision A. Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*, 2003.
15. US-EPA, *Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*, 2007.
16. J. M. Armitage, S. J. Hayward and F. Wania, *Environmental science & technology*, 2013, 47, 13546-13554.
17. T. F. Bidleman, *Environmental Science and Technology*, 1988, 22, 361-367.
18. S. Genualdi, S. C. Lee, M. Shoeib, A. Gawor, L. Ahrens and T. Harner, *Environmental Science and Technology*, 2010, 44, 5534-5539.
19. F. M. Jaward, G. Zhang, J. J. Nam, A. J. Sweetman, J. P. Obbard, Y. Kobara and K. C. Jones, *Environmental science & technology*, 2005, 39, 8638-8645.
20. A. Motelay-Massei, T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environmental science & technology*, 2005, 39, 5763-5773.
21. F. M. Jaward, N. J. Farrar, T. Harner, A. J. Sweetman and K. C. Jones, *Environmental Science and Technology*, 2004, 38, 34-41.
22. S. D. Choi, S. Y. Baek, Y. S. Chang, F. Wania, M. G. Ikonomou, Y. J. Yoon, B. K. Park and S. Hong, *Environmental science & technology*, 2008, 42, 7125-7131.
23. B. Gasic, C. Moeckel, M. MacLeod, J. Brunner, M. Scheringer, K. C. Jones and K. Hungerbuhler, *Environmental science & technology*, 2009, 43, 769-776.
24. L. Shen, F. Wania, Y. D. Lei, C. Teixeira, D. C. Muir and H. Xiao, *Environmental pollution*, 2006, 144, 434-444.
25. N. Tombesi, K. Pozo and T. Harner, *Atmospheric Pollution Research*, 2014, 5, 170-178.
26. M. Van den Berg, L. S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker and R. E. Peterson, *Toxicological sciences : an official journal of the Society of Toxicology*, 2006, 93, 223-241.
27. J. L. Barber, A. J. Sweetman, D. Van Wijk and K. C. Jones, *Science of the Total Environment*, 2005, 349, 1-44.
28. C. Shunthirasingham, R. Barra, G. Mendoza, M. Montory, C. E. Oyiliagu, Y. D. Lei and F. Wania, *Atmospheric Environment*, 2011, 45, 303-309.
29. M. Koblizkova, S. Genualdi, S. C. Lee and T. Harner, *Environmental Science and Technology*, 2012, 46, 391-396.
30. R. E. Bailey, *Chemosphere*, 2001, 43, 167-182.
31. B. T. Meyer C, J. Muller, G. R, W. I, P. J, T. K, M. L and C. G. M. D. R, *National Dioxin Program_Technical Report No. 1_Dioxins Emissions from Bushfires in Australia*, 2004.
32. R. R. Black, C. P. Meyer, A. Touati, B. K. Gullett, H. Fiedler and J. F. Mueller, *Chemosphere*, 2011, 83, 1331-1338.
33. R. R. Black, C. P. Meyer, A. Touati, B. K. Gullett, H. Fiedler and J. F. Mueller, *Environment international*, 2012, 38, 62-66.
34. T. Primbs, G. Wilson, D. Schmedding, C. Higginbotham and S. M. Simonich, *Environmental Science and Technology*, 2008, 42, 6519-6525.
35. F. M. Jaward, N. J. Farrar, T. Harner, A. J. Sweetman and K. C. Jones, *Environmental science & technology*, 2004, 38, 34-41.

36. X. Liu, G. Zhang, J. Li, L. L. Yu, Y. Xu, X. D. Li, Y. Kobara and K. C. Jones, *Environmental science & technology*, 2009, 43, 1316-1321.
37. G. L. Daly, Y. D. Lei, C. Teixeira, D. C. Muir, L. E. Castillo, L. M. Jantunen and F. Wania, *Environmental science & technology*, 2007, 41, 1124-1130.
38. A. Beyer, D. Mackay, M. Matthies, F. Wania and E. Webster, *Environmental Science and Technology*, 2000, 34, 699-703.
39. L. Shen and F. Wania, *Journal of Chemical and Engineering Data*, 2005, 50, 742-768.
40. J. C. Radcliff, *Pesticide Use in Australia*, 2002.
41. R. S. Kookana, S. Baskaran and R. Naidu, *Australian Journal of Soil Research*, 1998, 36, 715-764.
42. T. F. Bidleman, L. M. M. Jantunen, K. Wiberg, T. Harner, K. A. Brice, K. Su, R. L. Falconer, A. D. Leone, E. J. Aigner and W. J. Parkhurst, *Environmental Science and Technology*, 1998, 32, 1546-1548.
43. R. Bossi, C. A. Skjøth and H. Skov, *Environmental Sciences: Processes and Impacts*, 2013, 15, 2213-2219.
44. H. G. Yeo, M. Choi, M. Y. Chun and Y. Sunwoo, *Atmospheric Environment*, 2003, 37, 3831-3839.
45. J. Beard, V. Westley-Wise and G. Sullivan, *Australian Journal of Public Health*, 1995, 19, 357-362.
46. T. F. Bidleman, L. M. Jantunen, P. A. Helm, E. Brorstrom-Lunden and S. Juntto, *Environmental science & technology*, 2002, 36, 539-544.
47. P. Chakraborty, G. Zhang, J. Li, Y. Xu, X. Liu, S. Tanabe and K. C. Jones, *Environmental Science and Technology*, 2010, 44, 8038-8043.
48. S. Y. Baek, S. D. Choi and Y. S. Chang, *Environmental science & technology*, 2011, 45, 4475-4482.
49. L. E. A. R. Network, http://www.lindane.org/ world/countries/australia.htm#ANZEC, http://www.lindane.org/ world/countries/australia.htm#ANZEC.
50. K. Pozo, T. Harner, A. Rudolph, G. Oyola, V. H. Estellano, R. Ahumada-Rudolph, M. Garrido, K. Pozo, R. Mabilia and S. Focardi, *Atmospheric Pollution Research*, 2012, 3, 426-434.
51. H. A. Alegria, F. Wong, L. M. Jantunen, T. F. Bidleman, M. S. Figueroa, G. G. Bouchot, V. C. Moreno, S. M. Waliszewski and R. Infanzon, *Atmospheric Environment*, 2008, 42, 8810-8818.
52. Y. F. Li, M. T. Scholtz and B. J. Van Heyst, *Journal of Geophysical Research: Atmospheres*, 2000, 105, 6621-6632.
53. APVMA, *The reconsideration of approval of the active constituent Endosulfan, registrations of products containing Endosulfan and their associated labels_final review report and regulatory decision_review series 2*, 2005.
54. D. Murray, *Cotton Pest Control in Australia Before and After Bt cotton: Economic, Ecologic and Social Aspects*, 2005.
55. APVMA, ed. C. o. A. Gazette, 2010.
56. CottonAustralia, Australian Cotton Production Statistics, http://www.cnpa.embrapa.br/produtos/algodao/publicacoes/trabalhos_cba5/303.pdf.
57. APVMA, Mirex Chemical Review_8_Regulatory Decision, http://apvma.gov.au/node/1831.