DIOXINS AND WOODSMOKE IN AUSTRALIAN CITIES

John Gras[1], Jochen Müller[2], Robert Symons[3], Debbie Burniston[3], Chris Mobbs[4], and Andrew Ivory[4]

[1]CSIRO Atmospheric Research, Aspendale, Vic.
[2]National Research Centre for Environmental Toxicology, *Coopers Plains, Qld.*
[3]National Measurement Institute, Pymble, NSW.
[4]Australian Government Department of the Environment & Heritage, Canberra, ACT

Abstract

Polychlorinated dibenzo dioxins (PCDDs) and related species, polychlorinated dibenzo furans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs), are amongst the most toxic pollutants known. Previous measurements of these species in Australia's atmosphere have been limited to only a few locations. Results from a recent twelve-month study, funded by the Australian Government Department of the Environment and Heritage and conducted by CSIRO Atmospheric Research, have shown low concentrations for dioxin-like species, by world standards, for all the major Australian cities studied. Clear annual cycles of these species were observed with relatively elevated levels measured during the winter months. For the PCDD/PCDF congeners there appears to be a consistent link to a domestic smoke source.

Keywords: airborne, polychlorinated, dioxin, furan, woodsmoke

1. Introduction

Polychlorinated dibenzo dioxins and the related species, polychlorinated dibenzo furans (described subsequently as PCDD/F) and dioxin-like polychlorinated biphenyls (PCBs), referred to here collectively as dioxins, are amongst the most toxic pollutants known, falling into the wider set of "problem" species known as persistent organic pollutants or POPs. Most concerns about health effects of dioxins, as summarised, for example, by the World Health Organization (2004), arise from long term exposure, with suspected impacts on the reproduction, endocrine, immune and nervous systems. There is also evidence that some congeners, particularly 2,3,7,8-TCDD are, or may be, cancer-causing.

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty aimed at protecting human health and the environment; the convention includes dioxin-like species and was ratified by Australia on 20 May 2004. Article 5 of the Convention, requires parties to take actions to reduce, and, where feasible, eliminate releases of by-products POPs which include polychlorinated dibenzo dioxins, polychlorinated dibenzo furans and dioxin-like polychlorinated biphenyls (PCBs),

PCDD/Fs are not deliberately manufactured on an industrial scale but can be produced for example as contaminants in other processes. Likely sources of PCDD/F and their potential contributions to air in Australia have recently been reviewed (Environment Australia 2002) and updated (Bawden et al. 2004). In the 2002 review, biomass combustion (including prescribed and wildfires) was identified as contributing around 75% of total annual emissions to air. The 2004 revision reduces this contribution to around 48% although in both cases, combined combustion sources (which also include residential and industrial wood combustion, power generation, metals and sinter production) are expected to account for approximately 95% of total annual dioxin emissions to air. Given the potential importance of these combustion processes in Australian dioxin production and the obligations from the Stokholm Convention on POPs to reduce or where feasible eliminate emissions, understanding the magnitude of the contributions from the different combustion sources has a particular significance.

Dioxin-like PCBs have been used in industrial applications; with examples including various products such as the Monsanto Arochlor mixes (e.g. 1254) that previously found application as transformer and capacitor oils. Whilst these uses

have been substantially eliminated, some residual material may still be present either in previously contaminated sites or possibly decommissioned equipment. Dioxin-like PCBs were determined as part of the study but typically were not strongly correlated with PCDD/Fs or smoke tracers, and are not reported here.

The work described here sets out primarily to establish representative concentration levels for toxic dioxins and furans in Australian cities, using a uniform sampling approach and as much as practical, over the same sampling period. Concentrations of the 17 dioxin and furan congeners, with established toxicity factors (Van den Berg *et al*. 1998) the total (tetra to octa PCDD/F) homologue groups and the 12 dioxin-like PCB congeners were determined for a full annual cycle, in order to detect any seasonal factors and included a number of other species that might act as tracers for some known aerosol sources.

2. Previous Australasian measurements

There have been few determinations of the concentration of atmospheric dioxin-like species in Australian urban atmospheres and none previously with national scope, whereas Buckland et al. (1999) reported an extensive program conducted in New Zealand in the 1990s. These studies are summarised in Gras and Müller (2004) and the range of reported PCDD/F concentrations for urban and some industrial/urban environments from a number of countries are plotted here for comparison in Fig. 1. The data are plotted, as reported, in the older international toxic equivalence (I-TEQ) scale, which differs slightly from the now preferred WHO_{98}-TEQ scale (Van den Berg *et al*. 1998) and in which the data from this study are reported.

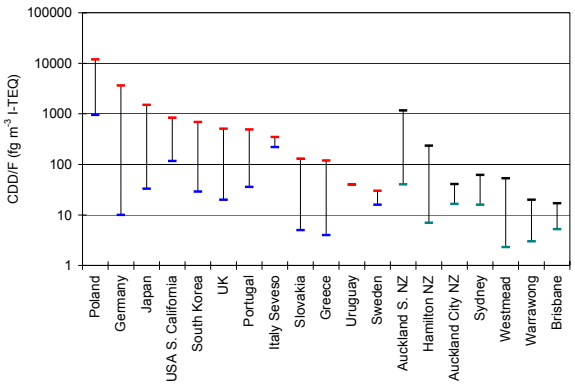

Fig. 1. Reported ranges for PCDD/F loadings in urban and industrial-urban locations (as I-TEQ). Loadings for Australian locations are the four points on the right. Original references are given in Gras and Müller (2004).

3. This study – experimental

Work reported here was carried out as part of the Australian National Dioxin Program, a twelve-month study, funded by the Australian Government Department of the Environment and Heritage and conducted by CSIRO Atmospheric Research and the National Research Centre for Environmental Toxicology. The ambient-air sampling component of the Program was aimed at covering a wide range of Australian environments, from remote through rural to urban. The focus was on representative locations and mainly included sites used for air quality compliance monitoring. The urban sites used included a number that are prodominantly residential as well as some that were industrial and some more mixed. The urban locations that comprise the basis for the present work are:

- Wattleup, in the Kwinana area, south of Perth, W.A. (industrial)
- Duncraig, Perth, W.A. (mid-sized urban)
- Eagle Farm, Brisbane, southeast Qld. (urban, light industrial)
- Westmead, Sydney, N.S.W. (major urban, some light industry impact from mixed industrial/urban air shed)
- Alphington, Melbourne, Vic. (major urban area, Yarra Valley)
- Netley, Adelaide S.A. (urban, light industrial).

3. 1 Instrumentation

Samplers used in the study were designed for combined gas and particle phase dioxin collection. They employ an open face quartz fibre filter, for aerosol with PUF-XAD2-PUF gas traps. Traps were constructed from PUF (polyurethane foam) plugs, typically 60 mm diameter x 25 mm long and 60 mm x 50 mm, with 10 g of XAD-2 resin per charge. The PUFs were pre-spiked using a range of isotopically-labelled surrogate standards.

Most samplers were operated at flow rates between 160-200 L min^{-1}, one exception was a pre-existing NRCET sampler, operated at Eagle Farm which was operated with a flow rate of around 73 L min^{-1}. All reported flow rates and concentrations are referenced to standard conditions (0 ºC, 1013 hPa). Integrated air flow was determined weekly, using built-in gas meters (typically Toyo MT5). Temperature and pressure values used for conversion to standard conditions are climatological values for the relevant month, at the nearest climate station.

Gas trap components were prepared at the Australian Govenrnment Analytical Laboratories (now National Measurement Institute) Sydney.

This comprised clean-up, a batch blank verification analysis, XAD-2 packing, spiking and trap assembly. Filters were baked at CSIRO at 400 ºC for 24 hours, conditioned then weighed at laboratory relative humidity (RH), typically 30-50% RH. Traps were shipped using clean aluminium-foil wrapping and air-tight metal canisters. Returning samples were stored in a freezer until the end of each sample month. Sample blanks representing approximately 10% of ambient samples were determined and other quality assurance procedures included the use of collocated samplers for 5% of samples and 5% of split aliquots for duplicates both of which were analysed independently (see Gras and Müller (2004).

The standard sampling protocol utilised one-month samples comprising a single gas trap combined with a series of one-week exposure filters covering the same period; this mitigates against loss of semivolatile aerosol phase material. At the Netley SA site the gas trap exposure was for two months with weekly filter changes.

4. Mean dioxin levels and seasonal cycle in Australian urban locations

Annual mean atmospheric PCDD/F concentrations for the Australian urban locations studied are plotted in Fig. 2.

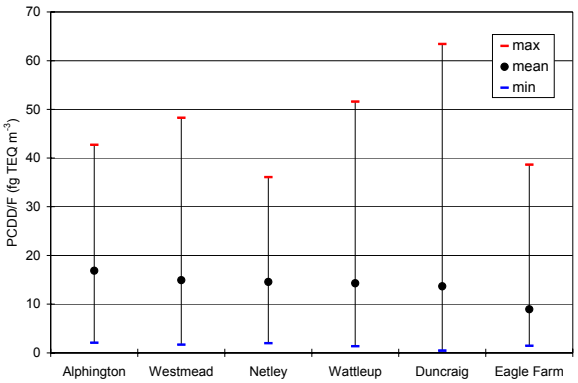

Fig. 2. Annual mean PCDD/F loadings, and maximum and minimum monthly loadings. as WHO_{98}-TEQ.

These annual mean levels show relatively small variation between the different cities studied, apart from Eagle Farm (Brisbane) the most northerly of the cities considered. Comparison with reported PCDD/F concentrations from other locations, as plotted in Fig. 1, show that Australian urban concentrations are at the low end of the typically observed range. Despite the low annual average levels, clear annual cycles in PCDD/F were observed in all of the Australian cities studied, with strongly elevated levels measured during the winter months. This is reflected in the minimum and maximum monthly values shown in Fig. 2, and the annual cycles in Fig. 3. Summer concentrations of PCDD/F were extremely small, the hotter months (Jan., Feb., Mar.), were typically 19% of the annual mean. Brisbane has an annual cycle similar to the more southern cities, but the winter increase is weaker, shorter and starts later. These are important clues to understanding the possible major sources of Australian urban dioxins.

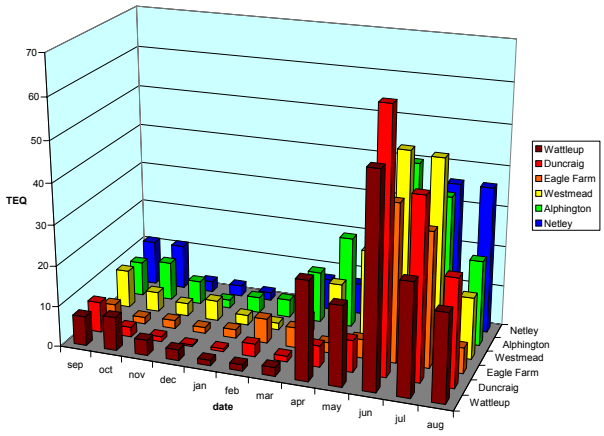

Fig. 3. Histogram of seasonal variation in PCDD/F loading by location.

A number of lines of evidence strongly suggest that the winter elevation of PCDD/F loadings result from residential wood combustion. Winter PCDD/F congener patterns, both the toxic congener and homologue groups, have a very consistent pattern for Duncraig, Wattleup, Westmead, Alphington, Netley and to some extent Eagle Farm. Homologue profiles are very similar to winter homologue profiles at Masterton and Christchurch N.Z., as reported by Buckland et al. (1999), who attribute these patterns to residential wood combustion. Directly relating source and ambient PCDD/F congener profiles is known to be problematic, however toxic congener profiles for eucalypt wood smoke, determined recently by Gras et al. (2002) and a pattern of elevated furans, decreasing with increasing chlorination and with a small peak around 1,2,3,4,6,7,8-HpCDF is similar to the Australian urban ambient congener profiles.

The form of the annual cycle is a strong qualitative indicator of an influence from wood combustion; quantitative indicators in the measurement series included total aerosol mass (TSP) as well as aerosol cation and anion species in the TSP, determined from aqueous extracts using ion chromatography. Aerosol potassium (K) is one potentially useful tracer for woodsmoke but there are possible interferences in this particular

measurement series because of the strong coarse mode contribution to TSP. Potassium from sea salt is readily corrected, using for example sodium or magnesium to calculate the expected concentration of potassium in the coarse mode sea-salt aerosol. Potassium from soil aerosol is more difficult with the present analysis suite, since there are no unambiguous soil tracers. Correcting measured potassium (K^+) only for sea-salt potassium (nssK) results in a correlation coefficient of r = 0.61 between nssK and total PCDD/F, and this is highly significant (n=64, sig = 0.000 t = 5.9). Factor analysis of the soluble species for these data shows significant association between fluoride (F^-) phosphate, calcium and nitrate, and this factor has been interpreted as representing the aerosol coarse mode. Fluoride is a known contaminant in phosphate fertilizer and soluble fluoride also comprises a small but variable fraction of the total fluoride in uncontaminated soils (typically 0.1-0.001, Cronin et al. 2000). A K/Fsol ratio of 1.87 was determined from multiple regression for K^+, which is equivalent to 2% of soluble F for average crustal composition. This was used to derive an empirical coarse fraction K, which with the measured nssK is designated as nssK* and is used as a smoke tracer. This tracer gives an improved correlation with total PCDD/F resulting in a coefficient of r = 0.74 (see Fig. 4). The second interference in this context is from open burning of biomass, which yields a lower PCDD/F emission factor (per unit fuel burnt) than burning in a closed appliance (Meyer et al. 2004). Whilst emissions from open biomass burning will have their own PCDD/F to nssK ratio, in the present context they will tend to reduce the correlation between PCDD/F and nssK* arising from combustion in heating appliances. A third factor potentially reducing correlations is that this analysis is taken over five different cities and some regional difference in source composition ratios is possible.

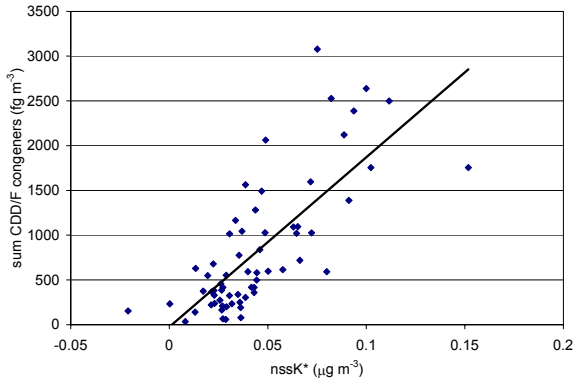

Fig. 4. Relationship between total PCDD/F congener concentrations and smoke indicator variable nssK* [see text for derivation].

5. Conclusions

Results from the 12-month study of toxic dioxin and furan concentrations in Australian cities has shown loadings that are at the low end of loadings reported from other urban and urban-industrial locations elsewhere in the world. Clear annual cycles were observed in PCDD/F loadings in the Australian cities, even as far north as Brisbane, and this pattern is interpreted as resulting from residential wood combustion for heating. This conclusion is supported by a statistically significant correlation of PCDD/F concentrations and non-sea salt potassium, a tracer for wood smoke as well as the similarity of homologue patterns with those observed in wood-smoke impacted cities in New Zealand and with source emission profiles from wood-heating appliances burning Australian hardwood fuels.

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