Atmospheric dioxins and dioxin-like PCBs at remote Australian locations

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Introduction

Dioxins are predominantly generated as unintended by-products of combustion processes and are usually emitted into the atmosphere. Consequently, atmospheric transport represents the primary route for transport of dioxins into the environment. Recent estimates suggest that in Australia, combustion sources could be expected to contribute up to 95% of the total air-borne dioxin emissions, with up to 75% from fossil fuel and biomass combustion alone[1]. The present studies carried out for Australia's National Dioxin Program will allow refinement of these estimates.

To date, little information has been available on the levels of dioxin-like chemicals in the Australian atmosphere, particularly at non-urban sites. In 2002 the Department of Environment and Heritage, Australia (DEH) initiated the National Dioxin Program in Australia with the aim of providing data on the levels of dioxin-like chemicals. This included a 12-month study on the levels of dioxins in ambient air. Here we report on the analytical results from four relatively remote sites, covering a range of climatic zones, from far northern to southern Australia.

Methods and Materials

Sampling Sites
Data from four sampling sites (see Fig. 1) are presented here:

- Berrimah, Northern Territory (a outer urban location in Darwin, located a remote rural region in far-northern Australia)
- Mutdapilly, south-east Queensland (an agricultural/grazing region near the south-western fringes of Brisbane)
- Boorolite, north-east Victoria (an agricultural/grazing area well removed from population centres; about 170 km north-east of Melbourne)
- Cape Grim, north-west Tasmania (a pristine, remote, location that receives clean maritime air from the Southern Ocean)

Samples were collected using a glass-fibre filter/adsorbent system (GFF/PUF/XAD-2) similar to the system that has been described and tested previously[2]. At Berrimah, Mutdapilly and Boorolite, samplers were run continuously at about 4 – 10 m^3 h^{-1}, usually collecting in excess of 3000 m^3 per month (corrected for pressure drop in the system). At Cape Grim the sampler was operated only for local winds from the clean marine sector (190° – 280°) and when total particle concentration was less than a seasonally-varying clean threshold value. Due to the extremely low levels encountered, a sampler operating at about 60 m^3 h^{-1} was used at this site. Noteably however, a burn-out of an electrical controller on a nearby sampler (3 m distant) that also operated only during clean conditions caused substantial contamination in samples from May and June 2003 and thus these samples have been discarded from the data (i.e. the mass of PCDD/PCDF collected on the trap increased by more than 3 orders of magnitudes from April to May due to this burnout).

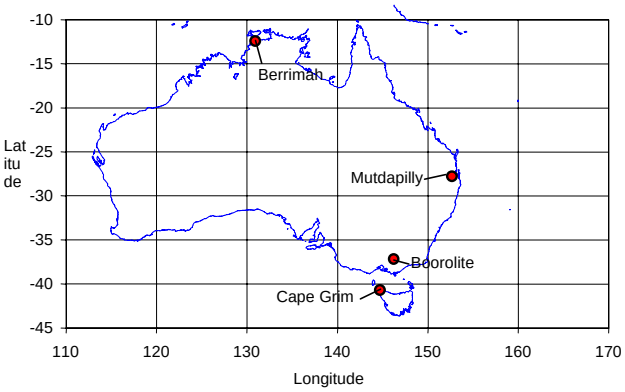

Figure 1 Map of Australia that includes the four sampling sites Berrimah, Mutdapilly, Boorolite and Cape Grim, representing remote and relatively non-urban atmospheric environments in Australia

Analysis of PCDD/PCDF and dioxin-like PCB Analyses

All analyses were conducted by the Australian Government Analytical Laboratories in Sydney. Standards used for calibration, quantification and determination of recovery of PCDD/PCDF and dioxin-like PCBs were sourced from Wellington Laboratories (Ontario, Canada). Solvents were purchased as pesticide-quality standard and used as received. All chromatographic columns were sourced from Fluid Management Systems (Waltham, MA, USA) and were used without further treatment. These comprised multi-layer (basic/neutral/acidic) silica, alumina and PX-21 carbon dispersed on celite. For extraction the filter/PUF/XAD-2 resin combinations were transferred to a large soxhlet extractor, spiked with a known amount of the respective PCDDs/PCDFs and dioxin-like PCB isotopically labeled $^{13}C_{12}$ surrogate spiking solutions and exhaustively extracted with an ethanol:toluene nmixture (68:32). The dried extracts were then cleaned-up on the Power-Prep™ system. Samples were analysed using GCMS (Agilent 6890 GC coupled with a MAT95XL HRMS). A DB-5 (J & W Scientific, Folsom, CA, USA) capillary column (60 m x 0.25 mm i.d., film thickness 0.25 µm) was used as the primary analytical column with a DB-Dioxin (J & W Scientific, Folsom, CA, USA) capillary column (60 m x 0.25 mm i.d., film thickness 0.15 µm) used as the secondary analytical column for quantification of those 2,3,7,8- CDD & CDF congeners not completely resolved on the DB-5 column. Resolution was maintained at 10,000 (10% valley definition) throughout the sample sequence. Multiple ion detection (MID) experiments were performed in the electron impact mode with monitoring of the exact masses of either M+ [M+2]+

or [M+4]+ ions for native and labeled compounds. Individual congeners were identified using the GC retention time and ion abundance ratios with reference to internal standards.

Results and Discussion

Dioxin-like chemicals were detectable in all air samples collected at the four sites. The concentration of the sum of detectable tetra-octachlorinated PCDD/PCDF (∑PCDD/Fs) ranged from about 3 fg m^{-3} in January 2003 at Cape Grim, to about 1700 fg m^{-3} at the Berrimah site, in September 2002. When expressed as TEQ, median concentrations for the 12-month period at the four sites ranged from <1 fg TEQ m^{-3} air at Cape Grim to 2.9 fg TEQ m^{-3} at Berrimah (Fig. 2). Overall the concentrations were slightly higher at the Berrimah and Mutdapilly Sites, both of which are within the greater vicinity of urbanised areas (i.e. Darwin and Brisbane respectively). The lowest PCDD/PCDF concentrations were observed at Cape Grim with highest concentrations in August (that is the Australian winter). The annual median concentrations of dioxin-like chemicals at Cape Grim and Boorolite were less than 1 fg TEQ $^{-3}$ air.

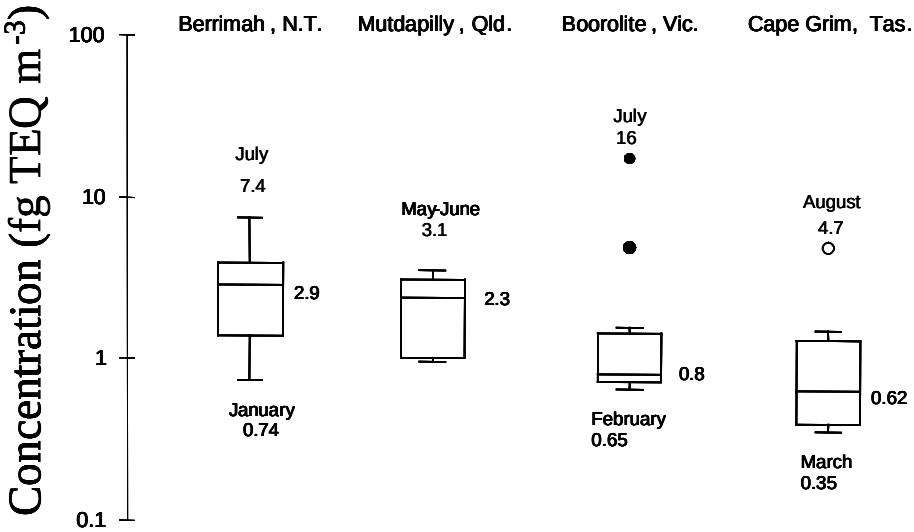

Figure 2: Box-Whisker plot of PCDD/PCDF concentration expressed as TEQ, in air samples collected from the four sites over a 12-month period. Data shown use middle bound values. Boxes represent the median, 25th and 75th percentiles, whiskers the 5th and 95th percentiles.

The annual pattern of dioxin-like chemicals shows a clear trend with the highest levels in late autumn and winter (May – August) and lowest levels in summer (December – March) (as shown in Figures 3a & b). The data suggest that seasonal variation is mainly due to an increase of PCDD/PCDF in winter. Lower chlorinated PCBs (i.e. PCB 71 and PCB 88) for example, showed a trend of higher concentration in summer and lower concentrations in winter months (data not shown). This suggests that dioxins are primarily emitted in the winter months, whereas

volatilisation from soils or water bodies may be a key source for lower chlorinated PCBs during the Australian summer.

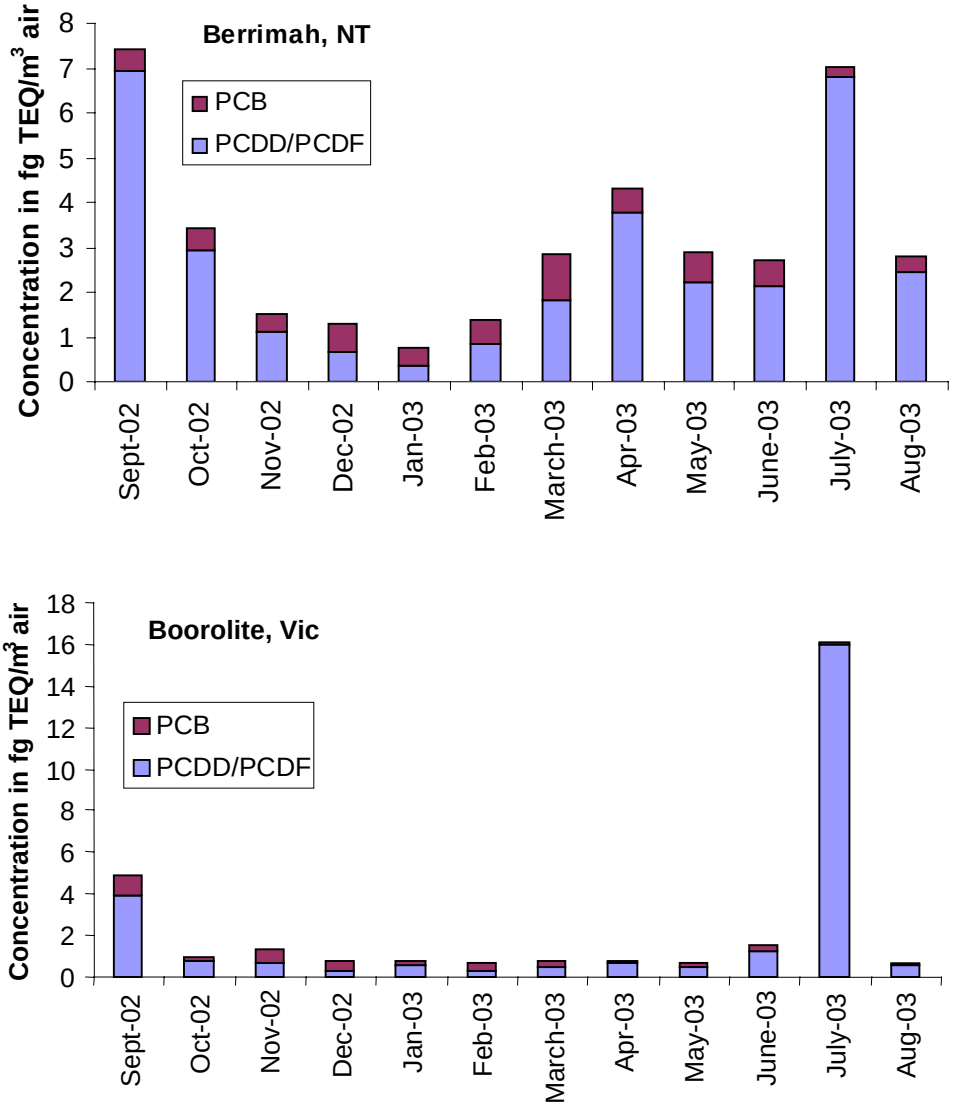

Figure 3 a & b: Concentration of dioxin-like chemicals expressed as fg TEQ m^{-3} air in samples from Berrimah (NT) and Boorolite (Vic), Australia.

A comparison with overseas data suggests that background levels of dioxin-like chemicals in Australian air are among the lowest observed in any industrialised country. For example, the mean concentration of PCDD/PCDF, as TEQ_{DF}, in clean Southern Ocean air sampled at Cape Grim, for September 2002 to August 2003 was less than 1.0 fg TEQ_{DF} m^{-3}. This is given as an upper limit and includes three times sample-blank noise for any congener's limit of detection (LOD), with half LOD for congeners less than the LOD. The data are not additionally blank-corrected for field blank concentrations. The mean field blank level was typically 0.7 fg TEQ_{DF} m^{-3} for the first six months samples and for the second six months 0.2 fg TEQ_{DF} m^{-3}. The corresponding three times the field blank standard deviation was 1.2 fg TEQ_{DF} m^{-3} for the first six months and for the second period around 0.3 fg TEQ_{DF} m^{-3}. The concentration for Cape Grim is slightly less than, but still consistent with, concentrations observed at the New Zealand reference site[3] and a reference site in a recent NSW EPA study[4]. The results are also similar to those reported for air samples collected at other remote southern hemisphere sites, such as Bird Island and Halley Bay[5].

Mean loadings of PCDD/PCDF at the rural/remote sites, Boorolite in north-east Victoria, Mutdapilly in south-east Queensland and Berrimah in the NT for September 2002 to August 2003, fall in the range of 1.5 to 2.2 fg TEQ_{DF} m^{-3}. These values, which are also not blank corrected (typical field blank level 0.6 fg TEQ_{DF} m^{-3}), are comparable with the cleanest New Zealand rural locations[3] and the Falkland Islands[5]. They are also much lower than the mean of 11–15 fg I-TE m^{-3} reported for rural locations in the USA, and using comparable treatment of samples less than the LOD[6].

In summary, the study found very low concentrations of dioxin-like chemicals at four sites around Australia that are not immediately in urban areas. The data show a clear seasonal trend for PCDD/PCDF with highest concentrations in winter and lowest concentrations in summer.

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References

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