National Dioxins Program

Technical Report No. 4
Dioxins in Ambient Air in Australia

A consultancy funded by the Australian Government
Department of the Environment and Heritage

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3. Inventory of Dioxins emissions in Australia, 2004
4. **Dioxins in Ambient Air in Australia**
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Foreword

When the Australian Government established the four year National Dioxins Program in 2001, our knowledge about the incidence of dioxins in Australia was very limited.

The aim of the program was to improve this knowledge base so that governments were in a better position to consider appropriate management actions. Starting in mid 2001, a range of studies were undertaken which involved measuring emissions from sources such as bushfires, as well as dioxin levels in the environment, food and population. The findings of these studies were used to shed light on the risk dioxins pose to our health and the environment.

This work has been completed and the findings are now presented in a series of twelve technical reports.

Having good information is essential if there is to be timely and effective action by governments; these studies are a start. Our next step is to foster informed debate on how we should tackle dioxins in Australia, as this is an obligation under the Stockholm Convention on Persistent Organic Pollutants. The Department of the Environment and Heritage will be working closely with other Australian Government, State and Territory agencies to take this step.

Ultimately, the effective management of dioxins will be the shared responsibility of all government jurisdictions with the support of the community and industry.

David Borthwick

David Borthwick

Secretary

Department of the Environment and Heritage

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- officers of the Chemical Assessment Section in DEH who assessed the ecological effects of dioxins
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Executive Summary

This study was a component of the National Dioxins Program that was tasked to quantify and assess the concentrations and relative chemical compositions of dioxin-like chemicals in ambient air in Australia.

This report is part of the first phase of the National Dioxins Program, which involves the determination of representative levels of dioxins in Australia. 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. A recent review has shown that, potentially, 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 (Environment Australia, 2002). Dioxin-like PCBs have not been subject to similar review in Australia; in general they can be expected to have a different evolution, including sources, transport and, potentially, fate.

The overall objective of this report was to characterise dioxin levels in ambient air in Australia, at various locations including metropolitan, agricultural and remote reference sites. The primary aims of the study included consolidation of the current state of knowledge on dioxin levels in ambient air and achieving a greater understanding of dioxin levels in ambient air, by direct sampling.

Sampling for this report was conducted over a twelve-month period to establish possible seasonal variations in dioxin concentration, related, for example, to emissions from sources such as wood heaters and bushfires. The basic sampling period was one month. The ten measurement sites represent metropolitan, agricultural and remote area air sheds, with eight of the ten sites situated at existing air-monitoring facilities. Samples were collected using high-volume samplers incorporating particulate and gas phase traps. Particulate phase collections were based on one-week exposure periods. Analyses, at the ultra-trace level, of toxic polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs or furans) and co-planar polychlorinated biphenyls (PCBs) were conducted by the Australian Government Analytical Laboratories (AGAL) Sydney. Data were collated and processed at CSIRO Atmospheric Research.

Samplers used in the ambient air study were designed and constructed to collect both gas and particle phase dioxins and dioxin-like PCBs using established semi-volatile species collection methodologies. Samplers utilised open face quartz fibre filters for condensed phase. The gas traps, used in conjunction with the filters, were constructed from a medium-density PUF (polyurethane foam) plug, a layer of XAD-2 resin and second PUF plug in a glass housing. The first PUF plug in each trap was pre-spiked using a range of isotopically-labelled surrogate standards for sampling loss determination.

Eleven samplers were deployed overall, including a duplicate sampler at one site (Alphington). The majority of samplers were operated at flow rates between 160-200 std. L min^{-1} (std. refers to standard volume, or reduced to STP) and an additional sampler, operating at approximately 1 m^3 min^{-1} was constructed for Cape Grim and operated from March 2003 to August 2003. Samplers in Queensland were operated at

around 73 std. L min^{-1}. The sampled air volume was determined weekly, using built-in calibrated gas meters (or orifice plate for the Cape Grim high-volume sampler).

Sampling sites used for the ambient sampling project, represent the three broad geographic regions of northern Australia, south-eastern Australia and south-west Western Australia, and priority air sheds represented include Darwin, south-east Queensland, Sydney, Port Phillip and Perth, with the later addition of Adelaide.

The ten sites used for the study were:

- Wattleup, in the Kwinana area, Perth, WA (industrial)
- Duncraig, Perth, WA (mid-sized urban)
- Berrimah, Darwin, NT (small urban within a remote rural region)
- Eagle Farm, Brisbane, south-east Qld (light industrial)
- Mutdapilly, south-east Qld (agricultural/grazing)
- Westmead, Sydney, NSW (major urban, some light industry impact from mixed industrial/urban air shed)
- Boorolite, lower north-east Vic (agricultural/grazing)
- Alphington, Melbourne, Vic (major urban area, Yarra Valley)
- Cape Grim, Tasmania (pristine remote)
- Netley, Adelaide SA (light industrial)

The nominal start date for the ambient program was 1 September 2002 and the end date for sampling was 31 August 2003 with trap changes nominally at the end of each calendar month. Some latitude in change dates (a few days) was allowed to meet local logistical requirements. The sampling program for Netley, SA, was incorporated as an addition to the main sampling program after the start of the main program, and was commissioned in January 2003 and ran until January 2004.

Quality control procedures were established and documented before the start of the sampling program and included a wide range of checks on both sampling and analytical procedures. In general, data collection and analysis went smoothly and most data quality goals were attained. Two filters from Queensland were lost in the mail - these represented only small fractions of the monthly samples for those sites and resulting concentrations could be substantially corrected. Also two months' samples (June - July) from the Sydney site, were analysed with incorrect filter and gas trap combinations; however, these data were also substantially correctable using separate gas and filter analyses for the complementary filter and trap combination, retaining effective monthly samples for that site (and providing some limited qualitative information on phase partitioning).

Findings

Concentrations of the 17 toxic dioxin and furan congeners, the total (tetra to octa CDD/F) homologue groups, the 12 dioxin-like PCB congeners and a suite of inorganic and light organic aerosol components were determined for a complete annual cycle. At Mutdapilly in Qld and Netley in SA, the sample period was adjusted to two-monthly integrals after the start of the study.

A major finding of this study is a very clear, strong, seasonal cycle in PCDD/PCDF concentrations, both as mass concentrations and TEQ, with a winter concentration maximum in all of the major population centres studied, from Perth, through Adelaide, Melbourne, Sydney and as far north as Brisbane. In these cities, the difference between winter maximum and summer minimum concentrations is large, and summer concentrations in general are very low by world standards.

The seasonal variation in PCDD/PCDF concentration, correlation with aerosol non-sea-salt potassium (nssK), a tracer for biomass burning, and association of PCDD/PCDF with nssK by factor analysis, all point to a residential wood smoke source for this strong winter enhancement. Congener patterns show strong resemblances to congener concentration patterns found in a study of wood smoke emissions from Australian residential wood heaters, by Gras et al. (2002) and to homologue patterns reported for emissions from Christchurch and Masterton, NZ during winter by Buckland et al. (1999).

Despite the winter enhancement in PCDD/PCDF, overall annual mean concentrations in the major cities are still very low by world standards. For example, for the two Perth locations annual mean concentrations, expressed as middle bound TEQs, are around 14 fg TEQ_{DF} m^{-3}, Eagle Farm (Brisbane) 9 fg TEQ_{DF} m^{-3}, Westmead (Sydney) around 15 fg TEQ_{DF} m^{-3}, Alphington (Melbourne) 17 fg TEQ_{DF} m^{-3} and Netley (Adelaide) 15 fg TEQ_{DF} m^{-3}. For comparison, for northern hemisphere urban locations, with a few exceptions, typical concentrations range from around 20 fg I-TE m^{-3} to several hundred fg I-TE m^{-3}, and in eastern Europe in the 1990s, values of several thousand fg I-TE m^{-3} were not uncommon. The Australian urban concentrations are also less than those in corresponding New Zealand urban sites, and more like concentrations observed at New Zealand rural sites by Buckland et al. (1999). The very low concentrations of dioxins in Southern Ocean air, in Australian rural locations, and urban locations in summer point to predominantly local sources for the observed dioxins.

Seasonal cycles in TEQ_{DF} were also observed in rural Queensland and rural Victoria although these were weaker than in the major urban locations. Likewise, a dry season to wet season difference was found in Darwin (the Berrimah site) with TEQ_{DF}, concentrations in the dry season around four times those found during the wet season. But, mean concentrations in Berrimah are very low (less than 3 fg TEQ_{DF} m^{-3} annual mean); hence, the impact of top-end dry season burning on PCDD/PCDF concentrations appears to be relatively minor (during this study).

Extremely low PCDD/PCDF concentrations were observed in clean marine air and also in rural locations removed from the major urban centres (typically less than 2 fg TEQ_{DF} m^{-3}). This indicates a very clean regional background, with the major sources being local and associated with the urban population.

The relative contributions of TEQ_{DF} and TEQ_{P} vary across the different locations. For the urban locations the PCB concentrations appear to be more location specific than the PCDD/PCDF concentrations. The SA site, Netley, has the highest dioxin-like PCB levels in ambient air of the locations studied and the highest fraction of PCBs in the $TEQ_{DF\&P}$.

A local pollution event at Cape Grim occurred in May - June 2003. This coincided with an electrical burn-out of a plastic-encapsulated electronic component assembly in a nearby sampler. Very high local loadings of heavier, highly chlorinated dioxins and furans resulted, predominantly in May with a minor carryover into June.

Overall, the one-year study shows that concentrations of PCDD/PCDF and dioxin-like PCBs in Australian air are very low by world standards. PCDD/PCDFs have a pronounced seasonal cycle with a winter maximum in most large Australian cities, and this appears to be largely due to wood burning for residential heating.

During the study period bushfire activity was very strong in both south-eastern and south-western Australia, notably over the summer of 2002-2003. Smoke from bushfire burning was reported from a number of sampling locations including Wattleup, Duncraig, Boorolite and Alphington. PCDD/PCDF concentrations do not show elevations as strong as those observed during winter, suggesting significant composition differences between smoke from open biomass burning and that from domestic burning.

Concentrations of dioxin-like PCBs in general did not correlate strongly with those of PCDD/PCDFs and were generally higher in the warmer seasons, compared with the winter maxima for the PCDD/PCDFs. PCB169 shows positive correlation with the PCDD/PCDFs and the smoke tracers. The general lack of correlation between concentrations of the dioxin-like PCBs and the dioxins, points to different sources or transformation histories for these species.

Glossary/Abbreviations

AGAL	Australian Government Analytical Laboratories.
BAPS	Baseline Air Pollution Station - Cape Grim, Tasmania.
Baseline	Clean oceanic air conditions at Cape Grim BAPS.
CAR-SV	CSIRO AR semi-volatile sampler.
CBD	Central Business District.
Congeners	Closely related chemicals derived from the same parent compound.
CSIRO	Commonwealth Scientific and Industrial Research Organisation.
CSIRO AR or CAR	CSIRO Atmospheric Research.
CSIRO-ET	CSIRO Energy Technology.
CSIRO-SE	CSIRO sustainable Ecosystems.
CSIRO-TERC	CSIRO Tropical Ecosystems Research Centre.
Dioxin-like PCBs	PCBs with a structure similar to that of dioxins, here includes only PCBs assigned a TEF by the WHO.
Dioxins	Common name for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans.
DQO	Data Quality Objective.
EPA-V	Victorian Environment Protection Authority
fg	Femto gram = 10^{-15} g.
Furan	Polychlorinated dibenzofuran.
Homologue group	A group of structurally related chemicals (for dioxins these have the same degree of chlorination).
HRGC	High Resolution Gas Chromatograph.
HRMS	High Resolution Mass Spectrometer.
Isomers	Compounds with the same molecular formula but different structure.
I-TE	Toxicity equivalencies using NATO-CCMS (1988) toxicity equivalency factors; most data prior to 1998 including the NZ studies reported in I-TEs which usually did not included PCBs.
IUPAC	International Union of Pure and Applied Chemistry.
LOD	Limit of detection. Here based on 3 times standard deviation of blank analysis.
Lower bound TEQ	Toxic equivalencies (TEQ) for which concentration of a non-detected congener assumed to be equal zero.

Middle bound TEQ	Toxic equivalencies (TEQ) for which concentration of a non-detected congener assumed to be equal to half the non detect value.
MOE Canada	Ministry of Environment Canada (second analysts).
NDP	National Dioxins Program.
NRCET	National Research Centre for Environmental Toxicology.
nss	Non-sea-salt.
nssK	Non-sea-salt potassium, example of smoke tracer.
NSW EPA	New South Wales Environment Protection Authority.
PCB	Polychlorinated biphenyl.
PCDD/PCDF	Polychlorinated dibenzo-*p*-dioxin and furan.
pg	Pico gram 10^{-12} g.
PUF	Polyurethane foam, used as part of the gas sampling system.
QC	Quality control.
STP	Standard temperature and temperature 0ºC, 1013 hPa.
Surrogate recovery	Percentage recovery for $^{13}C_{12}$ labelled surrogate standard.
TEF	Toxic equivalency factor for specific dioxin, furan or PCB. Defines the toxicity of each congener with dioxin-like biochemical and toxic responses, relative to the toxicity of the dioxin 2,3,7,8-TCDD (Van den Berg et al. 1998).
TEQs	Abbreviation of WHO$_{98}$-TEQ (in this report).
WHO$_{98}$-TEQ	World Health Organization toxic equivalent: the quantified level of each individual congener multiplied by the corresponding TEF. TEQs of each congener are summed to achieve and overall toxic equivalency for a sample (Van den Berg et al. 1998). In this document WHO$_{98}$-TEQ is abbreviated to 'TEQ'.
TEQ$_{DF}$	WHO$_{98}$-TEQ for dioxins and furans.
TEQ$_{DF\&P,}$ TEQ$_{DFP}$	WHO$_{98}$-TEQ for all analytes.
TEQ$_{PCB,}$ TEQ$_{P}$	WHO$_{98}$-TEQ for (dioxin-like) PCBs.
Upper bound TEQ	Toxic equivalencies (TEQ) for which concentration of a non-detected congener assumed to be equal to the non detect value.
XAD-2	Resin used as part of the gas sampling system.

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1 Introduction

1.1 Background

This project, "Dioxins in Ambient Air in Australia", is an integral part of a comprehensive National Dioxins Program being conducted by the Australian Government Department of the Environment and Heritage. Overall, the National Dioxins Program is a four-year activity set up to assess, and manage, dioxins and dioxin-like substances in Australia.

The aims of the National Dioxins Program are to:

- ensure protection of the health of the Australian population and environment from exposure to dioxins
- ensure that international obligations concerning dioxins are met
- complement work of other government agencies in protecting the integrity of Australia's food.

Activities of the National Dioxins Program comprise three phases:

- **Phase 1 -** determination of levels of dioxins in Australia
- **Phase 2** - assessment of the impact of dioxins on human health and the environment
- **Phase 3** - in light of the assessed impacts, reduction and where feasible, elimination of releases of dioxins in Australia.

"Dioxins" refer to the group of persistent chlorinated chemical compounds, polychlorinated dibenzodioxins (PCDD), which share certain similar chemical structures, properties and biological characteristics, including toxicity. For the purpose of the NDP the term "dioxins" is used in the broader sense and is also taken to include the closely related polychlorinated dibenzofurans (PCDF) and co-planar polychlorinated biphenyls (PCB). Several hundred of these compounds - or congeners exist, of which 29 are considered by the World Health Organization (WHO) to have significant toxicity (WHO, 1998). It is these 29 closely related toxic chemicals that are the subject of this report and they are listed in Table 1.1. The general formulae for PCCD and PCDF are presented in Figure 1.1; numbers 1-9 indicate the possible positions of the chlorine atoms. The general formulae for PCB is presented in Figure 1.2, numbers 2-6 (2'-6') indicate the possible positions of the chlorine atoms at ortho(o), meta(m) and para(p) positions, respectively.

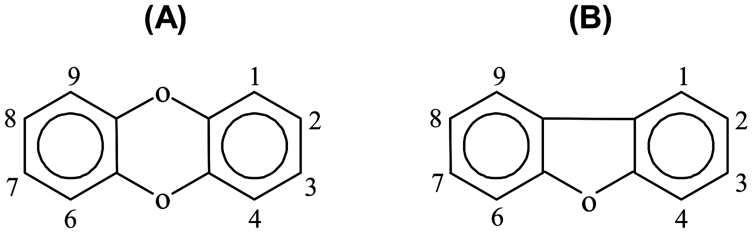

Figure 1.1 The structures of polychlorinated (A) dibenzo-p-dioxins and (B) dibenzofurans.

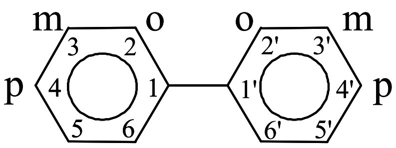

Figure 1.2 The structures of polychlorinated biphenyls (PCB).

Since dioxins occur as complex mixtures of congeners in most environmental media (air, water, soil), the concept of toxic equivalents (TEQs) has been developed. This concept allows the toxicity of a complex mixture to be expressed as a single number. Available animal-based toxicological data have been used to generate a set of weighting factors, each of which expresses the toxicity of a specific congener relative to an equivalent mass of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), the most studied and most toxic PCDD. Multiplication of the mass of the congener by its weighting factor (or toxic equivalents factor, TEF) yields the corresponding toxic equivalent for a given congener (TEQ) in a mixture. The formula for calculating TEQ is as follows:

$$\mathrm{TEQ} = ([\mathrm{PCDD}_i \times \mathrm{TEF}_i]_n) + ([\mathrm{PCDF}_i \times \mathrm{TEF}_i]_n) + ([\mathrm{PCB}_i \times \mathrm{TEFi}]_n)$$

The total toxicity (total TEQ) is the sum of the TEQs for all 17 congeners.

The most widely adopted system of TEF is that proposed by the North Atlantic Treaty Organisation (NATO) and known as the International Toxic Equivalents Factors (I-TEFs). This system has been updated and expanded by a WHO/IPCS expert group in 1997 and includes 12 dioxin-like PCB. This scheme also differentiates between mammalian, avian and aquatic organisms. The TEFs for humans for the 29 closely related chemicals that are the subject of this report are listed in Table 1.1.

A review of sources of dioxins and furans in Australia (Environment Australia, 2002) has shown that, from the limited data available, emissions of dioxins are expected to be low. A range of possible sources of dioxins in Australia was identified and these include bushfires and prescribed burning, residential wood combustion and industrial processes. The review also showed that potentially, these sources could be expected to contribute up to 95% of the total dioxin emissions, with up to 75% from fossil fuel and biomass combustion alone. Dioxin-like PCBs have not been subject to similar review in Australia, but in general, these species can be expected to have a significantly different history, including sources, transport and, potentially, fate.

Table 1.1 Dioxin, furans and PCB toxic equivalent factors (both I-TEF or NATO and WHO$_{98}$ TEF).

Congener	IUPAC No.	NATO CCMS or WH0$_{94}$-TEF	WHO$_{98}$-TEF (3)
Dioxins[a]			
2,3,7,8-TetraCDD [a]	-	1 (1)	1
1,2,3,7,8-PentaCDD	-	0.5	1
1,2,3,4,7,8-HexaCDD	-	0.1	0.1
1,2,3,6,7,8-HexaCDD	-	0.1	0.1
1,2,3,7,8,9-HexaCDD	-	0.1	0.1
1,2,3,4,6,7,8-HeptaCDD	-	0.01	0.01
OctaCDD	-	0.001	0.0001
Furans[b]			
2,3,7,8-TetraCDF [b]	-	0.1	0.1
1,2,3,7,8-PentaCDF	-	0.05	0.05
2,3,4,7,8-PentaCDF	-	0.5	0.5
1,2,3,4,7,8-HexaCDF	-	0.1	0.1
1,2,3,6,7,8-HexaCDF	-	0.1	0.1
1,2,3,7,8,9-HexaCDF	-	0.1	0.1
2,3,4,6,7,8-HexaCDF	-	0.1	0.1
1,2,3,4,6,7,8-HeptaCDF	-	0.01	0.01
1,2,3,4,7,8,9-HeptaCDF	-	0.01	0.01
OctaCDF	-	0.001	0.0001
Non-ortho PCB [c]			
3,3',4,4'-tetrachlorobiphenyl	PCB#77	0.0005 (2)	0.0001
3,4,4',5-tetrachlorobiphenyl	PCB#81	-	0.0001
3,3',4,4',5-pentachlorobiphenyl	PCB#126	0.1	0.1
3,3',4,4',5,5'-hexachlorobiphenyl	PCB#169	0.01	0.01
Mono-ortho PCB [c]			
2,3,3',4,4'-pentachlorobiphenyl	PCB#105	0.0001	0.0001
2,3,4,4',5-pentachlorobiphenyl	PCB#114	0.0005	0.0005
2,3',4,4',5-pentachlorobiphenyl	PCB#118	0.0001	0.0001
2',3,4,4',5-pentachlorobiphenyl	PCB#123	0.0001	0.0001
2,3,3',4,4',5-hexachlorobiphenyl	PCB#156	0.0005	0.0005
2,3,3',4,4',5'-hexachlorobiphenyl	PCB#157	0.0005	0.0005
2,3',4,4',5,5'-hexachlorobiphenyl	PCB#167	0.00001	0.00001
2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB#189	0.0001	0.0001

[1] NATO CCMS (1989) From Kurtz et al., (1990)
[2] WHO-TEF (1994) From Ahlborg et al., (1994)
[3] WHO-TEF (1998) From van den Berg et al., (1998)

[a] CDD – chlorinated dibenzo-*p*-dioxin
[b] CDF – chlorinated dibenzofuran
[c] PCB – polychlorinated biphenyl

1.2 Objectives

The overall objective of the “Dioxins in Ambient Air in Australia” report is to characterise dioxin levels in ambient air in Australia, at various locations, including metropolitan, agricultural and remote reference sites.

The project aims are to:

- consolidate the current state of knowledge on dioxin levels in ambient air, in Australia
- gain a greater understanding of dioxin levels in ambient air, in Australia, by direct sampling.

1.3 Project scope

The ambient air project, as designed, was implemented in four stages.

Stage 1: The measurement program.

Sampling was conducted over a twelve-month period, to account for possible seasonal variations in dioxin concentration related, for example, to emissions from sources such as wood heaters, bushfires and prescribed burns. The basic sampling period was one month, but at two of the locations the sampling period was two months. The ten measurement sites represent metropolitan, agricultural and remote area air sheds, with eight of the ten sites situated at existing air-monitoring facilities. Samples were collected using high-volume samplers incorporating conventional traps for both particulate and gas phase species. Particulate phase collections were based on one-week exposure periods, with the filters later combined to match the gas sampling basic frequency for each site.

Stage 2: Analysis.

All samples were analysed, at the ultra-trace level, to determine the concentrations of the 29 PCDDs, PCDFs and those PCBs assigned toxic equivalency factors by the WHO. These analyses were conducted by AGAL in Sydney, Australia.

Stage 3: Collation and processing of data.

Data on dioxin levels in ambient air obtained from Stage 2 were collated and processed at CSIRO Atmospheric Research (CAR).

Stage 4: Reporting of results and conclusions.

Results of the study of ambient air dioxin levels are principally reported in this final report.

2 Project design

2.1 Instrumentation and methods

Samplers used in the ambient air study were designed to collect both gas and particle phase dioxins using established collection procedures, based on semi-volatile species collection methodologies used at the National Research Centre for Environmental Toxicology (NRCET) and CAR. This comprises an open face filter for condensed phase using 102 mm diameter quartz fibre filters with no binders, specifically Pall 2500 QAT-UP, 102 mm, backed up by PUF-XAD2-PUF sandwich gas traps. Traps were constructed from medium-density PUF (polyurethane foam) plugs with a nominal density around 0.02-0.03 g cm^{-3}, and typically 60 mm OD x 25 mm long and 60 mm x 50 mm, with 10 g of XAD-2 resin per charge. The 50 mm PUF were pre-spiked using a range of isotopically-labelled surrogate standards for sampling loss determination. The CSIRO-Atmospheric Research designed semi-volatile sampler (CAR-SV) inlet section comprising the anodised aluminium filter holder and glass trap are shown in Figure 2.1. This figure shows a loaded trap with the PUF-XAD2-PUF sandwich.

Figure 2.1 CSIRO semi-volatiles sampling head.

Nine complete CAR-SV samplers were deployed, and an additional two CAR-SV inlet heads were constructed for existing NRCET samplers that were operated at Eagle Farm and Mutdapilly, Queensland. The majority of samplers were operated at flow rates between 160-200 L min^{-1} and an additional sampler, of the same overall design, but operating at approximately 1 m^{3} min^{-1} was constructed for Cape Grim. This higher-flow sampler operated from March 2003 until the end of the study. The NRCET samplers operated at around 73 L min^{-1}. Flow rates are referenced to STP conditions.

The integrated air flow was determined weekly, using built-in calibrated dry gas meters (typically Toyo MT5), except the Cape Grim high volume sampler. The high volume sampler at Cape Grim used a calibrated orifice plate with differential pressure logging. Temperature and pressure values that have been used for conversion to standard flow conditions are predominantly climatological values for the relevant month, at the nearest climate reporting station. For Boorolite and Cape Grim, temperature and pressure measured as part of the study were used.

CAR-SV samplers operate using 230V 50Hz mains power, with pumps rated at 0.8 kVA. Examples of the standard and higher flow rate samplers, as used in the study, are shown in Figure 2.2[1].

Figure 2.2 Examples of samplers used in the study.

Sampling procedures adopted for this study, in particular the use of monthly integrated samples, were consistent with the low concentrations of dioxins expected in most Australian air-sheds, with the expectation of fg TEQ m^{-3} levels in rural and remote regions and tens of fg TEQ m^{-3} levels in urban/industrial areas. At Cape Grim, where the volume of air sampled was heavily influenced by the frequency of clean maritime air conditions, the initial standard design sampler was replaced in February 2003 with a high-volume sampler utilising a larger-inlet trap system. This sampler design is similar to the CSIRO design used for the Bushfire Dioxin Sampling Project, incorporating a

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[1] The standard sampler, which operates at 200 L min^{-1}, is on the left and the higher flow sampler, typical flow rate 1 m^3 min^{-1}, is on the right.

trap diameter twice that of the standard sampler, combined with a high volume filter cassette. This modified design allowed an approximately four-fold increase in sample volume, whilst maintaining the same trap face velocity and transit time as in the gas trap in the standard sampler.

All gas trap components were prepared for sampling at AGAL, Sydney. This comprised clean-up, a batch blank verification analysis, XAD-2 packing, spiking and trap assembly. Cleaned traps were wrapped in pre-cleaned aluminium foil, labelled for shipping and sent to CAR. Filters were baked at 400 ºC for 24 hours, conditioned then weighed at laboratory relative humidity (RH), typically 30-50% RH. They were wrapped in pre-cleaned aluminium foil and shipped, together with the gas traps, to the sampling contacts. A log of trap number, and date sent, was maintained at CAR; see Tables B1 to B11 in Appendix B.

Traps were shipped out using clean air-tight metal canisters, with the wrapped traps packed in clean polyurethane foam. Filters were shipped in cleaned aluminium foil in polythene bags; either by air freight with the traps, or using next day Express Mail packs. Returning samples and log-sheets were sent to CAR Aspendale (apart from Westmead PUF traps which are delivered directly to AGAL). Samples were forwarded as a batch to AGAL. Filters were returned to CAR each week, after they were changed, using next day Express Mail packs. All of the filters were stored in a freezer at CAR until the end of the sample month. Traps were returned, by air freight, to CAR in the same air-tight metal containers that were used for shipping out the clean traps.

2.2 Sample collection sites

The overall National Dioxin Project design called for samples to be collected from three broad environments, with the majority of samples collected from the metropolitan and agricultural areas. The broad categories were:

- **metropolitan** (urban parks or open space in residential, light and heavy industrial areas in State capital cities and large regional centres)
- **agricultural** (grazing, broad-acre cropping and intensive horticulture areas)
- **remote reference areas** (national parks, State forests and other Crown lands not impacted by human activity).

Sampling sites used for the ambient sampling project, represent the three broad geographic regions of northern Australia, south-eastern Australia and south-west Western Australia, and priority air sheds represented include Darwin, south-east Queensland, Sydney, Port Phillip and Perth, with the later addition of Adelaide (Figure 2.3). All major Australian cities are located relatively close to the coast and, consequently, are influenced by maritime air masses. The selected sampling locations also reflect this population distribution and atmospheric environment.

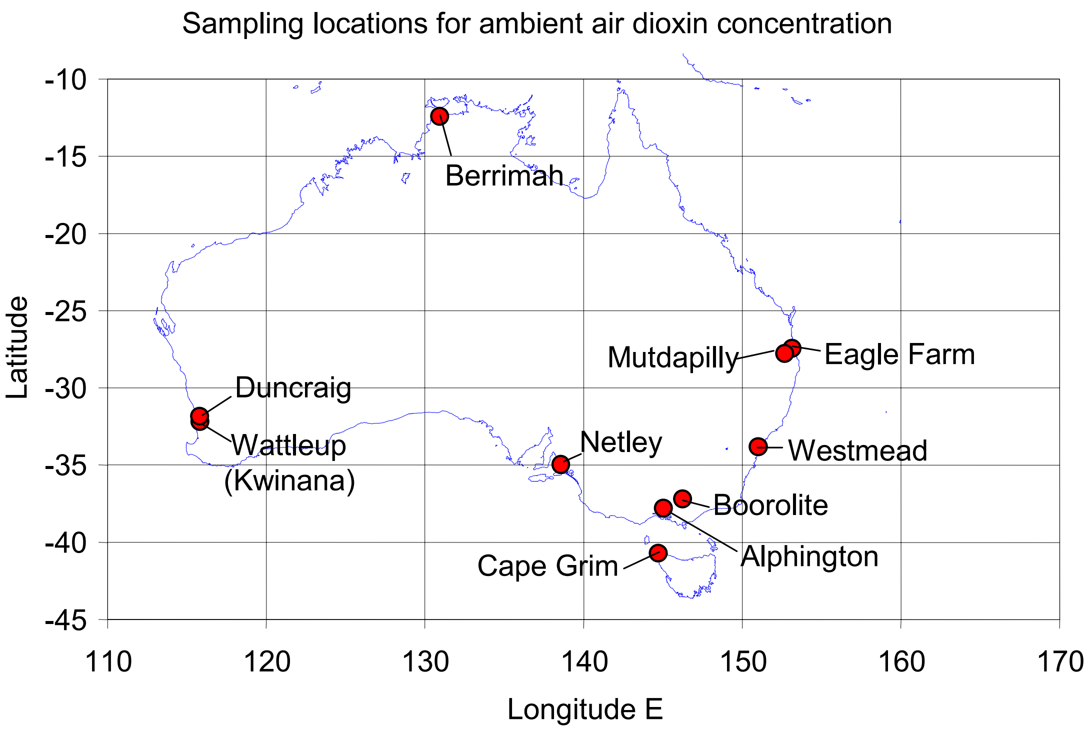

Figure 2.3 Map of sampling locations.

In all, ten sites were included in the study, and in addition to the major airshed sites, these also include a rural Victorian site and a background atmosphere site. The sites are:

- Wattleup, in the Kwinana area, south of Perth, WA (industrial)
- Duncraig, Perth, WA (mid-sized urban)
- Berrimah, Darwin, NT (small urban within a remote rural region)
- Eagle Farm, Brisbane, south-east Qld (urban, light industrial)
- Mutdapilly, south-east Qld (agricultural/grazing)
- Westmead, Sydney, NSW (major urban, some light industry impact from mixed industrial/urban air shed)
- Boorolite, lower north-east Vic (agricultural/grazing)
- Alphington, Melbourne, Vic (major urban area, Yarra Valley)
- Cape Grim, Tas (pristine remote)
- Netley, Adelaide SA (urban, light industrial).

Wattleup, Kwinana, WA. (Sampler operated by the Department of Environmental Protection [DEP] WA.). Kwinana is a major industrial precinct adjacent to Cockburn Sound, 35 km south of Perth, and 15 km south of Fremantle. The industrial region is about 12 km long (approximately north-south) by 2 km wide. Comprising 1,180 hectares, 80% is occupied by Alcoa with an alumina refinery, Cockburn Cement, BP oil refinery and Wesfarmers CSBP with ammonia and phosphate fertiliser production. Six air quality monitoring sites are maintained in the near vicinity, by the DEP and Kwinana Industrial Council. Wattleup, the site used for the dioxin sampling, is considered most representative of the general industrial strip.

A map of the Kwinana region and photograph of the Wattleup air quality sampling site, with dioxin sampler installed, are shown in Figure 2.4.

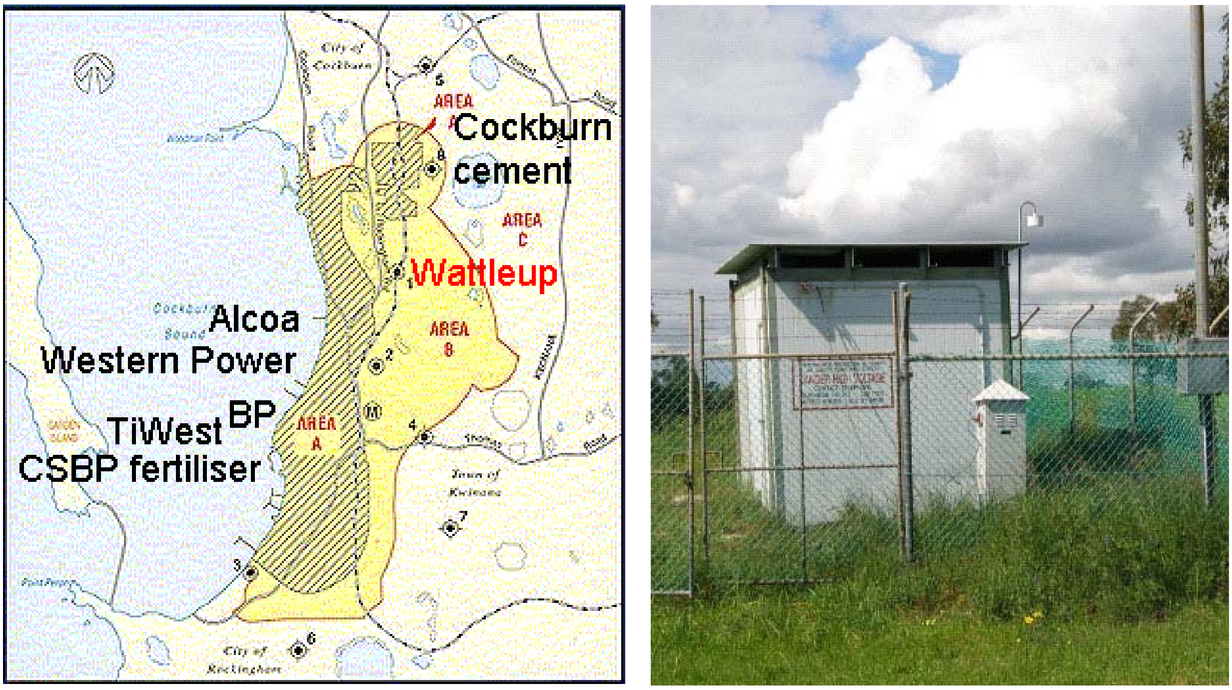

Figure 2.4 **Map of Kwinana area and Wattleup sampling site.**

Environmental areas for Kwinana, as indicated in Figure 2.4, are defined as follows:

AREA A - contains heavy industry
AREA B - a buffer area surrounding industry, plus other outlying land zoned for industrial use
AREA C - land used for predominantly rural and residential purposes.

Monitoring stations identified in Figure 2.4 are:

1) Wattleup*
2) Hope Valley*
3) North Rockingham*
4) Abercrombie Road, Postans
5) Miguel Road, Bibra Lake
6) Hillman Primary School, Hillman
7) Rhodes Park, Calista
8) Henderson Road, Munster.

Sites indicated with an * are operated by the DEP.

Duncraig, Perth, WA. (Sampler operated by the DEP). Duncraig is a Perth suburban residential area, approximately 15 km north of the Perth city centre. The area is subject to winter wood smoke and also to nocturnal drainage flows, potentially including vehicle emissions from the nearby Mitchell Freeway. Dioxin sampling was conducted at the DEP air-quality monitoring site. A site photograph is included in Figure 2.5.

Figure 2.5 **Perth and Duncraig air quality monitoring station.**

Berrimah, Darwin, NT (Sampler operated by CSIRO Sustainable Ecosystems). Darwin has a population of 82,400 (1996 Australian Bureau of Statistics census), and is located on the coast in a remote, tropical, rural region. Smoke from dry season burning is known to impact, significantly at times, on air quality. The sampling site at Berrimah, approximately 10 km north-east of the Darwin central business district (CBD), and 1 km east of Darwin airport, is located on the grounds of the CSIRO Tropical Ecosystems Research Centre (TERC). The area is close to the north-east edge of Darwin's residential area. TERC is located on Vanderlin Drive and about one third of the site (10 hectares) is covered by savannah woodland, one of the few areas of intact bushland in the Darwin suburbs. This site was used by the NT Department of Land Planning and Environment (with CAR) for a pilot study of air quality in 2000. A site photograph is included in Figure 2.6.

Figure 2.6 Dioxin sampler, Berrimah, NT.

Eagle Farm, south-east Queensland (Sampler operated by NRCET). Eagle Farm is a north-eastern suburb of Brisbane, approximately 7 km from the Brisbane CBD. It is bordered largely by Brisbane airport and the Brisbane River, and is categorised by the Queensland Environment Protection Agency (EPA) as a light-industrial area. The location of the Eagle Farm site is indicated on the Queensland EPA site location map and a photograph of the site are given in Figure 2.7.

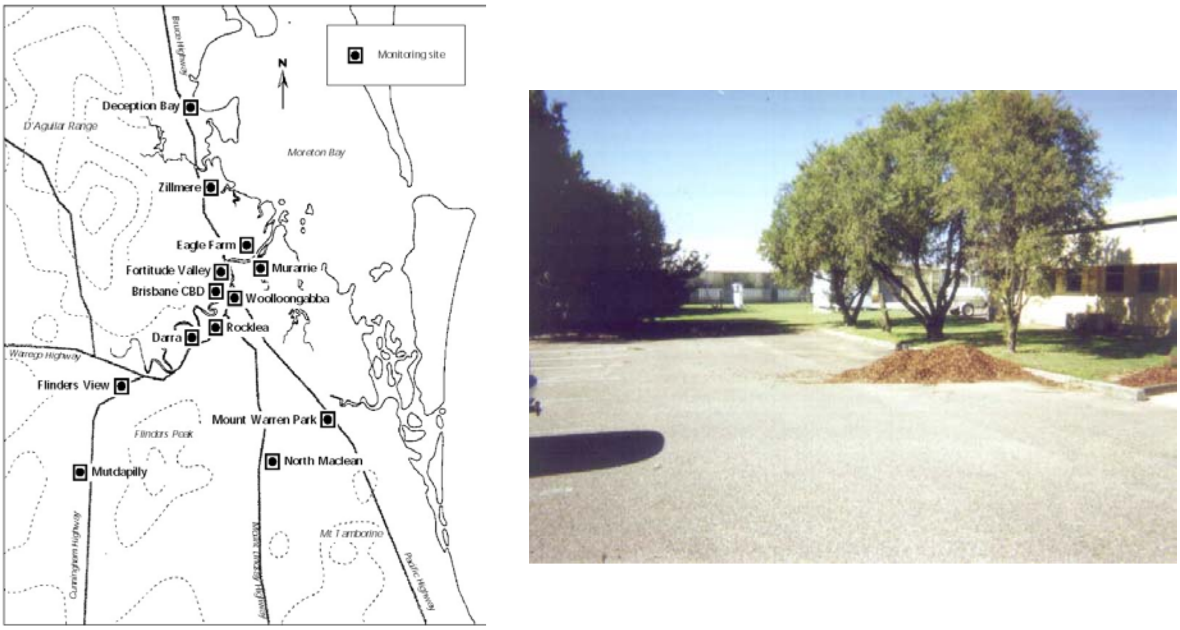

Figure 2.7 Sampling site locations and the Eagle Farm air quality measuring site.

Mutdapilly, south-east Queensland (Sampler operated by NRCET). The Queensland EPA air quality monitoring site at Mutdapilly is located in Gimpels Road, 55 km south-west of Brisbane, in rural south-east Queensland. The region is characterised by agricultural/grazing activities. The site location is approximately 150 m from the Cunningham Highway (Brisbane to Warwick). Rural sites were not selected to be totally free of all human activity (or potential sources). Mutdapilly represents many parts of the country where rural locations are a moderate distance from a regional centre, in this case, Ipswich and the Swanbank power station are both about 20 km away. Figure 2.8 is a photograph of the Mutdapilly air quality monitoring station.

Figure 2.8 The Mutdapilly air quality monitoring station, Queensland.

Westmead, Sydney and NSW (Sampler operated by CSIRO ET). The Westmead location is the NSW Department of Environment and Conservation (DEC)[2] air quality monitoring site on the Westmead Hospital grounds. Located in a residential area in Sydney's north-west (near Parramatta), the area is urban with some light industry in a mixed industrial/urban air shed.

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[2] Formally the Environment Protection Authority (EPA).

Figure 2.9 **The Westmead air quality monitoring site.**

The Westmead site has been a NSW DEC air quality station since 1980, and has been used for a previous NSW DEC study of dioxins. Figure 2.9 is a photograph of the Westmead air quality monitoring station, with the dioxin sampler shown on the right of the sampling building. Figure 2.10 illustrates the NSW DEC metropolitan samplings sites.

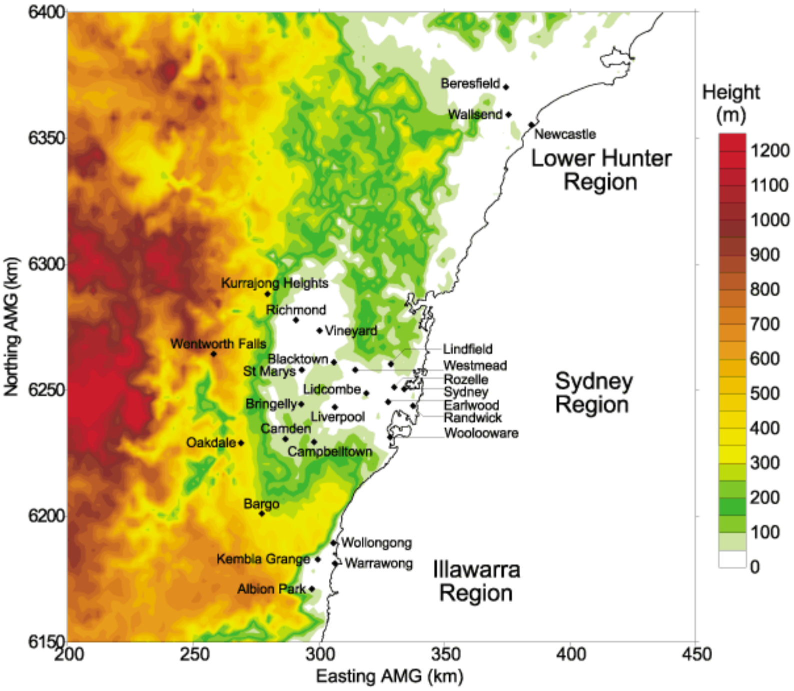

Figure 2.10 **Map of NSW DEC metropolitan sampling sites.**

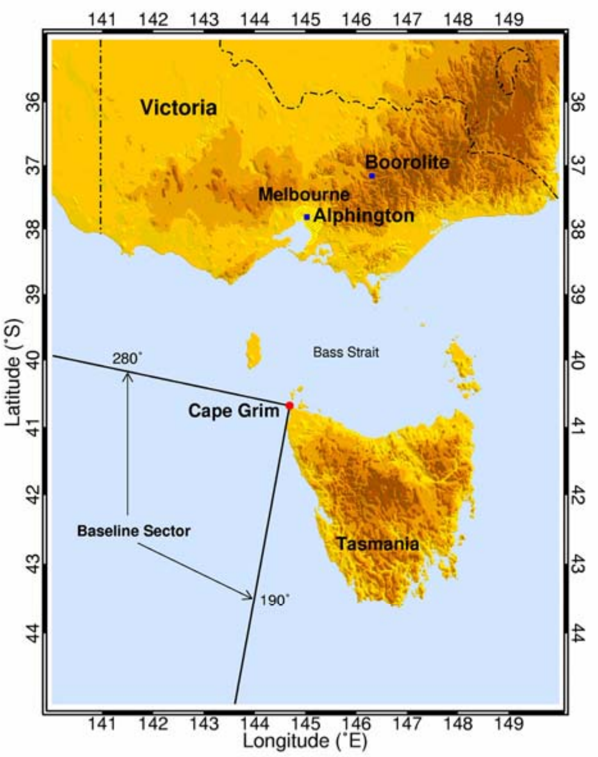

Figure 2.11 Victorian and Tasmanian sites (Boorolite, Alphington and Cape Grim).

Boorolite, lower north-east Victoria (Sampler operated by CAR). This site is located on a rural property in an agricultural/grazing region, approximately 20 km south of Mansfield. The sampling location is shown in Figure 2.11 and the area surrounding the sampling site is shown in the photograph given as Figure 2.12. The sampler is to the right of the shed at the left of the photograph.

Figure 2.12 The area around the Boorolite sampling location, Victoria.

Alphington, Melbourne, Victoria (Sampler operated by CAR). Alphington is a suburban area in the Yarra Valley, approximately 7 km from the Melbourne CBD. The site is subject to domestic wood smoke during the autumn-winter period. The sampler was located at the EPA Victoria Alphington Air Quality sampling station. The site location is shown in Figure 2.13.

Figure 2.13 The EPA-V Alphington air-quality monitoring site.

Cape Grim, Tasmania (Site operated by the Australian Baseline Atmospheric Pollution Station - BAPS). This site is located at the BAPS on the north-western tip of Tasmania. The location is indicated in Figure 2.11, and Figure 2.14 shows the dixon sampler installed on the roof deck of the Station. The area receives air from the remote Southern Ocean, representing a pristine remote location. During northerly and easterly conditions, air arriving at Cape Grim is influenced by anthropogenic activities, however, for the dioxin sampling project conditional sampling was used to ensure sampling only for the clean marine sector (local winds 190°-280°).

Figure 2.14 Dioxin sampler at Cape Grim Baseline Atmospheric Pollution Station.

Netley, SA (site operated by Environment Protection Authority [EPA] SA). This site was added after the start of the main program. The location, at the EPA laboratories on

Richmond Road, Netley, in west metropolitan Adelaide, is near Adelaide airport and is exposed to major roads and industry (see Figure 2.15 and Figure 2.16).

Figure 2.15 Dioxin sampler installed in the grounds of the SA Netley site.

Figure 2.16 Aerial view of the Netley site.

2.3 Sampling program implementation

The nominal start date for ambient sampling was 1 September 2002 and concluded on the 31 August 2003. The sampling program for Netley, SA, was added in January 2003, after the start of the main sampling program. Actual gas trap (PUF) and filter start and end dates are given in Tables B1 to B11, in Appendix B. The Cape Grim sampler was controlled by a "Baseline" switch (BL3) that only allowed sample collection for winds from 190º to 280º, at the 50 m level, and a total particle number less than the previous 5-year ninety percentile for the current month. This procedure was used to select only clean marine air from the south-west, for minimal anthropogenic impact. The frequency of clean marine air selected in this manner is indicated in Table B10, Appendix B, and ranged from 7.6% in May 2003 to 49% in January 2003.

2.4 Sample analysis

2.4.1 Analytical procedures - CSIRO AR

At CAR, the collected aerosol mass was determined gravimetrically by weighing the exposed filters after equilibration at laboratory RH conditions for 24 hours (typically 30-50% RH), the same conditions used for the determination of the pre-exposed filter mass. The balance used was a Sartorius LA130 S-F. A small plug (1.6% of the filter area) was later punched from each filter, using a pre-cleaned punch, for analysis of soluble inorganic aerosol components by ion-chromatography, at CAR. The CAR laboratory is NATA accredited for aerosol mass determination. The subsequent extractions and analyses for the dioxin and dioxin-like components were carried out at AGAL Sydney. All procedures were undertaken using clean conditions consistent with ultra-trace level determinations.

2.4.2 Analysis procedures at AGAL Sydney

At AGAL Sydney, the concentrations of the dioxin and dioxin-like species were determined by analysis, at the ultra-trace level, of combined aerosol and gas phase samples. The analytical methodology for the determination utilises isotopic dilution techniques and is modified from those described by the US EPA methods 1613B, 1668A and TO9A. The dioxin, furan and PCB congeners analysed are listed in Table 2.1, together with their TEFs, and in addition the tetra to octa PCDD/PCDF homologues were also determined. On return of the samples to AGAL, the sampling components were spiked with ^{13}C-labelled internal standards (filters, PUFs and XAD-2 resin) and extracted together using a hot soxhlet extraction in toluene. Clean-up involved partitioning with sulfuric acid then distilled water, followed by column chromatography on acid and base modified silica gels, neutral alumina and carbon dispersed on celite. Analyses for dioxins, and dioxin-like compounds, was performed using a high resolution Gas Chromatograph - high resolution Mass Spectrometer HRGC-HRMS (ThermoQuest Finnigan MAT95XL) that has a sensitivity for 2,3,7,8-TCDD of better than 10 fg with a signal to noise ratio of 10:1. Individual congeners were identified using the GC retention time and ion abundance ratios, with reference to internal standards. Quantitative analysis was performed using selected ion current profiles following a variety of methodologies that are congener specific and requiring calibration as described, for example, in US EPA Methods 1613B, TO-9A and 1668A. All laboratory procedures such as laboratory blanks, sample identification and chromatogram checking follow standard procedures laid down for the laboratory NATA accreditation for dioxin analyses. All analysis results are archived both in hard and electronic copy for future reference. The reference laboratory selected for analysing the duplicate quality control samples was the Ministry of the Environment, Laboratory Services Branch, Ontario, Canada (MOE).

Table 2.1 Dioxin, furan and PCB congeners analysed in the study.

Congener	WHO-TEF[3]
Dioxins	
2,3,7,8-TetraCDD	1
1,2,3,7,8-PentaCDD	1
1,2,3,4,7,8-HexaCDD	0.1
1,2,3,6,7,8-HexaCDD	0.1
1,2,3,7,8,9-HexaCDD	0.1
1,2,3,4,6,7,8-HeptaCDD	0.01
OctaCDD	0.0001
Furans	
2,3,7,8-TetraCDF	0.1
1,2,3,7,8-PentaCDF	0.05
2,3,4,7,8-PentaCDF	0.5
1,2,3,4,7,8-HexaCDF	0.1
1,2,3,6,7,8-HexaCDF	0.1
1,2,3,7,8,9-HexaCDF	0.1
2,3,4,6,7,8-HexaCDF	0.1
1,2,3,4,6,7,8-HeptaCDF	0.01
1,2,3,4,7,8,9-HeptaCDF	0.01
OctaCDF	0.0001

CDD - chlorinated dibenzo-*p*-dioxin
CDF - chlorinated dibenzofuran

Congener	IUPAC No.	WHO-TEF[3]
Non-ortho PCBs		
3,3',4,4'-tetrachlorobiphenyl	PCB#77	0.0001
3,4,4',5-tetrachlorobiphenyl	PCB#81	0.0001
3,3',4,4',5-pentachlorobiphenyl	PCB#126	0.1
3,3',4,4',5,5'-hexachlorobiphenyl	PCB#169	0.01
Mono-ortho PCBs		
2,3,3',4,4'-pentachlorobiphenyl	PCB#105	0.0001
2,3,4,4',5-pentachlorobiphenyl	PCB#114	0.0005
2,3',4,4',5-pentachlorobiphenyl	PCB#118	0.0001
2',3,4,4',5-pentachlorobiphenyl	PCB#123	0.0001
2,3,3',4,4',5-hexachlorobiphenyl	PCB#156	0.0005
2,3,3',4,4',5'-hexachlorobiphenyl	PCB#157	0.0005
2,3',4,4',5,5'-hexachlorobiphenyl	PCB#167	0.00001
2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB#189	0.0001

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[3] Van den Berg, M. et al. (1998)

2.5 Data quality

The data quality assurance plan for the study is included as Appendix A. This comprised a set of standard operating procedures, data quality objectives and quality control measures.

2.5.1 Quality Control procedures for Stage 1 (sampling program)

Field blanks

These are additional samples that were treated the same as the ambient samples, loaded into the sampler then unloaded, but with no air drawn through the sampler. Extraction and analyses were the same as for ambient samples (by the principal analyst, AGAL). Five field blanks, representing 5% of the ambient samples, were conducted at approximately equal intervals throughout the study (See Appendix D, Table D1). Concentrations of dioxins determined from the field blanks are given in Appendix D.

Collocated samples

Two CSIRO-SV samplers were operated side by side in the field, for five months at the Alphington (Vic) site. The paired samples were analysed using the standard procedures. One of each pair of samples was treated the same as the other normal samples, with extraction and analysis by the principal analysts (AGAL) and the second sample in each pair was analysed by the independent analysts, MOE. Five collocated samples were included representing 5% of the ambient samples.

Replicate analyses

Replicate samples include the five collocated samples plus three samples from the normal sample stream that were split into two aliquots after extraction and clean-up at AGAL (primary analysts). The replicate analyses were conducted by the independent analysts, MOE Canada. The results are illustrated in Figure 2.17[4].

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[4] In this graph, the five collected samples represented as filled symbols and three collected samples as open symbols.

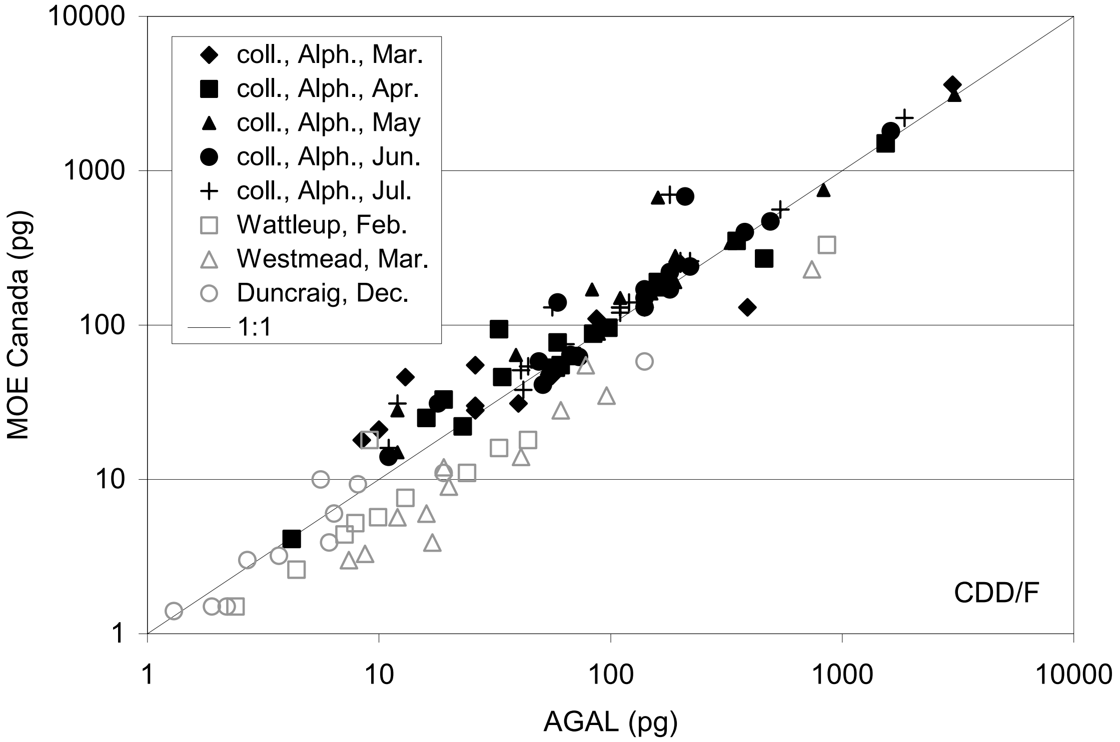

Figure 2.17 Results of replicate analyses for dioxin and furan congeners.

All replicate PCDD/PCDF congener analyses that returned above minimum detect levels in both replicate analyses are shown in Figure 2.18. The overall geometric mean ratio (for AGAL/MOE) for the PCDD/PCDF congeners is 1.00 with plus and minus one geometric standard deviation yielding ratios of 1.75 and 0.58. For the collocated samples alone, the geometric mean is 0.80 with plus and minus one geometric standard deviation corresponding to ratios of 1.21 and 0.53, respectively. A similar plot of all PCB replicate analyses is given in Figure 2.19. In this case the overall geometric mean concentration ratio (AGAL/MOE) is 1.15 with plus and minus one geometric standard deviation corresponding to ratios of 1.87 and 0.71. Similarly a plot of the total tetra to hepta dioxin and furan isomers is given in Figure 2.20. The overall geometric mean concentration ratio (AGAL/MOE) for this group was 1.05 with plus and minus one geometric standard deviation corresponding to ratios of 1.71 and 0.64. In all cases there appears to be some systematic difference between collocated and split aliquot replicates, that may indicate a storage loss effect.

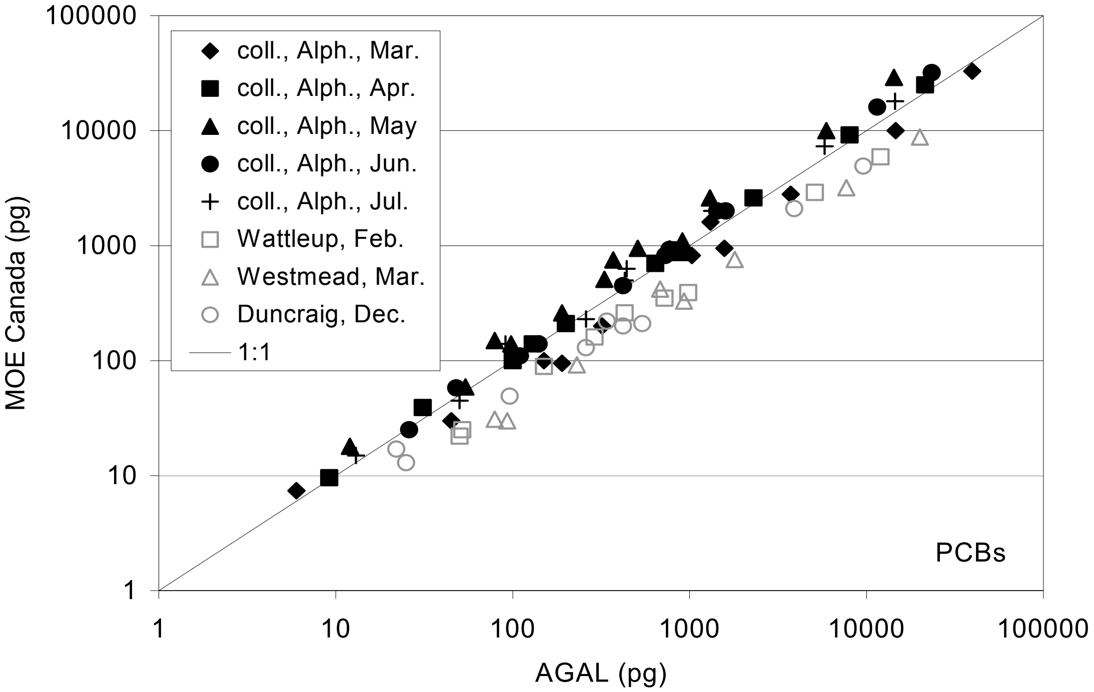

Figure 2.18 **Replicate analyses for dioxin-like PCBs.**

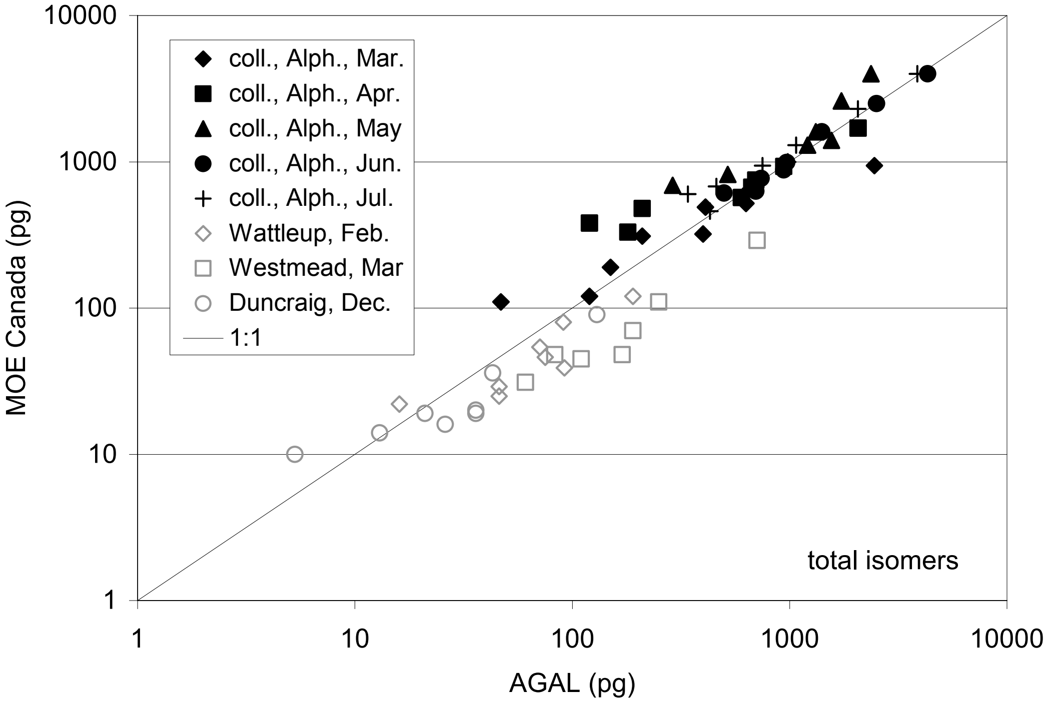

Figure 2.19 **Replicate analyses for total tetra to hepta isomers.**

Gas meters used to determine integrated flows in the CSIRO samplers were referenced to a CSIRO dry gas meter (S.I.M Brunt, model G6, S/N 07615) that was calibrated using a wet-test meter (CAR Aspendale, 14/5/02). Calibrated orifice plates, referenced to this initial calibration were supplied for subsequent flow checking in the field.

Differential pressure gauges were referenced to a Wallace and Tiernan absolute pressure sensor (Model FA129 S/N EE15626), located at CAR Aspendale. Flow checks during and at the end of the study were within expected limits.

2.5.2 Incorporated Quality Control procedures for Stage 2

The following objectives were adopted for the analysis and reporting of all samples and establishing limit of detection (LOD):

- Retention time of the analyte within one second of the retention time of the corresponding ^{13}C surrogate standard
- Ion ratio obtained for the analyte within ±10% (±20% for PCBs) of the theoretical ion ratio
- Signal-to-noise ratio greater than 3:1
- Levels of PCDD/PCDF and 'dioxin-like' PCB congeners in a sample greater than five times any level found in the corresponding laboratory blank analysed (three times the level in the blank for OCDD)
- Surrogate standard recoveries in the range 10-120% (objective).

2.5.3 Data Quality Objectives (DQOs)

Surrogate recovery

Ratios are reported in Appendix C, Tables C1 and C2. From 2,750 surrogate recovery determinations (for September 2002 to August 2003), the overall average surrogate recovery was 73%. Only 0.07% determinations had less than the 10% objective, and 1.3% had greater than the 120% objective. The overall minimum surrogate recovery was 8.2% and the overall maximum was 187%, surrogate recovery was not used as a basis for data rejection.

Intact sample return

Two filters (one each from Mutdapilly and Eagle Farm) that were returned to CAR from NRCET by Express Mail were lost in the post – these were subsequently delivered but too late for inclusion in the batch analysis. Reported concentration data include a correction for these samples. All gas traps were returned on time and intact. The Westmead July gas trap was inadvertently analysed together with the June filters samples, so subsequently the June gas trap and July filter were analysed separately. Combined gas plus particle concentrations were derived for June and July and these are reported, however the apportionment involves some approximation based on derived partitioning. The sum of June plus July monthly loadings as reported will be correct for the combined period.

Blank levels

As shown in Appendix D, concentrations of target compounds meet the DQO of equal to 2 - 20 pg for tetra-, penta-, and hexa- and 40 to 150 pg for hepta- and octa-CDDs for each pair of filter and trap assembly (for unexposed traps). Data reported are not blank corrected.

Laboratory blanks

Laboratory blanks were included as part of the analysis procedure and used to determine the limit of detection (LOD). LOD is three times the standard deviation of the target species in the laboratory blanks.

Overall sensitivity/LOD

This was determined from the five analysed field blanks. With an assumed volume flow of 6000 m^3 per sample, the overall sensitivity, taken as three times the blank standard deviation, is approximately 0.6 fg TEQ m^{-3} for PCDD/PCDF with the middle bound (½ LOD for values less than LOD) and 0.7 fg TEQ m^{-3} for PCDD/PCDF/PCDP with the middle bound.

Sampling precision

Precision in sampling, including flow determination, filter handling and analytical analysis for particle mass and inorganic species, can be evaluated from the five collocated samples run at Alphington from March to July 2003. Two examples are given in Figures 2.21 and 2.22 that show weekly mass and sodium concentrations from filter extracts on the Alphington (main) and Alphington-collocated samplers. The average ratio between particle mass concentrations for the two samplers was 0.994 ± 0.016 (one std. error of the mean) and for sodium the average ratio of mass concentrations was 0.986 ± 0.016, in both cases from 20 determinations.

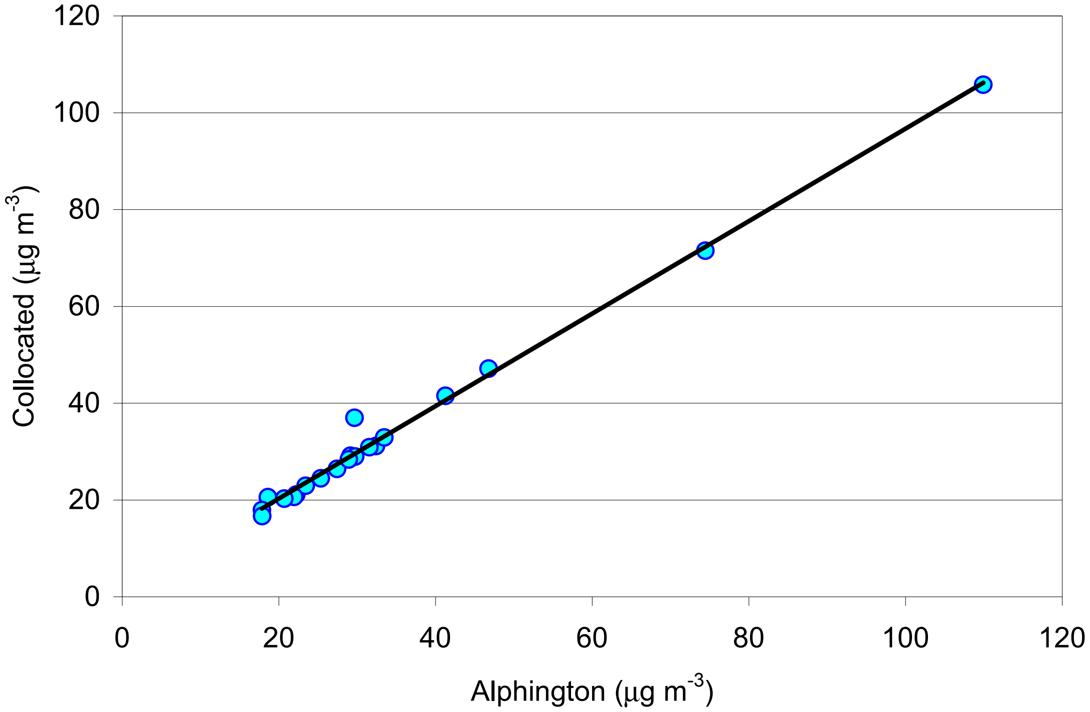

Figure 2.20 **One-week average mass concentrations.**

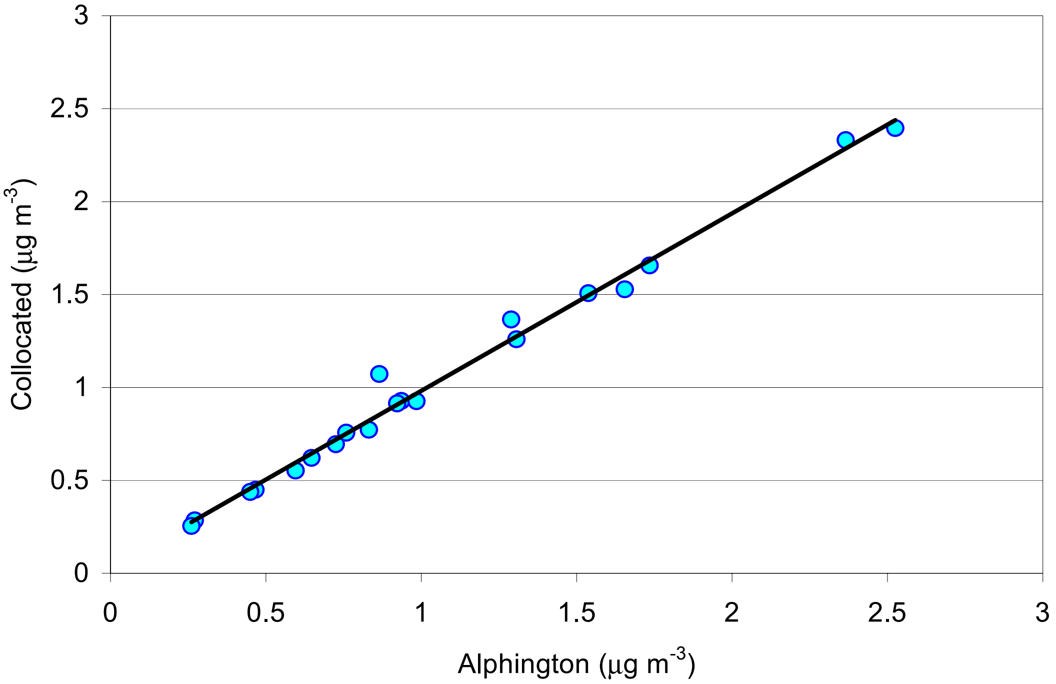

Figure 2.21 **One-week average sodium concentrations.**