National Dioxins Program

Technical Report No. 5
Dioxins in Soil in Australia

A consultancy funded by the Australian Government

Department of the Environment and Heritage

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Australian Government
Department of the Environment and Heritage

ISBN 0 642 54997 4

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1. Dioxins emissions from Bushfires in Australia
2. Dioxins emissions from Motor Vehicles in Australia
3. Inventory of Dioxin emissions in Australia 2004
4. Dioxins in Ambient Air in Australia
5. **Dioxins in Soils in Australia**
6. Dioxins in Aquatic Environments in Australia
7. Dioxins in Fauna in Australia
8. Dioxins in Agricultural Commodities in Australia
9. Dioxins in the Australian Population: Levels in Blood
10. Dioxins in the Australian Population: Levels in Human Milk
11. Ecological Risk Assessment of Dioxins in Australia
12. Human Health Risk Assessment of Dioxins in Australia

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Citation
This report sould be cited as follows:
Müller J, Muller, R, Goudkamp, K, Shaw M, Mortimer M, Haynes D, Burniston D, Symons R & Moore M, 2004, *Dioxins in Soils in Australia*, National Dioxins Program Technical Report No. 5, Australian Government Department of the Environment and Heritage, Canberra.

Foreword

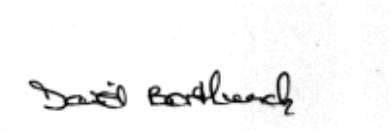
When the Australian Government established the four year National Dioxins Program in 2001, our knowledge about the incidence of dioxins in Australia was very limited.

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

Secretary

Department of the Environment and Heritage

Acknowledgements

The Department of the Environment and Heritage (DEH) would like to acknowledge the following individuals and organisations that contributed to the information studies and risk assessments under the National Dioxins Program:

- the project teams from the CSIRO, the National Research Centre for Environmental Toxicology and Pacific Air & Environment who undertook the studies assessing the levels of dioxins in the environment, the population and from emission sources, the overseas experts who provided advice to these organisations, and the many individuals across Australia who collected the samples in the field
- the Department of Agriculture, Fisheries and Forestry, who assessed the levels of dioxins in agricultural commodities
- Food Standards Australia New Zealand and the Department of Health and Ageing and who assessed the levels of dioxins in foods and assessed the health effects of dioxins
- officers of the Chemical Assessment Section in DEH who assessed the ecological effects of dioxins
- members of the National Dioxins Project Team which included representatives from the State and Territory environment protection agencies, the Australian Health Ministers Conference and the Primary Industries Ministers Council
- members of the National Dioxins Consultative Group which included representatives from industry and agricultural sectors, environment and public health groups and research institutions.

The Department would also like to especially thank Dr Heidelore Fiedler (UNEP Chemicals, Switzerland) and Dr Patrick Dyke (PD Consulting, United Kingdom) who provided valuable review on an early draft of this report.

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The National Research Centre for Environmental Toxicology (ENTOX) is cofunded by Queensland Health.

ENTOX would like to thank the following people for their assistance with the collection of soil samples and without whose help the project would not have been possible.

(NT) Jacob Nayinggul, Jonathan Nadji, Michael Banggalanag, Alistair Cameron (Department of Environment and Heritage); Sally Kirby and Judy Faulks (Department of Infrastructure Planning and Environment); Gary Cook (CSIRO); Lindsay Hutley and Jenny Brazier (Charles Darwin University); Chris Day (West Macdonnell NP); Madonna Mackay (Landcare); Chris Humphrey.

(QLD) Ray Clark, Helen Stephenson, Luke Nicholson, Jenny Keys, John Ferris, Graham Webb, Ingrid Minnesma, Andrew Thompson, Ian Bryant, Michelle Nissen (Environmental Protection Agency); Bruce Lansdown, Ian Wallace and David Phelps (Department of Primary Industries); Susanne Schmidt, John Hall, Boyd Wright (University of Queensland); Karen Kennedy, Melanie Shaw, Stephan Hartkopp and Johannes Riehle (National Research Centre for Environmental Toxicology); Mark Kleinschmidt (Landcare); Jon Marshall (Department of Natural Resources, Energy and Mines); Leo Duivenvoorden and John Rolfe (Central Queensland University); Des Connell (Griffith University); Peter Muller; Stephen Pugh.

(NSW) Cheryl Tang, Peter Scanes, Murray Root, Ross Johnson, Max Carpenter and Graham Sherwin (Environmental Protection Agency); Craig Miller (Department of Infrastructure, Planning and Natural Resources); Ingrid Witte and Louise Stayte (NSW National Parks and Wildlife Services); Ian Auldist (Hay Trees on the Plains Landcare); Bob Jemeer, Tim O'Kelly and Joy Gardner (State Forests of NSW); Philip Milling (Upper Hunter Landcare); Michelle Jefferies (Department of Land and Water Conservation); Nerida Reid, Neville Reid (Landcare); Ben Grounds (Healthy Cities Illawarra); Lana Collison (Maitland City Council); Irene Kreis (University of Wollongong); Bill Baker.

(ACT) Paul Story (Australian Plague Locust Commission).

(VIC) John Gras, Michelle Bald, Jenny Treeby, Bim Graham (CSIRO); Dianne Rose, Neil Biggins, Tony Robinson, Paul Moritz, John Williamson and Alex Leonard (Environmental Protection Agency); Ross Scott; Janine Dean and students (Gordon Institute of TAFE); Duncan McKenzie and assistants (Birds Australia); Ross Scott; Mark Fletcher (Department of Sustainability and Environment); Richard MacEwan and Renick Peries (Department of Natural Resources and Energy); Josephine Stokes and Dayanthi Nugegoda (RMIT University); Bill Incoll; Ian Schmidt.

(TAS) Jill Cainey (Bureau of Meteorology); Christine Coughanowr, Coleen Cole, John Dobson, Joseph Tranter (TAS Department of Primary Industries, Water and Environment); Chris Bolch, Danny Donaghy, Greg Kent, Karen Adamorewski (University of Tasmania); Anna Griggs (Huon Valley Council); Tanya von Ehrenstein.

(SA) David Ellis, Ray Correll (CSIRO); Tracey Steggles, Scott Nichols, Noel Johnston, Pru Tucker (River Murray Catchment Management Board); Don Maguire (SA Forestry); Duncan MacKenzie (Birds Australia Gluepot Reserve); Graham Moss (Kangaroo Island);

(WA) Andrew McTaggart, Brendan Oversby, Alan Burns, Clare Taylor, Christine Webb, Claire Thorstensen and Brad Iscoll (WA Water and Rivers Commission); Todd Simms and Felix Neuweiler (East Pilbara Shire

Council); David Wilson (City of Joondalup); Peter Crawford and David Allen (Laverton Shire Council); Mike Paxman (Kalbarri National Park).

Jessyca Bosscha; Jim Cullen.

We would also like to thank those involved with preparing and distributing sampling equipment: Kevin Rynne, Johannes Riehle, Tamara Ivastinovic, Sally Evans, Eva Holt.

Scott Stephens was responsible for the development of the MS Access database which proved invaluable for data storage and saved us a great deal of time when it came to data analysis, thank you Scott. Thanks also to Ulrike Bauer and Eva Holt for assisting with the editing of the final report.

For samples analysis we would like to thank staff of the AGAL Dioxin Analytical Unit: Masooma Trout, Alan Yates, Nino Piro, Gavin Stevenson, Rania Jaber, Jesuina De Araujo, Rozza Kaabi, Jun Du Fang, Shana Rogic, Michelle Kueh.

We are indebted to the Waite Institute, South Australia and Jan Skjemstad for the provision of historical soil samples.

For concept development, advice and support we thank Ray Correll, Warren Muller, Andrew McTaggert, Rai Kookana, Des Connell, Martin van den Berg, Mats Tysklind, Olaf Päpke, Graeme Batley, Michael McLachlan and John Gras.

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 Australian soils.

The project involved the systematic collection of several thousand soil cores by more than 50 individual sampling personnel using a standard sampling protocol. Samples were collected from 86 locations representative of airsheds and catchments based on the National Pollution Inventory. For the purposes of the study, the continent, including Tasmania, was divided into three geographic areas (Northern, South-Eastern, and South-Western), and soil samples were taken from locations in each geographic area that were representative of different land-uses (agricultural, urban, industrial, and remote). Further subdivisions were made of agricultural land-uses according to the predominant form of agriculture practice (grazing, cotton, vegetables, sugarcane, forestry, cereals). In addition, an archive of historical soil samples collected from a single location near Adelaide was assessed for evidence of changes in background levels of dioxin-like chemicals since the 1920s.

Chemical analysis of soil samples was primarily conducted by the Australian Government Analytical Laboratories, and a series of quality assurance/quality control checks were incorporated into the study including replicate sampling, replicate analysis and an interlaboratory comparison of analytical results using an overseas laboratory highly regarded for its experience in the analysis of dioxin-like chemicals in environmental samples. These checks showed high reproducibility in chemical analysis, and that the identification of individual dioxin-like chemicals and quantification of their concentrations in soil samples was reliable. However, the reproducibility of results from replicate sampling in the more highly contaminated locations was more variable, indicating the likelihood of historical or current point source contamination at or near some of the sites concerned.

Data was assessed both in terms of actual concentrations of dioxin-like chemicals as well as toxic equivalents. In addition, the patterns of component chemicals were evaluated, and assessments of contamination patterns were made in respect to geographic location and land-use differences.

Dioxin-like chemicals were found in most of the 116 Australian soils sampled, with middle bound concentrations ranging from the limit of detection 0.05 pg TEQ g^{-1} dm to 23 pg TEQ g^{-1} dm. Median concentrations of dioxin-like chemicals expressed as toxic equivalents in soils across all land-use types in the Northern and South-Eastern study regions were similar, but the median concentration in the South-Western study region was less. The greatest concentrations of dioxin-like chemicals were found in soils collected near centres of population within the South-East coastal area of Australia, whereas concentrations were consistently low in soils collected from locations in Western Australia and inland areas across all regions.

Data from the study showed that levels of dioxin-like chemicals in soils from urban and industrial locations were substantially higher relative to agricultural land-use and remote locations. This pattern was consistent regardless of whether levels were expressed as toxic equivalents or as concentrations. Across agricultural land-uses, concentrations of dioxin-like chemicals in soils were similar, with the exception of sugarcane growing, in which the concentration was substantially greater than other agricultural land-uses. However, other evidence suggests that contamination of sugarcane soils is not likely to be related to sugarcane cultivation since contamination extends throughout the coastal environment of Queensland. The formation process or specific source of the elevated levels of dioxins in these coastal soils remains unknown although natural formation processes may be involved.

Homologue and congener profiles for the PCDD/PCDF were strongly dominated by OCDD. Similarly, the tetra-heptachlorinated 2,3,7,8-chlorine substituted profiles are dominated by the highest chlorinated PCDD, 1,2,3,4,6,7,8-heptachloro dibenzodioxin. The source or formation processes by which dominance of higher chlorinated congeners could occur remains unresolved despite intensive studies by others. With regards to the TEQs, on average, more than 80% of the toxic equivalency across soil samples was attributed to 2,3,7,8-PCDD/PCDF.

Although there is no Australian guideline threshold for dioxin-like chemicals in soils, comparison of concentrations of dioxin-like chemicals in the NDP soil samples against a categorisation derived from German thresholds showed that only 15% of the Australian samples (all but one of which were from urban or industrial locations) exceeded the German derived target value of <5 pg TEQ g^{-1} dm.

The concentrations of dioxin-like chemicals in urban and industrial locations sampled as part of the NDP were similar to those reported in previous Australian studies and in the New Zealand Organochlorines Program. On the basis of toxic equivalents, concentrations of dioxin-like chemicals in Australian soils are on average much lower than those reported from many industrial locations internationally. On a global basis, they can be considered among the lowest background concentrations reported in soil from any industrialised nation.

Lower bound oncentrations of dioxin-like chemicals for the archived samples ranged from 0.54 to 3.8 pg TEQ g^{-1} dm. Interestingly, the oldest sample, collected in 1925, contained detectable concentrations of PCDD/PCDF as well as PCB. Also, the concentrations in the 1925 sample are greater than in the samples from the 1930s and 1940s. It is not clear how selective contamination of the oldest sample could have occurred and whether it is an artifact related to sampling or storage of the sample.

Glossary/Abbreviations

AGAL	Australian Government Analytical Laboratories.
ANZECC	Australian and New Zealand Environmental Protection Council, now replaced by the Environment Protection and Heritage Council. Representation includes environmental ministers from Australia and New Zealand.
CSIRO	Commonwealth Scientific and Industrial Research Organisation.
Congeners	Closely related chemicals derived from the same parent compound.
Dioxin	Common name for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF).
Dioxin-like	For the purpose of this study, 2,3,7,8-chlorine substituted PCDD/PCDF and non-ortho and mono-ortho PCB.
dm	Dry mass.
ENTOX	National Research Centre for Environmental Toxicology.
fm	Fresh mass.
Furan	Polychlorinated dibenzofuran (PCDF).
GC	Gas Chromatography.
Homologues	A group of structurally related chemicals that have the same degree of chlorination.
HRGC	High-resolution gas chromatography.
HRMS	High-resolution mass spectrometry.
Isomer	Chemical compound where the overall composition of the molecule is the same but the structure is different.
IPCS	International Programme on Chemical Safety.
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 did not included PCB.
I-TEF	See TEF but factors developed earlier by NATO-CCMS (1998).
IUPAC	International Union of Pure and Applied Chemistry.
LOD	Limit of detection, the lowest level at which a chemical can be measured in a sample by the analytical method used.
Lower bound TEQ	Toxic equivalencies (TEQ) for which the concentration of a non-detected congener is assumed to be zero. The remaining detected values are multiplied by the corresponding TEF value then summed to achieve the lower-bound TEQ (TEQ excluding LOD values).
Middle bound TEQ	Toxic equivalencies (TEQ) for which the concentration of a non-detected congener is assumed to be half the limit of detection. All values are multiplied by the corresponding TEF value then summed to achieve the middle-bound TEQ (TEQ including half LOD values).

MS	Mass Spectrometer.
NATO	North Atlantic Treaty Organisation
NDP	National Dioxins Program.
ng g^{-1}	Nanogram per gram, 10^{-9} g.
OCDD	Octachlorodibenzo-*p*-dioxin
OCDF	Octachlorodibenzofuran
PCB	Polychlorinated biphenyl.
∑PCB	Summed total of all PCB congeners that were analysed and detected
PCDD/PCDF	Polychlorinated dibenzo-*p*-dioxin and furan.
∑PCCD/PCDF	Summed total of all tetra-octachlorinated PCDD/PCDF congeners that were analysed and detected
pg g^{-1}	Picogram per gram, 10^{-12} g. Equal to nanogram per kilogram (ng kg^{-1}).
Stdev	Standard deviation.
TCDD	Tetrachlorodibenzo-*p*-dioxin
TEF	Toxic equivalency factor of a specific PCDD/PCDF 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).
TEQ	Abbreviation of WHO_{98}-TEQ (this document).
TOC	Total Organic Carbon (considered the sorption phase for hydrophobic substances such as dioxin-like chemicals in sediments).
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'.
WHO_{98}-TEQ_{DF}	WHO_{98}-TEQ for PCDD and PCDF.
WHO_{98}-TEQ_{PCB}	WHO_{98}-TEQ for PCB.
WHO_{98}-TEQ_{DF+PCB}	WHO_{98}-TEQ for all analytes.

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1. Introduction

1.1 Background

The first Australian inventory of dioxin emissions to air (*Sources of Dioxins and Furans in Australia: Air Emissions)* was published in 1998 (Environment Australia 1998). As there were few Australian data on dioxins, the preparation of that inventory relied heavily on overseas data, using release estimation methodology. The limited monitoring data available indicated that environmental concentrations were generally low, but that there was insufficient information to assess the impact of dioxins in Australia. At its meeting in December 2000, the Australian and New Zealand Environment and Conservation Council (ANZECC) requested the development of a discussion paper on dioxins for use in consultation with stakeholders. In April 2001, public meetings were held in several cities across Australia to seek public input into the development of a possible National Dioxins Program. These workshops noted the lack of information on dioxins in Australia and recommended that data be obtained on levels in the environment and the population. Following on from these consultations, a proposal for a National Dioxins Program was tabled at the meeting of ANZECC in June 2001. At this meeting, Council noted that the Australian Government would fund a National Dioxins Program (NDP) with $5 million over four years and that this program would generate data over the following two years which could be used to determine whether a specific regulatory approach would be required to manage dioxins. The NDP is being implemented by the Australian Government Department of the Environment and Heritage (DEH) in three phases:

- information gathering about the current levels of dioxins in Australia
- risk assessment using the information gathered as a basis to assess the potential risks of dioxins to the environment and human health
- development of measures to reduce, and where feasible, to eliminate the release of dioxins in Australia.

Under the information gathering phase, DEH commissioned organisations to undertake the following studies:

- Determination of ambient environmental levels (ambient air, aquatic, soils and fauna) of dioxins in Australia
- Determination of the levels of dioxins emissions from bushfires in Australia
- Determination of the levels of dioxin emissions from motor vehicles in Australia
- Determination of the levels of dioxins in the Australian population by analysis of blood serum
- Dioxins and dioxin-like compounds in pooled human milk samples.

Studies of dioxins in food by Food Standards Australia and New Zealand (FSANZ) and dioxins in agricultural commodities under the National Residues Survey by the Australian Government Department of Agriculture, Fisheries and Forestry (DAFF) also contributed valuable information on dioxins.

Dioxins

"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.

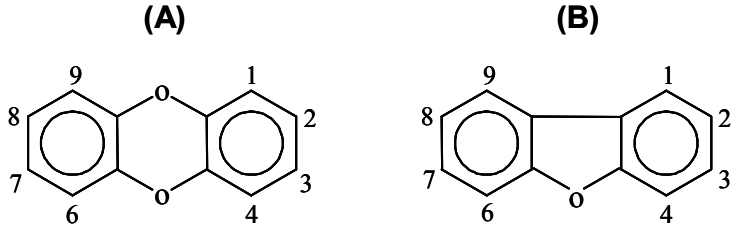


Figure 1.1 The structures of polychlorinated (A) dibenzo-p-dioxins and (B) dibenzofurans.

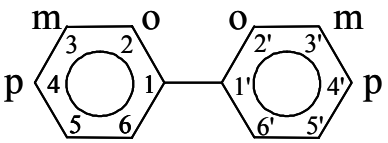


Figure 1.2 The structures of polychlorinated biphenyls (PCB).

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:

$$TEQ = ([PCDD_i \times TEF_i]_n) + ([PCDF_i \times TEF_i]_n) + ([PCB_i \times TEFi]_n)$$

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.

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

This study formed part of the Ambient Environmental Levels section of the Data Gathering and Consolidation phase of the NDP. The overall objective of the study was to determine ambient environmental levels of dioxins in Australian soils through characterisation of the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and dioxin-like polychlorinated biphenyls (PCB) in terms of concentrations and toxic equivalents in soils across a range of landforms, climates and land-uses.

Specific aims of the study were to:

- Increase understanding of background dioxin levels in Australian soils by direct sampling
- To compare analytical results with previous Australian studies and international data
- Analyse archived soil samples to determine historical evidence of dioxin contamination in Australia
- Standardise sampling analyses and reporting of dioxin data nationally.

1.3 Scope

A four-stage project plan was implemented in order to achieve the project aims:

Stage 1 – Sample collection

Composite samples were collected at all sampling locations to ensure samples were representative of the background at each location. Sampling was conducted within airsheds and catchments based on the National Pollution Inventory (NPI).

Historical evidence of soil dioxin contamination was determined through analysis of ten historical samples collected from the same location at the Waite Institute, South Australia. These samples were soils collected in 1925, 1935, 1945, 1950, 1956, 1963, 1973, 1981, 1983, and 2001.

Stage 2 – Sample analysis

Analysis of samples was undertaken at Australian Government Analytical Laboratories (AGAL) in Sydney to determine the concentrations of the 29 polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and co-planar polychlorinated biphenyls (PCB) as outlined in the analytical methodology at Appendix B.

Quality control/quality assurance was integrated into all phases of the sampling and analysis process. Duplicate samples (i.e. ‘A’ and ‘B’) were collected at each location to allow sampling reproducibility to be determined through the analysis of 20% of ‘B’ samples. Analytical reproducibility was determined through replicated analysis of 6 soil

samples at AGAL and through an interlaboratory calibration where 10% of the samples were analysed at the Ministry of the Environment, Laboratory Services Branch, Ontario, Canada.

Stage 3 – Collation and statistical analysis of the data

A database was prepared to include all site information recorded by sampling personnel and to store the analytical results. Site information included: GPS readings (latitude, longitude and altitude), vegetative cover, soil type, temperature range, average annual rainfall, and in information concerning possible PCDD/PCDF and/or PCB sources near the sampling location. The database was utilised for statistical analysis of results.

The current state of knowledge on dioxin levels in Australian environments was consolidated through a literature review of studies previously undertaken in Australia. A review of international literature was conducted and results obtained in this study were compared to those found in international environments. Study data were also compared with international regulatory guidelines.

Stage 4

Report preparation and presentation.

2. Project design

Samples were collected from 86 locations representing urban, industrial, agricultural and remote land-uses across Australia, across a range of climates and landforms. The sampling strategy is described under Section 2.2.2.

Seventy-six sampling locations were concentrated in priority airsheds and catchments, and including metropolitan (industrial and urban), agricultural and remote areas. A further ten samples were collected in remote areas of Australia to represent the remainder of the continent.

The sampling protocol was designed for the determination of background concentrations of dioxin and dioxin like chemicals in soil across a range of environments and land-uses. Sites that may have been subject to specific local contamination were avoided.

In addition, 10 historic samples were obtained from an archive of soils collected from an agricultural plot near the Waite Institute, South Australia.

2.1 Selection of sampling locations

Where possible, sampling locations were co-located with locations used to collect samples for parallel component studies for the National Dioxins Program, including aquatic, ambient air, fauna and bushfire studies. Co-location allowed correlations to be identified, potentially providing information on the fate, deposition and partitioning processes of chemicals between environmental phases.

Soil sampling sites were selected based on the following criteria:

- Compatibility with other studies, where possible samples were collected in the vicinity of aquatic, air, bushfire, and/or fauna study sampling sites
- Sampling locations were spread evenly across Australian regions (Northern, South Eastern, South Western)
- Population based sampling (covering key residential areas in all regions)
- Land-use based sampling. Samples were collected from:
  - industrial
  - urban
  - agricultural
  - remote.
- Environmental based sampling (covering remote environmental areas in various regions based on vegetation covers and types with special emphasis on fire resistant plants indicating a history of regular burning)
- Priority land-use subcategories were identified for each land-use and at least one of each was sampled for each region (Table 2.1).

Table 2.1 Priority land-uses identified for selection of sampling locations.

Land-use type	Priority land-use sub category
Urban	Capital cities and major towns, including coastal and inland population centres.
Industrial	Areas dominated by industry. No specific industries were targeted.
Agricultural	Sugarcane, cotton, grazing, forestry, cereals, horticulture.
Remote	Open forest, closed forest, inland, coastal, regions subject to regular burning and regions where fire is excluded.

Specific criteria were developed for the selection of industrial/urban, agricultural and remote sites to ensure potential localised contamination sources were avoided. These are listed in Appendix A. Table 2.2 summarises the number of samples analysed for each land-use and region, and Figure 2.1 displays the geographical distribution of sampling locations.

Table 2.2 Summary of the sampling strategy and number of samples analysed for the study.

Land-use	**Region**						**Total**
	Northern		**South-Eastern**		**South-Western**		
	A	**B**	**A**	**B**	**A**	**B**	
Industrial	4	2	12 +1*	6	2	1	27
Urban	4	2	12 +1*	6	2	-	26
Agricultural	5	-	15	1	2	-	23
Remote	6	-	10	-	3	-	19
Additional Remote[1]	6	-	2	-	1	-	9
Total	29		64 +2		11		104 +2

[1] Additional remote sampling locations were selected to specifically cover inland regions.
* Resampled sites Hobart Urban A and Hobart Industrial A.

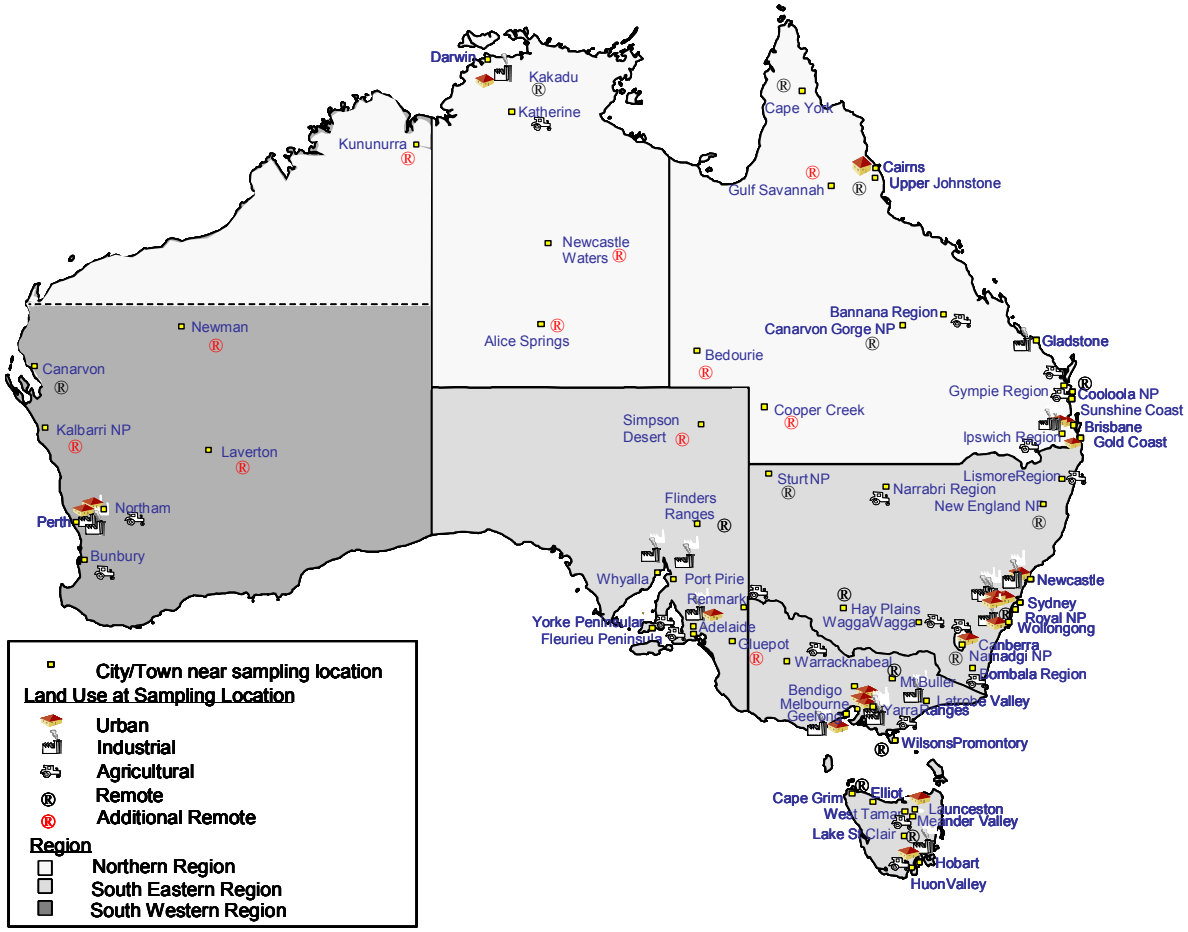


Figure 2.1 Conceptual representation of the geographical distribution of sampling locations.

2.2 Sample collection

2.2.1 Sampling personnel

The nation-wide sampling program was conducted by local sampling personnel. Sampling personnel were provided with instructions specific to the land-use type of the allocated sampling location (listed below). These instructions comprised audiovisual material together with comprehensive written instructions and detailed sampling site data sheets (Appendix A) to ensure consistent sampling methods were employed at all sites.

2.2.2 Sampling strategy

The sampling strategy was designed to ensure a sample representative of the land-use specified for each location. A sampling strategy based on that used by Buckland et al. (1998) was employed. Sampling personnel were responsible for the selection of sub-sampling sites (Figure 2.2) at each sampling location according to the prescribed study criteria. At each location two composite samples, 'A' and 'B', were collected. Each composite sample consisted of 18 soil cores, where six soil cores were collected from each

of the three sub-sampling sites. To ensure the samples were randomly distributed within sites, a triangular sampling configuration was used at each subsampling site (Figure 2.3). The soil cores were collected using aluminium tubes (15 cm length, 2.5 cm diameter), which were hammered into the ground to a depth of 10 cm, then withdrawn and sealed in aluminium foil to minimise potential contamination problems associated with the handling of tubes (see Appendix C for details).

Emphasis was placed on determining background levels. Those sites that may have been subject to unusual local contamination ('hotspots') were deliberately avoided. Potential 'hotspot' sources were identified as follows:

- vehicle emissions
- wood treatment (fences, poles, playgrounds, buildings etc.)
- other chemical treatment and/or chemical spraying
- burning, in particular, burning of plastics
- deposition of contaminated material
- draining of contaminated material and spillage
- application of biosolids (agricultural fields).

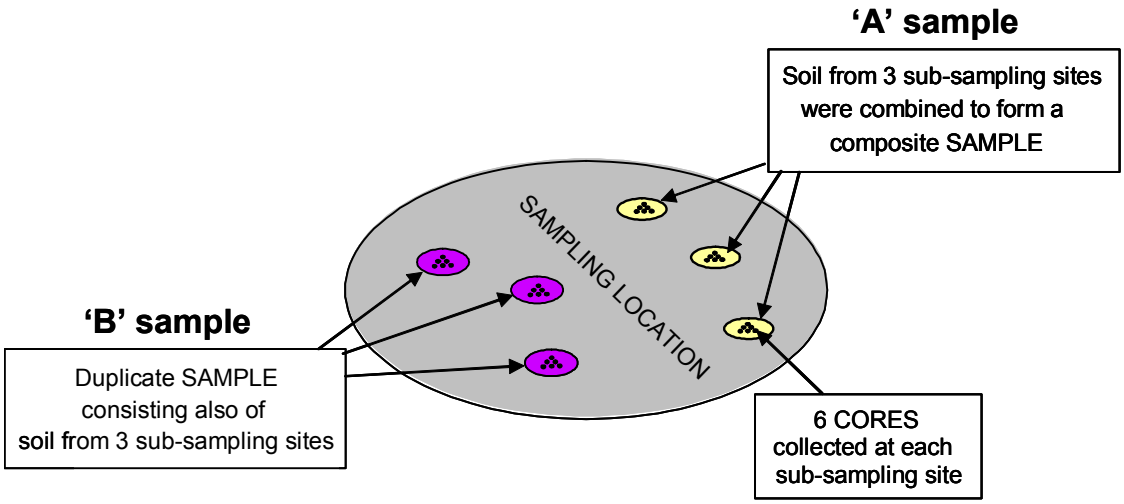


Figure 2.2 Sampling strategy for a given sampling location.

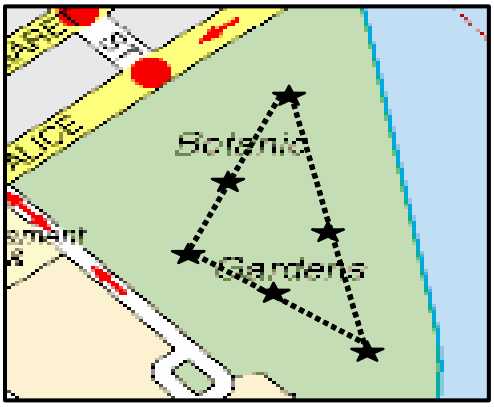


Figure 2.3 The triangular sub-sampling configuration consisting of six cores.

2.2.3 Sampling location information

Sampling personnel completed a sampling location information form (Appendix A). Details recorded include geographical information and parameters relevant to the deposition of dioxin-like chemicals, for example, rainfall (wet deposition), soil type (soil retention of contaminants) and parameters relevant to different land-uses (potential local sources).

Key plant communities present at the site were recorded along with the approximate percentage cover. Of particular interest for remote locations is the presence/absence of fire-adapted species, enabling investigation of forest fires as a potential source of dioxin and dioxin-like chemicals.

2.2.4 Historic samples

Archived historic soil samples were obtained from the same plot at the Waite Institute SA. Samples were collected in 1925, 1935, 1945, 1950, 1956, 1963, 1973, 1981, 1983 and 2001. Analysis of these archived soils allowed the determination of historical deposition of dioxin-like chemicals in soil. These samples were suitable for analysis as they periodically represented the last century and include samples collected prior to the manufacturing of organochlorines (prior to 1940's). Details concerning these samples are in Table A2.

2.3 Analysis, statistics and data quality

2.3.1 Analysis

Soil extracted from coring tubes representative of a site was pooled to form a composite sample and homogenised. Composite samples were freeze-dried, sieved through a 2 mm sieve and placed in individual solvent washed jars. Samples were then transported to AGAL for analysis.

The analytical methodology for the determination of PCDD/PCDF and PCB is based on quantification of the analytes through isotopic dilution techniques and is modified from those described by the USEPA methods 1613B and 1668A, respectively. For further details on the analytical methodologies and list of analytes refer to Appendix B.

Total organic carbon (TOC) was determined in the Queensland Health Scientific Services (QHSS) laboratory according to a standardised procedure (QHSS, 1996) (see Appendix B).

For all samples, data with quantified analytes were reported to two or three significant figures, whereas limit of detection data for non-quantified analytes were reported to one significant figure only.

For samples where non-detects were involved, total TEQs were calculated both with below limit of detection values excluded and also with half limit of detection values substituted.

2.3.2 Database and statistical analysis

A database (MS Access) was developed for storage and retrieval of data pertaining to the sampling location and analysis.

Statistical analysis was carried out using XL-Stat (supplementary Microsoft Excel 2000 package) and SYSTAT V7.0 (Wilkinson, 1996). In this study, the median concentration or TEQ is often presented rather than the mean, since the median is a "resistant" measure that is not sensitive to extreme observations, whereas the mean may be raised or lowered substantially by a single high or low sample result (see Box 1). Standard box and whisker plots were used for data presentation (see Box 2). Two-way analysis of variance (ANOVA) was used to explore differences in mean dioxin TEQ concentrations between regions (Northern, South Eastern and South Western) and adjacent land-use type (urban/industrial, agricultural and remote). Data were inspected for gross deviations from normality prior to analysis and where necessary, Log_{10} transformed.

Data obtained in this study was compared with data from the Organochlorines Program in New Zealand and other complementary overseas data. In particular, interpretation of the data was based on national standards of dioxin-like chemicals in soils such as those from European countries.

Box 1. Means and medians

Means and medians are two alternative ways to define the middle or "average" value for a set of samples.

The arithmetic **mean** is the sum of all values divided by the number of samples.

The **median** is the middle value of a set of samples arranged in order from the lowest to the highest. If there is an even number of samples then the median is the mean of the centre two values in the ordered list.

2.3.3 Data quality

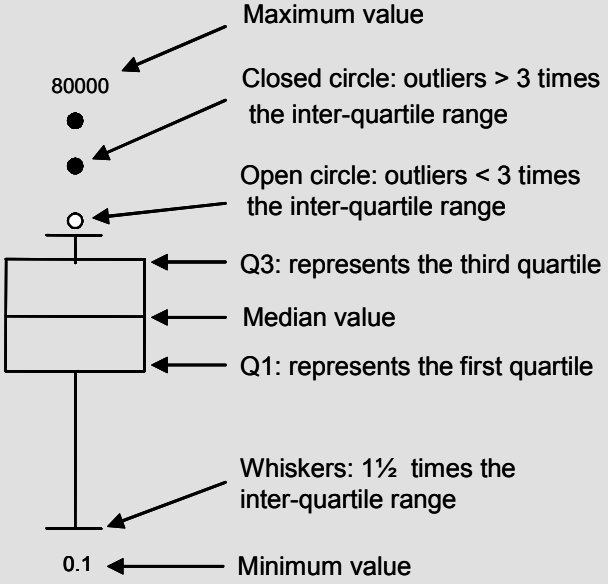
A number of procedures were implemented to avoid sample contamination. A chain of custody was established with a suitable labelling system to ensure that no samples were mixed up or misplaced. For a detailed description of the sample handling and quality assurance refer to Appendix C.

The study design allowed for the determination of both sampling and analytical reproducibility. Sampling reproducibility was evaluated through collection of duplicate samples at each sampling location. A total of eighteen 'B' samples were selected for evaluating the sampling reproducibility. It is important to note that in many cases 'B' samples were selected based on elevated levels of dioxin-like chemicals in the respective 'A' samples. Hence, the selection of 'B' samples was strongly biased toward urban and industrial locations and is likely to represent a worst-case scenario of sampling reproducibility. The concentrations detected in each 'B' sample were compared to those of the corresponding 'A' sample by calculating the mean normalised difference (see Box 3, and Tables C3 and D1-3). This comparison demonstrated that the sampling reproducibility was highly variable and the average of all eighteen mean normalised difference values was approximately 85% or in other words the difference between A and B samples was on average greater than a factor of two. This further indicates that either local historic or present point sources or the magnitude of local diffuse sources have substantially affected part of the results in samples from urban and industrial locations.

Box 2. Box and whisker plots

Box and whisker plots are a widely accepted way of presenting environmental data. They show where the data points are concentrated (the box) and the outlying values (the whiskers, open and closed circles). Box plots are often used to compare several sets of data.

Here we use a plot where the boxes represent the 25th and 75th percentiles. The top of the box in these plots is the 75th percentile (75% of the data fall below this line), while the bottom of the box represents the 25th percentile (25% of the data fall below this line). The line in the middle of the box represents the median (50% of the data fall above and 50% below this number).



The whiskers on the box extend to data points that are up to 1½ times the Inter Quartile Range (IQR). The IQR is defined as the difference between the 75th and the 25th percentiles, and is equal to the range of about half the data. Outliers, which are less than three times the IQR, are shown as open circles, while those greater than three times the IQR are shown as closed circles. The statistical and graphical package XL-Stat was used to produce all box plots and calculate percentiles.

The analytical reproducibility was determined through replicate analysis of six 'A' samples where both the original and the replicate samples were analysed by AGAL at different times. The results indicated good agreement in the repeated analysis of the samples with respect to the concentration expressed as TEQ, ∑PCDD/PCDF or ∑PCB, although the number of detectable congeners varied between the replicate analyses in two of the samples. Overall, the mean normalised difference between congeners detected in both replicates varied between 14% and 39% and is, thus, consistently low (see Tables C4 and D1 - D2).

Additionally, an inter-laboratory calibration was performed where eight 'A' samples analysed by AGAL were re-analysed by the Ministry of the Environment, Laboratory Services Branch, Ontario, Canada. The normalised difference was calculated for comparison of the AGAL result and the MoE-Canada result (Tables C5 and E1). Based on all results that were detectable by both laboratories (i.e. including all congeners and homologues) the mean normalised difference was less than 30% and no systematic differences between the results from the two laboratories was observable (i.e. neither laboratory was consistently higher or lower for any compounds).

Box 3. Normalised differences

In this report, comparisons between replicate samples or replicated analysis have been made using the normalised difference. The normalised difference between two samples is mathematically defined as:

$$\text{normalised difference (\%)} = \frac{\left|\text{value a} - \text{value b}\right|}{\frac{(\text{value a} + \text{value b})}{2}} \times 100$$

The table below provides a demonstration of the normalised difference (ND) values that would result from a range of differences in sample values.

Examples of normalised differences (ND) that would result from different sample values.

Sample A (pg g^{-1} dm)	Sample B (pg g^{-1} dm)	ND %
1.0	1.2	18
1.0	1.5	40
1.0	2.0	67
1.0	3.0	100
1.0	10.0	160
1.0	100.0	200

The mean normalised difference expresses the average normalised difference for all 29 congeners.

A direct comparison between the sampling reproducibility and the analytical reproducibility is illustrated in Figure 2.4 where 'A' and 'B' samples collected at location Sydney U3 (urban) were both analysed twice at AGAL (Figure 2.4 and Table D2). The results show that the error related to the analytical reproducibility between replicate analysis (defined by the standard deviation on the each of the bars) was much smaller than the 'error' or difference that was observed between the samples collected from the different sites representing the given location (i.e. Sydney U3). Hence, it can be concluded that despite

the emphasis on pooling 18 subsamples from 3 sites into one sample the largest error in this study is likely to be related to the selection of the specific sampling sites within a sampling location and is unlikely to be related to analytical errors.

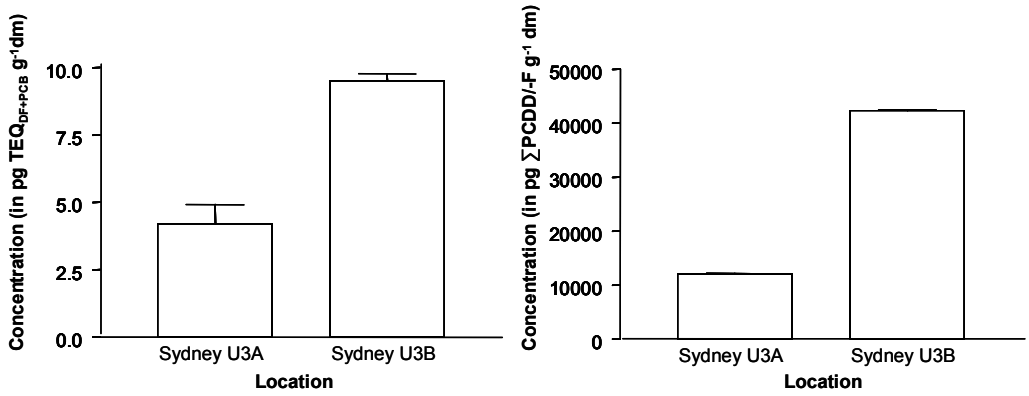


Figure 2.4 Results for replicate analysis of soil samples Sydney U3A & U3B.