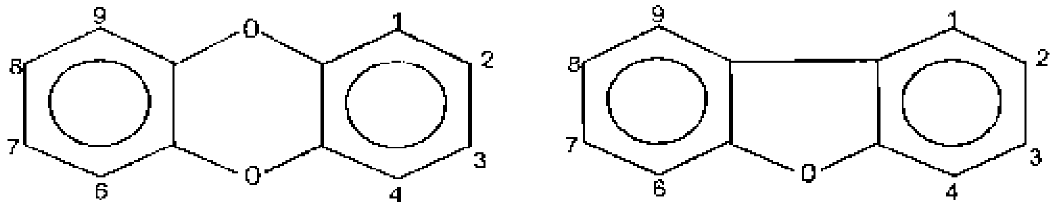
1. Introduction

Dioxins is a term used to describe a group of environmentally persistent chemicals that accumulate in the body fat of animals and humans and are resistant to the body's metabolism. They include compounds such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs) and co-planar polychlorinated biphenyl (PCBs). Dioxins are highly toxic substances generally found at such extremely low concentrations that they challenge the limits of scientific measurement.

In this study, laboratory analysis was limited to PCDD and PCDF compounds or 'congeners' which contain either a dibenzo-p-dioxin or dibenzofuran nucleus substituted with chlorine. The structures of dibenzo-p-dioxin and dibenzofuran are shown in Figure 1. Each of these molecules may have between 1 and 8 chlorine atoms bonded to them at any of the eight numbered positions (i.e. 1–4, 6–9) shown in Figure 1. Each individual compound resulting from this is termed a congener. There are 210 congeners in total with 75 congeners based on dibenzo-p-dioxin and 135 congeners based on dibenzofuran. Of these congeners, it has been found that it is only those with chlorine atoms in the 2, 3, 7 and 8 positions which exhibit toxic effects (i.e. 17 possible congeners in total, the most toxic of which is 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)). It is these 17 toxic congeners that are the primary focus of this study.



dibenzo-p-dioxin dibenzofuran

Figure 1: Structures of dibenzo-p-dioxin and dibenzofuran

Dioxins have never been intentionally produced, other than on a laboratory-scale basis for use in chemical analyses. Rather, they are produced as the unintended by-products of some human activities (mostly processes involving combustion) and from some natural activities such as bushfires and volcanic activity. Appendix A presents further information on sources of dioxins.

Over the past 10–20 years, programs have been in place in NSW and elsewhere to eliminate known sources of dioxins from the manufacture of chemicals including pesticides, emissions from waste incinerators and industry, and more diffuse sources such as backyard burning. These programs have resulted in significant reductions in dioxin emissions.

Dioxins usually occur as a complex mixture of congeners. To enable the relative toxicity of such a mixture of compounds to be expressed as a single number, the concept of toxic equivalents (TEQ) has been developed. The scheme used in this report was proposed by the North Atlantic Treaty Organisation/Committee on the Challenges of Modern Society, known as the International Toxic Equivalents Factor (I-TEF) scheme (Kutz et al 1990) and is the most widely adopted system. A toxic equivalent factor (TEF) has been given to each of the 17 congeners with chlorine atoms in the 2, 3, 7 and 8 positions. By definition, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic congener, has a TEF of 1. Other congeners have a TEF of between 0 and 1, depending on their relative toxicity (see Appendix B).

The total toxicity of a sample is calculated in two steps. Firstly, the concentration of each congener in the sample is multiplied by its TEF. Next, the total toxicity is calculated by adding together the contributing toxicity of each congener. This standardises the measurement so it can be used to compare results with other sites and international levels and goals.

Dioxins are highly persistent under normal environmental conditions and can be transported long distances in the atmosphere if they are bound to particulate material.

Several dioxin congeners cause adverse health effects in humans such as immune suppression, and reproductive and developmental effects. International experts have reached various conclusions on the carcinogenic classification of the most toxic congener—2,3,7,8-TCDD:

- The International Agency for Research on Cancer (IARC), the State of California and the US National Toxicology Program have classified 2,3,7,8-TCDD as a known human carcinogen (IARC 1997; CCR 1996; US DHHS 2001).
- The US EPA identified this compound as a human carcinogen under the Agency's draft risk assessment and risk characterisation (US EPA 2000a). The Agency's Science Advisory Board have since released a report that indicates that 50% of the Board do not agree with the 'known human carcinogen' assessment for 2,3,7,8-TCDD (US EPA 2001a).
- The FAO/WHO Expert Committee on Food Additives concluded that 2,3,7,8-TCDD is a cancer promoting agent rather than a genotoxic carcinogen (FAO/WHO 2001).

Dioxins appear on several national and international priority lists for air toxics, for example, the US EPA has identified 2,3,7,8-TCDD as one of 33 air toxics that present 'the greatest threat to public health in the largest number of urban areas' and Environment Australia has listed polychlorinated dioxins and furans as one of 28 priority pollutants (US EPA 2000b; Environment Australia 2001).

1.1 Project background and objectives

In September 2003, the EPA became part of the Department of Environment and Conservation (NSW). Since all research in this report was conducted before September 2003, the organisation is referred to as the EPA throughout.

Previously, there have been few measurements made of ambient dioxin concentrations in New South Wales (NSW). As part of the NSW EPA's Pilot Air Toxics Project (NSW EPA 1998) a few ambient samples were collected in the vicinity of suspected dioxin sources, but no systematic quantification of ambient concentrations was attempted.

The purpose of the study was to measure concentrations of the 17 toxic congeners (with chlorine atoms in the 2,3,7 and 8 positions) in ambient air at three sites chosen to reflect a range of distinctly different environments with respect to dioxin levels. The congener profiles for potential source identification were also investigated.

2. Materials and methods

2.1 Sampling sites

The following sites (see Figure 2) were chosen to reflect a range of distinct environments:

- **Rural background site:** the Siding Spring Observatory in central-western NSW, approximately 25 km west of Coonabarabran and approximately 400 km north-west of Sydney was chosen. The site is at an elevation of about 500 m and is surrounded on three sides by the Warrumbungles National Park. There is a main road running through the centre of the national park which carries major regional and tourist traffic. There is also a road running within 30 m of the sampling site, which observatory staff use at a rate of approximately three cars or less per hour. Tourist coaches are permitted to use this road to access a nearby lookout, but these coach movements number less than one a week.
- **Urban site:** the EPA's existing air quality monitoring station at Westmead was chosen. The site is in western Sydney, approximating the geographical centre of the Sydney Metropolitan Area. Any major industrial activity is 4–5 km away.
- **Urban site near an industrial source of dioxins:** the EPA's existing air quality monitoring station at Warrawong in the Illawarra region was chosen. The site is at the north-eastern end of Lake Illawarra, about 3 km south-east of the steelworks at Port Kembla (the largest known point source of dioxins in NSW). The site is on an open playing field but has houses, a main road and a major suburban shopping complex within 500 m.

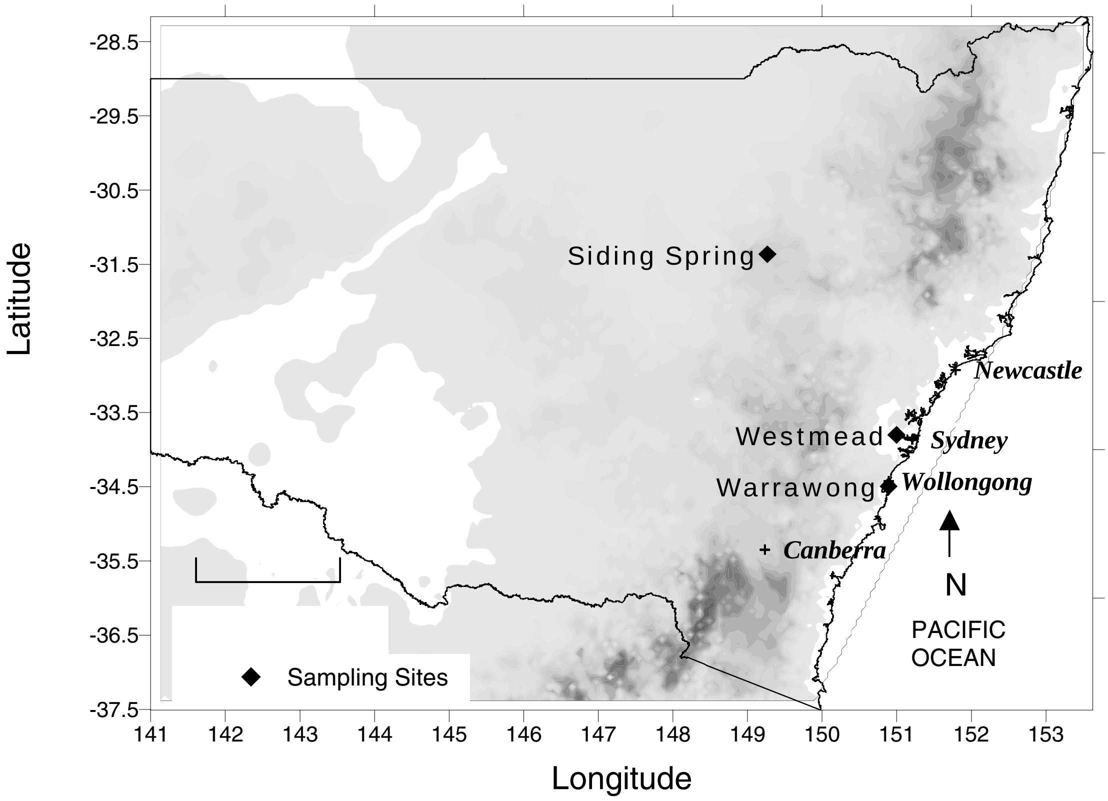


Figure 2: Map of New South Wales showing locations of sampling sites

2.2 Sampling schedule

Sampling for dioxins took place continuously from November 1998 to April 2000 at each site, with the exception of an approximate three-month period at each site in early 1999 caused by mechanical failure of the air sampler motors. There was also a one-week gap in sampling at Siding Spring in early November 1999 caused by a lightning strike.

Air was sampled continuously for 12 days at Westmead and Warrawong. Because the readings at Siding Spring were so low and the test methodology requires a sample to be taken which can provide a detectable concentration, samples at that site were taken continuously over 24 days. There were some occasional minor variations from these times as logistical arrangements determined.

2.3 Sampling and analytical procedures

Sample collection and analysis were in accordance with 'Method TO-9A—Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air' (US EPA 1999a).

A sample of air was drawn through a filter paper and an absorbent canister. The absorbent canister contained a mixed medium of polyurethane foam (PUF) and a cross-linked polystyrene resin (XAD-2). The canisters were pre-spiked with a range of isotopically labelled dioxin congeners, which were internal standards for the analysis.

Samples were collected at a flow rate of around 160–190 L/min. Air volumes sampled ranged from:

- 1900–7400 m^3 (average 5600 m^3) at Siding Spring
- 830–4000 m^3 (average 2900 m^3) at Warrawong
- 270–3600 m^3 (average 2500 m^3) at Westmead.

Details relating to the measurement of air flow and instrument calibration are provided in Appendix C.

Because of the extremely low concentrations of dioxins expected, extreme care had to be taken when handling the sampling equipment to avoid contamination. All apparatus was double rinsed with solvents and only handled with forceps or gloved hands. Specific details are provided in Appendix D.

The exposed canister and its accompanying filter were extracted together with ethanol/toluene (68:32) in the laboratory and analysed by high resolution gas chromatography/mass spectrometry. The data for each air sample was for the total sample (i.e. combined gaseous plus particulate phases). All analyses were conducted by the Institute of Environmental Science and Research Limited (ESR) of New Zealand which became AgriQuality New Zealand Limited during the course of the study. This laboratory is accredited by International Accreditation New Zealand.

The 17 congeners with chlorine atoms in the 2, 3, 7 and 8 positions were determined congener-specifically and reported as the mass of each congener collected on each canister/filter paper pair. These congeners are the ones which exhibit toxic effects, the most toxic of which is 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), and are the congeners for which toxic equivalent factors exist. Analysis in this report is based on the 17 2,3,7,8-congeners only.

Details of the analytical methodology are provided in Appendix E.

2.4 Data handling

Air flow data and sample chemical analysis data were combined in a database. The concentrations of dioxins in the sampled air were determined simply as the mass of dioxins (individual or groups of congeners) reported by the laboratory, divided by the volume of air which passed through the sampler over the sampling period. Database details are provided in Appendix F.

2.5 Measurement units and detection limits

Dioxin concentrations have been reported in femtograms per cubic metre (fg m^{-3}): one femtogram is 1×10^{-15}grams. To put this extremely small measure in perspective, 1 fg is to a gram as 1 milligram is to one million tonnes. Data are corrected for recovery of $^{13}C_{12}$ surrogate standards. Toxic equivalents are calculated using the international TEF scheme.

The laboratory detection limits varied from sample to sample and also by congener in each sample due to varying recovery efficiencies and mass spectral instrument performance. The range of detection limits for each dioxin and furan congener group is presented in Table 1. The largest range in detection limits occurred for the octa chlorinated dioxin congener with a range of 20,000–300,000 fg. This detection limit of 300,000 fg is also the highest detection limit for any congener.

Table 1: Range of detection limits for each 2,3,7,8-congener group

			Furan detection limits	
				Median (fg)
Tetra	600–8000	2000	400–20,000	2000
Penta	700–10,000	3000	400–4000	2000
Hexa	700–10,000	4000	400–10,000	2000
Hepta	4000–20,000	10,000	700–30,000	4000
Octa	20,000–300,000	95,000	2000–50,000	8000

A decision was necessary on how to deal with data where the mass of a particular congener or congener group in the sample was reported as less than a stated detection limit. Currently there are no internationally consistent approaches or available standards for dealing with non detects for dioxins. Three approaches were available and included:

- excluding non-detects
- assuming that non-detects are present at half the level of detection
- assuming non-detects are present at the level of detection.

Despite the long sampling periods, approximately 85% of individual congener results were below the detection limit at Siding Spring, 25% at Warrawong and 24% at Westmead. As a result, the technique(s) used to handle non detects had a significant impact on data relating to Siding Spring but showed little impact on levels at Warrawong and Westmead.

For this study it was decided to use the second technique, where the mass of non-detects was assumed to be half the stated detection limit. This is in accordance with an established US practice (BAAQMD 1995). All figures have been prepared using data that assume non-detects were present at half the limit of detection (calculated using individual sample and congener detection limits).

3. Results

3.1 Congener concentrations

Table 2 overleaf presents the average and median concentration of each congener at each of the three sites along with the respective maximum and minimum concentration. The number of non-detects for each congener at each site is also presented (a value of zero indicates that the congener was present in every sample at the site).

3.1.1 Congener profiles

A congener profile represents the proportion that each of the 2,3,7,8-congeners contributes to the total 2,3,7,8-congener concentration in each sample. Where profiles are based on more than one sample, the profile represents the average of the individual sample proportions (as opposed to the proportion of the average congener levels).

The method used for data reporting (where if a congener was below the detection limit, it was assumed to be present at half the detection limit) could have a significant influence on the congener profiles. Due to the varying detection limits, both by sample and by congener, the profiles may be skewed towards congeners with higher detection limits. The number of samples where each congener was below the limit of detection is presented in Appendix G.

Figure 3 on page 9 presents the profiles for each measurement site in NSW and shows that the octa chlorinated dioxin group dominates the profile for all sites. At Warrawong, however, while the octa chlorinated dioxin group dominates the profile, it is a lower proportion of the profile than at the other two sites, with the contribution from the chlorinated furan groups being higher. The higher detection limit for the octa chlorinated dioxin group should be noted especially for Siding Spring where this congener was below the detection limit in 73% of samples compared with 27% and 9% for Warrawong and Westmead respectively. There is greater uncertainty in the congener profile at Siding Spring, and in the relative contribution made by octa dioxin, compared with the other two sites.

No meaningful interpretation can be made of the congener profile for Siding Spring due to the high frequency of non-detects. The profile patterns for Westmead and Warrawong are different, suggesting that there are different mixes of dioxin and furan congeners, which may be indicative of different sources.

Table 2: 2,3,7,8-congener concentrations at each site (fg m^{-3})

[redacted]	[redacted]					[redacted]					Westmead				
[redacted]	[redacted]					[redacted]					34 (12-day)				
															Number of non-detects
2,3,7,8-TCDD	0.18	0.14	0.79	0.05	14	0.88	0.78	2.1	0.18	17	1.3	0.81	3.9	0.17	19
1,2,3,7,8-PeCDD	0.21	0.16	0.79	0.06	14	1.5	1.2	3.6	0.21	16	3.4	1.8	11	0.23	13
1,2,3,4,7,8-HxCDD	0.29	0.2	1.6	0.07	14	1.1	0.9	2.8	0.21	20	3.3	1.5	11	0.48	14
1,2,3,6,7,8-HxCDD	0.31	0.2	1.3	0.06	13	2.3	1.5	6.1	0.56	16	8.2	4.6	31	0.66	12
1,2,3,7,8,9-HxCDD	0.29	0.2	1.3	0.07	13	2.1	1.6	6.9	0.59	16	7.1	4.5	25	0.66	13
1,2,3,4,6,7,8-HpCDD	1.6	0.82	7.3	0.28	11	17	13	53	1.6	6	71	40	280	4.1	3
OCDD	11	7.8	33	1.4	11	69	60	180	12	9	270	210	830	35	3
2,3,7,8-TCDF	0.32	0.2	0.96	0.08	7	8.4	7.8	19	2.5	0	8.3	4.8	30	1.6	2
1,2,3,7,8-PeCDF	0.18	0.15	0.53	0.07	14	6.4	6.1	12	1.8	0	5.8	3.3	22	0.66	4
2,3,4,7,8-PeCDF	0.18	0.15	0.53	0.07	14	8.6	8.9	21	2.3	0	8.9	4.6	39	0.69	3
1,2,3,4,7,8-HxCDF	0.27	0.2	0.79	0.07	13	6.0	5.6	12	1.7	0	6.6	3.8	24	0.78	3
1,2,3,6,7,8-HxCDF	0.19	0.15	0.79	0.07	13	6.1	5.8	15	1.5	0	6.5	4.2	24	1.0	3
1,2,3,7,8,9-HxCDF	0.22	0.14	1.1	0.06	14	0.67	0.60	1.9	0.27	25	0.95	0.68	3.7	0.14	24
2,3,4,6,7,8-HxCDF	0.22	0.16	1.1	0.06	13	6.4	5.7	16	1.4	0	7.9	5.7	35	0.81	3
1,2,3,4,6,7,8-HpCDF	0.47	0.33	1.2	0.15	12	13	11	40	2.4	2	21	18	52	3.9	3
1,2,3,4,7,8,9-HpCDF	0.31	0.2	1.6	0.07	14	2.2	2.1	7.0	0.29	11	3.3	2.1	11	0.65	13
OCDF	0.80	0.65	2.1	0.19	12	9.8	8.4	25	1.6	5	40	19	430	1.8	3
															138/578

Note: ‘Number of non-detects’ assumes non-detects were present at half the limit of detection

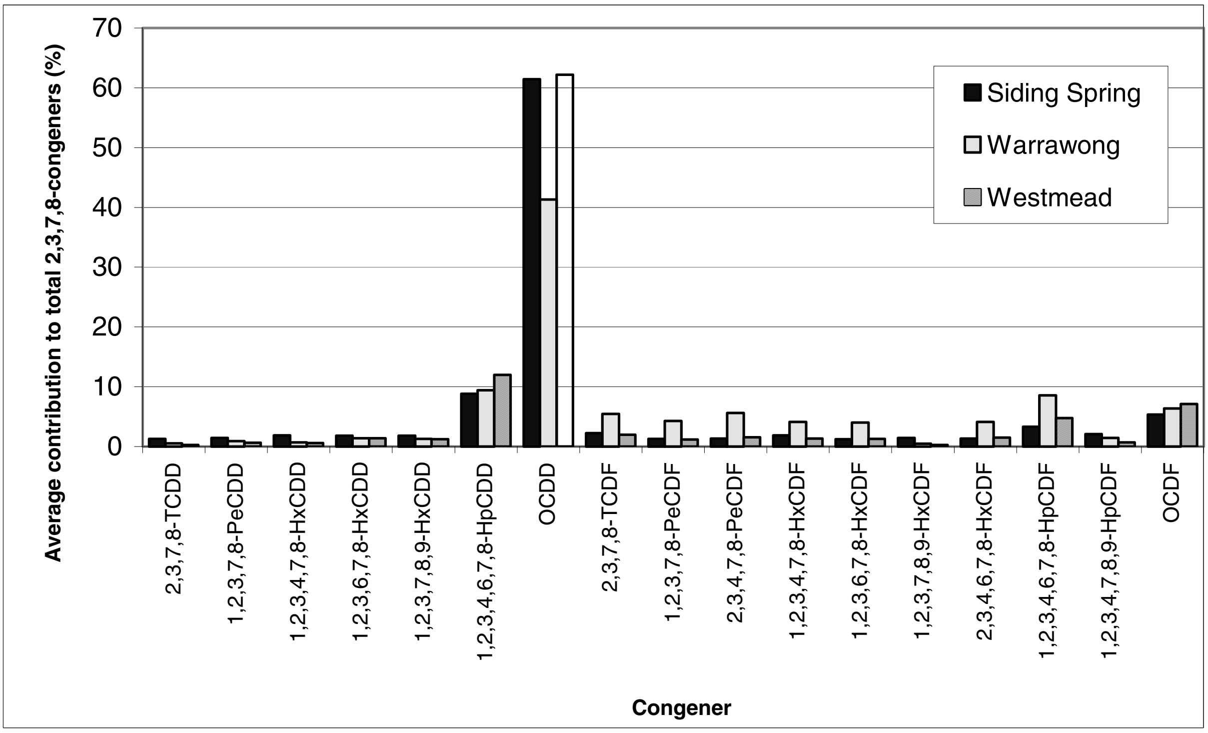


Figure 3: Congener profiles for total 2,3,7,8-congener concentrations at the three sampling sites

3.2 Total concentrations

Figure 4 on the next page shows the spread of data points for the total concentrations (fg m^{-3}) using a box and whisker plot. The lines of the box represent:

- the lower 25% of the data points (lower line of box)
- the median of the data (internal line in box)
- the upper 25% of the data points (upper edge of the box).

The whisker lines extend to the most extreme points within 1.5 inter-quartile ranges of the upper and lower quartiles. A circle marks the mean concentration.

The plot shows that the concentrations at Siding Spring are substantially lower than the concentrations at the other two sites. The Westmead site has a distribution of concentrations, which is skewed to higher concentrations when compared with Warrawong. Other evidence of the data skew at Westmead is the positive difference between the mean and median. Fifty percent of the data points from Westmead are higher than the maximum level at Warrawong. Levels at Siding Spring are low in comparison.

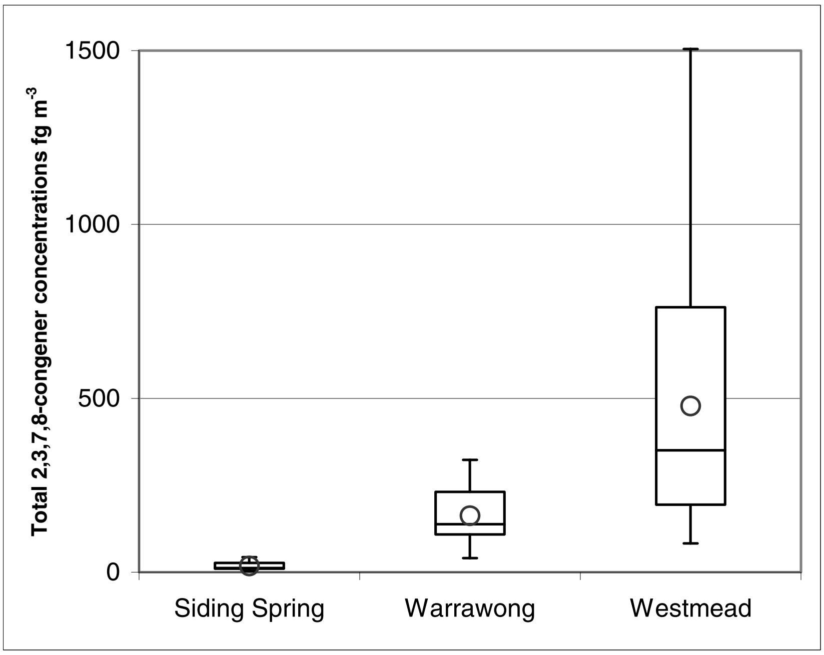


Figure 4: Total 2,3,7,8-congener concentrations at each site

Figure 5 overleaf presents changes in total 2,3,7,8-congener concentrations at each site during the course of the study. The dates shown are the dates in the middle of each sample period (for example, a mid-sample date of ‘12 June’ refers to a sample period from approximately 1–24 June for Siding Spring and 6–17 June for Warrawong or Westmead). The gap in sampling between January 1999 and April 1999 was due to motor failure. A table of these data is presented in Appendix H.

Siding Spring had much lower concentrations than the other two sites. The maximum concentration at Siding Spring of 43 fg m^{-3} was considerably less than the maximum of 320 fg m^{-3} at Warrawong and 1500 fg m^{-3} at Westmead.

Despite the proximity of the Port Kembla industrial complex, dioxin levels at Warrawong were lower than levels at Westmead. This may reflect the coastal location of Warrawong as well as the occurrence of meteorological conditions conducive to better dispersion during the measurement period (higher wind speeds were measured at the NSW EPA site at Warrawong compared with those measured at Westmead). In addition, the Illawarra region has a smaller population and therefore potentially fewer diffuse dioxin sources.

At both Warrawong and, in particular, Westmead, higher concentrations were observed in winter than in summer. This is likely to be attributable to poorer dispersion due to the effects of inversion layers, though increased emissions due to domestic heating may have also played a role.

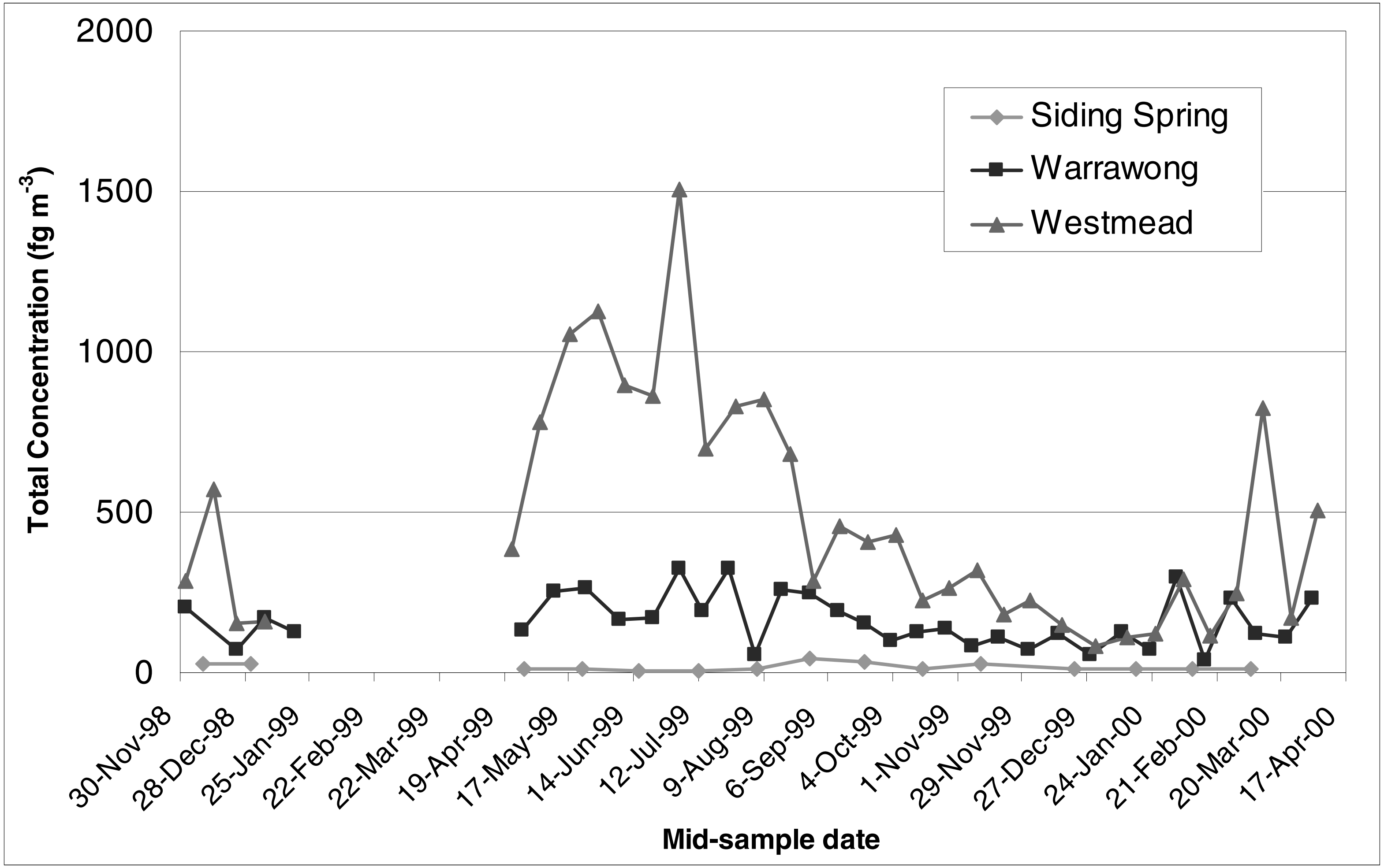


Figure 5: Variation in total 2,3,7,8-congener concentrations over time at Siding Spring, Warrawong and Westmead

3.3 Toxic equivalents

Figure 6 shows the spread of data points for the toxic equivalents (fg m^{-3}) using a box and whisker plot (see section 3.2 for explanation). Points more extreme than the whisker lines are marked with stars. Toxic equivalents were calculated using the international TEF (I-TEF) scheme and using congener concentrations based on the assumption that non-detected congeners were present at half the limit of detection.

I-TEQ levels at Siding Spring were markedly lower than those determined for the Warrawong and Westmead sites. Twenty-five percent of the data points from Westmead are higher than the maximum level at Warrawong. The Warrawong data contained a greater contribution from the more toxic congeners. However, because the total concentrations are significantly higher at Westmead, the overall toxic equivalents are higher at Westmead for more than 25% of the data.

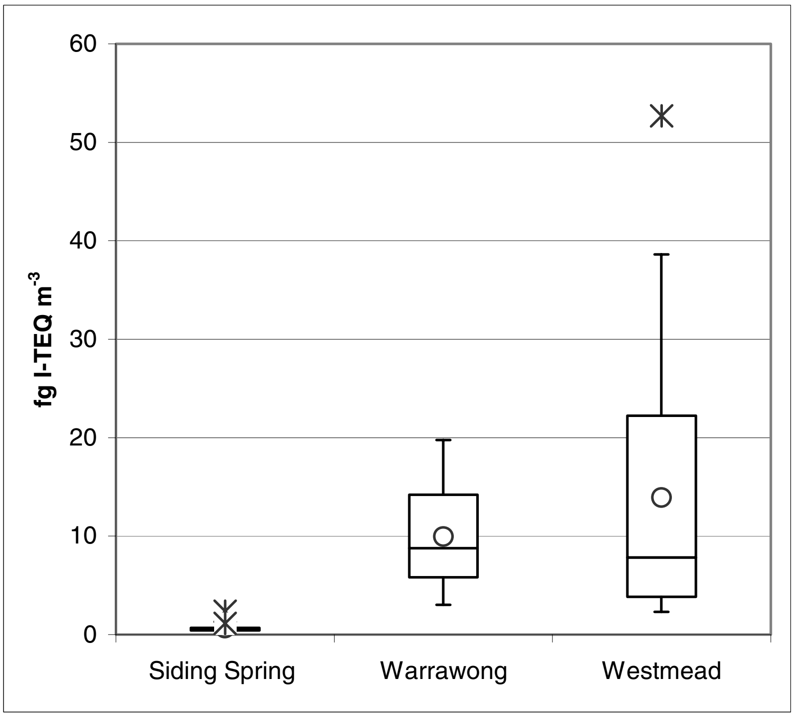


Figure 6: Toxic equivalent concentrations at each site

Figure 7 presents the individual contribution of each of the 17 congeners to the toxic equivalent concentrations for Warrawong and Westmead. The contribution of toxic equivalent concentrations at Siding Spring could not be reliably calculated due to the high proportion of non-detects and the low levels found when detected (see Table 2).

Note that in contrast to the dominance of OCDD in the overall congener profile (see Figure 3), OCDD makes a very small contribution to the overall TEQ concentration.

At Warrawong the congener 2,3,4,7,8-PeCDF (generally prevalent in combustion sources) is the most significant contributor to the toxic equivalent concentrations with an average contribution of over 40%. This congener also has the largest contribution to the toxic equivalents at Westmead. See discussion in section 4.4.3.

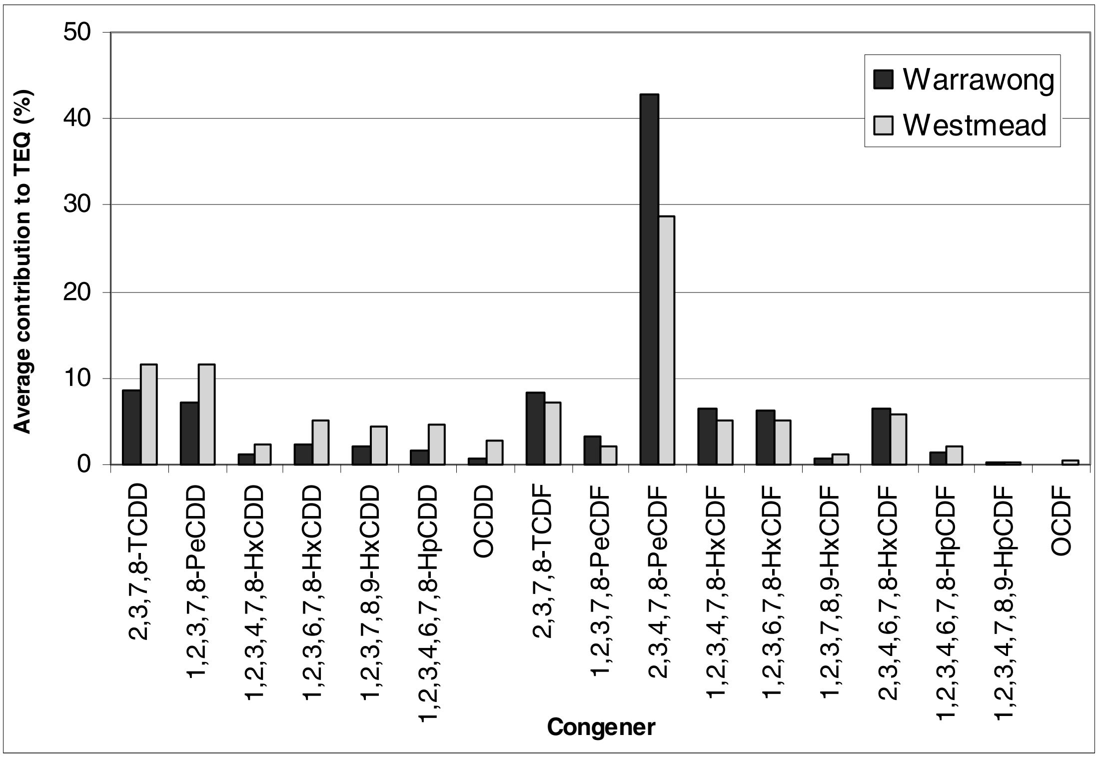


Figure 7: Contribution of individual 2,3,7,8-congeners to toxic equivalent concentrations

Figure 8 presents changes in the toxic equivalents over time at each site. The dates shown are the dates in the middle of each sample period (for example, a mid-sample date of '12 June' refers to a sample period from approximately 1–24 June for Siding Spring and 6–17 June for Warrawong or Westmead). Again, the winter peak in concentrations at Warrawong and Westmead can be observed. Siding Spring (mean value 0.64 fg m^{-3}) has much lower toxic equivalent concentrations than either Warrawong (mean value 10 fg m^{-3}) or Westmead (mean value 14 fg m^{-3}). A table of these data for figures 5 and 8 is presented in Appendix H.

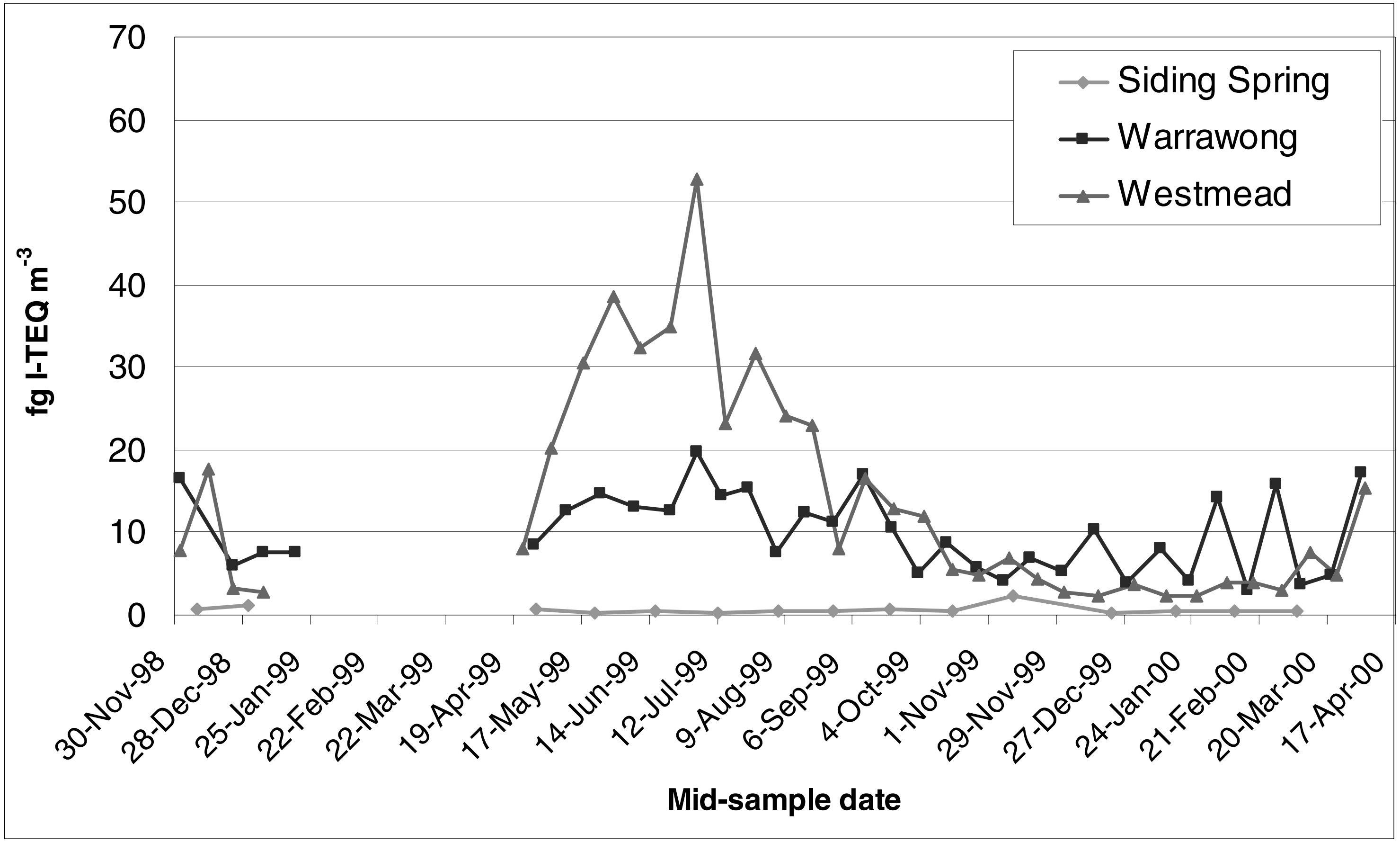


Figure 8: Changes in toxic equivalent (I-TEQ) concentrations over time at Siding Spring, Warrawong and Westmead

4. Discussion

4.1 Previous studies in NSW

Levels of dioxins in Sydney have previously been measured and reported (NSW EPA 1998; Taucher et al 1992). These studies were conducted in the early- to mid-1990s and had sample durations of less than one week. Sample sites were usually near sources such as waste incinerators that have since closed. This older data could not be expected to provide comparable data to make a valid or relevant point of comparison with the current study.

4.2 Comparison with overseas levels

Table 3 on the next page summarises the data collected in this study and similar data reported in several overseas studies. There are more data available from overseas but the data selected are the lowest reported for the relevant location type in the respective country.

Several areas of uncertainty should be considered when comparing levels with those collected in different studies. For example, two studies in Table 3 used different equivalency schemes for calculation of TEQ. The technique used for dealing with non-detects is important, especially for background sites with potentially more congeners below the detection limit. The method used for dealing with non-detects varies between studies and is often not reported. Other possible areas of uncertainty include siting classification definitions, nearby sources, sampling duration, measurement techniques and study objectives. The data therefore are not strictly comparable, but are broadly indicative.

It is evident from Table 3 that the levels of dioxins measured in this study were extremely low, especially considering that the overseas examples chosen were from the lower end of the data range.

The background levels measured at Siding Spring are among the lowest of any of the available results reviewed and are comparable with New Zealand and Connecticut, USA. European results of comparable locations were generally an order of magnitude higher.

The urban-industrial levels measured at Warrawong were lower than at comparable sites in all other places, including New Zealand, Belgium, Germany, Spain and the Netherlands.

The levels of dioxins measured at Westmead (urban site) were similar to those measured in the Netherlands, Sweden and New Zealand, but considerably lower than those in Japan (winter), UK (Belfast) and Poland (Cracow). The levels measured at Westmead were well below contemporary international goals.

Table 3: Comparison of data collected in this study with that reported from overseas

Site type	Country/Locale	Concentration fg I-TEQ m^{-3}			Original references
		Min	Max	Average	
					This study
Background	New Zealand	0.77	1.75	1.39	MFENZ 1999
Background	Netherlands	10	15		Bolt and De Jong 1993
Background/ country	USA, Connecticut	1.6*	3.6*		Maisel and Hunt 1996
Rural background	Germany, North-Rhine-Westfalia			19	Hiester *et a*l 1997
Rural	New Zealand	0.94	9.88	3.77	MFENZ 1999
Rural/ farmland	Austria, Vienna	11	96		Thanner and Moche 1996
Rural	Belgium, Flanders	46.3	190		Wevers et al 1993
Rural	Japan			255-375	Kurokawa et al. 1996
Rural	Spain, North-east, Catalonia (near MWI)			50	Abad et al. 1997
Rural	UK, Hazelrigg	nd	22		Department of Environment 1995
Remote coast	Sweden			2.6-4.4*	Broman et al 1991
					This study
	New Zealand	16.5	40.8	28.1	MFENZ 1999
	Austria, Ulmerfeld/ Hausmening	10.8	110		Thanner and Moche 1995
	Belgium, Flanders	17.5	194		Wevers et al 1993
	Germany, Baden-Wurttemburg	9	217		Wallenhorst et al 1997
	Japan (summer)	403	1310		Sugita et al 1993
	Japan (winter)	269	4240		Sugita et al 1993
	Netherlands	4	99		Bolt-Moekoet and De Jong 1993
	Sweden, Stockholm			13-24*	Broman et al 1991
	UK, Belfast	37	178		HMIP 1996
	UK, Stevenage	nd	800		Clayton et al 1993
	USA, Connecticut (Bridgeport)	10	290		Hunt and Maisel 1990
	Poland, Cracow	60	5740		Grochowalski and Chrzaszcz 1997
					This study
	New Zealand	40.3	1170	317	MFENZ 1999
	Belgium, Flanders	21.5	379		Wevers et al 1993
	Germany, North-Rhine-Westfalia	40	120		Hiester et al 1997
	Netherlands (close to MWI)	6	140		Bolt and De Jong 1992
	Spain, Catalonia			80-550	Abad et al. 1997

* Calculated using an alternate equivalency scheme
nd = not detected
Source: Adapted from table in MFENZ 1999.

4.3 Comparison with overseas goals or standards

There are no Australian goals or standards for ambient levels of dioxins against which to assess the NSW results. Similarly, there are not many overseas benchmarks. Goals that are available tend to use a range of different averaging periods and compounds.

Japan has an annual average goal of 600 I-TEQ fg m^{-3} (includes coplanar polychlorinated biphenyls) (MOEJ 1999). Ambient air concentrations of dioxins at all measured sites in NSW were well below this goal. The highest annual average concentration measured in this study (14 I-TEQ fg m^{-3} at Westmead) is only 2.5% of this yardstick. Note that this study did not include measurement of coplanar PCBs.

The Ontario Ministry of the Environment (Canada) has an Ambient Air Quality Criterion (AAQC) for dioxins of 5000 fg I-TEQ m^{-3} over 24 hours (OME 1999). Samples in this study were collected over 12 or 24 days and, while indicative, are not directly comparable with this goal. However, all measured levels in NSW were well below the goal. The maximum level measured (53 fg I-TEQ m^{-3} at Westmead over a 12-day sample period) was just 1% of the Canadian goal.

The Texas Natural Resource Conservation Commission (TNRCC) has developed Effects Screening Levels (ESLs) for ambient air. The TNRCC states that ESLs are not ambient air standards and are used as follows:

- if measured airborne levels do not exceed the screening level, adverse health or welfare effects would not be expected to result
- if ambient levels in air exceed the screening levels, it does not necessarily indicate a problem, but triggers a more in-depth review. The ESL for 2,3,7,8-TCDD is 30 fg m^{-3} based on an annual averaging period and is under review (TNRCC 2001).

The US EPA has developed two ambient air values for 2,3,7,8-TCDD. Region 6 Human Health Screening Levels (HHSL) address common human health exposure pathways (US EPA 2000c). Region 9 Preliminary Remediation Goals (PRGs) are risk-based tools for evaluating and cleaning up contaminated sites and are designed to estimate contaminant concentrations that are considered protective of humans over a lifetime. Exceeding a PRG suggests that further evaluation of the potential risks is appropriate (US EPA 1999b). The ambient air value set for 2,3,7,8-TCDD for both Region 6 and Region 9 is 45 fg m^{-3}.

Average levels of 2,3,7,8-TCDD in this study were well below all of these goals at all sites, with the highest average level of 1.3 fg m^{-3} found at Westmead.

4.4 Possible sources of dioxins

Congener profiles can sometimes be used to ‘fingerprint’ the source(s) of dioxins. Motor vehicles and several industrial, domestic and natural processes all contribute to the levels of dioxins in the atmosphere. There is a limited amount of information in the literature on congener profiles for various sources. A comprehensive source reconciliation analysis has not been conducted because a complete library of congener profiles for the full range of possible sources is not available. Further uncertainties associated with using congener profiles for source reconciliation include:

- the frequency of non-detects and the technique used for dealing with non-detects
- the influence of varying detection limits for each congener
- the possibility of similar profiles for different sources
- the likelihood that each site is influenced by several different sources and the combination of these might tend to blur congener fingerprints.

It was expected that the integrated steel works at Port Kembla would have an influence on concentrations at Warrawong, so profiles for two steel manufacturing facilities have been presented. Motor vehicles were expected to have some influence, especially in urban areas, so profiles for motor vehicles were plotted also. Other sources for which congener profiles are not available might also be influencing the data.

4.4.1 Motor vehicles

Figure 9 presents the congener profile for one sample collected by the NSW EPA over several days from the Sydney Harbour Tunnel in 1994. Figure 9 has been presented using a log scale as OCDD dominated the graph (contributing to almost 100% of the profile) making the contributions of the remaining congeners difficult to see. The Sydney Harbour Tunnel operators indicated that tunnel usage by heavy vehicles was much lower than the proportion of such vehicles in the total road fleet and so sampling from the tunnel was biased towards lighter vehicles and cars. It is also likely that the composition of the lighter vehicle fleet in NSW may have changed since 1994. The composition of the fuel has also changed during this time, with the reduction of lead in petrol. The uncertainty associated with the collection of only one sample must also be considered. In the one sample available, motor vehicle dioxin emissions were dominated by the octa chlorinated dioxin.

A New Zealand study of emissions from a motor vehicle running on unleaded fuel found that HpCDD had the highest contribution followed by OCDD, with other congeners having concentrations below the limit of detection (Bingham 1989).

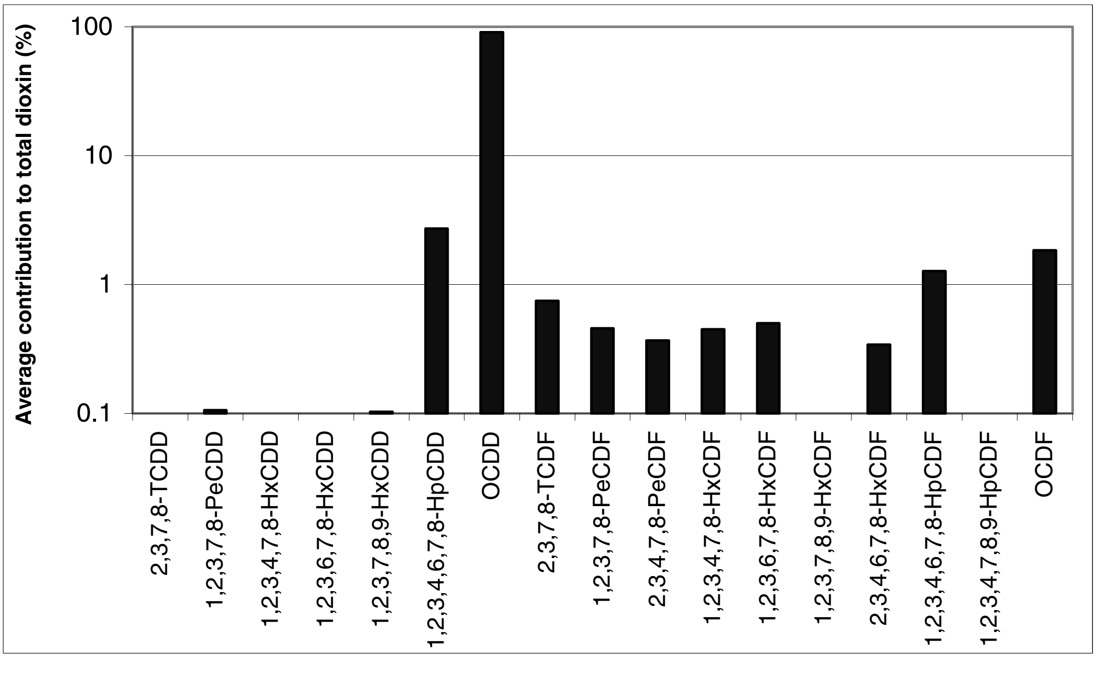


Figure 9: 2,3,7,8-congener profile for an air sample collected from the Sydney Harbour Tunnel, October 1994

Figure 10 presents the congener profile based on results from two overseas studies of motor vehicle emissions. In the first study, samples were collected in a tunnel in Norway in 1989 and represent motor vehicle exhaust (Oehme 1991). At the time of the measurements, unleaded petrol consisted of 25–30% of total petrol consumption. The second study was based on the emissions of one diesel vehicle and was collected under urban driving conditions (Ryan and Gullet 2000). The profiles are similar, especially for the octa dioxin and the hexa, hepta and octa furan groups.

When compared with the Sydney Harbour Tunnel sample a similar pattern emerges, although OCDD has a greater contribution in the Sydney sample.

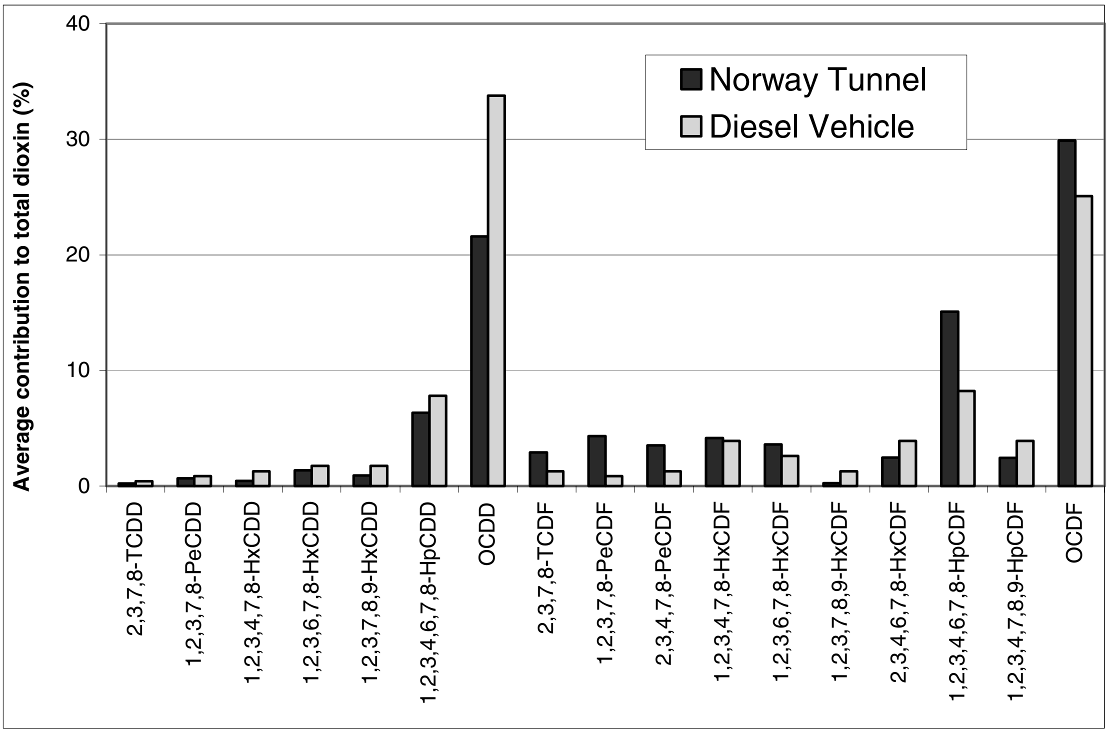


Figure 10: 2,3,7,8-congener profiles for overseas motor vehicle exhaust studies

4.4.2 Steel manufacturing

The largest integrated steelworks in the southern hemisphere (the BHP steelworks) are located in Port Kembla, approximately 3 km north-west of the Warrawong site, and there is a mini steel mill at Rooty Hill in western Sydney (approximately 15 km from the Westmead site). Congener profile data for these two facilities are presented in figures 11 and 12 respectively. The BHP Port Kembla profile was based on four samples collected in 1999 from the sinter plant stack (Egis 2000). The profile for the Sydney steel mill was based on three samples collected during 1999 from the baghouse stack (Sinclair Knight Merz 1999). The 17 congeners in both the Port Kembla and the Rooty Hill samples were found at levels above the limit of detection and therefore represent actual profiles.

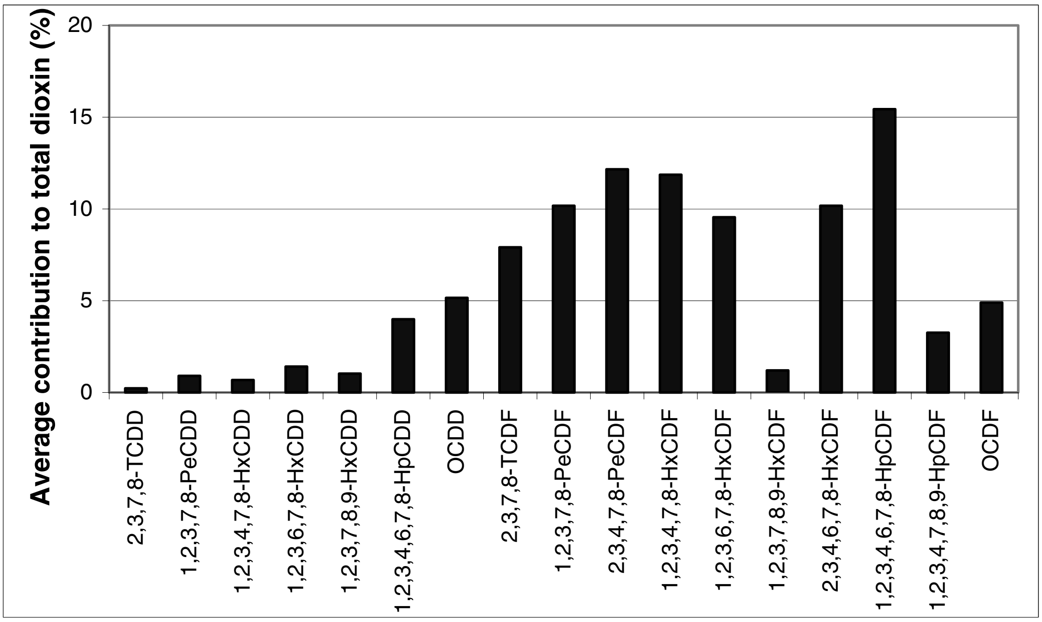


Figure 11:2,3,7,8-congener profile for BHP steelworks, Port Kembla sinter plant

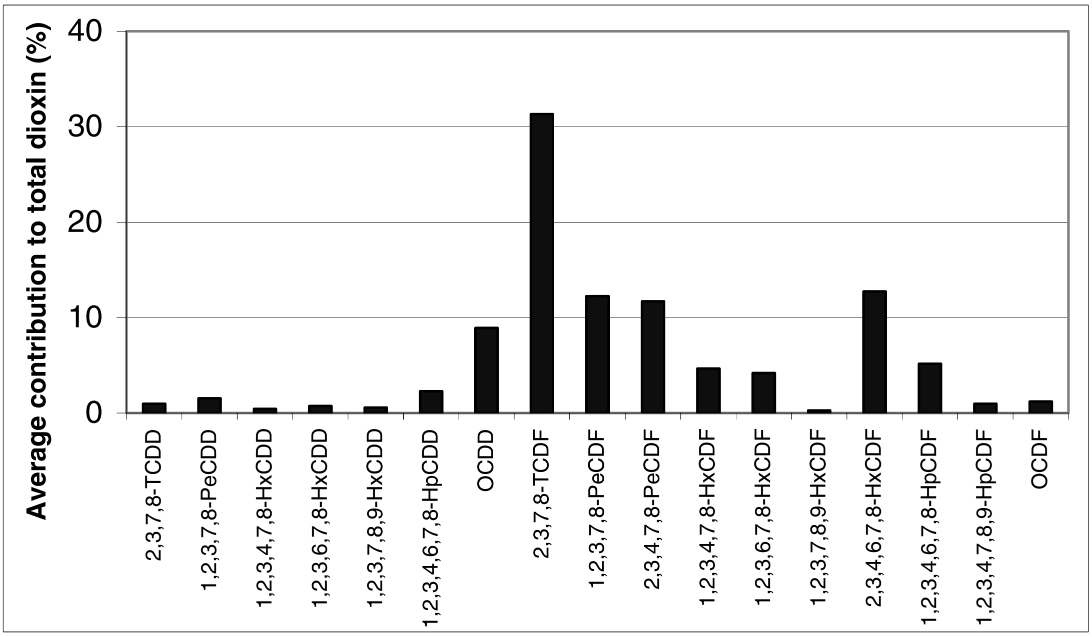


Figure 12: 2,3,7,8-congener profile for mini steel mill, Rooty Hill baghouse stack

Figures 11 and 12 indicate that dioxin congener profiles of steel making facilities are dominated by chlorinated furans. The chlorinated dioxins are almost entirely absent.

4.4.3 Congener profiles comparison

Figure 13 presents the congener profiles for total concentrations at Warrawong and Westmead separately (as opposed to Figure 3) for comparison with the source profiles. The congener profile for Siding Spring is less meaningful due to the high frequency of non-detects and has therefore been excluded.

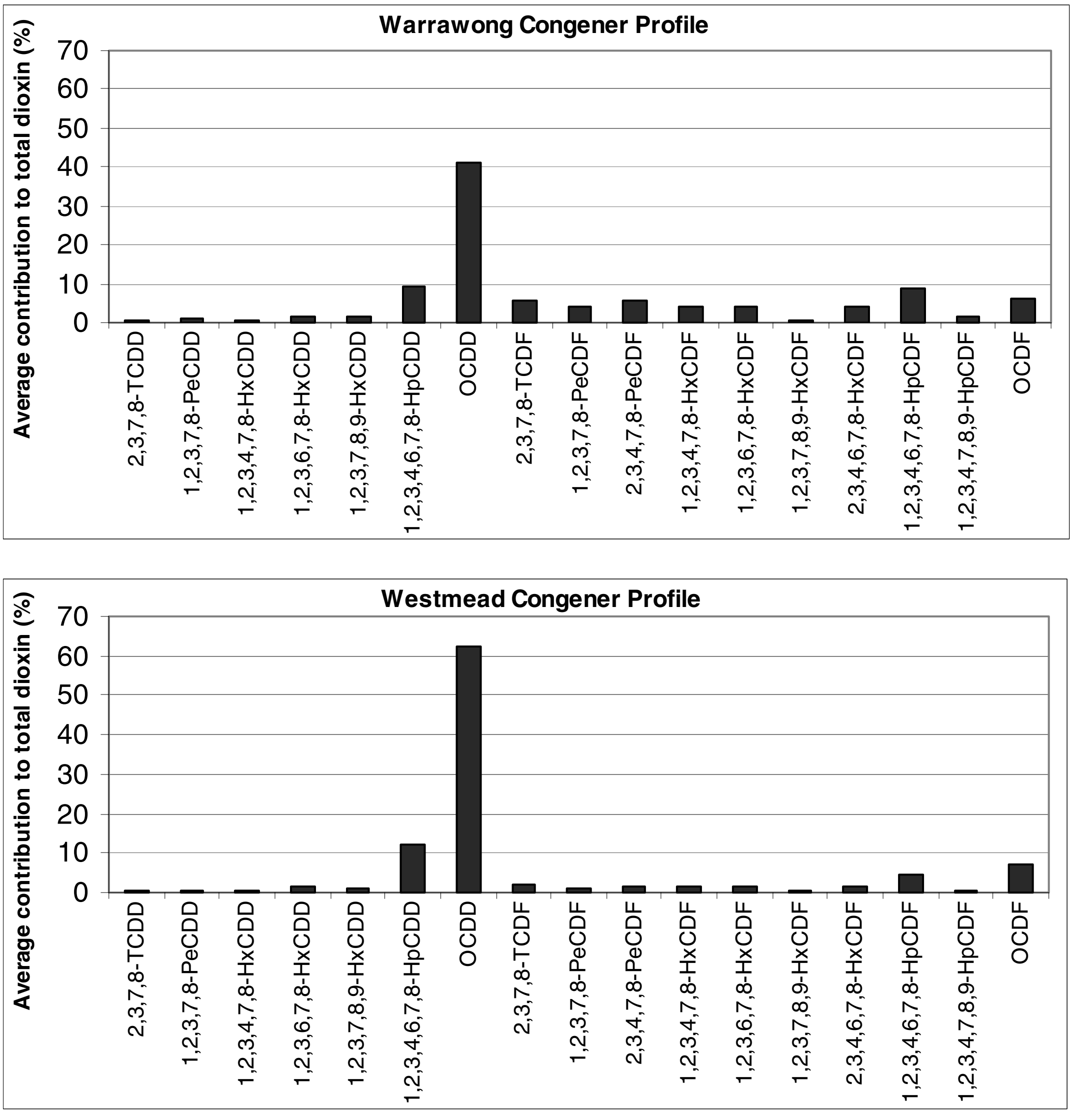


Figure 13: 2,3,7,8-congener profiles for Westmead and Warrawong

Siding Spring is in a relatively isolated part of NSW with minimal human activity close by. Since dioxins bound to particulate material can be transported long distances in the atmosphere, the extremely low levels of dioxins measured at Siding Spring would include contributions from a wide range of sources and would therefore be representative of a background level.

The congener profiles for Westmead and Warrawong suggest a contribution from a mix of sources. In comparison to available profiles, motor vehicles would appear to make a contribution at both Warrawong and Westmead. The profiles at both sites show a similar pattern to the profile for motor vehicles (see Figure 9) with the OCDD congener dominating the profiles. The profile for Warrawong would suggest that the steelworks nearby also make a contribution to the levels. The furan congener group at Warrawong shows a similar pattern to the profile for BHP (see Figure 11). This is also consistent with Figure 7, where PeCDF was influencing the toxic equivalents at Warrawong.

A recent study has also found that production of OCDD and HpCDD from pentachlorophenol in clouds and rain droplets is an important contributor to dioxin concentrations in air (Baker and Hites 2000). Pentachlorophenol is used in wood treatment and as a pesticide (CARB 1997). This may contribute to the dominance of OCDD at both sites.

5. Conclusion

A comparison between the three sampling sites of the dioxin results collected over 18 months indicates that, on a regional basis, the ambient dioxin levels are very low, and are in all cases a small fraction of contemporary overseas ambient standards for these substances. Comparison of dioxin results from this study with results obtained at comparable localities overseas also indicates that the ambient dioxin levels at these NSW locations are low.

The background levels measured at Siding Spring were among the lowest of any of the available results reviewed and were comparable with New Zealand and Connecticut, USA. European results of comparable locations were generally an order of magnitude higher.

The urban-industrial levels measured at Warrawong were lower than comparable results from all other jurisdictions, including New Zealand, Belgium, Germany, Spain and the Netherlands.

The urban levels measured at Westmead were comparable with those measured in the Netherlands, Sweden and New Zealand and were considerably lower than those in Japan (winter), UK (Belfast) and Poland (Cracow). The results obtained at Westmead were well below contemporary international goals.

Despite the proximity of the Port Kembla industrial complex, dioxin levels at Warrawong were lower than levels at Westmead. This may reflect the coastal location of Warrawong as well as the occurrence of meteorological conditions conducive to better dispersion during the measurement period (higher wind speeds occurred at Warrawong than Westmead). In addition, the Illawarra region has a smaller population and therefore potentially fewer diffuse dioxin sources.

A comprehensive source reconciliation analysis has not been conducted because a complete library of congener profiles for the full range of possible sources is not available. A profile for solid fuel heaters and bushfires are of importance for this work. Based on the congener profiles available, it appears that the low levels of dioxins are differently mixed for the urban and industrial sites, which may be indicative of different sources. The congener profiles for Westmead and Warrawong suggest a contribution from a mix of sources, including motor vehicles. The profile for Warrawong also indicates that the steelworks nearby contribute to the levels at this site. Other sources also likely to be contributing to dioxin levels at these sites include solid fuel heaters, other industrial and combustion processes and natural processes such as bushfires.

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Appendices

Appendix A—Sources of dioxins

Dioxins are released into the environment in a variety of ways and in varying quantities, depending on the source.

Dioxins have recently been found in clay deposits in the USA. No definitive experimental evidence has been brought forward to account for the presence of the dioxins from known anthropogenic sources or to explain the selective chemical synthesis of dioxins under the conditions inherent to the formation of clays some 40 million years ago (Ferrario 2000).

Studies of sediment deposits from freshwater lakes in the United States have generally shown CDD and CDF concentrations began to rise in the 1930s and 1940s, and then began to decline in some lakes in the 1960s and 1970s (Cleverly 1996).

Although these compounds are released from a variety of sources, the congener profiles of dioxins found in sediments have been linked to combustion sources (Hites 1991).

Dioxins have never been intentionally produced, other than on a laboratory-scale basis for use in chemical analyses. Rather, they are produced as the unintended by-products of some human activities (mostly processes involving combustion) or from some natural activities such as bushfires and volcanic activity. A recent study has also found that production of OCDD and HpCDD from pentachlorophenol in clouds and rain droplets is an important contributor to dioxin concentrations in air (Baker and Hites 2000).

A report by UNEP on dioxin and furan inventories categorised anthropogenic sources of dioxins and furans into nine major sectors (UNEP 1999):

- iron and steel—iron and steel plants including foundries, sinter and coke plants
- non-ferrous metals—primary and secondary plants for the generation of copper, aluminium, zinc and lead
- power plants—fuelled with coal, gas, crude oil and wood
- industrial combustion plants—industrial units fuelled with coal, gas, crude oil, sewage sludge and biomass for use on-site
- small combustion units—mostly domestic stoves and chimneys fired with coal, oil and gas
- waste incineration—includes incineration of municipal solid waste, hazardous waste, sewage sludge, hospital waste, waste wood and crematoria
- road transport—passenger cars, buses, trucks run on leaded petrol, unleaded petrol or diesel
- mineral products production—generation of cement, lime, glass and brick
- others—shredder plants, asphalt mixing, drying of green fodder, wood chips, chemical industry, accidental fires and prescribed burnings.

A study to investigate the sources of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions in Australia was conducted based on international inventory studies and the application of emission factors. For most sources the emission estimates were presented as a range and were indicative only as they were subject to considerable uncertainties. Based on the upper bound of each range, it was found that biomass combustion from prescribed burning and bushfires was potentially the most significant source of PCDD and PCDF in Australia, contributing approximately 75% to the total estimates. The next most significant sources in decreasing order were: cement production, residential wood combustion, coal combustion, sinter production, industrial wood combustion and lime production. These sources combined with prescribed burning and bushfires, accounted for approximately 95% of total emissions. Motor vehicles were estimated to contribute less than 1% of total emissions (Environment Australia 1998).

Appendix B—Toxic equivalents

In most environmental media, dioxins occur as complex mixtures of congeners. To enable the toxicity of a complex mixture to be expressed as a single number, the concept of toxic equivalents (TEQs) has been developed. Due to their structure these congeners cause health effects in organisms by way of an interaction with a receptor inside cells known as the Ah receptor. Different congeners interact with the receptor with different potencies and the concentration at which a particular congener will cause health effects is related to its ability to interact with this receptor. This common mechanism of action has enabled an approach to be developed to assess the possible health effects from exposure to mixtures of these congeners based on toxic equivalent factors (TEFs). Of the 210 possible congeners, only those with chlorine atoms in the 2, 3, 7 and 8 positions (i.e. 17 possible congeners in total) exhibit toxic effects through interaction with the Ah receptor.

The TEFs are based on assessments of the potency of each congener to interact with the Ah receptor relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic member of the group. The TEFs are essentially a set of weighting factors, each of which expresses the toxicity of a specific congener in terms of the mass of TCDD that would cause an equivalent toxic response. Multiplication of the concentration of the congener by its TEF yields the corresponding TEQ. The total toxicity of any mixture is then simply the sum of the individual congener TEQs.

The most widely adopted system of TEFs is that proposed by the North Atlantic Treaty Organisation/Committee on the Challenges of Modern Society (Kutz et al 1990) and known as the International Toxic Equivalents Factor (I-TEFs) scheme. This scheme has been expanded by the World Health Organisation (WHO) (Van den Berg et al 1998) to include factors for mammals (who are used as surrogates for humans), birds and fish. Table B1 lists the I-TEFs and WHO-TEFs for the 17 2,3,7,8-congeners. The most toxic congener—2,3,7,8-tetrachlorodibenzo-para-dioxin (2,3,7,8-TCDD)—is rated as 1. Other congeners are rated between 0 and 1, depending on their relative toxicity. The remaining 193 congeners have TEFs of zero.

Table 4: Toxic equivalent factors for dioxins

	-	**WHO-TEF (humans/mammals) (Van den Berg et al 1998)**
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0001

Notes

The name of each congener takes the form: [z,]-XxCDY
Where Xx can take the values T meaning tetra (i.e. 4)
Pe meaning penta (i.e. 5)
Hx meaning hexa (i.e. 6)
Hp meaning hepta (i.e. 7) or
O meaning octa (i.e. 8)
CD means chlorodibenzo
and Y can take the values D meaning dioxin; or
F meaning furan

Thus HpCDD means heptachlorodibenzodioxin
and PeCDF means pentachlorodibenzofuran

and further, the prefix digits (z) indicate the positions on the central molecule (dibenzo-p-dioxin or dibenzofuran—see Figure 1) to which the chlorine atoms are attached.

Appendix C—Air flow determination

C1. Introduction

Figure 14 overleaf indicates the nature of the sampling instrument. Apart from the sampling head, which holds the filter and absorbent canister, much of the detail of the instrument is associated with control and measurement of the air flow rate so total air flow volume through the canister/filter can be determined. The Magnehelic gauge indicates the pressure differential (in inches of water) across a venturi throat in the flow line. This reading relates to gas flow rate. To enable continuous reading of this pressure differential, a pressure transducer was fitted across the venturi throat in parallel with the Magnehelic gauge. The voltage from this transducer (0-1 VDC) was recorded on a data logger.

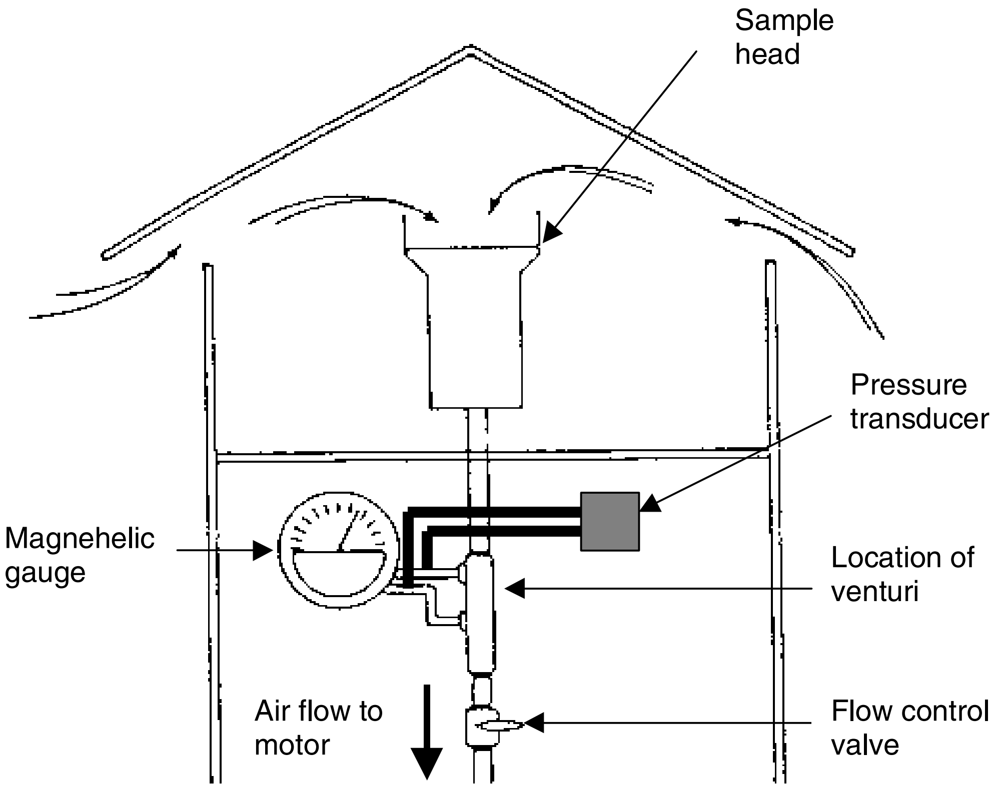

Figure 14: Diagram of PS-1 high volume air sampler

C2. Instrument calibration

C2.1 Calibration of air flow against Magnehelic gauge

The Magnehelic gauge gives a reading of the pressure differential which develops across the venturi as the air flows through the system. It was necessary to calibrate this for flow rates of between 100 and 200 litres/minute at approximately 27°C. Since the motor operates at a constant speed, the calibration needed to be carried out at the motor speed which was used in the field.

In the field, variation of air flow can occur due to three separate effects:

a) variations in the speed of the motor—such variations were expected to take the form of a slow drift as mechanical wear occurred
b) variations in air density due to normal fluctuations in atmospheric temperature and pressure
c) restrictions of the air flow due to the build up of particles on the sampling head filter paper.

To ensure that the motor speed remained effectively constant, a simple brass restrictor was made for each instrument. This restrictor could be fitted in the flow path in place of the sampling head. The restrictor had a constant bore and so served as a constant, if uncalibrated, flow controller. With the restrictor in place, the Magnehelic reading was set at 40 inches of water by adjusting the speed of the motor. This restrictor was left with each instrument and could be put in the flow path as needed to check that the flow was maintaining a constant value. Periodic checking indicated that the flow rate was quite stable and that motor wear was thus not an issue. Flow variations due to effects b) and c) above were allowed for by measurement of the air flow during the sampling period for each sample.

Calibration of the flow rate thus meant that the motor speed was carefully adjusted so the Magnehelic reading was 40 inches of water with the restrictor in place. This restrictor was then replaced by a standard orifice for which the pressure differential could be accurately and independently measured. This standard orifice also incorporated a flow control valve which could be used to alter the flow rate and thereby effectively mimic the effect of the build up of particles on the sampling head filter paper. Calibration consisted of taking a paired series of Magnehelic readings and standard orifice pressure differential readings over the range of air flows anticipated. The standard orifice pressure differential readings were immediately convertible to an air flow and thus a paired series of air flow and Magnehelic readings was obtained.

The flow rate through the venturi was given by the equation:

$$\text{Flow rate} = \text{Constant} * \sqrt{(\text{Magnehelic reading})}$$

The air flow and Magnehelic readings were graphed and the value of the constant obtained.

This was repeated for each instrument. The values of these constants were entered into the database.

C2.2 Calibration of the Magnehelic readings and the pressure transducer/ data logger combinations

The Magnehelic gauge can only be read when there is a human operator present. Since extended unattended operation was to occur, it was necessary to have regular values of these gauge readings so that air flow variations could be accommodated within air volume determinations. To achieve this, a pressure transducer was connected across the pressure tubes which connected the Magnehelic gauge to the instrument. A voltage, proportional to the Magnehelic reading, was thus produced.

A Hydromace TRS data logger was chosen to record these voltages. Signal output from the pressure transducer was connected to a head amplifier which converted the signal (0 to 1 V DC) into a frequency count between 0 and 4096. The data logger recorded this frequency count. Calibration could thus consist of 2 steps:

- calibration of the Magnehelic reading against pressure transducer voltage
- calibration of input voltage against frequency count for the head amplifier.

Since previous experience had shown these data loggers to be quite reliable, it was not anticipated that there would need to be any change of data logger or head amplifier for the entire sampling period and thus it was decided to calibrate each setup as a single unit—i.e. Magnehelic reading against frequency count.

To calibrate the instruments in this mode, the brass restrictor (see C2.1 above) was placed in the instrument. The motor speed was varied so that a series of Magnehelic readings and frequency counts, read from the LCD screen of the data logger, was obtained. The Magnehelic readings varied over the range from approximately 70 to 5 inches of water. Graphing of this data indicated that there was a slight curvature in the plot, especially at low values of the Magnehelic readings, so a cubic equation was fitted in each case. The values of the equation coefficients were entered into the database.

C3. Field air flow measurement and data handling

The Hydromace TRS data logger has its own internal registers which keep track of the month, day of the month and time (to the nearest minute). When it records a value it also records the time of day of that reading. At midnight, it also records the new day and month number. It requires that the operator keep an external record of the year.

In the field, the data logger was programmed to record the pressure transducer voltage (as a count) every hour. A data logger record for one day thus consisted of a midnight (day and month) mark followed by 24 time and voltage count pairs.

Each time a new sample canister and filter paper was put into a sampler, the memory pack of the data logger was exchanged also. Each memory pack was individually numbered. A manual record of the site and the start and finish dates and times for each memory pack was kept. These details were manually entered into the database.

When exchanging canisters, filter papers and data logger memory packs, the air flow was stopped by turning off the motor. A manual record of the Magnehelic gauge readings immediately prior to motor turn off and immediately after motor turn on was also taken.

Each high volume air sampler incorporated a motor run-time meter. The meter reading was recorded whenever the motor was turned off (generally when canisters etc were being exchanged). This served as a check on the operation time of the instrument as calculated from start and finish dates and times and thus also served as an internal check on the accuracy of data entry to the database.

At the office, the contents of the data logger memory pack were downloaded into a computer. Spreadsheet software was used to calculate time and date of each voltage count record, along with the memory pack ID number. These records were also stored in the database.

Appendix D—Sample handling

Since the anticipated concentrations of dioxins were so low, particular precautions had to be taken during sample handling to prevent contamination and to otherwise ensure sample integrity.

Sampling canisters consisted of a glass cylinder, 130 mm long x 57 mm wide, which was open at both ends and which had a stainless steel wire mesh perpendicular to the axis and about 10 mm from one end. This mesh provided a support for the polyurethane foam and XAD resin which served as the absorbent material for the dioxins. These canisters were impregnated with ^{13}C labelled dioxin congeners which were internal standards for the GC/MS analysis (see Appendix E for details). The canisters were supplied in bulk lots of 20 to 50 canisters. Canisters were individually sealed with laboratory sealing film and individually wrapped in bubble wrap plastic to prevent breakage. The bubble wrap and sealing film were only removed immediately before the canister was put into the sampling head (see Figure 15 on page 36). Exposed canisters had fresh sealing film applied and were bubble wrapped immediately after being removed from the sampling head. The sealing film helped prevent loss of standards and collected dioxins as well as preventing contamination from other volatile organic compounds.

With three sampling sites and 24- or 12-day sampling durations, approximately eight canisters were used, on average, per month. The batches of canisters as supplied thus lasted for two to six months. To prevent loss of internal standards prior to use and loss of absorbed dioxins after collection, both unused and exposed canisters (still film sealed and wrapped) were stored in a freezer. Canisters were transported to and from the field in polystyrene containers in the presence of ‘freezer bricks’, again to minimise losses of dioxins and standards by volatilisation. Exposed canisters were retained in the freezer until air freighted to the New Zealand laboratory in batches of about 8–12 canisters, i.e. about 4–6 weeks sampling effort. It was not possible to keep canisters under cooled conditions during transport to the laboratory. Delivery times to the laboratory were generally 24 to 36 hours. Advice from the laboratory was that such a period without cooling would have no effect on the results. Indeed, this advice was that much longer periods without cooling were permissible, however, samples were kept cool or frozen wherever possible since such freezing or cooling was relatively easy to arrange and it was felt to be a wise precaution.

The polyurethane foam and XAD resin used in the sampling canisters are extremely efficient at absorbing a wide range of volatile organic compounds and so exposure of the canisters to such compounds was kept to a minimum. As mentioned above, laboratory sealing film was used at all times to prevent vapours coming into contact with the absorbent materials when the canister was not actually in the sampler. Since humans can be a significant source of such volatile compounds (natural body oils, perfumes from deodorants, some soaps, shampoos, etc) field staff were instructed to avoid use of these materials when servicing samplers. In addition, when handling the sampling heads, silicone rubber gloves were always worn.

Figure 15 on page 36 shows an exploded view of the sampling head. When handling this head in the field, it was necessary to disassemble the head as indicated in Figure 15. The disassembled pieces were placed on a 50 cm square sheet of stainless steel which had been rinsed in nanograde acetone followed by nanograde hexane immediately prior to use. This rinsing removed any traces of organic matter which might have been adhering to the sheet and which could have contaminated the sampling head. The exposed filter paper was removed using forceps which had also been rinsed in the above solvents. This paper was replaced in the aluminium foil wrap it had been supplied in by the laboratory and which had been retained since that filter paper had been installed on the previous visit. When the exposed canister was removed from the sampling head, it was immediately sealed at both ends with laboratory sealing film. Prior to installing the new canister, all parts of the sampling head were rinsed in the above solvents. The sealing film was removed from the new canister which was then rapidly installed in the sampling head which in turn was rapidly re-assembled. The new filter paper was taken from its supplied foil wrap and using only washed forceps, was placed into position on the supporting mesh. The filter holding ring was then locked in position. The aluminium foil wrap was carefully re-folded and put aside ready to receive the filter once it had been used.

Both the canisters and the filter papers had unique identifying numbers allocated to them. When exchanging canisters and filters in the field, careful note of identifying numbers and times and dates of installation/removal were made for later entry in the database (see Appendix F). The identifying number on the canister was written on a label affixed to it, whereas for the filter, the identifying number was written on the foil wrap. It was thus crucial that the foil wrap be retained to re-wrap the exposed filter in each case.

A spare sampling head was available which permitted an assessment of the effectiveness of these handling procedures. Over the first few months of the overall sampling program, the spare head, with a new canister and filter in each case, was left in the sampler housing next to the operational head. This was retrieved when the site was next visited to exchange canisters and filters. This ‘handling blank’ was handled and analysed identically to exposed filters except that it was not exposed to the pumped air flow. In all, six ‘handling blanks’ were prepared, two at each of the sites. In five of the six ‘handling blanks’, all dioxin congeners or congener groups were reported to be below the laboratory detection limit. The use of ‘handling blanks’ was discontinued once it became apparent that contamination was not occurring.

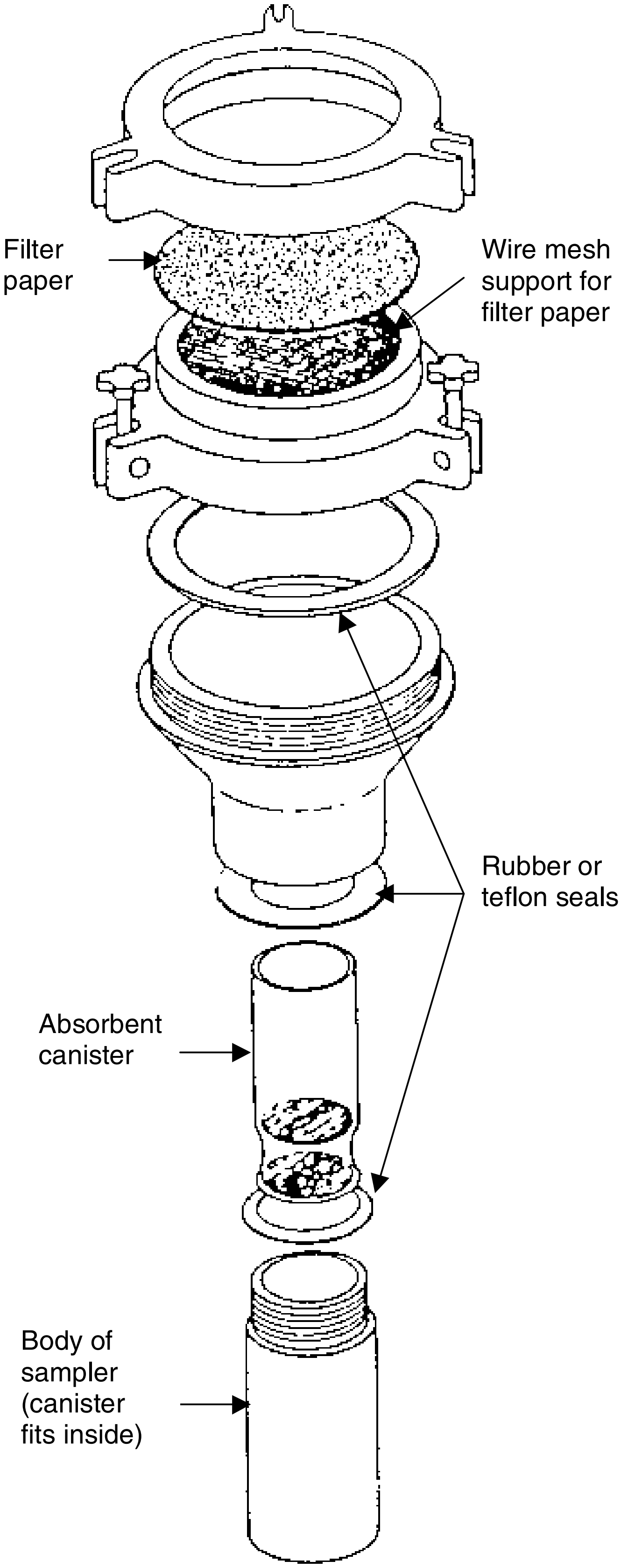

Figure 15: Exploded view of the high volume air sampler head

Appendix E—Analytical methods

E1. Collection media preparation

All absorbent cartridges and filters were prepared by the laboratory which conducted the analyses viz ESR/AgriQuality, of Wellington New Zealand.

PUF, XAD-2 resin and GF/C filters were precleaned prior to use. PUF discs as supplied (General Metal Works) were subjected to Soxhlet extraction for 20 hours with toluene (twice) then dried under vacuum. Resin (Supelco) was washed on a glass sinter funnel (16–20 times) with hot distilled water, then subjected to Soxhlet extraction for 20 hours with methanol, 20 hours with dichloromethane (DCM) and a further 20 hours with fresh DCM. The resin was dried in a fluid bed apparatus using oxygen-free nitrogen, passed first through a bed of activated charcoal.

The PUF and XAD-2 resin were packed into a cleaned glass sample cartridge as: bottom PUF, layer of XAD-2 resin, top PUF. The packed cartridge was spiked with a range of isotopically labelled PCDD, PCDF standards, (Wellington Laboratories-Ontario, Canada) prior to the collection of the sample. The nominal amounts of each surrogate standard added are given in Table 5. The sample cartridge was labelled with a unique identification number. The cartridge was sealed at each end with laboratory sealing film and then wrapped in bubble-wrap plastic for transportation to the NSW EPA. Upon receipt by the EPA, canisters were stored, as packed, in a freezer until required in the field.

GF/C filters (1.2 µm mesh) were precleaned by Soxhlet extraction with toluene for 20 hours and dried. Each filter was weighed, wrapped in hexane-rinsed aluminium foil and given a unique identification number prior to shipment to the NSW EPA.

Table 5: Nominal amounts of isotopically labelled surrogate standards added to each PUF/XAD-2 cartridge pre-sampling

			ng added
2,3,7,8-TCDD	0.5	2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDD	0.5	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.5	1,2,3,4,7,8-HxCDF	0.5
1,2,3,4,6,7,8-HpCDD	0.5	1,2,3,6,7,8-HxCDF	0.5
OCDD	1	2,3,4,6,7,8-HxCDF	0.5
		1,2,3,7,8,9-HxCDF	0.5
		1,2,3,4,6,7,8-HpCDF	0.5
		1,2,3,4,7,8,9-HpCDF	0.5

E2. Sample preparation

Following sample collection and receipt at the laboratory, samples were stored at 4 °C pending analysis. Each ambient air sample consisted of a single sample cartridge holding the PUF/XAD-2 adsorbent and a single filter. Each filter was dried to constant weight in a desiccator, weighed and the particulate content determined gravimetrically (see Figure 16 on page 38).

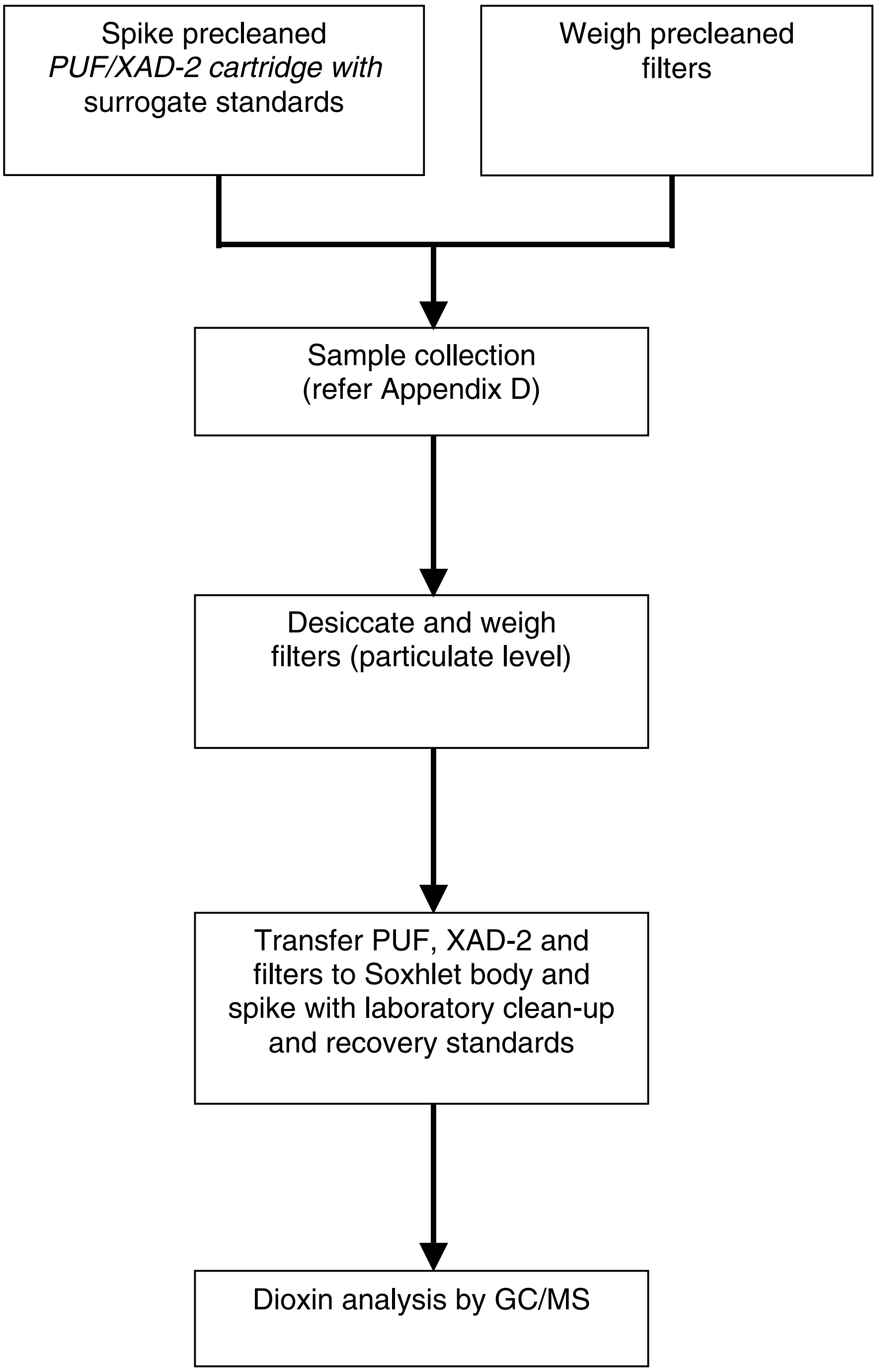

Figure 16: Sample collection and analysis scheme

E3. Sample extraction

PUF is an extremely efficient absorbent for a broad range of chlorinated organic compounds including chlorinated pesticides, chlorophenols, polychlorinated biphenyls and dioxins. The sample extraction and purification steps were only conducted for dioxins.

The PUF and XAD-2 adsorbents were removed from the glass cartridge and, along with the filters, were loaded into a Soxhlet body and spiked with an isotopically labelled extraction and clean-up recovery standard. The extraction and clean-up recovery standard added was 0.4 ng of $^{37}Cl_4$ 2,3,7,8-TCDD. The sample was Soxhlet extracted for 16 hours with ethanol/toluene (68:32).

The ethanol/toluene extracts were reduced using rotary evaporation. The ethanol/toluene extract was solvent-exchanged to hexane dried (anhydrous Na_2SO_4), and made up to volume with hexane.

The extract was then partitioned with concentrated sulphuric acid, washed with water, dried (anhydrous Na_2SO_4) and reduced by rotary evaporation. The extract was further purified by column chromatography as follows:

- acid and base modified silica gel (eluent: hexane)
- alumina (neutral) (eluent: hexane, 1:20 diethyl ether/hexane, diethyl ether)
- Carbopack C (18% dispersed on Celite 545) (eluent: hexane, 1:1 DCM/cyclohexane, 15:4:1 DCM/methanol/toluene, toluene)

Following purification, a volume of $^{13}C_{12}$ labelled laboratory recovery spike (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD) in tetradecane was added and the extract was reduced by rotary evaporation, blown down gently under a stream of nitrogen, and transferred to a vial for PCDD and PCDF analysis using capillary gas chromatography-high resolution mass spectrometry (GC/MS).

Extracts were analysed by GC/MS on an HP5890 Series II Plus GC interfaced to a Micromass Autospec Ultima high resolution mass spectrometer. All extracts were run on an Ultra2 or ZB-5 capillary column. If a peak was detected at the correct retention times for 2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF or 1,2,3,7,8,9-HxCDD, the extract was re-analysed on a SP2331 capillary column for full congener-specific quantification. Chromatographic conditions are given below (in Table 6), and the mass spectral ions monitored are detailed in Table 7.

Table 6: Chromatographic conditions

Column	25 m Ultra2 or ZB-5	60 m SP2331
Carrier gas head pressure	150 kPa	200 kPa
Injector temperature	260 ^{0}C	270 ^{0}C
Injection	2 µl splitless	2 µl splitless
Temperature program	Initial temp 210 ^{0}C (hold 4 min), 3 ^{0}C min -1 to 275 ^{0}C (11 min).	Initial temp 210 ^{0}C (hold 3.3 min), 3 ^{0}C min -1 to 255 ^{0}C (40 min).

Table 7: Ions monitored for dioxins

				^{13}C Confirmation ion (m/z)
TCDF	305.8987	303.9016	317.9389	315.9419
TCDD	321.8936	319.8965	333.9339	331.9368
PeCDF	339.8597	337.8626	351.9000	349.9029
PeCDD	355.8546	353.8575	367.8949	365.8978
HxCDF	373.8207	375.8178	385.8610	387.8580
HxCDD	389.8156	391.8127	401.8559	403.8530
HpCDF	407.7818	409.7788	419.8220	421.8191
HpCDD	423.7767	425.7737	435.8169	437.8140
OCDF	443.7398	441.7428		
OCDD	459.7347	457.7377	471.7750	469.7780

E4. Analyte identification and quantification criteria

For positive identification and quantification the following criteria must be met:

- the retention time of the analyte must be within one second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard
- the ion ratio obtained for the analyte must be ±10% of the theoretical ion ratio
- the signal to noise ratio must be greater than 3:1
- levels of dioxin congeners in a sample must be 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 must be in the range 25–150%.

E5. Quantification

Quantification was by the isotope dilution technique using the surrogate standards listed in Table 5. Relative response factors (RRFs) were calculated for each targeted analyte from a series of calibration standards analysed under the same conditions as the samples. Non 2,3,7,8-substituted dioxin congeners were quantified using the RRF of the first eluting surrogate standard in each mass spectral group. Targeting of all analytes was performed by the MS software (OPUS). Text files created by OPUS were electronically transferred to a customised spreadsheet for further data reduction and preparation of the final analytical report.

E6. Limits of detection

If no peak was distinguishable above the background noise at the retention time for a targeted analyte, the area was recorded as being less than the limit of detection. The limit of detection was calculated by multiplying by three the area of the section of baseline noise at the retention time of the analyte. If a peak was present at the correct retention time for the targeted analyte but failed to meet all analyte identification and quantification criteria, the area of that analyte was recorded and the calculated concentration was reported as a limit of detection.

E7. Surrogate standard recoveries

The recovery of each isotopically labelled surrogate standard (Table 5) and extraction and clean-up recovery standard, was calculated from the ratio of the area of the surrogate standard in the sample (normalised to its laboratory recovery spike) to the area of the surrogate standard in the calibration standards (normalised to its laboratory recovery spike).

E8. Quality control

- The batch size was typically 8–10 samples.
- A laboratory blank was analysed with each batch of samples.
- The GC/MS resolution, performance and sensitivity were established for each MS run.
- The recoveries of all isotopically labelled surrogate standards were calculated and reported.

Confidence levels for each congener are presented in Table 8.

Table 8: Confidence levels

Congener	Precision ± 2SD	Congener	Precision ± 2SD
2,3,7,8-TCDD	14%	2,3,7,8-TCDF	14%
1,2,3,7,8-PeCDD	5%	1,2,3,7,8-PeCDF	25%
1,2,3,4,7,8-HxCDD	27%	2,3,4,7,8-PeCDF	20%
1,2,3,6,7,8-HxCDD	12%	1,2,3,4,7,8-HxCDF	9%
1,2,3,7,8,9-HxCDD	12%	1,2,3,6,7,8-HxCDF	14%
1,2,3,4,6,7,8-HpCDD	10%	1,2,3,7,8,9-HxCDF	14%
OCDD	11%	2,3,4,6,7,8-HxCDF	10%
		1,2,3,4,6,7,8-HpCDF	6%
		1,2,3,4,7,8,9-HpCDF	10%
		OCDF	24%

E9. Data reporting

The data for each air sample is for the total sample (i.e. combined gaseous plus particulate phases). Data are corrected for recovery of $^{13}C_{12}$ surrogate standards. Laboratory data for detected analytes are reported to two or three significant figures and non-detected analytes are reported to one significant figure. Concentrations presented in this report are rounded to two significant figures.

Appendix F—Database design and operation

F1. Input data sources and forms

Data for entering into the database came from four separate sources:

a) manual records—these include all details relating to samples, data logger memory pack usage and visual observations of Magnehelic gauge readings

b) spreadsheet records of sample chemical analyses as provided by the laboratory (ESR, Wellington, New Zealand)
c) data logger records of digital counts relating to high volume air sampler pressure transducer voltages (see Appendix C).
d) calibration data—these include the calibration data for air flow and data logger/pressure transducer response (see Appendix C); these data also include basic information which should only need to be entered very infrequently such as instrument locations and data logger locations.

F2. Manual records

Manual records consisted of:

- samples (date and time of deployment and retrieval, site ID, canister and filter paper ID, motor run-time meter readings)
- data logger memory pack usage (site ID, dates and times of deployment and retrieval, memory pack ID number)
- visual observations of Magnehelic gauge readings.

Each of these types of records has its own table in the database. Data were entered into these tables on each occasion when a field visit was completed.

F3. Chemical analysis records

Results of chemical analyses were provided by ESR in the form of Excel spreadsheets. After some minor re-arrangement, the results could be directly imported into the relevant database table using a simple database query.

F4. Data logger records

As indicated in Appendix C, the data logger records consisted of a sequence of 24 pairs of time and count readings with each group of 24 readings headed by a new date reading. The time and date values were in an internal data logger format which required some pre-processing before they could be stored in the database. This pre-processing was accomplished in a spreadsheet template from which the data could be directly introduced into the relevant database table using a simple database query.

F5. Calibration data

These data were manually entered into the database tables. The nature of these data was that they were expected not to alter frequently, if at all, during the conduct of the sample collection and thus data entry was only expected to occur a few times over that period. Data in this category included details of instrument locations, installation and retrieval information regarding data loggers, instrument air flow calibration data and data logger/pressure transducer calibration data.

F6. Overall database operation

The overall database structure showing individual tables, the data stored within those tables and the relationships between the tables is shown in Figure 17.

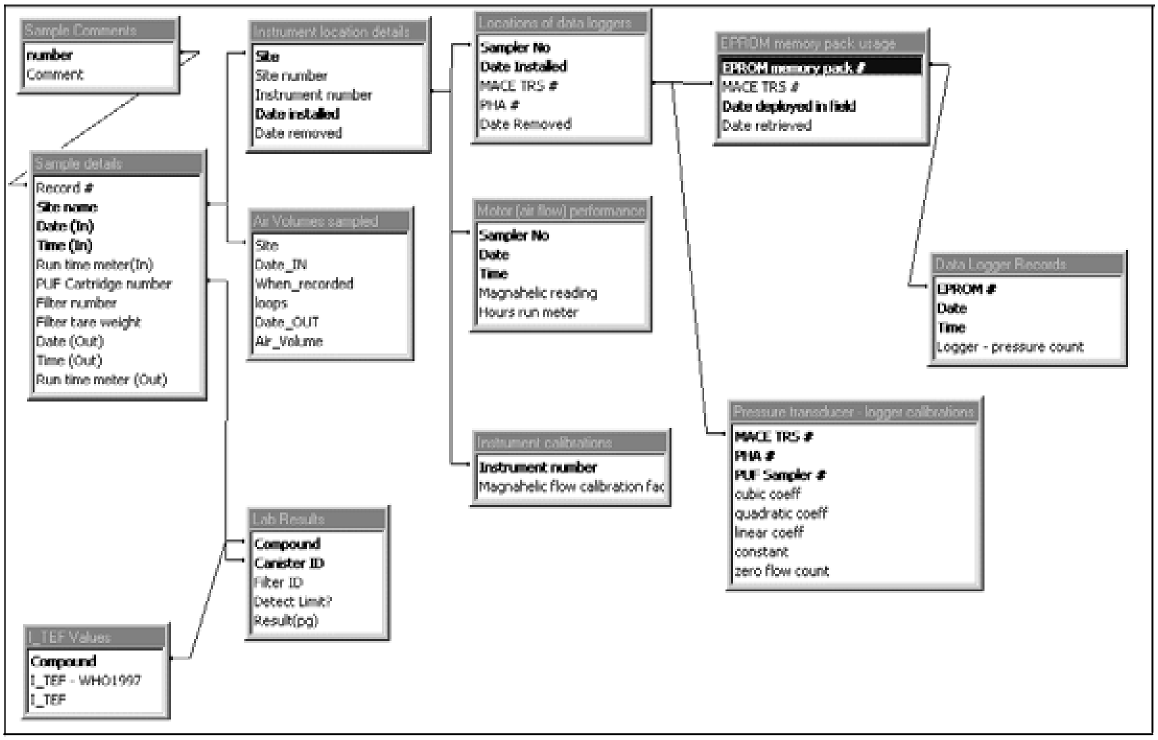

Figure 17: Database structure

Figure 18 outlines the logic flow in the calculation of the air concentrations. The text boxes at the top of the page, each with a bold text heading, represent different data input streams as outlined in sections F1 to F5 above. The text in italics in these boxes indicates the relevant data content in each stream. The flow of the arrows and lines indicates the way in which these individual data streams are joined and the nature of the intermediate data which are created. The calculation starts at the top right hand corner and works down. The process is as follows:

- the data logger count is converted to a Magnehelic gauge reading by the application of the data logger/pressure transducer calibration equation
- these calculated data are combined with the manual Magnehelic gauge readings to produce an intermediate file of date, time and gauge readings
- the instrument flow calibration factor is then used to convert these gauge readings to air flow rates, with their corresponding dates and times
- for each sample, these date, time and air flow readings are integrated to produce the total air volume which was sampled
- the chemical analysis data consist of the mass of each congener contained within the sample canister and its associated filter paper. These masses are converted to concentrations by dividing by the total sampled air volume
- the toxic equivalents were derived by multiplying the congener concentrations by their appropriate I-TEF
- the details relating to the individual samples are then used to ensure that the final reported air concentrations relate to a sample from a specific site and for a specific sampling period.

All these calculations were carried out in the database and each process was checked manually on a small data subset using spreadsheets.

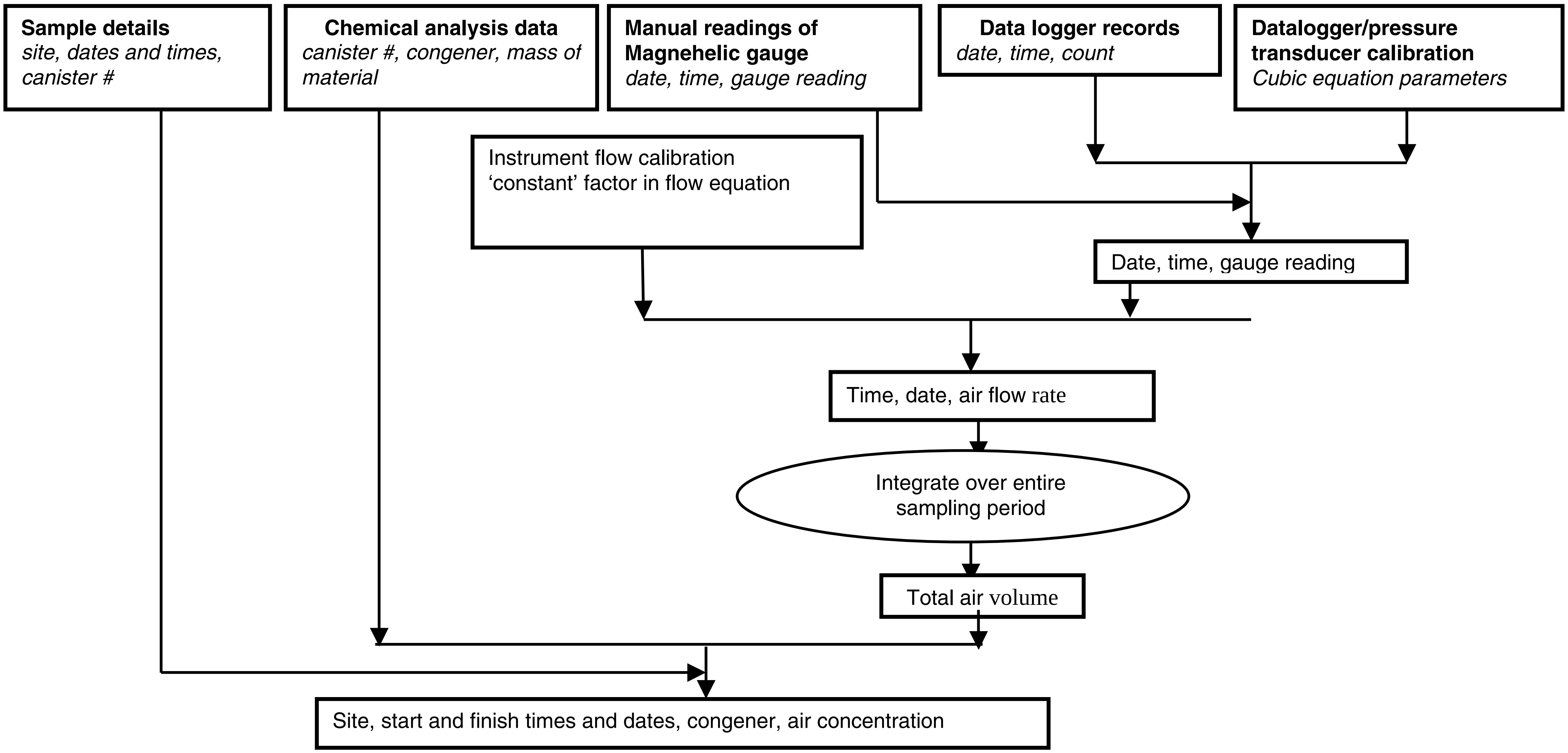

Figure 18: Database calculation logic flow

Appendix G—Number and percentage of samples below the detection limit

Congener	Siding Spring	Warrawong	Westmead
			n=34
2,3,7,8-TCDD	14 (93%)	17 (52%)	19 (56%)
1,2,3,7,8-PeCDD	14 (93%)	16 (48%)	13 (38%)
1,2,3,4,7,8-HxCDD	14 (93%)	20 (61%)	14 (41%)
1,2,3,6,7,8-HxCDD	13 (87%)	16 (48%)	12 (35%)
1,2,3,7,8,9-HxCDD	13 (87%)	16 (48%)	13 (38%)
1,2,3,4,6,7,8-HpCDD	11 (73%)	6 (18%)	3 (9%)
OCDD	11 (73%)	9 (27%)	3 (9%)
2,3,7,8-TCDF	7 (47%)	0 (0%)	2 (6%)
1,2,3,7,8-PeCDF	14 (93%)	0 (0%)	4 (12%)
2,3,4,7,8-PeCDF	14 (93%)	0 (0%)	3 (9%)
1,2,3,4,7,8-HxCDF	13 (87%)	0 (0%)	3 (9%)
1,2,3,6,7,8-HxCDF	13 (87%)	0 (0%)	3 (9%)
1,2,3,7,8,9-HxCDF	14 (93%)	25 (76%)	24 (71%)
2,3,4,6,7,8-HxCDF	13 (87%)	0 (0%)	3 (9%)
1,2,3,4,6,7,8-HpCDF	12 (80%)	2 (6%)	3 (9%)
1,2,3,4,7,8,9-HpCDF	14 (93%)	11 (33%)	13 (38%)
OCDF	12 (80%)	5 (15%)	3 (9%)
Total 2,3,7,8-congeners (17)	216 of 255 (85%)	143 of 561 (25%)	138 of 578 (24%)

Notes: if equal to 0 then the congener was detected in every sample at that site
n = number of samples.

Appendix H—2,3,7,8-congener concentrations and I-TEQS

						Westmead		
Middle sample date	Total 2,3,7,8-congener concentration fg m^{-3}	TEQ fg m^{-3}	Middle sample date	Total 2,3,7,8-congener concentration fg m^{-3}	TEQ fg m^{-3}	Middle sample date	Total 2,3,7,8-congener concentration fg m^{-3}	TEQ fg m^{-3}
9 Dec 98	28	0.6	2 Dec 98	200	16	2 Dec 98	290	7.7
			24 Dec 98	73	6.0	14 Dec 98	570	18
30 Dec 98	28	1.1	5 Jan 99	170	7.6	24 Dec 98	150	3.3
			18 Jan 99	120	7.6	5 Jan 99	160	2.7
28 Apr 99	12	0.7	27 Apr 99	130	8.4	22 Apr 99	380	7.9
			10 May 99	250	13	4 May 99	780	20
22 May 99	12	0.3	24 May 99	260	15	17 May 99	1100	31
			8 Jun 99	170	13	29 May 99	1100	39
16 Jun 99	6.0	0.4	22 Jun 99	170	13	10 Jun 99	890	32
			3 Jul 99	320	20	22 Jun 99	860	35
11 Jul 99	3.1	0.2	13 Jul 99	190	15	3 Jul 99	1500	53
			25 Jul 99	320	16	15 Jul 99	700	23
5 Aug 99	13	0.5	5 Aug 99	55	7.6	28 Jul 99	830	32
			17 Aug 99	260	13	9 Aug 99	850	24
29 Aug 99	43	0.4	28 Aug 99	250	11	20 Aug 99	680	23
			10 Sep 99	190	17	31 Aug 99	290	8.1
21 Sep 99	33	0.7	22 Sep 99	150	11	11 Sep 99	450	17
			2 Oct 99	99	5.0	23 Sep 99	410	13
17 Oct 99	9	0.4	14 Oct 99	130	8.8	5 Oct 99	430	12
			27 Oct 99	140	5.8	16 Oct 99	230	5.5
			7 Nov 99	81	4.1	28 Oct 99	260	4.7
11 Nov 99	26	2.4	18 Nov 99	110	6.8	9 Nov 99	320	6.9
			1 Dec 99	72	5.3	21 Nov 99	180	4.4
			14 Dec 99	120	10	2 Dec 99	230	2.7
21 Dec 99	9.7	0.3	28 Dec 99	57	3.8	16 Dec 99	150	2.3
			10 Jan 00	130	7.9	31 Dec 99	83	3.7
17 Jan 00	10	0.4	23 Jan 00	71	4.1	13 Jan 00	110	2.3
			3 Feb 00	300	14	25 Jan 00	120	2.3
10 Feb 00	11	0.5	16 Feb 00	40	3.0	7 Feb 00	290	4.0
			27 Feb 00	230	16	18 Feb 00	110	3.8
7 Mar 00	14	0.4	9 Mar 00	120	3.7	29 Feb 00	240	3.1
			21 Mar 00	110	4.9	12 Mar 00	820	7.5
			2 Apr 00	230	17	23 Mar 00	170	4.8
						4 Apr 00	500	15