3. Dioxin concentrations in Australian soils

3.1 Concentration of dioxin-like chemicals in Australia.

This section provides an analysis of the concentrations of dioxin-like chemicals in Australia across the 86 specific locations from which samples were collected for this study, as well as the 10 historic samples. Dioxin-like chemicals were detected in most of the 116 soil samples analysed (Table 3.1). Concentrations of PCDD/PCDF and dioxin-like PCB expressed as middle bound toxic equivalents ranged over several orders of magnitude from less than the limit of detection (about 0.05 pg g^{-1} depending on the specific sample) to 43 pg g^{-1} dm. It should be noted that the latter value is from the analysis of the original sample from the Hobart urban location. This concentration was regarded as anomalous not only because it was very much greater than those from any other study location, but also because the concentration in the sample from the Hobart industrial location was among the lowest of those from industrial locations. Analysis results from resampling both Hobart locations, taking soil from the same sites as used for the original sampling, indicated that the concentration for the Hobart urban location was within the range for urban sites at other study locations and confirmed the previous result in respect of the Hobart industrial location. Setting aside the concentration of dioxin-like chemicals at the Hobart urban location, the range of concentrations found in this study ranged from less than the limit of detection to a maximum of 23 pg TEQ g^{-1} dm (urban location at Wollongong, New South Wales)(Table D2).

3.1.1 Concentration of dioxin-like chemicals in different regions

The sampling locations covered three different regions in Australia, namely North, South-east and South-west with samples being collected in all three sampling regions covering all land-use types. The median concentration of dioxin-like chemicals expressed as TEQ_{DF+PCB} were 0.98, 0.74 and 0.21 pg g^{-1} dm in the North, South-east and South-west regions respectively, indicating that concentrations in soils of North and South-East regions were similar, whereas the concentration in the soils from the south-west region was less than both north and south-east concentrations (see Figure 3.1). Note that the Additional Remote locations are not included in this figure.

Table 3.1 Summary of the PCDD/PCDF and PCB concentrations.

This table includes the sum and the respective WHO_{98}-TEQs (pg g^{-1}, dm) in both lower bound (excl. LOD) and middle bound (incl. ½ LOD), for all samples combined, for the different land-use types and for the different regions.

		All samples	Land-use				Region		
			Indust.	Urban	Agricult.	Remote	N	SE	SW
∑PCDD/-F (Exc. LOD)	Min.	ND	21	3.4	ND	0.31	0.31	ND	2.1
	Max.	68000	50000	68000	8600	15000	68000	68000	5600
	Median	530	940	7000	130	56	1100	560	41
	Mean	6300	3300	13000	930	890	6700	7200	740
WHO_{98}-TEQ_{DF} (Exc. LOD)	Min.	ND	0.063	0.023	ND	0.00056	0.00056	ND	0.023
	Max.	42	11	42	4.0	5.0	10	42	1.4
	Median	0.47	1.3	3.2	0.097	0.046	0.86	0.61	0.13
	Mean	2.6	2.6	5.9	0.40	0.38	2.0	3.2	0.33
WHO_{98}-TEQ_{DF} (Inc. 1/2 LOD)	Min.	0.027	0.12	0.11	0.027	0.037	0.040	0.027	0.070
	Max.	42	11	42	4.2	5.1	10	42	1.7
	Median	0.61	1.6	3.2	0.20	0.22	0.87	0.76	0.23
	Mean	**2.7**	**2.7**	**6.0**	**0.52**	**0.50**	**2.1**	**3.4**	**0.42**
∑PCB (Exc. LOD)	Min.	ND	7.2	ND	ND	ND	ND	ND	ND
	Max.	2000	2000	2000	420	66	880	2000	180
	Median	27	160	260	1.8	1.5	2.9	66	1.8
	Mean	200	5800	370	25	5.1	78	280	23
WHO_{98}-TEQ_{PCB} (Exc. LOD)	Min.	ND	0.0050	ND	ND	ND	ND	ND	ND
	Max.	1.7	1.7	1.6	0.087	0.078	0.82	1.7	0.094
	Median	0.029	0.17	0.32	0.00070	0.00024	0.00045	0.13	0.0050
	Mean	0.23	0.36	0.41	0.0094	0.0054	0.086	0.34	0.025
WHO_{98}-TEQ_{PCB} (Inc. 1/2 LOD)	Min.	0.0012	0.015	0.0058	0.0037	0.0012	0.0012	0.0012	0.0020
	Max.	1.8	1.8	1.6	0.089	0.079	0.82	1.8	0.096
	Median	0.043	0.20	0.33	0.0097	0.0059	0.011	0.13	0.0097
	Mean	**0.25**	**0.37**	**0.42**	**0.015**	**0.011**	**0.096**	**0.35**	**0.029**
WHO_{98}-TEQ_{DF+PCB} (Exc. LOD)	Min.	ND	0.069	0.081	ND	0.00068	0.0010	ND	0.032
	Max.	42	11	42	4.1	5.2	11	42	1.4
	Median	0.55	2.1	3.7	0.13	0.047	0.86	0.90	0.13
	Mean	2.8	2.9	6.3	0.41	0.38	2.1	3.6	0.35
WHO_{98}-TEQ_{DF+PCB} (Inc. 1/2 LOD)	Min.	0.031	0.13	0.17	0.031	0.041	0.041	0.031	0.075
	Max.	43*	11	43*	4.3	5.2	11	43	1.7
	Median	0.74	2.2	3.7	0.21	0.24	0.88	1.0	0.29
	Mean	**3.0**	**3.1**	**6.4**	**0.54**	**0.51**	**2.3**	**3.7**	**0.45**

* Note that the original result for the Hobart sample of 43 pg TEQ g^{-1} is included in this table.

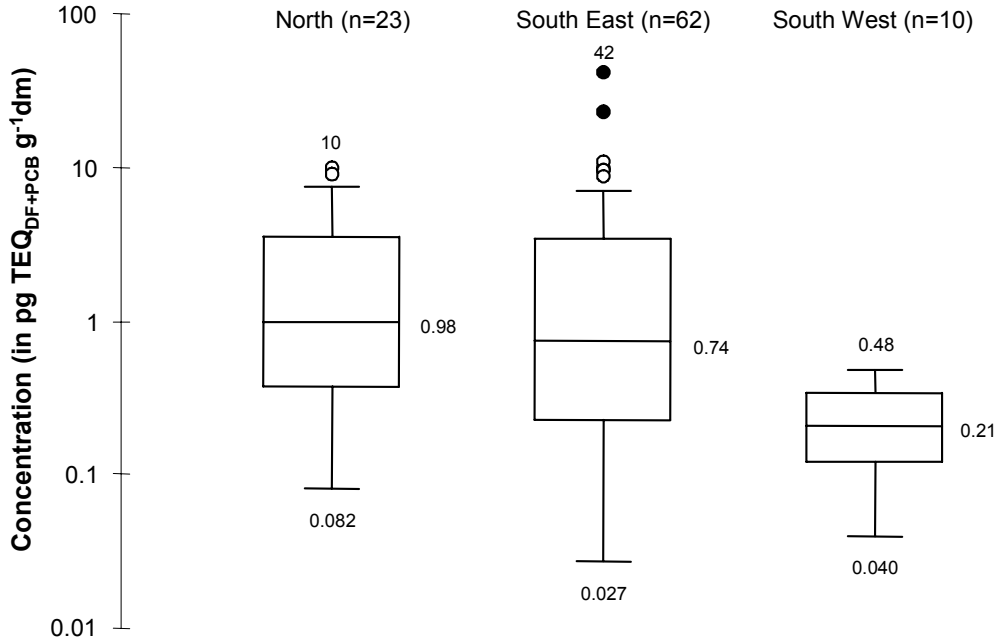

Figure 3.1 Concentration of dioxin-like chemicals in the North, South-East and South-West regions[1].

3.1.2 Concentration of dioxin-like chemicals in each state

The results can also be evaluated on the basis of concentration of dioxins in the various states and territories of Australia. Figure 3.2 provides a graphical representation comparing all samples from each state. The great within-state variability indicated by these box and whisker plots can be attributed to the inclusion of different land-use types and serves to illustrate the problematic nature of comparing all samples together. It is, therefore, important to assess the influence of land-use on the concentration of dioxin-like chemicals in soils in Australia.

[1] Expressed on a TEQ basis including half LOD values.

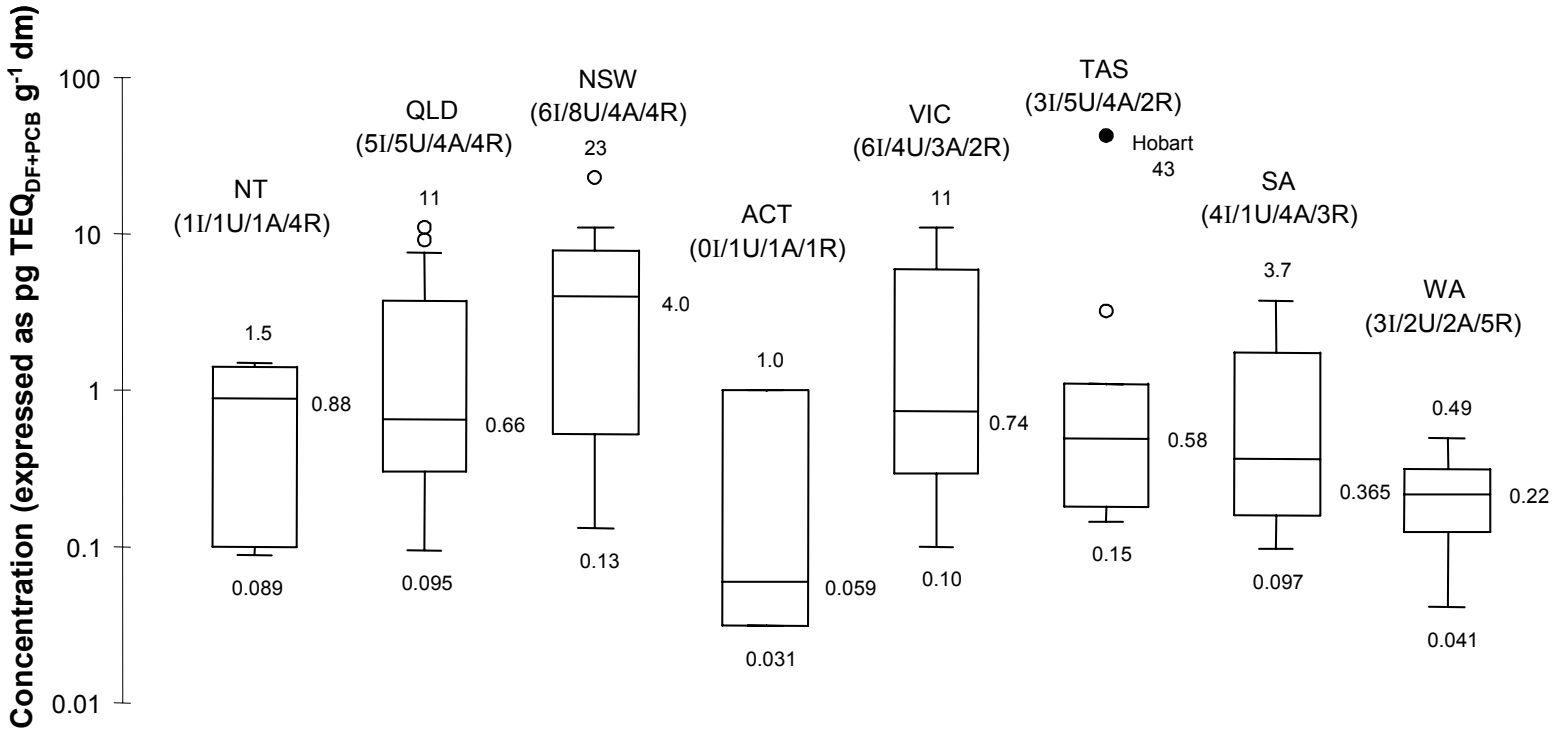

Figure 3.2 Concentration of dioxin-like chemicals in soil samples from all States/Territories in Australia.

The number of samples included for respective land-uses are given in brackets below the state name (i.e. 2I/1U/3A/4R represents 2 Industrial, 1 Urban, 3 Agricultural and 4 Remote locations).

3.1.3 Concentration of dioxin-like chemicals in soils representing different land-use types

Land-use was identified during the NDP's planning phase as a key parameter for the evaluation of background levels of dioxin-like chemicals in various environmental media. For the soil study, four key land-use types were differentiated: industrial, urban, agricultural and remote. Sampling locations within a given region were selected to represent one of these four land-use categories. It should, however, be noted that differentiation between the land-use categories (particularly between urban and industrial or agricultural and remote locations) can be problematical.

A plot of the results of the concentration of dioxin-like chemicals in soils representing different land-use types is presented in Figure 3.3, note that values include half LOD. The data shows that median concentrations of dioxin-like chemicals are substantially higher in soils that represent urban or industrial locations relative to those from agricultural and remote locations. However, median concentrations in soils from urban and industrial locations, or soils from agricultural and remote locations were similar (Table 3.2 and 3.3).

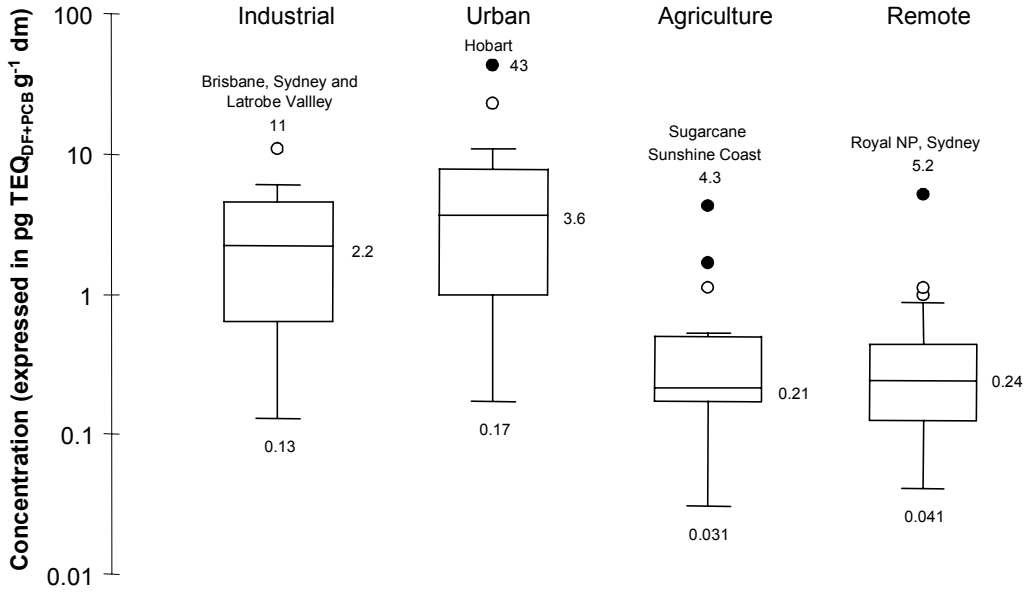

Figure 3.3 Concentration of dioxin-like chemicals in soil samples from different land-use categories.

The occurrence of higher levels of dioxin-like chemicals in urban and industrial locations relative to agricultural and remote locations is consistent irrespective of whether concentrations are express on a TEQ basis, or as a sum of detected PCDD/PCDF or the sum of detectable dioxin-like PCB. It is also noteworthy that PCB contributed to a greater extent to the TEQ in soils from industrial and urban locations with mean contributions to the TEQ_{DF+PCB} of 24% and 15%, respectively. In contrast, the contribution of PCB in soils from remote and agricultural areas was on average 5.8% and 5.3%, respectively.

Statistical analysis of the mean values obtained for different land-uses was undertaken using mean ∑PCDD/PCDF (pg g^{-1}), mean ∑PCB (pg g^{-1}) and mean TEQs. Two-way analysis of variance (ANOVA) was used to investigate differences across mean dioxin TEQ concentrations between sampling regions (North, South-East and South-West) and under different land-use categories (remote, agricultural, urban and industrial). Where PCDD/PCDF and PCB congener concentrations were less than detection limits, concentrations were set at half the detection limit. Data were inspected for gross deviation from normality and where necessary, log transformed (log_{10}) prior to analysis. Significant differences between means were determined using the Tukey HSD test procedure.

Two-way ANOVA and Tukey multiple comparison tests indicated that TEQs were significantly higher in samples collected in Northern and South-Eastern sampling regions compared with samples collected in the South-Western sampling region. TEQs were also significantly lower in samples collected in remote and agricultural areas compared with samples collected in industrial and urban areas (Tables 3.2 and 3.3).

Table 3.2 Summary of the two-way ANOVA of mean soil dioxin TEQs.

Source of variation	df	F ratio	P
Region (Northern, South-Eastern or South-Western)	2	9.6	<0.001
Land-use (remote, agricultural, industrial or urban)	3	11	<0.001
Interaction	6	1.3	0.26

Data log_{10} transformed prior to analysis.

Table 3.3 Results of Tukey multiple comparison of dioxin TEQs.

Land-use			Region		
Remote	Agricultural	Industrial	South-Western	Northern	South-Eastern

Mean concentrations of dioxin-like chemicals from land-use types or sampling regions joined by a thick underline were not significantly different.

3.1.4 Variation within land-uses

Agriculture

A comparison of the concentration of dioxin-like chemicals in soils representing different types of agriculture is presented in Figure 3.4. Soils from a sugarcane growing area showed substantially greater concentrations compared to all other agricultural soils. Similar results have been found in the mid and late 1990s in studies from Queensland (Müller et al. 1996). However, it is noteworthy that evidence from Prange et al. (2002) in a study of the formation of dioxins in Queensland, found 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 the work by Prange et al. (2002) suggests that natural formation processes may be involved. A

series of indirect evidence has been found that supports the hypothesis that natural formation is an important source for higher chlorinated PCDD/PCDF. The indirect evidence includes (Prange, 2003):

the congener profile is unique and could not be attributed to a specific source

- elevated levels of OCDD were found throughout a soil core including the deepest slice collected from several metres depth
- a mass balance indicates that the amount of OCDD in Queensland soils is in excess of global estimates
- the contamination is widespread and elevated levels were found in relatively remote locations along the coast
- no significant formation could be found in a simulation of a controlled bush fire.

In addition, Prange (2002) also evaluated natural formation in a laboratory incubation experiment and found a slight increase in the quantity of higher chlorinated dioxins. However, relatively high concentrations of OCDD in the material prior to the incubation make interpretation of these data difficult. Hence, the evidence that indicates natural formation to be the key source for the higher chlorinated PCDD is only indirect, and the process remains unidentified and is not considered further in this report.

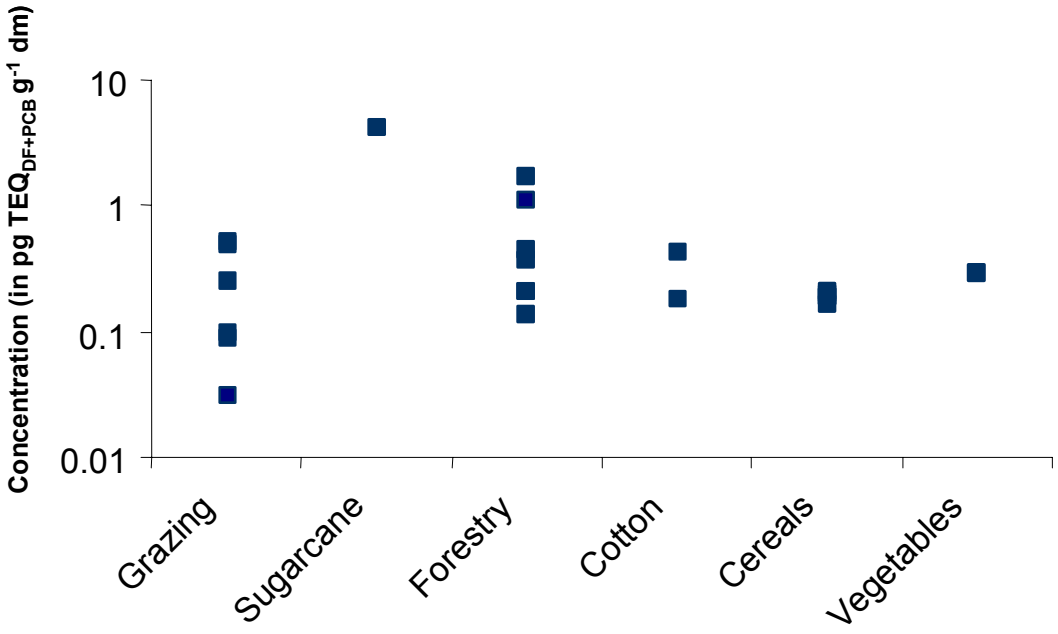

Figure 3.4 Toxic equivalents (TEQ_{DF+PCB}) of dioxin-like chemicals for specific types of agriculture.

Remote

Twenty-eight of the sampling locations in this study were defined as remote, for which a range of national parks and relatively undisturbed locations were selected. Criteria for defining a remote location are listed in Appendix A; it should be noted however, that there were some instances where these criteria were not adhered to. For example, one sample that was defined as remote originated from the Royal National Park, was less than the defined 60 km from an urban centre, being just outside Sydney. Not surprisingly, the sample from this remote location was found to be an elevated outlier for the remote data.

3.1.5 Contamination of coastal versus inland environments

The sampling locations can also be differentiated between those located in the coastal environment (between the sea and the first mountain range or < 100 km from the coast) and those in the inland environment (from the first mountain range inland or > 100 km from the coast). Such a comparison is particularly relevant in the light of recent work by Prange et al. (2001) which showed a widespread contamination of soils with higher chlorinated PCDD in Queensland's coastal environment but very low contamination in the inland environment.

A comparison of the levels of dioxin-like chemicals in inland and coastal samples is complicated by the fact that in Australia almost all urban centres are located in the coastal region whereas the inland region is sparsely populated. For example, in this study none of the 18 locations representing industrial areas and only 2 of 18 urban locations (Canberra and Bendigo) are defined as inland. By contrast the majority of agricultural (12 of 22) and remote (20 of 28) locations from which samples were collected are inland. Hence, for the purpose of comparing concentrations of dioxin-like chemicals between inland and coastal locations, analysis has been limited to the agricultural and remote sampling locations. Considering only these sampling locations, the data suggest elevated levels of dioxin-like chemicals occurred at coastal sampling locations when compared with inland samples (Figure 3.5). For example, when samples were ranked according to the sum of the PCDD/PCDF concentrations, the nine highest ranks were found in samples from locations in the coastal region. Conversely, it is interesting to note that the highest concentrations were found in the samples collected from Royal National Park (located near Sydney), agricultural and remote location in or near the Queensland Sunshine Coast and agricultural regions south of Adelaide. The difference between concentrations in samples from coastal and inland locations becomes less clear when locations are excluded that are within 200 km from urban centres. Excluding these data, no significant difference between coastal and inland concentrations was detectable at $p<0.05$.

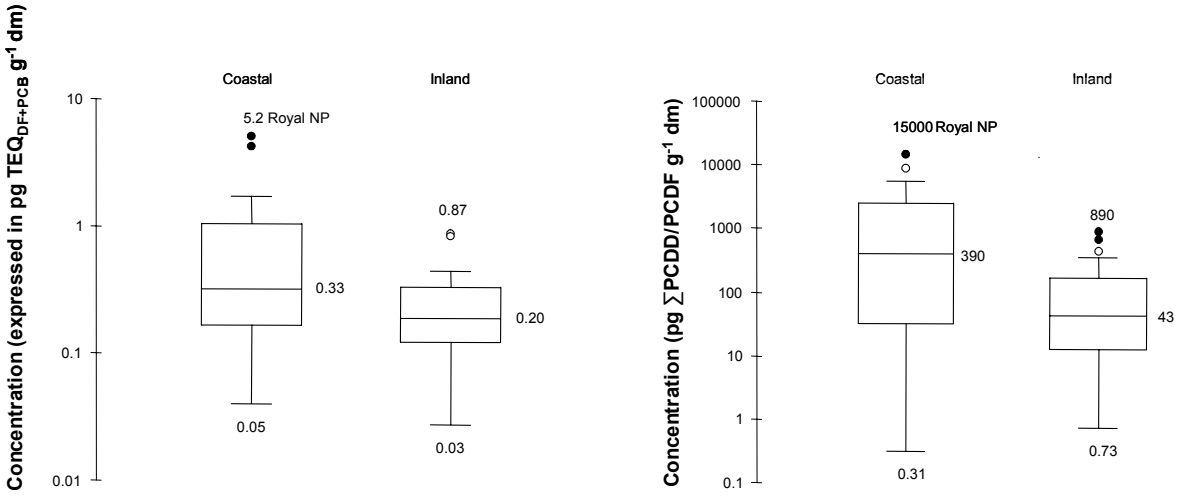

Figure 3.5 Comparison of the concentration of dioxin-like chemicals from coastal and inland areas.

Expressed as TEQs (left) and ∑PCDD/PCDF (right) in samples collected from agricultural and remote locations from coastal (n=20) and inland areas (n=32).

3.1.6 Geographical distribution

The geographical distribution of dioxin-like chemicals in locations representing different land-use types is presented graphically in Figures 3.6 to 3.9. These graphs summarise the findings that dioxin-like chemicals are highest in the urban environment of Australia (note that the scales on Figures 3.6 to 3.9 vary from figure to figure). In summary:

- concentrations of dioxin-like chemicals were greatest in soils near centres along the populated south-east coastal region of Australia
- concentrations were consistently low in locations from Western Australia and inland
- PCDD/PCDF consistently contributed more than 80% of the toxic equivalents to the total TEQs (TEQ_{DF+PCB}) in the soil samples.

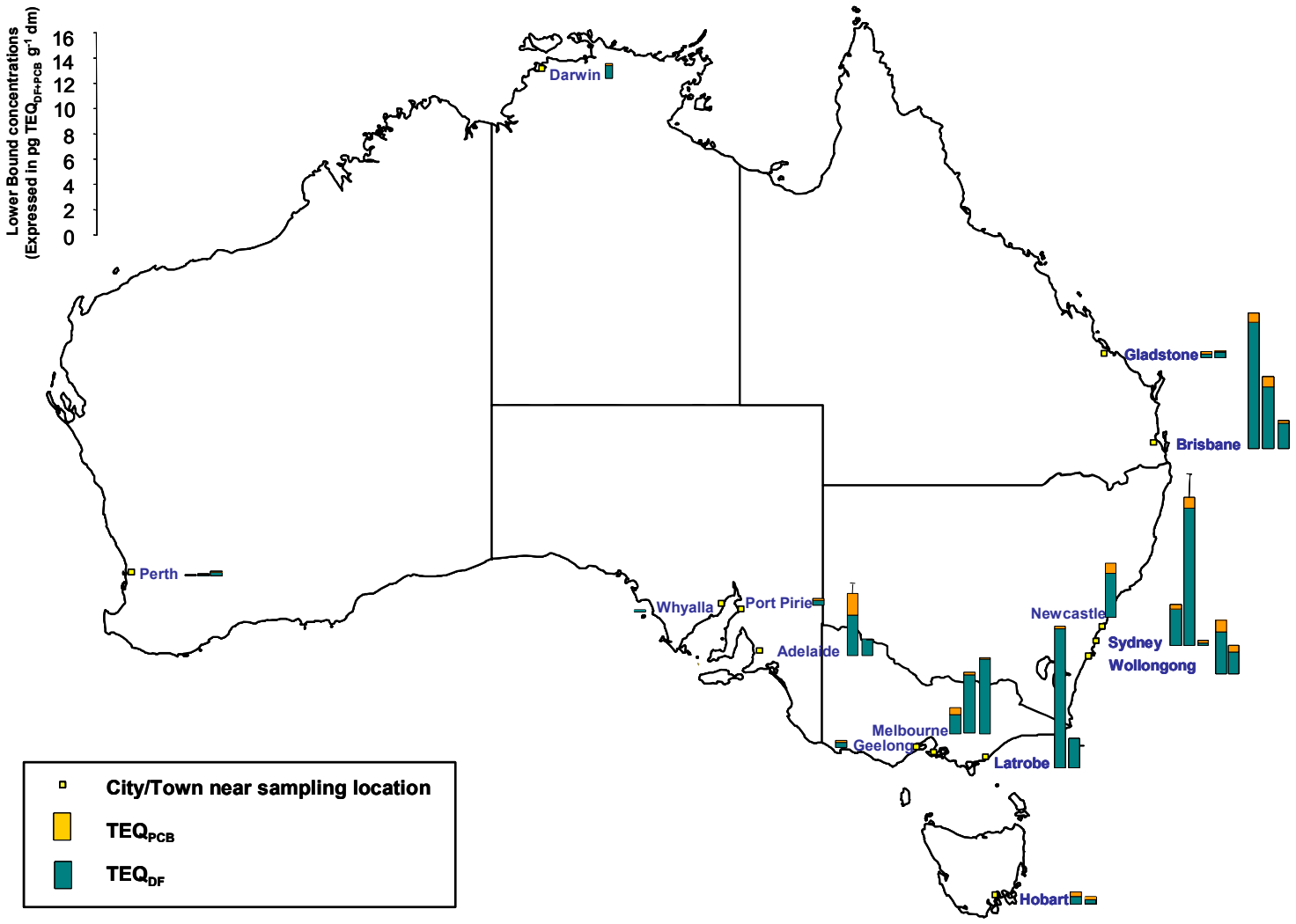

Figure 3.6 **Dioxin-like chemicals in samples from industrial locations.**

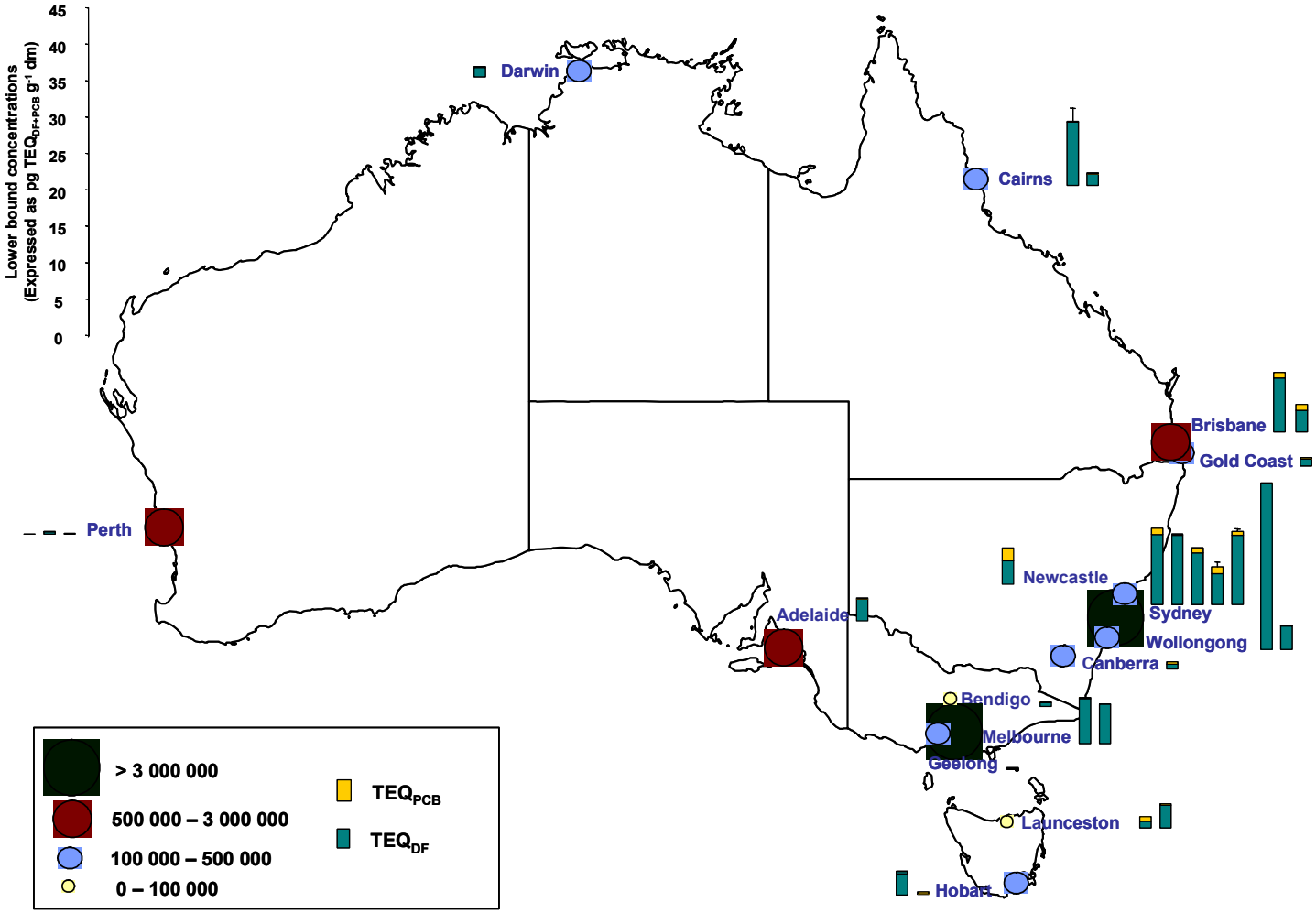

Figure 3.7 **Dioxin-like chemicals in samples from urban locations.**

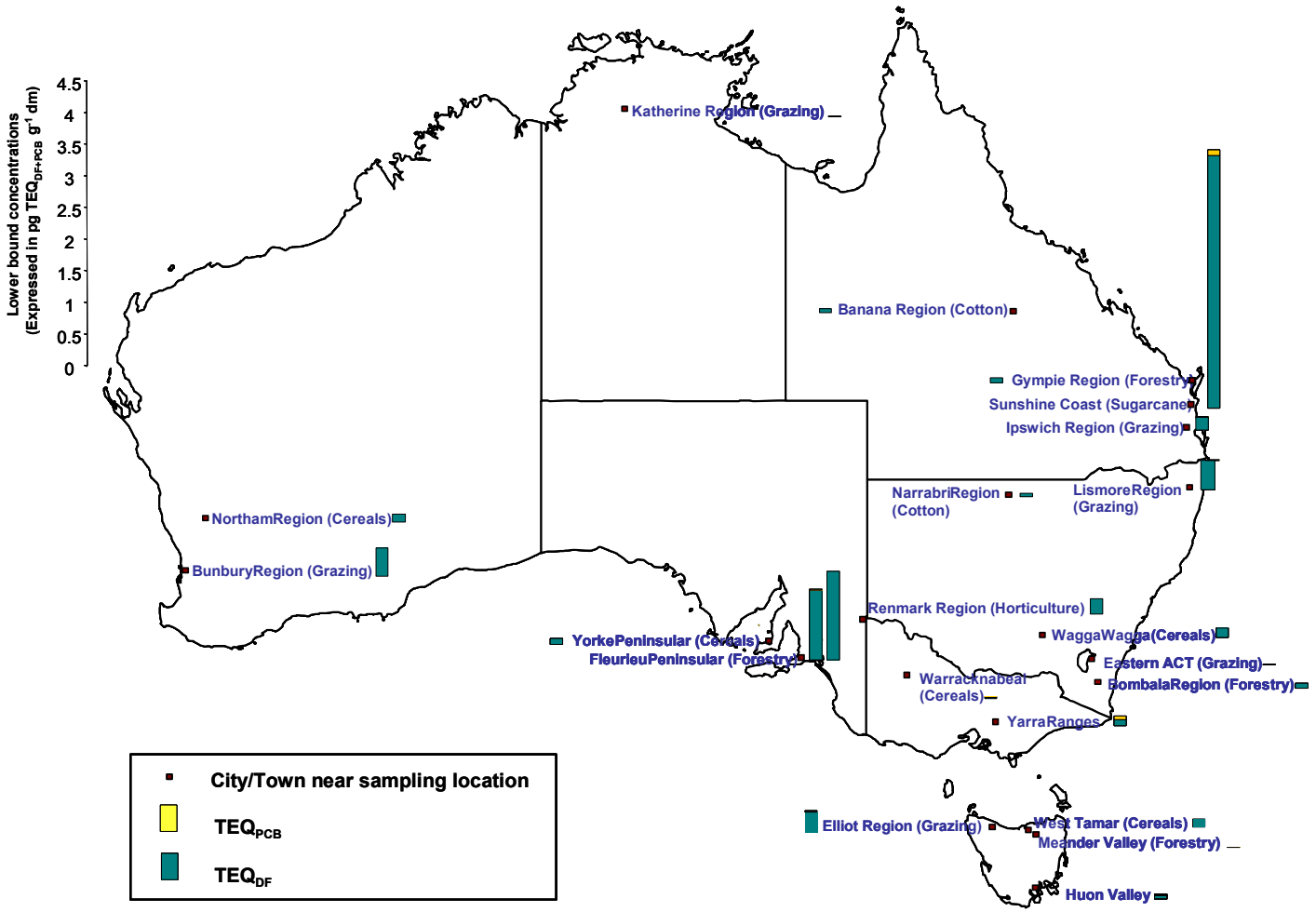

Figure 3.8 **Dioxin-like chemicals in samples from agricultural locations.**

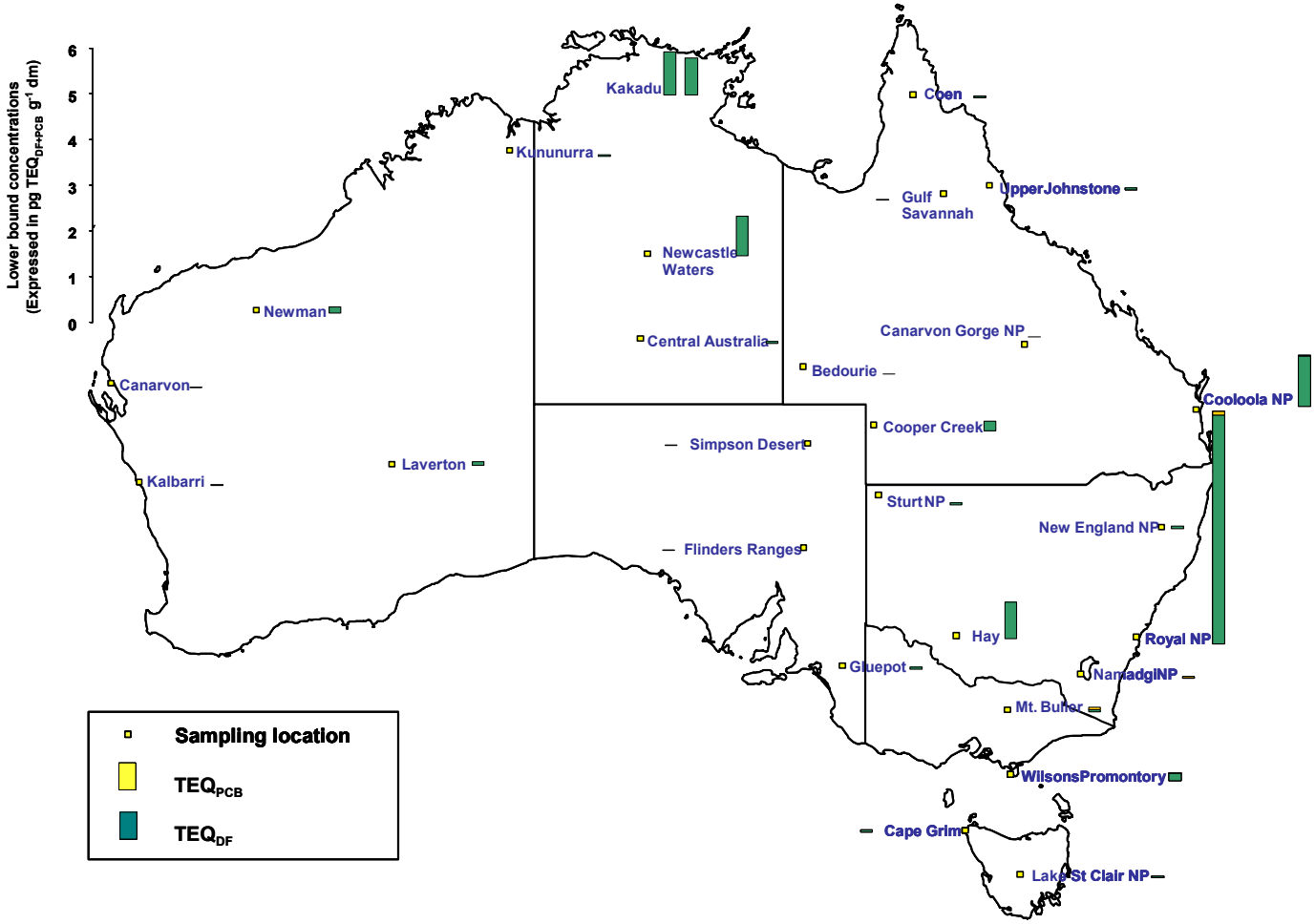

Figure 3.9 **Dioxin-like chemicals in samples from remote locations.**

3.1.7 Dioxin-like chemicals in historical soil samples

Dioxin-like chemicals are highly persistent in the environment and, hence, analysis of stored samples that have been collected in the past, or similarly, analysis of sample strata where deposition can be dated has been widely used to evaluate historic environmental concentrations, emissions, and depositional history. A key problem that may be encountered when evaluating historic contamination using archived historic samples is uncertainties regarding sample collection and storage that may, for example, have caused post-sampling contamination.

The 10 archived samples analysed for this study were collected since 1925 from a near-urban agricultural field near Adelaide, South Australia. Information concerning the depth of sampling is provided at Table A2. It is unfortunate that for most samples very little material was available, which may have affected the level of detection. Furthermore, repeat analysis, confirmation through interlaboratory calibration, and measurements of total organic carbon content were not possible for that reason.

Concentrations of dioxin-like chemicals ranged from 0.54 to 3.8 pg TEQ g^{-1} dm. The results of chemical analysis are presented in Figures 3.10 to 3.12 for TEQ, ∑PCDD/PCDF and ∑PCB; note that these are lower bound and exclude LOD values. 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 those 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. The relatively high result for the 1981 sample may be a result of this being a shallow near-surface profile (0-2.5 cm) whereas the other samples covered profiles of greater depth (0-10 cm and 0-23 cm).

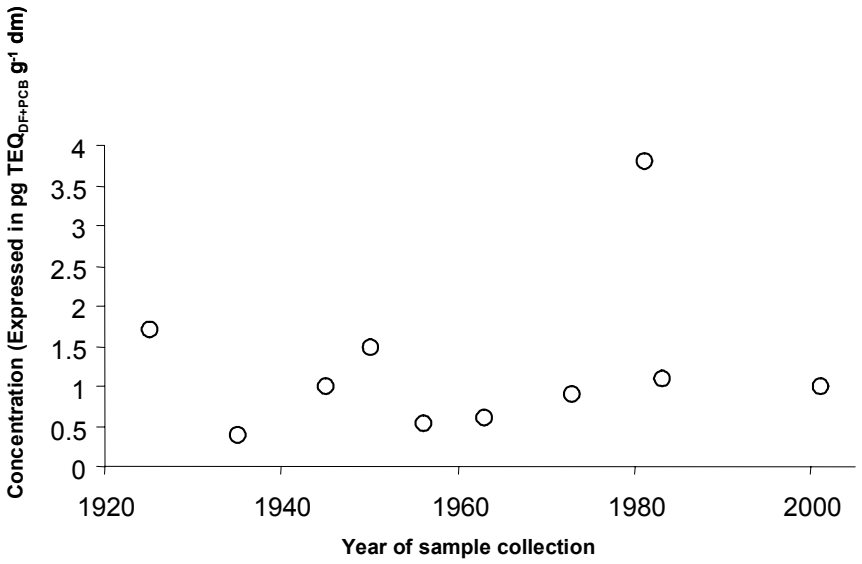

Figure 3.10 Concentration of dioxin-like chemicals in archived soil samples.

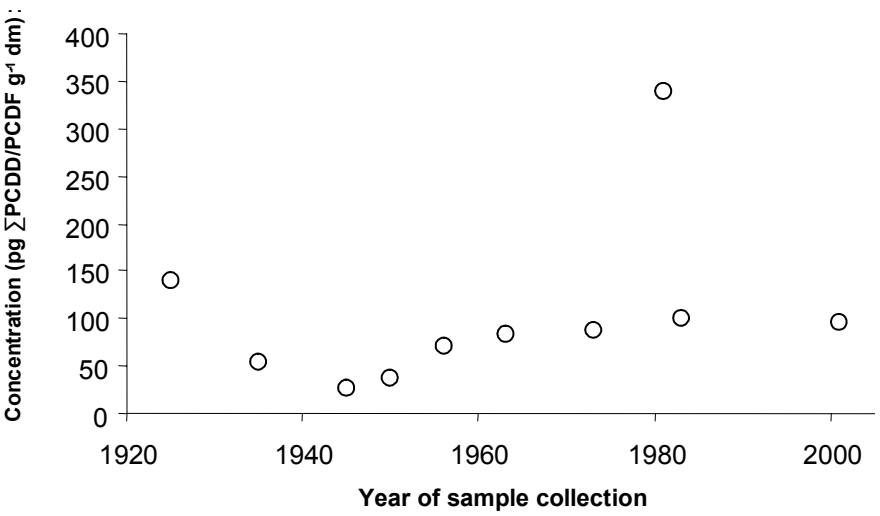

Figure 3.11 Concentration of ∑PCDD/PCDF in archived soil samples.

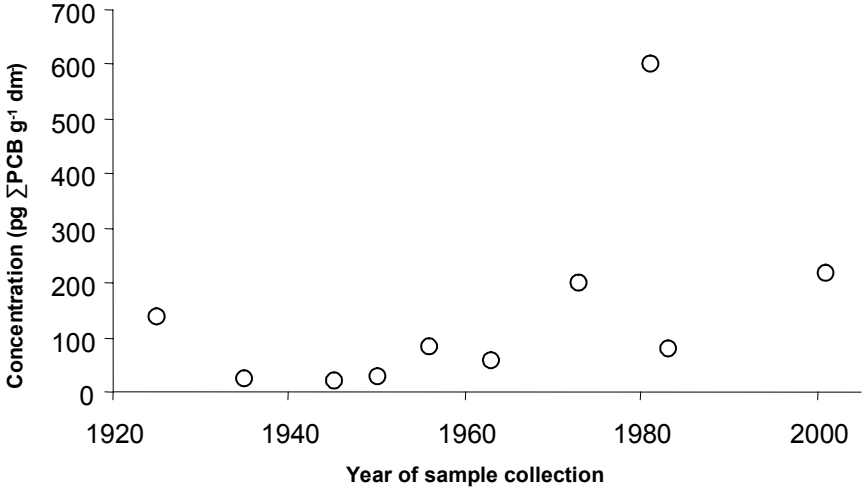

Figure 3.12 Concentration of ∑PCB in archived soil samples.

3.2 Characteristic patterns for dioxin-like chemicals in Australian soils.

3.2.1 Homologue and congener profiles

The specific sources of dioxin-like chemicals are often evaluated using PCDD/PCDF homologue and/or congener profiles (see Box 4). Typically in all samples that were collected in this study the PCDD/PCDF homologue profile as well as the congener profiles are overwhelmingly dominated by octachlorodibenzodioxin (OCDD), the highest

chlorinated PCDD. In the samples where OCDD was detectable, it contributed between 60% to greater than 99% of the ∑PCDD/PCDF (Fig. 3.13): Note that in Perth samples, OCDD was not detected and the LOD (i.e. 20 and 10 pg g^{-1} dm) was used to calculate homologue profiles for the two Perth samples.

Similarly the PCDD/PCDF congener profiles for the tetra - heptachlorinated 2,3,7,8-chlorine substituted PCDD/PCDF congeners are dominated by 1,2,3,4,6,7,8-heptachloro dibenzodioxin (Figures 3.14). This overwhelming dominance of the higher chlorinated PCDD in samples from Australia has been the subject of a range of studies in Queensland (Müller et al. 1999, Gaus et al. 2001, 2002, Prange et al. 2002). Despite intensive efforts examining soil cores as well as a range of formation processes including bush fire and natural formation processes, the source or process remain uncertain (Prange, 2003).

Interestingly, a closer inspection of the soil congener profiles obtained from this study indicates that the dominance of the higher chlorinated PCDD in both the homologue and the congener profile is less pronounced in samples from the more temperate regions such as Tasmania, South Australia and Western Australia. In fact, a comparison of samples from these more temperate environments show congener and homologue profiles similar to those reported from other temperate zones in the Northern Hemisphere as well as in New Zealand (i.e. Buckland et al. 1998). This shift from higher chlorinated PCDD/PCDF to lower chlorinated PCDD/PCDF is found in samples covering all land-use types including the remote sites where proximity to sources is particularly unlikely to have caused the specific profile (Figure 3.15). Hence, this result maybe seen as an indication that the domination of higher chlorinated PCDD in samples from the tropical regions is at least in part related to fate processes of the chemicals where the least volatile and most persistent PCDD accumulate specifically in tropical environments whereas the more volatile lower chlorinated PCDD/PCDF are transported from these environment to colder climates where they accumulate. In addition, a more rapid degradation of the lower chlorinated PCDD/PCDF in tropical environments may contribute to this observed shift in congener profile.

The congener profile for PCB is dominated by PCB#118 (approximately 50 to 70%) followed by PCB#105 (10 to 20%). No apparent differences in PCB profiles were observable between soils from different locations and an example of the typical PCB profiles for industrial soil samples is provided in Figures 3.16. Note that the four non-ortho chlorine substituted PCB are plotted on the left and the mono-ortho substituted PCB are plotted on the right hand side of the figure.

Box 4. Congener homologue and profiles

Congener and homologue profiles are useful tools for the determination of source and fate processes of dioxin-like chemicals, which may lead to accumulation in humans. Sometimes these profiles are compared to a "fingerprint", where the focus is not on the concentration but on the ratio of different dioxin-like chemicals to each other. Accordingly, in this document, profiles are presented by plotting the individual congener or homologue as the percent contribution it makes to the sum of a range of congeners or homologues.

Congeners and congener profiles

Congeners are individual compound members of the same chemical family. There are 75 possible different congeners of PCDD and 135 different congeners of PCDF. They differ according to their degree of chlorination (i.e. tetra-, penta-, hexa-, hepta- and octachlorinated compounds) and the position of chlorines in the molecule (i.e. 2,3,7,8-substituted compounds). There are a total of 7 PCDD and 10 PCDF congeners that are substituted in the 2,3,7,8-position. The congener profiles in this report show the percent contribution of each 2,3,7,8-substituted congener to the sum of the 15 2,3,7,8-chlorine substituted, tetra-heptachlorinated PCDD/PCDF concentration.

Homologues and homologue profiles

Homologues are a group of structurally related chemicals that have the same degree of chlorination (i.e. the same number of chlorines in the molecule). Within the PCDD/PCDF, each of the mono- to octachlorinated groups represent a homologue (i.e. there are 8 PCDD and 8 PCDF homologue groups, however since only PCDD/PCDF with > 3 chlorines the profiles are of concern, only 5 PCDD and 5 PCDF homologue groups are used). The homologue profiles in this report show the percent contribution of each tetra- to heptachlorinated homologue to the sum total PCDD/PCDF concentration.

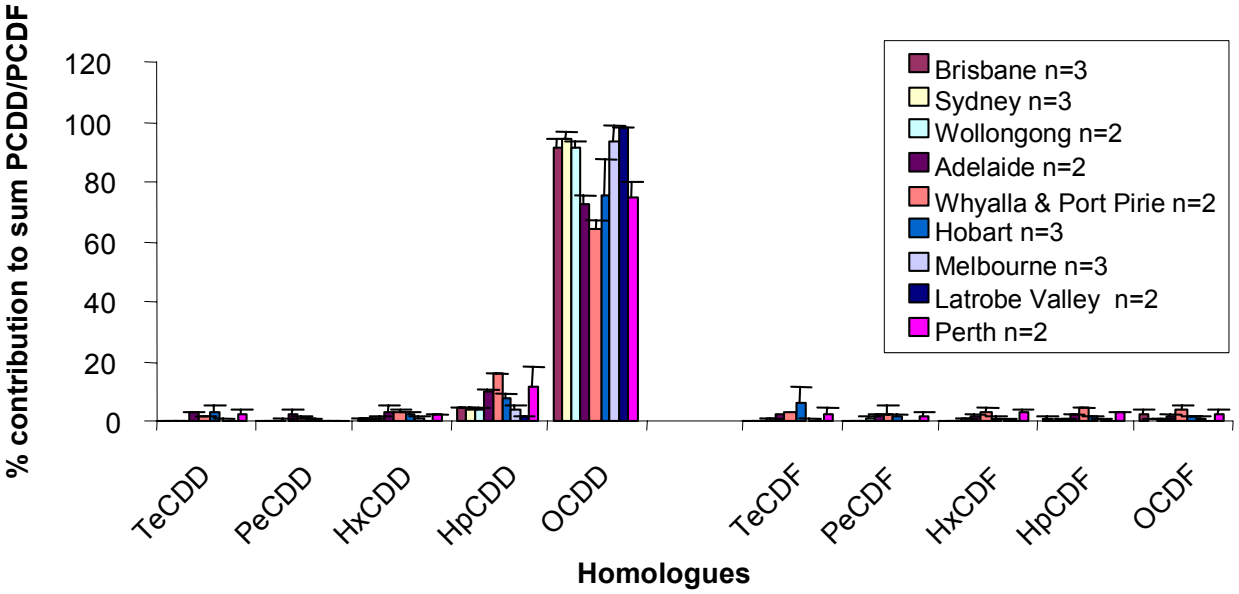

Figure 3.13 PCDD/PCDF homologue profile of soils for selected industrial locations.

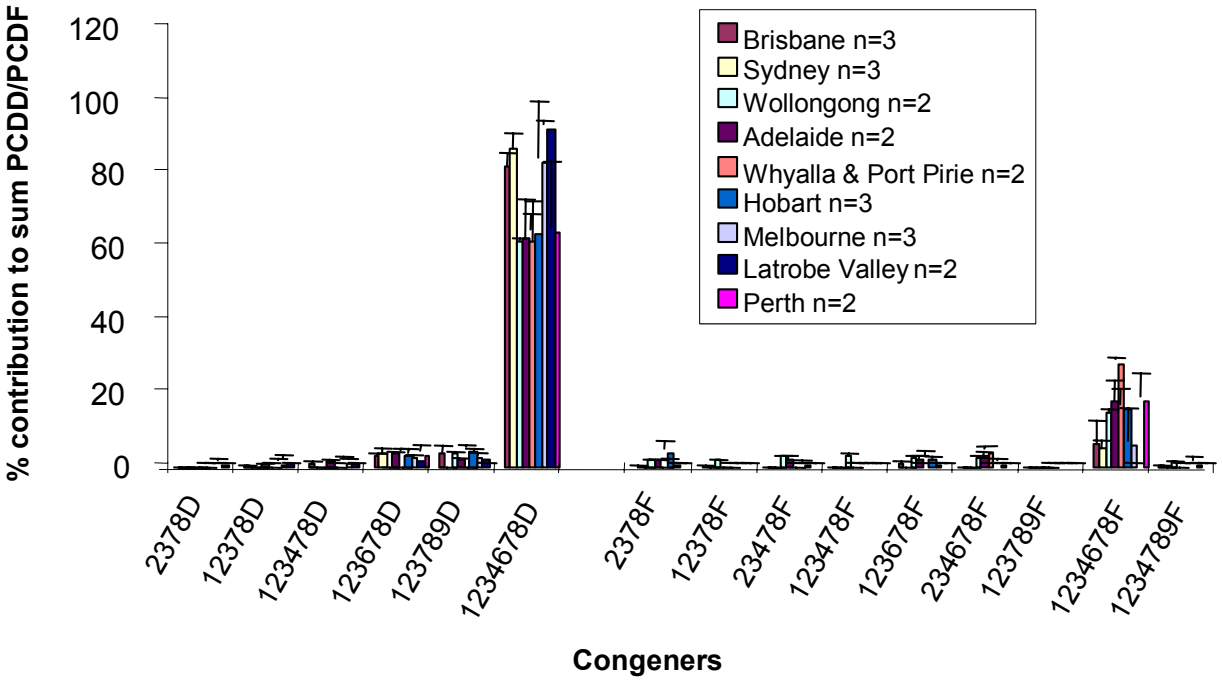

Figure 3.14 **PCDD/PCDF congener profile of soils for selected industrial locations.**

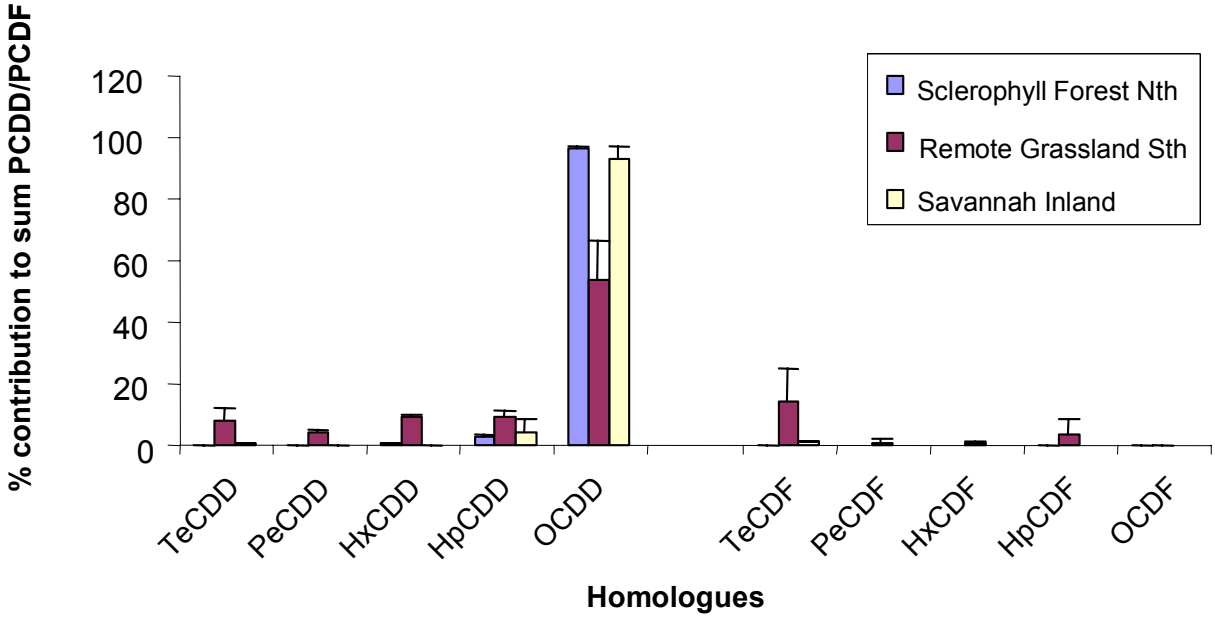

Figure 3.15 **PCDD/PCDF homologue profile for soils covering selected remote locations.**

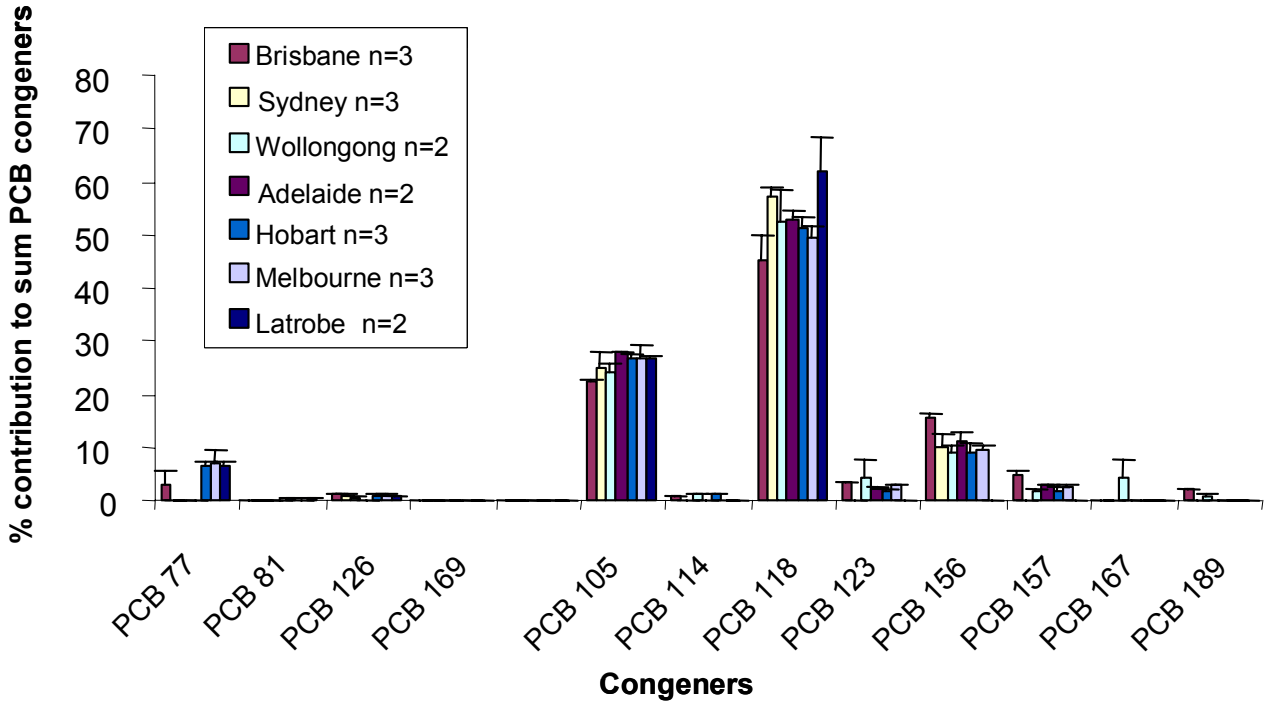

Figure 3.16 PCB congener profile in soils from industrial locations.

3.3 Comparison of Australian levels of dioxin-like chemicals with guidelines.

Contamination categories, which describe the levels of pollution associated with different contaminant concentrations, are a useful aid for interpreting the importance of field data. No Australian guideline exists for threshold levels of dioxin-like chemicals in soils. In Germany, reference values and recommended action for agricultural and horticultural land-uses were issued in 1992 and translated into governmental decrees in a number of Länder (Federal States in Germany) (Table 3.4) (Umweltbundesamt, 1992). These were as follows:

- For preventive reasons and as a long-term objective, the dioxin concentrations of soil used for agricultural purposes should be reduced to below 5 pg TEQ g^{-1}
- Cultivation of foodstuffs is not restricted in the case where the soil contains 5-40 pg g^{-1}. However, critical land uses, e.g. grazing management, should be avoided if increased dioxin levels were found in foodstuffs grown on such soils
- Limitations on the cultivation of certain feedstuffs and foodstuffs might be necessary if the dioxin contamination is above 40 pg TEQ g^{-1} soil. However, unlimited cultivation is allowed for plants with minimum dioxin transfer, e.g., corn.

In addition, guideline values were established for measures to be taken on children's playgrounds and in residential areas:

- Remediation of contaminated soil is required in playgrounds if the soil contains more than 100 pg TEQ g^{-1}. Remediation means sealing, decontamination or removal and replacement of contaminated soil
- In residential areas, such action should be taken if the soil is contaminated with more than 1,000 pg TEQ g^{-1}
- In industrial areas, the limit value was set to 10,000 pg TEQ g^{-1}.

Table 3.4 Reference values and recommended action for land-use and remediation of contaminated soil in Germany.

PCDD/PCDF (pg I-TE g^{-1} dm)	Recommended Action
<5	Target concentration
5-40	Control of products if dioxin transfer
>100	Soil removal and replacement on children playgrounds
>1,000	Soil removal and replacement in residential areas
>10,000	Soil removal and replacement independent of the location

In New Zealand, soil thresholds have been published in the *New Zealand Health and Environmental Guidelines for Selected Timber Treatment Chemicals* (Ministry for the Environment and Ministry of Health, 1997), based on protection of human health and incorporating the WHO tolerable daily intake for PCDD/PCDF of 10 pg/kg body wt/day (Table 3.5) (Buckland et al. 1998).

Table 3.5 New Zealand soil acceptance criteria.

	Agricultural	Residential	Industrial		
			Unpaved	Paved	Maintenance
PCDD/PCDF (pg I-TE g^{-1})	10	1500	18000	90000	21000

Most of the data collected in this study are within the levels set by Germany and the New Zealand soil criteria. Only one of the samples collected from agricultural and remote locations exceeded 5 pg TEQ g^{-1} dm. This sample, however, originated from the Royal National Park in the vicinity of Sydney and hence is clearly influenced by urban activities. Overall 37% of samples collected from urban locations and 18% of samples collected from industrial locations exceeded 5 pg TEQ g^{-1} dm and only one sample exceeded 40 pg TEQ g^{-1} dm. However, as discussed above, resampling of this location (Hobart urban) showed no elevation, and was consistent with the relatively low results found in other samples from Hobart.

3.4 Comparison of data from this study with other studies in Australia and overseas.

In this section, data gathered in this study are compared with both previous Australian studies and international publications (see Figure 3.17 and 3.18 and summary table in Appendix F). However, care needs to be taken not to over interpret the comparison between different studies or results from different countries. Such comparisons are always

complicated by a number of factors such as the definitions of land-use create. For example, what may be considered a remote sampling location in Central Europe would not either be considered a remote location in Australia or comply with the criteria for remote sites in this study. Furthermore, the aims of a study will usually determine the types of locations that will be included and, therefore, each study is to some extent unique. The complications in attempting to make a valid comparison include, but are not limited to:

- Differences in the aims of the study, for example determining background levels versus identification of contamination and potential hotspots
- Differences in the sampling strategy (including sampling depth, criteria for sampling, number of samples that are pooled, sampling equipment and methodology)
- Differences in the expression of results and the basis of the expression of results (i.e. ∑PCDD/PCDF and ∑PCB, individual congeners, TEQs or I-TE, basis of expression - dry mass versus organic carbon basis etc.)
- Difference in sampling period - data suggest a substantial decline in PCDD/PCDF and PCB soil concentration since the 1980s in many industrial countries (see Umweltbundesamt 2002)
- Differences in reporting or summarising results (i.e. mean, median, range, of TEQ, congeners and/or ∑PCDD/PCDF and PCB values may or may not be provided)
- Soil concentration data often do not follow normal distribution patterns.

In reality, few countries have carried out a comprehensive soil survey on dioxin-levels focusing on background soil concentrations. Here an attempt is made to compare the results from this study with results from some key studies, including limited studies conducted in Australia as well as studies from overseas including New Zealand, Asia, the Americas and Europe. The aim is to compare the results on the basis of similar land-use, however, it is noteworthy that, particularly for industrial and urban soils, many studies have aimed to detect sources rather then evaluate background concentrations. Such studies should therefore be considered as potentially biased towards sampling soils that are contaminated at levels which may exceed the average (background) concentration of the location and land-use in question.

3.4.1 Remote and agricultural soils

The data from this study did not show a significant difference in the concentration of dioxin-like chemicals between samples that were collected at locations designated as ‘remote’ to those designated as ‘agricultural’. Hence, remote and agricultural land-uses are combined in the discussion of the results from other studies (see Table F1) although there may well be differences in the contamination levels between agriculture and remote locations in other countries. See Figure 3.17 for a graphical representation of the results. Data for this figure was taken from minimum and maximum values from international studies included in Appendix F.

In Australia few studies have measured dioxin-like chemicals in soils at remote sites. Buckland et al. (1994) reported PCDD/PCDF concentrations for soil samples collected from a conservation area 40 km north of Sydney city following a bush fire and detected between 2.2-38.5 pg I-TE g^{-1} dm (28,000 pg ∑PCDD/PCDF g^{-1} dm) in these soils. However, the sampling location would have not passed the criteria for a remote location in this NDP study - and in fact the findings by Buckland et al. are similar to the levels that were found in this study in Royal National Park, just south of Sydney. Brzuzy and Hites (1996) reported the flux of dioxins in two rural soils in Victoria, and the data allowed recalculation of a soil concentration of about 4,000 pg ∑PCDD/PCDF g^{-1} dm.

Probably the most relevant study in Australia that included analysis of dioxin-like chemicals in samples from remote and agricultural soils areas was carried out by ENTOX. Following the discovery of unexpected elevated concentrations of PCDD/PCDF in soils from sugarcane farms (i.e. 6 and 10 pg I-TE g^{-1} dm and 5,000 and 9,200 pg ∑PCDD/PCDF g^{-1} dm), investigations started into the source and fate of the PCDD/PCDF. Following the initial results, Müller et al. (1999) analysed sediments/soils excavated from irrigation drains in sugarcane and cotton growing areas and found elevated levels of higher chlorinated PCDD in particular, in the samples from sugarcane growing areas relative to those from cotton growing areas (which, in contrast, showed elevated levels of many organochlorine pesticides). In order to evaluate the source of this contamination, Prange et al. (2002) analysed more than 30 soil samples covering various remote and agricultural locations such as national parks including rain forests and sclerophyll forest, savannah, *Melaleuca* wetlands and a peat swamp as well as grazing, forestry and sugarcane areas. Only selected samples were analysed for the full PCDD/PCDF profile. For most samples a GC-ECD method was used to quantify the dominant congener OCDD, the least toxic dioxin congener. As a result, concentrations are not available for all these soils on the basis of TEQs. However, Prange et al. found OCDD concentration ranging from about 8 pg g^{-1} dm to about 20,000 pg g^{-1} dm in samples from remote locations and the data demonstrated that the contamination is much higher in coastal soils in Queensland compared to inland soils (i.e. the median concentration in soils from coastal bushland was about 930 pg OCDD g^{-1} dm whereas all three inland soils showed very low levels of OCDD with a median concentration of 20 pg OCDD g^{-1} dm). Furthermore, although Prange's work also found consistently high concentrations of OCDD in sugarcane soils (median 5,300 pg OCDD g^{-1} dm) and related irrigation systems (median 7,200 pg OCDD g^{-1} dm) she concluded that the contamination is unlikely to be related to sugarcane farming practices (Prange et al., 2002; Prange, 2003). Overall, the dominance of the OCDD in coastal soils from at least the east coast of Australia, but also the elevated levels of dioxins in coastal zones and low levels in inland regions are in good agreement with the results from this study, although it is noteworthy that levels in Prange's study were much higher than in this study. This is most likely related to the fact that Prange's sampling concentrated on the coastal region of Queensland whereas the majority of the remote samples in the NDP soil study were collected at remote locations inland.

Sampling at remote or reference/pristine locations and agricultural sites was an important part of New Zealand's organochlorines program carried out from the mid to the late 1990s. For their study Buckland et al. (1998) collected 7 indigenous forest soils and 5 indigenous

grassland soils with concentrations of PCDD/PCDF expressed as I-TE ranging from about 0.17 to 1.99 pg g^{-1} dm for middle bound values (0.5 pg I-TE g^{-1} dm using lower bound values). The NZ results for pristine areas are somewhat similar to those from this Australian dioxins study if results are expressed on the basis of toxic equivalents. However, in comparison to NZ where the highest concentration of ∑PCDD/PCDF at remote indigenous grassland and forest sites were about 100 and 300 pg ∑PCDD/PCDF g^{-1} dm, respectively, results from this Australian study show more than 25 % of the samples from remote locations exceeded the maximum levels observed at pristine sites in NZ.

With respect to the agricultural soil data, the New Zealand study also found that, in general, the concentrations of PCDD/PCDF in pristine soils were not different from those in agricultural soil. The NZ study found one exception: in one agricultural sample the levels of PCDD/PCDF were substantially elevated with 9 pg I-TE g^{-1} dm. The elevated concentration in the NZ soil sample stemmed mainly from elevated levels of 2,3,7,8-TCDD and, thus, could be attributed to the use of contaminated 2,4,5-T for the control of weeds.

Results for concentrations of dioxin-like chemicals at remote and agricultural locations are available for many countries and have been reviewed extensively, for example by the WHO (1998) and International Agency for Research on Cancer (1997) and in the report of the NZ soil study (Buckland et al. 1998). An update and a comparison of results from this Australian study with some key international studies are provided below. See Figure 3.17 for a graphical representation of the results and Appendix F for a summary table of the results.

A major new report was recently published by Germany's Umweltbundesamt (2002). For soils the report summarises 2,502 soil analysis results covering the last two decades. The results include 1041 samples from soils that can be considered indicative of background concentrations, as these are not related to specific sources. The UBA report suggested that the concentration of PCDD/PCDF in the topsoil has substantially decreased in the period since 1985-1990 (median concentration 9 pg g^{-1} dm) to 1999 (median concentration 1 pg g^{-1} dm). In summary, median concentrations for cultivated land, grassland and forest in Germany are about 1, 2 and 4 pg I-TE g^{-1} dm, respectively, with the greatest concentration of about 25 pg g^{-1} dm in cultivated land and up to about 100 pg g^{-1} dm in forest soils. Notably these results are overall much less than the results of Rotard et al. (1994) who evaluated PCDD/PCDF in German agricultural and forest background soils and subsoils (i.e. 0-2 cm litter layer above the soil). Rotard et al. showed that background concentration of PCDD/PCDF in different cultivation types (forest, grassland and ploughland) in Germany ranged from about 10-110 pg I-TE g^{-1} dm. However, their study also demonstrated that the high results in forest soils were found only in the subsoil, whereas soil concentrations in the top 10 cm of the mineral soil combined (i.e. the soil that was sampled in both this Australian as well as the NZ study) was much lower (approximately one order of magnitude). The results of the recent UBA report (Umweltbundesamt, 2002) is also in good agreement with results from Boos et al. (1992) and Gälli et al. (1992 quoted in Buckland et al. 1998) all of which evaluated PCDD/PCDF in alpine soils.

In the Czech Republic, Holoubek et al. (2003) found a median level of in agricultural soils of 1.3 pg TEQ_{DF} g^{-1} dm with a maximum value of about 14 pg TEQ_{DF} g^{-1} dm, which is greater than that found in Australia.

For the United Kingdom, Buckland et al. (1998) quoted Her Majesty's Inspectorate of Pollution (HMIP)(1995) with levels of PCDD/PCDF from 0.78-18 pg I-TE g^{-1} dm (mean value of 5.2 pg I-TE). Recent studies of concentrations of dioxin-like chemicals in soils were also carried out in many other European countries including Spain, the UK, Greece and Poland. However, these studies concentrated on specific sources (Table F1).

In North America, the US EPA in their Dioxin Reassessment Document found that PCDD/PCDF levels in rural soils range typically from 0.1-6 pg TEQ_{DF} g^{-1} dm (mean value: 2.5 pg TEQ g^{-1} dm based on 252 samples). Rappe et al. (1997) analysed soils from rural areas in the southern Mississippi region and found a median concentration of 0.7 pg TEQ_{DF} g^{-1} dm (max. 23 pg TEQ g^{-1} dm). Tysklind et al. (2002) reported a median level of 3.3 pg TEQ g^{-1} dm in soils from wetlands in Mississippi (maximum 8.4 pg TEQ_{DF} g^{-1} dm, PCDD/PCDF only). Notably, the congener profiles in these soils were similar to those observed in studies from Queensland and the authors discuss natural formation processes. Recent studies in California covered the levels of dioxin-like chemicals in agricultural soils and found a median concentration of 2.6 pg TEQ g^{-1} dm (max. 5.5 pg TEQ g^{-1} dm) (Petreas et al. 2003). From Brazil, Braga et al. (2002) reported a concentration of 0.04 pg TEQ_{DF} g^{-1} dm (PCDD/PCDF) for a forest site that served as a control site.

Probably the largest volume of recent literature on dioxin-like chemicals in soils has come from Asian countries. For a study into landfills as a source for dioxin-like chemicals in the Philippines, Cambodia, India and Vietnam, Hung Minh et al. (2003) reported levels at control sites from each country in the range of 0.03 to 4.5 pg TEQ g^{-1} dm. A large quantity of work in the recent years has been carried out on dioxin contamination in Japan, Korea and China, though the focus has been on urban hotspots. In Japan, the Ministry of Environment conducted an environmental survey of dioxins that including 3031 points nation wide, with a soil survey of the general environment and a survey of the vicinity of pollution sources (http://www.env.go.jp/en/topic/dioxins.html). The survey found concentrations in soils ranging from < LOD to 1200 pg TEQ g^{-1} dm. However, to date no information has become available that allowed differentiation of study results on the basis of land-use. Sakurai et al. (1996) also had as a reference site, a paddy field where they found 2.5 pg I-TE g^{-1} dm. Furthermore, Seike et al. (2001) reported mean concentrations for dioxin-like chemicals in of 3.9 pg TEQ g^{-1} dm in forest soils (0.6-13 pg TEQ g^{-1} dm) and a mean concentration of 120 pg TEQ g^{-1} dm in paddy soils (4.5-230 pg TEQ g^{-1} dm).

For Korea, Im et al. (2002) found 0.2 pg TEQ g^{-1} dm in soil from a mountain top (control site). Also Choi et al. (2003) measured dioxin-like chemicals in soils collected from farmland sites in Korea and found concentrations ranging from < LOD to 43 pg TEQ_{DF} g^{-1} dm (mean value 2.3 pg TEQ g^{-1} dm).

In China, Chen et al. (2003) analysed 37 soils covering farmland and grass land with concentrations ranging from 0.1-3.7 pg TEQ g^{-1} dm (only PCDD/PCDF; mean values for

farmland and grassland were 0.87 and 0.48 pg TEQ g^{-1} dm, respectively). Wu et al. (2002) looked at two rural soil samples and found 0.1 and 0.29 pg TEQ g^{-1} dm.

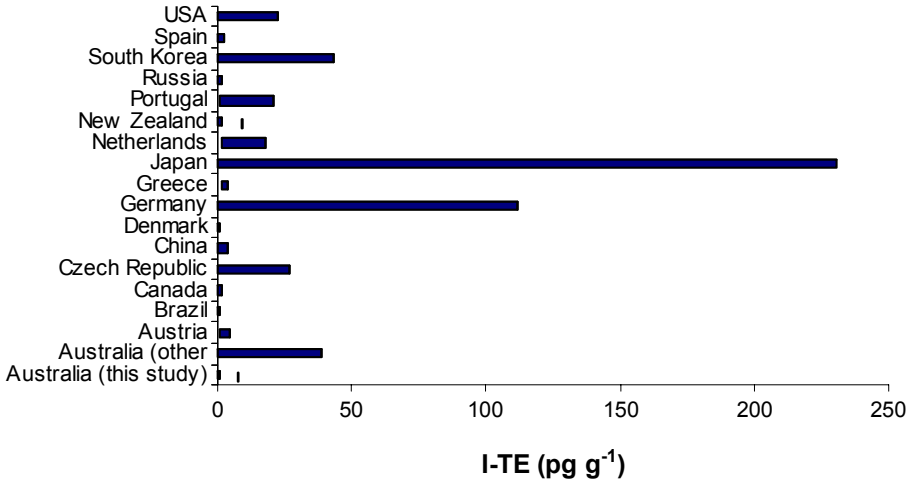

Figure 3.17 Australian versus international data for remote and agricultural land-uses.

3.4.2 Industrial and urban soils

Determination of background concentrations of dioxin-like chemicals in urban and industrial soils was a primary task in this study. As discussed previously, differences were not identified between the concentrations of dioxin-like chemicals between samples that were collected at urban/residential locations and those that were collected in industrial parts of cities, though it needs to be stressed again that specific point sources were avoided in this study, even in industrial locations. Due to the overall similarity in the concentration levels in urban and industrial locations in this study, these land-uses are combined for comparison with the results from other studies (Appendix D). See Figure 3.18 for a graphical representation of the results. Data for this figure was taken from minimum and maximum values in international studies included in Appendix F.

In Australia few studies are available that consider concentrations of dioxin-like chemicals in urban and/or industrial locations. Sund et al. (1993) examined PCDD/PCDF in Melbourne and reported levels between 1.8 and 8.2 pg I-TE g^{-1} dm in urban soils and between 0.1 and 2.1 pg I-TE g^{-1} dm in soils from industrial areas in Victoria. Buckland et al. (1994) in their study on soils after a bushfire analysed a sample from a roadside north of Sydney and detected about 43 pg I-TE g^{-1} dm in this soil sample. Prange (2003) reported OCDD concentrations for nine samples from industrial locations with a median concentration of 2300 pg OCDD g^{-1} dm. While Prange's results indicated elevated levels of OCDD in all samples collected from locations within urbanised and industrial regions, the result suggested that none of the specific activities investigated seemed to be associated with the elevated concentrations.

For New Zealand's Organochlorines Program the authors differentiated the sampling locations into provincial centres (n=8) and metropolitan centres (n=15) and with the

exception of an outlier (33 pg TEQ g^{-1} dm) found that soil concentrations ranged from 0.72-3.7 pg I-TE g^{-1} dm in soils from provincial centres and 0.26 to 6.7 pg I-TE g^{-1} dm in soils from metropolitan centres (only PCDD/PCDF) (Buckland et al. 1998). The NZ study also analysed PCB and found levels of PCB expressed as I-TE were < 0.3 pg g^{-1} dm in the soils from the provincial centres and up to about 1 pg g^{-1} dm in the soils from metropolitan centres.

In Germany the report by the Umweltbundesamt distinguishes soil sampling locations into a high density urbanised ("agglomeration") area, urbanised area and rural areas with median concentrations of 3, 2 and 1 pg I-TE g^{-1} dm in the respective zones (maximum concentrations of 112 pg I-TE g^{-1} dm for the high density urbanised area, 88 pg I-TE g^{-1} dm for the urbanised area and about 26 pg I-TE g^{-1} dm for the rural area) (UBA 2002). In addition, the UBA report separately discusses areas with specific contamination sources with a median concentration in 'industrial areas' of 4 pg I-TE g^{-1} dm (maximum concentration of 72 pg I-TE g^{-1} dm). Elsewhere in Europe, Boos et al. (1992) found between 2 and 6 pg I-TE g^{-1} dm in soil samples from urban outskirts and between about 4 and 13 pg I-TE g^{-1} dm in soils from industrial sites (PCDD/PCDF median concentrations of 3.5 and 5 pg I-TE g^{-1} dm, respectively).

From Denmark, Vikelsoe (2002) reported recently between 0.3 and 3 pg I-TE g^{-1} dm. For the UK, Stenhouse and Badshaw (1990) reported between 3 and 20 pg I-TE g^{-1} dm. Furthermore, Buckland et al. (1998) quoted reports by the HMIP studies that suggest that the levels of PCDD/PCDF in UK urban soils range from 4.9-87 pg I-TE g^{-1} dm. Much higher levels were found however in Newcastle in the UK approaching 1,900 pg TEQ g^{-1} dm, although the vicinity of a source is obvious in this study. In Spain, Schumacher et al. (2002, 2003) found between 0.2 and 0.8 pg I-TE g^{-1} dm in industrial area near a cement plant and up to 17 pg I-TE g^{-1} dm in the vicinity of waste incinerators.

In the Americas, the US EPA in their Dioxin Reassessment Document (US EPA, 2000) found that PCDD/PCDF levels in urban soils range typically from 2-21 pg TEQ_{DF} g^{-1} dm (mean value: 9.4 pg TEQ g^{-1} dm based on 171 samples). Birmingham (1990) measured PCDD/PCDF concentrations of up to 79 pg I-TE g^{-1} dm in soils from urban areas that were not considered industrial and up to about 102 pg I-TE g^{-1} dm in soils from industrial areas. Lorber et al. (1996) analysed soils from urban areas and found between 3 and 33 pg I-TE g^{-1} dm; whereas concentration in soils sampled from the vicinity of solid waste incinerators were contaminated at levels between 50 and 840 pg I-TE g^{-1} dm. From Brazil, Braga et al. (2002) reported between 0.2 and 2.1 pg I-TE g^{-1} dm.

From Asia, results from Korea found between 0.02 and 0.6 pg I-TE g^{-1} dm at industrial sites which is much lower than the results reported in a study from Im et al. (2002) who found between about 9 and 3,700 pg I-TE g^{-1} dm with a median concentration of 34 pg I-TE g^{-1} dm. A separated study by Kim et al. (2001) reported mean concentrations of 7.6 and 4 pg I-TE g^{-1} dm in soil samples from industrial and urban areas, respectively. From Japan, besides the study from the Ministry of Environment (http://www.env.go.jp/en/topic/dioxins.html), Ono et al. (2001) reported concentrations between 0.17 and 67 pg I-TE g^{-1} dm in soils from playgrounds in an urban centre and between 15 and 25 pg I-TE g^{-1} dm from soils collected from the side of a main road. Soil

concentrations in parklands near Beijing in China ranged from 0.42 to 2.3 pg I-TE g^{-1} dm (Chen et al. 2003). Amirov and Kruglov (2002) investigated dioxin-like chemicals in urban environments in Russia and reported mean concentrations ranging from 1.2 pg I-TE g^{-1} dm in Ukhta in the northern Urals to 3.7 pg I-TE g^{-1} dm in the city of Kurgan in western Siberia.

Figure 3.18 provides a summary of international data and compares results from this study to those from overseas and previous Australian studies. The concentrations of dioxin-like chemicals in soils collected specifically to evaluate background concentration in industrial and urban locations in Australia are similar to results reported previously from Australia and similar to results reported in the soil study for the NZ Organochlorines Program. On the basis of toxic equivalents, concentrations of dioxin-like chemicals are on average much lower than those reported from many industrial sites internationally and globally can be considered among the lowest background concentrations in urban and industrial locations.

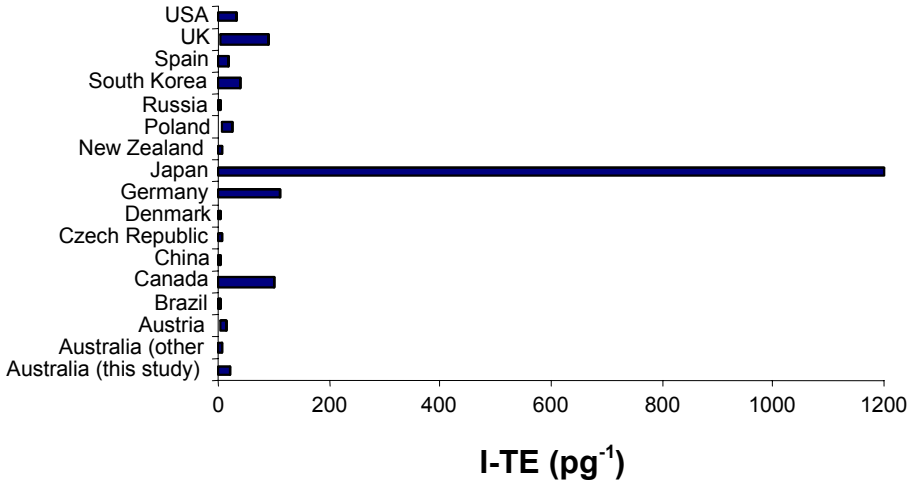

Figure 3.18 Australian versus international data for industrial and urban sampling locations.