Originally presented to the National Energy-from-Waste conference
18th – 19th July 2007, Manly, NSW, Australia

Dioxins and waste-to-energy plants – a reality check

B.R. Stanmore 51 McIvor Park Court Junortoun Vic 3551
03 5449 3742 stanmore@ uq.edu.au

Abstract

Waste combustion has a reputation for being a major contributor to the amount of dioxins (PCDD/F) in the environment, and opposition to WTE plants is often based on this perception. An examination of the relevant literature indicates that other sources are responsible. Dioxins are ubiquitous in the environment, and in Australia are formed predominantly in bushfires, especially in tropical, coastal regions. They are then redistributed across the continent. Over 90 % of human intake is from food such as meat, grains, fish and dairy products. A modern WTE plant would contribute a negligible amount to human PCDD/F intake in its neighbourhood.

Introduction

A major concern expressed by those likely to be impacted by the installation of a plant to burn municipal waste is that of 'dioxin' emissions. Dioxins or PCDD/F (a mixture of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) have a reputation for being emitted in significant quantities, and are conventionally regarded as being extremely toxic. This paper examines two aspects of the debate:

1 what is the extent of PCDD/F emissions from a modern WTE plant, and
2. what is the likely contribution these emissions make the total intake of PCDD/F by the surrounding population.

It should be noted that not all 'dioxins' are regarded as toxic, and a distinction between total mass and the ITEQ (or toxic) mass must be maintained. In the category of PCDD/F there are 75 dioxin compounds and 135 furan compounds, only 17 of which have been allocated toxicity factors. These factors relate the toxic effect of a particular compound to the toxicity of 2,3,7,8 tetrachloro dibenzo-*p*-dioxin (TCDD), which is arbitrarily given a factor of unity. The concentrations may be reported on the basis of the 'international' standard toxicity equivalent ITEQ, or the World Health standard WTEQ. There is little difference between them.

The mass of the toxic congeners or ITEQ then depends on the composition of the mixture. Natural PCDD/F is mostly octachloro dibenzo-*p*-dioxin OCDD, which has a toxicity factor of 0.001 i.e its toxicity is one thousandth of that of TCDD. The PCDD/F generated by waste combustion is typically higher in furans than in dioxins, and is a maximum around the pentachloro congeners (PeCDD/F). The ITEQ mass of MSW emissions is less than the total PCDD/F mass by a factor of about 0.01.

Before discussing the matter of WTE emissions, the widespread natural distribution of PCDD/F in the environment (both air and soil) should be noted.

The ubiquitous nature of PCDD/F

Samples of soil taken from sites in Queensland exhibit significant concentrations of PCDD/F, mostly as OCDD, see Figure 1 (Prange et al 2002). Gaus et al (2001) show from dated sediments in the Burdekin region that variations of PCDD concentrations in the cores over several centuries of depositional history were relatively small. Elevated PCDD levels were present in sediment slices from the early 17th century. Much of this material is believed to be formed during bushfires, and redistributed by subsequent fires (Prange et al 2005).

Ball clays which are used as extenders in chicken feed have been shown to contain high concentrations of PCDD/F e.g. Gadomski et al (2004) in the USA. These deposits are believed to be natural, and formed in-situ by non-thermal mechanisms (Holmstrand et al 2006). Similar ball and kaolinite clays in other countries, including Australia have also been shown to contain dioxins.

A study of the PCDD/F concentrations in grasses harvested and stored for over a century in the UK has been carried out by Hassanin et al (2006). Both the total mass and ITEQ mass are plotted by year from 1903 to 2004 in Figure 2. The values have been consistently falling and are now at a level which is one tenth of the value 100 years ago. Soils sampled in the UK in the 1880s have also been found to have significant dioxin concentrations.

The concentration of PCDD/F in Sydney's air was measured in the early nineties by Taucher et al (1992). Total PCDD/F values of 3 – 15 pg Nm^{-3} were recorded at different locations in the city, and ITEQ values of 0.016 – 0.062 pg Nm^{-3}. The corresponding values in urban Houston USA in 2004 were 0.9 to 1.2 pg m^{-3}, and they were removed from the air mostly by rain (Correa et al 2006).

An interesting investigation by Meharg and Killham (2003) of the peat ash remaining in domestic fireplaces on the now-abandoned western Scottish island of Hirta suggests that the highlands and islands produced about 1 kg of PCDD/F per annum through the eighteenth and nineteenth centuries. This compares with an estimate of 11 kg produced per annum by current WTE plants in the UK.

Emissions of PCDD/F from a modern WTE plant

The National Dioxins Review Program (ADEH 2004) found that of the estimated 1787 g_{TEQ} produced in Australia per annum, 1360 g_{TEQ} were generated in uncontrolled combustion processes, i.e. bushfires, controlled burns and agricultural waste combustion. This represents 76% of the total. Ferrous and non-ferrous metal production accounted for another 9%. The remainder was generated by chemicals production, power/heat generation, landfilling and incineration (medical waste and sewage sludge).

MSW contains PCDD/F. Figures from Spain (Abad et al 2002) range from 1.5 to 46 μg_{ITEQ} t^{-1}, with the medians in three campaigns being 3.2, 4.3 and 11.4 μg_{ITEQ} t^{-1}. The mean figure for the UK reported by Eduljee et al (1997) was 6.3 μg_{ITEQ} t^{-1}, or 6,300 ng_{ITEQ} t^{-1}. The collection of mostly German values reported by Giugliano et al (2002) ranges from 1.3 to 255 μg_{ITEQ} t^{-1}, with most values in the 10 to 50 μg_{ITEQ} t^{-1} range. Note that leachates from landfills in Korea (Choi and Lee 2006) have been found to contain between 4 and 46 pg_{ITEQ} per litre (or ng_{ITEQ} per m^3).

The dioxins present in MSW feed to a WTE plant are destroyed in the furnace. However they are newly formed in the fluegases emerging from the furnace in two temperature windows. In the heat exchangers they are generated from precursors such as chlorophenols in the gas phase at 900 to 600^{o}C. They are also the product of reactions in the flyash between unburned carbon, chloride salts and oxygen in the temperature range 400 to 200^{o}C. This is known as the *de novo* reaction. The dioxins can be removed by the addition of activated carbon before the fabric filter, or by catalytic destruction.

The universal limit for PCDD/F emissions from MSW combustion in Europe, Japan, the USA is 0.1 ng_{ITEQ} per Nm^3 of flue gas, measured dry and at 7% oxygen. Abad et al report a mean in Spain of 0.008 ng_{ITEQ} per Nm^3, Erbach in Germany (1988) 0.02 ng_{ITEQ} per Nm^3, and a Seghers plant in Austria 0.04 ng_{ITEQ} per Nm^3. The volume of gas produced during the combustion of a typical MSW is of the order of 4200 Nm^3 per tonne of MSW, measured dry and at 7% oxygen. The masses of ITEQ emitted by the plants above are therefore 0.034, 0.084 and 0.17 μg_{ITEQ} per tonne of MSW burned. Consonni et al (2005) give a mean value for four plants in Italy of 0.26 μg_{ITEQ} t^{-1}.

The bottom ash may be buried or used for civil works because, having experienced temperatures above 1000°C, it typically contains between 4 and 13 μg_{ITEQ} t^{-1} of dioxins (Abad et al 2002, Grosso et al 2007). There is little variation across WTE units. In comparison, the amount of PCDD/F present in the MSW is between 1.3 and 50 μg_{ITEQ} t^{-1}. However, the bottom ash represents only 20 to 30% of the mass of the initial MSW. Accepted guidelines for the PCDD/F content of soils is 3.9 pg_{ITEQ} g^{-1} i.e. 3.9 μg_{ITEQ} t^{-1} for residential soils, and 27 μg_{ITEQ} t^{-1} for industrial soils (Colson 2003). The flyash, including the activated carbon, is stabilised with cement to fix the metals, and buried in a secure landfill. This flyash constitutes only 1 to 2 % of the mass of the initial MSW. In the case of high contents in a feed MSW, a WTE plant can be net destroyer of dioxins.

The intake of PCDD/F by inhalation from WTE

The likely intake of PCDD/F by respiration of emissions from a WTE plant by a neighbour was roughly estimated by Porteous (2005), who considered the emission limit of 0.1 $ng_{ITEQ}Nm^{-3}$, the likely dilution factor at neighbouring ground level and the volume of air respired by human lungs. The resulting intake was 20 pg per annum, which is 0.04 % of the recommended WHO tolerable daily dose for a 70 kg person (van Leeuwen et al 2000). This finding is consistent with those of Reis et al (2007), who measured the dioxin levels in the blood of sample populations living near two WTE plants in Portugal. They found no significant difference between the samples and reference samples living remote from the plants. In fact the neighbours to a plant in the Azores contained blood levels about 60% of those in the reference sample in Lisbon, a large city. A similar negative result was obtained by a study of the impact on the surrounding inhabitants of a hazardous waste destruction unit in Spain (Ferré-Huguet et al, 2006).

When the impact of a gaseous emission is considered for licensing purposes, it is mandatory to carry out a dispersion modelling exercise. This calculates the likely concentrations at ground level around the source, using a turbulent dispersion model such as Ausplume. The emission rate of the pollutant in question, the meteorological conditions and the prevailing wind patterns are necessary inputs to this model.

Such an exercise was carried out for PCDD/F around the French city of Besançon in the valley of the Doubs river (Floret et al 2006). The WTE plant there has been in service since 1971, but the older more polluting furnaces have been shut down. Current emissions are much lower than those responsible for the historical deposition on surrounding soils. The river has cut a gorge through the limestone formations of the area, so that the prevailing winds blow either up the valley or down it. This makes modelling easier, and produces a distribution plot around the plant as shown in Figure 3. The predicted concentrations are extremely low, with a maximum contour range of 0.0004 to 0.0016 pg per m^3, and fall rapidly away from the plant.

The model was used not to study the PCDD/F inhaled, but that deposited on the ground. It therefore is concerned with the fallout of particulates carried away in the plume by the wind. Surface soil samples to a depth of 10 cm were taken at all the points marked with a black dot in Figure 3; there were 75 in total. The values ranged from 28.6 pg_{WTEQ} per kg of soil adjacent to the plant to 0.25 pg at the remotest points. Acceptable correlation between the predicted fallout and soil concentrations were found with the simple terrain to the northeast, but not with more complex terrain to the southwest. It was found that the PCDD/F concentrations in these soil samples were all within accepted limits for daily consumption . The only possible concern was the case for long-term residents living next to the plant who grew and ate their own vegetables over an extended period.

The most mechanism of PCDD/F intake is therefore not by inhalation, but through ingestion with food. The WHO website puts the figure for food at > 90 % of the total, and it is given as 99 % by Vahlberg et al (1996). This figure was arrived at by considering all the routes for takeup, with the contribution of the food chain being considered via the amounts of various foods eaten, and their typical PCDD/F concentrations.

The dioxin contents of four commercial meat samples, namely young chickens, young turkeys, market hogs and steers/heifers, which were analysed in the USA are reproduced in Table 1 (Hoffman et al 2006). The ITEQ values are reported in two columns, one with non-detect congeners shown as zero concentration, and the other with non-detect concentrations arbitrarily allocated to 0.5 of the detection limit. As expected, the latter show higher values. It can be seen from Table 1 that the concentrations in the first three species have decreased from the mid-nineties to 2003, while that in beef may have increased. The values in Australian meats were found to be similar, Table 1 (ADEH 2004).

PCDD/F becomes concentrated in lipids (body fat) after ingestion, with an estimated half-life in humans of 7 years (Mocarelli 2001). Its impact on living organisms is probably greater at a younger age, so that early nutrition assumes some importance. Hsu et al (2007) analysed breast milk donated by 37 Taiwanese women, and formula milk sourced from seven different countries. The WTEQ concentrations in formula milk are presented in Figure 4, and in average contain around 0.7 ng kg^{-1} of lipid. Breast milk was on average about 20 times higher in PCDD/F content than the formulas, with a mean of 15 ng kg^{-1} of lipid.

The concentration of WTEQ in the general population of Finland was evaluated by Kiviranta et al (2005) through samples taken from 420 participants. The mean concentration was found to be 29 ng_{WTEQ} per kg of body fat, higher than most Western countries. One important correlator was with the amount of fish eaten which originated in the Baltic Sea, especially Baltic herring. A correlation between residential location of the subject in relation to the Baltic and the content in mother's milk was also found.

The concentrations of PCDD/F in a range of Australian foods was found to be 15 to 20% of the EU standard maximum (ADEH 2004). The situation with fish was better, with a figure of only 5.7%. The mean concentration in Australia is about 11 ng_{WTEQ} per kg of body fat, and due to bio-accumulation, the values increase with age, see Figure 5 (ADEH 2000). There was little difference between the values of city and country dwellers, between genders and between geographical locations.

The situation regarding the impact of WTE emissions on ambient dioxins is summed up by Hassanin regarding his grass analyses: 'The declines in PCDD/F levels in these samples (a) pre-date the introduction of emission control measures on incinerators and other combustion sources in the UK; (b) appear to have been largely unaffected by them'. Similarly, Reis et al (2007) report after a study of the neighbours of two WTE plants in Portugal: 'Findings from this investigation also suggest that incineration does not impact on dioxin levels of nearby residents'.

As a result of their study, Ferré-Huguet et al (2006) conclude 'The comparison of the PCDD/F congener profiles corresponding to the baseline and current surveys as well as the human health risk assessment suggests that the HWI studied here does not mean additional risks either to the environment or to the population living in the vicinity of the facility. In fact, according to the results of a number of studies carried out in recent years from various countries it seems quite evident that the public concern over health risks due to exposure to PCDD/Fs emitted by modern MSWIs may be scientifically unjustified'. Finally, even the extreme toxicity of dioxins is open to question. For instance, the outcome of the Seveso incident in northern Italy, where significant exposures to TCDD were experienced by the local population after a runaway reaction in a pesticide manufacturing plant should be noted. In a report 23 years later by the supervising doctor (Mocarelli 2001), 'no clear-cut effects attributable to TCDD, besides chloracne have been observed'.

Conclusion

Dioxins or PCDD/F are distributed widely in nature, both in soils and vegetation as a result of fires, and naturally in some clays. They are present in both city and country air. The PCDD/F content of soils and vegetation is decreasing with time in industrialised areas, but remains roughly constant in remote areas. MSW contains significant amounts of PCDD/F. Estimates of the contribution of a WTE plant to the intake of PCDD/F to the human population near the emission source is miniscule, as the major source is through food. A wide range of foods such as meat, fish and dairy products all contribute to the burden. Concern about dioxin emissions should not constitute a reason for opposing the construction of a state-of-the-art WTE plant. In fact these plants can be net destroyers of dioxins.

References

Abad E., Adrados M.A., Caixach J. and **Rivera J.** (2002) "Dioxin abatement strategies and mass balance at a municipal waste management plant" Environ Sci Technol. 36, 92 - 99

ADEH, Australian Dept of Environment and Heritage, National Dioxins Program, Technical Reports (2004)

Choi K-I and **Lee D-H** (2006) "PCDD/F in leachates from Korean MSW landfills" Chemosphere 63, 1353-1360

Colson C.L. (2003) Internal report, Visy Ltd

Consonni S., Giugliano M. and **Grosso M.** (2005) "Alternative strategies for energy recovery from municipal solid waste. Part B: Emission and cost estimates" Waste Manage 25, 137-148

Correa O., Raun L., Rifai H., Suarez M., Holsen T. and **Koenig L.** (2006) "Depositional flux of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in an urban setting" Chemosphere 64, 1550-1561

Eduljee G.H., Dyke P. and **Cains P.W.** (1997) "The effect of changing waste management practices on PCDD/F releases from household waste recycling and disposal processes" Chemosphere, 34, 1615-1622

Ferré-Huguet N., Nadal M., Schumacher M. and Domingo J.L. (2006) "Environmental impact and human health risks of polychlorinated –*p*-dioxins and dibenzofurans in the vicinity of a hazardous waste incinerator: A case study" Environmental Science and Technology, 40, 61-66

Floret N., Viel J-F., Lucot E., Dudermel P-M., Cahn J-Y., Badot P-M. and **Mauny F.** (2006) "Dispersion modelling as a dioxin exposure indicator in the vicinity of a municipal solid waste incinerator. A validation study" Environmental Science and Technology 40, 2149-2155

Gadomski D., Tysklind M., Irvine R.L., Burns P.C. and **Andersson R.** (2004) "Investigations into the vertical distribution of PCDDs and mineralogy in three ball clay cores from the United States exhibiting the natural formation pattern" Environmental Science and Technology 38, 4956-4963

Gaus C, Brunskill G.I., Weber R., Päpke O. and **Müller J.F.** (2001) "Historical PCDD inputs and their source implications from dated sediment cores in Queensland (Australia)" Environmental Science and Technology 35, 4597-4603

Grosso M., Cernuschi S., Giugliano M., Lonati G. and **Rigamonti L.** (2007) "Environmental release and mass flux partitioning of PCDD/Fs during normal and transient operation of full scale waste to energy plants" Chemosphere 67, S118-S124

Giugliano M., Cernuschi S., Grosso M., Miglio R. and Aloigi E. (2002) "PCDD/F mass balance in the flue gas cleaning units of a MSW incineration plant" Chemosphere 46, 1321-1328

Hassanin A., Lee R.G.M., Johnston A.E. and **Jones K.C.** (2006) "Reductions and changing patterns of ambient PCDD/Fs in the UK: Evidence and implications" Chemosphere 65, 530-539

Hoffman M.K., Huwe J., Deyrup C.L., Lorentzsen M., Zaylskie R., Clinch N.R., Saunders P. and **Sutton W.R.** (2006) "Statistically designed survey of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and co-planar polychlorinated biphenyls in U.S. meat and poultry 2002-2003: Results, trends and implications" Environmental Science and Technology 40, 5340-5346

Holmstrand H., Gadomski D., Mandalakis M., Tysklind M., Irvine R.L., Andersson P. and **Gustafsson Ö** (2006) "Origin of PCDDs in ball clay assessed with compound-specific chlorine isotope analysis and radiocarbon dating" Environmental Science and Technology 40, 3730-3735

Hsu J-F., Guo Y-L, Liu C-H., Hu S-C., Wang J-N. and **Liao P-C.** (2007) "A comparison of PCDD/Fs exposure in infants via formula milk or breast milk feeding" Chemosphere 66, 311-319

Kiviranta H., Tuomisto J.T., Tuomisto J., Tukiainen E. and **Vartiainen T.** (2005) "Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls in the general population in Finland" Chemosphere 60, 854-869

Lin L-F., Lee W-J., Li H-W., Wang M-S. and **Chang-Chien** G-P. (2007) "Characterisation and inventory of PCDD/F emissions from coal-fired power plants and other sources in Taiwan" Chemosphere 68, 1642-1649

Meharg A.A and **Killham K.** (2003) "A pre-industrial source of dioxins and furans" Nature 42 Feb27, 909-10

Mocarelli P. (2001) "Seveso – a teaching story" Chemosphere 43, 391-402

Porteous A. (2005) "Why energy from waste incineration is an essential component of environmentally responsible waste management" Waste Management 25, 451-459

Prange J.A., Gaus C., Päpke O. and **Müller J.F.** (2002) "Investigations into the PCDD contamination of topsoil, river sediments and kaolinite clay in Queensland, Australia" Chemosphere 46, 1335-1342

Prange J.A., Gaus C., Weber R., Päpke O. and **Müller J.F.** (2005) "Assessing forest fire as a potential PCDD/F source in Queensland, Australia" Environmental Science and Technology 37, 4325-4329

Reis M.F., Miguel J.P., Sampaio C., Aguiar P., Melim J.M. and **Päpke O.** (2007) "Determinants of dioxins and furans in blood of non-occupationally exposed populations living near Portuguese solid waste incinerators" Chemosphere 67, S224-S230

Taucher J.A., Buckland S.J., Lister A.R., Porter L.J. and **Ferguson C.** (1992) "Levels of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in ambient air in Sydney, Australia" Chemosphere 25, 1361-1365

Vahlberg P.A., Drivas P.J., McCarthy S. and Watson A.Y. (1996) "Evaluating the health impacts of incinerator emissions" J Hazardous Materials, 47, 205-227

van Leeuwen R.X.F., Feeley M., Schrenk D., Larsen J.C., Farland W. and **Younes M.** (2000) "Dioxins: WHO's tolerable daily intake revisited" Chemosphere 40 1095-1101

Table 1 ITEQ Contents of four commercial meats (USA)
(ng_{ITEQ} per kg)

Class	Mid-1990s		2002-2003		Change (%)		Australia 2003
	* 0	½ LOD	* 0	½ LOD	* 0	½ LOD	
young chickens	0.65	0.94	0.22	0.29	- 66	- 69	0.33
young turkeys	1.32	1.53	0.55	0.59	- 58	- 61	-
market hogs	0.40	1.47	0.15	0.23	- 63	- 84	0.33
steers/heifers	0.68	1.38	0.83	0.87	+ 22	- 37	0.56

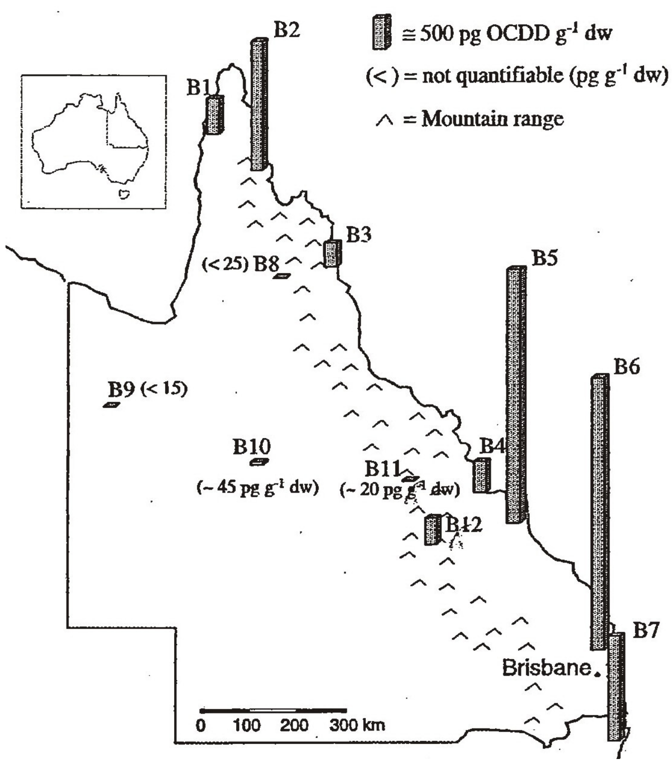

Figure 1 Natural PCDD/F concentrations in Queensland soil (ng kg^{-1} dry)

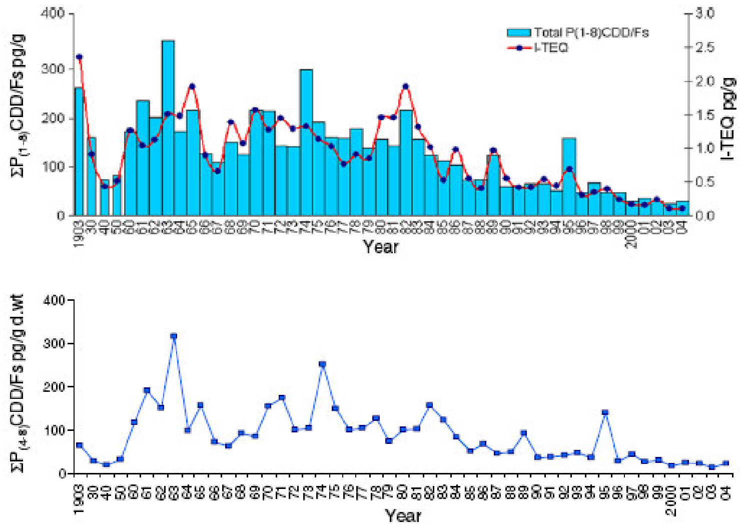

Figure 2 The 100 year history of the PCDD and PCDF content of grass in the UK

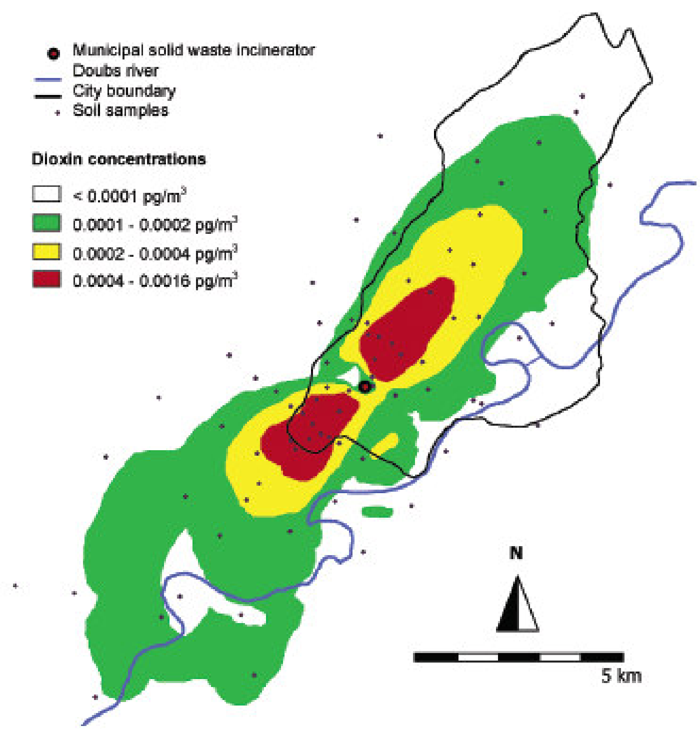

Figure 3 The concentration of PCDD/F in the air around a WTE plant in Besançon, France

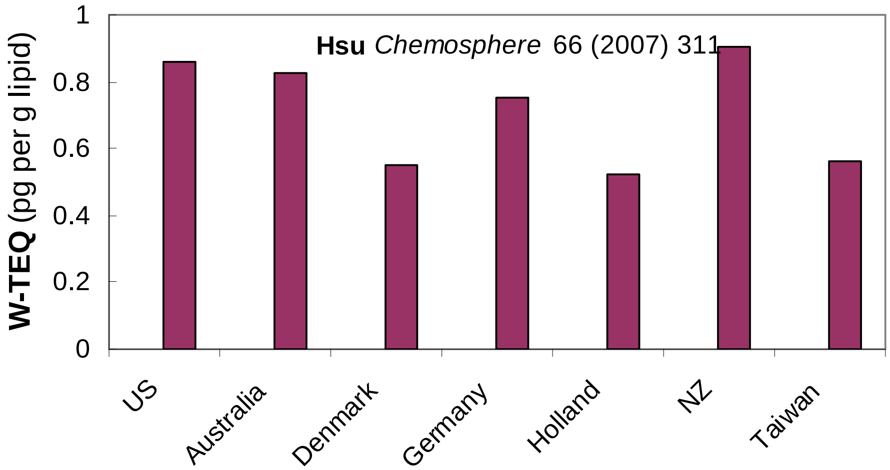

Figure 4 The WTEQ content of formula milk powders from 7 countries

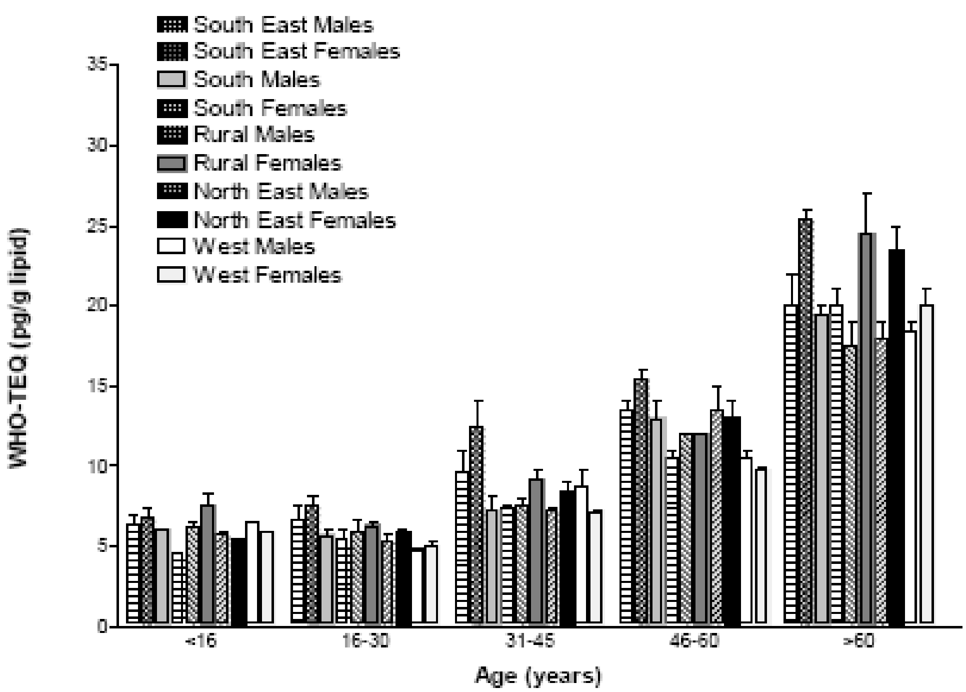

Figure 5 The WTEQ content in fat of the general Australian population by age
(the age groups range from 16 to 80+)