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Review of data relating to potential pollution of soil and effects on plants around a proposed biomass power plant at Manjimup, Western Australia

10th April 2008 (update)
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Prepared for Connell Wagner Pty Ltd

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1 Executive Summary

- This review was initiated by Connell Wagner Pty Ltd who requested CSIRO Land and Water to review the potential effects of pollutants predicted to be emitted from a proposed biomass power station at Manjimup, Western Australia, on plants and agricultural crops in the surrounding area.

- Several sources of contaminants and data for the atmospheric emissions from the proposed biomass power plant (BPP) were reviewed, namely particulates, nitrogen and sulfur oxides, persistent organic compounds, and (non-organic) trace elements (inorganic contaminants). Hazard quotients (HQs) were predicted for contaminants accumulating in soil over the life of the plant, using predicted environmental concentrations (PECs) and predicted no-effect concentrations (PNECs) derived from regulatory benchmarks.
- Particulates exert no direct toxicity to soil through physical effects as soil is composed primarily of particulate material – toxicity of particulates in soil is related wholly to chemical composition and transformations after deposition. To date, no jurisdiction has considered the hazard posed by particulates to the environment as significant enough to warrant development of air quality or soil quality PNECs to protect the environment. It was therefore difficult to assess hazard as no benchmarks are available against which to judge predicted emission data, but review of the literature indicated hazards are likely low, and restricted to areas very close to the plant.

- The predicted direct toxicity hazards from SO_2 emissions to plants and crops are predicted to be negligible. Intermittent and infrequent emissions (2% time) of SO_2 from the BPP could approach the WHO 24-hour air quality guideline (AQG) value (0.007 ppm), but this is a human-health based AQG and the hazard to crops cannot be assessed from this predicted HQ.
- The predicted direct toxicity hazard from NO_2 emissions to plants and crops are predicted to be acceptable. As the HQ varies from 0.3 to 0.5 (depending on whether background NO_2 is included), it is suggested that monitoring of NO_2 emissions be undertaken once the plant is operating to ensure predicted emissions are in line with actual emissions, and that actual emissions are within regulatory limits. Acidification of soils due to deposition of NO_2 and SO_2 was predicted to be negligible.

- The predicted soil toxicity hazards from PCDD/Fs emissions to agricultural crops are predicted to be negligible as the HQ is <0.1.

- It was not possible to predict hazard due to emission of PAHs to agricultural crops/plants as no ecological PNECs are available against which to judge predicted emission data and predicted soil concentrations. Given their physicochemical behaviour in soils, and the low increase in soil concentrations due to BPP emissions, predicted direct toxicity to plants is unlikely.

- For inorganic contaminants, predicted hazards posed by lifetime accumulation of As, Cd, Cu, Cr(III and VI), Hg, Ni, Pb, Se and Zn in soil due to emissions from the BPP are small. HQs could not be calculated as Australian PNECs for maximum soil concentrations of B, Co, Cr(VI), Fe, K, Mo, Na, P, Sb, and Ti are not available for phytotoxicity endpoints. However, hazards from these elements are also likely to be low due to:

    - the small predicted accumulation of contaminant in relation to ambient background concentrations;

    - the fact that some of these elements are structural components of soil minerals present in abundance in most soils and known to have low toxicity (Fe, K, Mn, Na, and P); and

    - many of the contaminants (Co, Ti) have low solubility or high soil:solution partitioning values which limit mobility and toxicity in soil.

2 Introduction

This review was initiated by Connell Wagner Pty Ltd (CW) in an E-mail dated 12th February 2008 with attached letter dated 7th February 2008 from Dr Neil McKenzie of CW to Prof. M.J. McLaughlin of CSIRO Land and Water (CSIRO). Terms of the review were confirmed in an E-mail from CSIRO to CW dated 11th March 2008 and accepted by CW via E-mail on 11th March 2008.

CSIRO agreed to deliver a report to CW detailing effects of pollutants from a proposed biomass power station at Manjimup, Western Australia, on plants in the surrounding area. The agreed time to review reports and prepare an assessment was three days.

Several sources of data and information were received from CW.

1) A report on air quality titled “Air Quality PER extract-nm” received via E-mail as a pdf file on 7th February 2008.

2) A letter requesting review titled “PER Cover Letter CSIRO Land and Water” received via E-mail as a pdf file on 7th February 2008. These data were subsequently updated (see 12, 13, 14 and 17 below).

3) A report titles “Draft Geotech Report – Golders” received via E-mail as a pdf file on 11th March 2008.

4) A letter titled “Biomass Power Station - GLC Qualification for Other Pollutants” received via E-mail as a pdf file on 11th March 2008.

5) A letter titled “Biomass Power Station - GLC Qualification for Other Pollutants” received via E-mail as a pdf file on 13th March 2008.

6) A report from Provisor’s investigation titled “Biomass Power Station – Air Pollution Effects on Grapes” ” received via E-mail as a pdf file (“Report Final Version”) on 13th March 2008.

7) A report/letter titled Report to Dan Pannell 140208” received via E-mail as a pdf file on 13th March 2008.

8) A report by Toxikos titled “Preliminary health risk assessment of air emissions from proposed Biomass Power Station, Manjimup” received via E-mail as a pdf file (“BPS HRA_TR170208-R3_130308 V3 SENT”) on 16th March 2008.

9) A report by Dr R.E. Smart titled “ Report on the possibility of air pollution from a biomass power station affecting neighbouring vineyards and wineries” received via E-mail as a Microsoft Word file (“Report Biomass burning 2”) on 16th March 2008.

10) Excel spreadsheet titled “SO_2 deposition calculation.xls” received via E-mail 19th March 2008.

11) Data on revised NO_2 deposition data received in an E-mail dated 30th March 2008.

12) Data on revised SO_2 deposition data received in an E-mail dated 1st April 2008.

13) Revised data in MS Word file titled "update table BPS_csiro.doc" received via E-mail 1st April 2008.

14) Revised data in MS Word file titled "Update(horticultural assessment) 040408.doc" received via E-mail 4th April 2008.

15) Data on revised NO_2 deposition data received in an E-mail dated 7th April 2008.

16) Revised data on pollutant emissions received in MS Word file "csiro.doc" via E-mail on 8th April 2008.

3 Scope of this review

Several sources of contaminants and data for the atmospheric emissions from the proposed biomass power plant (BPP) were reviewed, namely:

a) Particulates;

b) Nitrogen and sulfur oxides;

c) Persistent organic compounds; and

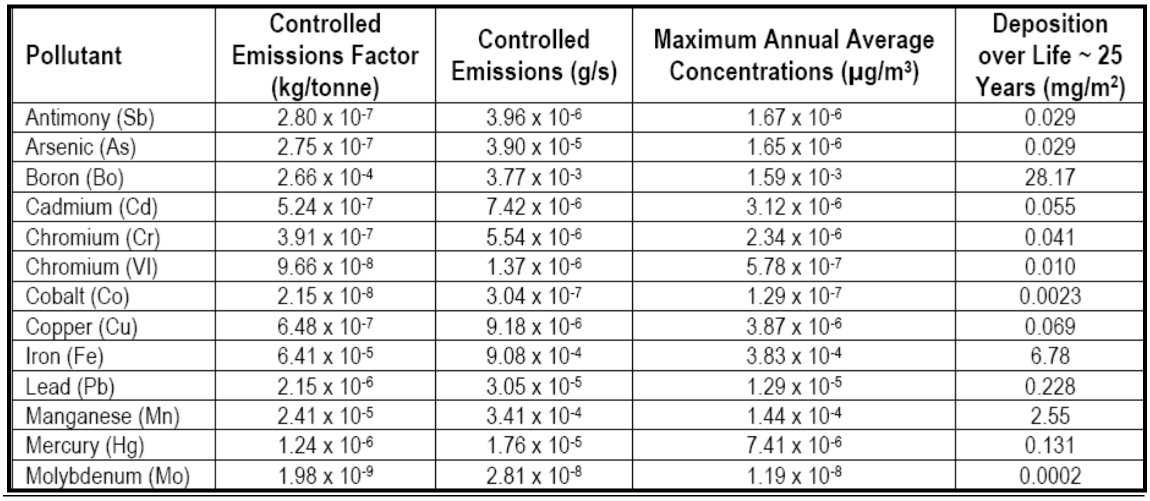
d) Non organic trace elements (inorganic contaminants).

4 Hazard identification

The information and reports provided by CW (see Section 2) identified several potential hazards to plants/ agricultural crops in the region as a result of emissions from the proposed BPP.

Hazard identified in relation to inorganic contaminants are outlined in Table 1.

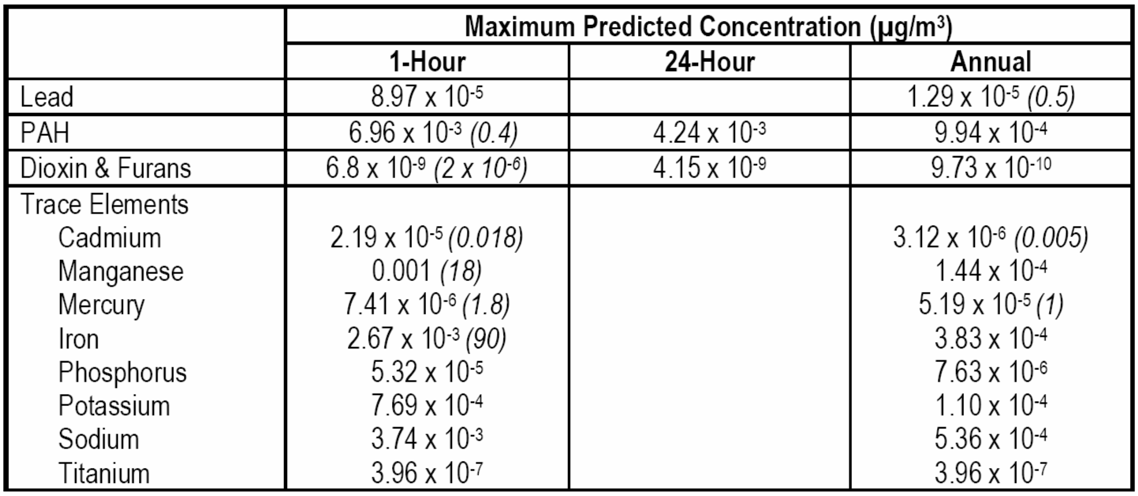
Table 1. Inorganic elements emitted from the proposed BPP and deposited on soils assuming a 22km by 22km deposition blanket (Source 5, Section 2).



Pollutant	Controlled Emissions Factor (kg/tonne)	Controlled Emissions (g/s)	Maximum Annual Average Concentrations (µg/m³)	Deposition over Life ~ 25 Years (mg/m²)
Antimony (Sb)	2.80×10^{-7}	3.96×10^{-6}	1.67×10^{-6}	0.029
Arsenic (As)	2.75×10^{-7}	3.90×10^{-5}	1.65×10^{-6}	0.029
Boron (Bo)	2.66×10^{-4}	3.77×10^{-3}	1.59×10^{-3}	28.17
Cadmium (Cd)	5.24×10^{-7}	7.42×10^{-6}	3.12×10^{-6}	0.055
Chromium (Cr)	3.91×10^{-7}	5.54×10^{-6}	2.34×10^{-6}	0.041
Chromium (VI)	9.66×10^{-8}	1.37×10^{-6}	5.78×10^{-7}	0.010
Cobalt (Co)	2.15×10^{-8}	3.04×10^{-7}	1.29×10^{-7}	0.0023
Copper (Cu)	6.48×10^{-7}	9.18×10^{-6}	3.87×10^{-6}	0.069
Iron (Fe)	6.41×10^{-5}	9.08×10^{-4}	3.83×10^{-4}	6.78
Lead (Pb)	2.15×10^{-6}	3.05×10^{-5}	1.29×10^{-5}	0.228
Manganese (Mn)	2.41×10^{-5}	3.41×10^{-4}	1.44×10^{-4}	2.55
Mercury (Hg)	1.24×10^{-6}	1.76×10^{-5}	7.41×10^{-6}	0.131
Molybdenum (Mo)	1.98×10^{-9}	2.81×10^{-8}	1.19×10^{-8}	0.0002

In addition, data on emissions of nitrous and sulfur oxides, particulates, polyaromatic hydrocarbons and dioxins/furans were also provided (Table 2).

Table 2. Predicted air concentrations of oxides of sulfur, and persistent organic contaminants emitted from the proposed BPP, with NSW regulatory levels for ambient air quality in parentheses (Source 16, Section 2).



	Maximum Predicted Concentration (µg/m³)		
	1-Hour	24-Hour	Annual
Lead	8.97×10^{-5}		1.29×10^{-5} *(0.5)*
PAH	6.96×10^{-3} *(0.4)*	4.24×10^{-3}	9.94×10^{-4}
Dioxin & Furans	6.8×10^{-9} *(2×10^{-6})*	4.15×10^{-9}	9.73×10^{-10}
Trace Elements			
Cadmium	2.19×10^{-5} *(0.018)*		3.12×10^{-6} *(0.005)*
Manganese	0.001 *(18)*		1.44×10^{-4}
Mercury	7.41×10^{-6} *(1.8)*		5.19×10^{-5} *(1)*
Iron	2.67×10^{-3} *(90)*		3.83×10^{-4}
Phosphorus	5.32×10^{-5}		7.63×10^{-6}
Potassium	7.69×10^{-4}		1.10×10^{-4}
Sodium	3.74×10^{-3}		5.36×10^{-4}
Titanium	3.96×10^{-7}		3.96×10^{-7}

Predicted emissions of SO_2 were also provided as follows (Source 2, Section 2).

Time period	µg/m³
1-hour	1.1
24-hour	0.3
Annual	0.3

Predicted emissions of nitrogen dioxide (NO_2) are shown in Table 3.

Table 3. Data for NO_2 and SO_2 emissions were also provided for NO_2 on 7th April 2008 (Source 16, Section 2) and for SO2 on 8th April 2008 (Source 16, Section 2) as follows.

Averaging period	NO_2 Ground Level Concentration (GLC) (ppb)			NEPM criteria
	Maximum	98th percentile	95th percentile	
1 hour	34.3	8.38	3.78	120
24 hour	12.9	0.38	-	-
Annual	1.66	-	-	30

Averaging Period	**SO_2 Ground Level Concentrations (ppb)**			**NEPM Criteria (ppb)**
	Maximum	**98th Percentile**	**95th Percentile**	
1 hour	27.8	4.17	1.74	200
24 hour	6.83	0.03		80
Annual	0.58			20

Annualised pollutant emissions of NO_x, particulates (PM10 – particles less than 10µm in diameter), sulfur dioxide (SO_2) and selected elements in relation to other point-source and diffuse-source emissions in the same area are shown in Table 4.

Table 4. Annualised pollutant emissions of NO_x, PM10, SO_2 and inorganics in relation to other point-source and diffuse-source emissions in the same area (Source 16, Section 2).

Pollutant (kg/yr)	**Industrial Sources**			**Diffuse Sources**	
	Biomass	**Sons of Gwalia**	**GUNNS**	**Shire of Manjimup**	**Bunbury Air Shed**
NO_x	850,000	70,000	8,000	1,400,000	66,000,000
PM10	56,700	290,000	26,000	16,000,000	170,000,000
SO_2	189,200	75,000	40	20,000	70,000,000
VOCs	58,700	5,500	720	12,000,000	140,000,000
CO	378,000	60,000	5,600	5,300,000	130,000,000
Lead	0.96	7.6	4.4	51,000	410,000
Dioxins/Furans	0.000073	0	0.00026	0.00026	0.0051
PAH	74	0.56	15	3,100	70,000
Trace Elements					
Manganese	10.8	750		58,800	510,000
Iron	28.6				
Phosphorus	0.57				360,000
Potassium	8.23				
Sodium	40.0				
Titanium	0.03				

Depositional life data were provided for NO_x (Source 10, Section 2) and SO_2 (Source 12, Section 2) pollutants, and were estimated as follows assuming a 22 km by 22 km deposition blanket:

SO_2 1935 mg/m^2/25y (wet+dry deposition)

NO_2 1293 mg/m^2/25y

5 Contaminant exposure pathways

For each element, depending on their physicochemical properties, their concentration in the combustion emissions, the extent of the contamination, the nature of the soil, the cropping system or land management, different exposure pathways will dominate. McLaughlin et al. (2000) suggested a prioritisation of the key risk pathways for several heavy metals in soil (Table 5).

It is important that the various pathways be considered and the priority risk pathways be identified for further evaluation in this review. This is a key action for defining the focus and scope of any subsequent risk assessment.

Table 5. Critical risk pathway assessment for heavy metal pollution of soils (McLaughlin et al., 2000).

Metal	Dominant risk pathway	Secondary risk pathway
Cd	Food chain transfer	Phyto- and eco-toxicity
Co	Food chain transfer	Phyto- and eco-toxicity
Cr	Phyto- and eco-toxicity	Leaching
Cu	Phyto- and eco-toxicity	Soil ingestion by animals/humans
Fe	Phyto- and eco-toxicity*	None
Hg	Soil ingestion by animals/humans	Leaching
Mn	Phyto- and eco-toxicity	Soil ingestion by animals/humans
Ni	Phyto- and eco-toxicity	Soil ingestion by animals/humans
Pb	Soil ingestion by animals/humans	Phyto- and eco-toxicity
Zn	Phyto- and eco-toxicity	Food chain transfer

* only in acid soils under reducing condition

A conceptual diagram of exposure pathways for atmospheric emissions from the BPP at Manjmup to plants/agricultural crops in the regions is shown in Figure 1.

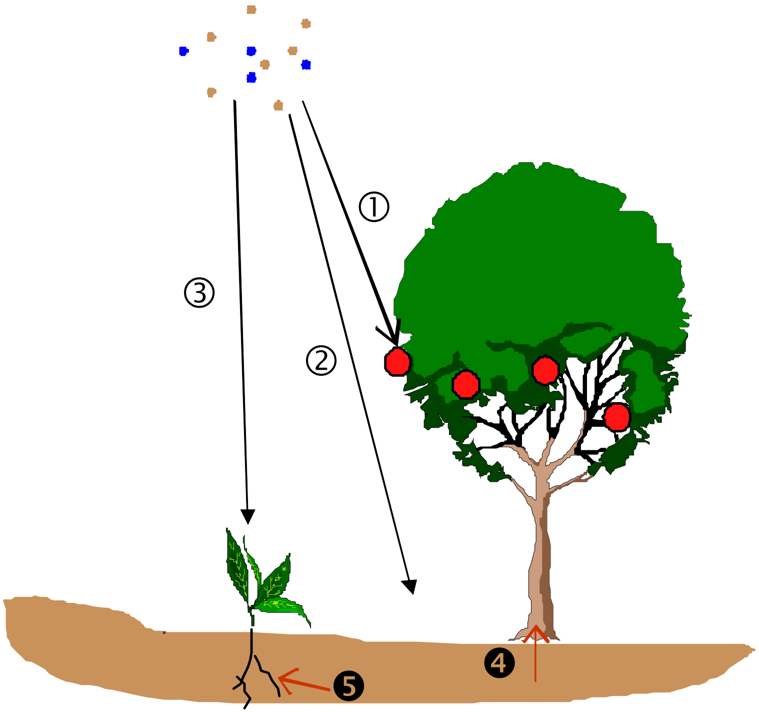


Figure 1. Exposure pathways considered for wet (blue) and dry (brown) deposition of contaminants to soil/plants.
① = direct deposition to fruit
② = direct deposition to soil and accumulation
③ = direct deposition to leaves
④ = plant uptake of contaminants by perennials
⑤ = plant uptake by annuals/vegetables

Pathway ① is of concern in relation to food quality (contamination of produce by dust and aerosols), pathway ② is of concern from soil accumulation of contaminants over the life of the BPP and potential adverse effects on plant growth, pathway ③ may affect both plant growth and food quality, and pathways ④ and ⑤ represent the exposure route through which soil accumulation affects root growth (and hence crop production), or plant uptake of contaminants (and hence food quality).

In general, plant uptake of surface accumulated soil contaminants by perennial species (④) is much less than annual species (⑤), due to their deeper rooting depth. Furthermore, foods produced by perennial species (usually fruits) also provides an additional barrier to contaminant transport to the food chain, as contaminants must pass from xylem (the transpirational water flow from roots to shoots) to phloem (which fills fruits). Hence exposure pathway ⑤ is higher risk than ④ for most of the contaminants listed in Section 4. Exceptions would be B, Cr(VI), and Se which are relatively more mobile.

Surface deposition of contaminants on plants/foods affecting food quality (pathways ① and ③) are limited to specific contaminants where terrestrial food quality standards exist in Australia (As, Cd, and Pb) (FSANZ - Food Standards Australia New Zealand, 2005), and direct toxicity effects of contaminants on plant function that could potentially affect crop production are also covered by these pathways. Gaseous contaminants (SO_2, NO_x) have a much greater chance of affecting plant function than particulate contaminants, due to ease of entry through stomata and cuticles (Saxe, 1994).

Phytotoxicity and soil-root-food transfer of contaminants (pathways ②, ④ and ⑤) relates to all soil-deposited contaminants, with certain contaminants presenting predominantly food quality hazards (i.e. As, Cd) while others present predominantly phytotoxicity hazards (e.g. B, Cu, Zn). This relates to the behaviour of the contaminant after addition to soil, and to the acquisition and transport characteristics of contaminants by plants (McLaughlin et al., 1996).

6 Physicochemical characteristics of contaminants that affect their uptake from soil and potential phytotoxicity

Under most conditions, the surfaces of the solid phase of soils are negatively charged that attracts positively charged elements or species to the solid phase and decreases their bioavailability and mobility (Figure 2).

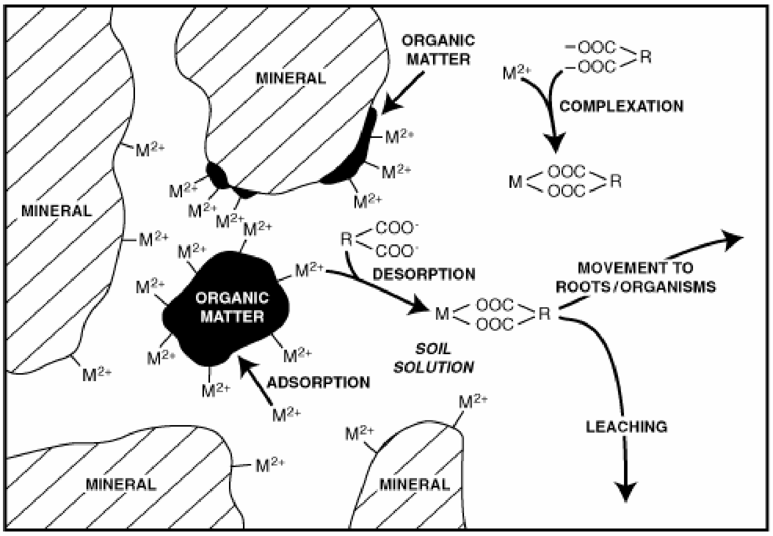


Figure 2. Soil binding sites and behaviour of a divalent cationic contaminant (M^{2+}) in soils.

These solid phases are aluminosilicate clay minerals, oxides and organic matter particles. In contrast, negatively charged species are repelled by the negative charges on the soil solid phase and so tend to remain in the aqueous phase which renders them highly bioavailable and mobile, except in net positively charged soils (e.g. oxide-rich subsoils) at low pH. Furthermore, the soil pH affects the binding of cationic and anionic species differently. In low pH soils, which are defined by an excess of positively charged H^+ ions, the H^+ competes with other cations for binding to the negatively charged sites on the soil solid phase, and so solubility of these cations tends to increase as the soil pH decreases. The same process causes the solubility of anions to decrease as the soil pH decreases because binding of H^+ ions to the solid phase decreases the negative charge on the solid phase. For this reason, soil pH has been termed a master variable in determining the fate of contaminants added to soil.

Iron and Mn oxides are markedly affected by soil redox potential and undergo both oxidation and reduction depending on soil conditions. This has important implications for the bioavailability and toxicity of Fe and Me as well as the many contaminants sorbed by their oxides.

A few key parameters are primarily responsible for determining availability/mobility of contaminants in the environment and the overall outcome of these can be assessed in part by looking at contaminant solubility in water, partitioning between soil gaseous-, aqueous- and solid-phases.

Solubility in water for a contaminant compound is described by a solubility product (K_{sp}), which is the molar product of the aqueous activities of the compounds constituent elements. Some contaminants have extremely insoluble compounds with very low K_{sp} values e.g. Pb, zirconium, so that these elements, when added to soil, form solid phase precipitates. Some schools of endeavour in soil science contend that all element availability in soils can be described by precipitation/dissolution-type reactions (Lindsay 1979).

The distribution of chemicals between aqueous and solid phases of soils can be described by the partitioning coefficient (the notation for this is Kd or Koc) where a high Kd or Koc indicates a high level of sorption to the soil solid phase relative to the concentration in the aqueous phase. Henry's Law determines the distribution of a contaminant between aqueous and gaseous phases of a soil.

$$Kd = \frac{\text{Contaminant on soil solid phase}}{\text{Contaminant in soil solution}}$$

and

$$Koc = \frac{\text{Contaminant on organic carbon}}{\text{Contaminant in soil solution}}$$

It must be stressed that partition coefficients are not constants, as they vary across soils due to variation in the amount and type of clay and organic matter, and due to the effect of soil pH on soil surface charge, and charge of the contaminant, and the effect of redox on soil surface properties and on oxidation state of elements or compounds with redox dependent behaviour e.g. As, Se.

Soil-contaminant interactions characterised by high Kd values mean that soils have high sorption or buffering capacities for added contaminants i.e. the ability of the soil solid-phase to maintain constant concentrations of contaminants in the soil solution through sorption reactions. The buffering capacity is an integrated measure of the total amount of contaminant, as well as the number and the strength of binding sites for that contaminant in the soil. The buffering capacity of a soil is derived from the charged components, which include iron and aluminium oxides, carbonates, clays and organic carbon.

Because of the preponderance of oxide materials in tropical soils, they tend to have amongst the highest buffering capacities (Kd) for cationic contaminants of all soil types at neutral to alkaline pH. In soils with a high buffering capacity, the phytoavailability of contaminants is limited.

6.1 Inorganic contaminants

As noted above, the behaviour of inorganic contaminants is determined largely by the contaminant's key physical and chemical characteristics (solubility, charge, redox state, etc.).

Many of the common contaminants in soils, in particular the heavy metals, are cationic in nature e.g. Cd, Cu, Ni, Pb, Zn, etc. (Table 6). The predominant charge on most metal contaminant ions is 2+. For this reason, bioavailability and mobility through soil, are determined primarily by soil pH, and are enhanced under acidic soil conditions. Compared to the alkali earth cations (e.g. Ca, Mg), most metals have high partition coefficients and are sorbed much more strongly to soil.

Table 6. Physical and chemical properties of 'heavy metals' (McLaughlin 2002).

Element	Symbol	Atomic No.	Atomic weight	Valence	Natural isotopes	Density (Mg m^{-3})	Melting point (^oC)	Dominant species in soil	Dominant species in soil solution	
									pH 3.5-6.0	pH 6.0-8.5
Cadmium	Cd	48	112.41	2	8	8.65	321	Cd^{2+}	Cd^{2+}, $CdCl^+$, $CdSO_4^0$	Cd^{2+}, $CdCl^+$, $CdSO_4^0$
Chromium	Cr	24	52.01	2,3,6	4	7.19	1,875	Cr^{3+},CrO_4^{2-}	Cr^{3+}, $CrOH^{2+}$	$Cr(OH)_{4-}$
Cobalt	Co	27	58.94	2,3	1	8.90	1,493	Co^{2+}	-	-
Copper	Cu	29	63.54	1,2	2	8.94	1,083	Cu^{2+}	Cu^{2+}, Cu-org.	Cu-hydroxy species, $CuCO_3^0$, Cu-org.
Iron	Fe	26	55.85	2,3	4	7.87	1,536	Fe^{2+}, Fe^{3+}	Fe-hydroxy species, Fe-org.	Fe-hydroxy species, Fe-org.
Lead	Pb	82	207.19	2,4	4	11.35	327	Pb^{2+}	Pb^{2+}, $PbSO_4^0$, Pb-org.	Pb-hydroxy and carbonate species, Pb-org.
Manganese	Mn	25	54.94	2,3,4,7	1	7.44	1,244	Mn^{2+}, Mn^{4+}	Mn^{2+}, $MnSO_4^0$, Mn-org.	Mn^{2+}, $MnSO_4^0$, $MnCO_3^0$
Mercury	Hg	80	200.61	1,2	7	13.54	-39	Hg^{2+}, $(CH_3)_2Hg$	-	-
Molybdenum	Mo	42	95.94	6	7	10.22	2,610	MoO_4^{2-}	-	-
Nickel	Ni	28	58.71	2,3	5	8.91	1,453	Ni^{2+}	Ni^{2+}, $NiSO_4^0$, Ni-org.	Ni^{2+}, $NiHCO_3^+$, $NiCO_3$
Zinc	Zn	30	65.37	2	5	7.14	420	Zn^{2+}	Zn^{2+}, $ZnSO_4^0$, Zn-org.	Zn^{2+}, Zn-hydroxy and carbonate species, Zn-org.

Oxidation converts the non-toxic Cr^{3+} ion to the toxic and carcinogenic Cr^{6+} oxyanion. This reaction has even more significance in soils as a strongly sorbed or precipitated cation (Cr^{3+}) is converted into a poorly sorbed or soluble anion (CrO_4^{2-}). However, even in aerobic soils, Cr^{3+} is thermodynamically the most stable state, so added Cr^{6+} ion is rapidly converted to Cr^{3+} in most soils.

6.2 Organic contaminants

An organic contaminant, once it is added to soil, can undergo the following processes:

- Sorption (binding) on soil particles;
- Degradation (biotic or abiotic);
- Biotransformation;
- Volatilisation; and
- Transfer via the soil solution and with colloids to surface- and/or ground-water.

These processes are influenced by a few important physicochemical characteristics of the compound and the soil, including the hydrophobicity of the compound (defined by octanol-water partition coefficients - K_{ow}), charge characteristics, the volatilisation ability (defined by Henry's Law constant), the organic carbon/matter content of soil and other factors affecting the persistence of the compound in the soil (often designated as the compound half-life).

K_{OW} is a measure of the propensity of the compound to partition between water and lipids (present in all cell membranes), and is measured by determining the partitioning of the compound between a hydrophobic liquid phase (*n*-octanol) and a hydrophilic liquid phase (water). The following is a general guide to the effect of log K_{OW} on the strength of sorption:

- $\log K_{OW} < 2.5$: weak sorption to soil;
- $2.5 < \log K_{OW} < 4$: medium sorption to soil; and
- $\log K_{OW} > 4$: strong sorption to soil.

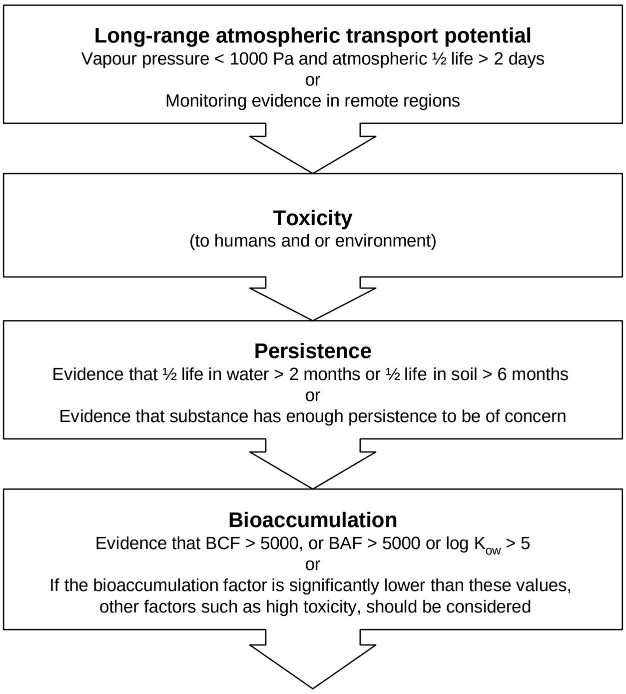
Similarly, the volatility of some of these molecules is characterised by the Henry's Law constant (Hc). This parameter, in combination with the log K_{OW}, will determine their potential for volatilisation loss into the atmosphere. Thus if

- $Hc>1.10^{-4}$ and $Hc/K_{OW} > 1.10^{-9}$: high volatility; and
- $Hc<1.10^{-4}$ and $Hc/K_{OW}<1.10^{-9}$: low volatility.

A few general points can be drawn:

- Most of the persistent organic pollutants (POPs e.g. PAHs, dioxins/furans) are non-polar, have very low aqueous solubility and will tend to sorb strongly on solid particles, especially organic matter in soil;
- The free molecules are unlikely to be dominant forms transported in water however;
- If the organic pollutant has a high molecular weight, its rate of transport to above ground plant parts is likely to be low, however it may accumulate in below ground plant components (e.g. roots and tubers); and
- Direct ingestion of persistent hydrophobic organic chemicals with soil particles (such as during animal grazing) and food chain transfer are important pathways for contaminant uptake. The discovery of organochlorine pesticide (dieldrin) residues in beef in 1980s is an example of such a pathway resulting in a major agricultural and trade issue impacting a major industry in Australia.

Hence, taking into account physicochemical characteristics and the toxicity potential of compounds can help to assess the risk profile of organic contaminants. They are summarised in Figure 3.



Note:
Log Kow : logarithm of octanol-water partition coefficient
BCF : Bioconcentration factor, which indicates aquatic organisms ability to take up chemical from water
BAF : Bioaccumulation factor, which is ratio of organism and water concentrations

Figure 3. Information to take into account when assessing the risk potential of an organic pollutant released in the environment (for instance, present in a fertilizer) (adapted from Vallack et al., 1998).

6.3 Ageing of contaminants in soil

After addition of a soluble contaminant to soil, sorption or precipitation reactions decrease the concentration of contaminant in the soil solution. These reactions are hypothetically reversible, so that if a contaminant is removed (either by plant uptake, volatilisation, or leaching), there will be desorption or dissolution of the contaminant from the solid phase in soil. It has been found that the rate of release of sorbed contaminants decreases with time, a phenomenon termed “ageing” or “fixation”, and this is manifest by increases in the partition coefficient with time.

For a contaminant that has been adsorbed, this increasing strength of binding to soil may be due to a rearrangement of the contaminant on the surface of the solid phase e.g. diffusion of metal into micropores on the surface of the soil mineral or organic material (Figure 4a). A related hypothesis is that the adsorbed metal slowly diffuses from the surface into the crystalline structure of soil minerals (Barrow 1987) (Figure 4b). Numerous studies have been conducted in laboratories that have demonstrated this phenomenon for both inorganic and organic contaminants, and there are suggestions that the rate of the ageing process is contaminant specific e.g.

Cd<Mo<Zn<Ni (Barrow, 1986; Barrow et al., 1989).

Precipitation reactions remove contaminants from soil solution through the formation of new solid phases, usually in association with a corresponding anion or cation already present in the soil solution. Precipitation reactions like those for adsorption, exhibit time dependent reaction rates – the longer the contaminant is in contact with the soil, the greater the stability of the solid phase formed (McLaughlin, 2001). Ageing is one reason P and Zn fertilizers must be added to soil repeatedly.

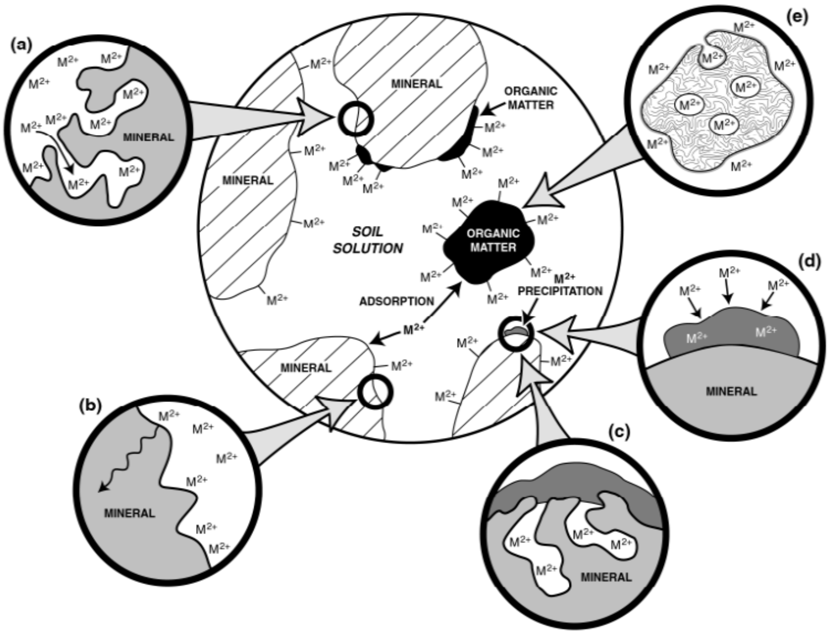


Figure 4. Sorption and ageing processes in soils, depicted for a cationic divalent metal (e.g. Cd). While the figure illustrates ageing for a metal it equally applies to organic contaminants. Sorption moves contaminants from solution to soil surfaces. Ageing moves contaminants from soil surfaces into the solid phase through (a) surface pore diffusion, (b) solid state diffusion, (c) occlusion of metals through precipitation of other phases, (d) precipitation of new metal solid phases, and (e) occlusion in organic matter.

For organic contaminants ageing is also well established, as the residues progressively become less bioavailable with increasing contact with soil or organic matter with a subsequent decrease in risk to the environment over time (Alexander, 2000). At the same time the so-called non-available fraction or bound residue increases with time (in the order of years). These trends have been schematically described in Figure 5. Some of the processes such as diffusion into micropores, entrapment or sequestration of organic compounds into the internal surfaces, and the bioavailability of organic contaminants in soils often decrease with time.

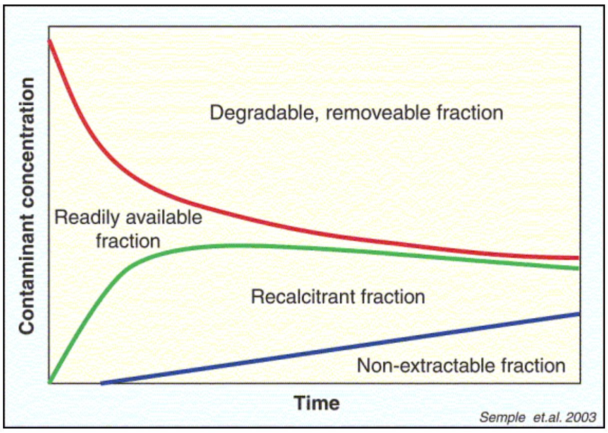


Figure 5. A schematic diagram showing the generalised behaviour of contaminants in soils with increasing time of contact. Note that with time (years) the non extractable fraction increases.

The outcome of ageing reactions for both inorganic and organic contaminants is that bioavailability slowly declines with time, so that where regulatory limits are set on the basis of 100% bioavailability (which if often the case), toxicity effects will be overpredicted by a greater degree the longer the contaminant resides in soil.

7 Hazard assessment of contaminants in atmospheric emissions from the biomass power plant

Predicted hazards from the emissions from the BPP were assessed using normal assessment procedures, by developing hazard quotients (HQs) for each contaminant of concern. To determine the HQs for all contaminants of concern, the following method was applied:

$$HQ = PEC/PNEC \qquad (1)$$

where HQ is the hazard quotient for the contaminant in question, PEC is the predicted environmental concentration of the contaminant and PNEC is the predicted no effect concentration, assumed to be benchmark concentrations for the contaminant in soil or air (given the exposure pathways identified above). A $HQ \geq 1.0$ was considered unacceptable, a $HQ < 1.0$ was considered acceptable, and a $HQ < 0.1$ was considered negligible.

As outlined in Section 2, CW provided data on a wide range of contaminants in emissions from the BPP at Manjimup, Western Australia. Each class of contaminant was assessed separately below.

7.1 Particulates

The main hazard of fine particulates is to human health, and air quality guidelines have been developed to assess this hazard. This is outside the scope of this review focussed on effects on plants/crops.

Particulates exert no direct toxicity to soil through physical effects as soil is composed primarily of particulate material – toxicity of particulates in soil is related wholly to chemical composition and transformations after deposition.

Particulates may have a direct toxicity effect on plants through “shading” of leaves and reducing photosynthetic activity (pathway ③, Figure 1). Plants can act as “filters” of atmospheric particulates (Adrizal et al. 2008) and this is likely to be greatest in the high dust deposition zones, and where rainfall is infrequent in the growing season (which reduces wash off of dust from leaves).

An excellent review of the effects of fine particulates on plants is by Beckett et al. (1988). They report only one study of fine particulates from fuel combustion affecting plant growth (Rick and Williams, 1974) where the effect was indirect – particulates apparently “wedging” open stomata at night and increasing exposure of the trees to gaseous pollutants.

Pandey and Pandey (1994) also examined the effect of air quality on plant growth and function, by correlating plant leaf area, damage and chlorophyll concentration to air quality at four locations in a large city in India. They found a negative correlation between concentrations of SO_2, ozone, NO_2 and total suspended particulates and plant health, but the design of the study failed to indicate if soil conditions at the different locations were also causal. It is worth noting that the lowest concentrations of airborne particulates measured by these authors at the least polluted (control) location (125 $\mu g/m^3$) is 4-fold higher than the concentrations predicted to be present due to emissions by the proposed BPP (Source 1, Section 2).

7.1.1 Conclusions for particulates

- *To date, no jurisdiction has considered the hazard posed by particulates to the environment as significant enough to warrant development of air quality or soil quality guidelines to protect the environment. It is therefore difficult to assess hazard as no benchmarks are available against which to judge predicted emission data, but review of the literature indicated hazards are likely low and restricted to areas very close to the plant.*

7.2 Oxides of nitrogen and sulfur

Oxides of nitrogen (N) comprise both nitric oxide (NO) and nitrogen dioxide (NO_2) and while these may be a source of nutrient N for plant growth through direct uptake from the atmosphere or via soil deposition and root uptake, they may be toxic to plants at high gaseous concentrations (pathway ③, Figure 1) (Wellburn, 1990). Nitric oxide may be formed in combustion processes but is oxidised in the atmosphere to NO_2, the more toxic species (Saxe, 1994).

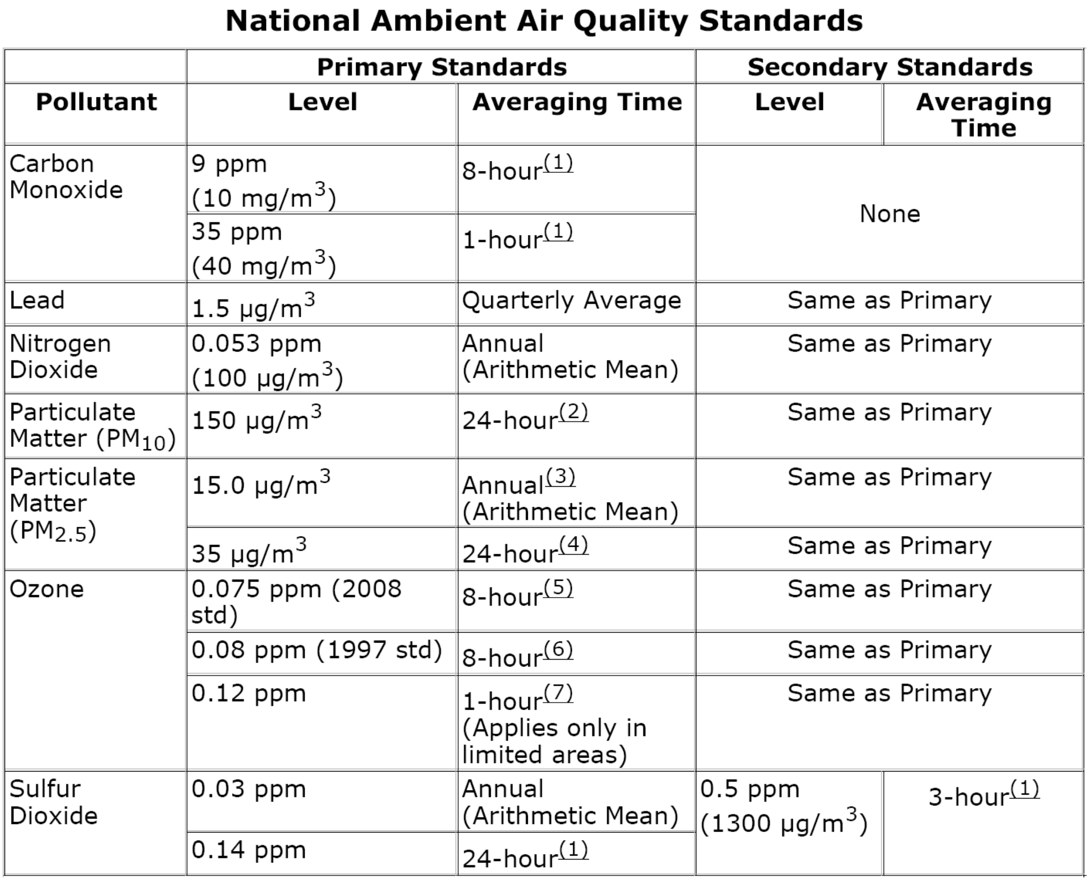
Short-term exposure to high concentrations of NO_2 does not affect plant growth, but prolonged exposure can and the mechanism appears to be related to the production of nitrite in the leaf cells (Wellburn, 1990)). A comparison of the effect of NO and NO_2 exposure (generated by glasshouse CO_2 enrichment and heating by combustion processes) to 35 different plant cultivars found growth stimulation in some cultivars but toxicity in the bulk of species investigated. It is of note that the concentrations of SO_2 and NO_2 measured by Pandey and Pandey (1994) discussed above, even at the most polluted location, were well below US EPA standards (Table 7) yet adverse effects were noted. The paper does not have adequate quality assurance on the analytical data, does not have adequate statistical presentation of results in my view, and does not take adequate account of co-variates in the soil that could affect plant growth, and therefore the data should be regarded with caution.

Sulfur dioxide (SO_2) emissions can affect plant growth through generation of acid in and on the leaf surface, and generally leads to scorching of the leaf.

Currently, the secondary United States National Ambient Air Quality Standard (NAAQS) set under the Clean Air Act (http://www.epa.gov/air/caa/) for sulfur oxides uses SO_2 as the chemical indicator and has an annual 3-h maximum average of 0.5 ppm. The secondary NAAQS for nitrogen oxides has NO_2 as the chemical indicator and is set same as the primary with an annual average of 0.053ppm. These secondary NAAQSs were set to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings (Table 7).

Since these standards were produced, secondary effects of S/N-oxide deposition have been evaluated. These relate to acidification of ecosystems caused by both NO_x and SO_2 deposition. Current examination of this process by the US EPA suggests that N and S loadings of less than 15 and 6 kg/ha/yr are needed to minimise adverse effects. No similar studies have been produced in Australia. For each mol of S deposited in soil as SO_2, 2 mols of protons (H^+) are generated. For each mol of N deposited in soil as NO_x, 1 mol of H^+ are generated. Hence per mole emission, oxides of sulfur are more acidifying.

Table 7. United States National Ambient Air Quality Standards (US EPA - **http://www.epa.gov/air/criteria.html**).



National Ambient Air Quality Standards

	Primary Standards		Secondary Standards	
Pollutant	**Level**	**Averaging Time**	**Level**	**Averaging Time**
Carbon Monoxide	9 ppm (10 mg/m^3)	8-hour(1)	None	
	35 ppm (40 mg/m^3)	1-hour(1)		
Lead	1.5 µg/m^3	Quarterly Average	Same as Primary	
Nitrogen Dioxide	0.053 ppm (100 µg/m^3)	Annual (Arithmetic Mean)	Same as Primary	
Particulate Matter (PM$_{10}$)	150 µg/m^3	24-hour(2)	Same as Primary	
Particulate Matter (PM$_{2.5}$)	15.0 µg/m^3	Annual(3) (Arithmetic Mean)	Same as Primary	
	35 µg/m^3	24-hour(4)	Same as Primary	
Ozone	0.075 ppm (2008 std)	8-hour(5)	Same as Primary	
	0.08 ppm (1997 std)	8-hour(6)	Same as Primary	
	0.12 ppm	1-hour(7) (Applies only in limited areas)	Same as Primary	
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm (1300 µg/m^3)	3-hour(1)
	0.14 ppm	24-hour(1)		

(1) Not to be exceeded more than once per year.

(2) Not to be exceeded more than once per year on average over 3 years.

(3) To attain this standard, the 3-year average of the weighted annual mean PM2.5 concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m3.

(4) To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m3 (effective December 17, 2006).

(5) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm. (effective 60 days after publication in the Federal Register)

(6) (a) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.

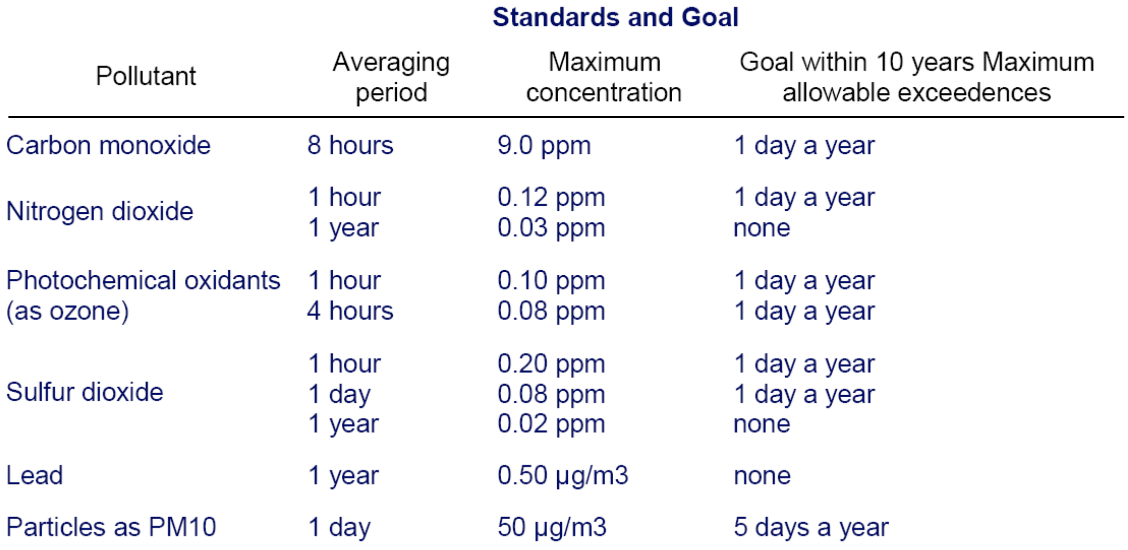
(b) The 1997 standard—and the implementation rules for that standard—will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.

(7) (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is $\leq$ 1.

(b) As of June 15, 2005 EPA revoked the 1-hour ozone standard in all areas except the 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

In Australia, ambient air quality is governed by the National Environmental Protection Measure (NEPM) for (http://www.ephc.gov.au/nepms/air/air_nepm.html). Current standards and goals are shown in Table 8. It should be noted that the current Ambient Air Quality NEPM in Australia does not consider ecological impacts, but this is currently under review. However, Australia's NEPM human health-based standards for SO_2 and NO_2 are more stringent that the US EPA secondary standards (designed to protect ecosystems and communities).

Table 8. Australia's National Environmental Protection Measure Ambient Air Quality Standards for the protection of human health.



	Standards and Goal		
Pollutant	Averaging period	Maximum concentration	Goal within 10 years Maximum allowable exceedences
Carbon monoxide	8 hours	9.0 ppm	1 day a year
Nitrogen dioxide	1 hour 1 year	0.12 ppm 0.03 ppm	1 day a year none
Photochemical oxidants (as ozone)	1 hour 4 hours	0.10 ppm 0.08 ppm	1 day a year 1 day a year
Sulfur dioxide	1 hour 1 day 1 year	0.20 ppm 0.08 ppm 0.02 ppm	1 day a year 1 day a year none
Lead	1 year	0.50 µg/m3	none
Particles as PM10	1 day	50 µg/m3	5 days a year

The World Health Organisation's most recent updated air quality standards ((World Health Organisation (WHO), 2006)) cite slightly more stringent standards than Australia for some contaminants as follows:

NO_2 1-hour mean limit = 200 µg/m^3 = 100 ppb = 0.10 ppm
NO_2 annual mean limit = 40 µg/m^3 = 20 ppb = 0.02 ppm

SO_2 24-hour mean limit = 20 µg/m^3 = 7.1 ppb = 0.007 ppm

7.2.1 Hazard characterisation for NO_2 and SO_2

Using the SO_2 and NO_x exposure data in Section 4, and using the NEPM standards for Australia (which protect human health only but are more stringent than US EPA standards to protect plants and communities), the following Hazard Quotients were calculated.

SO_2

PEC for SO_2 = 27.8 ppb (1 hour predicted maximum) 0.58 ppb (annual)

PNEC for SO_2 = 0.20 ppm = 200 ppb (NEPM 1 hour standard) or 30 ppb (NEPM annual)

HQ_{S02} = 0.14 (1 hour) or 0.03 (annual)

Using the much more stringent WHO air quality guidelines (AQG), the HQ (24 hour) for SO_2 was calculated to be 0.96. This is approaching 1.0, but the WHO AQG is based on protection of human health and not ecological health. It is also pertinent to note that the 98th percentile HQ is very low (<0.01), so that only very intermittent and infrequent emissions of SO_2 could approach the WHO air quality guideline.

NO_2

PEC = 34.3 ppb (1 hour predicted) or 1.7 ppb (annual).

PNEC for NO_2 = 120 ppb (NEPM 1 hour standard), or 30 ppb (NEPM annual standard)

HQ_{NO2} = 0.29 (1 hour) or 0.06 (annual)

Even using the slightly more stringent WHO air quality standards, the HQs calculated are <1 (~0.35). Furthermore, even if the data of Pandey and Pandey (1994) are accepted as valid, concentrations of SO_2 predicted to be present in air from emissions from the BPP are *15-fold lower,* and those for NO_2 *3-fold lower*, than those reported from the least polluted (control) location in the study of Pandey and Pandey (1994).

A further potential hazard from these compounds is the acidification of soil over time, and while not a serious threat, this may lead to lss of crop productivity unless limestone is applied to correct acidification.

Using the 25-year lifespan of the plant, the following depositional rates were estimated

SO_2	1935 mg/m^2/25y
NO_2	1293 mg/m^2/25y

These equate to a cumulative H^+ load of ~88 mmols H^+/m^2, which would require 44 mmols/m^2 $CaCO_3$ to neutralise the acidity produced. This is equivalent to ~44 kg lime per hectare, which is insignificant when placed in perspective of normal rates of acidification of agricultural soils in Australia (Helyar et al., 1990).

7.2.2 Conclusions for oxides of nitrogen and sulfur

- *The predicted direct toxicity hazards from SO_2 emissions to plants and crops are predicted to be negligible. Intermittent and infrequent emissions (2% time) of SO_2 from the BPP could approach the WHO 24-hour air quality guideline (AQG) value (0.007 ppm), but this is a human-health based AQG and the hazard to crops cannot be assessed from this predicted HQ.*
- *The predicted direct toxicity hazard from NO_2 emissions to plants and crops are predicted to be acceptable. As the HQ is ~0.3, it is suggested that monitoring of NO_2 emissions be undertaken once the plant is operating to ensure predicted emissions are in line with actual emissions, and that actual emissions are within regulatory limits.*
- *Acidification of soils due to deposition of NO_2 and SO_2 is predicted to be negligible.*

7.3 Persistent organic contaminants

7.3.1 Dioxins and furans

Polychlorinated dibenzo-para-dioxins, and polychlorinated dibenzo-para-furans (PCDD/Fs), commonly referred to as dioxins and furans, are chlorinated aromatic compounds. The dioxin group comprises 75 different compounds, and the furans, 135. Of these, 17 are reported to have adverse health effects (Vallack et al., 1998). PCDD/F are not commercially produced but are inadvertently formed as by-products of various industrial and combustion processes of compounds containing chloride. The most important sources of PCDD/F are from the combustion processes including bushfires, metal production, power generation and waste incineration. The recent National Dioxin Program (Dept. Environment and Heritage, 2004) has shown that low-level residues of these chemicals are widely distributed in Australian soils, fauna, air and water.

Since dioxins and furans are a complex mixture of many chemicals, concentrations of these chemicals are normally reported as toxic equivalent concentrations (TEQ) for the group of 17 congeners.

$$\mathrm{TEQ} = ([\mathrm{PCDD_i} \times \mathrm{TEF_i}]_n) + ([\mathrm{PCDF_i} \times \mathrm{TEF_i}]_n) + ([\mathrm{PCB_i} \times \mathrm{TEFi}]_n) \qquad (2)$$

There are no Australian standards for dioxins and furans in soils, but reference values and recommended action values (for remediation) have been produced by Germany (Muller et al., 2004). These values are 5 pg TEQ/g as a long-term target value for soils used for agricultural purposes, <40 pg TEQ/g for soils used for activities where dioxins could transfer through the food chain (e.g. grazing). New Zealand has produced criteria for agricultural soils of <10 pg TEQ/g. Crop cultivation and food chain transfer for most crops is low risk due to the very strong binding of these substances to soil.

A survey of these compounds in Australian soils has been conducted (Muller et al., 2004) and levels vary widely across the country. Soils in Western Australia had concentrations ranging from 0.04-0.49 (mean 0.22) pg TEQ/g.

7.3.2 Hazard characterisation for dioxins/furans

Using the annual exposure data in Table 3, and applying a similar deposition factor as for inorganic elements from BPP emissions, the deposition of PCDD/Fs over the life of the plant (25 years) is predicted to be 0.2 mg/ha in the assumed deposition area (22 km by 22 km).

Looking first at accumulation rates, assuming a lower soil background concentration in Manjimup of 0.04 pg TEQ/g from the national survey (Muller et al., 2004), the predicted lifetime deposition would increase soil concentrations by a maximum of ~0.13 pg TEQ/g.

Examining the soil concentrations in relation to overseas guidelines, predicted maximum soil concentrations (depending on background concentrations) would be in the range 0.17-0.62 pg TEQ/g with most of this being background concentrations at the upper end.

PEC for PCDD/Fs = 0.62 pg TEQ/g (upper background+deposition)

PNEC for PCDD/Fs = 10 pg TEQ/g (NZ agricultural soil guideline)

HQ = 0.062

7.3.3 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are formed mainly as by-products of incomplete combustion of materials containing carbon and hydrogen (e.g. coal, petrol, oil and wood). Emissions from anthropogenic activities predominate (fuel and road vehicle combustion, wood preservation, metal and steel industry) (Edwards, 1983), but PAHs are also the result of natural processes such as forest fires (Baek et al*.,* 1991). There are many PAHs but the US-EPA lists 16 as being priority pollutants to be screened in different environments and matrices.

For PCB, PCDD/F and PAHs, which are part of a bigger group of chemicals called persistent organic pollutants (POPs), the combination of high volatility and persistence (i.e. resistance to photolytic biological and chemical degradation) allow long-range atmospheric transport and make them ubiquitous in the environment. Therefore, they can be found in for example, green residues, tree cuttings, lawn clippings, as a result of aerial deposition (especially near highly industrialised areas, or major roads).

PAHs rarely exert direct toxicity to crops and plants due to their strong binding to soil after addition. The main hazard is to humans through ingestion of soil, or transfer through the food chain to humans. Hence, there are no air quality standards to assess direct risks from foliar toxicity of PAHs to agricultural crops or plants, nor are there soil standards to protect plants from toxicity expressed through the roots.

7.3.4 Conclusions for persistent organic contaminants

- *The predicted direct toxicity hazards from* PCDD/Fs *emissions to agricultural crops are predicted to be negligible as the HQ is <0.1.*
- *It was not possible to predict hazard due to emission of PAHs to agricultural crops/plants as no environmental benchmarks are available against which to judge predicted emission data and predicted soil concentrations.*

7.4 Inorganic contaminants

As noted in Section 5, the hazards posed by deposition of inorganic contaminants on plants or soil can be assessed by considering the key exposure pathways, which are dependent on the physico-chemical behaviour and crop uptake characteristics of each element. Many inorganics are essential elements for plant nutrition (Marschner 1995) and many are also structural minerals in soil. Hence addition of a small concentration of an element in relation to the background concentration of that element in soil is a first indicator of likely accumulation potential, and a first screen as to the potential hazard to plants and biota.

Background concentrations for a range of potential inorganic contaminants were sourced from CSIRO Land and Water's database. Information provided by CW (Source 3, Section 2) only provided a general overview of geology at the site and no information on surrounding soil conditions. Accordingly, ambient concentrations of elements were determined from a small survey of WA soils which included soils from the Manjimup area (CSIRO Land and Water data). Data from a total 29 samples (0-150mm depth) from horticultural soils in WA were collated to provide an indicative level of background concentrations for inorganic elements in the soils (Table 9).

Table 9. Data for ambient concentrations of inorganic elements in WA horticultural soils (CSIRO Land and Water data).

Element	Mean	Median	Min	Max	5th percentile
	---------------------------------- mg/kg				---------------------------------
Al	38792	39337	8033	53006	25537
Ca	1916	1675	467	4942	695
Cd	0.197	0.163	0.048	0.779	0.063
Co	2.6	2.5	1.4	4.5	1.7
Cr	59	41	5	264	5.4
Cu	13.4	10.3	3.0	38.1	3.4
Fe	14543	11816	0	29409	1585
Mg	308	271	64	640	119
Mn	177	147	32	488	52
Ni	15.8	13.7	2.5	47.5	4.3
P	887	794	327	1663	372
Pb	15.0	14.0	4.7	26.3	7.4
Zn	18.6	13.0	4.8	103.0	6.9

As soil data for the Manjimup area were not available, a conservative 5th percentile of the WA distribution was used, against which to judge soil accumulation of inorganic contaminants from the BPP emissions. Data for ambient concentrations of certain elements in WA soils were not readily available, so data were sourced from the literature for As, B, Cr(VI), K, Mo, Na, Sb, Se, and Ti (Taylor et al., 1983; Williams and Raupach, 1983; Panichev et al., 2003; Alloway 1995; McBride and Cherney, 2004). No reliable data for Cr(VI) concentrations in soils were found, so the detection limit of the analytical technique was used (Panichev et al. 2003) (Table 10).

The lifetime emissions of inorganic contaminants from Table 1 were converted into a predicted increase in soil concentration assuming mixing of the deposited contaminants into the top 100 mm soil and a bulk density in soil of 1300 kg/m^3. The lifetime increase in soil concentration was divided by the ambient concentration in soil (from 5th percentile or literature data) to determine an accumulation potential relative to ambient background concentrations expressed as a fraction of the ambient background concentration.

From the data in Table 10 it is evident that the contaminants most likely to be elevated relative to the ambient background are B, Hg, and Se, but the fractional increases even for these elements are <0.10 i.e. *the lifetime emissions of the BPP are predicted to increase ambient background concentrations by less than 10%.*

Table 10. Cumulative increase in soil concentrations of inorganic elements due to 25 years emission of contaminants (Table 1, Source 5, Section 2) in relation to the 5th percentile ambient background concentrations in soils in WA (Table 9).

	Increase in soil concn	5th percentile ambient concn	Typical soil ambient concn	Ambient concn used	Fractional lifetime increase in soil concentration
	------------------------------ mg/kg ----------------------------				
Antimony	2.2E-04		0.9	0.9	2.48E-04
Arsenic	2.2E-04		0.6	0.6	3.72E-04
Boron	2.2E-01		20	20	1.08E-02
Cadmium	4.2E-04	0.06		0.06	6.76E-03
Cobalt	1.8E-05	1.7		1.7	1.02E-05
Copper	5.3E-04	3.4		3.4	1.56E-04
Cr(III)	3.2E-04	5.4		5.4	5.85E-05
Cr(VI)	7.7E-05		0.03	0.03	2.56E-03
Iron	5.2E-02	1585		1585	3.29E-05
Lead	1.2E-02	7.4		7.4	1.64E-03
Manganese	2.0E-02	52		52.3	3.75E-04
Mercury	1.0E-03		0.1	0.1	7.02E-02
Molybdenum	1.5E-06		1.0	1.0	1.54E-06
Nickel	1.5E-04	4.3		4.3	3.60E-05
Phosphorus	1.0E-03	372		372	2.77E-06
Potassium	1.5E-02		400	400	3.72E-05
Selenium	3.7E-04		0.01	0.01	3.69E-02
Sodium	7.2E-02		100	100	7.25E-04
Titanium	5.4E-05		6000	6000	8.92E-09
Zinc	3.5E-03	6.9		6.9	5.13E-04

7.4.1 Hazard characterisation for inorganic contaminants

Not all the inorganic contaminants in the BPP emissions have regulatory limits, guideline or benchmark values for soil concentrations. In Australia, inorganic element concentrations in agricultural soils are not monitored or controlled, except where municipal biosolids are applied to land. On land receiving biosolids in WA, current limit values for inorganic contaminants in agricultural soils are as outlined in Table 11 (WA DEP 2002).

Table 11. Maximum allowable soil contaminant concentrations following biosolids application (WA DEP 2002).

Contaminant	**Maximum Allowable Soil Contaminant Concentration (mg/kg)***
Arsenic	20
Cadmium	1
Chromium (total)	100
Copper	100
Lead	150
Mercury	1
Nickel	60
Selenium	5
Zinc	200

Further to these guidelines published in 2002, CSIRO Land and Water has released revised maximum recommended contaminant concentrations for soils receiving biosolids for Cd, Cu and Zn, as a result of more recent research findings (see http://www.clw.csiro.au/research/biogeochemistry/assessment/biosolids/documents/DraftNBRPPositionPaperForPublicComment.pdf). These revised suggested limit values for these three elements have a much more robust scientific basis and take into account soil factors affecting contaminant bioavailability (as outlined in Section 6) and are protective of phytotoxicity, microbial toxicity and food chain contamination. Conservatively assuming the soils around Manjimup are sandy texture, acidic in nature, and have low ambient background concentrations (Table 9), the revised maximum recommended concentrations of Cd, Cu and Zn are assumed to be 0.5, 28 and 27 mg/kg.

Some elements have interim urban ecological investigation levels (EILs) defined in the NEPM (Assessment of Site Contamination), which act as a trigger for further investigation of soil at contaminated sites, based on potential risks to ecological receptors. Generally, these concentrations are equal to, or greater, than those in Table 10. Where two values were available, the lower benchmark was used (i.e. more conservative). One contaminant, Cr(VI), has an EIL defined but no limit listed for agricultural soils receiving biosolids.

Using the above values, the HQs for the inorganic elements having standards or limits could be calculated (Table 12). HQs could not be calculated as Australian PNEC values for maximum soil concentrations of B, Co, Cr(VI), Fe, K, Mo, Na, P, Sb, and Ti are not available for agricultural soils.

Table 12. Predicted environmental concentrations, predicted no effect concentrations and hazard quotients for inorganic elements emitted from the BPP at Manjimup.

	Soil concentration (PEC)	Limit value (PNEC)	Hazard quotient (HQ)
Antimony	0.9		
Arsenic	0.6	20	0.030
Boron	20		
Cadmium	0.06	0.5	0.126
Cobalt	1.7		
Copper	3.4	28	0.121
Cr(III)	5.4	100	0.054
Cr(VI)	0.03	1.0*	0.030
Iron	1586		
Lead	7.4	150	0.049
Manganese	52		
Mercury	0.10	1	0.101
Molybdenum	1.0		
Nickel	4.3	60	0.071
Phosphorus	372		
Potassium	400		
Selenium	0.01	5	0.002
Sodium	100		
Titanium	6000		
Zinc	6.9	27	0.255

* PNEC derived from EIL in Site Contamination NEPM.

7.4.2 Conclusions for inorganic contaminants

- *For inorganic contaminants, predicted hazards posed by lifetime accumulation of As, Cd, Cu, Cr(III and VI), Hg, Ni, Pb, Se and Zn in soil due to emissions from the BPP are small. HQs could not be calculated as Australian PNECs for maximum soil concentrations of B, Co, Cr(VI), Fe, K, Mo, Na, P, Sb, and Ti are not available for phytotoxicity endpoints. However, hazards from these elements are also likely to be low due to:*
  - *the small predicted accumulation of contaminant in relation to ambient background concentrations;*
  - *the fact that some of these elements are structural components of soil minerals present in abundance in most soils and known to have low toxicity (Fe, K, Mn, Na, and P); and*
  - *many of the contaminants (Co, Ti) have low solubility or high soil:solution partitioning values which limit mobility and toxicity in soil.*

8 References

Adrizal A, Patterson PH, Hulet RM, Bates RM, Myers CAB, Martin G, Shockey RL, Van Der Grinten M, Anderson DA, Thompson JR. Vegetative buffers for fan emissions from poultry farms: 2. Ammonia, dust and foliar nitrogen. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 2008; 43: 96-103.

Alexander M. Aging, bioavailability, and overestimation of risk from environmental pollutants. Environmental Science and Technology 2000; 34: 4259-4265.

Alloway BJ. Heavy Metals in Soils. 2nd Edition. Blackie Academic and Professional, Glasgow, 1995.

Baek SO, Field RA, Goldstone ME, Kirk PW, Lester JN, Perry R. A review of atmospheric polycyclic aromatic-hydrocarbons - sources, fate and behavior. Water Air and Soil Pollution 1991; 60: 279-300.

Barrow NJ. Testing a mechanistic model. 2. The effects of time and temperature on the reaction of zinc with a soil. Journal of Soil Science 1986; 37: 277-286.

Barrow NJ. Reactions with variable charge soils. Martinus Nijhoff Publishers, Dordrecht, the Netherlands, 1987.

Barrow NJ, Gerth J, Brummer GW. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II. Modelling the extent and rate of reaction. Journal of Soil Science 1989; 40: 437-450 .

Beckett KP, Freer-Smith PH, Taylor G. Urban woodlands: Their role in reducing the effects of particulate pollution. Environmental Pollution 1998; 99: 347-360.

Edwards NT. Polycyclic aromatic-hydrocarbons (PAHs) in the terrestrial environment - a review. Journal of Environmental Quality 1983; 12: 427-441.

FSANZ (Food Standards Australia New Zealand) . Australia New Zealand Food Standards Code, Standard 1.4.1, Contaminants and Natural Toxicants. 2005. verified 8th June 2005.

Helyar KR, Cregan PD, Godyn DL. Soil acidity in New South Wales-Current pH values and estimates of acidification rates. Australian Journal of Soil Research 1990; 28: 523-537.

Lindsay WL. Chemical Equilibria in Soils. John Wiley and Sons, New York, USA., 1979, 449.

Marschner H. Mineral nutrition of higher plants. Academic Press, USA, 1995.

McBride MB, Cherney J. Molybdenum, sulfur, and other trace elements in farm soils and forages after sewage sludge application. Communications in Soil Science and Plant Analysis 2004; 35: 517-535.

McLaughlin, MJ. Ageing of Metals in Soils Changes Bioavailability. Fact Sheet on Environmental Risk Assessment 4, 1-6. September 2001. Ontario, Canada, International Council on Metals and the Environment. 2001.

McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Australian Journal of Soil Research 2000; 38: 1037-1086.

McLaughlin MJ, Tiller KG, Naidu R, Stevens DG. Review: The behaviour and environmental impact of contaminants in fertilizers . Australian Journal of Soil Research 1996; 34: 1-54.

Muller, J, Muller, R, Goudkamp, K, Shaw, M, Mortimer, M, and Haynes, D. Australian Government Department of Environment and Heritage National Dioxins Program. Dioxins in Soil in Australia. 2004. Canberra, Australia, Commonwealth of Australia.

Pandey, J. and Pandey, U. Evaluation of air-pollution phytotoxicity in a seasonally dry tropical urban-environment. Environmental Monitoring and Assessment 1994; 33: 195-213.

Panichev N, Mandiwana K, Foukaridis G. Electrothermal atomic absorption spectrometric determination of Cr(VI) in soil after leaching of Cr(VI) species with carbon dioxide. Analytica Chimica Acta 2003; 491: 81-89.

Ricks GR, Williams RJ. Effects of atmospheric pollution on deciduous woodland .2. Effects of particulate matter upon stomatal diffusion resistance in leaves of *Quercus-petrea* (Mattuschka) Leibl. Environmental Pollution 1974; 6: 87-109.

Saxe H. Relative sensitivity of greenhouse pot plants to long-term exposures of NO-containing and NO_2-containing air. Environmental Pollution 1994; 85: 283-290.

Taylor RM, McKenzie RM, Fordham AW, Gillman GP. Oxide minerals. Soils: an Australian viewpoint CSIRO/Academic Press, Melbourne, Australia, 1983, pp. 309-334.

Vallack HW, Bakker DJ, Brandt I, Brostrom-Lunden E, Brouwer A, Bull KR, Gough C, Guardans R, Holoubek I, Jansson B, Koch R, Kuylenstierna J, Lecloux A, Mackay D, Mccutcheon P, Mocarelli P, Taalman RDF. Controlling persistent organic pollutants - what next? Environmental Toxicology and Pharmacology 1998; 6: 143-175.

Wellburn AR. Why are atmospheric oxides of nitrogen usually phytotoxic and not alternative fertilizers. New Phytologist 1990; 115: 395-429.

Western Australia Department of Environmental Protection. Western Australian guidelines for direct application of biosolids and biosolid products. Department of Environmental Protection, Perth, WA, 2002, 35.

Williams CH, Raupach M. Plant nutrients in Australian soils. Soils: an Australian viewpoint CSIRO/Academic Press, Melbourne, Australia, 1983, pp. 777-793.

World Health Organisation (WHO). WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. Global Update 2005. Summary of Risk Assessment. 2006. Geneva, Switzerland, World Health Organisation.

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