



Background and scope for establishing a list of prohibited substances and guideline limits for levels of contaminants in fertilizers

**April 2005**

**CSIRO Land and Water, Centre for Environmental Contaminants Research**

**Prepared for Product Safety and Integrity Committee,  
Fertilizer Working Group**

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**Final Scoping Report**

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**Robert Molloy, Mike McLaughlin, Michael Warne,  
Rebecca Hamon, Rai Kookana, Carine Saison**

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## Executive Summary

CSIRO's Centre for Environmental Contaminants Research was commissioned by the Fertilizer Working Group of the Product Safety and Integrity Committee (PSIC) in October 2004 to investigate the background and scope for establishing a list of prohibited substances and guideline limits for levels of contaminants in fertilizers.

The approach taken was to initiate discussion amongst the various stakeholders, by bringing together the available information on:

- the market for fertilizer and soil additives/amendments in Australia;
- classes of contaminants which are of concern;
- potential pathways and endpoints for those contaminants; and
- factors to be considered when assessing risk.

A Discussion Paper covering the background information along with key issues that required further discussion was released in February 2005. In addition to posting the paper on the CSIRO Land and Water website, it was distributed to key industry groups for comment.

To assist in resolving the issues and to seek consensus on a way forward, CSIRO hosted a workshop in Canberra, which was attended by members of the Fertilizer Working Group and the Industrial Residue Working Group.

As part of the process for developing a list of prohibited substances and guideline limits for contaminants six issues were raised for discussion. A brief summary of the key points is made for each issue, along with outcomes of the discussion.

CSIRO's Recommendations taking into consideration the outcomes of discussions with stakeholders, including manufacturers, distributors, users, waste management groups, and agricultural and environmental regulators are as follows:

1. That the ingredient approach should be used in determining which chemicals or materials should not be allowed in fertilizers. The concentration approach should be used in determining those chemicals or materials that can be present in fertilizers below certain guideline values;
2. The scope of adverse effects to be covered by this project are:
  - Increased release or bioavailability of contaminants leading to negative effects on soil ecosystems, aquatic ecosystems or plants, in the short or long term;
  - Accumulation or concentration in the food chain producing unacceptable contaminant levels from a trade or human health perspective;
  - Potential for contaminant mobilisation and off-site migration at concentrations sufficient to cause negative impacts on off-site ecosystems; and
  - Toxic to domestic animals, livestock and wildlife.
3. The mass concentration approach be used in combination with the proposed hazard assessment methodology as a mechanism for determining which chemicals or ingredients pose a potential hazard. Those chemicals that are indicated as posing a hazard would then be subject to a risk assessment using the critical load model.
4. The timeframe to be used in the critical load models is 100 years, however, it will be crucial that the issue be reassessed considerably before this period has elapsed.
5. The following agricultural systems are ranked in terms of relative importance and the order in which they should be assessed:
  - Horticulture – including recreational horticulture (turf, golf courses, sports fields, etc);
  - Sugar and other rotation crops;

- Dairy;
  - Livestock production for meat – predominantly cattle and sheep pasture grazing or stock feed;
  - Viticulture;
  - Cereal production;
  - Irrigated cropping – includes rice and cotton farming in the Murray Darling Basin;
  - Forestry – covers use of fertilizers in regeneration of forests and establishment of plantations; and
  - Aquaculture – is currently viewed as a low priority system however there are chemical/drug inputs and potential off-site effects in aquatic systems.
6. The recommended types of contaminants or sources of contaminants to be investigated in the first instance are:
- **Inorganic contaminants:** Essential elements, heavy metals, metalloids, radionuclides, rare earth elements and anionic elements. Specifically As, B, Cd, Cr, Cu, F, Hg, Ni, Pb, Se, and Zn;
  - **Organic contaminants:** Pesticides, persistent organic pollutants (e.g. PCBs, dioxins and furans, PAHs), flocculants, coagulants, surfactants, pharmaceutical and personal care products and other organic contaminants. Where appropriate (ie. chemicals with the same mode of action) the toxic equivalent approach should be used; and
  - **Sources of contaminants:** Raw materials of mineral fertilisers, mining and smelting by-products, energy wastes, and other industrial wastes.
7. We recommend that no biological contaminants be considered at this stage.

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# 1 Project Scope and Outline

CSIRO's Centre for Environmental Contaminants Research was commissioned in October 2004 by the Department of Agriculture, Fisheries and Forestry on behalf of the Fertilizer Working Group to investigate the background and scope for establishing a list of prohibited substances and guideline limits for levels of contaminants in fertilizers.

The Fertilizer Working Group was established under the Primary Industries Standing Committee (PISC) and has responsibility for developing a national approach to managing contaminants in fertilizer. The development of the standard is a key component of a broad policy framework developed by the Working Group to provide the basis for a nationally consistent risk-based approach to fertilizer regulation. Members of the Fertilizer Working Group are listed in Appendix A.

The terms of reference for the study cite the following aims:

1. To establish a list of prohibited substances that must not be added to or used as fertilizers (the negative list);
2. To establish a list of contaminants permitted in fertilizers with the provision that their concentrations, or annual loadings per unit area, do not exceed guideline limits (the positive list); and
3. To establish transparent and traceable procedures for achieving aims 1 and 2 and for future assessments.

Furthermore, the terms of reference for the study also cite the following desired outcomes:

1. A list of substances prohibited in fertilizers;
2. A list of contaminants that are allowed in fertilizers and their guideline limits in various fertilizers or their maximum permitted annual loading rates per unit area;
3. Transparent and traceable documentation for items 1 and 2; and
4. A transparent evaluation procedure and data requirements for future amendments or additions as new data become available or new developments occur.

Given the complexity of the issues associated with contaminants in fertilizers and soil additives, it was suggested that the project be undertaken in three phases. This will then allow effort to be focused on the issues of major concern and more detailed research and evaluation of the wider issues to be undertaken within a framework of continuous improvement.

As such, CSIRO was engaged to undertake Phase 1, which is the Scoping Study. A decision on the need for further work (Phase 2 and 3) will be made by the Fertilizer Working Group based on the outcomes of Phase 1, which is the subject of this report.

For the purposes of this document 'waste materials' are substances such as blast furnace slag, fly ash, mining waste, asbestos dust and waste quarry residues. Selected waste materials may be designated as 'prohibited substances.'

'Contaminants' are undesirable components of fertilizers or fertilizer ingredients. Examples are cadmium, mercury and dioxins. In order to develop guidelines and effectively monitor compliance with the guidelines analytical methods must be available for measuring contaminant levels in fertilizers and fertilizer ingredients.

## 1.1 Approach

The Scoping Study was undertaken to clarify the focus of the project given the potential breadth of substances or contaminants that may need to be considered, and the number of potential exposure pathways and endpoints to be protected. As such the first step of the project was to initiate discussion amongst the various stakeholders, by bringing together the available information on:

- the market for fertilizer and soil additives/amendments in Australia;
- classes of contaminants which are of concern;
- potential pathways and endpoints for those contaminants; and
- factors to be considered when assessing risk.

A summary of available information was presented in a Discussion Paper, which was posted on the CSIRO Land and Water website (<http://www.clw.csiro.au/cecr/publications>) and distributed to various stakeholders for comment. Included in the paper, were six issues which CSIRO believed required further discussion as part of the process for developing a list of prohibited substances and guideline limits for contaminants in fertilizer.

To assist in resolving the issues and to seek consensus on a way forward, CSIRO hosted a workshop in Canberra, which was attended by members of the Fertilizer Working Group and the Industrial Residue Working Group. A report on the workshop proceedings is provided in Appendix B while in Appendix C industry submissions and the response of CSIRO are presented.

The final task in Phase 1 is the writing of the Scoping Report, which brings together the information presented in the Discussion Paper, the deliberations from the workshop, and feedback provided by members of the two working groups and various industry stakeholders. It also includes recommendations for Phase 2.

## 1.2 Project Team

The Project Team, which comprised staff from CSIRO's Centre for Environmental Contaminants Research, combined a broad range of skills covering: environmental chemistry, contaminants and exposure pathways, bioavailability and associated risk assessment, along with knowledge, understanding and experience with fertilizers and soil additives. The project also drew on the combined experience and knowledge of the Fertilizer Working Group and the Industrial Residue Working Group (see Appendix A).

Project Team: Dr Mike McLaughlin (Project Leader) – soil geochemistry;

Mr Robert Molloy (Project Manager);

Dr Rebecca Hamon – contaminant bioavailability (inorganics);

Dr Carine Saison – contaminant bioavailability (organics);

Dr Michael Warne – ecotoxicology, and environmental quality guideline derivation; and

Dr Rai Kookana – organics, contaminant risk assessment.

## 2 Background

Following the publication of a series of articles in the Sydney Morning Herald in May 2002 regarding contaminants in industrial residues used as fertilizer, Standing Committee CEOs established a working group to develop a national standard for contaminants in fertilizer (PISC, 2004).

In earlier cases (e.g. reports in The Australian and Sunday Telegraph in 2002) industrial wastes containing high levels of cadmium and lead had been imported into Australia for sale as fertilizer. At that time fertilizers were registered and, at least in some States, the waste could not be sold when registration was refused. There had been earlier cases from 1986-87 where registration was refused because of heavy metal concentrations.

By the mid 1990s, State jurisdictions had repealed their fertilizer registration requirements, which inadvertently removed one of the safeguards against the disposal of industrial waste as fertilizer. Reliance was thus placed on environmental legislation to manage any risks associated with the application of waste materials to land. However, given Australia's drive for sustainability, most governments have now set goals for recycling and reuse of industrial waste. It is unclear, however, whether environmental regulators have sufficient processes in place to promote recycling of waste material and to avoid the disposal of hazardous waste material to land under the guise of fertilizers.

Previous legislation has generally been aimed at the manufacture and sale of fertilizers that are intended to improve the nutrient status or the condition of the soil. The legislation generally has not been framed to control the disposal of industrial waste, where the driving economic force is the disposal cost of wastes.

Australia's agricultural and pastoral lands are valuable assets and must be protected against contamination in the interests of long-term sustainable production. Rural lands must not be treated as a target or sink for the disposal of waste material classified as fertilizer (see fertilizer definition in box below). Therefore fertilizers should not be treated as vehicles for waste disposal. However, this does not preclude the conversion of waste or by-product materials to fertilizers. For a substance to be acceptable as a fertilizer, it must have a beneficial level of nutrient or deliver some other measurable soil benefit. Genuine fertilizers are designed to provide the correct dose of nutrients for the crop or to condition the soil (alter its chemical, physical or biological composition) for beneficial purposes.

A model definition of fertilizer

"Fertilizer" means:

(a) a substance that is manufactured, represented, supplied or used as a means of directly or indirectly: (i) fertilizing the soil; or (ii) supplying nutrients to plants; or (iii) conditioning the soil by altering the chemical, physical or biological composition of the soil; or

(b) a substance declared by regulation to be a fertilizer,

but does not include a substance excluded by regulation from the ambit of this definition.

Developed by the PSIC Fertilizer Working Group, 2004.

### 3 Fertilizer Industry

Fertilizers are one of the major physical inputs to Australian agricultural production and account for over 12% of the value of material and service inputs used. In 1999 Australian farmers used around 5.25 million tonnes of fertilizer products with a value of approximately \$2 billion. The Australian Farm Surveys Report (ABARE, 2003) stated that the average cost per Australian farm in 2001-02 was \$21,840. Costs ranged between States, with farmers in Western Australia paying the most at \$61,920 per farm.

The Australian fertilizer industry is made up of manufacturers, importers, blenders, retail distributors or agents, and contract applicators. It should be noted however, that all manufacturers import significant quantities of manufactured fertilizers. Both manufacturers and importers market through dealers and/or agents who provide farmers with a local service point and often employ advisory agronomists. Many manufacturers also operate regional distribution and blending service centres.

There are many solid, soluble, and liquid products used as fertilizers in Australia. The products may have organic or mineral origin. The majority of the major nutrients nitrogen (N), phosphorus (P), and potassium (K) are applied as solid mineral fertilizers. Significant quantities of nitrogen are also applied as anhydrous ammonia (gas in liquefied form under pressure).

Calcium (Ca), magnesium (Mg) and sulfur (S) are often referred to as secondary nutrients as they are generally needed in smaller amounts to N, P and K. Together the six nutrients are referred to as macronutrients.

Other elements needed by plants in very small amounts can be referred to as micronutrients or trace elements. The seven micronutrients are: boron (B), chlorine (Cl) (rarely are soils deficient in this element), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn).

Superphosphate is still the most common fertilizer used by farmers for pasture production because it contains both phosphorus and sulfur in readily available forms. Superphosphate is manufactured by treating phosphate rock with sulfuric acid and water to render the phosphorus in the mineral into a soluble form capable of being taken up by plants.

Superphosphate demand is very sensitive to rural commodity prices and the P is moderately immobile after application (in contrast to the more leachable nitrogen fertilizer that requires more regular application). This can result in demand doubling (or halving) from one year to the next. Generally, cropping regions are tending to use more concentrated phosphate fertilizers such as triple superphosphate and ammonium phosphates which contain little sulfur, although in some cases additional sulfur is added in other ways.

Concentrated phosphate fertilizers are produced in a similar way to superphosphate except that the phosphate in the rock is treated with phosphoric acid. The phosphogypsum produced as a by-product in this process is often used as a soil conditioner. Phosphoric acid is either reacted with ammonia to produce mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP) or used to treat phosphate rock to produce double and triple superphosphates.

Nitrogen fertilizers are manufactured by combining nitrogen (from the air) and hydrogen (from water, oil, coal or more often from natural gas) in the presence of a catalyst to form ammonia, the building block of most nitrogen fertilizers. The ammonia is then either used directly as a fertilizer, combined with carbon dioxide to form urea, with phosphoric acid to form mono and di-ammonium phosphate or with nitric acid to form ammonium nitrate.

The use of nitrogen fertilizers for cropping, particularly of cereals and sugar, has been increasing steadily and nitrogen use (tonnes of total nutrient) now exceeds phosphorus. The largest increase has been in urea, which now comprises half of the nitrogen fertilizer used in agriculture.

Use of ammonium phosphates, which are also an important source of phosphorus, has also significantly increased. The Australian industry offers many different fertilizer mixtures in which the major nutrients - nitrogen, phosphorus, potassium and sulfur - are combined in varying proportions. Essential trace elements are incorporated into fertilizers where a particular deficiency is indicated in the soil.

The total tonnage of the major fertilizer products (imported and domestic) used in Australia, and the total tonnage of nutrient elements in those products are listed in Table 1.

**Table 1. Tonnage of major imported and domestic fertilizer products used in 2002. (FIFA website).**

Product	Tonnes	Approximate Tonnage of Principal Elements				
		N	P	K	S	Ca
Urea	1,306,400	600,940	-	-	-	-
Single superphosphate	1,297,819	-	116,805	-	142,760	259,565
Di-ammonium phosphate (DAP)	730,009	131,400	146,000	-	10,950	-
Mono-ammonium phosphate (MAP)	558,796	55,880	122,935	-	8,380	-
Potassium chloride (muriate of potash)	340,788	-	-	170,395	-	-
Ammonium sulfate	237,908	49,960	-	-	57,100	-
Triple superphosphate	193,762	-	38,750	-	-	-
Anhydrous ammonia	84,115	68,970	-	-	-	-
<b>TOTAL</b>	<b>4,749,597</b>	<b>907,150</b>	<b>424,490</b>	<b>170,395</b>	<b>219,190</b>	<b>259,565</b>

### 3.1 Products to Improve Soil Quality

There is little information aggregated at the national level for soil conditioners and other soil amendments in Australia. This is a key gap in our knowledge of the contaminant inputs to soils receiving these products. The concentrations of the various chemicals within these products are likely to vary depending on the source of the material, and the level of processing required prior to use as a soil additive.

Traditional soil amendments within the agricultural industry include lime, dolomite and gypsum. However, the current trend is to make greater use of products developed from waste, such as compost, biosolids, and other wastes such as fly ash or iron slag. The following sections provide a brief summary of some of the major products used to improve soil quality.

#### 3.1.1 Lime

Lime, which is comprised mostly of calcium carbonate, is a common soil conditioner used to neutralise acidity and to improve soil structure. It also supplies plants with the important element calcium. Most fertilizers that contain nitrogen slowly acidify soils and it is important to correct for this. As soils become more acidic, hydrogen ion replaces valuable mineral elements, such as Ca and K; while other elements, such as phosphorus, may become less available to plants. Minor elements, such as Mn and to a lesser extent aluminium (Al), become more soluble in acidic soils and can be taken up in excessive quantities by

some plants. If large quantities of lime, or Ca salts such as gypsum, are mixed with the soil they improve its structure by forming more stable soil aggregates, thus making it easier for roots and water to penetrate. The amount of lime that is applied depends on both the acidity of the soil and its texture; for example a heavy soil needs more lime than a sandy soil.

Another liming material is hydrated lime, which is produced by reacting quicklime (CaO) with sufficient water to satisfy its chemical affinity for water, yet maintain it as a powder. The production process used also removes contaminants that are normally found in quicklime. Hydrated Lime, which is an extremely versatile chemical, is the most widely used and lowest cost alkali in the world.

The annual quantity of lime applied each year to Australian soils in 2001 and 2002 is presented in Table 2.

### 3.1.2 Dolomite

Dolomite is a naturally occurring product similar to lime. It differs because it contains much higher levels of magnesium carbonates, although the calcium content still exceeds the magnesium content. Dolomite is used instead of lime in situations where the Ca to Mg ratio needs correcting along with pH. Dolomite has a variable but high neutralising value depending on where the product is sourced. The annual quantity of dolomite applied each year to Australian soils in 2001 and 2002 is presented in Table 2.

### 3.1.3 Gypsum

Gypsum is a naturally occurring product high in calcium and sulfur in the form of calcium sulphate. It is used primarily for correcting sulfur deficiencies and improving soil structure. It comes in many different forms including sand, seed and crystal and is obtained from many different locations. Gypsum also helps improve soil structure and balance the soil by both adding Ca and displacing Na. When gypsum is applied, the Ca combines with clay particles, causing them to aggregate - improving soil structure. The sulfate in gypsum combines with Na, which is then carried away in the soil water.

Many Australian soils are high in Mg, and when combined with low concentrations of Ca, soils set hard when dry, limiting root access and inhibiting crop establishment. Gypsum is also used to restore the appropriate Ca to Mg ratio.

Australia currently produces about 4 million tonnes of gypsum annually, which is nearly triple the volume produced 10 years ago. Nearly a quarter of the production is exported. The annual quantity of gypsum applied each year to Australian soils in 2001 and 2002 is presented in Table 2.

Gypsum (also known as phosphogypsum) is a by-product in the manufacture of phosphoric acid for use in the production of high analysis phosphorus fertilisers. Annual usage of Phosphogypsum in Queensland is about 25 - 30 000 tonnes. Use in recent years has been depressed by dry weather and low farm incomes, as well as farmers' awareness that the product should not be used in vegetable or peanut production, or on acid soils because of elevated Cd.

Phosphogypsum typically contains higher concentrations of cadmium and radionuclides than naturally occurring gypsum, reflecting the higher concentration of these elements in the phosphate rock from which it was made. The actual concentrations depend on the source of the phosphate rock.

Phosphogypsum, which was produced at Newcastle and Brisbane until around 1990, was made from Nauru phosphate rock. It contained up to 15 mg/kg Cd (typically around 10 mg/kg Cd). The phosphogypsum that remains at Newcastle is no longer used in agriculture, sales of this product being confined to industrial use (washing coal). Phosphogypsum continues to be sourced from Brisbane, though the stockpile is diminishing. Incitec Pivot targets this product at inland grain and cotton cropping areas on alkaline clay soils, where the bioavailability of cadmium in the soil is low. Use on acid coastal soils, and in crops such as peanuts and vegetables is discouraged.

Since 2000, phosphogypsum has also been produced by WMC Fertilizers at their ammonium phosphate fertiliser plant in northwest Queensland. However, given the plant's remote location and associated freight costs, the product has minimal use in agriculture.

**Table 2. Use of lime, dolomite and gypsum in Australia for the years 2001 and 2002. (ABS 2001-02, Agricultural Commodities).**

Substance	Tonnes of material used in different years	
	2001	2002
Lime (acidity control)	1 745 000	2 353 000
Dolomite	155 000	197 000
Gypsum (soil conditioning)	1 376 000	1 715 000

### 3.1.4 Biosolids

Biosolids are solids containing predominantly organic, but also mineral components that are derived from sewage treatment processes and are in a state that they can be managed to utilise their nutrient, soil conditioning, energy, or other values. The application of this product to land has increased considerably over the last 15 years. An example of this is provided in Figure 1 where the trend is illustrated for NSW.

Currently, approximately 250,000 dry tonnes of biosolids are produced annually in Australia, with perhaps one third to one half of this being applied to land. Significant differences in the extent of land application exist between States however.

To facilitate the reuse of biosolids, each State has developed guidelines for their management and application. The guidelines published by EPA Victoria (2004) describe minimum requirements for biosolids land application, thereby ensuring sustainable management, but enabling access to the potential benefits of biosolids – addition of organic matter, nutrients, trace elements and improved moisture retention and holding capacity with subsequent improvements in soil structure and fertility.

In addition, The National Water Quality Management Strategy *Guidelines for Sewerage Systems Biosolids Management*, provide national guidelines and a uniform approach to the management of biosolids with the focus on the beneficial use of biosolids as a resource. The guidelines have been developed for water resource managers, sewerage authorities and regulators developing biosolids management systems. The guidelines were agreed to at the Natural Resource Management Ministerial Council in December 2004 and are due for public release in mid 2005.

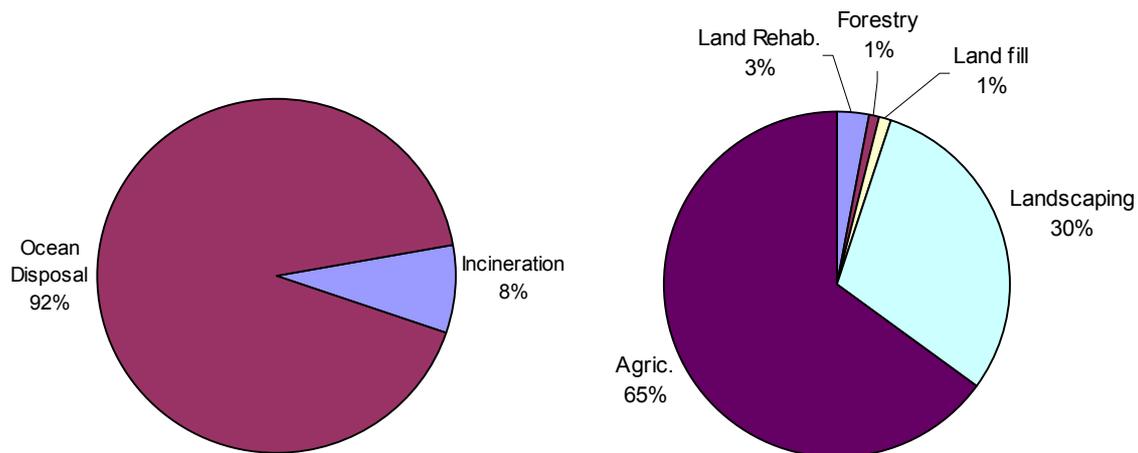


Figure 1. Biosolid use in New South Wales in 1988/89 (left) and 1998/99 (right).

### 3.1.5 Compost

Local Government is increasingly playing a vital role in diverting organic wastes away from landfill for recycling at composting facilities. A survey last year by the NSW Department of Environment and Conservation showed that the collection of garden plant residue in NSW had increased by an average of 19 per cent per year from 1998, through the progressive introduction of kerbside collection services. The survey also showed more than 1.3 million tonnes of organic materials were composted in NSW in 2002-03. Almost half of this (620,000 tonnes) consisted of household garden organic wastes, with most of the remainder (540,000 tonnes) coming from the agricultural and forestry industries. About 85 per cent of garden organics recycled in NSW were from the Sydney, Hunter, Central Coast and Illawarra regions (WME, 2004).

Ecocycle Victoria has reported that over 500,000 tonnes of organic waste is collected annually in Victoria (amount does not include proscribed wastes such as meat waste). Of this amount, some 78% ends up in a range of products used in landscaping, horticulture, agriculture and bioremediation. This includes compost (24%), mulch (31%), soils (17%) and potting mix (6%).

The use of compost and mulch has been increasing steadily over the past few years, given a greater awareness of its role in reducing water usage. Manures are mixed with composts in order to increase the nutrient concentration of the final product. Similarly composts are mixed with worm castings to produce higher value products. Compost is also blended with coal dust.

### 3.1.6 Manure

Manure from farm animals such as poultry, cattle and pigs, is used directly as fertilizers for agricultural purposes. It can also be mixed with compost to increase the composts' nutrient value as a soil additive. In addition to nutrients, manure may contain salts, metals, and to a lesser extent pharmaceutical products including antibiotics (Ying et al., 2002). The nature of manure and the requirement to manage its disposal has led to the development of numerous guidelines by various agencies - covering application rates and methods for assessing the benefits to come from the use of manure in agriculture.

Agricultural guidelines, (e.g. DPI Vic, 2004) suggest that where poultry litter is used as fertiliser and spread evenly across a pasture at rates consistent with such use, the pasture may be grazed by stock without contravening the ruminant feed ban or poultry litter ban. This ban has been put in place to reduce the risk of transmitting bovine spongiform encephalopathy, otherwise known as mad cow disease or BSE. This is also consistent with international standards that allow for meat and bone meal to be used as

pasture fertiliser but not as stock feed. Other precautions associated with the use of poultry manure is that stock be kept from the fertilised paddock for at least three weeks to minimise their risk of developing botulism, salmonellosis or mastitis. Ideally, the litter/manure should be ploughed into the soil and time given for the grass to grow to a height where close grazing to the ground will not occur (DPI Vic, 2004).

Similar guidelines have also been developed for the use of dairy shed effluent, which limit the application rates and establish protocols to reduce offsite contamination.

Pathogenic microorganisms found in land-applied manure can include bacteria, viruses and protozoa. These organisms may persist in the soil and be transported by runoff into surface and ground water (Mawdsley et al., 1995). Experimental work undertaken in the USA using liquid pig manure showed that organisms with a short persistence time were unlikely to survive in farm run-off; however the risk of offsite transport increased with species survival time (Gessel et al., 2004). Hence controlling manure application rate and method of application may be means to reduce the risk of pathogen transport.

### **3.1.7 Municipal solid waste**

There is an increasing drive to find alternative uses for municipal solid waste (MSW) as opposed to the current process of disposing to land fill. As such MSW is seen as a source product for compost and can be blended with organic wastes and other products to form composts and other soil products for agricultural use. Given the increasing number of alternative waste technologies coming on line, it is likely more organic waste will be available for use in agriculture.

A joint Working Group between COMPOST NSW and the NSW Alternative Waste Technology (AWT) Working Group has been formed to develop a roadmap for the utilisation of AWT organics - the organics rich stream produced by AWT processing of municipal solid waste (MSW) and commercial and industrial (C&I) waste streams. These processes are likely to produce an organic rich fraction containing nutrients and organic matter, which has the potential to improve soil physical, chemical and biological health. It is a prime requirement that any application to land of such material is genuinely beneficial and not harmful to the environment, human health or agriculture.

In the development of standards and, ultimately, markets for these organics, industry needs to be aware that promotion of any unsafe or harmful products would have a very negative impact on the acceptability and hence long term viability of AWT.

### **3.1.8 Fly ash**

Coal fired power stations produce large quantities of power fly ash. Increasing the effective utilisation of ash materials is fast becoming a priority for Australian ash producers particularly in the face of deregulating electricity market places (Heidrich, 2003). Of the 13.1 million tonnes of fly ash produced annually in Australia, some 3% is currently used in agriculture.

The composition of fly ash varies depending on the source of coal being burnt. In Australia, the majority of fly ash produced is about 65% silica, and 23% alumina. Other components include  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{SO}_3$ . Given the process by which it is created, fly ash may also contain dioxins and furans.

### **3.1.9 Kiln dust**

During the manufacture of cement, there is a by-product called kiln dust, potash lime or calfines. This by-product is ideal for use to neutralise substances, for pH control, and as a raw material for use in fertilizer production where a solid residue is not a concern. Its chemical properties vary depending on production conditions, and as with other products, it can contain heavy metals.

### 3.1.10 Mining and smelting by-products

Mining and smelting industries produce wastes that may have beneficial properties for land application. At present, there is no national inventory of these wastes, nor a compilation of their qualities.

A by-product from the process of refining bauxite to alumina, red mud, has been used as a soil amendment to enhance phosphorus retention in sandy soils (Snars et al., 2003). However, it does have possible detrimental effects for agricultural use, due to its inherent radioactivity and heavy metal content. But these risks can be minimised through low rates of application (20 t/ha once every 5 years) (WA EPA, 2000).

Iron and steel smelting produces about 3 million tonnes of slag annually, and there is an expectation that the use of this material for agricultural purposes will increase, given the current emphasis on waste utilisation.

## 4 Adverse Effects of Contaminants

An adverse effect is a deleterious effect on plants, plant products, animals, micro-organisms, human beings or the environment. Adverse effects may be chemical (e.g. accumulation of contaminant in soil), physical (e.g. damage to soil structure resulting in water repellence/waterlogging/increased erosion etc), biological (e.g. toxicity to biota) and social (e.g. public perception that produce is contaminated).

For this report, the definition of an adverse effect is restricted to the more direct effects from the use of a fertilizer. Thus, occupational health and safety risks associated with the manufacture, production or application of fertilizers containing harmful contaminants is outside the scope of this report.

The PISC Fertilizer Working Group drafted the following list of adverse effects, which were discussed with the various stakeholders.

#### 1. Adverse environmental impact:

- Accumulation in the soil (related to environmental action levels in the Assessment of Contaminated Sites National Environment Protection Measure);
- Increased bioavailability if the contaminant is toxic to plants or animals;
- Interaction with other chemicals and production of harmful by-products;
- Accumulation or concentration in the food-chain, producing unacceptable contaminant levels;
- Introduction of weeds, diseases or pests or conditions that favour them;
- Potential for mobilisation and off-site migration of contaminants; and
- Adverse effects on soil ecosystems, aquatic ecosystems and biota.

#### 2. Adverse human impact:

- Harmful to human health, through handling or in food;
- Accumulation or concentration in human food products; and
- Aesthetic issues, predominantly odour but possibly visual.

#### 3. Adverse agricultural impacts:

- Toxic to agricultural plants or animals;
- Accumulation in agricultural products;
- Likely to jeopardise marketing of agricultural products (e.g. through unacceptable contaminant levels or through products being perceived to be a risk to consumers); and
- Likely to jeopardise agricultural production (e.g. introducing weeds, diseases or pests or long-term impacts on soil health).

#### 4. Anticipated adverse impacts (a precautionary approach):

- Source of material known to consistently contain contaminants; and
- Otherwise unacceptable (i.e. adverse community reaction to use of material as a fertilizer).

In assessing an adverse effect of a contaminant, it is important to consider the pathways from an agricultural perspective. These include:

- Increased release or bioavailability of contaminants, if toxic to plants or animals, leading to adverse effects on soil ecosystems or plants, in the short or long term;
- Accumulation or concentration in the food chain producing unacceptable contaminant levels from a trade or human health perspective;
- Potential for contaminant mobilisation and off-site migration; and
- Toxic to domestic animals.

It is important not to define an adverse effect as merely accumulation of a contaminant in soil or food, since fertilizers are added to soils to increase concentrations of nutrients in plants and soils. For example, the use of zinc fertilizers is leading to an accumulation of zinc in Australian soils, but this is not seen as an adverse effect unless the concentrations of zinc exceed those found to be toxic to an organism deemed worth protecting. Similarly, use of copper fungicides in vineyards is leading to copper accumulation in these soils, but effects should not be considered adverse until vine production, other potential crop production, or other endpoints are deleteriously affected.

It is also important to recognise that establishing “adverse effect” levels or “loading” levels for contaminants could be an invitation to contaminate up to those levels. Hence an approach that develops maximal contamination guidelines but also adopts a “no-more-than-necessary” principle would be more acceptable from a sustainability perspective.

#### **Recommendation**

For the purpose of this project the following were defined as adverse effects:

- Increased release, mobility or bioavailability of contaminants leading to adverse effects on soil ecosystems or aquatic ecosystems in the short or long term;
- Accumulation or concentration in the food chain producing unacceptable contaminant levels from a trade, human health or ecological perspective;
- Potential for contaminant mobilisation and off-site migration at concentrations sufficient to cause negative impacts on off-site ecosystems; and
- Toxic to domestic animals, livestock and wildlife.

## 5 Contaminants of Concern

There are a vast number of chemicals that could be contaminants of fertilizers and have the potential to affect human and environmental health. However, rather than listing these individually, a brief description of the groups or families of chemicals that may be present in fertilizers and that are considered to pose a risk to the environment are provided below (Table 3).

**Table 3. Groups or families of chemicals that may be present in fertilizers, and that are considered to pose a risk to human and/or environmental health.**

Inorganic contaminants	Organic contaminants	Biological contaminants
<ul style="list-style-type: none"> <li>• Essential elements</li> <li>• Heavy metals</li> <li>• Metalloids</li> <li>• Radionuclides</li> <li>• Rare earth elements</li> <li>• Anionic elements</li> <li>• All other elements</li> </ul>	<ul style="list-style-type: none"> <li>• Pesticides</li> <li>• PCBs</li> <li>• Dioxins and furans</li> <li>• PAHs</li> <li>• Surfactants</li> <li>• Pharmaceutical and personal care products</li> <li>• Endocrine disruptors</li> </ul>	<ul style="list-style-type: none"> <li>• Pathogens</li> <li>• Viruses, prions, bacteria</li> <li>• Foreign sp. including weeds</li> </ul>

### 5.1 Inorganic Contaminants

All elements (Figure 2), even essential nutrients such as Cu, P and Zn, and their associated compounds have the potential to be of concern to human or ecological health. Whether they do cause detrimental effects or not depends on their concentration, bioavailability in a particular matrix, and duration and path of exposure to the target organism, and sensitivity of the target organism to a particular element.

A key difference between inorganic and organic contaminants is their persistence: even though certain types of organic chemicals may be slow to degrade, there is nevertheless the potential for degradation to less toxic forms whereas inorganic elements persist indefinitely. Hence pollution of a soil by an inorganic contaminant can only be decreased by physical removal of that contaminant through for example, leaching, volatilisation (applicable to only a few elements, including N, S, mercury (Hg) and selenium (Se)), or physical removal of the soil or crops which have taken up the inorganic element (the latter being the strategy used in phytoremediation of contaminated soil).

#### 5.1.1 Heavy metals

It is generally accepted that metals having a specific gravity (weight per unit volume) greater than  $5\text{mg m}^{-3}$  are termed heavy metals, although the term is often used, and misused, in many contexts (Duffus 2001). The heavy metal elements that naturally occur in soil include Cd, cobalt (Co), chromium (Cr), Cu, iron (Fe), Hg, Mn, Mo, nickel (Ni), lead (Pb) and Zn. These are located in the yellow and green areas of the periodic table shown in Figure 2. Many of these elements differ from the alkaline earth metals, which include Ca and Mg, in that they can exist in several valence states in soil (McLaughlin, 2003).

The term “heavy metals” is often used synonymously with the term “trace elements”, but this is incorrect as trace elements are generally defined as those elements normally occurring in soil at concentrations less than  $100\text{ mg kg}^{-1}$  (Logan, 2000), which precludes several heavy metals, including Cr, Fe and Mn. Arsenic (As) is often included in “heavy metals”, but is more correctly classified a metalloid along with Selenium (Se).

Some heavy metals are essential for either plant or animal survival (Co, Cr, Cu, Fe, Mn, Mo, Ni and Zn) while others are non-essential (Cd, Hg and Pb). Essential heavy metals can exert toxic effects by either being present at too low (deficient) or too high concentrations. Non-essential heavy metals in contrast, are generally toxic at low concentrations.

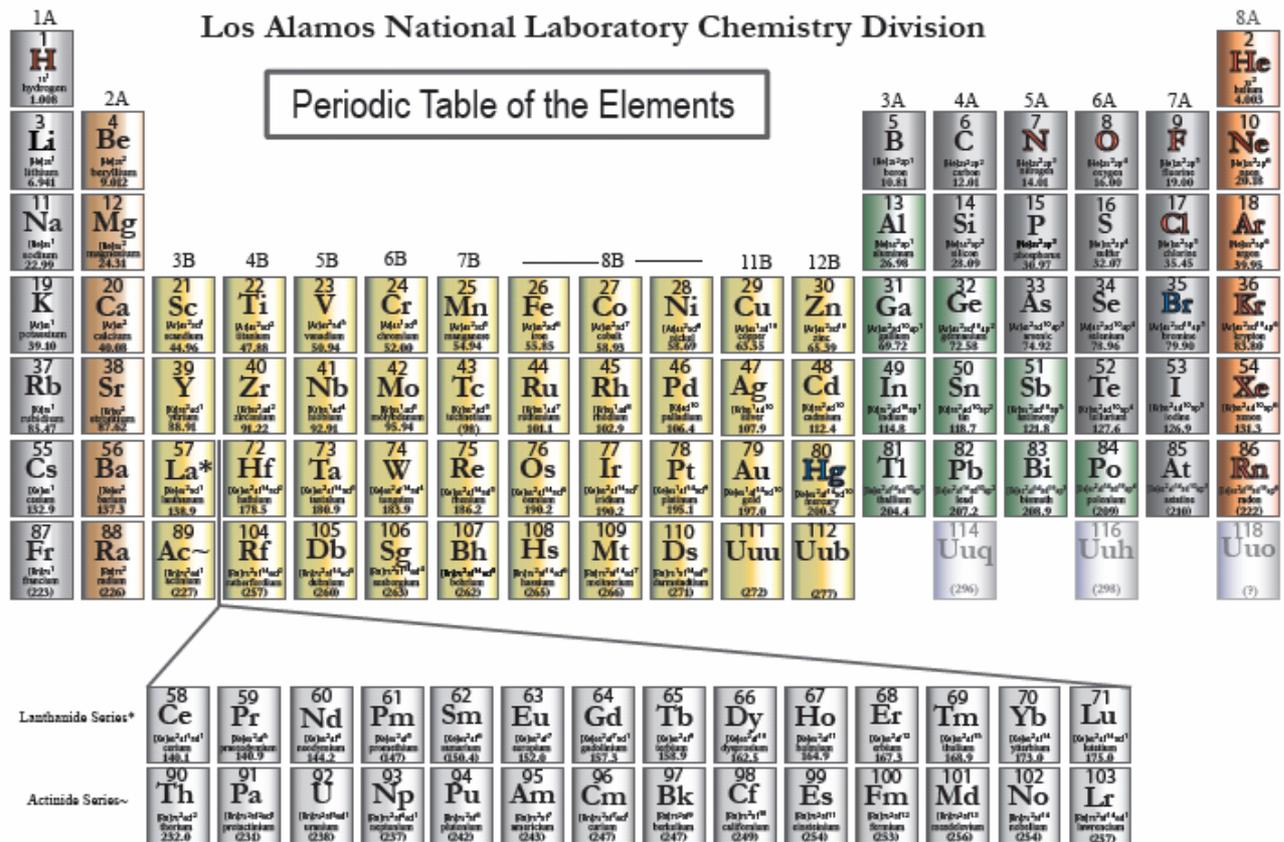


Figure 2. Periodic Table of the elements.

In the guidelines for regulating maximum allowable concentrations of contaminants in various environmental compartments, most attention to date has focused on the heavy metals. This attention is warranted, as organisms tend to be highly sensitive to heavy metals, which are already widespread in nature and sometimes at concentrations close to critical toxicity threshold levels for organisms. Hence, in some situations a relatively small increase above background concentrations for a particular heavy metal may result in adverse human or ecological health effects. Heavy metals also tend to be concentrated by the same forces that concentrate phosphorus into potential fertilizer sources such as rock phosphate ore deposits or sewage sludges and manures. To date, the removal of heavy metals from these products has not been widely practised; hence most manufactured phosphatic fertilizers, as well as by-products such as phosphogypsum and biosolids, may contain appreciable amounts of some heavy metals.

There are many other inputs to agricultural soils that are potential sources of heavy metals, including animal food supplements that contain arsenic (As), Cu and Zn, fungicides, agricultural limes, gypsums, composts, and other soil conditioners.

### 5.1.2 Metalloids

The metalloids are the group of elements that are located at the border of the green and grey areas in the Periodic Table (Figure 2) except Al, which is a metal. Of these, As is the element of most concern due to a combination of its moderately high natural abundance in the environment and toxicity. Arsenic, along with Cu and Cr, is still widely applied as a wood preservative (Cu-Cr-As-treatment) and historically it was used as a fungicide/pesticide and so it will be found in composts or other products that originate from treated materials. Arsenic is also commonly associated with iron-, base metal- and precious metal- ore

deposits and so may be concentrated in by-products from the mining industry. It should also be noted that As and Cr are both elements that commonly are found in different oxidation states in natural systems and their toxicity to organisms, bioavailability and mobility are very strongly controlled by their chemical form (e.g. oxidation state). For example, As (III) is more toxic than As (V), and Cr (VI) is more toxic than Cr (III).

### 5.1.3 Radionuclides

Radionuclides can be toxic as a result of their chemical properties but they are primarily of concern because they emit radiation that can damage DNA leading to carcinogenic and/or teratogenic impacts. Several naturally occurring radionuclides occur in soils including isotopes of potassium, uranium, thorium and radium. These are often found at higher concentrations in association with phosphate rock ores and can be transferred into the finished fertilizer product. Natural radionuclides may also be associated with mineralised zones and can be concentrated in by-products from for example, the aluminium and heavy mineral sands processing industries. There are also a large number of man-made radionuclides which have entered the environment as a result of nuclear weapons testing or releases from nuclear facilities, and others which are used commercially such as <sup>241</sup>americium (half-life 432 years) which is a component of household smoke detectors and <sup>60</sup>cobalt (half-life 5 years) which is used as a medical and industrial radiation source.

### 5.1.4 Rare earth elements

These are elements with atomic numbers between 57-71 (lanthanides) that except for promethium (atomic number 61, a short-lived radioisotope), are found naturally in the environment. Very little information is available regarding their toxicity and behaviour in the environment. What information is available was collated in a recent review (Sneller, 2000). This indicated a complete lack of toxicity data for terrestrial species but toxicity values in the range of 1 – 20 mg/L for fresh and marine aquatic species. However, with the advent and increasing accessibility of inductively coupled plasma mass spectrometry (ICP-MS) technology for analysis of these elements, the amount of data for these elements is likely to increase.

### 5.1.5 Anionic elements

Most of the elements in the groups described above tend to exist in cationic forms in the environment. Notable exceptions to this are the halogens (Group 7A in Figure 2 - fluorine (F), Cl and bromine (Br)), and the oxyanions (As, Cr, Mo and Se) which combine with oxygen to form stable negatively charged (anionic) species. The charge on any element or molecule has a large bearing on its behaviour in the environment and biota. Of the halogens, F is currently the element of greatest concern for vertebrates in agricultural systems due to its toxicity to these organisms and high concentration in phosphatic fertilizers. High concentrations of Cl can result in toxicity to plant and soil micro-organisms, and since many waste streams can be highly saline, it needs to be ensured that any potential fertilizer value from such streams is not compromised by excessive Cl levels.

### 5.1.6 Other elements

As mentioned above, all elements have the potential to cause detrimental human/ecological effects when present in high enough bioavailable concentrations. Elements which do not fit into the above groupings but which have been demonstrated to be of concern in some environments include Al, B and Na. Aluminium toxicity is largely responsible for poor plant growth at low soil pH (< 4.5), at higher soil pH values, Al is not soluble and hence not bioavailable to plants. Boron exists as the uncharged boric acid species in most soils. High concentrations of Na result in poor plant growth, but this is generally due to detrimental effects on soil structure which occur before Na toxicity *per se* becomes an issue.

## 5.2 Organic Contaminants

### 5.2.1 Pesticides

Pesticides, which include herbicides, fungicides, insecticides and other biocides are chemicals that can be found in straw, green plant residues (e.g. tree cuttings and lawn clippings), winery or distillery wastes (lies, stems and skins) and products or by-products of plant or animal (e.g. wool scouring) origin which have been treated with such chemicals.

The use of organochlorine pesticides, such as DDT and dieldrin, which were found to be persistent in the environment, have been gradually banned from agricultural and urban usage since the 1970s, but may still be present in wastes.

### 5.2.2 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a group of chlorinated hydrocarbons, consisting of 209 different congeners, whose physicochemical properties vary with their degree of chlorination (Vallack et al., 1998). They are industrial products and were formerly used widely as pesticide intermediates, as heat-transfer media, lubricants, solvents and dielectrics in electrical transformers. Due to their high persistence, they are found in many environmental compartments or matrices. However, it should be noted that The National Residue Survey (on animal fats) suggests that PCBs are not a contaminant of Australian agricultural systems.

### 5.2.3 Dioxins and furans

Polychlorinated dibenzo-para-dioxins, and polychlorinated dibenzo-para-furans (PCDD/F), 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.

### 5.2.4 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). These compounds can also be present in sewage sludges, depending on the waste stream (domestic or industrial).

### 5.2.5 Surfactants and by-products

Surfactants are major ingredients of domestic and industrial detergents that are used worldwide. Approximately two billion kilograms of surfactants are used annually (Ainsworth, 1992). The byproducts from these surfactants can occur in high concentrations in sewage derived biosolids. Levels ranging from 200 to 20,000 mg/kg (dry weight of biosolids) have been reported (Haigh, 1996).

Surfactants include, anionic (e.g. linear alkylbenzene sulfonates (LAS), alkane ethoxy sulfonates and secondary alkanesulphonates); nonionic (e.g. alcohol ethoxylates, alkylphenols (AP) including alkylphenol polyethoxylates and alkylphenol polyethoxycarboxylates); cationic (e.g. di-2-hydroxyethyl dimethyl ammonium chloride and quaternary esters) compounds.

LAS and APs are the surfactants most commonly found in the environment. There are some reports that indicate that these compounds are strongly bound (low bioavailability) but have relatively rapid degradation in biosolid-amended soils. Alkylphenols also exhibit endocrine disrupting properties, as they can mimic natural hormones and interfere with normal endocrine functioning of exposed organisms particularly sexual development and functioning.

### 5.2.6 Pharmaceuticals

Pharmaceuticals are a large group of compounds that are intentionally designed to have biological effects. When released to the environment they can interact with and bioaccumulate in other living organisms. Some of these compounds have a hormone mimicking effects on the reproductive system, even at very low concentrations (e.g.  $\text{ng.L}^{-1}$ ) (Halling-Sorensen et al., 1998), and thus are classified as endocrine disrupting chemicals (EDCs). The most likely route of these chemicals entering fertilizers is via biosolids and animal manures.

### 5.2.7 Endocrine-disrupting chemicals

Endocrine-disrupting chemicals (EDCs) is the collective term that includes all substances that adversely effect on the endocrine system of target organisms. For example this group includes metals, alkylphenols, natural and synthetic hormones, some pharmaceuticals (e.g. ethynylestradiol), as well as other organic compounds such as PCBs and pesticides. Some of these chemicals (e.g. heavy metals or hormones) may be present in animal manure and biosolids.

## 5.3 Biological Contaminants

### 5.3.1 Pathogens

Although beyond the scope of this document, the introduction of pathogenic bacteria (including salmonella, faecal coliforms), viruses, protozoa, helminthes (parasitic worms), and other parasites from faecal matter into potential soil amendments can be of concern. Pathogens can be found particularly in biosolids, if it has not been properly sterilised, and also through animal manure applied directly on agricultural lands. It should also be noted that composts, that don't use biosolids or manure, can still present a substantial pathogen risk as they provide an ideal environment once the composting process has ceased. High pathogen risk needs a source of pathogens and an environment to sustain them otherwise they will die off relatively rapidly.

### 5.3.2 Other biological contaminants

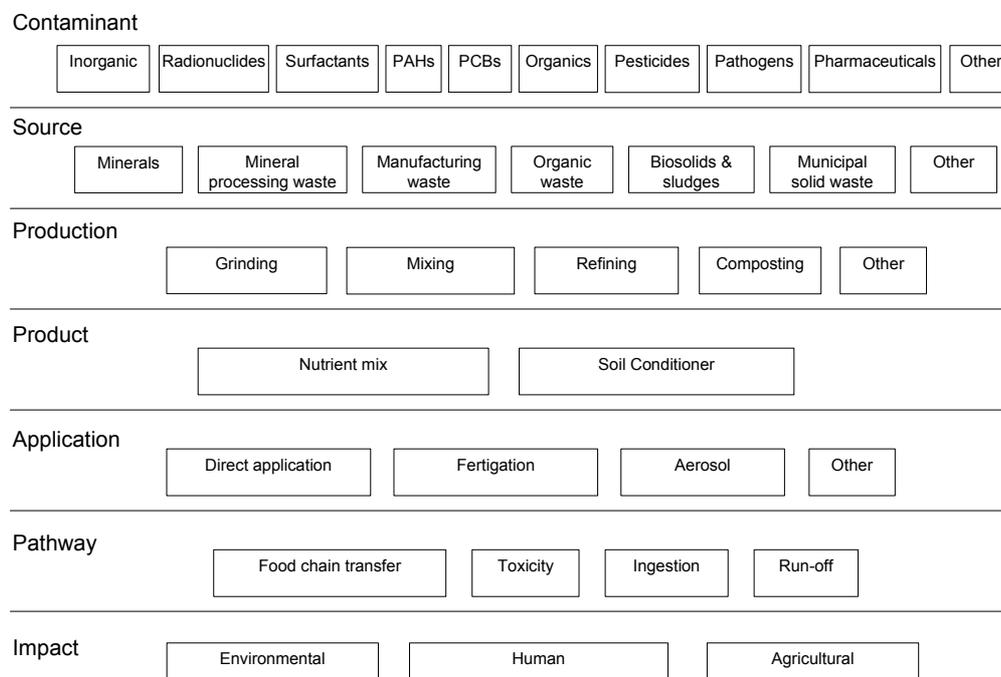
Plant and animal wastes used in composts and various soil amendments can be sources of non-pathogenic micro-organisms and pest species of animals and plants. The risk of this is reduced by appropriate production processes – e.g. length of time and temperature for composting. The prevention of

inappropriate material entering into the waste streams could also greatly reduce the chances of introducing such biological contaminants.

## 5.4 Sources of Contaminants

Understanding which contaminants pose the most risk and how much might be applied to land within or as a fertilizer will assist in developing a strategy for managing the associated risk.

Figure 3 provides a draft conceptual model of the pathways and stages in the transfer of contaminants from source to point of impact. One approach might be to focus on specific industry sectors that produce fertilizer ingredients that contain contaminants of concern. Alternatively the focus can be on the producers of fertilizers, and whether their methods could be improved to remove or make the contaminant non-toxic. Regulation may be further complicated by the differences between traditional producers of fertilizer and those that are producing a fertilizer as a means for recycling what was previously considered a waste product. These second type of producers are likely to form only a small component of the overall fertilizer market, but are likely to be dealing with products that have the potential to carry contaminants of concern.



**Figure 3. A draft conceptual model showing the layers or processes where the impact of contaminants might be investigated to reduce or remove the associated risk.**

### Recommendation

The types of contaminants or sources of contaminants to be investigated as a first priority are:

**Inorganic contaminants:** Essential elements, heavy metals, metalloids, radionuclides, rare earth elements and anionic elements. Specifically As, B, Cd, Cr, Cu, F, Hg, Ni, Pb, Se, and Zn.

**Organic contaminants:** Persistent organic pollutants (e.g. PCBs, dioxins and furans, PAHs), flocculants, coagulants, surfactants, pharmaceutical and personal care products, endocrine disruptors. Where appropriate (ie. chemicals with the same mode of action) the toxic equivalent approach should be used.

**Biological contaminants:** On advice from the FWG and IRWG we recommend that biological contaminants not be investigated as part of this project.

In terms of potential sources of contaminants we recommend that raw materials of mineral fertilisers, by-products of mining and smelting, energy wastes, and other industrial wastes are considered prior to examining biosolids, municipal solid waste, or food and green waste streams.

Future work in identifying contaminants of concern should draw on the knowledge and experience gained by related investigations, including the extensive work undertaken by the US EPA on chemicals of concern for biosolids (specifically the heavy metals and several organics), and also the work being done by the National Biosolids Research Programme (NBRP) in Australia.

## 6 Controlling Concentrations or Ingredients

In developing a strategy for controlling the inclusion of contaminants in fertilizers there are two main options available. These are the “ingredients” and “concentration” approaches. In the “ingredients” approach the presence of contaminants in fertilizers and soil amendments is controlled by specifying prohibited substances that cannot be used as fertilizers or as components of fertilizers. This can be taken further by prohibiting the use of any material that has been created using any of the banned substances in the manufacture of fertilizers.

Effectively the “ingredients” approach controls fertilizer quality through prohibiting the use of substances or ingredients, rather than contaminant concentrations or loadings to soil. This approach works well when contaminant concentrations in all possible ingredients are already known, but requires exemptions to be sought for many “safe” raw materials currently used in fertilizer production, where good quality, but prohibited, ingredients are already in use.

Contaminants *per se* are not a problem; rather, it is the rate/loading that is considered important, hence the alternative option is the “concentration” approach. This approach is also more conducive to the use of waste products (which include known contaminants) in fertilizers, when and where they are considered to be of no impact. However using the “concentration” approach requires a greater understanding of the environmental impact of contaminants. The circumstances, conditions and rates under which the fertilizer is intended to be used would also need to be understood.

The consensus reached was that a concentration approach is more practical as it allows the focus of risk to be based upon the end product rather than ingredients. However it was also recognised that some ingredients should clearly not be used in the production of fertilizers (e.g. asbestos). Hence a combined approach should be developed where a prohibited list of ingredients is produced, along with another list of concentration limits.

### Recommendation

That both the “ingredient” and “concentration” approaches should be used in this project. The “ingredient” approach should be used in deriving the list of compounds/ingredients that are not permitted in fertilizers. The “concentration” approach should be used to control permitted contaminants.

## 7 Potential Exposure

### 7.1 Pathways of Exposure

The transport and fate of contaminants present in a fertilizer once it is applied to soil will determine the potential exposures to living organisms. The potential pathways and endpoints that need to be considered are numerous, and a number have been identified at this stage as requiring evaluation.

For each family of contaminants, depending on their physicochemical properties, their concentration in the fertilizer, the way the fertilizer is incorporated in the soil (for example applied to the surface or mixed to depth), the extent of the contamination, the nature of the soil, the cropping system or land management, different exposure pathways will dominate. McLaughlin et al. (2000b) suggested a prioritisation of the key risk pathways for several heavy metals in soil (Table 4).

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 4. Critical risk pathway assessment for heavy metal pollution of soils, adapted from McLaughlin et al. (2000b).**

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

Pathways relevant to human/animal health include:

- Direct ingestion or dermal exposure during fertilizer application;
- Ingestion or dermal contact of fertilizer amended soil;
- Inhalation of particles and vapours in the air during and after fertilizer spreading and cultivation;
- Ingestion of plant and animal products produced on soil amended with fertilizers;
- Ingestion of animals/aquatic organisms (e.g. fish) affected by fertilizers either directly or indirectly; and
- Leaching or off-site migration of contaminants to potable water supplies from soils amended with fertilizers.

Environmental pathways include:

- Direct toxicity of fertilizer-derived contaminants to soil microflora e.g. bacteria such as *Rhizobium* spp. or fungi such as *mycorrhizae*;
- Direct ingestion and toxicity of fertilizer-derived contaminants to soil invertebrates;

- Toxicity of fertilizer-derived contaminants to crop, introduced and native plants;
- Indirect toxicity of fertilizer-derived contaminants to aquatic biota through runoff, leaching or dust deposition;
- Direct ingestion and toxicity of fertilizer-derived contaminants by domestic animals or native vertebrate fauna; and
- Secondary poisoning of domestic animals or native vertebrate fauna through ingestion of plant products, or soil flora or fauna, containing contaminants derived from fertilizer addition to soil.

Pathways for marketing/trade relate to the accumulation to levels in agricultural produce that exceed the Food Safety Australia New Zealand Maximum Residue Levels or Codex Maximum Levels.

## 7.2 Physicochemical Characteristics of Contaminants that Affect their Fate in Soil

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 4). 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 manganese 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 Mn as well as the many contaminants sorbed by their oxides. As both Fe and Mn are major structural metals in soil minerals, reduction of the Fe(III) and Mn(IV) species may change retention of many contaminants.

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. lead and 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).

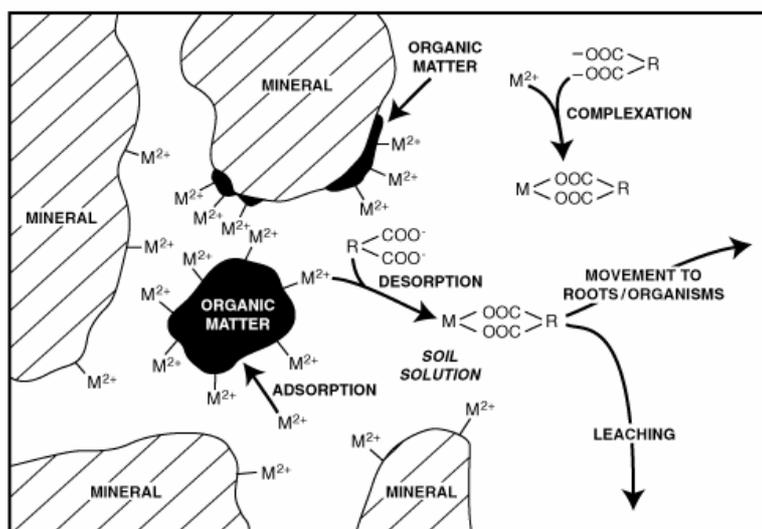


Figure 4. Soil binding sites and behaviour of a divalent cationic contaminant ( $M^{2+}$ ) in soils.

The distribution of chemicals between aqueous and solid phases of soils can be described by the partitioning coefficient (the notation for this is  $K_d$  or  $K_{oc}$ ) where a high  $K_d$  or  $K_{oc}$  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.

$$K_d = \frac{\text{Contaminant on soil solid phase}}{\text{Contaminant in soil solution}} \quad (1)$$

and

$$K_{oc} = \frac{\text{Contaminant on organic carbon}}{\text{Contaminant in soil solution}} \quad (2)$$

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 and Se.

Soils with high  $K_d$  values have a high sorption or buffering capacity for added contaminants i.e. the ability of the soil solid-phase to maintain constant concentrations of elements in the soil solution through sorption reactions. The buffering capacity is an integrated measure of the total amount of element, as well as the number and the strength of binding sites for that element 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 ( $K_d$ ) 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.

### 7.2.1 Inorganic contaminants

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

Many of the common contaminants in fertilizers, in particular the heavy metals, are cationic in nature e.g.

Cd, Cu, Ni, Pb, Zn etc. (Table 5). 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 5. Physical and chemical properties of heavy metals (McLaughlin, 2002).**

Element	Symbol	Atomic No.	Atomic weight	Valence	Natural isotopes	Density (mg m <sup>-3</sup> )	Melting point (°C)	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 <sup>2+</sup>	Cd <sup>2+</sup> , CdCl <sup>+</sup> , CdSO <sub>4</sub> <sup>0</sup>	Cd <sup>2+</sup> , CdCl <sup>+</sup> , CdSO <sub>4</sub>
Chromium	Cr	24	52.01	2,3,6	4	7.19	1,875	Cr <sup>3+</sup> , CrO <sub>4</sub> <sup>2-</sup>	Cr <sup>3+</sup> , CrOH <sup>2+</sup>	Cr(OH) <sub>4</sub>
Cobalt	Co	27	58.94	2,3	1	8.90	1,493	Co <sup>2+</sup>	-	-
Copper	Cu	29	63.54	1,2	2	8.94	1,083	Cu <sup>2+</sup>	Cu <sup>2+</sup> , Cu-org.	Cu-hydroxy species, CuCO <sub>3</sub> , Cu-org.
Iron	Fe	26	55.85	2,3	4	7.87	1,536	Fe <sup>2+</sup> , Fe <sup>3+</sup>	Fe-hydroxy species, Fe-org.	Fe-hydroxy species, Fe-org.
Lead	Pb	82	207.19	2,4	4	11.35	327	Pb <sup>2+</sup>	Pb <sup>2+</sup> , PbSO <sub>4</sub> <sup>0</sup> , Pb-org.	Pb-hydroxy and carbonate species, Pb-org.
Manganese	Mn	25	54.94	2,3,4,7	1	7.44	1,244	Mn <sup>2+</sup> , Mn <sup>4+</sup>	Mn <sup>2+</sup> , MnSO <sub>4</sub> <sup>0</sup> , Mn-org.	Mn <sup>2+</sup> , MnSO <sub>4</sub> , MnCO <sub>3</sub>
Mercury	Hg	80	200.61	1,2	7	13.54	-39	Hg <sup>2+</sup> , (CH <sub>3</sub> ) <sub>2</sub> Hg	-	-
Molybdenum	Mo	42	95.94	6	7	10.22	2,610	MoO <sub>4</sub> <sup>2-</sup>	-	-
Nickel	Ni	28	58.71	2,3	5	8.91	1,453	Ni <sup>2+</sup>	Ni <sup>2+</sup> , NiSO <sub>4</sub> <sup>0</sup> , Ni-org.	Ni <sup>2+</sup> , NiHCO <sub>3</sub> <sup>+</sup> , NiCO <sub>3</sub>
Zinc	Zn	30	65.37	2	5	7.14	420	Zn <sup>2+</sup>	Zn <sup>2+</sup> , ZnSO <sub>4</sub> <sup>0</sup> , Zn-org.	Zn <sup>2+</sup> , Zn-hydroxy and carbonate species, Zn-org.

Oxidation converts the non-toxic Cr<sup>3+</sup> ion to the toxic and carcinogenic Cr<sup>6+</sup> oxyanion. This reaction has even more significance in soils as a strongly sorbed or precipitated cation (Cr<sup>3+</sup>) is converted into a poorly sorbed or soluble anion (CrO<sub>4</sub><sup>2-</sup>). However, even in aerobic soils, Cr<sup>3+</sup> is thermodynamically the most stable state, so added Cr<sup>6+</sup> ion is rapidly converted to Cr<sup>3+</sup> in most soils.

### 7.2.2 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 log K<sub>OW</sub>), 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<sub>OW</sub> 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 ( $H_c$ ). This parameter, in combination with the  $\log K_{OW}$ , will determine their potential for volatilisation loss into the atmosphere. Thus if

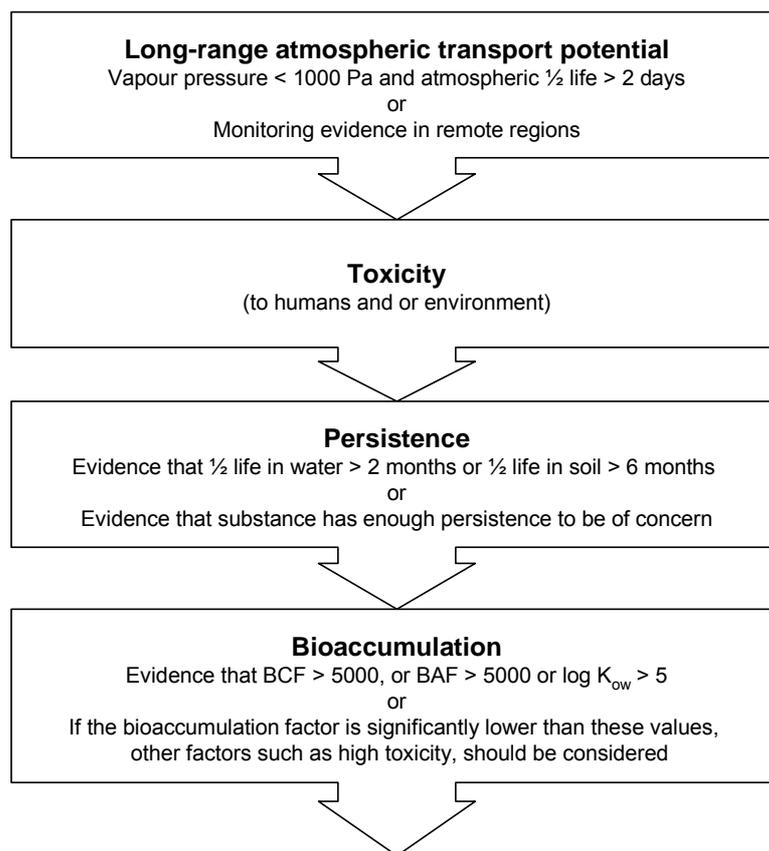
$H_c > 1.10^{-4}$  and  $H_c/K_{OW} > 1.10^{-9}$  : high volatility; and

$H_c < 1.10^{-4}$  and  $H_c/K_{OW} < 1.10^{-9}$  : low volatility.

A few general points can be drawn:

- Most of the persistent organic pollutants (POPs) are non-polar, have very low aqueous solubility and will tend to sorb strongly on solid particles, especially organic matter. For example, during sewage treatment the more hydrophobic and persistent organic compounds tend to partition on to sludge/biosolids during the treatment process;
- The free molecules are unlikely to be dominant forms transported in water however; the presence of dissolved organic molecules will facilitate their transport in water, because POPs will bind to these highly mobile organic particles (due to their high hydrophobicity). Furthermore, colloid movement can facilitate their off-site migration as the colloids are enriched in contaminant load. Consequently, an appreciable high concentration of contaminants can be found in surface- or ground-waters;
- 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 5.



Note:

Log K<sub>ow</sub> : 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 5. Information to take into account when assessing the risk potential of an organic pollutant released in the environment (e.g. present in a fertilizer) (adapted from Vallack et al., 1998).**

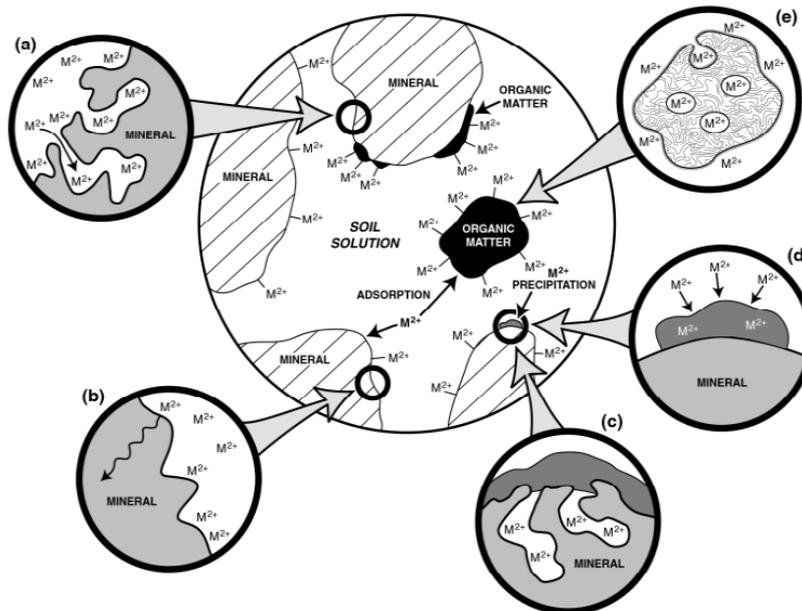
### 7.2.3 Ageing of contaminants in soil

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 6a). A related hypothesis is that the adsorbed metal slowly diffuses from the surface into the crystalline structure of soil minerals (Barrow, 1987) (Figure 6b). 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).

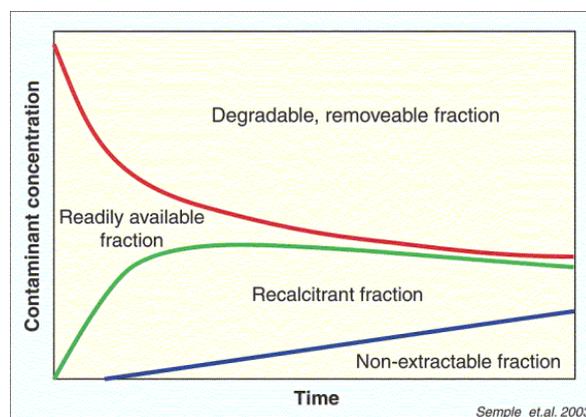
Precipitation reactions remove contaminants from soil solution through the formation of new solid phases, usually in association with a corresponding anion or cation already present in the soil solution.

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 6.** Sorption and ageing processes in soils, depicted for a cationic divalent metal (e.g. cadmium). 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. From McLaughlin (2001).

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; Ahmad et al., 2004). 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 7. 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 7.** A diagram showing the generalised behaviour of contaminants in soils with increasing time of contact. Note that with time (years) the non extractable fraction increases.

## 8 Process for Assessing the Hazard Posed by Contaminants

Risk assessments are typically conducted using a tiered or hierarchical framework such as that used by US EPA (1992), the Canadian Pest Management and Regulatory Agency (PMRA, 2000), and the Australian National Registration Authority (NRA, 1997). These consist of three consecutive components, a preliminary screening, a hazard assessment and a probabilistic risk assessment. Each step is more environmentally realistic than the preceding one and therefore provides a more realistic assessment of the potential threat posed by each chemical being considered. Chemicals posing a low threat to the environment are eliminated early in the process, thereby concentrating effort on the chemicals of greatest concern (Muschal and Warne, 2003).

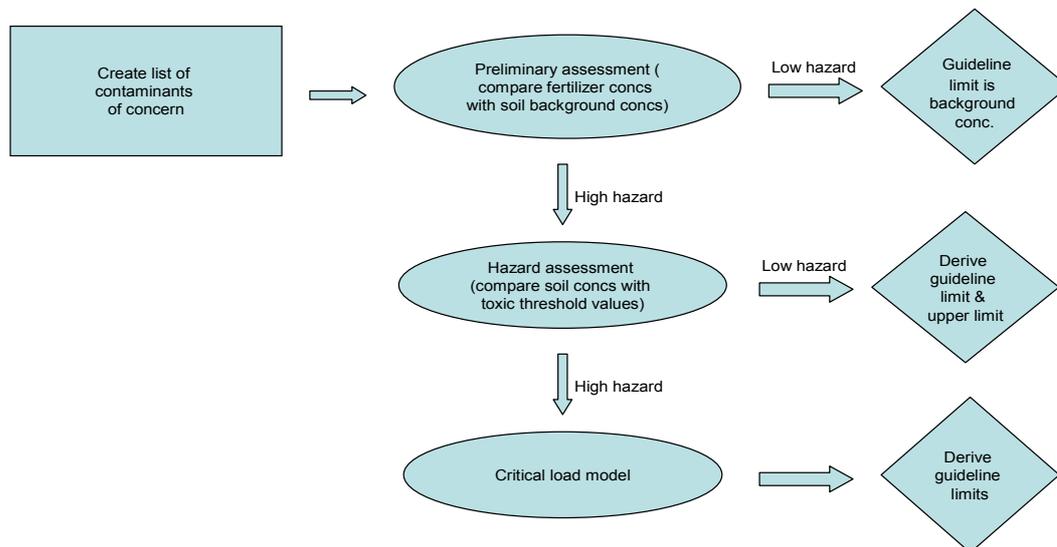
One of the required outcomes of this project is a set of guideline limits stating the maximum permissible level of contaminants in fertilizers. We propose to use the preliminary, hazard and risk assessment processes mentioned above, to calculate these guideline limits. How this will be done is illustrated in Figure 8 and details will be provided in the following material (Section 8.1 – 10 inclusive).

### 8.1 List of Contaminants of Concern

The first step that needs to be completed in order to be able to commence the process of assessing the hazard and risk posed by contaminants and deriving guideline limits is to formulate a list of contaminants of concern (LCC). The LCC will be decided on by the FWG and IRWG based on the recommendations made by CSIRO in this report (see recommendation in Section 5.4).

### 8.2 Preliminary Screening

As mentioned above, the first tier of the risk assessment is a preliminary screening, which provides a LCC for hazard assessment. The preliminary screening will consist of comparing the highest measured concentrations of contaminants in fertilizers against the lowest measured background concentration using values from the literature. Alternatively, an estimate of the background concentration such as that provided by the method developed by Hamon et al. (2004) could be used.



**Figure 8. Schematic of the process for assessing the hazard and risk posed by fertilizer contaminants and deriving guideline limits.**

The preliminary assessment would in fact use a hazard assessment method – the hazard quotient method developed by Urban and Cook (1986). Hazard quotients would be calculated using the following formula:

$$\text{HQ} = \frac{\text{highest estimated fertilizer concentration}}{\text{lowest background value or estimate of background}} \quad (3)$$

A HQ value greater than or equal to one means that the contaminant concentration in the fertilizer is greater than the background concentration and therefore it could accumulate over time to cause elevated soil concentrations. Such a scenario would be classed as posing a 'high' hazard. A HQ value of less than one means that the concentration in the fertilizer is less than the background concentration and given that the fertilizer is never applied on a 1:1 basis to soil, then there is no chance that the concentration of the contaminant in soil will increase over time. Such a scenario would be classed as posing a 'low' hazard.

Those contaminants that receive a high hazard classification will then be subject to the hazard assessment (Section 8.3). Those contaminants that receive a low hazard classification will not proceed to the hazard assessment; rather guideline limits will be derived. It is recommended that the guideline limit for the contaminant in fertilizers that have a low hazard should equal the conservative estimate of background concentration used in equation 3. However in order to be consistent with the "no more than necessary" principle it is recommended that fertilizer manufacturers not use ingredients that contain any higher contaminant concentration than is necessary.

### 8.3 Hazard Assessment

For the hazard assessment, the hazard quotient method that was previously used in the preliminary screening is again recommended with some slight modifications. This method is routinely used in the early stages of ecological risk assessments (e.g. Giesy et al., 1999; Solomon et al., 1996; Muschal and Warne, 2003). Hazard quotients would be calculated using the following formula:

$$\text{HQ} = \frac{\text{highest estimated environmental concentration}}{\text{lowest threshold value}} \quad (4)$$

where the lowest threshold value is the lowest toxicity value or the lowest environmental, food or human health guideline or standard (e.g. the Australian and NZ water quality guidelines, FSANZ guidelines, USEPA ECOSL values) for that contaminant. Given the two parameters used in Equation 2, the HQ values are conservative (i.e. tend to favour the environment).

There are two key differences between the hazard assessment conducted here and that conducted in the preliminary screening that improve the environmental realism of the assessment. First, estimates of the concentration of contaminants in soil (taking into account application rates, etc.) are used rather than simply the concentration in the fertilizer itself. Second, the estimated soil concentrations are compared to those concentrations that are known to cause toxic effects rather than simply background concentrations.

Depending on the chemical, there is the potential for off-site migration of some contaminants in fertilizers and therefore the hazard posed to both terrestrial and aquatic ecosystems will need to be assessed.

The hazard will be classed as low if the HQ is  $\leq 0.1$ , moderate when between 0.1 and 0.5 and high when the HQ  $> 0.5$ . The highest hazard classification that a contaminant receives from both the aquatic and terrestrial hazard assessments will become the overall assessment. A chemical that receives a high hazard classification will require further investigation, in the form of a probabilistic risk assessment and have its guideline limit derived from first principles (Section 9).

The HQ values are usually calculated using a series of environmental scenarios, of decreasing

environmental conservatism and increasing environmental realism (NRA, 1997). These scenarios are well established for the application of pesticides to both aquatic and terrestrial ecosystems but are not established for the application of fertilizers.

Based on experience with pesticides, the following scenarios for the application of fertilizers are proposed, but may change subsequently. A reasonably conservative scenario would be for a one hectare block of land to receive the maximum recommended application rate of fertilizer, at the maximum recommended frequency, for the maximum period of time that the soils are to be protected for, and assuming no loss of any of the chemicals added with the fertilizers. An equivalently conservative aquatic scenario would be for a one hectare pond that is homogeneously mixed to 15 cm deep to receive all of the fertilizer added in the terrestrial scenario. Contaminants that are determined to pose a low hazard under these scenarios are likely to be very safe. However, there are others contaminants that may pose a high hazard – for such chemicals the distribution coefficient of the contaminant will be used to generate more environmentally realistic concentrations for use in the hazard assessment. Only those that continue to pose a high hazard will be subject to probabilistic risk assessment and critical load modelling in Phase III of the project.

The depth of incorporation of the fertilizer in the soil will vary according to agricultural practice and this will modify the estimated environmental concentration and HQ values. The HQ analysis should be conducted for various agricultural systems (e.g. horticulture, dairy or dryland grazing). Given the variation in the composition of fertilizers the HQ analysis should also be conducted for each of the major types of fertilizer (e.g. phosphatic; trace element; biosolids, animal manures and composts; and soil amendments).

HQ analysis provides a quantitative assessment of whether deleterious environmental impacts could occur at a site under a given environmental scenario. They are not probabilistic statements of the likelihood of a toxic effect occurring or the likelihood of a certain size effect occurring.

Two sets of data are required to conduct a HQ analysis – threshold values and environmental concentration data (see Equation 4). Threshold values include toxicity data and various environmental, food and human health guidelines/standards. Toxicity data can be acquired by conducting searches of the US EPA ECOTOX (USEPA, 2004); Australasian Ecotoxicology (Warne et al., 1998; Warne and Westbury, 1999; Markich et al., 2002), and ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals) (ECETOC, 1993) databases in addition to searches of the literature. Likewise the various guidelines or standards will be obtained by conducting literature searches and contacting appropriate regulatory authorities. Estimated environmental concentrations of fertilizer contaminants can be determined using the above exposure scenarios and concentration data of contaminants in fertilizers and the rates and frequencies of fertilizer application. The latter data can be obtained by liaison with the Fertilizer Industry Federation of Australia and fertilizer manufacturers and importers.

One of the limitations that will be encountered is that the vast majority of toxicity data only measure the effects of direct exposure to chemicals absorbed from the ambient environment. The majority do not address the issue of real world exposures where organisms are exposed to the toxicants from both the ambient environment and from the food they consume. This is only a limitation for those chemicals that tend to accumulate in animal and plant tissue (ie. chemicals with high bioconcentration (BCF), bioaccumulation (BAF) or biomagnification (BMF) factors, or high octanol-water partition coefficients (Kow)). This limitation of the toxicity data is often carried through to the various guidelines and standards which are derived from the toxicity data. Thus, if the threshold data used to determine the HQ values do not account for accumulation then the hazard assessment will also fail to consider this. It is recommended that if there is not appropriate threshold data (that account for accumulation) all chemicals with a moderate to high potential to accumulate (BCF, BAF, BMF or Kow  $\geq 1000$ ) should automatically proceed to stage three where the guideline limits are derived from first principles.

BCF, BAF, BMF and Kow data for the contaminants undergoing hazard assessment will be obtained from

sources such as Hansch et al. (1995), Mackay et al. (1992a and b, 1993, 1995), Shiu et al. (1994), Tomlin (1994), Verschuere (1983) and Weast (1987). As there are often different estimates the mean or geometric mean of the published values will be used.

Guidelines for the control of contaminants in fertilizers and to protect soil quality that have been developed overseas could be used in Australia, however, their use could lead to either significant under- and/or over-protection of Australian soil and water quality. This could occur because:

- (1) Australian soils differ in a number of crucial physicochemical properties (including organic matter content, pH and clay mineralogy) to many European and North American soils. For example, most Australian soils contain less than 1.5% organic matter, which is very low for European soils.
- (2) Australian organisms can have different sensitivities to toxicants. A comprehensive comparison of the sensitivity of Australasian and non-Australasian aquatic species to metals and metalloids has shown statistically significant differences for a number of taxonomic groups and species (Hobbs et al., 2004).

The purpose of the hazard assessment is to identify those chemicals that pose a potential hazard to the environment. The hazard assessment is conservative, thus only chemicals that pose a "high hazard" warrant the development of guideline limits from first principles (see Section 9). For those chemicals that pose a "low" or "acceptable hazard" it would be advisable to derive two values - the guideline limit and an upper limit for contaminants in fertilizers. The guideline limit would effectively become the current maximum level of contamination in fertilizers – such an approach is consistent with the "no more than necessary" principle. The upper limit would be equal to the concentration of the chemical that corresponds to a HQ value of 0.5. The purpose of having the two values (ie. the guideline limit and upper limit) is that it may be necessary to change the source of a component of a fertilizer that may have a higher concentration of the chemical than is currently used. In such a case industry would need to determine the concentration of the contaminant and compare that to the upper limit. Provided the measured concentration in the new source was below the upper limit then it could be approved by the appropriate regulatory body. If, however, the measured concentration exceeded the upper limit then a guideline limit would have to be derived from first principles (as per the method described in Section 9) and the measured concentration compared to that.

### **Recommendation**

#### **Preliminary Screening**

That a preliminary screening process be conducted to identify those chemicals that could accumulate in the soil.

The background concentration be adopted as the guideline limit for contaminants that pose a low hazard.

Chemicals that pose a high hazard be subject to a hazard assessment.

#### **Hazard Assessment**

That a hazard assessment be conducted to identify those chemicals that could cause toxic effects.

The current levels of contamination in fertilizers be adopted as the guideline limit for contaminants that pose a low or acceptable hazard. An upper limit equal to the concentration in fertilizers that corresponds to a hazard quotient of 0.5 should also be derived.

Chemicals that pose a high hazard should be subject to further analysis in phase three of the project.

## 9 Methods to Determine Guideline Limits for Contaminants in Fertilizers from First Principles

There are three different approaches that can be used to determine the guideline limits for contaminants in fertilizers from first principles: the mass concentration; the mass balance; and the critical load approaches. A brief description of each of these approaches along with an assessment of the strengths and limitations of each approach are provided below.

### 9.1 Mass Concentration Approach

A mass concentration approach is perhaps the simplest form of assessing risk posed by contaminants in fertilizers, and requires no knowledge of contaminant behaviour, no information on rate of fertilizer application and no information on the characteristics of the soil conceptually receiving the contaminants. It assumes that deleterious impacts will occur if a contaminant occurs in a fertilizer at a concentration greater to that of the receiving soil, or against some other specified concentration. The main problem envisaged is the selection of reference concentration given the significant variation that occurs between different soil types and environments.

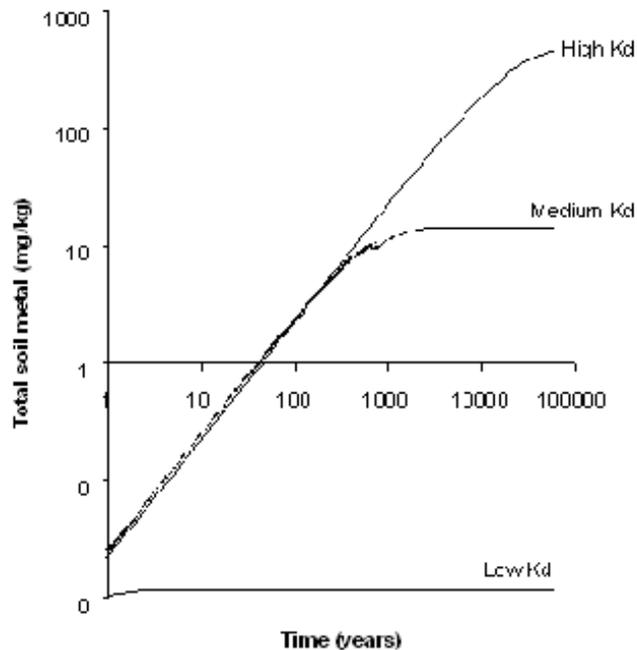
The mass concentration approach could be useful as part of a screening process, but is considered too simplistic to be used in deriving guideline limits for contaminants in fertilizers.

### 9.2 Mass Balance Modelling

The aim of mass balance modelling is to predict the change over time in soil concentrations of each element or compound. More detailed knowledge is needed of the fertilizer and other soil amendment inputs, contaminant behaviour (partitioning, uptake, leaching, volatilisation, etc.), crop uptake and crop partitioning (to harvested portions). For common contaminants, such modelling is possible and has been performed at farm-gate level for several contaminants in Europe (e.g. Bengtsson et al., 2003). National inputs of heavy metals have recently been assessed in UK agriculture by Nicholson et al. (2003), but outputs were not included in this work. The current proposed EU regulations for permissible Cd concentrations in phosphatic fertilizers were developed after extensive mass balance scenario modelling in European countries. Mass balance models adopt a “no net accumulation” criterion (ie. the concentration of a contaminant can not increase over time). This criterion could be very restrictive and inappropriate for some systems e.g. essential fertilizer elements Zn and Cu.

Mass balance models can be either static or dynamic. Static models consider present-day mass balances and do not take into account changes in soil concentrations, changes in crop off-take, and changes in other outputs (leaching, volatilisation, etc.) over time. Dynamic models are more realistic and account for time-dependent changes of the preceding variables and others. Dynamic models allow the calculation of steady state contaminant loads and concentrations; that is contaminant loads that lead to no net change in soil concentrations over time, when net inputs equal net outputs.

A key component of dynamic mass balances models is the assumed partitioning of the contaminant between solid, liquid and gaseous forms once added to soil. Given a set input, contaminants with low  $K_d$  values have low steady state soil concentrations (as leaching removes them from the soil) and contaminants with high  $K_d$  values have high steady state soil concentrations as leaching losses and plant uptake are minimal (Figure 9).



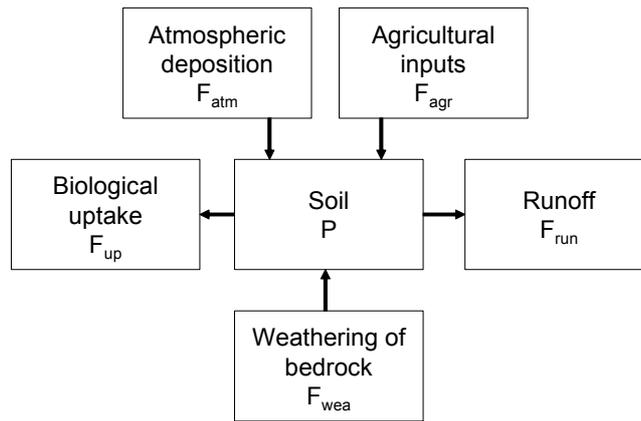
**Figure 9. Increase in soil concentration for metals having low (e.g. B and Se), medium (e.g. Cu and Zn) and high (e.g. Cr and Pb) partition coefficients (Kd values) given constant input (Smolders et al., 2004).**

To implement mass balance modelling requires detailed information on the concentrations of contaminants in fertilizers, knowledge of the partitioning of contaminant in soil, knowledge of exports of contaminants in harvested produce, soil erosion, leaching and/or volatilization, estimates of degradation or decay losses (if applicable) and estimates of surface run-off. Such data are often not available for each contaminant, which may necessitate assumptions being made for data poor contaminants.

Application of the mass balance modelling approach could be refined by implementing a pre-screening exercise to filter out contaminants of no concern. The approach would then focus on investigating the contaminants given a high hazard priority.

### 9.3 Critical Load Models

Critical load models (Figure 10) have been widely used in Europe for the assessment of permissible acid rain inputs from diffuse sources and are increasingly being used to assess critical loads of metal contaminants to soil from trans-boundary air pollution and other diffuse sources (e.g. de Vries et al., 1995, 1998; Paces, 1998). These models are basically dynamic mass balance models with a critical load assumed – usually a total concentration in soil corresponding to an ecological threshold value. There has been some criticism of this approach as a result of some of the assumptions made in the models (Cresser, 2000).



**Figure 10. Basic critical load model (from Paces, 1998).**

Critical load models are data-hungry, having the same requirements as the mass balance approach plus threshold effect data required to determine the critical load. For Australia the critical loads would have to be assumed as we do not have critical soil concentrations for any metal, except under State biosolid guidelines and under the National Environmental Protection Measure (1999) for human health protection. While the latter are risk-based, the former are not. State biosolid guidelines are based more on considerations of normal background concentrations in soils, and on limit values suggested from overseas jurisdictions (e.g. Europe).

Critical loads for ecological health have not yet been defined under the NEPM, and only interim urban ecological investigation levels have been suggested for some elements. Thus, even if a good dynamic model for contaminant accumulation in defined agricultural systems could be developed, we do not have good critical thresholds with which to calculate critical loads in fertilizers. Subsequently, adoption of this approach would require significant levels of investigation prior to its implementation.

Critical levels vary for human health, aquatic ecosystems, terrestrial ecosystems, and food standards, so choosing the appropriate levels may be contentious. It is also noted that the values provided in overseas literature may be misleading for Australian conditions, which often vary significantly (especially with soil types). Hence national values may need to be adjusted for regional or site specific conditions. Similar adjustments are prescribed in the Australian National Water Quality Management Guidelines (ANZECC & ARMCANZ, 2000).

#### **Recommendation**

That the concentration balance and mass balance approaches not be used to derive guideline limits for contaminants in fertilizers.

The critical load approach be used to derive guideline limits for those chemicals that are indicated as posing a high hazard by the hazard assessment.

## **10 Factors to be Considered When Assessing Hazard and Deriving Guideline Limits**

In a continent of the size of Australia, there are many diverse soil and environmental conditions. These produce different environmental factors that affect the risk of toxicity being expressed for any contaminant added to soil. Thus, some contaminants will pose greater risks in particular regions of Australia, and any hazard ranking or risk assessment needs to address this issue.

## 10.1 Background Concentrations

Inorganic and organic contaminants may exist in soils as a result of geogenic and other non-anthropogenic processes (e.g. bushfires). These background concentrations of elements are important determinants for risk assessment for two reasons. Firstly, for nutrient elements, organisms adapt to the background concentrations of elements in which they have evolved, so that toxicity thresholds for organisms in high background environments are greater than those adapted to low background environments (McLaughlin and Smolders, 2001). Secondly, strict single-value limits cannot be placed on some contaminants in soil, as they exist naturally over a wide range of concentrations (Figure 11) and a soil toxicity limit may easily fall within the background range.

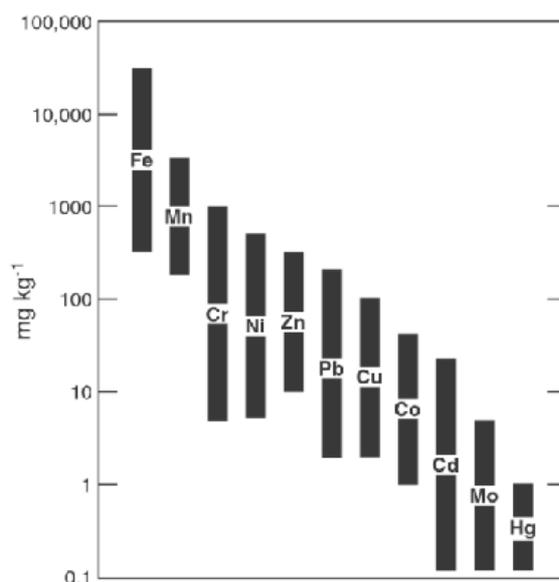


Figure 11. Range of background concentrations for metals in soil (from McLaughlin, 2002).

## 10.2 Temperature

Temperature affects contaminant persistence in soils directly by controlling contaminant transfer to the atmosphere (Henry's Law constant); and by its effect on contaminant solubility ( $K_{sp}$ ). Indirectly it controls microbial activity in soils which affects rates of degradation of organic pollutants, as well as controlling organic matter levels, which determines contaminant partitioning.

## 10.3 Rainfall

Rainfall directly affects contaminant mobility in soils. Rainfall leads to downward and lateral movement of contaminants to water supplies and aquatic ecosystems. Rainfall also indirectly affects contaminant mobility, through its effect on soil organic matter levels as a result of controls on primary productivity, and through its effect in controlling soil pH. For example, high rainfall environments are dominated by acidic soils, and low rainfall environments are dominated by alkaline soils.

## 10.4 Time Frame Used to Assess Sustainability

Most current human activities are unsustainable in perpetuity (e.g. fossil fuel use), and the issue of contaminants in fertilizers must seek a balance between sustainability issues on one hand and practicalities and economic issues on the other. Depending on the choice of the definition of "adverse effect", some defined time endpoint needs to be chosen if critical soil and fertilizer levels are to be based on ecotoxicity or food chain accumulation to a defined level. Critical loads of contaminants vary markedly

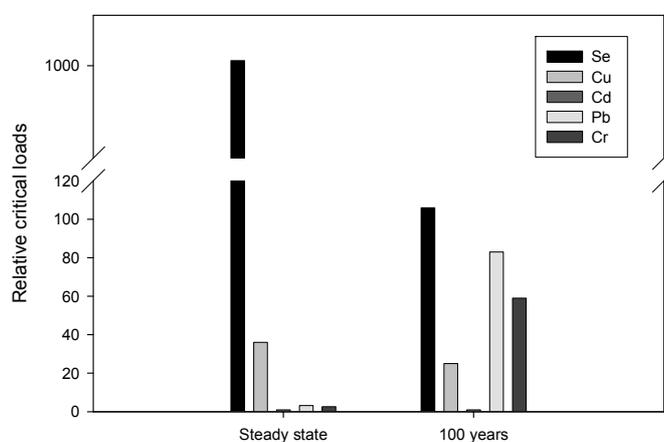
depending on the time frame chosen (Figure 12).

For a recent workshop on persistence, bioaccumulation and toxicity of contaminants hosted by the Society for Environmental Toxicology and Chemistry (SETAC), scenarios of soil accumulation of up to 100 years were chosen as a basis for making predictions, and for suggesting changes to the management of soils. The Australian and New Zealand guidelines for irrigation water (i.e. applied to agricultural land) are, similarly, devised to protect the soil for 20 and 100 years continual exposure (ANZECC & ARMCANZ, 2000). The Standing Committee on Agriculture and Resource Management's Cadmium in Agriculture Task Force used scenarios of up to 200 years to model changes in soil and crop cadmium concentrations in two model agricultural systems.

A time frame of 70 - 100 years would be a logical choice if dynamic models are chosen to assess contaminant accumulation in soils. Given the progressive development of science, it is likely that further research will improve the knowledge base within that time frame. It will therefore be crucial that any guidelines developed in this project be reviewed well before the 100 years has elapsed. This will be necessary in order to ensure that the guidelines reflect the scientific knowledge at that time and to ensure the sustainability of agricultural land. The Australian Water Quality Guidelines and National Environment Protection Measures are reviewed every five years. Such a timeframe might also be appropriate for the guidelines for contaminants in fertilizers however, this is a policy decision that the FWG should make.

### Recommendation

That a timeframe of 100 years be used in assessing the hazard and determining the guideline limits for contaminants in fertilizers.



**Figure 12. Critical loads of metals (relative to Cd = 1) to achieve soil ecotoxicological criteria at steady state and after 100 years of metal loading. The ecotoxicological soil criteria (Crommentuijn et al., 1997) are (in mg/kg): 0.8 for Se, 40 for Cu, 1.6 for Cd, 140 for Pb and 100 for Cr (III) (Smolders et al., 2004).**

## 10.5 Agricultural Systems to Focus on

Australia has many agro-ecological systems, with different inputs and crop husbandry practices. The impact of contaminants may vary depending on the nature of agro-ecological system, and the fertilizer practices in place for each particular system.

If static or dynamic models are used to assess contaminant accumulation and potential adverse effects, some focus needs to be given to key agricultural systems to limit the scope of subsequent work.

Irrespective of the model used, maximal benefit would be obtained from this project by focussing on those agro-ecological systems that have the greatest economic and environmental importance to Australia. In the following list agricultural systems are ranked highest to lowest according to their considered risk with respect to contaminants in fertilizers:

1. Horticulture – includes vegetables and flowers, features include having sensitive export markets, high fertilizer and soil amendment inputs, high water inputs, high potential leaching and high crop off-takes (also includes “recreational horticulture” which covers turf farms, golf courses and sports grounds).
2. Sugarcane with rotation cropping – these occur in high rainfall environments, have high fertilizer inputs, can involve rotation crops (e.g. peanuts), and may have sensitive off-site receptors (e.g. coastal reefs)
3. Dairy production – these are generally high rainfall environments (or irrigated) that have high fertilizer inputs and low contaminant off-takes.
4. Livestock production for meat – predominantly cattle and sheep pasture grazing or stock feed, market sensitivity to quality and customer perception.
5. Viticulture – these are very sensitive export markets, and have high water, fertilizer soil amendment and chemical use.
6. Cropping cereals/legumes – typical of the “wheat belt” in southern and western Australia. Features of this system include sensitive export markets for the produce, low crop off-takes of most contaminants, low leaching potential, but also low fertilizer and chemical inputs.
7. Irrigated cropping – includes rice and cotton farming in the Murray Darling Basin.
8. Forestry – covers use of fertilizers in regeneration of forests and establishment of plantations - low fertilizer and chemical inputs.
9. Aquaculture – fertilizers used to promote algal growth as food source for fish – chemical/drug inputs and off-site effects in aquatic systems.

#### **Recommendation**

The order in which the various agro-ecological systems should have the impacts of fertilizer contaminants assessed is:

1. Horticulture;
2. Sugar and other rotational crops;
3. Dairy;
4. Beef and sheep;
5. Viticulture;
6. Cereal production; and
7. Aquaculture.

Given the potential size of the project it is recommended that only the first three agro-ecological systems (horticulture, sugar and other rotational crops and dairy) be examined in the present study.

## **11 Conclusions and Recommendations**

1. There are data gaps regarding a national overview of the amounts and quality of soil amendments used from the composting and the waste management industries, and from other industrial sources.
2. There is a large list of potential contaminants of concern (see the recommendation after section 5.4) We therefore recommend that a qualitative preliminary screening and a quantitative hazard assessment be conducted to identify those contaminants of fertilizers for which the derivation of

guideline limits from first principles is warranted.

3. The ingredient approach should be used in determining which chemicals or materials should be prohibited in fertilizers. The concentration approach should be used to control those contaminants that are permitted in fertilisers.
4. In deriving the guideline limits we recommend that the following adverse effects and pathways are important and should be considered:
  - Increased bioavailability if toxic to plants or animals, leading to adverse effects on ecosystems in the short or long term;
  - Accumulation or concentration in the food chain producing unacceptable contaminant levels from a trade, environmental or human health perspective;
  - Potential for mobilisation and off-site migration; and
  - Direct toxicity to domestic animals.
5. That the physicochemical behaviour of contaminants be used to rank the relative importance of the above pathways with the highest ranked becoming the foci when deriving the guideline limits. We propose that contaminant partitioning in soil, and half-life for organic contaminants, be used as key properties.
6. Given the large number of organic contaminants that can be present in waste materials, we recommend that a limited number of model compounds be used to represent groups of organic contaminants.
7. That critical load models with a 100 year timeframe be developed and used to determine the guideline limits for chemicals that pose a high hazard. This would be done for horticulture, sugar/grain legume cropping under tropical conditions; and dairy production.

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## 13 Glossary

<b>Bioavailability</b>	The ability of a substance to interact with the biosystem of an organism. (Van Leeuwen and Hermens, 2000)
<b>Carcinogen</b>	A substance that causes cancer.
<b>Codex</b>	Codex Alimentarius Commission, established by the World Health Organisation and the Food and Agriculture Organisation, determines standards for internationally traded food commodities through the Codex Committee on food additives and contaminants.
<b>FSANZ</b>	Food Standards Australia New Zealand
<b>Isotope</b>	Different forms of a chemical element having the same number of protons in their atoms, but a different number of neutrons. All isotopes of a chemical element have essentially the same chemical properties.
<b>Lipid</b>	Any of a large group of organic compounds including fats. They generally have a greasy feeling and are sparingly soluble in water.
<b>Maximum Level(ML) and Maximum Residue Limit (MRL)</b>	These are the maximum level of a specified contaminant, or specified natural toxicant, which is permitted to be present in a nominated food expressed, unless otherwise specified, in milligrams of the contaminant or the natural toxicant per kilogram of the food (mg/kg).
<b>MSW</b>	Municipal solid waste
<b>NHMRC</b>	National Health and Medical Research Council
<b>pH</b>	Measure of the intensity of acidity/alkalinity. Values of 7 are neutral, above 7 are increasingly alkaline, while below 7 they are increasingly acidic.
<b>Precipitation</b>	The combination of a metal with an associated ion in soil pore water to form a new solid phase compound in soil e.g. calcium phosphates in soils containing lime
<b>Radioisotope</b>	Isotope of an element that is unstable and undergoes natural radioactive decay.
<b>Sorption</b>	A surface phenomenon that may be either absorption (penetration of one substance into the body of another) or adsorption (taking up of one substance at the surface of another), or a combination of the two.
<b>Teratogenic</b>	A substance that causes foetal abnormalities.

## Appendices

### Appendix A – Attendees at Workshop, Tuesday 8 March 2005, Canberra

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22.	Cecil Camilleri – Yalumba Wine Co	ccamilleri@yalumba.com
23.	Martin Shafron – FIFA	
24.	Phillip Owen – Industrial Galvanizers (FIFA)	
25.	David Ford – Impact Fertilizers (FIFA)	
26.	Enrico Rizzon – Incitec Pivot (FIFA)	
27.	Garry Kuhn – Incitec Pivot (FIFA)	
28.	Cameron Schuster – CSBP (FIFA)	
29.	Mike McLaughlin – CSIRO (FWG)	Mike.McLaughlin@csiro.au

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Organisations: Fertilizers Working Group (FWG); Industrial Residue Working Group (IRWG); Fertilizer Industry Federation of Australia (FIFA), University of Technology Sydney (UTS), Australasian Slag Association (ASA), Ash Development Association of Australia (ADAA), Department of Agriculture, Forestry and Fisheries (DAFF), Department of Primary Industries (DPI), Department of Environment and Conservation (DEC), Environment Protection Authority (EPA), Primary Industry & Resources (PIR), Environment Planning and Lands

**Appendix B - Control of Contaminants in Fertilizers Workshop Report**

Tuesday 8th March, 2005

CSIRO Land and Water, Pye Building, Black Mountain, Canberra.

**Program for the workshop:**

9.30	<b>Introduction</b> <ul style="list-style-type: none"> <li>• Steve McCutcheon – role of the Fertilizer Working Group and the regulatory context</li> <li>• Michael Warne – review of the discussion paper, and issues to resolve at the workshop</li> <li>• Roundtable listing of issues – consider those relevant to specific contaminant, industry or regions</li> </ul>	Facilitated by Robert Molloy
10.30	<b>Morning Tea</b>	
10.45	<b>Workshopping the questions:</b> <ul style="list-style-type: none"> <li>• Should fertilizer contaminants concentrations or fertilizer ingredients be controlled?</li> <li>• What should be defined as an adverse effect?</li> <li>• What time frame do we use to assess sustainability?</li> <li>• Which agricultural systems should be the focus of study?</li> <li>• Which contaminants and their sources need to be the focus of further investigation?</li> </ul>	Group work for 30 mins - 1 topic per group, then report back with 5 mins per group. Then open discussion.
12.45	<b>Lunch</b>	
1.30	<b>Discussion/Workshop</b> The merit of the three approaches that could be used in assessing the risk posed by contaminants in fertilizers <ul style="list-style-type: none"> <li>• Mass concentration approach</li> <li>• Mass balance modelling</li> <li>• Critical load models</li> </ul> Undertake quick ranking based on scientific rigour, ease of regulatory implementation, and practicality of using the method	Intro by Michael Warne (10 mins), then discuss as groups, then report back and open discussion  Survey sheet provided
3.30	<b>Summary &amp; Conclusions</b> <ul style="list-style-type: none"> <li>• Check off issues raised in earlier sessions</li> <li>• Summarise where we are at</li> </ul>	Steve McCutcheon & Mike McLaughlin to facilitate
4.00	<b>Close</b>	

**Notes from Presentation by Michael Warne**

- Background to the situation - Reports in various press highlighted the use of contaminated industrial wastes in fertilizers. Concern about human and environmental impacts.
- The PSIC FWG definition of a fertilizer:  
a substance that is manufactured, represented, supplied or used as a means of directly or indirectly:  
(i) fertilizing the soil; or (ii) supplying nutrients to plants; or (iii) conditioning the soil by altering the chemical, physical or biological composition of the soil; or  
- a substance declared by regulation to be a fertilizer,  
But does not include a substance excluded by regulation from the ambit of this definition

**Objectives of this workshop**

- Determine stakeholders concerns regarding contaminants in fertilizers.
- To seek input on key unresolved issues (UI 1 to 6).
- Use the outcomes of the workshop to help finalise recommendations for a process to establish:
  - a list of prohibited substances in fertilizers; and
  - guidelines for levels of contaminants or for ingredients permitted in fertilizers.

- UI 1      Should fertilizer contaminant concentrations or fertilizer ingredients be controlled?  
UI 2(a)    How adverse effects should be defined?  
UI 2(b)    What should be defined as an adverse effect?  
UI 3      Which type of approach should be used to assess the risk posed by contaminants in fertilizers?  
UI 4      What time frame should be used to assess sustainability?  
UI 5      Which agricultural systems should be the focus of study?  
UI 6      Which contaminants and their sources need to be the focus of further investigation?

**Issues Raised by participants:**

- Occupational exposure
- Copper based fertilizers
- Wastewater treatment sludge (e.g. Winery)
- Sewerage treatment sludge (biosolids)
- Lack of information on what wastes and how much applied to land – “scale of the problem”
- NSW Land Protection Proposal – an interim measure that will be superseded by the national approach
- Want a national approach to the issue rather than state by state
- National approach – consider different issues faced States & Territories
- State vs. regional perspective (e.g. coasts vs. semi-arid)
- Want a practical method re: implementation and not too narrow a focus
- Practical timeframe for implementation – to phase out any prohibited materials or to meet guidelines
- Focus should be on materials/chemicals being added to fertilizers having a benefit and being sustainable rather than simply on not causing harm
- Mixed method – ingredients & conc.
- Implications to markets (e.g. international) and trade are very important, QA requirements
- Scientific and market risk – appropriate balance
- Balance of scientific uncertainty and need for regulation necessities
- Regional use of wastes. Wastes could be regionally useful. Can the method deal with regional issues?
- Cost associated with implementing the proposed scheme and regulating
- Public perception – negative image of using wastes
- Regulations for changed waste management practices – e.g. municipal waste to compost
- How much damage already – where is the problem
- Why isn't current legislation sufficient

## Group 1 (Michael Warne)

### Should fertilizer contaminant concentrations or fertilizer ingredients be controlled?

- Ingredients present problems to suppliers because of complex supply chains. Those chemicals sourced from developing countries with poor QA/QC require additional checking prior to acceptance.
- Existing QA/QC procedures are final product based – concentrations may vary to those in the ingredients.
- Contaminants *per se* are not a problem; it is the rate/loading that is important. This makes product based controls logical.
- Ingredients themselves are not a problem – only when compared to concentrations at which harmful effects occur.
- The two approaches (ingredient vs. concentration) are not mutually exclusive –
  - List of prohibited chemicals will change over time, given the potential list is huge.
  - Can prohibit parent compound but what if it is incorporated into other products.
- Issue of chemical additives that are added to fertilizers that do not benefit agriculture – but help in making fertilizers. Don't want these to be caught up in this project.
- There are implications to industries that supply wastes/by-products for fertilizers
- Ingredients approach more likely to be more self monitored? Concentrations approach likely to be easier to monitor?
- What is inferred for chemicals that are not prohibited or there are no guidelines for? Are they approved?
- For prohibited substances you can only say that there is none present given a specific detection limit. So the detection limits may need to be specified.
- Staged approach – if can't develop scientifically based concentrations can reduce them on a practical basis.
- There are always going to be exceptions and clarifications required.

*In summary the ingredient approach could be used for developing the list of prohibited substances but it would be preferable to use the concentration approach for those chemicals that are to be permitted in fertilizers.*

## Group 2 (Carine Saison and Rebecca Hamon)

### How should adverse effects be defined?

- Adverse effects may be chemical (e.g. accumulation of contaminant in soil), physical (e.g. damage to soil structure resulting in water repellancy/waterlogging/increased erosion etc), biological (e.g. toxicity to biota) and social (e.g. public perception that produce is unclean)
- Whether accumulation in soils is an adverse effect or not is dependent on the type of contaminant; example of asbestos given where any accumulation would likely be considered as an adverse effect
- Accumulation in soil might also be an adverse effect if there is risk of offsite transport to sensitive receiving environment
- If don't have any toxicological data then should apply precautionary principle and assume that any accumulation in soil is an adverse effect until data-base can suggest otherwise
- Adverse effect could also occur during application of 'fertilizer'- dust a big issue for human health/public perception
- Also noted that adverse effect depends on what perspective you approach things: i.e. agriculture can be considered an adverse effect if you are looking from the environmental point of view

*Overall agreement that the adverse effects discussed in document were comprehensive (with addition of public perception issue) and appropriate (with caveat that accumulation in soils may constitute an adverse effect for some contaminants).*

### What time frame should be used to assess sustainability?

- If no accumulation allowed (mass balance) then this is not an issue i.e. time frame is in perpetuity
- If accumulation allowed then main issues would be intergenerational equity, likelihood of current land-use changing to more sensitive land-use, potential for creation of 'time bomb'

- Fertiliser benefit of material must outweigh detrimental effect of any contaminant

*In absence of anyway to reconcile this, thought that ~100 yr time frame seemed reasonable as long as regular monitoring and review took place, and as long as the potential for time bomb issues were borne in mind and modelled if possible*

*If accumulation allowed, thought that an intermediate value that is significantly below any critical load should be used as the endpoint for the ~100 yr time frame; thought that this approach would also receive greater public acceptance*

### **Group 3 (Mike McLaughlin)**

#### **Which agricultural systems should be the focus of study?**

In the following list agricultural systems were ranked according to their considered risk re: contaminants in fertilizers:

1. Horticulture – high input, peri-urban, sensitive markets
2. Sugar and other rotation crops – high inputs, effects mostly off-site (e.g. coastal reefs)
3. Dairy – high inputs, off-site issues, sensitive markets
4. Beef/sheep – market sensitivity, stockfeed issue
5. Viticulture – market sensitivity, perceptions
6. Cereal production – low input
7. Aquaculture – sleeper, chemical/drug inputs and off-site effects in marine systems

*In the discussion that followed the group presentation it was suggested that an 8<sup>th</sup> system covering forestry should be included, with it also given low priority. It was noted that recreational turf was a high user of fertilizers, but could be included with Horticulture (“recreational horticulture” which would also include sports fields etc).*

### **Group 4 (Rai Kookana)**

#### **Which contaminants and their sources need to be the focus of further investigation?**

- Contaminants – too many to list
  - Priorities - Next candidates
  - Organics – can they be represented by indicator compounds?
  - Biological contaminants
  - Weeds, virus, prions, Genetically modified organisms
  - General nature – salinity, pH etc
- 
- More of a potential problem than a current problem but needs to be dealt with.
  - Cd, Pb and Hg are relatively well dealt with by laws, and there are guidelines for other materials in most Aust and international jurisdictions.
  - Sources: Municipal solid waste, biosolids, mineral fertilisers
  - Do we need to look at sources (e.g. Inorganics, organics etc separately) or just simply look at contaminants where ever sourced? Big question?

*Priority contaminants that may need initial study include those that were listed in the slide (below), with a specific focus on:*

- *Inorganics: Hg, Pb, F, Ni, Cu, As, B, Se, Zn, Cr,*
- *Organics: POPs, flocculants/coagulants, approach could include total load of similar materials*

*Biologicals: considered in existing organics guidelines for compost etc, so low priority for now because it would need redefinition of waste.*



### UI 6 – Which contaminants and their sources need to be the focus of further investigation?

#### Inorganic contaminants

- Essential elements
- Heavy metals
- Metalloids
- Radionuclides
- Rare earth elements
- Anionic elements
- All other elements

#### Organic contaminants

- Pesticides
- PCBs
- Dioxins and furans
- PAHs
- Surfactants
- Pharmaceutical and personal care products
- Endocrine disruptors

#### Biological contaminants

- Pathogens
- Viruses, Prions, Bacteria
- Foreign sp. including weeds

### Unresolved Issue 3

Which type of approach should be used to assess the risk posed by contaminants in fertilizers?

- Mass concentration approach
- Mass balance modelling
- Critical load models

### Group 1 – Mass concentration approach

Discussion Points:

- Problem with the reference concentration in soil: what's the value? (e.g. if use "background" which concentration to choose as soil background because concentrations for inorganics can vary by three orders of magnitude)
- What's the background concentration for organic chemicals?
- If concentration in fertilizer is lower than in soil, then assumption is that concentration in soil is not going to increase, BUT, even if concentration of contaminant is low, it can build up, because of higher rate of use or solubility of the 'active fertiliser ingredients'
- Does not need to be a universal system : different approaches for different products
- Thought that each of the models under discussion had a potential role in the process and should not necessarily exclusively limit to one model
- Mass concentration can be useful for the industry as part of a screening process

Pros	Cons
<ul style="list-style-type: none"> <li>• Good initial screening (single number)</li> <li>• Simple</li> <li>• Cheap/cost effective</li> <li>• More transparent</li> <li>• Easy to explain in terms of practicality of using</li> <li>• Rigorous for its purpose</li> </ul>	<ul style="list-style-type: none"> <li>• Does not consider volumes</li> <li>• Does not address loading rates</li> <li>• Overly simplistic as a guideline</li> <li>• Need more information for background concentrations</li> </ul>

## Group 2 – Mass balance modelling

### Discussion Points:

- Not needed for all contaminants – need a pre-screen to filter out contaminants of no concern, prioritise on high hazard contaminants
- Information to construct a mass balance made may be lacking – assumptions may be made for data poor contaminants
- No net accumulation could be very restrictive and inappropriate for some systems e.g. essential fertilizer elements Zn, Cu.
- Accumulation is not necessarily an adverse effect so mass balance only may be flawed – critical load better

## Group 3 – Critical load model

### Discussion Points:

- Key difference to Mass Balance model is the increased emphasis on ecotoxicity and need for identifying the critical load
- About managing the contaminant balance remaining in the environment – how risk adverse you are
- Critical levels vary for human health, aquatic ecosystems, terrestrial ecosystems, food standards
- Using overseas literature values may be misleading for Aust. conditions
- Water quality guidelines a good base – considered as conservative, lowest common denominator, but can be modified
- Critical loads for soils – national value, but adjust for local soil properties
- Guidelines not absolutes – but once a number is on a page they can become de facto standards
- Is a potentially flexible system – along lines of WQGs
- Ease of use is dependent on having a critical value for specific contaminants e.g. cadmium in foods
- Work-around – pollution reduction program to allow for breaches
- Ease of incorporating risk for poorly studied contaminants – nearest representative

Pros	Cons
<ul style="list-style-type: none"> <li>• Mirrors the approach used for water quality</li> <li>• Established methodology (trigger based system)</li> <li>• Can be adjusted to site specific conditions</li> <li>• Can links to food standards</li> <li>• Confidence in approach and acceptability</li> <li>• Suitable for handling high risk scenarios – links to data availability issue</li> </ul>	<ul style="list-style-type: none"> <li>• We don't know if we have sufficient or appropriate critical loads data</li> <li>• A national guide might have limited applicability – forces need for site specific investigation</li> <li>• Labelling and application guides are more complex to develop, but better in the end</li> <li>• Risk the guideline becomes the standard</li> <li>• Statistical reliability and confidence in data may be lost – but this can be addressed</li> <li>• Seems the most expensive approach, because it requires upfront investment</li> </ul>

## Survey Feedback

Participants were invited to select the grade that they felt most applied to each of the three measures of the approaches (scientific rigour, ease of regulatory implementation, practicality of using the method) and then sum the corresponding values for each method. There were five categories for each - high, good, moderate, low and very low that corresponded to values of 5, 4, 3, 2, and 1. Thus the highest and lowest possible scores were 15 and 3 respectively.

The average results for each approach based on all replies were:

Mass concentration approach: 9.2  
 Mass balance modelling: 9.2  
 Critical load models: 11.1

When the responses were separated on the basis of the type of employer of the respondent (ie. fertilizer producer, user, regulator or other) the following results were obtained.

Regulator:	MC = 9.4	MB = 8.1	CL = 10.6
Producer:	MC = 9.3	MB = 9.7	CL = 10.7
Users:	MC = 7	MB = 14	CL = 15
Others:	MC = 9.3	MB = 9.3	CL = 12

Thus no matter whom the people worked for, the Critical Load (CL) approach was the preferred method for assessing the risk. However, it was evident from the discussions that there was strong support for the concept that the mass concentration approach could be used as a screening tool.

Attendees were also asked to evaluate the usefulness of the workshop. Possible ratings were highly useful, moderately useful, low usefulness and of no use. A total of 20 questionnaires were completed and returned. One respondent marked both highly and moderately useful – hence there were 21 values stated in the below summary. 17 respondents felt the workshop was highly useful, 2 felt it was moderately useful and 2 did not complete this question. Thus 17 out of 21 respondents (81%) rated the workshop as highly useful.

### Summary of the workshops findings regarding the six unresolved issues (by Mike McLaughlin)

The unresolved issues are stated in normal text while the summary of the findings are in bold.

1. Contaminant concentrations or ingredients?  
**Seems to be consensus on concentrations but some ingredients could be excluded outright**
2. Adverse effects?  
**As per discussion paper, but add OH&S issues and trade/market as very important adverse effects.**
3. Type of approach?  
**Initial mass concentration approach for screening chemicals, then use the critical load model for those chemicals that warrant further investigation.**
4. What time frame?  
**Consensus ~ 70-100 years, review of the outcomes of this project likely prior to this time period being reached.**
5. What agricultural systems?  
**As per discussion document, with the priorities indicated earlier in these minutes. New ones suggested were aquaculture, turf and forestry (lower priority) turf can be considered with sports fields as “recreational horticulture”.**
6. Which contaminants for further investigation?  
**A good start list is what is covered in the biosolids guidelines plus the list in the slide above.**

#### Overall:

- Inorganics – F, Ni, (only in some sources) Hg, Pb Cu, As, B, Se, Zn, Cr
- Organics – POPs, readily biodegradable compounds, flocculants/coagulants, where total load of “similar material” use indicator compound to represent a group/class
- Radioactive material

- **Contaminants associated with sources – includes: biosolids, municipal solid waste, mineral fertilisers, (others were also mentioned...slags/ashes/red muds ?)**

### CSIRO's Recommendations taking into consideration the outcomes of the Workshop

1. That the ingredient approach should be used in determining which chemicals or materials should not be allowed in fertilizers. The concentration approach should be used in determining those chemicals or materials that can be present in fertilizers below certain guideline values.
2. The following are the definitions of adverse effects:
  - Increased release or bioavailability of contaminants, if toxic to plants or animals, leading to adverse effects on soil ecosystems, aquatic ecosystems or plants, in the short or long term;
  - Accumulation or concentration in the food chain producing unacceptable contaminant levels from a trade or human health perspective;
  - Potential for contaminant mobilisation and off-site migration at concentrations sufficient to cause negative impacts on off-site ecosystems; and
  - Toxic to domestic animals, livestock and wildlife.
3. That the concentration balance approach be used in combination with the proposed hazard assessment methodology as a mechanism of determining which chemicals or ingredients pose a potential hazard. Those chemicals that are indicated as posing a hazard would then be subject to a risk assessment using the critical load model.
4. That the timeframe to be used in the critical load models is 100 years. However, it will be crucial that considerably before this period is reached that the issue be reassessed.
5. The following agricultural systems are ranked in terms of relative importance and the order in which they should be assessed.
  - Horticulture – high input, peri-urban, sensitive markets
  - Sugar and other rotation crops – high inputs, effects mostly off-site (e.g. coastal reefs)
  - Dairy – high inputs, off-site issues, sensitive markets
  - Beef/sheep – market sensitivity, stockfeed issue
  - Viticulture – market sensitivity, perceptions
  - Cereal production – low input
  - Aquaculture – is currently viewed as a low priority system however there are chemical/drug inputs and potential off-site effects in aquatic systems
6. The recommended types of contaminants or sources of contaminants to be investigated are:
  - **Inorganics:** Essential elements, heavy metals, metalloids, radionuclides, rare earth elements, anionic elements, all other elements - specifically Hg, Pb, F, Ni, Cu, As, B, Se, Zn, Cr.
  - **Organics:** Persistent organic pollutants (e.g. PCBs, dioxins and furans, PAHs), flocculants, coagulants, surfactants, pharmaceutical and personal care products, endocrine disruptors. Where appropriate (ie. chemicals with the same mode of action) the toxic equivalent approach should be used.
  - We recommend that biological contaminants could be considered at a later stage.
7. In terms of potential sources of contaminants we recommend that raw materials of mineral fertilisers, mining and smelting by-products, energy wastes, and other industrial wastes are considered prior to examining biosolids, municipal solid waste, food and green waste streams.

## Appendix C - Summary of Industry Submissions in Response to the Discussion Paper and how they were addressed in the Scoping Report

Respondent	Comment	Response
Craig Heidrich, Australasian Slag Association (ASA) and Ash Development Association of Australia (ADAA)	<ol style="list-style-type: none"> <li>1. Fertilizer definition is too broad.</li> <li>2. The recommended use of the ingredient and concentration approaches is supported.</li> <li>3. Questioned the validity of including aesthetics in the adverse effects.</li> <li>4 – 5. The recommended approaches and timeframe were supported.</li> <li>6. Supported the recommended agricultural systems but also suggested that forestry and recreational horticulture be included.</li> <li>7. Supported many but not all of the chemicals recommended for inclusion. No new chemicals were suggested.</li> <li>8. They support a national approach to dealing with contaminants in fertilizers.</li> </ol>	<ol style="list-style-type: none"> <li>1. Defining a fertilizer is not an objective of this study. The current definition is being considered by the Fertilizer Working Group.</li> <li>2. No response.</li> <li>3. Aesthetics was mentioned in the original project document released by the FWG. It was not one of the recommendations of the CSIRO report.</li> <li>4 - 5. No response required.</li> <li>6. Recreational horticulture was included in the horticulture system and recommended for inclusion in the CSIRO report. Forestry was not recommended for inclusion in the current study as there are other higher priority agricultural systems.</li> <li>7. We agree with their supported chemicals but feel that the additional chemicals recommended should be included in the project.</li> <li>8. No response required.</li> </ol>
Nick Ronan, Dairy Association	<ol style="list-style-type: none"> <li>1. The discussion paper states that it 'explores the reasoning behind and possible strategies for controlling the input of contaminants and prohibited substances in fertilizers and soil amendment products' however, this aim is not fully achieved, principally focussing on assembling knowledge of the role of fertilizers/nutrients, types of contaminants and their source, exposure and risk issues.</li> <li>2. They argue that contaminants should not be allowed into dairy products.</li> <li>3. Argue that the project should include the prevention of animal products being incorporated into fertilizers and subsequently eaten by ruminants.</li> <li>4 &amp; 5. That biosolids can contain contaminants and pose potential problems to the Dairy Industry and therefore should be included in the</li> </ol>	<ol style="list-style-type: none"> <li>1. The scope of the report was naturally limited to the boundaries placed on it by the FWG. The FWG made the policy decision, prior to the project commencing, that fertilizer contaminants would be controlled at the input stage.</li> <li>2. We agree it is important to achieve this and this is why the project was commenced.</li> <li>3. This issue has been included in the section of this report dealing with manures (section 3.1.6). However, this issues lies largely outside the scope of the project.</li> <li>4 &amp; 5. Biosolids are not within the scope of this project. They are already covered by the existing state biosolid guidelines.</li> <li>6. Recycled / reclaimed water are outside the scope of the project.</li> </ol>

	project. 6. Question whether recycled / reclaimed water should be included in the project.	
Brian McLoughlin, Iluka Pty Ltd	General support	None
Nancy Penney, WA Water Corporation	General support – modelling approaches for assessing risk may be problematic if data to validate model isn't available. Comments on contaminants of concern – knowledge to be gained from biosolids work. In addition to focusing on some key chemicals, broader ecological toxicity testing that attempts to assess the collective impact of a range of contaminants is needed.	Agreed and text amended where appropriate.