

1 **Application of phytotoxicity data to a new Australian soil quality**
2 **guideline framework for biosolids.**

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13

1 **Abstract**

2 To protect terrestrial ecosystems and humans from contaminants many countries and
3 jurisdictions have developed soil quality guidelines (SQGs). This study proposes a
4 new framework to derive SQGs and guidelines for amended soils and uses a case
5 study based on phytotoxicity data of copper (Cu) and zinc (Zn) from field studies to
6 illustrate how the framework could be applied. The proposed framework uses
7 normalisation relationships to account for the effects of soil properties on toxicity
8 data followed by a species sensitivity distribution (SSD) method to calculate a soil
9 added contaminant limit (soil ACL) for a standard soil. The normalisation equations
10 are then used to calculate soil ACLs for other soils. A soil amendment availability
11 factor (SAAF) is then calculated as the toxicity and bioavailability of pure
12 contaminants and contaminants in amendments can be different. The SAAF is used to
13 modify soil ACLs to ACLs for amended soils.

14

15 The framework was then used to calculate soil ACLs for copper (Cu) and zinc (Zn).
16 For soils with pH of 4-8 and OC content of 1-6%, the ACLs range from 8 mg/kg to
17 970 mg/kg added Cu. The SAAF for Cu was pH dependant and varied from 1.44 at
18 pH 4 to 2.15 at pH 8. For soils with pH of 4-8 and OC content of 1-6%, the ACLs for
19 amended soils range from 11 mg/kg to 2080 mg/kg added Cu. For soils with pH of 4-
20 8 and a CEC from 5-60, the ACLs for Zn ranged from 21 to 1470 mg/kg added Zn. A
21 SAAF of one was used for Zn as it concentrations in plant tissue and soil to water
22 partitioning showed no difference between biosolids and soluble Zn salt treatments,
23 indicating that Zn from biosolids and Zn salts are equally bioavailable to plants.

24

25

- 1 **Key words** – metals, phytotoxicity, soil, biosolids, soil quality guidelines, ecological
- 2 risk assessment
- 3
- 4

1 **Introduction**

2 The vast majority of soil quality guidelines (SQGs) consist of a single numerical limit
3 defining the maximum allowable rate of contaminant addition to soils, despite
4 ecotoxicological studies showing that bioavailability and therefore toxicity of
5 contaminants is often dependent on soil physicochemical characteristics. As a result,
6 the levels of protection afforded by current SQGs can vary markedly between sites
7 and lead to under- or over-protection.

8

9 The soil properties that have been most frequently shown to affect the toxicity of
10 metals to micro-organisms, plants and invertebrates are cation exchange capacity,
11 organic carbon content, clay content and soil pH. A series of studies (Smolders et al.,
12 2003; Smolders et al., 2004; EU, 2006; McLaughlin et al., 2006; Oorts et al., 2006;
13 Rooney et al., 2006; Song et al., 2006; Broos et al., 2007; Warne et al., 2008a; Warne
14 et al., 2008b) have developed quantitative normalisation relationships between metal
15 bioavailability, toxicity and uptake by organisms and soil properties. Incorporation of
16 these relationships into frameworks to derive SQGs will permit soil and site specific
17 guidelines to be derived. Such guidelines would give a more consistent level of
18 protection and predict risk to species more accurately, thus minimising both over- and
19 under-protection of terrestrial ecosystems. Very few of such guidelines are currently
20 in use. The approach adopted in Germany (BbodSchV, 1999) attempts to address the
21 variation in toxicity and bioavailability caused by soil properties by deriving soil
22 precautionary values for three soil type classes (sandy, sandy loam and a clay soil). A
23 similar approach has been advocated for the Netherlands (Bos et al. 2005) where soil
24 guidelines for zinc (Zn) would be based on three soil types (i.e. peat, sand and
25 loam/clay). Such broad classifications of soils do not necessarily address the

1 potentially large variation in soil properties such as CEC, pH and organic matter that
2 can occur within a class. Current Dutch SQGs are normalised using relationships
3 between soil characteristics and background concentrations, not relationships based
4 on toxicity data. In Flanders (northern part of Belgium) the SQGs for several metals
5 are soil specific (OVAM, 2005) and were derived using normalisation relationships
6 derived from toxicity data and include a leaching/ageing factor to overcome
7 laboratory to field differences (Erik Smolders, pers.comm.).

8

9 Current Australian national and state guidelines controlling metal contaminant
10 concentrations in biosolids and biosolid-amended soils (NSW EPA, 1997; SA EPA,
11 1997; DPIWE, 1999; WA DEP, 2002; EPA Vic 2004; NRMCC, 2004) are still based
12 on single values for all soil types and largely follow European regulations and
13 research (McLaughlin et al., 2000a). However, there are significant differences
14 between European and Australian agricultural soils (Taylor, 1983; McLaughlin et al.,
15 2000a) and Australian biota might be more sensitive to metal contaminants (Hobbs,
16 2006; Hobbs et al., 2004). European toxicity values to protect soil quality may
17 therefore be unsuitable for Australian soils, biota and climatic conditions. The
18 Australian National Biosolids Research Program (NBRP) was therefore established to
19 investigate the human and environmental benefits and risks of applying biosolids to
20 agricultural land and to develop critical soil metal concentrations, above which soil
21 quality is likely to be impaired.

22

23 This study proposes a new framework to derive soil- and/or site-specific SQGs and
24 guidelines for amended soils (SQG_{amended}). The framework includes the use of (a)
25 toxicity normalisation relationships (b) a species sensitivity distribution method (c) a

1 factor that accounts for temporal changes in contaminant bioavailability (d) a factor
2 that accounts for the difference in toxicity and bioavailability of purified
3 contaminants and the same contaminant in biosolids or other soil amendments and (e)
4 the ambient background concentration (ABC) of the contaminant in question.
5 Phytotoxicity data from the NBRP were then used as a case study of the proposed
6 framework to derive SQG and SQG_{amended} values for copper (Cu) and Zn.

7

8 **Box 1. Abbreviations used and their meanings**

- 9 ABC – ambient background concentration
- 10 ACL – added contaminant limit
- 11 ACL_{amended} – added contaminant limit for amended soils
- 12 ACL_{biosolids} – added contaminant limit for biosolids
- 13 BCF – bioconcentration factor
- 14 CLAR – contaminant limiting application rate of biosolids
- 15 EQG(s) – environmental quality guideline(s)
- 16 E values – isotopically exchangeable amount of a metal
- 17 NBRP – National Biosolids Research Program
- 18 PC_x – protective concentration for x percent of species
- 19 SAAF(s) –soil amendment availability factor(s)
- 20 SQG(s) – soil quality guideline(s)
- 21 SQG_{amended} – soil quality guideline for amended soils
- 22 SSD – species sensitivity distribution
- 23 STV(s) – soil trigger value(s)
- 24 STV_{amended} – soil trigger value(s) for amended soils
- 25 STV_{biosolids} – soil trigger value(s) for biosolids
- 26 WQG(s) – water quality guideline(s)

27

28

1 **Methods**

2 Data from the NBRP were used to derive SQGs and SQG_{amended} using the proposed
3 framework. Detailed descriptions of the NBRP field trials and the specific
4 methodologies of plant and soil analyses conducted have been provided in
5 McLaughlin et al. (2006) and Broos et al. (2007). Details on the development of
6 relationships between Cu and Zn toxicity and soil physicochemical properties for
7 micro-organisms and laboratory- and field-based wheat have been provided in Broos
8 et al. (2007), Warne et al. (2008a) and Warne et al. (2008b) respectively. An
9 assessment of the relative bioavailability of Cu and Zn from biosolids and metal salts
10 is in Heemsbergen et al. (in prep).

11

12 **Proposed framework for deriving quality guidelines for soil and amended soil**

13 Throughout this paper we use the terms SQG and SQG_{amended} as generic terms for the
14 overall process of protecting soils. The numerical limits for contaminants are termed
15 soil trigger values (STVs) because if they are exceeded further action is triggered.
16 The overall process of deriving STVs and STVs for amended soils (STV_{amended}) is
17 presented in Figure 1. While this study addresses phytotoxicity of Cu and Zn, a
18 similar framework has been developed for cadmium uptake in wheat (McLaughlin et
19 al., 2006). The NBRP will also be making recommendations regarding new biosolids
20 guidelines for nutrients, but as the type of data available are not amenable to this
21 framework a separate method will be used. Thus four separate sets of STVs will be
22 derived for soils receiving biosolids, and the most restrictive (i.e. permitting the
23 lowest amount of the soil amendment to be added) will be recommended as the
24 STV_{amended} (see Figure 1).

25

1 The proposed framework is presented in Figure 2. In brief, the steps are (1) collating
2 and assessing the quality and appropriateness of toxicity data, (2) assessing temporal
3 changes in toxicity and bioavailability, (3 - 4) deriving and implementing toxicity
4 normalising relationships across soils, (5) using a species sensitivity distribution
5 method to derive a concentration that provides the chosen level of protection to a
6 standardized soil (termed added contaminant limit – ACL), (6) deriving a set of soil
7 ACLs, (7) deriving one or more soil amendment bioavailability factors (SAAFs), (8)
8 applying the SAAF(s) to derive a suite of ACLs for soils receiving amendments, (9
9 and 10) determining and adding the ambient background concentrations (ABC) of the
10 contaminant to the suite of ACL values to calculate STVs. Steps 1 – 6 and 9 and 10
11 are common to the derivation of STVs but steps 7 and 8 are only required when the
12 bioavailability in the amendment is known and therefore one can derive an
13 amendment specific STV_{amended} .

14

15 The separation of naturally occurring concentrations of a contaminant and the added
16 contaminant in deriving STVs in our framework is based on the ‘added risk approach’
17 (Struijs et al., 1997; Crommentuijn et al., 1997). This approach assumes that the
18 availability of the ABC of a contaminant is zero or sufficiently close that it makes no
19 practical difference and that the background ‘has resulted in the biodiversity of
20 ecosystems or serves to fulfil the needs for micronutrients for the organisms in the
21 environment’ (Traas, 2001). Evidence supporting these assumptions has been
22 provided by Posthuma (1997), Crommentuijn et al. (2000b) and Warne et al. (2008b)
23 and by work showing that the availability of metal salts decreases over time through
24 aging processes (e.g. Mann and Ritchie, 1994; Posthuma, 1997; Song et al., 2006).
25 However, some studies did find that for microbial communities the background might

1 be important regarding tolerance to metals (Díaz-Raviña and Bååth, 1996; Bååth et
2 al., 1998; Rutgers et al. 1998; McLaughlin and Smolders, 2001; Rusk et al., 2004;
3 Fait et al., 2006; Broos et al. 2007). Some of these studies found positive relationships
4 between Zn background concentration and effect concentrations, which could indicate
5 that microbial communities in soils with relatively high background Zn have evolved
6 to be more tolerant to additional Zn. Although these studies have shown that
7 background concentration might not be completely chemically unavailable,
8 adaptation of microbial communities does not underestimate the ACL but it is more
9 likely to overprotect micro-organisms.

10

11 *Step 1 – Collating and assessing the quality and appropriateness of toxicity data*

12 All frameworks for deriving environmental quality guidelines (EQGs) have
13 procedures to assess the quality of the data. While they differ in specifics they are
14 generally fairly similar. These assess whether appropriate experimental design,
15 chemical analysis and statistics were used to generate the toxicity data. In the current
16 study, the quality of the data was assessed using the method outlined in Hobbs et al.
17 (2005) but adjusted to reflect important features for terrestrial toxicity data (Table 1).

18

19 The aim of SQGs and SQG_{amended} is to protect terrestrial organisms and ecosystems
20 from adverse effects caused by long term exposure to contamination. As such, SQGs
21 generally prefer to use chronic sub-lethal toxicity data (e.g. Roux et al., 1996;
22 ANZECC and ARMCANZ, 2000; EC, 2003; CCME, 2006). We also recommend the
23 use of this type of data. Most chronic sub-lethal toxicity data are hypotheses based
24 estimates (e.g. no observed effect concentrations – NOECs and lowest observed effect
25 concentrations - LOECs) rather than point estimates (e.g. EC50, LC20). Due to the

1 many limitations of NOEC and LOEC data it has been argued that they are
2 inappropriate for regulatory purposes (e.g. Hoekstra and Van Ewijk, 1993; Chapman
3 et al., 1996; Van der Hoeven et al., 1997). However, in the absence of alternative data
4 their use continues. As NOEC values typically correspond to a 10 to 30% effect
5 concentration (Hoekstra and Van Ewijk, 1993; Moore and Caux, 1997) normalisation
6 relationships based on NOEC/LOEC type data typically have lower r^2 values than
7 relationships based on point estimate data (Rooney et al., 2006). Therefore in the
8 proposed framework, point estimates of chronic sub-lethal toxicity that cause a 10 to
9 20 % effect should be used, but NOEC type data can be used if there is insufficient
10 appropriate point estimate data available.

11

12 If only higher adverse effect data are available (e.g. EC50 or LOEC data) then these
13 should be converted to EC10 / NOEC values with appropriate conversion factors,
14 such as those used in the Australian and New Zealand water quality guidelines
15 (WQGs) (Warne, 2000). Due to the general paucity of terrestrial ecotoxicology data, it
16 is proposed that if toxicity data are not expressed as single numbers but instead are
17 given as ranges, then the mean value of the range should be used. In certain studies,
18 the lowest toxicant concentration had already caused significant toxic effects and
19 therefore toxicity data is given as a $<$ or \leq value. If possible, the percentage effect that
20 the reported concentration caused should be determined and if the effect was between
21 0 - 30, the value should be treated as a NOEC. If the percentage was 30 – 40% the
22 value should be treated as a LOEC and $>$ 40 % it should be treated as an EC50 and
23 they should be converted accordingly. If in studies, the highest tested concentration
24 did not cause an effect on the species and the toxicity data is given as $>$ value, the

1 actual value can be treated as an EC10. This is proposed as it is a conservative
2 approach and will result in more toxicity data available for SQG derivation.

3

4 *Step 2 - Determining temporal changes in toxicity and bioavailability*

5 This step is only applicable if toxicity values have been measured over time, e.g. the
6 field-based measurements generated by the NBRP over consecutive crop years. There
7 are two scenarios in which determining the temporal changes in toxicity would be
8 appropriate. Firstly, to ensure that toxicity values measured when the contaminant is
9 most bioavailable and exerting the greatest toxicity on species are used to derive STV
10 and STV_{amended}. Secondly, where the contaminants have been in the soil for a
11 prolonged period (i.e. years or decades) it would be appropriate to determine an
12 ‘ageing factor’ to adjust toxicity data derived from experiments based on freshly
13 added (spiked) contaminants for any moderating effects of prolonged soil residence
14 times. In general a contaminant is most bioavailable immediately after application,
15 with ageing and degradation of organic contaminants occurring over time (e.g. Walter
16 et al, 2002; Smolders et al., 2003). However, increased toxicity is possible for organic
17 contaminants where metabolites can be more toxic than their parent compound, or
18 contaminants applied to unstable soil amendment matrices can be released through
19 degradation of the matrix (Chang et al., 1997; McBride, 2003).

20

21 *Step 3 - Developing normalisation relationships*

22 Normalisation relationships are empirical relationships between toxicity or
23 bioaccumulation data for a contaminant to a species and the physicochemical
24 properties of the soils where the tests were conducted. They have generally been
25 developed using linear regression analysis techniques including forward and

1 backward step-wise regression (e.g. Smolders et al., 2004; McLaughlin et al., 2006;
2 Rooney et al., 2006; Broos et al., 2007; Warne et al., 2008a; Warne et al., 2008b) or
3 partial least squares (PLS) regression techniques (e.g. Lock and Janssen, 2001). It is
4 important that only soil physicochemical properties that are not significantly
5 correlated with each other are used to develop normalisation relationships using the
6 above techniques. However, if Ridge regression is used then this requirement does
7 not apply (Basta et al., 2008). Researchers have generally only reported or
8 recommended the use of normalisation relationships that explain more than 50% of
9 the variation in toxicity values, i.e. they have coefficients of determination (r^2) or
10 adjusted coefficients of determination ($\text{adj } r^2$) greater than 0.5. If a relationship does
11 not explain at least 50% of the variation then using it to normalise other toxicity data
12 could introduce considerable error.

13

14 Normalisation relationships can, in principle, be developed for any combination of
15 contaminant, species, measure and endpoint of toxicity. However, while this is
16 possible, one should only develop normalisation relationships using ecologically
17 relevant species, measures and endpoints of toxicity for the ecosystem that is being
18 protected. In addition, it is preferable from an implementation point of view that
19 relatively easy and cheap to measure, accurate and repeatable soil properties are used
20 to derive normalisation relationships. The latter will ensure the relationships that end
21 up being used and do not place considerable additional costs on users.

22

23 *Step 4 - Normalising the toxicity data*

24 At this point the usual approach to derive an EQG is to enter the toxicity data that
25 have passed the screening into a SSD method and calculate concentrations that should

1 protect a selected percentage of species (e.g. ANZECC and ARMCANZ, 2000;
2 Crommentuijn, 2000a; CCME, 2006). However, terrestrial toxicity data will most
3 likely have been undertaken in a range of different soils and thus the variation in the
4 toxicity data will reflect both the inherent sensitivity of the species and the soil
5 properties that modify toxicity. Therefore, a concentration to hypothetically protect
6 95% of species (PC95 which is the equivalent of a hazard concentration of 5% - HC5)
7 derived using such data would not per se protect 95% of species but rather it would
8 hypothetically protect 95% of combinations of species and soil type. This problem
9 can be overcome by using relationships to normalise the data to a standard soil before
10 the data are entered into a SSD method. By normalising the data at this point, the
11 effect of soil properties on the available toxicity data will be minimised and the
12 resulting distribution of the data will reflect more closely the inherent sensitivity of
13 the test species. The properties of the standard soil that was selected to represent
14 Australian soils in the present study were: pH 6, clay content 10%, cation ion
15 exchange capacity 10 cmol_c/kg and organic carbon content 1%. It should be noted
16 however, that the selection of the standard soil does not have any effect on the final
17 TVs as these are extrapolated back to actual soil conditions (see step 6).

18

19 Each normalisation relationship is specific for a combination of a species and a
20 contaminant. A normalisation relationship typically takes the form:

21

$$22 \quad \textit{Effect of contaminant} = a \{ \textit{soil property} \} \pm b \quad [1]$$

23

24 where *a* is the gradient of the regression and *b* is the y-intercept. The effect of the
25 contaminant could be toxic effects or bioaccumulation of the contaminant. The y-

1 intercept is a measure of the inherent sensitivity of the test species used to derive the
2 normalisation relationship, with each species having a unique y-intercept.

3

4 Availability of normalisation relationships for contaminants in soil is limited to a few
5 species and a few contaminants. However, this can be overcome by applying the
6 relationships to other species than those for which they were derived (e.g. EU, 2006).

7 When applying normalisation relationships to other species, the toxicity data should
8 only be transformed using the gradient (i.e. a in eqtn 1) of the normalisation
9 relationships (EU, 2006). This practise should only be conducted if it could be
10 expected that the contaminant would have a similar effect on other species and the
11 application of the normalisation relationship leads to a decrease in the range of
12 toxicity or bioaccumulation values for the other species (EU, 2006). The application
13 of normalisation relationships for one species to another is preferably used within the
14 following taxonomic groups: 1) plants; 2) invertebrates without an exoskeleton (e.g.
15 annelida, nematoda, mollusca) and heterotrophic protists, (e.g. protozoa, amoeba); 3)
16 invertebrates with an exoskeleton (e.g. hexapoda, myriapoda, chelicerata, tardigrada);
17 and 4) microbial and fungal functional endpoints. This grouping is based on the body
18 structure and the exposure route of organisms to the contaminant i.e. being exposed
19 by the direct environment or through food.

20

21 If multiple normalisation relationships are available within a taxonomic group of
22 organisms, the most geographically appropriate normalisation relationships should be
23 applied to the toxicity data.

24

25 The following four potential scenarios for ACL derivation are possible:

- 1 1. if normalisation relationships for all 4 taxonomic groups are available and
2 each group meets the minimum data requirements to use the SSD approach,
3 then derive a set of ACL values for each group and merge them so that the
4 lowest ACL for the soil in question is adopted;
- 5 2. if normalisation relationships for all 4 taxonomic groups are available but at
6 least one group does not meet the minimum data requirements to use the SSD
7 approach, then apply the normalisation relationships. Combine data for the soil
8 invertebrates and soil processes in one SSD calculation. Crop species should
9 not be grouped with soil processes and soil invertebrates and remain separate
10 as they have a different protection factor. Then use the normalisation
11 relationships to derive a set of ACLs for each taxonomic group and merge
12 them so that the lowest ACL for the soil in question is adopted;
- 13 3. if normalisation relationships are available for some groups then apply them to
14 the appropriate data and then combine all the data (including the non-
15 normalised toxicity data) in one SSD calculation. Then use the normalisation
16 relationships to derive a set of ACLs for each group of organisms that have a
17 normalisation relationship and merge them so that the lowest ACL for the soil
18 in question is adopted;
- 19 4. if normalisation relationships are not available, then pool all data and derive
20 one generic ACL.

21

22 *Step 5 – Calculating a Protective Concentration*

23 A number of SSD methods have been developed and used to derive EQGs. Generally,
24 these have applied a single statistical distribution to toxicity data e.g. the log-logistic
25 (Aldenberg and Slob, 1993), log-normal (Wagner and Løkke, 1991; Aldenberg and

1 Jaworska, 2000) and log-triangular distributions (Stephan et al., 1985). However,
2 there is no theoretical reason why the distribution of species sensitivity should
3 conform to any specific statistical distribution. Shao (2000) therefore recommended
4 that the Burr Type III (BT III) family of distributions be used to derive EQGs as they
5 have a wide variety of shapes, include the log-logistic distribution and can
6 approximate the log-normal and log-triangular distributions. This method was used to
7 derive the Australian and New Zealand water quality guidelines (ANZECC and
8 ARMCANZ, 2000). Other authors (e.g. Maltby et al., 2003; Kwok et al., 2007) have
9 since also adopted a more flexible approach whereby the distribution that best fits the
10 data is used to derive the EQG or to determine the ecological risk. The Burr Type III
11 SSD (Campbell et al., 2000) is therefore recommended for use in the proposed
12 framework (software using Burrlioz method is freely available at
13 <http://www.cmis.csiro.au/Envir/BurrliOZ/Download1.htm>).

14

15 SSD methods are statistical approaches and therefore they become increasingly
16 unreliable as the number of data decreases. A number of studies (Newman et al.,
17 2000; Forbes and Calow, 2002; Wheeler et al., 2002) have yielded different estimates
18 of the minimum number of data points that are needed to obtain EQGs that do not
19 change markedly with the addition, removal or substitution of data. These estimates
20 range between 10 and 30 data points. However, for the majority of contaminants such
21 large datasets are not available so regulatory agencies have developed pragmatic
22 minimum data requirements. Generally, the minimum data requirements for SSD
23 methods used to derive WQGs is toxicity data for at least five species that belong to
24 at least four different taxonomic groups (Van de Plassche et al., 1993; OECD, 1995;
25 ANZECC and ARMCANZ, 2000), although data for eight species are required in the

1 US assessments (Stephan et al., 1985) and EU water quality guidelines require
2 toxicity data for at least ten species that belong to at least eight taxonomic groups
3 (EC, 2003). Due to the lack of terrestrial toxicity data, the Dutch reduced the
4 minimum data requirements to at least four species that belong to at least four
5 different taxonomic groups (Crommentuijn et al., 2000a). We recommend toxicity
6 data for at least 5 species preferably belonging to at least three taxonomic groups is
7 required.

8

9 For all SSD methodologies, a percentile of the distribution has to be chosen to
10 calculate the concentration that should theoretically protect a specified percentage of
11 species from harmful sub-lethal effects of a contaminant in the standard soil. The
12 chosen percentile used in SSDs to protect ecosystems and their functioning varies
13 between countries. For example, Canada has set the species protective percentage for
14 agricultural and residential land uses at 75% (CCME, 2006), while in the
15 Netherlands, the maximum permissible concentrations are based on protecting 95%
16 of species (Crommentuijn et al., 2000a). For agricultural land, contamination
17 concentrations should be kept sufficiently low that the production of the vast majority
18 of agricultural crops is not significantly impaired. Therefore a conservative approach
19 would be to protect a high percentage of crop species and we propose to protect 95%
20 ($PC_{95_{crop}}$). Although soil processes and soil invertebrates are important to ensure
21 nutrient cycling that sustains these crop species, tillage and the use of
22 pesticides/herbicides make it unrealistic to protect 95% of these processes and
23 species. Therefore we propose that 80% of invertebrate species and soil processes be
24 protected ($PC_{80_{soil\ org}}$) in agricultural soils. The separation of the crop species from
25 invertebrates and soil processes might result in insufficient data to use the SSD

1 approach. An alternative method to ensure an adequate level of protection should be
2 adopted. For example, within the NBRP a comparison was made between the toxicity
3 values of invertebrates in NBRP soils to the plant toxicity data. This comparison
4 showed that invertebrates were as sensitive as plants and were therefore protected by
5 the $PC_{95_{\text{crops}}}$. Furthermore, for the protection of soil processes we generated a
6 protective value for substrate induced respiration (SIR) by calculating a 95th
7 percentile of the SIR toxicity values measured in the NBRP soils using BurliOz SSD
8 methodology (Campbell et al., 2000).

9

10 The $PC_{95_{\text{crop}}}$ and the $PC_{80_{\text{soil org}}}$ are added contaminant limit (ACL) values (mg
11 added contaminant/kg soil). For bioaccumulating substances (e.g. cadmium)
12 contamination levels should be kept sufficiently low to prevent exceeding food
13 standards (see McLaughlin et al., 2006).

14

15 *Step 6 – Calculating a suite of ACL values*

16 In this step we create soil specific ACL values for contaminants where toxicity data
17 showed a clear relationship (i.e. statistically significant and $\text{adj } r^2 > 0.5$) with soil
18 properties. Therefore, this step is omitted if an appropriate normalisation relationship
19 is not available for a particular contaminant. If however, one or more normalisation
20 relationships are available they should be applied to the single reference ACL value
21 generated in step 5. For example, if the normalisation relationship was based on soil
22 pH, a series of ACLs would be generated for different soil pH values and if a
23 normalisation relationship was based on pH and CEC then a matrix of ACL values
24 would be derived for each combination of pH and CEC. Extrapolation of ACLs

1 beyond the range of the soil physicochemical properties used to develop the
2 normalisation relationships is not recommended.

3
4 For each taxonomic group (see step 5) that has a normalisation relationship a suite of
5 ACLs should be calculated. For a specific site or soil, the lowest ACL of these groups
6 should be used. If multiple normalisation relationships are available within a
7 taxonomic group then the normalisation relationship of the most relevant region
8 should be used to calculate a suite of ACLs.

9

10 *Step 7 - Calculation of a soil amendment availability factor*

11 The soil amendment (bio)availability factor (SAAF) refers to a factor that takes into
12 account the difference in bioavailability of contaminants in the soil amendment
13 compared to that of the pure form of the contaminant (e.g. metal salt) from which the
14 ACLs were derived. There are several methodologies to assess bioavailability of
15 metals in soils (McLaughlin et al. 2000b), including extraction techniques (e.g.
16 CaCl₂, NH₄-NO₃, chelates and soil solution extraction) (Degryse et al., 2003;
17 McBride et al. 2004), isotope dilution techniques (Hamon et al. 2002; Nolan et al.,
18 2003), membrane techniques and by measuring metal concentrations in organisms.
19 Currently there is no consensus in the literature on which methodology most
20 accurately describes the bioavailability of metals, as pathways of metal exposure and
21 routes of uptake may vary across organisms and the metals themselves (Sauvé et al.,
22 2000; Feng et al., 2005).

23

24 Soil extraction techniques have been reported in the literature as both good and bad
25 predictors of bioavailability and hence toxicity (Smit and Van Gestel, 1998; Lock and

1 Janssen, 2001; Zhang et al., 2001; Smolders et al., 2003; Smolders et al., 2004; Nolan
2 et al., 2005; Oorts et al., 2006; Zhao et al., 2006; Broos et al., 2007, Warne et al.
3 2008b). This is probably due to the fact that soil extraction techniques do not measure
4 the exchangeable solid phase pool which can be a very dominant bioavailable pool in
5 certain soils (Zhang et al., 2001; Nolan et al., 2005). Another complication with soil
6 extraction techniques is that potential complexation of contaminants with colloidal
7 particles and dissolved organic matter (DOM) has to be taken into account. As a
8 result, assessment of contaminant availability needs to not only consider potential
9 release of that contaminant from the soil amendment, but also consider the speciation
10 of the released contaminant and its subsequent partitioning between soil mineral and
11 organic phases (Merrington et al., 2003; Oliver et al., 2004). Techniques like diffuse
12 gradient in thin films (DGT) and isotopic dilution therefore seem more promising
13 than chemical extraction methods, as they take potential release of contaminants from
14 the soil amendment into account (Zhang et al., 2001; Oliver et al., 2004; Nolan et al.,
15 2005). Until the debate over which is the best method for determining bioavailability
16 has been resolved, the determination of SAAFs should be done on a case by case
17 basis. In such situations a weight of evidence approach (e.g. Menzie et al., 1996; Ruth
18 et al., 2006) is most appropriate.

19

20 The SAAF should be calculated using the following equation regardless of which
21 bioavailability measure was used:

$$22 \quad SAAF = \frac{\textit{Bioavailability in pure form}}{\textit{Bioavailability in soil amendment}} \quad [2]$$

23

24 The SAAF may or may not vary with soil properties and this needs to be examined in
25 determining the SAAF.

1 *Step 8 – Derivation of ACL value(s) for amended soil*

2 The SAAF can be a single value or can vary with soil or amended soil characteristics.
3 If the SAAF is a single value for a contaminant and there was no normalisation
4 relationship then the single ACL value (step 5) is multiplied by the SAAF to obtain
5 an ACL for amended soils (ACL_{amended}). If the SAAF is a single value for a
6 contaminant and there was a normalisation relationship the ACL values are multiplied
7 by the SAAF to obtain a suite of ACL_{amended} values. The approach is slightly different
8 if the SAAF varies with soil characteristics. In such situations the SAAF should be
9 calculated for the range of soils for which STVs are to be derived and the resulting
10 SAAFs should be multiplied by the appropriate soil ACL values to generate a suite of
11 ACL_{amended} values. It is possible that the soil properties that control the SAAF and the
12 ACL are different and it may be difficult or costly to measure the appropriate soil
13 property necessary to determine the SAAF. In such cases, an alternative would be for
14 the most conservative (i.e. lowest) SAAF or a percentile of the SAAF values (e.g. 95th
15 percentile) to be used to derive the ACL_{amended} values.

16

17 *Step 9 - Determining ambient background concentrations (ABCs)*

18 Concentrations of contaminants in topsoil are the sum of natural and anthropogenic
19 contributions. Some authors (e.g. Reimann and Garrett, 2005) argue that natural
20 background concentrations no longer exist anywhere in the world due to man's
21 activities and global transport of contaminants. Therefore, it has been argued that the
22 term ambient background concentration (ABC) rather than background concentration
23 should be used (e.g. Zhao et al., 2007).

24

1 The ABC can be measured directly or it can be estimated using models, although
2 direct measurement is preferred and should always be used if possible. The
3 complexity and problems associated with measuring the ABC are discussed in a
4 series of papers in Human and Ecological Risk Assessment Vol. 9, 2003 and by
5 Reimann and Garrett (2005). If reliable ABC values for a soil can not be obtained,
6 estimates from models are appropriate to use. We propose to use the model developed
7 by Hamon et al. (2004) in this Australian framework. However, other similar models
8 (e.g. Sterckeman et al., 2006; Zhao et al., 2007) would be more appropriate for other
9 countries.

10

11 Hamon et al. (2004) developed significant ($p < 0.05$) linear relationships between Fe or
12 Mn concentrations in soil determined by *aqua regia* digestion and the corresponding
13 concentrations of As, Co, Cr, Cu, Ni, Pb and Zn in 758 soils from Australia,
14 Malaysia, Namibia and Thailand. Ambient background concentrations were then
15 calculated using the equation that encompassed the upper 95th percentile of the data.
16 Zhao et al. (2007) argued that the Hamon et al. (2004) method is not a conservative
17 approach as the poorer the relationship the larger the 95th percentile will be, hence the
18 larger the estimates of ABC will be, potentially leading to under-protection of soils.
19 We agree and therefore suggest using the 50th percentile (i.e. the regression equation)
20 which are presented in Table 2, for ABC calculations.

21

22 Most organic contaminants of interest are xenobiotics, hence they have no natural
23 background concentration. Notable exceptions to this include lipids and fats,
24 hormones (e.g., oestrogen, testosterone), fatty acids, alcohols, hydrocarbons,
25 polycyclic aromatic hydrocarbons and dioxins. Therefore, ABCs for organic

1 contaminants will have to be generated by direct measurement or a default ABC of
2 zero (Crommentuijn et al., 2000b) could be assumed. For pyrogenic organic
3 contamination (e.g. contaminants arising from fire), a site-specific risk assessment
4 will have to determine if the measured soil concentrations are background
5 concentrations for that site/region. If a site-specific assessment is conducted then the
6 upper 80th percentile of the background concentrations should be used as the ABC as
7 per the Australian and New Zealand WQGs (ANZECC and ARMCANZ, 2000).
8 However, even if concentrations of organic contaminants are considered ABC, this
9 does not imply that there is no risk to the terrestrial biota.

10

11 *Step 10 - Calculating soil TVs or TVs for amended soil*

12 The ACL values determined in step 6 and 8 are based on added metal concentrations,
13 so the appropriate ABC must be added to them in order to obtain STVs or STV_{amended}
14 that are based on total contaminant concentrations:

15

$$16 \quad STV = ACL + ABC \quad [3]$$

17

18 where STV can be either a standard STV or STV_{amended} , the ACL can be either a
19 standard ACL or ACL_{amended} and ABC is the ambient background concentration of
20 the contaminant.

21

22 **Example calculations of STVs for amended soils using plant toxicity data**

23 *Derivation of STVs for Cu*

24 The cumulative distribution of EC10 data for all crops from the NBRP field trials
25 over the 3 harvests is presented in Figure 3 for Cu. There were no temporal changes

1 in the toxicity of Cu to wheat, therefore field-based normalisation relationships based
2 on wheat grown over the three years of the NBRP were developed. Furthermore,
3 EC10 data of laboratory based wheat bioassays, substrate induced nitrification and
4 substrate induced respiration showed no trend in time (data not shown).

5

6 Grain yield at harvest was used to derive soil TVs. Although plant growth at 8 weeks
7 and shoot yield, grain yield, protein content and 100 grain weight at harvest were
8 measured in the NBRP, we did not use these as insufficient high quality normalisation
9 relationships could be developed for plant growth at 8 weeks. Furthermore, shoot
10 yield was not measured at all sites and protein content and 100 grain weight were not
11 affected by Cu. The best normalisation relationships for field-based Cu EC10 and
12 EC20 (wheat grain yield) values were based on pH combined with log OC (Warne et
13 al., 2008b). The relationship for EC10 data was used to standardize the grain EC10
14 data; $EC10 = 0.56 + 0.31 * pH + 1.05 * \log OC$ (Warne et al., 2008b). The Cu EC10
15 values for each crop grown in the NBRP were normalised to the standard soil (pH 6
16 and OC =1 %) using the slopes of the pH and OC.

17

18 A single toxicity value is used in SSD methods to represent each species and
19 therefore geometric means were taken for species with multiple observations as
20 recommended by Van der Plassche et al. (1993) and the Australian and New Zealand
21 WQGs (ANZECC and ARMCANZ, 2000), see Table 3. The most sensitive species to
22 Cu grown in the NBRP trial were triticale and barley, while peanuts and sugar cane
23 were the most tolerant. The 95th percentile of these values, the ACL, was 35 mg/kg in
24 the standard soil. In comparison, the Flemish guideline value for the Australian
25 standard soil would result in 73 mg/kg but this is a total concentration including

1 background concentrations (OVAM, 2005). The Cu EC10 normalisation relationship
2 was used to calculate a matrix of ACL values based on pH and OC content in soils
3 (Table 4). For soils with soil pH of 4-8 and OC content of 1-6%, the ACLs range
4 from 8 mg/kg to 970 mg/kg added Cu.

5

6 We do not recommend extrapolating the normalisation relationships beyond the range
7 of soil properties from which they were derived. Therefore, for soils exceeding the
8 ranges of pH and OC of the matrix, the ACL of the closest setting of pH and OC
9 content in the matrix should be used for that soil.

10

11 To determine the SAAF we developed models relating the bioavailability of Cu to
12 soil physicochemical properties and compared the models for biosolids and metal
13 salts (Heemsbergen et al., in prep). This was done using the following methods to
14 estimate bioavailability (a) CaCl_2 extractable fraction, (b) soil solution concentration,
15 (c) plant tissue concentrations using linear regression analysis with groups, and (d)
16 isotopic dilutions measure using E values of Cu in biosolids (a measure of the
17 isotopically exchangeable Cu) from the work by Oliver et al. (2004). Plant tissue
18 concentrations showed that Cu concentrations were highly regulated and therefore not
19 a good measure to assess differences in bioavailability between biosolids and Cu
20 salts, as noted earlier by (McLaughlin et al., 2000b). Models of Kd (the ratio of total
21 soil concentration to the concentration in the soil solution) and CaCl_2 extractable
22 fractions of Cu showed higher solubility of Cu from biosolids than from the metal
23 salts. This was most probably due to the decomposition of biosolids resulting in high
24 concentrations of dissolved organic matter (DOM). Complexation of Cu by DOM can
25 markedly increase Cu solubility, however, it may not change or can even reduce Cu

1 bioavailability as biologically active free Cu^{2+} ion is complexed by DOM (Checkai et
2 al., 1987; Minnich et al., 1987; Laurie and Manthey, 1994). Therefore, the assessment
3 of biosolid Cu availability should consider both potential release of Cu from biosolids
4 and its speciation and partitioning to soil mineral and organic phases (Merrington et
5 al. 2003; Oliver et al. 2004). Furthermore, it is the bioavailability in the long term that
6 is most relevant for biosolids guidelines when labile organic matter compounds have
7 degraded and the biosolids have become relatively stable. Isotopic dilutions measures
8 (E values) might therefore give a more robust assessment of long term bioavailability
9 as E values measure the soluble plus exchangeable solid phase pool (Hamon et al.,
10 2002; Oliver et al., 2004). We therefore used the isotopically-exchangeable Cu in
11 Australian biosolids as reported by Oliver et al. (2004) to calculate a BCF.

12

13 As the labile fraction of Cu in biosolids decreases with increasing pH, Oliver et al.
14 (2004) calculated a SAAF for Australian biosolids by standardising all biosolids
15 exchangeable fractions to pH 4, a reasonable worst-case soil pH scenario for
16 Australian agricultural soils where liming is not a regular soil pH management
17 practice. The gradient of the relationship between pH and the exchangeable pool
18 varied with the biosolids and ranged from 23 to 59 mg/kg per unit pH change. To
19 calculate the maximum available Cu in all biosolids, they used the labile Cu in the
20 biosolids at the ambient biosolids pH, and assumed that all biosolids release Cu due
21 to acidification at the highest rate found (59 mg/kg per unit pH reduction) to produce
22 a maximum available Cu concentration in each biosolid at pH 4. We used these data
23 to calculate non-labile Cu in biosolids at various pH scenarios, expressed as a % of
24 the total Cu in the biosolids, using the pH 4 data above and normalising to other pH
25 values assuming non-labile Cu increases in biosolids at the *lowest* pH-dependent rate

1 observed by Oliver et al. (2004). This is conservative as most biosolids would have
2 more non-labile Cu at each pH than our values suggest. The non-labile Cu in each
3 biosolid, expressed as a % of total Cu, at each pH scenario was then plotted as a
4 cumulative frequency distribution and the 5th percentile value calculated using
5 BurrliOZ (Campbell et al., 2000) which then become the SAAF (Table 5). This again
6 represents a very conservative assessment of Cu availability in Australian biosolids at
7 various pH levels, as 95% of Australian biosolids will have more non-labile Cu than
8 these SAAF values.

9

10 Multiplying the Cu SAAFs (Table 5) with ACL values for Cu added to soil at the
11 same pH (Table 4) produces the $ACL_{\text{biosolids}}$ values (Table 6). The low biosolids
12 ACLs at low soil pH and OC contents occur because phytotoxicity of Cu is higher in
13 acidic soils with low organic matter and under these conditions the biosolids
14 availability factor is also low. To determine a $STV_{\text{biosolids}}$ for Cu either the measured
15 or estimated ABC is added to the appropriate $ACL_{\text{biosolids}}$. As the ABC is site specific,
16 it is not possible to provide a list of $STV_{\text{biosolids}}$ values.

17

18 For example, a soil with a pH of 6, OC content of 2%, and 10% Fe would result in a
19 ACL of 75 mg/kg added Cu (Table 4), and an ABC of 26 mg/kg Cu (Table 2)
20 resulting in a STV of 101 mg/kg Cu. The corresponding $STV_{\text{biosolids}}$ would be 146
21 mg/kg i.e. 120 mg/kg added Cu from the $ACL_{\text{biosolids}}$ (Table 6) and an ABC of 26
22 mg/kg.

23

24

25

1 *Derivation of TVs for Zn in soil*

2 The cumulative distribution of EC10 data for all crops from the NBRP field trials
3 over the 3 harvests is presented in Figure 4 for Zn. There were no temporal changes
4 in the toxicity of Zn to wheat, therefore field-based normalisation relationships based
5 on wheat grown over the three years of the NBRP were developed (Warne et al. 2008b).
6 They found that field-based phytotoxicity (EC10, EC20 and EC50) values were most
7 strongly related to pH and CEC. The Zn normalisation relationship for EC10 (grain
8 yield) values was used for the same reasons provided earlier for using the Cu EC10
9 normalisation relationships, $Zn\ EC10 = 0.48 + 0.27 * pH + 0.70 * \log\ CEC$ (Warne et
10 al, 2008b).

11

12 A single Zn toxicity value for each crop grown in the NBRP was obtained by
13 calculating the geometric mean of the EC10 values normalised to the standard soil (a
14 pH of 6 and CEC 10 cmol_c/kg) (Table 7). The most sensitive species to Zn were
15 barley and peanuts while sugar cane was not affected at the highest tested Zn
16 concentration (i.e. 3200 mg/kg total added Zn). The soil ACLs for Zn based on
17 protecting 95% of species for a variety of soils (pH 4 – 8 and CEC 3 – 60 cmol_c/kg)
18 are presented in Table 8 and range from 21 mg/kg added Zn to 1470 mg/kg added Zn.
19 The German soil precautionary values for Zn are 60, 150 and 200 mg/kg for sandy,
20 loam/silt and clay soils respectively (BbodSchV, 1999) and thus lie within the range
21 of values generated by the present study. As CEC increases with increasing clay
22 content, the German classification is similar to that proposed, and their values
23 correspond to the soil ACL values at a soil pH of approximately 5 (Table 8).

24

1 The biosolids availability factor for Zn was determined using the same approach as
2 for Cu except that no E values were available. Relative bioavailability of Zn from
3 biosolids determined using K_d values and CaCl_2 extractable fractions suggested
4 availability was lower than from the Zn salts at low pH and clay content (i.e. less than
5 20%) while at higher pH and clay contents biosolids Zn had a similar bioavailability
6 to Zn from added soluble salt (Heemsbergen et al., in prep). However, these initial
7 differences disappeared after 3 years. It is likely that the initial higher binding of Zn
8 in biosolids was due to elevated organic matter content which degraded over time
9 (Heemsbergen et al., in prep). Furthermore, initial plant uptake data showed that the
10 biosolids and metal salt Zn BCF values were significantly different ($p < 0.001$) at low
11 total soil Zn concentrations but were similar at high total soil Zn concentrations (i.e. \geq
12 60 mg/kg). Therefore to protect plants, irrespective of the total Zn soil concentration,
13 a Zn bioavailability factor of one was adopted and the Zn soil $\text{ACL}_{\text{biosolids}}$ are
14 numerically equal to the general Zn soil ACL values shown in Table 8.

15

16 As an example calculation: A soil with a pH of 6, a CEC of 10 (cmol_c/kg) and 10%
17 Fe content would result in a ACL of 120 mg/kg added Zn (Table 8), and an ABC of
18 41 mg/kg Zn (using the 50th percentile equation, Table 2), resulting in a soil TV of
19 161 mg/kg Zn. The corresponding TV for soils receiving biosolids would also be 161
20 mg/kg Zn as the biosolids availability factor is one.

21

22 **Implications of the proposed framework for use of biosolids on agricultural** 23 **fields**

24 The generated Cu and Zn $\text{ACL}_{\text{biosolids}}$ were both lower and higher than the current
25 single value guidelines in Australia for biosolids amended soils (100-200 mg/kg for

1 Cu and 200-250 mg/kg for Zn, NRMCC 2004). Alkaline soils and soils with high OC
2 contents or high CECs can accept greater loadings of Cu and Zn from biosolids than
3 sandy acidic soils with low OC content. These latter soil conditions have $ACL_{\text{biosolids}}$
4 below current national guidelines in Australia. This was also observed in the study of
5 food-chain transfer of Cd in the same NBRP sites where sandy acidic soils were also
6 identified as high risk (McLaughlin et al., 2006). On these soils, repeated biosolids
7 application is considered a higher potential risk in the long-term to both human and
8 environmental health, compared to other soil types, especially if lower grade
9 biosolids with high metal concentrations are applied. Some state biosolids guidelines
10 have a minimum soil pH limit below which soils can not receive biosolids, i.e. 5.5 in
11 South Australia (SA EPA, 1997), 5.0 in Western Australia (WA DEP, 2002) and 4.5
12 in Victoria (EPA Vic, 2004). Guidelines for maximum application rates for biosolids
13 consider both nutrients and contaminants in the soil and in the biosolids (Figure 1).
14 As indicated by Figure 1, the proposed framework can be used to protect other key
15 organisms types (e.g. micro-organisms, invertebrates) or exposure pathways (plant
16 uptake). The lowest set of derived guidelines of the different exposure pathways or
17 key organisms will be what applies to a particular soil or amended soil.

18

19 The calculation of contaminant limiting application rate of biosolids (CLAR) is quite
20 straightforward:

21

$$22 \quad CLAR = \frac{SM * (TV \text{ for amended soil} - AS)}{BCC} \quad [4]$$

23

1 where SM is the soil mass per hectare to the depth of biosolids incorporation
2 (tonnes/ha), AS is the application site soil contaminant concentration and BCC is the
3 biosolids contaminant concentration (equation modified from EPA Vic 2004).

4

5 The biosolids used in the NBRP generally had higher Zn than Cu concentrations
6 (Table 10). Comparing the Cu and Zn concentrations in biosolids to the proposed soil
7 TVs showed that, if these limits were adopted, Zn would be the contaminant most
8 likely to limit biosolids applications (in the long term) for almost all Australian soil
9 types regardless of pH, CEC and OC content. In contrast, Cu would limit biosolids
10 application in Western Australia due to the relatively high Cu contents of their
11 biosolids and because many of the local soils are acidic and have low organic carbon
12 contents. Generally in Australia (except for South Australia), nutrient loadings
13 currently limit biosolids application rates and soil metal limits will only impinge on
14 biosolid re-use programs if these materials are repeatedly applied to the same areas.

15

16 **Conclusion**

17 A scientifically-based framework for developing site- or soil-specific quality
18 guidelines for contaminants in soils and soils receiving amendments was developed.
19 The application of the framework was illustrated by developing Cu and Zn guidelines
20 to protect crops grown in soils receiving biosolids based on data derived from a multi-
21 year, field-based investigation of phytotoxicity and plant metal uptake in Australian
22 soils. The framework can also be used to derive guidelines to protect other organisms,
23 soil processes or human exposure pathways. The soil quality guidelines developed
24 rely on measurement not only of total metal concentrations in soil, but also of key soil
25 properties that control metal bioavailability, notably soil pH, organic carbon content

1 and CEC. The framework also acknowledges the different bioavailability of
2 contaminants in soil amendments compared to pure contaminant salts or compounds.

3

4

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11

12

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- 2 of trace metals in soils for risk assessment. *Environ Pollut* 2007;148:221-229.

1 Table 1. Questionnaire for assessing the quality of terrestrial toxicity data adapted
 2 from Hobbs et al 2005. The quality of a study will be considered unacceptable to
 3 derive soil and amended soil trigger values if the quality score is < 50%.

4

Question	credits
1 Was the duration of the exposure stated (e.g., 48 or 96 h)?	10 or 0
2 Was the biological endpoint (e.g., immobilization or population growth) stated and defined (10 marks)? Award 5 marks if the biological endpoint is only stated	10, 5 or 0
3 Was the biological effect stated (e.g., LC or NOEC)?	5 or 0
4 Was the biological effect quantified (e.g., 50% effect, 25% effect)? The effect for NOEC and LOEC data must be quantified	5 or 0
5 Were appropriate controls (e.g., a no-toxicant control and/or solvent control) used?	5 or 0
6 Was each control and contaminant concentration at least duplicated?	5 or 0
7 Were test acceptability criteria stated (e.g., mortality in controls must not exceed a certain percentage)? OR Were test acceptability criteria inferred (e.g., test method used [USEPA, OECD, ASTM etc] uses validation criteria) (award 2 marks). Note: Invalid data must not be included in the database	5, 2 or 0
8 Were the characteristics of the test organism (e.g., length, mass, age) stated?	5 or 0
9 Was the type of test media used stated?	5 or 0
10 Were the contaminant concentrations measured?	4 or 0
11 Were parallel reference contaminant toxicity tests conducted?	4 or 0
12 Was there a concentration–response relationship either observable or stated	4 or 0
13 Was an appropriate statistical method or model used to determine the toxicity?	4 or 0
14 For NOEC/LOEC data was the significance level 0.05 or less? OR For LC/EC/BEC data was an estimate of variability provided?	4 or 0
15 Were the following parameters measured? pH, OM or OC content Clay content CEC	3, 1 or 0 3, 1 or 0 3, 1 or 0 3, 1 or 0
16a Was the temperature measured and stated?	3 or 0
17 Was the grade or purity of the test chemical stated? For metal salts 3 points are automatically scored.	3 or 0
18 Were other cations and or major soil elements measured? Or Were known interacting elements on bioavailability measured (e.g. Mo for Cu and Cl for Cd)?	3 or 0
19 For spiked soils with metal salts: Were the soils leached after spiking	3 or 0
20 Was the incubation conditions and time of the soil stated	3, 1 or 0
Total score	
Total possible score for the various types of data and contaminants: 102	
Quality score ($[\text{Total score} / 102] * 100$)	
Quality class (H _80%, 51–79% A, U _ 50%)	

5

1 Table 2: Equations from Hamon et al. (2004) and the corresponding coefficient of
 2 determination (r^2) used to estimate ambient background concentrations of Arsenic
 3 (As), Cobalt (Co), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc
 4 (Zn) based on the 50th percentile of the data. The standard errors are given in
 5 brackets. Equations are based on the logarithm of the iron content or manganese (for
 6 Co) (x in %) and the logarithm of the element (y in mg/kg).

Element	Gradient	y intercept 50th percentile	r^2
As	0.547	0.507 (0.355)	0.5
Co	0.894	-1.409 (0.3063)	0.71
Cr	0.75	1.242 (0.364)	0.58
Cu	0.612	0.808 (0.284)	0.61
Ni	0.702	0.834 (0.311)	0.64
Pb	1.039	0.118 (0.3014)	0.66
Zn	0.589	1.024 (0.222)	0.61

1 Table 3: Crops grown in field trials of the Australian National Biosolids Research
2 Program with their corresponding geometric means of copper concentrations that
3 inhibited crop yield by 10% (EC10), the lowest observed EC10 and the number of
4 EC10 values for each species. All toxicity values are standardized to pH 6 and
5 organic carbon content of 1%.

Crop	Geometric means of EC10 values	Lowest EC10 value	Number of EC10 values
Barley	63.1	30.6	3
Canola	341	88.9	4
Cotton	245	245	1
Maize	175	175	1
Millet	377	377	1
Peanuts	521	406	2
Sorghum	385	385	1
Sugar cane	663	663	1
Triticale	32.4	32.4	1
Wheat	256	156	11

6

7

1 Table 4: Added contaminant limits (ACLs, mg/kg) values for added copper at each
2 combination of soil pH (4 – 8) and organic carbon content (0.5 – 6%) based on all
3 crops grown in the Australian National Biosolids Research Program. The ACLs
4 should theoretically protect 95% of species.

pH	Organic Carbon Content (%)			
	1	2	4	6
4.0	8	18	35	55
5.0	17	35	75	115
6.0	35	75	150	230
7.0	70	150	310	470
8.0	150	300	630	970

5

1 Table 5: The non-labile fraction and biosolids availability factors for copper at
2 different pH levels, based on E values from the study of Oliver et al. (2004).

3

pH	Cu non-labile fraction (% of total Cu)	Biosolids availability factor
4	21.9	1.28
5	30.1	1.43
6	38.8	1.63
7	47.0	1.89
8	53.4	2.15

4

- 1 Table 6: Added contaminant limits for biosolids amended soils ($ACL_{\text{biosolids}}$ mg/kg)
- 2 for copper at each combination of soil pH (4 – 8) and organic carbon contents (0.5 –
- 3 6%) based on all crops grown in the Australian National Biosolids Research Program.
- 4 The ACL should theoretically protect 95% of species.

pH	Organic Carbon Content (%)			
	1	2	4	6
4	11	23	47	72
5	25	50	107	164
6	60	120	249	381
7	135	282	585	896
8	315	653	1356	2078

1 Table 7: Crops grown in field trials of the Australian National Biosolids Research
 2 Program with their corresponding geometric means of zinc (Zn) concentrations that
 3 inhibited crop yield by 10% (EC10 values), lowest observed Zn EC10 and the number
 4 of Zn EC10 values. All values were standardized to pH 6 and cation exchange
 5 capacity of 10 cmol_c/kg.

Species	Geometric means of EC10 values	Lowest EC10 value	Number of EC10 values
Barley	129	20.5	3
Canola	223	143	4
Cotton	272	272	1
Maize	644	644	1
Millet	539	539	1
Peanuts	140	67.3	2
Sorghum	213	213	1
Sugar cane	3200 ¹	3200 ¹	1
Triticale	998	998	1
Wheat	640	293	11

6 ¹ the highest tested Zn concentration is presented here as no effect occurred at that
 7 concentration.

8

1 Table 8: Added contaminant limits for Zn added to soil (soil ACL, mg/kg) at each
 2 combination of soil pH (4 – 8) and cation exchange capacity (3 – 60 cmol_c/kg) based
 3 on all crops grown in the Australian National Biosolids Research Program. The soil
 4 ACL values are based on protecting 95% of species. The amended soil ACL values
 5 are equal to the soil ACL values as the biosolids availability factor is one.

pH	Cation exchange capacity (cmol _c /kg)				
	5	10	20	40	60
4	21	34	56	91	121
5	40	64	105	170	226
6	74	120	195	317	422
7	138	224	364	592	787
8	257	418	680	1106	1470

1 Table 9: Selected chemical properties of the biosolids used in the Australian National Biosolids Research Program.

Biosolids source and name	Sites applied	EC ^a	pH	Total C	Total N	KCL NH ₄ -N	KCL NO ₃ -N	CEC ^b	Total Cd	Total Cu	Total Zn
		(dS/m)	(CaCl ₂)	(%)	(%)	(mg/kg)	(mg/kg)	(cmol(+)/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Bolivar agitated air dried	SA sites	6.29	7.4	6.3	0.77	28	1690	35	1.8	315	435
Bolivar dried lagoon	SA sites	7.04	7.4	8.6	0.98	49	1370	28	2.2	340	500
Goulburn Valley Water	Dookie	3.79	7.1	6.5	0.83	89	1420	24	1.4	65	180
North East Water	Dookie	6.47	5.0	11.6	2.03	480	4010	49	0.9	100	300
Vic Dutson Downs Gippsland Water	Dutson Down	6.78	5.6	20.4	2.85	3280	3910	61	<0.5	70	180
Vic Dutson Downs East Gippsland Water	Dutson Down	4.10	4.6	10.6	1.25	82	2580	21	1.0	150	290
NSW Malabar STP -LSB 2002	NSW sites	4.06	7.6	20.2	1.55	1480	104	32	5.4	420	650
NSW Bondi STP dewatered cake 2003	NSW sites	5.92	6.2	28.7	2.50	3560	357	37	4.6	880	870
QLD Noosa	QLD sites	2.86	6.8	27.2	4.79	480	22	84	1.9	355	495
QLD Luggage Point	QLD sites	7.61	6.6	32.8	5.72	4660	3	68	3.5	830	1705
WA Woodman Point 2005	WA sites	4.39	6.9	32.2	5.17	4520	4	68	2.0	1500	900
WA Beenyup 2005	WA sites	4.34	6.8	34.7	5.54	4480	3	60	1.4	1170	615

2 ^a EC = electrical conductivity. ^b CEC = cation exchange capacity.

1 **Figure Captions:**

2

3 Figure 1: Overview of the proposed framework for deriving biosolid guidelines and
4 their implementation. Abbreviations: Cd = cadmium; ACL = added contaminant
5 limit.

6

7 Figures 2: The proposed framework for deriving soil and amended soil trigger values
8 (TVs). Steps seven and eight are omitted when soil TVs are to be derived.

9

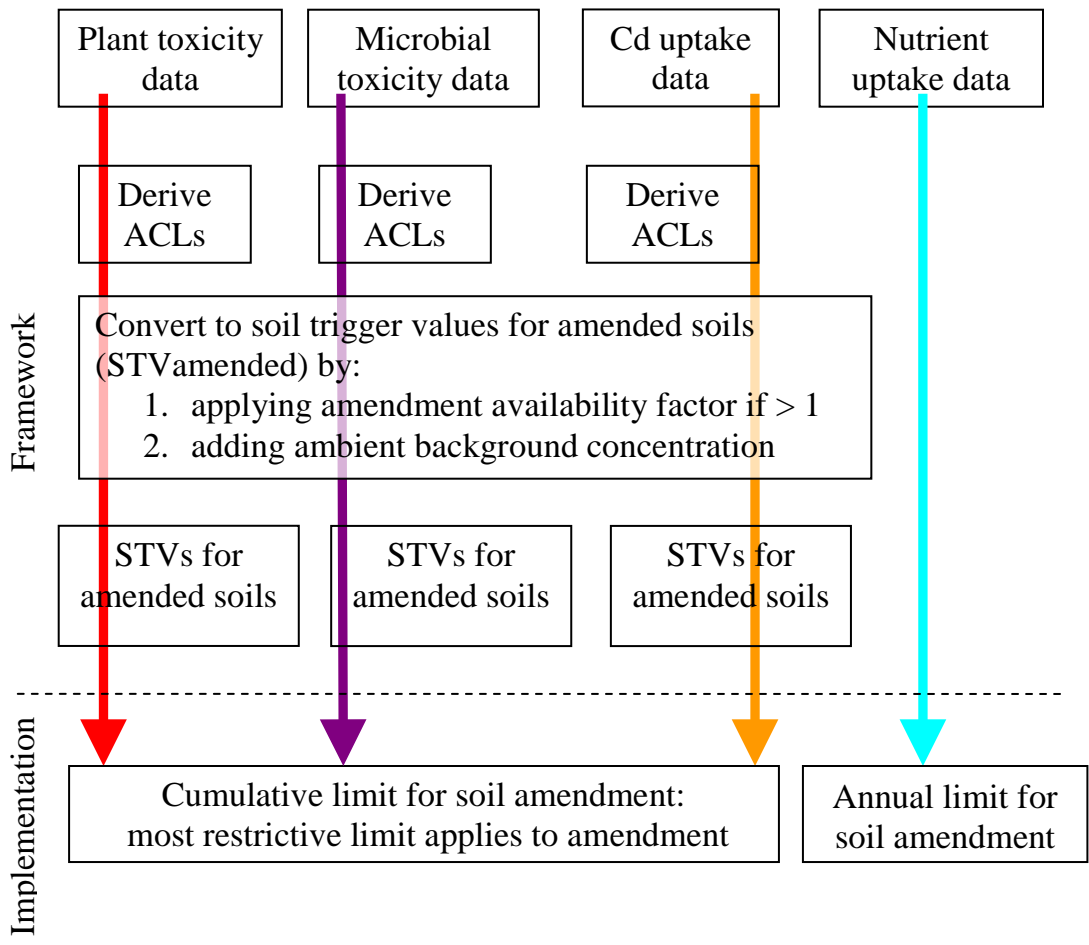
10 Figure 3: Cumulative percentage plot of normalised added Cu concentrations that
11 inhibited crop growth by 10% (EC10) for three harvests. Data for the first (T1),
12 second (T2) and third (T3) harvests have hollow diamonds, solid squares and solid
13 triangles respectively.

14

15 Figure 4: Cumulative percentage plot of normalised added Zn concentrations
16 measured that inhibited crop growth by 10% (EC10) for three harvests. Data for the
17 first (T1), second (T2) and third (T3) harvests have hollow diamonds, solid squares
18 and solid triangles respectively.

19

1 Figure 1.



- 2
- 3
- 4

1 Figure 2

2

3

1. Collation of toxicity data and assessment of its quality and appropriateness

2. Determine if temporal changes in toxicity occur. Select the most sensitive set of toxicity data.

3. Derive normalisation relationships by regress toxicity data against soil properties.

4. Normalise toxicity data of all species to a standard soil with specific characteristics

5. Use a species sensitivity distribution method to obtain a protective concentration (added contaminant limit – ACL)

6. Calculate ACL values for a range of soils using the normalisation relationships

If deriving soil TVs omit steps 7 & 8

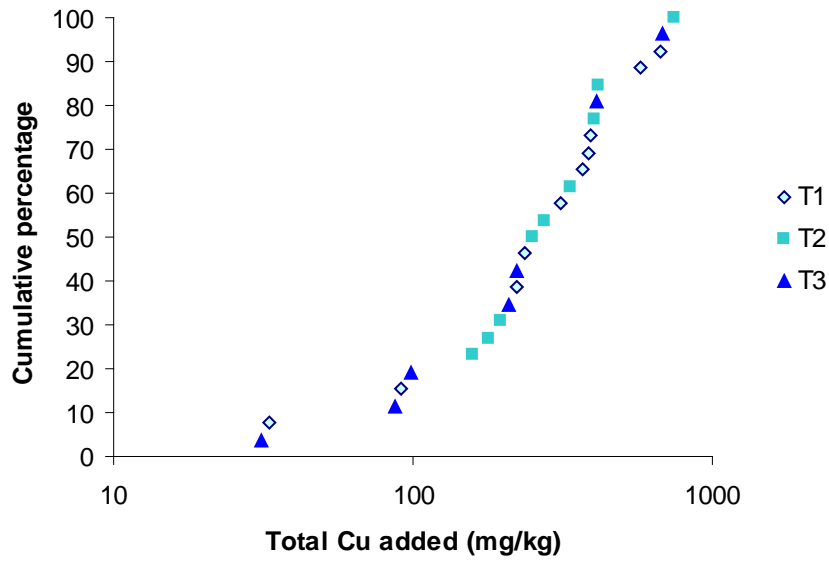
7. Derive a soil amendment (bio)availability factor (SAAF)

8. Multiply the SAAF and soil ACL values to derive ACL values for soil amendments

9. Determine the ambient background concentration (ABC) of the contaminant

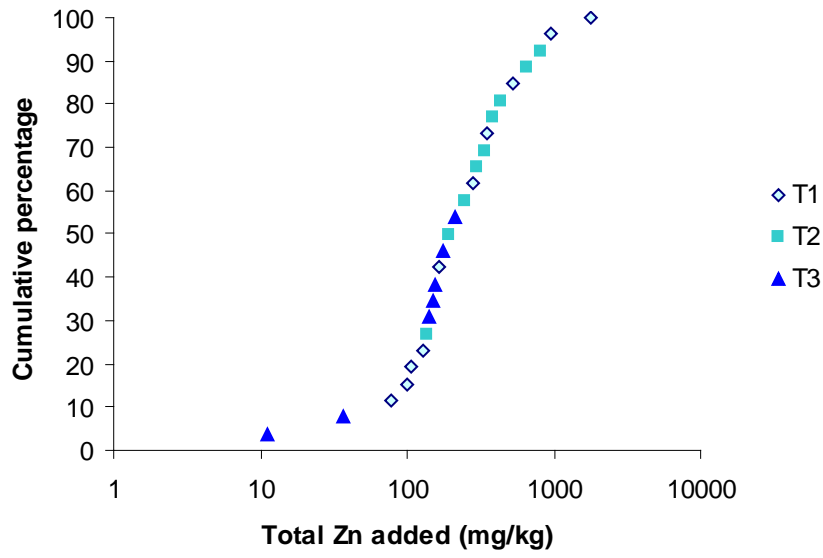
10. Add the ABC to the ACL values to calculate STVs

1 Figure 3



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3

1 Figure 4



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