

REUSING ROAD SWEEPINGS AND STORMWATER SEDIMENTS: REDUCING HEAVY METAL LEACHING

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ABSTRACT

Every year millions of dollars are spent by councils and road authorities landfilling thousands of tonnes of street sweepings and catchpit sediments. In addition to street sweepings, the last decade has seen a large increase in the number of storm water treatment devices, which as part of ongoing maintenance, will significantly increase the amount of contaminated road derived sediment (RDS) requiring costly landfill disposal. With numerous examples of successful RDS reuse applications in North America (landfill reductions waste by 90-95%); there is growing interest in NZ to implement environmentally responsible reuse options as an alternative to landfill disposal. A major challenge is to adequately stabilize the heavy metals (namely copper and zinc) to address environmental concerns regarding heavy metal mobilization. Compost was ineffective at stabilising zinc, but reduced copper leaching by up to 40% for RDS mixtures amended with 15% compost (dry weight). Phosphate amendment was largely ineffective and actually increased heavy metal mobilisation in most instances. Using an alkaline modifier to increase the leachate pH to 7.5-8 was found to be the most effective way of immobilising zinc (60-99% reduction), while a combination of compost (15%) and alkaline modifier (5-10%) reduced copper and lead leaching by ca. 60% and 50%, respectively. Based on potentially relevant international guidelines, carcinogenic PAH levels in Christchurch RDS would require a 2- to 3-fold dilution with clean material to ensure the most stringent guidelines were met (namely carcinogenic PAHs). Potential municipal wastes streams that could be used to incorporate RDS include greenwaste (composting) and wastewater treatment plant biosolids.

KEYWORDS

Street sweepings, heavy metals, reuse, RDS, contaminants, stabilization, leaching, guidelines

1 INTRODUCTION

1.1 GENERAL

Road runoff is a major contributor of suspended sediment and associated contaminants to urban stormwater. In order to reduce the environmental impacts of road runoff, road sweeping, catch pits and stormwater treatment devices (SWTDs) are used to capture this material before it is transported into aquatic receiving environments. For convenience, road sweepings and catchpit sediments are collectively referred to in this report as road-derived sediment or RDS.

The downside to reducing the amount of sediment transported to aquatic receiving environments is that road maintenance managers are faced with large amounts of road-derived sediment requiring costly disposal. As an example, for the 12 months ending October 2007, Christchurch City Council landfilled 7600 tonnes of RDS at a cost of ca. \$1.5m (S. McNeill pers. comm. 2007). This corresponds to ca. 4 tonnes of RDS/km/year being collected from Christchurch roadways, which indicates the potential scale of the problem when applied across the whole country. On a national scale, the tonnage of RDS disposed is expected to be at least comparable to the approximately 55,000 tonnes of waste water treatment biosolids produced from 'high-rate' wastewater treatment plants (WWTPs) in New Zealand each year (NZWWA 2003).

Current New Zealand guidelines (NZWWA 2003) specify that RDS is not suitable for cleanfills and, therefore, it must be disposed of in landfills. With increasing landfill charges, the cost of disposing of RDS is becoming an important issue for road waste generators; particularly in Christchurch where disposal costs are ca. \$200 per tonne of RDS. However, reducing landfilling costs is not the only driver for reusing RDS. There are potential benefits from reduced vehicle emissions (i.e., assuming reuse processing closer than landfill site), better alignment with national strategies on sustainability/waste reduction, and potential savings from generating product of value (i.e., compost) – thereby eliminating the need to purchase new material.

Many cities in the United States have already tackled the issue of dealing with RDS in more sustainable ways via various reuse and recycling applications. Alternatives to landfilling RDS include: daily cover material for lined or unlined landfills; fill materials for highway median strips and berm construction; fill for industrial, commercial and residential properties (in accordance with specific regulations); material used for spill cleanups; blending with other soil products to make topsoil; soil conditioner; component of compost; sand recovery; cleanfill disposal (as opposed to landfills); cement production; and aggregate in concrete and asphalt production. Utilising such sustainable approaches, the city of Bloomington, Minnesota reduced the amount of street sweepings landfilled by 90%. Various options for reusing, recycling and treating RDS have been reviewed by Depree (2008).

1.2 SUMMARY OF HEAVY METAL STABILISATION FROM PREVIOUS LTNZ RESEARCH

The research showed that with one 'worst case' Christchurch RDS sample (C2CP), there was considerable potential to stabilise heavy metals, in particular zinc, by simply adding low cost amending agents such as compost or phosphorus. A limitation of the two stabilisation methods trialled was increased DOC concentrations, which resulted in increased solubilisation of copper. Fortunately, the complexation of copper by DOC appears to result in a non-bioavailable (i.e., non-toxic) form of copper. The effectiveness of compost to potentially reduce the toxicity of RDS leachates is illustrated in Figure 1, which shows leachate toxicity plotted against particulate zinc concentration. C2CP, which contained 773 mg/kg of particulate zinc, was the most toxic leachate, however, the addition of 10% compost (reduced particulate zinc to ca. 700 mg/kg) reduced the

toxicity down to levels observed for RDS containing <300 mg/kg zinc. This demonstrated that although heavy metals cannot be 'treated out', they can be stabilised without having to add large amounts of clean diluting material.

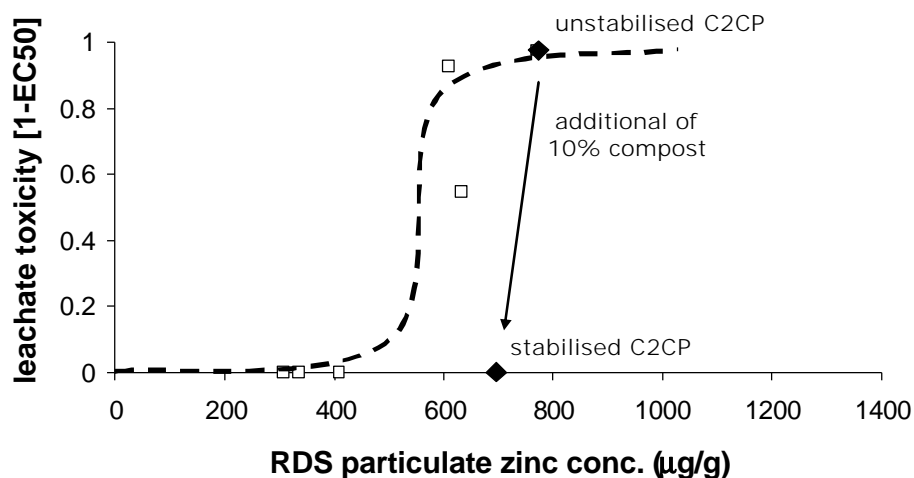


Figure 1: Leachate toxicity (relative scale) vs RDS particulate zinc concentrations: solid arrow indicates the stabilising effect of 10% compost on leachate toxicity of C2CP.

Relating leachate toxicity to RDS particulate zinc concentration, Figure 1 shows that leachate toxicity begins to increase at a particulate zinc concentration of ca. 400 mg/kg. This value is in good agreement with the NZ biosolids guidelines (post 2012 values), which specifies a maximum permitted zinc concentration of 300 mg/kg for grade 'a' biosolids (NZWWA, 2003).

Despite the useful data obtained, limitations of the stabilisation/amendment research component involved: only one RDS sample (C2CP); two amending agents trialled at one concentration; duplicate samples not run; and most importantly, a lack of control over leachate pH which can have a large effect on heavy metal solubilisation (especially zinc). As such, there are still unanswered questions such as:

- How representative was C2CP to RDS samples collected throughout Christchurch, and hence are simple amendment strategies applicable to a wider range of RDS, in particular street sweepings?
- What is the optimum loading of compost and/or phosphate?
- What influence did pH have on limiting the solubilisation of heavy metals in stabilised samples, and what amendments can maximise pH-related stabilisation of RDS?
- How can zinc be stabilised without increasing DOC and copper leaching?
- Should the focus of RDS reuse be more on contaminant dilution (to reduce risk) rather than contaminant stabilisation?

1.3 SCOPE OF CURRENT PROJECT

With previous work showing the potential of relatively simple amendment strategies to greatly reduce the toxicity (primarily via stabilising zinc) of RDS leachates, Christchurch City Council (CCC) wanted to investigate the applicability of these stabilisation strategies to a wider range of representative road sweeping samples from Christchurch. In addition, to attempt to answer some of the questions raised in Section 1.2.6, a more comprehensive set of experiments were required to examine the effectiveness of simple amending strategies to stabilise heavy metals. Road sweepings were the focus of this study as compared to catchpit sediments, streets sweepings are a larger and more manageable (no issues with sump water etc.) waste stream. Key components of the research project were:

- § Collect at least 10 representative samples of street sweepings from different areas throughout the city.
- § Characterise particle size distribution and analyse for, organic matter (OM), suite of heavy metals (including zinc, copper and lead), polycyclic aromatic hydrocarbons (PAHs), and total petroleum hydrocarbons (TPH).
- § Determine freshwater leaching of heavy metals (following US EPA SPLP procedure except using a more concentrated L/S ratio of 5).
- § Using at least 2 RDS samples, examine the effects of various stabilisation methods (i.e., amending agents) on the solubilisation of heavy metals. Amendments included multiple concentrations of compost, phosphate and alkalinity modifier (power station fly ash). The effect of pH was investigated (by adding either acid or base), to determine the importance of controlling pH in any reuse application.
- § Undertake experiments to determine the mechanism (biotic vs abiotic) for increased DOC in the presence of phosphate amending agents.
- § Analyse data and prepare an internally peer reviewed report that outlines the research results, summarises major findings and provides recommendations for advancing the reuse of RDS.

2 METHODS

2.1 RDS COLLECTION AND PROCESSING

2.1.1 COLLECTION

Samples were collected by vacuum sweeper truck, and general locations and traffic characteristics are summarised in Table 1. For each sample, a stock pile (Figure 2) consisting of 1-2 truck loads was sub-sampled using a spade. On average 5-10 spade loads were taken from different points from the stock pile and combined to give a wet

sample mass of ca. 10kg. Samples C1-C11 were collected in November 2008, while C2CP was an archived sample (Depree, 2008), which was originally collected (from a sump cleaning truck) in September 2006.

Table 1: Christchurch street sweeping sampling sites.

Sample	Description
C1	(SP5) South Western wards (1 load, arterials)
C2	(SP4) South Western wards (1 load, local)
C3	High traffic volume – Fitz, Cashel, Hereford, Moorehouse
C4	High traffic volume – New Brighton, Breezes
C5	Low traffic volume – Riverside area, River Rd
C6	Low volume traffic – Ajax, Achilles, Cooper, Bampton, Barclay, Belfield, Bramwell, Westcot, Gayhurst, Cresswell
C7	Low traffic volume – Eastern residential: Linwood, Tancred and English
C8	(SP2) CBD – standard sweepings (?) - 2 loads
C9	Low volume traffic – dish gutter
C10	High traffic volume (older stock pile)
C11	High traffic volume – Papanui, Harewood, Main North
C2CP ^a	High traffic volume – sump sediment from CBD

^a C2CP was an archived catchpit sediment sample original collected in 2006 (Depree, 2008).



Figure 2: Typical Christchurch street sweeping load that was sub-sampled.

2.1.2 PROCESSING

RDS samples were dried at ambient temperature (outdoors undercover) in large plastic trays (ca. 1200 x 600 mm) for approximately 2 weeks with daily mixing to facilitate drying. After this time, some samples (especially those containing high amounts of OM) were moved into the laboratory where removal of residual water was facilitated by the air conditioned environment. To be able to analyse representative sub-samples, samples were size fractionated in five fractions, <1mm, 1-5.6mm, 5.6-9mm, 9-20mm and >20mm, weighed and the particle size distribution (PSD) for each RDS sample determined. Combined, the <9mm fractions corresponded to 83% of the RDS dry mass (median value) and was therefore used for all further leaching and stabilising tests. To optimise sample homogeneity (so that experimental samples had the same composition as the original RDS material), all individual <9 mm RDS samples were composites prepared using the correct proportion of the four individual particle size fractions (<1, 1-5.6 and 5.6-9mm

RDS particulate samples C1-C11, and the corresponding freshwater leachates, were analysed for TPH, PAHs and heavy metals. Stabilisation trials were carried out on 2 representative samples C5, C11 and the archived RDS sample C2CP (to compare with original findings; Depree, 2008).

2.2 RDS PARTICULATE ANALYSES

2.2.1 HEAVY METALS

Particulate heavy metal concentrations of the three smallest size fractions (<1, 1-5.6 and 5.6-9mm) were measured by ICP-MS after a nitric/hydrochloric acid digestion in accordance with standard method US EPA 200.2 (Hill Laboratories). A sample size of ca. 2g was used for the more homogeneous <1mm fraction, whereas a 40-50g sample was extracted for the two larger size fractions. The total concentration of metals in the <9mm composite RDS sample was calculated from the relative mass contribution of the individual size fractions. A suite of six heavy metals were analysed, including cadmium, chromium, copper, lead, nickel and zinc, although discussion is limited to copper, lead and zinc.

2.2.2 PAHS AND TPH

Particulate PAHs analyses were carried out by Hill Laboratories (Hamilton) in accordance with standard methods US EPA 3540 and 3630. The PAHs analysed were the 16 priority PAHs listed by the US EPA, which include the following: naphthalene; acenaphthene; acenaphthylene; fluorene; phenanthrene; fluoranthene; pyrene; benz[a]anthracene; chrysene; benzo[b]fluoranthene; benzo[k]fluoranthene; benzo[a]pyrene; indeno[1,2,3-c,d]pyrene; dibenz[a,h]anthracene; benzo[g,h,i]-perylene. The seven underlined PAHs are classified as carcinogenic PAHs (cPAH).

Particulate TPH analyses were carried out by Hill Laboratories (Hamilton) using standard methods US EPA 8015B/NZ OIEWG. The method quantified the TPH in 3 carbon bands, C₇-C₉ (gasoline), C₁₀-C₁₄ (diesel) and C₁₅-C₃₆ (heavy).

2.2.3 ORGANIC MATTER (OM)

Organic matter was determined by the 'loss on ignition' method (Organic Laboratory, NIWA Hamilton). For <5.6mm size fractions, large samples (20–50g) were weighed in pre-weighed metal trays. The samples were heated to 100°C (to remove any water) and then reweighed. The dried RDS samples were then combusted at 400°C and reweighed – the difference between the dry (100°C) and combusted weight (400°C) being the amount of organic material present.

2.3 RDS EXTRACTIONS

2.3.1 TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

Toxicity characteristic leaching procedure (TCLP) and leachate metals analysis were carried out by Hill Laboratories (Hamilton) using the standard USEPA method 1311. Briefly, 100g of RDS were mixed with 2L (1:20 RDS to liquid ratio) of acidic extraction liquid (extraction fluid #1) for 18 hours. Extraction fluid #1 was prepared from a mixture of glacial acetic acid and NaOH with a pH of 4.93 ± 0.05. The acidic leachate mixture was then filtered and the filtrate analysed for the heavy metals; cadmium, chromium, nickel, copper, lead and zinc (via flame AAS).

2.3.2 FRESH WATER LEACHING AND STABILISATION TRIALS

The USEPA Method 1312, the Synthetic Precipitation Leaching Procedure (SPLP) is used to evaluate the potential for leaching metals into ground and surface waters, and like the TCLP method, utilises a L/S ratio of 20 (typically 100g extracted with 2L solvent). The method specifies slightly acidic extraction solution to mimic acid rain pH (unbuffered pH of 4.2 or 5, depending on region). However, in New Zealand, it is common for the test to be carried out using de-ionised (DI) water. To simulate more 'real world' conditions (i.e., low L/S ratio) a lower L/S ratio of 5 was used.

Mixtures consisting of RDS (100 or 200g) and phosphate/compost/fly-ash (Table 2) were moistened with 30% (w/w) of DI ultrapure water (18.2 M•) and equilibrated for 5 days. After 5 days the experimental mixtures were transferred to 2L glass bottles and DI water was added in a 5:1 ratio. The resulting suspension was placed on an orbital shaker (150 rpm) and allowed to equilibrate for 24 hours at ambient temperature (20-22°C). The samples were then centrifuged, filtered (0.45µm pore size cellulose acetate filters, Sartorius) and their equilibrium pH (Brand Orion, model 290A) and conductivity (HACH, model HQ40d) were measured. Filtered samples for metals were acidified with 0.2% HNO₃ (Aristar, analytical grade) and measured by ICP-MS with a dynamic reaction cell in accordance with standard method APHA 3125 B 21st ed. 2005 (Hill Laboratories, 2010 Stormwater Conference

Hamilton NZ). DOC was determined using catalytic oxidation and infrared detection in accordance with standard method APHA 5310 B 20th ed. 2005 (Hill Laboratories, Hamilton).

The compost (Dalton's Ltd "Just Compost") consisted of composted bark, saw dust, chicken manure and mushroom compost. The compost was added as percentage dry weight of the RDS without changing the 5:1 DI water to RDS ratio. The coal fly ash sample was sourced from the Huntly coal-fired power station.

Phosphate was added as a 1M buffer solution of sodium phosphate dibasic anhydrous (Na_2HPO_4 , Sigma-Aldrich) and sodium dihydrogen orthophosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, BDH Ltd UK) in DI water. To investigate the effect of pH on heavy metal mobility the pH of the experimental RDS suspensions was adjusted using HNO_3 (Aristar, analytical grade) and NaOH (Fluka, puriss pro analysi).

3 RESULTS AND DISCUSSION

3.1 CHARACTERISATION OF PARTICULATE PROPERTIES OF RDS

The purpose of this research was to characterise the variability of contaminants in a range of RDS (street sweepings in this instance) samples that were representative of the many types of 'environments' in Christchurch City. While parameters such as traffic density and catchment use (i.e., residential/commercial/industrial) are potentially important with respect to RDS contaminant concentration, this type of analysis/discussion was not part of this study.

3.1.1 SUMMARY OF CONTAMINANT CONCENTRATIONS

A summary of median particulate contaminant concentrations present in the 11 Christchurch RDS samples (C1-C11) is provided in Table 2.

Table 2: Summary of physical and chemical properties of Christchurch RDS (<9 mm, n=11).

parameter	median	interquartile range
% RDS mass <5.6mm	65	63-72
% RDS mass <9mm	83	81-85
organic matter (OM) %	8.6	6.4-13.8
TPH (mg/kg)	680	615-935
PAH ^a (mg/kg)	5.6	3.1-16.3
carcinogenic PAH ^b (mg/kg)	2.3	1.2-5.4
zinc (mg/kg)	212	174-267
copper (mg/kg)	35	24-46
lead (mg/kg)	112	77-138

^a PAH concentration refers to the sum of the 16 US EPA listed PAHs. ^b sum of 7 PAH, including benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, indenopyrene.

3.1.2 PARTICLE SIZE DISTRIBUTION AND ORGANIC MATTER CONTENT

The average particle size distribution (PSD) and the cumulative amount of RDS mass passing through each mesh size (1, 5.6, 9 and 20 mm) for C1-C11 is shown in Figure 3 and 4, respectively.

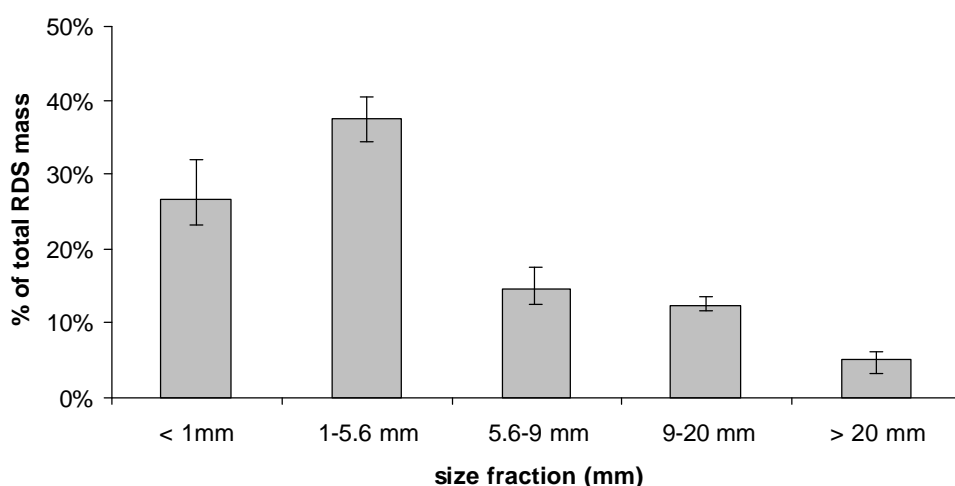


Figure 3: Median PSD of Christchurch RDS samples. Error bars represent upper and lower quartile values.

The PSD of C1-C11 indicated that the street sweepings were coarser compared to samples collected in 2006 (Depree, 2008), which is possible on account of the larger amount of organic detritus (vegetation) in the samples collected for this study

(December 2008). The median amount (interquartile range in parentheses) of RDS mass passing through a 1, 5.6 and 9mm mesh size was 27% (23-32), 65% (63-72) and 83% (81-85), respectively. All RDS recycling/reuse processes use 20-25 mm coarse screen to remove rubbish and vegetative debris. Using a 20mm screen on Christchurch RDS would result in 94-97% (lower/upper quartile range) of material being included for reuse processing, and 3-6% of the mass being diverted to landfill. Decreasing the screen size to 9-10 mm would increase the amount of landfill material to 15-19% of the total RDS mass.

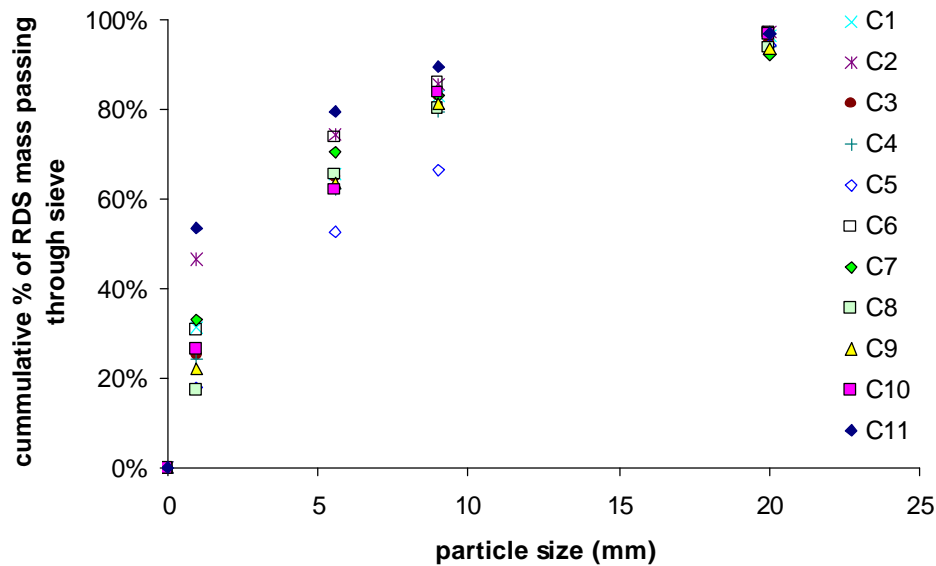


Figure 4: Cumulative PSD of individual Christchurch RDS samples (C1-C11).

Percent OM values for C1-C11 ranged from 3.7% to 26.5%. The median, lower and upper quartile percent OM was 8.6, 6.4 and 13.8%, respectively. The distribution of OM between particle sizes for each of the samples, based on median values, <1 and 1-5.6 mm fractions contained ca. 10% OM, while the coarser 5.6-9 mm fraction contain approximately half this amount (Figure 5).

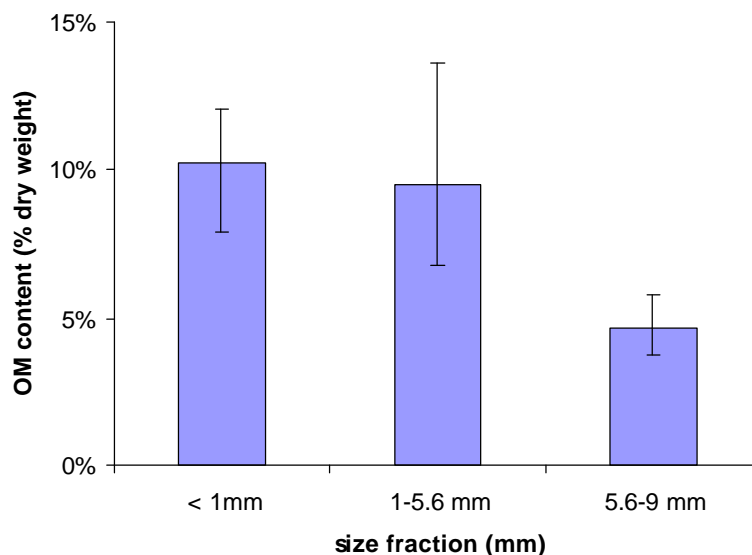


Figure 5: Median OM content for the three individual particle size fractions of RDS. Error bars for median data represent lower and upper quartile values.

3.1.3 PARTICULATE CONCENTRATIONS OF ORGANIC CONTAMINANTS

TPH

TPH concentrations in Christchurch RDS samples C1-C11 (<9mm) ranged from 370 to 1200 mg/kg, with a median and interquartile range of 680 mg/kg and 615-935 mg/kg, respectively (Figure 6). Of the three TPH fractions, C₇-C₉ (e.g., petrol), C₁₀-C₁₄ (e.g., diesel) and C₁₅-C₃₆ (e.g., oils, bitumen, plant waxes), the majority of the TPH (ca. 97%) in RDS samples were from the heaviest hydrocarbon fraction (C₁₅-C₃₆).

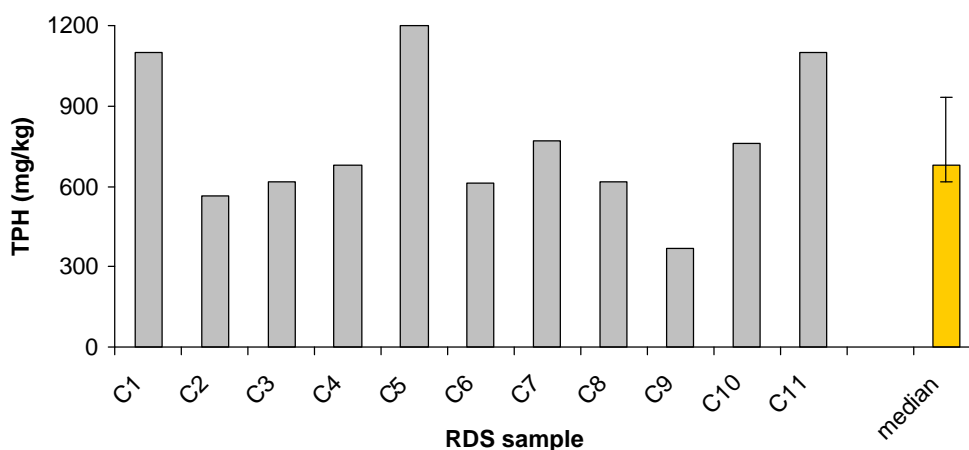


Figure 6: Particulate TPH concentrations for Christchurch RDS samples C1-C11. Error bars represent lower and upper quartile values.

Relative to guidelines used in the US, TPH concentrations in C1-C11 were very low, and well below maxima specified for Snohomish County (Washington) Class A street waste, and Oregon soil clean guidelines specify maximum TPH levels of 2750 and 10,000

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mg/kg, respectively. Collins and Moore (2000) listed RDS containing <1000 mg/kg TPH as one of the conditions for classifying the risk from reused RDS as 'low'. Accordingly, TPH are not considered a limitation (i.e., with respect to risk) for reusing Christchurch RDS.

PAHS

The concentration of PAHs (sum of the 16 listed by the US EPA) ranged from 1.8 to 41.7 mg/kg, with a median and interquartile range of 5.6 mg/kg and 3.1-16.3 mg/kg, respectively (Figure 7). The variation in PAH concentrations most likely reflects the mixture of RDS from newer 'flat' and older 'dished' type channels, with the latter being characterised by high PAH concentration in roadside soils and RDS because of legacy coal tar from road construction (Depree, 2006; Depree, 2007; Depree & Olsen, 2005; Depree et al. 2006). Coal tar-containing particulates is therefore the most likely cause of the large variation in PAH concentrations in RDS, as opposed to other catchment parameters such as land use and/or traffic volume.

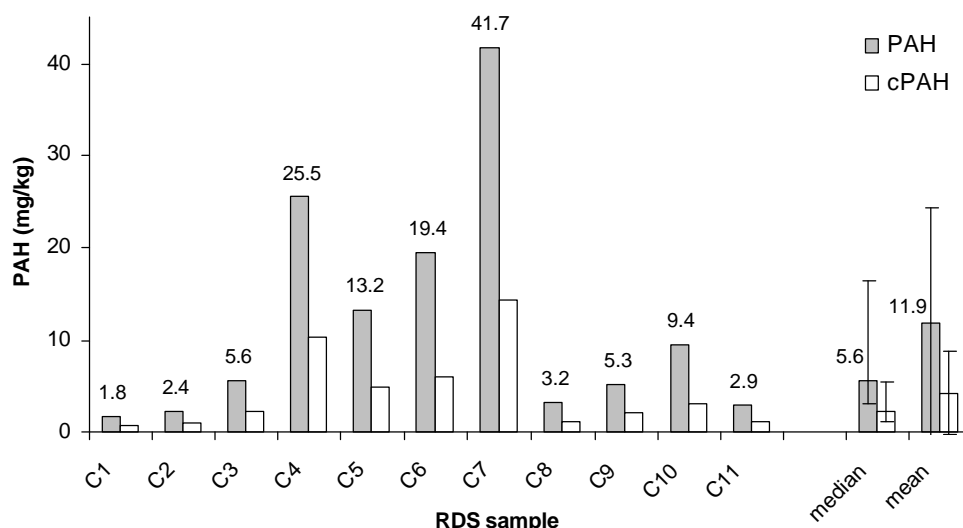


Figure 7: PAH and cPAH (carcinogenic PAHs) concentrations in Christchurch RDS samples C1-C11. Error bars represent lower and upper quartile values (median) and 1 SD (mean).

Particulate levels of PAHs in Christchurch RDS are of concern. Despite results indicating that PAH-contaminated roadside soils in Christchurch are not toxic to springtails (soil dwelling insect) at levels up to 1000 mg/kg of PAHs (Depree, 2007), the particulate concentrations do exceed some international soil quality guidelines (Table 2). The concentration of carcinogenic PAHs (cPAHs) in Christchurch RDS is a potential concern, since these account for ca. 38% of the total PAH concentration. The total concentration of cPAH for RDS samples C1-C11 ranged from 0.7 to 14.4 mg/kg, with a mean and interquartile range of 2.3 mg/kg and 1.2-5.4 mg/kg respectively. The mean concentration for the 11 RDS samples (assuming all stock piles were combined/mixed in equal quantities) was 4.3 ± 4.4 mg/kg (± 1 s.d.).

Table 2: Soil quality guidelines (Dutch and Canadian) and median concentrations of selected PAHs in RDS (road sweepings and catchpit sediments).

Contaminant	Dutch SQG ^a (µg/g)	Canadian SQGs (mg/kg)		C1-C11 RDS (mg/kg)	
		Residential / parkland	Commercial / industrial	Median conc. (interquartile range)	Maximum conc.
Phenanthrene	31	5 ^b	50 ^b	0.70 (0.44-1.55)	2.3
Benzo[a]anthracene ^c	2.5	1 ^b	10 ^b	0.38 (0.16-0.92)	2.5
Benzo[a]pyrene ^c	7.0	0.7	0.7	0.52 (0.25-1.4)	2.3

^a PAH values are SRC_{eco} values (i.e., ecological serious risk concentration. ^b Interim remediation criteria for soil that have not yet been replaced by Canadian SQGs. ^c carcinogenic PAHs

Most guidelines tend to specify maximum levels for individual cPAH compounds, which depending on the land use (residential vs industrial), are typically between 1 and 10 mg/kg. U.S. guidelines for cPAH in reused RDS are very restrictive (compared to heavy metal limits), for example Oregon DEP ‘soil cleanup’ guidelines (Collins and Moore, 2000) permit individual cPAH concentrations of between 0.1 (residential) and 1 mg/kg (industrial), and Snohomish County (Washington) specify a maximum total (sum of all 7 cPAH) of 1 mg/kg for Class A street waste (CWC, 1997).

3.1.4 PARTICULATE HEAVY METAL CONCENTRATIONS

Figure 8 shows the median heavy metal concentrations for the 11 RDS samples compared to the maximum concentrations specified by the NZ guidelines for grade ‘a’ biosolids (white bars) – which can be safely handled by the public and applied to land without risk of significant adverse effects – and the NZ landfill screening criteria (black bars). Based on these values, zinc is the heavy metal of greatest concern, followed by copper and lead.

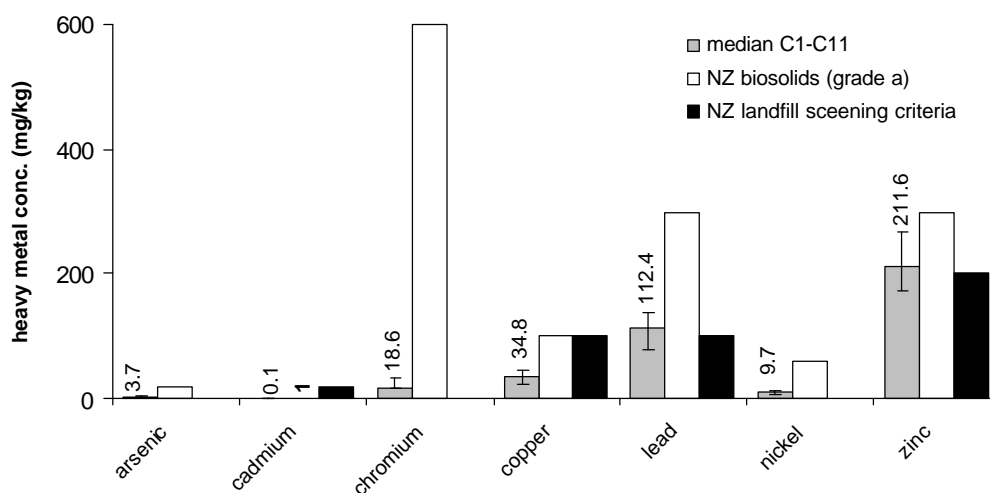


Figure 8: Median heavy metal concentrations in Christchurch RDS samples C1-C11 (grey bars) relative to maximum concentrations for i) NZ biosolids land application guidelines for grade 'a' material (white bars; NZWWA, 2003) and ii) NZ landfill screening criteria (black bars; MfE, 2004) – note the latter has no values for arsenic, chromium and nickel. Error bars represent lower and upper quartile concentration values.

The Minnesota Pollution Control Agency has defined dredged material 'soil reference values' (SRV) for determining suitability of various recovered sediments for reuse applications. As mentioned previously, sediments below Level 1 SRV values can be used on residential areas, and sediments below Level 2 SRV values can only be reused on properties with an industrial use category (Stollenwerk et al. 2009). Level 1 SRV values for copper and lead were similar to NZ biosolids values at 100 and 300 mg/kg, respectively; however, the SRV value for zinc was much greater at 8700 mg/kg. Level 2 SRV values were considerably higher, with maximum copper, lead and zinc concentrations of 9000, 700 and 75,000 mg/kg, respectively. Accordingly, the NZ biosolid limits ('a' grade) of 100 mg/kg for copper and 300 mg/kg for zinc and lead, are considered more relevant in assessing the suitability of RDS for reuse in NZ.

Although reuse options for RDS involve land application, it is still useful to consider NZ sediment quality guidelines, as there may be potential concern regarding the erosion and transfer of reused RDS to aquatic environments (i.e., incorporation into sediments). The ANZECC (2000) interim sediment quality guidelines (ISQG) contain respective 'low' and 'high' ISQG values of 200 and 410 mg/kg for zinc, 65 and 270 mg/kg for copper and 50 and 220 mg/kg for lead. It is emphasised, however, that inputs of reused RDS into aquatic environments are likely to be highly diluted when incorporated into sediments. Accordingly, soil and/or biosolid guidelines (for land application) are considered more relevant in the context of safely reusing RDS in NZ.

ZINC

The concentration of particulate zinc ranged from 136 to 1521 mg/kg, with a median and interquartile range of 212 mg/kg and 174-267 mg/kg, respectively. Using the 2012 NZ biosolids maximum zinc concentration of 300 mg/kg as a guiding value, then with the

exception of C5, a 50/50 blend of RDS with a clean material (e.g., compost or green waste prior to composting) would reduce RDS zinc concentrations to acceptable levels.

COPPER

Particulate copper concentrations in RDS had a median and interquartile range of 35 mg/kg and 24-46 mg/kg, respectively. Based on these concentrations, copper in Christchurch RDS does not exceed the guideline value for 'a' grade NZ biosolids (which can be applied to land without risk of significant adverse effects) without the need for dilution.

LEAD

Particulate lead concentrations in RDS had a median and interquartile range of 112 mg/kg and 77-138 mg/kg, respectively. The levels were comparable to street sweeping samples (n=16) from Auckland, Hamilton and Christchurch (Depree, 2008), which had a median and interquartile lead concentration of 117 mg/kg and 59-137 mg/kg, respectively. As with copper, the maximum concentration of lead (212 mg/kg) is well below the grade 'a' biosolids maximum value of 300 mg/kg, and as such, should not limit reuse application of RDS.

DISTRIBUTION OF HEAVY METALS BETWEEN PARTICLE SIZE FRACTIONS

There was a relative enrichment of heavy metal contaminants in the <1mm fraction – accounting for 32% of the particulate mass but 55-65% of the heavy metal load. Conversely, the coarse 5.6-9mm fraction was depleted in heavy metal contaminants – comprising 21% of the RDS particulate mass but only 3-5% of the zinc, copper and lead load (Figure 9).

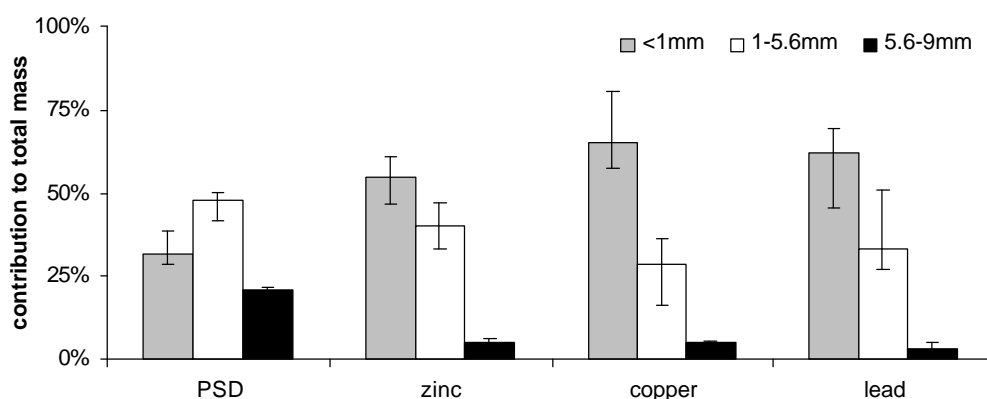


Figure 9: Particle size distribution of heavy metals in Christchurch RDS. Median values shown, error bars represent lower and upper quartile concentrations.

The concentrations of zinc, copper and lead in the 5.6-9mm fraction were, on average, 6 times lower for zinc, and 10-12 times lower for copper and lead, than the <1 mm fraction. The median particulate concentrations of zinc, copper and lead in the 5.6-9 mm fraction were 56, 7 and 16 mg/kg, respectively - compared to the <1mm fraction where the respective concentrations were 346, 74 and 188 mg/kg.

3.2 CONTAMINANT LEACHING FROM UNSTABILISED RDS

3.2.1 ACIDIC LEACHING CONDITIONS: TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

The TCLP method involves extracting the solid waste material with a buffered acidic solution (ca. pH 4-5) which mimics the leachate conditions in a landfill. While acidic conditions are not applicable to RDS reuse applications, such as general fill, compost and soil conditioners where rain water is the extraction medium, it was useful to determine acidic leaching for comparative purposes and also for determining compliance with at least NZ landfill guidelines before proceeding with alternative reuse applications.

The median leachate concentrations of zinc, copper and lead were 2.8, 0.08 and 0.10 mg/L (Figure 10), respectively, which were below the NZ landfill (class A) guidelines maxima of 5 mg/L (copper and lead) and 10 mg/L (zinc). The respective median (and interquartile range) leachate concentrations of zinc, copper and lead from that study (11 Christchurch RDS samples) were 4.7 (3.8-4.7) mg/L, 0.10 (0.06-0.15) mg/L and 0.17 (0.14-0.22) mg/L.

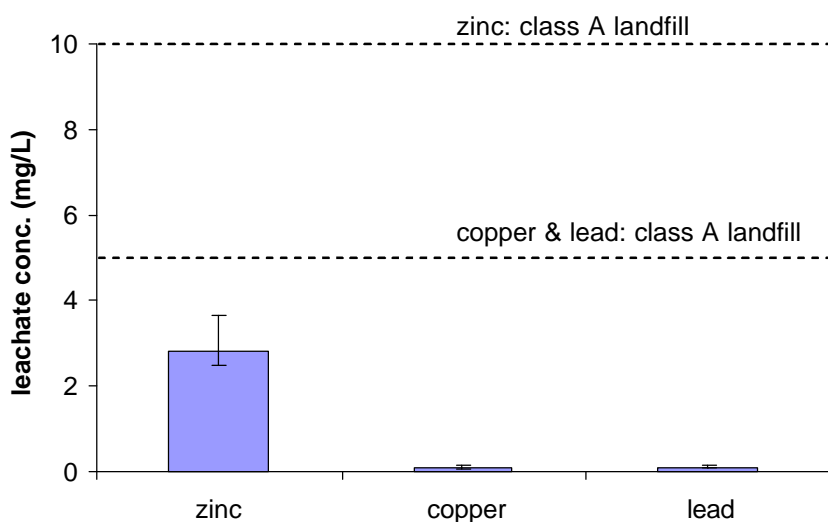


Figure 10: Median TCLP leachate concentrations of the heavy metals zinc, copper and lead. Error bars represent upper and lower quartile concentration values.

Under the TCLP acidic extraction conditions, zinc was the most mobile metal with ca. 17% of the total particulate zinc solubilised. In contrast, the amount of copper and lead solubilised was only ca. 4% and 2%, respectively, of the total particulate concentrations.

3.2.2 FRESH WATER LEACHING CONDITIONS: SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP)

As reuse applications for RDS generally involves placement of the material on or close to the soil surface. Rainwater (as opposed to acidic landfill leachates), either directly contacting the RDS or infiltrating down through the soil column, is the main mechanism

by which metal contaminants are mobilised. The US EPA developed the SPLP method to evaluate the potential for leaching metals into ground and surface waters. Modifications to the method used in this study included the use of de-ionised water as the extraction solvent and using a liquid to solid (L/S) ratio of 5 (cf. 20 of the SPLP method).

HEAVY METAL LEACHATE CONCENTRATIONS FROM UNSTABILISED RDS

The freshwater leachate concentrations for C1-C11 are provided in Table 3 – note that the units are µg/L, as opposed to mg/L that was used in section 3.2.1. The freshwater leaching experiments were carried out in duplicate and the reported concentrations represent the average leachate concentration.

Table 3: Heavy metal concentrations (µg/L) in freshwater leachates from Christchurch RDS samples C1-C11 (average concentrations from duplicate extractions).

RDS sample	Zinc (µg/L)	Copper (µg/L)	Lead (µg/L)
C1	185	35.5	9.4
C2	114	36	14.6
C3	120	29.5	13
C4	210	43	26
C5	420	109	42
C6	180	46.5	12
C7	335	54.5	34
C8	155	33.5	15.5
C9	103.5	29.5	6.8
C10	71.5	33.5	8.6
C11	165	92	11.5
Median (quartile range)	165 (117-198)	36 (34-51)	13 (10-21)
Mean (1 std dev)	187 (104)	49 (27)	18 (11)

The freshwater leachate concentrations of zinc were much lower than the TCLP concentrations (pH 4), reflecting the much lower solubility of zinc under the alkaline pH conditions (pH 8) of the freshwater extractions. The median leachate concentrations at pH 4 of 2800 µg/L decreased ca. 17-fold to 165 µg/L at pH 8 in freshwater. As such, for mobile, pH dependent metals like zinc, it is important that any reuse application prevents acidic leaching conditions from occurring.

The difference between acidic and freshwater leaching for lead and copper was less pronounced, which presumably reflects the ability of copper, and to a lesser extent lead, to form strong complexes with DOM. Numerous studies have reported that copper and lead form stable complexes with DOM resulting in a strong correlation between dissolved copper/lead and DOM concentrations in soil suspensions (Impellitteri et al. 2002; Jordan et al. 1997; Temminghoff et al. 1997; Yin et al. 2002).

3.2.3 POTENTIAL TOXICITY AND ENVIRONMENTAL CONCERN OF LEACHATES FROM UNSTABILISED RDS

By comparing the leachate concentrations of heavy metals with HC_{50} values (concentrations hazardous to 50% of aquatic organisms), it was apparent that copper and zinc are present at levels that may be toxic to some organisms (Figure 11). It is emphasised, however, that these heavy metal concentrations are from undiluted leachates, which in the real world would be subject to considerable dilution when discharged into receiving environments.

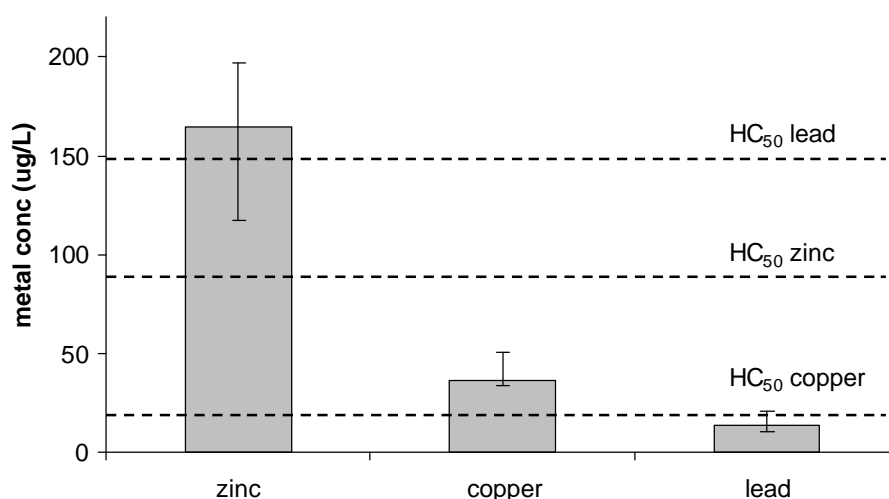


Figure 11: Comparison of undiluted metal leachate concentration compared to the 50% aquatic hazardous concentrations (HC_{50} values Verbruggen et al. 2001).

Toxicity studies using the leachates C1-C11 were undertaken using a freshwater algal (*P. subcapitata*) assay, which involved preparing a 50% dilution series, consisting of 10 concentrations ranging from 100% (i.e., full strength leachate) through to 0.2% (99.8% DI water) for each leachate. In general, when very dilute (i.e., <3%), the leachate solutions stimulate algal growth relative to control growth (Figure 12). At higher concentrations, algal growth declined and depending on the leachate, either decreased to a lower (i.e., C6) or higher (i.e., C4) level than growth in the respective controls. The various toxicological parameters from the algal toxicity assays are summarised in Table 4. At full strength (100%), five of the RDS leachates (C1, C3 and C9-C11) exhibited no toxicity (i.e., $LOEC > 100\%$). Based on Harrington-Hughes (2000) scheme, with the exception of C5, the Christchurch RDS samples were classified as having either a 'low' or 'moderate' potential for harm.

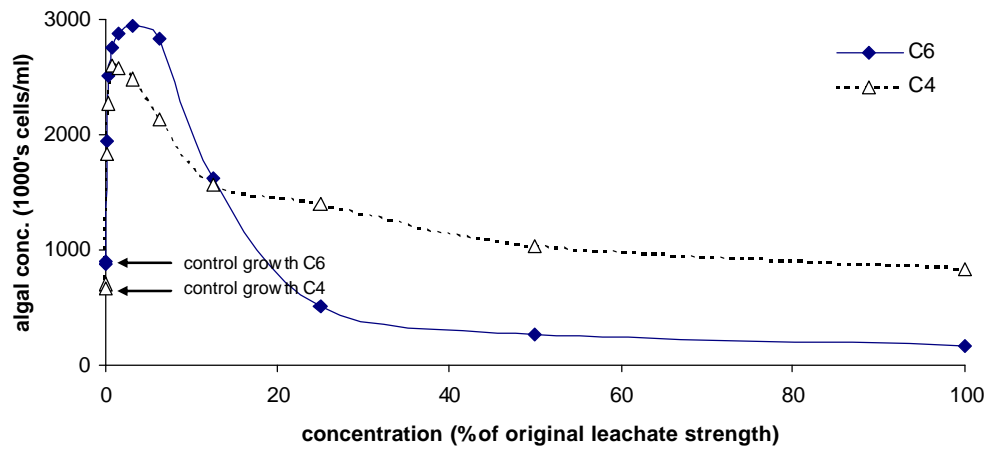


Figure 12: 'Dose-response' (fresh water alga, *P. subcapitata*) curves for RDS leachate solutions C4 and C6.

Table 4: Algal toxicity of freshwater RDS (C1-C11) leachate solutions.

RDS sample	EC ₅₀ (%) ^a	NOEC ^b (%)	LOEC ^c (%)	ChV ^d (%)
C1	>100	100	>100	
C2	>100	50	100	71
C3	82	25	50	35
C4	>100	100	>100	
C5	19	6.25	12.5	9
C6	31	12.5	25	18
C7	70	12.5	25	18
C8	>100	50	100	71
C9	>100	100	>100	
C10	>100	100	>100	
C11	>100	100	>100	

^a EC₅₀ (effective concentration, 50%) – the concentration (expressed as a percent of full-strength leachate) resulting in 50% algal growth inhibition compared to the control. The full-strength (or undiluted) leachate was assigned a concentration of 100%; ^b NOEC (no observed effect concentration); ^c LOEC (lowest observed effect concentration); ^d ChV (chronic value) – the geometric mean between NOEC and LOEC.

3.2.4 POTENTIAL TOXICITY OF RDS LEACHATES ENTERING AQUATIC RECEIVING ENVIRONMENTS

One of the main concerns about reusing mildly contaminated material such as biosolids and RDS is the potential for contaminants, especially heavy metals, to be mobilised and transferred into nearby receiving waters. Important considerations are therefore the dilution factor of the runoff/leachate when entering the receiving water body and relevant receiving water quality guidelines (WQG). ANZECC (2000) guidelines include target trigger values for 80, 90, 95 and 99% protection levels (Table 5). When assessing the potential for impacts of receiving waters it is normal to use a 95% protection level.

Table 5: ANZECC WQG freshwater trigger values ($\mu\text{g/L}$) for copper, lead and zinc.

metal	Level of protection (% of species)				Estimated receiving water conc. ($\mu\text{g/L}$) ^a from RDS leachate (10-fold dilution) ^b
	99%	95%	90%	80%	
copper	1.0	1.4	1.8	2.5	3.6 (3.4-5.1)
lead	1.0	3.4	5.6	9.4	1.3 (1.0-2.1)
zinc	2.4	8.0	15	31	17 (12-20)

^a median concentration (n=11) and lower and upper concentrations shown in parentheses. ^b conservative dilution factor of 10 has been used to estimate final receiving water concentrations (Holman, 1981) – however, with relatively low inputs of runoff potentially affected by the leaching of reused RDS, in reality the dilution factor of the original leachate concentrations would be much greater.

Based on a conservative receiving environment dilution factor of 10 (Holman 1981; ECETOC, 1994; EC, 1996) lead concentrations were below the 95% level of protection and zinc was below the 80% level of protection trigger value. The estimated receiving environment concentration of copper (3.6 $\mu\text{g/L}$) exceeded the 80% protection level trigger value of 2.5 $\mu\text{g/L}$; however, copper forms strong complexes with DOM that greatly reduces the amount of dissolved copper present as freely dissolved ions – the toxic form of dissolved metals.

In the absence of any reduced heavy metal bioavailability, Figure 13 shows that a dilution factor of ca. 35 is required to reduce the upper quartile concentration of leachate copper (51 $\mu\text{g/L}$) to a 95% level of species protection (1.4 $\mu\text{g/L}$). For zinc, a dilution factor of ca. 25 is required to reduce the original upper quartile leachate concentration (200 $\mu\text{g/L}$) to a 95% protection level in receiving waters (8.0 $\mu\text{g/L}$).

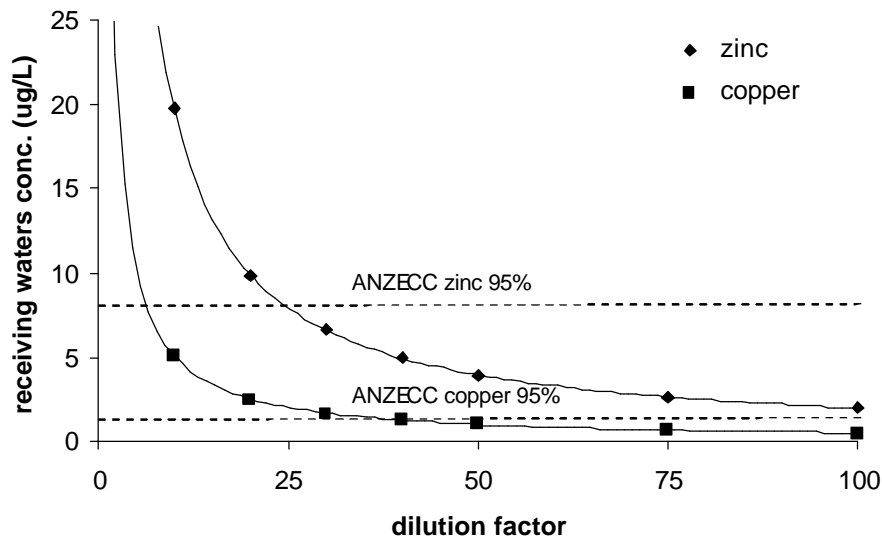


Figure 21: Theoretical receiving water concentrations of zinc and copper after dilution of the original RDS leachate (based on upper quartile concentrations).

3.3 STABILISATION OF RDS TO REDUCE CONTAMINANT MOBILITY

Whether making an assessment from the standpoint of particulate contaminants (e.g., comparing with biosolid guidelines) or mobilisation (and potential toxicity) of metals in leachates, it is apparent that there is the potential for adverse effects if reusing untreated or undiluted RDS (i.e., fill/compost etc.). While this risk could most likely be adequately managed by best management practices to control the conditions of use, it is more desirable to have a 'treatment train' that either stabilises and/or dilutes the contaminants in RDS sufficiently to enable safe and responsible reuse of the material.

The following are possible methods for reducing the potential environment risks of heavy metal contaminants in RDS (Depree, 2008):

1. **Physical entrapment:** involves locking up the metal contaminants by incorporating the RDS into a solid matrix such as concrete or asphalt.
2. **Dilution:** involves blending the RDS with clean material for the purpose of reducing particulate contaminant concentrations to a certain level (i.e., below a particular regulatory guideline value).
3. **Stabilisation:** involves adding chemicals/materials for the purpose of reducing the mobility of metals in RDS (via pH control, chemical modification and/or sorption). In contrast to 'dilution,' the focus is to reduce the concentration of leachate contaminants, even though the particulate concentrations may be comparable to unstabilised RDS.

The main focus of this section was to look at the effectiveness of different stabilisation treatments to reduce the mobility of zinc and copper. Lead concentrations were also analysed, but there was less focus on lead stabilisation since this it did not exceed the ANZECC 95% protection trigger value even when applying a conservative dilution factor of 10. Although there is some overlap between stabilisation and dilution, the relative importance of each depends on the final regulatory guidelines applied to RDS reuse. For example, if the guidelines stipulate maximum particulate concentrations of contaminants, then dilution will be more important. If, on the other hand, water quality standards are applied, then stabilisation methods can address contaminant solubilisation, irrespective of the actual particulate contaminant concentrations.

Stabilisation treatments included coal fly ash (alkalinity modifier), compost (humic-metal sorption), and phosphate (formation of insoluble metal phosphates). Of the 11 RDS samples, C5 and C11 were selected for the stabilisation trials, and to provide comparability with previous results (Depree, 2008), an archived sample of C2CP (refer to section 1.2.5) was used for selected stabilisation treatments. A more detailed account of the metal stabilising work, including boosted regression analyses on the data, has been published elsewhere (Rijkenberg and Depree, 2010).

3.3.1 STARTING POINT: PREVIOUS STABILISATION OF CHRISTCHURCH RDS SAMPLE (C2CP)

The previous study (Depree, 2008) trialled a limited number of treatments (phosphate and compost), on a catch pit sediment that yielded the most toxic leachate (L/S ratio of 20) – namely RDS sample C2CP. The limited number of amendments showed potentially promising results with 10- and 100-fold reductions in leached zinc concentrations and leachate toxicity (algal), respectively. However, Rijkenberg and Depree (2010) have reported that solution pH accounts for >90% of the leachate zinc concentration, suggesting the reductions reported by Depree (2008) may well reflect differences in leachate pH as opposed to phosphate or compost immobilisation mechanisms.

To determine whether similar stabilisation results could be achieved, archived samples of C2CP were mixed with different amending agents (0.1% phosphorus, 10% compost, and 10% compost + 10% fly ash) and extracted using an L/S ratio of 5. Leachate zinc and copper (and DOC) concentrations are summarised in Figures 14 and 15, respectively.

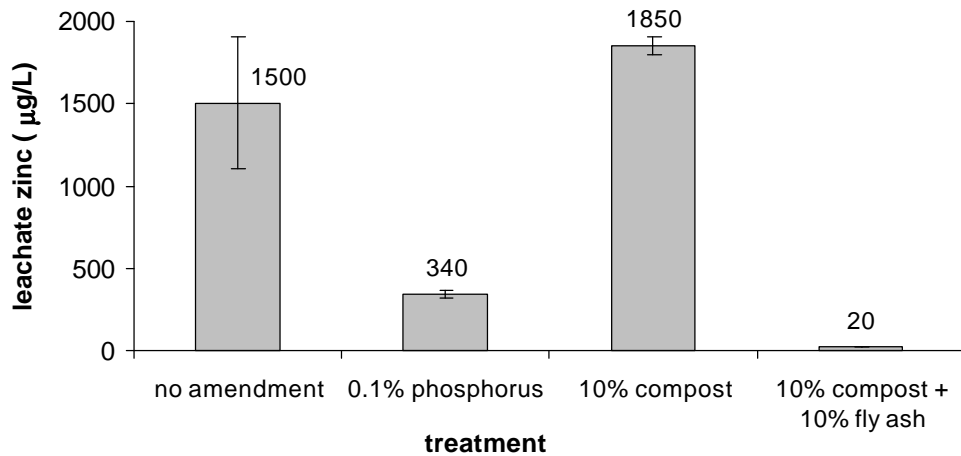


Figure 14: Effect of phosphate, compost and fly ash amendment on leachate zinc concentrations (µg/L) from Christchurch RDS sample C2CP (this study).

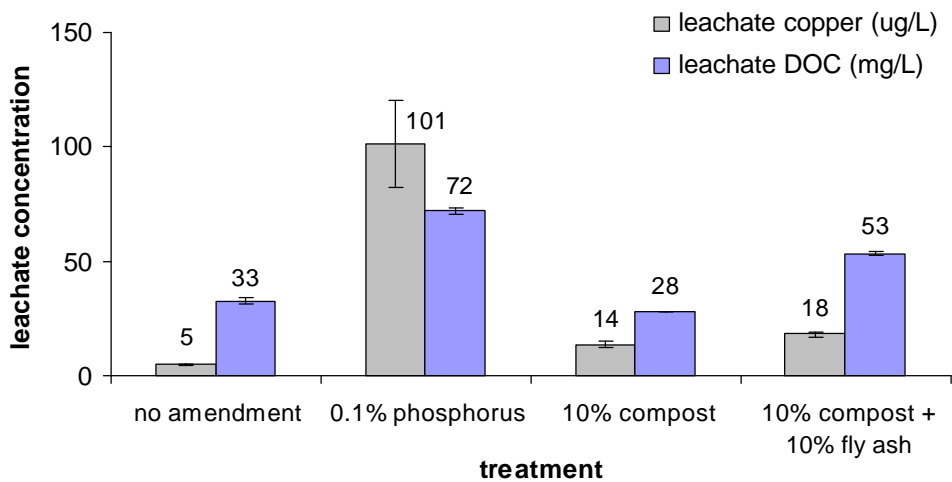


Figure 15: Effect of phosphate, compost and fly ash amendment on leachate copper (grey bars, µg/L) and DOC (blue bars, mg/L) concentrations from Christchurch RDS sample, C2CP (current study).

The most notable feature of the experiment was the complete lack of efficacy of compost to stabilise zinc leaching. In previous trials (Depree, 2008), this treatment reduced leachate zinc concentrations ca.10-fold (data not shown), however, in this study, the 10% compost treatment had no effect (Figure 14). In contrast, the 0.1% phosphorus (as phosphate) treatment yielded similar reductions in leachate zinc between the two sets of data for C2CP. The ineffectiveness of compost and phosphate to stabilised zinc in C5 and C11, (see results 3.3.2) strongly suggest that previously reported zinc stabilisation results using C2CP (Depree, 2008) were not the result of metal-OM binding or insoluble phosphate formation, but rather were attributable to differences in leachate pH. Although this raises questions as to the suitability of phosphate and compost as metal stabilising treatment options, it highlights the importance of controlling pH to suppress the leaching of zinc from RDS.

The combination of 10% compost + 10% fly ash (alkalinity modifier) reduced leachate zinc concentrations by ca. 99%; from 1500 (± 400) $\mu\text{g/L}$ in unstabilised C2CP to 20 (± 1) $\mu\text{g/L}$. The decreased solubility of zinc was on account of the leachate pH being raised from 6.7 to 8.2.

3.3.2 RDS SAMPLES C5 AND C11

Sample C2CP, a catchpit sediment, did not produce a lot of DOC under the freshwater extraction conditions – only 9 mg/L and 33 mg/L for L/S ratios of 20 and 5, respectively. DOC, along with pH, is an important parameter that controls the solubility, and hence mobility of heavy metals. DOC mobilisation is especially important for metals like copper that have a strong affinity for forming complexes with organic material (Impellitteri et al. 2002, Jordan et al. 1997, Temminghoff et al. 1997, Yin et al. 2002). Accordingly, RDS samples that generate higher levels of DOC may be more difficult to stabilise on account of over-riding DOC-metal solubilisation processes. To get a better understanding of how 'typical' Christchurch street sweepings respond to different stabilising treatments, C5 and C11 (325 and 115mg/L of DOC, respectively) were selected to further examine the efficacy of simple RDS stabilisation amendments.

3.3.3 'STABILISATION' BY PHOSPHATE AMENDMENT

Many studies have shown that phosphate amendment can be successfully used to stabilise heavy metals as lead and zinc in soils (Cotter-Howells and Caporn, 1996; Kumpiene et al. 2008). However, in the road sweeping samples C5 and C11, the leachate concentrations of copper, zinc and even lead all increased linearly with phosphate loading (Figure 16). The ineffectiveness of phosphate to immobilise zinc or lead was surprising, considering that 0.1% phosphorus (as phosphate) amendment of C2CP resulted in ca. 80% reduction in zinc solubilisation (Figure 14). The increase in metal concentrations was attributed to the phosphate-induced generation of DOC.

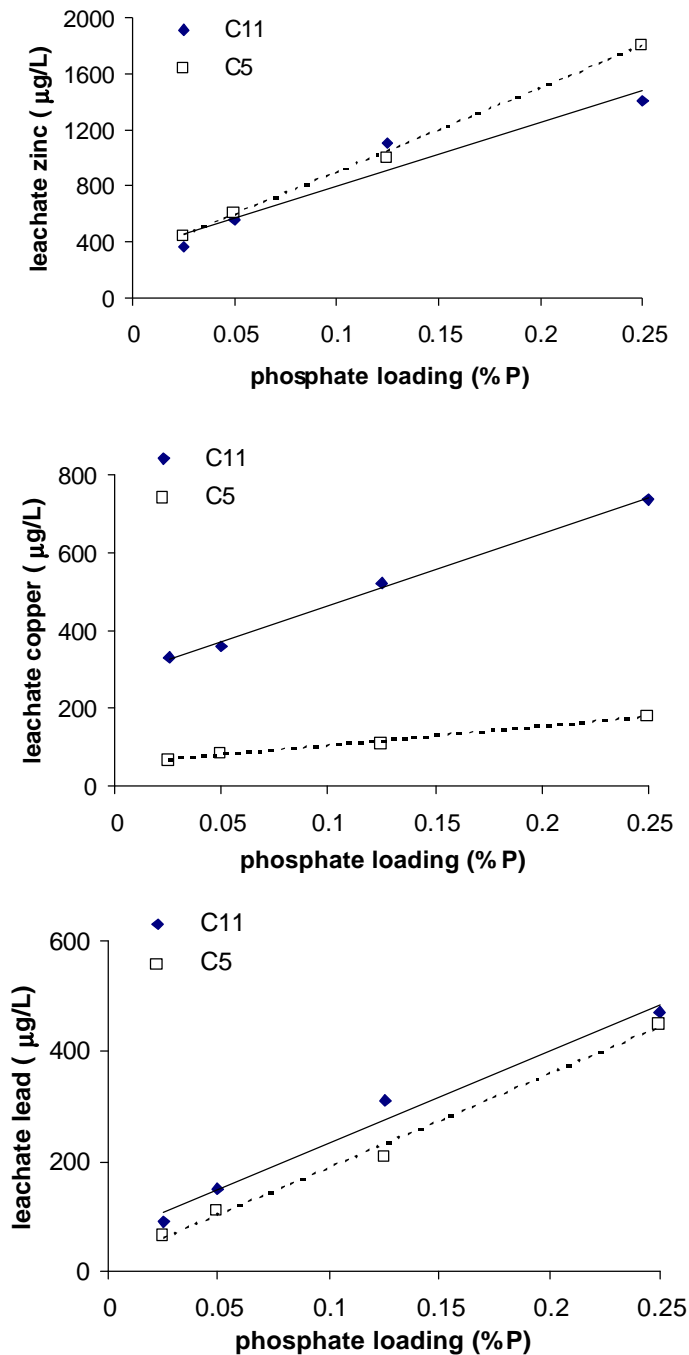


Figure 16: Effect of phosphate amendment on leachate concentrations of zinc (top), copper (middle) and lead (lower) from RDS samples C11 (w) and C5 (ú).

Overall, these results show that the successful use of phosphate amendment in heavy metal stabilisation depends on quantity and quality (i.e., fresh vs. humified) of OM present in RDS and the heavy metals that require stabilisation. In general, phosphate amendment will be unsuccessful in RDS that contain high amounts of fresh OM, as the release of high quantities of DOC will increase the mobilisation of heavy metals. Only when leached DOC concentrations are low, as for example with the C2CP sample (33 mg/L), metals may, depending on their affinity for DOC, be stabilised by a phosphate amendment.

3.3.4 STABILISATION BY COMPOST AMENDMENT

Consistent with C2CP compost stabilisation (Figure 14), the leached zinc concentration was not influenced by the addition of up to 30% compost (Figure 17). In C5 the zinc concentration in control (0% compost), 10% and 30% amended samples was 740, 670 and 750 $\mu\text{g/L}$, respectively. Likewise, for C11, the respective leachate zinc concentrations were 340, 330 and 430 $\mu\text{g/L}$ for 0, 10 and 30% compost amendments. Because it is unlikely that commercially composted materials would be significantly different (with respect to humified composition and hence metal binding), the ineffectiveness of compost to reduce zinc leaching in C5, C11 and C2CP indicates that i) previous conclusions (Depree, 2008) regarding compost stabilisation of zinc were incorrect, and ii) compost is not an effective amendment option for stabilising zinc in RDS. This is consistent with zinc being a relatively mobile metal that is easily out-competed by other cations (e.g., lead, copper) for adsorption sites (Cao et al. 2004).

With respect to the stabilisation of copper in the RDS samples C5 and C11, the inclusion of compost resulted in moderate decreases in leachate copper concentrations, with an optimal loading rate of between 10-20% (dry w/w). In C5, the leachate copper concentration decreased 45% from 92 $\mu\text{g/L}$ in the control (0% compost) to 51 $\mu\text{g/L}$ with 10% added compost. Increasing the compost loading did not improve copper immobilisation. For example, the concentration of copper was 60 $\mu\text{g/L}$ for the 30% compost amended sample. C11 was very similar with leachate copper decreasing 40% from 110 $\mu\text{g/L}$ in the control to 66 $\mu\text{g/L}$ with 15% added compost. The addition of 30% compost to C11 increased the leachate copper concentration slightly to 71 $\mu\text{g/L}$.

Similarly to what was observed for copper, compost amendment was also effective at reducing the leaching of lead from RDS sample C5. Relative to the 5% compost loading (control concentration value unreliable), increasing the loading to 30% decrease leachate lead 43%, from 160 $\mu\text{g/L}$ down to 91 $\mu\text{g/L}$. The addition of compost had no effect on the leachate lead concentrations of C11; however, the leachate concentration was relatively low in the non-amended RDS (ca. 20 $\mu\text{g/L}$).

Leachate copper and lead concentrations were reduced by ca. 40% when 10-20% of compost was added to RDS. Unfortunately, compost was ineffective at stabilising zinc, however, a combination of compost addition and pH control (via alkaline modifier) may be effective at reducing leachate concentrations of zinc, copper and lead.

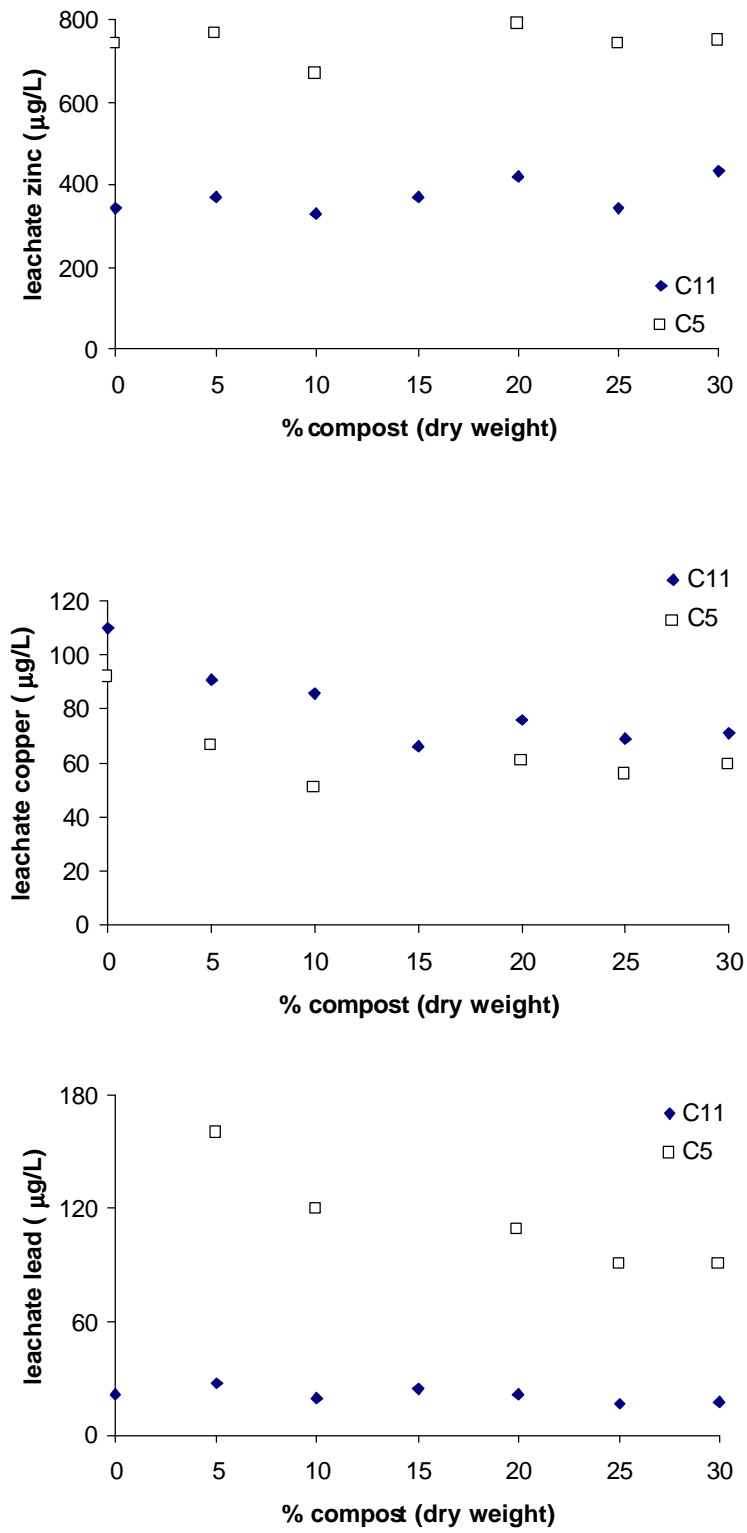
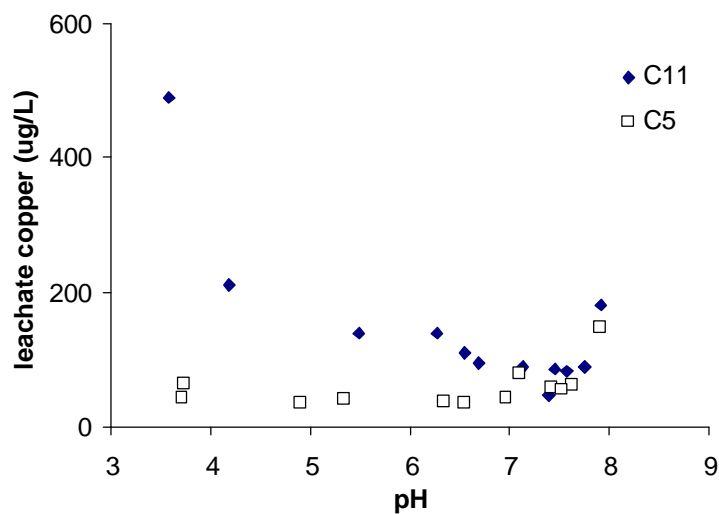


Figure 17: Effect of compost amendment on leachate concentrations of zinc (top), copper (middle) and lead (lower) from RDS samples C11 (w) and C5 (ú).

3.3.5 EFFECT OF PH ON SOLUBILISATION OF METALS FROM RDS

DOC and pH are the two most important factors determining the mobilisation of copper, lead and zinc from soils (Jordan et al. 1997; Sauve et al. 2000; Impellitteri et al. 2002; Linde et al. 2007). Although copper and lead are less impacted by pH changes than zinc, even relatively modest pH changes of between 6 and 8 cause the concentrations of copper and lead to vary by up to a factor of ca. 2 (Figure 18). This highlights the importance of maintaining constant pH when evaluating the stabilising efficacy of particular material. At leachate pH values <5 there was a large increase in heavy metal solubilisation from RDS C11.

Leachate pH had a more pronounced effect on zinc solubilisation from C5 and C11 (Figure 31). For example, leachate zinc concentrations from C11 at pH 7.9, 6.6, 5.5, 4.2 and 3.6 were 180, 1100, 6400, 12,000 and 24,000 µg/L, respectively. Although leachates of pH <5 are unlikely, Figure 19 (lower) shows the importance of maintaining leachate pH of 7-8. For C5, increasing the leachate pH from ca. 6.5 to 7.5 decreased the leachate zinc concentration 5-fold from 1100 to 210 µg/L. For C5 the decrease was less pronounced (2-fold, from 700 to 340 µg/L) presumably because of the competing influence from high DOC concentrations.



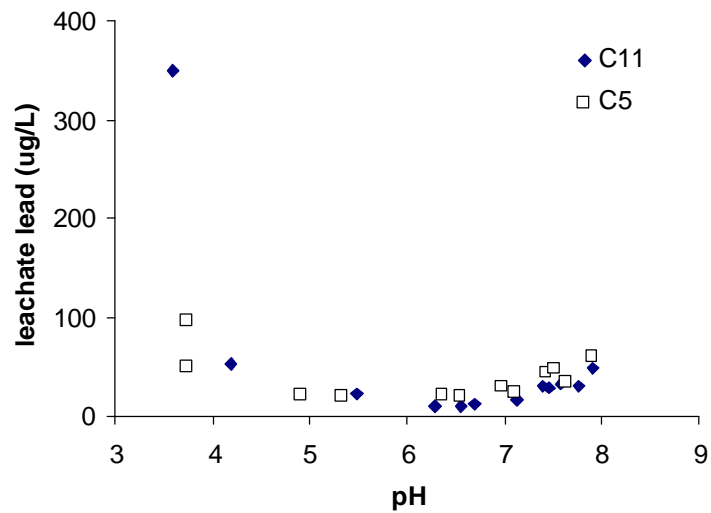
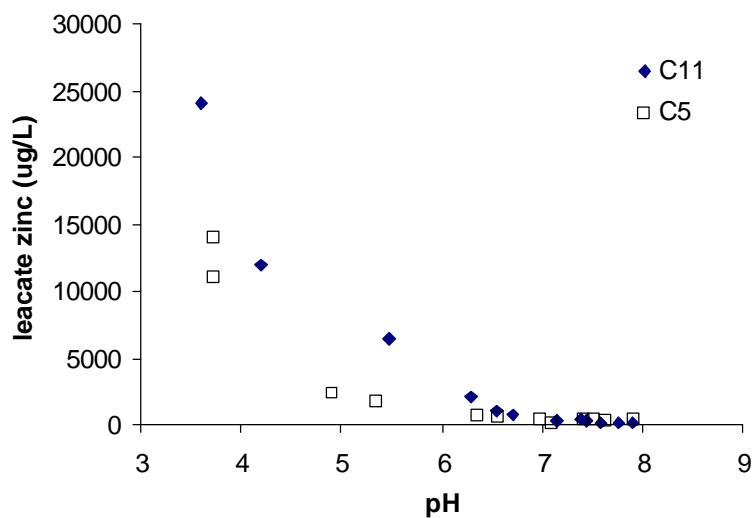


Figure 18: Effect of leachate pH on the solubility of copper and lead from RDS samples of C5 and C11 containing 15% compost (dry weight).

As a relatively abundant and mobile metal (Murakami et al. 2009), zinc is arguably the most problematic heavy metal limiting the reuse of RDS (with respect to both particulate and leachate concentrations), and therefore any stabilisation strategy should be effective against zinc. Phosphate and compost have previously been shown to reduce zinc leaching (Depree, 2008), however, these amendments were found to be ineffective in this study. Controlling leachate pH was the most effective way of reducing the solubility of zinc from RDS. For zinc the ideal pH was between 7 and 8, although with solubility increasing rapidly at pH values <7, a pH range of 7.5 to 8 is preferable. With respect to the other metals, C11 showed a copper leachate minimum at pH 7 to 7.5, with concentrations increasing at pH 8, while minimum leachate lead concentrations corresponded to pH of 6 to 6.5. While the concentration of lead is not a primary concern, copper is and therefore a pH of ca. 7.5 appears to be the optimum value for controlling both copper and zinc concentrations.



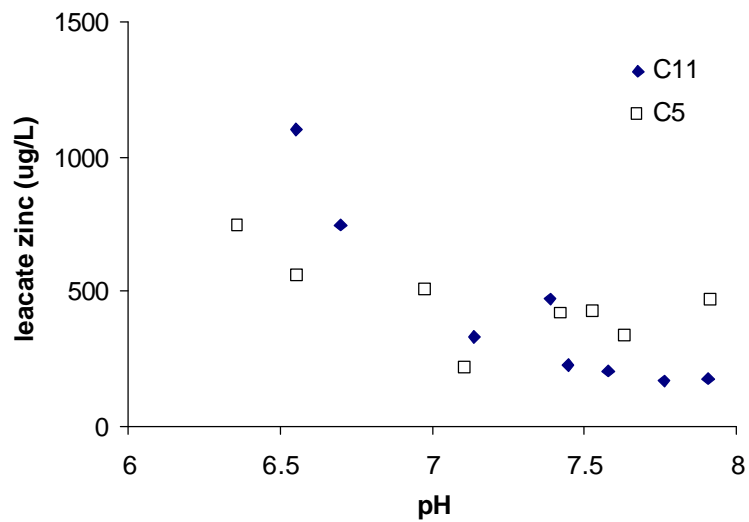
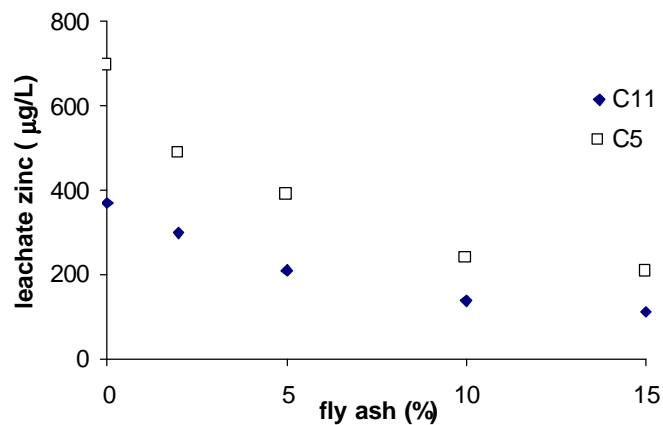


Figure 19: Effect of leachate pH on solubility of zinc from RDS samples C5 and C11 (lower plot shows detail in the 6-8 pH range).

3.3.6 STABILISATION USING ALKALINE MODIFIER (COAL FLY ASH)

Although limestone (CaCO_3) is the most commonly used alkaline material for increasing soil alkalinity, this study used coal fly ash, mainly because using a waste product was consistent with the whole concept of turning waste materials into usable materials. Therefore, in the absence of fly ash, limestone, calcium oxide or even wood ash (ca. 70% CaCO_3) can be used as an alkaline modifier.



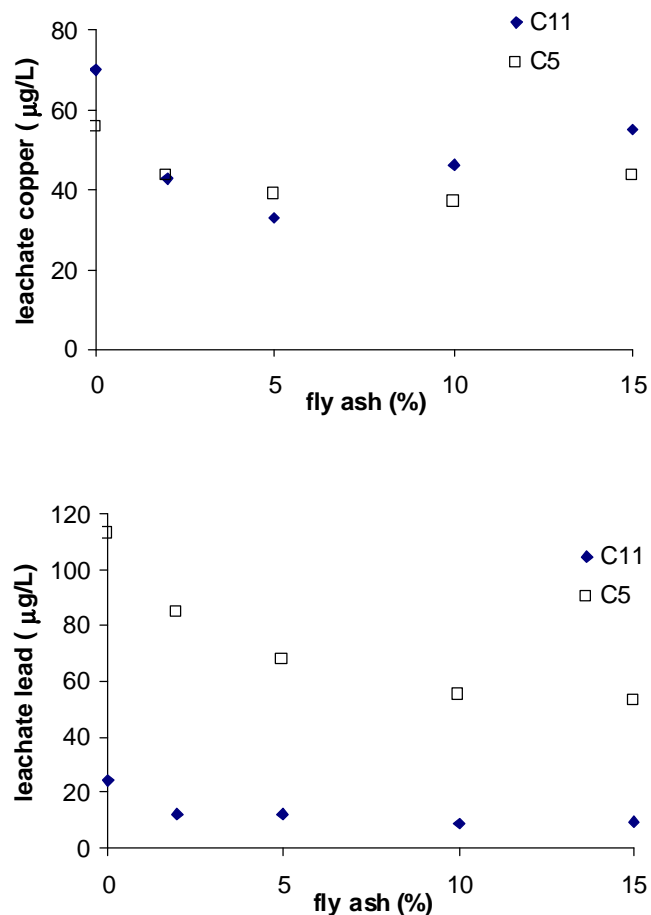


Figure 20: Effect of coal fly ash (alkaline modifier) on leachate zinc (top), copper (middle) and lead (bottom) concentrations from compost/RDS mixtures of C5 and C11. Control values (0% fly ash) were taken from the compost experiment (refer to Figure 29), which were run in a different experimental batch.

The addition of up to 15% fly ash to RDS mixed with 15% compost led to an increase in leachate pH of ca. 0.8 to 1 pH unit for both C5 and C11. The addition of 10% fly-ash to a mixture of C2CP with 10% compost increased the equilibrium pH from 6.5 to 8.2. The effect on heavy metal leachate concentrations of adding 2.5-15% fly ash to 10% compost mixtures of C5 and C11 are presented in Figure 20. The leachate zinc concentration decreased for fly ash loadings up to the maximum tested of 15%, which corresponded to a pH of 7.8 and 8.1 for C5 and C11, respectively. For C5 the reduction in leachate zinc for 10% (pH 7.8) and 15% (pH 8.1) fly ash amendments was 66 and 70%, respectively. Similarly, for C11 the concentration of leachate zinc for 10% (pH 7.6) and 15% (pH 7.8) fly ash amendments was 62% and 70%, respectively. In contrast leachate zinc was reduced 99% in C2CP with a 10% fly ash loading (refer to Figure 14). Presumably the higher efficacy is attributed to the much lower DOC concentrations, which otherwise facilitates the solubilisation of metals.

The copper leachate (Figure 20) concentration reached a minimum value with 5% fly ash for C11 (pH 7.5) and 10% for C5 (pH 7.6). At 10% loading, the level required to get better zinc stabilisation, the copper leachate concentration of C11 increased from 33 to

46 µg/L. With C2CP (refer to Figure 15), leachate copper increased slightly from 14 µg/L to 18 µg/L (10% fly ash). This increase was presumably on account of the DOC concentration increasing 2-fold (28 to 53 mg/L) under the alkaline conditions (pH 8.2).

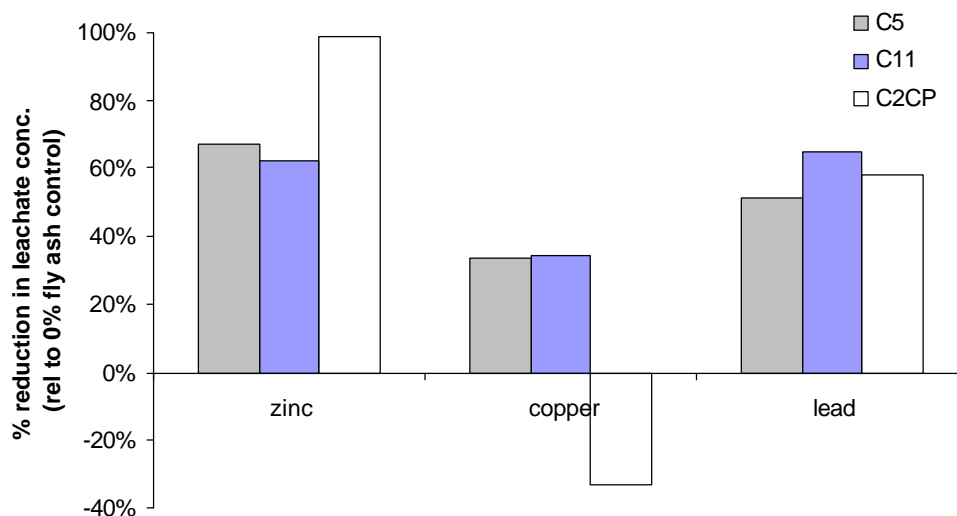


Figure 21: Effectiveness of adding 10% fly ash to reduce heavy metal leaching from different RDS/compost mixtures (% reduction relative to control mixture containing 0% fly ash).

The overall effectiveness of fly ash (10%) for stabilising heavy metals in RDS (relative to RDS/compost mixtures containing no fly ash) is summarised in Figure 21. Note that these estimates are relative to an RDS/compost mixture control and therefore do not include any beneficial effect from the compost, which was moderately effective at reducing copper, and to a lesser extent, lead. Accordingly, relative to unamended RDS (C5 and C11), the combined effectiveness of compost and fly ash at reducing leachate copper concentration was ca. 60%. Presumably the combined effectiveness for lead would be greater than that indicated in Figure 21, however, there was no reliable unamended control value for C5. Any practical application to stabilise zinc in RDS by changing alkalinity needs to be relatively long-lasting. Acidic soils amended with ca. 5% peat and 5% fly ash have been reported to maintain a neutral pH for at least 2 years (the duration of the study) during which time the average reduction in leached copper and lead was 98-99% (Kumpiene et al. 2007). Accordingly, there is considerable potential for the successful long-term stabilisation of zinc in RDS based on pH amendment.

3.4 STABILISATION VS DILUTION OF CONTAMINANTS IN RDS

Without any regulatory framework regarding RDS reuse in New Zealand it is unclear as to whether use should be based on particulate concentration maxima or mobility of contaminants and risk of exceeding relevant surface water quality guideline (WQG) values. If the former is applied, for example similar to the NZ biosolids guidelines, then dilution with clean material will almost certainly be required to reduce contaminants like

carcinogenic PAHs and, to a lesser extent, zinc and copper (refer to Table 12 and Figure 12, respectively). If the latter, then stabilisation and/or dilution could be used to ensure contaminant leaching, namely copper and zinc, does not exceed water quality guidelines (Table 16) – the difference being that particulate contaminant concentrations would be of little relevance.

Section 3.3 described a number of stabilisation trials, with phosphate, compost and alkaline modifiers. Based on the outcome of these trials, reductions in leachate concentrations of approximately 60-70%, 60% (C5 and C11 data) and 50% for zinc, copper and lead, respectively, should be attainable. Although higher removal efficiencies were observed for zinc in C2CP, this probably reflects lower leachate DOC concentrations (ca. 30 mg/L). By comparison, the average DOC concentration for the Christchurch street sweeping samples was 98 mg/L. Higher DOC concentrations facilitate the solubilisation of heavy metals, which lessens the effectiveness of stabilisation treatments.

In Section 3.2.4, it was concluded that using a conservative dilution factor of 10, the RDS copper and zinc leachate concentrations still exceeded the ANZECC WQG value at the 95% protection level. To determine whether stabilisation was effective enough on its own, the approximate 'stabilisation efficiencies' (i.e., percent reductions in leached metals) were used to calculate theoretical receiving water concentrations from stabilised RDS and then compared to the ANZECC 95% protection level WQG values (Table 6). Stabilisation was effective at reducing the receiving water concentration of zinc to just below the guideline value of 8.0 µg/L; however the concentration of copper remained a factor of ca. 1.5 higher than the guideline value of 1.4 µg/L. In this theoretical example, stabilisation reduced the required receiving environment dilution factor from ca. 25 to 9 for zinc, and from ca. 35 to 15 for copper (Figure 22). The concentration of lead from unstabilised RDS did not exceed the guideline value of 3.4 µg/L, although stabilisation resulted in a conservative concentration that was 3-times lower (1.1 µg/L).

Table 6: Theoretical receiving water concentrations of copper, zinc and lead from stabilised (alkaline modifier) RDS leachates (assuming 10-fold dilution, and upper quartile RDS concentration).

Metal	Approx. stabilisation effect (% reduction)	95% protection level WQG (ANZECC)	Estimated receiving water conc. from RDS leachate	
			unstabilised	stabilised
zinc	60-70	8.0	20	6-8
copper	60	1.4	5.1	2.1
lead	50	3.4	2.1	1.1

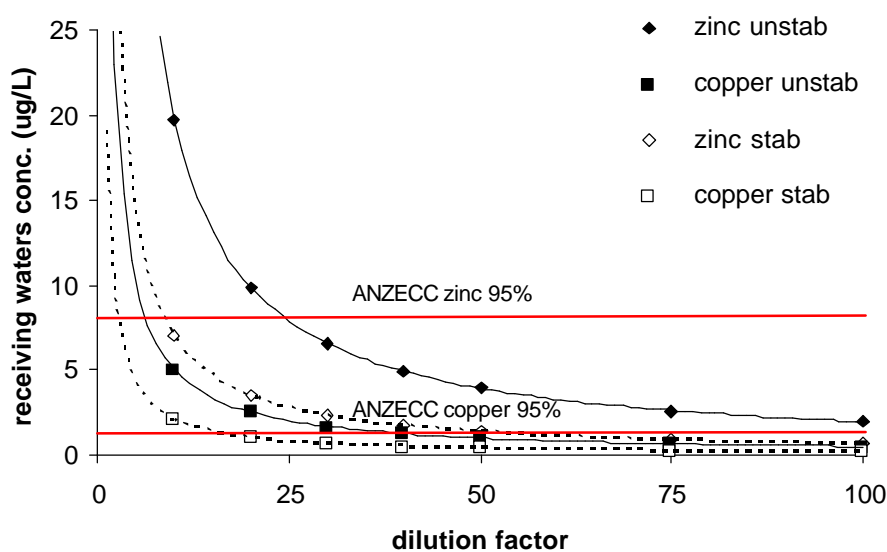


Figure 22: Comparison of stabilised and un-stabilised concentrations of zinc and copper in surface water based on different dilution factors of the RDS leachates (upper quartile concentrations used n=11).

Although the assumptions regarding mixing factors are overly conservative, based on the findings it is apparent that a combination of dilution and stabilisation is the best approach to ensure reuse of RDS represents no significant risks to the environment. Even if stabilisation treatments (i.e., phosphorus/compost/fly ash) were 99% effective at immobilising heavy metals, there is still the potential limitation that like with biosolids, reuse guidelines/consents may require compliance with particulate concentrations, in which case a 1:1 or possibly 2:1 dilution of RDS may be required to ensure compliance.

4 SUMMARY AND CONCLUSIONS

4.1 PHYSICAL CHARACTERISTICS

The particle size distribution of Christchurch RDS (n=11) corresponded to 94-97% of material passing through a 20mm screen. Thus assuming reuse of the RDS fraction <20mm, the amount of RDS landfilled could be reduced to <6% of the current total. Reducing the screen size from 20mm to 9mm (if required for removal of rubbish/sharps etc.), then the amount of material passing through the screen is reduced to 81-85% of the total RDS mass. The amount of particulate organic matter (OM) was approximately 6-14% (inter-quartile range).

4.2 PARTICULATE CONTAMINANT CONCENTRATIONS

Christchurch City RDS samples contained moderate concentrations of heavy metal contaminants. The upper quartile concentrations of the major heavy metals, zinc (267

mg/kg), copper (46 mg/kg) and lead (138 mg/kg) were lower than the contaminant New Zealand grade 'a' guidelines for biosolids that can be applied to land without risk of significant adverse effects. Grade 'a' biosolid limits for zinc, copper and lead are 300, 100 and 300 mg/kg, respectively. Christchurch RDS contained relatively high concentrations of PAHs with median and upper quartile concentrations of 5.6 and 16.3 mg/kg (n=11), respectively. The carcinogenic PAH benzo[a]pyrene (BaP) was potentially the most problematic with respect to reuse involving land-application. Although there are no readily available New Zealand guidelines, the upper quartile BaP concentration of 1.4 mg/kg exceeded the Canadian soil quality guideline value of 0.7 mg/kg two-fold. Based purely on particulate concentrations, at least a 1:1 or preferably a 2:1 (in case of BaP) dilution of RDS with clean materials would be prudent. This would ensure the concentration of organic and inorganic contaminants are well below any potentially relevant guideline and/or consent maxima. Although sediment quality guidelines are less relevant (than soil) for land application reuse option, the aforementioned dilution of the RDS would alleviate potential concerns of erosion and deposition of the material in aquatic environments. The ANZECC (2000) interim sediment quality guidelines (ISQG) specify 'low' trigger values for zinc, copper and lead of 200, 65 and 50 mg/kg, respectively. Accordingly, a 2:1 dilution reduces the upper quartiles concentrations in RDS below these 'low' risk trigger levels.

4.3 MOBILITY OF RDS OF CONTAMINANTS: METAL LEACHING

Leaching experiments were undertaken using a liquid-to-solid (L/S) ratio of five, yielding an upper quartile leaching concentration of zinc, copper and lead of 198, 51 and 21 µg/L, respectively. At 100% leachate strength (undiluted), only 4 of the 11 RDS samples exhibited toxicity to the fresh water alga *P. subcapitata*. In general, RDS leachates were classified as having either a 'low' or 'moderate' potential for harm (Harrington-Hughes, 2000).

Using a conservative 10-fold receiving environment dilution factor, theoretical surface water concentrations of RDS leachates were found to exceed the 95% protection level ANZECC WQG value for both copper and zinc, while lead was below the WQG value. Based on the upper quartile leachate concentrations of zinc and copper, a receiving environment dilution factor of approximately 25 and 35, respectively, would be required to ensure concentrations complied with ANZECC WQG maxima.

4.4 STABILISATION OF HEAVY METALS TO REDUCE LEACHING

Of the eleven RDS samples, C5 and C11 were selected for contaminant stabilisation experiments. Both samples contained DOC levels that were greater than the upper quartile concentration of 102 mg/L, which was considered an important parameter because DOC facilitates heavy metal solubilisation and therefore can negate some of the effectiveness of stabilisation treatments. Accordingly, the results with C5 and C11 most likely represent a conservative evaluation of stabilisation effectiveness, with better efficacy anticipated for lower DOC-yielding RDS. Additional information regarding the

metal stabilisation of Christchurch RDS samples is published elsewhere (Rijkenberg and Depree, 2010).

4.4.1 COMPOST

Compost used was ineffective at stabilising zinc RDS irrespective of the DOC concentration. For RDS that produced relatively high concentrations of leachate DOC (C5 and C11) the inclusion of compost had a negligible effect on DOC concentration and so the increased amount of metal binding particulate OM resulted in a net reduction in the concentration of copper by ca. 40%. Higher DOC concentrations in RDS leachates favour weaker binding between metals and the particulate material (weaker binding = more readily mobilised metals). As such, composting RDS (alone or as a component of a composting waste stream) should be advantageous since it should reduce the amount of DOC-generating, labile (i.e., fresh) OM.

4.4.2 PHOSPHATE

Phosphate amendment was only effective at stabilising zinc in C2CP (ca. 80% reduction in leached zinc), which contained a lower than average concentration of leachate DOC. For RDS samples with higher DOC concentrations (C5 and C11), increasing the phosphate amendment resulted in greater leachate concentrations of zinc, copper and lead. This destabilising effect of heavy metals was attributed to phosphate-induced production of DOC caused by anionic competition/displacement of OM from mineral surfaces (see also Rijkenberg and Depree (2010)). The tendency of phosphate to release relatively large amounts of DOC (and the associated increase in heavy metals) limits its potential as a stabilising amendment for RDS.

4.4.3 ALKALINITY MODIFIER (COAL FLY ASH)

Leachate pH is one of the most important factors determining the solubility of heavy metal contaminants. The concentration of zinc in RDS leachates decreased with increasing pH, with the reduction per pH unit being quite pronounced (i.e., 5-fold reduction in zinc on going from pH of 6.5 to 7.5). Although pH values higher than 8 would further reduce leachate zinc concentrations, highly alkaline amended RDS would be potentially harmful to animals and/or plants. In addition, higher pH values can produce DOC and, in turn, increase the solubilisation of heavy metals such as copper.

In order to use another waste material, coal fly ash was used to increase the pH of RDS/compost mixtures. As a rough guide, for every 5% coal fly ash (based on dry weight of RDS), the leachate pH increased ca. 0.3 pH units. A loading of 10% resulted in a leachate pH in the desired range of between 7.5 and 8. Increasing the loading to 15% fly ash improved zinc stabilisation, however, at the expense of increased copper solubilisation. For high DOC-yielding RDS (i.e., C5 and C11), the reduction in zinc, copper and lead were approximately 60-70, 60 and 50%, respectively. With low DOC-

yielding RDS, the alkaline stabilisation of zinc is potentially more effective, with 99% reduced zinc leaching observed for C2CP.

4.4.4 STABILISED LEACHING AND ANZECC GUIDELINES

Using a conservative 10-fold receiving environment dilution factor, theoretical surface water concentrations from stabilised RDS leachates (composts + alkaline modifier) for zinc would reduce from ca. 20 •g/L down to ca. 6-8 •g/L, which is comparable to the 95% WQG value of 8.0 •g/L. With respect to copper, stabilisation is estimated to reduce the receiving water concentration from 5.1 •g/L down to 2.1 •g/L, which is now only 1.5-times higher than the 95% WQG value of 1.4 •g/L. The dilution factor required to reduce the leachate copper concentration to below the 1.4 •g/L value decreased from ca. 35 for unstabilised RDS to ca. 15 in stabilised RDS (based on C5 and C11).

4.5 RECOMMENDATIONS

Despite RDS stabilisation treatments showing considerable merit, it is likely that any regulatory guidelines and/or consent conditions would most likely be based around particulate concentration (i.e., similar to NZ biosolids guidelines). If so, the main priority would be compliance with particulate concentrations, which would necessitate blending with other clean materials to dilute potentially problematic contaminants – such as zinc, copper and carcinogenic PAHs. Based on various guidelines (including soil quality), a 2:1 dilution (3-fold) of RDS would be required. Dilution of RDS is envisaged to proceed via one of two processes:

‘High dilution’: refers to the process of incorporating RDS into another processing stream (i.e., green waste composting) where RDS is only a very minor component (i.e., at least 10-fold dilution) in the final product. The high dilution would result in very low particulate concentrations of contaminants which are unlikely to have any potential for adverse environmental effects in reuse applications. Initial screening (refer to bullet point 1) below) of the RDS (prior to incorporation/dilution) and contaminant analysis of the final product are still recommended.

‘Low dilution’: refers to the process of where RDS is the primary waste stream and only the amount of diluting material required to meet guideline/consent conditions is added (e.g., 2-3 fold dilution). Although this report focuses on dilution with respect to reducing contaminant concentrations (both particulate and leachate), it may also relate to the addition of materials that improve the properties (i.e., drainage, organic matter etc.) of the final product. With respect to contaminants, general recommendations include:

- 1) RDS must first be screened to ensure adequate removal of rubbish – normal practice utilise 20-25 mm screens. This study never assessed the amount of rubbish that passed through the <20mm fraction. Accordingly, the required screen size should be determined to optimise the quality of the fraction of RDS

that is reused. Approximately 95% and 85% of RDS passed through 20 and 9mm sieves, respectively.

- 2) Compost has been shown to have a moderate stabilising effect (at least for copper and lead), and therefore using compost as a dilution material (as opposed to sand and/or soil) may have added benefits for immobilising/binding heavy metals. This does not preclude the addition of other materials to improve the 'fit for purpose' properties of the final RDS blend.
- 3) RDS contains a considerable amount of 'fresh' OM which tends to result in high concentrations of DOC. Accordingly, using RDS in a composting waste stream would be potentially better than simply blending the RDS with preformed compost. Other benefits of actually composting the RDS are the potential reduction (via 'cooking out') of organic contaminants such as TPH and PAHs.
- 4) The addition of an alkaline modifier (i.e., lime, wood ash, coal fly ash) should be considered to circumvent acidic (pH <7) leaching conditions (i.e., high metal solubilisation), which result in substantial higher heavy metal leaching. A fly-ash loading of 5-10% (based on dry weight of RDS) increased leachate pH to between 7.5 and 8.0, and was the only reliable method of reducing zinc mobility (by at least 60-70%).
- 5) Unlike 'high dilution' applications for RDS, 'low dilution' blends will still contain elevated levels of organic and inorganic contaminants, and therefore decisions (unless already defined by consent conditions etc.) need to be made regarding how the material will be used – that is, types of applications and restrictions on use. For example, NZ biosolids guidelines stipulate non-permitted applications for Grade 'Aa' biosolids. These include: i) within 20 m of any river, lake, wetland or artificial watercourse or the coastal marine area; ii) not onto land where there is a chance of the biosolids entering the water ; and iii) where there could be a discharge to any sensitive areas; including wahi tapu.
- 6) Contaminant testing should be undertaken on all RDS blended products – preferable before (i.e., screened RDS) and after blending/composting. In addition, it is emphasised that all contaminant mobility results, to date, have been based on short-term batch leaching (i.e., extraction) experiments. Column experiments or field lysimeters containing blended/stabilised RDS materials and receiving multiple cycles of simulated (or real) precipitation would give a much better understanding of contaminant mobilisation from RDS-based materials.

In summary, this research has identified the potential for Christchurch City Council to divert landfilled RDS by converting/incorporating it into useable products that, like high grade biosolids, can be applied to land without risk of significant adverse effects.

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