Contaminant characterisation and toxicity of road sweepings and catchpit sediments: Towards more sustainable reuse options

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Contaminant characterisation and toxicity of road sweepings and catchpit sediments: Towards more sustainable reuse options

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Executive summary

General remarks and the need for change

The main purpose of this research project was to characterise road-derived sediments, or RDS (road sweepings and catchpit sediments), in New Zealand, and based on the concentrations and toxicity of these contaminants, ascertain their suitability for reuse applications that have been implemented overseas. An important driver for reusing RDS is the rising costs of disposing of tens of thousands of tonnes of RDS in landfills. These economic pressures are highlighted by the current situation in Christchurch, where in the 12 months ending October 2007, ca. 7600 tonnes of RDS were landfilled at a cost of ca. \$1.5m. Increasing tipping charges at the nation's landfills will continue to put pressure on road maintenance budgets, with anecdotal evidence suggesting that roading managers may already be reducing sweeping maintenance in order to offset increasing costs. With up to four tonnes of RDS collected per km per year on the nation's roads, the long-term sustainability of landfilling all RDS in New Zealand is highly questionable.

Just as New Zealand has followed international trends in promoting the reuse of biosolids, it is timely for this country to look at the feasibility of implementing more sustainable approaches to managing the RDS waste stream. Through a change in thinking that views RDS as something of worth (ie a potential product) and not a waste product, cities in the United States (and Canada) have been successful in reducing the amount of RDS landfilled by 80–100%. The potential to reduce large amount of waste is consistent with the key aims of the *New Zealand waste strategy* (MfE 2002b).

RDS contaminant concentrations

The study analysed a total of 35 RDS samples collected from Auckland, Hamilton and Christchurch and represented streets carrying different volumes of traffic. The samples were analysed for TPH, PAH and heavy metals (lead, copper and zinc) and median, lower and upper quartile concentrations as shown in Table E1.

Table E1 Summary of contaminant concentrations (μg/g) in RDS.

Contaminant	Median	Lower quartile	Upper quartile
TPH	1220	935	1740
PAHs	6.3	3.2	11.2
lead	122	57	170
copper	67	41	119
zinc	422	303	555

There was very little difference between the contaminant loads in catchpit sediment and street sweepings, with zinc being the only significant difference – 336 μ g/g in sweepings vs 464 μ g/g in catchpit sediments. RDS from low trafficked streets (ie residential <500

vpd) contained two to three times less contaminants than RDS from higher trafficked streets (up to 10,000 vpd) and, therefore, may be more amenable for reuse applications.

Comparison of RDS contaminant levels with guideline criteria

The summary contaminant table clearly shows that RDS contain relatively high levels of contaminants, particularly heavy metals. Based on comparisons with a number of different environmental guidelines and contaminant criteria, it was concluded that the organic contaminants in RDS (ie total petroleum hydrocarbons and polycyclic aromatic hydrocarbons) do not represent a significant environmental risk. The focus was, therefore, switched exclusively to the three heavy metals – lead, copper and zinc.

Because reusing RDS involves placing contaminated material into some environmental compartment other than a Class A compliant landfill, it is necessary to have guidelines governing the safe reuse of such a material. It was concluded that the best starting point for the reuse of RDS in New Zealand was the *Guidelines for the application of biosolids to land in New Zealand* (NZWWA 2003). These guidelines specify maximum contaminant criteria for 'unrestricted use' biosolids (Grade 'a'), meaning they can be handled by the public and applied without consent without causing any adverse environment effects.

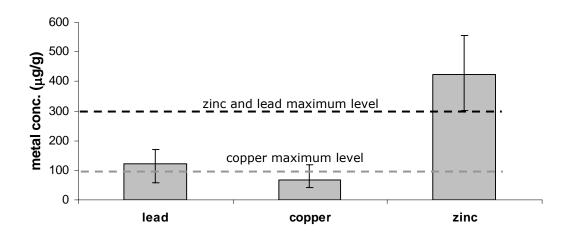


Figure E1 Median concentrations of heavy metals in RDS relative to maximum contaminant criteria of Grade 'a' biosolids ('error bars' represent upper and lower quartiles).

As can be seen in Figure E1, based on the biosolids guidelines, the most problematic contaminants that may limit the reuse of RDS are copper and, in particular, zinc. The concentration of lead in the RDS samples was well below the Grade 'a' limit of 300 μ g/g. All the contaminants were well below the Grade 'b' biosolids criteria of 300, 1250 and 1500 μ g/g for lead, copper and zinc respectively.

Reducing contaminant risks from reused RDS

Environmental concerns regarding the levels and mobility of zinc contaminants in RDS were confirmed in toxicity tests on the fresh water alga *Psuedokirchneriella subcapitata*.

Three of the eight RDS leachate samples tested were classified as toxic, with algal toxicity attributed to the concentration of the heavy metal zinc.

A toxicity threshold for RDS samples was estimated to occur at particulate zinc concentrations of ca. 550 μ g/g, which corresponded to the upper quartile concentration of the RDS samples (Figure E3). The estimated 'safe' concentration (ie no or minimal environmental effects) was estimated to be ca. 300 μ g/g of particulate zinc, which is consistent with the proposed 300 μ g/g limit for zinc in Grade 'a' biosolids (NZWWA 2003) Given that the lower quartile concentration of zinc in RDS was 303 μ g/g; approximately 75% of RDS samples in New Zealand may exceed the estimated 'safe' concentration.

Any RDS reuse options would, therefore, need to involve processes that mitigated the environmental risks posed by heavy metal contaminants, via one, or a combination of the following:

- 1. **Physically 'locking up' contaminated material**: Main applications involving using RDS as fine aggregate component in the manufacture of concrete and asphalt.
- Blending with clean materials: New Zealand biosolids guidelines permit blending
 with clean material to dilute contaminants and comply with guideline concentrations.
 Potential applications include using RDS as a component of compost, growing media
 or top soil.
- 3. Stabilisation (treatment) of metal contaminants: Adding materials for the specific purpose of immobilisation of metal contaminants, not simply diluting. Heavy metal immobilisation can be achieved by adding special metal binding phases (ie humic matter) or components that convert the metals to highly insoluble forms (ie phosphate materials).

Stabilisation trials showed that simply adding 10% compost to a toxic RDS sample (ie C2CP) reduced leachate zinc concentrations and toxicity by 14- and 220-fold, respectively. This simple compost stabilisation transformed one of the most toxic RDS samples into a non-toxic material that would presumably be suitable for most reuse options. Unless RDS is being used for the manufacture of asphalt or concrete, the reuse (including cleanfilling) of untreated and/or undiluted RDS is not recommended.

The future of reusing RDS in New Zealand is now dependent on the need or willingness of different groups of people to establish pilot studies and address aspects of RDS reuse that were beyond the scope of this report – such as costs and regulatory guidance.

Abstract

In 2006-07, 35 road-derived sediments (RDS) consisting of street sweepings and catchpit (ie sump) sediments, were collected from three cities in New Zealand; namely Auckland, Hamilton and Christchurch. The concentrations, mobility and toxicity of contaminants were determined in order to assess the suitability of RDS for certain reuse applications. The current situation in New Zealand is that all RDS must be disposed of in landfills. The RDS were analysed for total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs) and the heavy metals, lead, copper and zinc - with respective median (n=35) concentrations of 1220, 6.3, 122, 67, 422 μg/g. Comparisons with soil guideline values for ecological protection (Dutch and Canadian) and reuse of biosolids for land application (New Zealand), indicated that zinc will be the most problematic contaminant with respect to mitigating environmental risks in any reuse applications of RDS in New Zealand. Selected RDS freshwater leachates were toxic to the alga, Psuedokirchneriella subcapitata, at zinc concentrations of ca. 22-150 μg/L (EC₅₀), however, leachate toxicity was reduced up to 225-fold when amended, or 'stabilised' with 10% compost. Based on the results and potentially applicable guideline values, the reuse of RDS may be limited to applications that either physically (ie incorporation into concrete or asphalt) or chemically (ie addition of a 'stabilising' agents like compost or phosphate) immobilise problematic heavy metal contaminants, namely zinc.

1. Introduction

1.1 Background

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.

With the requirement to manage stormwater quality, sediment retention devices such as retention/detention ponds, infiltration trenches and swales are becoming increasingly promoted as solutions to address stormwater quality concerns (Auckland Regional Council 2003). In order for these STWDs to perform effectively, routine maintenance to remove accumulated sediment must be undertaken. Street sweeping is often largely done for reasons of aesthetics and for preventing the blockage of drains (ie from autumn leaves). However, with improvements in the efficiency of vacuum and regenerative sweeper truck technology to pick up fine particulate matter, sweeping is increasingly being seen as a way to reduce the amount of contaminants in stormwater. This is of particular relevance in catchments where it is not practical (or even possible) to retrofit conventional STWDs to reduce particulate contaminant loads in road runoff.

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 equates 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. Presumably the national tonnage of RDS disposed would exceed that of the 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. It is certainly already a major issue for Christchurch City Council where the landfilling charge for RDS is almost \$200 per tonne (S. McNeill pers. comm. 2007). Selected examples highlighting the increase in landfilling charges include: Masterton's Nursey Rd landfill site – charges have increased 58% from \$44 per tonne in 2004 to \$70 per tonne in 2005 (Masterton District Council 2005); Wellington landfill – disposal costs have increased 54–84% over a four-year period with charges increasing from \$43 (Northern landfill) and \$51 (Southern landfill) in 2002 to \$78 per tonne in 2006 (only

Southern landfill operating) – note that the 2006 tonnage charges actually peaked at \$101 in 2005; and Hastings landfill (Omaranui) –costs have increased 64% over a four-year period from \$44 per tonne in 2003 to \$72 per tonne in 2007.

Increasing landfill/waste station charges have resulted in the RDS disposal component accounting for up to 60–70% of the total cost of street sweeping contracts (B. Williamson pers. comm. 2007). One North Island sweeping contractor indicated that increasing disposal costs of RDS are already having a negative impact on the ability of some roading managers to maintain regular sweeping regimes – with increasing costs having to be offset with reduced sweeping frequency and/or coverage. Clearly any reduction in roadside maintenance is not desirable and, therefore, raises questions regarding the long-term economic sustainability of the current requirement of landfilling all RDS in New Zealand.

To further advance the transport sector's goals of sustainability and responsiveness to national waste management strategies, alternative uses for RDS in New Zealand need to be explored. As with all other waste streams, before road-derived waste is disposed of, careful consideration needs to be given to minimising the waste stream in accordance with the New Zealand waste management hierarchy. The hierarchy, in decreasing preference, is:

- reduction
- reuse
- recycling or materials recovery
- disposal.

With respect to road sweepings and sediment, reduction is not relevant; however, there has been very little emphasis (if any) in New Zealand on reuse or recycling (materials recovery) applications for road sweepings and sediment.

Many United States cities 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%. The various options for reusing, recycling and treating RDS are discussed in Section 1.3.

Despite the considerable amount of work dedicated to minimising the waste stream of RDS in North America, no such research has been undertaken in New Zealand.

Accordingly the main aim of this Land Transport New Zealand project was to undertake a preliminary investigation to determine the possible feasibility of reusing RDS in New Zealand. This was achieved by characterising contaminant concentrations, mobility

and even toxicity in representative samples of RDS and comparing these results with relevant national and international guideline values. Treatment options to stabilise contaminants and mitigate environmental concerns of contaminant migration were also undertaken.

1.2 Project objectives and report layout

The project was carried out between July 2006 and June 2007 and comprised the following seven objectives. To aid navigation the sections in the report corresponding to each of the objectives have been included.

- 1. Literature review: Summarise relevant literature on RDS contaminant levels, reusing and/or recycling of RDS; and also summarise potentially relevant national and international guidelines to provide a global context for the New Zealand research.
- \Rightarrow Section 1.3 Literature review typical RDS contaminant concentrations and reuse applications
- 2. Characterisation of New Zealand RDS: Collect and analyse representative RDS samples (from Auckland, Hamilton and Christchurch) for particle size distribution, organic matter, total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), and the heavy metals lead, copper and zinc. Comparison will determine whether there are significant differences in contaminant concentrations between cities, RDS type (ie sweepings vs catchpit) and daily traffic volumes.
- ⇒ Section 3.1 Characterisation I: Physical properties
- ⇒ Section 3.2 Characterisation II: Chemical contaminants
- 3. Comparison with guideline values ('1st tier' risk assessment): Using contaminant concentrations determined in Objective 2, assess the potential for reusing New Zealand RDS by comparison with relevant national and international guidelines. Potentially relevant guidelines include: ecological protection and human health guidelines for soil and sediment (New Zealand, Canadian and Dutch), New Zealand landfill guidelines, New Zealand biosolids guidelines and threshold concentrations from contaminated land cleanup guidelines.
- \Rightarrow Section 3.3 RDS risk assessment I: Comparison with guideline values

Objectives 4. 5 and 6 represent a '2nd tier' risk assessment.

- **4. Determination of RDS contaminant mobility:** Evaluate the risk of contaminant migration from RDS, by conducting leaching studies under both landfill conditions (ie acidic leaching via US EPA TCLP method) and fresh water leaching –the latter simulating contaminant leaching by rainwater (ie runoff/infiltration), which is more relevant for applications where RDS is reused as soil amendment, fill or compost.
- \Rightarrow Section 3.4 RDS risk assessment II: Freshwater leaching, toxicity and amendment studies
- \Rightarrow Section 3.4.1 Freshwater leaching of metals from RDS

- **5. Determination of the toxicity of selected RDS samples:** Evaluate the toxicity of freshwater leachates from selected RDS samples using the freshwater alga, *Pseudokirchneriella subcapitata*.
- ⇒ Section 3.4.2 Algal toxicity of freshwater leachates
- **6. Stabilisation of heavy metal contaminants in RDS:** Evaluate alternative treatment or stabilisation methods to immobilise RDS contaminants in order to reduce the environmental risk of contaminants being leached from reused RDS.
- ⇒ Section 3.4.3 Reducing metal leaching from RDS
- 7. Conclusions regarding the potential for reusing RDS in New Zealand: Using data from Objectives 1–6, recommend possible RDS reuse applications that respond to the requirements of economical feasibility and environmental protection, and also identify additional work that is regarded to advance such options in New Zealand.
- ⇒ Section 4 What it means for reusing RDS in New Zealand

1.3 Literature review – typical RDS contaminant concentrations and reuse applications

There are a number of aspects that need to be considered in order to ascertain which of the various reuse options for RDS are potentially suitable for New Zealand conditions. RDS is known to be contaminated with heavy metals and petroleum hydrocarbons, although virtually all studies have shown that the levels are below hazardous waste thresholds (Collins and Moore 2000). However, a cautious approach still needs to be taken. Even if RDS is not classified as a hazardous waste, this does not imply that it is free from environmentally harmful contaminants. This was aptly stated by Collins and Moore (Collins and Moore 2000) by the following comment, 'it may not glow in the dark, but that does not mean it's benign'.

When considering reuse options for RDS, contaminant levels must be considered to ensure the final end-use does not compromise the health of the public or the environment. With respect to implementing wide-scale reuse of RDS, key components include the:

- determination of contaminant concentrations in RDS
- identification of potential reuse applications
- understanding exposure/transport risks of RDS contaminants in reuse applications
- existence of specific guidelines governing the safe reuse of RDS.

Literature relating to these four key components is reviewed and discussed in the following sections.

1.3.1 Typical contaminant levels

A starting point for any discussion regarding the potential reuse of RDS is determining the concentration of contaminants routinely present in these materials. To facilitate comparisons with RDS contaminant concentrations determined as part of this study and to provide a broader international context, the concentrations of important contaminants has been reviewed and summarised in Sections 1.3.1.1 (organic contaminants) and 1.3.1.2 (heavy metal contaminants).

1.3.1.1 Organic contaminants – petroleum hydrocarbons (TPH and PAHs)

The main organic contaminants of interest in RDS are petroleum hydrocarbons. The total amount of petroleum hydrocarbons is referred to as TPH (total petroleum hydrocarbons) and includes all petroleum-derived compound types including, aromatic, polycyclic aromatic and aliphatic hydrocarbon compounds (which includes straight chain, branched and cyclic hydrocarbons). An important subset of compounds included in the 'TPH concentration' are PAHs (polycyclic aromatic hydrocarbons), which are environmentally persistent and potentially toxic contaminants listed as 'priority contaminants' by the United States Environmental Protection Agency (EPA). In this report, the term organic contaminants refer to petroleum hydrocarbons (ie TPH) and, in particular, the sub-group of hydrocarbons called PAHs.

While there is a large amount of literature on hydrocarbon concentrations in soils and receiving environment sediments, studies focusing specifically on RDS are relatively scarce. Many of the studies on urban runoff contaminants involve determining pollutant concentrations per litre of stormwater, rather than determining the contaminant concentration of the actual particulate phase. Selected studies that have analysed TPH and/or PAH concentrations in RDS (including 'street dust') are summarised in Table 1.1.

TPH concentrations

The concentration of TPH is reasonably constant (ie within a factor of 10) ranging from a few hundred to a few thousand micrograms per gram (Table 1.1). Based on the very limited number of studies, it is estimated that the median concentration of TPH in RDS is in the range $1000-2000~\mu g/g$. The concentration of TPH appears to be dependent on both traffic volume and catchment usage – with high volumes and industrial catchments resulting in the highest concentrations. For example, Latimer et al. (1990) reported TPH concentrations of 353, 1680 and 3490 $\mu g/g$ for road dust from residential, highway and industrial sites, respectively.

PAH concentrations

As can be seen from the values in Table 1.1 the concentration of PAHs in RDS varies considerably (ie 2–300 μ g/g), although most studies report median concentrations of between 5–8 μ g/g. Interestingly, the concentration of PAHs does not appear to be related to traffic volume, based on the observation that RDS from Tokyo roads with 100,000 vehicles per day (vpd) contained only 4 μ g/g of PAHs (Takada et al. 1991), whereas RDS from residential areas in Worcester, Massachusetts, with 9000 vpd contained 325 μ g/g of PAH (Mathisen et al. 1999). Assuming similar vehicle emissions in the two studies, it is

apparent that traffic was not the key contributor of PAHs to the Worcester road sediment sample. If not traffic, then what is the source of this variation in the concentration of PAHs in RDS?

Table 1.1 Hydrocarbon (TPH and PAH) concentrations in RDS (ie road sweepings, street dust and catchpit sediment).

TPH	PAH ^a	Comment	Reference	
(µg/g)	(µg/g)			
Street dust/	sweepings	,		
-	4.40	Dunedin (New Zealand)	Brown and Peake 2006	
(112-505)	30	Mixed land use type	Mathisen et al. 1999	
1054	7.7	Interstate/state highways	Hindin 1993	
	3.4	Road dust (>10,000 vpd)	Takada et al. 1991	
	16.7	Expressway: inside tunnel	Takada et al. 1991	
	3.4	Expressway: outside tunnel	Takada et al. 1991	
353		Residential	Latimer et al. 1990	
3490		Industrial	Latimer et al. 1990	
1680		Highway	Latimer et al. 1990	
	7.5	Street dust	Yang and Baumann 1995	
	(1.7-216)			
Catchpit sec	liments			
	3.8	Residential (500 vpd)	Karlsson and Viklander 2008	
	17	Arterial (25,500 vpd)	Karlsson and Viklander2008	
1788	_	Interstate/state highways	Hindin 1993	
-	6.53	Dunedin (New Zealand)	Brown and Peake 2006	
1620	7.1	Mixed land use type	Mathisen et al. 1999	
	(0-325)			

^a median or mean PAH concentration (concentration range in parentheses)

Possible reason for the large variation in PAHs - coal tar

As road abrasion is a contributor to PAHs in RDS, the type of binder and quantity of PAHs associated with the different binder can have a substantial effect of the amount of PAHs present in RDS. While bitumen is almost exclusively used in modern road construction, coal tar binders have also been widely used. Unlike bitumen that contains 20– $30~\mu g/g$ of total PAHs, coal tar binders typically contain in excess of $100,000~\mu g/g$ (>10%) of PAHs. Studies have shown that runoff particulates from coal tar surfaces can contain ca. 100 times more PAHs than those from a conventional bituminous surface (Mahler et al. 2005). This is the most likely explanation for the high concentrations of up to $325~\mu g/g$ of PAHs reported by Mathisen et al (1999) in the City of Worcester. In the United States, coal tar is still commonly used (millions of gallons annually in the State of Texas alone) for seal coats on asphalt car parking lots and driveways.

NIWA research has also shown the importance of coal tar as the major source of PAHs in runoff particulates in New Zealand, with PAH concentrations of $>200~\mu g/g$ for RDS

collected from older residential suburbs in Christchurch (Depree and Olsen 2005). In contrast, RDS from much more heavily trafficked road ways (eg SH1 and SH16) have been shown to contain much lower PAH concentrations of $3-5~\mu g/g$. This range is consistent with the $4.4~\mu g/g$ reported for street sweepings collected from Dunedin (Brown and Peake 2006) and, therefore, in the absence of coal-tar inputs, the concentrations of PAHs in RDS are expected to be ca. $5~\mu g/g$.

The reason for discussing the issue of coal tar is to bring attention to the fact that very high levels of PAHs in RDS are not typical of modern roads constructed from bitumen and, therefore, the observation of very high levels are indicative of coal tar type inputs. In Christchurch, even though the wearing course consists of a bitumen chip seal layer, coal tar contamination of road side soil (ie shoulders) provides a reservoir of contaminated material that still contributes to elevated PAHs concentrations in RDS (Depree et al. 2006). While a detailed discussion of coal tar contamination is beyond the scope of this research project, further details on coal tar in New Zealand's urban environment are covered elsewhere (Depree et al. 2006; Depree and Ahrens 2005, 2007; Ahrens and Depree 2006; Mahler et al. 2005).

All RDS samples collected for this current study were taken from streets where coal tar contaminants were not regarded as an issue and are, therefore, considered to be representative of RDS collected and disposed of in New Zealand.

Do catchpit sediments contain more hydrocarbons than street sweepings?

A commonly held perception is that catchpit sediments are significantly more polluted than road sweepings. This is supported by results from Mathisen et al. (1999) where TPH concentrations in sweepings ranged from 112–505 μ g/g, and the median concentration in catchpit sediments was 1620 μ g/g (Table 1.1). Furthermore, Hindin (1993) reported mean TPH concentrations in street sweepings and catchpit sediments of 1054 μ g/g and 1788 μ g/g, respectively.

However, an important consideration that is often overlooked when comparing contaminant concentrations in street sweepings and catchpit sediments is the efficiency of the sweeper truck to remove fine particle fractions of RDS. This is very important because contaminants are often enriched in the fine particle size fractions, hence low-efficiency sweepers will pick up only a small fraction of this contaminated material, leaving the majority behind to wash into catchpits – resulting in the relative depletion and enrichment of contaminants in sweeping and catchpit sediments, respectively. Examples of low-efficiency sweepers include mechanical sweeper trucks and high-efficiency sweepers include vacuum or regenerative air sweeper trucks.

The United States Geological Survey has conducted efficiency trials using both mechanical and vacuum sweeper trucks (Breault et al. 2005). For collecting particles less than 250 μ m, the efficiency of the mechanical sweeper was 10–13%, whereas the efficiency range of the vacuum sweeper truck was 75–93%. Therefore, a high-efficiency sweeper removes ca. 90% of the fines, resulting in similar particle size distributions, and hence similar

contaminant concentrations in street sweeping and catchpit sediments. In contrast, low-efficiency sweepers leave behind ca. 90% of the fines, which are ultimately incorporated and concentrated in catchpit sediments. The result is coarse particle size enrichment in street sweepings and fine particle size enrichment in catchpit sediments (or retention pond sediment). This is supported by Liebens (2001) who reported that the percentage of sand-sized particulates in street sweepings and retention pond sediments was 95% and 65%, respectively.

All street sweeping samples in this current study were collected using high-efficiency vacuum- or regenerative air-type street sweeping trucks (not mechanical sweepers). As such, any substantial differences in particle size distribution and contaminant concentrations between catchpit sediments and street sweepings were not anticipated.

1.3.1.2 Heavy metals - lead, copper and zinc

There is a considerable amount of literature devoted to heavy metal contaminants in RDS. Most studies include a large suite of heavy metals; however, for this study, analyses were limited to the three heavy metals that are most relevant with respect to road-derived contaminants, namely lead, copper and zinc. The concentrations of these three metals from various New Zealand and international studies are summarised in Table 1.2.

Fergusson and Kim (1995) carried out an extensive review of metal concentrations in street dust and reported typical concentration ranges for lead, copper and zinc of 500–4000 μ g/g, 100–300 μ g/g and 300–900 μ g/g, respectively. While the concentration ranges for copper and zinc are applicable to more recent studies, lead concentrations in RDS reported after ca. 2000 tend to be less than 200 μ g/g – significantly lower than the 500–4000 μ g/g range reported by Fergusson and Kim (1991) and the mean concentration of 1880 μ g/g (n=13) reported by Harrison (1979).

Lead, copper and zinc concentrations in RDS (includes road sweepings, street dust, catchpit sediments and retention pond/swale sediments).

Metal concentration ^a (μg/g)		Comment	Reference	
lead	copper	zinc		
		Stre	eet dust/sweepings	
1710	275	975	street dust	Harrison and Wilson 1985
1354	115	513	street dust, London	Thornton 1991
19.7 (5.2-94.1)	9.6 (2.4–43.5)	38.5 (6.8–108.5)	residential and commercial	Liebens 2001
1000	100	300	typical values	Sartor and Gaboury 1984
289	129	528	Dunedin (New Zealand)	Brown and Peake 2006
160	126	1170	residential/commercial	Li et al. 2001
249	124	962	25,000 vpd	Zanders 2005
(500-4000)	(100-300)	(300-900)	review (all types)	Fergusson and Kim 1991
1880 (920-3560)	143 (57-312)	534 (200-940)	urban (13 samples)	Harrison 1979
6630 (2200- 15,000)	206 (104–375)	1600 (1010-3725)	car parks (8 samples)	Harrison 1979
15-77	-	-	mixed land use type	Mathisen et al. 1999
123	14.9	47.8	residential	Latimer et al. 1990
1410	228	655	industrial	Latimer et al. 1990
840	90	336	highway	Latimer et al. 1990
106	167	434	13 kerbside samples	Sutherland et al. 2001
186	185	675	15 kerbside samples	Andrews and Sutherland 2004
		Catchp	it and SWTD sediments	
262	179	424	Dunedin (New Zealand)	Brown and Peake 2006
150			mixed land use type	Mathisen et al. 1999
(183-305)	(6.1-19.6)	(155-1282)	flood control sumps	Smith 2001
		(203-1090)	catchpit sediment	O'Riley et al. 2002
(218-1601)	(69-243)		runoff sediment	Jiries et al. 2001
59.7 (5.3–777)	16.7 (0-54.5)	114 (0.3-622)	SWTD pond sediment	Liebens 2001
68.3 (19.8–190)	14.1 (2.1-49.6)	101.1 (16-565.5)	swale sediment	Liebens 2001
112 and 160	286 and 426	888 and 1337	ponds A and B, respectively	Hares and Ward 2004

^a median or mean metal concentrations (concentration range in parentheses)

Removal of lead from petrol

The decreased concentrations of lead in RDS, reported in more recent studies, reflect the gradual removal of lead from petrol in various countries. Since Japan banned leaded

additives in petrol in 1986, other countries that have banned the addition of lead to petrol (the major source of vehicle derived lead emissions) include: Austria in 1990; Canada in 1993; the United States in 1995; and New Zealand in 1996. In countries where leaded petrol is banned, very high particulate concentrations of lead are presumably the result of legacy contamination or a non-vehicle related source (eg industrial emissions).

1.3.2 Alternatives to landfilling

Although there are many factors that need to be considered, the key to successfully implementing reuse strategies for roadwaste is a change in thinking. That is, 'roadwaste needs to be viewed as something of value (ie a potential product) rather than as a waste material needing disposal' (AASHTO 2004).

1.3.2.1 General considerations

Alternatives to landfill disposal of RDS need to be both economically and environmentally feasible. With respect to environmental feasibility, this is particularly relevant in the United States, where the liability from environmental impacts of waste is unending (ie 'cradle to grave'). Accordingly any cost savings from a potential reuse application (relative to landfilling) needs to be balanced against the significant advantage gained by disposal at a permitted solid waste landfill, which is the elimination of any future liability. Alternatives need to address concerns/risks of contaminants being mobilised (as particulates or in solution) from the site and distributed in the wider environment. To further limit any liability, reuse of roadwaste is often limited to applications that do not involve routine access or contact with people.

In relation to economic feasibility, the reuse option, to be practical, must be less expensive than the combined cost of disposal and purchase of new materials (which has been circumvented through reuse of roadwaste). This is an important consideration, because the feasibility of various options is dependent on landfill charges, which vary considerably between areas. For example, the landfill charge for roadwaste in Hamilton is \$65 per tonne, whereas in Christchurch the cost is ca. 150% higher at \$160 per tonne. Clearly there is considerably more scope (and incentive) to implement cost-effective RDS reuse strategies in Christchurch than there is in Hamilton.

Because cost savings are the main driver for reusing/recycling roadwaste, ideal solutions need to be either 'ready to use' applications, or ones that involve minimal processing and/or treatment. For example, in the United States, most states only require the removal of litter by coarse sieving the RDS through a 25 mm screen.

1.3.2.2 North America leading the way in reusing RDS

Most of the progress in the area of reusing roadwaste materials has been achieved in North America, in particular, the States of Florida (Liebens 2001), Washington (CWC 1997), Massachusetts (Mathisen et al. 1999) and Oregon (Collins and Moore 2000; Ghezzi et al. 2001), but also at a Federal level via the American Association of State Highway and Transportation Officials (AASHTO) and Federal Highway Administration. In 2004, AASHTO

released a comprehensive manual entitled *Environmental stewardship practices*, procedures, and policies for highway construction and maintenance (AASHTO 2004). The AASHTO report included a chapter entitled 'Roadside management and maintenance: Beyond vegetation' (Chapter 10), which provides considerable information on a number of different applications pertaining to the reuse, recycling and/or treatment of RDS. While this section provides a brief summary of potential reuse options and their implementation, the reader is encouraged to consult the aforementioned references for additional information and individual case studies. Some of the more commonly proposed or implemented reuse applications for RDS are summarised below.

1.3.2.3 Fill-type applications

Of the various options, the attraction of 'fill' applications is that it requires very little processing of roadwaste material and it is suitable for marginally contaminated material (AASHTO 2004). Recommended practices for this RDS reuse application include: rubbish removal; limited public access; stormwater (runoff) containment; limiting contaminant levels to state industrial site cleanup thresholds; mix and/or cap with uncontaminated fill material; and planting/mulching to limit erosion and/or dust emissions of the reused RDS material.

In the United States, an important consideration for reusing contaminated material, such as RDS, is the 'cradle to grave' liability. Accordingly, road waste generators must be sure that the reuse application of RDS does not pose any risk to the environment or human health. Authors of the AASHTO report (AASHTO 2004) reported that reusing RDS for the construction of roadside berm structures represented a low to moderate risk.

Example: Massachusetts

Massachusetts allows street sweeping to be used as poor grade trench fill. It is termed poor grade fill because it has a poor compaction rating, quickly loses volume and is marginally contaminated. Recommended practices include: limiting to commercial, industry or agency controlled, limited access sites; covering with uncontaminated soil cap (further limiting potential exposure/fugitive losses); using only under open ground (not beneath paved surfaces because of volume loss); and screening for rubbish prior to use. Massachusetts also uses street sweepings as fill material in highway median strips and verges that are not readily accessible by people. Street sweepings are placed on clay or soil bases (not sand or gravel free draining substrates) and are normally capped with non-contaminated material.

1.3.2.4 Daily cover at landfill sites

This is really only a pseudo-reuse option as it still ultimately involves the disposal of roadwaste at a landfill site. The potential benefit of this particular application is that some landfill sites offer reduced charges to dispose of relatively clean material that can be used for daily cover. Many landfills (including those in New Zealand), however, have an oversupply of cleanfill and so there is often very little difference in the cost of landfilling clean material vs general refuse. Because of this, daily cover at landfills is not considered a feasible reuse option in New Zealand.

1.3.2.5 Cleanfill disposal

Disposal of roadwaste in cleanfill sites (ie unlined construction and demolition landfills) may offer considerable savings in disposal costs; however, like daily cover applications, it is not a genuine reuse option because it is simply a lower cost method of disposal. Neither cleanfill disposal nor daily cover applications are consistent with a 'change in thinking' – that is, viewing RDS as something of value rather than as a waste material needing disposal.

In the United States, many former sand and gravel pits operating now as cleanfills are accepting RDS, despite the porous nature of the matrix (ie sand and gravel) and ready access to the water table making these sites inappropriate for the disposal of even mildly contaminated materials (AASHTO 2004). Consequently, at some of these cleanfill sites, contaminants have been virtually injected into the ground water, which has resulted in RDS being excavated from a number of such sites. In New Zealand, the national cleanfill guidelines (MfE 2002) specifically state that RDS sediments (both sweeping and catchpit sediments) are not suitable for disposing in cleanfills. Accordingly, cleanfill disposal of RDS is not considered a practical option for the sustainable management of RDS in New Zealand.

1.3.2.6 Compost/soil conditioner

Use of RDS for soil amending can reduce management costs substantially – reducing both landfilling costs and the need to purchase new materials. Most RDS has decent drainage characteristics, plentiful nutrients, good water retention and a good mix of particle sizes appropriate as an effective growing medium (AASHTO 2004). Risk of contaminant migration from the site can be effectively controlled by placing the product only in areas where risk of exposure is low and the potential for contaminant transport minimal.

Examples from the United States:

A number of municipalities in the United States either directly compost RDS or use processed RDS (eg screened and washed) to blend with compost. Colorado Springs, Colorado, has achieved a 100% reduction in the volume of catch pit sediments landfilled through the development of its own programme that involves the dewatering, screening and blending with compost (Mathisen et al. 1999).

The City of Long Beach, California, conducted a successful pilot programme that showed its street sweepings were suitable for generating compost. The city now diverts 95% of the 16,000 tonnes of sweepings collected annually to a composting facility where the final product is used for agricultural purposes (Kidwell-Ross 2006). However, it is important to note that the Long Beach process appears to compost the separated organic fraction (including paper) – the fines/dirt fraction is reused in other applications (ie they are not included in the composting process).

The Washington Department of Transportation mixes catch pit sediments ('vactor waste') with wood chips for an effective growing medium used in freeway infields and medians (Collins and Moore 2000). The addition of wood chips improves the growing media and

also fixes metals and petroleum compounds. Although no data is provided to support the contaminant-binding benefits of wood chips, assuming the wood reduces contaminant mobility/availability, this soil amendment application combines both 'treatment' and 'reuse' aspects of RDS management.

1.3.2.7 Cement and concrete production

Many of the environmental concerns relating to the reuse of contaminated RDS (eg contaminant exposure, transportation, leaching etc) are alleviated if they are physically locked into a solid matrix such as concrete or asphalt. There are two potential applications for incorporating RDS into concrete.

Cement

Cement production involves heating a mixture of limestone, silica, aluminates and ferric minerals feedstock materials to a temperature of ca. 1400 °C. The benefits of using RDS as a silica feedstock material is that it results in the thermal destruction of petroleum hydrocarbon contaminants (TPH and PAH), and heavy metal contaminants being incorporated into the cement and, ultimately, into a concrete matrix. A key to this reuse option, however, is consistency of supply, since kiln operation requires that the amount of organic matter in the feedstock is known. Cement manufacturers accepting RDS as feedstock often specify that it be free of over-sized materials and debris and tested for heavy metals to ensure they are not accepting hazardous waste (AASHTO 2004).

Concrete

RDS can also be incorporated directly into concrete as the main aggregate component. In 1996, the Kitsap County Public Works department made 260 *eco-blocks*, each weighing ca. 1400 kg, using a total of 390 tonnes of RDS (largely catchpit sediments). To improve strength, a small amount of washed crushed rock aggregate was added (<10%) with the remainder being RDS. The total cost of manufacturing the *eco-blocks* was US\$6500, compared with estimated landfill disposal charges of \$US15,580 for the 390 tonnes of RDS (CWC 1997).

Asphalt

Reuse of RDS as an aggregate component in asphalt production has been suggested; however, a limitation is the requirement for dry aggregate that is free of organic matter. In order to meet this requirement, a significant level of RDS processing would need to be carried out to dry and separate out the low-density organic material. Despite this potential issue, a joint study between University of Massachusetts (Civil and Environmental Engineering Department) and Mass Highway Department concluded that RDS (both street sweepings and catchpit sediments) could be reused as fine aggregates in asphalt. The conclusion was based on British pendulum number (BPN), bulk specific gravity, uncompacted void content and model mode load stresses (MMLS) rut testing (Sengupta et al. 2007). A significant benefit of asphalt incorporation is that it is conducive to using RDS that may contain relatively high concentrations of hydrocarbon contaminants because these will be insignificant compared with the hydrocarbon levels in the final bituminous product.

1.3.3 Treatment options for road-derived sediments (RDS)

Although not the focus of this research project, to minimise the risk of contaminants in RDS and to reduce certain contaminant concentrations to levels acceptable for reuse, a number of potential treatment options are possible.

1.3.3.1 Contaminant removal vs contaminant 'immobilisation'

First, it is important to emphasise that not all contaminant types can be broken down and removed via treatment processes. Degradation and thermal destruction are only applicable to organic contaminants (as opposed to heavy metals), namely hydrocarbons (or TPH). TPH, as the name suggests, is a measure of the total amount of petroleum hydrocarbons. This includes the relatively fast degrading 'aliphatic' (or non-aromatic) hydrocarbons, through to the significantly more environmentally persistent polycyclic aromatic hydrocarbons (PAHs).

Heavy metals, on the other hand, do not 'treat out,' breakdown or disappear over time – they remain in the RDS. The only way to reduce the concentration of metals is by washing, which removes a portion of the metals by either dissolving the metal or removing the very fine particulate fraction that it enriched with metal contaminants. Any benefits in reducing contaminant concentrations from washing are usually offset by the associated costs and complexity of treating waste water. Hence, the treatment approach for metals is based on reducing metal mobility – where 'mobility' refers to the tendency of the metal to leach or migrate from the RDS matrix. In this way, treated RDS may contain the same amount of metal contaminants, but they are locked more tightly into the solid matrix and, therefore, represent a significantly lower environmental risk. This is because leaching is a major vector for contaminant migration 'off site' and the bioavailable (and hence toxic) 'form' of metal contaminants is the *soluble* fraction – not the particulate bound, or *solid*, fraction. This approach is the basis for 'phosphate amendment' (Section 1.3.3.9), which reduces metal solubility by forming insoluble phosphates.

1.3.3.2 Typical treatment options that may facilitate RDS reuse

Examples of treatment and/or processing options for RDS that are discussed in the following sections include:

- screening/separation (1.3.3.3)
- washing (1.3.3.4)
- composting (1.3.3.5)
- passive remediation (1.3.3.6)
- active remediation (1.3.3.7)
- phytoremediation (1.3.3.8)
- phosphate amendment (1.3.3.9).

1.3.3.3 Screening/separation

All reuse options of RDS in the United States appear to require pre-screening to remove rubbish and organic material. Different screening technologies are available for screening wet and dry material. The various separation technologies available including, liquid, vibratory, air, and mechanical are reviewed elsewhere (CWC 1997). Of all the technologies discussed, mechanical separation using a trommel screening is considered the most effective piece of screening equipment for processing wet material such as RDS.

1.3.3.4 Washing

The majority of the metal and hydrocarbon contaminants are adsorbed onto the surface of particles and, therefore, cannot simply be washed or 'rinsed off' with water. While it is possible to enhance the solubilisation of organic and metal contaminants (ie using surfactants and acids, respectively), the main aim of washing treatments is to remove the fine particle size fraction. Fine particles (ie <63 μ m) have a greater surface area to volume ratio than larger particles and, therefore, contain greater concentrations of adsorbed contaminants, especially metals.

Washing RDS can remove this more contaminated fine fraction leaving the larger particle size fractions ready for reuse (Collins and Moore 2000). The major problem of this treatment is that it creates a secondary problem – effectively managing the wastewater that is now contaminated with fine particulate material. Besides evaporating the water in large ponds, the authors of *Roadwaste management: A tool for developing district plans* (Collins and Moore 2000) concluded there was no simple technology available to de-water the lighter suspended fines. Despite this limitation, there are situations where washing to remove fines can be economically feasible, such as recovery of winter street sand (see the City of Edmonton example below).

Example: City of Edmonton, Canada

The city places ca. 165,000 tonnes of winter street sand on its roadways annually, with ca. 115,000 tonnes recovered in street sweepings. Historically, only 25% of the material was reused, with the remaining 75% being landfilled. In 2002, 115,000 tonnes of street sand sweepings contaminated with salt, hydrocarbons, road litter, leaves, grass and soil were landfilled. This quantity corresponded to 60% of the total weight of materials landfilled annually, which if continued, would have a significantly detrimental effect on the service life of the city's landfill site.

In 2003, a pilot programme was undertaken to find a more cost-effective and environmentally sustainable solution. The city implemented a four-phase process consisting of waste removal, material washing, fines processing and clean sand dewatering and drying. Based on the pilot project results, of the ca. 115,000 tonnes of material collected, 101,000 tonnes (88%) will be diverted from landfill. Of this, 92,000 tonnes will be recoverable as street sand, 6900 tonnes as washed fine sand and 2300 tonnes as aggregate. The remaining 14,000 tonnes that will require landfilling consist of 9400 tonnes of silt and clay size particles and 4600 tonnes of road litter.

1.3.3.5 Composting

As mentioned in Section 1.3.2, composting processes involving RDS have been successfully implemented by various municipalities; however, most of these processes appear to involve the separation, and subsequent composting, of only the organic fraction. This is despite research findings by Hindin et al. (1993) that RDS is biologically active enough to compost (or 'cook out') on its own. Most hydrocarbons that collectively make up the 'TPH' total are fairly susceptible to microbial decomposition; however, notable exceptions are PAHs, which include the carcinogenic compounds chrysene, indeno[1,2,3-cd]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, benzo[a]anthracene, and benzo[a]pyrene.

Although composting does not significantly reduce the concentration of persistent organic contaminants (PAHs) and metals, the composting process generates humic materials that can bind, and hence reduce the bioavailability of both metals and PAHs (ie contaminant *stabilisation*). Because the presence of humic materials is important for contaminant immobilisation, it may not be necessary to actually compost RDS to attain these treatment benefits. Instead, simply blending RDS with ready-formed compost may be sufficient to stabilise the contaminants through interactions with the added humic material.

Such humic-contaminant interactions are presumably the reason for the claimed 'contaminant binding' benefits of the Washington State Department of Transportation practice of mixing catch pit sediments with wood chips for producing an effective growing medium (Collins and Moore 2000). In addition, the City of Portland (Oregon) conducted RDS composting trials (Ghezzi et al. 2001) using formulations ranging from 20% RDS: 80% organic matter, through to 100% RDS. Analyses conducted on runoff water from the compost cells revealed minimal concentrations of contaminants. The apparent immobilisation of RDS contaminants in this experiment may reflect the binding influence of humified organic matter.

The blending of contaminated RDS with pre-composted material to reduce metal availability was a key component of the research undertaken for this report (Section 3.4.3).

1.3.3.6 Passive bioremediation

This treatment option allows the natural microbes present in the RDS to break down hydrocarbon contaminants. It has been shown that RDS piles left to naturally bioremediate (ie natural attenuation) have had little or no detectable TPH within six months. PAHs are considerably more resistant to biological breakdown and, therefore, this method does not significantly reduce their concentration. Pre-screening of the RDS to remove rubbish is possibly beneficial to the passive remediation process because it aerates the RDS, increasing natural microbial decomposition of petroleum hydrocarbons (Collins and Moore 2000). Hindin (1993) reported mean TPH concentrations of 3215 μ g/g and 312 μ g/g for freshly collected and well weathered road sweepings, respectively.

1.3.3.7 Active bioremediation

Active bioremediation enhances the biodegradation of contaminants above the level that is normally possible through passive bioremediation. The enhanced degradation is achieved by technologies that include the following: the use of specialised microbes that degrade hydrocarbons with high efficiency; supply of additional nutrient that supports increased microbial activity; addition of surfactants that release bound chemicals; and addition of chemicals that help break down contaminants or provide chemical source of oxygen (eg peroxides). Active bioremediation is considered an expensive treatment option with limited relevance to treating RDS for further reuse (Collins and Moore 2000).

1.3.3.8 Phytoremediation

Phytoremediation involves using plants to treat contaminants (Krämer 2005; McGrath and Zhao 2003). A number of plant species have been identified that either remove or break down soil contaminants. For example, certain grass varieties are known to take up high amounts of lead, and mulberry bushes have been shown to breakdown carcinogenic PAHs in the rhyzosphere (the biologically active rot zone). As it is often a requirement to plant over sites where RDS have been reused (to reduce transportation of contaminated material), it makes sense to select plants that have the potential (over time) to reduce the concentrations of contaminants in the soil.

Unlike organic contaminants, metals cannot be broken down by plants – they can only be removed from the soil by being taken up and incorporated into plant tissue. To avoid redistribution of the metal contaminants, presumably the metals would need to be stored in permanent woody-type plant tissue. If stored in temporary tissues like leaves, then the metal would be deposited back onto the soil upon leaf abscission. Hence there appears to be limited scope to use grasses that require mowing since this may necessitate the collection and removal of clippings.

1.3.3.9 Phosphate amendment to reduce heavy metal solubility

Although this method has not been reported for the treatment of RDS, it has been extensively studied as a feasible in situ remediation technique for metal-contaminated soils. Metal mobility and bioavailability depend on soil chemistry and hence the mineral form of the metal (Berti and Cunningham 1997). It is, therefore, beneficial to add chemicals that can convert the more soluble and available form/s of heavy metals (ie copper, lead and zinc) into insoluble mineral forms. A considerable amount of work has focused on the addition of phosphate to contaminated soils to facilitate the formation of insoluble metal-phosphate minerals. Most of this work has involved lead-contaminated soils; however, reductions in the mobility of zinc have also been reported. McGowen et al. (2001) reported a 19-fold reduction in zinc mobility for a smelter-contaminated soil amended with only 0.05% phosphorus (added as diammonium phosphate fertiliser).

Because zinc is a major contaminant in RDS, phosphate addition to reduce contaminant mobility was trialled as part of this study (Section 3.4.3).

1.3.4 Regulatory guidelines for RDS reuse in the United States

There are very few regulatory guidelines specifically relating to acceptable contaminant levels for reusing RDS. Many state regulatory agencies appear to favour using soil (ie industrial) cleanup guidelines as a basis for assessing the suitability of reusing RDS in certain applications. The regulatory status of reusing RDS varies from agency to agency in relation to the following types of issues: requirement for contaminant screening for RDS being reused; pre-approved reuse application of RDS that does not require screening; reuse of catch pit sediments; the type of reuse applications; and restrictions on the placement of reused RDS materials.

Some examples of state regulations relevant to the reuse of RDS are outlined below, and serve as a useful starting point for how New Zealand could address reuse/recycling of RDS.

1.3.4.1 Massachusetts

The Department of Environmental Protection (DEP) *Reuse and disposal of street sweepings, final policy #BWP-94-092* states that street sweepings must either be disposed of in landfills; used as daily cover or fill in roadways; used as compost additive; or an application can be made for an alternate 'beneficial use' – subject to department approval. The reuse of street sweepings is subject to stipulations, such as use outside residential areas, placement above the water table, and placement outside buffer zone for wetlands and water supplies. The policy only refers to street sweepings and does not include catchpit sediments (Mathisen et al. 1999).

1.3.4.2 Oregon

The Oregon Department of Environmental Quality (DEQ) 'cleanup levels' define specific pollutants and the concentrations at which they become a significant risk to the environment and human health. Collins and Moore (2000) assert that assessing pollutant health risks is different from determining whether or not a material, such as RDS, can be placed into the environment (ie exceeding cleanup levels does not preclude reuse/recycling). Nonetheless the cleanup levels (Table 1.3) provide a useful starting point in assessing appropriate reuse options for contaminated materials.

Based on these cleanup levels and the typical contaminant levels in RDS, the most problematic contaminants limiting the reuse of RDS in Oregon are carcinogenic PAHs (cPAHs) and the heavy metals, lead and arsenic. It is unclear why the cleanup levels permit such high levels of metals such as copper (ie $10,000~\mu g/g$ for residential). In contrast, the screening criterion for copper in Class A landfills in New Zealand is only $100~\mu g/g$ (MfE 2004). With respect to TPH, Oregon DEQ has approved concentrations in the heavy oil range of up to $10,000~\mu g/g$ for reusing RDS.

Table 1.3 Oregon DEQ soil cleanup levels for carcinogenic PAHs and heavy metals (Collins and Moore 2000).

Contaminant	Residential (µg/g)	Industrial (µg/g)	Acceptable leachate conc. (µg/ml)
	PA	Hs	_
Benzo[a]anthrance	0.1	1.0	-
Benzo[a]pyrene	0.1	1.0	-
Benzo[b]fluoranthene	0.1	1.0	-
Benzo[b]fluoranthene	0.1	1.0	-
Benzo[k]fluoranthene	0.1	1.0	-
Chrysene	0.1	1.0	-
Dibenz[a,h]anthracene	0.1	1.0	-
Indenopyrene	0.1	1.0	-
	Heavy	metals	
Arsenic	0.4	3	0.004
Cadmium	100	1000	0.5
Chromium	1000	1500	10
Copper	10,000	80,000	100
Lead	200	2000	2

Collins and Moore (2000) proposed a 'rough and ready' method for assessing the risk of RDS, which consisted of the following *High, Medium, Low* classification system:

High = exceeds industrial cleanup standards, or is directly impacted by a petroleum spill or other toxic substance

Medium = exceeds only residential cleanup standards

Low = less than the residential standards and <1000 μ g/g of TPH.

1.3.4.3 Washington, Snohomish County

The state's solid waste statute prioritises the need to recycle rather than dispose of waste. The Snohomish Health District (Environmental Health Division, Solid Waste and Toxics Section) has defined a list of potential end uses of RDS depending on whether the material is classified as Class A or Class B street waste solids. The Class A street waste solid criteria are largely based on Model Toxics Control Act (MTCA) – Cleanup. These criteria have been developed by the Washington State Department of Ecology (Model Toxics Control Act – Cleanup, 2007) and are summarised in Table 1.4. Class A solids can be used, with restrictions (identified by number in parentheses) as: road subgrade or other road construction fill (1); street traction sand (1); pipe bedding (1) and (2); utility trench backfill (1) and (2); fill in commercial/industrial zones (1), (2) and (3); any approved reuse option for Class B street waste solids, and other end uses approved by the Health District. The restrictions (1–3) being as follows:

- 1. removal of litter and vegetative matter
- 2. end use should take into consideration potential human exposure both at the time of use and in the future

3. requires the following:

- completed fill must be 'encapsulated' with two feet or more of uncontaminated, relatively impervious soil
- completed fill site must be recorded on deed with Snohomish County Auditor's Office.

Class B street wastes are solids whose contaminant levels exceed Class A levels, but are not classified as dangerous/hazardous waste. Potential end-use options for Class B street waste solids are limited to pre-fabricated concrete, cement and asphalt manufacturing and daily cover at landfills (these applications are discussed in Section 1.3.2). In most instances, Grade B reuse activities would require submission of a recycling permit application to the Health District for review and approval.

Table 1.4 Maximum end-use contaminant levels for Class A street waste solids (CWC 1997, Appendix A).

Contaminant	Maximum concentration (μg/g)
Heavy fuel hydrocarbons (C ₂₄ -C ₃₀) ^a	2000
Diesel (C ₁₂ -C ₂₄) ^a	500
Gasoline (C ₆ -C ₁₂) ^a	250
Carcinogenic PAHs (total)	1.0
Arsenic	20
Cadmium	2.0
Lead	250
Mercury (inorganic)	1.0

^a maximum end-use contaminant levels for RDS defined by Snohomish Health District. Remaining values are method A cleanup values (unrestricted land use soil values), from the MTCA regulation.

1.3.4.4 Florida

A report by the Florida Centre for Solid and Hazardous Waste Management (Liebens 2001) outlined a number of potentially relevant federal and state regulations that may apply to the reuse of RDS. Of the various regulations and guidelines discussed by Liebens, the most relevant appear to be those pertaining to the reuse (ie land application) of sediments from waste waster treatment (ie biosolids).

Table 1.5	Contaminant ceiling concentrations and Class AA parameter concentrations
for biosolid	s in Florida (Florida DEP 1998).

Contaminant	Ceiling concentration (µg/g)	Class AA concentration (µg/g)
Arsenic	75	41
Cadmium	85	39
Copper	4300	1500
Lead	840	300
Mercury	57	17
Zinc	7500	2800

The biosolids regulations consist of two sets of concentration limits for heavy metal contaminants (Table 1.5):

- 1. maximum 'ceiling concentrations' for contaminants for environmental protection
- 2. a set of lower Class AA concentrations which are used to classify high-grade biosolids and biosolid blends.

These high-grade materials are classified as Class AA residuals and are suitable for distribution and marketing.

1.3.5 Potentially relevant guidelines for RDS management in New Zealand

1.3.5.1 Landfill criteria – hazardous vs non-hazardous classification

Currently all RDS in New Zealand are landfilled, therefore, it is beneficial to quickly review the national *Hazardous waste guidelines* – *landfill waste acceptance criteria* (MfE 2004). The landfill criteria are based on maximum permitted leachate concentrations using a toxicity characteristic leaching procedure (TCLP) test. The TCLP test mimics the acidic leaching conditions of a landfill, and it is determined using 50 g of material with 1 L of extraction solvent (acidic solution). Screening concentrations are the theoretical contaminant concentration that would need to be present in 50 g to exceed the maximum leaching concentration, and are simply obtained by multiplying the leachate concentration by 20 (note: units change from mg/L to mg/kg = μ g/g) – this is referred to as the 'rule of 20'. The screening criteria and leachability limits for Class A landfills (ie consistent with design standards outlined in MfE 2004) are summarised in Table 1.6. Materials exceeding the screening criteria are subject to TCLP analysis. If the leachate concentrations are less than the leachability limit then the material is classified *non-hazardous*. If greater than any of the limits in Table 1.6, the material is classified as *hazardous* and must be treated before it can be accepted for disposal in a landfill.

Table 1.6 Leachability limits and screening concentrations for Class A landfills in New Zealand (adapted from MfE 2004).

Contaminant	Screening criteria (solid) (µg/g)	Maximum leachate conc. (mg/L)
Cadmium	20	1
Copper	100	5
Lead	100	5
Mercury	4	0.2
Zinc	200	10
Naphthalene	200	10

The screening criteria values for copper ($100 \mu g/g$) and zinc ($200 \mu g/g$) are relatively low, especially when considering that typical concentration ranges of copper and zinc in RDS are $100-300 \mu g/g$ and $300-900 \mu g/g$, respectively. Based on these typical concentrations, RDS materials would require TCLP testing to determine if they were a hazardous waste material. Clearly there would be very limited scope for reusing RDS in New Zealand if it was technically classified as a hazardous waste material. However, it is emphasised that the screening criteria are based on the assumption that 100% of the metal contaminant is removed/solubilised by the leaching solution, which is definitely not the case. Nevertheless, it still highlights that RDS materials do contain significant amounts of environmental contaminants and that any reuse of them needs to address any potential risks.

An important component of this research project was to characterise total contaminant levels and, more importantly, the leachability of contaminants in representative samples of New Zealand RDS.

1.3.5.2 Biosolids guidelines and relevance to RDS reuse

Using the same approach as in Florida, a useful starting point for reuse guidelines for RDS are the regulations pertaining to the land application of sewage sludge, or biosolids. In 2003, the *Guidelines for the safe application of biosolids to land in New Zealand* were released by the New Zealand Water and Waste Association (NZWWA 2003), which introduced a dual classification system based on the *stabilisation* (Grade A or B) and *contaminant content* (Grade 'a' or 'b') of the biosolid material. *Stabilisation* refers to the extent of treatment to eliminate and/or reduce pathogens, vector attraction and offensive odours. The highest quality grade biosolids (Aa) are classified as 'unrestricted use biosolids', and can be safely handled by the public and applied to land without risk of significant adverse effects. Grades Ab, Ba and Bb are classified as 'restricted use biosolids', and can only be applied to land with site specific controls imposed in accordance with resource consent. Contaminant limits for Grade 'a' and 'b' biosolids are listed in Table 1.7.

Table 1.7 Maximum contaminant concentrations for Grade 'a' and Grade 'b' biosolid classification in New Zealand (adapted from NZWWA 2003).

Contaminant	Grac µg/g dry	Grade 'b' (μg/g dry weight)	
	Until 31/12/2012	After 31/12/2012	
Arsenic	20	20	30
Cadmium	3	1	10
Chromium	600	600	1500
Copper	300	100	1250
Lead	300	300	300
Mercury	2	1	7.5
Nickel	60	60	135
Zinc	600	300	1500

Although the typical contaminant range for copper ($100-300 \mu g/g$) and zinc ($300-900 \mu g/g$) in RDS (Fergusson and Kim 1991) may be outside the Grade 'a' criteria (certainly after 2012), they are well within the maximum concentrations for Grade 'b' biosolids. To facilitate the widespread reuse of RDS, it is desirable to find or develop applications that do not require resource consent. Hence it is beneficial to have a situation analogous to the Grade Aa biosolids, where RDS (or modified/blended RDS materials) can be classified as 'unrestricted use' materials.

If post-2012 Grade 'a' contaminant maxima were applied to the reuse of RDS in New Zealand, then based on typical concentrations of copper and zinc, a significant amount of blending with clean materials would probably be required. The biosolids guidelines state that blending the sludge with other substances (eg pumice, sand, subsoils, bark, sawdust or green waste) before, during or after treatment is an acceptable way of diluting contaminant levels in order to attain either the 'a' or 'b' biosolid contaminant grades. Apply this diluting approach to RDS may facilitate reuse options and, depending on the blending material (ie compost), may provide additional beneficial contaminant-immobilisation properties.

2. Methods

2.1 Sample collection

2.1.1 General

The aims of the RDS sampling programme were to:

- sample RDS from three major urban centres to determine 'typical' contaminant concentrations in New Zealand, thereby maximising the national relevance of the study
- sample both street sweepings and catchpit sediments from the same street sections to compare contaminant concentrations in the two major types of RDS
- sample RDS from streets with high (ie >10,000 vehicle per day, or vpd) and low (ca.
 500 vpd) traffic volumes to determine what effect this had on contaminant concentrations
- where possible, sample RDS that had been collected by commercial operators so that the samples were relevant to 'real world' RDS collected throughout New Zealand.

At all major sampling locations, four to six streets (or sweeping sectors) that satisfied the above traffic criteria were selected by city council and sweeping contractor personnel. Street traffic volumes were defined as: high ≥10,000 vpd; low <1000 vpd (although preferably <500 vpd); and medium ca. 1000−10,000 vpd. Sampling dates were as follows: Auckland – November 2007; Hamilton – October 2007 (street sweepings) and December 2007 (catchpit sediments); and Christchurch – September 2007.

The scope of the research project was to characterise RDS from three New Zealand cities and to determine the typical range of contaminant concentrations and how they varied by location, traffic volume and RDS type (ie catchpit sediment vs sweeping particulates). The total number of RDS samples was limited to 35, which was considered sufficient to enable meaningful comparisons between smaller subsets of RDS samples. The smallest group of RDS samples used to compare differences in medians consisted of eight RDS samples.

It is emphasised that the study offers a 'one-off' snapshot of contaminant concentrations at the sites sampled – it does not take into account any potential seasonal variations in contaminant concentrations. The author also acknowledges that catchment land use (ie whether predominately residential, commercial or industrial) also plays an important role in RDS contaminant concentrations. However, the extensive sampling required to incorporate these parameters was beyond the scope and resources of the research project.

2.1.1.1 Street sweepings

Street sweeping samples were collected by contractors using high efficiency vacuum (Johnson or Elgin) or regenerative air (Schwarz) sweeper trucks (Figure 2.1).



Figure 2.1 The two types of high efficiency sweeping technology used to collect samples – vacuum (left) and regenerative air (right). Note the 'sweep width' on the regenerative air sweeper is as wide as the truck.

Starting with an empty truck, the specified street (or sweeping sector) was swept and at the conclusion, 6–10 shovel loads were removed from the inspection hatch and combined in a large plastic bin (Figure 2.2). The composite sample was thoroughly mixed and a sub-sample (2–4 kg) removed and placed into a zip-lock plastic bag. The samples were transported back to the laboratory and stored at -20°C prior to processing.



Figure 2.2 Sampling the collected street sweepings from sweeper truck inspection hatch (left) and view of collected sweepings inside sweeper truck (right).

2.1.1.2 Catchpit sediments

The original project plan was to collect catchpit sediments using sump cleaning trucks that, starting from empty, cleaned out the catchpits along the same street section (or sweeping sector) used to collect the street sweeping samples. This method would have provided the best comparison between catchpit sediments and street sweeping samples; however, it was not possible for councils and/or contractors to work the extra sump

cleaning operations into their scheduled maintenance programmes. As a result, catchpit sediments were collected manually from at least three sumps on the street (or sweeping sector) from which each of the street sweeping samples had been collected (Figure 2.3). Approximately 2–3 kg of sediment were collected from each catchpit and placed in a ziplock plastic bag. The individual catchpit samples were composited (by mixing thoroughly in a large plastic bin) and a 2–3 kg subsample removed and placed in a zip-lock plastic bag. The composited catchpit samples were stored at -20°C prior to processing.



Figure 2.3 Manually sampling catchpit sediments (Christchurch, left and centre; Auckland, right).

2.1.2 Sampling locations

Auckland City

Street sweeping sites were identified and collected by Auckland City sweeping contractor, Metrowaste (using an Elgin vacuum sweeper truck). In addition to the paired samples of sweepings and catchpit sediments (sites A1 to A4), additional sites (A5 to A7) were collected and included: Northwestern motorway (SH16) street sweepings (provided by Fulton Hogan); a catchpit composite sample from a new residential suburb (provided by Interclean); and sediment from New Zealand's largest SWTD in Grafton Gully, Auckland (provided by MWH and Fulton Hogan), which is shown in Figure 2.4. With the exception of A5CP, all catchpit sediments were sampled manually using a shovel. Details of the sampling sites are given in Table 2.1.

Table 2.1 Details of RDS (sweepings = SW; catchpit sediments = CP) sampled from Auckland City.

Street	Site no. A = Auckland	RDS type	RDS sample abbreviation	Traffic volume ^a
Main RDS sample	es with 'paired' swee	pings and cate	hpit sediment sa	mples
New North Rd	A1	sweeping	A1SW	high
New North Rd	A1	catchpit	A1CP	high
Charles St	A2	sweeping	A2SW	medium
Charles St	A2	catchpit	A2CP	medium
Parnell Rd	А3	sweeping	A3SW	high
Parnell Rd	А3	catchpit	АЗСР	high
Carlton Core Rd	A4	sweeping	A4SW	medium
Carlton Core Rd	A4	catchpit	A4CP	medium
	'Non-paired' misco	ellaneous sam	oles	
New residential suburb	A5	catchpit	A5CP	low
North Western motorway	A6	sweeping	A6SW	high
Grafton Gully SWTD ^b	A7i	catchpit	А7СРі	high
Grafton Gully SWTD ^b	A7ii	catchpit	A7CPii	high

 $^{^{\}rm a}$ high >10,000 vpd; low <1000 vpd; and medium ca. 1000-10,000 vpd. $^{\rm b}$ Largest stormwater treatment device (SWTD) in New Zealand. Site A7i is the coarse inlet sediment and site A7ii is the finer sediment fraction in the forebay.



Figure 2.4 The 100 m long Grafton Gully SWTD, showing the fully uncovered inlet chamber (first compartment to the left) and the partially uncovered forebay chamber (in between the inlet and the Hiab truck).

2.1.2.1 Hamilton

Suitable sites (ranging in traffic volumes from ca. 250–24,000 vpd) were selected by Hamilton City Council personnel and the sweeping contractor, Excell Corporation (operating a Johnson vacuum sweeper truck). In addition to four Hamilton sites (H1–H4), a very low trafficked residential street (<200 vpd) was included from neighbouring

Ngaruawahia (provided by Unicus operating a Schwarz regenerative air sweeper). All catchpit samples (CP) were collected manually using a shovel. Details of the sampling sites are provided in Table 2.2.

Table 2.2 Details of RDS (sweepings = SW; catchpit sediments = CP) sampled from Hamilton and Ngaruawahia.

Street	Site no. H = Hamilton N = Ngaruawahia	RDS type	RDS sample abbreviation	Traffic volume ^a
Ulster St	H1	sweeping	H1SW	high
Ulster St	H1	catchpit	H1CP	high
Killarney Rd	H2	sweeping	H2SW	high
Killarney Rd	H2	catchpit	H2CP	high
Primrose and Lyon St	Н3	sweeping	H3SW	low
Primrose and Lyon St	Н3	catchpit	Н3СР	low
Victoria St	H4	sweeping	H4SW	medium-high ^b
Victoria St	H4	catchpit	H4CP	medium-high ^b
Newton Street	N1	sweeping	N1SW	low
Newton Street	N2	catchpit	N1CP	low

 $^{^{\}rm a}$ high >10,000 vpd; low <1000 vpd; and medium ca. 1000–10,000 vpd. $^{\rm b}$ 8250–11,300 vpd.

2.1.2.2 Christchurch

Suitable streets were identified by Christchurch City Council personnel and sweeping samples were collected by City Care (Schwarz regenerative air sweeper truck), except for C2SW which was collected by Excell Corporation using a Johnston vacuum sweeper. With the exception of C2CP which was sampled from a sump cleaning truck, all other catchpit sediments were manually collected. Details of the sampling sites are presented in Table 2.3.

Christchurch.

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Street/sector	Site no. C = Christchurch	RDS type	RDS sample abbreviation	Traffic volume ^a
Straven/Waimairi	C1	sweeping	C1SW	medium
Straven/Waimairi	C1	catchpit	C1CP	medium
CBD - sector	C2	sweeping	C2SW	high
CBD - sector	C2	catchpit	C2CP	high
Papanui Rd	C3	sweeping	C3SW	high
Papanui Rd	C3	catchpit	СЗСР	high
Condell/Greers/Normans	C4	sweeping	C4SW	low
Condell/Greers/Normans	C4i	catchpit	C4CPi	low
Condell/Greers/Normans	C4ii	catchpit	C4CPii	low
Nunweek residential	C5	sweeping	C5SW	low
Nunweek residential	C5	catchpit	C5CP	low

Details of RDS (sweepings = SW; catchpit sediments = CP) sampled from

2.2 Sample processing

2.2.1 General

Details of sample processing are illustrated Figure 2.5. Each of the 35 frozen RDS samples was de-thawed (1) and 2/3 of the sample removed for drying and processing (2). The remaining 1/3 of the sample was re-frozen and archived (1b). The majority of samples were dried to a constant weight in 40° C ovens, although catchpit samples that contained large amounts of water were lyophilised (freeze-dried). After drying, the total amount of RDS sediment was ca. 1-1.5 kg.

Prior to chemical analysis, it was necessary to determine the ideal size fraction cutoff that offered the best compromise between the analytical need for sample homogeneity (the need to be able to analyse representative subsamples) and the requirement to include as much of the RDS mass as possible to maintain 'real world' relevance. For example, the routinely used size cutoff of 500 μ m for metals analysis on sediments is useful for analytical precision, but would exclude a large percentage of RDS mass. To ensure 'real world' relevance, the project used a cutoff that included at least 75% of the mass of RDS. This was experimentally determined to be 5.6 mm (3).

All 35 RDS samples were analysed for TPH, PAHs and heavy metals, but only a representative subset of ca. eight samples were used for additional analyses (including contaminant analyses on individual particle size fraction), leaching and toxicity testing (Figure 2.5). The eight samples selected were chosen in accordance with the following criteria: contaminant concentrations between the 50th and 90th percentile range; samples from each of the three cities; and a similar number of street sweeping samples and catchpit sediments. The eight samples selected for further analysis were A2SW, H2SW, C1SW, C2SW, A2CP, A1CP, A7CPii and C2CP.

 $^{^{}a}$ high >10,000 vpd; low <1000 vpd; and medium ca. 1000–10,000 vpd.

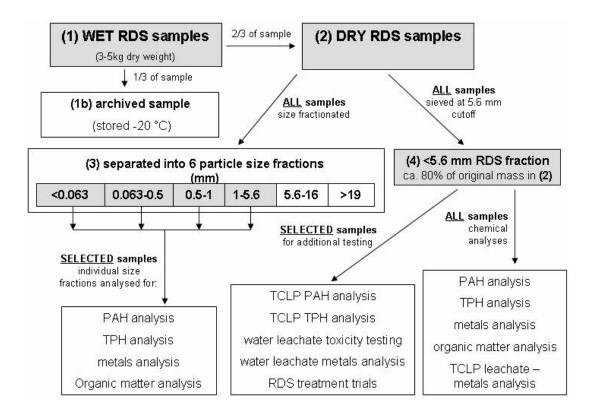


Figure 2.5: The processing and analytical pathways used for the RDS samples.

2.2.2 RDS sieving and size fractionation

A proportion of the total amount of each dried RDS sample (2) was fractionated through a stack of sieves with mesh sizes of 19 mm, 5.6 mm, 1.0 mm, 0.5 mm and 0.063 mm – resulting in six particle size fractions (3). The weight of all six particle size fractions was recorded and the percentage size distribution determined. Individual fractions (3) of selected samples were analysed for the parameters listed in Figure 2.5. Having ascertained that 5.6 mm cutoff included >75% of the RDS mass (3); the remaining quantity of whole dried RDS sample was sieved through a 5.6 mm sieve (4). The <5.6 mm fraction was used for all subsequent testing involving 'whole' RDS samples (4) in Figure 2.5.

2.3 Sample testing and analysis

2.3.1 General analytical procedures – heavy metals

2.3.1.1 Particulate analyses

Particulate metals concentrations in RDS were determined by the Landcare Environmental Laboratory (Palmerston North) using method 163 (Kovacs et al. 2000) which is similar to EPA SW 846 method 3050: Acid digestion of sediment, sludges and soils. The analytical suite of heavy metals consisted of cadmium, chromium, nickel, copper, lead and zinc. Briefly, weighed amounts RDS were treated with nitric acid and hydrogen peroxide to dissolve all heavy metals in the particulate matrix. The extraction filtrates were then analysed by flame or graphite furnace atomic absorption spectrometry (AAS).

2.3.1.2 TCLP leachate analysis

Toxicity characteristic leaching procedure (TCLP) is a relatively complicated leaching procedure that simulates conditions of wastes if they were to be disposed of in an ordinary sanitary landfill. TCLP extractions and metals analysis were performed by the Landcare Environmental Laboratory (Palmerston North) using the standard US EPA method 1311. Briefly, this method involved the following: Fifty grams of RDS were mixed with 1 L (1:20 RDS to extractant 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 suitability of extraction fluid #1 for the RDS samples was determined in accordance with Section 7.1.4 (of method 1311). This involves adding 96.5 ml of H_2O and 3.5 ml of 1N nitric acid to a 5 g sample of RDS – if the pH of this solution is <5, then extraction fluid #1 is sufficient to maintain a pH of <5 (mimicking landfill leaching conditions) for the duration of the TCLP extraction. The acidic leachate mixture was then filtered and the filtrate analysed for the heavy metals; chromium, nickel, copper, lead and zinc (via flame AAS).

2.3.1.3 Fresh water leachate analysis

Freshwater leachates were obtained via an analogous procedure to the TCLP method (Section 2.3.1.2) except de-ionised water was used as the extraction liquid (as opposed to acidic solution). The same extraction ratio of 50 g RDS to 1 L of extraction solution was used and where material was limited the quantities were scaled accordingly. Extractions were carried out in 2 L screw-cap Pyrex bottles (acid washed) and mixed on a shaker table for 18 hours before filtering through 0.45 µm glass fibre filters. A 10 ml subsample of the filtered leachate solution was 'preserved' with nitric acid and sent to Hill Laboratories (Hamilton) for heavy metal analysis. The metals (total arsenic, cadmium, chromium, copper, nickel, lead and zinc) were analysed in accordance with standard method APHA 3125 B 20th ed (1998) using ICP-MS.

The bulk of the filtered solution was not acidified and this was used for algal toxicity experiments (Section 2.3.3) and analysis of dissolved organic carbon (DOC) concentration. Leachate DOC was determined using method APHA 5310 B 20th ed (1998) (catalytic oxidation and infrared detection).

2.3.2 General analytical procedures – organics

2.3.2.1 Particulate analyses

A key to getting meaningful analyses is to ensure that the sample analysed is representative of the bulk sample. This was particularly important when analysing the <5.6 mm RDS (RDS (4) in Figure 2.5) because of the heterogeneous nature of the material. While 1-10 g samples are adequate for the analysis of homogeneous samples (ie individual size fractions), much larger sample sizes (ie 50-100 g) were used to analyse the <5.6 mm RDS.

Total petroleum hydrocarbons (TPH)

Particulate TPH analyses were carried out by Hill Laboratories (Hamilton) using standard methods US EPA 8015B/NZ OIEWG. Briefly, RDS were extracted with dichloromethane solvent using ultrasonication. The filtrates were analysed by gas chromatography equipped with a flame ionisation detector (GC-FID). The method quantified the TPH in 3 carbon bands, C_7 - C_9 (gasoline), C_{10} - C_{14} (diesel) and C_{15} - C_{36} (heavy).

Polycyclic aromatic hydrocarbons (PAH)

Particulate PAHs analyses were carried out by Hill Laboratories (Hamilton) in accordance with standard methods US EPA 3540 and 3630. Briefly, RDS were extracted with dichloromethane solvent using ultrasonication. The filtrates were cleaned up by silica gel chromatography and the PAHs quantified by gas chromatography mass spectrometry (GCMS) operated in selected-ion monitoring (SIM) acquisition mode. The PAHs analysed were the 16 priority PAHs listed by the US EPA, which include the following: naphthalene; acenaphthene; acenaphthylene; fluorene; phenanthrene; fluoranthene; pyrene; benza[a]anthracene; chrysene; benza[b]fluoranthene; benza[k]fluoranthene; benza[g,h,i]perylene. The seven underlined PAHs are classified as carcinogenic PAHs (cPAH).

Organic matter (OM)

Organic matter was determined by the 'loss on ignition' method (Organic Laboratory, NIWA Hamilton). For <5.6 mm size fractions, large samples (20-50 g) 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 $(100^{\circ}$ C) and combusted weight $(400^{\circ}$ C) being the amount of organic material present.

2.3.2.2 TCLP leachate analysis

The same procedure as outlined in Section 2.3.1.2, except the TCLP procedure (US EPA 1311) was carried out by Hill Laboratories (Hamilton) and the resulting filtrate was analysed for PAHs (16 US EPA) and TPH. Prior to analysis, the organic contaminants in the aqueous TCLP extracts were extracted into organic solvent (hexane). TPH (as above) were analysed by GC-FID using methods US EPA 8015B/NZ OIEWG (carbon bands). PAHs were analysed by GC-MS (operating in SIM acquisition mode) in accordance with US EPA TCLP method (modified).

2.3.3 Fresh water algal toxicity tests

Chronic toxicity testing of RDS leachates was determined using the fresh water alga, *Psuedokirchneriella subcapitata* (formerly known as *Selenastrum capricornutum*), by the Ecotoxicology Laboratory, NIWA (Hamilton) following NIWA Freshwater Algae Microplate Method #15.2. The freshwater leachates were prepared from selected RDS samples according to the method outlined in Section 2.3.1.3. A 50% dilution series, consisting of 10 concentrations ranging from 100% through to 0.2%, was prepared for each leachate. The dilutions were dispensed into a microplate (five replicates/dilution), then algal culture

at a concentration of 10,000 cells/ml was added to each dilution. After 72 hours of incubation at 24°C, the concentration of algae was measured using flow cytometry. Algal growth was measured as an increase in the concentration of algal cells. Algal growth tests are considered chronic tests because the effects are assessed over several generations during the exposure period. Toxicity data was analysed using $ToxCalc^{TM}$ statistical software and used to generate toxicological parameters including: NOEC (no observed effect concentration); LOEC (lowest observed effect concentration); ChV (chronic value) – the geometric mean between NOEC and LOEC; EC_{50} (effective concentration, 50%) – the concentration of a contaminant that results in a specified biological result (ie death, reduction in growth) in 50% of the test population compared to the control.

2.3.4 RDS amendment trials (contaminant stabilisation)

The leachate from C2CP (catchpit sediment from Christchurch CBD) exhibited the highest toxicity to algae and, therefore, this sample was used for amendment trials to determine whether the availability and toxicity of heavy metals could be reduced.

Two treatment amendment materials were trialled – compost and phosphate (Figure 2.5a). The compost was Dalton's brand compost purchased from The Warehouse. The phosphate was a mixture of potassium dihydrogenphosphate (KH_2PO_4) and disodium hydrogenphosphate (Na_2HPO_4) to maintain an extraction pH of 8. The compost was added to give a dry weight loading of 10% and 30% and phosphate was added at 0.1% and 0.5% (based on phosphorus content). The amendment trials of C2CP are listed in Table 2.4. To facilitate physical and chemical interactions between the contaminants and the stabilising material, water was added to the dry C2CP RDS to give a moisture content of ca. 30% (ca. 12 ml per 40 g of RDS). Two controls containing no amending agent were used, one with added moisture and one without.

Table 2.4	Treatment amendments of RDS sample C2CP.
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Sample	Stabilising agent	% of stabilising agent – based on:		
		mass of stabilising	dry weight ^a and	
		agent added	phosphorus content ^b	
Control (wet)	-	0	0	
Control (dry)	-	0	0	
10%-compost ^a	compost	20	10ª	
30%-compost ^a	compost	60	30ª	
0.1%-phosphorus ^b	phosphate	0.45	0.1 ^b	
0.5%-phosphorus ^b	phosphate	2.27	0.5 ^b	

^a The compost used contained 50% moisture. ^b The phosphate stabilising agent (potassium phosphate) contained ca. 22% of elemental phosphorus (P).

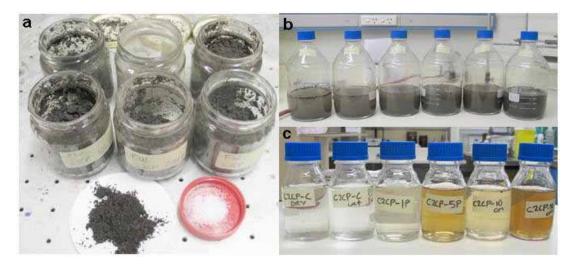


Figure 2.5 (a) Amendment of Christchurch CBD catchpit samples (C2CP) with compost (left foreground) and phosphate (right foreground). (b) Leachate mixtures following 18 h extraction. (c) Filtered leachates ready for metals analysis and toxicity testing.

The moistened RDS (C2CP) samples (40 g dry weight) were mixed with the appropriate amount of stabilising material in screw cap jars (Figure 2.5a). The mixtures were then left to 'age' for ca. five days, but were stirred/mixed twice daily to maintain adequate aeration. The aged treatments, all of which contained 40 g of RDS, were extracted with 800 ml of water according to the method described in Section 2.3.1.3. A portion of the filtered leachates was used for algal toxicity testing (refer to Section 2.3.3) and acid-stabilised aliquots of the leachates were sent to Hill Laboratories (Hamilton) for metals analysis (refer to Section 2.3.1.3).

2.3.5 Statistical analysis

To determine whether differences in the medians of different groups were significant, the non-parametric Mann-Whitney U test (also known as Mann-Whitney-Wilcoxon, Wilcoxon rank-sum, or Wilcoxon-Mann-Whitney test) was used to analyse the data (Datadesk® v6.1). The null hypothesis for this test is that the medians of the two groups (ie A and B) are the same ie Ho: median (A) = median (B). The alpha level for rejecting the null hypothesis is 0.05; hence for p values \le 0.05, the null hypothesis was rejected – ie the group medians were not equal.

3. Results and discussion

In addition to presenting the physical and characterisation data of the 35 RDS samples as a whole data set, where beneficial, the results are also compared by city, RDS sample type (ie sweeping vs catchpit sediment) and traffic volume (ie low, medium and high). Because typical contaminant concentrations have been reviewed in Chapter 1, the RDS characterisation results are presented in a largely descriptive format with minimal comparison to other literature studies. For comparisons of contaminant concentrations in New Zealand RDS with other literature studies the reader is encouraged to refer to concentrations and reference included in Table 1.1 (hydrocarbons) and Table 1.2 (metals).

3.1 Characterisation I: Physical properties

Detailed size fractionation data for RDS samples are listed in Table A.1 (Appendix A).

3.1.1 Particle size distribution

The median particle size distribution for all RDS showed a bimodal distribution at 5.6-1 mm and 0.5-0.063 mm, with the latter being the most abundant fraction (Figure 3.1).

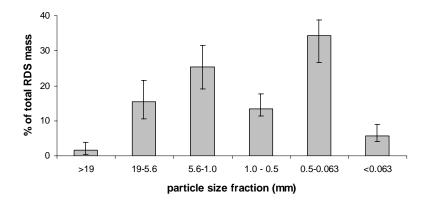


Figure 3.1 Median particle size distribution for all RDS (catchpit sediments and sweepings) – 'error bars' represent the upper and lower quartile range.

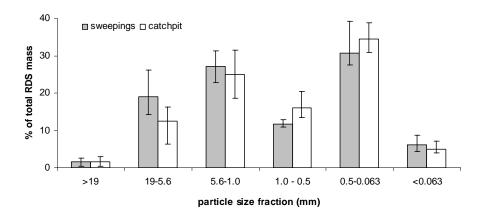


Figure 3.2 Median particle size distribution for street sweepings (grey bars) and catchpit sediments (white bars). 'Error bars' represent the upper and lower quartile range.

3.1.1.1 Particle size distribution: comparing RDS type

The comparison of particle size distribution between RDS sample types (Figure 3.2) indicated that, with the exception of the 1.0–0.5 mm fraction (p=0.006), there was no significant difference between catchpit sediments and street sweepings. This result is consistent with New Zealand sweepings being collected with high-efficiency sweeper trucks. Vacuum trucks have been shown to collect 90% of particles <250 μ m (Breault et al. 2005), meaning that there is limited scope for the enrichment of fine particulates in catchpit sediments. In contrast, low-efficiency mechanical sweepers only collect 10% of fines <250 μ m, leaving 90% of fine particulates behind to concentrate in catchpit sediments. The latter scenario is presumably why catchpit sediments in some United States studies have been reported to have much greater percentages of fine particulates and, therefore, higher concentrations of contaminants (refer to discussion in Section 1.3.1.1).

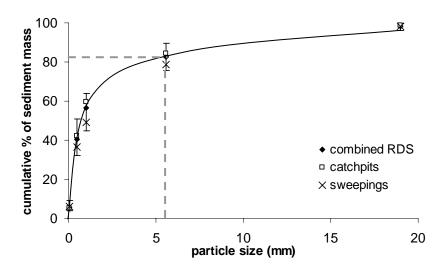


Figure 3.3 Median particle size cumulative distributions for RDS (combined, \spadesuit), catchpit sediments (\Box) and sweepings (x). 'Error bars' represent the upper and lower quartile range for the 'combined' data (curve is estimated best fit for 'combined' data).

Figure 3.3 shows that the median percentage of RDS mass passing through a 5.6 mm sieve was 82% (grey dashed line), with upper and lower quartiles of 76% and 90% (upper and lower quartile range of 76–90%). This exceeded the target to include at least 75% of the RDS to maximise the 'real world' relevance of the study.

3.1.1.2 Particle size distribution: comparing cities

Figure 3.4 shows the individual size fractions of all RDS for the three cities included in the study – Auckland, Hamilton and Christchurch. Based on the median values, Christchurch RDS appeared to be enriched in fine particulates (<0.5 mm), relative to Hamilton and Auckland RDS samples. Many of the differences in the median concentrations between Christchurch and Auckland, and between Christchurch and Hamilton were significant (p<0.05), although the real world significance of such differences is debatable given the relatively small sample sizes. One possible outcome of having a large proportion of fines in RDS may be that washing treatments targeting the removal of fines may result in greater percentage reductions of contaminant loads. There were no significant differences between the particle size distributions of RDS samples from Auckland and Hamilton.

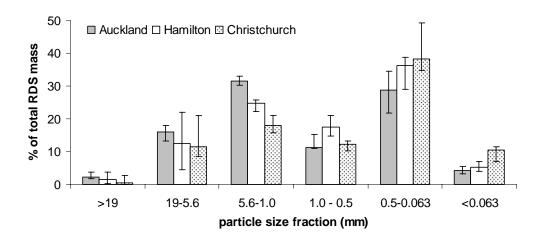


Figure 3.4 Median particle size distribution for RDS from Auckland (grey bars), Hamilton (white bars) and Christchurch (dotted bars) – excludes Ngaruawahia samples (N1SW and N1CP). 'Error bars' represent the upper and lower quartile range.

The RDS from all three cities showed a bimodal distribution at 0.5-0.063 mm and 5.6-1.0 mm. The coarser Auckland RDS differed from the other two cities in that the most dominant mass fraction was the 5.6-1.0 mm range particulates (as opposed to 0.5-0.063 mm for Hamilton and Christchurch).

3.1.2 Organic matter

3.1.2.1 All RDS samples: <5.6 mm fraction

In determining the feasibility of reusing RDS in New Zealand, a parameter of interest is the amount of organic matter present. Organic matter (OM) content was determined for all RDS (<5.6 mm) by determining the mass loss on combustion at 400°C (refer to Table A.2, Appendix A for individual OM values). Percent OM data is summarised in Figure 3.5.

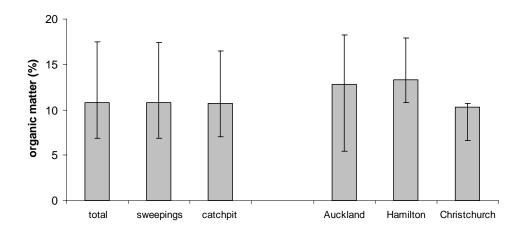


Figure 3.5 Median percent organic matter (OM) in RDS samples ('error bars' on the median bars represent lower and upper quartile range).

There was no significant difference in OM content between street sweepings (median 10.8%) and catchpit sediments (median 10.7%). The OM content of RDS from the three cities was also very similar, with no significant difference between the median OM values for Auckland (12.8%), Hamilton (13.3%) and Christchurch (10.3%).

3.1.2.2 Selected RDS samples: individual size fractions

The following RDS had their individual size fractions analysed for organic matter: A1SW; A2SW; A1CP; H3SW; H3CP; C1SW and C1CP (refer to Table A.3 for OM data for complete OM data set for individual fractions). The median percentage OM values for the particle size fractions were relatively constant, ranging from 8 to 10% (grey bars, Figure 3.6). The contribution of each particle size to total OM content followed the same bimodal distribution (white bars, Figure 3.6) observed for particle size mass distribution (refer to Figure 3.1).

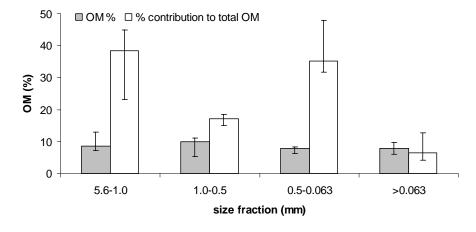


Figure 3.6 Percent organic matter (OM) in individual particle size fractions. Grey bars represent the median of 7 RDS samples ('error bars' represent the lower and upper quartile range).

Figure 3.7 shows the large variation that exists between individual samples. For example, the Auckland sample contained much higher amounts of organic matter in the coarser 5.6–1.0 mm fraction, while Hamilton and Christchurch sweepings contained ca. 50% of the OM in the finer 0.5–0.063 mm fraction. The distribution of organic matter will be highly dependent on the type of vegetation adjacent to the road and on the season. Presumably the distribution of OM in the Auckland sweeping sample was influenced by a recent deposition of vegetative matter (ie leaves, seeds or flowers).

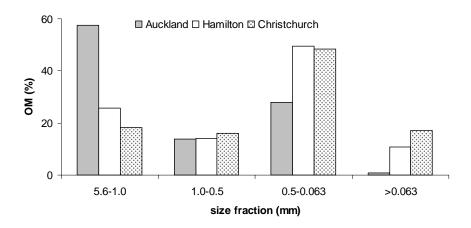


Figure 3.7 Contribution of particle sizes to total organic matter (OM) content in three individual RDS samples.

3.2 Characterisation II: Chemical contaminants

3.2.1 Total petroleum hydrocarbons (TPH)

TPH consist of three carbon ranges, C_7 - C_9 (petrol range), C_{10} - C_{14} (diesel range) and C_{15} - C_{36} (heavy oil range, including bitumen). Consistent with the findings of other studies, the petrol and diesel range hydrocarbons were all below detection limit (10– $30~\mu g/g$) in the RDS. The TPH concentrations were comprised of only 'heavy range' hydrocarbons (refer to Table A1.4 for individual TPH concentrations). The concentration of TPH in RDS ranged from 120 $\mu g/g$ in Ngaruawahia catchpit sediment N1CP, through to 5260 $\mu g/g$ in Auckland sweepings sample (A2SW – commercial site). The median, lower and upper quartile TPH concentrations were 1220 $\mu g/g$, 935 $\mu g/g$ and 1740 $\mu g/g$ respectively, which are comparable to the 1680 $\mu g/g$ mean reported by Latimer (1990) for highway RDS (refer to Table 1.1). TPH data for all samples, RDS type and city are summarised as median values in Figure 3.8.

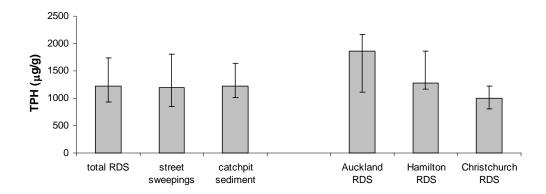


Figure 3.8 Median TPH concentrations (μ g/g) in RDS represented as: all samples (total RDS); type of RDS (sweeping/catchpit); and city of origin. 'Error bars' represent the lower and upper quartile range.

There were no significant differences between the median concentrations of TPH in catchpit sediments (1220 $\mu g/g$) and street sweepings (1190 $\mu g/g$), which is consistent with the similar particle size distribution of the two RDS types (Section 3.1.1). This indicates that, for at least TPH, the assumption that catchpit sediments are more contaminated than street sweepings is not correct in New Zealand where high-efficiency sweepers are used.

3.2.1.1 TPH: comparing RDS from different cities

On average, Auckland samples contained higher concentrations of TPH than those from either Hamilton or Christchurch – respective median concentrations were 1865 μ g/g, 1275 μ g/g and 1000 μ g/g. Despite considerable variation in Auckland RDS samples (ie interquartile range of 1055 μ g/g), the difference between the median TPH concentrations in Auckland and Christchurch RDS samples was significant (p=0.03). Reasons for the higher TPH concentrations in Auckland RDS samples are not apparent.

3.2.2 Polycyclic aromatic hydrocarbons (PAHs)

The total concentration of PAHs in RDS ranged from 0.2 μ g/g (H5SW and A5CP) to 30.5 μ g/g (A3CP). For all RDS samples, the median, lower and upper quartile PAH concentrations were 6.3 μ g/g, 3.2 μ g/g and 11.2 μ g/g, respectively, indicating that the highest concentrations (ie up to 30 μ g/g) were well above the typical range for New Zealand RDS (Figure 3.9). Previous NIWA research has shown that high concentrations of PAHs in RDS (ie >20-25 μ g/g) are probably attributable to coal tar contaminated particulates and are not typical of 'normal' RDS (Depree and Ahrens 2007).

The median PAH concentration in RDS from this study was consistent with the 3–8 μ g/g range reported by other researchers (refer Table 1.1 in Section 1.3.1.1). With respect to New Zealand studies, Brown and Peake (2006) reported mean PAH concentrations of 4.4 μ g/g (sweepings) and 6.5 μ g/g (catchpit sediments) for Dunedin RDS; and Depree and Ahrens (2003) reported concentrations of 3–6 μ g/g for RDS collected from New Zealand state highways (ie SH16, Auckland and SH1, Hamilton).

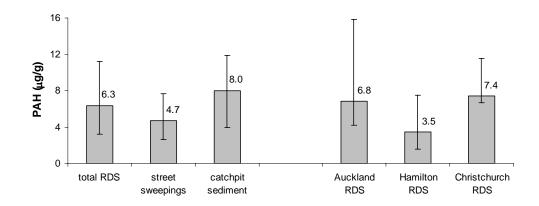


Figure 3.9 Median PAH (total) concentrations (μ g/g) in RDS represented as: all samples (total RDS); type of RDS (sweeping/catchpit); and city of origin. 'Error bars' represent the lower and upper quartile range.

Based on median values (Figure 3.9) catchpit sediments (8.0 ug/g) contained higher concentrations of PAHs than street sweepings (4.7 μ g/g); however, the difference was not significant (ie p=0.23) on account of the large variation in the concentrations. There were no significant differences between the median PAH concentrations in RDS from the three cities. The median and lower-upper quartile span of PAH concentrations were as follows: Auckland 6.8 μ g/g, 4.2–15.8 μ g/g; Hamilton 3.5 μ g/g, 1.6–7.5 μ g/g; and Christchurch 7.4 μ g/g, 6.7–11.5 μ g/g.

3.2.3 Heavy metals - lead, copper and zinc

The median concentration of lead, copper and zinc in RDS (total, sweepings and catchpit sediments) are summarised in Table 3.1. Heavy metal concentrations for individual RDS samples are given in Table A.6 (Appendix A). The levels of lead, copper and zinc found in this study were comparable to the other studies listed in Table 1.2 (Section 1.3.1.2) – the typical ranges for lead (post ban on leaded petrol), copper and zinc were estimated as $100-200~\mu g/g$, $100-300~\mu g/g$ and $300-900~\mu g/g$ respectively. With respect to New Zealand studies, Brown and Peake (2006) reported respective lead, copper and zinc concentrations of 289, 129, and 528 $\mu g/g$, for street sweepings and 262, 179 and 424 $\mu g/g$ for catchpit sediments.

As with the study by Brown and Peake (2006), the concentrations of lead in RDS reported in Table 3.1 are much lower than in many of the pre-1990 studies where lead petrol was a major source of lead in RDS. During this era, lead concentrations in RDS (and urban street dust) as high as ca. 4000 μ g/g were not uncommon. For example, in a review of the subject, Fergusson and Kim (1991) provided a typical lead concentration range of 500–4000 μ g/g, while Harrison (1979) reported 920–3560 μ g/g of lead in 13 urban street dust samples. Accordingly, the low concentrations of lead reported in this study (median of 122 μ g/g) reflect the 11-year absence of lead additives in petrol (leaded petrol banned in 1996).

Table 3.1 Median heavy metal concentrations (lower-upper quartile concentration range in parentheses) in RDS. Note: typical New Zealand soil concentrations are provided to highlight anthropogenic inputs over above background concentrations.

	Lead (µg/g)	Copper (µg/g)	Zinc (µg/g)
RDS (all samples)	122 (57–170)	67 (41–119)	422 (303-555)
Street sweepings	117 (59–137)	55 (36-129)	336 (283-426)
Catchpit sediments	133 (58-183)	85 (48-116)	464 (418-706)
New Zealand soils ^a	(10-30)	27 (1-76)	68 (7-97)

^a typical mean concentrations (range in parentheses)

A summary of lead, copper and zinc concentrations in RDS, categorised by total, type (ie sweepings vs catchpits) and city, are provided in Figures 3.10 (lead), 3.11 (copper) and 3.12 (zinc). Comparing street sweepings with catchpit sediments, the only significant difference (ie p < 0.05) in median concentrations of the three metals was for zinc (p = 0.03). The similarity in metal concentrations between road sweepings and catchpit sediments is consistent with PAH and TPH, and further supports the assertion that catchpit sediments in New Zealand are not significantly more contaminated than street sweepings. As mentioned previously, this is presumably because high-efficiency sweepers result in similar proportions of contaminated fine particulates in both sweepings and catchpit sediments.

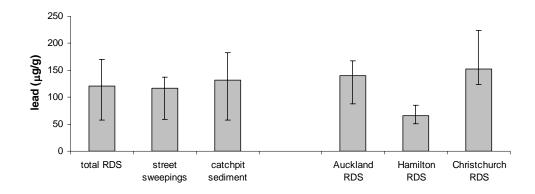


Figure 3.10 Median lead concentrations (μ g/g, dry weight) in RDS represented as: all samples (total RDS); type of RDS (sweeping/catchpit); and city of origin. 'Error bars' represent the lower and upper quartile range.

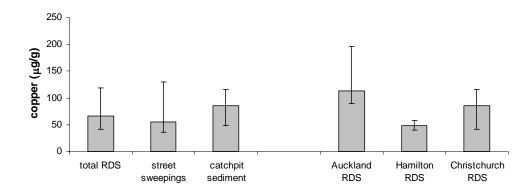


Figure 3.11 Median copper concentrations (µg/g, dry weight) in RDS represented as: all samples (total RDS); type of RDS (sweeping/catchpit); and city of origin. 'Error bars' represent the lower and upper quartile range.

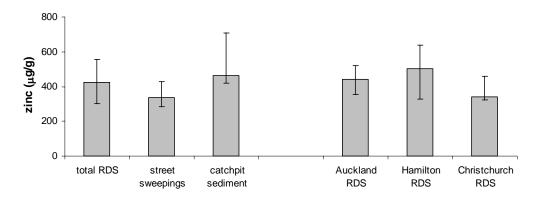


Figure 3.12 Median zinc concentrations (μ g/g, dry weight) in RDS represented as: all samples (total RDS); type of RDS (sweeping/catchpit); and city of origin. 'Error bars' represent the lower and upper quartile range.

There were significant differences between the median copper concentrations in RDS from different cities, with the order being Auckland > Christchurch > Hamilton. Hamilton also contained significantly lower concentrations of lead compared with Christchurch. There were no significant differences in the median RDS zinc concentrations for the three cities.

3.2.4 Contaminants in individual particle size fractions

Of the 35 total RDS samples, seven 'representative' samples – namely, A1SW, A2SW, A1CP, H3SW, H3CP, C1SW, and C1CP – were selected for further analysis to determine the particle size distribution of the contaminants. The seven samples were selected to include: a range of contaminants (generally higher than median levels); all three cities; and 'matched' sweeping/catchpit pairs for comparison. For each sample, the 5.6–1.0 mm, 1.0–0.50 mm, 0.50–0.063 mm and the <0.063 mm size fractions were analysed for TPH, PAHs and heavy metals. The contaminant concentrations for the individual particle size fractions are provided in Table A.7 (TPH), Table A.8 (PAHs) and Table A.9 (metals) in Appendix A.

3.2.4.1 TPH

As expected, the highest concentration of TPH in RDS was associated with the fine fraction (<63 μ m); containing, on average, twice the concentration of TPH than in the coarser particle size fractions (Figure 3.13). The coarser particle size fractions, that is 5.6–1.0, 1.0–0.5, and 0.5–0.063 mm fractions, all contained comparable amounts of TPH. Despite the enrichment of TPH in the fine particles, the percentage contribution to total TPH loading in RDS samples (grey bars, Figure 3.14) was largely determined by the particle size mass distribution (white bars, Figure 3.14). This result indicates that treatments such as washing to remove particulate fines will only reduce total TPH contaminant loadings by ca. 10%.

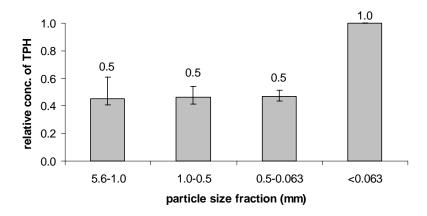


Figure 3.13 Relative concentrations of TPH contaminants in different particle size fractions. Data shown are median values – 'error bars' represent the lower and upper quartile range.

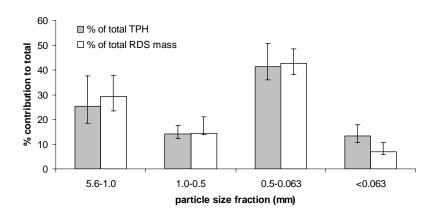


Figure 3.14 Contribution of particle size fractions to total TPH loading (grey bars) and total mass (white bars) of the RDS samples. Data shown are median values – 'error bars' represent the lower and upper quartile range.

3.2.4.2 PAHs

The highest concentrations of PAHs were associated with the fine fraction (<63 μ m), although the enrichment was less pronounced than for TPH (Figure 3.15). Compared with TPH distribution (Figure 3.13), the 0.5–1.0 mm fraction was enriched (70% of <63 μ m

value) and the 5.6-1.0 mm fraction was depleted (only 30% of $<63~\mu m$ value) in PAH contaminants. The different particle size distribution of PAH vs TPH is presumably indicative of the different sources that contribute to these two contaminant types.

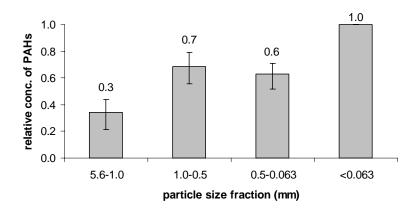


Figure 3.15 Relative concentrations of PAH contaminants in different particle size fractions. Data shown are median values – 'error bars' represent the lower and upper quartile range.

As for TPH, the percent contribution of each size fraction to the total PAH loading in the RDS samples (grey bars, Figure 3.16) was largely determined by the particle size mass distribution (white bars, Figure 3.16). Figure 3.16 shows that while containing the highest concentration of PAHs, the fine clay and silt fraction (<63 μ m) still accounts for only ca. 11% (median value) of the PAHs in RDS. The relatively small proportion of contaminants associated with the fines (ca. 10%) should be an important consideration when assessing the relative merits of treatment options such as sediment washing.

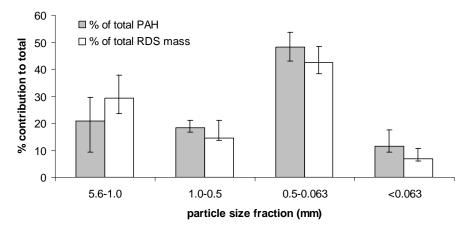


Figure 3.16 Contribution of particle size fractions to total PAH loading (grey bars) and total mass (white bars) of the RDS samples. Data shown are median values – 'error bars' represent the lower and upper quartile range.

3.2.4.3 Heavy metals

As expected, the highest concentration of metals resided in the silt/clay fraction ($<63 \mu m$), with this fraction containing ca. twice the metal concentrations of coarser fractions (Figure 3.17). However, at two sites (A2SW and C2SW) the larger particle size fractions

contained higher concentrations of lead. A2SW contained 889 μ g/g in the 0.5–0.063 mm fraction (cf. to 356 μ g/g in <63 μ m fraction) and C2SW contained 985 μ g/g of lead in the 5.6–1.0 mm fraction (cf. to only 222 μ g/g in <63 μ m fraction). These two results are the reason for the 'negative' error bar on the <0.063 mm size fraction for lead (Figure 3.17).

The concentrations of heavy metals in the <63 μ m particle size fraction ranged from 87–425 μ g/g for lead, 129–1233 μ g/g for copper, and 303–1307 μ g/g for zinc. The occurrence of the highest lead concentration (985 μ g/g) in the coarse 5.6–1.0 mm fraction of A2SW suggests that the sample may have contained a discrete object that contributed the majority of the lead in this coarse fraction – as opposed to a homogenous distribution of lead dispersed and/or adsorbed to the coarse particulate material.

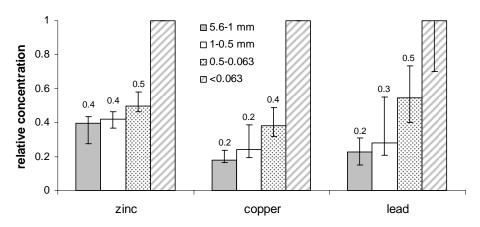


Figure 3.17 Relative concentrations (to the size fraction with the highest concentration) of zinc, copper and lead in different particle size fractions. Data shown are median values – 'error bars' represent the lower and upper quartile range.

Of the three metals, copper appeared to be most enriched in the <63 μ m fraction, relative to the three coarser fractions (Figure 3.17). This was confirmed in Figure 3.18 by the observation that the fine fraction accounted for >20% of the total copper loading in RDS. Although the <0.063 μ m fraction accounted for only ca. 7% (median) of the RDS mass, it contained 15%, 21% and 16% (median values) of the total RDS loading of lead, copper and zinc, respectively. The opposite trend was observed for the coarsest size fraction (5.6–1.0 mm), accounting for 30% of RDS mass, but only 14%, 17% and 21% (median values) of total amount of lead, copper and zinc, respectively. Despite the enrichment, removal of the fines is expected to only remove ca. 20% of heavy metals from RDS. It is worth noting that dry sieving can result in the fraction of fine particulate (<0.063 mm) being underestimated because it adheres to larger particles during the drying process.

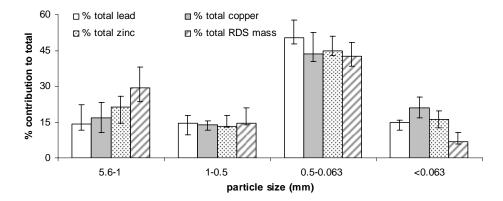


Figure 3.18 Contribution of particle size fractions to total loadings of lead, copper, zinc and total RDS mass. Data shown are median values – 'error bars' represent the lower and upper quartile range.

3.2.5 Effect of traffic volume on RDS contaminant levels

As a major source of contaminants in RDS is related to vehicles (soot emissions, tyre abrasion, road surface abrasion and brake pad wear), it is reasonable to assume that RDS collected from highly trafficked streets will contain significantly higher contaminant levels than RDS from low trafficked (ie residential) streets. For example, Latimer et al. (1990) reported TPH concentrations of $1680~\mu\text{g/g}$ and $353~\mu\text{g/g}$ for street dust from a highway and residential site, respectively. Heavy metals were also significantly reduced at the residential site, with zinc concentrations of $336~\mu\text{g/g}$ in highway dust and $48~\mu\text{g/g}$ in the residential street dust. The lower levels of contaminants in RDS from low trafficked residential sites may make these materials more amenable for reuse.

Catchment usage also influences contaminant levels in RDS with the general contaminant trend being industrial > commercial > residential. Catchment/street use (ie residential vs commercial vs industrial) was not taken into account when selecting sampling sites for this project – that is, the focus was exclusively on the effects of vehicle numbers. Accordingly, each traffic category (ie high, medium, low) may be comprised of RDS from different landuse types, but they were mainly a mixture of predominately commercial and residential. Only site A2 (Auckland) was in an industrial zone. The traffic classification of each site is given in Tables 2.1–2.3 (Section 2).

3.2.5.1 PAHs

Median PAH concentrations in RDS from sites with high, median and low traffic volumes were 11, 8 and 4 μ g/g, respectively (Figure 3.19). The large variation (particularly for the high traffic RDS) meant the difference in PAHs between high and medium sites was not significant (p=0.86). However, the concentration of PAHs in RDS from low trafficked sites was significantly lower than for either the high (p=0.04) or medium (p=0.01) trafficked sites. The concentration of PAHs was not directly related to traffic volumes – a ~20-fold reduction in vehicle numbers only resulting in a <3-fold reduction in PAHs. Karlsson and Viklander (2008) reported similar results from catchpit sediments collected from a residential area (ca. 500 vdp) and a major arterial (ca. 25,500 vpd), with median PAH

concentrations of 4 μ g/g and 17 μ g/g, respectively. For that study, the 50-fold decrease in vehicle numbers corresponded to a 4-fold reduction in the concentration of PAHs in RDS. However, if the unusually high naphthalene concentrations (ie 50% of the total PAHs) are subtracted, the respective total PAH concentrations for the residential and arterial road reduce to 2 μ g/g and 5 μ g/g. This corresponds to just a 2.5-fold reduction in PAHs despite a 50-fold reduction in traffic volume.

Although traffic and PAH concentrations are not directly related, the results of this study, and those of Karlsson and Viklander (2008), show that RDS from low trafficked streets (ie residential) contains ca. two times lower concentrations than material collected from main arterial roads. This may be beneficial with respect to selectively targeting RDS from low trafficked streets for reuse applications that need to reduce environmental concerns about carcinogenic PAHs.

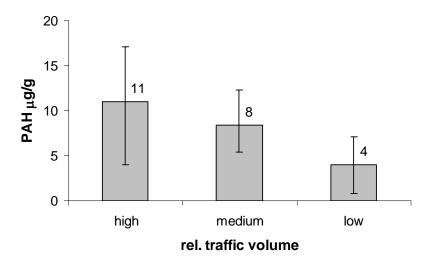


Figure 3.19 Effect of traffic volume on PAH concentrations in RDS. Data shown are median values – 'error bars' represent the lower and upper quartile range.

3.2.5.2 Heavy metals

The general trend of lower contaminant concentrations corresponding to low trafficked streets was generally observed, with lowest median concentrations corresponding to the RDS from low trafficked sites. There was very little differentiation between high and medium trafficked sites, with the latter generally exhibiting slightly higher concentrations (Figure 3.20). The median concentrations of lead and copper in RDS from low sites were significantly lower than those from medium and/or high sites; however, the difference in zinc concentrations was not significant. The median RDS zinc concentration at low sites was not significantly lower than either of the more highly trafficked sites. The weak correlation between metal concentrations and traffic volume could be due to a couple of reasons. Firstly, sources of metal include tyres and brake pads, therefore, the nature of site (corners, braking, gradient, intersections etc) will have a large impact on the amount of metals released per vehicle. For example, O'Riley et al (2002) reported zinc concentrations in catchpit sediments of 203 μ g/g and 240 μ g/g at two traffic light intersections, and 794 and 1090 μ g/g at two roundabout sites where tyre wear is much

more pronounced. Secondly, depending on the roofing material, a significant source of zinc (and potentially copper) in stormwater is thought to be derived from roof runoff (Kennedy et al. 2004). This non-vehicle related input of zinc may explain the relatively high concentrations observed in RDS from low trafficked sites (Figure 3.20).

For copper and lead, the low trafficked sites (ie residential), contained approximately onethird of the concentrations in RDS from sites with higher traffic volumes (ie 'high' and 'medium'). Hence, as concluded for PAHs, there may be an advantage in targeting RDS from low traffic volume streets to minimise since this material contains less contaminants and, therefore, is more amenable for potential reuse applications.

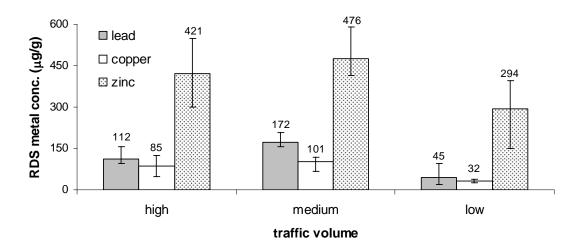


Figure 3.20 Contribution of particle size fractions to total loadings of lead, copper, zinc and total RDS mass. Data shown are median values – 'error bars' represent the lower and upper quartile range.

3.3 RDS risk assessment I: Comparison with guideline values

3.3.1 New Zealand landfill leaching guidelines

As a starting point, it is useful to compare the RDS collected in the study with New Zealand landfill guidelines. The landfill guidelines are based on the risk of high concentrations of contaminants leaching from materials under the acidic conditions typical of landfill leachates. Although not particularly relevant to RDS reuse applications, since the major mobilisation risk comes from rain water and not acidic landfill leachates, the landfill guidelines are considered a necessary starting point in the process – simply because the current situation requires that all RDS be landfilled in New Zealand.

Following on from the brief introduction of New Zealand landfill guidelines in Section 1.3.5.1, the landfill classification system divides landfills into two classes, each with different levels of environmental protection:

Class A landfills: landfills that meet the site selection and design standards outlined in the Centre for Advanced Engineering's (2000) landfill guidelines. These landfills are sited in areas to reduce the potential for adverse effects and are engineered to contain and/or collect landfill leachate and landfill gas.

Class B landfills: existing landfills that do not meet the site selection and design standards outlined in the Centre for Advanced Engineering's (2000) landfill guidelines. These landfills have limited or no engineered systems designed to collect landfill leachate or gases, and may be in areas that pose a risk to the environment.

Waste acceptance criteria for landfills are based on maximum contaminant concentrations in acidic leachates, which are normally assessed using the US EPA TCLP (toxicity characteristic leaching procedure) test. To limit the expense and complexity of analysis, 'screening limits' have been derived by multiplying the TCLP criteria by 20, based on the assumption that all the contaminant is transferred to the leachate. Although Class A criteria for selected contaminants were covered in Table 1.6, Table 3.2 contains Class A and Class B criteria (screening and TCLP limits) for the contaminants included in this study (MfE 2004). Naphthalene is the only PAH included because this is the most mobile PAH (ie highest water solubility) and is considered a risk driver for non-carcinogenic PAHs. Appendix B (MfE 2004) of the guideline document states that total benzo[a]pyrene (BaP) concentrations should be determined; however, no guideline value is provided.

Table 3.2 Total concentration (screening criteria) and leachability limits (TCLP) for Class A and Class B landfills (taken from Appendix A – MfE 2004)

Contaminant	Class A	landfills	Class B landfills	
	Screening Leachate conc. criteria (µg/g) (µg/ml)		Screening criteria (µg/g)	Leachate conc. (µg/ml)
Naphthalene	200	10	20	1
Lead	100	5	10	0.5
Copper	100	5	10	0.5
Zinc	200	10	20	1

3.3.1.1 PAHs

The highest total concentration of naphthalene in the RDS was 0.3 μ g/g (Appendix A, Table A.5), which is well below the screening criteria value of 200 μ g/g. Even if 100% of the naphthalene was mobilised, the maximum leachate concentration of <0.02 μ g/ml would be 60- and 600-fold lower than Class B and Class A criteria, respectively. This strongly indicates that PAHs (at least non-carcinogenic ones based naphthalene risk) in RDS are not an issue in regards to landfill disposal guidelines in New Zealand. This was subsequently confirmed by TCLP testing results on the seven RDS samples, A1CP, A2SW, A4SW, C1CP, C3SW and H3SW, where the highest detected concentration of naphthalene was 0.00008 μ g/ml (or 80 parts per trillion!).

3

3.3.1.2 Metals - screening criteria

In contrast to PAHs, the median concentrations of lead and zinc in RDS exceeded the screening criteria for Class A landfills (Figures 3.21 and 3.22). The median concentrations of lead, copper and zinc were 122 μ g/g, 67 μ g/g and 422 μ g/g. The median zinc concentration was more than twice the screening criteria value of 200 μ g/g. According to the waste acceptance decision process (MfE 2004), many of the RDS collected as part of this study would require TCLP testing to determine suitability for landfill disposal (Section 3.3.1.3). As mentioned, the screening criteria are a 'first estimate' based on theoretical maximum concentrations assuming that 100% of the metal contaminants are solubilised or extracted. In practice, however, only a relatively small fraction of the metal is extracted under these conditions (Section 3.3.1.3). Regardless of TCLP testing, the screening results indicate that RDS do contain significant concentrations of heavy metal contaminants, and as such, reusing this material will need to consider any potential environmental risks.

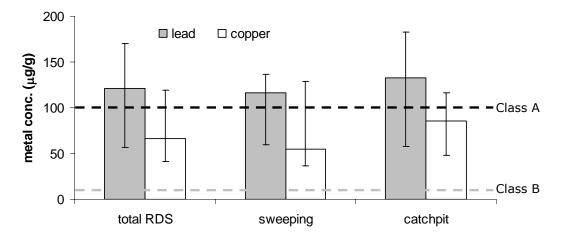


Figure 3.21 Median concentrations of lead and copper in RDS samples (total and separated into 'sweeping' and 'catchpit') compared with New Zealand screening criteria values for Class A (black dashed line, 100 μ g/g) and Class B (grey dashed line, 10 μ g/g) landfills. Data shown are median values – error bars represent the lower and upper quartile range.

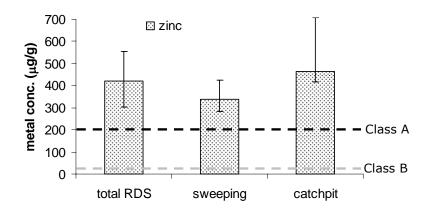


Figure 3.22 Median concentrations of zinc in RDS samples (total and separated into 'sweeping' and 'catchpit') compared with New Zealand screening criteria values for Class A (black dashed line, 200 μ g/g) and Class B (grey dashed line, 20 μ g/g) landfills. Data shown are median values – error bars represent the lower and upper quartile range.

3.3.1.3 Metals - leachate concentrations (TCLP)

Having exceeded the landfill screening concentrations, TCLP extractions using a weak acid solution were undertaken. Individual TCLP concentrations of lead, copper and zinc for all 35 RDS samples are listed in Table A.10 (Appendix A).

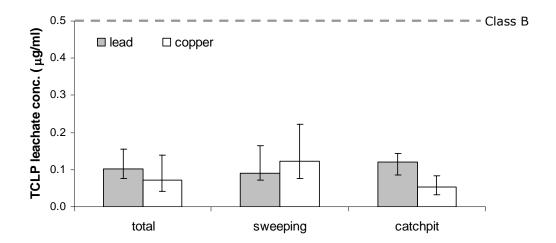


Figure 3.23 Median TCLP leachate concentrations of lead and copper in RDS samples (total and separated into 'sweeping' and 'catchpit') compared with the New Zealand guideline value for Class B landfills of 0.5 μ g/ml (grey dashed line). Class A leachate value of 5 μ g/ml is off-scale. Data shown are median values – error bars represent the lower and upper quartile range.

The median concentrations of lead and copper in TCLP leachates from the RDS samples were 0.10 μ g/ml and 0.07 μ g/ml, respectively. Both of these concentrations are well below the Class B landfill maximum value of 0.5 μ g/ml (Figure 3.23). The Class A landfill guideline value for lead and copper is 5 μ g/ml (off-scale). The median TCLP concentration of zinc was 4.6 μ g/ml, which is less than the Class A guideline value (10 μ g/ml), but significantly higher than the Class B value of 1 μ g/ml (Figure 3.24). On the basis of this

data, most RDS in New Zealand may not meet the requirements for disposal in Class B landfills.

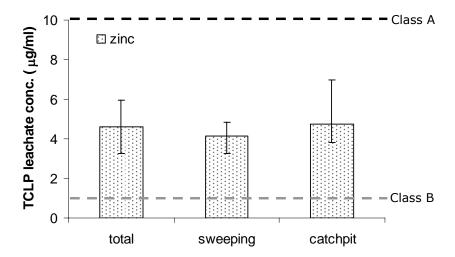


Figure 3.24 Median TCLP leachate concentrations of zinc in RDS samples (total and separated into 'sweeping' and 'catchpit') compared with New Zealand guideline values for Class A (black line, 10 µg/ml) and Class B (grey line, 1 µg/ml) landfills. Data shown are median values – error bars represent the lower and upper quartile range.

Zinc is more problematic than either copper or lead because it is ca. 10 times more mobile under the TCLP conditions (Figure 3.25), with 20% of total zinc mobilised compared to only ca. 2% for copper and lead. High particulate concentrations, combined with high mobility/solubility, make zinc the major limiting contaminant with respect to landfill disposal of RDS in New Zealand. An important consideration is whether similar high mobility of zinc is observed under freshwater leaching conditions, because this is more relevant for assessing risks of reusing RDS.

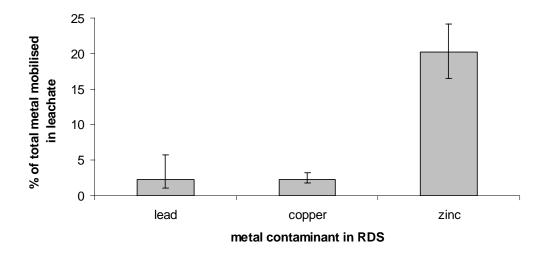


Figure 3.25 Percentage of total lead, copper and zinc mobilised by the TCLP leaching procedure. Data shown are median values – error bars represent the lower and upper quartile range.

3.3.2 International soil quality guidelines (Dutch and Canadian)

Having assessed the landfilling criteria for RDS, with many reuse options involving land application (eg as fill or component of compost etc), it is beneficial to compare New Zealand RDS contaminant levels with established soil/sediment guideline values.

Commonly used soil quality guidelines include those derived by Canadian and Dutch regulatory authorities. The Canadian soil quality guidelines (SQGs), produced by the Canadian Council of Ministers of the Environment (CCME 2007), are for the protection of both environmental and human health. Canadian SQG values have been derived for a range of landuse types with different 'sensitivities' to contaminants. The four landuse types are agricultural, residential/parkland, commercial and industrial land types (in the order of decreasing sensitivity). SQG values are defined as concentrations that should result in negligible risk to biota, their functions, or any interactions that are sustaining the health of ecosystems.

Dutch regulatory agencies have also developed comprehensive risk-based guidelines for protecting health and the environment (Lijzen et al. 2001; Verbruggen et al. 2001). The initial system of soil intervention values (ie if exceeded, remediation was required) has been superseded by serious risk concentrations (SRCs) that determine both environmental risk and human health risk. The final SRC_{eco} value is the lower of the two values, which is invariably the environmental risk concentration. The derivation of SRC values for metals is complicated by varying background levels and so to avoid unnecessary complexity, the older Dutch intervention values for lead, copper and zinc have been used.

The Canadian and Dutch SQGs for lead, copper, zinc, and selected PAHs are summarised in Table 3.3. To facilitate comparisons with RDS from this study (n=35), median, upper and lower quartile concentrations have been included.

The information in Table 3.3 further supports previous assertions that the most problematic contaminants in New Zealand RDS are heavy metals, in particular, zinc. For all 35 RDS samples, the median and upper quartile concentration of zinc was 422 μ g/g and 555 μ g/g, respectively. This is greater than the maximum SQG (Canadian) values for both residential/parkland (200 μ g/g) and commercial/industrial (360 μ g/g), but less than the Dutch intervention value for zinc in soil (720 μ g/g).

On the other hand, PAHs do not appear to be a significant issue since the upper quartile concentration of benzo[a]pyrene is less than the most stringent SQG value of $0.7~\mu g/g$. This is in contrast to the situation in states like Oregon where soil cleanup levels (refer to Table 1.3, Section 1.3.4.2) are low for PAHs (ie $0.1~\mu g/g$ for residential) and high for metals (e.g. $10,000~\mu g/g$ for copper). In states where these type of regulations apply, PAHs are often the limiting contaminants preventing, or complicating, the reuse of RDS.

Table 3.3	Soil quality guidelines (Dutch and Canadian) and median concentrations of
selected co	ntaminants in RDS (road sweepings and catchpit sediments).

Contaminant	Dutch SQG ^a	Canadian S	RDS ^d (µg/g)	
	(µg/g)	Residential/	Commercial/	Median (lower
		parkland	industrial	and upper
				quartiles)
		PAHs		
Phenanthrene	31	5 ^b	50 ^b	<u>0.57</u> (0.24-1.19)
Benzo[a]anthracene	2.5	1 ^b	10 ^b	<u>0.44</u> (0.20-0.78)
Benzo[a]pyrene	7.0	0.7	0.7	<u>0.31</u> (0.16-0.62)
		Metals		
Lead	530	140	260/600°	<u>122</u> (57-170)
Copper	190	63	91	<u>67</u> (41-119)
Zinc	720	200	360	<u>422</u> (302–555)

^a PAHs are SRC_{eco} values; metals are intervention values. ^b Interim remediation criteria for soil that have not yet been replaced by Canadian SQGs. ^c SQC for lead is 260 μ g/g and 600 μ g/g for commercial and residential landuse respectively. ^d the 35 RDS samples collected for this study.

3.3.3 New Zealand biosolids guidelines: metals

Guidelines for the application of biosolids are probably the most relevant of existing regulations that could be applied to reusing RDS in New Zealand. This is because biosolids are produced in large amounts, have beneficial uses and hence landfilling this material is inconsistent with the targets of *The New Zealand waste strategy* (MfE 2002b). As with RDS, biosolids contain elevated concentrations of metals, but adequate management of environmental risks through the development of maximum contaminant concentrations in *Guidelines for the safe application of biosolids to land in New Zealand* (NZWWA 2003) are facilitating the reuse of biosolids – ie application to agricultural land. As such, these guidelines provide a useful starting point for assessing the suitability of RDS for reuse options that involve application to land (eg soil amendment, fill and compost additive).

The New Zealand biosolids guidelines (introduced in Section 1.3.5.2) have two contaminant classifications, Grade 'a' and 'b'. Grade 'a' compliant materials can be designated *unrestricted use biosolids* (depending on the 'stabilisation' grade – refer to Section 1.3.5.2 for details), and can be handled by the general public and applied to land without risk of significant adverse effects. The land application of biosolids exceeding Grade 'a' limits requires resource consent (ie *restricted use*). The maximum concentrations of lead, copper and zinc permitted in biosolids for land application in New Zealand and, for comparison, Florida, are summarised in Table 3.4.

Table 3.4 Guideline values for biosolid application to land (New Zealand and Florida) and RDS concentrations of lead, copper and zinc.

	Maximum permitted conc. in biosolid (µg/g dry weight)			
	Lead	Copper	Zinc	
Biosolid 'Grade'				
NZ Grade 'a' (after 2012)	300	100	300	
NZ Grade 'a' (until 2012)	300	300	600	
NZ Grade 'b'	300	1250	1500	
Florida Class AA	300	1500	2800	
RDS (this study)	metal concer	ntrations in RDS (µg/g	dry weight) ^a	
Total RDS (n=35)	<u>122</u> (57-170)	<u>67</u> (41-119)	<u>422</u> (302-555)	
Street sweepings (n=16)	<u>117</u> (59-137)	<u>55</u> (36-129)	<u>336</u> (283-426)	
Catchpit sediment (n=19)	<u>133</u> (58-183)	<u>85</u> (48-116)	<u>464</u> (418-706)	
RDS – high traffic (n=11)	<u>112</u> (95-157)	<u>85</u> (49-124)	<u>421</u> (301-548)	
RDS – med traffic (n=10)	<u>172</u> (155-206)	<u>101</u> (69-120)	<u>475</u> (415-590)	
RDS – low traffic (n=11)	<u>45</u> (20-97)	<u>32</u> (26-37)	<u>294</u> (149-397)	

^a underlined value is median concentration with the upper and lower quartile concentration range in parentheses.

The biosolids guidelines (NZWWA 2003) specify restrictions on where these contaminated materials can be reused so as to further mitigate any potential adverse environmental effects. Non-permitted application areas include:

- within 20 m of any river, lake, wetland or artificial watercourse or the coastal marine area
- not onto land where there is a chance of the biosolids entering the water
- where there could be a discharge to any sensitive areas; including wahi tapu, archaeological sites and habitats of rare and endangered species.

3.3.3.1 How do RDS contaminants compare with biosolid guidelines?

All median and upper quartile concentrations for all three heavy metals are well below the Grade 'b' contaminant limits for biosolids. However, if applying the biosolids classifications, in order for RDS to be classified 'unrestricted use' this material would need to comply with Grade 'a' contaminant limits. To be realistic, 'unrestricted use' classification is probably needed to bring about a 'change in thinking' – that is, viewing RDS as something of value rather than a waste product.

Although the upper quartile concentrations for the heavy metals were generally below the pre-2012 Grade 'a' contaminant limits, these are only temporary limits that have been set to enable time for wastewater treatment plants to improve technology that will enable the permanent Grade 'a' criteria (post-2012 values) to be met. After 2012, the limits decrease three-fold for copper (300 μ g/g down to 100 μ g/g), two-fold for zinc (600 μ g/g down to 300 μ g/g) and remains unchanged for lead (300 μ g/g). After 2012, copper and

zinc concentrations in RDS are unlikely to meet Class 'a' contaminant levels. The median zinc concentration of 422 μ g/g in RDS easily exceeded the 300 μ g/g limit, while the upper quartile concentration of 555 μ g/g was almost a factor of 2 higher. For copper, the median RDS concentration (all samples) of 67 μ g/g was below the 100 μ g/g limit; however, the upper quartile concentrations for all samples (119 μ g/g), street sweepings (129 μ g/g) and catchpit sediments (116 μ g/g) exceeded the Grade 'a' limit. Although zinc levels were still exceeded by the upper quartile concentration (397 μ g/g), RDS from low trafficked streets is more likely to comply with Grade 'a' criteria. For example, the median zinc concentration was 294 μ g/g and the upper quartile concentration of copper was only 37 μ g/g.

3.3.3.2 Blending RDS with 'clean' material to reduce contaminant loads

Biosolids containing levels of metals that exceed contaminant criteria can be blended with other materials to dilute the contaminants to attain compliance. The actual wording of the biosolids guidelines is as follows:

The blending of sewage sludge with other substances (eg pumice, sand, subsoils, bark, sawdust, green waste) before, during or after treatment is an acceptable way of diluting contaminant levels in order to attain either the 'b' or 'a' biosolids contaminant grades. (NZWWA 2003).

The upper quartile zinc concentration of $555 \,\mu\text{g/g}$ in RDS (for all samples) suggests that 50/50 blends of RDS would be sufficient to reduce RDS contaminant levels below Grade 'a' contaminant limits. In addition, the choice of blending material may significantly reduce the mobility of certain metal contaminants – for example, the humic material in compost blends may reduce metal mobility via strong metal binding properties (refer Section 1.3.3.3).

3.3.3.3 Parallels between reusing biosolids and RDS

New Zealand produces ca. 55,000 tonnes of biosolids a year from 'high-rate' wastewater treatment plants (WWTPs) on a regular (weekly/monthly) basis. An additional 22,000 tonnes per year are periodically removed from small waste stabilisation ponds (NZWWA 2003). Of the 55,000 tonnes produced regularly (high-rate plants), only 20% is currently applied to land (ca. 50% agriculture and 50% production forests) with the remainder landfilled. In Europe and the United States, biosolid application rates to land are ca. 40%. In Sydney, over 90% of the biosolids are used beneficially, including ca. 50% applied to agriculture land (pastoral, cropping and forest land) and ca. 25% to the domestic market via compost products (NZWWA 2003). As such, there is considerable scope to increase the level of biosolids reuse in New Zealand, and presumably the New Zealand biosolids guidelines will facilitate this through the provision of accredited (via *Biosolids Quality Mark*, BQM) unrestricted use biosolids (ie Grade Aa) that can be applied to land as a 'permitted activity' (ie no resource consent required).

In New Zealand, Grade Aa biosolids can be added at a rate of 200 kg total N/ha/year (three-yearly average). Biosolids have an average nitrogen content of 3%, which equates to loading rates of ca. 7 tonnes of biosolids/ha/year. Although classified as unrestricted

use biosolids, the material cannot be placed within 20 m of a river, stream, wetland, artificial water course, coastal marine area, or any land where there is a likelihood of biosolids entering the water. The guidelines recommend that any proposals to apply lower grades of biosolids (or where conditions for the application of Grade Aa biosolids are not meet) be subject to a resource consent application for a discretionary activity. This would require an assessment of environmental effects (AEE) and provide a full opportunity for public scrutiny (ie objection and appeal).

There are obvious parallels between biosolids and RDS, that is, they are both relatively large waste streams that are mostly being disposed of in landfill despite having beneficial reuse options. The total tonnage of RDS disposed of annually in New Zealand is unclear, but to provide an indication of the quantities involved, Christchurch City Council disposed of 5468 tonnes of street sweepings and 2132 tonnes of catchpit sediments for the 12 months ending October 2007 – an annual total of 7600 tonnes from just one city. These tonnages are collected from ca. 1380 km of roads (based on 2756 km of kerb length), which equates to ca. 4 tonnes of RDS/km of road/year (McNeill pers comm. 2007). Based on these quantities, the total amount of RDS collected and disposed of nationally would most likely exceed the 55,000 tonnes of biosolids produced regularly from high-rate WWTPs.

Despite the amount of material involved, there are no regulatory guidelines, analogous to those for the application of biosolids to land, that promote and/or facilitate the reuse of RDS in New Zealand. Although it seems a reasonable approach, any decision as to the relevance of applying biosolid contaminant limits to reusing RDS; however, requires considerable input from the various regional (and central) regulatory agencies.

3.4 RDS risk assessment II: Freshwater leaching, toxicity and amendment studies

The comparison of contaminants in RDS (and TCLP leachates) with guideline values (Section 3.3) indicated that zinc was the most problematic contaminant when considering potential environmental effects of reusing RDS in New Zealand. As reuse options generally involve 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. This section details fresh water leaching experiments, including leachate contaminant concentrations and algal toxicity (*Psuedokirchneriella subcapitata*).

3.4.1 Freshwater leaching of metals from RDS

The results from the freshwater leaching tests on eight RDS samples are summarised in Table 3.5. Following similar procedures to the TCLP methodology, the same 20:1 ratio of solvent (in this case de-ionised water) to RDS was used. Typically, the freshwater leachates were prepared by adding 800 ml of water to 40 grams of RDS and agitating the resulting suspension for ca. 24 hours.

RDS sample ^a	Lead (µg/L)	Copper (µg/L)	Zinc (µg/L)
C1SW	10.1	87	210
H2SW	9.1	97.7	341
C2SW	13.4	177	566
A2CP	14.6	32.5	267
A1CP	19.1	45.7	230
A7CPii	1.2	15.5	177
A2SW	13.2	124	1070
C2CP	6.4	13.5	993
Median	12	66	304
Lower quartile	8	28	225
Upper quartile	14	104	673
HC ₅₀ ^b	150	18	89

^a Refer to Tables 2.1–2.3 for full RDS site details. ^b Hazardous concentration (μ g/L) to 50% of species – derived from numerous toxicity data sets using different aquatic organisms (Verbruggen et al. 2001).

The median (n=8) freshwater leachate concentrations of lead (12 μ g/L), copper (66 μ g/L) and zinc (304 μ g/L), were much lower than the corresponding TCLP concentrations (115, 120 and 6200 μ g/L, respectively). The percentage of heavy metals mobilised by fresh water, relative to TCLP solution, was 5%, 35% and 7% for lead, copper and zinc, respectively. The reason for the high percentage of copper in freshwater leachates was presumably because of the affinity of copper for dissolved organic carbon (DOC) – supported by the correlation coefficient (r^2) of 0.74 (data not shown).

A comparison of median freshwater leachate concentrations with HC_{50} values (concentration of a contaminant that is hazardous to 50% of species) indicated that copper and zinc were both present at potentially toxic concentrations (Figure 3.26). The HC_{50} values have been calculated using toxicity data from many studies involving different aquatic species (both marine and freshwater) and as such represent the concentration hazardous to 50% of aquatic species. This is in contrast to EC_{50} values (effective concentration causing 50% effects in the test population) that apply to the specific organism being tested. The HC_{50} values serve as the basis for the serious risk concentrations (SRC_{eco}) used in Dutch environmental guidelines (Section 3.3.2 and Table 3.3).

The leachate concentration of lead from RDS samples was well below the HC_{50} value, and hence is not considered a potential environmental risk when reusing these materials. It is worth noting that while leachate concentrations have been compared with HC_{50} values, the freshwater leachates prepared in this study were based on the TCLP methodology. That is, leaching conditions, and hence concentration of the leachates, were not part of a standard methodology to assess or accurately mimic the freshwater mobility and/or

toxicity of contaminants; or to compare with accepted toxicity value/guidelines. The purpose of the data presented in Figure 3.26 is two fold. First, to provide a starting point for determining what may be the most problematic heavy contaminants; and second, to provide 'baseline' metal leachate concentrations in order to ascertain whether subsequent RDS amendments significantly reduced mobility/toxicity of problematic metals.

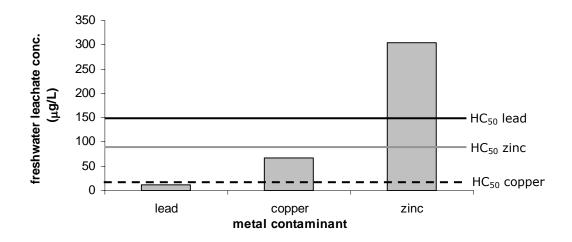


Figure 3.26 RDS freshwater leachate concentrations and HC_{50} values for lead, copper and zinc (data shown are median values, n=8).

3.4.2 Algal toxicity of freshwater leachates

Toxicity testing using the alga *Psuedokirchneriella subcapitata* was carried out using the same eight RDS freshwater leachates listed in Table 3.5. Starting with the undiluted leachates, 50% dilution series were prepared to give the following concentrations series: 100% (undiluted); 50%, 25%; 12.5%; 6.25%; 3.13%; 1.5%; 0.78%; 0.39%; and 0.2%. Using the statistical package $ToxCalc^{TM}$, the toxicity data from each leachate concentration series was used to derive the following toxicological parameters: NOEC (no observed effects concentration); LOEC (lowest observed effects concentration); ChV (chronic value) – the geometric mean between NOEC and LOEC; EC_{50} (effective concentration, 50%) – the concentration of a contaminant that results in a specified biological result (ie death, reduction in growth) in 50% of the test population compared with the control.

These are summarised in Table 3.6 – values >100% denote that the toxicity of the undiluted leachate was insufficient to enable this parameter to be determined. Note that the concentration is expressed as percentage (%) of the undiluted leachate concentration. For example, 100% = undiluted leachate, 25% = 4-fold dilution of original leachate, and 2% = 50-fold dilution of original leachate.

Table 3.6 Toxicological parameters of selected RDS freshwater leachates for the alga *Psuedokirchneriella subcapitata*. Units are the percentage (%) of the undiluted leachate concentration.

RDS sample	EC ₅₀ (%) ^a	EC ₅₀ (%) (w/v basis) ^b	NOEC° (%)	LOEC ^d (%)	ChV ^e (%)
C1SW	>100	>5	50	100	70.7
H2SW	45	2.25	12.5	25	17.7
C2SW	4.6	0.23	0.8	1.5	1.1
A2CP	>100	>5	100	>100	>100
A1CP	>100	>5	100	>100	>100
A7CPii	85.7	4.3	25	50	35.4
A2SW	7	0.35	0.8	1.5	1.1
C2CP	2.2	0.11	0.2	0.4	0.3

 $^{^{}a}$ 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 EC₅₀ % value based on the weight/volume (w/v) percent ratio of the extraction, which was 5% for the undiluted leachate (ie L/S ratio of 1/20); c NOEC (no observed effect concentration); d LOEC (lowest observed effect concentration); e ChV (chronic value) – the geometric mean between NOEC and LOEC.

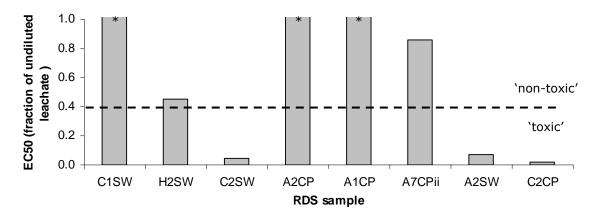


Figure 3.27 Concentration of original leachate required to inhibit 50% of the growth (EC₅₀ value) of the alga *Psuedokirchneriella subcapitata*. Concentrations are expressed as the fraction of the undiluted leachate. 'Toxicity threshold' estimate (dashed line) was adapted from the value determined by Kwan and Dutka (1992) for *Vibrio fischeri*.

To illustrate the differences in the algal toxicity of the eight RDS leachates, the EC_{50} data is plotted in Figure 3.27. Note that the EC_{50} concentrations are expressed as a *fraction of the full-strength leachate* and that the lower the EC_{50} value the more toxic the RDS leachate was to the algae. The open bars for samples C1SW, A2CP and A1CP (marked with *) indicate that the EC_{50} values for these RDS samples are greater than the full-strength (undiluted) leachate. That is, the undiluted leachates from these RDS samples were not sufficiently toxic to derive an EC_{50} value.

The toxicity of the leachates varied widely with EC $_{50}$ values ranging from 2.2% leachate strength (or 45-fold dilution of original leachate) for C2CP through to >100% for C1SW, A2CP and A1CP. The leachates of A2SW, C2SW and C2CP inhibited algal growth by 50% (ie EC $_{50}$) at leachate dilution factors of 14, 22 and 45, respectively. Undiluted leachates from the Auckland catchpit samples, A2CP and A1CP showed no adverse effects on algal growth (ie NOEC = 100%, and LOEC >100%), and the C1SW leachate only exhibited algal toxicity when undiluted (ie NOEC = 50% and LOEC = 100%).

The 'toxicity threshold' in Figure 3.27 (dashed line) is derived from the suggested 'non-toxic' EC_{50} threshold concentration of 2% (weight/volume basis) based on soil leachate toxicity testing using the bacterium V. fischeri (Kwan and Dutka 1992). This weight/volume-based EC_{50} value corresponds to an EC_{50} threshold concentration of 40% (based on percent of full-strength leachate) or 0.4 (based on fraction of full-strength leachate). This toxicity threshold is discussed in more detail under the heading 'Comparison with other studies'.

Applying copper and zinc concentrations in Table 3.5, approximate EC₅₀ concentrations (ie μ g/L rather than dilution %) were calculated (Table 3.7). These ranged from 0.3–44 μ g/L for copper, and 22–154 μ g/L for zinc. These are only approximations, because the leachates consisted of a mixture of metal contaminants and, therefore, the toxicity cannot be exclusively attributed to just one metal. The EC₅₀ concentrations determined in this study were comparable with those reported by De Schamphelaere et al. (2003) using the same freshwater alga, *P. subcapitata*. Depending on pH (varied between 6–8), those authors reported EC₅₀ values of 14–55 μ g/L for copper and 58-215 μ g/L for zinc. The median EC₅₀ concentrations of the RDS leachates (Table 3.7) were comparable with the aquatic organism HC₅₀ values for copper (18 μ g/L) and zinc (89 μ g/L) reported by Verbruggen et al. (2001).

Table 3.7 Approximate zinc and copper EC_{50} concentrations ($\mu g/L$) for Psuedokirchneriella subcapitata derived from EC_{50} leachate percentage values.

	Corresponding EC ₅₀ c	oncentrations (µg/L)
RDS sample	copper	zinc
H2SW	44.2	154
C2SW	8.1	26
A7CPii	13.3	152
A2SW	8.7	75
C2CP	0.3	22
Median	9	75

3.4.2.1 Choice of organism for toxicity testing

The green alga (*P. subcapitata*) was selected because it is relatively sensitive to zinc and, therefore, maximised the chance of observing toxicological responses from the RDS leachates. In contrast to the relative zinc sensitivity of *P. subcapitata*, another commonly used aquatic organism is the crustacean, *Daphnia magna*, which is much more tolerant of

zinc with EC₅₀ values of 1869–2690 μ g/L (De Schamphelaere et al. 2003). However, the aquatic organism HC₅₀ value of 89 μ g/L for zinc (derived from multiple studies and organisms) suggests that the toxicological response of the green algae is more representative than that of *Daphnia magna*. In addition, the algal growth tests are considered chronic tests (as opposed to acute) because the effects are assessed over several generations during the exposure period. Chronic testing is generally more environmentally relevant than short term (acute) toxicity testing.

3.4.2.2 Comparison with other studies

One of the most commonly used assay methods for determining the toxicity of aqueous extracts (ie leachates) from contaminated materials and waste products is the commercially available Microtox[®] assay (Microbics, Carlsbad, CA, US). The Microtox[®] assay is a bacterial test of acute toxicity that measures the luminescence of the marine bacteria *Vibrio fischeri*. The response of this bacterium has been measured for more than 1300 chemicals and environmental samples (Acheson et al. 2004). Typically, this assay involves taking 7 g of sediment and extracting with 35 ml of water, which corresponds to a 1:5 dilution (ie L/S ratio of 5), and a weight/volume (w/v) percentage of 20% for the full-strength leachate. The dilution series is then prepared using this w/v percent strength as the most concentrated sample. An EC₅₀ value of 5% (w/v) using the Microtox method, therefore, corresponds to the full-strength leachate being diluted by a factor of 4.

The 'w/v' percent dilution was used to derive the alternate set of EC₅₀ values provided in Table 3.6 (3rd column) for the RDS leachates, which ranged from 0.11% to >5%. Kwan and Dutka (1992) have suggested that a Microtox EC₅₀ value $\ge 2\%$ (w/v) is indicative of a non-toxic or 'clean' soil. Although this study (reported herein) did not use the Microtox bacterial assay, the 2% w/v EC₅₀ threshold corresponds to an EC₅₀ concentration of 40% (percent of full-strength leachate) or 0.4 (based on fraction of full-strength leachate), and has been used in Figures 3.27, 3.28, 3.30, 3.36 and 3.37. Note that this is only a proposed threshold value (Kwan and Dutka 1992) based on bacterial Microtox assay results – it is only used in this report as a possible 'guiding value'. It is emphasised that it is neither a recognised guideline nor accepted regulatory value for differentiating non-toxic and toxic materials.

Hindin (1993) used the Microtox assay to assess a large number of RDS samples, including fresh road sweepings, weathered road sweepings and catchpit sediments (ie vactor sludges). Reported EC_{50} values (w/v) for freshly collected street sweepings ranged from 1.0% to 40.8%, with a geometric mean of 9.0%. Catchpit sediments were similar, with EC_{50} values ranging from 3.6% to 35% and a geometric mean of 10.4%. Unfortunately, Hindin did not disclose details regarding the extraction conditions (ie L/S ratio) or the 'nature' of the dilution sequence used, and so it is difficult to make any meaningful comparisons between his data and that presented in this report.

A National Cooperative Highway Research Programme (Harrington-Hughes 2000) investigating the environmental impact of road construction and repair materials defined more stringent measures regarding the 'potential for harm' from leachates (Table 3.8).

The findings from that study were based on leachate toxicity testing using *Daphnia* and the same freshwater alga *P. subcapitata*. Using the classification scheme in Table 3.8, the potential for harm from the RDS samples listed in Table 3.6 (with defined EC_{50} values) is either 'extremely high' (C2SW, A2SW and C2CP) or 'high' (A7CPii and H2SW). Depending on the actual EC_{50} concentration of C1SW, A2CP and A1CP, which could not be determined given the toxicity of the undiluted leachate, these three samples would be classified as 'moderate' or 'low.'

Table 3.8 Summary of stabilisation trials using the RDS sample C2CP.

Potential for harm	EC ₅₀ % (A)	EC ₅₀ % (B)
	(% full strength leachate)	(% on w/v basis)
Extremely high	<10	<2.5
High	10-20	2.5-5
Moderate	20-75	5–19
Low	>75	>19

3.4.2.3 The main cause of leachate toxicity: copper or zinc?

Zinc and copper are present at concentrations in RDS freshwater leachates that are potentially toxic to aquatic organisms (refer to Figure 3.26). Of these two metals, comparisons with landfill, soil quality and biosolids guidelines have indicated that zinc is likely to be the most problematic. Assuming that a particular metal is largely responsible for leachate toxicity, specific amendment and treatment strategies can be devised that specifically target the immobilisation of that metal.

Dose-response curves that plot response on the y-axis and concentration on the x-axis (normally log-scale) typically show a sigmoid curve fit to the data. Dose-response curves for zinc and copper were obtained by plotting the concentration (log-scale) of the five toxic leachates against a measure of toxicity (Figure 3.28). The measure of toxicity, [1- EC_{50}], is simply the fraction of undiluted leachate required to effect 50% of algal growth in the controls (ie y-axis values in Figure 3.27) subtracted from 1 so that increasing y-axis values correspond to increasing toxicity (accordingly the 40% EC_{50} toxicity threshold now =0.6 on these plots). Note that the individual points of the dose-repose plots are for the five different leachates, as opposed to a dilution series of just one leachate.

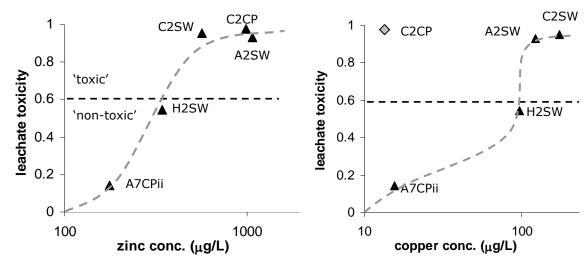


Figure 3.28 Dose-response curves (zinc, left and copper, right) plotted using the individual RDS leachates (ie not a dilution series from one leachate). The measure of toxicity (y-axis) is $[1-EC_{50}]$ where EC_{50} is defined as the fraction of undiluted leachate required to inhibit 50% of the control algal growth (fitted curve is estimated best fit). The estimated toxicity threshold (dashed line) was adapted from the value determined by Kwan and Dutka (1992) for *Vibrio fischeri*.

Of the five leachates included, zinc appeared to give a better dose-response curve fit than copper. The anomalously high toxicity of C2CP in the copper dose-response curve (grey diamond), which had a copper concentration of only 13.5 μ g/L, was attributable to the high zinc concentration of 993 μ g/L. Despite a possibly better dose-response curve fit for zinc, it was impossible to differentiate toxicity of the two metals because the concentrations of copper were strongly correlated with zinc (r^2 =0.82, Figure 3.29) to at least 566 μ g/L (ie C2SW). The higher zinc concentrations in C2CP and A2SW leachates (ca. 1000 μ g/L) were well outside the 'normal' zinc/copper correlation (grey diamonds in Figure 3.29) and as such, the toxicity of these leachates could probably be attributed exclusively to zinc. The inclusion of the two outlier samples (C2CP and A2SW) reduced the correlation coefficient (r^2) to 0.05.

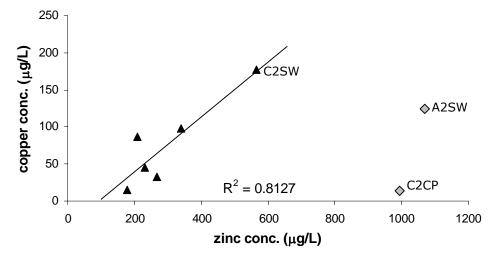


Figure 3.29 Correlation of copper and zinc concentrations from the freshwater leachates of selected RDS samples.

3.4.2.4 Copper-DOC binding and reduced bioavailability

Strong binding of copper to DOC, as evidenced by the correlation coefficient (r^2) of 0.74, further supports the assumption that zinc is the main cause of leachate toxicity. Many studies have shown that metals are not in a readily bioavailable state when present in solution as a metal-DOC complex. It is generally acknowledged that only the fraction of metal that is present in solution as the free metal ion is available for uptake by organisms (ie bioavailable) and hence potentially toxic. If a significant fraction of the copper in the leachate solution is present as a copper-DOC complex, then only a small fraction of the total copper concentration is bioavailable. The reduced bioavailability of copper with increasing DOC carbon is discussed in greater detail in Section 3.4.3.3.

3.4.2.5 Leachate toxicity and particulate zinc concentration

Assuming zinc is the most problematic contaminant in freshwater leachates, a useful parameter is to be able to relate easily measurable particulate concentrations with freshwater leachate toxicity. The plot of leachate toxicity vs particulate zinc concentrations showed a general trend of increasing leachate toxicity with higher particulate concentrations (Figure 3.30). The exception to this was the samples C2SW and low A7CPii (grey squares), which showed unexpectedly high and low leachate toxicity, respectively, based on the particulate zinc concentrations. Ignoring the two 'outlier' samples, the curve in Figure 3.30 shows a transition between toxic and non-toxic leachates occurs at $400-600~\mu\text{g/g}$ of particulate zinc (the shaded region represents the lower and upper quartile concentration range of zinc). The dashed curve in Figure 3.30 is an estimated best fit and yields a particulate threshold concentration of ca. 550 $\mu\text{g/g}$ of zinc. This threshold estimation is comparable to the upper quartile particulate zinc concentration (for all RDS samples, n=35), of 555 $\mu\text{g/g}$.

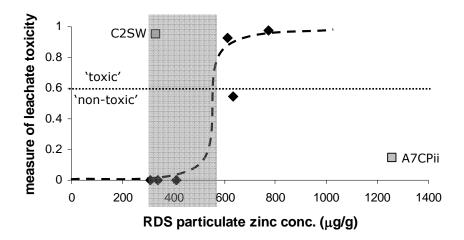


Figure 3.30 Leachate toxicity [1-EC₅₀] vs total particulate zinc concentrations in selected RDS samples (curve is estimated best fit). The grey shaded area represents the lower (302 μ g/g) and upper quartile (555 μ g/g) range for all RDS samples (n=35). Horizontal dashed line represents the estimated toxicity threshold value of 0.6 (adapted from the value determined by Kwan and Dutka (1992) for *Vibrio fischeri*).

This result indicates that ca. 25% of RDS in New Zealand may contain particulate zinc in high enough concentrations that the freshwater leachates (based on 50 g of RDS per litre) are toxic to green algae. As mentioned, the leachate toxicity data only applies to the green algal species tested, which is known to be very sensitive to zinc. It is likely that none of the RDS leachates would have shown significant toxicity if the more robust crustacean, *Daphnia magna* (EC $_{50}$ of 1869-2690 µg/L) had been used as the test organism. Regardless of the sensitivity of the test organism, the results strongly indicate the need for a cautious approach when considering potential reuse options of RDS.

One way to minimise the potential risk posed by the mobility of zinc would be to target RDS from streets that generate lower quantities of metal contaminants. RDS from low trafficked streets (ie largely residential) had median and upper quartile concentrations of 294 μ g /g and 397 μ g /g, respectively. Therefore, RDS from low trafficked streets are not expected to yield leachates that are toxic to green algae because these particulate zinc concentrations are below the estimated threshold value of 550 μ g/g (Figure 3.30).

3.4.3 Reducing metal leaching from RDS

Toxicity testing has shown that the concentration and mobility of copper and zinc in RDS are sufficiently high to represent a potential risk to the environment. An important attribute of metal contaminants is that, unlike organic contaminants (ie TPH and PAH), they cannot be removed via biotic and/or abiotic decomposition processes. The only practical ways to reduce the toxicity risks of metal contaminants is to 'treat' the RDS with components that 'lock up' the metals into a less mobile and/or bioavailable form, or as is permitted for biosolids, blend with sufficient quantities of clean material to 'dilute' the metals to acceptable levels.

The following are considered the most practicable methods for reducing the potential environment risks of heavy metal contaminants in RDS:

- Physically 'locking up' metals: Metals in RDS are physically incorporated into solid matrices. The major application examples involve using RDS as feedstock of fine aggregate for concrete or asphalt production. This application was discussed in Chapter 1 (Section 1.3.2.7). Assuming the demand exists, this represents a very effective way of reusing RDS while basically eliminating all environmental risks.
- 2. Blending to dilute metals: This simply involves blending RDS with clean materials at a ratio to reduce (via dilution) total metal concentrations below regulatory guideline limits. Based on the upper quartile concentration of zinc (555 μg/g) and the New Zealand guideline maximum for Grade `a' biosolids (300 μg/g after 2012), 50/50 blends would most likely result in acceptable concentrations of metals for RDS reuse options involving land application.
- 3. **Stabilisation of metals**: This involves the addition of chemicals and/or other materials for the purpose of reducing the mobility of metals in RDS. For example, the application of small quantities of phosphate converts soluble forms of metal contaminants into insoluble metal phosphates (refer to Section 1.3.3.7). This is

particularly effective for the immobilisation of lead in soils as lead phosphates have extremely low water solubility. Iron oxide (or equivalent source of iron) has also been used to immobilise metals such as zinc. This approach overlaps with method 2 'Blending to dilute metals' since the addition of clean materials invariably increases the surface area for metal binding.

The key difference between 2. *Blending* and 3. *Stabilisation*, is that *blending* is mass based and used to achieve compliance with guideline values for total particulate metal concentrations. For example, if the maximum permitted zinc concentration is $300 \,\mu\text{g/g}$ then a material containing ca. $550 \,\mu\text{g/g}$ needs to be blended with an equal mass of clean material to reduce concentrations by a factor of 2. The focus of *stabilisation* is to reduce the mobility of metals to some pre-determined value, which may be achieved without a significant reduction (or dilution) of the contaminants in the bulk particular phase. For example, the amount of phosphate added to stabilise contaminated soils is typically <1% by mass.

In practice, the applicability of either approach will ultimately depend on the specifics of any future RDS reuse guidelines or consent conditions imposed for 'restricted activities', that is, whether they are based exclusively on particulate metal totals or whether there is also provision to comply with maximum leachate metal concentrations and/or toxicity.

3.4.3.1 Metal leaching from stabilised RDS samples

The focus of the research project was to reduce the potential environmental risk of metals in RDS by using stabilisation methods. Leaching experiments (both TCLP and freshwater) have indicated that zinc is potentially the most problematic contaminant. Two immobilisation amendments were trialled – phosphate and compost. The RDS sample C2CP was selected because the freshwater leachate from this sample was one of most toxic towards the test green alga, *P. subcapitata* (refer to Figure 3.28) and as such represented a worst case scenario RDS rather than a typical RDS.

The basic procedure involved adding the stabilising agents to the RDS and adjusting the water content to ca. 30%. Samples were mixed regularly and aged for ca. five days prior to extraction. Two controls were used, one left 'dry' prior to extraction to compare with the original C2CP leachate, and the other had water added (ie 'wet') to provide equivalent control conditions to the moistened stabilised samples. All samples contained the exact same amount of C2CP RDS and were extracted with the same volume of freshwater.

Sample (all C2CP)	Stabilising agent	pH of leachate	Copper (µg/L)	Zinc (µg/L)
Control (wet)	-	6.4	9.5	2100
Control (dry)	-	6.4	14.6	1180
10%-compost ^a	compost	7.0	26.3	156
30%-compost ^a	compost	7.3	126.0	253
0.1%-phosphorus ^b	phosphate	6.5	18.6	224
0.5%-phosphorus ^b	phosphate	7.2	96.8	310
Original C2CP ^c	-		13.5	993

^a percentage loading based on dry weight of compost (contained 50% water). ^b percentage loading based on phosphorus. ^c unstabilised 'dry' control – this was the original C2CP RDS leachate (refer Section 3.4.1) and was extracted using the same procedure as 'control (dry)' and therefore it should contain comparable concentrations of copper and zinc (ie duplicate sample).

The contaminant stabilisation trials of C2CP and resulting leachate concentrations of copper and zinc are summarised in Table 3.9. Both the compost and phosphate stabilised RDS resulted in large decreases in leachate zinc concentrations. Relative to the 'wet' control, which contained 2100 μ g/L of zinc, stabilisation reduced leachate zinc concentrations by 85-93%. A major factor controlling the solubility and, therefore, mobility of zinc is pH (increasing solubility at acidic pH values). The pH of the leachates used in the stabilisation trial ranged from 6.4-7.3. This narrow pH range suggests that the observed reductions in leachate zinc concentrations (relative to the control samples) were not the result of pH differences. This was further supported by the much lower mobilisation of zinc from the 0.1% phosphorus-stabilised sample despite having essentially the same leachate pH as the two unstabilised controls (ie 6.5 vs 6.4). This is important because the purpose of the amendment trial was to reduce heavy metal mobility without potentially detrimental environmental effects such as large pH changes (either acidic or alkaline) in water that comes into contact with amended RDS (eg pore water, runoff and leachates).

In studies to immobilise lead in contaminated soils, Berti and Cunningham (1997) reported that potassium phosphate (KH_2PO_4) and natural humus (ie compost) have little impact on the pH of the leaching solution. Accordingly, their findings were influential in the choice of stabilising agents selected for this study.

The lower loadings of phosphorus and compost appeared to be more effective in immobilising zinc, with compost being the most effective of the two stabilising agents (at the concentrations trialled). The largest reduction in the amount of zinc mobilised was 10-fold for phosphate and 14-fold for compost stabilisation. In contrast, the amount of leachate copper actually increased for stabilised samples – increasing from 9.5 μ g/L ('wet' control) up to 126 μ g/L (0.5% phosphorus). The increased concentration of copper correlated to leachate DOC concentrations (see below). It is unclear why the 'wet' control leachate had twice as high zinc concentrations compared with the 'dry' control.

3.4.3.2 Increased leachate copper and dissolved organic carbon (DOC)

The reason stabilised RDS exhibited higher leachate concentrations of copper was because these samples released significantly larger amounts of DOC. As discussed earlier, copper readily forms complexes with DOC, which 'pulls' the copper into solution (ie facilitates solubilisation). The relationship between copper and DOC concentrations in the leachate solutions is shown in Figure 3.31.

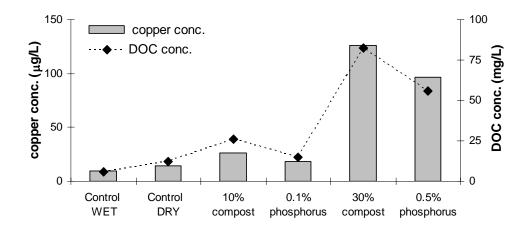


Figure 3.31 Copper and DOC leachate concentrations from C2CP stabilised and nonstabilised (controls) RDS samples.

The concentration of leachate copper seems to be determined exclusively by DOC levels $(r^2=0.97, Figure 3.32)$; overriding any increased insolubility (via phosphate) and binding (via compost) effects of added phosphate and compost, which should decrease metal concentrations (as observed for zinc).

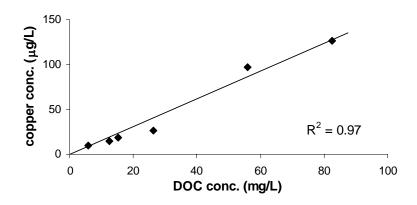


Figure 3.32 Correlation of copper and DOC leachate concentrations from C2CP stabilised and non-stabilised (controls) RDS samples.

The significance of copper being associated with DOC is that a large proportion of copper in the leachate solutions is not present as the free metal ions; instead it is present as DOC-copper complex. Unlike free metal ions that are bioavailable and toxic, the copper-DOC complex is considered to be too large and/or polar for organisms to take up.

Assuming this to be the case, much of the additional copper in the stabilised leachates was probably not in a form that is readily bioavailable or toxic (refer to Section 3.4.3.3).

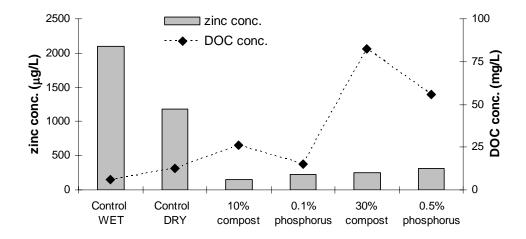


Figure 3.33 Zinc and DOC leachate concentrations from C2CP stabilised and non-stabilised (controls) RDS samples.

In contrast to copper, the leachate concentrations of zinc and DOC were not correlated (Figure 3.33), presumably because zinc has a lower binding affinity (ie partitioning coefficient) for DOC than copper. Brown et al. (1999) have shown that zinc binds 30 times less strongly than copper to the same type of DOC. Because of the low affinity of zinc for DOC, Kalbitz and Wennrich (1998) concluded that DOC is unimportant in the mobilisation of zinc from soil, which is consistent with the leaching results shown in Figure 3.33.

3.4.3.3 Algal toxicity of leachates from stabilised RDS samples (C2CP)

Four leachates, comprising the two unstabilised controls ('wet' and 'dry'), the 'low' phosphate and the 'low' compost stabilised samples, were evaluated for algal toxicity using the same procedure described in Section 3.4.2 (using P. subcapitata). The toxicological parameters ($ToxCalc^{TM}$) for the four leachates are summarised in Table 3.10. The addition of stabilising agents clearly resulted in significant reductions in leachate toxicity. While this was partly anticipated, on account of the 10- to 14-fold reductions in zinc concentrations, the effect on algal toxicity was much more pronounced. Compost stabilisation of C2CP, for example, resulted in reductions in leachate toxicity of 220-fold and 500-fold based on EC_{50} and LOEC values, respectively. The substantial decrease in the toxicity of stabilised leachates is clearly illustrated in the plot of algal toxicity versus leachate concentration (Figure 3.34).

Table 3.10 Algal toxicity (*P. subcapitata*) of leachates from stabilised and unstabilised RDS samples (C2CP). Units are the percentage (%) of the undiluted leachate concentration.

Sample (all C2CP)	EC ₅₀ (%) ^a	EC ₅₀ (%) (w/v basis) ^b	NOEC° (%)	LOEC ^d (%)	ChV ^e (%)
Original C2CP ^f	2.2	0.11	0.2	0.4	0.3
Control (dry)	1.2	0.06	0.2	0.4	0.3
Control (wet)	0.5	0.025	<0.2	0.2	-
0.1%-phosphorus	36.4	1.82	12.5	25	17.7
10%-compost	110 ⁹	5.5 ⁹	50	100	70.7

 $^{^{}a}$ EC₅₀ (effective concentration, 50%) – the concentration (expressed as a percent of full-strength leachate) resulting in 50% algal growth inhibition compared with the control. The full-strength (or undiluted) leachate was assigned a concentration of 100%; b EC₅₀ % value based on the weight/volume (w/v) percent ratio of the extraction, which was 5% for the undiluted leachate (ie L/S ratio of 1/20); c NOEC (no observed effect concentration); d LOEC (lowest observed effect concentration); e ChV (chronicvValue) – the geometric mean between NOEC and LOEC. f original 'non-stabilised' C2CP leachate (refer Table 3.6) – equivalent to 'control (dry)' (ie duplicate). g estimated via extrapolation.

Using the toxicity EC_{50} threshold value of 40% (or 2% based on 'Microtox' dilution protocol) to differentiate toxic vs non-toxic samples, the addition of 10% compost resulted in a non-toxic product, while the addition of 0.1% phosphate resulted in a marginal stabilised product (ie $EC_{50} = 36\%$). This is clearly illustrated in Figure 3.36.

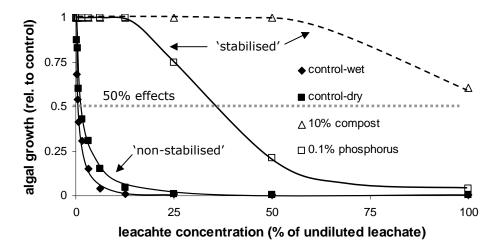


Figure 3.34 Algal toxicity vs leachate concentration for stabilised and non-stabilised (ie controls) RDS samples (C2CP).

The main cause of leachate toxicity: copper or zinc?

When this question was first raised in Section 3.4.2.1 it was difficult to ascertain from the toxicity experiments whether copper or zinc was primarily responsible for the observed algal toxicity, although the data seemed to favour the latter. A benefit of the stabilised experiments was that they enabled leachate copper to be eliminated as a source of toxicity since leachate toxicity was observed to actually decrease with increasing copper

concentrations. The inverse relationship (Figure 3.35) between toxicity and copper indicates that toxicity is not related to leachate copper because it is present mainly as a non-bioavailable DOC-copper complex.

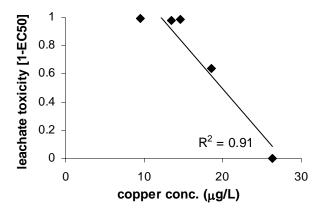


Figure 3.35 Dose-response curve showing the inverse relationship between algal toxicity and leachate copper concentrations.

The effect of DOC on copper toxicity is consistent with the findings of Tsiridis et al. (2006) who investigated the interactive toxic effects of heavy metals and dissolved humic materials (the metal binding component of DOC) on the bacterium *Vibrio fischeri*. The study found the toxicity of copper solutions decreased significantly in the presence of added DOC while the toxicity of zinc solutions remained almost constant. In the absence of DOC, the interactive toxic effects of binary mixtures of copper and zinc were found to be synergistic (ie greater than the sum of the combined toxicities). However, because of the strong binding efficiency of copper, the addition of DOC (above 1 mg/L) to these binary mixtures resulted in large decreases in toxicity because the bioavailable form (free copper ions) was removed (Tsiridis et al. 2006).

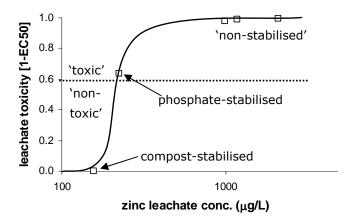


Figure 3.36 Dose-response curve showing the individual leachates from stabilised and non-stabilised C2CP RDS samples. Horizontal dashed line represents the estimated toxicity threshold value of 0.6 (adapted from Microtox® leachate soil assays using *Vibrio fischeri* – Kwan and Dutka 1992).

In contrast to copper, algal toxicity of the leachates was well correlated to the concentration of zinc (Figure 3.36). This is consistent with the low binding efficiency of zinc and, accordingly, the toxicity of zinc is not influenced by the presence of DOC (Tsiridis et al. 2006). This confirms zinc as the most problematic contaminant (with respect to algal toxicity at least) and hence measures to control zinc mobilisation are anticipated to be highly beneficial in mitigating potential environmental risks associated with reusing RDS.

Optimum loading rates for immobilising zinc

Although this preliminary experiment consisted of only two concentrations of the different stabilisation materials, the results showed that increasing the loading of these materials did not result in improved immobilisation of target heavy metals in RDS refer to Figures 3.31 (copper) and 3.33 (zinc). Altering the phosphate loading from 0.1% to 0.5% increased the leachate zinc concentration from 224 μ g/L to 310 μ g/L. Similarly, changing the compost loading from 10% to 30% increased the amount of zinc mobilised from 156 μg/L to 253 μg/L. Even if these increases are not significant (ie values are based on single replicates only), the results clearly show that increasing the amount of stabilising material beyond a certain level has no benefit with respect to zinc mobilisation in RDS. In fact adding excess stabilisation material may actually be detrimental to leachate quality because of increased DOC levels and the associated increase in the concentration of copper. Even if the copper is present in a nonbioavailable form, the mobilisation of any heavy metals from reused RDS will most likely be undesirable. It is, therefore, important to determine the optimal loading of a stabilising material that maximises the immobilisation of zinc (or other problematic heavy metal/s) and minimises potentially undesirable processes, such as the generation of DOC. In addition to minimising the amount of DOC, using the least amount of stabilising material will have potential cost benefits that may facilitate the costeffectiveness of this type of RDS pre-treatment process.

The best reductions in leachate zinc concentrations for phosphate and compost stabilised C2CP samples (relative to the 'wet' unstabilised sample) were 10- and 14-fold, respectively. Additional stabilisation trails would be required to determine whether similar or improved zinc immobilisation can be achieved by using even lower incorporation levels of phosphate or compost. With respect to the use of even lower amounts of stabilising agents, McGowan et al. (2001) reported effective zinc immobilisation (19-fold decrease) in contaminated soils using a phosphate loading of just 0.046%. The authors also noted that increasing the phosphate loading to 0.23% (5-fold increase) failed to further reduce the mobility of zinc, which is consistent with the results reported herein for C2CP RDS.

It is important to reiterate here that the type and loading of the stabilising agent needs to be controlled so as to avoid significant changes in pH. Stabilised RDS that produce acidic leachates will yield higher concentrations of heavy metals – for example, TCLP leaching conditions at pH 5 (ie landfill leachate pH) resulted in ca. 15 times higher concentrations of zinc than the equivalent freshwater leaching (pH ca. 8). In short, while immobilisation mechanisms such as sorption (eg compost) and chemical conversion (eg phosphate) are

potentially useful for stabilising heavy metal contaminants, amendments resulting in significant changes to leachate pH should be avoided.

A number of reuse applications involve composting RDS or blending RDS with pre-formed compost/organic matter. Despite general claims relating to contaminant immobilisation via absorption, there appears to be no rigorous scientific studies to confirm these benefits. This study has shown very effective reductions in leachate zinc concentrations and toxicity using compost loadings of only 10% (dry weight). This current study only permitted two concentrations to be trialled using just one type of compost. Accordingly, further experiments that include a wider range of compost loadings, different RDS samples, multiple replicates, and different types of compost are required in order to fully evaluate the heavy metal stabilising benefits of adding compost to RDS. Longer-term pilot scale experiments are required to determine whether the presence of compost, or even the organic vegetation originally present in the RDS, has the potential to generate acidic leachates. This is undesirable since it would result in increased mobilisation of heavy metals in RDS (relative to unstabilised RDS). The decomposition of organic matter can lower pH by the formation of organic acids; however, the benefit of compost is that it has already been partially degraded (ie humified) prior to blending with RDS. The potential for acidic leachates from compost-stabilised RDS is presumably small because of the refractory nature of the humified material and the relatively low loading rates required for effective zinc binding (eg 10% dry weight).

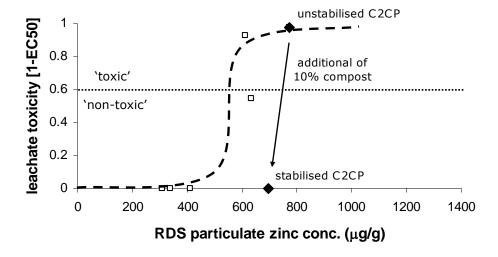


Figure 3.37 Leachate toxicity [1-EC $_{50}$] vs total particulate zinc concentrations: emphasising the stabilising effect of compost on leachate toxicity of C2CP.

It is important to reiterate that C2CP was selected as a worse case scenario RDS, as the leachate from this RDS sample was the most toxic of the eight samples originally tested. The simple addition of 10% compost to this sample resulted in a 200-fold decrease algal toxicity (based on EC_{50} data). The pronounced decrease in leachate toxicity from adding 10% compost is illustrated in Figure 3.37. This dose-response curve is based on particulate zinc concentrations (similar to Figure 3.30) and shows C2CP RDS shift from 'toxic' when untreated (773 μ g/g of zinc) to 'non-toxic' when compost-stabilised (ca. 700

 μ g/g of zinc because of 10% compost dilution). These results provide confirmation that, for zinc at least, the addition of humic matter does bind and immobilise a significant fraction of problematic heavy metals that would otherwise dissolve and contribute to leachate toxicity.

4. What it means for reusing RDS in New Zealand

4.1 General summary and the need for change

The main purpose of this research project was to characterise typical RDS in New Zealand and, based on the concentrations and toxicity of these contaminants, ascertain the suitability of RDS for potential reuse applications implemented overseas. An important driver for reusing RDS is the rising costs of disposing of tens-of-thousands of tonnes of RDS in landfills. These economic pressures are highlighted by the current situation in Christchurch, where in the 12 months ending October 2007, ca. 7600 tonnes of RDS were landfilled at a cost of ca. \$1.5m. Increases in tipping charges at the nation's landfills will continue to put pressure on road maintenance budgets, with anecdotal evidence suggesting that roading managers may already be reducing sweeping maintenance in order to offset increasing costs. With up to four tonnes of RDS collected per km per year on the nation's roads, the long-term sustainability of landfilling all RDS in New Zealand is questionable.

Just as New Zealand has followed international trends in promoting the reuse of biosolids, it is timely for this country to look at the feasibility of implementing more sustainable approaches to managing the RDS waste stream. Through a change in thinking that views RDS as a something of worth (ie a potential product) and not a waste product, cities in the United States (and Canada) have been successful in reducing the amount of RDS landfilled by 80–100%. The potential to reduce large amounts of waste is consistent with the key aims of *The New Zealand waste strategy*.

Work presented in Chapter 3 has shown that RDS in New Zealand does contain a relatively high amount of contaminants (Table 4.1) with the greatest risk probably coming from zinc – based on comparisons with biosolids guidelines for contaminants (NZWWA 2003). The relative concern regarding the concentration of zinc in RDS is illustrated in Figure 4.1. Except for zinc, there were no significant differences in the concentrations of contaminants present in catchpit sediments versus road sweepings.

Table 4.1 Summary of contaminar	t concentrations (µg/g) in RDS.
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Contaminant	Median	Lower quartile	Upper quartile
TPH	1220	935	1740
PAHs	6.3	3.2	11.2
lead	122	57	170
copper	67	41	119
zinc	422	303	555

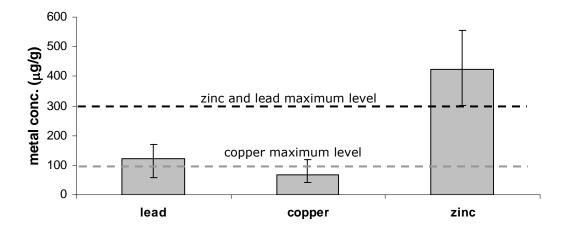


Figure 4.1 Median concentrations of heavy metals in RDS relative to maximum contaminant criteria of Grade 'a' biosolids ('error bars' represent upper and lower quartiles).

Based on toxicity guidelines for aqueous extracts, three of the eight RDS samples were classified as toxic (refer to Figure 3.27). Assuming zinc was largely responsible for the observed toxicity; the toxicity threshold for RDS samples appeared to occur at particulate zinc concentrations of ca. 550 μ g/g, which corresponded to the upper quartile concentration (Figure 4.2). The data shown indicated that although the toxicity threshold concentration was 550 μ g/g of zinc, the estimated 'safe' concentration was more likely to be around 300 μ g/g. Given that the lower quartile concentration of zinc in RDS was 303 μ g/g, this means that 75% of RDS samples may exceed this estimated 'safe' concentration. This is an important finding with respect to the way RDS may be reused in New Zealand, since clearly it is not advisable to use untreated and/or undiluted RDS directly in the environment.

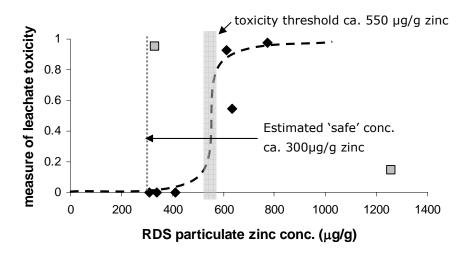


Figure 4.2 Toxicity of RDS leachates vs particulate zinc concentrations to determine the estimated 'safe' zinc concentration.

4.2 Cleanfill disposal

At the outset of this research project, a viable reuse option was disposing of RDS in cleanfills; however, the results from this study, and the finding from other studies, do not support cleanfilling RDS. Furthermore, it is the opinion of the author, that while disposing of RDS in cleanfills may address the growing costs of landfilling, it does not embrace longer-term environmental sustainability goals. Neither does this application respond to the need for a change in thinking, which views RDS as something of value (ie a potential product) rather than as a waste material needing disposal.

4.3 Reducing contaminant risks from reused RDS

In Section 3.4.3, three options were discussed that are considered relevant to reducing the risk of contaminants mobilised from reused RDS. These included (note all applications assume RDS is first pre-screened (ie 25 mm) to remove rubbish):

- 1. **Physically 'locking up' contaminated material** Main applications involve using RDS as fine aggregate component in the manufacture of concrete and bitumen.
- 2. **Blending with clean materials** The biosolids guidelines permit blending with clean material to dilute contaminant so that they comply with guideline concentrations. Potential applications include using RDS as a component of compost, growing media or top soil.
- 3. Stabilisation (treatment) of metal contaminants Adding materials for the specific purpose of immobilisation of metal contaminants, not simply diluting. Heavy metal immobilisation can be achieved by adding special metal binding phases (ie humic matter) or components that convert the metals to highly insoluble forms (ie phosphate materials).

With respect to option 3, the research showed that simply adding 10% compost to toxic RDS samples (ie C2CP) can reduce leachate zinc concentrations and toxicity by 14- and 220-fold, respectively. As clearly evident in Figure 3.37, this simple compost stabilisation transformed one of the most toxic RDS samples into a treated non-toxic material that is presumably conducive to many reuse options that involve land application.

With the ease and potential to eliminate toxicity concerns, treatment of RDS with small amounts of compost (or equivalent stabilisation agent) is considered a very useful way to address environmental concerns. Using stabilised RDS material (via option 3) as a feed stock for preparing blends (ie option 2) would further reduce risk because of the additive benefits of combining contaminant *stabilisation* and *dilution* approaches.

Based on contaminant concentrations, the only reuse options applicable to non-diluted (ie non-blended) or untreated RDS, are those that physically lock the RDS particles into a solid matrix. In doing so, the majority of the contaminants are effectively removed from any contaminant leaching/migration processes and, therefore, represent minimal risk to the environment. An example of this application was the use of catchpit sediments in the

construction of 'eco blocks' that were used by the municipality for various retaining applications.

4.4 Requirements to move RDS reuse forward in New Zealand

The purpose of this project has been to provide a scientific starting point for the possible implementation of more sustainable approaches to managing RDS. However, this will require buy-in from many end users and, more importantly, environmental agencies if it is to get off the ground. An initial aim of the project was to determine whether the current 'unsuitable for cleanfill' classification of RDS was necessary; however, as the project progressed, it became apparent more innovative options (that represent genuine reuse/recycling of a current waste stream) were required.

What is now required is the realisation of a need to find cost-effective alternatives, which will vary for different areas depending on current tonnage disposal costs and which will act as a catalyst for the formation of groups or consortia to establish pilot programmes to look into practical implementation aspects that were well beyond the scope of this research project. Consortia would ideally consist of regulators, scientists, industry partners (ie contractors) and waste generators (ie councils, Transit New Zealand etc) – with the common goal of changing the perception of RDS in New Zealand from a landfilled waste to something of value. Based on the outcomes of these pilot programmes, it would then be hoped that this would drive the need for the establishment of some national quidelines on reusing RDS – analogous to the biosolids guidelines.

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Appendix A RDS characterisation data tables

Table A.1 Particle size distribution of RDS samples

Sample		Part	icle size (mm)) distribution	by %	
	>19	19-5.6	5.6-1.0	1.0-0.5	0.5-0.063	<0.063
Auckland						
A1SW	1.7	16.5	30.3	11.0	34.8	5.6
A1CP	1.5	12.0	33.6	19.4	30.8	2.7
A2SW	7.8	25.5	31.4	9.3	22.1	3.9
A2CP	1.3	16.2	43.7	15.7	21.1	2.0
A3SW	3.6	15.4	31.4	11.1	33.8	4.7
АЗСР	2.4	12.5	29.4	13.4	37.8	4.6
A4SW	1.8	6.0	30.1	11.4	42.1	8.6
A4CP	2.0	15.6	31.8	25.9	21.5	3.2
A5CP	13.4	41.6	25.3	3.9	12.1	3.7
A6SW	3.8	18.4	33.3	11.3	26.7	6.5
Hamilton						
H1SW	8.2	30.9	25.8	11.7	21.3	2.0
H1CP	0.1	5.3	25.0	23.7	38.8	7.0
H2SW	4.1	11.9	20.1	14.5	38.3	11.2
H2CP	0.1	4.2	21.5	21.2	47.4	5.5
H3SW	1.5	3.5	23.9	18.8	43.4	9.0
НЗСР	3.0	12.9	24.7	19.9	34.4	5.1
H4SW	0.4	29.6	25.1	12.8	27.8	4.3
H4CP	5.1	15.6	18.6	16.1	37.9	6.6
H5SW	0.4	24.2	45.0	15.9	13.3	1.3
H5CP	1.7	3.5	31.5	26.3	33.1	4.0
N1SW	2.2	15.4	34.0	17.6	24.8	5.9
N1CP	1.2	22.7	33.3	20.4	17.3	5.0
Christchurc	h					
C1SW	0.0	3.3	11.4	12.8	61.1	11.5
C1CP	3.8	11.6	18.5	12.2	43.3	10.5
C2SW	7.3	19.5	29.0	9.5	27.8	6.8
C2CP	0.4	2.2	8.4	9.7	75.2	4.1
C3SW	0.2	20.2	19.1	6.2	38.3	16.0
СЗСР	0.0	10.5	15.8	12.2	49.8	11.7
C4SW	0.0	27.9	15.7	11.8	37.5	7.0
C4CPi	4.6	21.6	22.9	13.5	32.9	4.5
C4CPii	0.0	24.5	18.0	13.5	33.4	10.5
C5SW	1.6	10.7	16.3	10.6	48.8	11.9

Table A.2 Percentage of organic matter (OM) in RDS samples (<5.6 mm fraction).

			1	
RDS sample	Dry weight (g) 100°C	Ash weight (g) 400°C	Difference – OM	Percentage OM (%)
C1SW	36.991	34.713	(g) 2.278	6.2
C1CP	29.686	25.272	4.414	14.9
C2SW	32.909	29.523	3.386	10.3
C2CP	29.201	26.048	3.153	10.8
A3SW	37.004	33.995	3.009	8.1
C3CP	32.354	28.977	3.377	10.4
C4SW	37.423	34.795	2.628	7.0
C4CPi	34.800	31.076	3.724	10.7
C4CPii	26.278	20.939	5.339	20.3
C5SW	39.824	37.354	2.470	6.2
		44.734		
C5CP	46.645		1.911	4.1
H1SW	25.646	22.877	2.769	10.8
H1CP	16.155	14.605	1.550	9.6
H2SW	26.858	22.733	4.125	15.4
H2CP	28.193	25.711	2.482	8.8
H3SW	34.678	30.913	3.765	10.9
H3CP	25.605	20.983	4.622	18.1
H4SW	27.532	22.746	4.786	17.4
H4CP	32.753	29.080	3.673	11.2
H5SW	20.074	16.134	3.940	19.6
H5CP	17.195	13.167	4.028	23.4
N1SW	43.259	40.363	2.896	6.7
N1CP	60.197	59.143	1.054	1.8
A1SW	25.661	21.143	4.518	17.6
A1CP	40.178	36.867	3.311	8.2
A2SW	20.738	16.594	4.144	20.0
A2CP	42.537	40.051	2.486	5.8
A3SW	24.433	21.743	2.690	11.0
АЗСР	20.704	16.775	3.929	19.0
A4SW	20.829	17.080	3.749	18.0
A4CP	21.233	16.846	4.387	20.7
A5CP	57.843	56.417	1.426	2.5
A6SW	44.763	42.814	1.949	4.4
А7СРі	49.559	47.602	1.957	3.9
A7CPii	22.613	19.327	3.286	14.5

Table A.3 Percentage of organic matter (OM) in individual particle size fractions from seven RDS samples.

RDS sample	Dry weight	Ash weight	Difference =	Percentage OM
	(g) 100°C	(g) 400°C	OM (g)	(%)
A2SW 1.0-5.6mm	23.582	19.918	3.664	15.5
A2SW 0.5-1.0mm	21.447	18.738	2.709	12.6
A2SW 0.063-0.5mm	24.903	22.233	2.670	10.7
A2SW < 0.063mm	11.561	11.358	0.203	1.8
H3CP 1.0-5.6mm	26.552	22.058	4.494	16.9
H3CP 0.5-1.0mm	26.933	24.273	2.660	9.9
H3CP 0.063-0.5mm	29.771	27.321	2.450	8.2
H3CP < 0.063mm	17.004	15.678	1.326	7.8
H3SW 1.0-5.6mm	29.818	27.585	2.233	7.5
H3SW 0.5-1.0mm	32.634	30.941	1.693	5.2
H3SW 0.063-0.5mm	32.438	29.858	2.580	8.0
H3SW < 0.063mm	26.416	24.195	2.221	8.4
A1CP 1.0-5.6mm	39.839	37.496	2.343	5.9
A1CP 0.5-1.0mm	36.209	34.320	1.889	5.2
A1CP 0.063-0.5mm	36.987	34.812	2.175	5.9
A1CP < 0.063mm	23.951	20.931	3.020	12.6
C1SW 1.0-5.6mm	31.125	28.966	2.159	6.9
C1SW 0.5-1.0mm	32.466	30.696	1.770	5.5
C1SW 0.063-0.5mm	45.781	44.216	1.565	3.4
C1SW < 0.063mm	32.419	30.313	2.106	6.5
C1CP 1.0-5.6mm	30.762	28.138	2.624	8.5
C1CP 0.5-1.0mm	25.312	22.553	2.759	10.9
C1CP 0.063-0.5mm	34.072	31.178	2.894	8.5
C1CP < 0.063mm	25.505	22.725	2.780	10.9
A1SW 1.0-5.6mm	25.633	22.915	2.718	10.6
A1SW 0.5-1.0mm	25.070	22.259	2.811	11.2
A1SW 0.063-0.5mm	30.570	28.504	2.066	6.8
A1SW < 0.063mm	14.535	13.759	0.776	5.3

Table A.4 TPH concentrations in RDS samples (μ g/g dry weight).

RDS	TP	H carbon band (µg	/g)	Total TPH
sample	C ₇ -C ₉	C ₁₀ -C ₁₄	C ₁₅ -C ₃₆	(µg/g)
C1SW	< 10	< 20	730	730
C1CP	< 10	< 30	1040	1040
C2SW	< 8	20	2160	2180
C2CP	< 10	< 20	1730	1730
C3SW	< 10	< 20	1050	1050
СЗСР	< 10	< 30	1220	1220
C4SW	< 10	< 20	990	990
C4CPi	< 10	< 20	610	610
C4CPii	< 10	< 30	1000	1000
C5SW	< 10	< 20	880	880
C5CP	< 10	< 20	430	430
H1SW	11	20	1120	1150
H1CP	< 8	< 20	1100	1100
H2SW	< 10	< 20	1640	1650
H2CP	< 8	< 20	1300	1300
H3SW	< 10	< 20	710	710
Н3СР	< 10	< 20	1550	1550
H4SW	< 8	20	1230	1250
H4CP	< 10	< 30	2160	2160
H5SW	< 8	< 20	1210	1230
Н5СР	< 10	< 20	1560	1560
N1SW	< 10	< 20	460	460
N1CP	< 10	< 20	120	120
A1SW	< 8	20	1960	1980
A1CP	< 10	< 20	1550	1550
A2SW	< 10	< 30	5260	5260
A2CP	< 9	< 20	1120	1120
A3SW	< 10	< 30	1750	1750
A3CP	< 10	< 20	2520	2520
A4SW	< 9	< 20	2310	2310
A4CP	< 9	120	2380	2500
A5CP	< 9	< 20	210	210
A6SW	< 9	< 20	600	600
А7СРі	< 10	< 20	1060	1060
A7CPii	< 10	< 20	4190	4190

Table A.5 PAH concentrations in RDS samples (μ g/g dry weight).

РАН	C1SW	C1CP	C2SW	C2CP
Naphthalene	< 0.2	< 0.09	0.15	0.08
Acenaphthene	< 0.03	0.04	0.03	0.02
Acenaphthylene	0.06	0.07	0.08	0.05
Fluorene	0.1	0.19	0.1	0.11
Anthracene	0.16	0.27	0.19	0.12
Phenanthrene	1.3	1.56	1.71	0.84
Fluoranthene	1.92	2.03	2.42	1.24
Pyrene	1.65	1.87	2.09	1.09
Benzo[a]anthracene	0.5	1.04	0.8	0.44
Chrysene	0.6	0.98	0.68	0.4
Benzo[b]fluoranthene	1.03	2.02	1.68	0.86
Benzo[k]fluoranthene	0.21	0.4	0.4	0.13
Benzo[a]pyrene (BAP)	0.31	0.69	0.55	0.29
Dibenzo[a,h]anthracene	0.07	0.15	0.13	0.08
Indenopyrene	0.19	0.39	0.38	0.19
Benzo[g,h,i]perylene	0.48	0.67	0.74	0.39
Total	8.6	12.4	12.1	6.3
	C3SW	СЗСР	C4SW	C4CPi
Naphthalene	0.08	1 0 00	0.48	. 0.00
Naphulalene	0.00	< 0.09	0.70	< 0.08
Acenaphthene	0.07	0.03	0.04	< 0.02
Acenaphthene	0.07	0.03	0.04	< 0.02
Acenaphthene Acenaphthylene	0.07 0.07	0.03 0.09	0.04 0.06	< 0.02 0.03
Acenaphthene Acenaphthylene Fluorene	0.07 0.07 0.23	0.03 0.09 0.06	0.04 0.06 0.14	< 0.02 0.03 0.02
Acenaphthene Acenaphthylene Fluorene Anthracene	0.07 0.07 0.23 0.28	0.03 0.09 0.06 0.13	0.04 0.06 0.14 0.13	< 0.02 0.03 0.02 0.05
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene	0.07 0.07 0.23 0.28 2.8	0.03 0.09 0.06 0.13 1.05	0.04 0.06 0.14 0.13 1.37	< 0.02 0.03 0.02 0.05 0.36
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene	0.07 0.07 0.23 0.28 2.8 2.87	0.03 0.09 0.06 0.13 1.05 1.8	0.04 0.06 0.14 0.13 1.37 1.24	< 0.02 0.03 0.02 0.05 0.36 0.76
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene	0.07 0.07 0.23 0.28 2.8 2.87 2.64	0.03 0.09 0.06 0.13 1.05 1.8 1.6	0.04 0.06 0.14 0.13 1.37 1.24 1.11	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene	0.07 0.07 0.23 0.28 2.8 2.87 2.64 1.1	0.03 0.09 0.06 0.13 1.05 1.8 1.6 0.74	0.04 0.06 0.14 0.13 1.37 1.24 1.11 0.44	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68 0.31
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene	0.07 0.07 0.23 0.28 2.8 2.87 2.64 1.1 1.01	0.03 0.09 0.06 0.13 1.05 1.8 1.6 0.74 0.76	0.04 0.06 0.14 0.13 1.37 1.24 1.11 0.44 0.55	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68 0.31 0.32
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene	0.07 0.07 0.23 0.28 2.8 2.87 2.64 1.1 1.01 1.97	0.03 0.09 0.06 0.13 1.05 1.8 1.6 0.74 0.76 2.07	0.04 0.06 0.14 0.13 1.37 1.24 1.11 0.44 0.55 0.85	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68 0.31 0.32 0.8
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene	0.07 0.07 0.23 0.28 2.8 2.87 2.64 1.1 1.01 1.97 0.44	0.03 0.09 0.06 0.13 1.05 1.8 1.6 0.74 0.76 2.07 0.4	0.04 0.06 0.14 0.13 1.37 1.24 1.11 0.44 0.55 0.85 0.19	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68 0.31 0.32 0.8 0.15
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP)	0.07 0.07 0.23 0.28 2.8 2.87 2.64 1.1 1.01 1.97 0.44 0.76	0.03 0.09 0.06 0.13 1.05 1.8 1.6 0.74 0.76 2.07 0.4 0.72	0.04 0.06 0.14 0.13 1.37 1.24 1.11 0.44 0.55 0.85 0.19 0.26	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68 0.31 0.32 0.8 0.15 0.26
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP) Dibenzo[a,h]anthracene	0.07 0.07 0.23 0.28 2.8 2.87 2.64 1.1 1.01 1.97 0.44 0.76 0.12	0.03 0.09 0.06 0.13 1.05 1.8 1.6 0.74 0.76 2.07 0.4 0.72 0.13	0.04 0.06 0.14 0.13 1.37 1.24 1.11 0.44 0.55 0.85 0.19 0.26 0.05	< 0.02 0.03 0.02 0.05 0.36 0.76 0.68 0.31 0.32 0.8 0.15 0.26 0.06

Table A.5 (cont.) PAH concentrations in RDS samples (μ g/g dry weight).

РАН	C4CPii	C5SW	C5CP	H1SW
Naphthalene	< 0.09	< 0.07	< 0.07	< 0.06
Acenaphthene	< 0.02	0.02	< 0.01	< 0.01
Acenaphthylene	0.04	0.05	0.02	< 0.01
Fluorene	0.05	0.07	0.03	0.01
Anthracene	0.11	0.1	0.03	0.01
Phenanthrene	0.61	0.91	0.22	0.13
Fluoranthene	1.29	1.32	0.3	0.35
Pyrene	1.13	1.15	0.27	0.31
Benzo[a]anthracene	0.5	0.47	0.1	0.11
Chrysene	0.55	0.55	0.14	0.16
Benzo[b]fluoranthene	1.19	1.15	0.22	0.34
Benzo[k]fluoranthene	0.23	0.21	0.02	0.06
Benzo[a]pyrene (BAP)	0.4	0.39	0.06	0.11
Dibenzo[a,h]anthracene	0.1	0.07	0.02	0.02
Indenopyrene	0.28	0.22	0.03	0.08
Benzo[g,h,i]perylene	0.58	0.35	0.08	0.2
Total	7.1	7.0	1.5	1.9
	H1CP	H2SW	H2CP	H3SW
Naphthalene	H1CP < 0.05	H2SW < 0.07	H2CP < 0.05	H3SW < 0.08
Naphthalene Acenaphthene				
·	< 0.05	< 0.07	< 0.05	< 0.08
Acenaphthene	< 0.05 0.02	< 0.07 < 0.01	< 0.05 < 0.01	< 0.08 < 0.02
Acenaphthene Acenaphthylene	< 0.05 0.02 0.05	< 0.07 < 0.01 0.02	< 0.05 < 0.01 < 0.01	< 0.08 < 0.02 0.03
Acenaphthene Acenaphthylene Fluorene	< 0.05 0.02 0.05 0.04	< 0.07 < 0.01 0.02 0.02	< 0.05 < 0.01 < 0.01 < 0.01	< 0.08 < 0.02 0.03 0.02
Acenaphthene Acenaphthylene Fluorene Anthracene	< 0.05 0.02 0.05 0.04 0.2	< 0.07 < 0.01 0.02 0.02 0.03	< 0.05 < 0.01 < 0.01 < 0.01 0.01	< 0.08 < 0.02 0.03 0.02 0.09
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene	< 0.05 0.02 0.05 0.04 0.2 1.08	< 0.07 < 0.01 0.02 0.02 0.03 0.21	< 0.05 < 0.01 < 0.01 < 0.01 0.01 0.09	< 0.08 < 0.02 0.03 0.02 0.09 0.49
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59	< 0.05 < 0.01 < 0.01 < 0.01 0.01 0.09 0.31 0.28	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9 0.92	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59 0.13	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31 0.28 0.06	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2 0.45
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9 0.92 0.69	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59 0.13 0.22	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31 0.28 0.06 0.13	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2 0.45 0.54
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9 0.92 0.69 2.01	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59 0.13 0.22 0.44	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31 0.28 0.06 0.13 0.24	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2 0.45 0.54 0.69
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9 0.92 0.69 2.01 0.39	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59 0.13 0.22 0.44 0.05	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31 0.28 0.06 0.13 0.24 0.03	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2 0.45 0.54 0.69 0.26
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP)	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9 0.92 0.69 2.01 0.39 0.73	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59 0.13 0.22 0.44 0.05 0.11	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31 0.28 0.06 0.13 0.24 0.03 0.06	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2 0.45 0.54 0.69 0.26 0.43
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP) Dibenzo[a,h]anthracene	< 0.05 0.02 0.05 0.04 0.2 1.08 2.17 1.9 0.92 0.69 2.01 0.39 0.73 0.14	< 0.07 < 0.01 0.02 0.02 0.03 0.21 0.69 0.59 0.13 0.22 0.44 0.05 0.11 0.03	< 0.05 < 0.01 < 0.01 < 0.01 0.09 0.31 0.28 0.06 0.13 0.24 0.03 0.06 0.02	< 0.08 < 0.02 0.03 0.02 0.09 0.49 1.32 1.2 0.45 0.54 0.69 0.26 0.43 0.05

Table A.5 (cont.) PAH concentrations in RDS samples (μ g/g dry weight).

РАН	НЗСР	H4SW	Н4СР	H5SW
Naphthalene	< 0.07	< 0.06	0.16	< 0.06
Acenaphthene	0.02	0.01	0.02	< 0.01
Acenaphthylene	0.04	0.02	0.14	< 0.01
Fluorene	0.04	0.02	0.07	< 0.01
Anthracene	0.11	0.04	0.21	< 0.01
Phenanthrene	0.67	0.26	1.57	0.03
Fluoranthene	1.34	0.73	3.42	0.05
Pyrene	1.17	0.65	3.05	0.04
Benzo[a]anthracene	0.61	0.28	1.26	< 0.01
Chrysene	0.51	0.28	1.17	< 0.01
Benzo[b]fluoranthene	1.59	0.73	3.57	0.04
Benzo[k]fluoranthene	0.27	0.11	0.61	< 0.01
Benzo[a]pyrene (BAP)	0.52	0.29	1.09	< 0.01
Dibenzo[a,h]anthracene	0.11	0.06	0.24	< 0.01
Indenopyrene	0.36	0.22	0.84	< 0.01
Benzo[g,h,i]perylene	0.6	0.32	1.3	0.04
Total	8.0	4.0	18.7	0.2
	H5CP	N1SW	N1CP	A1SW
Naphthalene	< 0.07	< 0.07	0.33	< 0.05
Acenaphthene	< 0.01	< 0.01	0.04	< 0.01
Acenaphthylene	< 0.01	< 0.01	< 0.01	0.03
Fluorene	< 0.01	< 0.01	0.02	0.02
Anthracene	< 0.01	< 0.01	0.07	0.06
Phenanthrene	0.07	0.04	0.31	0.46
Fluoranthene	0.12	0.15	0.61	0.65
Pyrene	0.1	0.16	0.62	0.91
Benzo[a]anthracene	< 0.01	0.04	0.2	0.19
Chrysene	< 0.01	0.1	0.31	0.35
Benzo[b]fluoranthene	0.08	0.15	0.36	0.59
Benzo[k]fluoranthene	< 0.01	0.06	0.16	0.21
Benzo[a]pyrene (BAP)	0.02	0.06	0.22	0.24
		1	0.03	0.04
Dibenzo[a,h]anthracene	< 0.01	< 0.01	0.03	0.04
Dibenzo[a,h]anthracene Indenopyrene	< 0.01 < 0.01	< 0.01 0.05	0.14	0.21

Table A.5 (cont.) PAH concentrations in RDS samples (μ g/g dry weight).

РАН	A1CP	A2SW	A2CP	A3SW
Naphthalene	< 0.08	< 0.08	< 0.06	< 0.1
Acenaphthene	0.08	0.02	0.03	< 0.02
Acenaphthylene	0.26	0.04	0.22	0.03
Fluorene	0.16	0.03	0.05	0.02
Anthracene	0.51	0.11	0.23	0.06
Phenanthrene	2.31	0.54	1.08	0.49
Fluoranthene	4.35	0.78	2.57	0.62
Pyrene	3.91	1.07	2.41	0.79
Benzo[a]anthracene	1.26	0.21	0.77	0.16
Chrysene	1.85	0.34	1.12	0.27
Benzo[b]fluoranthene	2.98	0.7	1.91	0.53
Benzo[k]fluoranthene	1.09	0.24	0.68	0.19
Benzo[a]pyrene (BAP)	1.43	0.27	0.9	0.21
Dibenzo[a,h]anthracene	0.25	0.04	0.18	0.02
Indenopyrene	1.14	0.24	0.78	0.18
Benzo[g,h,i]perylene	1.47	0.44	1.02	0.33
Total	23.1	5.1	14.0	3.9
	A3CP	A4SW	A4CP	A5CP
Naphthalene	A3CP 0.1	A4SW 0.11	A4CP < 0.06	A5CP < 0.06
Naphthalene Acenaphthene				
·	0.1	0.11	< 0.06	< 0.06
Acenaphthene	0.1 0.07	0.11 0.06	< 0.06 0.01	< 0.06 < 0.01
Acenaphthene Acenaphthylene	0.1 0.07 0.44	0.11 0.06 0.29	< 0.06 0.01 0.09	< 0.06 < 0.01 < 0.01
Acenaphthene Acenaphthylene Fluorene	0.1 0.07 0.44 0.12	0.11 0.06 0.29 0.12	< 0.06 0.01 0.09 0.02	< 0.06 < 0.01 < 0.01 < 0.01
Acenaphthene Acenaphthylene Fluorene Anthracene	0.1 0.07 0.44 0.12 0.55	0.11 0.06 0.29 0.12 0.37	< 0.06 0.01 0.09 0.02 0.13	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene	0.1 0.07 0.44 0.12 0.55 2.15	0.11 0.06 0.29 0.12 0.37 1.87	< 0.06 0.01 0.09 0.02 0.13 0.32	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 0.03
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene	0.1 0.07 0.44 0.12 0.55 2.15 5.68	0.11 0.06 0.29 0.12 0.37 1.87 3.97	< 0.06 0.01 0.09 0.02 0.13 0.32 1.42	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56	< 0.06 0.01 0.09 0.02 0.13 0.32 1.42 1.44	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06 0.07
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12 1.69	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56 1.08	< 0.06 0.01 0.09 0.02 0.13 0.32 1.42 1.44 0.42	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06 0.07 < 0.01
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12 1.69 2.36	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56 1.08 1.65	< 0.06 0.01 0.09 0.02 0.13 0.32 1.42 1.44 0.42 0.66	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06 0.07 < 0.01 < 0.01
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12 1.69 2.36 4.53	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56 1.08 1.65 3.11	< 0.06 0.01 0.09 0.02 0.13 0.32 1.42 1.44 0.42 0.66 1.38	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06 0.07 < 0.01 < 0.01 0.03
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12 1.69 2.36 4.53 1.64	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56 1.08 1.65 3.11 1.09	< 0.06	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06 0.07 < 0.01 < 0.01 0.03 < 0.01
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP)	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12 1.69 2.36 4.53 1.64 1.91	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56 1.08 1.65 3.11 1.09 1.3	< 0.06	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03 0.06 0.07 < 0.01 < 0.01 0.03 < 0.01 0.03
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP) Dibenzo[a,h]anthracene	0.1 0.07 0.44 0.12 0.55 2.15 5.68 5.12 1.69 2.36 4.53 1.64 1.91 0.38	0.11 0.06 0.29 0.12 0.37 1.87 3.97 3.56 1.08 1.65 3.11 1.09 1.3 0.25	< 0.06	< 0.06 < 0.01 < 0.01 < 0.01 < 0.01 < 0.03

Table A.5 (cont.) PAH concentrations in RDS samples (μ g/g dry weight).

PAH	A6SW	A7CPi	A7CPii
Naphthalene	< 0.06	< 0.08	0.1
Acenaphthene	< 0.01	0.02	0.03
Acenaphthylene	0.03	0.05	0.08
Fluorene	0.02	0.04	0.06
Anthracene	0.03	0.1	0.11
Phenanthrene	0.16	0.57	0.6
Fluoranthene	0.34	1.06	1.67
Pyrene	0.36	1.01	1.95
Benzo[a]anthracene	0.1	0.29	0.41
Chrysene	0.09	0.34	0.73
Benzo[b]fluoranthene	0.24	0.64	1.58
Benzo[k]fluoranthene	0.09	0.24	0.5
Benzo[a]pyrene (BAP)	0.11	0.32	0.47
Dibenzo[a,h]anthracene	< 0.01	0.05	0.09
Indenopyrene	0.09	0.26	0.44
Benzo[g,h,i]perylene	0.31	0.4	0.93
Total	2.0	5.4	9.8

Table A.6 Concentrations ($\mu g/g$ dry weight) of lead, copper and zinc in RDS.

RDS	heavy metal concentration (µg/g)			
sample	lead	copper	zinc	
A1SW	128	208	371	
A2SW	162	384	611	
A3SW	132	206	441	
A4SW	211	120	528	
A6SW	17.8	50.4	162	
C1SW	153	94.6	340	
C2SW	280	156	333	
C3SW	112	44.2	292	
C4SW	122	38.0	342	
C5SW	125	28.7	312	
H1SW	88.5	60.8	259	
H2SW	64.0	59.2	635	
H3SW	34.9	22.4	148	
H4SW	101	47.0	421	
H5SW	16.7	31.5	294	
N1SW	45.2	30.6	221	
A1CP	101	94.5	311	
A2CP	162	74.4	413	
АЗСР	183	123	515	
A4CP	182	108	487	
A5CP	15.1	35.8	136	
А7СРі	50.1	97.9	442	
A7CPii	149	193	1259	
C1CP	255	66.6	464	
C2CP	192	118	773	
СЗСР	350	85.2	875	
C4CPi	133	124	451	
C4CPii	178	115	450	
C5CP	22.7	21.7	150	
H1CP	66.5	47.9	582	
H2CP	46.5	48.7	422	
НЗСР	65.0	55.6	640	
Н4СР	1385	124	4186	
Н5СР	72.6	37.0	1039	
N1CP	9.8	13.2	118	

Table A.7 Concentrations ($\mu g/g$ dry weight) of TPH in individual particle size fractions of selected RDS samples.

RDS	Particle size	TPF	ł carbon band (µg	1/ g)	Total TPH
sample	fraction (mm)	C ₇ -C ₉	C ₁₀ -C ₁₄	C ₁₅ -C ₃₆	(µg/g)
A1CP	<0.063	< 9	< 20	7950	7950
A1CP	0.063-0.5	< 9	< 20	2990	2990
A1CP	0.5-1	< 9	< 20	2740	2740
A1CP	1-5.6	< 7	< 10	1680	1680
A1SW	<0.063	< 8	40	5990	6040
A1SW	0.063-0.5	< 9	< 20	2820	2820
A1SW	0.5-1	< 9	20	2480	2510
A1SW	1-5.6	< 8	50	2520	2570
A2SW	<0.063	16	70	16600	16700
A2SW	0.063-0.5	< 9	30	7670	7700
A2SW	0.5-1	< 9	40	8910	8950
A2SW	1-5.6	< 8	50	7500	7550
C1CP	<0.063	< 9	< 20	4130	4130
C1CP	0.063-0.5	< 9	< 20	2260	2260
C1CP	0.5-1	< 9	< 20	2330	2340
C1CP	1-5.6	< 7	< 10	1610	1620
C1SW	<0.063	< 9	< 20	2360	2360
C1SW	0.063-0.5	< 8	< 20	1130	1130
C1SW	0.5-1	< 9	< 20	970	970
C1SW	1-5.6	< 7	21	1420	1440
Н3СР	<0.063	< 9	< 20	4140	4150
Н3СР	0.063-0.5	< 9	< 20	1900	1900
Н3СР	0.5-1	< 8	< 20	2530	2530
Н3СР	1-5.6	< 9	< 20	4640	4650
H3SW	<0.063	< 9	< 20	1940	1940
H3SW	0.063-0.5	< 9	< 20	1580	1580
H3SW	0.5-1	< 9	< 20	900	900
H3SW	1-5.6	< 7	< 10	1180	1180

Table A.8 Concentrations ($\mu g/g$ dry weight) of PAHs in individual particle size fractions of selected RDS samples.

РАН	A1CP	A1CP	A1CP	A1CP
	<0.063 mm	0.063-0.5 mm	0.5-1 mm	1-5.6 mm
Naphthalene	0.083	0.056	0.061	0.039
Acenaphthene	0.038	0.032	0.052	0.0537
Acenaphthylene	0.31	0.162	0.217	0.106
Fluorene	0.075	0.058	0.083	0.125
Anthracene	1.88	1.53	2.3	3.03
Phenanthrene	0.272	0.204	0.341	0.346
Fluoranthene	5.24	2.64	4.56	3.61
Pyrene	7.28	3.87	5.48	3.85
Benzo[a]anthracene	4.81	2.36	3.35	1.55
Chrysene	3.29	1.36	1.86	1.42
Benzo[b]fluoranthene	9.33	4.81	6.03	2.27
Benzo[k]fluoranthene	2.34	0.838	0.877	1.06
Benzo[a]pyrene (BAP)	4.53	2.05	2.91	1.72
Dibenzo[a,h]anthracene	0.351	0.169	0.19	0.219
Indenopyrene	1.41	0.627	0.712	0.952
Benzo[g,h,i]perylene	3.63	1.57	1.7	1.11
Total	44.9	22.3	30.7	21.5
	A1SW	A1SW	A1SW	A1SW
DVH		_		
РАН	<0.063 mm	0.063-0.5 mm	0.5-1 mm	1-5.6 mm
Naphthalene	< 0.063 mm 0.026		0.5-1 mm 0.02	1-5.6 mm 0.005
		0.063-0.5 mm		
Naphthalene	0.026	0.063-0.5 mm 0.017	0.02	0.005
Naphthalene Acenaphthene	0.026 0.01	0.063-0.5 mm 0.017 0.006	0.02 0.011	0.005 0.0014
Naphthalene Acenaphthene Acenaphthylene	0.026 0.01 0.061	0.063-0.5 mm 0.017 0.006 0.032	0.02 0.011 0.058	0.005 0.0014 0.0073
Naphthalene Acenaphthene Acenaphthylene Fluorene	0.026 0.01 0.061 0.028	0.063-0.5 mm 0.017 0.006 0.032 0.023	0.02 0.011 0.058 0.036	0.005 0.0014 0.0073 0.0058
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene	0.026 0.01 0.061 0.028 0.85	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692	0.02 0.011 0.058 0.036 1.14	0.005 0.0014 0.0073 0.0058 0.177
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene	0.026 0.01 0.061 0.028 0.85 0.063	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055	0.02 0.011 0.058 0.036 1.14 0.091	0.005 0.0014 0.0073 0.0058 0.177 0.049
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene	0.026 0.01 0.061 0.028 0.85 0.063 0.688	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532	0.02 0.011 0.058 0.036 1.14 0.091 0.748	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34 0.78	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983 0.535	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22 0.598	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548 0.286
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34 0.78 0.403	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983 0.535 0.318	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22 0.598 0.406	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548 0.286 0.157
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34 0.78 0.403 1.41	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983 0.535 0.318 0.912	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22 0.598 0.406 0.94	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548 0.286 0.157 0.427
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34 0.78 0.403 1.41 0.298	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983 0.535 0.318 0.912 0.199	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22 0.598 0.406 0.94 0.182	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548 0.286 0.157 0.427 0.115
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP)	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34 0.78 0.403 1.41 0.298 0.942	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983 0.535 0.318 0.912 0.199 0.583	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22 0.598 0.406 0.94 0.182 0.565	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548 0.286 0.157 0.427 0.115 0.252
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP) Dibenzo[a,h]anthracene	0.026 0.01 0.061 0.028 0.85 0.063 0.688 1.34 0.78 0.403 1.41 0.298 0.942 0.085	0.063-0.5 mm 0.017 0.006 0.032 0.023 0.692 0.055 0.532 0.983 0.535 0.318 0.912 0.199 0.583 0.06	0.02 0.011 0.058 0.036 1.14 0.091 0.748 1.22 0.598 0.406 0.94 0.182 0.565 0.051	0.005 0.0014 0.0073 0.0058 0.177 0.049 0.384 0.548 0.286 0.157 0.427 0.115 0.252 0.0293

Table A.8 $\,$ (cont.) Concentrations (µg/g dry weight) of PAHs in individual particle size fractions of selected RDS samples.

РАН	A2SW	A2SW	A2SW	A2SW
	<0.063 mm	0.063-0.5 um	0.5-1 mm	1-5.6 mm
Naphthalene	0.041	0.028	0.028	0.012
Acenaphthene	0.013	0.008	0.009	0.0026
Acenaphthylene	0.063	0.035	0.031	0.0149
Fluorene	0.053	0.043	0.041	0.0131
Anthracene	1.21	0.998	0.883	0.251
Phenanthrene	0.073	0.073	0.092	0.0827
Fluoranthene	0.666	0.521	0.648	0.452
Pyrene	1.4	1.01	1.24	0.622
Benzo[a]anthracene	0.655	0.57	0.524	0.321
Chrysene	0.338	0.257	0.323	0.158
Benzo[b]fluoranthene	1.09	0.79	0.777	0.457
Benzo[k]fluoranthene	0.235	0.157	0.157	0.129
Benzo[a]pyrene (BAP)	0.782	0.424	0.604	0.197
Dibenzo[a,h]anthracene	0.087	0.045	0.059	0.0279
Indenopyrene	0.295	0.143	0.185	0.0931
Benzo[g,h,i]perylene	0.939	0.579	0.578	0.339
Total	7.9	5.7	6.2	3.2
ДΔН	C1CP	C1CP	C1CP	C1CP
РАН	C1CP <0.063 mm	C1CP 0.063-0.5 mm	C1CP 0.5-1 mm	C1CP 1-5.6 mm
PAH Naphthalene				
	<0.063 mm	0.063-0.5 mm	0.5-1 mm	1-5.6 mm
Naphthalene	< 0.063 mm 0.089	0.063-0.5 mm 0.073	0.5-1 mm 0.053	1-5.6 mm 0.009
Naphthalene Acenaphthene	<0.063 mm 0.089 0.061	0.063-0.5 mm 0.073 0.046	0.5-1 mm 0.053 0.03	1-5.6 mm 0.009 0.0075
Naphthalene Acenaphthene Acenaphthylene	<0.063 mm 0.089 0.061 0.152	0.063-0.5 mm 0.073 0.046 0.097	0.5-1 mm 0.053 0.03 0.067	1-5.6 mm 0.009 0.0075 0.0152
Naphthalene Acenaphthene Acenaphthylene Fluorene	<0.063 mm 0.089 0.061 0.152 0.258	0.063-0.5 mm 0.073 0.046 0.097 0.2	0.5-1 mm 0.053 0.03 0.067 0.111	1-5.6 mm 0.009 0.0075 0.0152 0.0326
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene	<0.063 mm 0.089 0.061 0.152 0.258 2.43	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79	0.5-1 mm 0.053 0.03 0.067 0.111 0.928	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11 2.81	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22 1.82	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18 0.85	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291 0.241
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11 2.81 1.41	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22 1.82 0.948	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18 0.85 0.489	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291 0.241 0.144
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11 2.81 1.41 3.09	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22 1.82 0.948 1.84	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18 0.85 0.489 1.37	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291 0.241 0.144 0.365
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11 2.81 1.41 3.09 1.09	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22 1.82 0.948 1.84 0.7	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18 0.85 0.489 1.37 0.374	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291 0.241 0.144 0.365 0.107
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[a]pyrene (BAP)	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11 2.81 1.41 3.09 1.09 1.54	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22 1.82 0.948 1.84 0.7 1.03	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18 0.85 0.489 1.37 0.374 0.674	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291 0.241 0.144 0.365 0.107 0.225
Naphthalene Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP) Dibenzo[a,h]anthracene	<0.063 mm 0.089 0.061 0.152 0.258 2.43 0.414 3.55 4.11 2.81 1.41 3.09 1.09 1.54 0.215	0.063-0.5 mm 0.073 0.046 0.097 0.2 1.79 0.295 2.11 2.22 1.82 0.948 1.84 0.7 1.03 0.148	0.5-1 mm 0.053 0.03 0.067 0.111 0.928 0.168 1.12 1.18 0.85 0.489 1.37 0.374 0.674 0.091	1-5.6 mm 0.009 0.0075 0.0152 0.0326 0.259 0.0454 0.305 0.291 0.241 0.144 0.365 0.107 0.225 0.0265

Table A.8 $\,$ (cont.) Concentrations (µg/g dry weight) of PAHs in individual particle size fractions of selected RDS samples.

PAH	C1SW	C1SW	C1SW	C1SW
	<0.063 mm	0.063-0.5 mm	0.5-1 mm	1-5.6 mm
Naphthalene	0.025	0.034	0.039	0.007
Acenaphthene	0.012	0.008	0.012	0.0017
Acenaphthylene	0.046	0.022	0.021	0.0055
Fluorene	0.039	0.025	0.046	0.0109
Anthracene	0.647	0.443	0.756	0.198
Phenanthrene	0.098	0.071	0.137	0.023
Fluoranthene	1.14	0.641	0.723	0.272
Pyrene	1.15	0.645	0.663	0.259
Benzo[a]anthracene	0.881	0.376	0.564	0.179
Chrysene	0.355	0.213	0.226	0.0821
Benzo[b]fluoranthene	1.31	0.494	0.87	0.21
Benzo[k]fluoranthene	0.333	0.155	0.249	0.0585
Benzo[a]pyrene (BAP)	0.439	0.274	0.305	0.121
Dibenzo[a,h]anthracene	0.061	0.031	0.052	0.0163
Indenopyrene	0.195	0.101	0.149	0.0372
Benzo[g,h,i]perylene	0.584	0.272	0.186	0.117
Total	7.3	3.8	5.0	1.6
РАН	НЗСР	НЗСР	НЗСР	НЗСР
IAII				
	<0.063 mm	0.063-0.5 mm	0.5-1 mm	1-5.6 mm
Naphthalene	< 0.063 mm 0.036	0.063-0.5 mm 0.02	0.5-1 mm 0.014	1-5.6 mm 0.01
Naphthalene Acenaphthene				
-	0.036	0.02	0.014	0.01
Acenaphthene	0.036 0.012	0.02 0.007	0.014 0.009	0.01 0.0021
Acenaphthene Acenaphthylene	0.036 0.012 0.067	0.02 0.007 0.034	0.014 0.009 0.026	0.01 0.0021 0.0152
Acenaphthene Acenaphthylene Fluorene	0.036 0.012 0.067 0.028	0.02 0.007 0.034 0.018	0.014 0.009 0.026 0.017	0.01 0.0021 0.0152 0.01
Acenaphthene Acenaphthylene Fluorene Anthracene	0.036 0.012 0.067 0.028 0.551	0.02 0.007 0.034 0.018 0.382	0.014 0.009 0.026 0.017 0.451	0.01 0.0021 0.0152 0.01 0.189
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene	0.036 0.012 0.067 0.028 0.551 0.103	0.02 0.007 0.034 0.018 0.382 0.067	0.014 0.009 0.026 0.017 0.451 0.074	0.01 0.0021 0.0152 0.01 0.189 0.038
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene	0.036 0.012 0.067 0.028 0.551 0.103 1.5	0.02 0.007 0.034 0.018 0.382 0.067 0.839	0.014 0.009 0.026 0.017 0.451 0.074 0.8	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14 2.23	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09 0.985	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06 1.09	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543 0.47
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14 2.23 0.873	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09 0.985 0.508	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06 1.09 0.557	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543 0.47 0.22
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14 2.23 0.873 2.96	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09 0.985 0.508 1.88	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06 1.09 0.557 1.28	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543 0.47 0.22 0.524
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14 2.23 0.873 2.96 0.955	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09 0.985 0.508 1.88 0.407	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06 1.09 0.557 1.28 0.327	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543 0.47 0.22 0.524 0.184
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP)	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14 2.23 0.873 2.96 0.955 2.18	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09 0.985 0.508 1.88 0.407 1.04	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06 1.09 0.557 1.28 0.327 0.738	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543 0.47 0.22 0.524 0.184 0.425
Acenaphthene Acenaphthylene Fluorene Anthracene Phenanthrene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene (BAP) Dibenzo[a,h]anthracene	0.036 0.012 0.067 0.028 0.551 0.103 1.5 2.14 2.23 0.873 2.96 0.955 2.18 0.291	0.02 0.007 0.034 0.018 0.382 0.067 0.839 1.09 0.985 0.508 1.88 0.407 1.04 0.13	0.014 0.009 0.026 0.017 0.451 0.074 0.8 1.06 1.09 0.557 1.28 0.327 0.738 0.073	0.01 0.0021 0.0152 0.01 0.189 0.038 0.513 0.543 0.47 0.22 0.524 0.184 0.425 0.0276

Table A.8 $\,$ (cont.) Concentrations (µg/g dry weight) of PAHs in individual particle size fractions of selected RDS samples.

РАН	H3SW	H3SW	H3SW	H3SW
	<0.063 mm	0.063-0.5 mm	0.5-1 mm	1-5.6 mm
Naphthalene	0.018	0.018	0.008	0.006
Acenaphthene	0.008	0.007	0.007	0.0281
Acenaphthylene	0.042	0.041	0.034	0.0393
Fluorene	0.017	0.016	0.016	0.052
Anthracene	0.388	0.488	0.618	1.21
Phenanthrene	0.058	0.076	0.099	0.161
Fluoranthene	0.903	1.14	1.23	1.57
Pyrene	1.18	1.39	1.38	1.38
Benzo[a]anthracene	0.814	0.955	0.799	0.859
Chrysene	0.403	0.477	0.444	0.582
Benzo[b]fluoranthene	1.12	0.989	0.711	0.958
Benzo[k]fluoranthene	0.298	0.277	0.209	0.283
Benzo[a]pyrene (BAP)	0.81	0.879	0.596	0.645
Dibenzo[a,h]anthracene	0.092	0.086	0.053	0.0497
Indenopyrene	0.366	0.313	0.211	0.186
Benzo[g,h,i]perylene	0.637	0.568	0.408	0.412
Total	7.2	7.7	6.8	8.4

Table A.9 Concentrations (μ g/g dry weight) of lead, copper and zinc in individual particle size fractions of selected RDS samples.

RDS	Size	heavy metal conce	entration (µg/g)	
sample	fraction (mm)	lead	copper	zinc
C1SW	<0.063	222	238	543
C1SW	0.063-0.5	128	140	261
C1SW	0.5-1	154	85.4	230
C1SW	1-5.6	985	57.2	260
C1CP	<0.063	426	279	994
C1CP	0.063-0.5	345	91.4	547
C1CP	0.5-1	379	115	632
C1CP	1-5.6	140	44.7	253
H3SW	<0.063	86.9	129	303
H3SW	0.063-0.5	57.2	39.9	185
H3SW	0.5-1	24.2	31.0	109
H3SW	1-5.6	19.9	30.0	120
НЗСР	<0.063	176	290	1307
НЗСР	0.063-0.5	79.3	111	652
НЗСР	0.5-1	54.9	52.9	495
НЗСР	1-5.6	51.7	51.3	544
A1SW	<0.063	332	1233	944
A1SW	0.063-0.5	182	469	426
A1SW	0.5-1	262	252	396
A1SW	1-5.6	49.9	119	282
A1CP	<0.063	425	487	1232
A1CP	0.063-0.5	150	115	371
A1CP	0.5-1	69.0	73.7	325
A1CP	1-5.6	64.1	81.8	170
A2SW	<0.063	356	888	1267
A2SW	0.063-0.5	889	565	789
A2SW	0.5-1	225	1272	646
A2SW	1-5.6	122	369	577
C1SW	<0.063	222	238	543
C1SW	0.063-0.5	128	140	261
C1SW	0.5-1	154	85.4	230
C1SW	1-5.6	985	57.2	260
C1CP	<0.063	426	279	994
C1CP	0.063-0.5	345	91.4	547
C1CP	0.5-1	379	115	632

Table A.10 Leachate (TCLP) concentrations of lead, copper and zinc from RDS ($\mu g/ml$).

RDS	metal leacha	ate concentration (µ	g/ml)
sample	lead	copper	zinc
A1SW	0.043	0.228	4.31
A1CP	0.087	0.104	3.05
A2SW	0.061	0.466	6.69
A2CP	2.01	0.066	6.62
A3SW	0.068	0.219	5.61
A3CP	0.061	0.142	4.59
A4SW	0.058	0.160	4.21
A4CP	0.123	0.147	4.93
A5CP	0.061	0.030	0.79
A6SW	0.091	0.090	1.15
A7CPi	0.120	0.053	7.30
A7CPii	0.129	0.047	18.3
C1SW	0.234	0.309	4.03
C1CP	0.150	0.063	3.20
C2SW	0.917	0.549	6.63
C2CP	0.101	0.036	4.75
C3SW	0.212	0.170	4.46
C3CP	0.266	0.057	8.75
C4SW	0.161	0.071	3.66
C4CPi	0.172	0.122	4.75
C4CPii	0.136	0.099	4.42
C5SW	0.177	0.107	4.61
C5CP	0.084	0.021	1.51
H1SW	0.096	0.098	3.18
H1CP	0.130	0.027	6.17
H2SW	0.078	0.137	5.78
H2CP	0.096	0.059	4.66
H3SW	0.077	0.038	0.97
Н3СР	0.104	0.041	5.47
H4SW	0.141	0.078	3.29
H4CP	5.35	0.024	67.1
H5SW	0.074	0.049	3.35
Н5СР	0.055	0.038	7.79
N1SW	0.088	0.043	1.53
N1CP	0.041	0.017	1.15

Appendix B: Abbreviations and acronyms

AASHTO American Association or State Highway and Transportation Officials

BPN British pendulum number

CCME Canadian Council of Ministers of the Environment

CWC Clean Washington Centre

DEP Department of Environmental Protection

DEQ Department of Environmental Quality (Oregon)

DOC dissolved organic carbon

DOT Department of Transportation

EPA Environmental Protection Agency

GCMS gas chromatography mass spectrometry

HC₅₀ hazardous concentration to 50% of species

MfE Ministry for the Environment (New Zealand)

NZWWA New Zealand Water and Waste Association

ODOT Oregon Department of Transportation

PAHs polycyclic aromatic hydrocarbons

RDS road-derived sediment

RIVM National Institute of Public Health and the Environment (Netherlands)

SQG sediment quality guideline
SRC serious risk concentration
SWTD stormwater treatment device

TCLP toxicity characteristic leaching procedure

TPH total petroleum hydrocarbons

μg/g micrograms per gram μg/L micrograms per litre vpd vehicles per day

WWTPs wastewater treatment plants