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Road-deposited sediments in an urban environment: A first look at sequentially extracted element loads in grain size fractions

Ross A. Sutherland[a,*], Filip M.G. Tack[b], Alan D. Ziegler[c]

[a] *University of Hawaii at Manoa, Geomorphology Laboratory, Department of Geography, 2424 Maile Way, Honolulu, HI 96822, USA*
[b] *Ghent University, Laboratory of Analytical Chemistry and Applied Ecochemistry, Coupure Links-653, B-9000 Gent, Belgium*
[c] *National University of Singapore, Geography Department, AS2, #03-01, 1 Arts Link, Kent Ridge, Singapore 117570, Singapore*

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ABSTRACT

Sediments stored in urban drainage basins are important environmental archives for assessing contamination. Few studies have examined the geochemical fractionation of metals in individual grain size classes of solid environmental media. This is the first study of road sediments to quantify the mass loading of Al, Cu, Pb, and Zn in individual grain size classes (<63 μm to 1000–2000 μm) and partition contributions amongst four sequentially extracted fractions (acid extractable, reducible, oxidizable, and residual). The optimized BCR sequential extraction procedure was applied to road sediments from Palolo Valley, Oahu, Hawaii. Road sediments from this non-industrialized drainage basin exhibited significant enrichment in Cu, Pb, and Zn. Metal mass loading results indicate that the <63 μm grain size class dominated almost all fraction loads for a given element. The residual fraction dominated the Al loading for this geogenic element. The reducible fraction, associated with Fe and Mn oxides, was the most important component for Cu, Pb, and Zn loading. These results have direct implications for environmental planners charged with reducing sediment-associated contaminant transport in urbanized drainage basins.

1. Introduction

Road-deposited sediment (RDS), inappropriately named “road dust”, is recognized as an important source of contamination in urban environments [1,2]. Road sediments are a complex environmental media. Their composition reflects inputs from a variety of sources, including water transported material from surrounding soils and slopes, dry and wet atmospheric deposition, biological inputs, road surface wear, road paint degradation, vehicle wear (tires, body, brake linings, etc.), vehicle fluid and particulate emissions, and inputs from the wear of sidewalks and buildings [3]. Road sediment is a valuable environmental archive as this material is located on paved areas that are directly connected to a city’s storm drainage system, and they have been identified as the primary source of urban nonpoint pollutants entering the receiving waters of the U.S. [4].

Many studies of solid environmental media, including RDS, have focussed on total digestions to characterize trace metal concentrations [5–12]. Today sequential extraction information is considered to be invaluable in assessing contamination levels and superior to a single total digestion. Gibson and Farmer [13] noted some measure of the availability and mobility of trace metals is required if informed judgments are to be made about the construction of environmental guidelines for potential toxic hazards and about the chemical behavior and fate of trace element contaminants in soil. Despite experimental uncertainty with all presently available methods for solid phase metal fractionation [14], they are a useful tool for predicting long-term adverse effects from contaminated solid material [15].

Several studies have used different sequential extraction procedures to examine metal concentrations in RDS [16–21]. Sutherland et al. [3] were the first to apply the standardized (optimized) BCR (Bureau Communitaire de Référence, or the European Community Bureau of Reference) procedure to road sediments. This standardized procedure has subsequently been applied to RDS in a variety of geographic locations, e.g., in Manchester, UK [22], Kayseri, Turkey [23], Barcelona, Spain [24], Thessaloniki, Greece [25]; Tokyo, Japan [26], and Beijing, China [27]. A standardized sequential extraction procedure, if followed closely, allows researchers to directly compare data between sites. Additionally, the development of certified reference materials (CRMs) has allowed researchers to calibrate their data with certified or indicative element concentrations.

Typically sequential extraction procedures have been applied to assess element concentrations in bulk RDS samples, i.e., <2 mm [1,3,24,26,28,29]. However, following the lead of Sutherland [30] there has been a recent increase in studies quantifying various inorganic elements in road sediments that have been grain-size fractionated [31–41]. Interest in grain size characteristics is related

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* Corresponding author. Tel.: +1 808 956 6070; fax: +1 808 956 3512.
E-mail address: Sutherla@Hawaii.edu (R.A. Sutherland).

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Table 1
Physico-chemical properties of individual road-deposited sediment samples from Palolo Valley, Oahu, Hawaii (<2 mm).

Site code	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	pH	OC (g/kg)	$CaCO_3$ (g/kg)	CEC ($cmol_c$/kg)	Al^b (mg/kg)	Cu^b (mg/kg)	Pb^b (mg/kg)	Zn^b (mg/kg)
P11[a]	646	290	64	7.4	95.8	56.2	24.8	20,800	378	2346	806
P2[a]	633	308	59	7.5	93.6	98.0	25.8	24,200	644	1692	867
P14[a]	588	339	73	7.7	74.9	75.0	31.3	29,100	1147	1376	3154
P7[a]	732	216	52	7.9	63.0	122	21.5	23,800	116	950	299
P1[a]	722	247	31	6.8	128	78.0	31.0	12,100	662	523	537
P6[a]	690	265	45	6.9	103	103	24.0	20,900	595	495	916
P20	631	297	72	7.8	85.1	49.4	26.1	26,500	924	419	472
P19	606	340	54	9.5	95.5	188	38.6	21,500	316	397	636
P16[a]	706	252	42	7.5	99.7	157	27.7	19,800	233	361	506
P13	439	468	93	7.7	80.7	120	44.3	24,750	299	275	665
P5	522	312	166	7.6	58.4	59.0	43.2	32,100	274	275	465
P15	413	434	153	7.9	74.4	85.0	27.3	25,500	298	252	466
P4	667	287	46	7.5	93.4	73.0	23.0	20,300	412	239	685
P9	771	212	17	7.7	313	70.0	77.2	12,400	509	230	436
P12	584	380	36	7.8	98.7	143	24.0	20,700	243	207	430
P8	688	274	38	7.4	99.9	86.0	28.7	23,500	155	183	362
P3	709	231	60	7.9	66.6	73.5	7.1	27,700	385	164	681
P17	625	313	62	7.9	97.7	89.0	28.5	23,300	156	152	377
P10	705	242	53	6.8	132	83.0	38.6	20,400	283	149	416
P18	676	271	53	7.4	110	57.0	27.1	24,100	158	59	250

Note: Sample ordering is based on Pb concentration ranking, i.e., from high to low.

[a] Road-deposited sediment samples selected for sequential extraction of individual grain size fractions.

[b] Al, Cu, Pb and Zn were determined using an aqua regia digestion, and the mean concentration of two replicates is presented.

to fluid transport theory, as it is well known that sediment grain size is an important factor controlling entrainment and transport thresholds [42]. Additionally, from the contaminant literature it is apparent that there is a grain size control on metal sorption and biotic ingestion, and thus bioavailability. Sutherland [30] further explored Pb loading in grain size fractions of road sediments. Loading combines element concentrations, on a grain size basis, with data on the mass percent of individual grain size classes. However, to our knowledge there has been no systematic examination of element loads in grain size fractions of RDS that have undergone sequential extraction, specifically by the optimized BCR approach. Our justification for examining element loads is that concentration alone does not tell the entire contaminant story. For example, the reducible phase of a particular grain size fraction may have a high element concentration, but when combined with a low sediment mass, the overall element mass loading may be negligible. These data have implications for establishing best management practices for reducing particle-associated contamination of receiving water bodies via urban roadway runoff.

The primary objective of this investigation was to characterize the fractionation patterns of known inorganic contaminants (Cu, Pb, and Zn) with grain size in a non-industrialized catchment. Road sediment was selected as the environmental media for study based on its availability, ease of sampling, and its ability to discern legacy and contemporaneous contributions of inorganic contaminants to the urban environment and receiving water bodies. The sub-objectives of this study were to:

- quantify element concentrations in acid extractable, reducible, oxidizable, and residual fractions in bulk RDSs;
- examine concentration variations in operationally defined fractions as a function of grain size; and
- assess grain size control on fraction element loadings.

2. Materials and methods

2.1. Study site

Oahu is the third largest island in the state of Hawaii, US, and Palolo Valley drainage basin occupies approximately 11.4 km^2 in southeastern Oahu. This is a non-industrialized basin with land use consisting of about 55% undeveloped conservation land, 41% is urbanized, and 4% is in agriculture [43]. Palolo Valley is carved into the remnants of the Koolau Shield Volcano, which forms the eastern mountain range of Oahu. The Koolau Volcano is between 1.8 and 2.7 million years old and is dominantly composed of tholeiitic basalts [44]. Annual rainfall at an elevation of 303 m in the valley is approximately 3380 mm, with high rainfall months being November (9.5%), December (9.8%), March (9.9%), and April (10.1%). Several soil orders are observed in the valley, including entisols, histosols, inceptisols, mollisols, oxisols, ultisols, and vertisols [45].

2.2. Road-deposited sediment sampling and preparation

The collection of road sediment from Palolo Valley was documented previously by Sutherland [30]. Twenty curbside sites were sampled to provide a representative coverage of traffic levels anticipated in the basin (selected sample sites are shown in Appendix A, an electronic Supplementary file). Over a curb length of about 1 m, samples up to 600 g were collected using an acid-washed Nalgene scoop.

Aliquots of individual RDSs were oven-dried at 105 °C to a constant mass and passed through an acid-washed 2 mm nylon sieve. Basic physico-chemical properties (texture, pH, organic carbon content, $CaCO_3$, and cation exchange capacity) for the bulk (<2 mm) samples were determined following methods described by Sutherland and Tolosa [2]. Data are shown in Table 1. Separate aliquots of RDS for grain size fractionation were oven-dried at ≤40 °C for 7 days following the procedure of Sutherland et al. [3]. Samples were passed through a 2 mm nylon sieve. Two subsamples were isolated, one was treated as a bulk sample, and the other was further separated into six grain size fractions. Grain size partitioning followed the procedure of Sutherland [30]. Briefly, 50–100 g were dry sieved for 10 min using a W.S. Tyler Ro-Tap (Mentor, OH) sieve-shaker and a nest of new stainless steel sieves. The fractions isolated and their sedimentological classes were: <63 μm (silt and clay), 63–125 μm (very fine sand), 125–250 μm (fine sand), 250–500 μm (medium sand), 500–1000 μm (coarse sand), and 1000–2000 μm (very coarse sand). To prevent cross contamination, sieves were thoroughly washed with 1 M HCl, soaked in distilled water for 0.5 h, and oven-dried between successive samples. Bulk samples and individual grain size fractions were ground in a Pica Blender Mill

(Model 2601, Cianflone Scientific Instruments Corp., Pittsburgh, PA) for 5-min in 30 mL tungsten carbide vials with tungsten carbide balls to enhance homogeneity during digestions. Vials were thoroughly cleaned after sample grinding following the procedures outlined by Obenauf et al. [46]. Specifically, 4 g of 99.99% pure SiO_2 (<300 μm) (CERAC, Milwaukee, WI) was mixed together with hot distilled water (10 mL) and metal-free detergent (≈1 mL), and ground for 2 min. Vials were washed repeatedly with distilled water, oven dried, and placed in a desiccator to cool to room temperature.

2.3. Road-deposited sediment chemical analysis and quality control

Two replicates (0.5 g) for each of 20 bulk samples (dried at ≤40 °C) were digested with aqua regia ($3HCl{:}1HNO_3$) and analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Four elements were examined in detail for this study. Aluminum was selected because of its high element concentration in basaltic rocks, and limited input from anthropogenic sources, and it is assumed to be primarily geogenic. The remaining three elements (Cu, Pb and Zn) were selected based on previous studies on Oahu indicating their anthropogenic enrichment in various environmental media [2,6,47,48].

Precision and pseudo-accuracy were determined on 5 replicates of SRM 2710 (Montana soil – highly elevated trace element concentrations) from the U.S. National Institute of Standards and Technology (NIST), and 5 replicates of BCR-483 (sewage sludge amended soil) from the European Institute for Reference Materials and Measurements (IRMM). Precision was defined as (standard deviation/mean) × 100. Pseudo-accuracy was computed as [(measured concentration − informational concentration)/informational concentration] × 100. Aliquots of SRM 2710 and BCR-483 were analyzed "as is", and results were adjusted for moisture content by drying 1-g aliquots of the two CRMs at 105 °C for 24 h. Informational values for SRM 2710 were reported in Gills [49], and indicative values for BCR-423 were tabulated in Rauret et al. [50]. Data for the four elements analyzed were both precise and accurate. Precision values for SRM 2710 were as follows: Al = 1.6%, Cu = 2.4%, Pb = 1.3%, and Zn = 1.3%; pseudo-accuracy values relative to US EPA 3050 median values were −4.4% (Al), 3.4% (Cu), 2.8% (Pb), and 7.6% (Zn). Precision values for BCR-483 were as follows: Al = 3.7%, Cu = 8.7%, Pb = 5.6%, and Zn = 2.7%; pseudo-accuracy values relative to indicative values were 3.4% (Cu), 1.3% Pb, and −12.3% (Zn).

Seven of the 20 size fractionated RDS samples were randomly selected and analyzed by the BCR 3-step plus aqua regia sequential extraction procedure according to the experimental details outlined in Rauret et al. [51]. Briefly, four operationally defined fractions were sequentially extracted using a standardized procedure; these included acid extractable (0.11 mol/L acetic acid), reducible (0.5 mol/L hydroxylamine hydrochloride), oxidizable (8.8 mol/L hydrogen peroxide + 1.0 mol/L ammonium acetate), and residual (aqua regia). Aluminum, Cu, Pb, and Zn were analyzed by flame (air/acetylene gas, except for Al where N_2O/acetylene was used) atomic absorption spectrometry (FAAS). For each extract, external standards prepared in the corresponding extracting solution were used for calibration.

Quality control data for the optimized BCR procedure was assessed using five replicates, from the same bottle, of the CRM BCR-483. The 1-g aliquots of BCR-483 were dried at 105 °C for 24 h as suggested by Rauret et al. [52]. From this, a mean correction "to dry mass" was obtained and applied to all analytical values reported in this work (i.e., element concentration per g dry sediment). Precision was determined as before, and pseudo-accuracy was determined using the indicative values reported by Rauret et al. [50]. A detailed summary of precision and accuracy of the BCR procedure is given in Table 2. Pseudo-accuracy determination of Al in BCR-483 for the BCR procedure could not be determined because no indicative values were available.

Table 2
Mean fraction-specific quality control (QC) data [precision[a] and pseudo-accuracy[a]] for the optimized BCR sequential extraction procedure for Al, Cu, Pb, and Zn in BCR-483 (sewage sludge amended soil).

Metal/QC[b]	Acid extractable (%)	Reducible (%)	Oxidizable (%)	Residual (%)
Al precision	4.3	2.5	9.0	2.1
Al accuracy[c]				
Cu precision	2.9	5.0	9.4	8.5
Cu accuracy	−11.3	−1.3	−7.1	−11.8
Pb precision	BDL[d]	3.5	8.5	9.3
Pb accuracy	BDL[d]	−2.2	−7.4	−10.9
Zn precision	4.1	7.6	3.3	1.6
Zn accuracy	−1.0	−0.6	−7.0	−8.5

[a] Precision and (pseudo) accuracy are as defined in the text.

[b] Pseudo-accuracy was determined using the indicative values in Rauret et al. [50].

[c] No data were available for Al in BCR-483.

[d] Concentrations of Pb in this fraction were below the detection limits for FAAS, i.e., 2 mg/kg.

2.4. Road-deposited sediment element grain-size and geochemical fraction loading

Concentration data from the four sequentially extracted phases of Al, Cu, Pb and Zn that were associated with the seven RDS samples that were grain-sized fractionated (mass determinations for each of the 6 size classes for a given sample) were used to compute element loads. A modified form of the grain size fraction load (GSF_{Load}) equation presented in Sutherland [30] was applied in this study:

$$GSF_{Load} = \left[\frac{\text{element}_{i,f} \times GS_i}{\Sigma \text{element}_{i,f} \times GS_i}\right] \times 100$$

where $\text{element}_{i,f}$ is the concentration of a given element (Al, Cu, Pb, or Zn) in an individual grain size fraction (e.g. <63 μm) in one of the four sequentially extracted fractions (mg/kg); and GS_i is the mass percentage of an individual fraction, which has limits of 0–100%. Therefore, for a given element in a given RDS sample, the summation of the four sequentially extracted fractions per grain size weighted fraction = 100%.

3. Results and discussion

3.1. Element concentrations in bulk road sediment samples

Concentrations of Al, Cu, Pb, and Zn from an aqua regia digestion of the <2 mm portion of 20 road-sediment samples are shown in Table 1 (mean values of two replicates are provided). The mean ± 1 standard deviation Al concentration was 22,670 ± 4800 mg/kg (median = 23,400 mg/kg; min and max = 12,100 and 32,100 mg/kg, respectively), Cu = 409 ± 269 mg/kg (median = 308 mg/kg; min and max = 116 and 1147 mg/kg, respectively), Pb = 537 ± 576 mg/kg (median = 275 mg/kg; min and max = 59 and 2348 mg/kg, respectively), and Zn = 671 ± 613 mg/kg (median = 489 mg/kg; min and max = 250 and 3154 mg/kg, respectively).

Copper, Pb and Zn were significantly enriched compared to baseline data for the underlying basaltic rocks, Cu ≈ 100 mg/kg, Pb < 10 mg/kg, and Zn < 180 mg/kg (Sutherland [6]). Lead isotope analysis of these road sediments has shown that the dominant source of Pb was from Pb gasoline additives [47], i.e., legacy Pb. Vehicle emissions, past and contemporaneous, archived in the surrounding urban soil environment are currently being mobilized

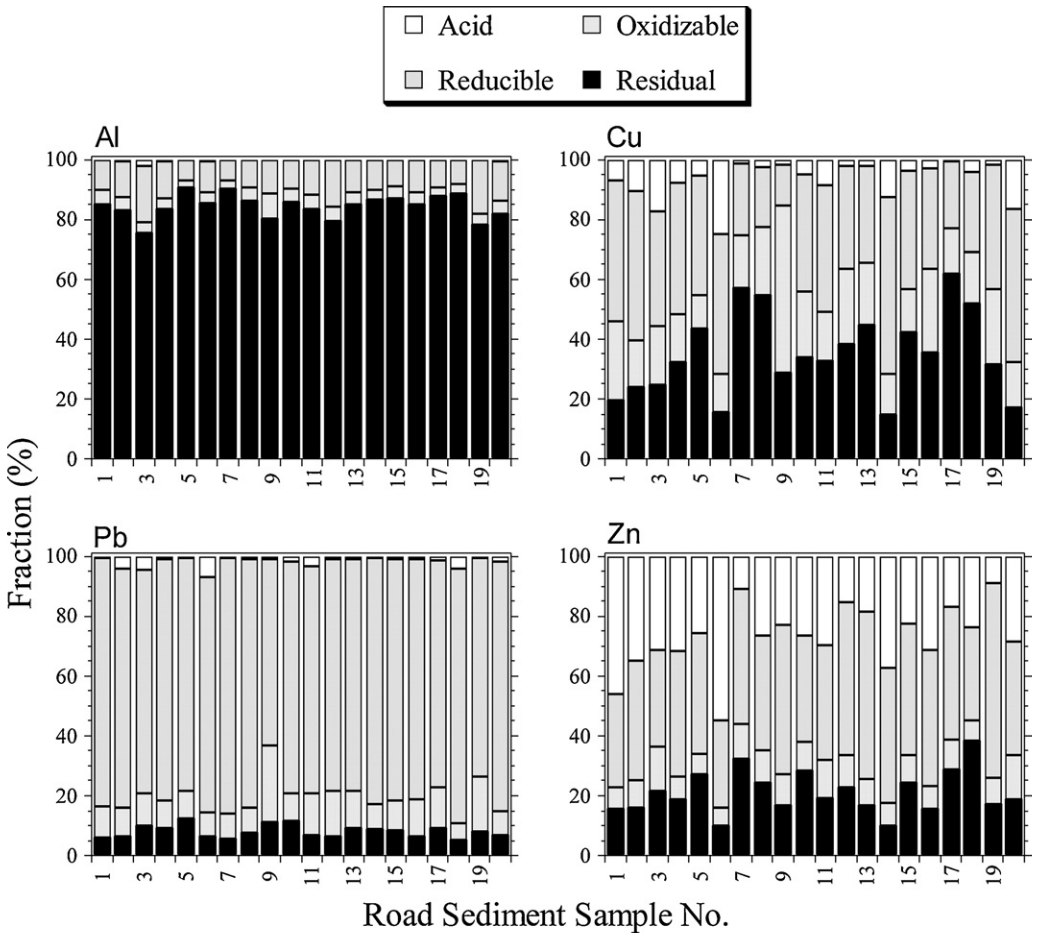

Fig. 1. Optimized BCR 3-step plus aqua regia sequential extraction of 20 road-deposited sediments from Palolo Valley, Oahu, Hawaii (<2 mm). Note ‘Acid’ represents the acid extractable fraction.

by surface erosional processes. This has important environmental implications for contaminant transport in Hawaii, because sediments stored temporarily on roads are directly routed to streams by way of storm drains during runoff events.

3.2. Metal concentrations in sequentially extracted fractions of bulk road sediment samples

Partitioning of the sequentially extracted fractions for each of the 20 bulk RDS samples is shown in Fig. 1, with average contributions displayed in Fig. 2. As expected the residual fraction was dominant for Al, and the actual proportion is underestimated as a total digestion with HF was not used in this study. The proportion of Al in the different phases decreases in the following order: residual > reducible > oxidizable > acid extractable. Comparison of Al sequentially extracted with the optimized BCR approach for an adjoining watershed (Manoa Valley) indicated a similar phase partitioning (Table 3).

The reducible fraction was the dominant phase for Cu, Pb, and Zn in RDS < 2 mm in Palolo Valley. The acid extractable fraction was a minor component for Pb (≈2%) and Cu (≈7%), but significant for Zn (≈27%). Results for the anthropogenically enhanced elements in the RDS samples from Palolo Valley can be directly compared to those from the literature for other RDSs extracted with the optimized BCR approach (Table 3). The partitioning of Cu in Palolo Valley was similar to the data from Kayseri, Turkey, and Hangzhou, China despite the higher average concentration in Palolo RDSs, i.e., 409 mg/kg compared to 207 mg/kg from Hangzhou, and 84 mg/kg from Kayseri. Road sediments from Barcelona had the greatest residual Cu percentage (80%) followed by Manoa Valley (45%). Lead from the present study had the lowest acid exchangeable fraction at 2%, compared to 4–18% for RDS in other geographic locations. The reducible fraction was the dominant phase for five of the six RDS studies summarized in Table 3, with the highest values in Hangzhou (66%), Manoa Valley (71%), and the current study (79%). The most typical Pb fraction ranking was: reducible > oxidizable > residual > acid exchangeable.

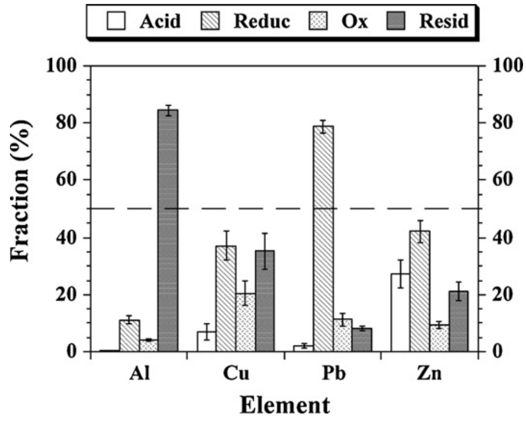

Fig. 2. Sequentially extracted fractions for Al, Cu, Pb, and Zn from 20 road-deposited sediment samples (<2 mm). Average values with corresponding standard errors shown.

Table 3
Comparison of the optimized BCR sequentially extracted fractions of Al, Cu, Pb, and Zn for Palolo Valley road-deposited sediments to data from the literature.

Elements/RDS study[a]	Acid exchangeable (%)	Reducible (%)	Oxidizable (%)	Residual (%)	Average concentration (mg/kg)
Al					
This study	0.4 ± 0.1[b]	11.1 ± 0.7	4.0 ± 0.5	84.5 ± 0.9	22,670
Sutherland et al. [3]	0.7 ± 0.1	15.1 ± 1.5	5.5 ± 0.7	78.7 ± 2.1	26,110
Cu					
This study	7.0 ± 1.4	37.2 ± 2.6	20.5 ± 2.2	35.3 ± 3.1	409
Kartal et al. [23]	6.0	43.6	25.5	24.9	84.2
Perez et al. [24]	1.9	8.2	10.3	79.6	670
Sutherland et al. [3]	4.9 ± 1.2	23.6 ± 3.1	26.2 ± 3.2	45.4 ± 3.9	163
Zhang and Hao [53]	7.3	44.6	26.8	21.3	207
Pb					
This study	1.9 ± 0.4	78.7 ± 1.2	11.3 ± 1.0	8.1 ± 0.5	537
Kartal et al. [23]	8.9	58.3	16.4	16.4	415
Perez et al. [24]	4.1	53.4	25.8	16.8	380
Sutherland et al. [3]	4.7 ± 1.2	71.0 ± 6.1	15.8 ± 4.0	8.5 ± 1.6	133
Tokalioglu and Kartal [20]	18.3	29.2	29.8	22.7	74.9
Zhang and Hao [53]	7.3	66.4	13.6	12.7	522
Zn					
This study	27.2 ± 2.5	42.1 ± 2.0	9.5 ± 0.6	21.2 ± 1.6	671
Kartal et al. [23]	25.1	55.1	9.6	10.2	443
Perez et al. [24]	28.8	28.9	14.1	28.3	640
Sutherland et al. [3]	32.7 ± 2.2	36.6 ± 1.5	8.3 ± 1.3	22.4 ± 2.1	471
Tokalioglu and Kartal [20]	33.2	29.7	20.9	16.2	113
Zhang and Hao [53]	26.7	42.5	13.2	17.6	344

[a] Kartal et al. [23], Kayseri, Turkey, <74 μm, $n = 33$; Perez et al. [24], Barcelona, Spain, <2 mm, $n = 13$; Sutherland et al. [3], Manoa Valley, Oahu, Hawaii, <2 mm, $n = 13$; Tokalioglu and Kartal [20], Organized Industrial District, Kayseri, Turkey, <2 mm, $n = 29$; Zhang and Hao [53], commercial zone, Hangzhou, China, <2 mm, $n = 5$.

[b] Average ± one standard error.

Zinc extractable contents typically followed the following fraction ordering: reducible > acid exchangeable > residual > oxidizable, even though the average concentrations between literature studies varied 6-fold, from 113 to 671 mg/kg. Zinc would be the most mobile of the anthropogenically impacted elements examined in this study, with between 25 and 33% associated with the most readily available fraction, i.e., acid exchangeable. An overall labile component can be defined by summing the percentages of each element in the first three phases of the BCR approach. In the RDS studies summarized in Table 3, the proportion of labile Pb ranged from 77 to 92%, for Zn 72 to 90%, and for Cu 20 to 79%.

3.3. Grain-size variations of metal concentrations in sequentially extracted fractions

Concentrations of the anthropogenically impacted elements for the seven RDS samples are shown in Fig. 3 for the grain size classes, and also for the bulk composition (i.e., < 2 mm). It is evident that the coarse grain size fractions, typically >500 μm, have lower concentrations than the finer classes. The clay plus silt (<63 μm) and the very fine sand (63–125 μm) fractions have the highest concentrations of Cu and Zn. This is a common concentration pattern documented in the literature, and is usually explained by increased sorption capacity as specific surface area increases with decreasing grain size [54]. Lead exhibited a more complex pattern, with concentrations in the <63 μm fraction less than those between 63 and 500 μm. This may reflect contributions of Pb from sources additional to gas additives. Sutherland et al. [47] found the Pb isotope signatures of the three most concentrated samples (P2, P11, and P14; Table 1) to be distinctly different from the other RDS samples, and suggested that breakdown of leaded wheel weights (cf. Root [55]) may account for the pattern. If indeed this represents an additional source of Pb to specific sample sites in Palolo Valley, breakdown processes would need to preferentially produce material of sizes between 63 and 500 μm.

A stacked bar graph (Fig. 4) displays the variation in Cu, Pb and Zn concentrations for each of the four sequentially extracted phases per grain size class. It is clear that the residual component is proportionally greater for Cu followed by Zn and Pb. This is similar to the pattern displayed by the bulk sediment samples (Fig. 1). The average Pb concentration in the residual fractions of all grain sizes (67 ± 60 mg/kg) is substantially greater than those displayed by the baseline soils in the area (≈11 mg/kg) or the baseline values for the basaltic rocks (≤ 10 mg/kg). Lead in the residual fraction exceeded the baseline values in all fractions by factors ranging from 2-fold (500–1000 μm) to 12-fold (<63 μm), the exception was the 1000–2000 μm class where Pb was at about 3 mg/kg. These data

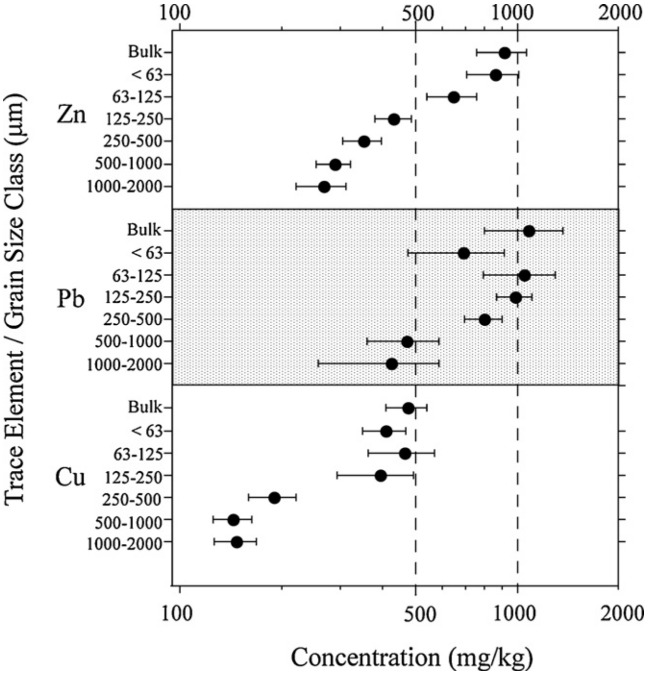

Fig. 3. Grain size partitioning of trace metal concentrations in the seven road-deposited sediments. Filled circles represent median values and error bars are the median absolute deviations from the median (MAD). 'Bulk' reflects the data for the <2 mm fraction for seven road sediments.

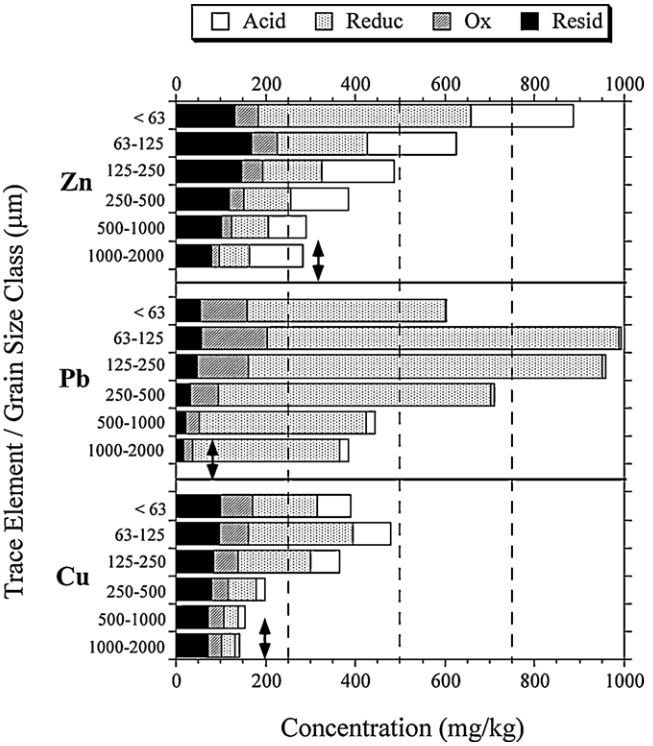

Fig. 4. Variation in geochemical fraction concentrations with grain size for the seven road-deposited sediments. Note 'Acid' represents the acid extractable fraction, 'Reduc' the reducible fraction, 'Ox' the oxidizable fraction, and 'Resid' the residual fraction.

suggest that some of the anthropogenic Pb released to the watershed has become incorporated into the residual fraction for grain sizes < 1 mm, and this component would not be typically available to biota. The quantity of Pb translocations to the residual fraction (aging) increased with decreased grain size. This pattern was not apparent for Cu or Zn. Average Cu (101 ± 69 mg/kg) and Zn (140 ± 76 mg/kg) concentrations in the residual fraction of RDS were not statistically different from baseline Hawaiian basalt data, which are 100 and 180 mg/kg, respectively.

Trace metals dissolved from the reducible fraction would be commonly occluded in Mn oxides, the easily reducible Mn phase, and in amorphous or partly amorphous Fe oxides [56]. The reducible fraction dominated storage of Pb in the RDSs of Palolo Valley (Fig. 4). Proportional contributions of the reducible fraction range from about 74% for the <63 μm grain size class to 86% for the 250–500 μm class. Reducible Pb concentrations were substantial, with a range from 328 mg/kg for the coarsest grain size class to 790 mg/kg for the 125–250 μm size class. In themselves, the Pb concentrations associated with the reducible fraction significantly exceed the consensus-based sediment quality guidelines for Pb in freshwater ecosystems. For example, probable effects concentration (PEC) level established by MacDonald et al. [57] for Pb (PEC_{Pb}) was 128 mg/kg, and those for Cu (PEC_{Cu}) and Zn (PEC_{Zn}) are 149 mg/kg, and 459 mg/kg, respectively. Element concentrations above their associated PEC value would be expected to be toxic to bottom-dwelling aquatic organisms. On average, PEC_{Cu}, PEC_{Pb}, and PEC_{Zn} were not exceeded in the acid exchangeable fraction for any of the grain size classes. In the reducible fraction, PEC_{Cu} was exceeded by all fractions <250 μm; Pb concentrations exceeded PEC_{Pb} in all grain size classes; and PEC_{Zn} was only exceeded for the <63 μm grain size class. For the oxidizable fraction, only PEC_{Pb} was exceeded in the 63–125 grain size class. Finally, PEC levels were not exceeded in the residual fraction of the RDSs examined.

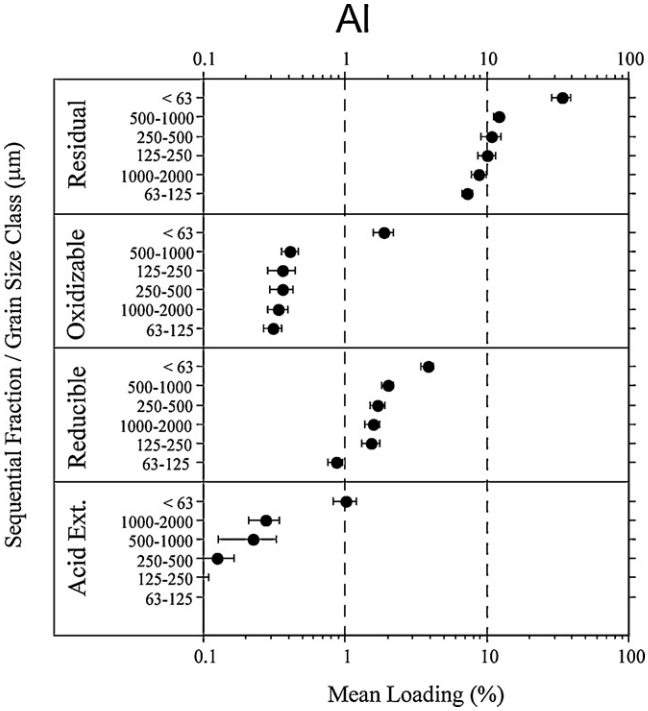

Fig. 5. Grain size variation in Al loading for the four sequentially extracted fractions of seven road-deposited sediments. Filled circles represent mean values and error bars are ±one standard error about the mean. Note the *X*-axis is logarithmic.

3.4. Grain-size partitioning of metal mass loads (GSF_{Load}) in sequentially extracted fractions

The subset of seven RDS samples had grain size distributions that were statistically similar to those for the complete data set of 20 samples (data not shown). Mean percentages (±1 standard error, SE) for the grain size classes were: <63 μm = 34.3 ± 2.0%; 63–125 μm = 8.6 ± 0.8%; 125–250 μm = 13.2 ± 1.2%; 250–500 μm = 15.5 ± 1.2%; 500–1000 μm = 16.4 ± 0.9%; and 1000–2000 μm = 12.0 ± 1.3%. Mean fraction loading percentages for the six grain size classes for Al, Cu, Pb, and Zn are shown in Figs. 5–8. Each sequentially extracted fraction is presented as a separate panel with individual loadings for grain size classes ranked from high to low. This facilitates visualization of the dominant geochemical fraction and variations in contributions with respect to grain size.

For the geogenic element Al the grain-size partitioning of load for the four sequentially extracted fractions are shown in Fig. 5. It is clear that the acid extractable component contributed an insignificant amount to all grain sizes (≤1%), and that Al partitioning was dominated by the residual fraction, followed by the reducible fraction.

Copper loading was more equally distributed between geochemical fractions (Fig. 6). Most individual grain size classes, regardless of chemical association, contributed from 1 to 6% to the total loading. The exception was the <63 μm size class, which contributed 6–15% of the total Cu loading. The dominance of the oxidizable fraction commonly noted in the literature for concentration studies [1,19,27,28,58–61] was not shown by these loading data. The reducible (34.5%) and residual (34.5%) fractions had equal Cu loadings, and both exceeded the loading in the oxidizable fraction by 2-fold (17.4%).

Lead loading was dominated by the reducible fraction, with an average of 76 ± 2% for all grain sizes combined (Fig. 7). Individual grain size contributions of the reducible fraction ranged from about 7% for the 63–125 μm class, to about 29% for the <63 μm class. The oxidizable component was the next largest geochemical fraction for

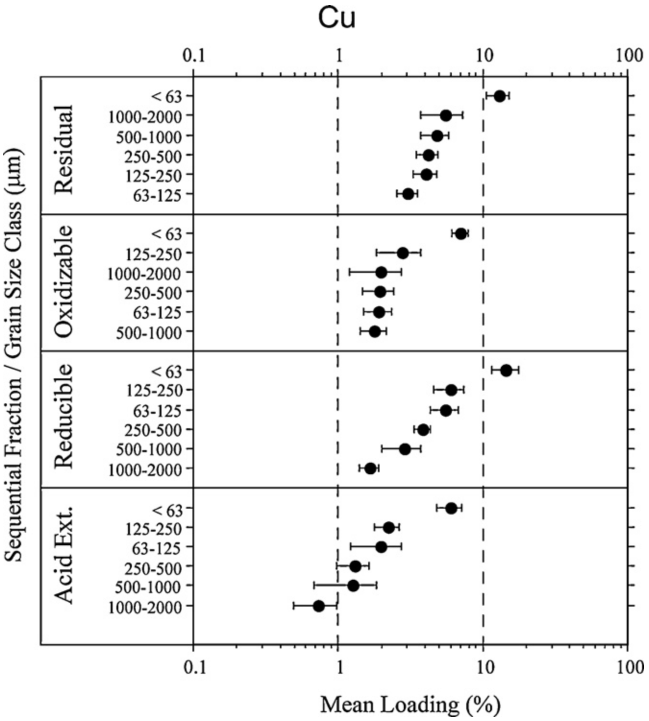

Fig. 6. Grain size variation in Cu loading for the four sequentially extracted fractions of seven road-deposited sediments. Filled circles represent mean values and error bars are ±one standard error about the mean. Note the *X*-axis is logarithmic.

Pb (12 ± 2%), followed by the residual fraction (9 ± 1%), and finally the acid extractable fraction (3 ± 1%). Loading in the <63 μm class dominated all chemical components except for the acid extractable fraction. Besides the significance of the <63 μm fraction, there was no consistent decrease in Pb loading with increased grain size.

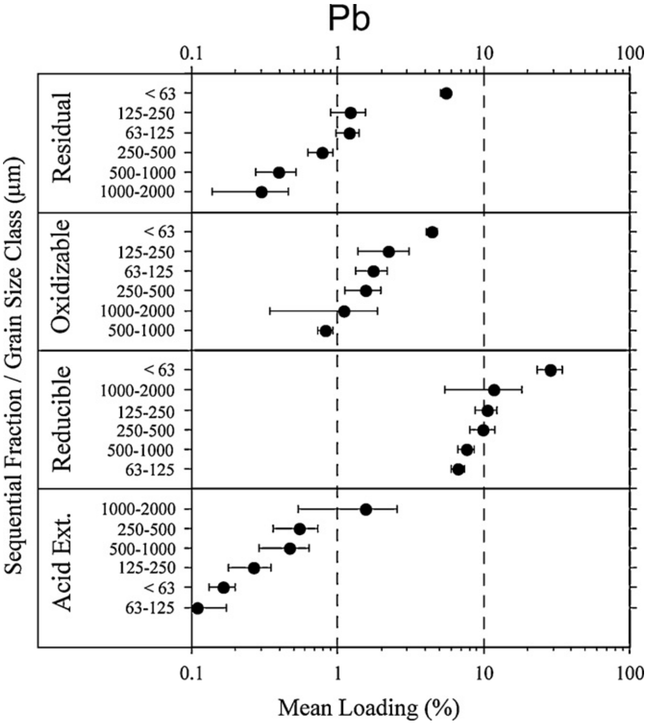

Fig. 7. Grain size variation in Pb loading for the four sequentially extracted fractions of seven road-deposited sediments. Filled circles represent mean values and error bars are ±one standard error about the mean. Note the *X*-axis is logarithmic.

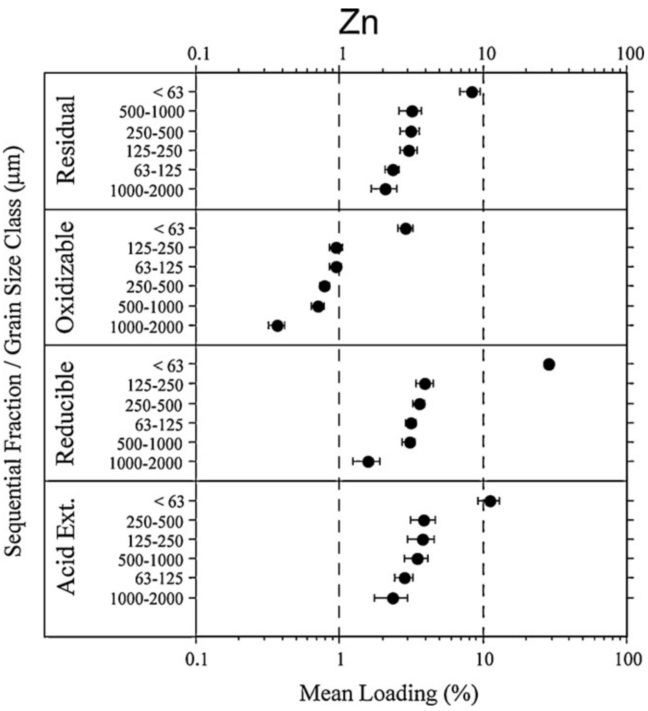

Fig. 8. Grain size variation in Zn loading for the four sequentially extracted fractions of seven road-deposited sediments. Filled circles represent mean values and error bars are ±one standard error about the mean. Note the *X*-axis is logarithmic.

The oxidizable component was the least important for Zn loading in RDSs of Palolo Valley (Fig. 8), with no grain size class contributing more than 3% to the total loading. The reducible Zn fraction was the most significant accounting for 44% of the total Zn load, with the <63 μm size class dominant. The Zn acid extractable fraction was proportionally greater than that for Cu (2-fold difference) and for Pb (9-fold difference). The acid extractable component is the most readily (bio)available sequentially extracted fraction. This is environmentally significant as increases in the hydrogen ion concentration associated with acid precipitation, or anywhere else along the storm runoff path will enhance Zn mobility. Additionally, 11% of the total Zn loading was associated with the <63 μm acid extractable fraction. This is notable because this is the sediment size class that would be most widely digested and assimilated by aquatic biota, especially benthic feeders.

Unfortunately no comparable load data from the literature are known to the authors for grain size and operationally defined fractions in solid environmental media. Thus, the data presented in this study will provide a baseline for future comparisons with the optimized BCR approach.

4. Conclusions

On a concentration basis the road sediments were enriched with Cu, Pb, and Zn. Reducible fractions of the road sediments had Pb concentrations exceeding probable effects levels for adverse impacts on biota. The geogenic element, Al, was primarily associated with the residual fraction. For the first time mass loads of Al, Cu, Pb, and Zn in road sediments were determined on a grain size basis for four sequentially extracted fractions. The <63 μm grain size class had the highest loading for all metals examined for each of the four geochemical fractions. For Cu, Pb, and Zn the reducible fraction was the most important metal phase, but the detailed fraction ranking was element dependent. For Cu, the sequence was: reducible = residual > oxidizable > acid extractable. For Pb, the ordering was: reducible ≫ oxidizable ≅ residual ≫ acid extractable, and for Zn, reducible > acid extractable > residual ≫ oxidizable.

The results from this metal load partitioning study are significant, because road runoff in Hawaii is routed to storm drains that are directly connected to the fluvial network. Thus, increased acidity, especially for Zn, or changes in redox potential, for Cu and Pb, will greatly enhance the solubility of the anthropogenically impacted elements examined in this study, especially in the <63 μm grain size class. To reduce contaminant loading to fluvial networks in Hawaii, environmental planners need to focus their attention on ways to reduce the flushing of fines (<63 μm) from road surfaces, because in the Palolo system this grain size class accounted for 30–40% of total mass (<2 mm) of sediment. Street sweeping is currently the best management practice used by the City and County of Honolulu to reduce transport of sediment to aquatic systems. Though potentially effective for coarse grain sizes, sweeping is inefficient for fines and thus will have little influence on the most critical size class and its labile metal associations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2012.04.066.

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