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Sequential Extraction of Lead from Grain Size Fractionated River Sediments Using the Optimized BCR Procedure

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Abstract Fluvial bed sediments are widely used for characterizing anthropogenic contaminant signals in urban watersheds. This study presents the first preliminary examination of sequentially extracted Pb from grain size fractionated bed sediments using the optimized (standardized) BCR procedure. Baseline sediment samples and samples from the vicinity of three storm-sewer outlets in Nuuanu Stream, Honolulu, Hawaii, were examined. The weighted average Pb liberated from four sequentially extracted phases was 144±26 mg/kg (±SD). These Pb concentrations are high compared to 3 mg/kg leached by a 0.5 M HCl solution, and 13 mg/kg from a 4-acid total digestion of baseline sediments. Over a 1.8 km section of stream channel, land use variations and traffic density differences had little impact on the magnitude of Pb in specific phases for each of the six grain size fractions examined. Regardless of grain size or spatial location, Pb in the reducible phase exceeded that in oxidizable, residual and acid extractable phases. Weighted reducible Pb concentrations for three sewer outlet sites ranged from 69 to 92 mg/kg, and this phase typically accounted for 70–80% of all labile Pb. The <63 μm grain size class did not exhibit the highest Pb concentration, instead this was found in either the 125–250 μm or 500–1,000 μm fractions. Examining bed sediment phase associations of Pb over a smaller length dimension (i.e., 40 m) centered around one sewer outlet, indicated higher concentrations at the outlet (180 mg/kg) compared to upstream (132 mg/kg) or downstream (150 mg/kg). The differences were primarily associated with higher Pb concentrations in the reducible and oxidizable phases of the coarse sand fractions (500–2,000 μm) at the outlet. Overall, all data point to a significant anthropogenic signal for Pb in bed sediments in the urbanized section of Nuuanu Stream.

Keywords Bed sediments · Contamination · Grain size fractions · Reducible phase · Storm-sewer outlets

1 Introduction

Bed sediments in river systems are the preferred media for geochemical investigations, as they act as both sink and source of metals. To understand metal

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behavior in river systems, researchers must examine the chemical partitioning and dynamics of metals within the sediment matrix. Assessment of the potential environmental impact of contaminated bed sediments requires information on bed sediment stability, sediment availability, transport capacity, sediment caliber and water chemistry. Additionally, geochemical information restricted only to the determination of total element concentrations associated with bed sediments is not sufficient for impact assessment, because metals of environmental significance are distributed over the various chemical compounds and minerals in sediments (Salomons and Forstner 1980). The chemical form of the metal in the sediment is what determines its behavior in the environment, its mobilization capacity, and its bioavailability (Rauret et al. 1989).

One approach to decipher contaminant signals in environmental media has been to apply 'non-selective' single reagent (partial) leaches (e.g., Agemian and Chau 1976; Malo 1977; Sutherland et al. 2001, 2004). However, greater insights on metal phase associations can be obtained from sequential extractions. Following the influential publication of Tessier et al. (1979), sequential extractions have become a commonly applied approach in environmental geochemistry. The use of sequential extractions, though generally labor intensive and time consuming, can contribute insights into the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals (Filgueiras et al. 2002).

A plethora of sequential extraction procedures exist in the literature, with between three and eight extractants used in sequence, from least aggressive to progressively more destructive and least specific. The 'Tessier-type' 5-step procedure is the most commonly applied sequential approach. However, as it is not standardized there have been innumerable variations to the original procedure. This makes comparisons between studies problematic. A significant advance was the standardization and harmonization of a 3-step sequential procedure in the late 1980s and early 1990s (Ure et al. 1993; Quevauviller et al. 1994). This procedure partitions elements into the following operationally defined phases: acid extractable, reducible, and oxidizable. The residue following step three, i.e., the residual phase, is commonly digested by aqua regia. This 3-step plus aqua regia extraction procedure is commonly referred to as the BCR approach (European Community Bureau of Reference, now known as the Standards, Measurements and Testing Programme). A key component of the BCR procedure was the development of an environmental certified reference material (CRM) from lake sediment (BCR-601; Quevauviller et al. 1997). This CRM had certified concentrations for specific elements in each of the various phases. This was critical for laboratory quality control/quality assurance (QC/QA), and facilitated widespread adoption, particularly in Europe. Enhancements were made to the original BCR approach to address reproducibility problems, primarily in step two (reducible phase). Thus a new optimized BCR approach has superceded the original sequential extraction procedure, and a new CRM was developed, BCR-701 (Rauret et al. 1999). This optimized approach has been applied to a wide range of solid environmental media: coastal and marine sediments (Guevara-Riba et al. 2004; Morillo et al. 2004; Adamo et al. 2005); fluvial sediments (Morillo et al. 2002a; Bird et al. 2003); lake sediments (Sahuquillo et al. 2000; Pueyo et al. 2001; Hjorth 2004); road-deposited sediments (Sutherland et al. 2000, 2004; Kartal et al. 2006); sewage sludge (van Hullebusch et al. 2005; Kazi et al. 2006); and soils (Sutherland and Tack 2000; Andersen et al. 2002; Du Laing et al. 2002; Pueyo et al. 2003; Davidson et al. 2006; Yuangen et al. 2006).

Fluvial bed sediments are an important environmental archive for deciphering the contaminant history of anthropogenic activities in watersheds. Bed sediment grain size is seen as an important 'lumped' variable controlling trace metal concentrations in bed sediments. Typically investigations have shown an increase in concentration with decreasing grain size (Horowitz 1991). Several studies have partitioned bed sediments into several grain size fractions and analyzed them using single leach, pseudo-total or total digestions (Ellaway et al. 1982; Chakrapani and Subramanian 1993; Vaithiyanathan et al. 1993; Singh et al. 1999; Orescanin et al. 2004). Others have isolated a specific grain size, typically the <63 μm fraction, and applied the 'Tessier-type' sequential extraction procedure (Ellaway et al. 1982; Birch et al. 2000; Chen et al. 2000; Klavins et al. 2000; Korfali and Davies 2000; Akcay et al. 2003; Lee et al. 2003; Peng et al. 2004; Glosinska et al. 2005). Application of the original and optimized BCR procedure to fluvial bed sediments has been mostly restricted to Europe (Table 1). Only a limited number of studies have applied sequential extraction procedures to several grain size fractions isolated from a given bed sediment sample, however none of them have applied the BCR approach (e.g., Brook and Moore 1988; Stone and Droppo 1996; Galvez-Cloutier and Dube 1998; Murray et al. 1999; Song et al. 1999; Lin et al. 2003).

The objectives of this study are to examine phase associations of Pb in different grain size fractions of bed sediments using the optimized BCR approach; and to explore the spatial variability of Pb associated with bed sediments in the vicinity of storm-sewer outlets.

2 Materials and Methods

2.1 Study Area

Situated on the southern side of the Koolau volcanic range on the island of Oahu, Nuuanu Valley is a long, deep valley, formed through the fluvial action of Nuuanu Stream, Waolani Stream, and many other smaller systems. Much of the valley is covered with layers of alluvial deposits and soils. The underlying geology consists of basaltic lavas from two main eruption phases: the Koolau Basalts and the Honolulu Volcanic Series. The Koolau Basalts formed during

Table 1 Summary of studies applying the BCR original and optimized sequential extraction procedure to river bed sediments for Pb analysis

Reference	River & location	Sample no.	Grain size (μm)[c]	Dominant phase[d]	Pb (mg/kg)
López-Sánchez et al. (1993)[a]	Besos River, Spain	3	NS	Resid & Ox	NS[c]
Davidson et al. (1994)[a]	River Clyde, England	3	<63	Ox	111
Thomas et al. (1994)[a]	Tenes Rivers, Spain	1	<63	Ox[e]	624
Thomas et al. (1994)[a]	Besos River, Spain	1	<63	Ox[e]	82
Bodog et al. (1997)[a]	River Malom, Hungary	14	NS	Resid	16–85
Ramos et al. (1999)[a]	Ebro River, Spain	7	<2,000	Various	5–57
da Silva et al. (2002)[a]	Tiete River, Brazil	4	<60	Resid	43–119
da Silva et al. (2002)[a]	Pinheiros River, Brazil	2	<60	Resid	143 & 147
Gardolinski et al. (2002)[a]	Buffalo River (SRM 2704)	15	<150	Reduc	161
Tuzen (2003)[a]	River Yesilirmak, Turkey	4	<2,000	Ox	30[f]
Dali-Youcef et al. (2004)[a]	Fafna River, Algeria	4	<63	Resid	14–27
Elass et al. (2004)[a]	Fes River, Morocco	5	<250	Ox & Resid	23–612
Elass et al. (2004)[a]	Sebou River, Morocco	5	<250	Resid	40–387
Filgueiras et al. (2004)[a]	Louro River, Spain	11	<50	Resid	44–91
Gismera et al. (2004)[a]	Jarama River, Spain	4	Bulk	Reduc, Ox, Resid	20–64
dos Reis et al. (2005)[a]	Agueda River, Portugal	44	<63	Ox	NS[c]
Morillo et al. (2002a)[b]	Tinto River, Spain	14	<63	Resid	17–13,400
Morillo et al. (2002b)[b]	Odiel River, Spain	17	<63	Resid	46–1,180
Ryan et al. (2002)[b]	Mud Creek, NY, USA	2	NS	Reduc	9.4 & 11.9
Bird et al. (2003)[b]	River Lapus, Hungary	10	<63	Reduc	3,630[f]
Bird et al. (2003)[b]	Rivers Somes, Romania	7	<63	Reduc	97[f]
Bird et al. (2003)[b]	River Tisa, Romania	16	<63	Reduc	38[f]
Mossop and Davidson (2003)[b]	White Cart River, England	1	NS	Reduc	40
Cook and Parker (2006)[b]	Canal WCO4, England	1	Bulk	Ox[e]	974
Cook and Parker (2006)[b]	Canal TM53, England	1	Bulk	Ox[e]	29
Cook and Parker (2006)[b]	Canal FR, France	1	Bulk	Ox[e]	5,800

[a] Original BCR procedure

[b] Optimized BCR procedure

[c] NS indicates values were not stated.

[d] Resid is the residual phase, Ox is the oxidizable phase, and Reduc is the reducible phase.

[e] Only the first 3-steps of the BCR procedure were applied, i.e., no residual phase was extracted.

[f] Represents mean value

the main shield building stage of the Koolau Range and are composed of tholeiitic and olivine basalts, while the Honolulu Volcanic Series is part of the post-erosional rejuvenation stage of the Koolau Volcano and consists of Mg and Fe-rich nephelinites, melilite nephelinites, basanites, and alkalic olivine basalts (Macdonald et al. 1983). From these parent materials, a variety of soils have formed in Nuuanu Valley (Foote et al. 1972), including Ultisols, Mollisols, and small outcrops of Vertisols.

In general, Hawaii's streams have steep gradients, receive high precipitation inputs in their mountainous headwater areas, respond rapidly to precipitation inputs, and exhibit very little sediment build-up in the upper reaches. In urbanized sections of Hawaiian watersheds, streams are channelized and receive direct sediment inputs from road surfaces via storm drain outlets. Nuuanu Stream is about 10 km long, with the lowermost ~1 km completely channelized to the mouth of the stream at Honolulu Harbor. Portions of the stream are partially channelized at higher elevations, usually with bank stabilization.

Nuuanu Valley is one of the oldest developed valleys on Oahu, with the first development between 1900 and 1910. There has been little change in land use since 1985, as limited land is available for new development (Andrews 2002). According to the US Geological Survey, 51% of the land in Nuuanu watershed is classified as "other" (forested in the upper watershed), while 49% is classified as "developed." Of the area considered "developed" in the lower watershed, approximately 9% is commercial, 6% is manufacturing/industry, 14% is open space, 16% is public infrastructure, 46% is residential, and 9% is social services (Anthony, personal communication). There is a general transition in land use from forest in the headwaters, to residential, to mixed residential and commercial as you approach the stream mouth at Honolulu Harbor.

According to Brasher and Anthony (2000), the population density of Nuuanu Valley is 1,287 persons per km^2, and for the 11.7 km^2 watershed this is equivalent to a population of ~15,000. However, there are some areas of higher population densities, reaching up to 5,000 residents per km^2 (State of Hawaii 2000).

The major transportation artery in Nuuanu Valley is the Pali Highway, with a daily traffic density of about 46,000 vehicles (State of Hawaii 2000). Daily volumes are also available for major roads crossing the stream, including north and south bound traffic on Nuuanu Ave. 7660–9700; east and west bound traffic on Vineyard Boulevard 10,850–15,880; and east and west bound traffic on Beretania Street 3440–19,500 (Okaneku, personal communication).

2.2 Contaminant History

In a reconnaissance study by the National Water-Quality Assessment (NAWQA) Program, a composited sediment sample from Nuuanu Stream was found to have the highest level of Pb of any stream surveyed in Hawaii (n=24) at 220 mg/kg (US Geological Survey 2004). In terms of organochlorine pesticides, Nuuanu Stream bed sediments had the highest levels of *cis*-Chlordane, *trans*-Chlordane, Dieldrin, Endrin, Heptachlor epoxide, and *trans*-Nonachlor of five systems sampled. In addition, Nuuanu Stream had concentrations of PCBs that were at least one order of magnitude higher than the others, at 951 μg/kg (Brasher and Anthony 2000). Andrews and Sutherland (2004) found Pb to be the most enriched trace metal in the road-deposited sediments and fluvial bed sediments in the watershed. Compared to baseline Pb concentrations leached by 0.5 M cold HCl of <10 mg/kg, road sediments averaged 445 mg/kg, with a maximum value of 3,140 mg/kg. Stream bed sediments had average Pb values of 133 mg/kg, with a maximum of 332 mg/kg.

2.3 Sample Collection and Processing

The details of the bed sampling of Nuuanu Stream are reported in Andrews and Sutherland (2004). Thus only a brief description is presented. Bed sediment samples were collected in 2002, under baseflow conditions. Baseline samples were collected from a tributary to Nuuanu Stream in the headwaters of the watershed, above all residential, commercial, and industrial areas. Originally, 10 sites were sampled to a depth of 5 cm with six individual cores sampled per site, and these were composited. All composited samples were analyzed using a 0.5 M HCl leach and three samples were totally digested using a 4-acid procedure.

Seven storm-sewer outlet sites were examined in the original study by Andrews and Sutherland (2004). Outlets were selected based on access, the presence of sediment deposition zones, and a direct and obvious connection from the road inlet to the storm-sewer outlet. Three of these sites have been reexamined in the present study (Judd, Vineyard and Beretania) using sampling methods similar to those used in the baseline sites. The Judd outlet primarily drains residential areas, has the lowest traffic density and is located 2 km upstream of the mouth of Nuuanu Stream. Vineyard and Beretania outlets are located nearer to the mouth of Nuuanu Stream and Honolulu Harbor. Vineyard is 400 m upstream and Beretania 200 m upstream from the outlet, and both sites drain mostly commercial land uses and have high traffic densities as previously noted. To explore more local spatial variations about a single sewer outlet, sediment samples were collected at the Beretania outlet and 20 m upstream and downstream of the outlet.

In the laboratory, samples were oven-dried at 40°C. Dried samples were gently disaggregated and passed through a 2-mm stainless steel sieve. The material retained on the 2-mm sieve was discarded. All material passing the 2-mm sieve was further sieved with a nest of stainless steel sieves for 10 min on a Ro-Tap shaker (W.S. Tyler, Mentor, OH). The six fractions retained for analysis and their sedimentological equivalents in parentheses were: <63 μm (silt and clay; coded C1 in subsequent figures), 63–125 μm (very fine sand; C2), 125–250 μm (fine sand; C3), 250–500 μm (medium sand; C4), 500–1,000 μm (coarse sand; C5), and 1,000–2,000 μm (very coarse sand; C6). Samples >63 μm were ground in a Pica Blender Mill (Cianflone Scientific Instruments, Pittsburg, PA) for 5-min in 30 mL tungsten carbide vials, with tungsten carbide balls to enhance homogeneity during digestions. All material was subsequently passed through a 63-μm nylon mesh screen. The mass in each of the grain size fractions was determined to a precision of 0.001 g.

2.4 Analytical Techniques

Baseline samples (<63 μm) and 13 samples of various grain sizes from the two sewer outlets were digested using a partial extraction procedure. Samples of 0.50 g were agitated with 10 mL of 0.5 M HCl for 1 h at 20°C (Sutherland 2002). A dilute HCl leach liberates adsorbed detrital and non-detrital carbonate-bound metals and much of the Fe/Mn oxide and organic-associated metals while minimizing the loss of residual silicate-bound metals (Sutherland and Tolosa 2000). Each sample solution was filtered and analyzed for elements with inductively coupled plasma-atomic emission spectrometry. Five replicates of a stream sediment CRM 'NCS DC73317' (GBW07307), produced by the China National Analysis Center for Iron, with a Pb concentration of 350 mg/kg (total digestion) were analyzed with a mean precision of 6%. The single HCl leach was applied to provide a rapid comparison to the more prolonged BCR sequential extraction procedure.

Bed sediment samples and three replicates of CRM BCR-601 and four replicates of BCR-701 were submitted by the first author to the second author's laboratory and analyzed "blindly." This procedure precluded any special handling of CRMs and thus results will describe the typical precision and accuracy of the optimized BCR procedure in this laboratory. One-gram samples were analyzed "as is" following the protocol defined in Table 2, with a minor modification of the residual digestion step. In this study we added 7.5 mL of 6 M HCl, and 2.5 mL of 14 M HNO_3 (Ure 1990); while the suggested procedure (Rauret et al. 2000b) uses 7.0 mL of 12 M HCl and 2.3 mL of 15.8 M HNO_3. Two or three 1 g samples of each CRM were dried at 105°C for 24 h. 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).

Four operationally defined fractions were identified, acid extractable, reducible, oxidizable, and residual. Eight metals (Al, Co, Cu, Fe, Mn, Ni, Pb and Zn) were originally analyzed by flame atomic absorption spectrometry (Varian SpectrAA-10, Palo Alto, CA; FAAS) equipped with deuterium background correction – though only results from Pb are fully reported in this study. Fraction specific detection limits, defined as three times the standard deviation of a reading near the blank, were 4 mg/kg for Pb in the first three steps of the procedure and 5 mg/kg in the residual phase. Data below detection limits were replaced with half the detection limit concentration.

Precision of Pb measurements, in each of the four steps, were based on measurements of CRM aliquots from a single bottle. Precision was defined as: (standard deviation/mean)×100. Accuracy was based on measured phase-specific element concentrations relative to recently published indicative values for BCR-601 using the optimized BCR procedure, and certified values for BCR-701. Accuracy was computed as: [(measured concentration – certified concentration)/certified concentration]×100. Precision and

Table 2 Chemical reagents and analytical conditions for the optimized BCR sequential extraction procedure with an aqua regia digestion (after Sutherland and Tack 2002)[a]

Step	Operational definition	Chemical reagents and conditions
1	Acid extractable	1-g aliquot, 40 mL 0.11 M acetic acid, shake for 16 h at 22±5°C. Separate extract from the solid residue by centrifugation at 3,000×*g* for 20 min.
2	Reducible	To Step 1 residue add 40 mL 0.5 M $NH_2OH{\bullet}HCl$ from a 1 L solution containing 25 mL 2 M HNO_3 (pH≈ 1.5), shake for 16 h at 22±5°C. Centrifuge extract as per Step 1.
3	Oxidizable	To Step 2 residue add 10 mL H_2O_2 (pH 2–3), 1 h at room temperature, heat to 85±2°C for 1 h; add a further 10 mL H_2O_2 and heat to 85±2°C for 1 h; add 50 mL 1 M NH_4OAc (pH 2) and shake for 16 h at 22±5°C. Centrifuge extract as per Step 1.
4	Residual	To Step 3 residue add 3 mL distilled H_2O, 7.5 mL 6 M HCl, and 2.5 mL 14 M HNO_3; leave overnight at 20° C, boil under reflux for 2 h, cool and filter

[a] Steps 1 to 3 are based on the protocol described fully in Rauret et al. (1999); and for the residual fraction (Step 4) the source of the procedure was (Ure 1990). Note Step 4 differs slightly from the aqua regia digestion suggested by Rauret et al. (2000b), which included 7.0 mL 12 M HCl and 2.3 mL 15.8 M HNO_3.

accuracy could not be determined for the acid extractable phase (step 1) in either BCR 601 or 701, as certified Pb concentrations of 2.3 and 3.18 mg/kg were below detection limits of the analytical approach used. This was not a concern as it turns out no samples in this study had acid extractable Pb concentrations greater than the detection limit. For the remaining steps, Pb precision was ≤13%, and accuracy was ±8% of indicative or certified values (Table 3).

Organic matter contents on the <63 µm fraction of bed sediments were estimated using the loss-on-ignition technique (LOI_{OM}; Sutherland 1999). Approximately 0.5 g was placed in a dried and weighed ceramic dish and then in a muffle furnace, set at 450°C, for a minimum of 16 h. Samples were cooled in a dessicator and re-weighed. The difference in mass was used as an index of organic matter. The cation exchange capacity (CEC) of the <63 µm fraction was determined using the ammonium acetate (NH_4OAc) sodium acetate (NaOAc) method (van Reeuwijk 1992).

To establish the general water chemistry of the system, five sites were sampled during baseflow conditions, from the headwaters (baseline area) to the furthest downstream storm-sewer outlet (Beretania). Electrical conductivity (EC), pH, and trace element concentrations by ICP-MS were determined on unfiltered samples. Further details are given in Andrews (2002).

2.5 Characterizing Contaminant Signals

To establish the degree of contamination of bed sediment samples from Nuuanu Stream, Pb concentrations were compared to those from baseline sites in the headwaters of the watershed. Two digestion procedures were applied. The first involved leaching the <63 µm fraction of baseline bed sediment samples with 0.5 M HCl (mean Pb=3 mg/kg), and a total 4-acid digestion of three samples (mean Pb=13 mg/kg). These baseline concentrations are used to define two enrichment ratios, ER_{HCl} and the more conservative

Table 3 Precision and accuracy measurements for Pb using the standardized BCR sequential extraction procedure and certified reference materials BCR-601 (*n*=3) and BCR-701 (*n*=4)

Phase	BCR-601 Pb (mg/kg)[a]	BCR-601 precision (%)	BCR-601 accuracy (%)	BCR-701 Pb (mg/kg)[b]	BCR-701 precision (%)	BCR-701 accuracy (%)
Reducible	205.0	3.6	−2.1	126.0	3.2	−3.7
Oxidizable	19.7	5.3	+2.4	9.3	13.2	−4.0
Residual	38.0	8.5	−8.2	11.0	10.1	−1.8

[a] Indicative values from Rauret et al. (2000a).

[b] Certified values from Rauret et al. (2001).

ER_{Total}. Values greater than 1 indicate enrichment above baseline conditions. Data from sequential extractions from the baseline sites were inconclusive as concentrations were typically below detection limits for several phases. Thus, baseline HCl or total digestion concentrations were used in enrichment ratio computations.

Another approach that has been widely applied in the environmental literature is to compare results from an investigation to generic sediment quality guidelines (SQGs). These SQGs are empirically based and rely on field sediment chemistry paired with field or laboratory biological effects data (Burton 2002). Recently, consensus based SQGs have been developed for freshwater ecosystems in the US (MacDonald et al. 2000). Two SQGs for a given element define three potential effects ‘fields.’ For example, MacDonald et al. (2000) define two SQGs for Pb. They are a threshold effect concentration (TEC, 35.8 mg/kg) and a probable effect concentration (PEC, 128 mg/kg). Sediments with concentrations ≤ TEC are not expected to have harmful effects on sediment-dwelling organisms. Sediment-associated Pb concentrations between TEC and PEC are expected to produce occasional harmful effects on sediment-dwelling organisms, while Pb concentrations greater than PEC are expected to produce frequent harmful effects. It should be emphasized that no data from Hawaiian streams were included in establishing the SQGs, the SQGs are based on total digestion procedures, and no data are provided on grain size. Thus the use of SQGs in this study is to place the Pb concentrations from Nuuanu Stream into a relative perspective.

3 Results and Discussion

3.1 Background Sediment and Water Chemistry

The grain size distribution for the Judd and Vineyard outlet samples are plotted alongside the average values for the three sites associated with Beretania sewer outlet (Fig. 1). Beretania samples were the finest with an average sample mass in the <63 μm fraction (i.e., C1) of 14±4%. This compares to 0.7% for the Judd outlet sample, and 2.5% for the Vineyard outlet sample. Vineyard had the largest mass percent in the coarsest fraction (1–2 mm; C6) at 53%, followed by Judd (34%), and by Beretania (20±8%).

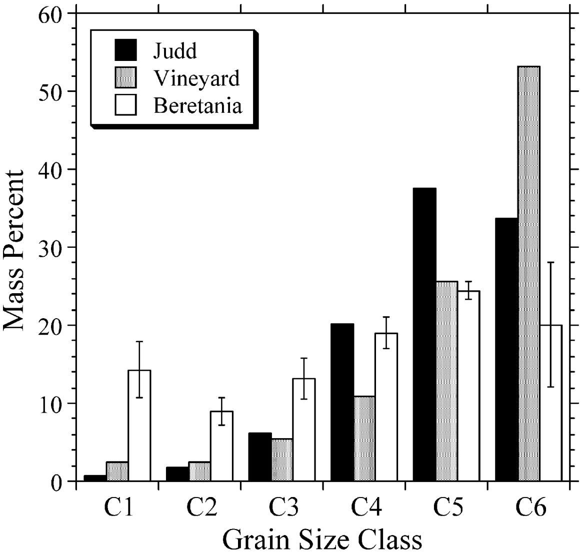

Fig. 1 Mean grain size distributions of bed sediments at the Judd Street sewer outlet, the Vineyard Boulevard outlet, and at three sites associated with the Beretania Street sewer outlet. Error bars reflect ± one standard deviation. *C1* represents <63 μm fraction (silt and clay-sized particles); *C2*, 63–125 μm (very fine sand-sized particles); *C3*, 125–250 μm (fine sand-sized particles); *C4*, 250–500 μm (medium sand-sized particles); *C5*, 500–1,000 μm (coarse sand-sized particles); and *C6*, 1,000–2,000 μm (very coarse sand-sized particles)

The baseline bed sediment sites had the lowest average CEC, at 27±3 cmol/kg, compared to a mean of 39±1.9 cmol/kg with a range from 36 to 43 cmol/kg in the urbanized stream section. The bed sediments associated with the Judd St. outlet (n=7) had the lowest organic matter content $LOI_{OM} = 12 \pm 1.5\%$. Mean LOI_{OM} values for the baseline sites (n=10), sites around the Vineyard outlet (n=7), and around the Beretania outlet (n=7) were 20±1.9, 18±3.7, and 25±5.4%, respectively.

Water pH varied minimally at the five sample locations (8.0 to 8.1). Temperature was lowest at the shaded baseline site (17°C), and 3 to 7°C warmer downstream in the urbanized stream sites. The EC varied significantly with distance downstream. Values in the headwaters were 100 μS/cm, at 1.1 km upstream of the stream outlet ECs ranged from 200 to 450 μS/cm, at 600 m upstream of the mouth EC was 9,400 μS/cm, and at the Beretania storm-sewer outlet, 200 m upstream from the mouth, the EC reached 220 mS/cm. The salinity gradient resulted from the salt water wedge that is associated with tidal fluctuations. Lead in unfiltered samples ranged from <0.1 μg/L in the headwaters to 1.1 μg/L at the Beretania sewer outlet.

3.2 Comparison between Pb Leached by HCl and Extracted with the BCR Procedure

Thirteen samples, six from around the Vineyard sewer outlet, and seven from around the Beretania outlet were analyzed with 0.5 M HCl and the 4-step BCR procedure. The HCl procedure takes only 1 h for leaching, compared to about 50 h for all steps of the BCR procedure. The average Pb leached by HCl was 133±48 mg/kg, and this was substantially greater than baseline Pb values of 3 mg/kg for the HCl leach and 13 mg/kg for a total digestion. Phases sequentially extracted were summed and compared to Pb leached by HCl; recoveries were 78% from step 1 and 2 of the BCR procedure, 103% from steps 1–3, and 126% from the sum of all steps 1–4. Spearman correlation coefficients (r_s) between Pb leached by HCl and that extracted using combinations of BCR phases were highly significant. For example, HCl vs. steps 1–2, r_s=0.78, p=0.0073; HCl vs. steps 1–3, r_s=0.94, p=0.0011; HCl vs. steps 1–4, r_s=0.96, p=0.0009. The strong associations are depicted in Fig. 2. The Wilcoxon paired test indicated that the HCl approach leached significantly more Pb than the summation of Pb from the first two steps of the BCR procedure (p=0.0024), and significantly less than the sum of Pb from all four steps of the BCR procedure (p=0.0037). However, there was no significant difference between Pb leached by HCl and the sum of the first three steps of the BCR procedure (p=0.65). The elements extracted in the first three steps of the BCR procedure are considered labile. Thus in this system the HCl leach provides a rapid, cost-effective approach to defining the labile phases of Pb in bed sediments. Before adopting the dilute HCl approach for all bed sediments, it is imperative for researchers to conduct a preliminary investigation to establish the degree of association between anthropogenic metals leached by dilute HCl and the labile fractions liberated by the optimized BCR approach. As an example, recent data from Cook and Parker (2006) indicates that this relationship may not hold for all environments. These authors found that the 0.5 M HCl leach removed 35 times less Pb than the sum of the first three steps of the optimized BCR procedure for a canal sediment contaminated by waste from a metal processing plant in France.

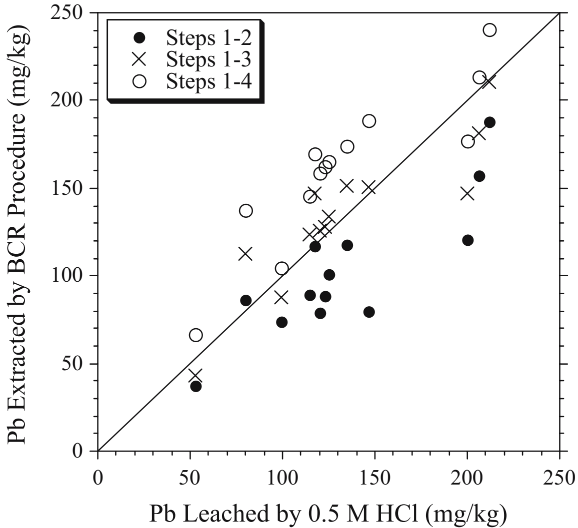

Fig. 2 Scattergram illustrating the relationship between Pb leached by 0.5 M HCl and that sequentially extracted by the optimized BCR procedure for 13 bed sediment samples from Nuuanu Stream, Hawaii. Steps 1–2, represents the sum of Pb in the acid extractable and reducible phases; Steps 1–3, represents the sum of Pb in steps 1–2 plus the oxidizable phase; and Steps 1–4, represents the sum of Pb in steps 1–3 plus the residual phase. The *diagonal line* (1:1) is for reference

3.3 Downstream Spatial Variation in Sequentially Extracted Pb

Sediment samples at three outlets were grain size fractionated and sequentially extracted for Pb. Data are shown in Figs. 3, 4 and 5. No data are available for the <63 μm fraction from the Judd outlet sample (Fig. 3), as sample mass was inadequate following other geochemical analyses. It is apparent that the maximum Pb concentrations, representing the sum of the four sequentially extracted steps did not occur in the finest grain size fraction, i.e., C1. Maximum Pb concentration occurred in grain size class C5 (500–1,000 μm) for Judd (232 mg/kg) and Beretania (334 mg/kg; Fig. 5) outlets; and in C3 (125–250 μm) for Vineyard outlet (240 mg/kg; Fig. 4). This was somewhat unexpected given the typical increase in concentration with decreased grain size (Horowitz 1991). But this may reflect aggregation of particles in the different size classes; simple mechanical sieving will not isolate individual primary particles but only aggregates or flocs (Droppo and Leppard 2004). These particle associations may be distributed throughout the size ranges separated in this study. In each of the outlet samples, the coarsest grain size fraction, C6 (1–2 mm)

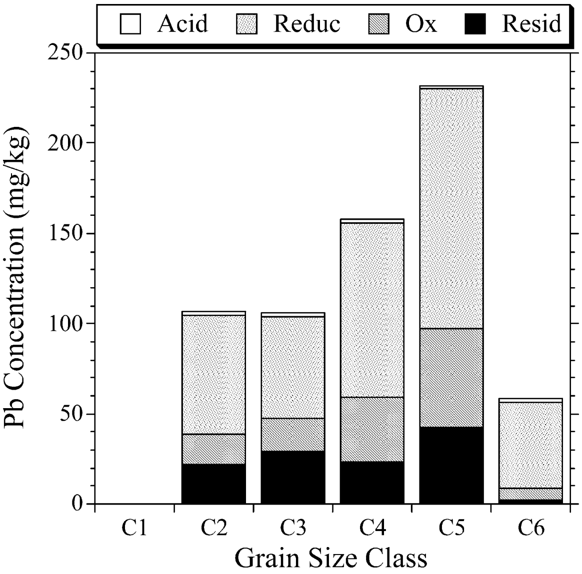

Fig. 3 Cumulative stack graph of Pb concentrations extracted from four phases from bed sediment at the Judd Street outlet. Acid represents acid extractable phase, *Reduc* the reducible phase, *Ox* the oxidizable phase, and *Resid* the residual phase. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm

had the lowest total Pb concentration, and this increased downstream from 59 mg/kg at Judd, to 67 mg/kg at Vineyard, to 116 mg/kg at Beretania.

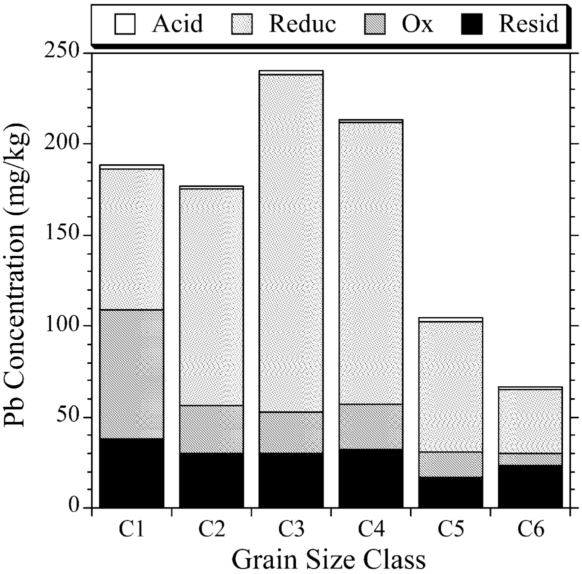

Fig. 4 Cumulative stack graph of Pb concentrations extracted from four phases from bed sediment at the Vineyard Boulevard outlet. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm

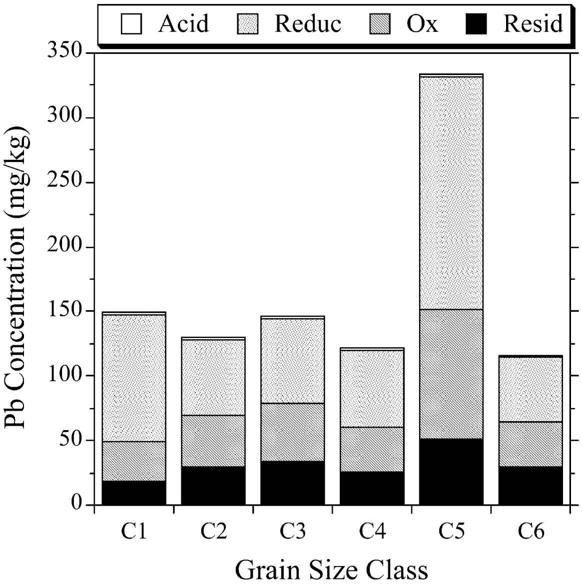

Fig. 5 Cumulative stack graph of Pb concentrations extracted from four phases from bed sediment at the Beretania Street outlet. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm

Lead concentrations and mass per grain size fraction were used to establish weighted Pb contents for the BCR phases. The spatial variation of Pb in reducible, oxidizable and residual phases are shown in Fig. 6. No data were plotted for the acid extractable phase, as all measurements were below the detection limit of 4 mg/kg. Three panels form Fig. 6, with each panel reflecting a given sequentially extracted phase with the spatial arrangement in each panel reflecting upstream (Judd) to downstream (Beretania) locations. No clear downstream pattern in Pb content is apparent from the three phases displayed in Fig. 6. However, weighted concentrations are typically higher for each of the phases at the outlet furthest downstream (Beretania). The Pb associated with the reducible phase was greater than either the oxidizable or residual phases for each of the outlets. Weighted Pb extracted from the reducible phase was lowest at Vineyard (69 mg/kg) and similar between the Judd (91 mg/kg) and Beretania (92 mg/kg) outlet sites. The oxidizable Pb content was lowest at the Vineyard outlet (13 mg/kg), which was approximately 2.4 times less than at Judd and 4.0 times lower than that at Beretania. It is noteworthy that the average residually-associated Pb concentrations in all three outlet samples were significantly greater (24 to 34 mg/kg)

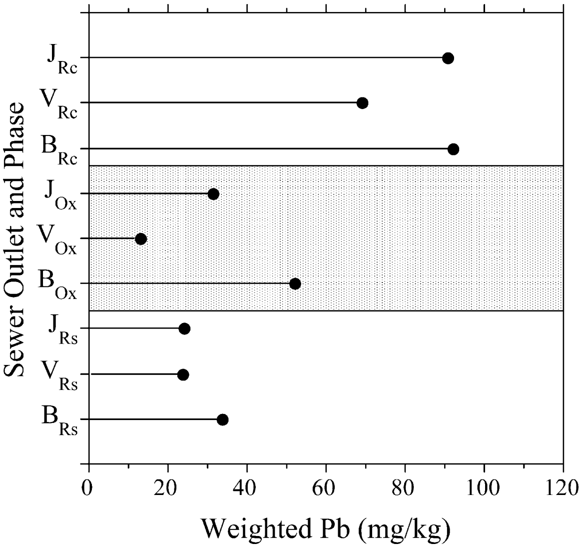

Fig. 6 Three-tiered dotplot of weighted Pb concentrations in three sequentially extracted phases for the Judd (*J*), Vineyard (*V*) and Beretania (*B*) outlets. *Rc* represents reducible, *Ox* oxidizable, and *Rs* residual

than the baseline Pb extracted by a total digestion (13 mg/kg). These differences may reflect different source area contributions and/or the incorporation of some portion of the anthropogenic Pb within the BCR residual fraction. The sum of the outlet-associated Pb in all phases of the BCR approach followed the sequence of Beretania (180 mg/kg)>Judd (148 mg/kg)>Vineyard (108 mg/kg).

Data from this study can be compared with caution to those in Table 1, only for the optimized BCR sequential approach. The extraction efficiency of Pb from the reducible phase in the original procedure is considerably lower than that from the new approach (Sutherland and Tack 2003), as the optimized approach has a lower pH and an increased concentration of hydroxylamine hydrochloride (0.5 vs. 0.1 M). Dominance of Pb in the reducible phase of Nuuanu bed sediments compares well with data from very different fluvial environments, e.g., the east coast of the US (Ryan et al. 2002), Hungary and Romania (Bird et al. 2003), and England (Mossop and Davidson 2003).

A ternary plot was used to display the relative proportions of the three important sequentially extracted phases for each of the grain size fractions associated with three storm-sewer outlets (Fig. 7). The majority of grain size fractions for a given outlet plot as discrete entities as described by ellipses. The deviations from the individual outlet groupings were typically in either the finest (<63 μm; C1) or coarsest (1–2 mm; C6) fractions. From viewing the three ellipses, there appears to be a shift in the centroid of each ellipse to an increased reducible Pb proportion from Beretania to Judd to Vineyard outlets. This does not follow a spatially-oriented upstream to downstream pattern. As a group, Pb sorbed to sediments about the Vineyard outlet would be the most environmentally mobile. The partitioning of Pb, weighted over grain size for each outlet is shown in Fig. 8. The reducible Pb phase at the Vineyard outlet accounts for about 64% of all extracted lead, or about 82% of the labile Pb. Sixty percent of the extractable Pb in the Judd outlet sediments is associated with the reducible phase, or 73% of the labile Pb. Beretania outlet sediments contain the lowest proportion of reducible Pb extracted (about 51%), or about 63% of the labile fraction. The oxidizable phase of the Beretania sediments accounted for 36% of the Pb, compared to 25% for Judd, and only 16% for the Vineyard outlet sediments. This may reflect the greater concentration of organic matter at this site, i.e., LOI_{OM} of 25% vs. 12–18% for Judd and Vineyard. The percentage of Pb associated with the residual phase varied minimally between sites, i.e., 16 to 22%.

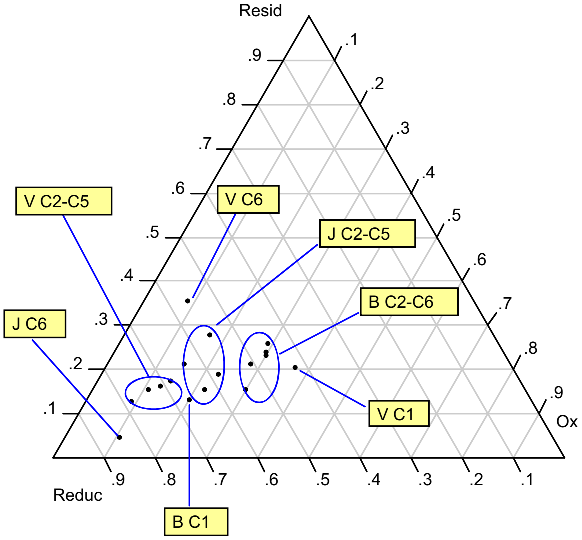

Fig. 7 Ternary plot for proportions of reducible (*Reduc*), oxidizable (*Ox*), and residual (*Resid*) Pb for all grain size fractions (*n*=17) of bed sediments at three storm-sewer outlets (*B*, Beretania; *J*, Judd; and *V*, Vineyard). C1–C6 represent grain size classes previously described

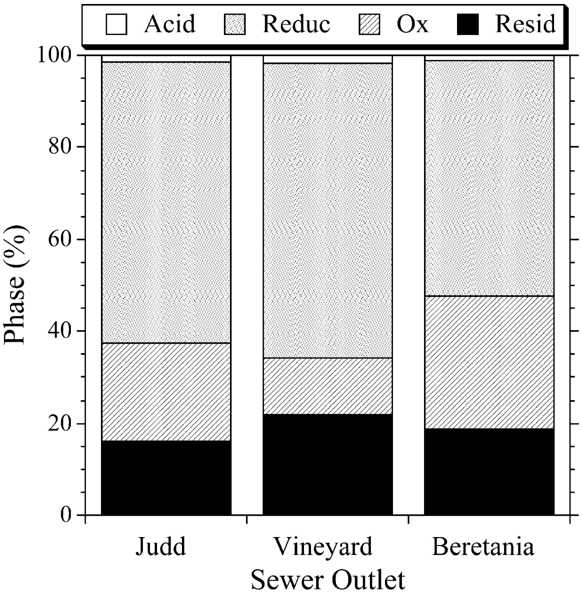

Fig. 8 Cumulative stack graph of bed sediment-associated (weighted) Pb percentages extracted from four phases at the Judd, Vineyard and Beretania storm-sewer outlets. *Acid* represents the acid extractable phase, *Reduc* the reducible phase, *Ox* the oxidizable phase, and *Resid* the residual phase

3.3.1 Lead Contaminant Signals for Outlet Samples

Assuming the average HCl and total Pb extracted from the <63 μm fraction of baseline bed sediments, 3 and 13 mg/kg, respectively, are representative of all grain size fractions, enrichment ratios can be determined. The weighted Pb ER_{HCl} values for the sum of four BCR steps for Beretania, Judd and Vineyard outlets were 60, 49, and 36, respectively; and ER_{Total} were 14, 11, and 8, respectively. These data reflect significant anthropogenic enhancement, regardless of sample location in Nuuanu Stream.

Lead concentrations extracted from individual bed sediment grain size fractions by the sum of the 4-step BCR procedure were compared to consensus-based SQGs. Though the 4-step procedure does not recover all Pb from the sediment matrix, the average recovery of the 4-step procedure compared to a total acid digestion ($n=13$) for Nuuanu bed sediments was 90% (range 71–98%; Sutherland, unpublished data). For the Judd outlet, all grain size fractions had Pb concentrations above TEC, three fractions fell between the TEC and PEC limits, and two fractions (250–500 μm and 1–2 mm) exceeded the PEC value of 128 mg/kg. For the Vineyard and Beretania outlet samples, Pb for two of the six fractions fell within the TEC–PEC 'field', and the remaining four fractions exceeded PEC. For Vineyard, PEC was exceeded by all fractions <500 μm, and for Beretania samples <250 μm and between 500 and 1,000 μm. Therefore approximately 60% of the individual fractions analyzed around storm-sewer outlets in Nuuanu would have Pb concentrations potentially harmful to sediment-dwelling organisms.

3.4 Spatial Variation in Pb Phases about One Outlet

Samples 20 m upstream and 20 m downstream of the previously examined Beretania outlet site were sequentially extracted for Pb from six grain size fractions. The intent was to establish whether there was any small scale (over 40 m) spatial differences in Pb associations in Nuuanu bed sediments centered about an outlet. Spatial patterns in phase-associated Pb concentrations are shown in Figs. 9, 10 and 11 for individual grain size fractions. As before, the reducible phase dominated the Pb partitioning for all grain size fractions, regardless of spatial location about the storm-sewer outlet. On average the weighted reducible phase accounted for 50±8% of the Pb stored in bed sediments at the outlet, with a range from 43% in the 1–2 mm fraction to 65% in the <63 μm fraction. At the

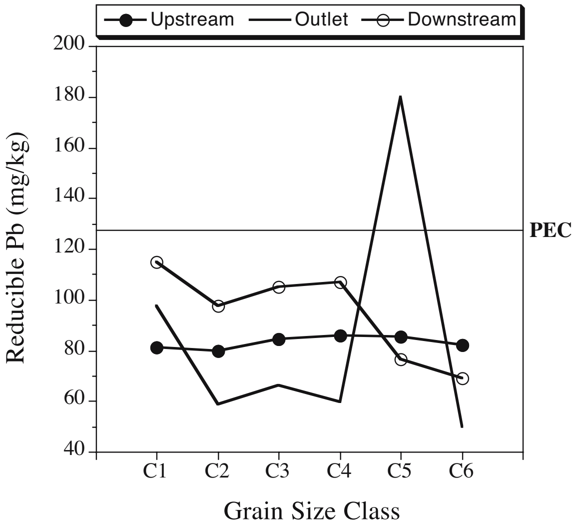

Fig. 9 Variation in Pb extracted from the reducible phase of bed sediments at three locations about the Beretania storm-sewer outlet, i.e., 20 m upstream, at the outlet, and 20 m downstream of the outlet. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm. PEC represents the probable effect concentration

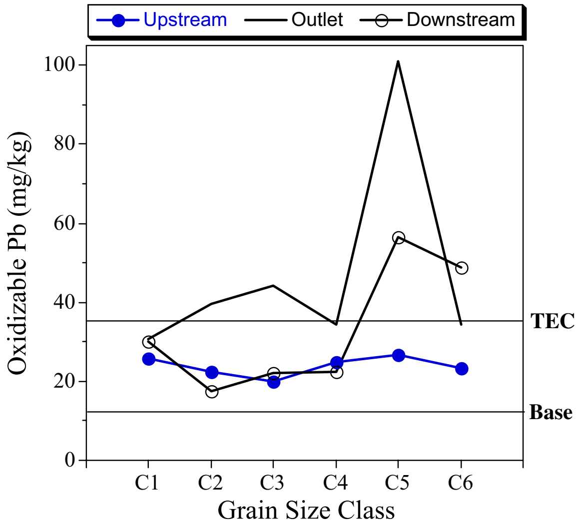

Fig. 10 Variation in Pb extracted from the oxidizable phase of bed sediments at three locations about the Beretania storm-sewer outlet. Base reflects the baseline Pb concentration (13 mg/kg) for bed sediments in Nuuanu watershed extracted with a 4-acid digestion procedure. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm. TEC represents the threshold effect concentration and Base is the (total) baseline concentration

upstream site reducible Pb accounted for 64±3% of all Pb, with a range from 60% for the 500–1,000 μm fraction to 66% for the 125–250 μm fraction. For the downstream site, reducible Pb accounted for 64±12% of total Pb, with a range from 48% in the 1–2 mm fraction, to 76% in the 63–125 μm fraction. Figure 9 indicates reducible Pb concentrations were highest downstream of the outlet in fractions <500 μm (C1–C4), while the maximum concentration occurred in the 500–1,000 μm fraction (C5) at the outlet (180 mg/kg).

The weighted oxidizable phase accounted for between 18±1% (upstream) and 28±4% (outlet) of all Pb. The oxidizable Pb phase (Fig. 10) was greatest at the storm-sewer outlet for all grain size fractions <1,000 μm (C1–C5), with the peak concentration (101 mg/kg) recorded in the 500–1,000 μm fraction (C5).

The residual phase accounted for between 13±3% (downstream) and 20±5% (outlet) of all Pb stored in bed sediment sites. Residual phase Pb was highest at the outlet for all grain sizes >63 μm (Fig. 11), and peaked in the 500–1,000 μm fraction (C5) at 51 mg/kg. For all grain size fractions, expect the 63–125 μm fraction (C2) at the downstream site, residual Pb exceeded the total amount of Pb extracted from baseline sites (13 mg/kg). For three sites, the weighted residual Pb concentration was highest at

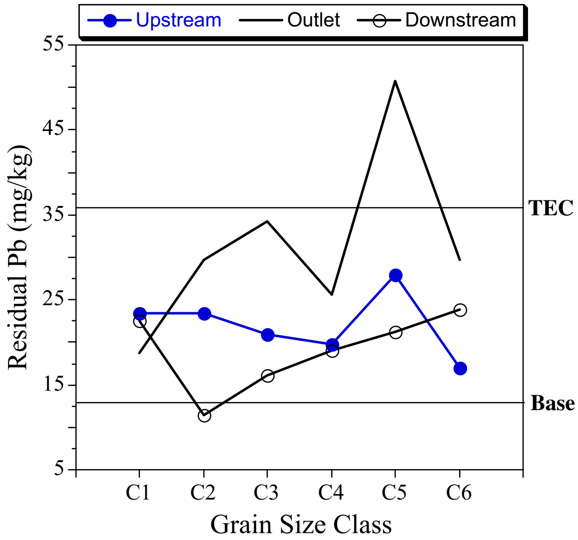

Fig. 11 Variation in Pb extracted from the reducible phase of bed sediments at three locations about the Beretania storm-sewer outlet. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm. TEC and Base as before

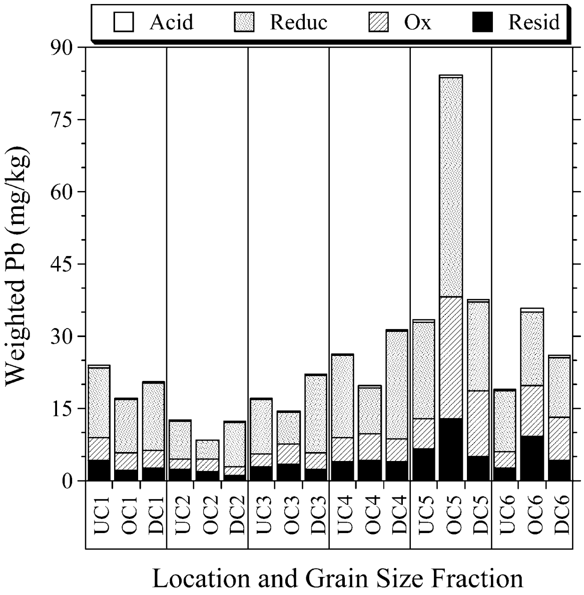

Fig. 12 Cumulative stack graph of bed sediment-associated (weighted) Pb concentrations extracted from four phases at a site 20 m upstream (*U*) of the Beretania outlet, at the outlet (*O*), and at a site 20 m downstream (*D*) from the outlet. *Acid* represents the acid extractable phase, *Reduc* the reducible phase, *Ox* the oxidizable phase, and *Resid* the residual phase. Grain size classes are: *C1*, <63 μm; *C2*, 63–125 μm; *C3*, 125–250 μm; *C4*, 250–500 μm; *C5*, 500–1,000 μm; and *C6*, 1,000–2,000 μm

the outlet (34 mg/kg), compared to 23 mg/kg at the upstream site, and 20 mg/kg at the downstream site. Given that the residual phase Pb concentrations exceed the baseline value of 13 mg/kg, it appears that some portion of the anthropogenic Pb has become preferentially associated with the residual phase. This preferential association was particularly noticeable in some of the coarser sediment fractions 500–1,000 μm (C5) and 1,000–2,000 μm (C6), especially at the outlet (Fig. 12). An alternative explanation to preferential sorption of gasoline era anthropogenic Pb to the residual phase, may be a different source of Pb that has a significant non-labile Pb phase. One potential source may be leaded wheel weights lost from motor vehicles to curbside areas of roads. Root (2000) was the first to draw attention to this potential Pb source, as individual wheel weights weigh up to 113 g and are easily abraded into tiny pieces on road surfaces. Recently, Bleiwas (2006) noted that leaded wheel-weights are an alloy made with 5% Sb, and are made from recycled automobile batteries. Additionally, he estimated that in 2003, approximately 65,000 Mg of lead wheel weights were in use on 232 million registered US vehicles, and about 2,000 Mg of Pb were lost to roadways in the US. To our knowledge there have been no published studies that have examined the toxicity or the phase partitioning of Pb from wheel weights. But their contribution to streams in Hawaii cannot be discounted, as there is a direct connection between most road surfaces and streams via storm drains.

Lead weighted by concentration and grain size for each of the three sample sites associated with the Beretaina sewer outlet are shown in Fig. 12. Data were arranged to compare weighted phase concentrations upstream (U), at the outlet (O), and downstream (D) on a grain size basis from fine (C1=<63 μm) to coarse (C6=1–2 mm). It is apparent that the weighted Pb concentrations were greater upstream or downstream of the outlet for all grain size fractions <500 μm (i.e., C1 to C4), but concentrations were greatest at the outlet in the two coarsest sand-sized fractions (500–2,000 μm; C5 and C6). Summing all phases for the six grain size fractions for a given sample location produced Pb values of 132 mg/kg upstream of the outlet, 180 mg/kg at the outlet, and 150 mg/kg downstream of the outlet. As previously observed for the Judd, Vineyard and Beretania outlet samples, the samples from upstream or downstream of an outlet are also anthropogenically enriched.

4 Conclusions

This study represents the first examination of Pb concentrations in grain size fractionated fluvial bed sediments from North America using the optimized BCR sequential extraction procedure. A weak HCl leach was shown to provide a rapid assessment of labile Pb in Nuuanu Stream bed sediments, but lacked the phase resolution provided by the BCR procedure. Maximum Pb concentrations did not occur in the finest grain size fraction examined (<63 μm).

The reducible phase of all grain size fractions dominated Pb storage in Nuuanu bed sediments. The dominance of this phase corroborates recent work on river sediments using the optimized approach for single grain size fractions.

Over a distance of about 1.8 km, three outlets were sampled and no clear spatial patterns in sequentially extracted Pb were observed. Thus, at this spatial scale, land use (residential vs. commercial) and traffic density (low vs. high) had limited influence on Pb contaminant signals. In fact, the site with the highest traffic density (Vineyard) had the lowest weighted reducible and oxidizable Pb concentrations.

More detailed spatial investigations centered around a single outlet, over a distance of 40 m, indicated little difference in weighted reducible Pb, with values ranging from 84 mg/kg at the upstream site, to 93 mg/kg at the downstream site. Summing all grain sizes and phase-associated concentration data indicated that the outlet had about 16% greater Pb content than the downstream site, and 26% greater Pb than the upstream site. This pattern may reflect greater dilution above and below the outlet with less contaminated sediment, and sediment redistribution below the outlet may have been limited following a sequence of storm events that occurred 1-week before the sampling campaign was conducted. Regardless, all bed sediment samples exhibited significant Pb contamination in the lower 2 km of Nuuanu Stream.

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