A comparison of geochemical information obtained from two fluvial bed sediment fractions

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Abstract A total of 121 bed sediment samples were collected from a 5.8-km stretch of Manoa Stream, Hawaii. Samples were physically partitioned into two grain-size fractions, <63 μm and 63–125 μm, acid digested and analyzed by ICP-AES and FAAS. Non-parametric matched-pair statistical testing and correlation analysis were used to assess differences and strengths of association between the two fractions for Al, Ba, Cu, Fe, Mn, Ni, Pb, Ti and Zn. Results indicated statistically significant differences between fractions for all elements except Mn. Concentrations were significantly greater in the <63 μm fraction for Al, Cu, Pb, Ti and Zn, while Ba, Fe and Ni were higher in the 63–125 μm fraction. Though some elements had statistically significant differences between fractions (Al, Ba, Fe and Zn) percentage differences were in the range of analytical precision of the instrument and thus differences were not practically significant. Correlation analysis indicated strong positive associations for all elements between the two fractions ($p < 0.0001$). Three contamination indices indicated similar degrees of pollution for each size fraction for four elements having an anthropogenic signal (Ba, Cu, Pb and Zn). The environmental information obtained from the 63–125 μm fraction was essentially equivalent to that from the <63 μm fraction. In this system it is clear that both bed sediment fractions indicate anthropogenic enrichment of trace metals, especially Pb, and further supports previous research that has found that aquatic sediments are critical median for tracing sources of pollution.

Key words Fluvial bed sediments · Contamination indices · Grain-size partitioning · Non-parametric statistics · Manoa Stream

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Introduction

The environmental and geochemical importance of trace element accumulations in bed sediments of rivers is unquestionable. Support for this statement comes from an extensive examination of publications between 1971–1998 dealing with "heavy metals" in active fluvial bed sediments. Comparable bodies of literature exist for lake, reservoir, estuary and oceanic systems. From the fluvial literature there has been a significant increase in the number of publications over the last 30 years, and the frequency of publication has increased from less than one per year during the early 1970s to approximately six per year during the most recent time period, 1996–1998 (Fig. 1). This increase primarily stems from the linkages between metal concentrations and ecosystem health, and includes issues such as contamination, nonpoint source pollution, biological magnification and toxicity.

Bed sediments are widely known as a significant and important archive of geochemical information. Analysis of bed sediments provides investigators with data to characterize the degree of anthropogenic influence and may allow for the identification of particular pollution sources.
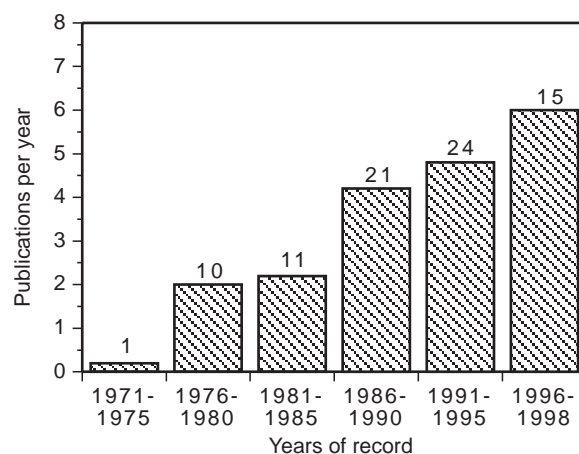

Fig. 1
Temporal variation in the annual number of scientific articles published over the period from 1971 to 1998. Note that the numeric values attached to individual bars represent the total number of publications in a given five-year period except for the 2.5 year period from 1996 to mid-1998. A complete list of the source material consulted can be found in the Appendix

However, a number of methodological problems exist in examining and comparing trace metal concentrations in bed sediments (Barbanti and Bothner 1993). An influential physical property controlling element concentration is sediment grain-size. As Horowitz (1991) states, one of the most significant factors controlling both suspended- and bottom-sediment capacity for concentrating and retaining trace elements is grain-size. As noted widely in the geochemical literature, there is a very strong positive association between decreasing particle size and a concomitant increase in trace element concentration.

Literature review – the issue of grain-size

Presently, there is no widely accepted standardized approach to bed sediment collection and grain-size separation for elemental analysis. This, combined with a variety of different dissolution procedures and chemometric issues, complicates attempts to compare data from a range of systems. Shelton and Capel (1994) advocate reporting trace element data for the < 63 μm fraction (> 4 Φ), which includes both the silt (2–63 μm, 4–9 Φ) and clay (< 2 μm, > 9 Φ) fractions, after wet sieving. Note the descriptive grain-size categories used in this paper follow the Wentworth size classes tabulated in Folk (1974). An examination of the literature indicated that the most widely analyzed sediment fraction was < 63 μm, with 30 of the 82 publications examined reporting elemental analyses for this fraction. However, in total there were 78 different fractions examined, including the granule fraction > 2000 μm (< -1.0 Φ, Moriarty and Hanson 1988), sand 63–2000 μm (4.0 to -1.0 Φ, Crawford and Lenat 1989), silt (Padmalal and Seralathan 1995) and clay (Horowitz and Elrick 1987). A variety of techniques including sieving (wet and dry), settling and decanting, centrifuging, and the use of cyclosizers and air elutriators have allowed for an almost limitless range of sediment fractions to be isolated and analyzed. In fact, 29 studies present concentration data for more than one fraction, with Wilber and Hunter (1979) reporting analyses for nine separate fractions ranging from > 2000 μm to < 0.15 μm. Rarely are there any statistical comparisons between concentrations from the different fractions. Furthermore, there is a total absence of information comparing the degree of pollution, as estimated with "pollution indices", for different grain-size fractions.

Objectives

Based on significant gaps noted in the fluvial bed-sediment literature the following objectives have been defined for this study:

1. To statistically compare, with non-parametric procedures, selected element concentrations for two commonly reported bed sediment fractions from an urban stream.
2. To assess the degree of anthropogenic pollution as estimated by various contamination indices for the two fractions.

Study area

Manoa basin is located in southeast Oahu, Hawaii and is drained by a third-order perennial stream with a planimetric area of about 15 km^2 (Fig. 2). Two headwater sub-basins, here termed Waihi and Waiakeakua, drain areas of 2.75 and 2.90 km^2, respectively. A distinct rainfall gradient exists in the basin and, over a distance of less than 8 km, the annual rainfall increases from about 100 cm (at 24 m above sea level, ASL) to about 400 cm (at 152 m ASL) in the Waihi sub-basin. Manoa Stream is designated Inland Waters-Class 2 in the Hawaii Administration Rules, Title 11, as waters that are to be protected for recreational purposes, propagation of fish, shellfish and aquatic life, agricultural and industrial water supplies, shipping, and navigation (Hawaii Department of Health 1990).

Conservation and undeveloped lands account for about 55–60% of Manoa basin, commercial developments about 2–3%, education and parks about 10%, and the remainder is residential area. Based on land use, traffic intensity, frequency of storm sewer outlets draining directly into the stream and anthropogenic activities Manoa was divided into four separate stream zones. The upper undisturbed headwater zone, residential zone, commercial-institutional zone, and the lower zone; with the latter zone being the most influenced by anthropogenic contaminants.

Manoa Valley is carved into the remnants of the Koolau Shield Volcano that forms the eastern spine of Oahu. Koolau Volcano is composed primarily of shield-type tholeiite basalts (Koolau Basalt) with the subaerial part constructed between 1.8 and 2.7 Ma ago (Lanphere and Dalrymple 1980; Frey and others 1994). The Honolulu Volcanic Series represents $< 1\%$ of the Koolau Shield Volcano, and comprises the post-erosional volcanism on the shield, with the lavas and tuffs < 1 Ma (Clague and Frey 1982). The Honolulu Volcanics broke from about 37 separate vents or groups of vents at different times after the Koolau Shield was "dead" and much dissected (Jackson and Wright 1970). These more recent volcanics are characterized by a nephelinitic suite of rocks (Clague and Frey 1982). The Sugarloaf vent (nr. 37) is the one that is most relevant to this study since lava flows spread out on the floor of Manoa Valley to form a broad, nearly level surface from the basin outlet to about 2.8 km upstream. The most widely cited age for the Sugarloaf flow is 67 ka based on potassium-argon (K-Ar) dating by Gramlich and others (1971). The soils that have developed in Manoa Valley have formed on rocks of very different ages.

Fig. 2
Study area location map, Manoa drainage basin, Oahu, Hawaii.
Note every tenth sample site is indicated by a solid "dot"; this
represents a distance of approximately 500 m

Six soil orders have been identified from maps of Manoa
Valley published by Foote and others (1972). The soils
classified as "rocky mountain land, rocky land, and cin-
der lavas" have been designated in this study as Entisols.
The areal abundance of soil orders in Manoa basin is as
follows: Entisol (45%) >Inceptisol (28%) >Ultisol (20%)
>Oxisol (5%) >Mollisol (1%) >Vertisol (<1%).

Materials and methods

Sample collection and processing
Systematic sampling was used to collect bed sediment
samples at 50-m intervals from the outlet of Manoa
Stream during baseflow on three successive days. A total
of 117 sites were included in the sampling array, covering
a distance of 5.8 km. Samples from depositional zones in
the main third-order channel and second-order segment
of Waihi Stream were collected. Samples from three loca-
tions could not be collected due to cement (box-type)
channelization. In addition to the main channel sites,
samples from two minor ephemeral tributaries were col-
lected as they entered the main channel, and samples
were also collected from the mouth of seven storm drains
entering the main channel.

A clear 10-cm internal-diameter Plexiglas tube sampler was used to collect three separate 5-cm cores at each sampling site. Cores were composited, double bagged and mixed thoroughly prior to transport to the laboratory, where they were cold stored at about 5 °C prior to processing. Several splits were made using a Teflon spatula in Teflon pans from each sample, with the split for element analyses placed in acid washed beakers and dried for 48 h at 40 °C. Samples were lightly crumbled with latex gloves to break up weak aggregates and dry-sieved through acid washed nylon sieves. Samples were physically partitioned to isolate the two grain-size fractions, < 63 μm and 63–125 μm.

Analytical techniques

Bed sediment fractions (mass 0.5 g) were ground using a mixer-mill with tungsten carbide bowl and balls for 2 min. Ground samples were digested using trace metal grade nitric (HNO_3), perchloric ($HClO_4$), and hydrofluoric (HF) acids to dryness overnight on a hot plate. The residue was solubilized with hydrochloric (HCl) acid and diluted to volume. Metals (except Pb) were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and Pb by flame atomic absorption spectrometry (FAAS).

Quality control procedures for elements in bed sediment included analyses of two standard reference materials (SRMs), National Institute of Standards (NIST) SRM 2704 collected from Buffalo River, NY (Epstein and others 1989) and the Canadian Certified Reference Materials Project (CCRMP) STSD-2 collected from Hirok Stream, BC (Lynch 1990). Accuracy and precision for the nine elements examined in this study are shown in Table 1, and these are based on 18 duplicate samples of SRM 2704 and 17 duplicates of STSD-2. Additionally, 24 field duplicate

samples were interspersed randomly within sample batches. The elements reported in Table 1 reflect a mix of major "conservative" elements (Al, Fe and Ti) commonly used for geochemical normalization; those as hydrous oxides that may significantly influence sorption processes (Al, Fe and Mn); minor elements which have shown no anthropogenic signal in Manoa Stream (Ni); and those minor elements with varying degrees of anthropogenic contamination (Ba, Cu, Pb and Zn).

Precision for all elements from the SRM samples was excellent with a range from 2–6% for STSD-2, and 3–7% for SRM 2704. Instrumental accuracy was very good for most elements with a range from –11% (Ba) to +14% (Ni) for STSD-2, and from –10% (Ti) to +3% (Ni) for SRM 2704.

Statistical differences in grain-size element concentrations

Several approaches were used to compare element concentrations for the two grain-size fractions. The non-parametric Wilcoxon (matched-pair) signed rank test was used to compare population differences in 121 samples. The Spearman rank order correlation statistic (r_s) was calculated to assess the strength of association, or lack of, between the fractions. Scattergrams are shown for selected elements so the reader gets a better visual assessment of the relationships. For individual elements, statistical results are presented for pair-wise subtractions of VFS concentrations from SiCl concentrations. Positive concentration differences indicate SiCl fraction values exceeded those in the VFS fraction. Differences are statistically summarized and selected histograms are presented.

Indicators of sediment contamination

A number of indices have been developed to characterize the degree of sediment contamination in aquatic sedi-

Table 1
Elemental analyses, precision and accuracy for geochemical standard reference samples measured in this study

Element	Units	Minimum reporting limit	STSD-2[a] $\bar{X} \pm 1$ SD[c] this study	STSD-2 $\bar{X} \pm 1$ SD[d] certified	STSD-2 Precision[e] CV (%)	STSD-2 Accuracy[f] (%)	SRM 2704[b] $\bar{X} \pm 1$ SD[g] this study	SRM 2704 $\bar{X} \pm 95\%$ CI[h] certified	SRM 2704 Precision[e] CV (%)	SRM 2704 Accuracy[f] (%)
Al	%	0.01	8.69 ± 0.19	8.52 ± 0.21	2.2	+ 2.0	6.16 ± 0.19	6.11 ± 0.16	3.2	+ 0.8
Ba	mg kg^{-1}	10	480 ± 30	540 ± 43	5.5	− 10.7	380 ± 30	414 ± 12	7.1	− 8.0
Cu	mg kg^{-1}	1	49 ± 3	47 ± 5	5.1	+ 3.2	96 ± 4	98.6 ± 5.0	4.1	− 2.5
Fe	%	0.01	4.97 ± 0.16	5.2 ± 0.3	3.2	− 4.4	3.96 ± 0.15	4.11 ± 0.10	3.8	− 3.6
Mn	mg kg^{-1}	5	970 ± 30	1060 ± 60	3.1	− 8.9	530 ± 21	555 ± 19	4.0	− 4.7
Ni	mg kg^{-1}	1	60 ± 3	53 ± 6	4.2	+ 14.0	45 ± 3	44.1 ± 3.0	5.9	+ 2.7
Pb	mg kg^{-1}	2	63 ± 2	66 ± 4	3.7	− 5.3	149 ± 7.1	161 ± 17	4.8	− 7.5
Ti	%	0.01	0.45 ± 0.02	0.49 ± 0.04	4.1	− 7.6	0.41 ± 0.02	0.457 ± 0.018	4.9	− 10.3
Zn	mg kg^{-1}	2	240 ± 8	246 ± 21	3.3	− 2.4	421 ± 14	438 ± 12	3.3	− 3.9

[a] STSD-2 is a geochemical stream sediment reference sample from the CCRMP
[b] SRM 2704 is a standard reference material (Buffalo River sediment) issued by the NIST
[c] $\bar{X} \pm 1$ SD represents the arithmetic mean plus/minus one standard deviation for 17 duplicates
[d] Certified values as reported by Lynch (1990)
[e] Precision is estimated by the coefficient of variation
$CV = [SD/\bar{X}] \cdot 100$

[f] Accuracy (bias) is estimated using the equation of Gill and Ramsey (1997):
$$\left[\frac{\bar{X}_{This\ Study} - \bar{X}_{Certified}}{\bar{X}_{Certified}} \right] \cdot 100$$
[g] Based on 18 duplicates
[h] $\bar{X} \pm 95\%$ CI represents the arithmetic mean plus/minus 95% confidence intervals as tabulated by Epstein and others (1989)

ments, but only limited data are available comparing the information extracted from these indices for different sediment size fractions. One of the simplest approaches was developed by Håkanson (1984) to assess the degree of pollution of various elements in lake sediment from Sweden. It is based on the concentrations associated with specific percentiles of the cumulative distribution curve for a given element. The index of pollution (PI) is defined as:

$$PI = \left[\frac{P_{90} - P_{10}}{P_{10}} \right] \qquad (1)$$

where P_{90} is the 90th percentile of the concentration distribution for a given element, and P_{10} is the 10th percentile. The P_{10} values can be considered as a rough approximation, when other data are not available, for the background concentration of the element.

Håkanson (1984) states that unpolluted lake sediments will have comparatively low PI-values, but no guidelines were presented. In the present study PI values were computed for the SiCl (PI_{SiCl}) and VFS (PI_{VFS}) fractions for the minor elements exhibiting at least a minor anthropogenic signal (Ba, Cu, Pb and Zn). Additionally, PI-values were computed for the three major elements that have previously been used as conservative elements to normalize geochemical sediment data, Al (Schropp and others 1990), Fe (White and Tittlebaum 1985), and Ti (Horowitz and others 1988). Normalized PI values (Norm PI) for both sediment fractions were determined in this study to overcome the shortcomings of the original PI value, and this is defined as follows:

$$\text{Norm PI} = \left[\frac{P_{n,f}}{MPI_{CE,f}} \right] \qquad (2)$$

where **n** represents the element with an anthropogenic signal, **f** the grain-size fraction (SiCl or VFS), and $MPI_{CE,f}$ is the median pollution index for three conservative elements for a given grain-size fraction. The advantages of Norm PI over the original PI equation are that both granulometric and mineralogical normalization procedures are included in the same index and the degree of contamination is defined relative to 1.0. Values of Norm PI ≤ 1 reflect no contamination, while values >1 reflect increasing pollution.

The original index of geoaccumulation (I_{geo}; cf. Förstner and others 1990) has been adapted to produce a modified index of geoaccumulation (MI_{geo}) and this is defined as follows:

$$MI_{geo} = \log_2 \left[\frac{C_{n,f}}{1.5 \cdot BE_n} \right] \qquad (3)$$

where C_n is the concentration for element **n** in grain-size fraction **f**, BE_n is the best estimate of background element concentrations for the two geologic outcrops in Manoa basin (Table 2). The factor 1.5 in Eq. (3) is used because of possible variations in the baseline (BE_n) data due to lithogenic effects (cf. Salomons and Förstner 1984). The original index used the <2-μm bed sediment fraction;

Table 2

Best estimates of baseline metal concentrations for the Koolau Basalts and the Honolulu Volcanics (Sugarloaf flow) in Manoa drainage basin

Element	Units	Koolau Basalts	Honolulu Volcanics
Al	%	7.72	5.83
Ba	mg kg^{-1}	100	250
Cu	mg kg^{-1}	100	100
Ni	mg kg^{-1}	190	240
Pb	mg kg^{-1}	6	7
Zn	mg kg^{-1}	110	180

and the geochemical background values were derived from fossil argillaceous sediment (average shale). These background values would not be appropriate for a basin dominated by igneous extrusive rocks. The following classification is used for MI_{geo} and follows that of I_{geo} reported by Förstner and others (1990): <0 = practically unpolluted; 0–1 = unpolluted to moderately polluted; 1–2 = moderately polluted; 2–3 = moderately to strongly polluted; 3–4 = strongly polluted; 4–5 = strong to very strongly polluted; and >5 very strongly polluted.

A normalized enrichment ratio (ER) equation was developed for a given element following the work of Lee and others (1994) and is defined as:

$$ER = \frac{\left[\dfrac{C_{n,f}\ \text{Sample}}{C_{Al,f}\ \text{Sample}} \right]}{\left[\dfrac{BE_n\ \text{Background}}{BE_{Al}\ \text{Background}} \right]} \qquad (4)$$

where $C_{n,f}$ is as before; $C_{Al,f}$ is the aluminum concentration in the <63 μm (SiCl) bed sediment fraction or the 63–125 μm fraction (VFS); BE_n Background is as before; and BE_{Al} Background is the best estimate of the concentration of Al in the Koolau Basalts or Honolulu Volcanics. Best estimate values are shown in Table 2. Aluminum was used as a conservative element in this study since it was the most accurately and the most precisely measured major element, and also it is the most commonly used normalizing element in the geochemical literature.

There is no accepted pollution ranking system or categorization of degree of pollution based on the enrichment ratio methodology. Thus, a five-category system is proposed here: ER <2 = depletion to minimal enrichment suggestive of no or minimal pollution; ER 2–5 = moderate enrichment, suggestive of moderate pollution; ER 5–20 = significant enrichment, suggestive of a significant pollution signal; ER 20–40 = very highly enriched, indicating a very strong pollution signal; and ER >40 = extremely enriched, indicating an extreme pollution signal.

Results

Concentration data and statistical test results for the nine elements compared between the two size fractions are shown in Table 3. The pair-wise Wilcoxon test indicated that concentrations for eight of the elements (Al, Ba, Cu, Fe, Ni, Pb, Ti and Zn) differed significantly between fractions. Thus the population median concentration difference between SiCl and VFS was not equal to zero. Only Mn exhibited a population median concentration equal to zero, and thus SiCl and VFS Mn concentrations came from the same parent population. Median element concentrations were significantly greater in the VFS fraction for Ba, Fe and Ni; while concentrations were significantly greater in the SiCl fraction for Al, Cu, Pb, Ti and Zn (Table 3). Barium, Cu and Zn are considered to have a minor anthropogenic signal in the <63-μm bed sediment fraction, while Pb has a major signal many times above background levels.

Histograms of concentration differences are shown for Ni and Pb in Fig. 2. Nickel (Fig. 3a) is an element that reflects only mineralogical control throughout the basin, and most samples had higher Ni values in the VFS fraction, with a maximum difference of 181 mg kg^{-1}. The histogram for Pb (Fig. 3b) indicates that the SiCl fraction typically had higher values, usually differences were <20 mg kg^{-1} but one sample had a concentration difference of 530 mg kg^{-1} (not shown in Fig. 3b). This sample was collected from a minor tributary 5 km from the basin outlet and was directly influenced by illegal dumping of metal pipes on the stream bed.

The spatial variation in concentration ratios for Fe and Pb in the two size fractions are shown in Fig. 4. Iron is typical of those metals with a SiCl to VFS ratio <1.0 (Fig. 4a); with only 14% of the sites examined having higher concentrations in the SiCl fraction (Table 3). Note the stippled areas shown in Fig. 4 represent the 95% confidence bands about the mean ratio and the solid lines
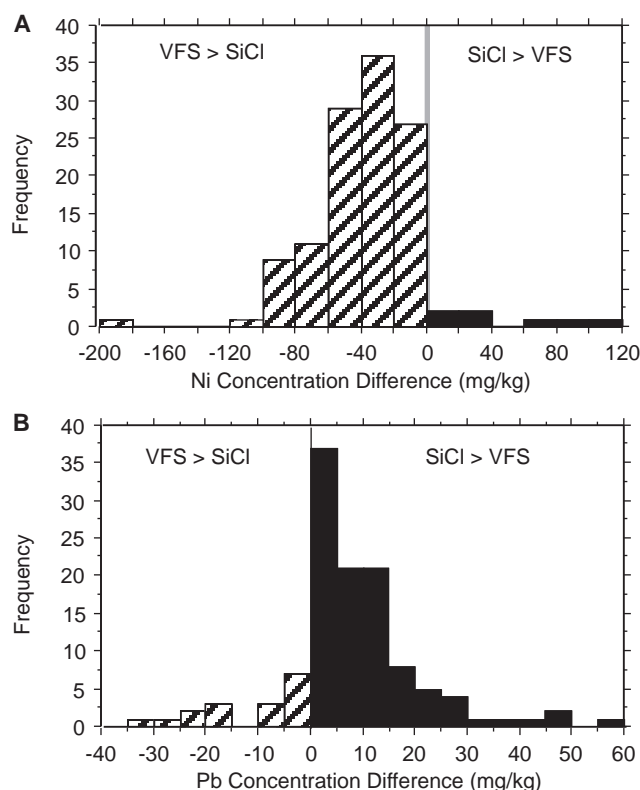

Fig. 3
a Histogram of bed sediment sample sites with Ni concentration differences greater in the very fine sand (VFS) fraction or in the silt + clay (SiCl) fraction from Manoa Stream; and (**b**) Pb concentration differences. Note two Pb "outliers" are not plotted, these are –160 and +530 mg kg^{-1}

represent equivalence in metal concentration between the two fractions. No strong linear associations were observed in the SiCl/VFS ratios for the nine elements. However, some minor cyclicity can be noted in the Pb data (Fig. 4b).

Table 3
Concentrations of trace elements in two grain size fractions and statistical associations for Manoa Stream bed sediments

Statistics-tests	Al	Ba	Cu	Fe	Mn	Ni	Pb	Ti	Zn
Median SiCl[a]	9.36	210	191	13.48	1750	321	52	2.92	242
Range SiCl[a]	8.05–10.90	121–430	133–267	11.31–15.83	1130–3060	278–439	5–1080	2.07–3.50	162–510
Median VFS[a]	8.96	221	162	14.07	1710	356	45	2.54	236
Range VFS[a]	6.25–11.15	132–596	130–263	11.83–19.13	1210–2680	222–493	5–545	2.18–3.28	164–512
Wilcoxon p-value[b]	<0.0001	<0.0001	<0.0001	<0.0001	0.54	<0.0001	<0.0001	<0.0001	<0.0001
Spearman r_s[c]	0.64	0.85	0.67	0.71	0.71	0.47	0.91	0.66	0.81
Spearman p-value[c]	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Sites SiCl>VFS (%)[d]	73.6	14.9	97.5	14.0	48.8	5.8	76.0	94.2	70.2
Median concentration difference[a,e]	+0.42	−11	+27	−0.65	−5	−38	+7	+0.36	+8

[a] Concentrations for Al, Fe and Ti are in %, concentrations for all other elements are mg kg^{-1}
[b] The Wilcoxon probability-value indicates that the ranked (matched pair) differences for the silt + clay (SiCl) fraction and the very fine sand (VFS) fraction populations are significant when the value is less than 0.05

[c] The Spearman rank order correlation coefficient indicates a significant monotonic association between pair-wise element concentrations when the p-value is less than 0.05
[d] The number of sample sites with a greater concentration in the SiCl grain size fraction
[e] The median concentration difference is positive when concentrations in the SiCl fraction exceed the VFS fraction
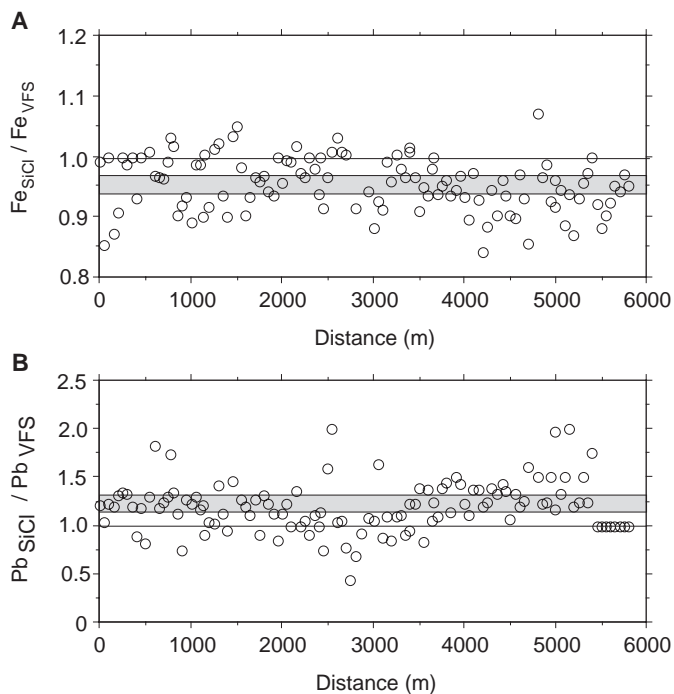
Fig. 4
a Spatial variation of Fe in the silt + clay (SiCl) fraction relative to the very fine sand (VFS) fraction in Manoa Stream bed sediment; and (**b**) Pb. Note *stippled area* in both plots represents the 95% confidence band about the mean ratio of SiCl to VFS for Fe and Pb

Fig. 5
a Scattergram of Fe in the silt + clay (SiCl) fraction relative to the very fine sand (VFS) fraction in Manoa Stream bed sediment, the r_s value is the Spearman rank order correlation coefficient; and (**b**) Pb

The magnitude of the Spearman correlation coefficients (Table 3) indicate that there were strong positive associations between element concentrations in the two fractions, with all r_s-values significant at p-levels <0.0001. This suggests that the probability of getting monotonic associations of such a magnitude simply by chance are less than 1 in 10000. Scattergrams for two elements Fe and Pb (Figs. 5a, b) visually reinforce the strong associations between the size fractions.

The degree of contamination for four elements in two bed-sediment fractions was assessed using three indices (Norm PI, MI_{geo} and ER) and data are summarized in Table 4. The normalized index of pollution indicates that of the four elements examined Pb is by far the most serious contaminant. The Norm PI values of the two sediment fractions differ minimally in magnitude and exhibit the same sequence of elemental pollution, i.e. Pb$>>$Ba$>$Zn$>$Cu. The median MI_{geo} values for the two fractions (Table 4) differ minimally and the range of values are similar. The main point to be made is that MI_{geo} for Pb is an order of magnitude greater ($\log_2$ scale) than for Ba, Cu and Zn as assessed by both fractions. A detailed breakdown of the number of sample sites within each of the MI_{geo} categories for each element and fraction appears in Table 5. Few significant differences exist in the number of sites falling into the seven categories for Ba, Cu and Zn. The only significant discrepancy appears in MI_{geo} category 3–4 (strongly polluted) for Pb; using the
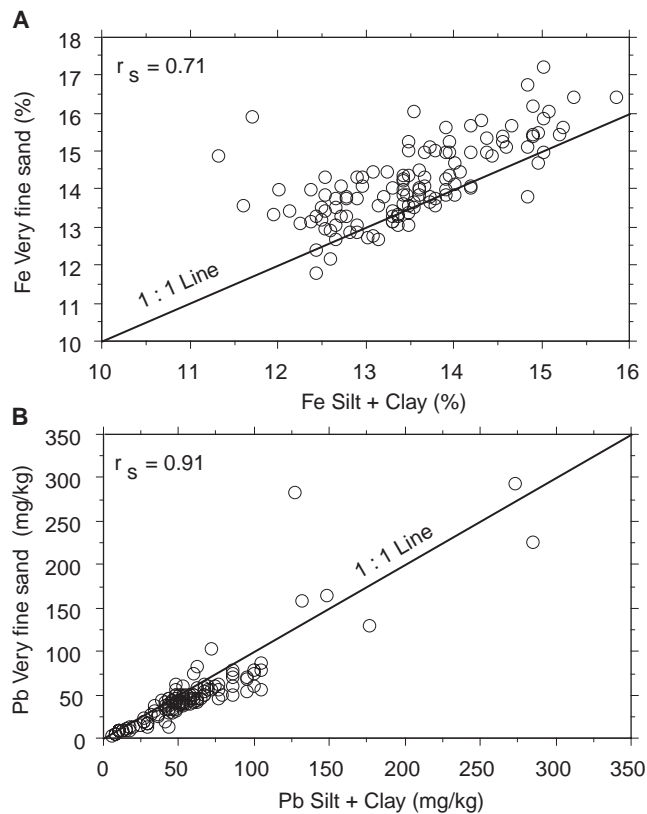
SiCl fraction 19 of 121 sites (15.7%) fall within this category but only 7 or 5.8% of all sites in the VFS fraction. Despite this difference an investigator would draw the same overall conclusion about the 'pollution status' of the sediments with respect to Pb. Enrichment ratio data (Tables 4 and 6) indicate that Pb is by far the most significant contaminant in the Manoa system regardless of fraction examined and supports the results from the other contamination indices.

Discussion and conclusion

Two approaches were used to examine differences in element concentrations in two grain-size fractions of bed sediments from Manoa Stream, Hawaii. The first being a statistical hypothesis testing approach, and the second an examination of contamination indices. The statistical approach was used because it is the standard in environmental studies. However, some have argued that many statistically significant differences reported in the literature are of absolutely no significance (Lachman 1993). This stems from the confusion over statistically significant and practically significant. McBride and others

Table 4
Contamination indices for the silt + clay (SiCl) and very fine sand (VFS) fraction of Manoa Stream bed sediments

Index	Ba	Cu	Pb	Zn	Al	Fe	Ti
PI_{SiCl} [a]	0.44	0.30	5.36	0.38	0.16	0.20	0.20
PI_{VFS} [a]	0.53	0.28	6.39	0.34	0.22	0.20	0.23
Norm PI_{SiCl} [b]	2.22	1.54	27.37	1.91	–	–	–
Norm PI_{VFS} [b]	2.37	1.26	28.79	1.54	–	–	–
Median MI_{geo} SiCl [c]	0.15	0.35	2.42	0.38	–	–	–
Range MI_{geo} SiCl	−0.57 to 1.44	−0.17 to 0.83	−0.93 to 6.91	−0.27 to 1.63	–	–	–
Median MI_{geo} VFS [c]	0.24	0.11	2.25	0.32	–	–	–
Range MI_{geo} VFS	−0.57 to 1.79	−0.21 to 0.81	−0.93 to 5.92	−0.36 to 1.63	–	–	–
Median ER_{SiCl} [d]	1.32	1.45	6.23	1.48	–	–	–
Range ER_{SiCl}	0.74–3.68	1.06–2.41	0.64–164	0.81–4.18	–	–	–
Median ER_{VFS} [d]	1.43	1.30	5.85	1.56	–	–	–
Range ER_{VFS}	0.82–5.40	1.07–2.85	0.63–86.5	0.81–4.84	–	–	–

[a] Index of pollution calculated from Eq. (1)
[b] Normalized index of pollution calculated from Eq. (2)
[c] Modified index of geoaccumulation calculated from Eq. (3)
[d] Normalized enrichment ratio calculated from Eq. (4)

Table 5
Number of bed sediment sample sites in seven categories of the modified index of geoaccumulation (MI_{geo}) for four elements and two bed sediment fractions from Manoa Stream, Oahu, Hawaii. MI_{geo} values were determined using Eq. (3), with values <0 practically unpolluted; 0–1 unpolluted to moderately polluted; 1–2 moderately polluted; 2–3 moderately or strongly polluted; 3–4 strongly polluted; 4–5 strong to very strongly polluted; >5 very strongly polluted (cf. Förstner and others 1990). SiCl represents the silt + clay bed sediment fraction (<63 μm) and VFS is the very fine sand bed sediment fraction (63–125 μm). Values in parentheses represent the percentage of sites in each category, with a total number of sites sampled = 121

Element – grain size	MI_{geo} <0	MI_{geo} 0–1	MI_{geo} 1–2	MI_{geo} 2–3	MI_{geo} 3–4	MI_{geo} 4–5	MI_{geo} >5
Ba-SiCl	53 (43.8)	67 (55.4)	1 (0.8)	–	–	–	–
Ba-VFS	45 (37.2)	74 (61.2)	2 (1.6)	–	–	–	–
Cu-SiCl	2 (1.6)	119 (98.4)	–	–	–	–	–
Cu-VFS	12 (9.9)	109 (90.1)	–	–	–	–	–
Pb-SiCl	3 (2.5)	11 (9.1)	15 (12.4)	69 (57.0)	19 (15.7)	3 (2.5)	1 (0.8)
Pb-VFS	3 (2.5)	15 (12.4)	20 (16.5)	70 (57.9)	7 (5.8)	4 (3.3)	2 (1.6)
Zn-SiCl	7 (5.8)	110 (90.9)	4 (3.3)	–	–	–	–
Zn-VFS	12 (9.9)	108 (89.3)	1 (0.8)	–	–	–	–

(1993) discuss nuances of these terms, and we need to ask whether the differences we achieve, though "statistically significant" are of practical or theoretical significance. This is a difficult question to address and in many environmental situations adequate information are not available. This discussion is important but commonly overlooked in the field of environmental analysis, especially when issues of analytical precision and accuracy are considered.

Data in Table 3 indicate that only Mn concentration was not statistically different between the two grain-size fractions, i.e. a median difference of only 5 mg kg^{-1} for 121 paired analyses. This represents a difference in median concentrations of only 2.3% between the SiCl and VFS fractions for Mn, a value that is less than the level of precision for this element (Table 1). Results indicated that there were statistical differences in concentrations between the fractions for some elements but these differences were in the order of precision for the ICP-AES technique, i.e. Al (median difference between fractions = 4.5%), Ba (5.0%), Fe (4.1%) and Zn (2.5%). Therefore it is doubtful whether these differences are meaningful because of the confounding factor of analytical precision. Median differences between the two size fractions for Cu (15%), Ni (9.8%), Pb (13.5%) and Ti (13.0%) were statistically significant and they exceeded instrument precision by two to three times. But whether the median Pb concentration difference of 7 mg kg^{-1} (Pb$_{SiCl}$ = 52 vs. Pb$_{VFS}$ = 45 mg kg^{-1}) between the fractions has geochemical meaning or ecotoxicological significance is unclear. Correlation analysis was used to examine the strength of association between metal concentrations in the two size fractions. Data showed strong positive monotonic associations, thus as the concentration of a given element in one fraction increased at a specific sample site there was a concomitant increase in the element in the other fraction. Lead showed the strongest association between fractions, this was important because Pb was the element most influenced by human activities in the basin.

Table 6
Number of bed sediment sample sites in five categories of the normalized enrichment ratio (ER) for four elements and two bed sediment fractions from Manoa Stream, Oahu, Hawaii. ER values were determined using Eq. (4), with <2 representing sites with no or minimal pollution; 2–5 represents sites moderately polluted; 5–20 represents sites with significant pollution; 20–40 represents sites with very strong pollution; and >40 represents those sites that are extremely polluted. SiCl represents the silt + clay bed sediment fraction (<63 μm) and VFS represents the very fine sand bed sediment fraction (63–125 μm). Values in parentheses represent the percentage of sites in each category, with a total number of sites sampled = 121

Element-grain size	ER <2	ER 2–5	ER 5–20	ER 20–40	ER >40
Ba-SiCl	117 (96.7)	4 (3.3)	–	–	–
Ba-VFS	111 (91.7)	9 (7.5)	1 (0.8)	–	–
Cu-SiCl	113 (93.4)	8 (6.6)	–	–	–
Cu-VFS	119 (98.3)	2 (1.7)	–	–	–
Pb-SiCl	12 (9.9)	24 (19.8)	82 (67.8)	1 (0.8)	2 (1.7)
Pb-VFS	15 (12.4)	25 (20.7)	77 (63.6)	1 (0.8)	3 (2.5)
Zn-SiCl	107 (88.4)	14 (11.6)	–	–	–
Zn-VFS	104 (86.0)	17 (14.0)	–	–	–

Contamination indices were used to assess the amount of environmental information that could be extracted from each of the two different grain-size fractions with regards to degree of pollution. Such indices are a critical part of environmental management and allows authorities to make informed decisions on whether sites require further toxicological investigation, or whether remediation is required. The three indices differ in their computation, but all point to Pb as the element of concern in both fractions of Manoa bed sediments. For MI_{geo} SiCl 92, of 121 sample sites were classified as being moderately/strongly to very strongly polluted for Pb, and 83 of 121 sites using the VFS fraction. From a management perspective these differences are trivial. For Ba, Cu and Zn the median MI_{geo} differences between SiCl and VFS fractions were small, and would not on their own constitute any environment hazard accept if there was some form of synergistic relationship with Pb. The same conclusions drawn from an examination of the MI_{geo} data are applicable to the enrichment ratio data presented in Table 6.

To conclude, statistical and possibly geochemically significant concentration differences were observed for four of the nine elements analyzed (Cu, Ni, Pb and Ti) when values in the <63-μm (silt + clay) and the 63–125-μm (very fine sand) bed sediment fractions of Manoa Stream were compared. However, statistical associations between the two fractions were strong for all elements and from a management perspective the conclusions drawn concerning degree of contamination would be similar regardless of fraction examined. Therefore, for Manoa bed sediments the choice of grain-size fraction to be analyzed should be based on issues such as ease of sample collection, ease of preparation and quantity required for a range of analytical procedures. The quantity issue may be particularly relevant in sand bed or coarser stream seg-

ments. In such streams the silt and clay contribution to the entire grain-size distribution is typically small <<1%; this may not pose a sampling problem if inductively coupled plasma-mass spectrometry (ICP-MS) is used, where <200 mg of material will suffice for analysis. However, if major element oxide determinations are required the technique of choice is X-ray fluorescence (XRF), which commonly requires 5–10 g for a meta-borate fusion. This sample mass may not be available for the <63-μm fraction unless large kilogram-size samples are collected, making field sampling rather onerous. In selected environments the quantity problem could be obviated if fine sands were substituted. Another key issue of environmental concern is the relationship between bed sediment size fractions and those processed by benthic feeders. Contamination of aquatic species in coarse sand or gravel bed streams may only be weakly linked to the clays or silts since they would be expected to have small mass and thus small metal loads. On the other hand the more abundant fine sand fractions would have higher mass loadings and would in these situations be more closely linked to biotic contamination and thus worthy of detailed examination.

Appendix

The following literature was used to generate the information displayed in Fig. 1.

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