



Metal extraction from road-deposited sediments using nine partial decomposition procedures

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Abstract

Nine partial decomposition procedures and a total digestion treatment were applied to road-deposited sediments. The objective was to define a parsimonious, time-efficient decomposition procedure that (1) has limited impact on the alumino-silicate matrix and/or refractory-associated fractions, (2) has metal recoveries independent of CaCO_3 content, and (3) produces high anthropogenic signals for known contaminants (e.g., Cu, Pb and Zn). The 9 digestions varied from weak single reagents (0.11 M acetic acid) to strong multi-step procedures (BCR 3-step plus aqua regia). Eight metals were examined: Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn. Cold (room temperature) 0.5 M HCl shaken over a 1-h period with a solid-to-solution ratio of 1 g:20 ml, was judged superior based on the defined criteria. This simple, rapid treatment had limited impact on the residual matrix (mean and 95% confidence interval for Al recovery was $6 \pm 1\%$); recoveries of all elements examined were independent of CaCO_3 content; the treatment produced high mean extraction efficiencies for Cu ($58 \pm 9\%$), Pb ($84 \pm 5\%$), and Zn ($73 \pm 7\%$), and produced high anthropogenic signals. Thus, dilute HCl can be widely recommended as an optimal partial decomposition procedure for assessing non-residual fractions of complex solid media.

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1. Introduction

Significant effort has been expended to develop partial digestion procedures for solid media. The procedures that are available reflect different investigative goals, including establishing baseline contaminant data, assessing bioavailability, characterizing element mobility in the vadose or phreatic zones, quantifying anthropogenic signals, and detecting signature anomalies (e.g., in geochemical prospecting). Many of these needs are met through the application of reagents, either as single leaches or sequentially. The common thread through these studies is that partial decomposition procedures, rather than total sample mineralization, are simpler, safer, and provide more meaningful environmental information.

A number of studies have applied more than one single leach partial digestion procedure to aliquots of solid sample media (Ray et al., 1957; Agemian and Chau, 1976; Lahann, 1976; Norvell, 1984; Szefer et al., 1995; de Kreji et al., 1993; Adami et al., 1999; Brunori et al., 1999; Gray et al., 1999; Tam and Yao, 1999; Száková et al., 2000; Sutherland et al., 2001; Madrid et al., 2002; Imperato et al., 2003). Although, no general consensus has been reached as to the most suitable single leach for examining anthropogenic trace element concentrations of solid media, dilute HCl is one of the most commonly applied partial treatments in the environmental/geochemical literature (Sutherland et al., 2001). The wide adoption of this inorganic acid can be traced to the studies of Agemian and Chau (1976; 1977), Luoma and Bryan (1981), and Chester et al. (1985).

An alternative approach to single reagent partial digestions is to apply chemical extractants of various types sequentially to the sample, each successive treat-

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ment being more drastic in chemical action or of a different nature than is the previous one (Chao, 1984). From an environmental perspective, sequential extractions have proven valuable in quantifying operationally-defined metal fractions in solid media, e.g., acid soluble, reducible, oxidizable, and residual (Pickering, 1986; Beckett, 1989; Tack and Verloo, 1995). However, these procedures are not without problems, such as read-sorption, and non-specificity (Tack and Verloo, 1995); and they are tedious and time consuming (Tack et al., 1996). Additionally, minor differences between closely related sequential extraction procedures can cause significant differences in the magnitude of the operationally defined metal fractions (Sutherland and Tack, 2003).

A limited number of studies have compared metal release by single extractants with those from sequentially extracted fractions. Both, Van Valin and Morse (1982), and Stone and Marsalek (1996); compared metal recoveries from 0.5 M HCl treatments to those from the sum of the first four steps of the Tessier et al. (1979) procedure. Recently, Sutherland (2002) found that a 0.5 M HCl treatment when compared to the first 3 steps of the optimized BCR approach (BCR is the European Community Bureau of Reference, now known as the Standards, Measurements, and Testing Program) removed statistically similar amounts of Cu, Pb and Zn.

The above studies suggest further exploration is needed of the application of various reagents to metal removal from environmental media. The objective of this study is to identify the most suitable digestion procedure, based on the following criteria: simplicity and time efficiency; limited digestion of the alumino-silicate matrix; metal recovery independent of CaCO_3 content; and high recovery of anthropogenic trace elements. This work significantly extends the prior studies of Sutherland et al. (2001) and Sutherland (2002).

2. Study site

Palolo Valley watershed (11.4 km²) is located in SE Oahu. Land use consists of 55% undeveloped conservation land, 41% urbanized area, and 4% agricultural land (Ikeno, 1996). In 1990, Palolo had 4097 households and a resident population of 13034 (State of Hawaii, 1998). Of 2640 housing units in 1980, 80.1% were single family; 10.6%, apartment buildings; 8.6%, duplexes; and 0.7%, townhouses (City and County of Honolulu, 1980). Streets in Palolo Valley are scheduled for street sweeping on a weekly basis, subject to availability of equipment and personnel (G. Takayesu, City and County of Honolulu, Personal Communication, 1999). However, there are several narrow streets within the valley with numerous parked and abandoned vehicles, preventing implementation of a comprehensive street sweeping program. Storm event runoff from roads is

directly input into stream channels via storm sewers. A storm runoff study has shown that streams in this valley are affected more adversely by urban runoff than neighboring systems (Ikeno, 1996).

Palolo 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). Post-erosional volcanism on the shield from the Kaaui Crater eruption (Honolulu Volcanic Series) represents a small fraction of the Koolau Shield Volcano (Macdonald et al., 1983). These more recent volcanics are characterized by a nephelinitic suite of rocks (Clague and Frey, 1982).

3. Methodology

3.1. Sampling and sample preparation

Road sediment samples from 20 curbside sites were collected over a curb length of about 1 m using a Nalgene® scoop and placed in plastic bags for transport to the laboratory. Sites were selected to provide representative coverage of all traffic levels anticipated in the watershed. Sample masses ranged from 300 to 600 g. Subsamples were oven-dried at 105 °C to a constant mass (~24 h) and passed through an acid-washed 2000 µm nylon sieve. All bulk (<2-mm) road sediment samples were analyzed for texture, organic C, pH, and cation exchange capacity using the methods described by Sutherland et al. (2000). Calcium carbonate was analyzed using the procedure defined by Singh et al. (1996).

Road sediment samples used for elemental analysis and grain size analysis were oven-dried at ≤40 °C for 7 days. Samples were passed through an acid-washed 2000 µm nylon sieve to isolate a bulk sample. All material was then 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 pass a 63 µm nylon mesh sieve. Three individual samples were ground simultaneously. Vials were thoroughly cleaned after sample grinding following the procedures outlined by Obenauf et al. (1999). Specifically, 4 g of 99.99% pure SiO_2 (<50 mesh) (CER-AC™, 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.

3.2. Suite of applied digestions

The 9 partial digestions applied to the road sediments are described in Table 1. They represent a range of approaches commonly applied in the environmental literature. The treatments are divided into 3 strength

Table 1
Summary of the 9 partial digestion procedures applied to the aliquots of 20 road-deposited sediments

Partial digestion	Description	Reference
<i>Weak</i>		
Acetic acid	1 g:40 ml of 0.11 M acetic acid, shake for 16 h at 22±5 °C, followed by flame atomic absorption spectrometry (AAS).	Rauret et al. (1999)
EDTA	2 g:20 ml of 0.05 M EDTA (pH 7), shake for 1 h at room temperature, followed by flame AAS.	Singh et al. (1996)
<i>Intermediate</i>		
Cold HCl	0.5 g:10 ml of 0.5 M HCl, shake for 1 h at room temperature, followed by ICP-AES.	Sutherland (2002)
BCR 2-step	To the residue from the acetic acid procedure (above) add 40 ml 0.5 M NH ₂ OH·HCl from a 1 l solution containing 25 ml 2 M HNO ₃ (pH ≈1.5), shake for 16 h at 22±5 °C, followed by flame AAS.	Rauret et al. (1999)
BCR Labile	To the residue from BCR 2-step add 20 ml H ₂ O ₂ (pH 2–3) over 2 h at room temperature, heat to 85±2 °C for 1 h; add 50 ml 1 M NH ₄ OAc (pH 2) and shake for 16 h at 22±5 °C, follow by flame AAS.	Rauret et al. (1999)
Hot HCl	0.5 g:10 ml of 0.5 M HCl, heat in a water bath (90–95 °C) for 1 h, followed by ICP-AES.	Agemian & Chau (1976)
<i>Strong</i>		
EPA 3050	1 g:10 ml of 1:1 HNO ₃ , heat for 0.25 h at 95±5 °C on a hot plate, add 5 ml concentrated HNO ₃ and heat for a further 0.5 h. Repeatedly add 30% H ₂ O ₂ (≤10 ml) and heat to 95 °C, follow by ICP-AES.	USEPA (1995)
Nitric/HCl	0.5 g:10 ml of 1:1 concentrated HNO ₃ and HCl, water bath heated for 1 h at 90–95 °C, follow by ICP-AES.	This study
BCR 4-step	To the residue from BCR labile (above) add 3 ml H ₂ O, 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, follow by flame AAS.	Ure (1990)

classes: weak (2), intermediate (4), and strong (3). For all digestions, 8 elements were studied: Al, Co, Cu, Fe, Mn, Ni, Pb and Zn. A 0.5 M HCl leach was selected over weaker concentrations of this acid, because prior work has shown that 0.1 M HCl can be effectively neutralized by carbonates, thereby preventing metal removal from sources other than carbonates (Ellis et al., 1967; McNeal et al., 1985). Additionally, Sholkovitz (1989) showed that readsorption of rare earth elements occurred at HCl concentrations <0.2 M. To determine recoveries of the partial digestion procedures, a total digestion procedure was applied. To 0.50 g aliquots of road sediment, a solution of 18:10:3:6 H₂O–HF–HClO₄–HNO₃ was heated to fuming on a hot plate and taken to dryness. The residue was dissolved in a mixture of 2:2:2 HCl–HNO₃–H₂O by heating in a boiling water bath for 30 min. The solution was analyzed using inductively coupled plasma-atomic emission spectrography (ICP-AES).

3.3. Quality control

Precision was estimated with the coefficient of variation for each of the partial digestion procedures using repeated measurements of certified reference materials. Precision data were acceptable (Table 2) with all means ≤8%. Precision and accuracy data for the total digestion of GSD-7 (fluvial sediment) certified by the China

National Analysis Center for Iron and Steel are also shown in Table 2. Precision for the 8 metals was ≤4.6%, and accuracy ranged from –3.9% for Al to +6.1% for Ni and Pb.

4. Results and discussion

The road sediments represent complex environmental media, and therefore, are a good test material for assessing various digestion procedures. Road sediments potentially contain material eroded from surrounding soils, weathered road and sidewalk materials, organics, material contributed directly from vehicle and tire wear, and deposition of exhaust emissions. The texture of the road sediments (Table 3) was dominated by sand (64%), with lesser amounts of silt (30%) and clay (6%). Median pH was 7.6, with a range from 6.8 to 9.5. Organic C and CaCO₃ contents were high with mean values of 10.3% and 9.3%, respectively. Cation exchange capacities were high with a mean of 31 cmol_c kg⁻¹, and a wide range from 7 to 77 cmol_c kg⁻¹.

4.1. Criteria I: Digestion of the alumino-silicate matrix

Recoveries of Al (i.e., Al partial decomposition ÷ Al total digestion) for the 9 digestion procedures is used as

Table 2
Mean precision (coefficient of variation) of 9 partial digestion procedures, and precision and accuracy for a total digestion

Digestion	CRM	Description	Al (%)	Co (%)	Cu (%)	Fe (%)	Mn (%)	Ni (%)	Pb (%)	Zn (%)
Acetic acid	CW 7 (5) ^a	Road dust	3.1	2.7	0.86	1.8	1.5	2.3	1.9	0.93
EDTA	CRM 601 (5)	Lake sediment	8.2	7.5	0.61	5.1	1.2	4.5	3.1	0.66
BCR 2-step	CW 7 (5)	Road dust	2.1	1.4	0.84	0.97	1.8	1.8	5.2	0.56
Cold HCl	GSD-7 (7)	Stream sediment	3.3	6.2	7.3	4.6	4.2	6.2	3.4	4.3
BCR Labile	CW 7 (5)	Road dust	1.5	2.1	0.63	0.55	1.6	1.2	4.2	0.55
Hot HCl	GSD-7 (5)	Stream sediment	0.76	3.2	2.2	0.96	0.77	1.9	1.1	1.2
EPA 3050	SRM 2711 (6)	Soil	1.34	4.1	0.83	1.2	0.67	0.91	1.0	0.62
HNO ₃ /HCl	SRM 2710 (5)	Soil	1.6	7.4	2.4	1.8	1.6	0.00	1.3	1.3
BCR 4-step	CW 7 (5)	Road dust	2.2	1.5	0.46	3.0	0.80	2.4	4.2	0.53
Total	GSD-7 (20)	Stream sediment	2.9	4.3	4.1	3.8	2.8	2.6	3.0	4.6
			[−3.9] ^b	[−2.2]	[−1.7]	[+1.1]	[+3.8]	[+6.1]	[+6.1]	[+1.3]

^a Values in parentheses represent the number of sample replications.

^b Values in square brackets represent accuracy values computed relative to published certified total digestion concentrations.

a proxy for breakdown of the alumino-silicate matrix. Anthropogenic contributions of Al to the road environment are considered negligible. Aluminum liberated by partial digestions is therefore assumed to be primarily from the lithogenic fraction and not bioavailable. Reagents with limited breakdown of the silicate lattice will have low recoveries of Al. This is considered a favorable condition, as the elements simultaneously extracted will come from pools other than from the residual fraction.

The mean Al concentrations and 95% confidence intervals for the 9 partial digestions and one total digestion are shown in Fig. 1a. Aluminum data, plotted on a log₁₀ scale, range over several orders of magnitude from 28±6 mg/kg for EDTA to 61,000±5000 mg/kg for a total digestion. Recoveries indicate the “weak” reagents, EDTA and acetic acid, removed less than 0.2% of the total Al (Fig. 1b). Aluminum recovery by EDTA was significantly lower ($\alpha=0.05$) than that for acetic acid (0.05±0.02% vs. 0.19±0.08%). For the

“intermediate” strength reagent group, the cold HCl treatment and the BCR 2-step procedure (acetic acid plus acidic hydroxylamine hydrochloride) removed statistically similar ($\alpha=0.05$) amounts of Al (~6%; Fig. 2a), but significantly lower amounts than the sum of the first three steps of the BCR procedure (BCR labile), i.e., ~8%. These 3 partial digestions all removed significantly less Al than the hot 0.5 M HCl leach (~17%; Fig. 2a).

The group of “strong” digestions removed 2.2- to 3.1-fold more Al from the road sediments than the strongest (hot HCl) of the intermediate digestions (Figs. 1b and 2b). The ordering of the strong digestions for Al recovery was: sum of BCR 4-step > EPA 3050 > concentrated HNO₃/HCl. None of these digestions can be considered “total” because on average less than 53% of the Al was recovered from the alumino-silicate matrix.

In summary, EDTA and acetic acid treatments meet the first criteria of limited digestion of the silicate matrix, followed by the cold HCl and BCR 2-step procedures. In addition to limited breakdown of the lattice the most suitable procedure must not be negatively influenced by CaCO₃ content, and must remove significant amounts of anthropogenically derived metals. These criteria will be explored below.

Table 3
Summary of baseline physico-chemical properties of 20 road-deposited sediments (<2 mm) from Palolo watershed, Oahu, Hawaii

Properties ^a	Units	Mean±95% CI	Minimum	Maximum
Sand	g/kg	638±43	413	771
Silt	g/kg	299±68	212	468
Clay	g/kg	63±37	17	166
pH		7.6±0.1 ^b	6.8	9.5
OC	g/kg	103±25	58	313
CaCO ₃	g/kg	93±17	49	188
CEC	cmol _c kg ⁻¹	31±6	7.1	77.2

^a OC is organic carbon, CaCO₃ is calcium carbonate, CEC is cation exchange capacity.

^b Median plus/minus values represent 95% confidence intervals about the median.

4.2. Criteria II: Influence of CaCO₃ content on metal recovery

The generally high, but variable, CaCO₃ contents (Table 3) in the road sediments reflect contributions from weathered road surfaces and sidewalks. High CaCO₃ may adversely influence the removal of metals, particularly contaminants, in other non-residual fractions. As previously noted, dilute acids may be effectively buffered by CaCO₃, thereby significantly reducing removal of metals from the reducible or oxidizable fractions. Metal removal would then be sample-specific

rather than reagent-specific. Thus, metal recovery of known contaminants should not be significantly correlated with CaCO₃ content. Bussen et al. (2000) observed that median concentrations ($\pm 95\%$ confidence intervals about the median) for Cu (286 ± 70 mg/kg), Pb (290 ± 116 mg/kg) and Zn (547 ± 116 mg/kg) in Palolo road sediments were well above background (geogenic)

levels reported for the watershed by Sutherland (2000), Cu ≈ 100 mg/kg, Pb ≤ 10 mg/kg, and Zn ~ 180 mg/kg.

The nonparametric Spearman correlation coefficient (r_s) was used to characterize monotonic association between individual recoveries of Cu, Pb, and Zn for the 4 digestions that had limited influence on the aluminosilicate matrix (i.e., acetic acid, EDTA, cold HCl, and

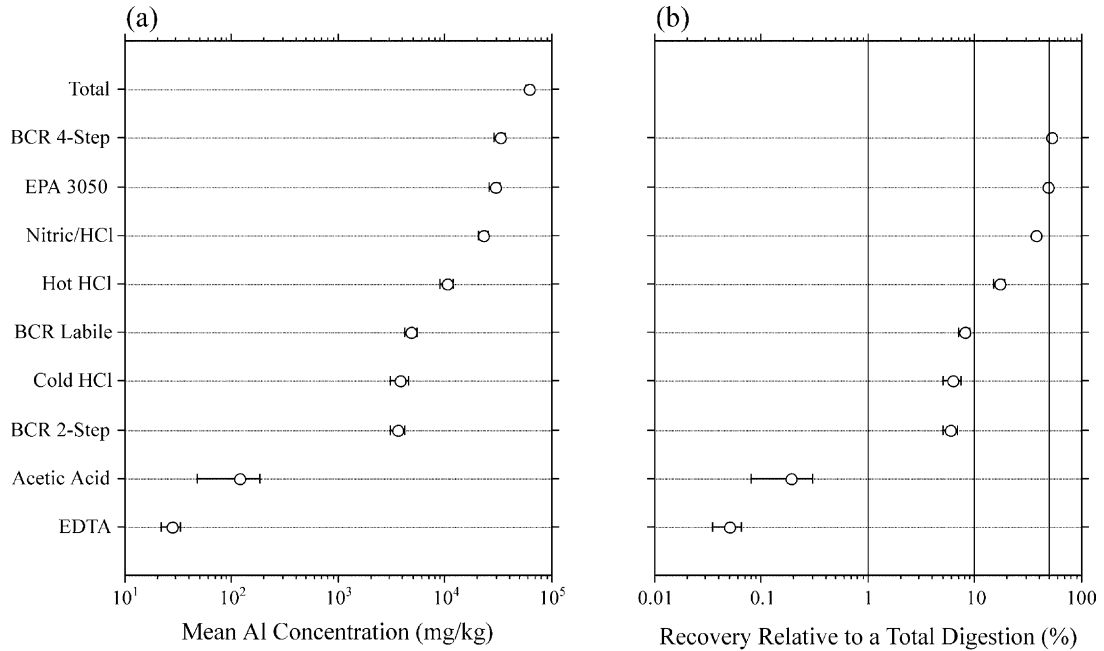


Fig. 1. (a) Ranked dotplot of mean Al concentrations liberated by 9 partial digestions and a total digestion of road-deposited sediments from Palolo watershed, Oahu, Hawaii. Error bars represent 95% confidence intervals. (b) Mean recoveries of the 9 partial digestion procedures. Vertical lines at 1%, 10%, and 50% are to facilitate visualization. Note the log₁₀ scale for both X-axes.

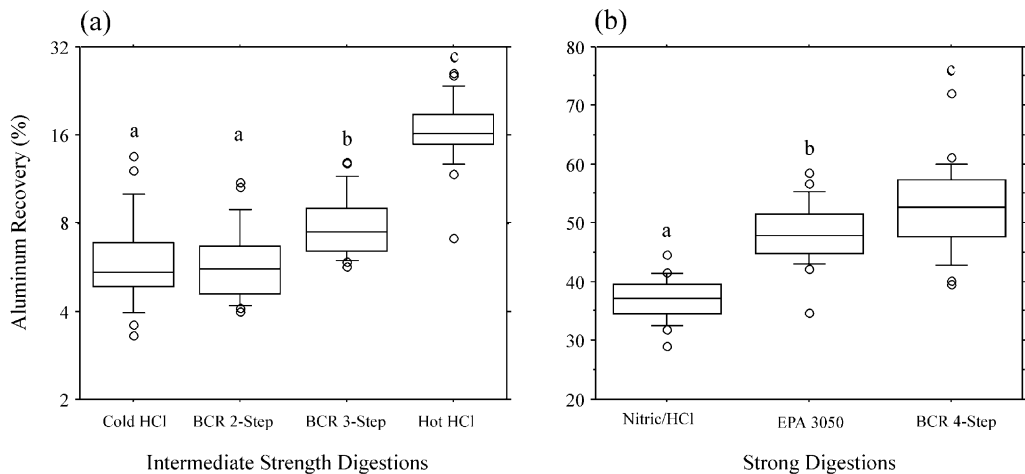


Fig. 2. (a) Boxplots of the 4 “intermediate” strength digestions for Al removal from road sediments. Note log₂ Y-axis. Boxplots with the same letter are not significantly different at an α -level of 0.05. (b) Boxplots of the 3 “strong” digestions for Al removal from road sediments. Boxplots with the same letter are not significantly different at an α -level of 0.05. Note that statistical relationships in plots (a) and (b) are not intercomparable.

Table 4

Spearman correlations (r_s) between 8 metal recoveries and calcium carbonate content for 4 partial digestions (2 ‘weak’ and 2 ‘intermediate’ strength digestions) for 20 road-deposited sediments

Element	EDTA	Acetic acid	Cold HCl	BCR 2-Step
Al	−0.61 (0.008) ^a	−0.56 (0.01)	0.07 (0.75)	0.17 (0.46)
Co	−0.25 (0.28)	0.46 (0.04)	−0.10 (0.66)	0.26 (0.27)
Cu	−0.50 (0.03)	−0.45 (0.05)	−0.13 (0.58)	−0.17 (0.45)
Fe	−0.61 (0.008)	0.09 (0.70)	0.24 (0.30)	0.09 (0.69)
Mn	−0.47 (0.04)	−0.03 (0.89)	−0.17 (0.47)	−0.08 (0.74)
Ni	−0.19 (0.40)	0.01 (0.97)	0.23 (0.33)	0.11 (0.64)
Pb	−0.73 (0.001)	0.06 (0.80)	−0.21 (0.35)	0.18 (0.44)
Zn	−0.38 (0.10)	−0.32 (0.16)	0.08 (0.71)	0.21 (0.36)

^a Values in parentheses represent *P*-values for the Spearman test, and those considered statistically significant (α -value ≤ 0.05) are underlined.

BCR 2-step). The r_s -values and corresponding *P*-values are summarized in Table 4. Only cold HCl and the BCR 2-step procedures exhibited no statistically significant correlation between metal recovery and CaCO₃ content. For the EDTA leach, 5 of the 8 elements showed a statistically significant ($\alpha=0.05$) decrease in recovery with increasing CaCO₃ content (i.e., Al, Cu, Fe, Mn, and Pb). Copper and Pb are particularly critical because they are known contaminants in road sediments, thus the concentrations of these metals liberated by EDTA are confounded by differing CaCO₃ contents between samples. For the final procedure, acetic acid, recoveries for Al, Co and Cu decreased significantly with increased CaCO₃ content. Although the weak extractions (EDTA and acetic acid) had little influence on the alumino-silicate matrix (Criteria I) their recoveries varied with CaCO₃ content for some metals (Criteria II). This is particularly important for EDTA, because recovery of Fe and Mn (both potential contributors to the oxidizable fraction) decreased, and 2 of the 3 major contaminants in the watershed (Cu and Pb) also decreased with increased CaCO₃. Applicability of EDTA to complex media with varying CaCO₃ contents is therefore questionable.

Cold HCl and the BCR 2-step procedures are shown to be superior to the two weak reagents because their metal removal is independent of CaCO₃ content (Table 4). Additionally, the remaining digestions also showed no statistically significant relationship between metal recovery and CaCO₃ content (data not shown). However, these digestions caused significant breakdown of the lattice structure (Figs. 1 and 2).

4.3. Criteria III: metal contaminant recoveries

In addition to minimal digestion of the alumino-silicate matrix, and independence of metal recovery with CaCO₃ content, a superior partial digestion procedure will exhibit high recoveries of known anthropogenically contributed metals. EDTA and acetic acid treatments

removed significantly less Cu, Pb, and Zn from the road sediments than the intermediate or strong reagents (Fig. 3 a–c). Acetic acid recovered only $7\pm 3\%$ of Cu, $2\pm 1\%$ of Pb, and $29\pm 6\%$ of Zn. These values are far too low given the baseline values of these metals in the watershed. In general, EDTA recoveries were also low, although significantly higher ($\alpha=0.05$) than acetic acid for Cu ($27\pm 5\%$) and Pb ($33\pm 7\%$), and statistically similar for Zn ($26\pm 6\%$).

Within the intermediate strength reagent group, a comparison of the cold HCl leach with the BCR 2-step leach indicated significantly greater removal of Cu (58% vs. 44%, *P*-value=0.0001), and Pb (84% vs. 77%, *P*-value=0.05) by the HCl procedure, but statistically similar amounts of Zn (73% vs. 73%, *P*-value=0.85). While all remaining digestions had greater recoveries than the cold HCl procedure, all caused substantial breakdown of the lattice. To balance contaminant recovery with lattice breakdown the anthropogenic signal index (ASI) was developed:

$$ASI_n = \frac{\left[\frac{\text{Partial Digestion}_n}{\text{Total Digestion}_n} \right]}{\left[\frac{\text{Partial Digestion}_{Al}}{\text{Total Digestion}_{Al}} \right]}$$

Aluminum is used to normalize the ASI and ‘n’ represents one of the 3 environmental contaminants (Cu, Pb or Zn). The same partial digestion procedure is used in the numerator and denominator. Low ASI values (i.e., ≤ 1) indicate the partial digestion procedure is insensitive with significant breakdown of the lattice and/or limited removal of a given contaminant. Partial digestions with ASI-values > 1 are considered superior. Weaker extractants such as acetic acid and EDTA are not expected to extract non-lattice elements to a large extent and were therefore not evaluated accordingly. Indeed, recovery of certain elements were a function of CaCO₃ content, and overall recoveries were low for Cu,

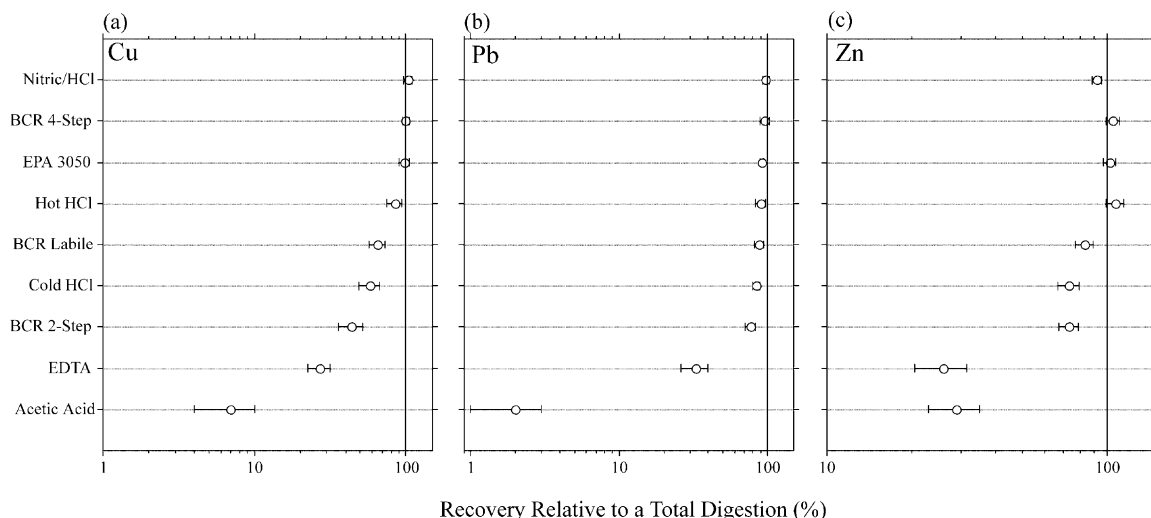


Fig. 3. Mean recovery of 9 partial digestion procedures relative to a total digestion for (a) Cu, (b) Pb, and (c) Zn in road sediments. Note \log_{10} X-axis; error bars represent 95% confidence intervals.

Table 5

Mean and 95% confidence intervals of the anthropogenic signal index (ASI is dimensionless) for 7 partial decomposition procedures for 20 road-deposited sediments

Decomposition procedure	ASI _{Cu}	ASI _{Pb}	ASI _{Zn}
Cold HCl	10.2±2.2	15.1±2.4	13.1±2.0
BCR 2-Step	7.8±1.5	14.1±2.2	13.1±1.6
BCR Labile	8.4±1.2	11.6±1.6	10.8±1.1
Hot HCl	5.2±0.6	5.6±0.8	6.7±0.9
HNO ₃ /HCl	2.6±0.2	2.8±0.2	3.0±0.2
EPA 3050	2.1±0.2	1.9±0.1	2.1±0.1
BCR 4-Step	1.9±0.2	1.8±0.2	2.0±0.2

Pb and Zn.

Mean values of ASI and 95% confidence intervals for the remaining 7 partial digestions are shown in Table 5. The ASI-values were highest for the cold HCl leach, and the intermediate strength digestions in general. The cold HCl ASI_{Cu} was significantly greater than either the BCR 2-step or BCR labile (sum of 3 steps). However, no statistically significant difference was observed for Pb (P -value = 0.14) or Zn (P -value = 0.77) between the cold HCl and BCR 2-step procedures.

5. Conclusions

Different strength partial digestions were applied to a complex solid media (road-deposited sediment) to identify the most appropriate procedure to liberate geo-environmentally meaningful amounts of metals. The 1-h

cold HCl digestion procedure was the most appropriate for use with road sediments. Recommendation of the cold HCl procedure was based on the assessment of 4 major criteria: (I) minimal removal of Al from the aluminosilicate matrix; (II) metal recoveries were not significantly influenced by CaCO₃ content; (III) high metal recoveries were obtained for known contaminants; and (IV) the procedure was simple, time-efficient, and cost-effective.

The cold HCl approach produced results most similar to a more complicated two-step optimized, sequential procedure (BCR 2-step; ≈ 32-h). Lead and Zn recoveries were statistically similar between the two procedures, but Cu recovery was significantly greater for the cold HCl procedure. It can be inferred that HCl liberates Pb and Zn from the acid soluble and reducible fractions that are targeted by the BCR 2-step. However, cold HCl removed some portion of Cu that was associated with the oxidizable fraction, but not liberated by the BCR 2-step treatment. The cold HCl procedure removed significantly less Cu than the BCR 3-step procedure (sum of acid soluble + reducible + oxidizable), 58% vs 65%, thus only the easily removed oxidizable fraction is liberated by the cold HCl procedure. This is environmentally meaningful because the metals associated with the more refractory organic compounds would not be readily available.

The two weakest decomposition procedures considered (0.05 M EDTA and 0.11 M acetic acid) removed negligible amounts of Al from the lattice. However, contaminant recoveries were low, and specific metal recoveries were dependent on CaCO₃ content. This is considered a major drawback to the general application

of these approaches for estimating the labile metal contents of solid media with all but minimal CaCO₃ content.

Cold HCl has the potential to be more widely integrated into contaminant monitoring studies. Development of standard reference materials with certified dilute HCl metal concentrations will facilitate the incorporation of this procedure in future environmental investigations. Availability of reference materials for quality assurance coupled with a standardized methodology would produce a simple procedure that could be widely applied, and produce environmentally meaningful results that are globally comparable.

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References

- Adami, G., Barbieri, P., Reisenhofer, E., 1999. A comparison on five sediment decomposition procedures for determining anthropogenic trace metal pollution. *Internat. J. Environ. Anal. Chem.* 75, 251–260.
- Agemian, H., Chau, A.S.Y., 1976. Evaluation of extraction techniques for the determination of metals in aquatic sediments. *Analyst* 101, 761–767.
- Agemian, H., Chau, A.S.Y., 1977. A study of different analytical extraction methods for nondetriral heavy metals in aquatic sediments. *Arch. Environ. Contam. Toxicol.* 6, 69–82.
- Beckett, P.H.T., 1989. The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils. *Adv. Soil Sci.* 9, 143–176.
- Brunori, C., Balzamo, S., Morabiot, R., 1999. Comparison between different leaching/extraction tests for the evaluation of metal release from fly ash. *Internat. J. Environ. Anal. Chem.* 75, 19–31.
- Bussen, J.O., Sutherland, R.A., Tack, F.M.G., 2000. Heavy metal pollution in road deposited sediments, Palolo Valley, Honolulu, HI. In: Nriagu, J. (Ed.), Eleventh Annual Int. Conf. on Heavy Metals in the Environment. August 6–10, 2000. U. Michigan, School of Public Health, Ann Arbor, Michigan (CD-ROM).
- Chao, T.T., 1984. Use of partial dissolution techniques in geochemical exploration. *J. Geochem. Explor.* 20, 101–135.
- Chester, R., Kudoja, W.M., Thomas, A., Towner, J., 1985. Pollution reconnaissance in stream sediments using non-residual trace metals. *Environ. Poll. (B)* 10, 213–238.
- City and County of Honolulu, 1980. Neighborhood Data Book Palolo. City and County of Honolulu, Hawaii.
- Clague, D.A., Frey, F.A., 1982. Petrology and trace element geochemistry of the Honolulu Volcanics, Oahu: implications for the mantle below Hawaii. *J. Petrol.* 23, 447–504.
- de Kreij, C., Martignon, G., van Elderen, C.W., 1993. Comparison of water, DTPA, and nitric acid as extractants to assess the availability of copper in peat substrates. *Commun. Soil Sci. Plant Anal* 24, 227–236.
- Ellis, A.J., Tooms, J.S., Webb, J.S., Bicknell, J.V., 1967. Application of solution experiments in geochemical prospecting. *Trans. Inst. Min. Metall., Sect B* 76, 25–39.
- Gray, D.J., Wildman, J.E., Longman, G.D., 1999. Selective and partial extraction analyses of transported overburden for gold exploration in the Yilgarn Craton, Western Australia. *J. Geochem. Explor.* 67, 51–66.
- Ikeno, D.E., 1996. Urban Runoff in Manoa and Palolo Streams. M.Sc. Thesis in Civil Engineering, U. Hawaii, Hawaii, USA.
- Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., Violante, P., 2003. Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environ. Poll* 124, 247–256.
- Lahann, R.W., 1976. The effect of trace metal extraction procedures on clay minerals. *J. Environ. Sci. Health A11*, 639–662.
- Luoma, S., Bryan, G.W., 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *Sci. Total Environ.* 17, 165–196.
- Macdonald, G., Abbott, A.T., Peterson, F.L., 1983. Volcanoes in the Sea-The Geology of Hawaii. 2nd Edition. U. Hawaii Press, Honolulu, Hawaii.
- Madrid, L., Díaz-Barrientos, E., Madrid, F., 2002. Distribution of heavy metal content of urban soils in parks of Seville. *Chemosphere* 49, 1301–1308.
- McNeal, J.M., Severson, R.C., Gough, L.P., 1985. The occurrence of extractable elements in soils from the northern Great Plains. *Soil Sci. Soc. Am. J.* 49, 873–881.
- Norvell, W.A., 1984. Comparison of chelating agents as extractants for metals in diverse soil materials. *Soil Sci. Soc. Am. J.* 48, 1285–1292.
- Obenauf, R.H., Bostwick, R., Fithian, W., DeStefano, M., McCormack, J.D., Selem, D. (Eds.), 1999. SPEX CertiPrep Handbook of Sample Preparation and Handling. SPEX CertiPrep, Inc, Metuchen, NJ.
- Pickering, W.F., 1986. Metal ion speciation-soils and sediments (a review). *Ore Geol. Rev.* 1, 83–146.
- Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three-step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* 1, 57–61.
- Ray, S., Gault, H.R., Dodd, C.G., 1957. The separation of clay minerals from carbonate rocks. *Am. Mineral.* 42, 681–686.
- Sholkovitz, E.R., 1989. Artifacts associated with the chemical leaching of sediments for rare-earth elements. *Chem. Geol.* 77, 47–51.
- Singh, S.P., Tack, F.M.G., Verloo, M.G., 1996. Solid-phase distribution of heavy metals as affected by single reagent extraction in dredged sediment derived surface soils. *Chem. Spec. Bioavail* 8, 37–43.

- State of Hawaii, 1998. State of Hawaii Data Book 1996-A Statistical Abstract. Department of Business, Economic Development and Tourism, State of Hawaii, USA.
- Stone, M., Marsalek, J., 1996. Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. *Water Air Soil Pollut* 87, 149–169.
- Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol.* 39, 611–627.
- Sutherland, R.A., 2002. Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. *Appl. Geochem.* 17, 353–365.
- Sutherland, R.A., Tack, F.M.G., 2003. Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Adv. Environ. Res.* 8, 37–50.
- Sutherland, R.A., Tack, F.M.G., Tolosa, C.A., Verloo, M.G., 2000. Operationally defined metal fractions in road deposited sediment, Honolulu, Hawaii. *J. Environ. Qual.* 29, 1431–1439.
- Sutherland, R.A., Tack, F.M.G., Tolosa, C.A., Verloo, M.G., 2001. Metal extraction from road sediment using different strength reagents. *Environ. Monit. Assess* 71, 221–242.
- Szaková, J., Tlustos, P., Balík, J., Pavlíková, D., Balíková, M., 2000. Efficiency of extractants to release As, Cd and Zn from main soil compartments. *Analisis* 28, 808–812.
- Szefer, P., Glasby, G.P., Pempkowiak, J., Kaliszan, R., 1995. Extraction studies of heavy-metal pollutants in surficial sediments from the southern Baltic Sea off Poland. *Chem. Geol.* 120, 111–126.
- Tack, F.M.G., Verloo, M.G., 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *Internat. J. Environ. Anal. Chem.* 59, 225–238.
- Tack, F.M.G., Vossius, H.A.H., Verloo, M.G., 1996. A comparison between sediment metal fractions, obtained from sequential extraction and estimated from single extractions. *Internat. J. Environ. Anal. Chem.* 63, 61–66.
- Tam, N.F.Y., Yao, M.W.Y., 1999. Three digestion methods to determine concentrations of Cu, Zn, Cd, Ni, Pb, Cr, Mn, and Fe in mangrove sediments from Sai Keng, Chek Keng, and Sha Tau Kok, Hong Kong. *Bull. Environ. Contam. Toxicol.* 62, 708–718.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 848–851.
- Ure, A.M., 1990. Methods of analysis for heavy metals in soils. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*. Blackie and Son, Glasgow, pp. 40–73.
- US Environmental Protection Agency (USEPA), 1995. Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods, Vol. 1A. Office of Solid Waste and Emergency Response, USEPA, Washington, DC, SW-846.
- Van Valin, R., Morse, J.W., 1982. An investigation of methods commonly used for the selective removal and characterization of trace metals in sediments. *Mar. Chem.* 11, 535–564.