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TECHNICAL ARTICLE

Trace Element Scavenging in Dry Wash Surficial Sediments in an Arid Region of Southern Nevada, USA

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Abstract Sediment samples were collected from a dry wash in Nelson, Nevada where the Techatticup Mine and Mill operated between 1850 and 1960. Samples were used to evaluate movement and behavior of certain metals and metalloids including aluminum, arsenic, barium, cadmium, copper, iron, manganese, lead, and vanadium. The data show that some metals and metalloids are more concentrated on larger particles whereas others show the opposite tendency. For example, As was greatest on silt fractions and least on coarse fractions, while Se was detected only on silts. Chromium, Cu, Fe, Mn, Pb, and Zn concentrations all increased with decreasing particle size (silt $>$ sand $>$ coarse), whereas Al, Ba, and V showed the opposite trend (silt $<$ sands $<$ coarse).

Keywords Mining · Metals and metalloids · Sediment transport · Particle size distribution · Nelson · Nevada

Introduction

The transport and subsequent mobilization of metals and metalloids, hereafter referred to as trace elements (TEs), are crucial when assessing risks posed by mine sites in any environment, but particularly in arid to hyperarid regions. Abandoned mined sites are known sources of TE contaminants (Giuliano et al. 2007; Larios et al. 2012; Sims 2010). Studies of such sites have predominantly been in humid regions where transport beyond source areas is well documented (Chopin and Alloway 2007; Kim et al. 2011; Modis and Vatalis 2014). Geochemical studies of humid mining regions show transport of TEs in the sediment/pore-water interface as a result of the interaction between TEs, AMD, Al-, Fe- and Mn-oxides, and oxyhydroxides (e.g. Johannesson and Tang 2009).

However, these studies did not assess arid regions. Transport of sediments containing TEs in arid environments primarily occurs during infrequent storm events when sediments are mobilized during flash flooding (Kim et al. 2011; Larios et al. 2012; Slowey et al. 2007). Arid climates that receive little precipitation can still produce major storm events that generate large surface flows for a short period of time and can transport sediment over great distances (Navarro-Hervás et al. 2012; Sims et al. 2013). While wind and overland flow can both transport sediment, desert environments tend to have a reduced wind transport due to a thin crust of salts that form on anthropogenically derived sediments (Ordõnez et al. 1915; Yu and Steinberger 2012).

A previous study of the Nelson, Nevada site showed that sediments had moved at least 6000 m from the source materials (Sims et al. 2013). Studies have shown that TE transfer (trace element scavenging) from particle-to-particle at the sediment/pore-water interface in sediment–water

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interactions occur during storm events in arid climates (Khalil et al. 2013; Navarro-Hervás et al. 2012). Trace element scavenging occurs when TEs are adsorbed on particle surfaces as ions or ionic complexes due to the presence of oxide or oxyhydroxide coatings (Nowinski et al. 2010, 2013). This sediment/pore-water interaction can be significant where substantial advective or convective activities occur (Khalil et al. 2013). However, it has been previously suggested that the threat of impact to the wider environment is insignificant in arid regions due to little if any AMD (Ross 2008).

Storm events that cause flash flooding in desert washes (also known as arroyos, these are the narrow, constricted dry beds of intermittent streams) are the dominant mechanism of sediment transport in arid environments; however, sediment transport is dissimilar from the scavenging mechanism (Reheis 2006). Sanchez-Martinez et al. (2013) and Slowey et al. (2007) showed that TEs are commonly transported in surficial sediments during storm events and thus have the potential to affect wider areas. However, such studies did not evaluate the interaction of tailings with local geology in arid climates over time (Camm et al. 2003a, 2004b; Larios et al. 2012).

Nelson, Nevada was chosen for this study due to large-scale mining operations at the Techatticup Mine and Mill, which operated between 1850 and 1960 (Greene 1975). The Techatticup Wash was chosen for this research as it has only one mine and mill site located at the head of the system. A detailed overview of the mining operation, including its ore and tailing processes, can be found in Sims (2011). This study assessed distance, particle size, and depth to determine transport mechanisms in an arid environment. The evaluation of the interaction of tailings mixed in with local, naturally occurring sediments at the sediment/pore-water interface is vital to contamination assessment, even in an arid region. The goal of this research was to provide a broader view of such transport, assessing vertical movement, particle size distribution, and TE interactions (trace element scavenging) with tailings and locally derived sediments transported by water in an arid region. Evaluating the interaction of tailings with the local geology, its transport mechanisms, and the interaction of tailings at the pore-water interface will provide a better understanding of overall impact in arid environments over time.

Environmental Setting

Geology

Clark County is located within the larger central Basin and Range tectonic setting of southern Nevada, which is characterized by narrow faulted mountains adjacent to flat arid valleys (Longwell et al. 1965). This is a structurally complex area that resulted from tectonic extension beginning around 18 million years ago during the Miocene (Morikawa 1993). The Nelson area is part of a widespread stratovolcano complex characterized by thick sequences of Tertiary volcanic rocks sitting on top of Precambrian basement rocks (Anderson 1971; Hansen 1962; Longwell et al. 1965). The youngest of the volcanic layers includes rhyolite, basalt, and andesite from the Mount Davis Formation that erupted between 12 and 15 million years ago (Anderson 1971; Anderson et al. 1972; Darvall 1991; Morikawa 1993). Basalts and rhyolites, which erupted during the later stages of tectonic extension overlie the volcanic sequence within the area. Surface sediments consist of volcanically-derived sands and gravels deposited through fluvial action from local geology (Anderson 1971; Longwell et al. 1965).

Hydrology

Southern Nevada lies within the southern edge of the Great Basin, an area where topography controls the regional hydrologic setting and results in a closed system with no significant external drainage. Streams in the higher elevations either drain into surface sinks in the basins or recharge shallow groundwater. The area averages 7 cm per year of precipitation (Longwell et al. 1965); however, current precipitation is much less than that as the area has been in severe drought conditions since 2000 (NWS 2014). Although most of the annual precipitation occurs during the winter months, intense thunderstorms can deliver a lot of rainfall within a short period of time, often leading to flood events (Longwell et al. 1965).

Water within the study area flows west to east and discharges into Lake Mojave, an artificial lake created by the construction of the Davis Dam in 1953 (BOR 1995). The hydrologically isolated Techatticup Wash has one abandoned mine and tailings storage facility at its western boundary, and no major tributaries (Longwell et al. 1965). Groundwater within the area is confined to localized shallow perched aquifers, with groundwater movement between washes being restricted by the overall synclinal structure (Bell and Smith 1980).

Sediment Composition

Sediments in dry washes are composed of poorly eroded bedrock from local sources deposited during high energy storm events (Navarro-Hervás et al. 2012). The exposed bedrock is covered with a dark coating of desert varnish, as is typical of arid regions. Desert varnish consists of Al-, Fe- and Mn-oxides and oxyhydroxides and according to research, builds up at 1 μm per 1000 years (Nowinski et al. 2010, 2013; Sparks 2003; Thiagarajan and Lee 2004). A previous study at this site found aeolian silts are also found at the surface and extend to a depth of approximately 15–45 cm (Sims 2011). Sediments are slightly alkaline, with a pH between 7.9 and 8.4, contain 1–2 % calcium carbonate, and have <1 % organic matter from the hyperarid climate (Sims 2011). Surface sediments contain <0.1 % moisture, indicating that aqueous phase transport of TEs is not a concern for most of the year (Sims et al.2013). Wash sediments contain 6.7–7.8 % silt; 64.4–66 % sand, and 26.8–28.5 % coarse fractions (Sims 2011).

Materials and Methods

Samples were collected for this study in March, 2013 from Bureau of Land Management (BLM) lands. The sampling strategy was designed to assess the concentrations of TEs in local background and source areas, and the extent of its migration in the Techatticup Wash. Seventy-two samples from eight locations were collected from within the Techatticup Wash to determine whether contaminants were transported downgradient from the source material (Fig. 1). A smaller number of samples were collected to augment a previous, more in-depth evaluation of horizontal distribution (Sims et al. 2013). Each sampling point was located 10 m apart at two different locations within the wash and was sampled at intervals of 0–10 cm, 10–20 cm, and 20–30 cm below the ground surface. Each sample was sieved for site specific fractions of silt, sand, and coarse fractions (<0.05 mm, 0.051–0.5 mm, >0.51–8 mm, respectively). Any particle >8 mm in diameter was discarded due to limited surface area.

Three background samples were collected approximately 1000 m up-gradient from the Techatticup Wash source materials so that background concentrations could be properly measured without anthropogenic influence (Fig. 1). Background samples were treated with the same methods as wash samples for particle size and analytical procedures so that local materials and possibly, desert varnish, could be evaluated. A sample was collected from the Techatticup Mine tailings source to evaluate the

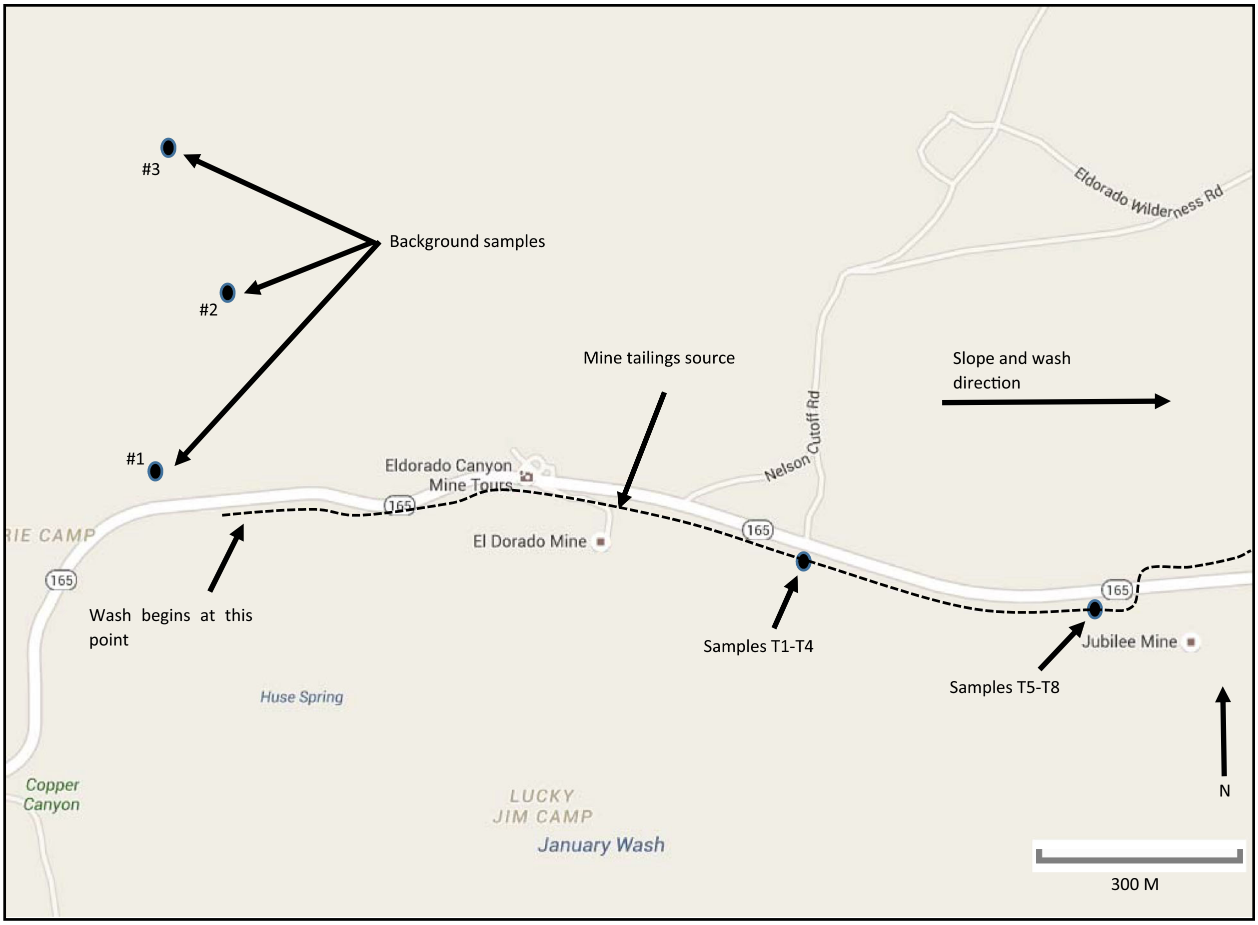

Fig. 1 Techatticup wash sampling locations (Google 2014)

Table 1 Background average concentrations (mg kg^{-1}) for samples collected from wash sediments

Element	Background								
	0–10 cm below surface			10–20 cm below surface			20–30 cm below surface		
	Silt	Sand	Coarse	Silt	Sand	Coarse	Silt	Sand	Coarse
Al	1450	749	220	1495	526	248	1498	574	138
As	1.25	2.6	1.5	0.35	0.85	–	1	0.7	0.4
Ba	34	20.1	3.5	36	11	9.2	39	10	3.3
Cd	0.01	0.06	–	–	–	–	–	–	–
Cu	12.4	3.2	0.9	9.8	2	0.5	8.8	2.4	0.8
Cr	1.05	0.6	0.1	1	0.23	–	1.2	0.2	–
Fe	600	369	121	730	179	84	655	278	90
Mn	158	88	93	138	74	12	178	48	12.9
Pb	15.1	5.4	0.65	18.2	5.2	0.3	15.8	5.9	1.6
Se	2.0	1	–	1.25	0.9	0.2	1.5	0.2	–
V	2.4	1.2	0.4	2.3	2.2	0.7	2.6	1.2	0.8
Zn	12.4	4.8	1.1	8.9	3.1	1.42	10	3.3	0.9

Averages are across all three background samples, fractionated for silts, sand and coarse

– Denotes below detection limits per USEPA method 3050B followed by 6010

Table 2 Processed tailing concentrations (mg kg^{-1}), detection limits and crustal abundances

Elements	Processed tailing cm below surface			IDL	Crustal averages
	0–10	10–20	20–30		
Al	1268	1200	1820	1.0	69[a]
As	3.3	2.8	3.6	0.01	2.0[c]
Ba	6.8	6.5	20	0.05	480[d]
Cd	6.2	6.0	4.5	0.01	0.1[e]
Cu	77	76	70	0.01	2[b]
Cr	4.2	3.5	3.4	0.01	20[c]
Fe	3104	2950	2955	1.0	9800[b]
Mn	265	256	370	0.01	720[a]
Pb	259	271	264	0.01	16[a]
Se	–	–	2.5	0.01	0.05[c]
V	2.3	2.5	3.8	0.01	20[b]
Zn	750	760	510	1.0	120[a]

IDL instrument detection limit; tailings materials are classified as silts due to the milling procedures and therefore, no other fractions are present

– Denotes below detection limits per USEPA method 3050B followed by 6010

[a] Schropp (1988), [b] Sparks (2003), [c] Thornton (1983), [d] Chaffee and Berry (2006), [e] Li (2000)

anthropogenic effects on TE concentrations. Source tailings are primarily composed of silt particles (4–62 µm) from milling processes.

Sediment samples were processed according to USEPA Solid Waste 846 (SW-846) protocols, including quality control (USEPA 1997). TEs were extracted by USEPA method 3050B (hot aqua-regia digestion) and analyzed by USEPA method 6010B using an inductively coupled plasma-optical emission spectrometer (USEPA 1997). Instrument calibration consisted of six points across a concentration range (including a blank) and was fitted by linear regression (R^2) > 0.995 (USEPA 1997). Analytical integrity was verified with a certified reference sample (RTC Corporation: CRM022-020, Sample 5, lot D522). The quality control sample measures within specified windows (±15 %) and exceeded specified requirements. Samples were analyzed in triplicate with a required relative standard deviation (RSD) of <20 % to qualify as acceptable (USEPA 1997).

Finally, principle components analysis (PCA) was used to describe groupings between TEs and particle size (Shapiro and Wilk 1965). As a result of the nature of sample heteroscedasticity, the mean of concentrations was not a suitable measure of their central location and thus could not be used in the statistical method when investigating the effect of particle sizes (Kruskal and Wallis 1952; Levene 1960; Shapiro and Wilk 1965).

Results and Discussion

Metal and Metalloid Background Levels

Background concentrations (Table 1) were below crustal abundances (Table 2) for Ba, Cd, Cr, Fe, Mn, V, and Zn, whereas Al, As, Cu, and Se exceeded crustal abundances. Crustal abundances are only global averages and do not represent a specific area. With regard to size fractions, background samples contained, on average, 7.1 % silt, 65.8 % sand, and 27.1 % coarse fractions, similar to samples taken from the eight locations along the wash.

Locations where TEs were detected in wash sediments (Fig. 1: T1 through T8) at, or above, background concentrations, are likely the result of tailings eroding into the wash system from source materials according to Horowitz et al. (1993). It is possible that geogenic outcroppings down-gradient of the mine contain TEs; however, such outcroppings are unlikely to significantly affect the overall

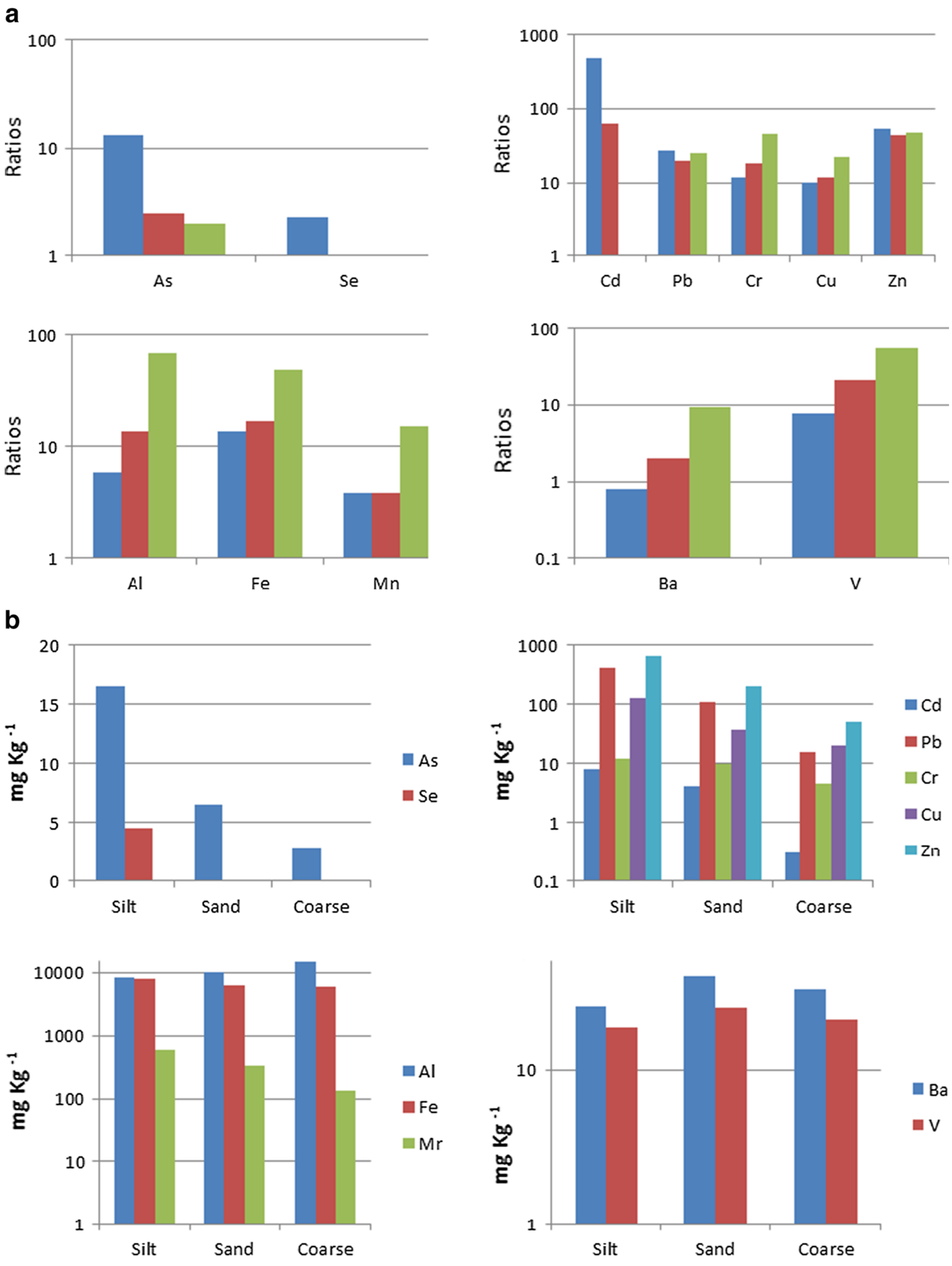

Fig. 2 **a** TE ratios concentrations in wash sediments to to their background levels on silt, sand and coarse fractions. **b** TE concentrations (mg kg^{-1}) on silt, sand and coarse fractions

dataset (Horowitz et al. 1993; Moreno-Jiḿenez et al. 2009; Taylor and Kesterton 2002).

Metals and Metalloids in Sediments

TEs in the source material were above background levels (Tables 1 and 2) except for Se, a TE that is ubiquitous in the Nelson area (Sims et al. 2013). Data show that Al, As, Ba, Cd, Cu, Cr, Fe, Mn, Pb, V, and Zn were above background concentrations (supplementary Table 1), indicating that contaminants detected in the wash sediments are from the source materials. The data further show that TEs have been redistributed throughout the sediments horizontally, vertically, and across particle fractions, except for Cd.

Cadmium was highest in the 0–10 cm level but decreased in concentration in the 10–20 and 20–30 cm levels, and decreased with distance from source materials and with increasing particle size. Data shows As and Se concentrations were higher on silt fractions, with As concentration decreasing as particle size increased (e.g. 2.9, 6.5, and 17 mg kg^{-1} on coarse, sand, and silt fractions, respectively, at T-1). Selenium was mainly detected on silt with little or none detected on sand or coarse fractions. Figure 2a illustrates enrichment of As and Se ratios relative to background levels; however, Fig. 2b shows As and Se concentrations were higher on silt fractions, which was not unexpected. Studies of metalloids (e.g. As, Se) in similar environments have found this same behavior with regard to As and Se (Ingri et al. 2014).

Data shows that the silt fraction had higher concentrations of Fe than the sand or coarse fractions. This could be contributing to the higher concentrations of metalloids found on the silt particles. Oxyanions (e.g. As, Se) are susceptible to adsorption on Fe-oxides (FeO$_x$) under appropriate conditions (Manceau and Combes 1988; Vinson et al. 2011). Bowell (1994) suggests that high levels of Fe in volcanic sediments could be a mechanism for FeO$_x$—metalloid interactions where sediment pH is close to neutral. Sediment pH in the Techatticup Wash ranges from 7.9 to 8.4 (Sims 2011).

Metalloid (e.g. As, Se) migration is restricted by strong sorption to Fe- and Al-oxides in sulfide-rich deposits (Modis and Vatalis 2014). Sorption of As and Se is likely where a synergistic effect of aridity, Fe-hydrates, and Al-oxides occurs (Fei et al. 2014; Sadiq 1997; Vinson et al. 2011). It is plausible that As and Se are correlated to the higher concentrations of Fe in the silts, possibly as Fe-oxides.

Aluminum increased with grain size, as illustrated at location T-1 (8550, 10,150, and 15,100 mg kg^{-1} for silt, sand, and coarse fractions, respectively; Fig. 2b). Unlike Al, Fe, Mn, and Zn decreased from silt to sand to coarse particles (8095, 6150, and 5900 mg Fe kg^{-1}, 595, 340, and 135 mg Mn kg^{-1}, respectively; Fig. 2b). Data show a similar pattern of TE behavior for Al, Fe, and Mn to that reported by Fei et al. (2014), who found that crustal metals

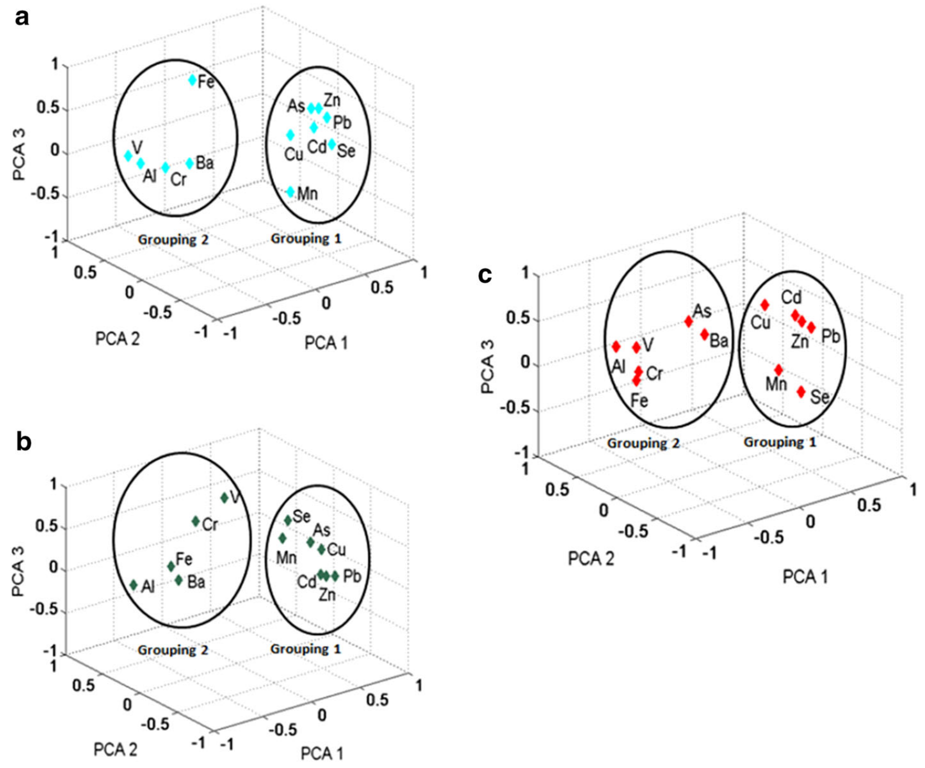

Fig. 3 PCA analysis showing groupings of TEs with silt fraction. **a** is silts, **b** is sands, and **c** is coarse

(e.g. Al, Fe, Mn) exist as metal-oxide species in volcanic areas, such as the study area, thereby affecting TE-oxide adsorption processes. The study area therefore provides ideal conditions for TE scavenging.

Cadmium, Cr, Pb, and Zn followed similar trends to Fe and Mn (Fig. 2a, b; supplementary Table 1). When comparing Cd ratios to background levels, Cd was highest in the 0–10 cm level at location T-1 (8.1, 4.2, and 0.3 mg kg^{-1} Cd, respectively). Cd and Fe-oxides are linked because Cd binds with Fe-oxides more readily than with Al- or Mn-oxides (Yu et al. 2006), and the silt fractions contained the highest Fe concentrations.

Cadmium scavenging takes place in two phases; first, a fast adsorption followed by a second, slower process when Cd is abundant (Vidal et al. 2009; Warren and Zimmerman 1994; Yu et al. 2006). It is likely that Cd is being scavenged in the surficial silt fraction because of its lower background concentration. Since Cd background levels are nearly non-detectable, it can be presumed that any elevated Cd concentrations are anthropogenic in origin. It is plausible that the Fe-oxides in the sediment influences scavenging of Cd, restricting sorbed Cd to the uppermost levels of the sediment profile.

Lead was consistently higher in silts, decreasing in concentration as particle size increased (e.g. T-1; 410, 109, and 16 mg kg^{-1}, respectively on silt, sand, and coarse fractions; Fig. 2a, b; supplementary Table 1). Its distribution could be correlated with Mn-oxide scavenging (Dong et al. 2003; Oyanedel-Craver and Smith 2006). It is plausible that Pb is competing for adsorption (reactive) sites with other cations and therefore could be adsorbed by Mn-oxides.

Chromium and Cu concentrations also decreased with increasing particle size (12, 10, and 4.5 mg kg^{-1} Cr; 129, 38 and 20 mg kg^{-1} Cu on silt, sand, and coarse fractions, respectively). Wayne et al. (2006) established a link between Fe- and Mn-oxides with Cr and Cu adsorption. Their research indicates that Fe- and Mn-oxides can control Cr and Cu distribution in the sediment profile.

Barium and V concentrations distinctly increased in coarser fractions (26, 40, and 33 mg kg^{-1} Ba and 19, 25, and 20 mg kg^{-1} V in silt, sand, and coarse fractions, respectively; Fig. 2a), exhibiting a similar distribution pattern to Al. Barium and V are attracted to Al-oxides (Jones et al. 2011; Rango et al. 2013; Vidal et al. 2009), so it is likely that Ba and V are being adsorbed by the abundant Al-oxides.

Principle components analysis (PCA) was applied to each particle size fraction (silt, sand, and coarse fractions; Fig. 3) and showed that the variability of all 12 TE concentrations can be effectively described (up to 70 %) by three principal components. Data show two main groupings of elements. Group 1 shows Mn associated with As, Cd, Cu, Pb, Se, and Zn, similar to what was found by Dong et al. (2003) and Oyanedel-Craver and Smith (2006). Group 2 shows Al associated with Cr, Ba, and V, with Fe (Fig. 3a, b) showing a slightly weaker association, similar to what was observed by Wayne et al. (2006) and Fei et al. (2014). Both groupings are consistent across silt, sand, and coarse fractions; however, As migrates from group 1 to group 2 in coarse fractions (Fig. 3). This is not unexpected as studies show oxyanions are more susceptible to adsorption on Fe-oxides (Ingri et al. 2014; Vinson et al. 2011). It is likely that the Fe-oxides are providing more reactive sites for the As, and that a lack of weathering of sediment minerals explains the grain size finding (Navarro-Hervás et al. 2012).

It appears that the movement of TEs in wash sediments is controlled by TE scavenging; for example, desert varnish found on rock substrate is composed predominantly of Al-, Fe-, and Mn-oxides and oxyhydroxides (Hoar et al. 2011; Nowinski 2009; Nowinski et al. 2012). Studies by Wayne et al. (2006) and Nowinski et al. (2010) showed that these oxide coatings provide reactive TE scavenging sites. This area contains poorly weathered sediments eroded from local geology coated with desert varnish (Anderson 1971; Hansen 1962). It is possible that the transport of TEs is driven not only by the physical transport of tailings, but also the surficial composition of the desert varnish.

Conclusions

Physical migration of tailings is only one method of movement of bed sediments in arid environments. Poorly weathered local sediments coated with desert varnish contributes to TE scavenging from mine tailings to larger particles. It appears that Al- oxides are scavenging Ba and V, whereas Fe- and Mn-oxides are scavenging As, Cd, Cu, Cr, Pb, Se, and possibly Zn during sediment transport in desert washes from storm events. Even in areas with limited precipitation, TE interactions with oxides must occur at the sediment/pore-water interface during the infrequent storm events. A synergistic effect of aridity and a short-term sediment/pore-water interface during storm events in the presence of oxides/oxyhydroxides might be driving the metal and metalloid scavenging. Additional studies of oxide metals and TE scavenging from tailings to bed sediments coated with desert varnish should provide valuable insight into the phenomenon of metals and metalloid scavenging in arid environments.

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