Geochemical partitioning of potentially toxic metals in soils and sediments from the Anka area, north-western Nigeria

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Abstract

The partitioning of Cr, Cu, Mn, Ni, Pb and Zn between different geochemical phases in soils and sediments from five artisanal mining contaminated villages in the Anka area, north-western Nigeria has been investigated. This is aimed at determining the ease with which these elements can be mobilized into the environment. Twenty five samples were subjected to sequential extraction procedures and the concentration of the elements in the exchangeable, carbonate and Fe/Mn oxides fractions determined using inductively coupled plasma-optical emission spectrometry. Total elemental concentration was measured by x-ray fluorescence spectrometry. The results show that the carbonate phase is the most geochemically significant in terms of the sequestration of majority of the elements, especially, Pb, Cu and Zn. This is followed by the Fe/Mn oxides and the finally the exchangeable fractions in that order. Generally, the lability of the elements was found to decrease in the order Pb > Cu > Zn > Mn > Ni > Cr, mainly controlled by the release of the elements from the carbonate and oxide phases. This indicates possible risk of mobilization of the elements under reducing, slightly acidic environmental conditions. In spite of the high concentration of the elements, especially Pb, Cu and Zn obtained in the carbonate and oxide fractions, less than 50 % of their total concentration is easily mobilisable. The remainder is held within less labile geochemical phase within the matrices. This further confirms that the sequential extraction protocols are better environmental assessment tools compared to determination of total concentrations alone. Remediation technologies aimed at reducing the acid susceptibility of these materials should be pursued in order to minimize the impact of the metals on the environment and health of the local population.

Keywords: geochemical, partitioning, mobilization, sequential extraction, metals, artisanal mining.

Introduction

Knowledge of total concentration of potentially toxic elements in environmental matrices alone is not enough to assess their mobilization, bioaccessibility and the environmental and human health risks they pose (Ullrich et al., 1999). In order to assess the mobilization of heavy metals held within soils and sediments and their possible environmental and health effects, it is necessary to establish the forms in which the elements exist. This has led to the shift of attention from determination of total or near total metal contents to techniques aimed at quantifying element distribution among solid geochemical phases. Sequential extraction protocols (SEPs) have been used with some success to determine the geochemical partitioning of elements within different fractions, namely, exchangeable, carbonate, iron-manganese oxides, organic matter bound and residual fractions.

Several sequential extraction protocols have been developed over the last few decades. The work of Tessier et al (1979) has been adapted and modified by many subsequent workers (example, Ullrich et al, 1999; Singh et al, 1999; Martley et al, 2004; Hou et al, 2006). But various previous workers (e.g. Nirel and Morel, 1990; Whalley and Grant, 1994; Kerstan, 2002) have highlighted the issue of possible non-specificity of the reagents, along with analyte reabsorption after release. However, this operationally defined speciation, though not able to definitively determine the specific mineralogical phases to which potentially toxic elements are bound (Ure and Davidson, 2002), is still a useful tool in

the determination of the ease with which toxic species may be mobilized from environmental matrices. The progressively increasing rigour of the procedures provides a means for evaluating the mobility of metals and other toxic elements in geologic materials.

The methods used in this work are based on combinations of these earlier works and only the exchangeable, carbonate and iron/ manganese oxides fractions were determined, because they are considered to be the most readily mobilized in the environment. Organic matter/ sulfide bound fraction and the residual fraction comprising of metals held within silicate mineral frameworks or some resistates have not been measured. These are not readily solubilised and released to the environment under a reasonable span of time (Tessier et al., 1979) and thus pose little environmental problem (Martley et al., 2004).

Most previous researches on the geochemistry of heavy metals in Nigeria have focused mainly on the spatial variation of the concentration of these elements in geologic materials (e.g. Ntekim, 1993; Tijani et al., 2006; Odewande and Abimbola, 2008). Little attention has been paid to the geochemical fractionation of these elements. There is the need to understand the solid state partitioning of these elements in soils and sediments, especially in the Anka area of north-western Nigeria, where artisanal mining has led to severe contamination of many villages. This work is therefore aimed at determining the fractionation of Cr, Cu, Mn, Ni, Pb and Zn in mining contaminated soils and stream sediments from five villages in the Anka area of north-western Nigeria.

The Study area

The study area lies between latitude $11^o51'N$ and $12^o08'N$, and longitude $5^o51'E$ and $6^o08'E$ and is characterized by generally gentle relief. The main surface water body in the area is the Anka River but there are numerous seasonal streams or channels which cut the entire landscape that are used as sources of water for domestic, irrigation and livestock watering purposes. Vegetation in the entire region is generally sparse, and has been described by Russ (1957) as savannah forest together with scrubs, which thin out in a northerly direction, with semi- deciduous high forests along streams and depressions. Generally, the inhabitants of this area are farmers, who are engaged in the cultivation of a large number of cereal and vegetable crops.

Geologically, the area falls within the Anka Schist Belt and Holt et al. (1978) have summarized the lithology in the area to include metaconglomerates, sandstones, slates, phyllites and acid volcanics. According to Turner (1983), the metaconglomerates form units of up to 150-200 m, interbedded with feldspathic metasandstones and contain rounded to angular fragments of granites, quartzites, quartz, phyllites and volcanics. Gold in this area is hosted by schists, phyllites and quarzites related to sub-regional structural elements subsidiary to the Anka fault (Garba, 2003) and metaconglomerates (Russ, 1957). Trace metal concentration in altered wall rock reported by Garba (2003) of 647-5410 ppm Cu; 7550-22600 ppm Pb; 1.5-8.6 ppm Ag and 123-6320 ppb Au show that the ores are very rich in lead and copper minerals.

Methodology

Twenty five soil and stream sediment samples were collected from five villages (Abare, Bagega, Dareta, Tsunke and Tungar Daji) in the Anka area, where artisanal gold mining has led to contamination of the environment. At each point, three top soil and sediment samples were collected and subsequently mixed up to form a composite sample. Sample locations in terms of geographic coordinates were obtained using a handheld GPS device (Garmin etrex). The data allowed the production of a sampling map (Figure 1) using Surfer version 9.1.325 Surface Mapping System (Golden Software, Inc., 2009).
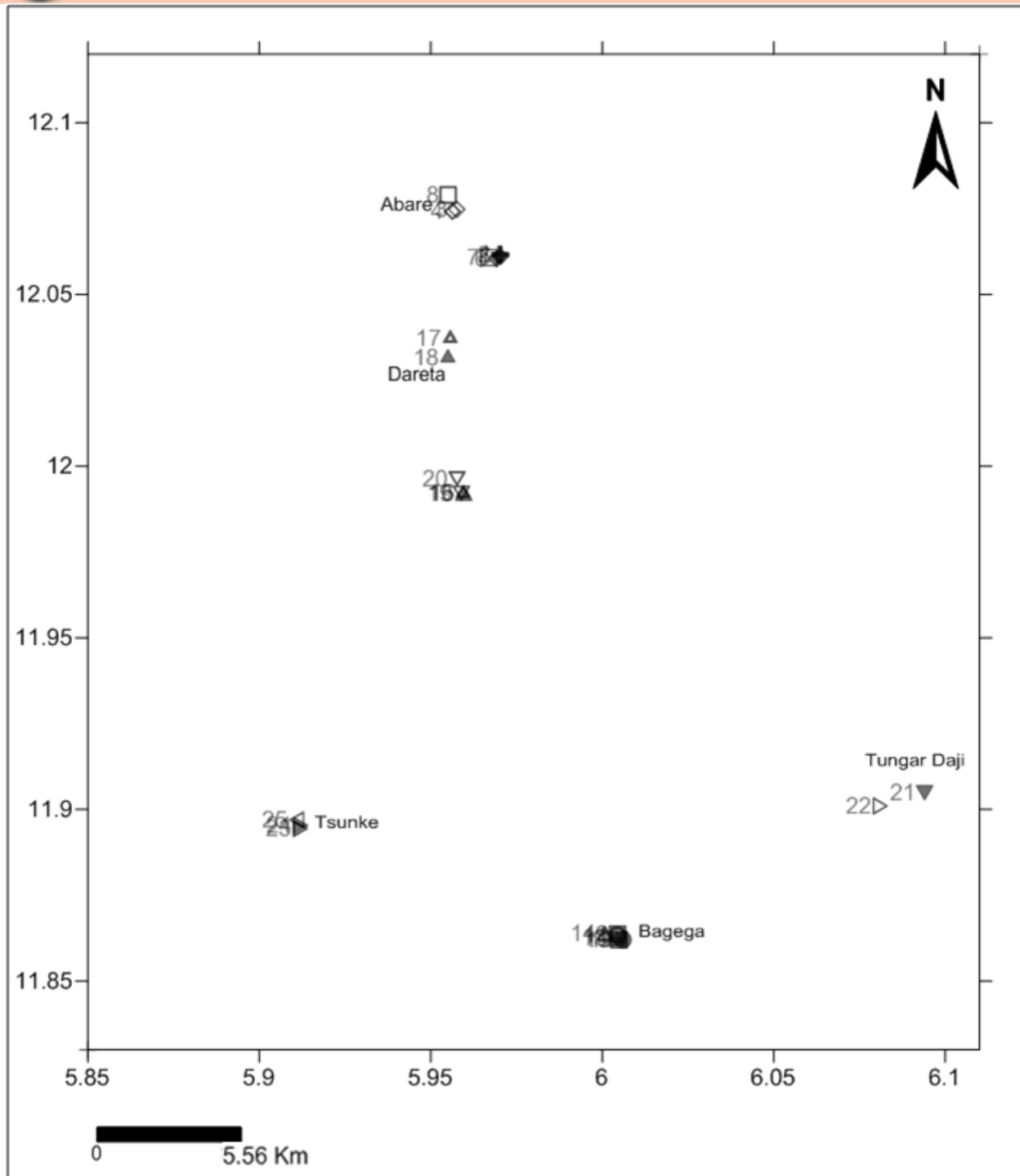
Figure 1 Location of samples within the study area, including locality names.

Total concentration of Cr, Cu, Mn, Ni, Pb and Zn was measured on pressed sample powder pellets, using x-ray fluorescence (XRF) spectrometry. The sequential extraction experiments were performed as follows:

Exchangeable (adsorptive) Fraction

A 1g portion of (< 63 μm) soil sample was extracted in a 50 mL polypropylene centrifuge tube using 8 mL of 0.5M magnesium chloride ($MgCl_2$) at pH value of 7 and room temperature with continuous agitation for 20 minutes.

Carbonate Fraction

To determine the amount of metals held in this phase, the soil residue from the exchangeable experiments was extracted using 40ml 1M ammonium acetate (NH_4OAc) at pH 5 and room

temperature for 2 hours. All through the period, the caps were kept tight and the vials subjected to continuous agitation.

Fe-Mn Oxides (reducible) Fraction

The reducible fraction was determined by subjecting the residue from the carbonate fraction test to extraction using 20 mL 0.04M hydroxylamine hydrochloride ($NH_2OH. HCl$) in 25% (v/v) acetic acid (HOAc). Temperature was kept at 96 $\pm3^oC$ for 4 hours and caps on tightly (Martley et al., 2004). Every 30 minutes, the pressure was vented and the samples shaken.

The extraction was achieved for each fraction by centrifuging (Tessier et al., 1979) at 4800 rpm for 30 minutes followed in each case by collection of the supernatant into a sample vial using a pipette to minimize sample loss. The sample was then stored in a fridge at 4^oC until analysis was carried out using ICP-OES. Between successive extractions, the sample was rinsed with 10 mL milliQ water and centrifuged for 15 minutes and the supernatant discarded.

To check method reproducibility for each of the steps, three aliquots of a certified reference material, STSD-2 (stream sediment) were extracted in triplicate. The results show that the measurements are more reproducible for all elements in the Fe/Mn oxide fractions compared to the carbonate and exchangeable fractions, with residual standard deviations (RSD) generally below 5 %, except for As. The high RSD values obtained for some of the elements in the exchangeable and carbonate fractions is interpreted to be a result of very low concentration. The lower the concentration, the more difficult it is to obtain reproducible results.

Results and Discussion
Exchangeable fraction

Elements held within the exchangeable fraction of soils and sediments are the most mobile and readily available for uptake in the environment. However, concentration of elements associated with this fraction is generally very low, ranging from nearly zero for Cr in all the samples up to about 0 to 5 % (mean, 1 %) for Cu and 0 to 16 % (mean, 2.2 %) for manganese. The percentage of Ni associated with the exchangeable fraction ranges from 0.35 % to about 6 % with a mean of 1.36 %, while the range for Pb is 0 to 6 % with an average of about 1 %. Similar low values of between 0 and 4 % (mean, 1.4 %) were obtained for Zn in this fraction. The partitioning of metals in this phase was found to decrease in the order Mn > Ni > Zn > Cu > Pb > Cr.

The results obtained for the exchangeable fraction are similar to those reported by Singh et al. (1999) for Cu, Mn and Zn in sediments of the Damodar River in India; Maskall and Thornton (1998) for Pb and Zn in soils contaminated by historical lead smelting in parts of Derbyshire, England and Clwyd, Wales, UK. Burt et al. (2003) obtained similar results for Cr, Cu, Pb and Zn in smelter-contaminated soils from Anaconda and Deer Lodge Valley, Montana, USA and Navas and Lindhorfer (2003) for Mn, Zn and Cr in semi-arid soils of the central Ebro Valley, Spain. Ullrich et al. (1999) also found low to moderate values for Pb and Zn in the exchangeable fraction in soils from an area of Pb/Zn mining and smelting near Bytom, Upper Silesia, Poland, although they reported these to increase significantly below pH 6.
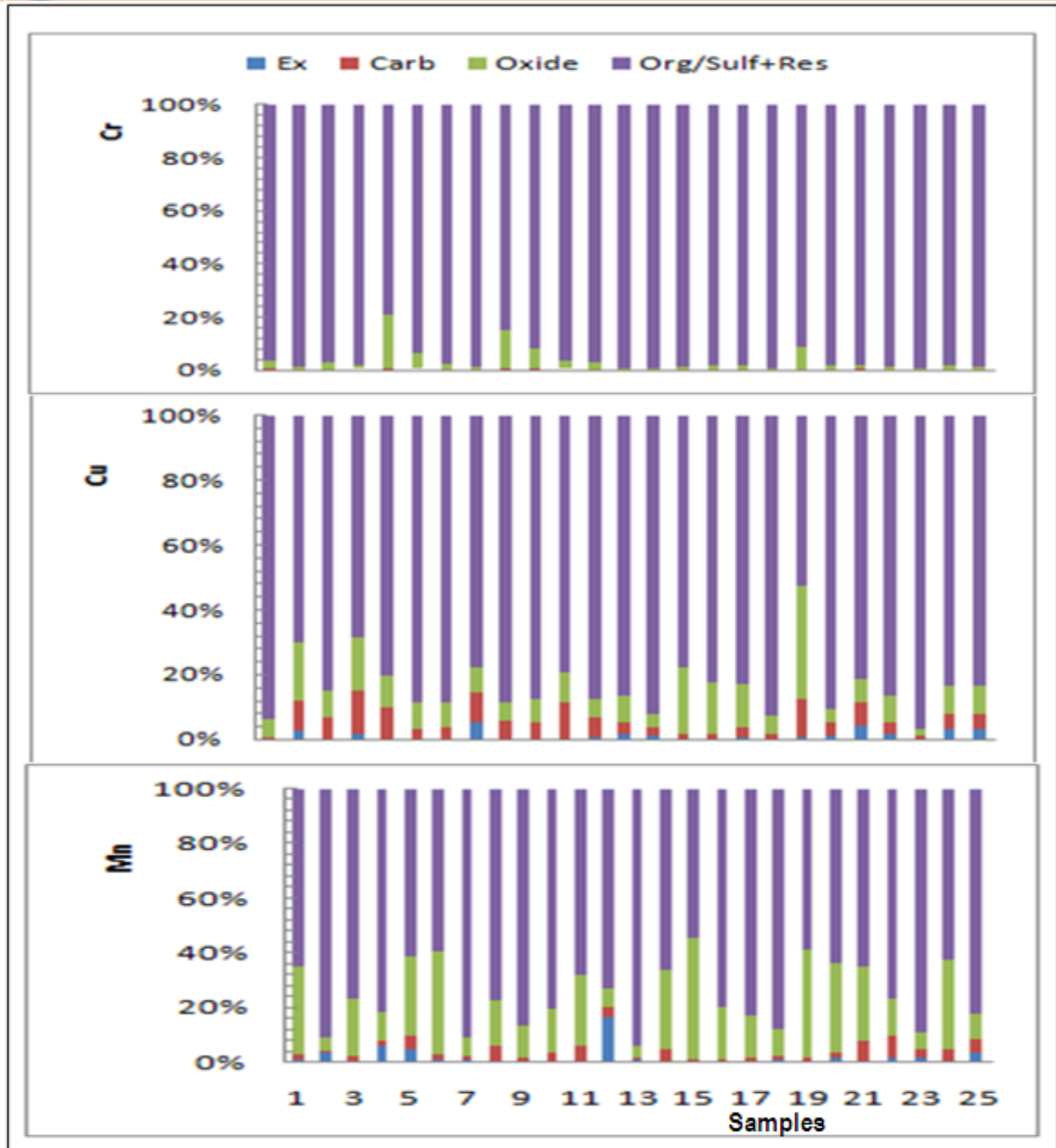
Figure 2 Partitioning of potentially toxic elements in three labile phases in soils and sediments from five villages in the Anka area, north-western Nigeria. In this work, the Org/Sulf+Res fraction is the difference between the sum of the SEP steps and the total concentration of each element. Locations of the samples are shown in figure 1.
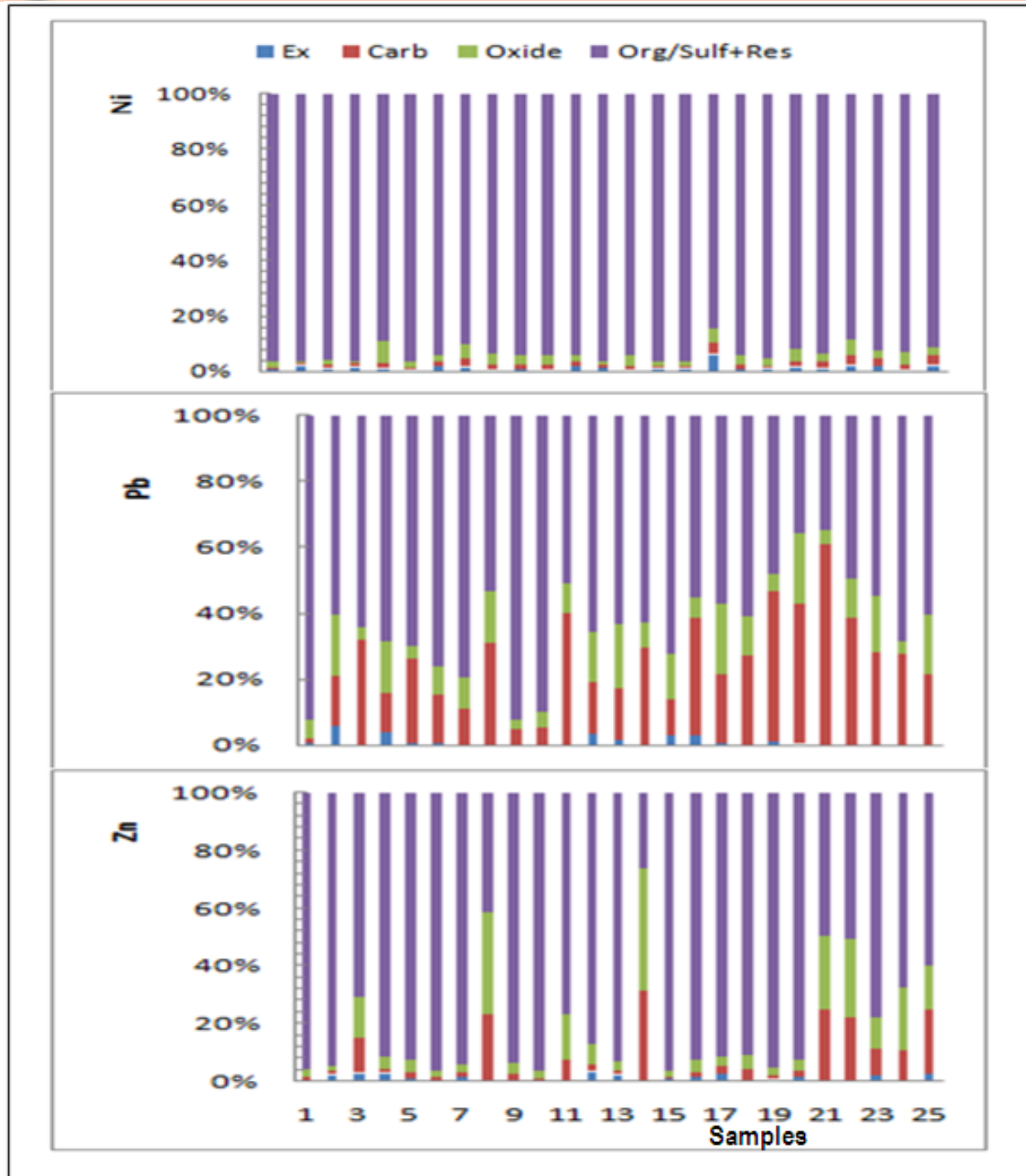
Figure 2(cont'd)

Most of the elements measured, with the exception of Mn have shown very low association with this phase in all samples. It seems also that the fact that the samples have generally high total concentrations of some of the elements, especially Pb and Cu, did not affect their distribution in terms of the exchangeable fraction. The low mobilization of all the elements in this step (Fig. 2) may be due in part, to the relatively high pH (4.89 – 9.24) obtained for the Anka soils, which may decrease the solubility and availability of most metals and their ability to form chelates (Burt et al., 2003; Forstner and Whittmann, 1983). The generally low alumina and base contents of these soils and sediments (Waziri, 2012) may be an indication of the paucity of fine grained clay mineral particles in the sample matrix, which in turn limits the ability of the soils to sorb trace elements both in terms of low surface area: volume ratios and negatively charged surfaces.

However, the possibility that these results are affected to some extent by extraction methods cannot be ruled out. For example, the 0.5 M $MgCl_2$ may not have been able to completely extract metals bound to this fraction over the 30 minute period used, and some of the metals associated with this phase may end up extracted together with the carbonate fraction. The exchangeable fraction is therefore the least geochemically significant of the three phases determined in the soils and sediments of the Anka area. Mobilization of contaminants bound to this fraction is therefore considered less likely to cause any serious environmental and/or human health problems of metal toxicity in the area.

Carbonate fraction

This is the second most labile fraction of heavy metals and according to Singh et al. (1999), it may account for over 50 % of non-lithogenic heavy metals in polluted sediments. The carbonate fraction contributed a significant amount of most of the elements measured in these samples (Fig. 2), accounting for between 0 to 21 % (mean 6 %) of total Cu in the samples similar to the about 20 % obtained by Van-Herreweghe et al. (2002) in contaminated soils from Flanders, northern Belgium. Most of the extractable Pb was found to be associated with this fraction (Figure 2), ranging from 1.5 to 61 % of total Pb in the samples with an average extractability of 24.56 %. Zinc too showed a relatively strong association with this phase, with about 8 % of the total zinc extracted in this step (range, 0.6 to 32 %). Manganese, Ni and Cr showed weaker association with the carbonate fraction compared to the rest, with mean values of 2.91 %, 1.74 % and 0.24 % respectively. The results show that Pb has the strongest affinity with this fraction, and the concentration of carbonate bound metals was found to decrease in the order Pb > Zn > Cu > Mn > Ni > Cr.

The very strong association of Pb with this phase (Figure 2) is probably due to the abundance of secondary lead carbonates in the ore that has been processed for gold by local artisanal miners (Plumlee and Morman, 2011), which serves as a source of contamination of soils and sediments in the area. Cerussite ($PbCO_3$) has been shown to be among the most readily solubilised carbonate minerals under acidic conditions compared to for example, calcite and aragonite (Plumlee, 1999). This also appears to be the reason for the relatively high concentrations of Cu and Zn in this phase in the Anka samples. The strong association of Pb and Zn with this phase is consistent with the findings of Li et al. (2001) in urban soils and road dusts in Hong Kong, although they did not find much Cu in the fraction.

The results show that this fraction is geochemically very significant in terms of the mobilization of potentially toxic elements into the environment. In this area, mainly Pb, but also Cu and Zn have been found to be labile and likely to become readily available for uptake by plants and passed on through the food chain. Based on these results, it is not envisaged that any environmental problems can occur due to the mobilization of Cr, Ni and Mn from this fraction due to their low association with the phase.

Fe/Mn Oxide fraction

The Fe and Mn oxide fraction is also known as the reducible phase and constitutes a significant sink for heavy metals in soils and sediments. It represents the contents of each element bound to iron and manganese oxides that would be mobilized if the conditions in the solid matrix became more reducing (Anju and Banerjee, 2010) because the oxides are thermodynamically unstable under anoxic conditions (Tessier et al., 1979). Manganese oxides have been reported (Hudson-Edwards, 2000) to take up heavy metals mainly through the agency of adsorption, cation exchange and co-precipitation. But depending on the efficiency of the previous extractions, the amount of each element extracted in the step may include portions from the carbonate and exchangeable fractions. This has the tendency to make results obtained in this step either too high or too low; depending on whether the carbonate bound and exchangeable fractions have been completely removed, or whether in fact some oxide bound metals were co-extracted during the carbonate step.

Nearly all the elements have shown strong to very strong association with this phase (Figure 2). The strongest affinity is shown by Mn with a mean of 20.04 % (range, 4 to 44 %). Except in two samples in

which 96% and 35 % was extracted in this step, the percent extractability of Cu in this phase ranges generally from 2 to18 % (mean, 13.55 %). Zn also shows a wide range of values, between 1.9 and 42 % with an average of 10.64 %, lower than 11.06 % for Pb (range, 3 to 21%). About 0.5 to 20 % (mean, 3.45%) of total Cr was found to be associated with the oxide phase, while Ni was much less soluble with only 0.5 to 8 % (mean, 3.19%) recovered in this step.

The association of the elements with this phase generally appears to follow the order Mn > Cu > Pb > Zn > Cr > Ni. However, when the two samples with high to very high Cu concentration are taken out, Pb shows stronger affinity to the phase than does Cu, which is in agreement with the findings of Li et al. (2001). Contrary to these data, their result shows that the phase has a stronger affinity for Zn compared to Cu. However, experiments by Murray (1975) and McKenzie (1980) have shown that the affinity of manganese oxides for heavy metals decreases in the order Pb > Cu > Zn > Ni, which is broadly similar to that obtained in this work. McKenzie (1980) found that Pb was more strongly adsorbed by manganese oxides than by iron oxides, and the partitioning of Pb onto the oxides was much stronger than that for other metals studied. This is similar to the results of O'Reilly and Hochella (2003), who concluded that Mn-oxides are generally more efficient sorbents of Pb than Fe-oxides. Tessier et al. (1979) also obtained relatively high levels of Cu, Ni, Pb and Mn in this fraction for bottom sediments from Saint-Marcel and Pierreville, Canada, with more than 20 % of total of each of Cu, Ni and Pb and 15-24 % Mn found to be associated with the fraction.

The mobilization of potentially toxic elements from this fraction is dependent on the pH and oxidation-reduction (redox) conditions of the environment. Redox reactions have a controlling influence on the solubility and eventual mobilization of some trace elements in different geologic systems (Krauskopf and Bird, 2003). For example, the reduction of Mn- and Fe- oxides can lead to their mobilization, with oxides of Mn III and IV being more soluble than Fe III oxides (Hudson-Edwards, 2000). Low pH (acidic conditions) will then ensure that these ions do not form precipitates with carbonates, sulphates, chlorides or some of the other anions commonly present in natural solutions (Krauskopf, 1957). This has implication for the release of associated heavy metals and other potentially toxic elements bound to these oxides in soils and stream sediments into surface and ground water systems or making them phytoavailable. The results have shown that this phase is geochemically very significant in terms of the sequestration of most of the PTEs measured. Any changes in Eh conditions, causing the reduction of Fe/Mn oxides in the soils and sediments in the area may lead to the mobilization of mainly Cu, Pb and Zn in the five villages of the Anka area. The results did not, however, show any risks of metal toxicity associated with the release of Ni and Cr from this fraction in soils from the area.

Recovery and relative mobility

Element recovery was calculated in order to determine the amount of contaminants held within the more labile fractions relative to the less reactive forms. While sequential extraction procedures do not extract elements bound to a given solid fraction, they may be used to infer the mobility of metals under changing environmental conditions, such as pH and Eh (Anju and Banerjee, 2010). Considering that only the more labile fractions were extracted in this work, the partitioning of elements in each of the three fractions, and sum of the three steps expressed as a percentage of the total concentration, are used in estimating the possible risk of metal toxicity associated with its mobilization from labile repositories. Although the sulphide / organic matter bound fraction is not considered as being very labile, oxidation of sulphide minerals, will mean that metals held in that fraction are going to become more susceptible to mobilization.

Recovery is calculated according to the equation:

$$Recovery = \frac{(\sum Sequential\ extraction\ procedure\ steps)}{Total\ concentration} \times 100$$

Although Cu recovery seems to span a wide range (3.3-118.6%), nearly 80% of the samples have values not exceeding the mean of 20.6%, indicating that the larger values are contributed by just few samples. Similarly, the amount of Pb dissolved across the three steps generally falls between 20 and 65 % (mean 38%) of total metal concentration, with only three samples with very high total concentrations (~60, 000 – 120, 000µg Pb/g) giving recoveries of between 8 and 10 %. The high solubility of Pb is to a large extent, due to the dissolution of Pb from the carbonate fraction, but also the oxide phases. This has the potential to make the metal more environmentally accessible, through for example drinking water, hand-to-mouth ingestion of contaminated soils and sediments and uptake by crops, thus increasing the risk of Pb toxicity in the area.

The amount of manganese recovered is relatively high, ranging from 5.9 to 45.4 % (mean 25.2 %). This is contributed mainly by the metal extracted from the Fe/Mn oxide phases by hydroxylamine hydrochloride which is thought to be specific to Fe/Mn oxides, but also some significant input from the carbonate and to a lesser extent, exchangeable fractions. The mobilization of Zn is highly variable across the samples, ranging from 4 to 74 % (mean, 22 %), without any clear pattern. The result for Ni is in the range of 3.3 to 15.2 % (mean, 10.2 %). The dissolution of Cr in the study area has been found to be very low, yielding recoveries in the range of 0.6 to 20 % with mean value of 3.2 %, reflecting the very low concentration of Cr in all the three fractions. These recovery values obtained for Cr and Ni are not commensurate with their total concentrations in the soils and sediments: the results therefore show that the two metals are bound to less labile fractions. Based on the generally low loss on ignition (LOI, %) obtained for these soils (Waziri, 2012), the organic matter fraction is less likely to be a significant store for these elements; the bulk of their concentration is expected to reside within the residual silicate mineral phases. This is consistent with the findings of previous workers (Morillo et al. 2002; Shikazono et al., 2012) in sediments of Odiel River, Spain and Tamagawa River in central Japan respectively. Burt et al. (2003) found that > 80 % Cr and > 78 % Ni are bound to the residual fraction in soils from the Anaconda and Deer-Lodge Valley, Montana, USA. The low solubility of Ni and Cr in all the samples, points to their low accessibility in the environment and therefore are considered to be potentially of low toxicity in the area.

In spite of the high concentrations obtained for some of the elements, the results show that less than 50 % of the total concentration of most of the elements is easily mobilisable. For example, the percentage of total Cr, Cu and Ni that remained intact in the samples after the three extractions is estimated to be approximately 97 %, 79 % and 93 % respectively. The same for Mn, Pb and Zn is 75 %, 62 % and 78 %. The fact that more than 50 % of the total concentration of all the elements is held within the less labile phases, illustrates the difficulty of assessing the risk posed by toxic elements on the basis of their total concentration in geologic materials. However, Pb and to a lesser extent Cu, is likely to become more mobile in the Anka area in the future due to oxidation of sulfide minerals in the soils. Metal sulphides are said to be easily oxidizable under surficial conditions to soluble sulphides and sulphates (Anju and Banerjee, 2010) that are subsequently mobilized into the environment.

Scanning electron microscopy analysis (Figure 3) has shown that the soils in the area contain fine particles of galena (PbS), which were introduced into the soils through the extraction of gold from lead rich ores. These results confirm that the sequential extraction protocols, despite their apparent shortcomings are better predictors of the environmental and human health impacts of heavy metals and other toxic elements in soils and stream sediments compared to using total concentration alone (Tessier et al., 1979; Ullrich et al., 1999; Singh et al., 1999; Romaguera et al., 2008).
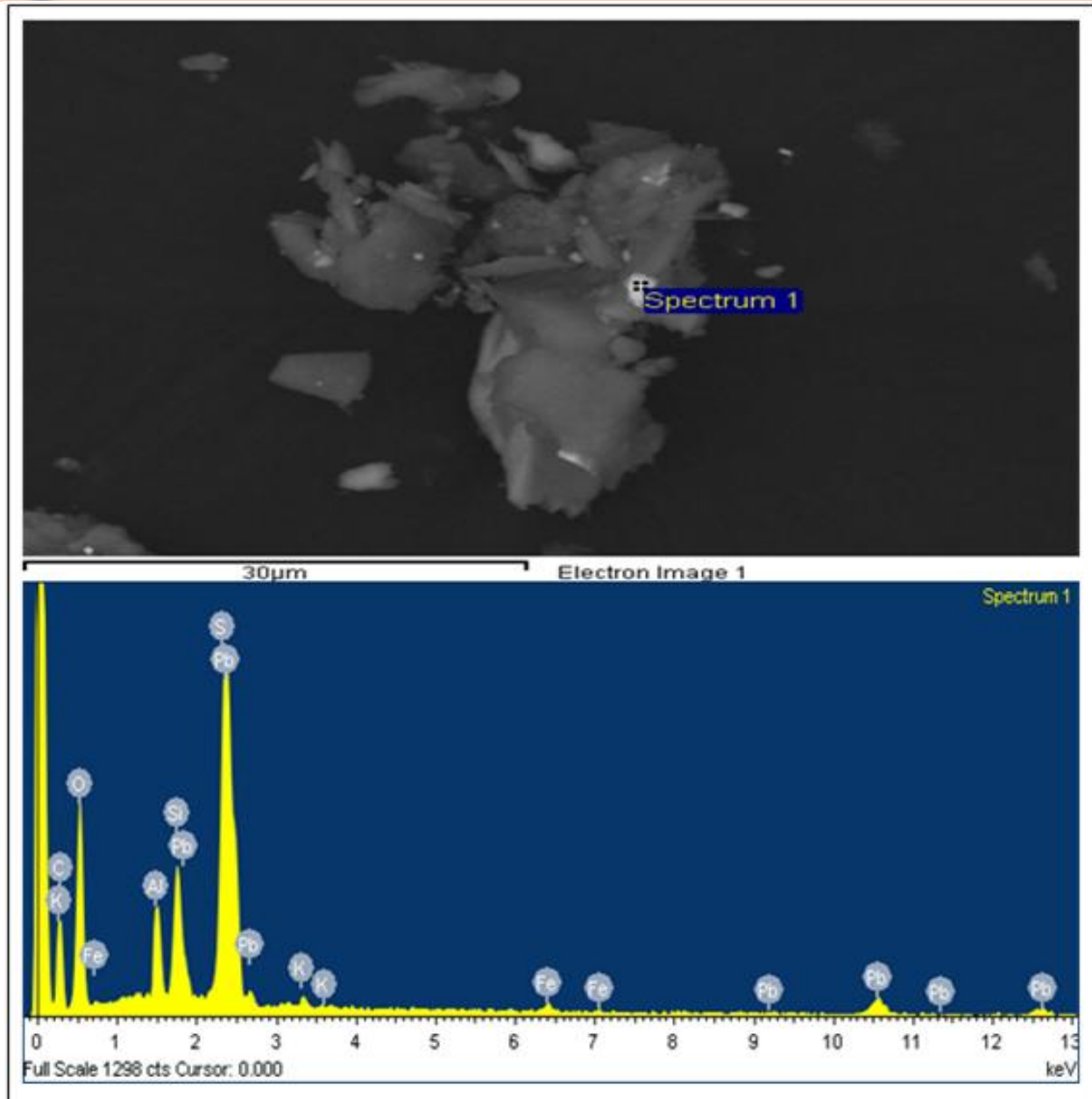
 Figure 3 Scanning electron micrograph and energy dispersive spectra showing a fine galena particle and its chemical signature.

Conclusion

The aim of this paper has been to study the geochemical partitioning of potentially toxic elements (Cr, Cu, Ni, Pb and Zn) in soils and sediments from the Anka area of north-western Nigeria. Unlike most previous studies, this work considered only those portions of contaminant elements associated with the three most labile fractions, namely, the exchangeable, carbonate and Fe/Mn oxide bound fractions.

Most of the elements are generally weakly associated with the exchangeable fraction. This is thought to be on the one hand, a result of the paucity of fine clay particles and exchangeable base cations, which have been depleted by leaching into deeper horizons of the tropical weathering profile and overland runoff. On the other hand, the soils may not have had long enough to interact with contaminant elements, which have only recently been introduced into the environment by artisanal mining to allow for the sorption of trace metal ions onto sorbent particles.

There is, however, a strong association of most of the elements, especially Pb and Zn with the carbonate fraction in soils and sediments of the Anka area. The high concentration of Pb obtained in this step is thought to be due to presence, in the contaminating ores, of highly soluble secondary Pb carbonates. This has a serious implication for the mobility and bioaccessibility of the metal. The Fe/Mn oxides phase showed strong to very strong association with most of the elements. Manganese partitions more strongly into this phase compared to the other elements. The generally strong partitioning of elements into this phase may be an indication of the strong affinity between the Fe/Mn oxides and trace elements, or the presence of secondary oxide minerals in the contaminating ores. However, there is the possibility that the concentration in this step is affected by the co-extraction of portions of elements held within the previous two phases.

In spite of the high concentrations of some of the elements obtained in the carbonate and oxide phases, less than 50 % of the total concentrations of all the elements were extracted across the three extraction steps. This shows that the bulk of the elements is held within, or associated with, the less labile organic matter/ sulfide and residual silicate fractions. The elements associated with these low solubility phases are not likely to be of serious environmental and human health concern over short periods, although some may become more mobile over the long term. However, these results have shown that in spite of earlier criticisms, sequential extraction procedures are useful in inferring the ease with which contaminant elements are mobilized; making them better indicators of the ecological and human health risks of potentially toxic elements.

Acknowledgements

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