Environmental Geochemistry of Soils and Stream Sediments from Anka and Birnin-Gwari Artisanal Gold Mining Areas, NW Nigeria

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Abstract

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By

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The geochemistry of surface soils and stream sediments from two areas in the north-western Nigeria Schist Belt was studied in order to assess the environmental impact of artisanal mining of quartz-gold-sulfide mineralization. XRF determination of total elemental concentration was carried out, along with sequential extraction procedures (SEPs) and *in vitro* bioaccessibility tests using ICP-AES. The results show that the soils in both the Anka and Birnin-Gwari area are highly enriched in silica, zirconium and markedly depleted in base cations due to intense tropical weathering. The results further show that artisanal mining has only caused severe contamination, especially with respect to Pb and Cu, in the Anka area, highlighting the importance of mineralogical differences in the ore deposits. Most trace elements partition strongly into the carbonate and Fe/Mn oxides fractions in samples from the Anka area, indicating possible risk of mobilization under reducing, slightly acidic conditions; the exchangeable phase being the least significant in both areas. Very high bioaccessibility values, which correlate strongly with the sums of the SEP steps, were obtained for Pb, Cu and to a lesser extent, As and Mn in soils of the Anka area and the minimal risk levels and tolerable daily intakes are greatly exceeded. Low pH was found to enhance the bioaccessibility of Pb, Cr and Cu, while rising pH appears to favour the release of As. Only the bioaccessibility of Cr was found to change with the length of extraction time and the ratio of the mass of sample to extraction fluid volume only affects the extraction of As. The results show significant human health risks, mostly in the Anka area due to processing of ores and improper disposal of tailings. Ore processing at the mine sites and an end to using the tailings as construction materials may reduce the exposure of the local population to potentially toxic elements.

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Chapter One

Introduction and Literature Review

1.1 Background

The environmental and health implications of mining have long been studied and scientific literature (e.g, Kelly, 1988; Thornton, 1996; Dudca and Adriano, 1997; Lottermoser, 2007; Plumlee and Morman, 2011) is full of documented cases of damage to the environment and human health directly linked to mining related pollution. Since the advent of civilization, we have continually exploited minerals and rocks for the production of goods, energy and building materials (Hudson-Edwards et al., 2011) with its attendant environmental consequences. Base metal mining results in a variety of wastes, ranging from host rock debris and its associated gangue minerals, dusts from milling, to slags resulting from smelting operations. These, often potentially toxic element (PTE, Alloway, 1995) laden wastes serve as sources of contamination of the environment and provide pathways for human exposure. In many parts of the world, metalliferous mining activities have been shown to lead to heavy metal contamination of soils, sediments and water (Adriano, 1986; Thornton, 1996; Jung, 2001; Bird et al., 2003; Dolenec et al., 2007). Heavy metal in soil is one of the environmental problems resulting from mining on a global scale.

In the Tsofon Birnin-Gwari and Anka regions and many other parts of Nigeria, exploitation of gold and associated sulfide minerals by artisans is a common practice and is thought to introduce associated PTEs into the soils and stream sediments in the area. Environmental problems related to artisanal gold mining are widely reported in the developing world, for example, Ghana (Hilson, 2002; Babut et al., 2003); Ecuador (Appleton et al., 2001) and the Brazilian Amazon (Hinton et al., 2003). As a result, elevated levels of the PTEs may be found in and around the metalliferous mines due to the dispersion of mine wastes down slope by surface runoff, wind action and effluent drainage into nearby soils and open water systems (Jung, 2001). One implication of having excessive levels of these elements in soils is that crops may take them up and pass them through the food chain to human beings. Another route of transmission to humans, especially children, is hand to mouth ingestion, in addition to contamination of surface and groundwater resources and inhalation of dusts. These elements are known to be toxic to plants (Radojevic and Bashkin, 1999; Berman, 1980) and animals if taken up beyond certain limits. They pose potential health risk to local residents, because they can accumulate in the body to cause heavy metal poisoning.

Little, if anything has been done to investigate the environmental impact of artisanal gold mining in general and soil heavy metal concentrations and bioaccessibility in these areas of Nigeria. Most previous work in the area has focused mainly on the geology (e.g. Russ, 1957; Truswell and Cope, 1963; McCurry and Wright, 1977; Ogezi, 1977; Holt et al., 1978; Rahman and Ocan, 1978; Turner, 1983; Fitches et al., 1985) and mineralization (Woakes et al., 1987), especially in relation to gold occurrences or deposits (Russ, 1957; Garba, 2000; 2002; 2003; Danbatta et al., 2009) to mention but a few. Not much attention has been paid to the possible implications of artisanal gold and base metal mining in the area and the effect it will have on the quality of the environment and human health. It is often viewed by many as a small-scale industry, incapable of posing any significant environmental and human health risks. As pointed out by Olade (1987), most studies on the biogeochemical cycling of heavy metals have been within temperate or sub-tropical ecosystems and therefore little is known about their behavior in the semi-arid tropics, such as northern Nigeria. A recent outbreak of acute lead poisoning among rural dwellers of the Anka area, which killed hundreds of children (UNEP/OCHA, 2010) has been traced to activities of the locals who try to extract gold from a mainly galena-chalcopyrite ore deposit. In fact, the work conducted by UNEP reported concentrations of up to 60,000 µg/g lead in the soil of some villages while the Blacksmith Institute (2011) reported soil lead concentrations in seven villages to be in excess of 100,000 µg/g, resulting in blood lead levels in children generally exceeding the internationally acceptable limit of 10 µg/dl (Fig.1).

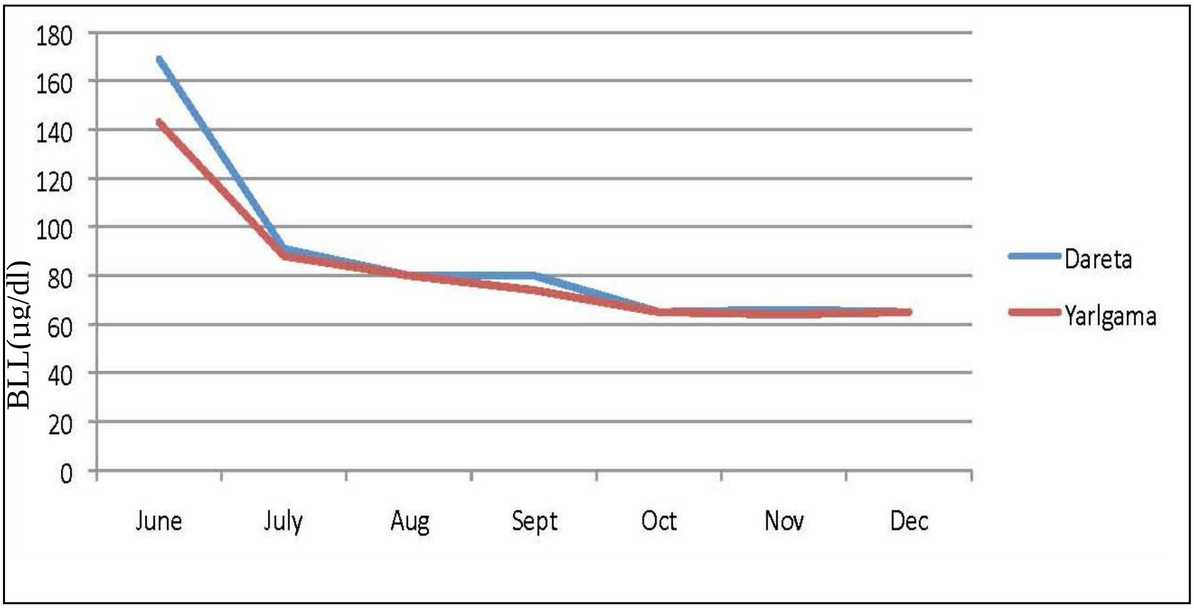

Figure 1 Average blood lead levels (µg/dl) in children in two villages of Anka area, north-western Nigeria contaminated by artisanal gold mining over seven months in 2010 (from Blacksmith Institute, 2011)

It is therefore vital to study the effect of these small-scale mines on the quality of the environment and the possible human health risks incident upon potentially toxic element contamination of soils and sediments in the area. To address this gap, the present work has investigated the geochemistry of soils and sediments from Anka and Birnin-Gwari areas within the north-western Nigeria schist belts, both famous for artisanal gold mining. The work involved the determination of the spatial distribution of the elements in soils and sediments, along with their geochemical partitioning in different solid phases, which is a measure of their mobility. Their relative *in vitro* bioaccessibility was estimated using physiologically-based extraction tests.

1.2 Aim of the work

The aim of this work is to assess the environmental and human health risks posed by artisanal mining in parts of the Nigerian north-west region. The geochemistry of soils and stream sediments in two mining areas was studied in terms of the total contaminant distribution, comparing the concentration with reference values in order to determine the extent of contamination. Geochemical mobility and relative bioaccessibility were estimated using sequential extraction procedures (SEPs) and *in vitro* extraction procedure.

1.3 The Study Area

1.3.1 Location and general geography

The Tsofon Birnin-Gwari study area (Fig. 2) is located in Birnin-Gwari local government area of Kaduna state in north-western Nigeria. It lies between latitude 10^o55’N and 11^o05’N and longitude 6^o45’E and 6^o52’E. The altitude of the area ranges from 518.16 m to 712.28 m above mean sea level and is traversed by the Birnin-Gwari/ Funtua road. The area, which covers about 226 km^2, is characterized by granitic inselbergs and roughly north-south trending ridges, often in conformity with the general trend in the Nigerian Basement Complex. It is drained mainly by the Kureta and Gora Rivers which are fed by a number of other tributary channels such as the Baigado and Abuya Rivers (FSN, 1967).

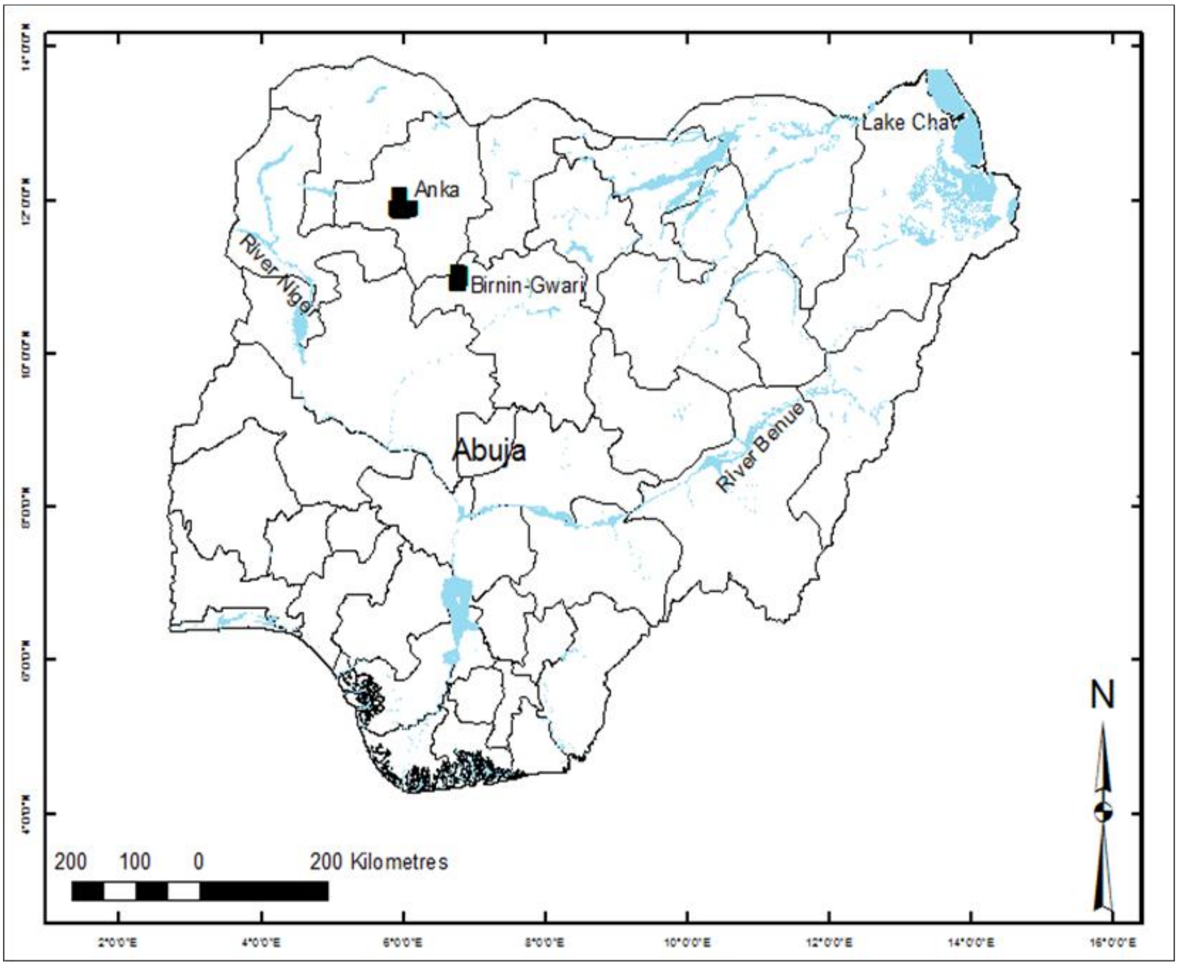

Figure 2 Outline map of Nigeria showing the location of the two study areas. Detailed maps of the areas are presented in Figure 8 (modified from DivaGIS).

The second site which lies to the northwest of the Birnin-Gwari site (Fig.2) and covering about 990 km^2 is in the Anka local government area of Zamfara state also in the north-western part of Nigeria. It falls between latitude 11^{o}51’N and 12^{o}08’N, and longitude 5^{o}51’E and 6^{o}08’E and is characterized by generally gentler relief compared to the Tsofon Birnin-Gwari area. The main surface water body in the area is the Anka River, which lies about a kilometer to the north of the town from which it derives its name, but there are numerous seasonal streams or channels which cut the entire landscape that feed into the main river and many are used as sources of water for domestic use, irrigation and livestock watering, especially during the wet season. A small number of these streams, such as the one at Abare village were observed to remain running well into the dry season. 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.

1.3.2 Geology of the study area

1.3.2.1 Regional setting

The study area is in the schist belt of the Nigerian basement complex which is part of the Pan-African mobile belt, sandwiched between the West African craton and the Congo Craton. This Neoproterozoic to early Phanerozoic belt is covered in many places by Cretaceous and younger sedimentary rocks. It has been described by McCurry and Wright (1977) as a system of synclinorial belts of low-grade metasediments downfolded into high-grade gneisses and migmatites, the whole intruded by batholitic granites. This was further explained by Woakes et al., (1987, Fig. 3) who summarized the major geologic units in the area to include a polycylic metamorphic migmatite- gneiss basement, with entrained supra-crustal remains, ranging in age from Archaean (2700 Ma) to Palaeoproterozoic (2000 Ma). This suite of rocks which constitutes about 60% of the Nigerian basement (Rahman and Ocan, 1978) consisting of gneisses, migmatites and quartzites is of medium to high grade amphibolite facies metamorphism. It is followed upwardly by the low- grade, deformed schist belts developed mostly in the western flanks of Nigeria. These upper Proterozoic generally north-south trending belts, have been infolded into the migmatite- gneiss basement complex. Metamorphism in these belts is generally of low grade, falling within the green-schist facies and characterized mainly (Turner, 1983) by schists, phyllites, banded iron formations, carbonate rocks and mafic metavolcanics which are now in the form of amhibolites and meta-conglomerates. These and the migmatite-gneiss basement have been cut by Pan-African granites. The syn- to late tectonic igneous intrusions include mainly granites, granodiorites, diorites and some gabbro, syenites and charnokites. Some unmetamorphosed volcanic and hypabyssal rocks dated as late Pan-African by McCurry and Wright (1977) overlie or intrude the basement rocks in the Anka area of north-western Nigeria.

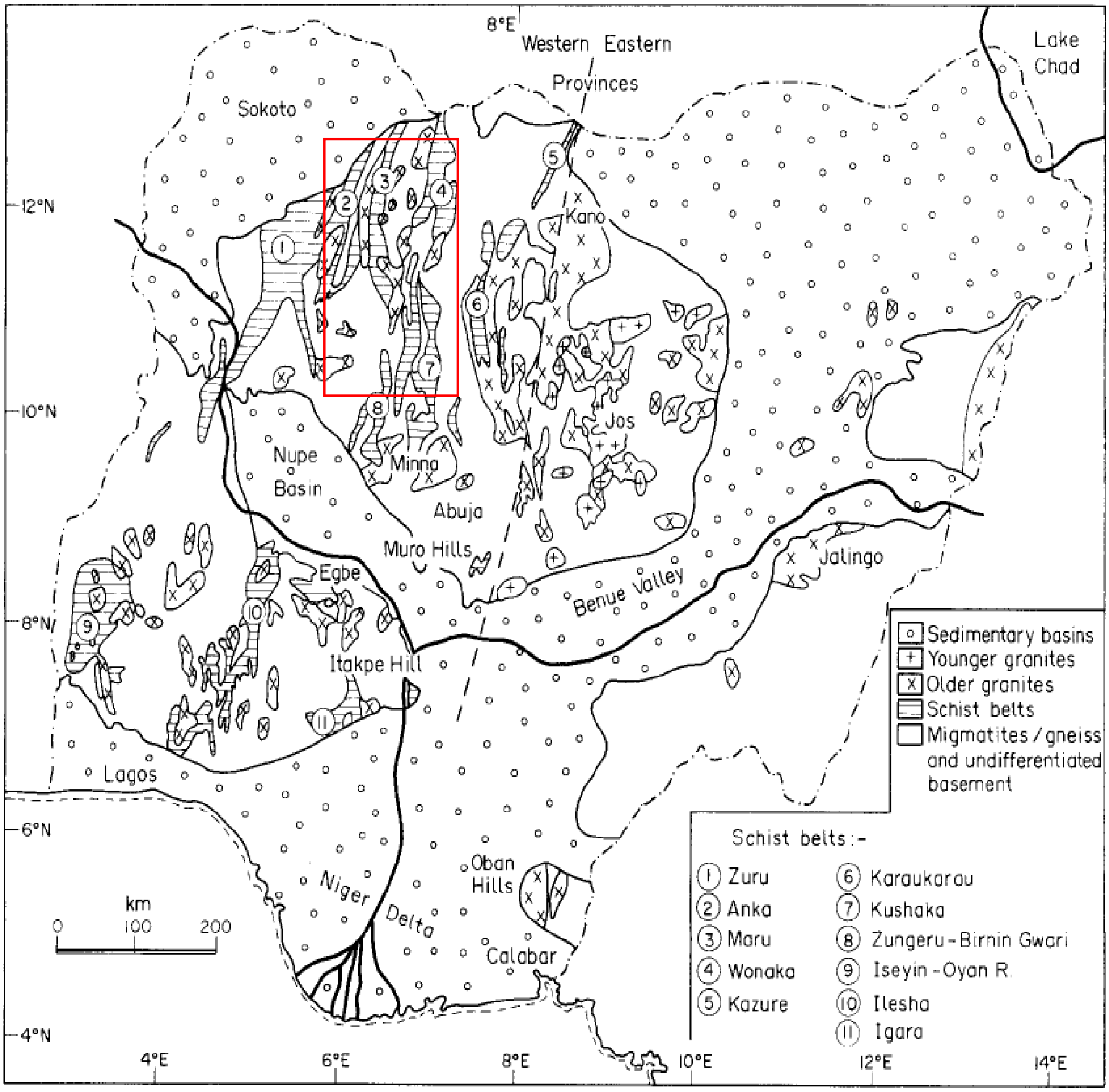

Figure 3 Outline geological map of Nigeria. The Anka (2) and Kushaka (7) Schist Belts in the box at the top left have been described in this work as the study sites. Reproduced from Woakes et al. (1987) with permission from Elsevier Limited, Oxford.

1.3.2.2 Local geology and mineralization

The study sites for this work lie within the Anka and Kushaka schist belts of north-western Nigeria. These belts although of different ages, have generally similar lithologies (Fig. 3&4a-c) and mineral paragenesis. They have both, like many other similar belts in Nigeria and the entire West African region been the focus of artisanal gold exploitation for several decades.

The Anka schist belt is the more westerly of the two and Holt et al. (1978, in Turner 1983) has summarized the lithology in the area to include metaconglomerates, sandstones, slates, phyllites and acid violcanics. 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. Fitches et al. (1985) report that the belt is composed chiefly of poorly exposed, homogenous quiet-water argillites, associated with coarse clastics and a province of acid-intermediate volcanic and intrusive rocks. The coarse clastics are said to generally overlie the argillites, but are intercalated with the latter in the lower parts of the coarse clastic layers (Fitches et al., 1985). The coarse clastics in the form of green and purple grits interbedded with shales and siltstones predominate in the eastern flanks of the belt, whereas in the west, phyllites are the dominant lithology (Turner, 1983). The age of this belt is not very certain, but Turner (1983) has reported a Rb/Sr date of 450±50Ma obtained by Ogezi (1977) as placing the metamorphism in the late Pan-African.

As with the other schist belts in the western part of Nigeria, gold and sulfide mineralization have been identified and exploited in the Anka area. 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). The gold mineralizing fluids were interpreted, based on Na_2O/Al_2O_3-K_2O/Al_2O_3 discrimination diagram and inter-lithophile elements ratios to be of metamorphic origin (Danbatta et al., 2009). The mineralized concordant veins are generally short, not exceeding half a kilometre of strike length and 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, mostly galena which has been observed during field work and also chalcopyrite.

The Kushaka schist belt on its part is characterized by a number of curved schist belts. It is underlain mainly by semi-pelitic biotite muscovite schist, along with phyllites, metasiltstones and graphitic schists (Turner, 1983). Interbedded with these units is a banded iron formation and the thick amphibolites in part of the area have been interpreted by Turner as indication of large volcanic accumulation. Truswell and Cope (1963) have described the rocks in the area as lying in a number of N-S trending isoclinal fold structures; pelitic metasediments been the dominant lithology, with the presence however of both psammites, pelites and amphibolites. The metasediments in this area, like those in the other belts have been extensively invaded by granites and granodiorites of the Pan-African series and the belt has been placed by Turner (1983) in the Kibaran (1100 ± 200 Ma). The granites were observed to form very prominent geomorphological features especially in the southern part of the study area, while to the north-west, the older migmatite-gneiss basement outcrops. According to Garba (2000) the entire sequence in this area has been cut and displaced by the NE-SW trending Kalangai transcurrent fault.

Figure 4 Some common rock types in the study area: (a) slumping schist blocks on the banks of Kureta river near Tsofon Birnin-Gwari, showing original bedding; (b) outcrops of the older granites near the village of Jenruwa, south of Tsofon Birnin-Gwari and (c) schist and quartzite exposed in artisanal mine east of Dareta village in the Anka area (Photos by author).

The Tsofon Birnin-Gwari area which is in the Kushaka schist belt is associated with extensive mineralization. Woakes and Bafor (1983) have named it as one of the areas associated with gold mineralization within the Nigerian schist belt. Elueze (1981a) and Bafor (1981) reported the presence of sulphide minerals in the schist belts. The Tsofon Birnin-Gwari (TBG) gold-sulphide-quartz reef mineralization is the most extensive in Nigeria with a strike length of over 7 km and the mineralization is hosted by graphitic and micaceous phyllites of the Kushaka schist belt of the northwestern Nigeria Pan-African (600 ± 150 Ma) terrane (Garba, 2002). The mineralization appears to lie in several narrow, near parallel shear zones, exploiting strong vertical foliation parallel to the axial planes of the fold structures (Garba, 2000). The mineral deposits, especially gold, have over the years been exploited by small-scale mining outfits. The Tsofon Birnin-Gwari area has had active gold mines since the 1930s and was reported to have yielded over 600 ounces (over 17kg) of reef and alluvial gold between 1932 and 1940 using the cyanide process (Russ, 1957). This, and the neighboring Kwaga site are still been exploited by artisanal miners. Gold in this area is generally associated with pyrite and minor sphalerite, chalcopyrite, pyrrhotite, galena and magnetite (Garba, 2003), with quartz, potassic feldspar and carbonaceous matter constituting the gangue minerals.

1.4 Heavy Metals in the environment

One of the major environmental problems in parts of the world at present is the high levels of heavy metals in soils and other components of the environment. The term “heavy metals” describes a group of metallic elements and metalloids with considerably high densities- typically exceeding 6g/cm^3. Elements such as arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc have been shown to be toxic to both human beings and plants, in spite of some of them being essential elements.

1.4.1 Routes of entry of heavy metals into soil

There are various ways by which heavy metals find their way into soils. According to Ward (1995), soils and sediments are considered as sinks for trace elements (including heavy metals), and therefore they play an important role in the environmental recycling of elements. The routes of entry have been classified into two broad categories-namely, natural and cultural (anthropogenic).

Naturally, heavy metals are introduced into soils through the weathering of rocks. According to Olade (1987), the overall abundance of trace elements in surficial materials depends initially on their concentrations in bedrocks and mineralized zones. Rocks are aggregates of minerals and the minerals are composed of certain elements including heavy metals. Weathering processes release these metals from the mineral systems and they end up in the environment as metal solutions in surface water, solids, and suspensions or adsorbed to soil particles (Fifield, 1995). Soils overlying certain rock types are generally richer in heavy metals. For example, the chromium content of soils overlying chromite bearing rocks (serpentinites) is higher than other soils, and a similar situation exists for lead in galena rich areas (Radojevic and Bashkin, 1999).

Cultural or anthropogenic sources of heavy metal pollution are linked to the activities of man. Mining is one such human activity which introduces metals into the environment. Because of the large volumes of materials handled, mining and smelting activities give rise to varying degrees of contamination of soil, air and water that lead to perturbations in the cycling of metals in the surficial environment (Thornton, 1996). Ciccu et al. (2003) have pointed at acid mine drainage, tailing embankments, mining rock dumps and metallurgical waste piles as some of the sources of pollution, posing serious threats to the environment.

The gradual abandonment of mines and the lack of maintenance or failure to adopt appropriate safety measures have increased the risk of pollution spreading to areas far removed from the mining sites. Mining introduces contaminants, including PTEs into the environment through low grade ore, overburden and barren rocks heaps; tailings heaps and acid mine drainage, especially where sulfide-bearing mine tailings are involved (Anju and Banerjee, 2010).

The type and abundance of contaminants from mines is directly linked to the geologic characteristics of the deposit being mined and type of host rock, local climatic conditions and the processing methods and chemicals used (Lottermoser, 2010; Plumlee and Morman, 2011). For example, in humid environments acid mine drainage (AMD) is generated by the oxidation of sulfide-bearing minerals in mine wastes exposed to weathering conditions, resulting in low quality effluents characterized by acidic pH and a high level of dissolved metals (Razo et al., 2003).

Figure 5 Pathways of contaminant elements into the environment from artisanal mining in the study area: a; abandoned mine pit, b; mineralized rock moved in sacks to processing sites, c; crushing and grinding mineralized rock in order to extract ore, and c; using gravity method along a stream channel to separate minerals in a slurry of powdered rock (Photos a, b and c are by the author; d, courtesy of Kabir Isa).

In artisanal gold mining areas of the world, the indiscriminate use of amalgamation to separate gold from associated minerals has been widely blamed for the introduction of mercury into the environment (Appleton et al., 2001; Hinton et al., 2003; Babut et al., 2003, Wu et al., 2011). In drier climates however, the problem is not much about AMD, but the movement of contaminants through fluvial and aeolian processes (Razo et al., 2003). Artisanal mining and beneficiation methods, such as those shown in Figure 5 (a-d) above are often very crude and under little or no regulation at all, leading to widespread improper disposal of mine wastes and contamination (Hilson, 2002).

1.4.2 Sediment and contaminant transport

Sediment transport is an important means through which contaminants are moved mostly in clastic form, but also hydromorphically from source to areas where their ecological and human health risks are felt. Erosion and transport of contaminated soils ensure that contaminants are taken to areas far away from their source environment (Breshears et al., 2003) and this has implication for human exposure pathways. The sparse vegetation cover in semi-arid environments, such as the study area for this work, which is, in itself a result of scant precipitation in the area, provides little, if any protection to soils against the erosive action of wind and water.

Both water and wind transport operates in much the same way, involving in the first instance detachment of soil particles by water or wind action. The detached particle is subsequently transported either as overland flow or aerosol movement and eventually deposited when the water and wind velocities drop (Breshears, 2003). In semi-arid environments, the process is event-based, often triggered, especially for water transport, by occasional intense weather phenomena such as a storm, although wind transport may be a more frequent occurrence compared to intense rainfall events.

Fluvial transport in this area is expected to be dominated by overland runoff during rainfall. Rainfall may not be regular in the area, but when it occurs, it is very intense and the erosive effectiveness of the rain is exacerbated by the intensity and the sparse vegetation cover of hill slopes: rapid run off results even from low rainfall events (Tooth, 2000). The dominance of overland run off makes it easier to move particles down slope and into temporary storage within the mostly ephemeral streams that are common features of the area. Once within the ephemeral channels, contaminated particles are further transported downstream either as bed load or as suspension within the water column depending on the energy of the transporting medium, particle characteristics and the nature of the stream bed. These streams carry very high sediment loads due to abundant supply from overland run-off and bed scouring and the concentration of sediment in the water increases as the flood discharge increases (Mather, 2007).

Figure 6 An ephemeral stream near Tsofon Birnin-Gwari: (a) dry stream channel; (b) the same channel upstream of location (a) few days later following some rainfall events. Rocks and vegetation on the stream bed provide the roughness needed for turbulent flow, thus enhancing sediment entrainment (Photos by the author).

High energy, turbulent flows over rough stream beds (Fig. 6) are better able to keep more particles, especially medium to fine fractions suspended within the water column and therefore transported longer distances compared to quieter laminar flow which moves sediments mainly by traction. The streams often overflow their banks, and when the energy of the transporting medium wanes, deposit the suspended fine contaminated load along floodplains as permanent deposits where they impact on soil, surface and ground water quality (Hudson-Edwards, 2000), or until they are recycled by future flood events. According to Razo et al. (2004) heavy rain falls during short rainy seasons contribute largely to the dispersion of pollutants in a very extensive area, in this way impacting not only streambeds and water bodies but also agricultural fields and urban soils. Physical dispersion and dissolution of minerals from waste rock and tailings repositories are very important pathways of contaminants (Fig. 7) into surrounding environments (Lottermoser and Ashley, 2005; Lottermoser et al., 2005) with the possibility of long term off-site release of contaminants (Lottermoser, 2010).

Wind transport has the potential to move contamination over longer distances distributing it over wide areas, due on the one hand, to the multidirectional nature of wind flow and on another, the ability to move finer particles vertically as a suspension (Breshears et al., 2003), especially in drier climatic regions. According to EPA (2005), the amount of a contaminant to be re-suspended by wind erosion is a function of the moisture content of the soil, vegetation cover and wind velocity; along with particle size, contaminant concentration in the soil and the areal extent of the contamination.

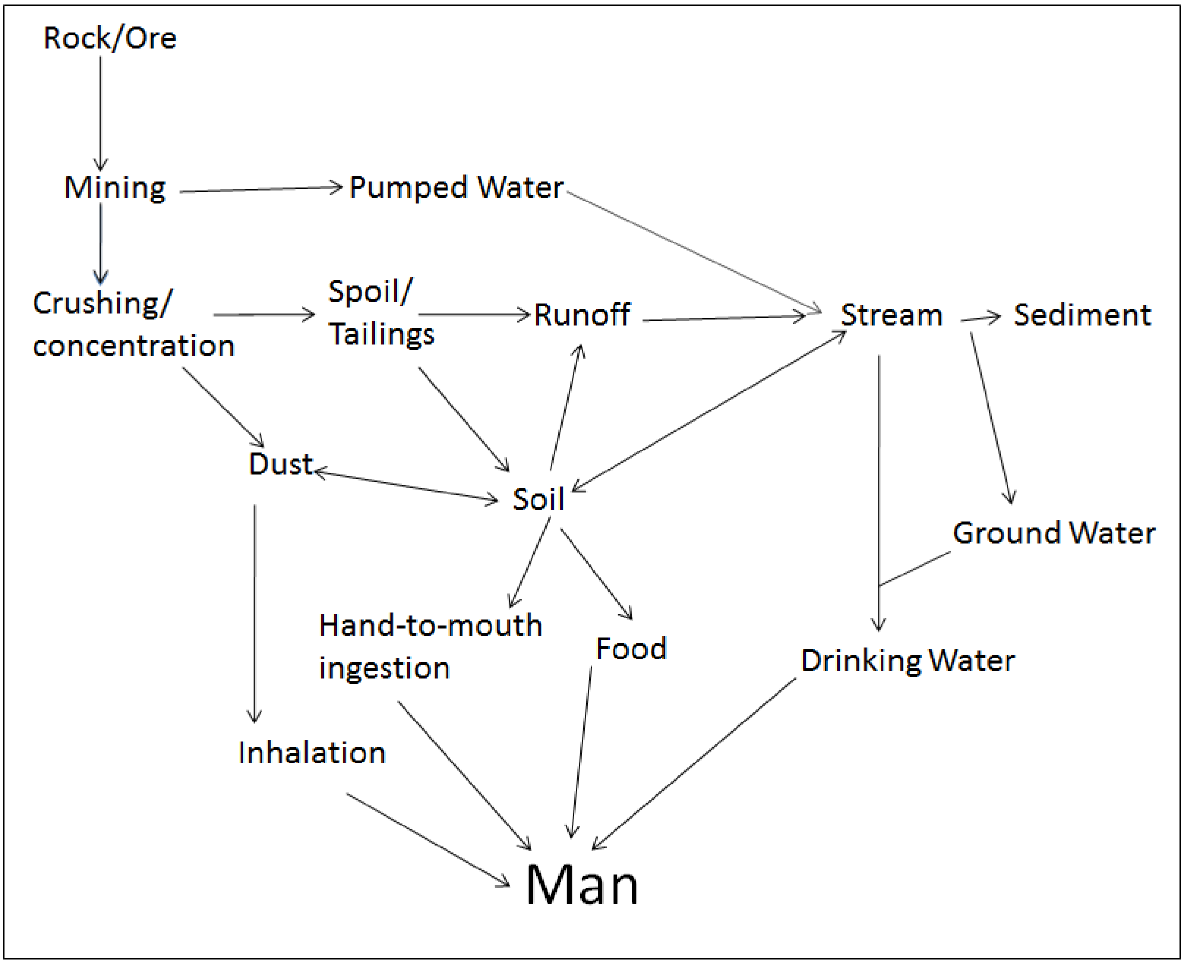

Figure 7 Transport to the environment and main human exposure pathways for potentially toxic elements in the study area (modified from Kelly, 1988)

Irrespective of the transport mechanisms, mine-related contaminants will almost inevitably get to populations living in an area through a number of pathways (Fig.7). Plumlee and Morman (2011) have summarized the pathways to include hand-to-mouth ingestion, inhalation and consumption of food grown on contaminated soils as well as drinking contaminated water. Exposure to heavy metals is normally chronic due to food chain transfer, however acute poisoning through ingestion or dermal contact though rare is possible (USDA, 2000). Hand-to-mouth ingestion and inhalation of fine particles have been blamed for recent acute lead poisoning in villages contaminated with mine wastes in Anka area of north-western Nigeria due to extensive dispersion of lead dust in the villages during grinding of the ore into fine powders (UNEP/OCHA, 2010). This is likely to continue for a long time, in spite of remediation attempts made by the authorities because the villagers reportedly use the contaminated powders as building materials for their dwellings, thus turning their homes into contaminant repositories. This is similar to the scenario reported in Kabwe, Zambia (WMC, 2006; Brannan, 2008 quoted by Plumlee and Morman, 2011) where the soils and sediments in the city were heavily contaminated with lead due to mining and processing of lead-zinc ores, leading to serious lead poisoning in children.

1.4.3 Mobility and Toxicity of heavy metals

The geochemical mobility of heavy metals is controlled by a number of factors. Forstner (1987) has identified pH, redox potential and the presence of organic chelators as environmental conditions controlling the movement of heavy metals. For example, in low pH soils and sediments, heavy metals are thought to be more mobile and therefore their bioavailability and toxicity is enhanced. Soil type plays an important role in this regard. The metals are more easily transported and taken up by plants in coarse grained soils than in the finer grained types (RCEP, 1996). The low mobility rate of metals in fine grained soils such as silt and clay may be due to the soils organic content and the net negative charges on the soil particles. According to Singh et al. (1999), metals are generally believed to associate more with finer grained soils due mainly to sorption, co-precipitation and complexing of the metals on particle surfaces and coatings. Smaller grains have a larger surface area: volume ratio and therefore show higher concentrations of metals. Clay minerals may contain low levels of trace elements as structural components but their surface properties (area and electrical charge) play a vital role in regulating the buffer and sink properties of soils (Ward, 1995). Sharma et al. (2000) have also reported positive relationship between metal concentration and smaller soil particles, with the silt-clay fraction showing the strongest correlation.

Heavy metals exist in different chemical forms within soils and sediments. Pueyo et al. (2004) have explained that the forms in which the metals exist (speciation) influences their mobility and toxicity compared to the total element content. It has long been established for example that mercury is more toxic in its organic form [CH_3Hg^+ or $(CH_2)_2Hg$]. This has therefore led to a paradigm shift from simple determination of total metal concentration to more detailed fractionation studies about the physiochemical forms of elements which is required to understand their environmental behavior, including mobility, pathways and bioavailability (Anju and Banerjee, 2010). The well-known Minimata accident in Japan was linked to the consumption of methyl mercury in shell fish. Chromium also behaves in a similar manner with the hexavalent form of the metal being considered to be more toxic and carcinogenic than the trivalent form because it is more readily absorbed and transported across cell membranes (Plumlee and Ziegler, 2004).

1.4.4 **Sequential Geochemical Extraction Tests**

Knowledge of total metal concentration in environmental matrices alone is not enough in assessing the bioavailability, mobilization and the human risk in an environment. Neither does the total concentration provide a good indication of the levels of metals potentially available to plants (Ullrich et al., 1999). In order to assess the possible effects of heavy metals and their complexities in soils, it is necessary to establish the forms in which the elements exist in the soils. In the last few decades, attention has shifted from determination of total or near total metal contents in soils to techniques aimed at quantifying the metal distribution among solid chemical phases, such as exchangeable, carbonate, iron-manganese oxides and the organic fractions.

Sequential extraction protocols (SEPs) have been used with some success to determine the geochemical partitioning of metals in soils, the sources of the metals and to estimate the potential environmental hazard (Kuo et al., 1983; Hickey and Kittrick, 1984; Adamo et al., 1996; Henderson et al., 1998; Li and Thornton, 2001; Martley et al., 2004) and in sediments (Tessier et al., 1979; Singh et al., 1998) among others. However, many workers have pointed out some factors that limit the interpretation of sequential extractions. Martley et al. (2004) summarized these factors as follows:

- Limited selectivity of extractants, such that metals bound to a particular phase may be partially dissolved in different leaches;
- Possible redistribution of trace elements among phases during extraction with a particular physiochemical phase;
- Influence of soil type and grain size on the efficiency of the extraction protocols;
- Results are likely to be influenced by the choice of reagents, extraction time and ratio of extractant to sample; and
- High metal content in a sample may lead to saturation of the extractant, thus, leading to incomplete extraction.

1.5.5 *In Vitro* Extraction Tests

In vitro bioaccessibility tests (IVBA) are inexpensive, physiologically-based extraction tests (PBET) designed to estimate the bioaccessibility of elements along exposure pathways (Morman et al., 2009). This is achieved by measuring the geochemical reactivity of the materials in simulated body fluids such as saliva, lung fluids and gastric juices or blood plasma. It is used as a proxy for the more complicated, expensive and often ethically constrained measurements of bioavailability using *in vivo* methods involving the use of animal or human subjects.

The term bioaccessibility in relation to human exposure by ingestion has been defined by Ruby et al. (1999) as the fraction of a potential toxicant in earth materials that becomes solubilized in the stomach or lungs, thus, becoming available for absorption. This is closely related to geoavailability, which is the portion of an element's total content in an earth material that can be liberated to the surface or near surface environment through mechanical, chemical or biological processes (Morman et al., 2009). The two concepts are related to the susceptibility and availability of the resident mineral phases to break down through chemical weathering processes, which then mobilize the elements and release them into the environment. For a given toxicant such as a potentially toxic element, the total concentration in an earth material is far more than the quantity eventually absorbed into the circulatory system of a subject (Plumlee and Ziegler, 2004). This means that, bioavailability < bioaccessibility < total concentration of a contaminant in an earth material.

Several methods of performing the *in vitro* studies have been reported in the geochemical literature. Some advanced the use of complex fluids to simulate gastric fluids. For example, Medlin (1997) used a fluid containing pepsin, admixed with citric, malic, lactic, acetic and hydrochloric acids. The method of Drexler and Brattin (2007) which was adopted by Morman et al. (2009) advances the combination of concentrated hydrochloric acid and glycine in deionised water. The approach of EPA (2008) involved combinations of sodium chloride, pepsin with hydrochloric acid and sodium bicarbonate, bile salts and pancreatin for the stomach and intestinal phases respectively. This two stage procedure earlier reported by Cave et al. (2006) was adopted by Button et al. (2009), while investigating the risk to humans at arsenic contaminated sites at a former mine at the Devon Great Consols, southwest England. However, the EPA (2008) in a subsequent study appeared to question the necessity of using the complex fluids. They argued that when the bioaccessibility of a series of test substances were compared using 0.4M glycine buffer at (pH 1.5) with and without the enzymes and metabolic acids, no significant difference was observed. They therefore concluded that the simplified buffer employed in the procedure is appropriate, even though it lacked some constituents known to be present in gastric fluids and that is the method adopted in this work.

1.5 Thesis outline

In this Chapter, the problems associated with artisanal small-scale exploitation of mineral resources have been examined, including a review of pertinent literature. The focus has been on two areas in the NW Nigerian Schist Belt where gold, often associated with sulfides in quartz veins is won by local artisanal miners, with attendant environmental and human health consequences. The work progresses in Chapter 2, with a detailed description of the research methods used, including fieldwork and laboratory experiments. In Chapters 3, 4 and 5, the results of laboratory experiments have been presented and discussed, beginning with the bulk soil and sediment geochemistry and continuing through geochemical partitioning studies and ending with *in vitro* bioaccessibility results. Finally, the main conclusions drawn from the results of this work are presented in Chapter 6, along with identified possible future research areas.

Chapter two

Methodology

2.1 Introduction

In this chapter, the methods employed in this work are outlined. Fieldwork was conducted in two stages, first during April and May, 2010 in the Birnin-Gwari area and subsequently in December of the same year in Anka area. On both occasions, field reconnaissance was carried out, followed by the collection of top soil and stream sediment samples. The samples were analyzed for their elemental and mineralogical contents using a variety of techniques, including x-ray diffraction (XRD) spectrometry, scanning electron microcopy (SEM), x-ray fluorescence (XRF) spectrometry and inductively coupled plasma-optical emission (ICP-OES) spectrometry. Figure 9 summarizes the main analytical methods used in this work. This is in addition to drying, pH measurement and the determination of organic matter content in the form of loss-on-ignition (LOI).

2.2 Fieldwork

(a) Field reconnaissance was carried out to improve on the information derived from the desk study; and

(b) Sample collection using a pre-determined programme. This took the form of simple random sampling along topographic lows and flood plains of streams. Top soil and sediment samples were collected from 0 to 15cm using a plastic trowel and placed in plastic self-seal bags. Care was taken to exclude surface vegetation, fresh litter, roots and rock fragments (Kelly and Hudson, 2007; Salminen, 2008). The method is a combination of exploratory and random sampling, where discrete grab samples were collected, generally aimed at checking the presence or absence of contamination (Swyngedouw and Crepin, 2008). At each sampling point, three samples were collected at the apices of a roughly equilateral triangle with sides one meter long and subsequently mixed up to make a composite sample. This was done in order to get a representative sample and check against local variability. Control (background) samples were collected from a nearby area, adjudged to be unaffected by the contamination (pristine) but with similar lithology and soil type as the study site. In the Birnin-Gwari area, five samples were collected from termite mounds (or ant hills) which occur in abundance within the study area. The aim is to gain knowledge of the distribution of different chemical species at depth since the burrowing animals have brought materials from deeper horizons of the soil or even bedrock. Each termite mound was sampled by collecting small pieces at different levels and mixing them to make a composite sample. In all, a total of 131 soil and sediment samples were collected, comprising of 86 from Birnin-Gwari and 45 from Anka area.

The location of each sample was indicated on a topographic base map of the area and geographic coordinates in the form of Latitude and Longitude were recorded using hand held global position system (GPS). These were subsequently used to produce the sample location maps (Fig. 8a&b) using ArcGIS (ArcMap^{TM}10.1) for Desktop from Environmental System Research Institute (ESRI, 2012). Details of the coordinates and sample description are presented in Appendix 1.

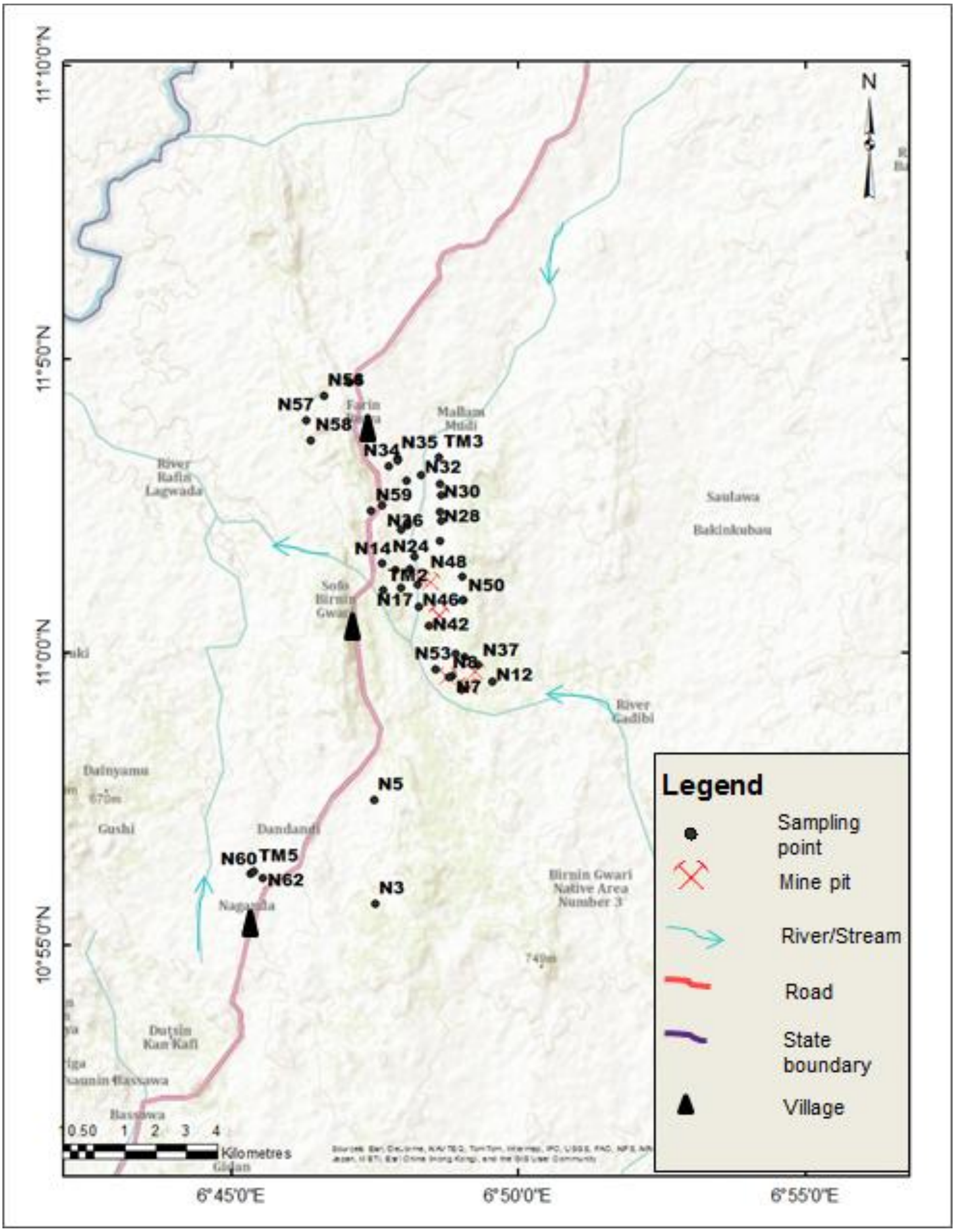

Figure 8a Map of Birnin-Gwari study area showing sampling sites and some artisanal mine pits. The location of this area in Nigeria has been indicated in Figure 2 (modified from ESRI, 2012).

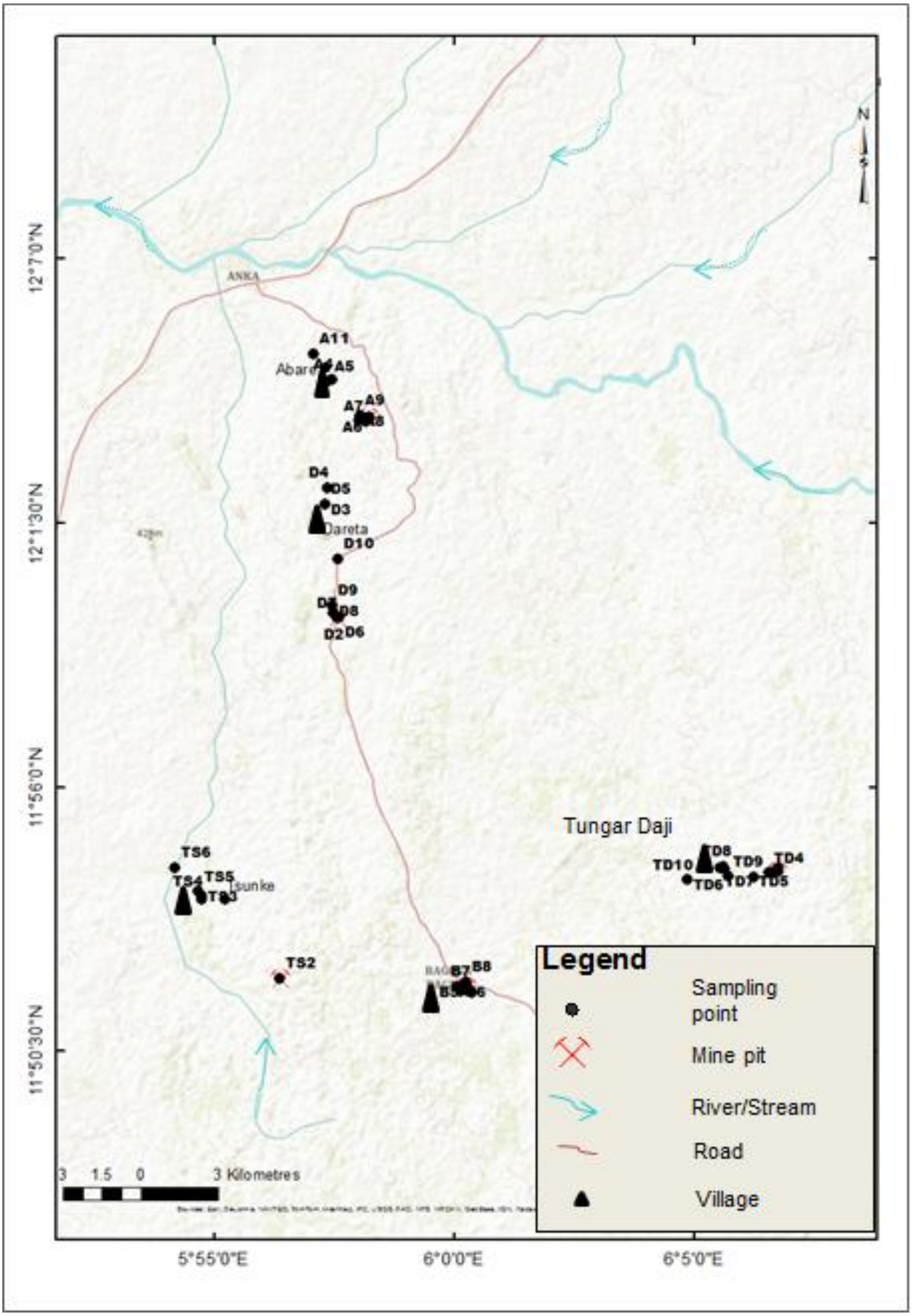

Figure 8b Map of the Anka study area showing sampling sites and location of some artisanal mine pits. The location of this area in Nigeria has been indicated in Figure 2 (modified from ESRI, 2012).

2.3 Sample preparation

2.3.1 Drying

The samples were subjected to a two stage drying process. To make the soil and sediment samples ready for sieving, they were air dried at room temperature. Samples were placed in plastic containers labeled with sample numbers and air dried in the laboratory. The second phase of drying was done on the sieved material in order to further expel moisture and make them suitable for final preparation and analysis. The samples were placed in disposable foil type containers and oven dried over night at a temperature of about 50^{o}C.

2.3.2 Disaggregation and sieving

The dried samples were subsequently disaggregated by pressing with a plastic gardeners scoop inside the containers. This was done in order to break lumps of soils, especially for those samples which were very wet when collected. It was followed by removal of rock fragments, pebbles and organic debris from the samples prior to sieving. 2 mm and 63 µm stainless steel sieves were used to sieve the samples by closing the lid and manually shaking the assembly for about 3 minutes until all the <63 µm fraction has been received in the pan. The finer fraction (<63 µm) was then scooped from the receiving pan into clean, self-seal poly bags and labeled appropriately. Prior to analysis, the sieved test material was further dried overnight in an oven at 100^{o}C in order to eliminate any moisture content. Between samples, the sieve, pan, lid and scoop were thoroughly cleaned, first using a plastic brush followed by wiping with clean, dry laboratory blue rolls. The aim of this was to eliminate or minimize cross sample contamination.

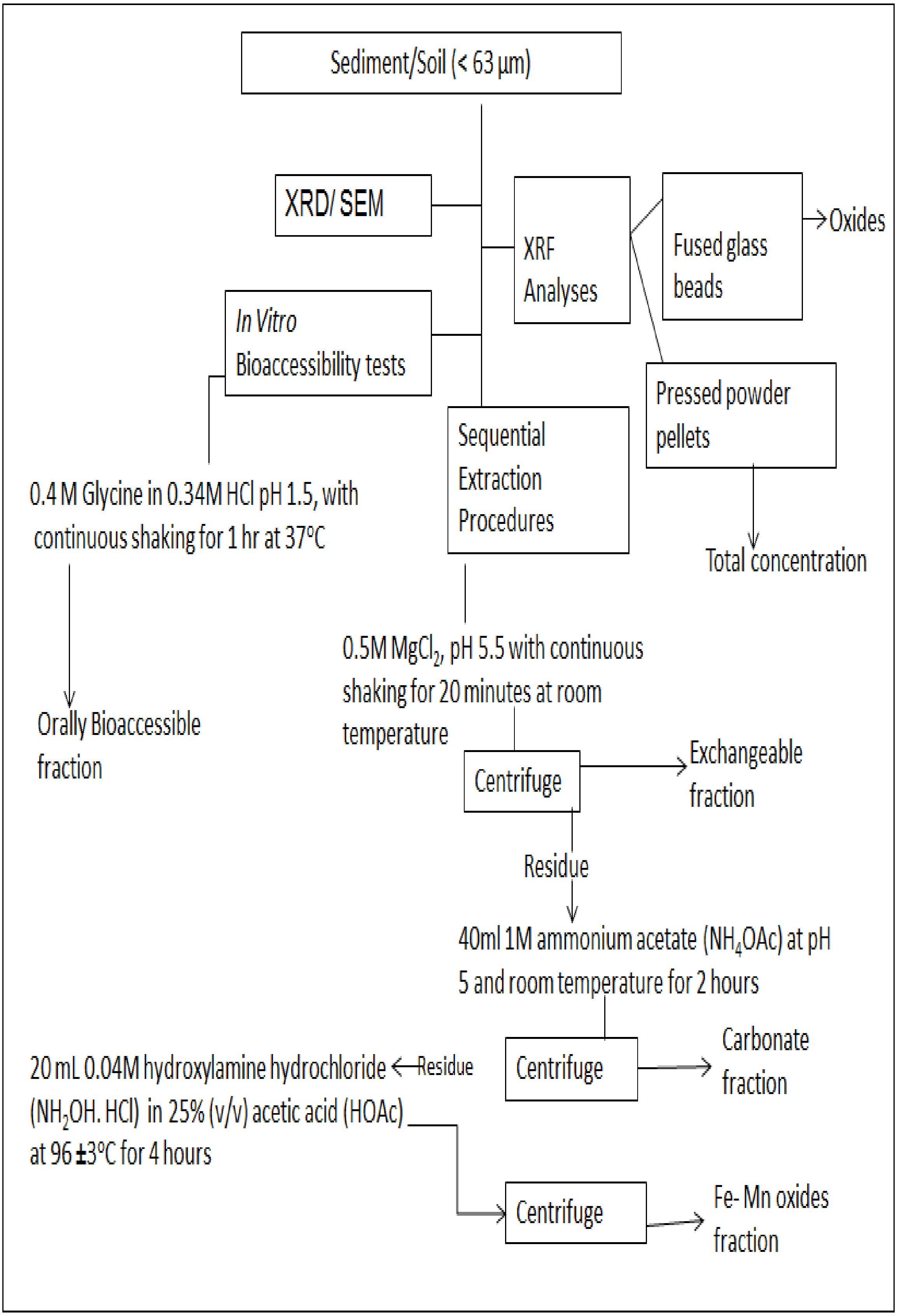

Fig 9 Summary of the analytical procedures used in this work.

2.4 Determination of pH

1g of soil was weighed into a beaker. To this, 10ml of milliQ water was added and stirred vigorously. The mixture was allowed to stand for 30 minutes until supernatant had formed. The pH meter was calibrated using two point calibration with buffer solutions of pH 7 and 4. The electrode was then immersed in the supernatant and measurement taken. Care was taken to ensure that the electrode was not in contact with soil, since this could cause an error of up to 1 pH unit (Radojevic and Bashkin, 1999).

2.5 Determination of organic matter content

The weight of an empty, clean, and dry porcelain dish (W_P) was determined. A portion of an oven-dried (100^{o}C) test material was placed in the porcelain dish and the weight of the dish and soil specimen (W_{PDS}) determined and recorded. The dish was then placed in a muffle furnace and the temperature gradually increased to 300^{o}C (J. Andrews, personal communication). The specimen was left in the furnace overnight. The furnace was the switched off and the specimens allowed to cool to room temperature. The weight of the dish containing the ash (burned soil) (W_{PA}) was determined and recorded.

The loss-on-ignition (LOI) which is a proxy for organic matter content of the sample was then calculated as follows (Reddy, 2002):

Weight of the dry soil, $W_D = W_{PDS} - W_P$ ....Eq 1

Weight of the ashed (burned) soil, $W_A = W_{PA} - W_P$ ....Eq 2

Weight of organic matter, $W_O = W_D - W_A$...........................Eq 3

The percentage organic matter, $OM(\%) = W_O/W_D \times 100$ Eq4

2.6 Powder X-ray Diffraction Analysis

The mineral composition of the soil samples was determined using X-ray diffraction spectrometry (XRD). About 0.5g of a fine soil sample was mixed with distilled water to make slurry. The soil paste was then spread evenly on an alcohol cleaned, dry glass slide and allowed to dry (Andrews, 2009). This was then mounted on the X-ray diffractometer (Thermo ARL). Samples were X-rayed from 5 to 65^o 2θ using Cu K-alpha radiation, with a step size of 0.02 degrees two theta, and a count time of at least two seconds per step using a scintillation counter. The results were interpreted using the WinXRD 2.0-5 computer program and manually using published tables of mineral d-spacings of major reflections of common minerals, d Å (Brown and Brindley, 1980).

2.7 Scanning Electron Microscopy

A scanning electron microscope equipped with an energy dispersive x-ray spectrometer (SEM/EDS) was used to check the distribution of minerals, especially those contributing potentially toxic elements (PTEs) in the samples (Fig. 10). The fine powder sample was sprinkled on sticky carbon tabs on aluminum sample stubs and then carbon coated to allow for flow of electrons. The samples were then viewed and the elemental content of sites of interest was obtained using the in-built spectrometer.

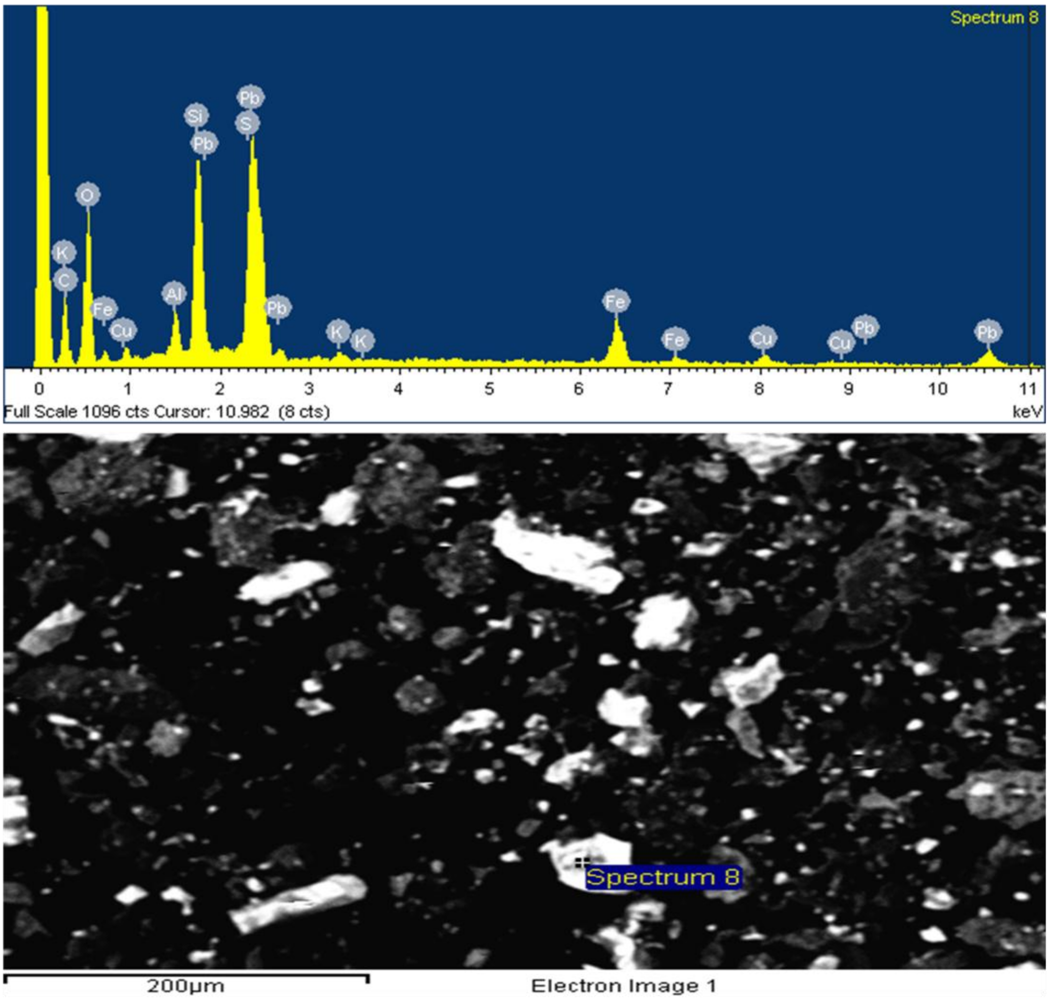

Figure 10 SEM micrograph and EDS spectra for a highly contaminated soil sample from Anka area, showing wide spread lead minerals (light particles) in the sample. The particle sizes, generally less than 200 µm make them very suitable for hand-to-mouth ingestion and amenable to suspension as dusts.

2.8 X-ray Fluorescence Spectrometry

Determination of total or near total concentration of the trace elements and major oxides in soils and sediments was carried ou by x-ray fluorescence (XRF) spectrometry method.

In order to determine total trace element concentration, pressed powder pellets were prepared. The procedure involved mixing 7.5 g of the sieved, oven-dried sample with three (3) cellulose tablets in a ratio of 1 cellulose tablet to 2.50 g of sample and grinding the mixture in an agate mill (Retsch RS 200) for 1 minute. This was followed by pressing the powder into 25 mm pellets using a hydraulic press at a pressure of 20 tons. The cellulose serves dual purposes as a binder and also reduces absorption of the target material (Potts and Webb, 1992; Funtua, 2001).

Glass beads were prepared for determination of major constituents. This involved the mixing of approximately 7.60g Lithium borate flux with 0.40g of the sample in a platinum crucible. The mixture was then fused on an air-acetylene flame (800 to 1200^{o}C) for fifteen (15) minutes so that the flux melts and the sample dissolves (Bruker axs, 2004); the melt was allowed to cool into a one-phase glass bead.

Analysis was carried out using a high performance sequential wavelength dispersive XRF spectrometer, S4 PIONEER from Bruker AXS, Germany. This was done using the default GEO-QUANT program for trace elements and the Beads-majors program for the major elemental constituents (oxides), with both running on the SPECTRA^{plus} XRF software. The GEO-QUANT method provides quantitative analyses of a suite of 22 trace elements in a sample, with a typical analysis time of about 30 minutes per sample. The quantification limits (LOQ) for the trace elements measured in this work are 10 μg/g for As, Sc, Cr, V, Ni, Cu, Nb, Mo, Sr, Rb, Th, U, Y, La and Ce; 9 μg/g Zn; 5 μg/g Pb; 24 μg/g Ba and 6 μg/g Zr. In order to allow for data analysis, LOQ values have been replaced with half the values for some of the trace elements (Nehls and Ackland, 1973; Kusner, 1976; USEPA, 2000). While those data points may not be very reliable, this is probably a better alternative to assigning zero concentration or removing the affected samples from the database.

However, for some samples with very high contents of lead and copper, beyond the upper calibration range of the GEOQUANT method (1000 µg/g Cu and 2500 µg/g Pb), a semi-quantitative method was used to estimate their total concentrations. This involved preparation of glass beads and determining Pb and Cu concentration as major oxides. The quantification limits for this method are 0.01 % Cu and 0.02 % Pb respectively. The major constituents program determines the ten (10) major elements as their oxides with a run time of approximately 20 minutes per sample. The set-up consists of a 75µm ultra-thin x-ray tube source and a LiF 220 high resolution analyzer crystal detector applicable for Ti or V Kα to Mo Kα which gives higher resolution and reduces spectrum overlap interferences. This is coupled with a sealed proportional counter and a scintillation counter.

In order to check analytical accuracy, four certified reference materials (CRMs) were always included among each batch of samples (n = 10). These are SDO-1, W2a, MESS-2 and STSD-2 for the trace elements and major elements (STSD-2 was not used for major elements). However, because the certificate of analysis of MESS-2 is missing a large number of both major and trace elements, its use was discontinued. The measured results of most of the elements for the remaining CRMs (Fig.11, Appendix 2) show very good agreement with the certified values, therefore showing good measurement accuracy, as indicated by the R^2 values and the slopes of the lines. The SDO-1 (shale) and STSD-2 (stream sediment) are thought to closely reflect the samples used in this work in terms of matrix.

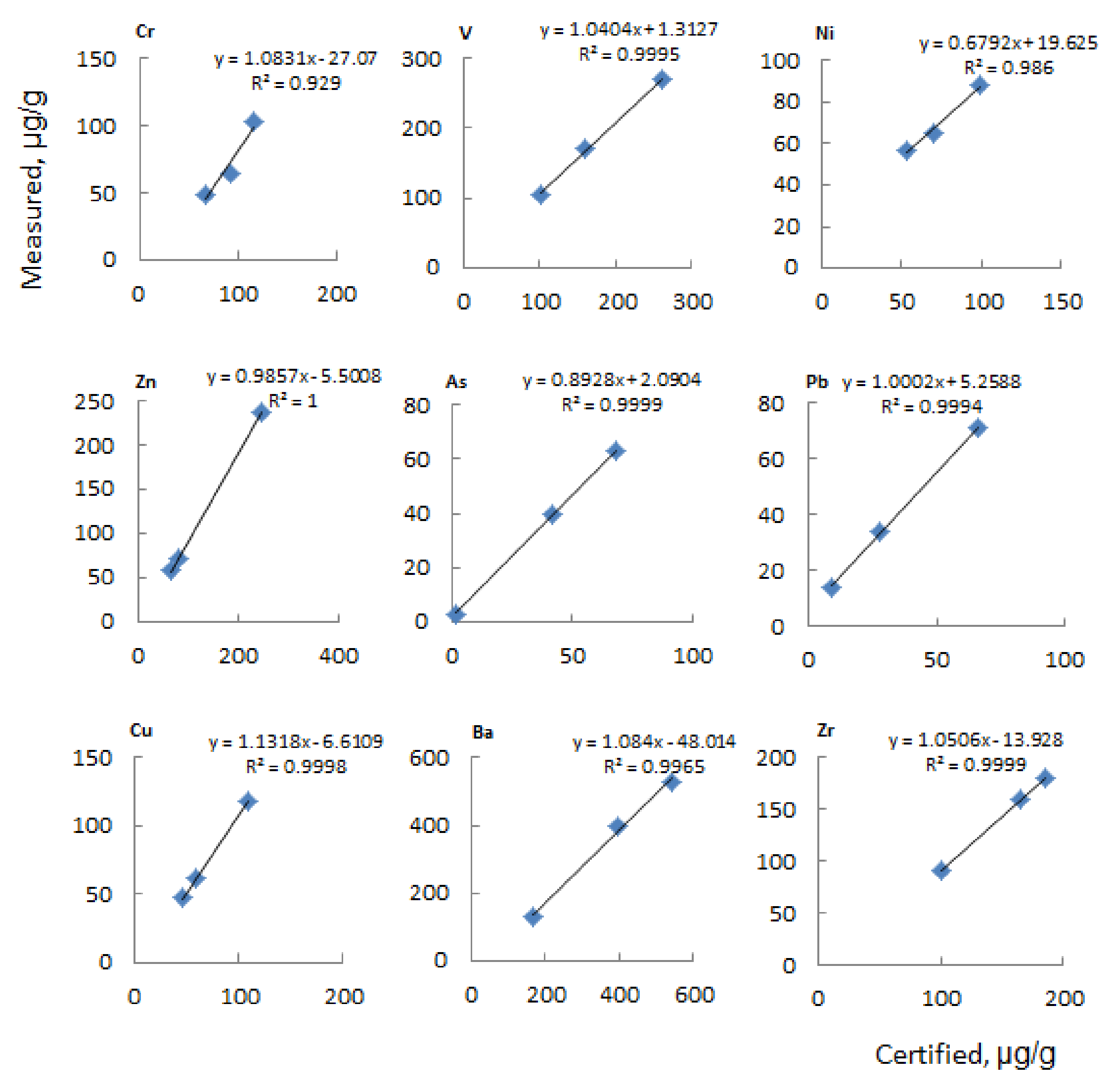

Figure 11 Plot of measured versus certified concentrations of trace elements in three certified reference materials: a, SDO-1 (shale, USGS); b, W2a (diabase, USGS); and c, STSD-2 (stream sediment, NRC, Canada). The table of data is presented in Appendix 2.

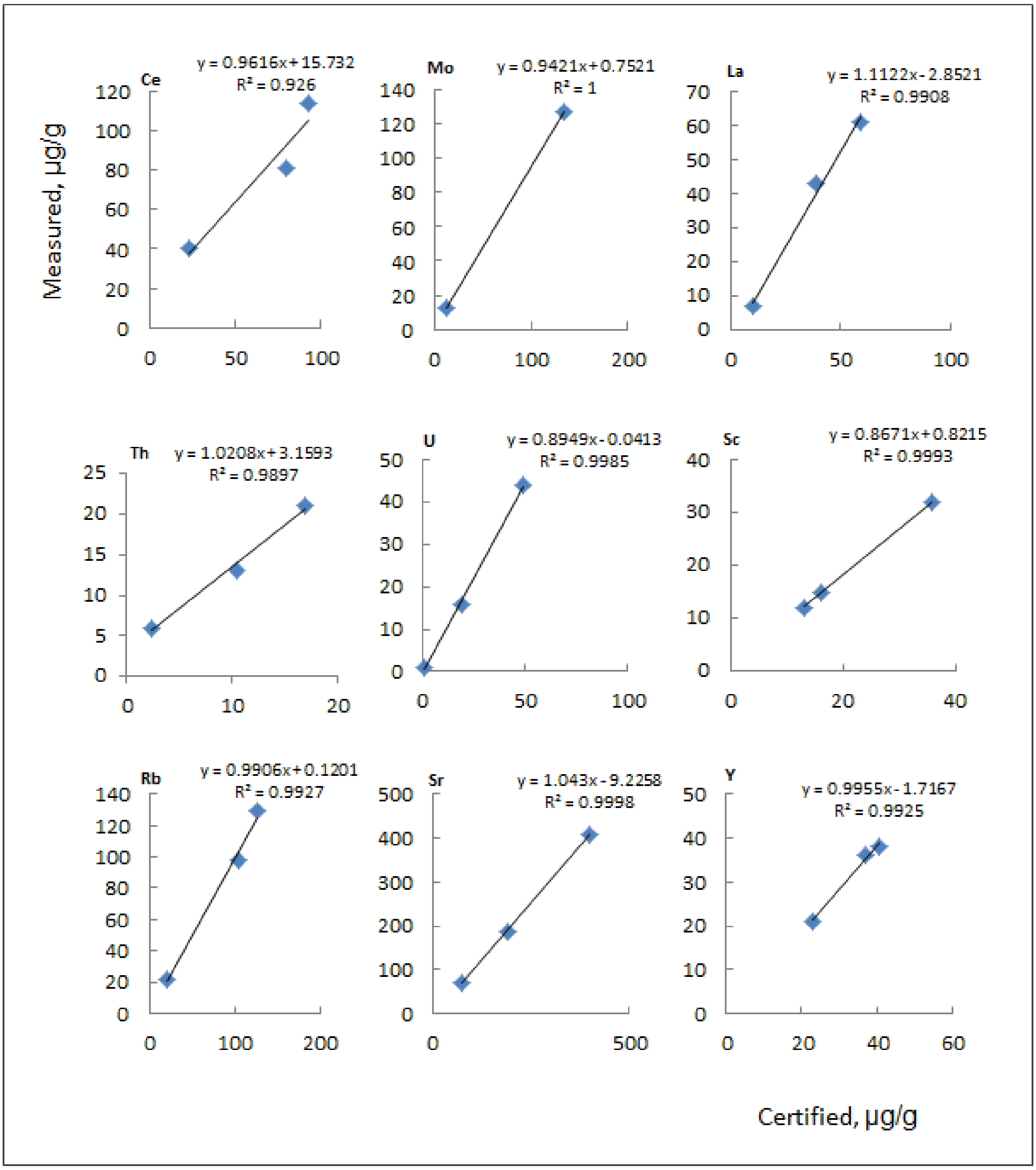

Figure 11 continued

2.9 Sequential Extraction Procedures

2.9.1 Introduction

Sequential extraction procedures are meant to determine the geochemical partitioning of elements into the exchangeable, carbonate, Fe/Mn oxides, sulfides, organic and possibly residual (lithic) fractions. Several 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). 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 in this 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 as they are not readily solubilized 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).

2.9.2 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.

2.9.3 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.

2.9.4 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 ±3^{o}C 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 vile using a pipette to minimize sample loss. The sample was then stored in a fridge at 4^{o}C until analysis was carried out using ICP-OES. Between successive extractions, the sample was rinsed with about 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 (Table 1) 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.

Table1 Reproducibility of the sequential extraction procedures for a certified reference material, STSD-2. Exch - Exchangeable fraction, Carb - Carbonate fraction and Oxide – Fe/Mn Oxides fraction. All units are μg/g except where otherwise stated.

	As	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
Exch	bdl	0.01	0.13	10.4	0.22	0.09	0.27
Exch	0.01	0.03	0.12	10.4	0.21	0.08	0.26
Exch	0.03	0.02	0.15	10.5	0.23	0.16	0.26
Mean	0.02	0.03	0.13	10.41	0.22	0.12	0.26
StDev	0.01	0.00	0.01	0.05	0.01	0.04	0.00
RSD%	**26.1**	**19.0**	**11.0**	**0.5**	**4.6**	**34.6**	**0.5**
Carb	2.83	0.14	1.49	34.12	0.96	4.93	3.24
Carb	2.73	0.15	1.44	32.57	0.88	3.65	3.04
Carb	3.30	0.24	1.92	38.39	0.95	8.39	3.62
Mean	3.01	0.20	1.68	35.48	0.92	6.02	3.33
StDev	0.28	0.05	0.24	2.91	0.04	2.37	0.29
RSD%	**9.5**	**23.1**	**14.3**	**8.2**	**3.9**	**39.4**	**8.7**
Oxide	5.06	1.69	3.08	298.79	3.48	11.48	11.44
Oxide	5.73	1.71	3.15	302.23	3.41	11.25	11.64
Oxide	6.49	1.75	3.12	325.34	3.52	11.44	11.84
Mean	6.11	1.73	3.13	313.79	3.46	11.34	11.74
StDev	0.38	0.02	0.02	11.56	0.05	0.09	0.10
RSD%	**6.2**	**1.1**	**0.5**	**3.7**	**1.5**	**0.8**	**0.9**

2.10 *In vitro* Bioaccessibility Tests

Physiologically-Based Extraction Techniques to assess the bioaccessibility of the elements and their toxicity. This involved laboratory simulation of gut fluids and using them to leach/ extract metals from the soils. Several procedures have been developed for in vitro testing of bioaccessible metals, among them are those by Drexler and Brattin (2007), USEPA (2007a,b; 2008), BARGE (2008).

The soil samples were air dried and sieved to < 60 µm. Gastric fluids were simulated by adding approximately 60 ml concentrated hydrochloric acid to 2 L of 0.4 M glycine solution. The glycine solution was prepared by adding 60.06g of glycine to 1.9 L of deionized water and the solution made up to 2L. The solution was then warmed in an incubator to a temperature of 37^{o}C and its pH adjusted to 1.5± 0.05 by drop-wise addition of concentrated hydrochloric acid.

The test material (1 g of the < 60 µm soil) and 50 ml of the extraction fluid were placed in a high density, wide mouthed Nalgene bottles. The bottles were tightly closed and shaken well to ensure that there was no leakage and that no soil was caked at the bottom of the bottle. The bottles were then placed into a temperature controlled incubator (37 ±2°C) and shaken side-to-side at 300 rpm for 1 hour. After 1 hour, the bottles were removed and placed upright on a bench top to allow the soil to settle at the bottom. A 15 ml aliquot of the supernatant was withdrawn using a syringe and filtered using a Luer-Lok attachment fitted with 0.45µm cellulose acetate filter to remove any particulate matter. The extraction solutions were stored in a fridge at about 4°C until they were analyzed and Figure 12 shows method precision on replicate measurements.

2.10.1 Effect of pH on *In Vitro* bioaccessibility

The gastric pH is said to range between 1 and 5 units depending on the presence or absence of food (USEPA, 2008; Washington et al. 2001), with the fasted condition giving lower pH values. This experiment was conducted at three pH values; 1.50, 2.20 and 2.90 which were achieved by successively reducing the volume of concentrated hydrochloric acid used (from 60ml to 30ml and 15ml) while keeping weight of glycine and total solution volume constant. A set of fifteen samples was used in this study, where three equal aliquots of each sample were each extracted with the solutions of varying pH in an incubator for one hour at 37°C with constant shaking. In order to test the precision of the method, three samples in each batch were extracted in triplicate and residual standard deviation (RSD) was found to be generally below 10%.

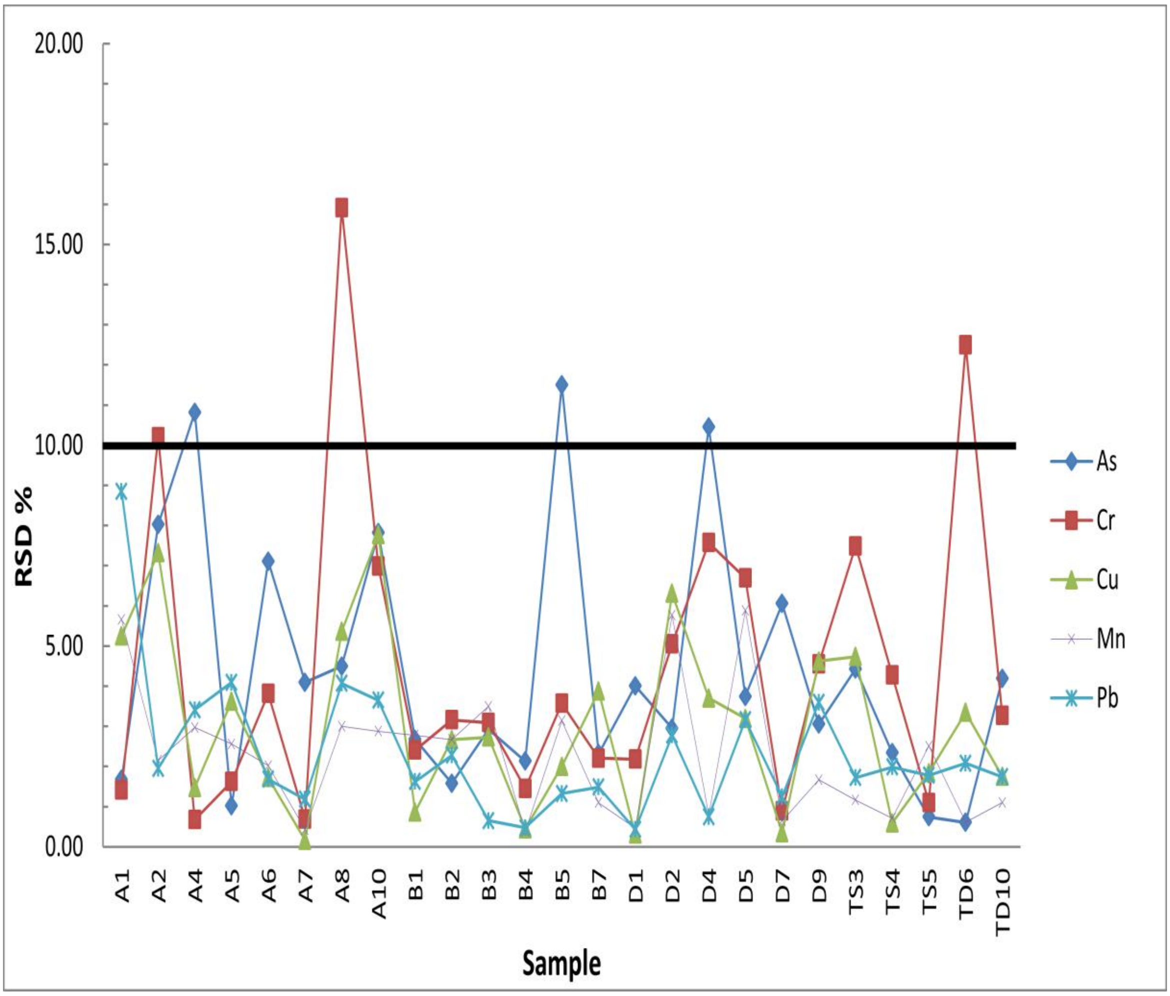

Figure 12 Precision of replicate *in vitro* measurements for five elements indicated as residual standard deviation, RSD %. Notice that most of the points lie well within an acceptable limit of 10% (Lu et al., 2011) **indicated by the solid horizontal line, except for arsenic and chromium in few samples.**

2.10.2 Effect of solid: fluid ratio on *In Vitro* bioaccessibility

To test the possibility that ratio of test material weight in the extraction bottle to volume of extraction fluid has an impact on contaminant solubilization, this experiment was conducted using three solid to fluid ratios. In addition to the 1:50 (1g test material: 50ml of extraction solution) adopted in 2.10 above, extraction was also carried out on a sub-set (n=10) of the samples used above at 0.5g: 50ml and 1g: 25ml test material to extraction solution respectively. The procedure involved placing three aliquots of the test material and adding the required volume of extraction solution. The set-up was then incubated for one hour at 37^{o}C with constant agitation, after 10ml aliquots of the supernatant were collected and filtered for analysis.

2.10.3 Effect of incubation time on *in vitro* bioaccessibility

In order to study the effect of incubation time on the *in vitro* bioaccessibility of contaminant elements, the extraction process was repeated at different time intervals. This is aimed at testing the impact of time of contact between the test material and extraction solution, within the stomach emptying time which is reported to be about 1 hour (USEPA, 2008) and between 30 minutes and a few hours (Drexler and Brattin, 2007) for a child. For this purpose, a sub-set (n=10) of the samples used in 2.10 above were subjected to incubation for one hour and two hours and finally left standing on bench top for 17 hours. The procedure involved placing 1g of the test material into a bottle and adding 50ml of the extraction solution prepared as above and incubating for one hour. After the first hour, the bottles were removed and placed on the bench top as usual to cool and allow the materials to settle. A 10 ml aliquot was then collected and filtered into sample vials. The remaining solution was then returned to incubator and shaken for another hour and a second 10 ml aliquot collected for analysis. Another aliquot was collected the following day after the set up was left to stand on bench for 17 hours.

2.11 ICP-OES Analysis

All sequential extraction and *in vitro* bioaccessibility solutions were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro CCD Simultaneous spectrometer, equipped with a Varian Sample Preparation System (SPS-5) for As(188.980 nm), Cr(267.716 nm), Cu(324.754 nm, 327.395 nm), Ni(231.604 nm), Mn(259.372 nm), Pb(220.353 nm) and Zn(213.857 nm). This spectrometer features a Charge Coupled Device (CCD) detector, high resolution echelle polychromator and a rugged 40 MHz RF system. The CCD detector has continuous wave length coverage, from 167nm to 789nm, which helps to easily eliminate spectral interferences (EVISA, 2010). The limits of detection (LOD) for the measurement in parts per billion (ppb) are 1.59 (As), 0.11 (Cr), 0.18-0.67 (Cu), 0.23 (Mn), 0.72 (Ni), 1.07 (Pb) and 0.51 for Zn. Calibration standards were prepared using commercially available analytical grade stock solutions from Fisher Scientific, UK. In order to the check the quality of the analyses, an analytical spike was included within each batch of samples, coupled with at least three blank samples (milliQ) water in each case and replicate measurements were done on samples selected at random. The analytical blank gave values generally very close to the LOD for all elements. The residual standard deviation (RSD) for the duplicate measurements on blanks and samples has generally been within or slightly above the acceptable limit of 10% (Lu et al. 2011) or 15% (Smith et al. 2009), thus indicating good method precision.

2.12 Statistical and Graphical Treatment of Data

The geochemical data was submitted to multivariate statistical analysis using SPSS (PASW 18) for Windows using methods described by Field (2009). Descriptive statistics (DS), correlation matrix (CM), principal component factor analysis (PCFA) and One-way repeat-measures ANOVA were performed on the data. While carrying out DS, CM and PCFA, it was assumed that the data was normally distributed and therefore no normalization was done before statistical treatment. For the repeat-measures ANOVA, a correction for data sphericity was carried out using Bonferroni method. Descriptive statistics provide a summary of the data in terms of its statistical parameters of minimum and maximum, mean and standard deviation. Correlation matrix was used to obtain the Pearson relationship between the elements on the one hand and with organic matter content of the sediments on the other. The PCFA was performed in order to identify possible sources and fate of the various elements (geogenic, anthropogenic or both). Repeat-measures ANOVA was performed in order to assess the effect of pH, time and solid to fluid ratio on element bioaccessibility. Similarly, the effect of grain size on total elemental concentration evaluated using this method. Multi- element graphs of the data were plotted using the chart option in Microsoft Office Excel 2007.

Chapter Three

Results: Bulk Geochemistry

3.1 Introduction

Soils and stream sediments from the Anka and Tsofon Birnin-Gwari areas of NW Nigeria were analyzed in order to assess the environmental impact of artisanal gold mining and processing. A total of 101 samples, consisting of 56 from the Birnin-Gwari and 45 from the Anka areas were analyzed for total element composition using x-ray fluorescence (XRF) spectrometry. The aim was to determine the distribution of major and trace elements in soils and stream sediments in these areas. The organic matter content (LOI %) of all the samples was determined by measuring the weight loss of a sample ignited in a furnace to burn off the volatile components. In order to identify and possibly quantify some of the mineral phases, a subset of the samples was studied using powder x-ray diffraction (XRD) analysis. Details of the analytical procedures have been given in Chapter 2. An observation of the results from both the Anka and Birnin-Gwari areas shows that the data is generally not normally distributed (Fig.13 a&b). As a result, the mean may not a good measure of the centre of the distribution for most of the elements and is therefore presented along with the median in the summary tables.

3.2 Mineralogy and Major Element Geochemistry

Table 2 (a and b) present the summary statistics of the concentrations of major and trace elements, organic matter contents and pH for the soil and sediment samples from the Anka and Birnin-Gwari areas of NW Nigeria. The tables present the results of this work, along with the crustal averages (Andrews et al., 2004; Taylor and McLennan, 1985, 1995; Wedepohl, 1995) and soil guideline values for some of the potentially toxic elements (ICRCL; USEPA) and the concentration of the elements in stream sediments from a similar terrane in central Nigeria recently published by Lapworth et al. (2012).

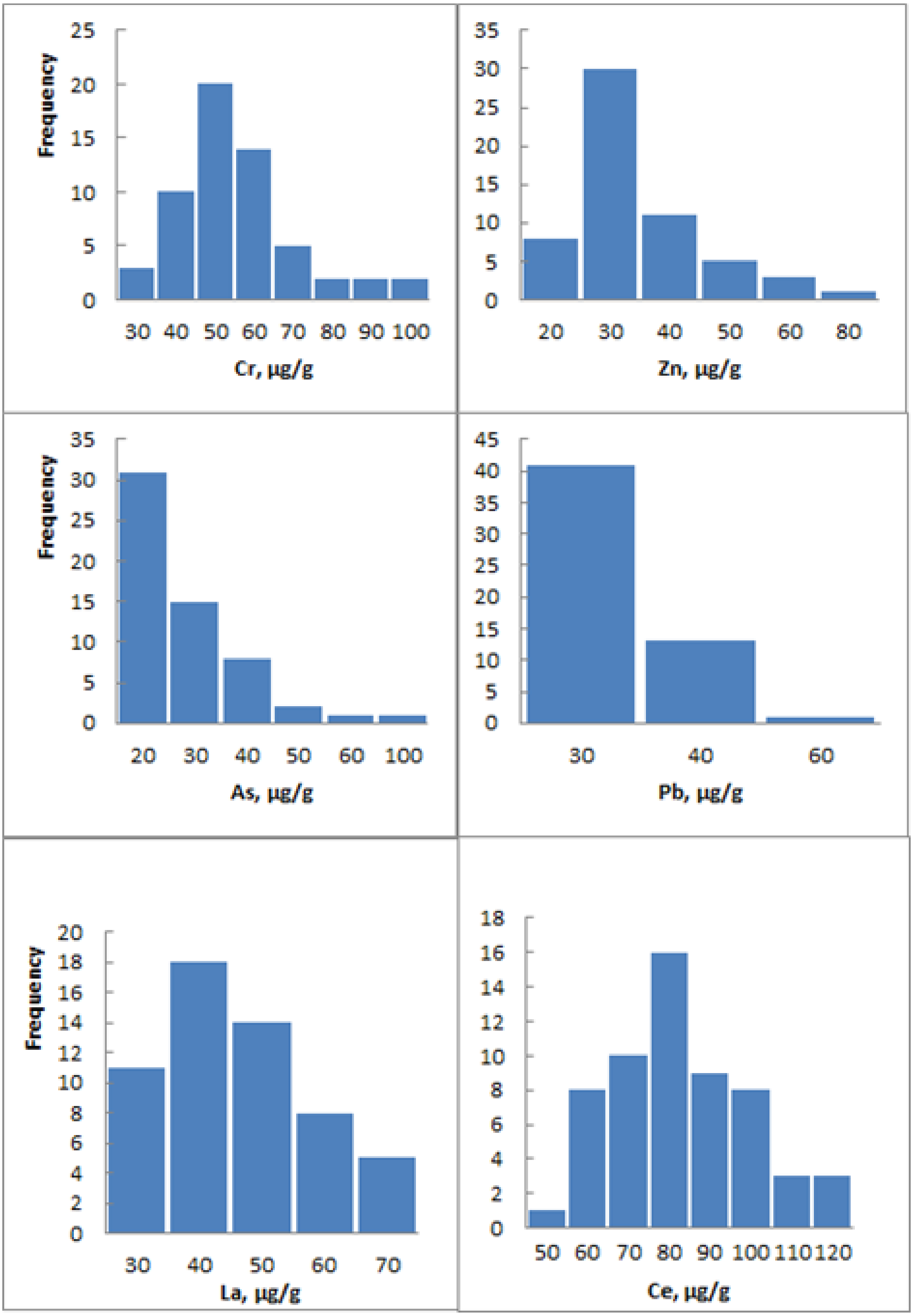

Figure 13a Histograms showing the non-normal nature of the distribution of trace elements data in the samples from the Birnin-Gwari area.

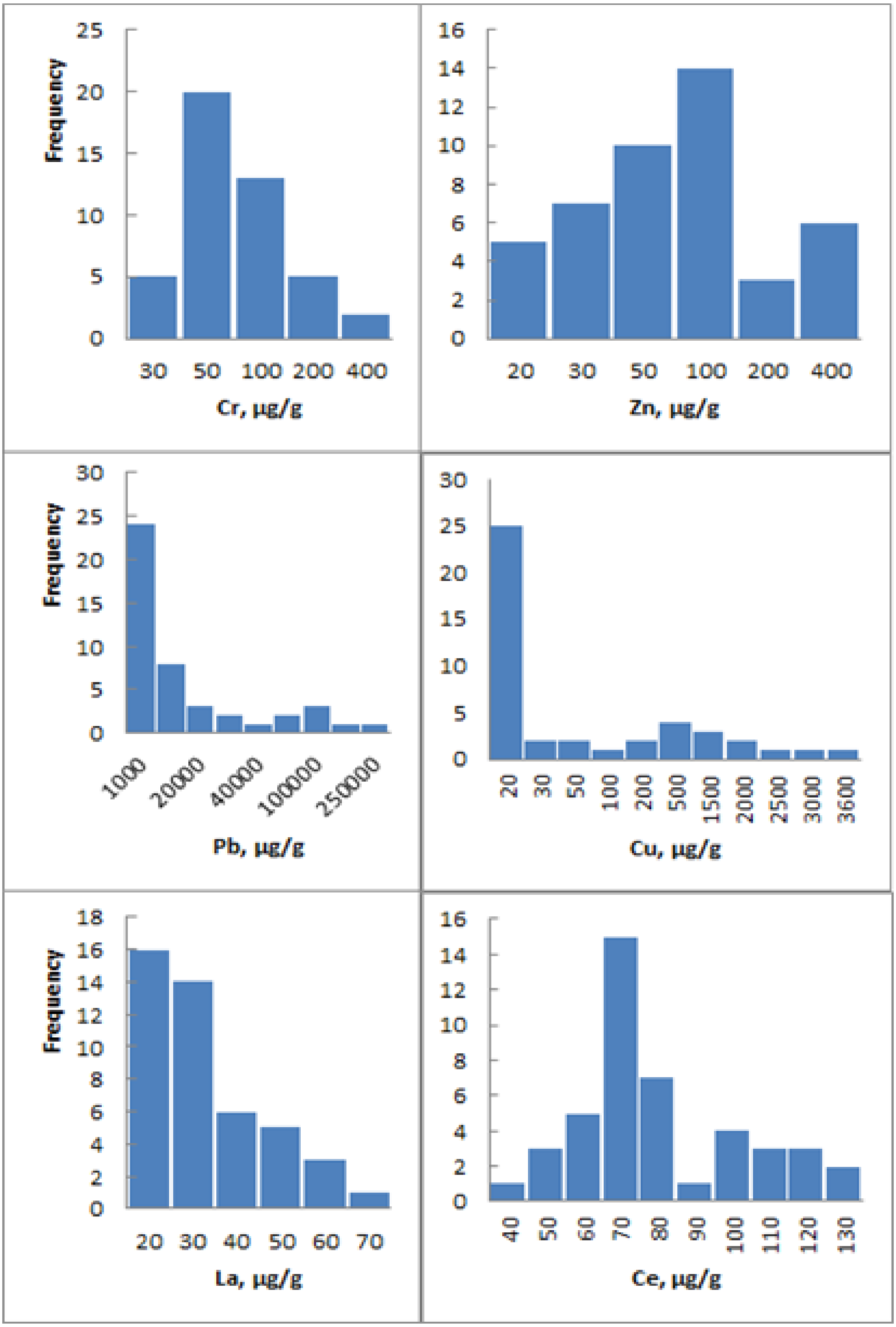

Figure 13b Histograms showing the non-normal nature of the distribution of trace elements data in the samples from the Anka area.

The data show that for the Anka area (Table 2a), the mean (± std. dev) concentrations (wt %) of SiO_2, TiO2, Al_2O_3 and Fe_2O_3 are 75.3 ± 11, 1.1 ± 0.5, 8.6 ± 4 and 4.5± 2.6 respectively. The results for MgO, CaO, K_2O and Na_2O are 0.5 ± 0.9, 0.7 ± 0.1, 1.8 ± 0.7 and 0.3 ± 0.5, while MnO and LOI give 0.1± 0.1 and 4.8 ± 2.2 respectively. Similarly, Table 1b shows that for the Birnin-Gwari area, the results for SiO_2, TiO2, Al_2O_3 and Fe_2O_3 are 78.4 ± 8 wt %, 1.2 ± 0.4 wt %, 9.2 ± 4 wt % and 4.6 ± 3 wt % respectively. The results further show that the mean concentrations of MgO, CaO, K_2O, Na_2O, MnO and LOI are similar to those obtained in the Anka area. A major feature of these results is the elevated silica contents and depletion in alumina and the alkalis relative to their published crustal average values (Andrews et al., 2004; Taylor and McLennan, 1985, 1995; Wedepohl, 1995). Similarly, the soils of this area have generally low organic matter content as indicated by the low mean percentage loss on ignition, LOI %. Iron content is however similar to the global average values.

The high silica contents, coupled with depletion in alumina and the alkalis, relative to the upper continental crust, is a reflection of the preponderance of quartz relative to feldspar, mafic, carbonate and clay minerals in the soils and sediments from the two areas, as shown by the powder XRD results (Fig. 14). The very high silica concentrations in soils and sediments from both the Anka and Birnin-Gwari areas are similar to those obtained by Tijani et al. (2006) for bedrock and soils overlying granite-gneiss and pegmatite (60.3-72.2 %) and schist-quartzite (81-91.3 %) in SW Nigeria. The results are similar (except for SiO_2) to those reported for stream sediments in central Nigeria (Table 1a&b) by Lapworth et al. (2012), who attributed the depletion in aluminum and the alkalis in the sediments relative to the upper continental crust, to the maturity of the chemical weathering process, which involves the progressive loss of the alkalis accompanied by an enrichment of sesquioxides (Tijani et al., 2006). Many previous workers (e.g. Price and Velbel, 2003;

Tijani et al, 2006) have used the chemical index of alteration, CIA (Nesbitt and Young, 1982) as a measure of the degree of weathering and is calculated according to the equation:

$$CIA = \frac{\mathrm{Al2O3}}{Al2O3+CaO+Na2O+K2O} \times 100 \text{ ....Eq 5.}$$

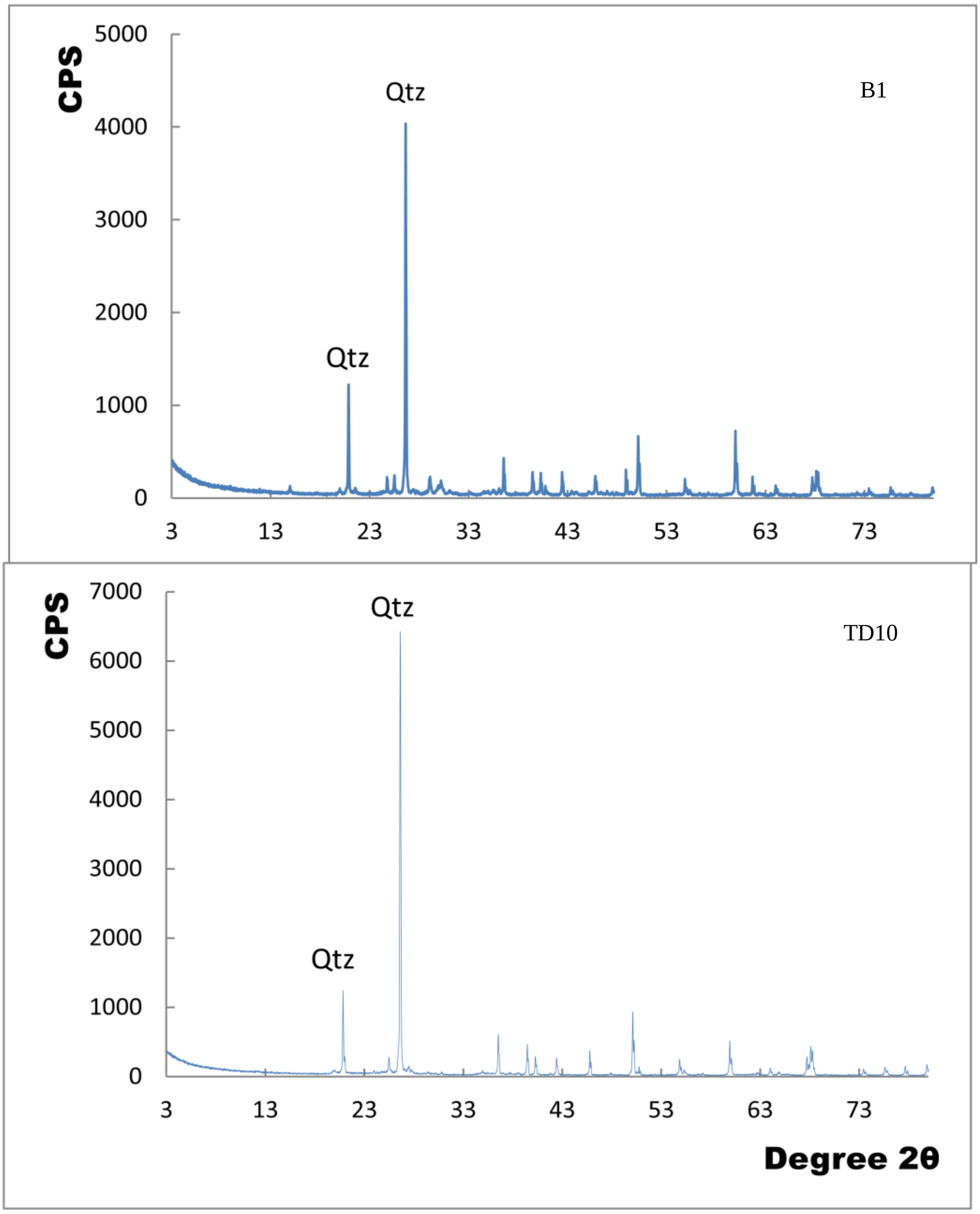

Figure 14 Powder x-ray diffraction patterns for randomly selected samples from Anka area, NW Nigeria showing the dominance of quartz (Qtz) in the samples.

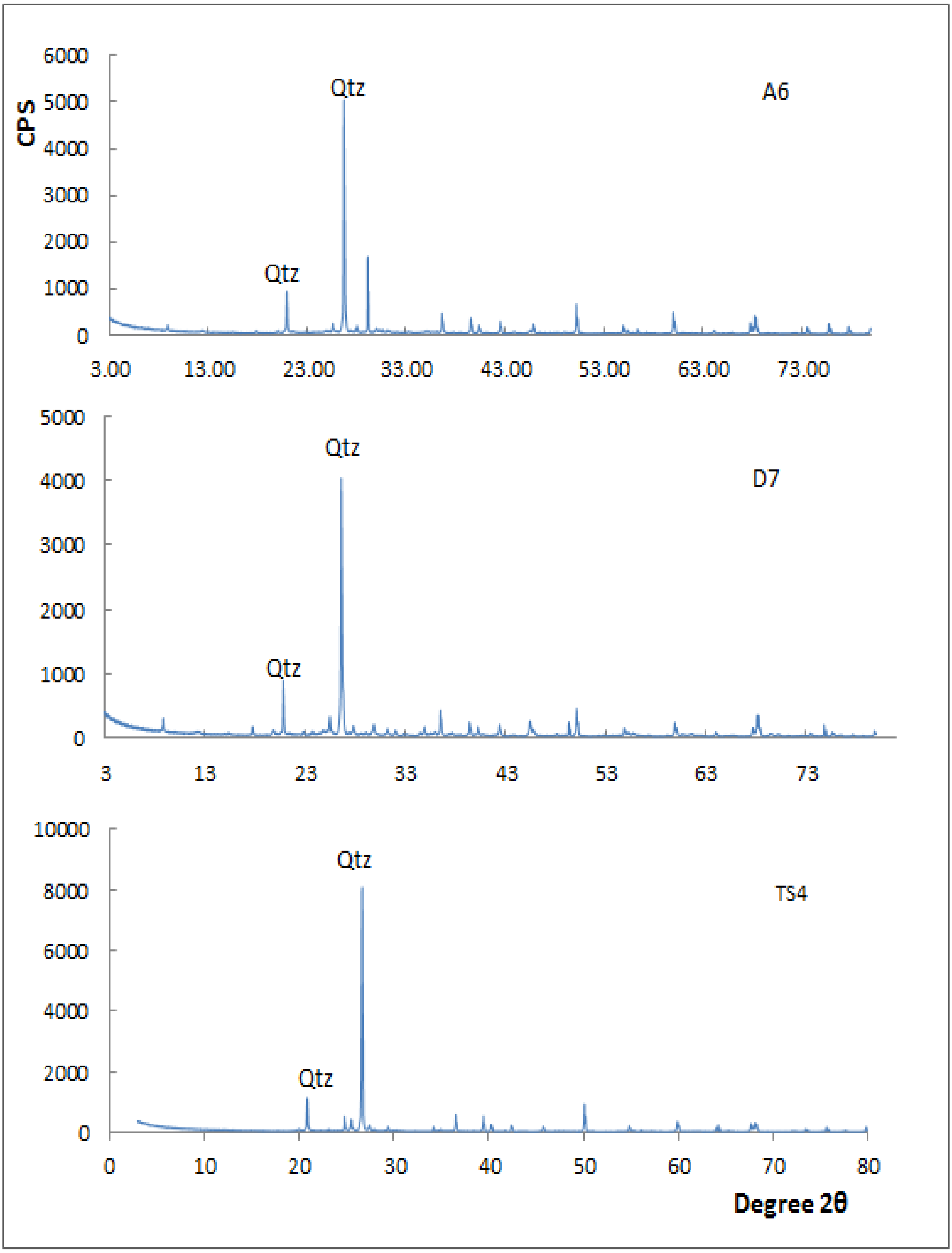

Figure 14 cont'd.

The computed CIA values for the Anka samples range from 60.3 to 89.6 (mean, 75.1), while for the Birnin-Gwari area the values lie between 69.1 and 88.3, with a mean of 79. These generally indicate that the soils and sediments from both study areas have undergone intense weathering and removal of alkali metals from feldspars by aggressive soil solutions (Nesbitt and Young, 1982), with the Birnin-Gwari samples again appearing to be more weathered. It may also be a result of considerable leaching of bases in the upper horizons of the soils as evidenced by low base saturation and low pH values (Pullan, 1970), which leaves the soils enriched in silica. The mean pH value obtained for the Anka samples is 6.7 ± 1: whether this is sufficiently low to cause the leaching of base cations faster than they are re-supplied by weathering (Kirchner, 1992; 1995) is not clear.

An observation of the whole data (Appendix 3 & 5) shows that the Birnin-Gwari samples are slightly more depleted in Mg, Ca and Na compared to the samples from the Anka area, while the two areas have broadly similar K concentrations. Given the broadly similar geology and climate of the two areas, topography is thought to be a contributory factor: the higher relief of the Birnin-Gwari area facilitating greater loss of base cations through overland runoff, which is consistent with the higher mean CIA value obtained for the area. Similarly, the results for three termite mound samples (TM2, TM3 and TM5) from the Birnin-Gwari area (Appendix 5), although few in number, have high alumina concentrations (~ 11 – 16.5 wt %) compared to most of the surface soil samples, but their alkali contents do not differ significantly from those of the surface soils and stream sediments. A possible reason for this is the origin of the termataria samples from deeper soil environments that have not undergone leaching relative to the top soils.

Table 2a Summary of XRF data for major (wt. %) and trace elements ($\mu g\ g^{-1}$) in soils and sediments from Anka area, NW Nigeria, along with published concentrations and soil guideline values for some potentially toxic elements.

Element	**This work**					**Cont. Crust**			**Soils**		**Sediment**
	Min	Max	Mean	Med	Std. Dev.	**a**	**b**[*]	**c**	**d**	**e**	**f**[*]
SiO_2	40	89	75.3	77.4	11	65	66	62			59.5
TiO_2	0.2	2.9	1.1	1.0	0.5	0.6	0.5	0.7			1.7
Al_2O_3	3.7	18.1	8.6	7.4	4	15	15	15			10.9
MnO	0	0.5	0.1	0.6	0.1		0.1	0.1			0.1
MgO	0.1	6.4	0.5	0.3	0.9	2.4	2.2	3.7			0.5
Fe_2O_3	1.2	10.5	4.5	4.0	2.6	4.9	5	6.3			4.5
CaO	0.1	5.8	0.7	0.4	1.0	4.1	4.2	5.5			1.2
P_2O_5	0	1.6	0.24	0.09	0.4		0.2	0.2			0.04
K_2O	0.4	4.3	1.8	1.8	0.7	3.1	3.4	2.4			2.3
Na_2O	0	2.4	0.3	0.2	0.5	3.5	3.9	3.2			
LOI	1.6	10.51	4.8	4.5	2.2						
pH	4.9	9.24	6.7	6.6	1.0						
Sc	10	28	11	5	3.3		11	16			
V	24	213	78	67	45		60	98			80.4
Cr	17	327	72	48	60		35	126	54	68	56.4
Ni	10	175	35	27	30		20	56	19	22	16.9
Cu	10	3600	506	14	958		25	25	25	22	16.5
Zn	13	395	83	52	90		71	65	60	66	41
As	10	533	25	5	78		1.5		10		1.62
Rb	10	139	47	52	31		112	78			76.7
Sr	34	312	115	95	69		350	333			201
Zr	122	4367	1321	638	928		190	203			2100
Nb	10	35	19	21	6		25	19			29.1
Mo	10	23	10	10	2		1.5				0.73
Ba	272	2320	813	566	626		550	584			808
La	10	64	27	26	14		30	30			99.9
Ce	39	160	78	67	26		64	60			211
Pb	22	221600	17522	497	40161		20	15	19	30	28
Th	5	10766	597	23	1736		11	8.5			40.8
U	<10	<10	<10	<10	0		2.8	1.7			8.09

a: Andrews et al, 2004; b: Upper continental crust, Taylor and McLennan, 1985, 1995; c: Wedepohl, 1995; d: ICRCL/DEFRA Trigger concentrations for domestic gardens/allotments ; e: US EPA soil guideline values; f: stream sediments from central Nigeria (Lapworth et al., 2012). *Major elements oxides worked out from elemental concentrations.

Table 2b Summary of XRF data for major (wt.%) and trace elements ($\mu g\ g^{-1}$) in soils and sediments from Birnin-Gwari area, NW Nigeria, along with published concentrations and soil guideline values for some potentially toxic elements.

Element	**This work**					**Cont. Crust**			**Soils**		**Sediment**
	Min	Max	Mean	Med	Std. Dev.	**a**	**b***	**c**	**d**	**e**	**f***
SiO_2	64.6	92.2	78.4	79.4	8	65	66	62			59.5
TiO_2	0.2	2.0	1.2	1.2	0.4	0.6	0.5	0.7			1.7
Al_2O_3	4.0	17.6	9.2	8.1	4	15	15	15			10.9
MnO	0.01	0.7	0.1	0.08	0.1		0.1	0.1			0.1
MgO	0.1	0.9	0.3	0.2	0.2	2.4	2.2	3.7			0.5
Fe_2O_3	0.8	12.1	4.6	3.4	3	4.9	5	6.3			4.5
CaO	0.03	0.6	0.2	0.2	0.1	4.1	4.2	5.5			1.2
P_2O_5	0.01	0.1	0.05	0.04	0.02		0.2	0.2			0.04
K_2O	0.9	3.4	1.8	1.76	0.5	3.1	3.4	2.4			2.3
Na_2O	0.1	0.5	0.2	0.2	0.1	3.5	3.9	3.2			-
LOI	1.3	9.3	5	4.4	2						-
Sc	10	18	11	10	2		11	16			-
V	24	127	58	56	20		60	98			80.4
Cr	28	100	51	48	15		35	126	54	68	56.4
Ni	10	30	16	15	6		20	56	19	22	16.9
Cu	10	40	11	10	5		25	25	25	22	16.5
Zn	15	77	30	27.5	12		71	65	60	66	41
As	10	94	24	19	14		1.5		10	-	1.62
Rb	31	148	74	67	28		112	78			76.7
Sr	23	127	56	52	19		350	333			201
Zr	251	4656	1597	1321	1207		190	203			2100
Nb	10	38	23	23	6		25	19			29.1
Mo	10	10	10	10	0		1.5				0.73
Ba	162	849	467	447.5	146		550	584			808
La	20	67	39	37	12		30	30			99.9
Ce	40	115	77	76.5	16		64	60			211
Pb	20	53	28	28	5		20	15	19	30	28
Th	10	45	21	19	8		11	8.5			40.8
U	10	10	10	10	0		2.8	1.7			8.09

a: Andrews et al, 2004; b: Upper continental crust, Taylor and McLennan, 1985, 1995; c: Wedepohl, 1995; d: ICRCL/DEFRA Trigger concentrations for domestic gardens/allotments ; e: US EPA soil guideline values; f: stream sediments from central Nigeria (Lapworth et al., 2012). *Major elements oxides worked out from elemental concentrations.

Termites are known to actively transport materials rich in clay minerals from deeper regolith to the surface horizons (Sako et al., 2009).

The low organic matter content of the soils is consistent with the findings of Pullan (1970) perhaps due to the sparse vegetation cover of the area, which is further exacerbated by intensive slash and burn agricultural practices which destroy the organic matter and overgrazing by cattle. According to Andrews et al. (2004), soil organic matter is mainly contributed by vegetation, although they note that most soils contain less than 5 wt % organic matter. The destroyed organic material may have also facilitated the removal of elements such as K, Ca, Mg and Na through leaching and overland runoff, thus, helping to explain their depletion in these soils. The paucity of exchangeable metals in these soils may be the reason for the low partitioning of heavy metals with the exchangeable fraction obtained in this work (Chapter 4). This might also have implications for water chemistry in the catchment; water pH may be lowered due to low buffering capacity of the surface soils and sediments.

3.3.1 Trace Element Geochemistry

The results of potentially toxic element analysis are summarized in Table 1a&b, along with published concentrations and trigger and / or guideline soil concentrations for As and five heavy metals. The data shows that the concentration of Pb, Cu, As, Cr and Zn in the Anka samples (Table 2a) ranges from 22 to 221,600 µg/g with a mean (± standard deviation) of 17,522 ± 40,161 µg/g; 10 to 3600 with a mean of 506 ± 958 µg/g; 10 to 533 with a mean of 25 ± 78 µg/g; 17 to 327 with a mean of 72 ± 60 µg/g and 13 to 395 µg/g with a mean of 83 ± 90 µg/g respectively, while the concentration of Ni ranges from 10 to 175 µg/g with a mean of 35 ± 30 µg/g. These concentrations are generally higher than those obtained for these elements from the Birnin-Gwari area, except for As, which has comparatively higher concentrations in the area. In fact higher mean As concentration in the Anka area is as a result of few anomalous samples which cause a positive skewing of the data set. The concentrations of Pb and Cu in particular are very high in the samples from Anka compared to those from the Birnin-Gwari study area. Similarly the mean concentrations of all the above six elements obtained from the Anka samples are above their crustal concentrations (Taylor and McLennan, 1985, 1995; Wedepohl, 1995), except for Cr which has a mean concentration less than 126 µg/g (Wedepohl, 1995).

In the Birnin-Gwari area however, only Pb and As have mean concentrations above the published crustal abundances (Table 2b), whereas the concentration of Cr exceeded only the Taylor and McLennan (1995) value of 35 µg/g. The results were also compared with the trigger and guideline value for potentially toxic elements in soils (ICRCL; US EPA) and this shows that the concentration of Pb in the Anka area is above the values set for soils by both the Interdepartmental Committee for the Reclamation of Contaminated Land (ICRCL) in the UK and the United States Environmental Protection Agency (US EPA), while the concentration of Cu exceeds only the ICRCL trigger concentration for domestic gardens and allotments. The elevated levels of these elements in soils and sediments, beyond the maximum allowable limits, especially Pb and Cu in the Anka area pose serious environmental and human health problems. Recently, acute Pb poisoning which resulted in the death of hundreds of children has been reported in several villages in the Anka area (UNEP/OCHA, 2010), owing to contamination of soils within residential areas by artisanal processing of Pb- (Plumlee and Morman, 2011) and Cu- rich gold ores. On the other hand, the concentrations of Cr, Ni and Zn from both study areas are within the limits set by both regulatory bodies.

In both study areas, the mean concentration of As is above the limit set for domestic gardens and allotments (ICRCL), although the majority of samples from the Anka area have levels below or within the set limits compared to those from Birnin-Gwari area. The mining of gold is an important source of As in the environment (Inam et al., 2011; Carvalho et al., 2009), but the results of this work do not show a significant elevation of As concentration in areas severely affected by artisanal gold processing, especially in the Anka area. Only a few samples have relatively high As contents, the maximum being 533 µg As/g. In the Birnin-Gwari area where As content of soils and sediments is consistently above the trigger concentrations (ICRCL, Appendix 6), there is no significant variation between As concentration in soils and sediments in the vicinity of the mine pits (Fig. 8a) and in those from background areas.

The Anka and Birnin-Gwari areas have broadly similar geology and the same artisanal mining methods have been and are still been used in both areas to win gold from hydrothermal veins. However, the results of this work show a marked difference in the way this activity has impacted on the chemical quality of soils and sediments in the two areas, with the Anka area experiencing intense contamination, especially with Pb and Cu, compared to the Birnin-Gwari area. This can be attributed to the mineralogy and geochemistry of the deposits being exploited: the Anka ores are clearly richer in Pb- and Cu- sulfides than those of the Birnin-Gwari area. According to Garba (2003), the wall rocks of the Anka deposits contain elevated levels of Cu (647-5410 µg/g) and Pb (7550-22600 µg/g), but the gold in Birnin-Gwari is associated with only minor sphalerite, chalcopyrite, pyrrhotite, galena and magnetite. Lead and Cu concentrations of up to 22 % and 0.4 % respectively were obtained in some of the Anka samples, and scanning electron microscopy analysis (with energy dispersive spectrometry, EDS) shows widespread presence of galena (and probable chalcopyrite) particles in the soils and sediments. Similarly, results of sequential extraction experiments (Chapter 4) show high concentrations of Pb in the carbonate fraction, due to the presence of very soluble secondary Pb carbonates (Plumlee and Morman, 2011). As contaminants were introduced into the soils only recently, the carbonate is likely to control the release of Pb in the immediate future depending on the pH of surface or meteoric water in the area. But as weathering progresses with time, the oxidation of fine galena particles exposed to the atmosphere, for example, to anglesite ($PbSO_4$, Plumlee, 1999) is expected to make Pb even more mobile and therefore available for uptake. The results therefore underscore the importance of deposit mineralogy and chemistry to the environmental geology of mineral deposits (Plumlee, 1999).

The concentrations of Zr, Th and, to a lesser extent, Ba have been found to be very high in both study areas (Table 2a&b), although the Anka samples have generally higher concentrations of the three elements. Mean concentrations (± standard deviation) of Zr and Th in both the Anka and Birnin-Gwari areas are greater than the crustal abundances (Taylor and McLennan, 1995; Wedepohl, 1995), whereas the concentration of Ba is only elevated above baseline concentrations in the Anka area. These results, except for Th in the Anka area, are broadly very similar to those obtained by Lapworth et al. (2012) for stream sediments in a survey in central Nigeria. The possible sources of these elements in the areas is not clear, but heavy minerals like zircon and monazite are likely sources of Zr and Th, while Ba may have been contributed by feldspars or associated barites mineralization. According to Key et al. (2012), anomalously high levels of Zr found in stream sediments in Nigeria may not be a reflection of the concentration of the element and other heavy mineral borne elements in surrounding Basement rocks. They instead interpreted it to be a product of intense tropical-chemical weathering, and persistent physical weathering aided by wet season flash floods and dry season winds, which effectively removed most of the clay minerals, thus, leaving the sediments enriched in zircon and the other resistates. The concentration of Zr obtained in this work for three metasedimentary rock samples, R1, R2 and R3 (Appendix 6) from the Birnin-Gwari area ranges from 251 to 276 µg Zr/g, similar to the results obtained by Key et al. (2012) for older granite samples from the Minna area in central Nigeria and Tijani et al. (2006) for schist-quartzites in SW Nigeria: further supporting the argument that the high Zr content of soils and sediments in the area does not indicate the presence of anomalous concentrations of the element in the bedrocks.

While this may help to explain the high Zr concentrations found in both the Anka and Birnin-Gwari areas, it does not account for the high concentrations of Th and its strong association with Pb and Cu in soils and sediments contaminated by artisanal gold mining and processing in the Anka area. The high concentration of Th, without a corresponding enrichment in associated elements such as U, La, Ce and Nb is a geochemically unusual situation. This, along with the strong correlation between Th and Pb in the samples could signify that the XRF determination of Th has been affected by interferent species, typically, Bi and Ag (Gawen Jenkin, personal communication). Under suitable conditions Ag and Bi may be present in galena in substantial amounts in solid solution (Foord et al., 1988). The substitution of Bi^{3+} for Pb^{2+} is made possible by the Bi^{3+}-Ag^{+} couple (Blackburn and Schwendeman, 1977) and is generally thought to function according to the scheme $2Pb^{2+} \leftrightarrow Bi^{3+} + Ag^{+}$ (Foord et al., 1988). Other than by ionic substitution for Pb, the presence of Ag and Bi may be accounted for by coexistence in solid solution of galena and matildite, $AgBiS_2$ (Blackburn and Schwendeman, 1977; Foord et al., 1988). However, when the six samples with the highest Th concentrations were scanned on a Wavelength Dispersive XRF Spectrometer, no silver or bismuth peaks were detected at detection limits of 100 µg/g Ag and 200 µg/g Bi, respectively. It is therefore still not clear what is responsible for the elevated Th values in some of the samples from Anka area. While it is still postulated that there may have been interferences on the determination of Th, no empirical data has been obtained to support the argument.

In the Anka area, the concentration of Ba appears to co-vary with those of Cu and Pb, such that samples with high Cu and Pb levels also have elevated Ba concentrations (Fig. 15, Appendix 4). This is perhaps as a result of associated barite mineralization or the presence of Ba in K-feldspar. Irrespective of their sources, the elevated levels of these metals in soils and sediments of the study area may present some environmental and human health problems. Thorium for example may be a source of radioactivity, with attendant long term adverse health effects. The concentrations of most of the remaining elements in both study areas (Table 2a&b) are low compared to the crustal baseline values, the exception being La and Ce in the Anka area and V and Ce in the Birnin-Gwari area. While the concentrations of Mo and U in both areas appear to be above the baseline values, it is important to note that the figures represent instrument detection limits and therefore may not necessarily be accurate.

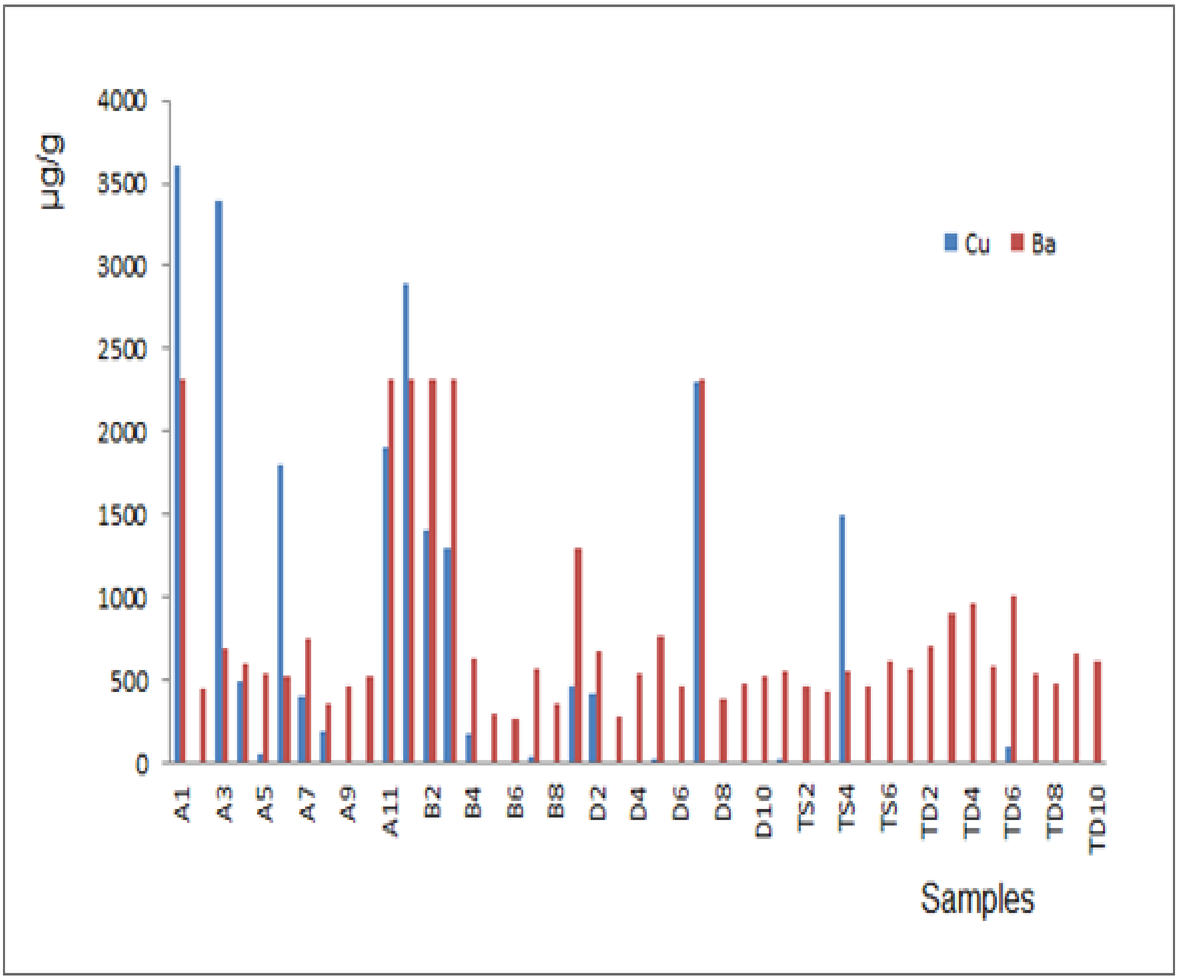

Figure 15 Relationship between Cu and Ba in samples from Anka area, northwestern Nigeria. See Fig.8b for location of of the samples.

3.3.2 Enrichment ratios

Element enrichment ratios (Albright, 2004; Tijani et al., 2006) were calculated in order to assess the extent of enrichment and /or depletion of trace elements in the soils of the two study areas relative to their crustal concentrations. In this work, the Upper Continental Crust concentrations of the elements published by Taylor and McLennan (1995) were used as baseline or background values and the enrichment ratio (ER) was calculated using the equations:

$$ER = \frac{\boldsymbol{Cn}}{\boldsymbol{Bn}} \text{ .... } \textbf{Eq 6},$$

where C_n is the concentration of an element measured in a sample and B_n is the background or baseline concentration, in this case, the upper crustal concentration of the element (Taylor and McLennan, 1985, 1995).

The results are summarized in Table 3 and show the factor by which the concentration of an element in the samples from the two areas exceeds their crustal abundances. Details of the results are available in Appendix 7 and 9. An enrichment ratio, ER of 1 indicates that the soil or sediment is neither enriched nor depleted in a particular element relative to the average crustal concentration. On the other hand an ER of > 1 or < 1 is an indication of enrichment or depletion, as the case may be. Based on this criterion, and using the mean ER values, only four elements (Rb, Sr, Nb and La) are found to be depleted in the soils and sediments from the Anka area, whereas all the remaining elements are enriched relative to the their crustal abundance. The ER for Pb (Table 3), which is about 900 times the crustal average concentration, is an indication of the severity of Pb contamination of the soils and sediments of the area.

The results further show that other elements with very high enrichments include Th (56 times), Cu (20 times) and Zr which is found to be about 7 times more concentrated in these samples, compared to its average abundance in upper crustal environments. The high levels of Pb and Cu in the soils and sediments of the Anka area has already been noted and it is linked to the artisanal mining activities in the area. Although the results indicate very strong enrichment in As, its concentration in the area is generally low; the high mean ER value is obviously affected by few samples with anomalously high concentrations of the metalloid.

Table 3 Summary of enrichment ratios, ER for the samples from Anka and Birnin-Gwari areas, NW Nigeria

	Enrichment ratios, ER					
	Anka (n = 45)			**Birnin-Gwari (n = 56)**		
Element	Min	Max	Mean	Min	Max	Mean
Sc	<0.9	2.5	1.0	<0.9	1.4	0.9
V	0.4	3.5	1.3	0.4	1.7	0.96
Cr	0.5	9.3	2.0	0.8	2.9	1.5
Ni	0.3	8.7	1.7	0.5	1.5	0.8
Cu	<0.4	14	20.2	<0.4	1.2	0.4
Zn	0.2	5.6	1.7	0.23	1.1	0.4
As	6.7	355.3	16.4	6.7	62.7	16.2
Rb	<0.1	1.2	0.4	0.3	1.3	0.7
Sr	0.1	0.9	0.3	0.1	0.4	0.2
Y	0.8	5.3	2.7	0.7	3.3	1.7
Zr	0.6	22.9	6.9	1.4	24.5	9.0
Nb	0.4	1.4	0.7	0.6	1.5	0.9
Mo	<6.7	15.3	6.9	<6.7	<6.7	<6.7
Ba	0.5	4.2	1.5	0.4	1.5	0.9
La	0.3	2.1	0.9	0.8	2.2	1.3
Ce	0.6	2.5	1.2	0.8	1.8	1.2
Pb	1.1	11080	876	1.0	2.6	1.4
Th	0.5	1006.17	55.8	1.1	4.2	2.0
U	<3.6	<3.6	<3.6	<3.6	<3.6	<3.6

Min: minimum; Max: maximum.

Furthermore, the enrichment data for Mo and U may not necessarily be a true reflection of their abundance in the samples from the Anka area. The concentration was found to be generally low and the value used in the computation of their ER is the lower limit of detection of the instrument.

Compared with the Anka area, the Birnin-Gwari study site has more elements at concentrations generally below their average crustal values. Seven elements (Sc, V, Ni, Rb, Sr, Nb and Ba) have mean enrichments ratios of less than 1 and are therefore depleted with respect to upper continental crust. The results (Table 3) show that As is the most enriched element relative to the baseline value, with an ER of 16. This tallies very closely with the generally higher As concentrations obtained in the Birnin-Gwari samples compared to those from Anka. The concentration of Zr in the Birnin-Gwari is about 9 times its upper crustal concentration, slightly higher than that found for the Anka area. Unlike in the Anka area, the Birnin-Gwari samples are only slightly enriched in Th (2 times) and Pb (1.4 times), while Cu is depleted relative to the continental crust with an ER of 0.4; further indicating that artisanal mining activities have not contaminated the environment with these elements as it did in the Anka area.

3.3.3 Index of geoaccumulation

One of the methods used in estimating the enrichment of the concentration of an element above the background or baseline values is to calculate the index of geoaccumulation, I_{geo}, proposed by Muller (1969). This method is used to assess the severity of pollution using seven enrichment classes based on an increase on the numerical value of the scale (Table 3).

Table 4 Classes of the index of geoaccumulation, I_{geo} (Muller, 1969).

I_{geo} value	I_{geo} class	Pollution intensity
>5	6	Extremely polluted
4–5	5	Strongly to extremely polluted
3–4	4	Strongly polluted
2–3	3	Moderately to strongly polluted
1–2	2	Moderately polluted
0–1	1	Unpolluted to moderately polluted
0	0	Unpolluted

The index of geoaccumulation, I_{geo} was calculated for all the samples from the Anka and Birnin-Gwari areas according to the equations (Muller, 1969):

$$\boldsymbol{I_{geo} = \mathbf{Log2}\left(\frac{Cn}{1.5Bn}\right)} \text{ .... } \mathbf{Eq\ 7,}$$

where C_n is the concentration of the element measured in a sample and B_n is its concentration in some reference sample or background concentration, which in this case is the average crustal value (Table 2a&b, Taylor and McLennan, 1985, 1995), while 1.5 is a constant which is introduced to minimize the effect of the variation of background values (Abrahim and Parker, 2008). Table 5 is a summary of the results for both Anka and Birnin-Gwari areas, where as the complete results are presented in appendix 6 and 8.

Based on the I_{geo} classes in Table 4, the results of this work (Table 5) show that both the Anka and Birnin-Gwari areas may have problems relating to As contamination, although as noted earlier on, only few samples in the Anka area have significantly high levels of As. The mean I_{geo} value of 3.3 for the Birnin-Gwari area falls within class 4 of the Muller, 1969 scale, indicating that the soils from this area are strongly polluted with respect to As. The mean for the Anka soils on the other hand corresponds to class 2 or moderately polluted. However, in some sample points in both study areas (Appendix 8 & 10), the results correspond to class 6 or very strongly polluted, as indicated by maximum I_{geo} values > 5.

Table 5 Summary of indices of geoaccumulation, I_{geo} for the samples from Anka and Birnin-Gwari areas, NW Nigeria

Element	Indices of geoaccumulation, I_{geo}					
	Anka (n= 45)			**Birnin-Gwari (n = 56)**		
	Min	Max	Mean	Min	Max	Mean
Sc	-0.7	0.8	-0.6	-0.7	-0.1	-0.7
V	-1.9	1.2	-0.4	-1.9	-0.2	-0.7
Cr	-1.6	2.6	0.1	-0.9	0.9	-0.1
Ni	-1.5	2.5	-0.1	-1.6	0	-1
Cu	-1.9	**6.6**	**0.5**	-1.9	-0.4	-1.8
Zn	-3.0	1.9	-0.9	-2.7	-0.5	-1.9
As	**2.1**	**7.9**	**2.5**	**2.1**	**5.4**	**3.3**
Rb	-4.2	-0.3	-2.3	-2.4	-0.2	-1.2
Sr	-3.9	-0.7	-2.4	-4.2	-2.0	-3.3
Y	-0.9	1.8	0.3	-1.0	1.1	0.1
Zr	-1.2	3.9	1.9	-0.1	4.0	2.2
Nb	-1.9	-0.1	-1.1	-1.3	0.0	-0.7
Mo	2.1	3.3	2.2	2.1	2.1	2.1
Ba	-1.6	1.5	0.3	-1.9	0.0	-0.8
La	-2.2	0.5	-0.9	-0.9	0.6	-0.2
Ce	-1.3	0.7	-0.4	-0.8	0.3	-0.3
Pb	**-0.4**	**12.8**	**5.1**	-0.5	0.8	-0.1
Th	-1.7	9.4	2.1	-0.4	1.5	0.3
U	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2

Min: minimum; Max: maximum.

However, only the Anka area has pollution problem with respect to Pb, with a mean I_{geo} value of 5.1, corresponding to class 6 of the Muller (1969) scale or very strongly polluted. In fact, at more than 45 % of the sample sites, the value is far greater than the maximum I_{geo} value of 5 proposed by Muller (1969), similar to the trend already noticed with the enrichment ratios. The maximum value of 12.8 underscores the intensity of Pb pollution in this area due to artisanal mining and processing of lead-rich gold ores (Plumlee and Morman, 2011). All samples from the Birnin-Gwari area on the other hand have values below 1, corresponding to unpolluted to moderately polluted conditions, showing that the area has no problem with respect to Pb contamination of surface soils and stream sediments.

The mean index of geoaccumulation for Cu in both the Anka and Birnin-Gwari areas is below 1, indicating no pollution to moderate pollution. But about a third of the Anka samples, mainly those from Abare and Bagega sampling sites (Fig. 8b), actually have values generally falling between 2.2 (moderately to strongly polluted) and 6.6 (very strongly polluted), consistent with the total concentration data and enrichment ratios. A plot of the I_{geo} values for Pb and Cu in the area (Fig. 16) shows a similar, though not exact pattern of Pb and Cu enrichment and/ or depletion in soils of the area. The close association of the two metals in these samples is an indication that the soils were contaminated by the processing of similar ores, rich in Pb and Cu minerals.

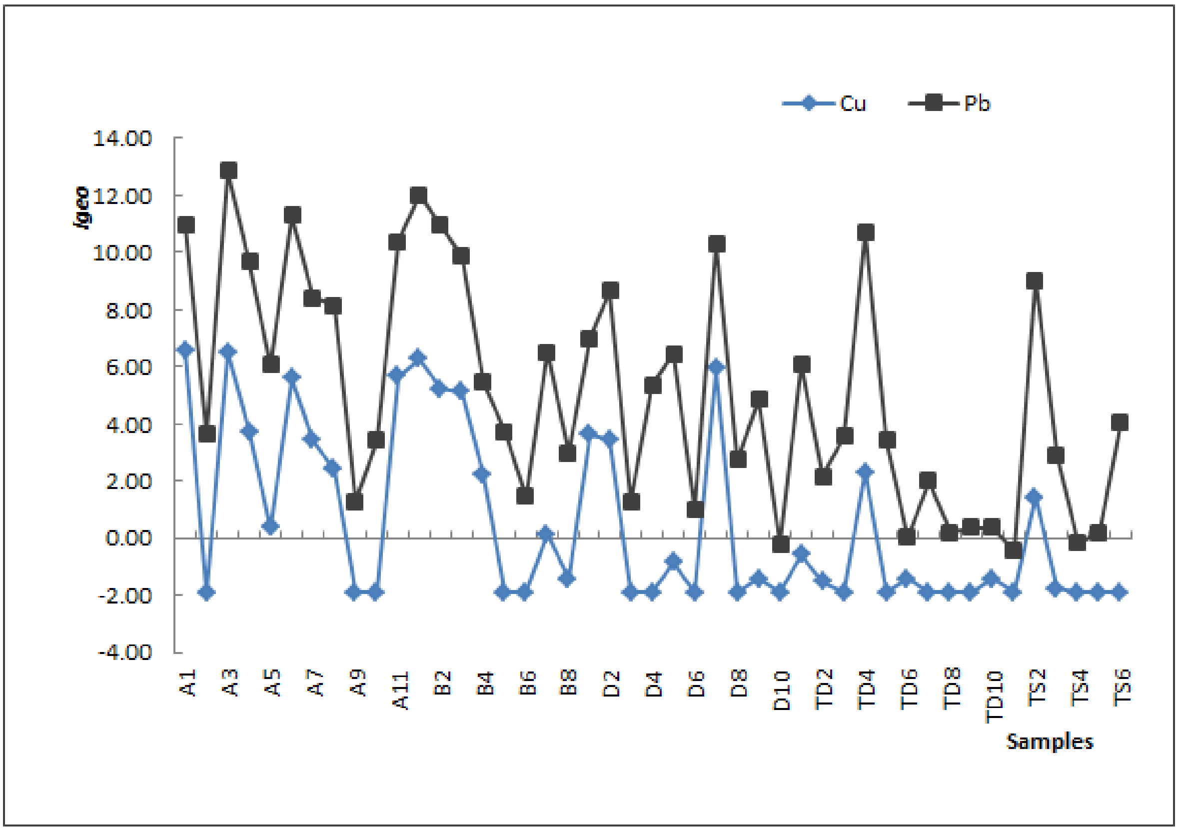

Figure 16 Plot of indices of geoaccumulation (I_{geo}) of Pb and Cu in samples from the Anka area, NW Nigeria, showing very similar pattern of enrichment of the two elements in the samples.

The results for Sc, V, Rb and Sr in both study areas fall within class 0 of the scale, showing that there has not been any contamination of the soils with these elements. Similarly, the results show that both areas are not polluted by Cr, Zn, Y and Ba except in few places in the Anka area, where these elements are found to cause moderate to strong pollution. Similar results were obtained for Zr, Th and U in the Birnin-Gwari area.

3.4 Geochemical association

An attempt was made to hunt for geochemical associations using the data from both Anka and Birnin-Gwari study sites. This was done with a view to determining the possible sources of elements, especially potentially toxic elements in the soils and sediments of the two areas. Multivariate statistical methods in the form of correlation matrix (CM), principal component analysis (PCA), along with hierarchical cluster analysis (HCA) were used to classify the elements into groups that may signify common origin. All multivariate statistical tests were performed using SPSS (PASW Statistics 18) for Windows.

3.4.1 Correlation Analysis

Spearman correlation (r_s) was used in order to assess the strength of the relationships between different elements (Gong et al., 2010), particularly as it relates to the effect of artisanal mining activities. This non-parametric correlation method was chosen in order to avoid problems associated with non-normally distributed (Fig. 13) data (Field, 2009). The Spearman correlation coefficient, r_s, is significant in all cases reported in this section at 0.01 level of significance (that is, $p = 0.01$).

The results show that for the Anka area, there is a very strong relationship between Pb and each of Cu and P_2O_5 and to a lesser extent Fe_2O_3, with r_s values of 0.89, 0.95, 0.84 and 0.50 respectively. These elements also show strong to very strong correlation with each other, the correlation coefficients being 0.66 for Cu/Fe and 0.62 for Fe/ P_2O_5. While correlation does not necessarily indicate causality, in theory it is expected that a strong positive correlation between two or more elements will indicate similar source or origin (Wu et al., 2011). These relationships, especially the strong association of Pb and Cu which is consistent with the findings of Wu et al. (2011), are thought to be a reflection of the contamination of the soils and sediments of this area already noted in section 3.3 above. Similar results were obtained (Section 3.4.2) using principal component analysis, along with cluster analysis. In the Birnin-Gwari area however, this relationship was not found, with only Cu and Fe_2O_3 exhibiting a fairly strong correlation ($r_s = 0.45$, $p < 0.01$), further confirming the observation that gold exploitation in the Birnin-Gwari area has not had a similar effect on soil and sediment chemistry compared to that observed in the Anka area.

An interesting feature of the correlation data for Birnin-Gwari area is the very strong correlation observed between the lithophile elements Y, Nb, Th, TiO_2, Zr, Ce and La, with the correlation coefficient between Y and the other elements ranging from 0.51 to 0.92 ($p = 0.01$). When compared with each other, the relationships were also found to be very strong, with the correlation coefficients of Nb/Th, TiO_2/Zr, Nb/TiO_2 and La/Ce being 0.91, 0.81, 0.89 and 0.83 respectively. The close association of these elements in the samples from the Birnin-Gwari area may be an indication of the effect of resistant heavy minerals from felsic rocks (mainly granites and gneisses) on the geochemistry of soils and sediments in the area.

Similarly, there is a strong positive correlation between iron oxide and manganese oxide in each study area ($r_s = 0.77$ for Anka and 0.76 for Birnin-Gwari, $p = 0.01$) and between the two oxides and each of Sc, V, Cr, Ni, Cu, Zn and to a lesser extent, Sr. This shows the importance of Fe/Mn oxides in controlling the geochemistry of trace elements in soils and sediments (Lapworth et al., 2012), although the correlation appears to be stronger between iron oxide and the trace elements than between them and manganese oxide. These relationships, as well as those between the trace elements and magnesium oxide are similar to the loadings of component 1 of the principal component factor analysis for both study areas.

The results do not show any particularly strong correlation between As and any other element in both study sites, probably indicating a different source. The highest coefficients of correlation obtained are 0.39 and 0.41 for As/TiO2 in the Anka and Birnin-Gwari areas respectively. Considering that the concentration of As in samples from the Birnin-Gwari area have been consistently higher than those of majority of the other trace elements (Appendix 6), which resulted in high ER and I_{geo} values (Section 3.3.3); the seeming lack of association with other elements, including the major oxides is probably an indication of a different origin or source for the metalloid in the soils and sediments of the area. It is speculated that a possible source of As in these soils and sediments is the use of pesticides in farmlands.

3.4.2 Principal component and cluster analysis

Based on the high concentrations of some elements obtained in certain sampling sites and the strong correlation between the elements indicated by the Spearman correlation matrix, the data was treated using principal component analysis, along with hierarchical cluster analysis to further assess the relationship patterns. Varimax orthogonal rotation with Kaiser normalization was applied to the PCA in order to minimize the effects of non-normal data (Gong et al., 2010), especially the effects of high concentrations, and components were extracted for both the Anka and Birnin-Gwari areas based on Kaiser's default Eigenvalue of 1 (Field, 2009). On the other hand, CA was performed using the Squared Euclidean Distance method. The results are presented in Tables 6 and 7a &b and Figure 17.

For the Anka samples, seven components explaining 88 % of the variance were extracted (Table 6). However, only four of the seven components, representing about 67 % of the variance have significant loadings of elements and when the test was repeated by specifying only four factors, a similar distribution was obtained, with a total variance of about 73 %. Therefore only the first four components are interpreted in this work.

The factor loadings (Table 7a) show that component 1 which explains 22 % of the variance is strongly positively correlated with MgO, CaO, Cr, Sc, Ni, Na_2O, Al_2O_3 and V. The second component also explains about 22 % of the variance and is very strongly positively correlated with Pb, P_2O_5, Cu, Th, Fe_2O_3 and Mn. Both C1 and C2 have a strong negative correlation with SiO_2. Components 3 and 4, both explaining about 11 % of the variance are correlated with TiO2, Nb, Zr and La, Ce, K2O, Sr respectively.

Table 6 Total variance explained for element contents in soils and stream sediments from Anka and Birnin-Gwari areas of NW Nigeria.

Anka									
Comp	Initial Eigenvalue			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% Var	Cumul %	Total	% Var	Cumul %	Total	% Var	Cumul%
1	9.2	32.8	32.8	9.2	32.8	32.8	6.2	22.2	22.2
2	5.1	18.3	51.1	5.1	18.3	51.1	6.1	21.8	44.0
3	3.3	11.7	62.9	3.3	11.7	62.9	3.2	11.5	55.5
4	2.5	8.8	71.7	2.5	8.8	71.7	3.2	11.4	66.9
5	1.9	6.8	78.5	1.9	6.8	78.5	2.5	9.0	75.9
6	1.6	5.6	84.1	1.6	5.6	84.1	1.9	6.7	82.6
7	1.2	4.3	88.4	1.2	4.3	88.4	1.6	5.7	88.4
8	0.8	2.8	91.1						
Birnin-Gwari									
Comp	Initial Eigenvalue			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% Var	Cumul %	Total	% Var	Cumul %	Total	% Var	Cumul%
1	9.6	34.4	34.4	9.6	34.4	34.4	6.6	23.5	23.5
2	5.7	20.4	54.8	5.7	20.4	54.8	5.7	20.2	43.7
3	3.8	13.5	68.3	3.8	13.5	68.3	5.2	18.5	62.2
4	2.7	9.7	78.0	2.7	9.7	78.0	3.2	11.5	73.6
5	1.6	5.7	83.7	1.6	5.7	83.7	2.8	10.1	83.7
6	0.9	3.2	86.9						

In contrast, five components were extracted for the Birnin-Gwari area (Table 6, 7b) and they account for about 84 % of the variance. Component 1 is associated with the loadings of P_2O_5, CaO, MgO, Fe_2O_3, MnO, along with Zn and Ni, while component 2 is strongly positively correlated with Y, Nb, Th, TiO_2, Zr, La and Ce. The third component is associated mainly with Sc, Al_2O_3, V, Cr, Cu, along with less strong correlation with Ni, Rb and K_2O. The last two components have Sr, Ba, Pb, K_2O and As, Na_2O and Rb respectively.

Principal component analysis does not show with certainly what controls the distribution of elements in environmental matrices, but useful inferences may be drawn from the data. Probably, the most interesting aspect of this result is component 2 for the Anka area, which is strongly correlated with the two most important elements in the ores, the processing of which leads to the contamination of soils and sediments in the area. The strong association of Pb and Cu, along with P_2O_5, Fe_2O_3 and MnO in this component further strengthens the findings from the Spearman correlation matrix and closely similar pattern of Pb and Cu enrichment/ depletion highlighted by the geoaccumulation indices (Fig. 16), and this is, to a large extent supported by results of cluster analysis (Fig. 17). However, the loading of U and Th in different components in Table 6a and at opposite ends of Figure 17 is clearly due to the uncertainty about the XRF measurement of Th, which has already been noted. That this pattern is not observed for the Birnin-Gwari area goes on to confirm the importance of mineralogy and chemistry in controlling the environmental effects of mineral deposits. The possible source of Th in the samples from Anka area has not become any clearer as a result of these tests, but it appears to be related to the Pb-Cu ores and its mineralogy and geochemistry may need to be further investigated in order to assess possible radioactivity risks.

Component 1 for the Anka area is correlated with the loadings for MgO, CaO, Cr, Sc, Ni, Na_2O, Al_2O_3, V as well as some Fe_2O_3. The same component for the Birnin-Gwari area has the association of P_2O_5, Fe_2O_3, MnO, Zn, Ni, MgO and CaO and to some extent, La and V. The correlation of this component in both cases with MgO and CaO (Table 7a&b) may be an indication of the similar lithology, probably the acidic igneous rocks and their metamorphic products (Zibret and Sajn, 2010). But the presence of Al, Cr as well as Fe in the Anka case (Table 7a), similar to the association in component 3 in the Birnin-Gwari area may well be an indication of the low grade metamorphic hosts of the mineralization.

The association of the lithophile elements Y, Nb, Th, Ti, Zr, Ce and La in component 2 in the Birnin-Gwari area (Table 7b) has already been observed from the correlation matrix and is again interpreted as an indication of the influence of the granitic rocks (Zibret and Sajn, 2010) and heavy mineral grains concentrated by placer processes on the chemistry of soils and sediments in the area. In the Anka area however, the interpretation becomes rather difficult because the correlation of these elements straddles two groups and therefore no clear pattern is readily observable. The strong positive correlation between component 4 in the Birnin-Gwari area and Sr, Ba, Pb and K_2O is similar to the pattern in the correlation matrix for the area and may indicate that the distribution of these elements in the soils and sediments of the area is controlled by clay minerals and mica (Lapworth et al., 2012). This further strengthens the view that Pb in the Birnin-Gwari samples may not be related to the artisanal mining, but is contributed by lithogenic sources, such as the weathering of mica.

Table 7a Rotated component matrix[a] for element contents in soils and stream sediments from Anka area, NW Nigeria

Element	Component						
	1	2	3	4	5	6	7
MgO	0.93						
CaO	0.88					0.33	
Cr	0.85						
Sc	0.85						
Ni	0.83						
Na_2O	0.69						
Al_2O_3	0.61			0.55			0.44
V	0.56	0.40			0.53		
Pb		0.92					
P_2O_5		0.89					
Cu		0.88					
Th		0.85					
SiO_2	-0.53	-0.69					
Fe_2O_3	0.54	0.63			0.46		
MnO	0.35	0.53		0.49			
TiO_2			0.87				
Nb			0.87				
Zr			0.58				
Ce				0.86			
La			0.42	0.76			
K_2O				0.63			0.35
Sr	0.43			0.61			
As					0.77		
Ba		0.41			0.59		
pH						0.89	
Zn						0.79	
Rb							0.69
LOI	0.33	0.45			0.39	0.39	0.49

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 15 iterations.

Table 7b Rotated component matrix[a] for element contents in soils and stream sediments from Birnin-Gwari area, NW Nigeria

Element	Component				
	1	2	3	4	5
P_2O_5	0.93				
Fe_2O_3	0.93				
MnO	0.91				
Zn	0.80				
LOI	0.79				
Ni	0.78		0.52		
SiO_2	-0.72		-0.58		
MgO	0.54				0.50
CaO	0.54				
Y		0.95			
Nb		0.94			
Th		0.93			
TiO_2		0.91			
Zr		0.84			
Ce		0.81			
La	0.47	0.66			
Sc			0.91		
Al_2O_3			0.81		
V	0.49		0.81		
Cr			0.74		0.49
Cu			0.65		
Sr				0.90	
Ba				0.82	
Pb				0.75	
K_2O			0.52	0.56	0.53
As					0.83
Na_2O					0.72
Rb			0.58		0.63

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 6 iterations.

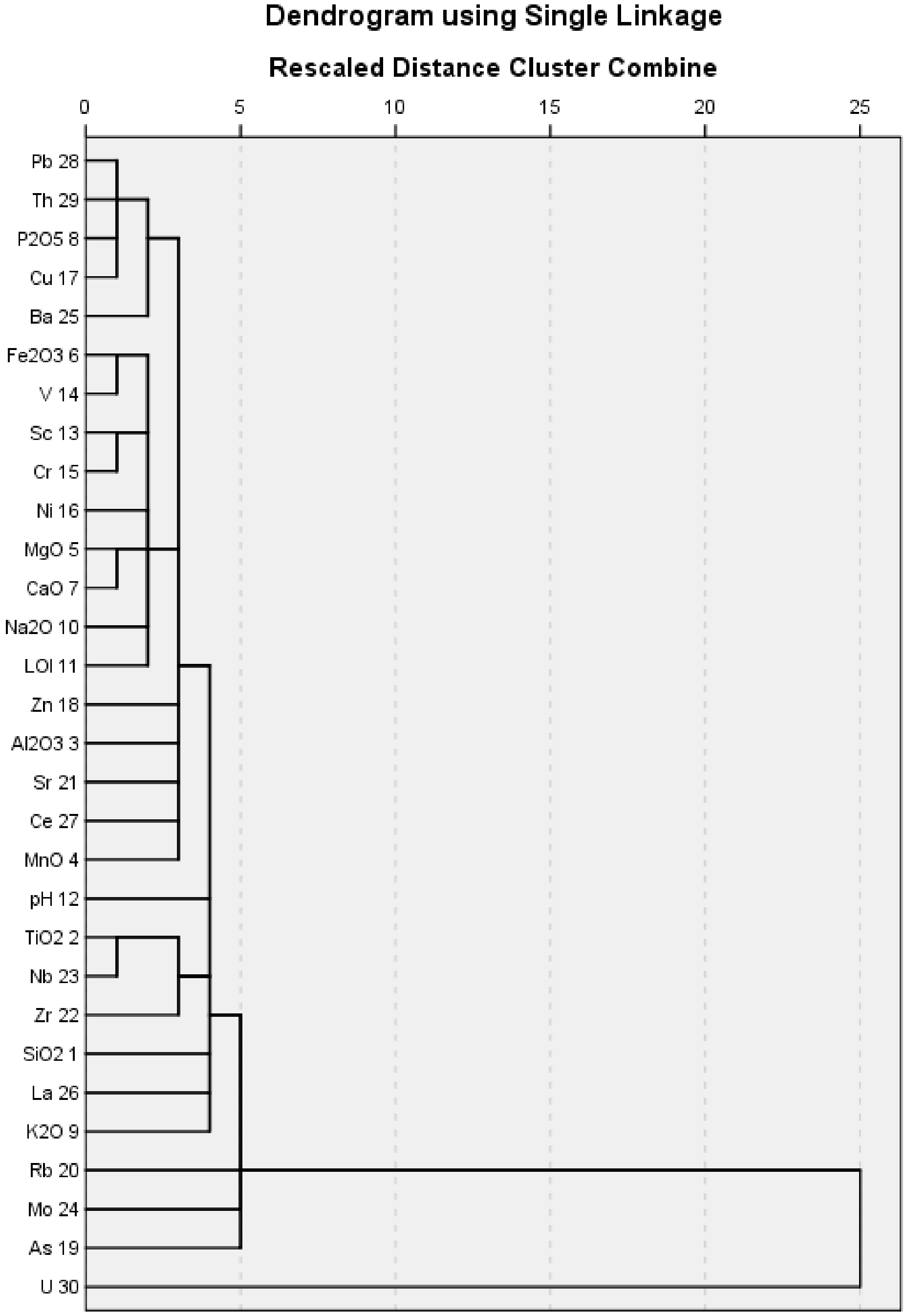

Figure 17 Dendrogram showing the result of cluster analysis performed on the Anka data. This shows similar pattern to the results of principal component analysis (Table 3.6a). Note for example the clustering of Pb, Cu and P at the top end of the plot. The loading of Th and U at opposite ends of the plot is clearly a result of the effect of high Pb concentration on Th data already noted at page 69.

3.5 Chapter summary

The results presented in this Chapter show that surface soils and sediments from both the Anka and Birnin-Gwari areas are depleted in base cations and alumina, but enriched in silica, relative to the upper continental crust, consistent with the findings of other workers in Nigeria. This is attributed to intensive tropical chemical weathering, coupled with physical removal of fine clay minerals through the combined effect of wet season overland runoff and dry season winds on the one hand, and the movement of base cations into deeper horizons of soils through leaching. This may have implications for surface water quality by lowering of pH due to reduced capacity of soils to supply alkalis and the mobility of contaminant trace elements. The same mechanism is identified as the reason for the high concentration of Zr found in soils and sediments of both study areas; the bedrocks were found not to have high concentrations of zirconium.

There is clear evidence, in the form of high concentrations of Pb and Cu, high enrichment ratios and indices of geoaccumulation, that artisanal mining and processing of Pb-Cu rich ores in the Anka area has resulted in serious Pb and Cu and to a lesser extent, As contamination of soils and sediments. However, this activity has not had the same effect in the Birnin-Gwari area, where Pb and Cu concentrations are generally low. Similarly, high concentrations of Th obtained in samples from Anka and the very strong positive correlation of Th with Pb and Cu, and the loading of these elements in the same factor of the principal component analysis is an indication that the concentration of Th in the ores is high. There is therefore the need to investigate the geochemistry and mineralogy of this metal in the ores and the contaminated media in order to understand the potential human health risks associated with it, especially in terms of radioactivity.

The main concern identified in the Birnin-Gwari area is the comparatively high As concentrations in soils and sediments, which does not appear to be controlled by the artisanal gold mining activities. In the next two chapters (Chapter 4 &5), the environmental and human health risks of some of the potentially toxic elements have been further investigated, by using sequential extractions protocols (SEPs) and *in vitro* bioaccessibility (IVBA) tests.

Chapter Four

Results: Geochemical partitioning of heavy metals

4.1 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.

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.

In this chapter, results of geochemical fractionation experiments showing the percentages of potentially toxic elements thought to be associated with the exchangeable, carbonate and iron- manganese oxides fractions are presented. A total of thirty nine (39) samples were analyzed in order to compare geochemical partitioning between contaminated and near pristine samples. Twenty five soil and stream sediment samples collected from villages in the Anka area, where artisanal gold mining has led to contamination of soils, in and around living compounds, were extracted using the sequential extraction protocols (SEPs). Details of the methods used have been outlined in chapter two and the results are summarized in Figure 18a. A further batch of 14 less contaminated samples from the Birnin-Gwari area was also analyzed and the results (Fig. 18b) compared with those from the Anka area. As highlighted in chapter two, the fraction of elements held within sulphide/ organic matter and residual phases have not been determined, chiefly because they are considered to be of comparatively low mobility and therefore less likely to constitute immediate environmental or human health concerns.

4.2 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, in the samples from Anka area, the amount of elements associated with this fraction is generally very low, ranging from nearly zero for As and 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 > As and Cr.

In the Birnin-Gwari samples, the proportion of metals associated with the exchangeable fraction is similarly very low, especially for As, Cr and Pb; their concentration in this fraction generally falling below the detection limit. Mn however shows some significant concentration in this fraction similar to that in the Anka samples; the extracted amounts ranging from 0.2 to 12 % (mean, 3.28 %) of total Mn in the samples. Partitioning of Cu, Ni and Zn in this phase have been found to be comparatively lower with only 0 to 1 % (mean, 0.62 %) of total Cu extracted in this step. The range of extractability for Ni and Zn is 0 to 3 % with mean values of 1.67 % and 1.57 % respectively. Based on these results, the fractionation of the metals with respect to the exchangeable fraction is found to decrease in the order Mn > Ni > Zn > Cu > Cr, As and Pb.

The results obtained for the exchangeable fraction in this work 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) 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. No significant differences appear to exist in the way metals partition in the exchangeable fraction in samples from the two study areas.

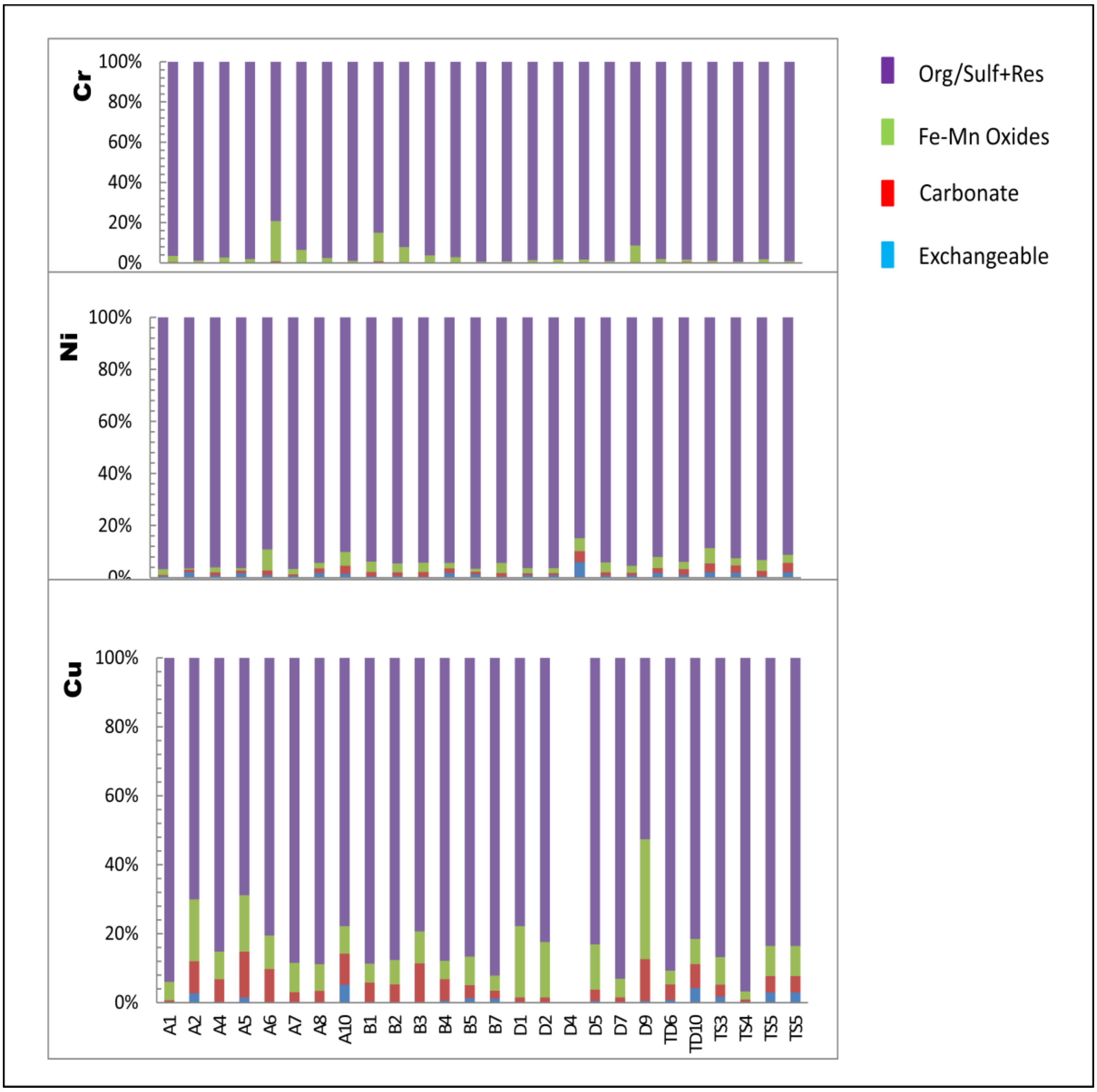

Figure 18a Partitioning of potentially toxic elements in three labile phases in soils and sediments of Anka area, north-western Nigeria. In this work, the Org/Sulf+Res fraction is the difference between the sum of the SEP steps and the near total concentration of each element. Locations of the samples are shown in figure 8b.

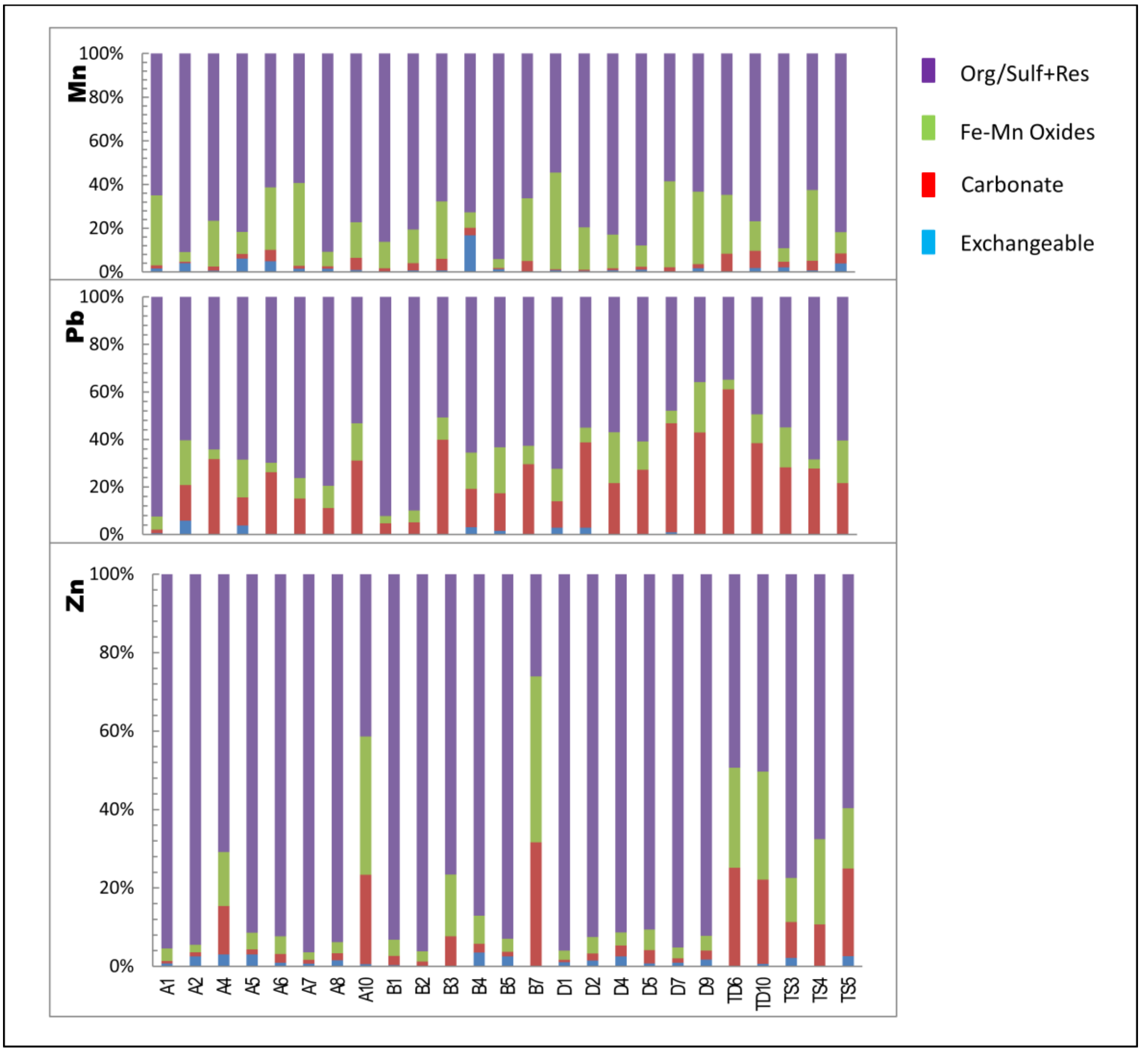

Figure 16a(cont'd)

Most of the elements measured, with the exception of Mn have shown very low association with this phase in all samples, irrespective of the area they came from (Fig. 18a& Fig. 18b). It seems also that the fact that the samples from Anka had generally higher total concentrations of some of the elements, especially Pb and Cu, did not affect their distribution in terms of the exchangeable fraction. Similarly, comparatively higher total As concentration in the samples from Birnin-Gwari did not appear to enhance its concentration in this phase relative to the samples from Anka.

The low mobilization of all the elements in this step from both areas (Fig. 18a& Fig. 18b) may be due in part, to the relatively high pH (4.89 – 9.24) obtained for the Anka samples, which may decrease the solubility and availability of most metals and their ability to form chelates (Burt et al., 2003; Forstner and Whittmann, 1983). This may be a reflection of the influence of broadly similar geology, climate and therefore soil type. The generally low alumina and base contents of these samples (Chapter 3) 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 and Birnin-Gwari areas of north-western Nigeria. Mobilization of contaminants bound to this fraction is therefore considered to unlikely to cause any serious environmental and/or human health problems of metal toxicity in the two areas; although it may limit the availability of essential elements to plants and subsequently livestock.

4.3 Carbonate fraction

This is the second most labile fraction of heavy metals which can be both authigenic and detrital. According to Singh et al (1999), this fraction 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. 18a), accounting for between 1 and 40 % (mean, 21.6 %) of total As and 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 (Fig.18a), 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 a strongest affinity with this fraction, and the amount of carbonate bound metals was found to follow the order Pb > As > Zn > Cu > Mn > Ni > Cr.

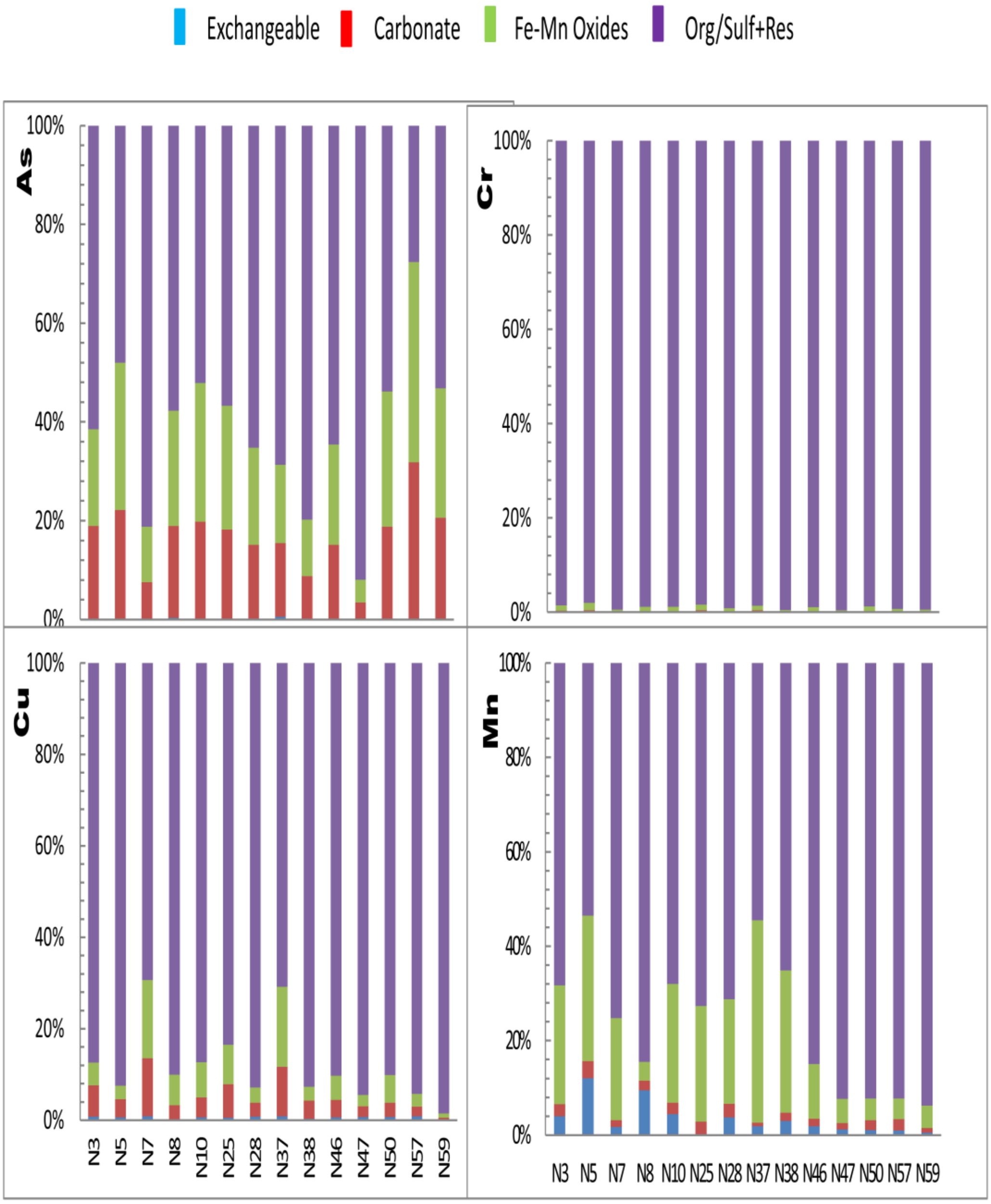

Figure 18b Partitioning of potentially toxic elements in three labile phases in soils and sediments from Birnin-Gwari area, north-western Nigeria. In this work, the Org/Sulf+Res fraction is the difference between the sum of the SEP steps and the near total concentration of each element. Locations of the samples are shown in figure 8a.

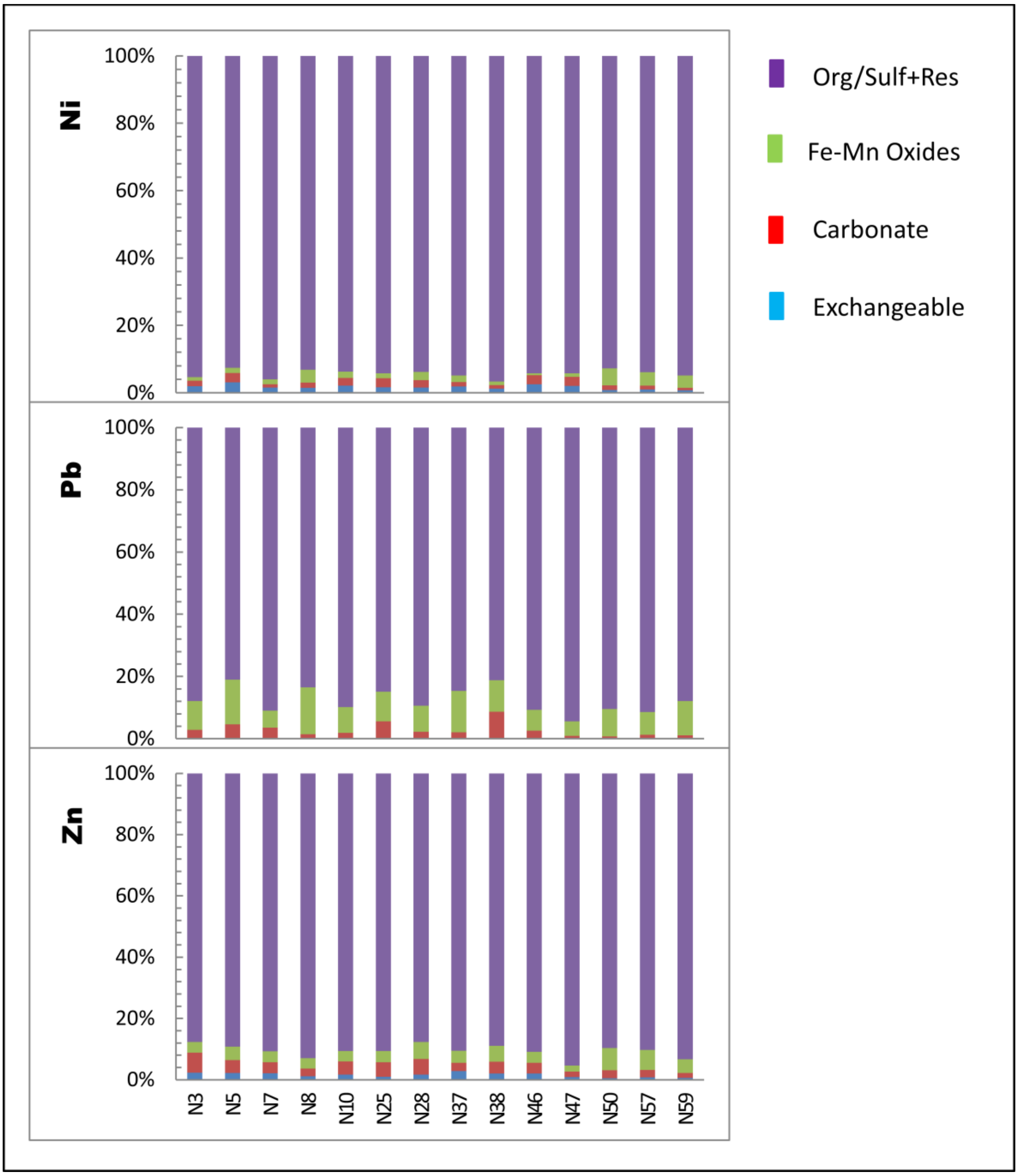

Figure 18b (cont'd)

In the case of the Birnin-Gwari samples (Fig. 18b), the partitioning of most of the metals in this fraction is generally not strong, except for As which showed considerable lability; with 3.5 to 32 % (mean, 16.68 %) of the total As extracted in this phase. This is followed by Cu (0.4-13 %, mean 4.86 %) and Zn (1-7 %) with an average of 3.51 %. The results for Pb, Mn and Ni are 0.5 to 9 % (mean, 2.80 %), 0.7 to 3.7 % (mean, 2.04 %) and 0.5 to 3 % (mean, 1.79 %) respectively; while Cr has the lowest solubility of between 0.1 and 0.4 % (mean, 0.23 %,). The association of metals with this phase was therefore found to follow the order As > Cu > Zn > Pb >Mn > Ni > Cr.

The very strong association of Pb with this phase in samples from Anka area (Fig. 18a) 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 due to the similarity of their ionic charge with that of Pb and possibly Ca. 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 data from Anka however contrast markedly with the results from the Birnin-Gwari area, where the affinity of Pb, Cu and Zn for this fraction was found to be comparatively low in all samples. This is probably due in part to the low total concentrations of these metals in the soils and sediments of the area, but it may also be an indication of a geogenic input of the metals, where the elements are held within structures of less labile minerals. The reason for the strong fractionation of As in this phase observed for both sample areas is not clear, but it may be a result of the metalloid occurring in the form of readily soluble arsenate or oxide minerals. On the contrary, the results for Mn, Ni and Cr across the two sites are broadly similar, showing generally low concentrations in the carbonate fraction. Cr has consistently been the least soluble of all the elements measured in both the Anka and Birnin-Gwari areas.

The results show that this fraction is geochemically very significant in terms of the mobilization of potentially toxic elements into the environment, particularly in the Anka area. In this area, mainly Pb, but also Cu, Zn and As have been found to be labile and likely to become readily available for uptake by plants and passed on through the food chain. In the Birnin-Gwari area however, only As was found to have significant association with this phase and its release is considered to be the main environmental concern in the area. Overall, based on these results, we do not envisage any environmental problems related to the mobilization of Cr, Ni and Mn from this fraction in either area due to their low association with the phase.

4.4 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). Mn oxides have been reported (Hudson-Edwards, 2000) to take up heavy metals mainly through the agency of adsorption, cation exchange and coprecipitation. 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 measured in the samples from the Anka area have shown a strong to very strong association with this phase (Fig. 18a). The strongest affinity is shown by As with a range of 2.2 to 67 % (mean, 32.70 %), followed 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.

Based on the mean of the percent extraction, the association of the elements with this phase generally appears to follow the order As > Mn > Cu > Pb > Zn > Cr > Ni. However, when the two samples with high to very high Cu values are taken out, then Pb will appear to show 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 for samples from Anka, but more especially the Birnin-Gwari area. McKenzie (1980) has 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.

Similar to its behaviour in the Anka samples, As shows a strong affinity for the Fe/Mn oxide fraction in the Birnin-Gwari area (Fig. 18b) relative to the other elements: about 4.5 to 41 % (mean, 21.67 %) of the total As was extracted in this step. This is very similar to that of Mn, which has a percentage extraction in this step of between 4 and 43 % (mean 18.36 %). Compared with As and Mn, most of the other elements show generally weaker association with this phase, with only Pb showing slightly significant partitioning to the oxide minerals; 4.5 to 15 % (mean 9.44 %) of total lead was dissolved by the treatment with hydroxylamine hydrochloride. However, compared with results from Anka, the Birnin-Gwari samples have more Pb associated with Fe-Mn oxides than with carbonate phases. This is followed closely by Cu (0.9 to 18 %, mean 6.39 %) and Zn (1.90 to 7.4 %) with an average of 4.31 %, while the solubility of Ni ranges from 0.6 to 5 % (mean 2.23 %). Cr has consistently been least soluble in these samples, with only 0.2 to 1.6 % (mean 0.79 %) of the total Cr associated with this phase. Based on the mean values, the strength of the affinity of metals with the Fe/Mn oxide minerals in the samples from Birnin-Gwari area was found to decrease in the order As > Mn > Pb > Cu > Zn > Ni > Cr.

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 met in natural solutions (Krauskopf, 1957). This has implication for the release of associated heavy metals and other potentially toxic elements bound to Fe/Mn oxides in soils and stream sediments into surface and ground water systems or making them phytoavailable. The results of this work have shown that this phase is geochemically very significant in terms of the sequestration of most of the PTEs measured in the samples from both the Anka and Birnin-Gwari areas, and 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 As and Mn in the Birnin-Gwari area and Cu, Pb and Zn in the Anka region. The results did not, however, show any risks of metal toxicity associated with the release of Ni and Cr from this fraction in samples from either area.

4.5 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. It is worth noting that although the sulphide / organic matter bound fraction was not considered in this work as being very labile, oxidation of sulphide minerals, especially in the Anka area, will mean that metals held in that fraction will become more susceptible to mobilization.

Recovery is calculated according to the equation:

$$Recovery = \frac{(\sum Sequential\ extraction\ procedure\ steps)}{Total\ concentration} \times \mathbf{100} \qquad \textbf{Eq 8}.$$

The result summarized in Table 8 shows that for samples from Anka, the amount of As extracted in the three steps as a percent of total concentration ranges from 3.50 to 204 % with a mean of 97.1 %. The very high percentage recoveries recorded for As in most of the samples are almost certainly due to the use of total arsenic concentration estimated at half the detection limit. The true concentration of As may be higher than the estimated 5 μg/g. For the few samples with total concentration above the instrument detection limit of 10 μg As/g, the recoveries were found to be generally below 50 %, whereas in one sample with over 500 μg As/g, only 3.5 % was extracted across the three steps. Similarly, the results for the Birnin-Gwari samples show that the amount of As extracted across the three fractions is high, ranging between 8 and 73 %, with an average of 38.4 % of total As in the soils and sediments of the area. However, unlike the case with the Anka samples, the recovery values obtained for As in the Birnin-Gwari area do not suffer from the problem of estimated total concentrations; the mean total As concentration in these samples is 26.8 µg/g, well above the instrument detection limit of 10 µg/g.

A similar pattern was observed for Cu and Pb, where samples with higher total concentrations gave comparatively lower recoveries relative to those with low concentrations, especially those close to, or below, the detection limits. Although Cu recovery seems to span a wide range (3.3-118.6%, Table 8) in the Anka samples, 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, while for the Birnin-Gwari area, Cu recovery was slightly lower, falling in the range of 1.5 to 31 % (mean, 11.9 %). Discounting the samples from Anka with very high values, the difference between the two data sets is quite small. However, the data indicates that there is more likely to be problems of Cu toxicity in the Anka area than in Birnin-Gwari, because of the existence of the metal in comparatively more labile forms in the former area.

Table 8 Results of recovery calculation for the three step extraction of samples from Anka and Birnin-Gwari areas.

Element	Anka area		Birnin-Gwari area	
	Range	Mean	Range	Mean
As	3.6 – 204	97.1	8 - 73	38.4
Cr	0.6 - 20.8	3.6	0.4 - 2	1
Cu	3.3 - 118.6	20.6	1.50 - 30.7	11.9
Ni	3.3 - 15.2	6.6	3.4 - 7.4	5.7
Mn	6 - 45.5	25.2	6.3 - 46.5	23.7
Pb	8 – 65	38	5.6 - 19	12.3
Zn	4 – 74	22	4.6 - 12.4	9.4

Similarly, the amount of Pb dissolved across the three steps generally falls between 20 and 65 % (mean, 38%) of total metal in the Anka samples, with only three samples with very high total concentrations (~60, 000 – 120, 000 μg Pb/g) giving recoveries of between 8 and 10 %. In the Birnin-Gwari samples, however, the recovery of Pb is comparatively low, falling between 5.6 and 19 % (mean, 12.3 %). Overall, Pb was found to be very soluble in the Anka samples, to a large extent contributed by the dissolution of Pb from the carbonate fraction, but also the oxide phases. The high rates of mobilization of Pb in the Anka area have 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. *In vitro* bioaccessibility of Pb in selected samples from this area has been found (Chapter 5) to be very high, resulting in the minimal risk level for Pb being exceeded in all samples. In the Birnin-Gwari area however, Pb toxicity is less likely to be a problem, due to the generally low total concentrations coupled with its low mobility in the samples as indicated by these data.

The amount of manganese recovered in both the Anka and Birnin-Gwari samples is relatively high, ranging from 5.9 to 45.4 % (mean, 25.2 %, Table 8) and 6 to 47 % with a mean of 23.7 % for the two areas respectively. 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 in the Anka samples is highly variable across the samples, ranging from 4 to 74 % (mean, 22 %), without any clear pattern. In the Birnin-Gwari samples, however, Zn recovery was very low, only 4.5 to 12.5 % (mean, 9.4 %) being mobilized.

The result for Ni in the Anka area is in the range of 3.3 to 15.2 % (mean, 10.2 %), slightly higher than 3.3 to 7.5 % (mean, 5.7 %) for samples from Birnin-Gwari area. The dissolution of Cr in both study sites has been found to be very low, yielding recoveries in the range of 0.6 to 20 % with mean value of 3.2 % for the Anka samples and 0.4 to 2 % (mean, 1.0 %) for Birnin-Gwari respectively, 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 samples from both areas: the results therefore show that the two metals are bound to less labile fractions in the soils. Giving the generally low loss on ignition (LOI, %) obtained for these samples (Chapter 3), the organic matter bound 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, 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 and Burt et al. (2003) who 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 from both areas, points to their low accessibility in the environment and therefore are considered to be potentially of low toxicity in both areas.

In spite of the high concentrations obtained for some of the elements, especially in the Anka samples, the results (Table 8) show that less than 50 % of the total concentration of most of the elements is easily mobilizable. In the Anka area for example, the percentage of total As, Cr, Cu and Ni that remained intact in the samples after the three extractions is estimated to be approximately 3 %, 97 %, 79 % and 93 % respectively. The same for Mn, Pb and Zn is 75 %, 62 % and 78 % respectively. The figures are even higher for the Birnin-Gwari samples, ranging from about 62 % for As to 99 % for Cr. The fact that more than 50 % of the total concentration of all the elements, except As in the Anka area, 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.

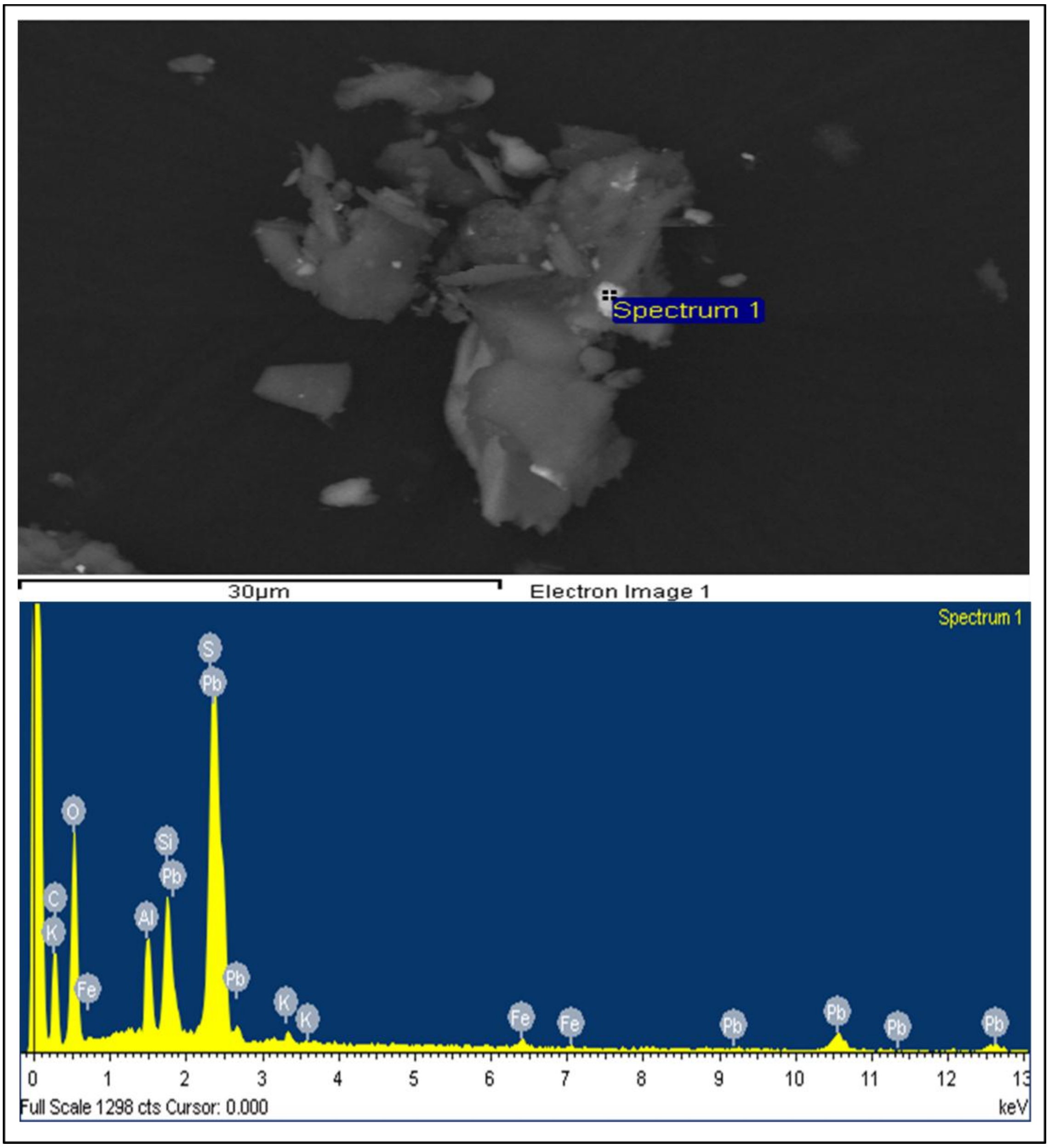

Figure 19 Scanning electron micrograph and energy dispersive spectra showing a fine galena particle and its chemical signature.

Scanning electron microscopy analysis (Fig.19) has shown that the soils in the area contain fine particles of galena (PbS), which was introduced into the soils through the extraction of gold from lead rich ores. These results, along with the *in vitro* bioaccessibility results presented in Chapter 5 confirm that the sequential extraction protocols, despite their apparent shortcomings are better predictors of the mobilization and human bioaccessibility 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).

4.6 Chapter Summary

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

The results show that in both study areas, most of the elements are generally weakly associated with the exchangeable fraction of the soils and sediments. 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, soils, most especially in the Anka area, 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 (Plumlee and Morman, 2011). This has a serious implication for the mobility and bioaccessibility of the metal and is considered to be the main reason for the high bioaccessible Pb obtained in this work (Chapter 5). Only As showed a significantly strong affinity for this phase in the samples from the Birnin-Gwari area; all the other elements only weakly portioning into the carbonate fraction. This is probably an indication of geogenic contribution of the elements into the soils, as opposed to the clearly anthropogenic signature of the samples from the Anka area.

The Fe/Mn oxides phase showed strong to very strong association with most of the elements in the Anka area, but slightly less so for the Birnin-Gwari study area. As and Mn partition more strongly into this phase in both study areas compared to the other elements. Similarly, Pb was found to be associated more with this fraction in the Birnin-Gwari soils and sediments, compared to its partitioning in the carbonate fraction in the same area, which contrasts with its behaviour in the Anka area. The generally strong partitioning of elements into this phase, particularly in the Anka area 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 (Plumlee and Morman, 2011). However, there is the possibility that the yield in this step is affected by the co-extraction of portions of elements held within the previous two phases.

The results show that despite 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, the 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, compared to the determination of total concentrations alone. Their risk assessment potential may be further enhanced if they are combined with the *in vitro* bioaccessibility measurements discussed in the next chapter.

Chapter Five

Results: *In vitro* Bioaccessibility of Heavy Metals

5.1 Introduction

The bioaccessibility of arsenic, chromium, copper, manganese, nickel, lead and zinc in the soils and sediments of the Anka area was determined using *in vitro* extraction procedure described in the materials and methods section. In this chapter, the results are presented, beginning with the bioaccessibility and estimated contaminant daily intake for a child 2-6 years old. The relationship between total concentration presented in chapter three and bioaccessible concentrations of potential toxicants is presented in the form of a correlation matrix and its implication examined. The effects of physicochemical variables, namely, pH, time and the ratio of solid test material weight to extraction fluid volume on contaminant bioaccessibility are presented in the next section.

5.2 Bioaccessibility

The bioaccessible concentration of potentially toxic elements in the samples is presented in Appendix 13 and the same concentrations for lead and copper are shown in Figure 20 plotted against their total concentration. The range and mean (± standard deviation) of oral bioaccessible concentration of arsenic, chromium, copper and manganese measured in 25 samples from the Anka area are 0.9 to 14.1 μg/g (mean 2.4 ± 2.7 μg/g), 0.1 to 8.7 (mean 2.2 ± 2.7 μg/g), 1.5 to 384.6 μg/g (mean 87.1 ± 121.8 μg/g) and 20.2 to 335.9 μg/g (mean 112.7 ± 90.6 μg/g) respectively. For nickel, lead and zinc, the values lie between 0.2 and 5.3 μg/g (mean 1.5 ± 1.4 μg/g), 197.5 and 41740 μg/g (mean, 9731.7 ± 12058 μg/g) and 0.8 and 295.2 μg/g (mean 37 ± 71.6 μg/g) respectively.

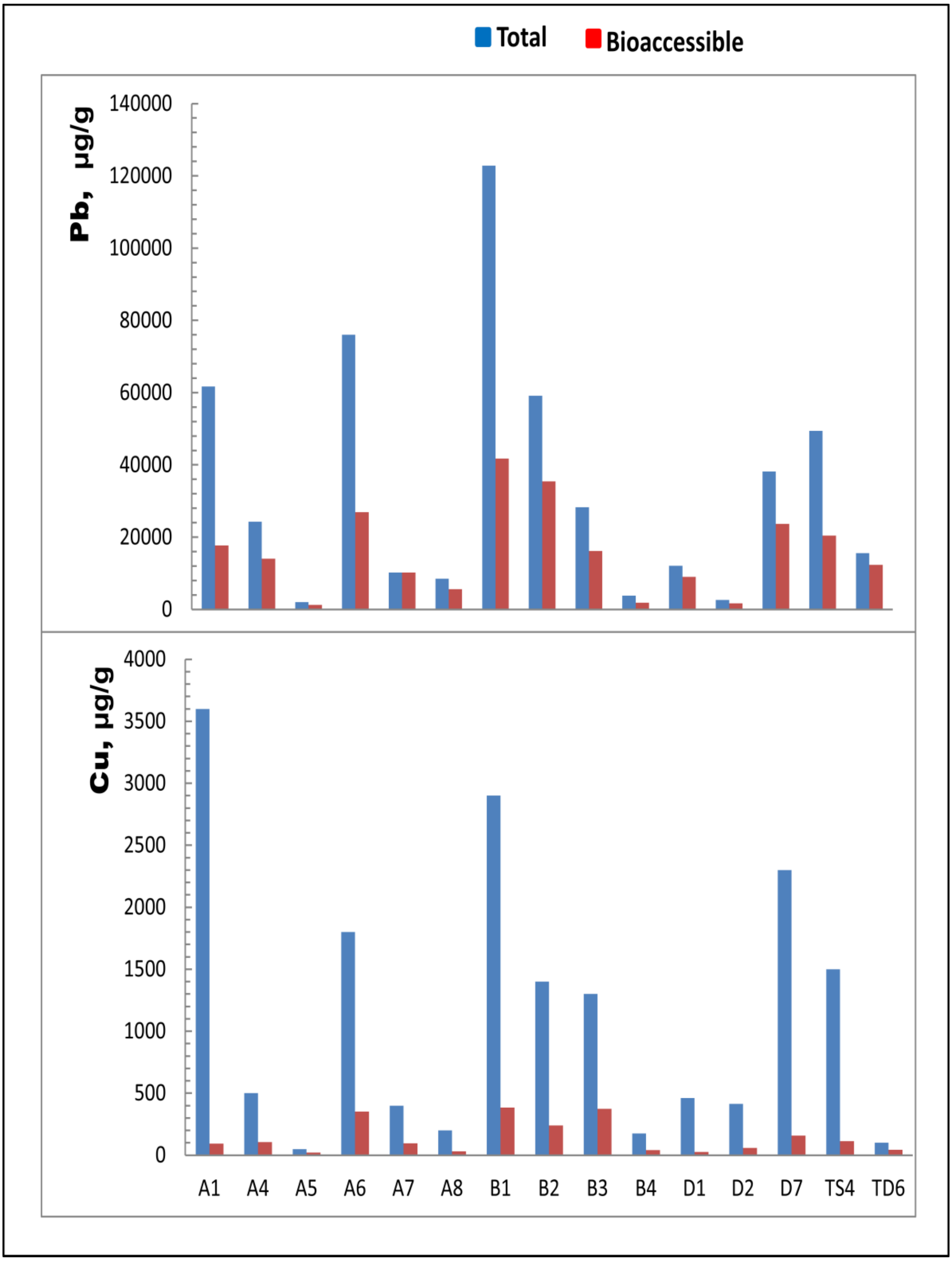

Figure 20 Total and *in vitro* bioaccessible lead and copper concentrations in randomly selected samples from the different sampling sites in the Anka area.

5.2.1 Human Bioaccessible fraction

The human bioaccessible fraction (HBA%) which is the proportion of arsenic, chromium, copper, manganese, nickel, lead and zinc that is extracted into the simulated gastric fluid as a percentage of their total concentration in the 25 soil and sediment samples was worked out according to the equations:

$$\%\mathbf{BA} = \frac{\textbf{Concentration in extraction solution},\mu g/g}{\textbf{total concentration in sample},\mu g/g} \times \mathbf{100} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{Eq 9.}$$

The bioaccessibility (BA%) for these elements is presented in Table 9 and it shows that the range of arsenic bioaccessibility is 2.6 to 105.1 %, the mean of 29.1 % appearing to be a better indication of the bioaccessibility on a sample-by-sample basis. Chromium bioaccessibility is generally low, falling between 0.2 and 17.1 % with an average of 3.5 %; while the minimum bioaccessibility for copper is 2.6 %, the maximum been 92.0%. The mean of 30.3 % again reflects the fact that the variability of copper bioaccessibility in all the samples is not as wide spread as indicated by the range; with only few samples having very high values. The range is 3.2 to 37.3 % (mean, 15.1 %) for manganese and 1 to 11% (mean, 4.3 %) for nickel. In this work, lead has the highest bioaccessibility, which ranges from 28.7 to 100.4 % (mean, 60.3 %) while the result for zinc is between 2.2 and 74.7 % with an average of 21.1 %.

The bioaccessibility values above 100%, especially for arsenic may be in part a result of the use of an estimated total concentration in samples with low concentrations, which is taken as half the limit of quantification of the XRF instrument (Nehls and Akland, 1973; Kushner, 1976), but could as well have resulted from sample heterogeneity (Morman et al., 2009).

Table 9 *In vitro* bioaccessibility (IVBA%) of potentially toxic elements in soils and sediment of Anka at pH 1.50.

Sample	As	Cr	Cu	Mn	Ni	Pb	Zn
A1	29.1	3.2	2.6	9.3	1.1	28.7	6.0
A2	7.5	0.3	29.0	8.2	1.1	65.3	3.7
A4	28.3	2.8	21.0	11.5	11.1	57.6	43.2
A5	25.7	0.9	41.8	19.3	2.6	60.6	7.3
A6	27.0	15.1	19.6	32.7	6.6	35.5	9.3
A7	30.2	8.8	23.8	16.9	2.0	100.4	4.3
A8	24.5	1.5	15.0	7.7	5.1	66.0	9.9
A10	21.2	0.7	70.4	19.3	6.1	68.1	58.4
B1	97.2	11.2	13.3	8.5	4.7	34.0	8.7
B2	11.5	4.3	17.2	15.2	3.9	60.0	4.5
B3	2.6	2.5	28.7	27.9	5.9	57.1	25.8
B4	4.1	1.0	23.5	27.6	5.4	52.3	10.8
B5	7.8	0.2	32.3	4.1	2.3	59.0	6.1
B7	46.1	0.7	19.7	18.2	4.0	56.8	58.0
D1	26.9	1.4	5.9	3.4	1.0	49.2	2.2
D2	28.4	2.3	13.8	3.2	1.7	74.2	10.6
D4	18.1	1.0	92.0	5.1	3.4	69.3	4.7
D5	33.6	0.7	28.0	7.5	2.1	65.6	9.2
D7	26.3	17.1	6.9	9.7	1.9	61.9	6.6
D9	19.7	0.8	34.5	10.4	2.8	66.0	4.4
TS3	9.3	0.3	42.2	9.9	4.7	69.8	21.8
TS4	75.0	8.2	7.5	26.5	5.0	41.4	42.0
TS5	9.5	0.4	45.5	18.5	4.7	60.4	43.2
TD6	105.1	2.3	43.6	37.3	8.2	78.9	74.7
TD10	12.9	0.8	79.2	20.9	9.8	69.0	52.5
Min	2.6	0.2	2.6	3.2	1.0	28.7	2.2
Max	105.1	17.1	92.0	37.3	11.1	100.4	74.7
Mean	29.1	3.5	30.3	15.1	4.3	60.3	21.1

Although As bioaccessibility obtained in this work appears to be widely variable, in reality only four samples have above 40 % bioaccessibility, with the majority of the samples falling around 10-35 %. These values for As compare well with the results of Button et al. (2009), who obtained values in the range of 10-34 % human bioaccessible As in contaminated soils from the Devon Great Consols in south-west England and 42% from an uncontaminated comparison site at Nottingham, also in England. Arsenic can occur in many primary or secondary minerals either as a dominant or trace component (Plumlee or Morman, 2011) and results of gastric extraction show that the arsenate and oxide forms are more readily bioaccessible while arseno-pyrite and the crystalline iron arsenate (scorodite) have lower solubility respectively (Plumlee and Ziegler, 2004).

Similarly, except for four of these twenty five samples, the results show a rather close agreement with the data of Morman et al. (2009), where Cr bioaccessibility in background soils was reported to range between 0.3-3.5 percent for the < 2mm fraction and 0.5-7.5 percent for the < 250 μm fraction, whereas the mean value obtained in this study is 3.5 %. A similar result was obtained by Sialelli et al. (2010), where less than 3% of the near total chromium was available in the gastric leachate of soils in Glasgow, UK. In spite of its relatively high total concentration in the samples, which is in turn a reflection of the natural abundance of the element especially in basalt and shale (Callender, 2004), Cr appears to have low solubility and therefore bioaccessibility. The fact that Cr^{3+} is able to form stable crystalline oxyhydroxides with iron and aluminium (Callender, 2004) may explain why it is less soluble, but it could equally point to the possibility of Cr in these samples residing in less soluble oxide mineral structures, such as chromite.

The higher bioaccessibility of lead across all the samples (Table 9) is in part a function of the higher total concentration of the element in the samples (Fig. 20). But it is also influenced by the abundance of very labile residual lead oxide and lead carbonate minerals in the ores reported by Plumlee and Morman (2011) and also confirmed by strong partitioning of lead into these phases seen during the SEPs experiments (Chapter 4) in this work. Casteel et al. (2006) have shown that oral lead bioaccessibility in human children is highest in lead carbonates and lead associated with manganese oxides. According to them, lead phosphates and oxide minerals and lead associated with iron oxides show intermediate bioaccessibilities, while lead sulphides and silicates (residual phases) are the least bioaccessible. The mean lead bioaccessibility obtained in this work is very similar to that reported (64 %) for mining contaminated soils in Brazil and 75-80 % for a certified reference soil, SRM 2710 by Bosso and Enzweiler (2008) using the PBET method, while the mean lead bioaccessibility of 39.1 % for urban soils in Guanzhou, China (Lu et al., 2011) is also within the range obtained here. Similarly, gastric bioaccessibilities of between 23 and 69 % obtained in lead-rich mine wastes by Jaggard (2012) are also broadly similar to the results of this work. However the results of this study are higher than median lead bioaccessibilities of 23 % for the < 2 mm and 18 % for < 250 μm fractions respectively obtained by Morman et al. (2009) from uncontaminated background soils in the United States, which is perhaps a pointer to the important role mineralogy and total element concentration can play in its bioaccessibility.

In this study, copper exhibited the second highest bioaccessibility, it too has high total concentration in samples (Fig. 20), owing to the fact that the contamination results from the extraction of gold from ores rich in Pb and Cu minerals. Like Pb, the bioaccessibility of Cu, is higher when present in the carbonate minerals, such as malachite and azurite compared to the sulphide minerals chalcopyrite and chalcochite, although some sulphate minerals of Cu have been shown to be very soluble (Plumlee and Ziegler, 2004). The mobilization of Zn and Ni are also enhanced by the presence of carbonate and sulphate phases in soils and sediments compared to the sulphide minerals (Plumlee and Ziegler, 2004).

5.2.2 Correlation Analysis

A Pearson correlation analysis was carried out (significant at $p = 0.01$) between total elemental concentration in the samples and the bioaccessible concentration. The results indicate that there is a generally strong to very strong positive correlation between total concentration and bioaccessibility of most of the elements, with correlation coefficients of 0.89 for As, 0.70 for Cu, 0.74 for Ni, 0.94 for Pb and 0.86 for Zn. This relationship is depicted in Figure 20 for lead and copper, where in all samples, there is a generally positive linear relationship between total lead and bioaccessible lead (less so for copper). However, the plot shows a more linear relationship between total and bioaccessible lead than for copper, especially in samples with relatively lower total lead concentration. But the relationship appears to be less linear in samples with very high total lead contents. The relationship is, however, not so strong for manganese ($r = 0.45$) and totally absent for chromium ($r = 0.07$) which may show that these two elements are not contributed by the mine wastes, but come largely from geogenic sources. The strong relationships which appear to exist between the total and bioaccessible concentrations especially for Pb, but also Cu, Zn, Ni and As may be a result of the introduction of the elements into soils and sediments during the processing of ores, the higher bioaccessibilities occur because the elements had relatively short time to bind to soil and sediment phases (Button et al., 2009). The results do not show any correlation between the bioaccessible concentration of the elements and soil pH except for Zn ($r = 0.70$, $p < 0.01$), indicating that the pH of the soils and sediments may not have any effect on the bioaccessibility of the elements.

Similarly, the correlation analysis reveals a generally strong to very strong relationship between the bioaccessible concentration of these elements and their concentration in two of the three fractions determined in the sequential extraction procedures (SEPs, Chapter 4) and the sum of the three fractions. The correlation (at $p = 0.01$ level of significance) between the bioaccessible and carbonate fraction concentrations range from $r = 0.60$ for Pb to 0.99 for Zn (the values for As, Cr, Cu, Mn and Ni been 0.98, 0.70, 0.97, 0.91 and 0.89 respectively). For the relationship with the Fe/Mn oxide fraction, the range is 0.73 for Ni to 0.99 for Zn, the r values for As, Cr, Cu and Pb been 0.96, 0.89, 0.77 and 0.92 respectively. Mn exhibits a different behaviour, showing a rather weak correlation (r = 0.41) between the bioaccessible and oxide bound concentrations. This may be due to very high concentrations of manganese in the Fe/Mn fraction of the SEPs, occasioned by the fact that the extraction step was developed specifically for manganese and iron oxides bound metals. All the elements showed a weak correlation with the exchangeable fraction, with only Cu, Pb and Mn showing fairly strong relationship (r= 0.46, 0.48, and 0.49 respectively). That manganese has the strongest correlation with this fraction may be an indication of stronger geogenic contribution of the element in the samples relative to the others.

When all the three SEP fractions were combined, the sums correlated positively strongly with the bioaccessible concentration, the r values generally lying between 0.58 for Mn and 0.99 for Zn. This strong relationship between the results, such as that for Pb (Fig. 21) from the two different leaching protocols may be used as a check on the quality of each of the extraction methods. While the sequential extraction procedures try to mimic mobilization of contaminants from the natural geologic environment, the *in vitro* bioaccessibility tests explore the release of these species into body fluids, in this case, gastric juices. However, the object of both schemes is to estimate the risk to human health associated with the uptake of contaminants from geological materials. The strong agreement between these datasets raises the question of whether one of the methods could be used as a proxy for the other, especially where rapid screening is needed to guide decision making about the existence of human health risks. Under such conditions, the *in vitro* bioaccessibility test may be a method of choice because the procedure is less time consuming and more reproducible (Fig. 12) compared to the SEPs. However, the *in vitro* method generally seems to yield higher concentrations as indicated by the slope of Figure 21, relative to the sum of the SEPs. This is mainly due to the lower pH of the (1.5) of the bioaccessibility solutions, which is unlikely to be achieved in the natural environmental settings which the SEPs attempt to mimic, except for example, under the influence of acid rock drainage.

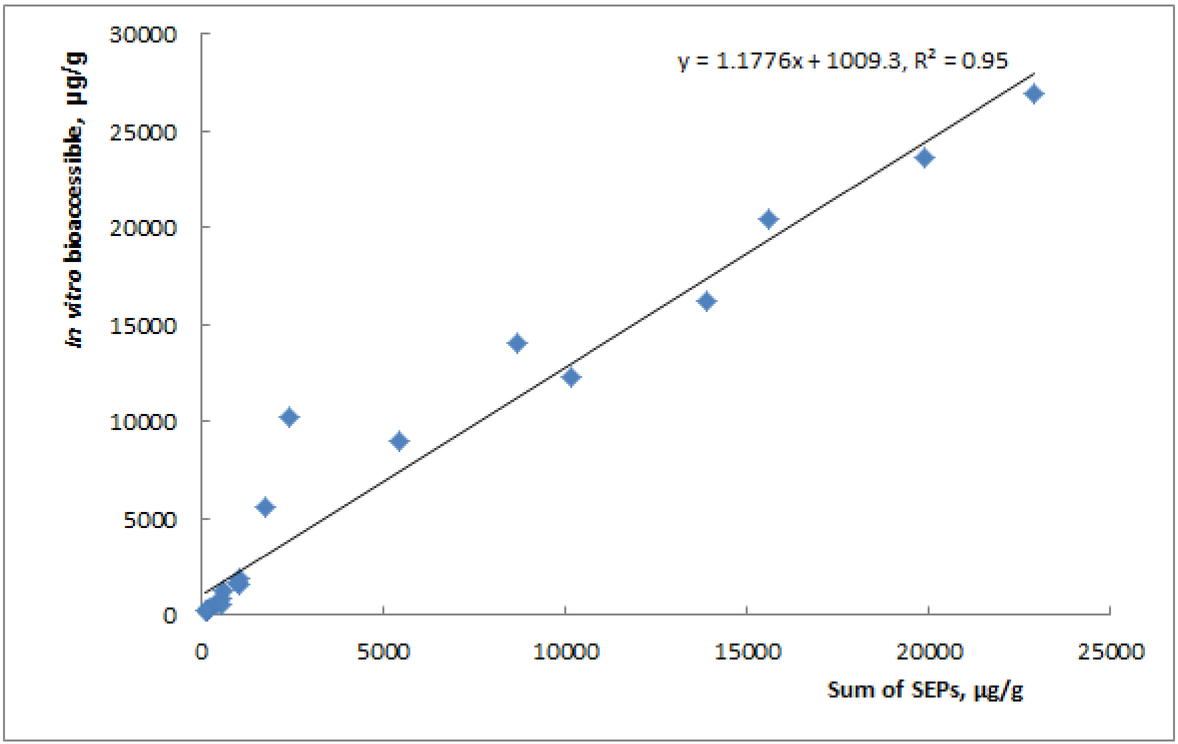

Figure 21 Relationship between measured bioaccessible concentration of Pb and the sum of its concentration in the three SEP extraction steps.

5.3 Physicochemical controls on oral bioaccessibility

The physicochemical parameters that are likely to affect the oral bioaccessibility of contaminants have been identified by previous workers (e.g, Drexler and Brattin, 2007) to include the pH of the extraction solution, extraction temperature, and length of extraction time; the feed or fast status and the ratio of the extraction fluid to the weight of test material. Different schemes have been proposed in the literature, using various combinations of these variables. In this work, the effects of pH, extraction time and solid/ fluid ratio have been investigated and the results are presented in the sections that follow in the form of comparison graphs.

5.3.1 Effect of pH

The bioaccessibility of six potentially toxic elements at three pH levels is presented in Figure 22 (a-g) and Appendix 14. This indicates that Cr, as expected is most accessible at the lower pH of 1.5, followed pH 2.9 and pH 2.2 in that order. The situation is completely different for As, where the extraction of the element seems to be enhanced with increasing pH, with the trend showing a decrease in As bioaccessibility as the pH decreases from 2.9 to 1.5. A similar but not exactly the same behaviour is exhibited by Mn, Ni and Zn (Fig. 22), where the highest of the three pH levels appear to leach out more of the metals compared to the more acidic treatments. Cu and Pb extraction on their part have a more linear relationship with the pH of the extraction solution, generally decreasing as the pH of the solution increases, except in few samples, especially B2, where the bioaccessible concentration of Pb appears to rise with the rising of pH. Repeat Measures ANOVA was performed on this data in order to verify the observations made from the graphs. While the results of this statistical test (Table 10) could not discriminate which pH level was more effective in extracting the elements, it does show that pH has a significant effect ($p < 0.05$) on the leaching of As, Cr, Cu and Pb, but not of Mn, Ni and Zn. The link between the two data sets is not very clear, but a pattern seems to form for Cr, Cu and Pb which shows that pH has had an effect on their solubilization. It becomes more difficult to explain the pattern in terms of the effect on As and to some extent Mn, Ni and Zn, because of the irregular nature of the responses.

Table 10 Result of one-way repeated- measures analysis of variance on the effects of pH, time and solid to fluid ratio on *in vitro* bioaccessibility of some potentially toxic elements

Element	***pH***	***Time***	***Solid : Fluid***
As	F(1.06, 20.17) = 7.06, $p < 0.05$	F(1.92, 17.31) = 2.79, $p > 0.05$	F(1.65, 14.80) = 210.65, $p <0.05$
Cr	F(1.21, 22.95) = 11.28, $p < 0.05$	F(1.20, 10.83) = 141.13, $p < 0.05$	F(1.23, 11.09) =3.14, $p > 0.05$
Ni	F(1.03, 19.49) = 5.85, $p > 0.05$	F(1.01, 9.09) = 7.13, $p < 0.05$	F(1.20, 9.63) = 14.20, $p < 0.05$
Cu	F(1.02, 19.37) = 12.95, $p < 0.05$	F(1.01, 9.10) = 6.99, $p < 0.05$	F(1.90, 17.10) = 1.23, $p > 0.05$
Mn	F(1.01, 19.12) = 4.04, $p > 0.05$	F(1.04, 9.33) = 4.58, $p > 0.05$	F(1.02, 9.15) = 2.54, $p > 0.05$
Pb	F(1.47, 27.94) = 4.40, $p < 0.05$	F(1.00, 9.00) = 1.31, $p > 0.05$	F(1.12, 10.06) = 0.65, $p > 0.05$
Zn	F(1.00, 18.03) = 3.34, $p > 0.05$	F(1.00, 8.04) = 4025, $p > 0.05$	-

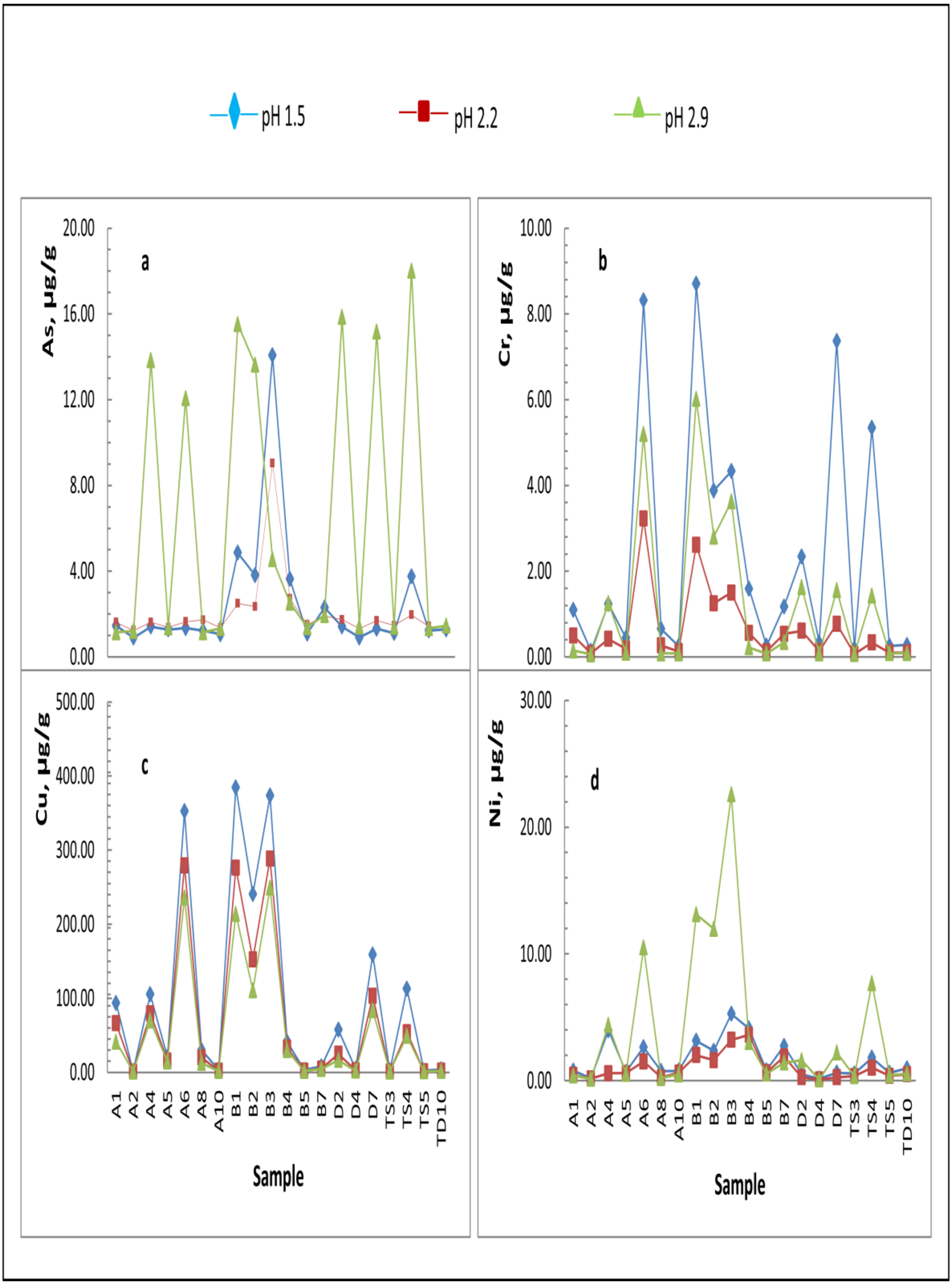

Figure 22 Effect of pH on the bioaccessibilityof potentially toxic elements in soils and sediments: a, arsenic; b, chromium; c, copper and d, nickel.

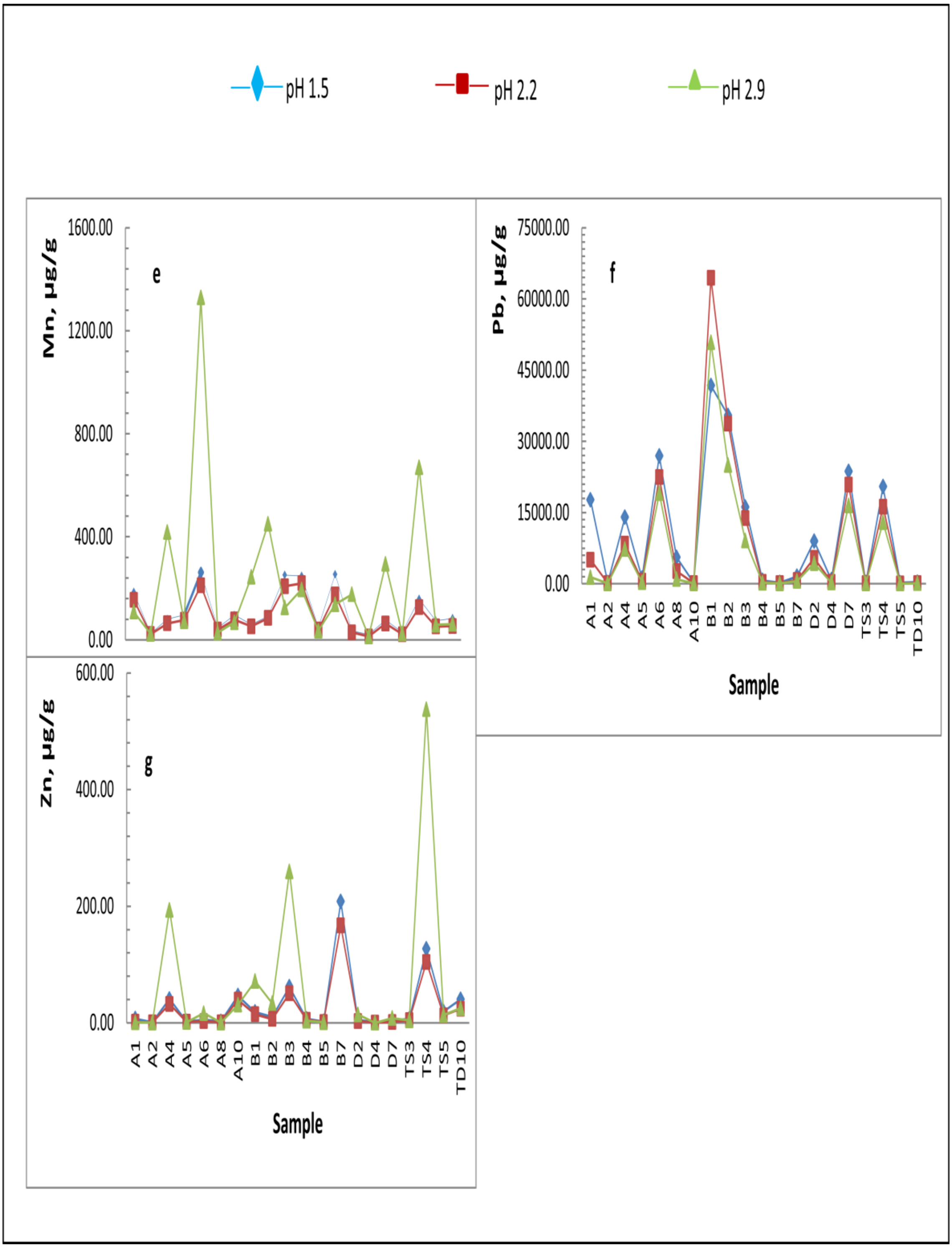

Figure 22 (continued): e, manganese; f, lead and g, zinc.

According to Drexler and Brattin (2007) human gastric pH generally falls between 1 and 4 under fasted conditions, but may reach 5 for a few hours after the intake of food. The pH range used in this work therefore falls within the fasted range and in general, a reduction in pH is expected to result in an increase in the dissolution of contaminant elements from an earth material. The effect of gastric pH is important when assessing the risk associated with ingestion of soil borne toxic elements, especially in economically deprived areas (Bosso and Enzweiler, 2008) such as this study area. In such areas, irregular feeding habits, often exemplified by the skipping of certain meals, means stomach pH remains low enough over long periods of time to ensure effective dissolution of contaminants incidentally ingested by children. Turner (2011) points out, however, that the pH dependence of mobilization in the gastric environment is metal specific: co-variation of pH and chloride concentration in the human stomach allows the formation of very soluble metal chlorocomplexes. According to Plumlee and Ziegler (2004), within the acidic human stomach, most base metals, including Pb, Fe, Cu, Zn, Cd, Ni and Co are likely to be complexed chiefly by chloride. Turner (2011) reports that the accessibilities of Cr and Pb are more sensitive to pH, showing significant reduction in going from low to high pH, but Zn accessibility is comparatively less affected. This is similar to the results of this work, which show Cr and Pb accessibilities decreasing with increase in pH, but not that of Zn (Fig. 22).

5.3.2 Effect of incubation time

Three sample incubation times were used to assess the effect of extraction time on accessibilities of elements in soils against the background of the reported half-time of stomach emptying time in human beings of about 1 hour (Washington et al., 2001). The results presented in Figure 23 (a-g) and Appendix 15 show that the accessibility of Cr changed consistently with length of time of extraction, the highest values obtained when the set up was left standing for seventeen hours. Among the other elements tested, only Cu and Mn showed marginal increases in accessibility after 2 hours and 17 hours compared to the 1 hour extraction time. The solubility of As, Pb and Zn remained unchanged over the entire period (Fig. 23). Repeated Measures ANOVA analysis (Table 10, $p < 0.05$) indicates the length of extraction time was not a significant factor affecting As, Mn, Pb and Zn solubilization, but it did affect the mobilization of Cr $F(1.20, 10.83) = 141.13$, $p < 0.05$ and to a lesser extent, Cu, $F(1.01, 9.10) = 6.99$, $p < 0.05$. The high F value for Cr shows the high significance of incubation time on the bioaccessibility of the element in these samples (Fig.23b).

Stomach emptying rate or residence time is said to be a complex function of the degree of smooth muscle stimulation, humoral signalling in the gut, and food composition if present, time of day and other physiological factors (Drexler and Brattin, 2007). Whatever the factors controlling stomach emptying, it does appear that for most of the elements studied in this work, longer extraction time does not enhance their accessibility. Drexler and Brattin (2007) and US EPA (2008) also found no significant difference in the *in vitro* bioaccessibility of Pb when the time was varied from 1 to 4 hours and therefore adopted an extraction time of 1 hour, in order to minimize testing time.

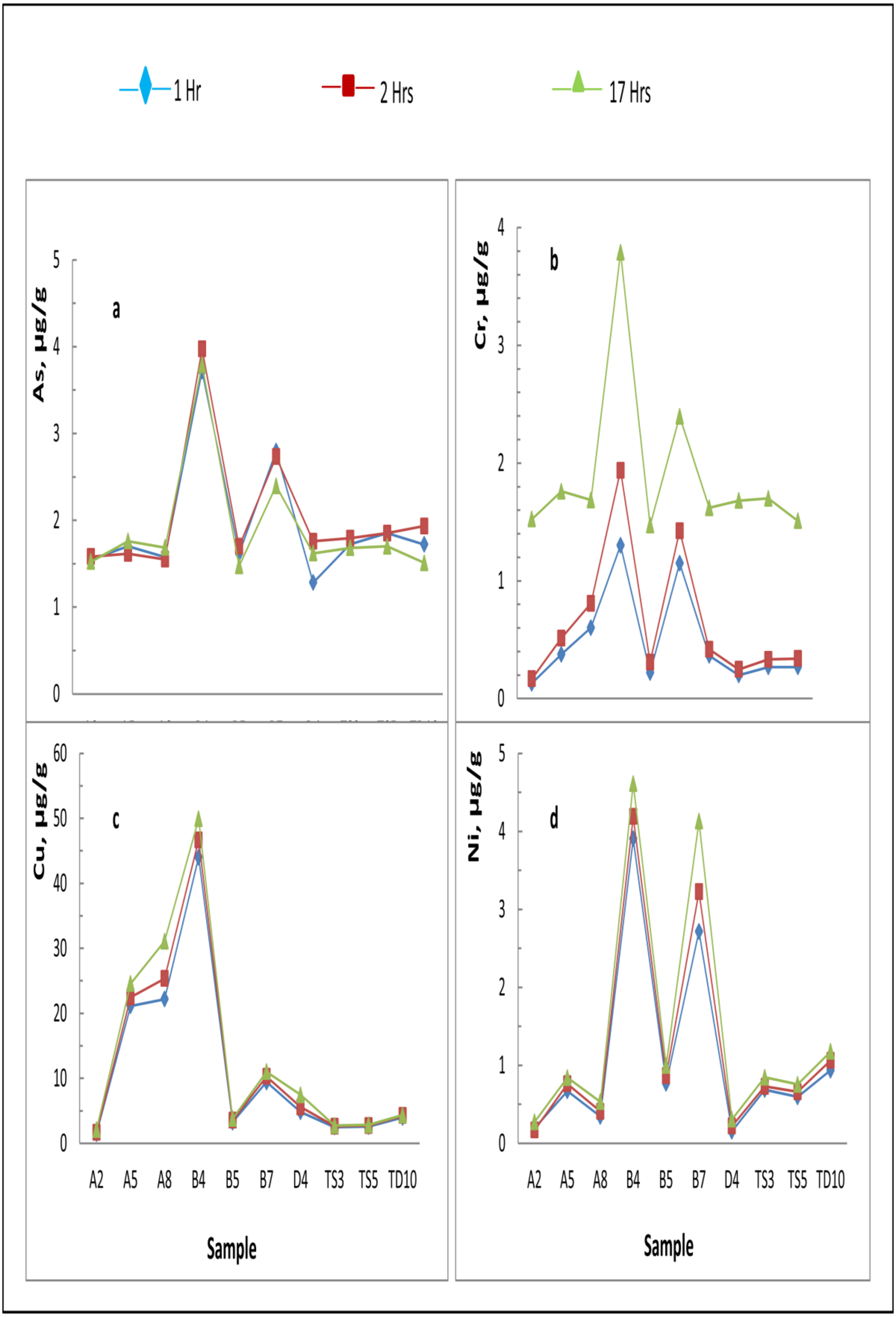

Figure 23 Effect of incubation time on bioaccessibility of potentially toxic elements in soils and sediments: a, arsenic; b, chromium, c, copper and d, nickel. Notice the jump in chromium mobilization after samples were left to stand overnight.

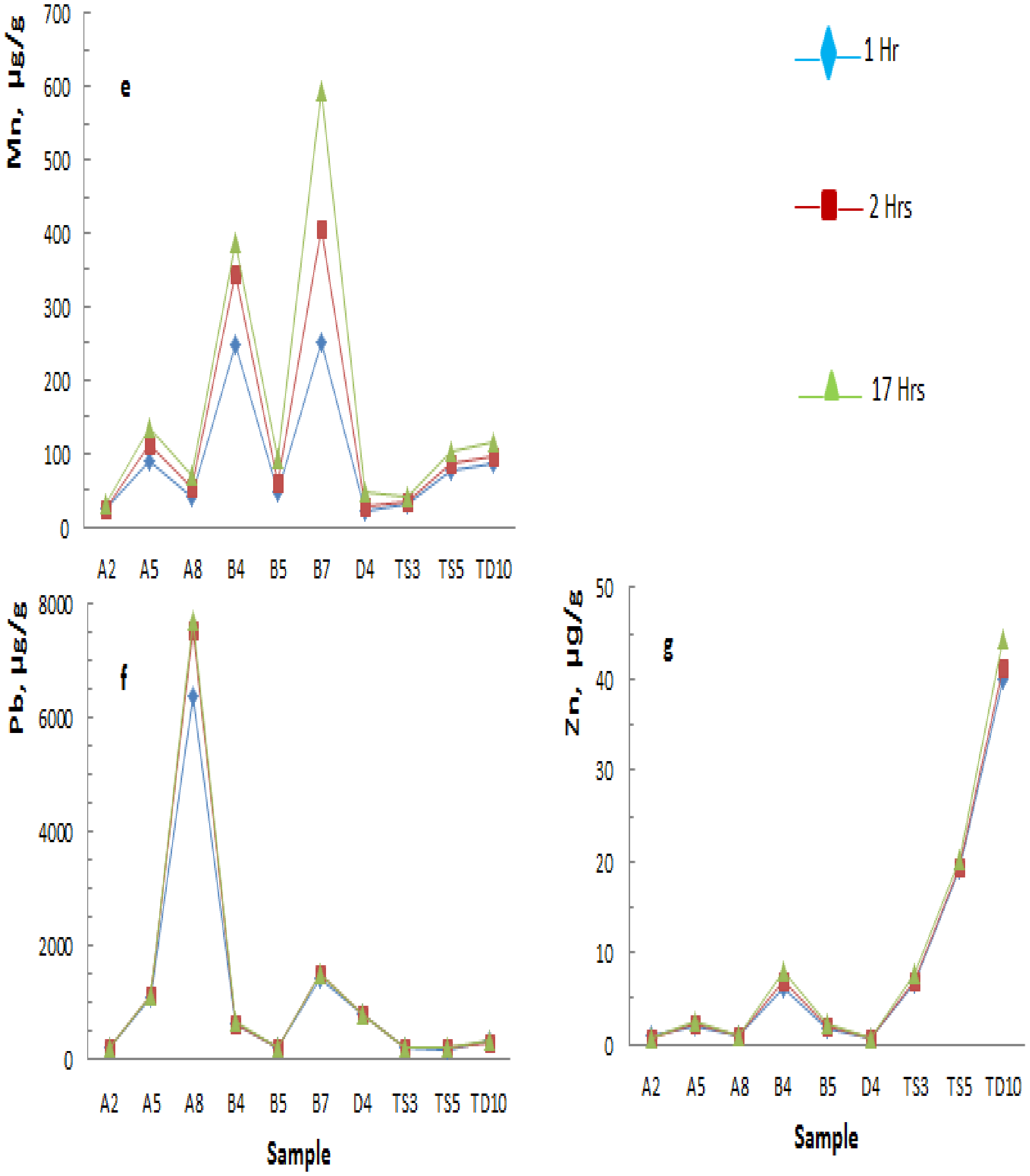

Figure 23 (continued): e, manganese; f, lead and g, zinc. The different shape of the zinc plot is as a result of removal of a sample which appeared to be an outlier.

5.3.3 Effect of solid: fluid ratio

The ratio of fluids to solid in the human stomach varies depending on feeding status and the amount of contaminated earth material ingested. In this work, the effect of solid/ fluid ratio on the accessibility of PTEs was investigated using three combinations of the test material to the extraction fluid. The results are presented in Figure 24 (a-f) and Appendix 16 and these show that As mobilization decreased as the weight of the test material increased against the volume of the extraction solution in the order 0.5 g: 50 mL > 1 g :50 mL > 1 g : 25 mL respectively. However, this pattern is restricted to As and to an insignificant extent Ni; as the accessibilities of Cr, Cu, Mn and Pb did not appear to change with variation in the ratio of solid sample to extraction fluid volume (Fig. 21). Results of One-way Repeat Measures ANOVA (Table 10) confirmed these observations. Arsenic mobilization in the three treatments is very significantly different $F(1.65, 14.80) = 210.65$, $p < 0.05$, but only slightly so for Ni $F(1.20, 9.63) = 14.20$, $p < 0.05$, whereas the concentrations of each of Cr, Cu, Mn and Pb were not significantly different across the three combinations of sample to extraction fluid (Fig. 24).

A wide range of ratios have been reported in the literature, ranging from 1: 100 to 1: 500 (Turner, 2011) and as high as 1: 1000 (Wragg et al., 2011). Drexler and Brattin (2007) performed tests on a variety of standard reference materials and reported no significant variation in the *in vitro* bioaccessibility with soil masses as low as 0.2 g per 100 mL of extraction fluid (1:500). Because actual test materials may not be as homogenous as reference materials and because of weighing errors, they proposed a ratio of no less than 0.4 g test material per 100 mL of fluid to reduce possible variability in bioaccessibility. However, Wragg et al. (2011) have reported the use of a ratio of 1: 1000 in order to eliminate poor reproducibility occasioned by high As concentration in soils contaminated with mine wastes and slag, although they too acknowledged the possible effects of sample in-homogeneity. The use of ratios of between 1: 25 to 1: 100 (Fig. 24) in this work did not result in a significant difference in bioaccessibility, except for As and to a lesser extent, Ni. The comparatively lower total Pb concentration in samples used for this experiment may have helped to avoid the problem of extraction fluid saturation and lead chloride precipitation (Drexler and Brattin, 2007; US EPA, 2008) reflected in samples with highly soluble Pb minerals such as lead acetate, lead oxide and lead carbonates . Even when a ratio of 1 g in 25 mL fluid was used, no significant difference was observed in spite of the presence of more sample mass and surface area. Unless one is dealing with highly contaminated samples exceeding the 50,000 μg Pb/g limit set by previous workers, it appears that the ratios used in this work are useful when there is limited sample supply.

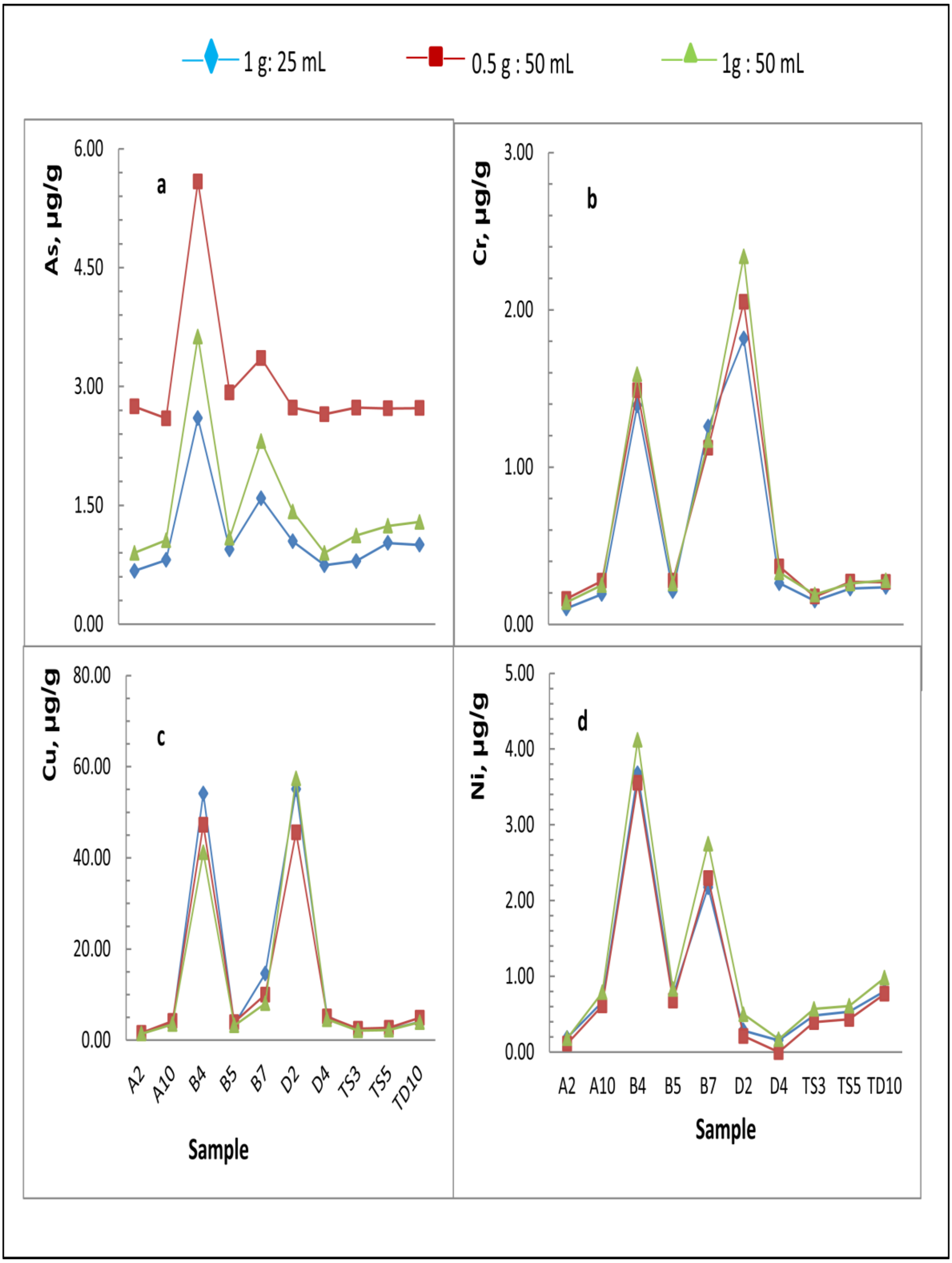

Figure 24 Effect of solid: fluid ratio on the bioaccessibility of potentially toxic elements in soils and sediments: a, arsenic; b, chromium; c, copper and d, nickel.

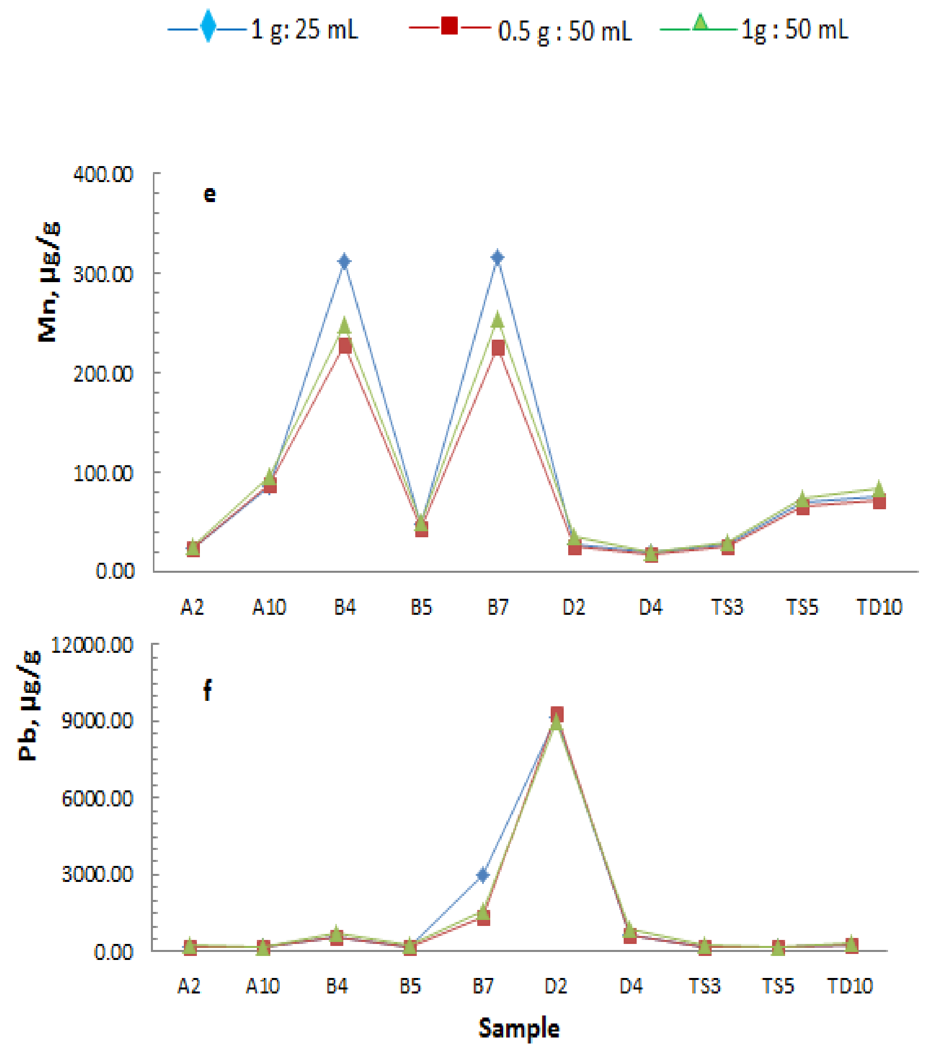

Figure 24 (continued): e, manganese and f, lead.

5.4 Contaminant Daily Intake

The chemical or contaminant daily intake is used to assess the exposure of humans, especially children to contaminant elements through ingestion of contaminated soil. For a child 2 to 6 years old, weighing 17.8 kg (USEPA, 1997), the daily chemical intake (CDI, µg $kg^{-1}day^{-1}$) is calculated using the following formula:

$$\boldsymbol{CDI = \frac{CS \times IR \times BA \times EF}{BW} \times CF} \text{ ……………………………………………………...} \textbf{Eq 10},$$

where CS is the total concentration of the contaminant element in the sample (µg/g), IR is the ingestion rate set at (USEPA, 2002) 200 mg soil per day, BA is the mean bioaccessibility of the element in the test materials, EF represent the exposure frequency, in this case 0.5 (182 days per year, Hemond and Solo-Gabriele, 2004), BW denotes body weight and CF is the unit conversion factor (10^{-3}).

The CDI estimates for this work are shown in Table 11 including the range, mean and the minimal risk levels, tolerable daily intake or lowest observable adverse effect levels (MRL; TDI; LOAEL, µg $kg^{-1}day^{-1}$) for the elements. These show that children exposed to these soils are likely to ingest between 0.8 to 87.2 µg As /kg per day with a mean of 5.2 µg/kg/day, while the range for chromium is 0.6 to 3.5 µg/kg/day, the average being 1.5 µg Cr /kg per day. The results show that the CDI for copper ranges between 0.9 and 612.5 µg Cu /kg per day with an average dose of 117.2 µg /kg/day. Manganese intake is estimated to fall between 25.5 and 170.2 µg Mn /kg /day with a mean of 64.8 µg Mn/kg/day. For nickel, the results range from 0.1 to 2.2 µg Ni /kg per day, with a mean daily intake of 0.9 µg Ni/kg.

Table 11 Estimated contaminant daily intake (CDI, µg/Kg/day) for children 2-6 years old living in the contaminated villages, at a gastric pH of 1.5.

Sample	As	Cr	Cu	Mn	Ni	Pb	Zn
A1	0.8	0.7	612.5	170.2	1.7	20895	14.5
A2	2.0	0.8	0.9	25.5	0.4	128	3.2
A4	0.8	0.9	85.1	59.6	0.9	8229	11.3
A5	0.8	1.0	8.3	42.5	0.7	685	3.9
A6	0.8	1.1	306.2	68.1	1.0	25738	6.9
A7	0.8	0.9	68.1	59.6	1.3	3454	10.9
A8	0.8	0.9	34.0	51.0	0.4	2879	3.2
A10	0.8	0.7	0.9	42.5	0.3	111	9.5
B1	0.8	1.6	493.4	59.6	1.6	41587	25.4
B2	5.4	1.8	238.2	51.0	1.4	20015	27.4
B3	87.2	3.5	221.2	97.4	2.2	9584	28.5
B4	14.6	3.2	29.8	76.6	1.8	451	7.7
B5	2.3	2.8	1.7	102.1	0.9	136	4.6
B7	0.8	3.5	7.0	119.1	1.7	938	42.6
D1	0.8	1.7	78.4	68.1	0.8	1287	7.8
D2	0.8	2.0	70.6	93.6	0.7	4098	5.8
D4	0.8	0.7	0.9	34.0	0.1	417	1.9
D5	0.8	1.6	3.6	68.1	0.8	881	5.2
D7	0.8	0.9	391.3	68.1	0.8	12937	6.6
D9	0.8	1.0	2.4	42.5	0.4	291	2.7
TS3	2.0	1.4	0.9	25.5	0.3	121	3.8
TS4	0.8	1.3	255.2	51.0	0.9	16730	35.8
TS5	2.1	1.2	0.9	34.0	0.3	111	5.3
TD6	0.8	0.6	17.0	76.6	0.5	5283	46.9
TD10	1.6	0.7	0.9	34.0	0.2	168	9.1
Min	0.8	0.6	0.9	25.5	0.1	111	1.9
Max	87.2	3.5	612.5	170.2	2.2	41587	46.9
Mean	5.2	1.4	117.2	64.8	0.9	7086	13.2
Median	0.8	1.1	29.8	59.6	0.8	1287	7.7
MRL	**0.3**	**1**	**10**	**60$^+$**	**12***	**~3.6***	**300**

MRL- minimal risk levels (ATSDR, 2008); ***TDI-** Tolerable daily intake worked out from the provisional tolerable weekly intake (PTWI) of 25 µg/kg (DEFRA, 2002). $^+$**LOAEL-** lowest observable adverse effect level (Greger, 1998).

More significant however, is the data for lead, which shows that the possible daily intake of lead from soil ranges from 110 to 41,585μg Pb /kg per day with a mean of 7,086 μg Pb /kg of body weight daily. The situation is less severe for zinc, having values in the range of 1.9 to 46.9μg/kg/day and a mean of 13.2μg Zn/kg/day.

The mean values for arsenic, chromium and copper generally exceed the oral chronic minimal risk levels (MRLs) published by ATSDR (2008) of 0.30, 1.00 and 10.00 μg/kg/day respectively and tolerable daily intake (TDI) of ~3.6 μg/kg/day for lead worked out from a provisional tolerable weekly intake (PTWI) of 25 μg/kg body weight (DEFRA, 2002). However, the mean CDI of 13.2 μg Zn /kg/day is very much within the 300 μg/kg/day oral minimal risk level for zinc. No oral MRLs or TDI have been found for manganese, but using the lowest observable adverse effect level (LOAEL, Greger, 1998) of 60 μg Mn/kg/day, it is apparent that the mean CDI of 64.8 μg Mn /kg/day is likely to result in some adverse health effects. The TDI for Ni of 12 μg /kg /day (EA, 2005) is far greater than the mean CDI obtained in this study.

The results (Table 11) show that at all the sample sites, the tolerable daily intake of Pb is far exceeded. This may explain the excessively high blood lead levels reported by the Blacksmith Institute (Chapter 1, Fig.1) in children of the affected villages leading to high levels of childhood mortalities. This is brought about by a combination of high total lead concentration in the soils and sediments of the area and the abundance of highly soluble secondary lead carbonate and lead oxide minerals within the ores (Plumlee and Morman, 2011) resulting in high extractability of lead observed in both the PBET and SEPs studies carried out in this work. Similarly, all the samples have CDI values above MRL for arsenic, although the magnitude is not as high as in the case of lead except in three samples (B2, B3 & B4), which have consistently shown high loadings for arsenic. For copper, 64% of the samples have exceeded the set limits, with some of them showing very high loadings. The pattern for chromium is similar to that of arsenic in terms of magnitude, although only 56% of the samples have CDI values in excess of the published MRLs. Fewer samples representing 44% of total exceeded the LOAEL for manganese, while all of the samples have values below the MRL for zinc and TDI for nickel, indicating that no chronic health effects may result from the two elements as a result of hand-to-mouth transmission of the soils.

These estimates have been based on an assumption that the only way of transmission is through the ingestion of fine particles which stick to the hands of children. But the daily ingestion of soil in these villages may be higher than the conservative figure of 200 mg per day used in this estimate, due to the possibility of other routes of exposure, such as eating poorly washed vegetables and the deliberate consumption of soil, called geophagy. Where poor people live in contaminated areas such as this study site, sub-nutrition and direct contact with wastes and soils are common (Bosso and Enzweiler, 2008). This may result in the ingestion of up to 10 g of soil in a single day (US EPA, 2002) leading to much higher contaminant uptake. If the latter scenario is taken into account, the health risks posed by the ingestion of these soils will be much higher than this data indicates, considering especially the very high levels of bioaccessible lead, copper and arsenic.

5.5 Chapter summary

A total of 25 samples of soils and sediments contaminated by artisanal mining and processing of Pb-Cu rich gold ores in the Anka area of north-western Nigeria were subjected to *in vitro* bioaccessibility tests. The results show very high bioaccessible concentrations and therefore in vitro bioaccessibility (IVBA) for Pb and Cu, and to a lesser extent, As and Mn. The high levels of bioaccessibility for Pb and Cu are influenced in part by high concentrations of the elements in the soils and sediments of the area, and by the presence in the contaminating ores, of highly soluble secondary oxide and carbonate minerals. Multivariate statistical analysis shows generally strong positive correlation between total and bioaccessible concentrations of most of the elements tested, except for

Mn which showed weak correlation and Cr, for which no correlation was observed. The very poor correlation between total and bioaccessible concentration of Cr is a reflection of the low solubility of the element, probably occasioned by its presence in the structures of less labile minerals such as silicates that are unrelated to the contaminating Pb-Cu-Au ores. Furthermore, the bioaccessible concentration is found to correlate strongly with the concentrations of these elements in either of the carbonate or Fe-Mn oxide fractions and the sums of the three fractions determined; correlation with the exchangeable fraction is generally weak.

An investigation into the effects of three physicochemical factors on *in vitro* bioaccessibility shows that the effect of varying pH changes from one element to another. The solubility of Cr, Pb and Cu are enhanced by lowering the pH, not so for As, Mn, Ni and Zn. In fact, the bioaccessible concentration of As increased significantly with a rise in pH. On the other hand, the length of extraction time was found to significantly influence the dissolution of Cr, its bioaccessible concentration increasing with increase in the length of time of contact between the sample and the simulated gastric fluid. However, the results do not show the same behaviour for the other elements, only Cu and Mn show marginal increase in bioaccessible concentration with time. Similarly, the results show that only the concentration of As is influenced by the variation in the ratio of sample mass to extraction fluid volume, it being highest at 0.5g sample: 50 mL of extraction solution. All other elements showed no significant difference in concentration due to the variation in this parameter. This has implication for the choice of optimum sample to fluid to fluid combination, especially in situations involving low sample supply.

Estimates of the chemical daily intake (CDI), which is the quantity of bioaccessible potentially toxic elements (PTEs) a child in the study area is likely to be exposed to daily through the agency of hand-to-mouth ingestion of contaminated soils indicate that for most of the elements, the tolerable limits have been exceeded. The situation is, however, very serious with respect to Pb and Cu, and to a lesser extent, As and Mn because the estimated CDI values show that even the ingestion of much smaller amounts of the contaminated soils can result in the delivery of dangerously high doses of bioaccessible PTEs. This is especially true for Pb, but also Cu with mean CDI values of 7086 µg /kg /day and 117.2 µg /kg /day against the tolerable daily intake and minimal risk level of ~3.6 µg /kg /day and 10 µg /kg /day respectively.

These results have highlighted the problems associated with the contamination of soils in residential areas and farm lands in artisanal mining communities in north-western Nigeria. Considering that the CDI estimates have been based on hand-to-mouth ingestion scenario alone, while neglecting other routes of exposure especially in these socio-economically deprived areas such as the consumption of improperly washed vegetables, deliberate consumption of soil, inhalation of dusts both indoor and outdoor, and drinking contaminated surface water, the bioaccessible amounts of these elements, especially Pb and Cu ingested by children and even adults in these communities may have been underestimated.

Chapter Six

Conclusions and further studies

6.1 Summary and Conclusions

The work in this thesis has focused on the environmental geochemistry of surface soils and stream sediments in the Anka and Birnin-Gwari areas of north-western Nigeria. The operation included determination of bulk geochemistry, geochemical partitioning and *in vitro* human oral bioaccessibility estimates of some potentially toxic elements. The following conclusions can be drawn from the experimental results:

- Intense tropical weathering, aided by the physical removal of fine clay particles by wet season overland runoff and dry season winds, and the leaching of bases, has led to enrichment in silica and marked depletion in Mg, Ca, Na and K. This has similarly led to very high soil and sediment Zr concentrations due to surficial processes which preferentially accumulate detrital zircon and other heavy mineral grains.

- Artisanal gold mining and processing has led to extensive Pb and Cu contamination of surface soils and stream sediments in and around a large number of communities in the Anka area, but this has not been found for the Birnin-Gwari area.

- In both study areas, a weak association exists between PTEs and the exchangeable fraction in soils and sediments due mainly, to the paucity of fine clay particles and depletion in exchangeable base cations.

- Most of the elements, especially Pb and Zn in the Anka area and As in the Birnin-Gwari area partition strongly into the carbonate geochemical phase, indicating a high potential for mobilization of contaminants under slightly acidic environmental conditions.

- Reducing environmental conditions may lead to the release of high concentrations of contaminant elements found to be associated with the Fe/Mn Oxides in these study areas.

- *In vitro* bioaccessibility experiments show very high bioaccessibility for Pb and Cu, and to a lesser extent As and Mn, in soils and sediments from the Anka area.

- Change in pH has different effects on the *in vitro* bioaccessibility of different elements. The bioaccessibility of Cr, Pb and Cu is higher at low pH, whereas that of As is enhanced by the rise in pH value. There is no evidence to show that the bioaccessibility of Mn, Ni and Zn have been affected by the range of pH used in this work.

- The length of contact time between the solid sample and the simulated gastric fluid does not appear to have a significant effect on the extraction of Pb, Cu, As, Mn, Ni and Zn, but it does clearly influence the amount of Cr extracted into the solution.

- The ratio of solid sample mass to extraction fluid volume is not an important constraint on the bioaccessibility of Pb, Cu, Ni, Mn, Zn and Cr, but it significantly affects the release of As into the gastric fluids. A ratio of 0.5 g sample to 50 mL extraction solution was found to give the highest bioaccessible concentration of As.

- In the contaminated villages of the Anka area, hand-to-mouth ingestion of soils by children delivers dangerously high doses of bioaccessible PTEs, especially Pb and Cu into the gastric fluids. The chemical daily intake estimates show that the tolerable daily limits have been exceeded for most of the elements.

The prevalence of artisanal mining of gold and associated base metals in these study areas has adverse environmental and human health consequences. Compared with the crustal averages and soil guideline values, the soils and sediments in the mining communities of the Anka area have suffered extensive contamination with potentially toxic elements, especially Pb and Cu. The very high concentration of Pb and Cu in soils within living compounds and surrounding farmlands in communities such as Abare and Bagega is a serious threat to the health and wellbeing of the population, particularly children. Grinding of ores using machines hitherto employed for food processing, the resultant dust generation and the indiscriminate disposal of the mineralized waste rock powders within compounds and along stream channels are all important pathways for human exposure to contaminant elements. In these semi-arid tropical environments, dust re-suspension by dry season winds ensures constant availability of inhalable contaminants, while transport of the soils and sediments by wet season floods, following storm events disperses contaminated materials to areas far away from their sources.

The results of this study show however, that the effects of artisanal mining are not the same everywhere. While the activity has resulted in severe contamination of soils and stream sediments in the Anka area, with adverse health consequences, the main problem in the Birnin-Gwari region is the creation of badlands. The chains of relatively deep mine pits, often filled with water during the wet season, are not only unsightly, but render the land virtually useless and even dangerous to humans and livestock. This therefore underscores the importance of site specific assessment of the environmental effects of artisanal mining in Nigeria and elsewhere in the world.

One reason why remediation attempts may not completely clean up the contaminated villages is the practice of using the mineralized powders for the construction of dwellings. Where such mud houses and perimeter walls are built, they can constitute a long term local source of contaminants due to the erosion of particles from exposed walls. As well as stopping this, the local population, especially those involved in artisanal mining could help to reduce contamination of their villages by processing the ore at the mine sites. The mineralized waste rock powders could then be disposed of in the mine pits, where eventual natural re-vegetation may in the long term, help to reduce the mobility of contaminant elements. A possible incentive to processing the ore at the mine sites will be provision of water, which at the moment is only available through water wells in the villages and ephemeral streams.

In spite of the high concentrations of some of the elements, such as Pb, Zn and As obtained in the carbonate and Fe-Mn oxides fractions, less than 50 % of the total concentrations of all the elements were extracted across the three sequential extraction steps. The bulk of the elements in the soils and sediments of the two study areas is therefore held within less labile organic matter/ sulfide fraction and in the structures of residual silicates and other resistates. This is a confirmation that not all elements present in geological materials are readily mobilizable and biogeoaccessible. The results show that despite apparent weaknesses, sequential extraction procedures are useful in assessing the environmental and human health risks associated with PTEs in soils and sediments. However, because of the very high concentration of Pb and Cu in most of the samples from the Anka area, a real risk exists even at these levels of bioaccessibility. For example, up to 40,000 μg/g Pb has been obtained as the sum of the three SEP steps. In interpreting the results therefore, it is important to consider the percentage recoveries along with elemental concentration in individual samples. The results show that given a reducing, slightly acidic environmental condition, dangerously high doses of Pb and Cu can be mobilized from Fe/Mn oxides and carbonate phases and become readily available for uptake by plants, animals and eventually humans.

In vitro bioaccessibility measurement based on hand-to-mouth ingestion of soils in the contaminated Anka villages has also given high concentrations of PTEs, especially, Pb and

Cu. In most of the samples, the concentrations have been higher than the sums of the three SEP steps, but there is a generally strong relationship between the two datasets. The higher concentration obtained *in vitro* is a function of the lower pH of the simulated gastric fluids, and in nature, bioaccessibility may even be enhanced by the near anoxic condition of the human stomach. In spite of the more aggressive nature of the *in vitro* extraction test, the results compare favourably with those from the SEPs and both datasets indicate similar levels of environmental and human health risks posed by exposure to soils and sediments contaminated by artisanal mining. Compared with the SEPs, the *in vitro* bioaccessibility extraction test is faster, less operationally demanding and probably even more easily reproducible. This may make it a preferred method where quick screening is needed to guide risk assessment and remediation planning. But to gain a broader understanding of the problem, it needs to be used along with other techniques (such as SEPs) that are capable of providing an insight into the different geochemical phases that exist in the contaminated media. The strong correlation between the sums of the SEP steps, which is mainly contributed by the concentration of PTEs in the carbonate and Fe/Mn oxide fractions and the *in vitro* bioaccessible fraction, underscores the importance of mineralogy in determining the bioaccessibility of contaminant elements. This is further buttressed by the fact that the correlation between bioaccessible concentration and the sum of SEPs is generally stronger than that between the former and the total element concentration in the samples. This is consistent with the results of previous workers, who found for example, that Pb is more readily released from cerrusite ($PbCO_3$) compared to galena (PbS).

The chemical daily intake (CDI), computed for children in the Anka area based on hand-to-mouth ingestion of contaminated soil shows that the tolerable daily limits for Pb, Cu, Mn, As and Cr have been exceeded. The mean CDI for Pb was found to be nearly 2000 times the tolerable daily intake for a 2-6 year child weighing 17.8 kg; the minimum value being about 31 times the limit. These results, along with those for Cu and to a lesser extent, Mn, As and Cr, further highlight the severity of the contamination of soils in the affected villages. Hand-to-mouth ingestion is the only exposure scenario investigated in this study. However, given the poor socioeconomic status of the residents of this study area, children and even adults can be exposed to lethal doses of PTEs through consumption of improperly washed vegetables, inhalation of indoor and outdoor dusts and drinking contaminated surface water. Similarly, factors such as low body weights due to sub-nutrition together with poor sanitation, which may increase the exposure frequency, are likely to increase the risks. While high blood lead levels have been reported in children in these villages by a combined team from the UNEP/OCHA, Blacksmiths Institute and other organizations, it will be interesting to study adult subjects, especially those actively involved with ore processing in order to assess possible chronic Pb and other PTE toxicity.

The results of this work underscore the need to study more closely, the effects of artisanal mining and processing of ores on the quality of the environment and the attendant human health consequences. Determining the spatial distribution of mining related potentially toxic elements relative to baseline concentrations, together with an assessment of their geochemical partitioning and *in vitro* bioaccessibility would be useful for artisanal mining areas in Nigeria and other parts of the developing world. The knowledge gained can guide remediation efforts and help to mitigate the harm to resident populations of contaminated areas.

6.2 Further studies

This work has investigated the geochemistry of soils and stream sediments in the artisanal gold mining areas of Anka and Birnin-Gwari in north-western Nigeria. However, further studies are required in order to increase our understanding of the environmental and human health risks brought about by the artisanal mining activities, especially in the Anka area. It is recommended that future investigations may include, but are not limited to the following:

1. Further geochemical fractionation and speciation studies should be carried to identify and estimate the abundances of the different phases or minerals in the contaminated soils in order to better understand the possible mobilization of contaminants in the area.
2. Future *in vitro* tests should be extended to include intestinal and lung phases. This will shed more light on the bioaccessibility of the contaminants.
3. Field and laboratory based experiments to investigate the immobilization of potentially toxic elements (PTEs) in soils of the Anka area using locally available materials such as phosphate nodules from the neighbouring Sokoto Basin, bone phosphate and eggshells. In these soils, treatment with phosphate may help in the immobilization of Pb which has been found to be the major contaminant, through the formation of pyromorphite [$Pb_5 (PO_4)_3Cl$].
4. Field sampling and laboratory based experiments to shed light on the uptake of potentially toxic elements (PTEs) by crops and livestock and their possible transmission through the food chain.
5. Continued, long term monitoring of the distribution of PTEs in surface soils and stream sediments in the contaminated villages of the Anka area, with a view to understanding their dispersal or attenuation, especially in areas where remediation has been attempted.
6. Finally, to expand the study to other areas in Nigeria where artisanal mining activities are prevalent in order to establish a database of the possible harmful effects of the unregulated small-scale exploitation of mineral resources by artisans.

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Appendix 1a Location and description of samples from the Anka area, northwestern Nigeria

Sample	Latitude	Longitude	Location	Sample description
A1	12.06167	5.97041	Abare	Soil, near mine pit
A2	12.06160	5.97010	Abare	Soil, generally dark brown
A3	12.06130	5.96940	Abare	Soil, generally dark brown
A4	12.07477	5.95755	Abare	Soil, brown, close to abandoned milling area
A5	12.07418	5.95628	Abare	Soil, in farmland downslope from A4
A6	12.06103	5.97031	Abare	Sediment downstream from mine pit
A7	12.06038	5.96915	Abare	Sediment downstream from A6
A8	12.06072	5.96690	Abare	Sediment downstream of A7
A9	12.06216	5.96707	Abare	Soil, reddish brown
A10	12.07894	5.95503	Abare	Farmland soil
A11	12.08375	5.95094	Abare	Contaminated soil removed to a dump site
B1	11.86370	6.00440	Bagega	Soil, light brown
B2	11.86210	6.00490	Bagega	Soil, light brown
B3	11.86340	6.00440	Bagega	Soil, light brown
B4	11.86206	6.00598	Bagega	Stream sediment
B5	11.86253	6.00405	Bagega	Farmland soil, light brown
B6	11.86235	6.00216	Bagega	Farmland soil, light brown
B7	11.86392	6.00077	Bagega	Brown soil, within village
B8	11.86571	6.00410	Bagega	Soil, near a house
D1	11.99210	5.95960	Dareta	Soil, near mine pit
D2	11.99210	5.95940	Dareta	Soil, near mine pit
D3	12.03140	5.95500	Dareta	Soil within village
D4	12.03719	5.95566	Dareta	Soil close to old milling site
D5	12.03155	5.95496	Dareta	Soil around water well in the village
D6	11.99212	5.95991	Dareta	Brown soils, near mine pit
D7	11.99204	5.95890	Dareta	Sediment, downstream of D6
D8	11.99382	5.95788	Dareta	Sediment, downstream of D7
D9	11.99630	5.95763	Dareta	Sediment, downstream of D8
D10	12.01258	5.95936	Dareta	Background soil, brown, near gully
TD1	11.90410	6.11270	Tungar Daji	Soil, near mine pit
TD2	11.90498	6.11247	Tungar Daji	Sediment, downstream of mine pit
TD3	11.90390	6.11126	Tungar Daji	Sediment, downstream of TD2
TD4	11.90345	6.10934	Tungar Daji	Sediment, downstream of TD3
TD5	11.90182	6.10392	Tungar Daji	Brown farmland soil
TD6	11.90487	6.09398	Tungar Daji	Soil, brown, within a compound
TD7	11.90516	6.09236	Tungar Daji	Materials scrapped from walls of a house
TD8	11.90573	6.09332	Tungar Daji	Soil, brown in farmland near village
TD9	11.90216	6.09496	Tungar Daji	Sediment
TD10	11.90103	6.08111	Tungar Daji	Soil from reclamation dumpsite
TS1	11.89413	5.92010	Tsunke	Soil from reclamation dumpsite
TS2	11.86685	5.93946	Tsunke	Soil, close to mine pit
TS3	11.89445	5.91198	Tsunke	Farmland soil
TS4	11.89537	5.91207	Tsunke	Soil within a compound
TS5	11.89697	5.91084	Tsunke	Soil, close to TS4 site
TS6	11.90530	5.90292	Tsunke	Sediment, from background area

Appendix 1b Location and description of samples from the Birnin-Gwari area, northwestern Nigeria

Sample	Latitude	Longitude	Location	Sample description
N3	10.9286	6.7919	B-Gwari	Stream bank soil, brown
N5	10.9581	6.7914	B-Gwari	Stream sediment
N7	10.9933	6.8142	B-Gwari	Sediment+mine waste rock
N8	10.9928	6.8131	B-Gwari	Sediment, downstream of N7
N9	10.9903	6.8192	B-Gwari	Sediment, downstream of N8
N10	10.9950	6.8208	B-Gwari	Sediment, downstream of N9
N12	10.9917	6.8258	B-Gwari	Soil
N14	11.0253	6.7939	B-Gwari	Soil
N15	11.0233	6.7975	B-Gwari	Stream bank soils
N15b	11.0233	6.7978	B-Gwari	"
N16	11.0183	6.7992	B-Gwari	River bank deposits, light brown
N17	11.0131	6.8044	B-Gwari	Soil
N20	11.0211	6.8050	B-Gwari	Soil
N21	11.0272	6.8031	B-Gwari	Stream sediment
N22	11.0236	6.8019	B-Gwari	Sediment, upstream of N21
N23	11.0316	6.8106	B-Gwari	River bank soils
N24	11.0350	6.7992	B-Gwari	Soil, upstream of N23
N25	11.0361	6.8011	B-Gwari	Sediment
N25b	11.0372	6.8011	B-Gwari	"
N27	11.0375	6.8108	B-Gwari	Sediment
N28	11.0400	6.8106	B-Gwari	Soil on farmland
N29	11.0447	6.8108	B-Gwari	Sediment on river bank
N30	11.0480	6.8106	B-Gwari	River bed sediment
N30b	11.0488	6.8008	B-Gwari	"
N32	11.0505	6.8050	B-Gwari	Soil
N34	11.0531	6.7956	B-Gwari	Soil, base of ridge
N35	11.0553	6.7983	B-Gwari	Pebbly brown soil
N35b	11.0544	6.7983	B-Gwari	"
N36	11.0417	6.7939	B-Gwari	Soil
N37	10.9964	6.8217	B-Gwari	Flood plain soils, farmland
N38	10.9986	6.8178	B-Gwari	Sediment from small channel
N39	10.9894	6.8167	B-Gwari	River bank soils
N42	11.0075	6.8072	B-Gwari	Soil on farmland, close to river bank
N43	11.0108	6.8106	B-Gwari	Waste rock heap, mostly of phyllites
N46	11.0192	6.8042	B-Gwari	Soil
N47	11.0203	6.8080	B-Gwari	Soil, close to mine pit
N48	11.0214	6.8169	B-Gwari	Soil
N50	11.0147	6.8175	B-Gwari	Pebbly brown soil
N50b	11.0147	6.8172	B-Gwari	"

Appendix 1b cont’d

Sample	**Latitude**	**Longitude**	**Location**	**Sample description**
N51	10.9997	6.8150	B-Gwari	Channel sediment
N53	10.9953	6.8094	B-Gwari	Farmland soil
N54	11.0775	6.7869	B-Gwari	Farmland soil, light brown
N55	11.0769	6.7844	B-Gwari	Soil, upslope from N54
N55b	11.0769	6.7842	B-Gwari	"
N56	11.0731	6.7769	B-Gwari	Channel sediment
N57	11.0661	6.7719	B-Gwari	Light brown soil
N58	11.0603	6.7731	B-Gwari	Brown soils
N59	11.0403	6.7906	B-Gwari	Grey-looking soils, base of hill
N60	10.9369	6.7556	B-Gwari	Farmland soil, light brown
N62	10.9358	6.7592	B-Gwari	"
TM2	11.0177	6.7941	B-Gwari	Termite mount soil
TM3	11.0556	6.8103	B-Gwari	"
TM5	10.9378	6.7567	B-Gwari	"
R1	10.97722	6.7986	B-Gwari	Rock, altered phyllite
R2	"	"	B-Gwari	"
R3	11.01083	6.8105	B-Gwari	"

Appendix 2 XRF measurement accuracy on three certified reference materials (oxides, wt %, trace elements, µg/g)

Element	**SDO-1(Shale, USGS)**		**W2a(Diabase, USGS)**		**STSD-2(S/sediment(NRCC)**	
	Certified	Measured	Certified	Measured	Certified	Measured
MgO	1.54	1.51	6.37	6.38	nd	nd
Al2O3	12.27	12.34	15.45	15.27	nd	nd
SiO2	49.28	49.36	52.68	52.27	nd	nd
P2O5	0.11	0.13	0.14	0.13	nd	nd
CaO	1.05	1.07	10.86	10.65	nd	nd
TiO2	0.71	0.71	1.06	1.04	nd	nd
MnO	0.04	0.04	0.167	0.16	nd	nd
K2O	3.35	3.40	0.63	0.64	nd	nd
Fe2O3	9.34	9.81	10.83	10.84	nd	nd
Na2O	0.38	0.67	2.2	2.5	nd	nd
Sc	13.2	12	36	32	16	15
V	160	170	260	271	101	105
Cr	66.4	49	92	64	116	103
Ni	99.5	88	70	65	53	57
Cu	60.2	61	110	118	47	47
Zn	64.1	58	80	73	246	237
As	68.5	63	1.2	3	42	40
Rb	126	129	21	22	104	98
Sr	75.1	71	190	186	400	409
Y	40.6	38	23	21	37	36
Zr	165	160	100	91	185	180
Nb	36.6	14	7.9	10	20	20
Mo	134	127	na	3	13	13
Ba	397	396	170	131	540	529
La	38.5	43	10	7	59	61
Ce	79.3	81	23	40	93	114
Pb	27.9	34	9.3	14	66	71
Th	10.5	13	2.4	6	17	21
U	48.8	44	0.5	1	19	16

Note: nd = not determined, na = not available.

Appendix 3 Major elements concentration (wt. %) in soils and sediments from the Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	SiO_2	TiO_2	Al_2O_3	MnO	MgO	Fe_2O_3	CaO	P_2O_5	K_2O	Na_2O	LOI	Total
A1	55.25	0.73	15.32	0.46	0.69	8.99	0.17	1.58	2.53	0.09	7.04	92.85
A2	84.81	1.29	7.46	0.03	0.15	2.53	0.35	0.03	1.53	<0.05	3.24	101.42
A3	40.21	0.18	4.46	0.12	0.11	9.58	0.25	1.08	0.55	<0.05	8.71	65.25
A4	81.87	1.75	4.91	0.07	0.12	3.42	0.17	0.31	1.48	0.16	2.68	99.42
A5	80.44	1.09	8.66	0.05	0.25	3.35	0.18	0.06	1.85	0.23	4.05	100.21
A6	70.27	0.57	6.36	0.08	0.31	7.48	0.16	1.14	1.13	0.03	3.76	99.07
A7	80.69	0.84	7.35	0.07	0.3	4.17	0.2	0.19	1.22	0.2	3.83	100.12
A8	86.14	1.83	4.49	0.06	0.11	2.48	0.13	0.15	1.22	0.05	1.84	99.37
A9	81.80	1.15	9.50	0.03	0.19	2.17	0.09	0.02	1.63	0.07	3.60	100.25
A10	84.79	1.02	5.93	0.05	0.19	2.03	0.54	0.10	1.79	0.17	3.99	100.60
A11	73.33	0.72	6.60	0.04	0.31	5.43	0.60	0.37	1.67	0.14	5.63	94.84
B1	62.58	0.39	3.74	0.07	0.16	7.98	0.46	1.27	0.51	<0.05	6.59	83.75
B2	70.87	0.75	6.24	0.06	0.33	7.46	0.44	0.45	1.03	<0.05	6.01	93.64
B3	61.79	1.00	11.22	0.09	0.72	10.41	1.11	0.45	1.79	<0.05	9.12	97.70
B4	58.76	1.43	16.43	0.09	0.60	10.48	0.38	0.10	1.47	<0.05	10.51	100.25
B5	80.76	2.86	6.34	0.12	0.23	5.13	0.21	0.06	1.20	0.19	3.24	100.34
B6	79.55	2.37	6.86	0.11	0.32	5.22	0.29	0.07	1.05	0.05	4.64	100.53
B7	63.65	1.79	9.72	0.14	1.01	7.93	3.43	0.38	2.15	0.19	9.85	100.24
B8	77.17	2.23	7.12	0.11	0.31	7.57	0.42	0.08	1.38	0.05	4.18	100.62
D1	64.6	0.52	17.97	0.08	1.02	6.27	0.64	0.12	4.3	<0.05	4.82	100.34
D2	76.07	1.98	8.98	0.11	0.4	5.3	1.6	0.18	1.38	0.07	3.64	99.71
D3	51.63	0.79	18.14	0.16	6.37	8.45	5.82	0.05	0.4	2.44	6.35	100.60
D4	88.97	1.04	4.78	0.04	0.10	1.58	0.14	0.03	1.84	0.19	1.56	100.27
D5	73.54	1.55	10.12	0.08	0.89	5.29	1.04	0.09	2.00	0.89	4.01	99.50
D6	77.29	1.33	9.77	0.06	0.34	4.34	0.91	0.03	1.38	0.41	4.51	100.37
D7	63.57	0.76	13.16	0.08	0.63	5.95	0.41	0.29	3.16	0.13	6.28	98.47
D8	82.94	1.36	6.23	0.07	0.25	3.34	0.85	0.03	1.32	0.35	2.31	99.05
D9	83.76	1.02	6.96	0.05	0.27	3.05	0.60	0.03	1.54	0.36	2.92	100.56
D10	89.05	0.85	4.87	0.04	0.08	1.20	0.20	0.02	1.79	0.17	1.72	99.99
TD1	83.79	0.65	8.15	0.02	0.25	2.16	0.7	0.02	1.82	0.7	2.80	101.06
TD2	76.43	0.87	10.68	0.06	0.60	3.04	0.82	0.04	2.18	0.84	4.62	100.18
TD3	69.60	0.78	13.05	0.12	0.99	4.49	1.90	0.07	2.19	1.49	5.32	100.00
TD4	66.64	0.82	14.88	0.11	1.25	5.28	1.34	0.09	2.88	1.47	5.46	100.22
TD5	88.00	0.85	5.25	0.03	0.10	1.21	0.24	0.02	2.17	0.33	1.68	99.88
TD6	77.38	0.9	5.74	0.09	0.45	1.74	1.15	0.28	2.44	0.19	8.62	100.55
TD7	72.06	1.08	12.64	0.05	0.44	4.01	0.63	0.10	2.26	0.13	7.06	100.46
TD8	88.35	1.13	4.59	0.04	0.09	1.26	0.15	0.03	1.92	0.25	1.79	99.60
TD9	79.87	1.09	9.40	0.06	0.27	2.69	0.32	0.04	2.27	0.43	4.03	100.47
TD10	83.56	0.99	5.88	0.04	0.23	1.70	0.57	0.13	2.12	0.24	5.13	100.59
TS1	77.77	0.98	8.44	0.06	0.43	3.02	0.62	0.20	2.39	0.28	5.95	100.14
TS2	79.98	1.15	8.96	0.05	0.38	3.17	0.18	0.04	1.54	0.12	5.06	100.63
TS3	86.30	1.09	5.65	0.03	0.15	1.79	0.20	0.04	1.76	0.16	2.99	100.16
TS4	73.35	0.91	6.3	0.06	0.32	3.89	1.12	0.71	1.88	0.18	5.7	99.51
TS5	85.40	1.06	6.27	0.04	0.18	1.99	0.23	0.07	1.90	0.28	3.82	101.24
TS6	72.99	1.03	11.17	0.08	0.77	4.49	0.77	0.07	1.95	0.62	5.93	99.87
Mean	75.28	1.12	8.59	0.08	0.53	4.54	0.73	0.24	1.78	0.32	4.81	98.53
Min	40.21	0.18	3.74	0.02	0.08	1.2	0.09	0.02	0.4	0.03	1.56	65.25
Max	89.05	2.86	18.14	0.46	6.37	10.48	5.82	1.58	4.3	2.44	10.51	101.42
PAAS	62.80	1.00	18.90	0.11	2.20	6.50	1.30	0.16	3.70	1.20	6.00	103.87

Note: For samples A1, A3, A4, A6, A8, A11, B1-B3, D7 and TS4, their totals should be read in conjunction with the lead and copper concentrations in Appendix 2 below.

Appendix 4 Trace element concentration (µg/g) in soils and sediments of Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	pH	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Zr
DL		10	10	10	10	10	9	10	10	10	6
A1	5.15	10	165	34	72	3600	122	5	5	233	472
A2	5.08	5	43	42	17	5	27	12	52	52	1816*
A3	5.63	5	88	17	74	3400	130	5	5	143	122
A4	6.97	5	53	44	36	500	95	5	5	66	4009*
A5	5.32	5	60	48	27	49	33	5	57	58	1011*
A6	6.08	11	86	55	40	1800	58	5	5	62	1457*
A7		5	95	45	52	400	92	5	5	104	854
A8	6.33	5	43	45	15	200	27	5	5	44	4367*
A9	5.27	5	38	39	18	5	28	13	58	45	1833*
A10	7.49	5	37	36	13	5	80	5	54	81	1460*
A11	6.36	5	196	28	40	1900	128	5	5	177	1017*
B1	6.68	12	111	78	67	2900	214	5	5	106	276
B2	6.44	11	123	90	60	1400	231	33	5	106	638
B3	7.39	14	148	176	90	1300	240	533	5	128	307
B4	4.89	21	213	159	76	175	65	89	71	56	458
B5	5.80	11	77	139	36	10	39	14	48	35	1587*
B6	7.03	12	75	123	41	5	59	11	48	36	1067*
B7	9.24	16	124	177	69	41	359	5	58	169	962
B8	7.85	11	124	224	51	14	61	14	56	40	1714*
D1		16	119	87	34	461	66	5	139	159	382
D2	6.28	14	88	100	30	415	49	5	5	232	3253*
D3	7.48	28	158	327	175	5	75	5	10	262	126
D4	7.29	5	33	34	5	5	16	5	51	63	1691*
D5	7.65	5	75	78	32	21	44	5	66	111	3502*
D6	6.45	11	70	62	16	5	24	13	47	133	1241*
D7	6.28	5	78	43	33	2300	56	5	5	243	603
D8	6.37	5	58	63	17	5	24	13	40	90	2068*
D9	6.95	10	53	50	18	14	23	5	46	82	1228*
D10	**6.11**	**5**	**28**	**28**	**5**	**5**	**16**	**10**	**52**	**64**	**549**
TS1	8.32	5	53	61	24	25	52	5	68	94	970
TS2	6.24	5	49	40	15	13	31	5	45	34	939
TS3	7.17	5	38	68	12	5	32	12	55	57	1586*
TS4	8.29	5	60	65	36	1500	302	5	5	131	1525*
TS5	7.20	5	40	58	13	5	45	13	58	61	1404*
TS6	**6.62**	**11**	**79**	**90**	**32**	**14**	**48**	**10**	**80**	**114**	**938**
TD1	6.08	5	39	26	10	5	20	5	56	148	754
TD2	5.31	5	67	40	15	5	34	5	86	165	1076*
TD3	6.04	5	87	44	19	5	46	5	85	312	889
TD4	6.57	5	96	45	23	14	55	5	114	257	789
TD5	6.77	5	32	27	5	5	13	11	60	83	1303*
TD6	8.52	5	34	32	21	100	395	5	18	166	1444*
TD7	8.2	5	67	50	25	11	72	5	91	95	959
TD8	6.71	5	24	32	28	5	17	15	58	65	1905*
TD9	5.44	5	45	45	14	5	27	11	86	106	1343*
TD10	7.80	5	33	36	10	5	77	10	64	94	1532*
UCC		**11**	**60**	**35**	**20**	**25**	**71**	**1.5**	**112**	**350**	**190**
PAAS		**16**	**150**	**110**	**55**	**90**	**85**		**160**	**200**	**210**

***Above upper calibration range of the instrument.**

Appendix 4 continued

Sample	Nb	Mo	Ba	La	Ce	Pb	Th	U
DL	10	10	24	10	10	20	10	10
A1	<10	<10	2315	59	116	61700	1664*	<10
A2	24	<10	455	30	67	378	25	<10
A3	<10	<10	695	10	39	221600	10766*	<10
A4	26	<10	597	53	100	24300	565	<10
A5	20	<10	537	10	65	2023	48	<10
A6	18	<10	528	27	64	76000	407	<10
A7	<10	<10	753	20	60	10200	2140*	<10
A8	30	<10	352	64	101	8500	214	<10
A9	24	<10	467	31	73	74	21	<10
A10	20	<10	523	26	67	327	21	<10
A11	<10	10	2319	10	127	40300	942	<10
B1	<10	23	2317	10	67	122800	4287*	<10
B2	<10	11	2318	10	87	59100	1604*	<10
B3	14	10	2316	27	99	28300	678	<10
B4	22	10	637	34	104	1333	55	<10
B5	35	<10	305	10	48	403	23	<10
B6	26	<10	272	22	41	83	12	<10
B7	22	<10	573	23	76	2771	59	<10
B8	30	<10	355	23	63	236	21	<10
D1	11	<10	1295	31	80	3800	74	<10
D2	25	10	675	51	116	12100	278	<10
D3	<10	<10	288	10	59	73	<10	<10
D4	20	<10	545	23	63	1232	39	<10
D5	25	<10	776	44	97	2600	77	<10
D6	21	<10	470	28	62	61	17	<10
D7	<10	10	2320	20	160	38200	892	<10
D8	21	<10	396	26	71	204	22	<10
D9	19	<10	488	10	61	858	29	<10
D10	**16**	**<10**	**519**	**20**	**48**	**26**	**<10**	**<10**
TS1	21	<10	562	32	68	2038	48	<10
TS2	20	<10	468	21	54	137	12	<10
TS3	21	<10	432	10	62	357	24	<10
TS4	12	<10	562	26	66	49400	1276*	<10
TS5	21	<10	471	26	64	327	23	<10
TS6	**22**	**<10**	**614**	**47**	**95**	**31**	**16**	**<10**
TD1	15	<10	566	20	61	120	<10	<10
TD2	18	<10	710	37	110	35	16	<10
TD3	16	<10	906	35	120	39	14	<10
TD4	15	<10	968	47	121	39	18	<10
TD5	17	<10	589	10	64	22	14	<10
TD6	17	<10	1013	20	76	15600	334	<10
TD7	24	<10	547	43	76	225	20	<10
TD8	22	<10	482	24	55	27	18	<10
TD9	22	<10	665	43	73	35	20	<10
TD10	20	<10	618	20	56	497	27	<10
UCC	**25**	**1.5**	**550**	**30**	**64**	**20**	**10.7**	**2.8**
PAAS	**1.9**		**650**		**64**	**20**	**14.6**	**3.1**

***Above upper calibration range of the instrument.**

Appendix 5 Major elements concentration (wt.%) in soils and sediments from Birnin-Gwari area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	SiO2	TiO2	Al2O3	MnO	MgO	Fe2O3	CaO	P2O5	K2O	Na2O	LOI	Total
N3	74.96	1.47	10.88	0.1	0.22	4.91	0.14	0.04	1.68	0.27	5.99	100.66
N5	78.23	1	9.75	0.09	0.18	3.21	0.15	0.04	2.6	0.32	4.99	100.56
N7	69.9	0.77	16.88	0.03	0.47	3.87	0.04	0.04	3.39	0.34	4.21	99.9
N8	68.36	1.2	14.68	0.33	0.38	6.27	0.1	0.05	2.19	0.21	6.85	100.62
N9	71.12	0.88	16.12	0.03	0.3	4.17	0.05	0.04	3	0.3	4.29	100.3
N10	82.58	1.15	7.68	0.08	0.24	3.02	0.24	0.03	1.88	0.26	3.16	100.32
N12	83.07	1.69	6.97	0.1	0.19	3.12	0.24	0.04	1.76	0.29	2.88	100.35
N14	69.34	1.03	8.92	0.46	0.24	11.18	0.33	0.14	1.03	0.21	8.38	101.26
N15	78.14	1.05	9.63	0.11	0.3	4.12	0.25	0.04	2.13	0.33	4.12	100.22
N15b	71.4	1.03	12.96	0.21	0.36	5.81	0.17	0.05	2.20	0.30	6.17	100.62
N16	83.23	1.33	6.91	0.08	0.21	2.96	0.26	0.04	1.85	0.29	3.25	100.41
N17	78.9	1.26	8.94	0.11	0.29	3.85	0.27	0.04	2.03	0.28	4.40	100.33
N20	82.44	1.64	7.31	0.06	0.19	3.03	0.19	0.03	1.87	0.3	nd	97.06
N21	83.1	1.98	6.74	0.07	0.18	3.12	0.20	0.04	1.70	0.26	2.67	100.05
N22	81.14	1.7	7.83	0.07	0.2	3.49	0.21	0.04	1.85	0.25	nd	96.78
N23	87.51	1.84	4.92	0.06	0.12	2.23	0.2	0.03	1.45	0.21	nd	98.57
N24	83.35	1.25	7.33	0.05	0.19	2.84	0.19	0.03	1.75	0.24	3.01	100.23
N25	83.7	1.29	7.33	0.07	0.22	3.02	0.23	0.03	1.84	0.23	2.93	100.87
N25b	86.68	1.93	5.25	0.06	0.12	2.32	0.2	0.04	1.58	0.23	nd	98.41
N27	80.6	1.19	8.67	0.07	0.25	3.51	0.23	0.03	1.91	0.24	3.75	100.46
N28	80.53	1.4	7.41	0.09	0.27	3.64	0.3	0.05	1.84	0.32	nd	95.85
N29	87.09	1.93	5.1	0.06	0.11	2.33	0.18	0.03	1.52	0.19	nd	98.54
N30	89.28	1.64	4.47	0.05	0.1	1.91	0.18	0.03	1.52	0.22	nd	99.4
N30b	85.63	1.91	5.42	0.07	0.14	2.69	0.19	0.04	1.49	0.32	nd	97.9
N32	79.91	1.87	7.67	0.08	0.27	3.59	0.24	0.05	1.74	0.33	nd	95.75
N34	73.96	1.15	10.29	0.08	0.31	3.01	0.57	0.07	1.72	0.28	9.26	100.7
N35	64.6	0.96	13.40	0.49	0.33	10.92	0.14	0.08	1.44	0.20	8.39	100.93
N35B	69.66	1.04	11.49	0.49	0.28	8.81	0.24	0.07	1.45	0.29	7.11	100.93
N36	69.13	0.66	15.36	0.11	0.83	5.75	0.1	0.04	3.34	0.2	5.04	100.56
N37	78.8	1.18	9.84	0.15	0.25	4.28	0.14	0.03	1.99	0.26	3.74	100.67
N38	65.3	1.17	17.56	0.08	0.40	6.32	0.08	0.05	3.35	0.28	5.90	100.45
N39	83.16	1.22	7.53	0.08	0.2	2.94	0.27	0.03	1.88	0.3	2.75	100.36
N42	85.37	1.43	5.92	0.1	0.15	2.52	0.22	0.03	1.76	0.23	2.87	100.6
N43	77.5	1.08	11.56	0.05	0.29	3.29	0.11	0.03	2.12	0.36	3.87	100.27
N46	86.8	1.30	5.37	0.05	0.12	2.21	0.16	0.03	1.54	0.19	2.00	99.8
N47	74.12	1.3	11.78	0.07	0.53	5.33	0.12	0.05	2.48	0.35	3.88	100.01
N48	80.44	1.36	8.12	0.13	0.23	3.33	0.23	0.05	1.19	0.21	5.54	100.83

nd: not determined

Appendix 5 continued

Sample	SiO2	TiO2	Al2O3	MnO	MgO	Fe2O3	CaO	P2O5	K2O	Na2O	LOI	Total
N50	67.91	1.04	10.64	0.46	0.42	10.68	0.31	0.1	1.39	0.17	7.76	100.88
N50b	73.47	1.21	8.01	0.32	0.36	9.23	0.4	0.09	1.37	0.17	6.04	100.67
N51	67.65	1.34	12.46	0.44	0.38	10.15	0.14	0.09	1.63	0.17	6.38	100.83
N53	86.59	1.15	5.95	0.08	0.13	2.46	0.1	0.03	1.64	0.21	2.31	100.65
N54	90.44	1.27	4	0.05	0.12	1.27	0.17	0.04	1.48	0.14	nd	98.98
N55	85.0	0.97	5.92	0.16	0.15	2.76	0.15	0.06	1.15	0.14	4.41	100.84
N55b	89.35	1.24	4.15	0.12	0.08	2.41	0.05	0.03	0.85	0.1	2.05	100.43
N56	65.3	0.68	11.75	0.67	0.85	12.09	0.24	0.09	2.14	0.51	6.68	101.03
N57	66.5	0.95	10.20	0.39	0.49	11.16	0.47	0.08	1.75	0.34	8.72	101.02
N58	77.6	0.99	7.58	0.18	0.36	5.39	0.35	0.06	1.40	0.18	6.83	100.89
N59	68.5	0.90	11.10	0.34	0.62	11.13	0.15	0.10	1.84	0.22	6.17	101.03
N60	78.7	1.09	8.45	0.04	0.19	2.00	0.30	0.05	2.30	0.22	7.28	100.57
N62	87.08	1.17	5.69	0.04	0.09	1.64	0.12	0.03	1.9	0.23	nd	97.99
TM2	64.83	1.39	16.41	0.16	0.35	7.49	0.16	0.05	2.01	0.22	7.25	100.32
TM3	71.2	1.52	13.78	0.08	0.29	5.44	0.09	0.05	1.8	0.21	5.96	100.42
TM5	70.81	1.23	15.17	0.03	0.27	3.65	0.15	0.04	2.18	0.18	7.18	100.89
R1	86.5	0.28	8.15	0.02	0.24	1.06	0.05	0.03	1.48	0.36	2.55	100.72
R2	92.19	0.21	5.09	0.01	0.19	0.84	0.03	0.01	1.14	0.12	1.26	101.09
R3	88.96	0.26	6.78	0.02	0.21	1.09	0.04	0.01	1.3	0.21	1.98	100.86
PAAS	62.80	1.00	18.90	0.11	2.20	6.50	1.30	0.16	3.70	1.20	6.00	103.87

PAAS: Post Archaean Australian Average Shale

Appendix 6 Trace elements concentration (µg/g) in soils and sediments from Birnin-Gwari area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y
DL	10	10	10	10	10	9	10	10	10	10
N3	11	79	57	16	<10	28	19	64	53	35
N5	<10	45	35	10	<10	29	15	89	127	31
N7	12	85	92	19	<10	30	43	148	80	21
N8	12	87	69	28	18	38	19	96	52	37
N9	13	80	77	15	<10	26	37	131	60	18
N10	<10	49	45	14	<10	24	17	66	52	33
N12	<10	48	48	13	<10	24	23	61	47	53
N14	<10	66	48	22	<10	37	39	48	49	37
N15	<10	60	49	17	<10	28	14	81	57	32
N15b	10	76	58	22	<10	35	13	92	59	33
N16	<10	50	45	12	<10	24	17	64	51	41
N17	10	61	51	16	<10	28	18	76	56	41
N20	<10	52	48	14	<10	26	26	63	51	61
N21	<10	53	51	13	<10	27	36	57	48	73
N22	<10	60	51	15	<10	27	22	65	51	58
N23	<10	41	46	11	<10	21	31	45	39	63
N24	<10	48	44	13	<10	22	20	62	49	41
N25	<10	49	45	13	<10	23	19	63	55	38
N25b	<10	42	45	11	<10	23	35	49	43	71
N27	<10	57	49	16	<10	25	16	70	54	36
N28	<10	58	57	15	<10	30	22	67	56	43
N29	<10	42	46	11	<10	21	30	48	42	67
N30	<10	37	42	10	<10	19	26	43	43	53
N30b	<10	46	46	11	<10	22	31	48	40	64
N32	10	61	57	17	<10	28	31	64	63	67
N34	<10	55	61	15	<10	42	13	70	69	29
N35	13	78	55	25	<10	38	19	79	45	32
N35B	10	72	56	20	<10	36	18	74	53	26
N36	13	68	52	16	<10	42	11	134	41	23
N37	<10	62	51	18	<10	29	24	77	53	36
N38	15	102	100	22	13	36	38	144	63	24
N39	<10	50	46	<10	<10	21	28	68	48	33
N42	<10	39	39	11	<10	22	21	60	52	39
N43	10	59	68	14	<10	32	48	108	48	25
N46	<10	38	39	10	<10	20	22	51	46	39
N47	10	63	72	12	<10	50	94	137	65	16
N48	<10	52	46	17	<10	26	17	56	43	33

Appendix 6 continued

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y
N50	10	78	54	28	<10	52	17	82	60	29
N50b	<10	67	50	20	<10	45	14	70	65	25
N51	14	96	60	30	19	52	16	95	51	33
N53	<10	37	34	11	<10	21	16	55	52	27
N54	<10	24	31	<10	<10	16	22	45	49	39
N55	<10	35	29	11	<10	23	17	45	43	29
N55b	<10	29	28	<10	<10	19	22	31	29	37
N56	11	77	62	30	11	51	53	112	59	21
N57	<10	74	48	19	<10	43	10	81	110	27
N58	<10	47	35	15	<10	38	11	67	60	23
N59	10	81	59	29	29	77	16	123	39	20
N60	<10	42	38	12	<10	22	11	76	113	33
N62	<10	33	33	<10	<10	18	17	56	67	37
TM2	18	127	81	23	40	32	29	78	44	32
TM3	13	82	82	27	<10	35	22	100	49	39
TM5	<10	65	48	19	<10	29	10	90	83	37
R1	<10	38	32	<10	<10	16	15	48	98	14
R2	<10	32	29	<10	<10	15	18	43	23	<10
R3	<10	39	33	<10	<10	16	14	48	58	11
	Zr	**Nb**	**Mo**	**Ba**	**La**	**Ce**	**Pb**	**Th**	**U**	
	6	10	10	24	10	10	20	10	10	
N3	1344*	27	<10	407	48	93	31	22	<10	
N5	1648*	21	<10	849	26	83	53	20	<10	
N7	476	15	<10	785	45	80	27	14	<10	
N8	830	24	<10	509	62	105	31	21	<10	
N9	505	18	<10	580	36	67	27	17	<10	
N10	1366*	24	<10	463	31	74	28	18	<10	
N12	3254*	38	<10	415	50	92	29	29	<10	
N14	792	21	<10	398	52	71	28	16	<10	
N15	1098*	23	<10	539	35	82	30	19	<10	
N15b	768	23	<10	578	47	84	29	18	<10	
N16	2048*	26	<10	460	34	78	29	24	<10	
N17	1681	28	<10	532	41	86	32	22	<10	
N20	3134	29	<10	447	57	100	31	33	<10	
N21	4154	33	<10	383	64	113	31	41	<10	
N22	2723	30	<10	429	48	93	28	31	<10	
N23	4435	30	<10	327	50	94	27	38	<10	
N24	2010*	24	<10	424	37	84	27	24	<10	
N25	1879	24	<10	451	35	72	30	21	<10	
N25b	4656	31	<10	366	53	104	27	45	<10	

***Above calibration limit.**

Appendix 6 continued

Sample	Zr	Nb	Mo	Ba	La	Ce	Pb	Th	U
N27	1467	23	<10	480	35	72	29	20	<10
N28	2370	25	<10	467	43	92	31	26	<10
N29	4266	31	<10	355	51	95	27	39	<10
N30	3255	27	<10	357	35	73	26	30	<10
N30b	4321	31	<10	344	55	99	28	39	<10
N32	3755	31	<10	456	67	115	32	39	<10
N34	888	20	<10	478	37	71	26	16	<10
N35	562	20	<10	448	55	77	27	17	<10
N35B	609	21	<10	476	42	73	25	15	<10
N36	371	17	<10	614	28	61	24	16	<10
N37	1348	23	<10	506	41	83	30	20	<10
N38	953	23	<10	675	39	69	34	19	<10
N39	1899*	26	<10	433	35	76	29	19	<10
N42	2099*	27	<10	437	31	72	28	21	<10
N43	1343	19	<10	374	25	56	26	17	<10
N46	2106	23	<10	374	24	67	28	23	<10
N47	596	20	<10	379	37	69	34	15	<10
N48	1234*	25	<10	295	31	77	26	16	<10
N50	555	19	<10	649	42	75	27	15	<10
N50b	691	19	<10	513	36	63	22	13	<10
N51	658	22	<10	586	51	83	26	16	<10
N53	1150*	21	<10	398	23	59	23	15	<10
N54	2131	23	<10	315	26	60	22	19	<10
N55	986	20	<10	358	25	56	23	13	<10
N55b	1755	22	<10	224	23	54	21	16	<10
N56	388	15	<10	669	41	78	26	12	<10
N57	760	19	<10	843	42	82	28	15	<10
N58	645	17	<10	405	25	58	24	12	<10
N59	261	17	<10	505	34	57	21	13	<10
N60	1424	23	<10	788	34	77	37	19	<10
N62	2034	22	<10	494	27	68	33	21	<10
TM2	395	22	<10	447	38	69	28	16	<10
TM3	1240*	28	<10	404	67	101	26	21	<10
TM5	1299*	27	<10	631	41	85	38	22	<10
R1	276	<10	<10	254	21	62	23	<10	<10
R2	251	<10	<10	162	<20	40	20	<10	<10
R3	262	<10	<10	214	<20	54	22	<10	<10

Appendix 7 Enrichment ratios, ER for trace elements in soils and sediments from Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Zr
A1	0.91	2.75	0.97	3.60	144.00	1.72	6.67	0.09	0.67	2.48
A2	0.91	0.72	1.20	0.85	0.40	0.38	8.00	0.46	0.15	9.56
A3	0.91	1.47	0.49	3.70	136.00	1.83	6.67	0.09	0.41	0.64
A4	0.91	0.88	1.26	1.80	20.00	1.34	6.67	0.09	0.19	21.10
A5	0.91	1.00	1.37	1.35	1.96	0.46	6.67	0.51	0.17	5.32
A6	1.00	1.43	1.57	2.00	72.00	0.82	6.67	0.09	0.18	7.67
A7	0.91	1.58	1.29	2.60	16.00	1.30	6.67	0.09	0.30	4.49
A8	0.91	0.72	1.29	0.75	8.00	0.38	6.67	0.09	0.13	22.98
A9	0.91	0.63	1.11	0.90	0.40	0.39	8.67	0.52	0.13	9.65
A10	0.91	0.62	1.03	0.65	0.40	1.13	6.67	0.48	0.23	7.68
A11	0.91	3.27	0.80	2.00	76.00	1.80	6.67	0.09	0.51	5.35
B1	1.09	1.85	2.23	3.35	116.00	3.01	6.67	0.09	0.30	1.45
B2	1.00	2.05	2.57	3.00	56.00	3.25	22.00	0.09	0.30	3.36
B3	1.27	2.47	5.03	4.50	52.00	3.38	355.33	0.09	0.37	1.62
B4	1.91	3.55	4.54	3.80	7.00	0.92	59.33	0.63	0.16	2.41
B5	1.00	1.28	3.97	1.80	0.40	0.55	9.33	0.43	0.10	8.35
B6	1.09	1.25	3.51	2.05	0.40	0.83	7.33	0.43	0.10	5.62
B7	1.45	2.07	5.06	3.45	1.64	5.06	6.67	0.52	0.48	5.06
B8	1.00	2.07	6.40	2.55	0.56	0.86	9.33	0.50	0.11	9.02
D1	1.45	1.98	2.49	1.70	18.44	0.93	6.67	1.24	0.45	2.01
D2	1.27	1.47	2.86	1.50	16.60	0.69	6.67	0.09	0.66	17.12
D3	2.55	2.63	9.34	8.75	0.40	1.06	6.67	0.09	0.75	0.66
D4	0.91	0.55	0.97	0.25	0.40	0.23	6.67	0.46	0.18	8.90
D5	0.91	1.25	2.23	1.60	0.84	0.62	6.67	0.59	0.32	18.43
D6	1.00	1.17	1.77	0.80	0.40	0.34	8.67	0.42	0.38	6.53
D7	0.91	1.30	1.23	1.65	92.00	0.79	6.67	0.09	0.69	3.17
D8	0.91	0.97	1.80	0.85	0.40	0.34	8.67	0.36	0.26	10.88
D9	0.91	0.88	1.43	0.90	0.56	0.32	6.67	0.41	0.23	6.46
D10	0.91	0.47	0.80	0.25	0.40	0.23	6.67	0.46	0.18	2.89
TD1	0.91	0.88	1.74	1.20	1.00	0.73	6.67	0.61	0.27	5.11
TD2	0.91	0.82	1.14	0.75	0.52	0.44	6.67	0.40	0.10	4.94
TD3	0.91	0.63	1.94	0.60	0.40	0.45	8.00	0.49	0.16	8.35
TD4	0.91	1.00	1.86	1.80	60.00	4.25	6.67	0.09	0.37	8.03
TD5	0.91	0.67	1.66	0.65	0.40	0.63	8.67	0.52	0.17	7.39
TD6	1.00	1.32	2.57	1.60	0.56	0.68	6.67	0.71	0.33	4.94
TD7	0.91	0.65	0.74	0.50	0.40	0.28	6.67	0.50	0.42	3.97
TD8	0.91	1.12	1.14	0.75	0.40	0.48	6.67	0.77	0.47	5.66
TD9	0.91	1.45	1.26	0.95	0.40	0.65	6.67	0.76	0.89	4.68
TD10	0.91	1.60	1.29	1.15	0.56	0.77	6.67	1.02	0.73	4.15
TS1	0.91	0.53	0.77	0.25	0.40	0.18	7.33	0.54	0.24	6.86
TS2	0.91	0.57	0.91	1.05	4.00	5.56	6.67	0.16	0.47	7.60
TS3	0.91	1.12	1.43	1.25	0.44	1.01	6.67	0.81	0.27	5.05
TS4	0.91	0.40	0.91	1.40	0.40	0.24	10.00	0.52	0.19	10.03
TS5	0.91	0.75	1.29	0.70	0.40	0.38	7.33	0.77	0.30	7.07
TS6	0.91	0.55	1.03	0.50	0.40	1.08	6.67	0.57	0.27	8.06
Min	0.91	0.40	0.49	0.25	0.40	0.18	6.67	0.09	0.10	0.64
Max	2.55	3.55	9.34	8.75	144.00	5.56	355.33	1.24	0.89	22.98
Mean	1.03	1.30	2.05	1.73	20.23	1.17	16.40	0.42	0.33	6.95

Appendix 7 continued

Sample	Nb	Mo	Y	Ba	La	Ce	Pb	Th	U
A1	0.40	6.67	5.18	4.21	1.97	1.81	3085.00	155.51	3.57
A2	0.96	6.67	1.59	0.83	1.00	1.05	18.90	2.34	3.57
A3	0.40	6.67	5.32	1.26	0.33	0.61	11080.00	1006.17	3.57
A4	1.04	6.67	4.32	1.09	1.77	1.56	1215.00	52.80	3.57
A5	0.80	6.67	1.41	0.98	0.33	1.02	101.15	4.49	3.57
A6	0.72	6.67	2.50	0.96	0.90	1.00	3800.00	38.04	3.57
A7	0.40	6.67	5.23	1.37	0.67	0.94	510.00	200.00	3.57
A8	1.20	6.67	3.59	0.64	2.13	1.58	425.00	20.00	3.57
A9	0.96	6.67	1.91	0.85	1.03	1.14	3.70	1.96	3.57
A10	0.80	6.67	1.27	0.95	0.87	1.05	16.35	1.96	3.57
A11	0.40	6.67	3.36	4.22	0.33	1.98	2015.00	88.04	3.57
B1	0.40	15.33	5.27	4.21	0.33	1.05	6140.00	400.65	3.57
B2	0.40	7.33	4.55	4.21	0.33	1.36	2955.00	149.91	3.57
B3	0.56	6.67	2.50	4.21	0.90	1.55	1415.00	63.36	3.57
B4	0.88	6.67	1.27	1.16	1.13	1.63	66.65	5.14	3.57
B5	1.40	6.67	1.45	0.55	0.33	0.75	20.15	2.15	3.57
B6	1.04	6.67	1.09	0.49	0.73	0.64	4.15	1.12	3.57
B7	0.88	6.67	1.18	1.04	0.77	1.19	138.55	5.51	3.57
B8	1.20	6.67	1.27	0.65	0.77	0.98	11.80	1.96	3.57
D1	0.44	6.67	1.36	2.35	1.03	1.25	190.00	6.92	3.57
D2	1.00	6.67	3.59	1.23	1.70	1.81	605.00	25.98	3.57
D3	0.40	6.67	1.14	0.52	0.33	0.92	3.65	0.47	3.57
D4	0.80	6.67	1.55	0.99	0.77	0.98	61.60	3.64	3.57
D5	1.00	6.67	2.09	1.41	1.47	1.52	130.00	7.20	3.57
D6	0.84	6.67	1.45	0.85	0.93	0.97	3.05	1.59	3.57
D7	0.40	6.67	3.41	4.22	0.67	2.50	1910.00	83.36	3.57
D8	0.84	6.67	1.59	0.72	0.87	1.11	10.20	2.06	3.57
D9	0.76	6.67	1.23	0.89	0.33	0.95	42.90	2.71	3.57
D10	0.64	6.67	0.77	0.94	0.67	0.75	1.30	0.47	3.57
TD1	0.84	6.67	1.45	1.02	1.07	1.06	101.90	4.49	3.57
TD2	0.80	6.67	1.86	0.85	0.70	0.84	6.85	1.12	3.57
TD3	0.84	6.67	1.45	0.79	0.33	0.97	17.85	2.24	3.57
TD4	0.48	6.67	4.59	1.02	0.87	1.03	2470.00	119.25	3.57
TD5	0.84	6.67	1.41	0.86	0.87	1.00	16.35	2.15	3.57
TD6	0.88	6.67	1.59	1.12	1.57	1.48	1.55	1.50	3.57
TD7	0.60	6.67	0.82	1.03	0.67	0.95	6.00	0.47	3.57
TD8	0.72	6.67	1.09	1.29	1.23	1.72	1.75	1.50	3.57
TD9	0.64	6.67	0.91	1.65	1.17	1.88	1.95	1.31	3.57
TD10	0.60	6.67	0.82	1.76	1.57	1.89	1.95	1.68	3.57
TS1	0.68	6.67	1.00	1.07	0.33	1.00	1.10	1.31	3.57
TS2	0.68	6.67	2.27	1.84	0.67	1.19	780.00	31.21	3.57
TS3	0.96	6.67	1.41	0.99	1.43	1.19	11.25	1.87	3.57
TS4	0.88	6.67	1.68	0.88	0.80	0.86	1.35	1.68	3.57
TS5	0.88	6.67	1.55	1.21	1.43	1.14	1.75	1.87	3.57
TS6	0.80	6.67	1.32	1.12	0.67	0.88	24.85	2.52	3.57
Min	0.40	6.67	0.77	0.49	0.33	0.61	1.10	0.47	3.57
Max	1.40	15.33	5.32	4.22	2.13	2.50	11080.00	1006.17	3.57
Mean	0.76	6.87	2.17	1.48	0.91	1.22	876.12	55.82	3.57

Appendix 8 Indices of geoaccumulation, I_{geo} for trace elements in soils and sediments from Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Zr
A1	-0.72	0.87	-0.63	1.26	6.58	0.20	2.15	-4.07	-1.17	0.73
A2	-0.72	-1.07	-0.32	-0.82	-1.91	-1.98	2.42	-1.69	-3.34	2.67
A3	-0.72	-0.03	-1.63	1.30	6.50	0.29	2.15	-4.07	-1.88	-1.22
A4	-0.72	-0.76	-0.25	0.26	3.74	-0.16	2.15	-4.07	-2.99	3.81
A5	-0.72	-0.58	-0.13	-0.15	0.39	-1.69	2.15	-1.56	-3.18	1.83
A6	-0.58	-0.07	0.07	0.42	5.58	-0.88	2.15	-4.07	-3.08	2.35
A7	-0.72	0.08	-0.22	0.79	3.42	-0.21	2.15	-4.07	-2.34	1.58
A8	-0.72	-1.07	-0.22	-1.00	2.42	-1.98	2.15	-4.07	-3.58	3.94
A9	-0.72	-1.24	-0.43	-0.74	-1.91	-1.93	2.53	-1.53	-3.54	2.69
A10	-0.72	-1.28	-0.54	-1.21	-1.91	-0.41	2.15	-1.64	-2.70	2.36
A11	-0.72	1.12	-0.91	0.42	5.66	0.27	2.15	-4.07	-1.57	1.84
B1	-0.46	0.30	0.57	1.16	6.27	1.01	2.15	-4.07	-2.31	-0.05
B2	-0.58	0.45	0.78	1.00	5.22	1.12	3.87	-4.07	-2.31	1.16
B3	-0.24	0.72	1.75	1.58	5.12	1.17	7.89	-4.07	-2.04	0.11
B4	0.35	1.24	1.60	1.34	2.22	-0.71	5.31	-1.24	-3.23	0.68
B5	-0.58	-0.23	1.40	0.26	-1.91	-1.45	2.64	-1.81	-3.91	2.48
B6	-0.46	-0.26	1.23	0.45	-1.91	-0.85	2.29	-1.81	-3.87	1.90
B7	-0.04	0.46	1.75	1.20	0.13	1.75	2.15	-1.53	-1.64	1.76
B8	-0.58	0.46	2.09	0.77	-1.42	-0.80	2.64	-1.58	-3.71	2.59
D1	-0.04	0.40	0.73	0.18	3.62	-0.69	2.15	-0.27	-1.72	0.42
D2	-0.24	-0.03	0.93	0.00	3.47	-1.12	2.15	-4.07	-1.18	3.51
D3	0.76	0.81	2.64	2.54	-1.91	-0.51	2.15	-4.07	-1.00	-1.18
D4	-0.72	-1.45	-0.63	-1.58	-1.91	-2.73	2.15	-1.72	-3.06	2.57
D5	-0.72	-0.26	0.57	0.09	-0.84	-1.28	2.15	-1.35	-2.24	3.62
D6	-0.58	-0.36	0.24	-0.91	-1.91	-2.15	2.53	-1.84	-1.98	2.12
D7	-0.72	-0.21	-0.29	0.14	5.94	-0.93	2.15	-4.07	-1.11	1.08
D8	-0.72	-0.63	0.26	-0.82	-1.91	-2.15	2.53	-2.07	-2.54	2.86
D9	-0.72	-0.76	-0.07	-0.74	-1.42	-2.21	2.15	-1.87	-2.68	2.11
D10	-0.72	-1.68	-0.91	-1.58	-1.91	-2.73	2.15	-1.69	-3.04	0.95
TD1	-0.72	-0.76	0.22	-0.32	-0.58	-1.03	2.15	-1.30	-2.48	1.77
TD2	-0.72	-0.88	-0.39	-1.00	-1.53	-1.78	2.15	-1.90	-3.95	1.72
TD3	-0.72	-1.24	0.37	-1.32	-1.91	-1.73	2.42	-1.61	-3.20	2.48
TD4	-0.72	-0.58	0.31	0.26	2.32	1.50	2.15	-4.07	-2.00	2.42
TD5	-0.72	-1.17	0.14	-1.21	-1.91	-1.24	2.53	-1.53	-3.11	2.30
TD6	-0.58	-0.19	0.78	0.09	-1.42	-1.15	2.15	-1.07	-2.20	1.72
TD7	-0.72	-1.21	-1.01	-1.58	-1.91	-2.41	2.15	-1.58	-1.83	1.40
TD8	-0.72	-0.43	-0.39	-1.00	-1.91	-1.65	2.15	-0.97	-1.67	1.92
TD9	-0.72	-0.05	-0.25	-0.66	-1.91	-1.21	2.15	-0.98	-0.75	1.64
TD10	-0.72	0.09	-0.22	-0.38	-1.42	-0.95	2.15	-0.56	-1.03	1.47
TS1	-0.72	-1.49	-0.96	-1.58	-1.91	-3.03	2.29	-1.49	-2.66	2.19
TS2	-0.72	-1.40	-0.71	-0.51	1.42	1.89	2.15	-3.22	-1.66	2.34
TS3	-0.72	-0.43	-0.07	-0.26	-1.77	-0.56	2.15	-0.88	-2.47	1.75
TS4	-0.72	-1.91	-0.71	-0.10	-1.91	-2.65	2.74	-1.53	-3.01	2.74
TS5	-0.72	-1.00	-0.22	-1.10	-1.91	-1.98	2.29	-0.97	-2.31	2.24
TS6	-0.72	-1.45	-0.54	-1.58	-1.91	-0.47	2.15	-1.39	-2.48	2.43
Min	-0.72	-1.91	-1.63	-1.58	-1.91	-3.03	2.15	-4.07	-3.95	-1.22
Max	0.76	1.24	2.64	2.54	6.58	1.89	7.89	-0.27	-0.75	3.94
Mean	-0.58	-0.43	0.13	-0.15	0.52	-0.94	2.48	-2.29	-2.44	1.86

Appendix 8 continued

Sample	Nb	Mo	Y	Ba	La	Ce	Pb	Th	U
A1	-1.91	2.15	1.79	1.49	0.39	0.27	11.01	6.70	1.25
A2	-0.64	2.15	0.08	-0.86	-0.58	-0.52	3.66	0.64	1.25
A3	-1.91	2.15	1.83	-0.25	-2.17	-1.30	12.85	9.39	1.25
A4	-0.53	2.15	1.53	-0.47	0.24	0.06	9.66	5.14	1.25
A5	-0.91	2.15	-0.09	-0.62	-2.17	-0.56	6.08	1.58	1.25
A6	-1.06	2.15	0.74	-0.64	-0.74	-0.58	11.31	4.66	1.25
A7	-1.91	2.15	1.80	-0.13	-1.17	-0.68	8.41	7.06	1.25
A8	-0.32	2.15	1.26	-1.23	0.51	0.07	8.15	3.74	1.25
A9	-0.64	2.15	0.35	-0.82	-0.54	-0.40	1.30	0.39	1.25
A10	-0.91	2.15	-0.24	-0.66	-0.79	-0.52	3.45	0.39	1.25
A11	-1.91	2.15	1.17	1.49	-2.17	0.40	10.39	5.88	1.25
B1	-1.91	3.35	1.81	1.49	-2.17	-0.52	12.00	8.06	1.25
B2	-1.91	2.29	1.60	1.49	-2.17	-0.14	10.94	6.64	1.25
B3	-1.42	2.15	0.74	1.49	-0.74	0.04	9.88	5.40	1.25
B4	-0.77	2.15	-0.24	-0.37	-0.40	0.12	5.47	1.78	1.25
B5	-0.10	2.15	-0.04	-1.44	-2.17	-1.00	3.75	0.52	1.25
B6	-0.53	2.15	-0.46	-1.60	-1.03	-1.23	1.47	-0.42	1.25
B7	-0.77	2.15	-0.34	-0.53	-0.97	-0.34	6.53	1.88	1.25
B8	-0.32	2.15	-0.24	-1.22	-0.97	-0.61	2.98	0.39	1.25
D1	-1.77	2.15	-0.14	0.65	-0.54	-0.26	6.98	2.20	1.25
D2	-0.58	2.15	1.26	-0.29	0.18	0.27	8.66	4.11	1.25
D3	-1.91	2.15	-0.40	-1.52	-2.17	-0.70	1.28	-1.68	1.25
D4	-0.91	2.15	0.04	-0.60	-0.97	-0.61	5.36	1.28	1.25
D5	-0.58	2.15	0.48	-0.09	-0.03	0.01	6.44	2.26	1.25
D6	-0.84	2.15	-0.04	-0.81	-0.68	-0.63	1.02	0.08	1.25
D7	-1.91	2.15	1.18	1.49	-1.17	0.74	10.31	5.80	1.25
D8	-0.84	2.15	0.08	-1.06	-0.79	-0.44	2.77	0.45	1.25
D9	-0.98	2.15	-0.29	-0.76	-2.17	-0.65	4.84	0.85	1.25
D10	-1.23	2.15	-0.96	-0.67	-1.17	-1.00	-0.21	-1.68	1.25
TD1	-0.84	2.15	-0.04	-0.55	-0.49	-0.50	6.09	1.58	1.25
TD2	-0.91	2.15	0.31	-0.82	-1.10	-0.83	2.19	-0.42	1.25
TD3	-0.84	2.15	-0.04	-0.93	-2.17	-0.63	3.57	0.58	1.25
TD4	-1.64	2.15	1.61	-0.55	-0.79	-0.54	10.69	6.31	1.25
TD5	-0.84	2.15	-0.09	-0.81	-0.79	-0.58	3.45	0.52	1.25
TD6	-0.77	2.15	0.08	-0.43	0.06	-0.02	0.05	0.00	1.25
TD7	-1.32	2.15	-0.87	-0.54	-1.17	-0.65	2.00	-1.68	1.25
TD8	-1.06	2.15	-0.46	-0.22	-0.28	0.20	0.22	0.00	1.25
TD9	-1.23	2.15	-0.72	0.14	-0.36	0.32	0.38	-0.20	1.25
TD10	-1.32	2.15	-0.87	0.23	0.06	0.33	0.38	0.17	1.25
TS1	-1.14	2.15	-0.58	-0.49	-2.17	-0.58	-0.45	-0.20	1.25
TS2	-1.14	2.15	0.60	0.30	-1.17	-0.34	9.02	4.38	1.25
TS3	-0.64	2.15	-0.09	-0.59	-0.07	-0.34	2.91	0.32	1.25
TS4	-0.77	2.15	0.17	-0.78	-0.91	-0.80	-0.15	0.17	1.25
TS5	-0.77	2.15	0.04	-0.31	-0.07	-0.40	0.22	0.32	1.25
TS6	-0.91	2.15	-0.19	-0.42	-1.17	-0.78	4.05	0.75	1.25
Min	-1.91	2.15	-0.96	-1.60	-2.17	-1.30	-0.45	-1.68	1.25
Max	-0.10	3.35	1.83	1.49	0.51	0.74	12.85	9.39	1.25
Mean	-1.07	2.18	0.29	-0.31	-0.93	-0.37	5.14	2.13	1.25

Appendix 9 Enrichment ratios, ER for trace elements in soils and sediments from Birnin-Gwari area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y
N3	1.00	1.32	1.63	0.80	0.40	0.39	12.67	0.57	0.15	1.59
N5	0.91	0.75	1.00	0.50	0.40	0.41	10.00	0.79	0.36	1.41
N7	1.09	1.42	2.63	0.95	0.40	0.42	28.67	1.32	0.23	0.95
N8	1.09	1.45	1.97	1.40	0.72	0.54	12.67	0.86	0.15	1.68
N9	1.18	1.33	2.20	0.75	0.40	0.37	24.67	1.17	0.17	0.82
N10	0.91	0.82	1.29	0.70	0.40	0.34	11.33	0.59	0.15	1.50
N12	0.91	0.80	1.37	0.65	0.40	0.34	15.33	0.54	0.13	2.41
N14	0.91	1.10	1.37	1.10	0.40	0.52	26.00	0.43	0.14	1.68
N15	0.91	1.00	1.40	0.85	0.40	0.39	9.33	0.72	0.16	1.45
N15b	0.91	1.27	1.66	1.10	0.40	0.49	8.67	0.82	0.17	1.50
N16	0.91	0.83	1.29	0.60	0.40	0.34	11.33	0.57	0.15	1.86
N17	0.91	1.02	1.46	0.80	0.40	0.39	12.00	0.68	0.16	1.86
N20	0.91	0.87	1.37	0.70	0.40	0.37	17.33	0.56	0.15	2.77
N21	0.91	0.88	1.46	0.65	0.40	0.38	24.00	0.51	0.14	3.32
N22	0.91	1.00	1.46	0.75	0.40	0.38	14.67	0.58	0.15	2.64
N23	0.91	0.68	1.31	0.55	0.40	0.30	20.67	0.40	0.11	2.86
N24	0.91	0.80	1.26	0.65	0.40	0.31	13.33	0.55	0.14	1.86
N25	0.91	0.82	1.29	0.65	0.40	0.32	12.67	0.56	0.16	1.73
N25b	0.91	0.70	1.29	0.55	0.40	0.32	23.33	0.44	0.12	3.23
N27	0.91	0.95	1.40	0.80	0.40	0.35	10.67	0.63	0.15	1.64
N28	0.91	0.97	1.63	0.75	0.40	0.42	14.67	0.60	0.16	1.95
N29	0.91	0.70	1.31	0.55	0.40	0.30	20.00	0.43	0.12	3.05
N30	0.91	0.62	1.20	0.50	0.40	0.27	17.33	0.38	0.12	2.41
N30b	0.91	0.77	1.31	0.55	0.40	0.31	20.67	0.43	0.11	2.91
N32	0.91	1.02	1.63	0.85	0.40	0.39	20.67	0.57	0.18	3.05
N34	0.91	0.92	1.74	0.75	0.40	0.59	8.67	0.63	0.20	1.32
N35	1.18	1.30	1.57	1.25	0.40	0.54	12.67	0.71	0.13	1.45
N35B	0.91	1.20	1.60	1.00	0.40	0.51	12.00	0.66	0.15	1.18
N36	1.18	1.13	1.49	0.80	0.40	0.59	7.33	1.20	0.12	1.05
N37	0.91	1.03	1.46	0.90	0.40	0.41	16.00	0.69	0.15	1.64
N38	1.36	1.70	2.86	1.10	0.52	0.51	25.33	1.29	0.18	1.09
N39	0.91	0.83	1.31	0.50	0.40	0.30	18.67	0.61	0.14	1.50
N42	0.91	0.65	1.11	0.55	0.40	0.31	14.00	0.54	0.15	1.77
N43	0.91	0.98	1.94	0.70	0.40	0.45	32.00	0.96	0.14	1.14
N46	0.91	0.63	1.11	0.50	0.40	0.28	14.67	0.46	0.13	1.77
N47	0.91	1.05	2.06	0.60	0.40	0.70	62.67	1.22	0.19	0.73
N48	0.91	0.87	1.31	0.85	0.40	0.37	11.33	0.50	0.12	1.50
N50	0.91	1.30	1.54	1.40	0.40	0.73	11.33	0.73	0.17	1.32
N50b	0.91	1.12	1.43	1.00	0.40	0.63	9.33	0.63	0.19	1.14
N51	1.27	1.60	1.71	1.50	0.76	0.73	10.67	0.85	0.15	1.50
N53	0.91	0.62	0.97	0.55	0.40	0.30	10.67	0.49	0.15	1.23
N54	0.91	0.40	0.89	0.50	0.40	0.23	14.67	0.40	0.14	1.77
N55	0.91	0.58	0.83	0.55	0.40	0.32	11.33	0.40	0.12	1.32
N55b	0.91	0.48	0.80	0.50	0.40	0.27	14.67	0.28	0.08	1.68

Appendix 9 continued

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y
N56	1.00	1.28	1.77	1.50	0.44	0.72	35.33	1.00	0.17	0.95
N57	0.91	1.23	1.37	0.95	0.40	0.61	6.67	0.72	0.31	1.23
N58	0.91	0.78	1.00	0.75	0.40	0.54	7.33	0.60	0.17	1.05
N59	0.91	1.35	1.69	1.45	1.16	1.08	10.67	1.10	0.11	0.91
N60	0.91	0.70	1.09	0.60	0.40	0.31	7.33	0.68	0.32	1.50
N62	0.91	0.55	0.94	0.50	0.40	0.25	11.33	0.50	0.19	1.68
Min	0.91	0.40	0.80	0.50	0.40	0.23	6.67	0.28	0.08	0.73
Max	1.36	1.70	2.86	1.50	1.16	1.08	62.67	1.32	0.36	3.32
Mean	0.95	0.96	1.46	0.80	0.43	0.43	16.19	0.67	0.16	1.71
	Zr	**Nb**	**Mo**	**Ba**	**La**	**Ce**	**Pb**	**Th**	**U**	
N3	7.07	1.08	6.67	0.74	1.60	1.45	1.55	2.06	3.57	
N5	8.67	0.84	6.67	1.54	0.87	1.30	2.65	1.87	3.57	
N7	2.51	0.60	6.67	1.43	1.50	1.25	1.35	1.31	3.57	
N8	4.37	0.96	6.67	0.93	2.07	1.64	1.55	1.96	3.57	
N9	2.66	0.72	6.67	1.05	1.20	1.05	1.35	1.59	3.57	
N10	7.19	0.96	6.67	0.84	1.03	1.16	1.40	1.68	3.57	
N12	17.13	1.52	6.67	0.75	1.67	1.44	1.45	2.71	3.57	
N14	4.17	0.84	6.67	0.72	1.73	1.11	1.40	1.50	3.57	
N15	5.78	0.92	6.67	0.98	1.17	1.28	1.50	1.78	3.57	
N15b	4.04	0.92	6.67	1.05	1.57	1.31	1.45	1.68	3.57	
N16	10.78	1.04	6.67	0.84	1.13	1.22	1.45	2.24	3.57	
N17	8.85	1.12	6.67	0.97	1.37	1.34	1.60	2.06	3.57	
N20	16.49	1.16	6.67	0.81	1.90	1.56	1.55	3.08	3.57	
N21	21.86	1.32	6.67	0.70	2.13	1.77	1.55	3.83	3.57	
N22	14.33	1.20	6.67	0.78	1.60	1.45	1.40	2.90	3.57	
N23	23.34	1.20	6.67	0.59	1.67	1.47	1.35	3.55	3.57	
N24	10.58	0.96	6.67	0.77	1.23	1.31	1.35	2.24	3.57	
N25	9.89	0.96	6.67	0.82	1.17	1.13	1.50	1.96	3.57	
N25b	24.51	1.24	6.67	0.67	1.77	1.63	1.35	4.21	3.57	
N27	7.72	0.92	6.67	0.87	1.17	1.13	1.45	1.87	3.57	
N28	12.47	1.00	6.67	0.85	1.43	1.44	1.55	2.43	3.57	
N29	22.45	1.24	6.67	0.65	1.70	1.48	1.35	3.64	3.57	
N30	17.13	1.08	6.67	0.65	1.17	1.14	1.30	2.80	3.57	
N30b	22.74	1.24	6.67	0.63	1.83	1.55	1.40	3.64	3.57	
N32	19.76	1.24	6.67	0.83	2.23	1.80	1.60	3.64	3.57	

Appendix 9 continued

Sample	Zr	Nb	Mo	Ba	La	Ce	Pb	Th	U
N34	4.67	0.80	6.67	0.87	1.23	1.11	1.30	1.50	3.57
N35	2.96	0.80	6.67	0.81	1.83	1.20	1.35	1.59	3.57
N35B	3.21	0.84	6.67	0.87	1.40	1.14	1.25	1.40	3.57
N36	1.95	0.68	6.67	1.12	0.93	0.95	1.20	1.50	3.57
N37	7.09	0.92	6.67	0.92	1.37	1.30	1.50	1.87	3.57
N38	5.02	0.92	6.67	1.23	1.30	1.08	1.70	1.78	3.57
N39	9.99	1.04	6.67	0.79	1.17	1.19	1.45	1.78	3.57
N42	11.05	1.08	6.67	0.79	1.03	1.13	1.40	1.96	3.57
N43	7.07	0.76	6.67	0.68	0.83	0.88	1.30	1.59	3.57
N46	11.08	0.92	6.67	0.68	0.80	1.05	1.40	2.15	3.57
N47	3.14	0.80	6.67	0.69	1.23	1.08	1.70	1.40	3.57
N48	6.49	1.00	6.67	0.54	1.03	1.20	1.30	1.50	3.57
N50	2.92	0.76	6.67	1.18	1.40	1.17	1.35	1.40	3.57
N50b	3.64	0.76	6.67	0.93	1.20	0.98	1.10	1.21	3.57
N51	3.46	0.88	6.67	1.07	1.70	1.30	1.30	1.50	3.57
N53	6.05	0.84	6.67	0.72	0.77	0.92	1.15	1.40	3.57
N54	11.22	0.92	6.67	0.57	0.87	0.94	1.10	1.78	3.57
N55	5.19	0.80	6.67	0.65	0.83	0.88	1.15	1.21	3.57
N55b	9.24	0.88	6.67	0.41	0.77	0.84	1.05	1.50	3.57
N56	2.04	0.60	6.67	1.22	1.37	1.22	1.30	1.12	3.57
N57	4.00	0.76	6.67	1.53	1.40	1.28	1.40	1.40	3.57
N58	3.39	0.68	6.67	0.74	0.83	0.91	1.20	1.12	3.57
N59	1.37	0.68	6.67	0.92	1.13	0.89	1.05	1.21	3.57
N60	7.49	0.92	6.67	1.43	1.13	1.20	1.85	1.78	3.57
N62	10.71	0.88	6.67	0.90	0.90	1.06	1.65	1.96	3.57
Min	1.37	0.60	6.67	0.41	0.77	0.84	1.05	1.12	3.57
Max	24.51	1.52	6.67	1.54	2.23	1.80	2.65	4.21	3.57
Mean	9.02	0.94	6.67	0.87	1.33	1.23	1.42	2.02	3.57

Appendix 10 Indices of geoaccumulation, I_{geo} for trace elements in soils and sediments from Birnin-Gwari area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y
N3	-0.58	-0.19	0.12	-0.91	-1.91	-1.93	3.08	-1.39	-3.31	0.08
N5	-0.72	-1	-0.58	-1.58	-1.91	-1.88	2.74	-0.92	-2.05	-0.09
N7	-0.46	-0.08	0.81	-0.66	-1.91	-1.83	4.26	-0.18	-2.71	-0.65
N8	-0.46	-0.05	0.39	-0.1	-1.06	-1.49	3.08	-0.81	-3.34	0.17
N9	-0.34	-0.17	0.55	-1	-1.91	-2.03	4.04	-0.36	-3.13	-0.87
N10	-0.72	-0.88	-0.22	-1.1	-1.91	-2.15	2.92	-1.35	-3.34	0
N12	-0.72	-0.91	-0.13	-1.21	-1.91	-2.15	3.35	-1.46	-3.48	0.68
N14	-0.72	-0.45	-0.13	-0.45	-1.91	-1.53	4.12	-1.81	-3.42	0.17
N15	-0.72	-0.58	-0.1	-0.82	-1.91	-1.93	2.64	-1.05	-3.2	-0.04
N15b	-0.72	-0.24	0.14	-0.45	-1.91	-1.61	2.53	-0.87	-3.15	0
N16	-0.72	-0.85	-0.22	-1.32	-1.91	-2.15	2.92	-1.39	-3.36	0.31
N17	-0.72	-0.56	-0.04	-0.91	-1.91	-1.93	3	-1.14	-3.23	0.31
N20	-0.72	-0.79	-0.13	-1.1	-1.91	-2.03	3.53	-1.42	-3.36	0.89
N21	-0.72	-0.76	-0.04	-1.21	-1.91	-1.98	4	-1.56	-3.45	1.15
N22	-0.72	-0.58	-0.04	-1	-1.91	-1.98	3.29	-1.37	-3.36	0.81
N23	-0.72	-1.13	-0.19	-1.45	-1.91	-2.34	3.78	-1.9	-3.75	0.93
N24	-0.72	-0.91	-0.25	-1.21	-1.91	-2.28	3.15	-1.44	-3.42	0.31
N25	-0.72	-0.88	-0.22	-1.21	-1.91	-2.21	3.08	-1.42	-3.25	0.2
N25b	-0.72	-1.1	-0.22	-1.45	-1.91	-2.21	3.96	-1.78	-3.61	1.11
N27	-0.72	-0.66	-0.1	-0.91	-1.91	-2.09	2.83	-1.26	-3.28	0.13
N28	-0.72	-0.63	0.12	-1	-1.91	-1.83	3.29	-1.33	-3.23	0.38
N29	-0.72	-1.1	-0.19	-1.45	-1.91	-2.34	3.74	-1.81	-3.64	1.02
N30	-0.72	-1.28	-0.32	-1.58	-1.91	-2.49	3.53	-1.97	-3.61	0.68
N30b	-0.72	-0.97	-0.19	-1.45	-1.91	-2.28	3.78	-1.81	-3.71	0.96
N32	-0.72	-0.56	0.12	-0.82	-1.91	-1.93	3.78	-1.39	-3.06	1.02
N34	-0.72	-0.71	0.22	-1	-1.91	-1.34	2.53	-1.26	-2.93	-0.19
N35	-0.34	-0.21	0.07	-0.26	-1.91	-1.49	3.08	-1.09	-3.54	-0.04
N35B	-0.72	-0.32	0.09	-0.58	-1.91	-1.56	3	-1.18	-3.31	-0.34
N36	-0.34	-0.4	-0.01	-0.91	-1.91	-1.34	2.29	-0.33	-3.68	-0.52
N37	-0.72	-0.54	-0.04	-0.74	-1.91	-1.88	3.42	-1.13	-3.31	0.13
N38	-0.14	0.18	0.93	-0.45	-1.53	-1.56	4.08	-0.22	-3.06	-0.46
N39	-0.72	-0.85	-0.19	-1.58	-1.91	-2.34	3.64	-1.3	-3.45	0
N42	-0.72	-1.21	-0.43	-1.45	-1.91	-2.28	3.22	-1.49	-3.34	0.24
N43	-0.72	-0.61	0.37	-1.1	-1.91	-1.73	4.42	-0.64	-3.45	-0.4
N46	-0.72	-1.24	-0.43	-1.58	-1.91	-2.41	3.29	-1.72	-3.51	0.24
N47	-0.72	-0.51	0.46	-1.32	-1.91	-1.09	5.38	-0.29	-3.01	-1.04
N48	-0.72	-0.79	-0.19	-0.82	-1.91	-2.03	2.92	-1.58	-3.61	0
N50	-0.72	-0.21	0.04	-0.1	-1.91	-1.03	2.92	-1.03	-3.13	-0.19
N50b	-0.72	-0.43	-0.07	-0.58	-1.91	-1.24	2.64	-1.26	-3.01	-0.4
N51	-0.24	0.09	0.19	0	-0.98	-1.03	2.83	-0.82	-3.36	0
N53	-0.72	-1.28	-0.63	-1.45	-1.91	-2.34	2.83	-1.61	-3.34	-0.29
N54	-0.72	-1.91	-0.76	-1.58	-1.91	-2.73	3.29	-1.9	-3.42	0.24
N55	-0.72	-1.36	-0.86	-1.45	-1.91	-2.21	2.92	-1.9	-3.61	-0.19
N55b	-0.72	-1.63	-0.91	-1.58	-1.91	-2.49	3.29	-2.44	-4.18	0.17

Appendix 10 continued

Sample	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Y
N56	-0.58	-0.23	0.24	0	-1.77	-1.06	4.56	-0.58	-3.15	-0.65
N57	-0.72	-0.28	-0.13	-0.66	-1.91	-1.31	2.15	-1.05	-2.25	-0.29
N58	-0.72	-0.94	-0.58	-1	-1.91	-1.49	2.29	-1.33	-3.13	-0.52
N59	-0.72	-0.15	0.17	-0.05	-0.37	-0.47	2.83	-0.45	-3.75	-0.72
N60	-0.72	-1.1	-0.47	-1.32	-1.91	-2.28	2.29	-1.14	-2.22	0
N62	-0.72	-1.45	-0.67	-1.58	-1.91	-2.56	2.92	-1.58	-2.97	0.17
Min	-0.72	-1.91	-0.91	-1.58	-1.91	-2.73	2.15	-2.44	-4.18	-1.04
Max	-0.14	0.18	0.93	0	-0.37	-0.47	5.38	-0.18	-2.05	1.15
Mean	-0.66	-0.71	-0.09	-0.99	-1.83	-1.88	3.27	-1.25	-3.28	0.09

	Zr	Nb	Mo	Ba	La	Ce	Pb	Th	U
N3	2.24	-0.47	2.15	-1.02	0.09	-0.05	0.05	0.45	1.25
N5	2.53	-0.84	2.15	0.04	-0.79	-0.21	0.82	0.32	1.25
N7	0.74	-1.32	2.15	-0.07	0	-0.26	-0.15	-0.2	1.25
N8	1.54	-0.64	2.15	-0.7	0.46	0.13	0.05	0.39	1.25
N9	0.83	-1.06	2.15	-0.51	-0.32	-0.52	-0.15	0.08	1.25
N10	2.26	-0.64	2.15	-0.83	-0.54	-0.38	-0.1	0.17	1.25
N12	3.51	0.02	2.15	-0.99	0.15	-0.06	-0.05	0.85	1.25
N14	1.47	-0.84	2.15	-1.05	0.21	-0.44	-0.1	0	1.25
N15	1.95	-0.71	2.15	-0.61	-0.36	-0.23	0	0.24	1.25
N15b	1.43	-0.71	2.15	-0.51	0.06	-0.19	-0.05	0.17	1.25
N16	2.85	-0.53	2.15	-0.84	-0.4	-0.3	-0.05	0.58	1.25
N17	2.56	-0.42	2.15	-0.63	-0.13	-0.16	0.09	0.45	1.25
N20	3.46	-0.37	2.15	-0.88	0.34	0.06	0.05	1.04	1.25
N21	3.87	-0.18	2.15	-1.11	0.51	0.24	0.05	1.35	1.25
N22	3.26	-0.32	2.15	-0.94	0.09	-0.05	-0.1	0.95	1.25
N23	3.96	-0.32	2.15	-1.34	0.15	-0.03	-0.15	1.24	1.25
N24	2.82	-0.64	2.15	-0.96	-0.28	-0.19	-0.15	0.58	1.25
N25	2.72	-0.64	2.15	-0.87	-0.36	-0.42	0	0.39	1.25
N25b	4.03	-0.27	2.15	-1.17	0.24	0.12	-0.15	1.49	1.25
N27	2.36	-0.71	2.15	-0.78	-0.36	-0.42	-0.05	0.32	1.25
N28	3.06	-0.58	2.15	-0.82	-0.07	-0.06	0.05	0.7	1.25
N29	3.9	-0.27	2.15	-1.22	0.18	-0.02	-0.15	1.28	1.25
N30	3.51	-0.47	2.15	-1.21	-0.36	-0.4	-0.21	0.9	1.25
N30b	3.92	-0.27	2.15	-1.26	0.29	0.04	-0.1	1.28	1.25
N32	3.72	-0.27	2.15	-0.86	0.57	0.26	0.09	1.28	1.25

Appendix 10 continued

Sample	Zr	Nb	Mo	Ba	La	Ce	Pb	Th	U
N34	1.64	-0.91	2.15	-0.79	-0.28	-0.44	-0.21	0	1.25
N35	0.98	-0.91	2.15	-0.88	0.29	-0.32	-0.15	0.08	1.25
N35B	1.1	-0.84	2.15	-0.79	-0.1	-0.4	-0.26	-0.1	1.25
N36	0.38	-1.14	2.15	-0.43	-0.68	-0.65	-0.32	0	1.25
N37	2.24	-0.71	2.15	-0.71	-0.13	-0.21	0	0.32	1.25
N38	1.74	-0.71	2.15	-0.29	-0.21	-0.48	0.18	0.24	1.25
N39	2.74	-0.53	2.15	-0.93	-0.36	-0.34	-0.05	0.24	1.25
N42	2.88	-0.47	2.15	-0.92	-0.54	-0.42	-0.1	0.39	1.25
N43	2.24	-0.98	2.15	-1.14	-0.85	-0.78	-0.21	0.08	1.25
N46	2.89	-0.71	2.15	-1.14	-0.91	-0.52	-0.1	0.52	1.25
N47	1.06	-0.91	2.15	-1.12	-0.28	-0.48	0.18	-0.1	1.25
N48	2.11	-0.58	2.15	-1.48	-0.54	-0.32	-0.21	0	1.25
N50	0.96	-0.98	2.15	-0.35	-0.1	-0.36	-0.15	-0.1	1.25
N50b	1.28	-0.98	2.15	-0.69	-0.32	-0.61	-0.45	-0.3	1.25
N51	1.21	-0.77	2.15	-0.49	0.18	-0.21	-0.21	0	1.25
N53	2.01	-0.84	2.15	-1.05	-0.97	-0.7	-0.38	-0.1	1.25
N54	2.9	-0.71	2.15	-1.39	-0.79	-0.68	-0.45	0.24	1.25
N55	1.79	-0.91	2.15	-1.2	-0.85	-0.78	-0.38	-0.3	1.25
N55b	2.62	-0.77	2.15	-1.88	-0.97	-0.83	-0.51	0	1.25
N56	0.45	-1.32	2.15	-0.3	-0.13	-0.3	-0.21	-0.42	1.25
N57	1.42	-0.98	2.15	0.03	-0.1	-0.23	-0.1	-0.1	1.25
N58	1.18	-1.14	2.15	-1.03	-0.85	-0.73	-0.32	-0.42	1.25
N59	-0.13	-1.14	2.15	-0.71	-0.4	-0.75	-0.51	-0.3	1.25
N60	2.32	-0.71	2.15	-0.07	-0.4	-0.32	0.3	0.24	1.25
N62	2.84	-0.77	2.15	-0.74	-0.74	-0.5	0.14	0.39	1.25
Min	-0.13	-1.32	2.15	-1.88	-0.97	-0.83	-0.51	-0.42	1.25
Max	4.03	0.02	2.15	0.04	0.57	0.26	0.82	1.49	1.25
Mean	2.23	-0.7	2.15	-0.83	-0.23	-0.32	-0.1	0.34	1.25

Appendix 11 Geochemical partitioning (µg/g) of selected trace elements in soils and sediments from Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	Arsenic					Chromium				
Sample	Ex	Carb	Oxide	Sum	% Recov	Ex	Carb	Oxide	Sum	% Recov
A1	0.06	2.14	3.46	5.67	113.33	0.01	0.14	1.04	1.20	3.52
A2	bdl	2.42	2.31	4.72	39.37	0.02	0.06	0.41	0.49	1.17
A4	bdl	2.40	3.37	5.77	115.34	0.02	0.08	1.10	1.21	2.74
A5	bdl	2.31	3.87	6.18	123.51	0.03	0.11	0.77	0.91	1.90
A6	0.04	2.31	3.57	5.92	118.45	bdl	0.40	11.04	11.44	20.80
A7	bdl	2.14	3.28	5.42	108.39	0.03	0.13	2.72	2.88	6.40
A8	bdl	2.11	3.07	5.19	103.75	bdl	0.07	1.05	1.12	2.49
A10	0.07	2.64	3.57	6.28	125.57	0.02	0.05	0.32	0.39	1.08
B1	bdl	3.01	6.70	9.71	194.26	0.02	0.58	11.14	11.74	15.05
B2	bdl	2.98	6.04	9.02	27.34	0.02	0.36	6.73	7.11	7.90
B3	bdl	7.18	11.69	18.87	3.54	0.02	0.53	6.00	6.56	3.73
B4	0.06	3.01	5.44	8.51	9.57	bdl	0.38	4.17	4.55	2.86
B5	bdl	2.41	3.63	6.03	43.09	0.02	0.08	0.73	0.83	0.60
B7	bdl	2.87	3.14	6.01	120.24	0.03	0.21	1.09	1.33	0.75
D1	0.12	2.38	4.51	7.01	140.28	bdl	0.12	1.07	1.19	1.37
D2	bdl	2.08	3.53	5.61	112.23	bdl	0.12	1.57	1.69	1.69
D4	bdl	2.31	2.68	4.99	99.75	0.02	0.05	0.51	0.57	1.69
D5	bdl	2.43	3.85	6.28	125.67	0.02	0.07	0.56	0.66	0.85
D7	bdl	2.49	4.13	6.62	132.39	bdl	0.12	3.58	3.70	8.61
D9	bdl	2.28	2.97	5.25	104.94	0.02	0.10	0.82	0.95	1.90
TD6	0.25	3.96	5.98	10.19	203.83	0.03	0.15	0.35	0.52	1.64
TD10	bdl	2.50	3.31	5.81	58.12	bdl	0.06	0.33	0.38	1.07
TS3	bdl	2.41	3.47	5.87	48.95	0.02	0.05	0.36	0.43	0.63
TS4	bdl	2.68	4.17	6.86	137.13	0.02	0.08	1.03	1.13	1.74
TS5	bdl	2.39	3.27	5.66	43.55	0.03	0.06	0.45	0.54	0.93
Min	0.04	2.08	2.31	4.72	3.54	0.01	0.05	0.32	0.38	0.60
Max	0.25	7.18	11.69	18.87	203.83	0.03	0.58	11.14	11.74	20.80
Mean	0.12	2.81	4.42	7.26	97.13	0.02	0.17	2.23	2.41	3.15

Appendix 11 continued

Sample	Copper					Manganese				
	Ex	Carb	Oxide	Sum	% Recov	Ex	Carb	Oxide	Sum	% Recov
A1	2.58	20.63	193.46	216.66	6.02	30.09	30.51	640.45	701.05	35.05
A2	0.14	0.47	0.90	1.50	29.98	11.89	1.97	13.55	27.41	9.14
A4	0.79	33.07	39.95	73.81	14.76	3.87	13.07	146.92	163.86	23.41
A5	0.74	6.51	8.04	15.29	31.20	30.75	10.45	50.11	91.30	18.26
A6	2.28	172.96	175.45	350.69	19.48	39.31	41.63	228.82	309.76	38.72
A7	0.19	11.98	33.89	46.06	11.51	10.11	9.57	265.00	284.68	40.67
A8	0.16	6.59	15.61	22.37	11.18	8.69	6.57	40.10	55.35	9.23
A10	0.26	0.45	0.40	1.11	22.19	4.44	27.62	81.73	113.79	22.76
B1	0.55	167.13	160.19	327.87	11.31	0.97	10.35	85.12	96.44	13.78
B2	0.48	73.30	99.22	173.01	12.36	3.84	19.92	92.94	116.70	19.45
B3	1.06	146.57	120.84	268.46	20.65	6.22	47.73	236.14	290.09	32.23
B4	1.11	10.79	9.41	21.31	12.18	150.74	31.35	63.49	245.58	27.29
B5	0.13	0.38	0.83	1.34	13.35	15.28	6.40	48.96	70.65	5.89
B7	0.48	0.95	1.80	3.22	7.86	3.28	66.21	402.09	471.59	33.68
D1	0.34	6.50	95.46	102.30	22.19	5.89	4.30	353.36	363.55	45.44
D2	0.22	6.13	66.48	72.83	17.55	4.55	5.99	214.23	224.77	20.43
D4	0.06	1.04	4.83	5.93	118.58	3.32	3.31	61.74	68.37	17.09
D5	0.12	0.68	2.75	3.55	16.90	8.27	10.43	78.26	96.95	12.12
D7	0.41	34.06	125.82	160.30	6.97	2.58	14.31	314.84	331.73	41.47
D9	0.08	1.69	4.87	6.63	47.39	8.27	9.62	165.69	183.58	36.72
TD6	0.84	4.47	3.95	9.26	9.26	1.52	73.01	242.89	317.42	35.27
TD10	0.21	0.35	0.36	0.92	18.47	7.07	31.33	54.31	92.70	23.18
TS3	0.09	0.17	0.40	0.66	13.22	6.31	7.84	18.49	32.64	10.88
TS4	0.97	13.11	34.87	48.95	3.26	3.84	27.00	194.41	225.25	37.54
TS5	0.15	0.24	0.44	0.82	16.45	15.60	18.24	38.82	72.66	18.16
Min	0.06	0.17	0.36	0.66	3.26	0.97	1.97	13.55	27.41	5.89
Max	2.58	172.96	193.46	350.69	118.58	150.74	73.01	640.45	701.05	45.44
Mean	0.39	24.33	39.12	63.84	20.64	13.54	21.55	152.63	187.72	25.16

Appendix 11 continued

Sample	Nickel					Lead				
	Ex	Carb	Oxide	Sum	% Recov	Ex	Carb	Oxide	Sum	% Recov
A1	0.48	0.25	1.64	2.36	3.28	291	941	3418	4649	8
A2	0.35	0.17	0.09	0.60	3.56	22	56	71	150	40
A4	0.32	0.41	0.70	1.43	3.98	47	7666	978	8691	36
A5	0.45	0.29	0.24	0.98	3.65	77	238	323	638	32
A6	0.40	0.70	3.24	4.35	10.87	208	19739	2990	22937	30
A7	0.32	0.34	1.09	1.74	3.35	32	1510	886	2428	24
A8	0.27	0.26	0.32	0.85	5.65	9	937	795	1741	20
A10	0.19	0.40	0.69	1.28	9.83	1	101	51	153	47
B1	0.40	1.01	2.70	4.11	6.14	123	5663	3748	9534	8
B2	0.39	0.86	2.01	3.26	5.44	105	2905	2951	5961	10
B3	0.32	1.66	3.22	5.19	5.76	9	11271	2652	13931	49
B4	1.35	1.36	1.62	4.33	5.70	41	215	203	459	34
B5	0.44	0.35	0.43	1.23	3.41	6	64	78	148	37
B7	0.30	0.93	2.66	3.89	5.64	0	818	217	1035	37
D1	0.33	0.24	0.69	1.25	3.69	108	424	518	1050	28
D2	0.30	0.23	0.57	1.10	3.65	348	4336	752	5436	45
D4	0.30	0.21	0.25	0.76	15.11	4	262	264	530	43
D5	0.23	0.44	1.21	1.88	5.86	2	705	313	1019	39
D7	0.29	0.30	0.90	1.50	4.54	353	17512	2049	19914	52
D9	0.31	0.35	0.77	1.44	7.97	2	366	182	550	64
TD6	0.21	0.48	0.58	1.27	6.07	2	9528	635	10164	65
TD10	0.20	0.34	0.59	1.13	11.31	1	191	60	251	51
TS3	0.23	0.33	0.34	0.89	7.43	1	100	60	161	45
TS4	0.20	0.71	1.51	2.41	6.70	1	13680	1953	15634	32
TS5	0.27	0.46	0.41	1.14	8.79	0	70	59	129	40
Min	0.19	0.17	0.09	0.60	3.28	0	56	51	129	8
Max	1.35	1.66	3.24	5.19	15.11	353	19739	3748	22937	65
Mean	0.34	0.56	1.13	2.03	6.60	57	3533	921	4511	38

Appendix 11 continued

Sample	**Zinc**				
	Ex	Carb	Oxide	Sum	% Recov
A1	0.91	0.76	3.93	5.60	5
A2	0.68	0.28	0.52	1.48	5
A4	2.89	11.74	13.08	27.71	29
A5	1.00	0.43	1.41	2.84	9
A6	0.56	1.29	2.61	4.45	8
A7	0.66	0.90	1.75	3.31	4
A8	0.42	0.48	0.77	1.68	6
A10	0.47	18.24	28.21	46.92	59
B1	0.64	5.01	8.86	14.51	7
B2	0.48	2.46	5.92	8.87	4
B3	0.39	17.98	37.89	56.26	23
B4	2.30	1.46	4.65	8.40	13
B5	0.99	0.46	1.29	2.74	7
B7	0.39	113.23	151.74	265.36	74
D1	0.69	0.42	1.54	2.65	4
D2	0.74	0.87	2.06	3.67	7
D4	0.41	0.44	0.54	1.39	9
D5	0.33	1.49	2.31	4.13	9
D7	0.51	0.65	1.54	2.70	5
D9	0.40	0.53	0.87	1.79	8
TD6	0.40	98.84	100.86	200.10	51
TD10	0.48	16.57	21.22	38.27	50
TS3	0.69	2.93	3.59	7.22	23
TS4	0.37	31.97	65.56	97.90	32
TS5	1.18	10.05	6.92	18.15	40
Min	0.33	0.28	0.52	1.39	4
Max	2.89	113.23	151.74	265.36	74
Mean	0.65	16.25	22.40	39.30	22

Appendix 12 Geochemical partitioning (µg/g) of selected trace elements in soils and sediments of Birnin-Gwari area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

	Arsenic					Chromium				
	Ex	Carb	Oxide	Sum	%Recov	Ex	Carb	Oxide	Sum	%Recov
N3	bdl	3.59	3.72	7.32	38.50	0.02	0.16	0.64	0.82	1.44
N5	bdl	3.33	4.47	7.80	51.97	bdl	0.13	0.56	0.69	1.98
N7	bdl	3.23	4.85	8.08	18.79	bdl	0.11	0.37	0.49	0.53
N8	0.07	3.52	4.44	8.03	42.24	bdl	0.13	0.65	0.79	1.14
N10	bdl	3.37	4.78	8.15	47.92	bdl	0.12	0.39	0.51	1.12
N25	bdl	3.46	4.76	8.21	43.23	0.02	0.17	0.52	0.71	1.57
N28	bdl	3.32	4.34	7.65	34.79	bdl	0.11	0.36	0.48	0.83
N37	0.14	3.57	3.81	7.52	31.34	0.03	0.17	0.51	0.72	1.40
N38	bdl	3.32	4.37	7.69	20.25	bdl	0.12	0.35	0.47	0.47
N46	bdl	3.32	4.47	7.79	35.43	bdl	0.11	0.32	0.42	1.08
N47	bdl	3.25	4.34	7.59	8.07	0.01	0.09	0.18	0.28	0.39
N50	bdl	3.19	4.66	7.85	46.15	0.02	0.12	0.54	0.68	1.25
N57	bdl	3.18	4.06	7.24	72.36	bdl	0.10	0.24	0.34	0.70
N59	bdl	3.29	4.19	7.48	46.77	bdl	0.09	0.22	0.30	0.52
Min	0.07	3.18	3.72	6.97	8.07	0.01	0.09	0.18	0.28	0.39
Max	0.14	3.59	4.85	8.58	72.36	0.03	0.17	0.65	0.86	1.98
Mean	0.10	3.35	4.37	7.83	38.42	0.02	0.12	0.42	0.56	1.03

Appendix 12 continued

Sample	Copper					Manganese				
	Ex	Carb	Oxide	Sum	%Recov	Ex	Carb	Oxide	Sum	%Recov
N3	0.04	0.34	0.25	0.63	12.60	39.45	25.98	251.49	316.92	1.69
N5	0.03	0.20	0.15	0.38	7.60	108.21	33.06	277.27	418.54	46.50
N7	0.04	0.63	0.85	1.53	30.68	5.04	4.32	64.96	74.32	24.77
N8	0.04	0.55	1.21	1.80	10.00	313.49	65.70	133.59	512.78	15.54
N10	0.03	0.22	0.38	0.63	12.68	35.16	19.34	201.32	255.82	31.98
N25	0.03	0.37	0.43	0.83	16.54	1.26	18.91	171.26	191.43	27.35
N28	0.04	0.15	0.17	0.36	7.15	33.99	25.45	199.56	258.99	28.78
N37	0.04	0.54	0.88	1.46	29.22	27.86	11.04	643.54	682.44	45.50
N38	0.04	0.52	0.40	0.95	7.33	23.92	13.81	241.46	279.19	34.90
N46	0.03	0.19	0.27	0.49	9.76	9.45	7.87	58.08	75.39	15.08
N47	0.04	0.12	0.12	0.28	5.52	8.23	9.52	36.10	53.85	7.69
N50	0.04	0.16	0.30	0.49	9.89	46.95	98.26	209.94	355.15	7.72
N57	0.04	0.11	0.14	0.29	5.73	36.43	94.59	171.66	302.68	7.76
N59	0.03	0.13	0.27	0.43	1.50	18.28	32.74	161.39	212.41	6.25
Min	0.03	0.11	0.12	0.26	1.50	1.26	4.32	36.10	53.85	6.25
Max	0.04	0.63	1.21	1.89	30.68	313.49	98.26	643.54	682.44	46.50
Mean	0.04	0.30	0.42	0.75	11.87	50.55	32.90	201.54	284.99	23.68

Appendix 12 continued

Sample	Nickel					Lead				
	Ex	Carb	Oxide	Sum	%Recov	Ex	Carb	Oxide	Sum	%Recov
N3	0.31	0.27	0.16	0.74	4.62	0.07	0.82	2.85	3.75	12.08
N5	0.31	0.28	0.16	0.74	7.41	Bdl	2.47	7.59	10.06	18.98
N7	0.30	0.17	0.29	0.76	3.98	Bdl	0.96	1.48	2.44	9.03
N8	0.41	0.43	1.07	1.91	6.84	0.05	0.39	4.67	5.12	16.50
N10	0.30	0.32	0.26	0.88	6.29	Bdl	0.52	2.32	2.84	10.14
N25	0.21	0.35	0.19	0.75	5.77	Bdl	1.69	2.85	4.54	15.13
N28	0.23	0.34	0.36	0.92	6.14	Bdl	0.70	2.58	3.29	10.60
N37	0.33	0.23	0.36	0.93	5.14	Bdl	0.61	4.00	4.61	15.35
N38	0.26	0.23	0.24	0.74	3.36	Bdl	2.96	3.45	6.41	18.84
N46	0.25	0.27	0.06	0.58	5.80	Bdl	0.72	1.89	2.61	9.33
N47	0.25	0.32	0.13	0.70	5.81	Bdl	0.32	1.57	1.89	5.57
N50	0.21	0.39	1.42	2.02	7.22	Bdl	0.20	2.38	2.58	9.55
N57	0.18	0.21	0.77	1.17	6.14	Bdl	0.35	2.06	2.42	8.63
N59	0.21	0.22	1.06	1.50	5.16	Bdl	0.23	2.31	2.54	12.10
Min	0.18	0.17	0.06	0.42	3.36	0.05	0.20	1.48	1.73	5.57
Max	0.41	0.43	1.42	2.26	7.41	0.07	2.96	7.59	10.62	18.98
Mean	0.27	0.29	0.47	1.02	5.69	0.06	0.92	3.00	3.99	12.27

Appendix 12 continued

Sample	**Zinc**				
	Ex	Carb	Oxide	Sum	%Recov
N3	0.65	1.83	0.97	3.45	12.33
N5	0.65	1.20	1.27	3.13	10.79
N7	0.65	1.08	1.05	2.78	9.25
N8	0.43	0.94	1.31	2.68	7.05
N10	0.40	1.02	0.82	2.25	9.38
N25	0.23	1.08	0.84	2.15	9.34
N28	0.51	1.54	1.65	3.70	12.32
N37	0.84	0.76	1.14	2.73	9.43
N38	0.74	1.39	1.85	3.98	11.06
N46	0.41	0.69	0.71	1.82	9.08
N47	0.43	0.89	0.97	2.30	4.59
N50	0.29	1.31	3.81	5.41	10.40
N57	0.32	1.05	2.82	4.19	9.75
N59	0.46	1.24	3.44	5.14	6.67
Min	0.23	0.69	0.71	1.63	4.59
Max	0.84	1.83	3.81	6.47	12.33
Mean	0.50	1.15	1.62	3.26	9.39

Appendix 13 Bioaccessible concentration of selected trace elements in soils and sediments of Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	As	Cr	Cu	Mn	Ni	Pb	Zn
A1	1.5	1.1	93.6	185.1	0.8	17702	7.3
A2	0.9	0.1	1.4	24.6	0.2	247	1.0
A4	1.4	1.2	105.2	80.3	4.0	14007	41.1
A5	1.3	0.4	20.5	96.3	0.7	1226	2.4
A6	1.4	8.3	352.4	261.8	2.6	26948	5.4
A7	1.5	3.9	95.2	118.2	1.0	10239	3.9
A8	1.2	0.7	30.0	46.4	0.8	5612	2.7
A10	1.1	0.3	3.5	96.3	0.8	223	46.7
B1	4.9	8.7	384.6	59.7	3.1	41740	18.7
B2	3.8	3.9	240.7	91.5	2.4	35470	10.4
B3	14.1	4.3	373.4	251.3	5.3	16173	61.9
B4	3.6	1.6	41.2	248.2	4.1	697	7.0
B5	1.1	0.3	3.2	48.9	0.8	238	2.4
B7	2.3	1.2	8.1	254.5	2.7	1574	208.3
D1	1.3	1.2	27.3	27.0	0.4	1869	1.5
D2	1.4	2.3	57.4	35.0	0.5	8978	5.2
D4	0.9	0.3	4.6	20.2	0.2	853	0.8
D5	1.7	0.5	5.9	59.9	0.7	1705	4.0
D7	1.3	7.4	159.1	77.2	0.6	23662	3.7
D9	1.0	0.4	4.8	52.0	0.5	566	1.0
TS3	1.1	0.2	2.1	29.6	0.6	249	7.0
TS4	3.7	5.3	113.0	159.0	1.8	20464	126.7
TS5	1.2	0.3	2.3	74.1	0.6	198	19.4
TD6	5.3	0.7	43.6	335.9	1.7	12312	295.2
TD10	1.3	0.3	4.0	83.6	1.0	343	40.4
Min	0.9	0.1	1.4	20.2	0.2	198	0.8
Max	14.1	8.7	384.6	335.9	5.3	41740	295.2
Mean	2.4	2.2	87.1	112.7	1.5	9732	37.0
SD	2.7	2.7	121.8	90.6	1.4	12058	71.6

Appendix 14 Effect of pH on the in vitro bioaccessibility of selected trace elements in soils and sediments of Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	As			Cr			Ni		
	pH1.5	pH2.2	pH2.9	pH1.5	pH2.2	pH2.9	pH1.5	pH2.2	pH2.9
A1	1.46	1.61	1.15	1.09	0.50	0.15	0.80	0.45	0.42
A2	0.90	1.24	1.21	0.14	0.09	0.06	0.18	0.17	0.15
A4	1.41	1.62	13.85	1.24	0.42	1.26	3.98	0.60	4.41
A5	1.28	1.38	1.38	0.44	0.19	0.10	0.70	0.59	0.55
A6	1.35	1.64	12.07	8.31	3.23	5.20	2.65	1.52	10.51
A8	1.22	1.73	1.15	0.65	0.27	0.08	0.76	0.26	0.21
A10	1.06	1.36	1.34	0.25	0.13	0.08	0.79	0.63	0.49
B1	4.86	2.49	15.53	8.70	2.62	6.02	3.15	2.01	13.13
B2	3.81	2.35	13.62	3.88	1.25	2.80	2.37	1.63	11.98
B3	14.08	9.04	4.56	4.33	1.50	3.63	5.27	3.22	22.58
B4	3.63	2.73	2.53	1.59	0.56	0.22	4.12	3.61	3.04
B5	1.09	1.51	1.38	0.26	0.13	0.08	0.83	0.66	0.55
B7	2.31	1.92	1.95	1.17	0.54	0.34	2.75	1.90	1.43
D2	1.42	1.74	15.85	2.34	0.61	1.63	0.50	0.27	1.62
D4	0.90	1.32	1.42	0.33	0.13	0.08	0.17	0.10	0.10
D7	1.32	1.70	15.18	7.37	0.77	1.56	0.64	0.27	2.23
TS3	1.12	1.47	1.40	0.19	0.07	0.07	0.57	0.36	0.37
TS4	3.75	1.96	18.01	5.35	0.34	1.43	1.82	1.04	7.69
TS5	1.24	1.43	1.34	0.26	0.10	0.09	0.61	0.39	0.44
TD10	1.29	1.37	1.46	0.28	0.10	0.09	0.98	0.51	0.56

	Cu			Mn			Zn		
	pH1.5	pH2.2	pH2.9	pH1.5	pH2.2	pH2.9	pH1.5	pH2.2	pH2.9
A1	93.57	66.21	41.47	185.07	155.31	108.88	7.29	1.81	1.06
A2	1.45	1.06	0.96	24.65	22.26	22.68	1.00	0.83	0.35
A4	105.21	79.55	69.88	80.27	63.70	418.25	41.08	32.34	193.69
A5	20.50	15.96	14.28	96.31	77.44	71.91	2.40	1.89	1.13
A6	352.36	279.34	236.40	261.79	211.15	1328.80	5.40	3.26	16.59
A8	30.02	19.80	12.70	46.44	39.18	27.54	2.68	1.12	0.42
A10	3.52	2.18	1.70	96.27	78.46	68.30	46.72	39.57	31.06
B1	384.56	276.33	213.83	59.69	51.94	244.06	18.65	14.83	71.67
B2	240.74	152.44	110.77	91.47	84.50	450.47	10.41	6.76	33.68
B3	373.38	288.31	249.27	251.27	207.78	125.41	61.87	50.50	259.83
B4	41.18	33.18	29.67	248.17	219.75	195.58	6.99	5.19	3.59
B5	3.23	2.15	1.79	48.90	39.19	34.96	2.38	1.66	1.04
B7	8.07	4.90	4.53	254.51	175.56	138.27	208.30	167.02	
D2	57.44	25.03	16.48	35.00	28.78	176.51	5.20	3.07	14.43
D4	4.60	2.86	2.17	20.23	13.24	12.67	0.76	0.43	0.20
D7	159.07	103.06	83.65	77.25	63.26	294.03	3.71	1.60	8.16
TS3	2.11	1.10	0.98	29.62	21.70	23.43	6.98	4.40	4.10
TS4	113.01	54.16	49.16	159.03	126.05	669.45	126.74	104.51	538.09
TS5	2.27	1.44	1.27	74.07	51.86	58.41	19.43	12.77	13.47
TD10	3.96	2.04	1.90	83.59	53.46	61.45	40.43	24.21	25.44

Appendix 14 continued

Sample	Pb		
	pH1.5	pH2.2	pH2.9
A1	17702.00	5060	1410
A2	246.89	145.42	70
A4	14007.33	8439	7306
A5	1226.10	638.91	301
A6	26948.00	22450	19078
A8	5611.97	2690	983
A10	222.63	130.60	71
B1	41740.00	64408	50872
B2	35469.67	33704	25023
B3	16173.33	13832	9136
B4	696.50	384.44	212
B5	237.60	137.41	69
B7	1573.67	783.72	584
D2	8977.57	5442	4350
D4	853.26	403.07	255
D7	23662.00	20870	16512
TS3	249.31	106.49	74
TS4	20464.00	16236	12963
TS5	197.51	79.20	53
TD10	342.70	156.18	121

Appendix 15 Effect of the time of extraction on the in vitro bioaccessibility of selected trace elements in soils and sediments of Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	As			Cr			Cu		
	1hr	2hrs	17hrs	1hr	2hrs	17hrs	1hr	2hrs	17hrs
A2	1.55	1.58	1.52	0.13	0.17	1.52	1.48	1.66	2.11
A5	1.7	1.62	1.76	0.38	0.51	1.76	21.1	22.5	24.6
A8	1.58	1.55	1.69	0.6	0.81	1.69	22.2	25.4	31.1
B4	3.72	3.97	3.79	1.3	1.94	3.79	44	46.7	49.9
B5	1.62	1.7	1.47	0.22	0.31	1.47	3.24	3.54	3.79
B7	2.8	2.73	2.4	1.15	1.43	2.4	9.42	10.3	11
D4	1.28	1.76	1.62	0.37	0.42	1.62	4.85	5.6	7.46
TS3	1.72	1.79	1.68	0.2	0.25	1.68	2.5	2.64	2.74
TS5	1.85	1.85	1.7	0.27	0.33	1.7	2.58	2.73	2.83
TD10	1.72	1.93	1.51	0.27	0.34	1.51	3.98	4.25	4.34
	Mn			**Pb**					
	1hr	2hrs	17hrs	1hr	2hrs	17hrs			
A2	24.9	26.4	32.8	233	237	241			
A5	91.1	112	134	1108	1142	1146			
A8	40.7	52.9	71.1	6374	7542	7722			
B4	247	347	387	619	655	675			
B5	47.5	62	93.1	218	225	230			
B7	251	405	593.02	1449	1503	1510			
D4	20.2	28	46.7	811	809	810			
TS3	31.4	35.2	41.2	237	237	241			
TS5	77.6	87	104	201	203	207			
TD10	86.3	94.6	116	328	326	329			
	Ni			**Zn**					
	1hr	2hrs	17hrs	1hr	2hrs	17hrs			
A2	0.19	0.17	0.27	0.86	0.77	0.7			
A5	0.67	0.76	0.84	2.06	2.24	2.59			
A8	0.34	0.41	0.53	0.98	0.92	1			
B4	3.9	4.19	4.61	6.11	6.83	8.05			
B5	0.77	0.87	1	1.87	2.02	2.37			
B7	2.72	3.23	4.13	-	-	-			
D4	0.16	0.22	0.31	0.73	0.63	0.64			
TS3	0.69	0.73	0.85	6.78	7.07	7.69			
TS5	0.6	0.66	0.76	19.2	19.4	20.1			
TD10	0.94	1.06	1.18	39.9	41.3	44.5			

Appendix 16 Effect of the ratio of solid sample mass to extraction fluid volume on the in vitro bioaccessibility of selected trace elements in soils and sediments of Anka area, NW Nigeria. Details of samples can be found in Appendix 1 and Figure 8.

Sample	As			Cr		
	1g/25mL	0.5g/50mL	1g/50mL	1g/25mL	0.5g/50mL	1g/50mL
A2	0.67	2.75	0.90	0.10	0.16	0.14
A10	0.81	2.60	1.06	0.19	0.28	0.25
B4	2.60	5.59	3.63	1.39	1.49	1.59
B5	0.94	2.92	1.09	0.21	0.28	0.26
B7	1.59	3.36	2.31	1.26	1.12	1.17
D2	1.05	2.73	1.42	1.82	2.05	2.34
D4	0.74	2.65	0.90	0.26	0.37	0.33
TS3	0.80	2.73	1.12	0.15	0.18	0.19
TS5	1.03	2.72	1.24	0.23	0.27	0.26
TD10	1.00	2.73	1.29	0.24	0.27	0.28

	Cu			Pb		
	1g/25mL	0.5g/50mL	1g/50mL	1g/25mL	0.5g/50mL	1g/50mL
A2	1.53	1.61	1.45	218.07	211.69	246.9
A10	3.55	4.20	3.52	180.66	177.45	222.6
B4	54.11	47.25	41.18	578.73	580.38	696.5
B5	3.47	3.97	3.23	196.69	188.51	237.6
B7	14.61	9.98	8.07	3018.70	1349.70	1574
D2	55.08	45.61	57.44	9124.30	9333.60	8978
D4	5.28	5.17	4.6	686.32	672.84	853.3
TS3	2.18	2.50	2.11	202.23	208.05	249.3
TS5	2.35	2.71	2.27	160.14	160.51	197.5
TD10	4.07	4.94	3.96	275.79	262.70	342.7

	Mn			Ni		
	1g/25mL	0.5g/50mL	1g/50mL	1g/25mL	0.5g/50mL	1g/50mL
A2	23.11	23.05	24.65	0.19	0.11	0.18
A10	85.87	87.98	96.27	0.66	0.61	0.79
B4	311.77	227.32	248.17	3.68	3.55	4.12
B5	47.34	43.25	48.90	0.76	0.68	0.83
B7	316.01	227.09	254.51	2.18	2.30	2.75
D2	28.30	26.08	35.00	0.29	0.21	0.50
D4	18.94	17.59	20.23	0.15	bdl	0.17
TS3	28.34	24.85	29.62	0.48	0.40	0.57
TS5	69.43	65.24	74.07	0.53	0.43	0.61
TD10	76.54	72.60	83.59	0.80	0.77	0.98