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SEASONAL VARIATION OF SOME HEAVY METALS IN SOILS AROUND GOLD MINE IN DARETA-ANKA, ZAMFARA STATE, NIGERIA

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Abstract: Seasonal assessment of the levels of some heavy metals (Zn, Pb, Fe, Cu and Cd) in soils caused by mining activities in Dareta village of Anka local government area of Zamfara state-Nigeria was carried out using Atomic Absorption Spectrophotometry (AAS) technique. The mean concentration of metals in the soil during dry season was; 94.23 ± 24.37, 67.32 ± 47.06, 746.21 ± 27.87, 720.09 ± 51.87 and 6.25 ± 4.67 mg/kg for Zn, Cu, Fe, Pb and Cd, respectively; while 76.15 ± 9.37, 61.87 ± 13.38, 619.45 ± 94.31, 464.66 ± 34.57 and 5.86 ± 2.32 mg/kg was recorded for rainy season samples. The concentration of some of the metals analyzed are quite above the maximum permissible limit set by World Health Organization (WHO) and National Environmental Standards and Regulations Enforcement Agency (NASREA) and therefore such soil is considered contaminated by those heavy metals.

Keywords: Atomic absorption spectroscopy, goldmine, heavy metals, seasonal variation, soils

Introduction

Mining and agriculture have continued to supply most of the basic raw materials used by modern civilization, however, the discovery of precious stones has make rural farmers to abandoned their farms and support their livelihoods by the exploitation of natural resources in their vicinity which often result in environmental degradation.

Mining is the extraction of valuable minerals and other substances from the ground. The mining industry continues to supply many of the basic raw materials used by modern civilization (Willard, 2005). However, unless adequate precautions are taken mining can be accompanied by serious negative impacts on the environment and human health (Bakau, 1993). Most people in rural areas in sub-Saharan Africa are poverty stricken, they support their livelihoods by the exploitation of natural resources in their vicinity which often result in environmental degradation (Thomas *et al.*, 2003).

Artisanal and small-scale mining (ASM) refers to informal mining activities carried out by individuals, groups, families or cooperatives using low technology or with minimal machinery. It is difficult to estimate the extent of ASM due to the lack of a common definition, its use of seasonal and occasional workers, and a lack of official statistics. In 1999 there were reported 13 million people working directly in ASM, with the livelihoods of a further 80-100 million people affected indirectly (Thomas *et al*., 2003). A more recent estimate notes that these numbers have likely risen in response to higher gold and commodity prices, and that there are now at least 25 million artisanal miners, with 150-170 million people indirectly reliant on ASM. In Africa, increased participation in ASM has been linked to poverty, decline in the viability of agriculture, or as a way to supplement agricultural income (Thomas *et al*., 2003).

Anthropogenic heavy metal contamination is becoming widespread with ubiquitous nature of heavy metals in the environment. Anthropogenic sources of heavy metal pollution include but not limited to mining, iron smelting, fossil burning and municipal and industrial waste disposal (Abdu and Yusuf, 2013). During mining, a fine grind of the ore is often necessary to release metals and minerals, so the mining industry produces enormous quantities of fine rock particles, in sizes ranging from sand-sized down to as low as a few microns (USEPA, 1994). These fine-grained wastes are known as "tailings". By far, the larger proportion of ore mined in most industry sectors ultimately becomes tailings that must be disposed of. In the gold industry, only a few hundreds of an ounce of gold may be produced for every ton of dry tailings generated (USEPA, 1994). Tailings need to be properly managed because they constitute a major source of release of many trace elements into the environment (Antwi-Agyei *et al.*, 2009).

During mining, the ores and minerals are explored thereby freeing these heavy metals. It is therefore known that, the soil over a gold mining region is always polluted by heavy metals, which are released from gold mining activities. It's also believed that the activity of Cyprus Mining Cooperation in Lefke was responsible for air, water and land pollution of the area (Stone, 2000). Potential environmental impacts of mining on the environment include poisonous air emission, fugitive dust blown to the surrounding area, non-reused overburdens, waste rocks, tailings, loss of plant population, reduction in localized groundwater recharge and loss of fish population from water pollution (Rasheed and Amuda 2014). Because these metals are toxic to living organisms, there are several cases where pollutant's related ingestion of contaminated food has led to human death. Such researches on ecological risk assessment of heavy metals in the polluted soil had gotten more and more attention. It was found that the results of the ecological risk assessment can reveal the possibility for soil to be polluted, and even for the ecology to be harmed by concerned heavy metals (Yao-guo *et al.*, 2010).

Soil is a natural resource essential for the food production and global economy; it also plays many important roles in the environment. As being situated at the interface between the atmosphere and the lithosphere it acts as a filter and a buffer and may weaken and degrade environmentally harmful compounds protecting the air quality. It also has an interface with hydrosphere and therefore it affects surface and groundwater quality. Furthermore, soil as a part of biosphere, provides nutrient-bearing environment that sustains the growth of plant and animals. As a habitat and protecting media of flora and fauna, it contributes to the maintaining of the global nutrient cycling as well as biomass production whether by natural vegetation growing or plant cultivation. Beside these ecological functions, soil is ground to build and live on, it is raw material and reserve of cultural heritage (Monika and Marija, 2011). Because soil quality and its utilization are directly linked, each of above mentioned functions or use mode requires a certain soil quality level. Otherwise, any change of soil quality may affect its utilization potential (Harris *et al*., 1996). A healthy soil is essential for human health because what is in the soil affects the health, safety and quality of the food that is derived from the soil

(Uduma and Jimoh, 2014).Out of total degraded land on the global scale that are estimated to 1,965 mha, about 55% was water eroded, about 28% wind eroded, and about 12% is polluted by chemicals (Adriano *et al.*, 1995). From the standpoint of soil degradation, the presence of some trace elements in a toxic concentration may be due to both natural and anthropogenic factors. Therefore, it may become quite difficult to discriminate among the different causes.

The aim of this work is to determine the levels and seasonal variation of heavy metals (Zn, Pb, Fe, Cu and Cd) in soil collected from Dareta village of Anka local government area of Zamfara state where mining activities by local miners are being held and compare the result obtained with national (e.g. NASREA, DPR) and international (e.g. WHO) standard guide lines.

Materials and Methods

Reagents

All reagents (HNO_3, HCl,$HClO_4$) and all metal salts used in this study were of analytical grade purity and used without further purification. Deionized water used was prepared in a Milli-Di Millipore machine (SAS 67120 MOLSHEM, France). All glassware and plastic containers were washed with detergent, rinsed with distilled water and then soaked in 10% HNO_3 for 24 h. Finally, the materials were washed with deionized water and dried in an oven at 80ºC for 24 h.

Study area

The study area (Fig. 1) is within the coordinates range between longitude 5°48E to 600°53E and latitude 11°58N to 12°15N, Anka local government of Zamfara state Nigeria.

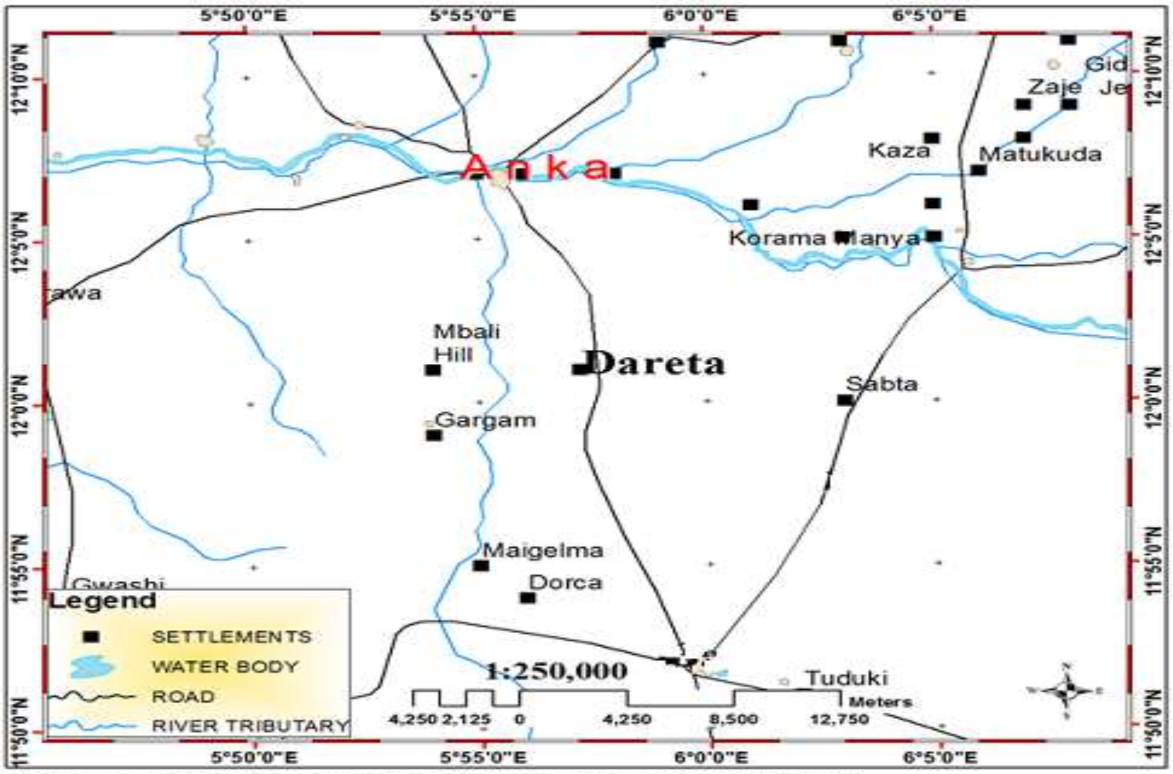


FIGURE 1: MAP OF ANKA LOCAL GOVT. SHOWING STUDY AREAS

source: digitized and cliped from Administrative Database/Nigeria Shapefile

Fig. 1: Map of Anka local government showing the study area

Sampling procedure

Soil samples were collected during the dry and raining seasons from Dareta village in Anka Local Government area of Zamfara State. The Soil samples were collected at a depth of 10 cm from the residential, farms and the mining sites of the village under study and stored in a polythene bag (Ayodele and Gaya, 1998). A background soil sample was also collected at a distance of about two kilometers from the ore processing areas around the village.

Sample pre-treatment

The soil samples were air dried, ground and sieved using a 2 mm mesh. The samples were then oven dried at 65°C until a constant weight was obtained and kept for further analysis (Dahiru *et al.*, 2013).

Digestion of soil samples

To 100 mg of the ground soil sample in a 100 mL beaker, 2 mL of concentrated HNO_3 and 6 mL concentrated HCl were added and the beaker covered with watch glass. The solution was heated to dryness on a sand-bath at a temperature of 250ºC in a fume cupboard and then left to cool. Exactly 2 mL of HCl were added to re-dissolve the dry sample. Finally, 10 mL of distilled water was added and heated for 5 min. The extract was cooled; the content filtered into 25 mL volumetric flask and made up to mark with distilled water (Lare *et al.*, 2013).

Results and Discussion

Table 1 presents the concentrations in mg/kg of all metals determined in the soils obtained from various sampling sites.

Table 1: Heavy metals concentration (mg/kg) in soil samples analyzed

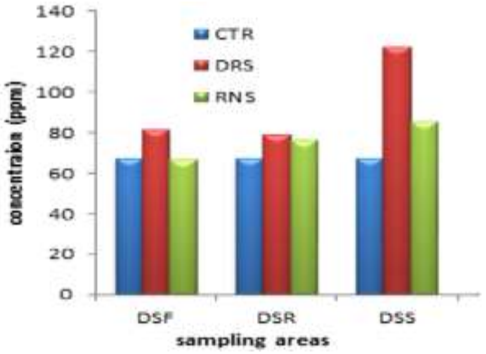
Site	Zn			Cu			Fe			Cd			Pb		
	CTR	DRS	RNS	CTR	DRS	RNS	CTR	DRS	RNS	CTR	DRS	RNS	CTR	DRS	RNS
DSS	67.187	122.333	85.489	39.482	115.071	76.563	107.426	900.565	721.859	0.680	9.633	7.522	71.439	1321.517	862.431
DFS	67.187	81.490	66.748	39.482	65.923	50.367	107.426	484.490	600.333	0.680	6.250	6.867	71.439	452.142	257.667
DRS	67.187	78.876	76.222	39.482	20.973	58.685	107.426	853.600	536.167	0.680	4.670	3.204	71.439	386.638	273.889

DSS = Mining Site, DFS = Farm Site, DRS = Residential Area, CTR = Control, DRS = Dry Season, RNS = Rainy Season

Metals in the soil

Figures 2 to 6 show the mean concentration of zinc, copper, iron, lead, and cadmium in soils from Dareta village at different seasons.

From Fig. 2, results obtained in the dry season exhibit elevated mean concentration of zinc (94.23 ± 24.37 mg/kg) than the corresponding rainy season (76.15 ± 9.37 mg/kg). This could be due to the fact that the zinc metal might have dissolved and disperse into surrounding streams as a result of rainwater runoff and percolation through contaminated soil (Mark *et al*., 2014). Generally the level of zinc for both seasons at all sampling points (residential, farms and the mining sites) in the community is higher compared to the background soil, this indicates that the activities of the local miners contribute to the increase in the levels of heavy metals at and around the mining areas. In a similar study, Antwi-Agyei *et al.* (2009) reported the mean concentration of 168.1 ± 108.7 mg/kg for Zn metal around goldmine tailings dams at Obuasi, Ghana which is quite higher than the ones obtained in this work (94.23 ± 24.37 and 76.15 ± 9.37 mg/kg for dry and rainy seasons respectively). Yao-guo *et al.* (2010) also reported 118.6 ± 85.26 mg/kg as the mean concentration of Zn in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. The concentration of Zn obtained in the present work did not exceed the maximum allowable values of 300 – 600 mg/kg set by Environmental Standards and Regulations Enforcement Agency (NASREA) and 200 mg/kg by World Health Organization (WHO) (Ezigbo, 2011).



CTR=Control (Background); DRS=Dry season concentration; RNS=Rainy season concentration; DSF=Dareta Farm soil; DSR=Dareta Residential soil; DSS=Dareta Mining site

Fig. 2: Concentration of zinc in soil samples analyzed

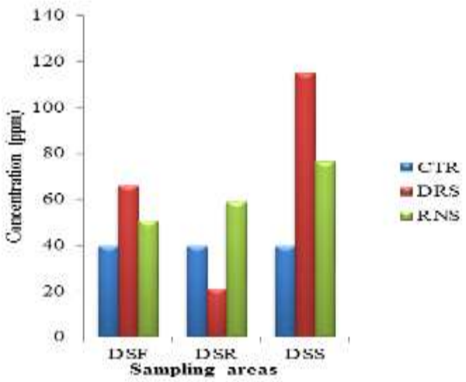


Fig. 3: Concentration of copper in soil samples analyzed

With the exception of residential area, the same trend of high concentration of the metal (Cu) in the dry season compared to the raining season was observed (Fig. 3). The observed high concentrations of Cu during the dry season could be probably due to the dissolution, dispersion and accumulation or retention of the metal by the soil (Mark *et al*., 2014). The mean concentration of Cu in two similar studies have been reported as 71.44 ± 15.8 and 54.13 ± 11.18 mg/kg (Antwi-Agyei *et al.,* 2009; Yao-guo *et al.,* 2010) which are in agreement with the mean concentration of 67.32 ± 47.06 and 61.87 ± 13.38 mg/kg obtained in this work. With the exception of DSS in the dry season, the concentrations of Cu were below the maximum allowable value of 100 mg/kg (Chiroma *et al.*, 2014).

During the rainy season, it obvious from Fig. 4 that the highest Fe concentration in the soil was observed in the mining site followed by the farm site and the lowest in the residential area with 619.45 ± 94.31 mg/kg as the mean concentration, but for the dry season however, the residential area emerged second to the highest with corresponding mean concentration of 746.21 ± 27.87 mg/kg. The results reported in this work show similarities to those reported by Tobias *et al.* (2013) who revealed the mean concentration of Fe in the soil of Aba city to be 784.09 ± 45.74 mg/kg. Practically, the concentrations of Fe for both dry and rainy seasons were below the maximum allowable value of 5000 mg/kg established by NASREA (Ezigbo, 2011).

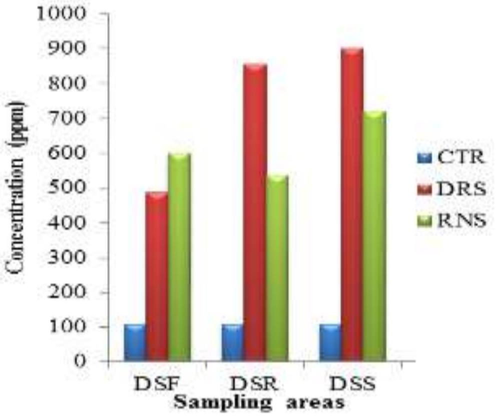


Fig. 4: Concentration of iron in soil samples analyzed

From Fig. 5, the concentration of Pb during the dry season was highest in all the three sampling sites which follow the order mining site > farm site > residential area. However for the rainy season, the trend was observed as mining site > residential area > farm site. The mean Pb concentrations for the dry and rainy seasons detected in this work are 720.09 ± 51.87 and 464.66 ± 34.57 mg/kg, respectively. Higher average value of 1266 mg/kg for Pb from contaminated farmlands of Abare village where mining activities are also being carried out in Zamfara State, Nigeria was reported by Abdu and Yusuf (2013). The concentrations of Pb for DSR and DSF in both seasons obtained from this research were slightly below the maximum allowable values of 500 mg/kg set by NASREA (Ezigbo, 2011); however the concentrations of Pb for DSS in all seasons have exceeded the limit as seen in Fig. 5.

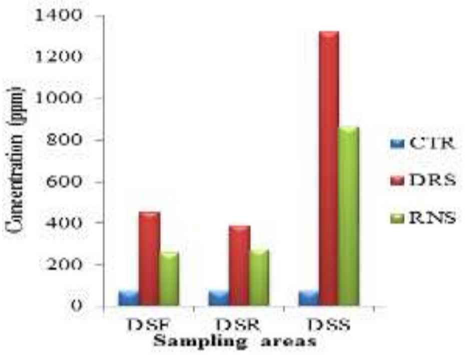


Fig. 5: Concentration of lead in soil samples analyzed

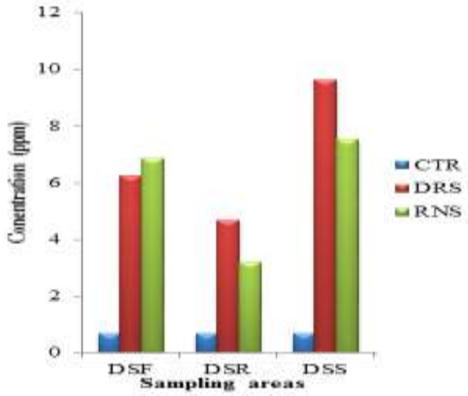


Fig. 6: Concentration of cadmium in soil samples analyzed

The mining site (DSS) and the farmland (DSF) of Dareta for the two seasons (Fig. 6) show cadmium concentrations higher than the range of 3 – 6 mg/kg cadmium in soil set by NASREA but below 10 mg/kg set by WHO (Ezigbo, 2011). However, for both dry and rainy seasons the concentrations are within the limits in the case of residential soil (DSR). The mean Cd concentrations of 6.25 ± 4.67 and 5.86 ± 2.32 mg/kg reported in this work are higher than the value discovered by Yao-guo *et al.* (2010) as 0.55 ± 0.31 for soil samples from a gold mining region.

Conclusion

Soil samples collected from Dareta village in Anka local government of Zamfara state were found to have an elevated concentration of heavy metals compared to the background concentration obtained in samples collected at a distance of about two kilometers from the last residential and ore/mineral processing areas. The concentrations of heavy metals in soil varied significantly within the sampling sites suggesting human factor in the dispersion of these heavy metals as suggested by UNEP (2010). Almost all the rainy season results have been found to be comparatively lower than the corresponding dry season concentration which could be attributed to the dissolution and dispersion of the metals into the surrounding streams as a result of rainwater runoff and percolation through contaminated soil.

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Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

References

Abdu N & Yusuf AA 2013. Human health risk characterization of lead pollution in contaminated farmlands of Abare Village, Zamfara State, Nigeria. *Afr. J. Envtal. Sci. and Techn.,* 7(9): 911-916.

Adriano DC, Chlopecka A, Kaplan DI, Clijsters H & Vangronsveld J 1995. Soil Contamination and Remediation: Philosophy, Science and Technology. Third International Conference on the Biogeochemistry of Trace Elements, Paris, 15-19 May, 1995. (INRA editions, Paris, France), pp. 317-322.

Antwi-Agyei P, Hogarh JN & Foli G 2009. Trace elements contamination of soils around gold mine tailings dams at Obuasi, Ghana. *Afr. J. Envtal. Sci. and Techn.*, 3(11): 353-359.

Ayodele JT & Gaya UM 1998. Chromium, manganese and zinc in Kano municipality street Dust, Nigeria. *J. Chem. Soc.,* 23: 24-34.

Bakau F 1993. Pollution Prevention and Abatement Guideline for the Mining Industry Jointly Sponsored by World Bank. UNIDO and UNEP.

Chiroma TM, Ebewele R & Hymore FK 2014. Comparative assessment of heavy metal levels in soil, vegetables and urban grey waste water used for irrigation in Yola and Kano. *Int. Refereed J. Engr. and Sci.*, 3(2): 01-09.

Dahiru MF, BirninYauri UA & Sani MD 2013. Cadmium, copper, lead and zinc levels in sorghum and millet grown in the city of Kano and its environs. *Global Adv. Res. J. Envtal. Sci. and Toxicol.*, 2(3): 82-85.

Ezigbo VO 2011. Determination of the trace metal concentration in the soil of Nnewi North local government area. *J. Basic Physical Res.*, 2(1): 82-85.

Harris RFD, Karlen DL & Mulla DJ 1996. *A Conceptual Framework for Assessment and Management of Soil Quality and Health, Methods for Assessing Soil Quality*. Ed. Doran JW, AJ Jones. Soil Science Society of America, Special Publication, 49: 61-82.

Lare U, Tsuwang K, Gusikit R & Mangs A 2013. Lead and mercury contamination associated with artisanal gold mining in Anka, Zamfara State, North-western Nigeria: The continued unabated Zamfara lead poisoning. *J. Earth Sci. and Engr.,* 3: 764-775.

Mark OAO, Raymond LN, Ugoeze UE & Adamu S 2014. Heavy metal contaminations of drinking water sources due to illegal gold mining activities in Zamfara State Nigeria. *J. Chem. and Biochem.*, 2(1): 31-44.

Monika Z & Marija R 2011. Soil Contamination by Trace Metals: Geochemical Behaviour as an Element of Risk Assessment, Earth and Environmental Sciences. Available from: http://www.intechopen.com/books/earth-and-environmental-sciences/soilcontamination-by-trace-metals-geochemical-behaviour-as-an-element-of-risk-assessment. Accessed on 25.06.2015.

Rasheed AI & Amuda AK 2014. Impacts of Artisanal Mining on Some Heavy Metals Concentration in Surface Water in Kutcheri, Zamfara State North-Western Nigeria. *Acad. J. Interdisc. Stu.*, 3(7): 74.

Stone L 2000. The Social Effects of Mining and the CMC Mine Problem. pp 212.

Thomas H Felix H & Michael P 2003. Artisanal & Small-Scale Mining, Challenges and Opportunities. Mining Minerals and Sustainable Development Projekt-Consult GmbH January 2003. No. 70 available at;*http://pubs.iied.org/pdfs/9268IIED.pdf.*

Tobias I, Ndubuisi E, Ezejiofor AN, Udebuani 1AC, Ezeji1 EU, Ayalogbu1 EA, Azuwuike, CO, Adjero LA, Ihejirika CE, Ujowundu CO, Nwaogu LA & Ngwogu KO 2013. Environmental metals pollutants load of a densely populated and heavily industrialized commercial city of Aba, Nigeria. *J. Toxicol. and Envtal. Health Sci.*, 5(1): 1-11.

Uduma AU & Jimoh WLO 2014. Assessment of Pb enrichment and depletion in selected contaminated arable soils of Nigeria using calcium as a reference element. *World J. Agric. Res.*, 2(1): 5-11.

USEPA 1994. Design and Evaluation of Tailings Dams. Technical Report – EPA530-R-94-038. USEPA, Office of Solid Waste, Special Waste Branch, Washington DC.

Willard L 2005. An Introduction to Geology and Hard Rock Mining Rocky Mountain Mineral Law Foundation. Science and Technology Series.

Yao-guo W, You-ning X & Zhang J 2010. Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. *Trans. Nonferrous Met. Soc. China*, 20: 688−694.