



# Multielemental Analysis of Limestone and Soil Samples of Kitui South (Kenya) Limestone Deposits

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(Received Oct 2012; Published Dec 2012)

## ABSTRACT

The results of analysis of heavy metal in limestone and soil samples from the limestone deposit areas of Kitui South, Kenya were reported in this paper. The analysis was carried out to assess the environmental impact of heavy metals in the region and provide necessary data on the extent of their spread that could be used as a basis for monitoring occupational exposure and the and subsequent environmental impact once mining and processing of limestone in the region starts. Limestone and soils were sampled from three major limestone deposit areas in the region of Kituvwi, Mwanyani and Ndulukuni and analyzed for heavy elemental content using <sup>109</sup>Cd radioisotope excited EDXRF spectrometry technique in which sample pellets were directly irradiated. The major elements detected in soils were Ti, Mn, Cu, Zn, and Pb, while in limestone they were; Ti Mn and Zn.

**Key words:** EDXRF, Limestone, Heavy Toxic metals, Environmental impact

DOI:10.14331/ijfps.2012.330036

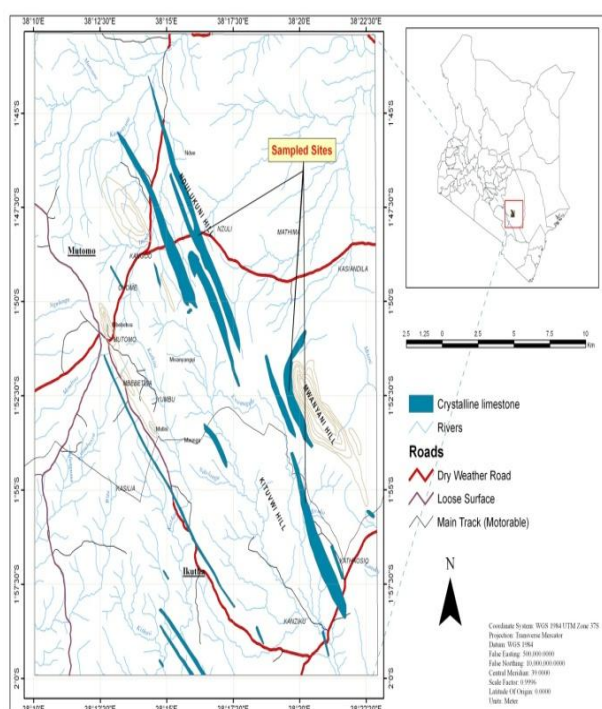
## INTRODUCTION

Limestone mining has been associated with enhancement of heavy toxic metals in soils. During limestone mining the size reduction process like crushing increases the surface area of the reaction between rock/mineral particles thereby accelerating oxidation and/ or chemical weathering and hence the immobilization of metals to the environment. The damping of mine tailings and mine waters pose a great risk of increasing the concentration of these heavy toxic metals in surrounding soils and water. At low concentrations, some of the metals are essential to plants, animals and humans but at above recommended levels they can be toxic.

The environmental effect of limestone mining and processing has been studied to determine its impacts in relation to soil and water pollution by heavy toxic metals in various parts of the world (Colbourn & Thornton, 1978; Li & Thornton, 1993; Prasad & Bose, 2001) In Sormour district of Himachal Pradesh, India, a study on the effect of limestone mining on heavy metal concentration in nine spring and eight surface water samples that was done showed lower heavy metal pollution index than the maximum permitted levels (Prasad & Bose, 2001). Subsequent studies in England and

Hungary on the heavy metal content of karst soils on limestone deposit areas have shown that the metal concentrations and distribution continuously changed with time. The contamination of large areas of agricultural soils in England comes from mining (Colbourn & Thornton, 1978). A similar study in the region indicated that the heavy metal content of limestone was originally not too high (Kabata-Pendias, 2000). Further investigation later indicated increased concentration of the metals in limestone. Based on the earlier investigation, the heavy metal contents of karst soils in Hungary was found to be higher than it should be originating from the parent rock alone (Bárányi-Kevei, Goldie, Hoyk, & Zseni, 2001). The multi-elemental contamination of soils (for example of brown earth on carboniferous limestone) is affected by the underlying mineralization rock, by mining activities producing widespread contamination and by smelter pollution (Li & Thornton, 1993). In South Jordan, a study of heavy metal distribution in soils around a cement factory in Qadissiya area showed relatively high concentration of lead, zinc and cadmium in soil samples of the investigated area were related to anthropogenic activities sources such as the cement industry, agricultural activities and traffic emissions. Lead, zinc and cadmium had the

highest concentration in areas close to the cement factory (Al-Khashman & Shawabkeh, 2006). Heavy toxic metal assessment is therefore necessary before mining activities in order to provide information on environmental impact assessment and monitoring of their enhancement during mining and processing. Kitui South is situated next to Tsavo East national park and borders the main Athi River bordering Kibwezi and Kitui Central districts of Kenya. The study area is the limestone deposits of Kitui South district of Kenya. Crystalline limestone outcrops in the area and the major bands are continuous over considerable distances with the major bands being found in the Kitui- Kanziku hills. The limestone deposits were discovered in 1957 (Saggerson, 1957). Since then no mining and processing activities of the limestone have been done probably due to poor social amenities such as lack of good road network, electricity among other factors. However, in recent years these limestone deposits have attracted various limestone mining and processing companies which have set plants within the region. This study aimed at assessing the environmental impact of heavy toxic metals in the limestone deposit areas of Ndulukuni, Mwanyani and Kituvwi Hills found in Kitui South District, Kitui County-Kenya (See figure 1) using EDXRF spectrometry before the start of the mining process in a view to make recommendations on possible pollution effects during the mining and processing of the limestone which was due to start by the time of the study. This study aimed at assessing the environmental impact of heavy toxic metals in the limestone deposit areas of Ndulukuni, Mwanyani and Kituvwi Hills found in Kitui South District, Kitui County-Kenya (See Figure.1) using EDXRF spectrometry before the start of the mining process in a view to make recommendations on possible pollution effects during the mining and processing of the limestone which was due to start by the time of the study.



**Fig.1** Simplified geological map of Kitui South limestone deposit areas (Saggerson, 1957)

## MATERIALS AND METHODS

A total of 90 samples were collected (45 limestone and 45 soil) 15 samples of soil from Ndulukuni, 15 from Mwanyani and 15 from Kituvwi hills, while the limestone samples consisted of 15 samples from each of the region. The limestone samples were collected from limestone rock outcrops in Kituvwi and Ndulukuni while samples from Mwanyani were collected from the various exploration sites with help of exploration workers of the Athi River cement company. Soil samples were collected from the same sites at depth of between 0-15cm making a total of 15 samples from Ndulukuni, 15 from Mwanyani and 15 from Kituvwi.

The samples were dried and pulverized into fine powder before being sieved to obtain a powdered matrix of particle size  $<75 \mu\text{m}$ . Three pellets of mass between 0.3-0.5g and diameter 25mm were prepared from each sample for analysis using Energy Dispersive X-Ray Fluorescence (EDXRF).

The EDXRF spectrometer used in this study consisted of  $^{109}\text{Cd}$  as the excitation source; Canberra Si (Li) detector, an ORTEC spectroscopy shaping amplifier model 571, ORTEC high voltage supply bias model 475, ORTEC liquid nitrogen monitor and a Canberra multichannel analyzer (S-100) interfaced with a 486 channel personal computer (Bárány-Kevei et al., 2001)

The crystal is molded in a vacuum tight cryostat of liquid nitrogen maintained at a temperature of 77 K ( $-200^{\circ}\text{C}$ ), which assists in reducing the electronic noise and keeping the lithium atoms in the silicon and the lattice point while the diode is depleted of the charge carriers and in effect it becomes an ionizing chamber (Pettersson & Selin-Lindgren, 2007). According to Beckhoff, Kanngießer, Langhoff, Wedell, and Wolff (2006) Multichannel analyzer (MCA) measures the heights of the amplitude of different pulses and stores the results in memory counters called channels. The number of times the pulses of the same height range has been detected is accumulated in the corresponding analyzer memory resulting into a pulse height distribution. The pulse height distribution is converted into the X-ray energy spectrum by appropriate MCA calibration. The MCA also includes a microprocessor, which is preprogrammed to perform single data analysis operations such as energy calibration, integration and subtraction of background (Beckhoff et al., 2006). Each pellet was run for 1800s and the spectra collected by the Canberra detector with energy resolution of 195 eV for (Mn-K $\alpha$ ) X rays at 5.9 keV. Characteristic X-ray spectra obtained from the samples were evaluated by nonlinear least squares fitting using the AXIL-QXAS code (Van Grieken & Markowicz, 2001).

## RESULTS AND DISCUSSION

Various heavy metals were found to exist in different quantities in both limestone and soil samples: Ti, Mn, Pb, Cu, Zn and Pb. The concentrations are presented in table 1. Table 2 shows the detection limits of the different metals. The results indicate that the Ti existed in soil samples from the three sampling regions with concentration of 7040 mg/kg, in Mwanyani, 6291 mg/kg in Kituvwi and 6288 mg/kg in Ndulukuni. On the other hand, Ti was found to be below detection limits for limestone samples from Kituvwi and Ndulukuni and an average concentration of 2643 mg/kg in

Mwanyani. The soil Ti content was therefore about 3 times higher than the limestone content in this region. Soil metal content is influenced by weathering and other geochemical process undergone by the rocks and minerals within the region. In this view, the soil Ti content in this area therefore could not be attributed to the limestone rocks but other rocks found within the region. Mn was found at detectable levels in soil from all the three regions with average concentrations 874 mg/kg, 925 mg/kg and 1126 mg/kg for the sites Kituvwi, Mwanyani and Ndulukuni respectively. However, for limestone Mn was below detection limits for samples from Kituvwi and Ndulukuni and a concentration of 909 mg/kg for Mwanyani. The results show that Mn was generally more abundant in soil than in limestone for each particular region showing that the soil Mn could have originated from other rocks within the region and not the limestone ore. These results are similar to the results reported in Hungary (Bárány-Kevei et al., 2001). Copper was found to be below detection limits for all the limestone from all the regions sampled.

It was also noted that Cu was below detection limits for soil samples from Kituvwi and Ndulukuni. However, Cu in soil samples from Mwanyani was found to have an average concentration of 66 mg/kg which is below the soil metal limits set by the United States Environmental Protection Agency (Adler, Landman, & Cameron, 1993) of 75 mg/kg. Thus the soils could be considered not contaminated with copper. It is thus inferred that the origin of copper in soils was weathering and other geochemical processes of other rocks and mineralization and not the limestone ore. These results support the results obtained in Hungary (Kabata-Pendias, 2000; Li & Thornton, 1993). Zinc was found in soil samples from all the three regions at average concentrations 78 mg/kg for Kituvwi, 147 mg/kg for Mwanyani and 100 mg/kg for Ndulukuni. For the limestone samples, Zn was below detection limits for samples from Kituvwi and Ndulukuni while the concentration of Zn for limestone in Mwanyani was 93 mg/kg.

**Table.1** Metal Concentration in soils and limestone from Kituvwi, Mwanyani and Ndulukuni

Element		Kituvwi		Mwanyani		Ndulukuni	
		Limestone	Soil	Limestone	Soil	Limestone	Soil
Ti	Max	BDL	9084±638	4255±385	17290±1022	BDL	9664±861
	Min	BDL	4266±387	1666±333	2461±314	BDL	3145±334
	Aver	BDL	6291±518	2643±404	7040±542	BDL	6288±537
Mn	Max	BDL	1540±126	1101±133	2760±178	BDL	2586±169
	Min	BDL	422±65	308±85	393±63	BDL	387±71
	Aver	BDL	874±91	909±110	925±89	BDL	1126±153
Cu	Max	BDL	BDL	BDL	86±15	BDL	BDL
	Min	BDL	BDL	BDL	43±12	BDL	BDL
	Aver	BDL	BDL	BDL	66±15	BDL	BDL
Zn	Max	BDL	103±12	144±16	170±21	BDL	174±17
	Min	BDL	33±9	48±9	34±11	BDL	42±11
	Aver	BDL	78±12	93±13	147±23	BDL	100±16
Pb	Max	BDL	BDL	BDL	72±5	BDL	BDL
	Min	BDL	BDL	BDL	20±7	BDL	BDL
	Aver	BDL	BDL	BDL	38±8	BDL	BDL

BDL: Below Detection Limits

Heavy metals in soils originate from mineralization of the region as well as weathering of rocks found within the area. Human activities such as farming may also contribute heavy metals in soils and water. However, the region under study is a hilly land where apart from occasional grazing no farming activities take place. The limestone within the region has not been mined though various limestone mining and processing companies are in the process of setting up mining and processing plants in the area. This implies that the soil heavy toxic metal content is mainly due to natural processes such as weathering and other geochemical processes of the rocks found within. The high concentration of all heavy toxic Zn, Pb, Cu, Ti and Mn, in soils as compared to limestone, are from the same sampling points indicate that the soil metal content was higher than it could have been if it originated from the limestone ores. These facts were also observed in other studies (Kabata-Pendias, 2000). Although the soil heavy metal content for the metals Zn, Pb and Cu were found to be below the United States Environmental Protection Agency limits of 75 mg/kg, 100 mg/kg and 200 mg/kg for Cu, Pb and Zn respectively (Adler et al., 1993) the levels

were close to the limits showing that a little enhancement of the heavy metals could raise their concentration beyond the limits. In conclusion, it was noted that soils from the region were not contaminated with metals Pb, Zn, Cu, Mn and Ti however great care should be taken to avoid enhancing the metal levels to toxic amounts through human activities. Mining and processing of the limestone in this region is due to start. This may result into enhancement of the metals through dumping of mine tailings in the region owing to the fact that the tailings shall be composed of rocks and other minerals found within the region other than limestone ores. The spread of heavy metals is a common phenomenon near factories due to dumping of mine tailings. Zn, Cu and Pb and Cd concentrations have been shown to be enhanced and to have increased as well as spread to nearby areas (Al-Khashman & Shawabkeh, 2006).

The area is hilly but surrounded by arable land with a number of seasonal streams from which the people get water for their daily. This poses a great danger to the people living within the area as well as animals as some of these heavy metals may be washed into the rivers making them available

to humans and biota. We recommend controlled dumping of mine tailings, mine water and any other effluence from the factories so as to ensure that the heavy metals do not spread to the neighboring arable land and water bodies. Frequent monitoring is also essential for environmental impact assessment once the mining and processing starts.

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## ACKNOWLEDGEMENT

We wish to thank the institute of Nuclear Science and technology, University of Nairobi for funding this project.