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Full Length Research Paper

Assessment of toxic heavy metal loading in topsoil samples within the vicinity of a limestone quarry in South Western Nigeria

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Loading of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe in topsoil samples (TS) collected from the vicinity of limestone quarry in South Western Nigeria was investigated. Thirty TS were sampled within ½ km radius from exploration area and 5 background samples from undeveloped area 10 km away from the study area. Limestone rock samples (RK) were also analyzed for metals' content. All samples were pretreated and leached with appropriate acid solutions for some properties. All leachates were analyzed with atomic absorption spectrophotomer (AAS) technique. Soil pH ranged from 6.65 to 8.23, sand from 55.8 to 75.0%, silt from 16.6 to 34.6%, clay from 8.43 to 13.6%, and organic matter from 0.97 to 4.84%, respectively. These properties compared with those of background samples. Rock samples (RK) showed high Fe and Mn enrichment. Metals levels (mg/kg) in TS with background levels in parenthesis ranged as follows: 11.5 to 27.7 (10.5) Pb, 0.28 to 3.18 (0.55) Cd, 12.1 to 17.4 (5.50) Cr, 80.6 to 55.8 (3.81) Cu, 8.93 to 23.5 (11.1) Co, 262 to 710 (637) Mn, 6.34 to 17.4 (6.10) Ni, 36.0 to 620 (24.4) Zn, and 6585 to 13440 (4563) Fe. The elevated enrichment suggests influence from exploration activities. Residual phase showed highest enrichment for all metals possibly, because of high sand content. Positive correlations were shown between all metals, except Mn and Cd that were negative. Geoaccumulation index rating showed <0 for Mn denoting uncontamination, while others ranged from 1 to 2 indicating moderate contamination.

Key words: Heavy metals, limestone, quarry, topsoil, pollution.

INTRODUCTION

Quarrying of different useful minerals like limestone from underground deposits is an old technology that has been in existence since antiquity (Ekmekçi, 1993). The Egyptians and the Romans of old used a lot of quarried materials in the construction of the huge pyramids of numbers, temples, and monuments that are preserved till today.

However, there are several adverse effects quarrying activities have brought to bear on humans and the entire ecosystem. Dust from quarrying has been reported to stall the growth and flowering of crops, because it settles on surfaces of leaves thereby interfering with the normal photosynthetic and other exchanges that take place at the leaf and atmosphere interface (Madhaven and Sanjay, 2005). Quarry dust has also been found to cause a killer disease called 'silicosis', especially among quarry workers through inhalation of minute dust particles (0.1 to 150 µm) high in silica (Durvasula, 1990; Madhaven and Sanjay, 2005). Occurrence of other respiratory and skin problems among manual stone-quarrying workers has been reported (Ugbogu et al., 2009). Heavy metals contamination of the environment from acid mine drainage produced from exposure of certain sulphide minerals mostly pyrite and arsenopyrite to air and water in both active and abandoned quarry/mine sites has been investigated by Sengupta (1992) and Zuhairi et al. (2009). Zuhairi et al. (2009) reported that, the

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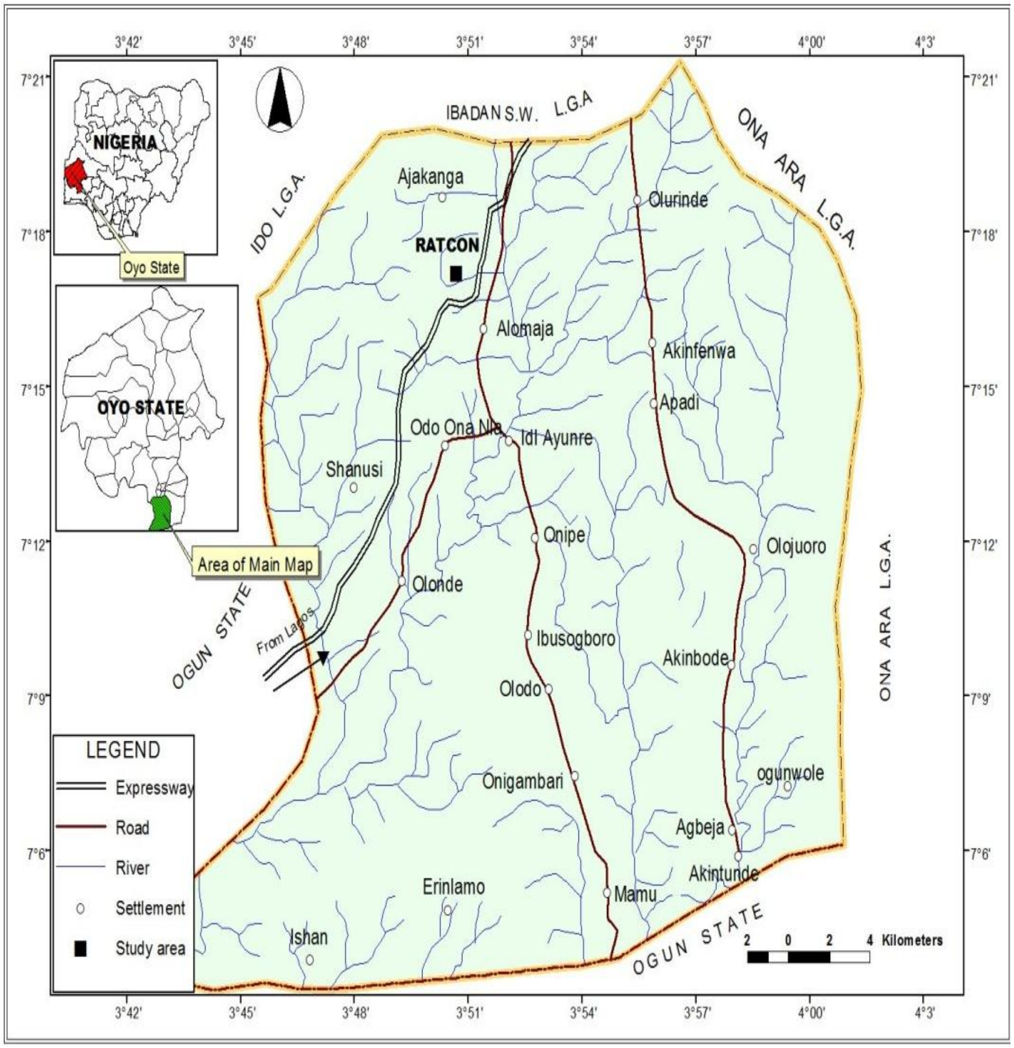

Figure 1. Map showing the location of the study area.

concentrations of As, Cu, Fe, Mn, Pb, and Zn in surface water, soil, and mine tailings exceeded regulatory limits. Recently, a limestone quarry in Florida was discovered to have been associated with exposure of hazardous levels of Hg metal (ENS, 2007).

Due to increasing demand for limestone for various construction activities in Nigeria, proportional increase in quarrying and extraction of limestone by opencast methods have been intensified in the last few decades. Determination of levels of radionuclides and gamma radiation and their rates in selected limestone quarries in Ibadan, Nigeria has been reported (Jibiri and Okorie, 2006).

There is dearth in information on the impact of limestone and other mineral explorations on the surrounding environment in terms of heavy metals pollution in Nigeria. There is need to investigate the baseline concentrations of toxic heavy metals within the vicinity of quarry sites. This would form a database on pollution statuses of the toxic heavy metals within the surrounding environment of quarries and serve as reference point for future studies and comparison.

This study assessed the levels of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe in topsoil samples of a major limestone quarry in Oluyole Local Government Area, Oyo State, Nigeria. Some statistical tools were also applied on the data to study the relationship between metals, distance from exploration zone, and level of pollution compared with the background levels.

MATERIALS AND METHODS

Description of the study area

Ratcon limestone quarry was selected as the study area, because it is one of the largest quarries in Oyo State and is located at Oluyole Local Government area of Oyo State, Nigeria (Figure 1). The study area is located on 7°13' N and 3°52' E. It falls in the basement

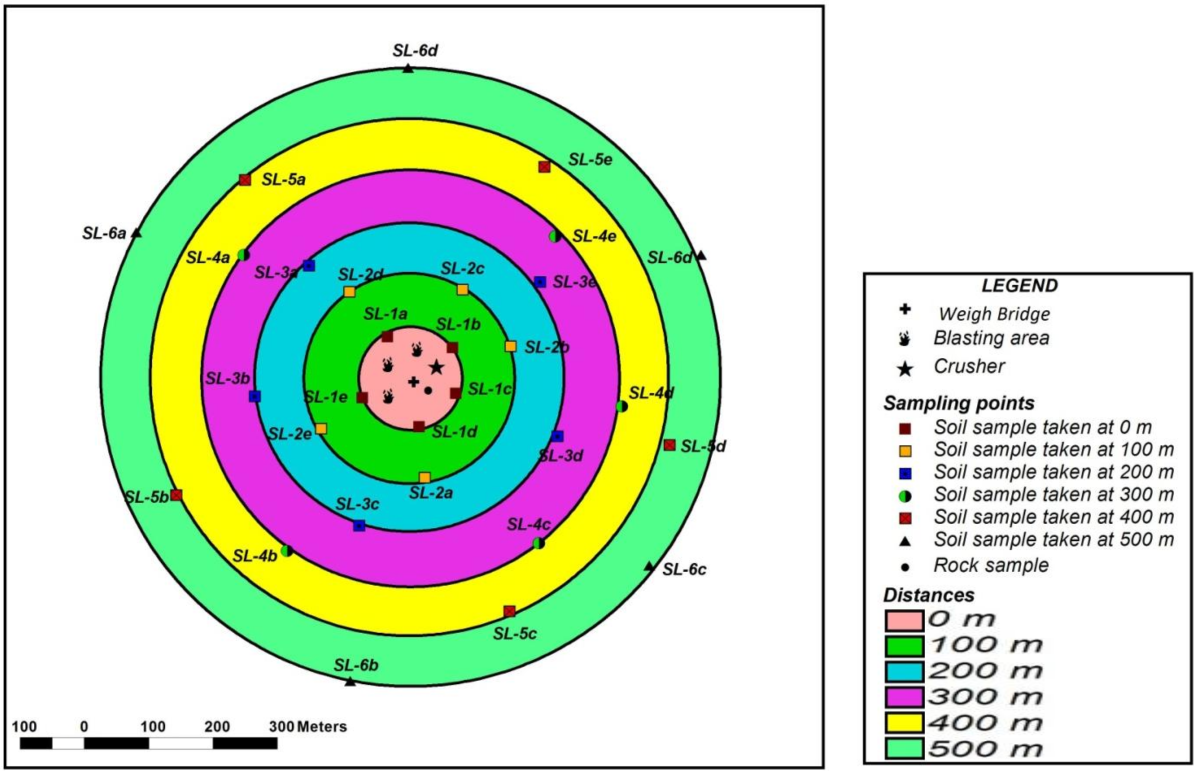

Figure 2. Map showing sampling points.

complex of geological setting characterised mainly by metamorphic rocks with few intrusion of granites and porphyrites. Generally, 75% of the rocks in the area are banded gneisses, while granite gneisses and quartzite share the remaining 25% (Oyewole, 1970). The quarry covers an area of 150 km^2 with a work-force of about 450 people (Interview with Quarry management, 2010). The quarry is surrounded with rural settlement, but there is evidence of urbanization as few modern residential buildings are springing up here and there within the vicinity of the quarry. Blasting operations are carried out once or twice a week depending on demand. The quarry site is characterized with blasting and crushing equipment, weigh bridge/loading station, limestone deposit, and heap of quarried limestone chippings.

Sampling design, collection, and preparation

A total of 30 topsoil samples (0 to 15 cm depth) were collected systematically ½ km from the crushing/blasting zone as shown in Figure 2. Five topsoil samples were obtained within the crushing/blasting arena and represented as samples at zero meter. Subsequent 5 topsoil samples each were collected within radii of 100, 200, 300, 400, and 500 m away from the crushing and blasting zone (Figure 2). All these samples added up to the 30 samples mentioned earlier. Samples at each point were collected randomly and combined to form composite samples. The average and standard deviation of each parameter determined in the 6 distances studied were denoted as SL-1 (0 m), SL-2 (100 m), SL-3 (200 m), SL-4 (300 m), SL-5 (400 m), and SL-6 (500 m). Five background topsoil samples were also collected from an undeveloped location about 10 km from the study area. Five limestone rock samples were also collected from different sections of deposit of quarried materials. A plastic hand trowel was used to scoop the samples and they were stored in polythene bags and transported to the laboratory immediately for pretreatment and analyses. Sampling implements and other work surfaces were always thoroughly cleaned between samples during sample preparations and analyses. All samples were safely transported to the laboratory and spread on a pre-cleaned surface. Soil samples were air-dried and grinded using agate mortar. They were sieved using nylon sieve with 0.5 mm mesh size.

Analyses of heavy metals and other soil properties

The pH of soil samples was determined by adopting the method by International Institute of Tropical Agriculture, Nigeria (IITA, 1979). The method involved taking the pH of 1:1 soil: deionized water extracts with a calibrated pH meter. Particle size analysis was done using the hydrometer method (IITA, 1979). Organic matter was determined in the soil samples according to Walkey and Black (1934) method. Ecologically significant fraction of all metals was leached by weighing 5.0 g of each sample into an acid washed bottle containing 50.0 ml of 2 M HNO$_3$. This setup was covered and placed in boiling water bath for 2 h. Intermittent agitation was carried out after every 20 min to make sure all soil particles were exposed to leaching solution. Each sample was cooled after 2 h and filtered with Whatman No 1 filter paper (Adie and Osibanjo, 2009; Andersson, 1976). Leachates from all samples were stored in plastic containers and kept in fridge (4°C) until metal analysis, using Buck Scientific (model 200A) atomic absorption spectrophotomer (AAS) using air acetylene flame at the optimal wavelengths of each metal. Standards used to calibrate the AAS were obtained as commercial BDH stock metal solutions from which working standards were prepared by appropriate dilution. The sequential extraction of metals on ten selected soil samples was determined

Table 1. Soil properties of topsoil samples within the vicinity of a limestone quarry.

Sample code	pH	Organic matter (%)	Sand (%)	Clay (%)	Silt (%)
SL-1	8.23 ± 0.75	1.01 ± 0.61	65.4 ± 2.68	13.6 ± 5.7	21.0 ± 4.8
SL-2	8.02 ± 1.03	0.97 ± 0.87	55.8 ± 23.3	9.62 ± 6.07	34.6 ± 23.1
SL-3	6.94 ± 0.79	2.77 ± 2.80	59.0 ± 23.2	12.4 ± 10.1	28.6 ± 7.6
SL-4	6.91 ± 0.38	3.00 ± 1.67	75.0 ± 6.69	8.43 ± 3.29	16.6 ± 4.8
SL-5	6.65 ± 0.79	2.46 ± 0.90	71.8 ± 16.6	10.1 ± 9.7	18.2 ± 7.1
SL-6	6.73 ± 0.60	4.84 ± 2.11	64.2 ± 17.1	9.65 ± 6.69	25.6 ± 14.3
Background	6.87 ± 0.35	3.31 ± 1.73	77.6 ± 4.2	5.05 ± 1.41	17.4 ± 2.8
RK	8.74 ± 0.52	na	na	na	na

na: Not applicable.

according to the popular Tessier et al. (1979) method and was analyzed with flame AAS. Blank samples (sample containing all reagents except the soil sample) were carried through all methods, analyzed and subtracted from the sample. This was done to check reagent and environmental interferences.

Risk assessment

Geoaccumulation index (I_{geo}) and Bray-Curtis similarity and distance index were used to assess the extent of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe pollution of topsoil within the vicinity of the study area. Geoaccumulation index (I_{geo}), first used by Muller in1969 is a tool that provides the extent of pollution of soil with regards to the background concentrations of the polluting metals. Geoaccumulation index is given mathematically as:

$$Geoaccumulation\,index\,(I_{geo}) = log_2\left[\frac{C_n}{1.5 \times B_n}\right]$$

where C_n is the average concentration of metal in the soil and B_n is the background concentration of the metal. The geoaccumulation index consists of six (6) descriptive classes is as shown in Table 3.

Bray-Curtis similarity and distance index were employed to established distance categorization and variability of the metal dataset. The distribution of data was tested with the analysis of variance (P = 0.05).

Correlation studies on heavy metals

Spearmen correlation was carried out to evaluate interelement association. The distribution of data was tested with the analysis of variance (P = 0.05). All statistical treatment mentioned earlier were performed using Microsoft Excel (2007 version) and Paleontological statistics software (PAST version 1.38).

Recovery studies

Analytical procedures used for analysis of metals were validated by conducting a spike recovery test on three soil samples with different concentrations of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe. Accurately, 5.0 g of triplicate soil samples previously analyzed for metals' content were spiked with metals' concentrations in such a manner that would make significant increment for each metal in the spiked sample. Samples were dried, grinded and taken through the same leaching procedure as unspiked samples. The filtered leachates were also analyzed for metals with flame AAS using air-acetylene flame. Percentage recovery was calculated as:

$$Recovery\,(\%) = \frac{Metal\ concentration\ \ in\ spiked\ sample}{metal\ concnetration\ \ in\ unspiked\ +amount\ \ spiked} \times 100$$

RESULTS AND DISCUSSION

Soil properties

The result of properties of topsoil samples within the vicinity of a major quarry in Nigeria is presented in Table 1. Average pH ranged from 6.65 to 8.23 for topsoil samples within a spherical span of ½ km away from the blasting and crushing area. The average pH of background soil was 6.87 ± 0.35, while that of the quarried limestone represented as RK in Table 1 was 8.74 ± 0.52. pH decreased with increase in distance from the blasting and crushing area. pH values of topsoil samples within 100 m from the exploration zone were comparable with RK, while pH values of soil samples farther than this distance were more alkaline. This indicates great influence from RK which is alkaline in nature. A sharp decrease in pH occurred in topsoil samples (200 m) and farther from the exploration arena and comparable with the background pH. This suggests lesser influence from RK. Generally, most metals do not exist in free form in the pH range of 6.0 to 9.0 (Porteus, 1985). The pH for all topsoil samples analyzed in this study fell within this pH range. It therefore implies that, there would be less leaching of metals from the topsoil towards subsoil and subsequently ground water as most of them would not be in solution.

The organic matter content of topsoil samples in the present study as shown in Table 1 ranged from 0.97 to 4.84% comparable with average of 3.31 ± 1.73% for background soil. Soil organic matter (SOM) is usually rich in humic materials with multiple functional groups. These functional groups have the ability to complex metals thereby retaining them in soil (Evans, 1989). Therefore, the higher the SOM content, the higher the ability of that soil to retain metals within it. The SOM was rather low in

Table 2. Average concentrations (mg/kg) of heavy metals in topsoil samples within the vicinity of a limestone quarry.

Sample code	Distance from crusher (meter)	Pb	Cd	Cr	Cu	Co	Mn	Ni	Zn	Fe
SL-1	0	19.6 ± 8.3	0.53 ± 0.30	17.4 ± 7.9	14.2 ± 8.5	23.5 ± 13.1	710 ± 424	13.5 ± 3.4	42.2 ± 7.8	13440 ± 1720
SL-2	100	11.8 ± 1.2	0.63 ± 0.33	9.25 ± 4.86	7.61 ± 5.03	9.83 ± 5.16	262 ± 155	11.0 ± 6.9	40.9 ± 18.7	14680 ± 4870
SL-3	200	27.7 ± 30.0	0.34 ± 0.18	17.2 ± 9.0	55.8 ± 86.8	13.0 ± 4.6	555 ± 251	17.4 ± 11.8	62.0 ± 65.2	17854 ± 10547
SL-4	300	13.5 ± 3.6	0.28 ± 0.11	7.98 ± 1.80	12.4 ± 12.3	13.6 ± 7.7	657 ± 370	6.34 ± 3.00	36.0 ± 19.4	6767 ± 1046
SL-5	400	11.9 ± 9.2	1.95 ± 0.96	6.94 ± 4.28	9.50 ± 11.2	8.93 ± 5.19	445 ± 257	6.73 ± 5.99	39.2 ± 52.6	6585 ± 6097
SL-6	500	11.5 ± 6.5	3.18 ± 3.43	12.1 ± 11.6	8.06 ± 4.36	11.5 ± 6.0	446 ± 278	10.5 ± 5.8	37.1 ± 17.3	7995 ± 4370
Background	Unpolluted	10.5 ± 4.3	0.55 ± 0.57	5.50 ± 1.24	3.81 ± 2.10	11.1 ± 2.7	637 ± 159	6.10 ± 2.30	24.4 ± 0.1	4563 ± 164
RK	-	8.13 ± 1.21	0.53 ± 0.24	9.45 ± 7.84	8.87 ± 1.64	10.4 ± 1.3	303 ± 15	13.4 ± 1.6	53.9 ± 15.2	18338 ± 1962

n = 5.

the present study for all soil samples suggesting lesser retention of metals within the soil.

The particle size analysis for all topsoil samples studied was in the order: 55.8 to 75.0% > 16.6 to 34.6% > 8.43 to 13.6% for sand, silt, and clay, respectively. These sizes compared with the background soil confirming that they were from the same geographical region and also indicating little or no interferences from the exploration activities. Soil high in sand retains fewer metals within it (Wenzel, 2005).

Metals in soil

The average concentrations of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe in topsoil samples within a depth of 0 to 15 cm from the study area are presented in Table 2. The concentrations of the various metals showed a wide range of variation with variable patterns in the order: Fe >>> Mn >> Zn > Cu > Pb > Co > Cr > Ni > Cd. There is no particular pattern in variation for each metal with increase in distance from the blasting and crushing area (Figure 2). This suggests that the dispersion of metals from the source could have been, majorly, by wind which disperses dust containing metals in all directions at different magnitude, space, and time. Samples between 0 to 200 m seem to show higher concentrations for most metals than samples farther away, probably because of their closeness to the exploration area and leaching of metals from quarry tailings which were found within this distance. Analysis of the quarry material (RK) showed conspicuously high level of Fe as compared to other metals investigated. Iron level in topsoil samples analyzed up to 500 m (Table 2) away from the crushing and blasting arena showed level almost in double fold when compared with the background level. The variation in the concentrations of Fe, Mn, Zn, and Cd in the Fe-rich RK (Table 2) showed similar inclination as concentrations in topsoil samples for all sampling points studied. The trend shown by these metals could be as a result of their high content in topsoil samples, possibly leached from RK or transferred by wind during blasting and crushing. Cd conspicuously indicated high levels at 100 and 500 m from the exploration area. It is thought that the source of Cd in these two sampling distances is a non point source. The soil particle size and organic matter content of topsoil samples in this study support leaching, but pH range of 6.65 to 8.23 for all soil samples suggests that most metals might not be free in solution (Porteus, 1985).

Speciation of metals in topsoil

Table 3 presents the result of speciation studies conducted on ten topsoil samples from a limestone quarry environment. Speciation studies of metals is a useful tool normally used to know the concentrations of pollutants in various fractions of soil, water and sediments samples. It gives an estimate of the amount of metals available to ecological materials. The amount of any metal concentration available depicts the toxicity level for that metal. In this study, the average bioavailable concentrations (exchangeable + carbonate bound + reducible + oxidizable) in percentage for all metals are shown in Table 3 in decreasing order as Ni (72.2%), Pb (68.2%), Cd (64.4%), Mn (59.8%), Cr (58.0%), Zn

Table 3. Average speciation (% in geochemical phases) of the heavy metals in topsoil samples.

Phase	Pb	Cd	Cr	Cu	Co	Mn	Ni	Zn	Fe
Exchangeable	21.9	14.7	9.28	2.89	0.21	1.67	11.9	2.67	5.94
Carbonate bound	8.99	14.7	8.40	1.27	18.5	30.5	11.9	13.5	4.15
Reducible	22.4	31.6	29.8	6.93	12.7	10.3	26.4	11.0	19.4
Oxidizable	14.9	3.35	10.5	13.3	6.52	17.2	22.0	19.7	15.3
Residual	31.8	35.6	42.0	75.6	62.0	40.3	27.9	53.2	55.2

Table 4. Geoaccumulation index (I_{geo}) of heavy metals in topsoil samples aroud a limestone quarry.

Sample code	Pb	Cd	Cr	Cu	Co	Mn	Ni	Zn	Fe
SL-1	0.31	-0.64	1.08	1.31	0.50	-0.43	0.57	0.20	0.97
SL-2	-0.42	-0.40	0.16	0.41	-0.76	-1.89	0.26	0.16	1.10
SL-3	-0.22	-1.32	1.06	3.28	-0.36	-0.79	0.93	0.76	1.38
SL-4	-0.22	-1.56	-0.04	1.12	-0.29	-0.54	-0.54	-0.03	-0.01
SL-5	-0.40	1.24	-0.25	0.73	-0.89	-1.09	-0.43	0.10	-0.06
SL-6	-0.45	1.94	0.56	0.19	-0.54	-1.09	0.20	0.01	0.23

Igeo is classified into six descriptive classes as follows: < 0 = practically uncontaminated; 0 to 1 = uncontaminated to slightly contaminated; 1 to 2 = moderately contaminated; 2 to 3 = moderately to strongly contaminated; 3 to 4 = strongly contaminated; 4 to 5 = strongly to very strongly contaminated; >5 = very strongly contaminated.

(46.9%), Fe (44.8%), Co (37.9%), and Cu (24.4%). Considering metal concentration in each fraction, residual phase showed the highest metal content of all metals studied possibly due to the sandy nature of topsoil. Metals largely reside in mineral lattice structures of sand resistant to acid digestion (McBride et al, 1997). There are also high percentage abundances of most metals studied in the reducible phase (Table 3). Metals in this fraction are bound to oxides of Fe and Mn in soil. It is well established that Fe and Mn oxides exist as nodules, concretions or cement between particles, or simply as coating on particles. These oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions, hence, changes of anoxic conditions of the soil will either influence the release or retention of elements in the reducible phase (Charlatchka and Cambier, 2000; Tessier et al., 1979). The high percentage abundances of metals in the reducible phase certainly is influenced by the high concentrations of Fe and Mn in the soil (Table 2). Onianwa (2001) also reported high Pb abundance in this phase in relation to the other phases.The percentage in the exchangeable phase indicates the level that is most easily available to ecological materials. Metals' percentage abundances in the exchangeable phase were Pb (21.9%) > Cd (14.7%) > Ni (11.9%) > Cr (9.28%) > Fe (5.94%) > Cu (2.89%) > Zn (2.67%) > Mn (1.67%) > Co (0.21%). This may not be unconnected with the pH of all the topsoil samples studied, which exist within 6.0 to 9.0. In this range, most metals are not in free form (Porteus, 1985). The low percentage abundances exhibited by some metals in the oxidizable phase (organic-bound phase) could be attributed to the low organic matter load of soil. Many of the metals studied have low abundances in the carbonate bound phase except Mn (30.5%) and Co (18.5%) which showed relatively high percentage abundances.

Risk assessment

Geoaccumulation accumulation index (I_{geo}) rating is presented in Table 4. Here, the content accepted as background is multiplied in each case by a factor (1.5) in order to account for natural fluctuations of a given metal in the environment and as well as small anthropogenic influences (Loska et al., 2003). Geoaccumulation accumulation index (I_{geo}) rating indicated that all topsoil samples analyzed ranged from practically uncontaminated (< 0) to moderately contaminated (1 to 2). All metals showed varying enrichment from the limestone exploration activities except Mn that showed I_{geo} of < 0 for all samples implying that all samples were practically uncontaminated by Mn. This suggests that Mn input in the soil is associated with the parent material that formed the soil or other natural or small anthropogenic non point sources. A similar spatial distribution of Ni in soils around an industrial facility in Mexico has been reported to be attributed to input from parental rocks in the surrounding (Morton-Bermea, 2010).

Table 5. Recovery studies.

S/N	Metal	Average percentage recovery
1	Pb	96.3 ± 4.18
2	Cd	90.4 ± 4.67
3	Cr	91.6 ± 7.22
4	Cu	99.5 ± 10.2
5	Co	93.9 ± 7.36
6	Ni	99.4 ± 8.93

n = 3.

Table 6. Soil quality criteria for some countries compared with present study.

Country/Definition	Pb	Cu	Cd	Cr	Co	Ni	Zn	Reference
Canada (industrial)	600	91	22	87	-	50		CCME (1999)
Canada (residential)	140	63	10	64	-	50		CCME (1999)
Canada (commercial)	260	91	22	87	-	50		CCME (1999)
Norway	50	100	1.0	100	-	30		Reimann et al. (1997)
Netherland (action level)	530	190	12	380	240	210		Reimann et al. (1997)
Switzerland (guide value)	50	50	0.8	-	-	-		FOEFL (1987)
EU limit (6≤ pH<7)	70	50	1	60	-	50	150	EU, Brussels (2000)
Present study (Mean)	16.0	17.9	1.15	11.8	13.4	10.9	42.9	Present study
Present study (Range)	11.5 - 27.7	8.06 - 55.8	0.28 - 1.95	6.94 - 17.4	8.93 - 23.5	6.34 - 17.4	36.0 - 62.0	Present study

Source: Onianwa, 2001.

Recovery studies

The result of the spike recovery test is presented in Table 5. The summary of the result is Pb (96.3 ± 4.18%), Cu (99.5 ± 10.2%), Cr (91.6 ± 7.22%), Cd (89.4 ± 4.67%), Co (93.9 ± 7.36%), and Ni (99.4 ± 8.93%). The percentage recoveries for some of the metals were within 100 ± 10% (Lena and Gade, 1997), a limit that demonstrates that the uncertainties in the methods of analyses used were within acceptable limits.

Soil quality criteria

The average levels for all metals studied were within the limits set by European Union (EU) and some countries as depicted in Table 6 except for Cd which exceeded EU, Norway, and Switzerland limits. The levels of metals in the present study demonstrate that there may be little or no potential toxicity risk posed from the exploration of limestone in this environment, however, as conditions become favourable (eg. more acidic pH, weathering of the rock, etc), the possibility of higher leaching potential of these metals from topsoil into subsoil and eventually into ground water could be experienced. Also, continuous piling up on topsoil of dust containing traces of these metals would at a point threaten the environment. The moderate contamination of topsoil depicted by I_{geo} rating as shown in Table 4 is a clear indication that the exploration activities is introducing some amount of metals unto the soil.

Table 7. Intermetal and sampling points association.

Parameter		Pb	Cd	Cr	Cu	Co	Mn	Ni	Zn	Fe
Spearman correlation	Pb	1	-	-	-	-	-	-	-	-
	Cd	-0.521	1	-	-	-	-	-	-	-
	Cr	0.820[a]	-0.241	1	-	-	-	-	-	-
	Cu	0.931[a]	-0.411	0.626[a]	1	-	-	-	-	-
	Co	0.427[a]	-0.380	0.695[a]	0.080	1	-	-	-	-
	Mn	0.467[a]	-0.358	0.462[a]	0.254	0.774[a]	1	-	-	-
	Ni	0.850[a]	-0.291	0.907[a]	0.766[a]	0.380[a]	0.121	1	-	-
	Zn	0.920[a]	-0.404	0.664[a]	0.968[a]	0.073	0.103	0.851[a]	1	-
	Fe	0.751[a]	-0.538	0.716[a]	0.681[a]	0.267	-0.068	0.909[a]	0.808[a]	1
		SL-1	**SL-2**	**SL-3**	**SL-4**	**SL-5**	**SL-6**			
Bray-Curtis similarity and distance index	SL-1	1	0.941	0.858	0.690	0.665	0.748	-	-	-
	SL-2	0.941	1	0.894	0.631	0.626	0.708	-	-	-
	SL-3	0.858	0.894	1	0.568	0.553	0.629	-	-	-
	SL-4	0.690	0.631	0.568	1	0.972	0.909	-	-	-
	SL-5	0.665	0.626	0.553	0.972	1	0.909	-	-	-
	SL-6	0.748	0.708	0.629	0.909	0.909	1	-	-	-

[a] Significant at $P < 0.05$.

Continuous monitoring of the top and sub soils is inevitable to always know the metals' levels.

Correlation studies

Table 7 shows the Spearman's correlation coefficient for all metals analyzed at 95% significance level and Bray-Curtis similarity and distance index. All the metals correlate positively at varying degrees except Cd and Mn that indicate negative correlation with most metals at 95% significance level. The moderate to strong positive correlation exhibited by most metals depict common origin. Correlation exhibited by Cd and Mn suggests input from a non point source.

The Bray-Curtis similarity and distance index (Table 7) showed that there were no significant differences in the metal distribution across the sample locations.

Conclusion

The input of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe in topsoil samples within the vicinity of a limestone quarry was investigated. The pH of the soil indicated that most of the metals would not exist in free form, while other soil properties like particle size and organic matter load support leaching of metals from the topsoil. All metals levels showed varying enrichment in topsoil samples investigated when compared with the background levels. Pollution statuses for all metals according to geoaccumulation index (I_{geo}) rating ranged from practically uncontaminated to moderately contaminated. It is thought that Mn is associated with parent material of soil as indicated by I_{geo} for all soil with a rating of < 0 denoting practically uncontaminated. Speciation studies indicated high percentage abundances in residual phase, because of high sand content. All metals were within regulatory limits, except Cd that exceeded when com-pared with some countries' limits. Continuous monitoring and control of the quarrying activities is important to check the metals' content which could pose threat soon with continuous piling up of dust on topsoil and leaching by acid rain (high CO_2, SO_2, and NO_X in the air).

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