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Article

Trace Metal Levels in Soils within an Abandoned Steel Industry Environment

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Abstract: Background concentrations of trace elements in soils are important due to recent interest in contamination potential and toxic effect of these elements on humans and the environment. Trace metals in soils within an abandoned steel industry environment were studied. Ten metals (Fe, Ni, Mn, Zn, Al, Co, Pb, Cd, Cr and Cu) were analyzed using Atomic Absorption Spectrophotometer (A.A.S). The findings revealed that the average concentrations of Fe, Ni, Mn, Zn, Al, Co, Pb, Cd, Cr and Cu in soil samples were 206.48±25.32 mg/kg, 24.01±5.11 mg/kg, 25.55±5.23 mg/kg, 69.71±17.12 mg/kg, 32.54±6.42 mg/kg, 7.72±3.68 mg/kg, 3.68±2.55 mg/kg, 7.50±2.62 mg/kg, 48.48±25.48 mg/kg and 92.67±28.57 mg/kg respectively. Levels of these trace metals in the industrial environment were generally higher than those in the control site, an indication that the activities of steel production and associated manufacturing processes which took place when the industry was operational, contributed to the observed higher levels of trace metals in the industry environment. This study aims at determining the levels of some trace metals in the soil and to ascertain the pollution status and the effect of trace metals in the environment.

Keywords: Trace metals, soils, environment, steel industry, pollution

1. Introduction

Soils vary across the landscape, therefore each soil contains unique trace element concentrations based on its parent material and other soil-forming factors that may have added or removed these elements from the soil. High background concentrations of trace elements, whether natural or anthropogenic, could result in mobilization and release into surface and subsurface waters and subsequent incorporation into the food chain. Soil factors such as organic matter, type and amount of clay, pH and cation exchange capacity (CEC) influence the quantity of trace elements available for mobilization and release or sorption in a soil. Several studies document gradual increases in the trace element contents of agricultural and forested soils due to waste applications (Berthelsen *et al.*, 1995; Chang *et al.*, 1984; McBride, 1995). While essential in small quantities for plant growth, micronutrients like copper (Cu), manganese (Mn), molybdenum (Mo), and zinc (Zn) can be toxic at high concentrations in the soil. Some elements not known to be essential to plant growth, such as arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and selenium (Se), also are toxic at high concentrations or under certain environmental conditions in the soil. The extent of soil pollution by heavy metals and base metal ions some of which are soil micronutrients is very alarming. It has been observed that the larger the urban area, the lower the quality of the environment.

Steel is an alloy that contains more than 50% of iron and 0.03-1.5% of carbon and to obtain the properties described for different purposes, other metals are usually added (Umland and Bellama, 1996). Some of these metals include; Manganese, Zinc, Nickel, Chromium, Tin, Tungsten, and Vanadium. Manganese is the only metal without any substitute that is used as a deoxidizing and desulfuring agent in the manufacture of steel. Zinc is used in galvanizing steel to give a protective coating against corrosion. Nickel is used in making stainless steel and high temperature alloys of steel. Chromium is used also for making stainless steel. Tin is used in protective coating for steel and tungsten is used to produce very tough steel (Leet *et al., 1982*). Vanadium used in the manufacture of steel makes the metal more ductile and resistant to shock (Anusiem, 2000). These metals can be accumulated in the soil through waste from steel production. According to Udosen *et al.*, (1990), heavy metals in soils are associated with geometrical cycles and biological processes and could be greatly influenced by industrial activities.

Plants in turn are capable of absorbing these metals from the soil (Kalulu and Abdullahi, 2004). These metals could be leached into the soil when they undergo chemical reactions and could come in direct contact with roots of plants (Udosen, 1991). When these plants in the form of vegetables, are eaten by man, trace metals become bioaccumulated and eventually result in several ailments which may subsequently end up in death (Odiette, 1999; Udosen, 1998). Plants can accumulate some of these metals which are not injurious to them, but may be poisonous to animals grazing on the plants (Raven and Evert, 1976). The iron-steel industry was of concern because of its location close to where rural populace farm. The distant of the steel industry to the water source of the community is worrisome.

Apart from the building and cemented areas, all other areas in the abandoned steel industry are now used for agricultural purposes. Some of the wastes emanating from steel production are spread over some parts of the environment particularly on water-logged soil. Trace metals present in the waste may therefore accumulate in the soil environment. Hence, the soils in this environment are presumed to be polluted with trace metals. This study is therefore to assess the trace metal levels in soil within the abandoned steel industry environment. Again, heavy metals discharged into our environment including their distribution, reaction in the ecosystem and subsequent uptake and distribution in soils are of great concern for human health, (Udosen *et al.,* 2007). Specifically, the aims of the study are: (i) to determine the levels of some trace metals in soil within the abandoned steel company environment (ii) to ascertain the pollution status and the effect of the trace metals in the environment. (iii) to recommend some remedies to the pollution problem of the environment.

2. Materials and Methods

2.1. Study Area

Qua-Steel Industry Limited was one of the major Steel producing industries in the South-South zone of Nigeria located along Ibeno road in Eket Local Government Area of Akwa Ibom State. The industry was commissioned in 1978, and was known for the production of steel and also for other manufacturing businesses. The major raw material used by this steel industry was steel billets. Some of the wastes generated by this industry were spread in some parts of the environment to check water-logging within the premises. Because of the lack of raw materials due to the closure of Delta Steel Company (DSC) Aladja – Warri in June 1996, as a result of the non-functionality of the major plants and machineries in the industry, Qua-Steel products Limited was closed down in 1996 and has remained abandoned till now. The premises of the abandoned industry are now used for agricultural purposes.

2.2. Sample Collection

Soil sampling was carried out by collecting portions of soil using a soil auger of length 15 cm at each location. The samples were put into polyethylene bags, labeled and taken to the laboratory for pre-treatment and analysis. Sampling was carried out within this environment from three different locations for three consecutive months (September to November). Soils samples were collected in triplicate from each location. Control samples were also collected about 10 km away from the industry. The description of samples is listed in table 1 below.

Table 1. Description of samples

Symbol	Description
SA 1	First soil sample at location A
SA 2	Second soil sample at location A
SA 3	Third soil sample at location B
SB 1	First soil sample at location B
SB 2	Second soil sample at location B
SB 3	Third soil sample at location B
SC 1	First soil sample at location C
SC 2	Second soil sample at location C
SC 3	Third soil sample at location C
SCLT 1	First soil sample at control site
SCLT 2	Second soil sample at control site
SA	Average soil sample at location A
SB	Average soil sample at location B
SC	Average soil sample at location C
SCLT	Average soil sample at control site

2.3. Sample Treatment and Analysis

All soil samples were air-dried at ambient laboratory temperature. Soil samples were ground using mortar and pestle and sieved to pass through 2 mm sieve and stored for chemical analysis. Each soil sample (2 g) was placed in a Teflon beaker and digestion was carried out using concentrated nitric (10 cm^3) and concentrated perchloric (5 cm^3) acids in the ratio of 2:1. This was allowed to cool before leaching the residue with 5 cm^3 of 20% HNO_3. Digested samples were filtered and made up to 50 cm^3 with deionized water. A blank determination was treated in the same method but without sample. Solution of samples were then taken and aspirated into Atomic Adsorption Spectrophotometer (Unicam Solaar A.A.S 969 model) for analyzing metals. Blank determination was also carried out as in a similar way as described above except for the omission of the sample. A calibration graph was plotted for each element using measured absorbance and the corresponding concentration. The calibration curve was used to determine the concentration of the metal.

3. Results and Discussion

3.1. Results

The analysis results of samples collected in different time are shown in tables 2-4 below. Table 5 shows the mean values of the concentration of metals.

Table 2: Concentrations of metals in soil samples obtained from Qua-Steel Industry environment and control site (mg/kg) in September.

Sample ID	Fe	Ni	Mn	Zn	Al	Co	Pb	Cd	Cr	Cu
SA 1	200.80	19.64	32.88	57.01	39.57	12.02	3.51	8.88	78.00	111.81
SA 2	233.32	26.86	36.77	52.46	37.22	12.41	2.96	7.46	74.64	119.93
SA 3	199.53	20.70	22.29	54.26	41.63	10.86	5.64	7.79	76.19	96.74
SB 1	237.42	33.45	33.83	88.78	31.94	4.09	0.28	4.23	43.52	113.72
SB 2	228.74	30.64	31.91	92.94	29.60	4.92	0.06	5.01	38.63	115.01
SB 3	221.13	25.14	25.36	83.17	32.55	4.70	2.58	4.73	50.84	97.75
SC 1	181.00	20.73	18.54	67.51	25.54	7.31	8.50	11.20	27.52	89.34
SC 2	182.10	22.71	26.21	64.71	26.90	6.75	2.63	8.22	24.17	95.24
SC 3	174.25	16.25	16.01	66.54	27.95	6.40	7.04	10.10	26.06	75.47
SCTL 1	51.11	4.20	5.33	25.61	16.67	2.62	0.03	2.74	16.45	35.22
SCTL 2	53.17	2.55	8.23	24.77	12.42	2.36	0.02	2.62	11.15	27.14

Table 3: Concentrations of metals in soil samples obtained from Qua-Steel Industry environment and control site (mg/kg) in October

Sample ID	Fe	Ni	Mn	Zn	Al	Co	Pb	Cd	Cr	Cu
SA 1	200.81	19.63	32.85	57.02	39.56	12.01	3.50	8.87	78.01	111.80
SA 2	233.30	26.85	36.79	52.48	37.23	12.43	2.94	7.45	74.66	119.95
SA 3	199.54	20.71	22.30	54.24	41.63	10.85	5.67	7.79	76.16	96.73
SB 1	237.40	33.46	33.84	88.79	31.93	4.11	0.30	4.24	43.54	113.72
SB 2	228.75	30.65	31.90	92.92	29.62	4.93	0.04	5.00	38.63	115.03
SB 3	221.14	25.12	25.37	83.18	32.54	4.68	2.57	4.73	50.82	97.73
SC 1	180.01	20.73	18.56	67.49	25.55	7.30	8.51	11.18	27.50	89.33
SC 2	183.10	22.70	26.20	64.69	26.98	6.75	2.63	8.24	24.16	95.26
SC 3	174.24	16.26	15.99	66.52	27.95	6.42	7.04	10.08	26.09	75.45
SCTL 1	50.10	4.18	5.32	25.60	16.69	2.64	0.02	2.75	16.45	35.20
SCTL 2	54.18	2.57	8.24	24.78	12.40	2.34	0.03	2.61	11.15	27.16

Table 4: Concentrations of metal in soil samples obtained from Qua-Steel Industry environment and control site (mg/kg) in November

Sample ID	Fe	Ni	Mn	Zn	Al	Co	Pb	Cd	Cr	Cu
SA 1	200.83	19.65	32.87	57.03	39.58	12.03	3.52	8.89	78.01	111.82
SA 2	233.31	26.86	36.78	52.47	37.22	12.42	2.95	7.45	74.65	119.94
SA 3	199.51	20.69	22.29	54.25	41.62	10.84	5.64	7.78	76.17	96.72
SB 1	237.51	33.47	33.85	88.80	31.95	4.10	0.29	4.24	43.53	113.73
SB 2	228.76	30.66	31.89	92.93	29.61	4.93	0.05	5.02	38.64	115.02
SB 3	221.10	25.10	25.36	83.16	32.53	4.69	2.58	4.71	50.82	97.73
SC 1	180.00	20.74	18.55	67.50	25.56	7.32	8.52	11.19	27.51	89.35
SC 2	183.09	22.72	26.20	64.70	26.89	6.74	2.61	8.23	24.17	95.25
SC 3	174.26	16.23	16.00	66.56	27.96	6.41	7.05	10.08	26.07	75.45
SCTL 1	50.12	4.19	5.34	25.62	16.68	2.63	0.03	2.76	16.47	35.21
SCTL 2	54.16	2.56	8.22	24.76	12.41	2.35	0.02	2.60	11.13	27.15

Table 5: Mean concentrations of Fe, Ni, Mn, Zn, Al, Co, Pb, Cd, Cr and Cu in soil samples obtained from Qua-Steel Industry Environment and control site (Mg/Kg).

Sample	Fe	Ni	Mn	Zn	Al	Co	Pb	Cd	Cr	Cu
1	211.22 ±16.78	22.40 ±3.37	30.65 ±6.49	54.58± 1.99	39.47± 1.91	11.76 ±0.71	4.04± 1.23	8.04± 0.65	76.28± 1.46	109.49± 10.20
2	229.10 ±7.06	29.74 ±3.67	30.37 ±3.85	88.30± 4.24	31.36± 1.34	4.57± 0.37	0.97± 1.21	4.66± 0.34	44.33± 5.32	108.83± 8.34
3	179.12 ±3.82	19.90 ±2.27	20.25 ±4.60	66.25± 1.23	26.80± 1.04	6.82± 0.39	6.06± 2.65	9.80± 1.30	25.92± 1.45	86.68±8.80
Control	52.14± 1.93	3.38 ±0.89	6.78± 1.59	25.19± 0.46	14.55± 2.34	2.49± 0.15	0.03± 0.00	2.68± 0.08	13.80± 2.90	31.18±4.41
Mean	206.48	24.01	25.55	69.71	32.54	7.72	3.68	7.50	48.84	92.67
S. D	25.32	5.11	5.23	17.12	6.42	3.68	2.55	2.61	25.48	28.57
C. V (%)	12.26	21.28	20.47	24.56	19.73	47.67	69.29	34.80	52.17	30.83

S. D - Standard Deviation
C. V – Coefficient of Variation

Table 6: Correlation Matrix between Heavy Metals in soil samples from Qua-Steel Industry environment (r at $p < 0.05$)

	Fe	Ni	Mn	Zn	Al	Co	Pb	Cd	Cr	Cu
Fe	1.000									
Ni	0.905	1.000								
Mn	0.927	0.679	1.000							
Zn	0.511	0.828	0.152	1.000						
Al	0.502	0.086	0.790	-0.487	1.000					
Co	-0.148	-0.554	0.234	-0.925	0.781	1.000				
Pb	-0.960	-0.988	-0.785	-0.732	-0.240	0.419	1.000			
Cd	-0.942	-0.995	-0.747	-0.770	-0.182	0.471	0.998	1.000		
Cr	0.588	0.093	0.794	-0.481	1.000	0.777	-0.246	-0.188	1.000	
Cu	0.931	0.688	1.000	0.1040	0.782	0.222	-0.792	-0.755	0.786	1.000

Source: Udosen et al., (2012)

3.2. Discussion

The concentrations of metals in soils at the abandoned steel industry environment and the control site indicate that there is an evidence of relative increase in the concentrations of trace metals in soils at the abandoned steel industry environment compared to the control site. The metals considered in this study include the metals which are micronutrients such as iron and zinc, and the non-essential/toxic trace metals which are toxic to plant when present in the soil at concentrations above tolerance level. The latter class of trace metals includes lead and nickel. Based on the results (Table 5), there was a significant difference between the concentrations of all the metals at the abandoned steel environment and the control site in all the samples (Udosen et al., 2012).

The mean level of Fe in the soil from all the locations of the study area was 206±25.32 mg/kg. Of all the metals analyzed in this study, Fe showed the highest concentration. This could be attributed to the fact that Fe was the major raw material used in the manufacture of steel, as observed by Joesten et al., (1991) that steel is an alloy of Fe. The low coefficient of variation of Fe in the soil samples, 12.26% shows that this metal is stable and will be present in this environment for a long time. Although Fe is not generally considered as soil pollutant because of its high background levels (Huamain et al., 1999) the relatively high concentration of Fe observed in the soil samples from this study area calls for concern.

The natural range for the concentration of nickel in soil is 10-1000 mg/kg (Vecera et al., 1999). The mean level of nickel in the soil samples was 24.01±5.11 mg/kg. This value is within the natural limit of nickel in soil. Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts, nickel can become mildly toxic. Ingestion of nickel may cause hyperglyanemia, depression of the central nervous system and kidney damage (Vincoli, 1995). The presence of nicked in this study area might be due to its use in the steel industry in making stainless steel and high temperature alloys of steel.

The permissible range for the concentration of manganese in soil is 100-4,000 mg/kg (Vecera et al., 1999). At the abandoned steel industry environment, the mean level of Mn in the soil samples was 25.55±5.23 mg/kg and 6.78±1.59 mg/kg at the control site. These values are within the permissible limit. The presence of Mn in this environment might be as a result of its use in the steel industry as it is the only metal without any substitute that is used as a deoxidizing and desulfuring agent in the manufacture of steel (Lee et al., 1982). Exposure to manganese has been indicated to cause lack of control of the bladder (Ayodele and Gaya, 1998) and transient psychiatric disturbances, among other effects (Nelson et al., 1993).

The natural range for the concentration of zinc in soil is 10-300 mg/kg (Vecera et al., 1999). The mean level of Zn in soil samples of the study area (69.71±17.12 mg/kg) was higher than the level of Zn at the control site (25.19±0.46 mg/kg). These values are within the permissible limit of Zn in soil. The high level of Zn observed in this environment than in the control site might be due to the use of Zn in galvanizing steel (Lee et al., 1982). Zinc although being an essential trace element in low concentration, is toxic in high concentration (Oborn et al., 2005). Ingestion of Zinc in excess of 12 mg per day may cause lung disturbance (Eka and Udotong, 2003). Apart from the use of zinc in galvanizing steel, its use as an additive in lubricating oil (Ayodele and Gaya, 1998) may also be responsible for the observed level of Zn in this environment.

The mean level of Al in the soil samples of this study area was 32.54±6.42 mg/kg. The low coefficient of variation of aluminum (19.73 mg/kg) in the soil shows that Al will persist in this environment. Exposure to high concentrations of Al through repeated inhalation may result in aluminosis or lung fibrosis. Other hazards associated with exposure to Al are accumulation of aluminum particles in the kidney and Alzheimer's disease (Vincoli, 1995).

The mean concentrations of cobalt in the study area and in the control site were found to be 7.72±3.68 and 2.49±0.15 mg/kg respectively. These values were within the permissible natural limit of cobalt in soil (1-40 mg/kg) (Vecera et al., 1999). Exposure to Co may cause dermatitis and diseases of the blood cell (Avila, 1992).

The mean concentrations of lead in both the soil samples (3.68±2.55 mg/kg) and the control site (0.03±0.00 mg/kg) were within the permissible limit of lead in soil (2-200 mg/kg). the presence of lead in this environment may have been due to automobile emission and industrial emission (Joesten et al., 1991). Chronic exposure to lead can lead to chronic lead poisoning, which will result in memory loss and restlessness. Lead has been found to inhibit enzymatic activity (Vincoli, 1995). The pollution of soil by lead is a serious problem that has been given much attention by environmental chemists. This is due to the fact lead is a cumulative pollutant (Dara, 1993) and the continuous disposal of lead containing waste into the environment should be discouraged.

The natural permissible limit of cadmium in soil is 0.01 to 3.00 mg/kg. The mean concentration of cadmium in the soil samples of the study area (7.5±2.61 mg/kg) is higher than the permissible limit of cadmium in soil. The soil is therefore considered to be polluted by cadmium. Exposure to high cadmium levels may result in disease known as osteoporosis (Akesson et al., 2006). Cadmium is regarded as the most hazardous trace element and its poisoning causes damage to kidney and heart and prolonged exposure results in loss of calcium from the bone (Udoessien, 2003). Cadmium derives its toxicological properties from its chemical similarity to zinc, an essential micronutrient for plants, animals and humans.

The mean concentrations of chromium in both the soil samples (48.84±25.48 mg/kg) and the control site (13.80±2.90 mg/kg) are within the permissible range of chromium in soil (5-3000 mg/kg) (Vecera et al., 1999). The high level of chromium in the abandoned steel environment compared to the control site is largely due to its use in the industry in making stainless steel when the industry was operational. Dudka and Andiano (1997) reported high concentrations of chromium (30-4560 mg/kg) in soil from chromium smelting industry in Japan. Exposure to chromium has been found to cause dermatitis (Ayodele and Gaya, 1998), perforation of nasal septa and kidney damage among other diseases (Vincoli, 1995).

The permissible natural range of copper in soil is 2-100 mg/kg (Vecera et al., 1999). The mean concentrations of copper in both the soil samples and the control site are 92.67±28.57 and 31.18±4.41 mg/kg respectively. The high level of copper in the study area compared to the control site could be as a result of the activities of the steel industry when the industry was operational. High amount of copper in an environment as indicated in this study area might be toxic to man and other organisms. Raven and Evert (1976) observed that high concentration of copper is toxic to plants. Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Excess of copper in the body has been found to cause Wilson's disease (Moore et al., 2005).

A correlation study between the metals in the soil samples studied is shown in Table 6. From the result, some metals were strongly correlated while some showed negative correlation. For example, there were strong correlations between Fe and Ni ($r=0.905$ $p,<0.05$), Fe and Mn ($r=0.927$, $p<0.05$), Fe and Zn ($r=0.511$, $p<0.05$), Fe and Cu ($r=0.931$, $p<0.05$), Ni and Zn ($r=0.828$, $p<0.05$), Ni and Mn ($r=0.679$, $p<0.05$). Among the pairs of metals that were negatively correlated were Fe and Pb (r= -

0.960, $p<0.05$), Ni and Pb ($r= -0.988$, $p<0.05$), Cd and Cu ($r= -0.755$, $p<0.05$), Mn and Pb ($r= -0.747$, $p<0.05$).

4. Conclusion

The concentrations of trace metals were observed to be higher in soils at the abandoned steel industry environment compared to the control site. This implies that the activities that took place when the steel industry was operational have a significant impact on the environment. The levels of trace metals obtained in this environment may affect human health since the crops grown in this environment are continuously consumed. Thus, there is need for bioremediation of this environment and the suspension of all agricultural activities in this environment to avoid transmission of these metals to man through the food chain.

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