ENVIRONMENTAL TOXICANTS IN SOILS AND WATERS OF SELECTED INDUSTRIAL AREAS IN NIGERIA.

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Abstract— *Soil and water samples were taken from different industrial locations typically polluted by environmental toxicants in Nigeria to study the presence of environmental toxicants, human exposure and their health effects on man, plant and animals. Soil analyses for colour, compaction, moisture and pH profile as well as water conductivity chloride, hardness, chemical oxygen demand, phosphate, alkalinity, sulphate, and potentially harmful elements (Ni, Zn, Pb, Fe, Cr, Cu, Mn, Ba, As, Co and Se) were carried out using the Atomic Absorption Spectrophotometry (AAS), Association of Officials of Analytical Chemists (AOAC). Bacteriological analysis for the presence of Escherichia coli and infrared detection of carbon hydrogen, oxygen, nitrogen and sulphur were also studied. Results showed the water and soil pH range of 3.08 to 3.80 and may be unsuitable for planting as against pH of 5.5 to 7.0 that can support plant growth. The levels of zinc (0.59 mg kg−1); Ni (0.24 mg kg−1); Se (0.9 mg kg−1) and lead (0.15 to 0.91 mg kg−1) dissolution into the water and soil samples were similarly observed with the lead permissible dose varies between 0.05 to 0.51 mg kg−1. The analysis describes the percentage of both positive and negative effects of these chemicals as 55.3% and 45.94%, respectively. Apart from the higher acidic content above permissible levels of some trace metals in all samples, the microbiological presence of Escherichia coli bacteria in all the samples can only serves as potential dangers to human health.*

Keywords— *"environment", "pollution", "toxicant", "health", "bacteria"*

I. Introduction

In developing countries, the heavy health risk due to the exposures to environmental pollution is usually higher where lack of investment in trendy technology, weak environmental legislation combines with impoverishment to cause high pollution levels. Association between environmental pollution and health outcome are however, complex and often poorly characterized. Levels of exposure, for example are often uncertain or unknown as a result of the lack of detailed monitoring and inevitable variations within any population group. Exposures may occur via a range of pathways and exposure processes [1]. Individual pollutants maybe implicated in a wide range of health effects, whereas few diseases are directly attributable to single pollutants [2] - [4]. Long latency times, the effects of cumulative exposures, and multiple exposures to different pollutants which might act synergistically all create difficulties in unravelling associations between environmental pollution and health [5]. About 8-9% of the total disease burden maybe attributed to pollution but considerably more in developing countries unsafe water, poor sanitation and poor hygiene are seen to be the major sources of exposure, along with indoor air pollution [6], [7].

Despite the major efforts that have been made over recent years to clean up the environment, pollution remains a major problem and poses continuing risks to health [8]. The problems are undoubtedly greatest in the developing world where traditional sources of pollution such as industrial emissions poor sanitation, inadequate waste management, contaminated water supplies and exposures to indoor air pollution from biomass fuels affect large numbers of people however, and environmental pollution persists most especially amongst poorer sectors of society [9] - [11]. The need to address the health risk associated with environmental pollution and check becomes more urgent; thus brought the objective of this work as human beings become the victims of various water borne diseases such as typhoid, cholera, dysentery, hepatitis, jaundice etc. The presence of acids/alkalis in water destroys the microorganisms thereby hindering the self-purification process in the rivers or water bodies; agriculture is affected badly due to polluted water. Poisonous industrial wastes are present in water bodies thus affect the quality of underground water for drinking, phytoplankton and animals living in fresh water [12].

The degree of toxicity can vary depending on where the organism is found within its food web. Bio-accumulation occurs when molecular compounds are stored in an organism's fatty tissues over time, this leads to the establishment of a trophic cascade and the bio magnifications of specific toxicants. Bio-degradation releases CO_2 and water as by-products into the environment. This process is typically limited in areas affected by environmental toxicants but the harmful effects of chemical and biological agents can include toxicants from pollutants, insecticides, pesticides and fertilizers, all of which can impact an organism and its community through shifts in species diversity and abundance [13].

In this study, it is our hope to investigate the relationship between the available trace elements and soil/water environment in selected industrial densely populated areas to further provide exposure data on possible land utilisation, remediation, management and likely health issues that trace elements may pose.

II. Materials and Method

A. Study area.

The studies were carried out around industrial areas of Kwara, Delta and Lagos States of Nigeria particularly around industrial sites of Global Soap and Detergent, Kamwire Industrial Limited and Olak Industrial limited, Olayiwola Pharmacy, Nestle Oregun, Kwara Chemicals, PZ Plc Ikeja, Petro Chemical Carbon, Haffertestile, Delta Steel, Inocome Phactory, Challeran Plc, Warri Refinery, Kam Industry, Pepsi Bottling Company, Nigeria Gas and Tuyil Pharmaceutical.

B. Sample collection

During systematic sampling for sample collection, the collections were done very early in the morning for water and soil to avoid human interference. Soil and well water samples were collected every two months for each of the sampling sites between October, 2019 and March, 2020. The pH measurements were taken on both samples at the points of collection. The soil profiles were excavated using a wooden spatula and a spade to trim the soil layer by layer. The soil samples were naturally air dried and sieved soil particles (< 2 mm) in the laboratory for analysis. The samples were packed in an air tight container to avoid further contaminations.

C. Sample preparation

1) *Chemicals and Reagents;* All chemicals solvents used were of analytical reagent grade or the highest purity available. Doubly distilled de-ionized water, which is non-absorbent under ultraviolet radiation, was used throughout. Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$, followed by washing with concentrated HNO_3 and rinsed several times with de-ionized water.

2) *Acid digestion;* An air-dried homogenized soil sample (100 g) was weighed accurately and placed in a 100 mL Micro-Kjeldahl flask. The sample was digested in the presence of oxidizing agent using Association of Officials of Analytical Chemists method [14]. The content of the flask was filtered through a Whatman No. 42 filter paper into a 25 mL calibrated flask and neutralized with dilute HNO3 solution. It was then diluted up to the mark with de-ionized water. Suitable aliquots (1–2 mL) were transferred into a 10 mL calibrated flask. The iron content was then determined using EDTA as a masking agent.

3) *Water analysis;* Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottles containing 1 mL of concentrated nitric acid. A 1000 mL stock solution (1000 mg mL−1) of Iron was prepared by dissolving 1.0 g of Fe. (purity 99.999%) in aqua regia by warming, evaporating the solution to dryness, dissolving the residue in hydrochloric acid, evaporating the solution to half its volume, cooling and diluting with water to 1000 mL in calibrated flask [17]. Working solutions were prepared by appropriate dilution of standard solution.

4) *Instrumental analysis;* A series of standard solutions of a neutral aqueous solution containing 0.1–300 µg of each elements in a 10 mL calibrated flask was mixed with 10–25-fold molar excess of the BSOPD solution (preferably 1.0 mL of 3.16 × 10−4 M) BSOPD reagent, 1–3.5 mL (preferably 2 mL) of 10% TX-100 solution, 0.5–1.2 mL (preferably 0.5 mL) of 4 M H_2SO4. The mixture was diluted to the mark with de-ionized water. Using Atomic Absorption Spectrometry (AAS), after standing for 10 min the absorbance was measured at 490 nm against a corresponding reagent blank. The iron content in samples was determined using a concurrently prepared calibration graph

5) *Data processing/analysis;* The one-way Analysis of Variance (ANOVA), SPSS 17 used to evaluate data with the Software StatSoft, Inc. (USA). Differences at $p<0.05$ were considered significant.

III. Results and Discussion

Soil analysis for pH, moisture, colour, soil structure, compaction and texture as well as water parameters such as pH, conductivity, chloride, hardness, chemical oxygen demand (COD), phosphate, alkalinity, sulphate, mineral contents (Ni, Zn, Pb, Fe, Cr, Cu, Mn, Ba, As, Co and Se) and bacteriological analysis were carried out. Infrared detection of carbon hydrogen, oxygen, nitrogen and sulphur were also detected using the Atomic Absorption Spectrophotometry (AAS), Association of Officials of Analytical Chemists [14] at the Prof. Julius Okojie Central Research Laboratory, Federal University of Technology, FUTA, Akure, Nigeria.

Observations showed that human exposure to industrial toxics waste were enormous which may pose danger on human health. The results obtained from samples from different area showed that the level at which the toxicity and pollutant content in surface and underground waters and soils in those areas can pose danger to the health of the people that lives around those places. Raymond and Felix (2011) reported the heavy metals in the metal contaminated soils and the permissible dose as shown in Table I

TABLE 1
SOIL CONCENTRATION RANGES AND REGULATORY GUIDELINES FOR SOME HEAVY METALS [15]

Metals	Soil concentration range (mg kg^{-1})	Regulatory limits
Pb	1.00–69 000	600
Cd	0.10–345	600
Cr	0.05–3 950	100
Hg	<0.01–1 800	270
Zn	150–5 000	1500

Lead (Pb) – absorption of lead into the body produces greater degree of anaemia as well as decreasing of metallic enzymes activities (Khalid et al., 2019). Also causes intestinal tract infection. zinc (Zn) - there could be kidney and stomach damages, skin burning, itching and tingling selenium (Se) could cause nail changes loss of energy and irritability at every time on the victim. Nickel (Ni) – exposition of body to nickel by inhalation can lead to asthma attacks, this is commonly found among the villagers that consume stream/river water from other works. Other macro nutrients elements such as iron (Fe), magnesium (Mg), calcium (Ca) and others must be consume at a permissible dosage to avoid negative effect or contradictions from trace elements. The dissolution of these trace metals is above the permissible dose the well water around the industrial area are dangerous to human health as it poses a great danger [10], [16].

Lar [16] also reported the trace elements with the health and environmental risk in Nigeria. Also, Raymond and Felix [15] reviewed the sources, chemistry, risks and best available strategies for remediation heavy metals in contaminated soils and suggested remediation of heavy metal contaminated soils to reduce the associated risks for agricultural production, and enhance food security. Table II show the concentrations of lead, chromium, arsenic, zinc, cadmium, copper, mercury and nickel etc that were commonly found in contaminated soils and the results compare with the levels of heavy metals in wastewater and soil samples found in past findings [15], [16]. In Table III and IV, the microbiological results showed that different bacterial were isolated from the water samples to ascertain the types of bacterial that were present in the water which serves as potential dangers to human health such as Escherichia coli (E. coli) [17], [18].

TABLE II
CONCENTRATION OF METALS (mg/L) IN WATER (WAI – WA15) AND SOIL (mg/Kg) SAMPLES (X1 – X13)

Sample	Ni	Zn	Pb	Fe	Cr	Cu	Cd	Mn	Ba	As	Co	Se
WA1	0.02	0.62	0.11	1.50	ND	0.06	ND	0.03	20.00	ND	0.02	0.59
WA2	0.04	0.33	0.03	0.96	ND	0.07	ND	0.04	16.30	ND	0.01	0.62
WA3	0.07	0.23	0.06	0.38	ND	0.03	ND	0.03	18.00	ND	0.02	0.84
WA4	0.06	0.22	0.15	0.41	ND	ND	ND	0.06	21.60	ND	0.01	0.50
WA5	0.09	0.11	0.02	0.52	ND	ND	ND	0.06	29.70	ND	0.01	0.91
WA6	0.10	0.24	ND	1.54	ND	ND	ND	0.11	18.40	ND	0.02	0.88
WA7	0.09	0.25	ND	0.28	0.08	0.14	ND	0.07	19.60	ND	ND	0.74
WA8	0.12	0.37	ND	0.61	ND	ND	ND	0.12	24.00	ND	ND	0.54
WA9	0.18	0.59	ND	1.32	ND	ND	0.01	0.14	22.30	ND	0.01	0.51
WA11	0.24	0.53	ND	1.66	ND	0.05	ND	0.17	25.70	ND	ND	0.83
WA12	0.05	0.34	ND	0.30	ND	0.02	ND	0.06	13.80	ND	ND	0.65
WA13A	0.10	0.11	ND	0.40	ND	0.01	ND	0.05	12.20	ND	ND	0.65
WA13B	0.12	0.29	ND	0.64	ND	0.01	ND	0.03	17.40	ND	0.01	0.51
WA14	0.13	0.49	ND	0.53	0.02	ND	ND	0.09	16.90	ND	ND	0.55
WA15	0.13	0.40	0.08	0.91	ND	0.01	0.01	0.17	30.20	ND	ND	0.65
X1	3.76	457.00	1.00	254.00	0.10	2.08	0.02	1.21	21.20	0.01	0.14	ND
X2	0.78	48.00	5.98	272.00	0.05	0.32	0.01	2.34	29.40	0.01	0.10	0.61
X3	4.36	1.00	0.49	144.00	ND	2.50	0.01	1.85	19.40	ND	0.04	0.47
X4	9.04	49.50	10.27	1130.00	ND	4.50	ND	6.00	65.30	ND	0.13	ND
X5	0.26	0.50	0.36	204.00	0.05	0.06	0.01	5.00	18.60	ND	0.08	ND
X6	0.98	4.50	11.23	284.00	0.06	0.56	0.02	1.45	29.50	ND	0.04	0.58
X7	0.75	10.50	3.86	325.00	ND	0.83	0.01	4.00	33.20	ND	0.07	ND
X8	3.31	31.50	11.79	429.00	ND	3.50	0.01	1.45	34.20	ND	0.04	ND
X9	7.79	189.50	9.00	841.00	ND	4.50	0.01	7.00	53.30	0.02	0.19	ND
X10	5.38	114.50	2.00	1224.00	0.03	11.50	0.02	16.00	115.00	ND	0.28	ND
X11	0.50	2.00	0.60	557.00	0.10	0.54	0.02	4.50	57.00	ND	0.04	ND
X12	0.48	1.00	0.59	330.00	0.45	0.48	0.02	1.93	51.30	ND	0.02	ND
X13	10.82	14.00	0.40	6.74	6.17	1.56	0.02	2.23	82.20	ND	1.87	ND

Key: **WA1- W15** = Water samples and **X1 – X13.** Soil samples from different locations. **ND** = Not detected

TABLE III
ISOLATED BACTERIA ON DIFFERENT WATER SAMPLES CODED WITH LETTER A - M

Samples	Coagulase (+ ve) Staphylococcus	Pseudomonas	Salmonella	Enterococcus	E. coli	Revival microorganism
A	-	-	-	-	-	+
B	-	-	-	-	-	+
C	-	-	-	+	+	+
D	-	-	+	-	-	+
E	-	-	-	-	-	+
F	+	+	-	+	+	+
G	-	-	-	+	-	+
H	-	-	-	+	-	+
I	+	+	-	+	-	+
J	-	-	-	+	-	+
K	-	-	-	+	-	+
L	-	-	-	-	-	+
M	+	+	-	-	-	+
Keys + = Microbial presence. - =Microbial absence. Escherichia coli – (+)						

TABLE IV
MICROBIOLOGICAL LABORATORY RESULT OF DIFFERENT WATER SAMPLES (CFU/ML) CODED WITH LETTER A – M

Water samples	Total coli form	Total viable count	Total Staphylococci count	Total Salmonepla count	Total Pseudomonas count	Total enterococcus count	Total E.coli count
A	0.00	3.0×10^0	0.00	0.00	0.00	0.00	0.00
B	0.00	8.9×10^3	0.00	0.00	0.00	0.00	0.00
C	$1.0x10^1$	5.0×10^0	0.00	0.00	0.00	5.0×10^0	5.0×10^0
D	0.00	$14.8x10^3$	0.00	7.4×10^3	0.00	0.00	0.00
E	0.00	$16.5x10^3$	0.00	0.00	0.00	0.00	0.00
F	$2.2x10^1$	$15.6x10^1$	$2.0x10^0$	0.00	$2.0x10^1$	$1.8x10^1$	$4.0x10^0$
G	$1.8x10^1$	$2.6x10^1$	0.00	0.00	0.00	$1.8x10^1$	0.00
H	$2.0x10^0$	$14.7x10^3$	0.00	0.00	0.00	$2.0x10^0$	0.00
I	$7.2x10^1$	$9.6x10^0$	1.1×10^1	0.00	2.2×10^0	7.2×10^1	0.00
J	$1.0x10^0$	3.0×10^0	0.00	0.00	0.00	1.0×10^0	0.00
K	$2.0x10^0$	2.8×10^1	0.00	0.00	0.00	2.0×10^0	0.00
L	0.00	7.0×10^0	0.00	0.00	0.00	0.00	0.00
M	0.00	22.4×10^3	1.0×10^0	0.00	14.9×10^1	0.00	0.00
AGAR USED	LACTOSE BROTH E.M.B AGAR	NUTRIENT AGAR	MANNITOL AGAR (MSA)	SALMONELLA SHIGELLA AGAR (SSA)	NUTRIENT AGAR	NUTRIENT AGAR EMB AGAR	

Soil optimum pH level that support plant growth are between 5.5 to 7.0 while the experimental results ranges between 6.08 to 6.72 for each of the samples obtained from different locations. The mean values of pH recorded were found to be higher in water sample than soil sample.

This shows that the soil sample is slightly acidic, while the water is slightly basic, which could be attributed to the fact that the buffering capacity of soil has been overwhelmed by the exchange of positive ions attached to soil particles by the hydrogen ion from the water source. The chlorides, phosphate and sulphate results contents caused the water around the area to be hard, with high pH measurement thus made it unsuitable for drinking (Table V and VI). Animals living in fresh water such as streams, rivers around the place are reduced while plankton's doses not grow around the area at all [17]. Specific plants cannot even survive there growth in such area thus seized to grow henceforth.

TABLE V
DIFFERENT PARAMETERS OF WATER SAMPLES CODED WITH LETTER WAI – WA15

Water samples	pH	Conductivity (US/CM)	Chloride (MG/L)	Hardness (MG/L)	COD (MG/L)	Phosphate (MG/L)	Alkalinity (MG/L)	Sulphate (MG/L)
WA1	6.69	650	12.4	18.20	106	3.0	2.95	60.48
WA2	6.44	650	23.3	16.20	102	3.8	2.34	46.08
WA3	6.55	634	6.9	15.40	120	3.4	2.16	39.36
WA4	6.75	679	39.7	9.40	110	3.0	1.16	49.92
WA5	6.46	657	7.4	15.0	96	3.0	2.14	107.5
WA6	6.08	665	23.3	7.60	92	4.6	1.36	25.92
WA7	6.72	666	8.4	9.00	122	7.6	1.34	37.40
WA8	6.19	678	24.3	5.00	114	5.4	2.13	72.00
WA9	6.61	638	16.37	9.80	116	7.0	0.80	79.68
WA11	6.15	663	20.8	4.60	88	1.4	3.36	63.36
WA12	6.33	666	28.5	3.40	108	2.6	2.17	55.68
WA13A	6.73	655	6.20	6.20	118	9.8	1.84	97.92
WA13B	6.50	659	12.6	6.00	112	7.0	2.42	52.80
WA14	6.67	686	4.6	18.00	86	3.4	2.43	58.56
WA15	6.72	658	6.20	5.00	114	9.0	1.50	58.56

TABLE VI
DIFFERENT PARAMETERS OF SOIL SAMPLES

Sample	**Sand (%)**	**Clay (%)**	**Slit (%)**	**Soil profile**	**Sand (g/kg)**	**Clay (g/kg)**	**Slit (g/kg)**
Tuyil	60.80	27.20	12.00	Sandy,Clay, Loamy	608.00	272.00	120.00
Haffer	56.80	27.20	16.00	Sandy,Clay, Loamy	568.00	272.00	160.00
Warri	48.80	27.20	24.00	Clay Loam	488.00	272.00	240.00

TOC – Total Organic Carbon,; OM – Organic Matter; CEC – Contaminant of Emerging Concern.

A. *Analysis of variance (ANOVA) of metal concentration between soil and water samples*

Sample	**pH**	**TOC (%)**	**OM (%)**	**P (mg/kg)**	**K (mg/kg)**	**Na cmol/kg**	**Ca (cmol/kg)**	**Mg (cmol/kg)**	**CEC**	**EA**
Tuyil	3.80	0.48	0.83	9.64	0.23	0.46	3.00	1.10	6.25	5.13
Haffer	3.46	0.54	0.92	16.02	0.27	0.44	4.40	2.00	11.26	4.96
Warri	3.08	2.62	4.52	5.83	0.21	0.66	1.40	0.60	13.16	10.30

In Table VII, it was observed there was significant difference in the percentage of soil sample taken to consideration their various processing control, since the p-value (1.000) was more that α (0.05) we therefore, rejected H_o

TABLE VII
ONE-WAY ANOVA: SAMPLE 3 VERSUS C2

Source	DF	SS	MS	F	P
C2	2	0	0	0.00	1.000
Error	15	657484	43832		
Total	17	657484			
	S = 209.4	R - Sq = 0.008	R - Sq (adj) = 0.008		

In Table VIII, the analysis of variance shows clearly the justification of minerals content were not significantly different to each other since the analysis of the result shows that p-value (0.000) compared to the level of significant (α=0.05), we therefore accepted the Null hypothesis (H_0). The descriptive statistics also testified to the variation among these mineral constituents from each samples and their average values are varies as well. Conclusively, mineral constituents made contribution to the environmental toxicants with human exposure and their possible health effects.

TABLE VIII

Source	DF	SS	MS	F	P
Sample1	10	838034	83803	5.37	0.000
Error	236	3685736	15618		
Total	246	4523770			
	S = 125.0	R - Sq = 18.53%	R - Sq (adj) = 15.078		

ONE-WAY ANOVA: SAMPLE 1 VERSUS C2

In Table IX, and from the analysis carried out, we discovered the soil parameter taken from each of the company location were significantly different since p-value (0.761) was more than α (0.05).

TABLE IX
ONE-WAY ANOVA: SAMPLES 2 VERSUS C1

Source	DF	SS	MS	F	P
C1	2	10.4	5.2	0.29	0.761
Error	27	510.6	18.9		
Total	29	521.0			
	S = 4.349	R-SQ = 2.00%	R-SQ(ADJ) = 0.00%		

In Table X, ANOVA shows there was difference in the company that were using the chemical for their processing since the p-value (1.000) was more than significant level (α=0.05) so, we rejected H_o based on the hypothesis testing which justified the claim. But there was no significant difference among the chemical reaction to their processing since the p-value (0.000) favorably compared to the significant level (α=0.05), therefore we did not reject Ho to justified the claim. In conclusion, the analysis describes the percentage of both positive and negative effects of these chemicals as 55.3% and 45.94%, respectively.

TABLE 10
Two – One -way Anova : Samples 1 versus C2

Source	DF	SS	MS	F	P
Company	15	61912	4127	0.18	1.0000
Chemical	7	2970713	424388	18.18	0.0000
Error	105	2451224	23345		
Total	127	5483849			
	S=152.8	R-SQ =55.30%	R-SQ (ADJ)=45.94%		

Conclusions

The heavy metal concentration differs according to the point of collection of samples as water moves through soil and rock; it dissolves some amounts of minerals and holds them in solution. The research findings made it clear that the contamination of this water body with the heavy metals were primarily due to the leachate discharged from the soil and possibly from the surrounding industrial effluents. The geological formation of the industrial area had a greater influence in the content of heavy metal in the water and soil samples. This study concludes that industrial wastes are major sources of environmental toxicants of which human are exposed to danger as it has health effects. It is therefore, suggestive that release of toxicants to the environment can be monitored through governmental and non-governmental agencies in other to curb or stop such act totally.

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