JASEM ISSN 1119-8362

Full-text Available Online at www.ajol.info and www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage. *Dec.* 2016
Vol. 20 (4) 31-37

An appraisal of Physicochemical Parameters and some Trace metals at the Disposal Points of Five Industrial Effluents in Trans-Amadi Industrial Area of Port Harcourt, Nigeria.

[*1]CHIKWE, TN; [2]ONOJAKE MC

[1]*Department of Pure and Industrial Chemistry,*
University of Port Harcourt,
P.M.B 5323, Choba, Port Harcourt, Nigeria
**Corresponding author.ononed@yahoo.com;mudiaga.onojake@uniport.edu.ng*
Tel: +2348035404696) (phone +234-8035478512; e-mail: templechikwe@yahoo.co.uk)

ABSTRACT: Industrial effluent samples collected from the disposal point of five different companies in Trans-Amadi industrial area of Port Harcourt were analyzed to investigate effect on the environment. The analyzed effluent samples showed results of the physicochemical parameters and trace metals in the ranges : (pH 3.60 - 6.90), electrical conductivity (406.00 – 722.00 µs/cm), total dissolved solid (194.00-347.00 mg/l); total suspended solid (>1067.00), chloride (14.20-151.10mg/l), sulphate (20.40-25.30 mg/l), nitrate (3.00-3.20 mg/l), total organic carbon (4.57-1556.00 mg/l), chemical oxygen demand (20.00-6225.00 mg/l), iron (1.26-1.68 mg/l), zinc (0.02 mg/l), copper (0.06 mg/l), lead (0.38mg/l), nickel (0.56-0.93mg/l), cadmium (0.09-0.34mg/l), chromium (0.19 mg/l) and sodium (11.45-20.77mg/l). The results obtained were compared with World Health Organization and United State Environmental Protection Act (USEPA), maximum permissible limits. Results showed that pH, chloride, conductivity and total organic carbon values of samples from three industries were above the maximum permissible limit while TSS values of samples from the five industries were above specification. Only one Industry produced an effluent with a chemical oxygen demand within the allowable limit. Some heavy metals like Nickel, Cadmium, and Chromium were also above the USEPA maximum permissible limit. Total suspended solids were determined using Pressure Millipore Vacuum Pump Assembly (NACE TM-01-73), Concentrations of Chloride, Sulphate, Nitrate, Total organic carbon (TOC) and Chemical Oxygen Demand (COD) were determined using a DR 2800 Spectrophotometer. Heavy metals were determined using Atomic absorption spectrometer (Perkin–Elmer model 2280/2380 model). © JASEM

http://dx.doi.org/10.4314/jasem.v21i1.4

KeyWords: Heavy metals, Industrial effluents, Pollution, Spectrophotometer, Physicochemical, Concentration.

The quest for industrialization and urbanization has impacted on the environment which is our natural resource. The uncontrolled and indiscriminate disposal waste matter into our surrounding, water bodies and atmosphere if unchecked can cause portends undesirable health effects to man and his ecosystem at large. Industrial effluents are wastewater generated as a result of industrial activities. Industrial wastes have the potential to contribute strong acid to a water body and may cause dented effects on both the fauna and flora. Disposal of waste material into water bodies as well as effluents from industrial activities and urbanization in developing countries have gradually led to deterioration of the water quality in recent years (Onojake *et al.*, 2011). The direct release of industrial effluents into rivers and the streams in an arbitrary manner without predetermining the impact of such discharges on animal and plant life is a growing third world environmental problem (Onojake and Frank, 2013). These effluents are the major sources of pollution and destruction of fragile environment. Various researches on trace and heavy metals in industrial effluents have shown that they are toxic to both man and aquatic life which result in the contamination of the food chain (Novick 1999; WHO, 2000)

A heavy metal is usually regarded as a metal with a relatively high density (>7g/cm3), atomic weight (>20) or atomic number. Some heavy metals, such as cadmium, mercury and lead, are notably toxic while others trace metals like Co, Cr, Cu, Fe, Mn, Ni and Zn are essential as micronutrients which are beneficial to plants and animals, but can be toxic in large amounts or certain forms (Bonetti *et al.,* 2009; Onojake and Frank, 2013). Heavy metals are major source of pollution not just because they are toxic above a relatively certain concentration but also because they are persistent, remaining in the

*Corresponding author email: ononed@yahoo.com

environment long after the source of pollution has been removed (Voutsinou-Taliadouri, 1981). Potential sources of heavy metal include mining and industrial wastes, agricultural runoff, occupational exposure and contact with lead-based paints (Brady and Holum, 1995). Anthropogenic sources of heavy metals include waste derived fuels and municipal wastes (Baldwin and Marshal, 1999).

This study is aimed at evaluating the physicochemical parameters and some trace metals at the disposal points of five industrial effluents in Trans-Amadi industrial area of Port Harcourt, Nigeria.

MATERIALS AND METHODS

Sample Collection: Effluent samples were obtained from five different Industries at Trans Amadi Industrial Layout in Port Harcourt Metropolis. Samples were obtained from two Brewing Industries labeled Sample1 and Sample 2 respectively, two Paint Industries labeled Sample 3 and Sample 4 respectively. A sample was obtained from a Beverage Industry labeled Sample 5. Three sets of representative samples were collected in each location with a sealed container to avoid evaporation of volatile components

Sample Preparation: The industrial effluents obtained were agitated several times to ensure homogeneity. 100 ml of each of the industrial effluents were used for pH, conductivity and heavy metal determination. 500 ml of effluent sample from each disposal point was used for TSS determination while 1 ml of effluent sample from each disposal point was used for TOC and COD determination. For the determination of chloride, nitrate and sulphate concentrations, Powder pillows corresponding to the parameter to be determined was introduced into 1 ml of effluent sample respectively (obtained from each disposal point) and stirred for an amount of time depending on the parameter.

Sample Analyses: *pH Determination*: An Inolab pH meter with an automatic temperature compensation probe was immersed into the beaker containing the sample. Time was allowed for the pH meter to gain stability then the reading was recorded.

Determination of Electrical Conductivity: An Inolab Conductivity meter was calibrated with the appropriate buffer solution. The probe was immersed into the beaker containing the sample. Time was allowed for the conductivity meter to gain stability then conductivity recorded.

Determination of Total Suspended Solids (TSS) (ASTM D5907, 2013): A membrane filter paper of 0.45 µm was placed in a dish and dried in an oven at 100 – 105 ^{0}C for One hour. The dish and the filter paper were then transferred to a dessicator to cool for 15 minutes. The membrane filter paper was weighed and weight recorded as B in grams. Filtering apparatus was assembled and connected to a suction pump. The membrane filter paper was placed on the funnel of the filtering apparatus. 500 ml of the industrial effluent was collected in a clean beaker. The sample was filtered though the weighed membranes filter paper while the pump was on. The membrane filter paper containing residue was carefully transferred to the same dish. The dish, membrane filter paper and residue were dried in an oven at 100 – 105 ^{0}C for two hours and then transferred to a dessicator to cool for 15 minutes. The membrane filter paper and residue were weighed and weight recorded as A in grams.

$$\text{Total suspended solids, mg/L} = \frac{(A - B) \times 1000 \times 1000}{\text{Vol. of Effluent Sample}}$$

*Determination of Chloride, Nitrate, Sulphate, Total Organic Carbon and Chemical Oxygen Demand with DR 2800 Spectrophotometer:*The Concentrations of Chloride, Nitrate, Sulphate, Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) were determined using DR 2800 Spectrophotometer. The DR 2800 has two cell compartments.. The sample containing the already reacted powder pillow was reinserted into the cell compartment. The cell compartment was shut and the 'READ' icon clicked. The concentration of the parameter to be determined pops up immediately. Powder pillows are not required for Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) determination.

Determination of Heavy Metals using Atomic Absorption Spectrophotometer (AAS)

100mL of each of the effluent sample was transferred into Pyrex beakers and 10ml of concentrated HNO_3 added to digest complexes formed between heavy metals and organic constituents. The samples were heated to the lowest possible volume (about 20 ml). The beakers were allowed to cool and another 5ml of concentrated HNO_3 was added to each sample. Heating was continued with addition of concentrated Nitric acid as necessary until digestion was complete. The samples were evaporated again to dryness and the beakers were cooled, followed by addition of 5ml HCl solution (1:1 v/v) . The solutions were warmed and 5ml of 5M NaOH was added, then filtered. The filtrates were transferred to 100ml volumetric flasks respectively and diluted to the mark with distilled water. 10 mg/l Standard Solutions of each of the heavy metals to be determined was prepared from their respective stock solutions (1000mg/l). Concentrations of Fe, Zn, Cu, Ni, Cd, Na, Cr, and Pb were determined using Perkin–Elmer model 2280/2380 atomic absorption spectrophometer (AAS) and calibrated against the standard solution (Lenore *et al.,* 1999).

RESULTS AND DISCUSSION

Table 1: Physicochemical Properties of Industrial Effluents from Trans - Amadi Industrial Layout.

	Samples					
Parameters	**1**	**2**	**3**	**4**	**5**	**WHO Specification**
pH	3.60	3.90	6.80	6.90	6.30	(6.0-9.0)
Conductivity	406.00	722.00	497.00	509.00	562.00	≤ 500
TDS	194.00	347.00	237.00	243.00	268.00	≤ 500
TSS	>1067.00	>1067.00	>1067.00	>1067.00	1067.00	≤ 350
Chloride (Cl-)	151.10	136.90	14.20	16.50	19.80	≤ 100
Sulphate ($S0_4^{2-}$)	22.90	25.30	20.40	23.90	20.50	(300-600)
Nitrate ($N0_3^{2-}$)	3.20	3.00	3.15	3.00	3.90	≤ 10
COD	3440.00	6225.00	365.00	240.00	20.00	≤ 120
TOC	864.00	1556.00	91.61	60.53	4.57	≤ 75

Conductivity (µS/cm), all other parameters are in (mg/l). Sample Temperature is maintained at 20- 23.2^{0}C

Table 2: Heavy Metals concentration in mg/l in Industrial Effluents from Trans -Amadi Industrial Layout

	Samples					
Parameters	**1**	**2**	**3**	**4**	**5**	**USEPA SPEC.**
Fe	1.68	1.26	1.47	1.26	1.47	≤ 2
Zn	0.02	0.02	0.02	0.02	0.02	≤ 2
Cu	0.06	0.06	0.06	0.06	0.06	≤ 0.5
Ni	0.74	0.56	0.93	0.56	0.74	≤ 0.1
Cd	0.32	0.34	0.09	0.21	0.28	≤ 0.01
Na	11.45	19.3	12.74	11.52	20.77	≤ 200
Cr	0.19	0.19	0.19	0.19	0.19	≤ 0.05
Pb	0.38	0.38	0.38	0.38	0.38	≤ 0.05

Results are averages obtained from multiple measurements and are validated using the standard deviation of each parameter. pH is a numeric scale used to specify the acidity or basicity of an aqueous solution. It is approximately the negative of the logarithm to base 10 of the molar concentration, measured in units of moles per liter, of hydrogen ions (Adebayo *et al.,* 2007). All organisms are subject to the amount of acidity of stream water and function best within a given range (Portman *et al.,* 1997). Table 1 shows that the pH of the effluent obtained from the two brewing Companies (Samples 1 & 2) were extremely acidic (3.6 -3.9) according to the United States Environmental Protection Agency . This classification also considers the Mean pH of the sewage obtained from the five industries as strongly acidic (Covington *et al.,* 1985). The acceptable pH range for the discharge of industrial wastewater to the Publicly Owned Treatment Works (POTW) collection system, as regulated in many industrial waste or sewer-use ordinances is in the range of 6.0 to 9.0. Results obtained from Table1 shows that the pH of the effluent obtained from Samples 3, 4 and 5 (two paint industries and a beverage industry) were within specification. The discharge of acidic effluents into the environment will result in damage to sewer over time; such discharges can eventually corrode the pipe completely, causing infiltration and contamination of the groundwater or infiltration of the groundwater into the sewer where the groundwater level is above the depth of the sewer (Akinola *et al.,* 1981). Industrial discharge violations of pH will also increase the maintenance requirements on pumps in the pumping stations. The damage to the pumps could eventually cause their failure, resulting in sewer break up and raw wastewater overflows (Aina, 1992).

Conductivity is an indicator of water quality, especially a function of the amount of dissolved salt, and can be used to monitor processes in the wastewater treatment that causes changes in total salt concentration and thus changes in conductivity (Hendricsk and David, 2007). Reduction of conductivity due to biological nitrogen removal will consume alkalinity or hydroxide ions. If the amount of available alkalinity is high enough (one mole alkalinity per mole ammonia) biological N-removal through nitrification followed by denitrification will give a decrease of conductivity with 842 µSm 2 /g N (Aina, 1992). Many municipalities requires that industries and similar enterprises which discharges sewage to the wastewater net, measure conductivity and that it is not allowed to be higher than 500 µS/m (Hellström *et al,* 2001). Table 1 show that only industrial effluents from the two brewing industries (Sample 1 & 2) meet specification in terms of conductivity (≤ 500 µS/m). Too high conductivity causes corrosion problem in the sewage pipe network. The variation of conductivity in the wastewater can be caused by variation of the ion content. Ions that cause conductivity are hydrogen H+, hydroxide OH- and nutrients such as phosphate and nitrate. The hydrogen and hydroxide ion contribution to conductivity is a function of pH (Nordstrom, *et al.,* 1999).

Total dissolved solid (TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a filter with two-micrometer pore conductivity (Hendricsk and David, 2007). According to World Health Organization (WHO), the acceptable TDS for effluents from natural gas Industries is ≤ 500mg/l and for other industries is ≤ 2000 mg/l (WHO, 1987). Table 1 shows that the TDS of the effluents produced from the five industries were all within WHO specification.

Total suspended solid (TSS) refers to the dry-weight of particles trapped by a filter. It is a water quality parameter used to assess the quality of wastewater after treatment in a wastewater treatment plant. It is listed as a conventional pollutant in the U.S. Clean Water Act (Hendricsk and David, 2007). According to World Health Organization (WHO), the acceptable TSS for industrial effluents is ≤ 350mg/l (WHO, 1987). Table 1 shows that the TSS of the industrial effluents from five industries was above specification therefore require treatment. If the discharge from a manufacturing process contains large amounts of fibrous or stringy materials, heavy solids, adhesives, or grease which constitutes the TSS, plugging of the sewer system may result. Plugging may occur just downstream of the discharge or in the pumping station (Abdulrzzak, 2007). Fibrous or stringy materials get caught on rough surfaces and soon build up by entangling more solids. These types of materials can also find themselves around pump impellers or shafts causing the pump to fail. If problems are occurring, it may be an indication of a problem with the manufacturing process or that the waste should have been pretreated prior to discharge (Hendricsk and David, 2007).

Non metallic parameters like Concentrations of Chloride, Sulphate, Nitrate as well as Chemical oxygen demand and Total organic carbon of effluent samples are important in determining the quality of effluent samples released into the environment through the Publicly Owned Treatment Works (POTW) (Hendricsk and David, 2007). The chloride ion is formed when the element chlorine (a halogen) gains an electron or when a compound such as hydrogen chloride is dissolved in water or other polar solvents. Chloride salts such as sodium chloride are often very soluble in water (Chen and Jensen, 2001). According to WHO, the acceptable Chloride concentration for industrial effluent is 100 mg/l (WHO, 1987). Table 1 show that the Chloride concentration of the industrial effluent from two brewing companies (Sample 1 and Sample 2) was above specification; however the Mean Chloride concentration from the five industries under review was within specification. High chloride concentration can cause corrosion in the sewage pipe network (Abdulrzzak, 2007).

In many Countries, the amount of sulphate that can be discharged to a sewer is limited to 300 – 600 mg/l in accordance to WHO Specification. This is restricted because of the effect of Sulphate ions on the waste water recirculation system (Clair *et al.,* 2003). Sulphate ions form Sulphate – Aluminate complexes that swell and crack concrete made from non resistant cement. The actual sulphate concentration of the effluent depends on the amount of salt used and degree of dilution with rinse waters (Munawar *et al.,* 1993). Table 1 shows that the sulphate concentration of all effluent samples from the five industries were within the permissible limit of WHO. This is expected as effluents from Wool textile industries have high sulphate concentration due to the processes of dyeing and carbonizing. The Companies considered in this study do not fall under the Textile Industry (Lori, 1991).

Most nitrogen in wastewater takes the form of ammonia or urea; however, nitrates are included. Nitrates are oxidized forms of nitrogen, commonly associated with Nitrogen, Phosphorus and Potassium fertilizers (Kornaros and Lyberatos, 1998). If excess nitrates are not removed, discharge of the untreated wastewater will cause excess algae growth in rivers and streams. This excess algae depletes oxygen, resulting in the death of fish and other important organisms, as well as odor problems (Randall and Buth, 1984). According to United States Environmental Protection Agency, the maximum acceptable Nitrate Concentration for Industrial effluent is 10 mg/l. Table 1 shows that all the

Industrial effluents obtained from the five Industries were within the permissible limit stipulated for Nitrate.

In recent times, due to the increase of pollution by discharging large amount of various chemicals, oxidizable organic substances of different matter into the aquatic system, Biochemical Oxygen Demand (BOD) values alone do not give a clear picture of organic matter content in effluent sample (Hendricsk and David, 2007). The presence of various toxicants in the sample may severely affect the validity of BOD test. Hence, Chemical oxygen demand (COD) test is a better estimate of organic matter which needs no sophistication and is time saving. COD which is the oxygen consumed (OC) does not differentiate the stable organic matter from the unstable form, therefore the COD value are not directly comparable to that of BOD (Akinola *et al.,* 1981). According to the United States Environmental Protection Agency, the maximum acceptable COD for Industrial effluent is 120 mg/l. Table 1 shows that only Sample 5 (effluent from the Beverage Industry) was within acceptable limit. High COD results in the death of useful organic matter within the ecosystem (Randall and Buth, 1984).

Total organic carbon (TOC) is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality. TOC may also refer to the amount of carbon in waste water, soil pharmaceutical products etc (Seiter *et al.,* 2004). Due to the passage of the U.S. Safe Drinking Water Act in 2001, TOC analysis emerged as a quick and accurate alternative to the classical but more lengthy biological oxygen demand (BOD) and Chemical oxygen demand (COD) tests traditionally reserved for assessing the pollution potential of wastewaters (USEPA, 2009). Total organic carbon (TOC) will not determine which particular compounds are present (most samples are complex mixtures which contain thousands of different organic carbon compounds), rather it informs the user of the sum of all organic carbon within the compounds (Sugimura, 1988). Industries which discharge liquid waste into a surface water body are required to monitor TOC. According to the United States Environmental Protection Agency (EPA) the maximum permissible TOC for Industrial Effluent is 75 mg/l (USEPA, 2009). Table 1 show that only Samples 4 and 5 were within permissible range.

Heavy metals concentration present in the Industrial effluent obtained from the five industries are shown in table 2. USEPA 2009 specifies a maximum concentration of 2 mg/l, 2 mg/l, 0.5 mg/l, 0.1 mg/l, 0.01 mg/l, 200 mg/l, 0.05 mg/l and 0.05mg/l for iron, Zinc, Copper, Nickel, Cadmium, Sodium, Chromium and Lead respectively. The Table shows that only the concentrations of Iron, Zinc, Copper and Sodium in the Industrial effluents obtained from the five Industries are within the permissible limit of the USEPA. The other heavy metals like Nickel, Cadmium, Chromium and Lead are above the maximum permissible limit. Heavy metal contamination has been recognized as a major environmental concern due to their pervasiveness and persistence, these heavy metals are not biodegradable; hence there is a need to develop such remediation technique, which should be efficient, economical and rapidly deployable in a wide range of physical settings (Bonchev and Kamenska, 1981). The toxicity of Heavy metals depend on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals (Pacyna, 1996). Owing to their high toxicity, Cadmium, Chromium and Lead rank among the priority metals of public health concern they are considered systemic toxicants known to induce multiple organ damage, even at lower levels of exposure (Goyer, 2001). They are also classified as human carcinogens according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer (USEPA, 2009). Copper serves as an essential co-factor for several oxidative stress-related enzymes including catalase, superoxide dismutase, peroxidase, cytochrome coxidases, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase (Stern, 2010). Cu(II), and reduced state, Cu(I), is used by cuproenzymes involved in redox reactions (Harvey and McArdle, 2008). However, it is this property of copper that also makes it potentially toxic because the transitions between Cu(II) and Cu(I) can result in the generation of superoxide and hydroxyl radicals (Tchounwou *et al.,* 2008) . Also, excessive exposure to copper has been linked to cellular damage leading to Wilson disease in humans. Heavy metals such as Iron, Nickel, Sodium and Zinc are essential nutrients that are required for various biochemical and physiological functions. Inadequate supply of these micro-nutrients results in a variety of deficiency diseases or syndromes however exposure to these metals at concentrations above permissible limit could result to various health problems (WHO 2000).

Conclusion: The release of Industrial effluents is inevitable in every industrial operation. All Industrial effluents end up back in the environment (Munawar *et al.,* 1993). The level of physicochemical parameters and heavy metals in Industrial effluents are key indicators that ascertain how safe these effluents are both to humans and the environment.

Introducing Industrial effluents that do not meet World Environmental Standard can result to high level of damage both to the route of discharge and the environment.

Acknowledgements: The authors wish to appreciate the management and DIABLOSS Chemical Laboratory 24 Azubuike Wosu Street, OFF Alcon Road Woji Port Harcourt for their assistance, support and use of their laboratory that enable this work to be completed on schedule.

REFERENCES

Abdulrzzak, A (2007). Dairy Industry Effluents Treatment. *Thesis. UTCB University, Bucharest-Romania pp 100-180.*

Adebayo, OT; Balogun, AM; Olubiyi, OA (2007).Chemical Analysis of Some Industrial Effluents that discharged into Lagos Lagoon, Nigeria. *Research Journal of Environmental Sciences, 1: pp 196-199.*

Aina, EOA (1992). Halting industrial pollution in Nigeria which way FEPA. In: Towards IndustrialPollution Abatement in Nigeria. *Aina, E.O.A. and N.O. Adedipe (Eds.), pp:13-19.*

Akinola, AA; John, AO; Titilope, O (1981). Chemical composition of agricultural waste products contaminating water sources. Proceedings of the 2nd National Conference on Water Pollution, Kaduna, Nigeria. *Federal Ministry Water Resources, pp: 198-210.*

ASTM D5907-13. (2013). Standard Test Methods for Filterable Matter (Total Dissolved Solids) and Nonfilterable Matter (Total Suspended Solids) in Water. *ASTM International, West Conshohocken, PA. pp 4-10.*

Baldwin, D R; Marshall, WJ (1999). Heavy metal poisoning and its laboratory investigation. *Annals of Clinical Biochemistry, vol. 36, no. 3, pp. 267–300.*

Bonchev, D; Kamenska, V (1981). Predicting the properties of the 113–120 transactinide elements. *The Journal of Physical Chemistry, vol. 85, no. 9, pp. 1177–1186.*

Bonetti, A; Leone, R; Muggia, F; Howell, S B (2009). Platinum and Other Heavy Metal Compounds in Cancer Chemotherapy: Molecular Mechanisms and Clinical Applications''. *Humana Press, New York, ISBN 978-1-60327-458-6.*

Brady, JE; Holum, JR (1995). Chemistry: The Study of Matter and its Changes. *2nd ed., John Wiley & Sons, New York, ISBN 0-471-10042-0. Pp 35-40.*

Chen, WL; Jensen, JN (2001). Effect of chlorine demand on the breakpoint curve: Model development, validation with nitrite, and application to municipal wastewater. *Water Environ. Res.*, 73(6), 721.

Clair, NS; Perry, LM; Gene, FP (2003). Chemistry for Environmental Engineering and Science. *(5th ed.). New York: McGraw-Hill. ISBN 0-07-248066-1. pp44.*

Covington, AK; Bates, RG; Durst, RA (1985). Definitions of pH scales, standard reference values, measurement of pH, and related terminology. *Pure Appl. Chem.* ***57*** *(3): 531–542.*

Goyer, RA (2001): Toxic effects of metals. In: Klaassen CD, editor. Cassarett and Doull's Toxicology: The Basic Science of Poisons. *New York: McGraw-Hill Publisher: pp. 811–867.*

Harvey, LJ; McArdle, HJ (2008). Biomarkers of copper status: a brief update. *Br J Nutr.; 99(S3):S10–S13. [PubMed]*

Hellström *et al.,* **(**2001) **.** Lack of Pericytes Leads to Endothelial Hyperplasia and Abnormal Vascular Morphogenesis.'' *JCB vol. 153 no. 3* ***543-554.***

Hendricks, I; David, W (2007). Water Treatment Unit Processes: Physical and Chemical. *Boca Raton, FL: CRC Press, pp 44–62.*

Lenore, SC; Arnold, EG; Andrew, DE (1999). Standard Methods for Examination of Water &Wastewater (20th ed.). *Washington, DC: American Public Health Association. ISBN 0-87553-235-7. pp 10-12.*

Lori, JA (1991). The textile industry and water pollution. *Proceedings of the 2nd National Environmental Seminar. FEPA, FMH, NAT Water Resources Institute, WITO, (ES'91), Kaduna State Water Board.pp: 11-13.*

Munawar, L; McCarthy, W; Gilron, G (1993). Assessing the impact of sewage effluent on the ecosystem health of the Toronto Waterfront

(Ashbridges Bay), Lake Ontario. *Journal of Aquatic Ecosystem Stress and Recovery* (Formerly *Journal of Aquatic Ecosystem Health*). *Springer Netherlands. Volume 2, pp 4*

Nordstrom, D; Kirk, A; Charles, N (1999). Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. *Proceedings of the National Academy of Sciences of the United States of America. PNAS.* ***96*** *(7): 3455–62.*

Novick, R (1999) Overview and the Health in Europe in the 1990s, World Health Organisation, Europe Regional Office, Copenhagen, *EUR/ICP/EH/CO 02 02 05/6 pp.20*

Onojake, MC; Frank, O (2013). Assessment of heavy metals in a soil contaminated by oil spill: a case study in Nigeria. *Chemistry and Ecology, 29 (3), 246-254.*

Onojake, MC; Ukerun, SO; Iwuoha, G (2011): A Statistical Approach for Evaluation of the Effects of Industrial and Municipal Wastes on Warri Rivers, Niger Delta, Nigeria. *Water Qual Expo Health. 3:91–99.*

Pacyna, JM (1996): Monitoring and assessment of metal contaminants in the air. In: Chang LW, Magos L, Suzuli T, editors. *Toxicology of Metals. Boca Raton, FL: CRC Press;. pp. 9–28.*

Portman, JE; Biney, I; Zabi, S (1997). State of the marine environment in the West and central African region. *UNEP Regional Sea Reports and Studies, No.108,pp2-5.*

Randall, CW; Buth, D (1984). Nitrite buildup in activated sludge resulting from temperature effects. *J. Water Pollut. Control Fed.*, *56(9),1039.*

Seiter, K; Hensen, C; Schröter, J; Zabel, M (2004). Organic carbon content in surface sediments—defining regional provinces. *Deep-Sea Research Part I: Oceanographic Research Papers* ***51*** *(12): 2001–2026.*

Stern, BR (2010). Essentiality and toxicity in copper health risk assessment: overview, update and regulatory considerations. *Toxicol Environ Health A.;73(2):114–127. [PubMed].*

Tchounwou, P; Newsome, C; Williams, J; Glass, K (2008). Copper-induced cytotoxicit and transcriptional activation of stress genes in human liver carcinoma cells. *Metal Ions Biol Med.;10:285–290. [PMC free article] [PubMed]*

U.S. Environmental Protection Agency (USEPA) (2009). Cincinnati, OH. Method 415.3: Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water. *Revision 1.2. Document no. EPA/600/R-09/122.*

WHO (World Health Organization). (1987). Environmental health criteria No. 70: Principles for the safety assessment of food additives and contaminants in food. *Geneva. pp 02-20.*

WHO (2000): WHO Air Quality Guidelines, 2nd Edition, World Health Organization, Europe Regional Office, Copenhagen

Voutsinou-Taliadouri (1981). Metals, Metalloids, and Radionuclides in the Baltic Sea Escosystem. *J. Elsevier Vol 5 pp 40-55.*