PRINT ISSN 1119-8362
Electronic ISSN 2659-1499

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 29 (3) 807-816 Mar. 2025

Physicochemical Parameters and Heavy Metals Content of Sediment, Water and Fauna of Printer Waste Toner Burdened Drainage System and its Receiving River around Mile 1 Diobu, Port Harcourt, Rivers State, Nigeria

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ABSTRACT: The objective of this paper was to evaluate some physicochemical parameters and heavy metals content of sediment, water and fauna of waste toner burdened drainage and its receiving river around Mile 1 Diobu, Rivers State, Nigeria using appropriate standard techniques. Results from the study area found pH levels to be within WHO set limits in both waste water and sediments. Nitrate levels were below WHO set limits. In contrast, Phosphate, EC and TDS were above the WHO permissible limits. Heavy metals content of waste water and sediments found Zn to be below WHO permissible limits. Ni, Mn, Pb, Fe and Cd were all above WHO limits. Zn, Ni, Mn, Pb, Fe and Cd were all above WHO limits in periwinkle (*Tympanotonusfucastus*), periwinkle shells, fish (*Elopssenegalensis*), orange crab (*Cardisomaarmatum*) and black crab (*Callinectesamnicola).* EDXRF characterization of waste toner shows a concentration of 35.4% of Fe_2O_3; MnO with a concentration of 20.56% and ZnO with a concentration of 15.1% among other toxic metallic oxides observed. The study recommended that further research should be carried out to ascertain the impacts of micro plastics, heavy metals and PAHs in receiving stream where drainage empties into.

DOI: https://dx.doi.org/10.4314/jasem.v29i3.16

Cite this Article as: OKAFOR, C. C; KONNE, J. L; JACK, I. R (2025). Physicochemical Parameters and Heavy Metals Content of Sediment, Water and Fauna of Printer Waste Toner Burdened Drainage System and its Receiving River around Mile 1 Diobu, Port Harcourt, Rivers State, Nigeria. *J. Appl. Sci. Environ. Manage.* 29 (3) 807-816

Dates: Received: 29 April 2024; Revised: 12 February 2025; Accepted: 10 March 2025; Published: 31 March 2025

Keywords: Heavy Metals; Sediment pollution; Water contamination; Waste Toner; Drainage; Physicochemical Parameters

More than 1.1 billion cartridges are sold every year, of which more than 500 million end up in landfills worldwide. Cartridges can be easily remanufactured up to 2–3 times, substantially reducing the number of cartridges going to landfills. However, waste toner powder (WTP) residue is hardly recycled and represents 8% wt of the printer cartridges (Assis *et al*., 2012). Waste toner generated from copiers and printers is a category of e-waste that has proven to be problematic due to its favored disposal techniques. The plastic waste and toner dust are disposed of using methods such as incineration and landfilling, they cause soil and water pollution leading to a multitude of health hazards (Babar *et al.*, 2019). Inkjet printers use printing inks, which contain chemicals such as butyl urea, cyclohexanone, ethoxylated acetylenic diols, ethylene diamine tetra-acetic acid, ethylene glycol, and several sulfur-containing dyes. During the printing process, many volatile organic solvents are released. Most of the components in printing inks are

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harmful chemicals, which pollute the environment (Aydemir and Ozsoy, 2020). Simple household inkjet printers contain two cartridges; one for black and the other for cyan, magenta, and yellow. If one of the colours is completed, the second cartridge has to be replaced altogether. The same is true in the case of high-end inkjet printers containing multiple cartridges for better colour reproduction in flex and photographs. Frequent replacement of multiple cartridges on depletion of even one colour results in bulk disposal of cartridges, thereby causing serious environmental pollution. The toner is used in photocopiers to form the latent electrical image on the drum. The paper picks up the toner particles (image), when it slides over the drum. Nearly 10% of toner particles are left over the drum for a normal document.The thermal properties of the toner should be soft for the fuser to bind and hard enough so that the toner particles are not fused in the photo receptor at the developmental stage (Krishnaraj and Vaira-Vignesh, 2015). The major component of toners is the resin (45-90%), which binds and fixes the toner onto the receiver, usually paper, thus creating a permanent image. The most commonly used binder resins are polystyrene, styrene acrylate copolymers, styrene-methacrylate copolymers, polyesters, epoxy resins, acrylics and urethanes. Styrene-acrylic copolymers have been most widely used because of their low cost and the ability to control the tribo-electric charge (Vucinic *et al.,* 2013). The toner is either in the dry form or wet form. Dry toners consist of acrylic and styrene powders together with colour pigments. Liquid toners consist of acrylic resins with added dye pigments to provide bright colour images. Colorants of toner powders may be either dyes or pigments or a combination of the two. Due to their high solubility in polymer resins as a colorant for black toner carbon black or iron oxide are used. Pigments used in chromatic toner powders in most cases are subject to commercial secret (Yordanova *et al*., 2019). Ewers and Nowak (2006) stated that waste toner powder is complex mixture of iron oxide, carbon black (which serves as pigment), polymethyl methacrylate (PMMA) ($C_5H_8O_2$) n, amorphous silica whose function is to serve as an additive, pigments (titanium hydroxide), polypropylene (C_3H_6) n, waxes, styrene acrylate copolymer ($C_8H_8.C_3H_4O_2$) n and some specific metal salts whose function is to control the electromagnetic properties. The toner is either in the dry form or wet form. Dry toners consist of acrylic and styrene powders together with colour pigments. Liquid toners consist of acrylic resins with added dye pigments to provide bright colour images. Laser printers are available in monocomponent and dual component models. In the former, toner powder and magnetic particles are mixed in a single printer drum. In the latter model, these are kept in separate drums and mixed with a developer while printing. Plastic resins constitute a major portion (45–90%) of toner powder and are generally made of styrene and acrylic polymers (Yordanova *et al*., 2019). Magnetic properties are imparted to the toner through iron oxide ingredients. In addition, various metals and semiconductors are added to the toner powder to induce triboelectric and superflow properties (Nakadate *et al*., 2018). Such a combination of organic and inorganic materials makes the toner powder stable and steadily fixes it to papers. Nevertheless, these ingredients render the toner nearly nondegradable and eco-unfriendly, posing serious environmental threats. Moreover, their small particle size (~10 μm) leads to serious respiratory problems and lung damage (Pirela *et al*., 2017). Toner waste is one of the major electronic waste materials posing serious environmental threat and health hazards. Globally, only about 20–30% of toner waste is recycled, while the remaining percentage is dumped in landfills. Recycling options are limited due to the desirably engineered durability of toners, ascribed to a complicated composition of chemicals, carbon black, and plastic particles, which in turn creates critical challenges in recycling. The World Health Organization has classified toner waste as class 2B carcinogen due to its potential health hazard (Parthasarathy, 2021).

There is paucity of data on waste toner laden drainage contents and its effect to the environment in the study area and Nigeria at large. There's is also assumption that the waste toner laden drainage empties itself into Receiving River in the environment, thereby polluting the river and endangering aquatic lives. However, the recycling and reuse of waste toner is difficult in this region and the only available method of disposing is in landfill and drainages. Therefore, the objective of this paper was to evaluate the physicochemical parameters and heavy metals content of sediment, water and fauna of printer waste toner burdened drainages system and it's receiving River around Mile One Diobu, Port Harcourt, Rivers State, Nigeria.

MATERIALS AND METHODS

Description of Study Area: Diobu is located in Port Harcourt City Local Government Area (PHALGA) of Rivers State in Nigeria. It is a densely populated neighborhood consisting of Mile 1, Mile 2 and Mile 3 good streets network. It houses two major markets in Port Harcourt; the Mile 1 and Mile 3 markets as well as the Ikokwu spare parts market and the Mile 3 timber market. It is the hub of commercial activities in Port Harcourt. Diobu is bordered by new

Government residential area (GRA) to the East, D/Line to the North-East, Rivers StateUniversity to the North-West, Old G.R.A to the East, Eagle Island to the South-West.

Mile one Diobu is located between Latitudes 40 47' 24"N and 40 49' 00" N, and longitudes between 60 59' 00" E and 70 01' 00", with an elevation of 468m.The area has the same weather condition like Port Harcourt as a region the climatic condition is the tropical climate. Mile One features a humid tropical climate with rainfall starting from the month of February through the month of November, while only the months of December and January truly qualifies as dry seasonmonths in the city. Rainfall is seasonal, variable, and heavy in Mile one Diobu. The mean annual temperature for Mile one Diobu is 26°C just as the case of Port Harcourt. It has approximately 30 streets and one of the largest markets in Port Harcourt. The market is surrounded by residential buildings, banks, Police Station, recreational park, commonly known as Isaac Boro Park, and car parks. Mile one in Diobu is a residential and commercial area as it attracts traders from different parts of Port Harcourt for the purposes of business transactions. Businessmen converge on daily basis to transact their businesses (Chukwu-Okeah, 2012). The map of the study area is shown in figure 1.

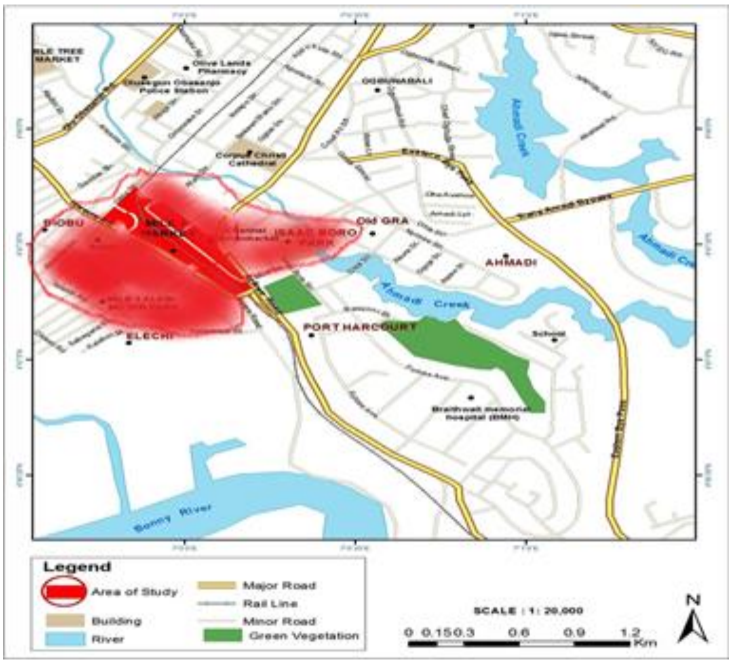

Fig.1: Map of Port Harcourt Showing Study Area (Field Survey, 2024).

Sample Collection: Samples from the study were water, sediment, periwinkle, periwinkle shells, black crab, orange crab, fish and waste toner. The samples were collected at different strategic location of the study area. The samples were collected taking into consideration apparent evidence of waste toner disposal carried out in the study area. Eight (8) waste water samples Samples were collected at 8 stations identified as (1) Urualla by Abakaliki Junction (2) Ikwerre Street (3)Njemanze by Awgu Street(4) Ojike by Abakaliki Street (5) Udi Street (6) Urualla by Illoabuchi Street (7) Urualla/Ojike/Elechi Water Front(8) Urualla/OjikeElechi Water Bodywith a pre-rinsed 1 litre plastic containers for the analysis of physicochemical parameters. Samples for heavy metals analysis were collected with 1 litre containers prerinsed with HNO_3 stored with 0.5% concentrated HNO_3. This was to stabilize the oxidation states of the metals. All the samples were transported with ice packs within an hour to the laboratory.

Sediments were collected with the aid of a plastic trowel to a depth of 0.5cm. Sediment samples were collected from the drains and at different locations where the drains empty into. The samples were immediately wrapped in aluminum foil to avoid contamination and taken to the laboratory.

The periwinkle (*Tympanotonusfucastus*), orange crab (*Cardisomaarmatum*) and black crab (*Callinectesamnicola*) were picked from the top of mud and few centimeters below the surface respectively. Fish (*Elopssenegalensis*) samples were caught with hand held net. Sorting of samples of similar sizes from the site were done by hand and rinsed with water and were placed in a locally made basket called “Kun” which were labeled according.

Three (3) waste toner samples from waste toner boxes of printing machines were collected from printing press within business center of Mile on Diobu Port Harcourt; considering the three (3) predominant toner types.

Physicochemical Analysis: The research adopted the method proposed by American Public Health Association (APHA) (1998).

The temperature of water and sediments samples was taken immediately on site using a thermometer calibrated indegree Celsius while the pH was determined using a pH meter (model HI 98130 Hanna).

Total dissolve solids were performed using a conductivity meter. The automated menu of the conductivity meterwas switched on to total dissolved solid. A volume of 100 cm^3 of the sample was poured into the beakerand the electrode which is part of the conductivity meter was introduced into the sample. The result ofthe total dissolved solid of the water and sediment sample shown on the display were noted (APHA, 1998).

Electrical conductivity was measured with conductivity Scan Meter model 1560. The probe of the meter was rinsed with demineralized water, for each measurement. The probe was thereafter immersed in the sample contained in a clean beaker and the instrument switched on for a stabilized digital display value expressed in µS/cm (Golterman*et al.*, 1978).

Nitrate (NO_3^-) was determined using Colorimetric Method.Ten (10) cm^3 of the water sample was transferred into 25ml volumetric flask. Then 2ml of Brucine reagent (dimethoxystrychnine-$C_{23}H_{26}O_4N_2.2H_2O$) was added, followed by the addition of 10ml of concentrated H_2SO_4. The content was mixed for about 30 seconds and allowed to stand for 30 minutes. The flask was air cooled for 15 minutes, made up to the mark, and the absorbance was measured by portable datalogying spectrophotometer model DR/2023 at the wavelength of 470nm. Standard nitrate solution was prepared by dissolving 0.8g of KNO_3 in 500 mL of distilled water. 0.5 mL of chloroform was added in order to preserve it. Aliquots having concentrations range of 0.01-2.0M of (NO_3^-) were prepared from stock solution and used to obtain a calibration curve. The absorbance obtained for each sample was compared to the calibration curve and the concentration of nitrate in each sample was obtained.

To determine Phosphate (PO_4^{3-}), standards WERE prepared using a phosphate standard solution of 3mg/L as phosphate (PO_4^{3-}). This isequivalent to a concentration of 1mg/L of phosphorus. The concentration and result from the procedurewere expressed in mg/L. Six (6) standard concentrations were prepared for every sampling data in the rangeof expected results. A serial dilution was prepared with varying: 0.00, 0.04, 0.08,0.12, 0.16, and 0.20. About 30 mL of the phosphate standard solution were poured into a 50 mL beaker.1-, 2-, 3-, 4-, and 5-mL Class A volumetric pipette was used to transfer a corresponding volume ofphosphate standard solution to each 25-mL volumetric flask.

Determination of Heavy Metals: The concentration (mg/L) of Pb, Ni, Cd, Mn, Fe and Zn in the water, sediments and faunas’ samples was determined usingthe atomic absorption spectrophotomer (Flame AAS) Model: S4=71096. The flame used for theanalysis was air-acetylene mixture. A standard solution ranging from 0.2 - 5.0mg/L was prepared forcalibration curves of the various metals. The hollow cathode lamp for the respective metals wasinstalled. A wavelength dial as specified by the analytical methodology was set. The instrument wasturn on, and the hollow cathode lamp was applied which started becoming warm until energy sourcewas stabilized for 10 - 20min. A 10cm, single-slot burner head was used by direct air-acetylene flamesmethod. The concentrated and digested samples were then aspirated and the actualconcentrations were obtained by referring to the calibration graph and necessary calculations.

Statistical Data Analysis: The IBM SPSS statistics was used to calculate the mean concentrations, standard deviation and standard error of mean and presented on tables and graphs.

Characterization of Waste Toner Samples: Elemental and chemical composition of toner powder was based on EDXRF analysis.

RESULTS AND DISCUSSION

The levels of physicochemical properties in waste water and sediments samples from the study are shown in Fig. 2 to 7. pH of sediment ranged from ranged from 6.83±0.21 to 7.36±0.11 with a mean of 7.10±0.12, while pH of waste water ranged from 6.57±0.07 to 7.30±0.0 with a mean of 7±0.06. The electrical conductivity (µS/cm) ranged from 234±1.32 to 5900±5.33 in sediment with a mean of

1564.13±4.3 while electrical conductivity for waste water (µS/cm) ranged from 844±5.32 to 26200±8.57 with a mean of 8168.5±6.32.

The temperature (℃) ranged from 27.5±0.22 to 27.7±0.22 in sediment with a mean of 27.61±0.22 while the temperature (℃) of waste water ranged from 20.5±2.32 to 24.8±2.12 with a mean of 23±2.38.

Total dissolved solids (mg/kg) ranged from 117±5.73 to 2950±34.31 with a mean of 781.36±14.34 in sediments while total dissolved solids (mg/L) of waste water ranged from 424±8.33 to 31000±18.32 with a mean of 4090.75±9.35.

Nitrate (mg/kg) for sediment ranged from 0.2±0.01 to 3.55±0.21 with a mean of 2.41±0.18 while nitrate in waste water (mg/L) ranged from 0.2±0.0 to 1.34±0.08 with a mean of 0.66±0.08.

Phosphate (mg/kg) for sediment ranged from 3.50±0.08 to 16±0.07 with a mean of 7.53±0.09 while the phosphate for waste water (mg/L) ranged from 2±0.08 to 21.5±0.06 with a mean of 13.16±1.06.

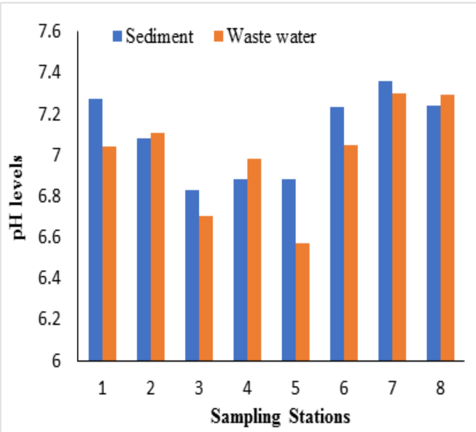

Fig.2: pH Levels of Sediment and Waste Water

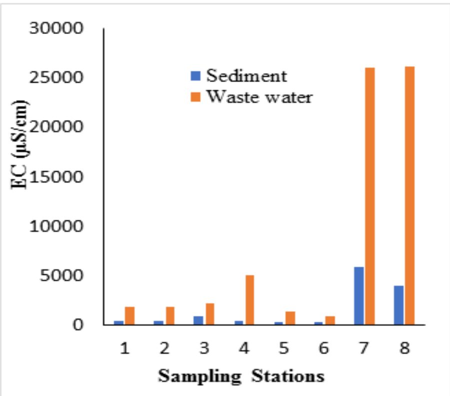

Fig.3: Electrical Conductivity Levels of Sediment and Waste Water

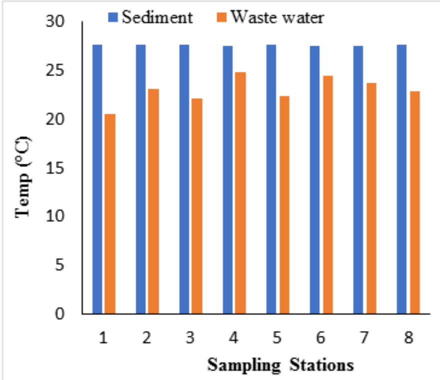

Fig.4: Temperature Levels of Sediment and Waste Water

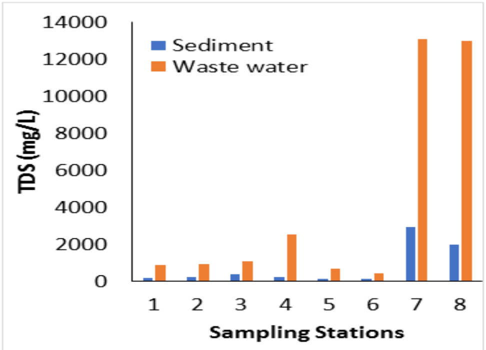

Fig.5: TDS Levels of Sediment and Waste Water

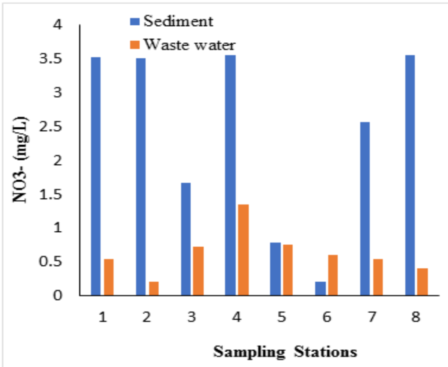

Fig.6: Nitrate Levels in Sediment and Waste Water

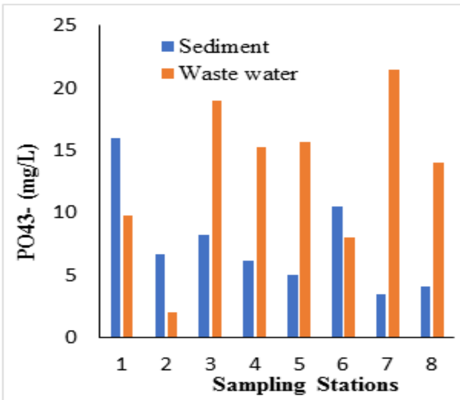

Fig.7: Phosphate Levels in Sediment and Waste Water

pH is a significant factor that impacts many biological and chemical processes. It is a water quality assessment parameter which is very important in evaluating water supply and treatment (Gray, 2020). The results from the study show that pH of the sediment samples ranged from 6.83±0.21 at station 3 to 7.36±0.11 at station 7 with a mean of 7.10±0.12. The pH of waste water ranged from 6.57±0.07 at station 5 to 7.3±0.0 at station 7 with a mean of 7±0.06. The mean pH levels of water and sediments were all within 6.5 – 8.5 which is WHO acceptable limits with sediment quality guidelines. Electrical Conductivity (µS/cm) ranged from 234±1.32 at station 6 to 5900±5.33 at station 7 in sediments with a mean of 1564.13±4.3. The EC (µS/cm) of water ranged from 844±5.32 at station 6 to 26200±8.57 at station 8 with a mean of 8168.5±6.32. The mean levels of EC (µS/cm) of water and sediments were above WHO acceptable limits with sediment quality guidelines of 500 µS/cm. This result shows that they are unsuitable for irrigation and other purposes. High conductivity results in this study shows that high quality of dissolved organic substances in ionized form could reach the water body. The temperature (oC) ranged from 27.5±0.22 to 27.7±0.22 in sediment with a mean of 27.61±0.22 while the temperature (oC) of water ranged from 20.5±2.32 to 24.8±2.12 with a mean of 23±2.38. The temperature levels obtained across the station for sediments and water was within WHO acceptable limits. Temperature reflects the reduction in solubility of gases in water. Amplification of taste and colour and also controls the rate of chemical reaction. High temperature enhances the growth of microorganisms and may increase problems related to taste, odour, colour and corrosion (WHO, 2011). Total dissolved solids (TDS) (mg/L) are the inorganic matter and small amounts of organic matter present in water in form of a solution. Results from the studies shows TDS (mg/kg) of sediments from 117±5.73 at station 6 to 2950±34.31 at station 7 with a mean of 781.36±14.34. The TDS (mg/L) of water ranged from 424±8.33 at station 6 to 13100±18.32 at staion 7 with a mean of 4090.75±9.35. The values of TDS exceeded WHO limits except station 5 and 6 of the sediments. Stations 7 and 8 for water and sediment showed very high values. The high values of TDS contribute in reducing the water clearness which contributes in reducing photosynthetic activities, perhaps leading to increase in temperature of the water (Aremu*et al.,* 2014). Nitrate levels recorded in the sediments ranged from 0.2±0.01mg/kg to 3.55±0.21mg/kg with a mean of 2.41±0.18mg/kg. The nitrate in water ranged from 0.2±0.0mg/L to 1.34±0.08mg/L with a mean of 0.66±0.08mg/L. The nitrate levels recorded were below the standard limits of WHO with sediment quality guidelines of 50mg/L. Phosphate levels recorded in the sediments ranged from 3.5±0.08mg/kg to 16±0.07mg/kg with a mean value of 7.53±0.09mg/kg. The phosphate levels in water ranged from 2±0.08mg/L to 21.5±0.06mg/L with a mean of 13.16±1.06mg/L. The values reported in the study for waste water and sediments exceed the recommended limit by WHO which is 0.5mg/L. *Heavy Metals:* The concentrations of heavy metals for waste water, sediments and fauna: periwinkle (*Tympanotonus fucastus*), periwinkle shells, fish (*Elops senegalensis*), orange crab (*Cardisoma armatum*) and black crab (*Callinectes amnicola*) is presented in Table 1 to 3 and Fig. 8 to 12. The concentrations of zinc in waste water in all stations ranges from 0.002±0.22±0.0 to 1.35±0.02mg/L, in sediments it ranges from 0.204±0.03 to 1.843±0.04mg/kg while fauna was 2.43±0.08 to 5.12±0.08mg/kg. The concentrations of nickel in waste water ranges from 0.023±0.01 to 0.862±0.02mg/L, in sediments it ranges from 0.029±0.01 to 0.745±0.06mg/kg while fauna was 2.042±0.14 to 4.605±01.41mg/kg. A manganese concentration ranges from 0.001±0.0 to 0.983±0.04mg/L in waste water, in sediments it ranges from 0.023±0.0 to 0.663±0.06mg/kg while fauna was 1.26±0.06 to 3.60±0.06mg/kg. Lead concentration in waste water ranges from 0.118±0.01 to 1.422±0.06mg/L, in sediments it ranges from 0.182±0.02 to 0.576±0.04mg/L while fauna was 1.483±0.09 to 3.043±0.06mg/kg. Iron concentration in waste water ranges from 1.128±0.08 to 5.106±1.83mg/L, in sediments it ranges from 21.495±4.12 to 94.048±6.13mgkg while fauna was 0.392±0.06 to 3.012±0.08mg/kg. The concentrations of cadmium ranges from 0.058±0.01 to 0.239±0.06mg/L in waste water, in sediments it ranges from 0.042±0.01 to 0.233±0.04mg/kg while fauna ranges from 0.043±0.02 to 0.484±0.03mg/kg.

Zinc (Zn) is one of the trace elements the body needs in minute quantity. It is known popularly as a booster to the immune system. However, excess quantity of it causes diarrhea in humans (Edori and Kpee, 2016). Results from the study in water, sediments and fauna: periwinkle (*Tympanotonusfucastus*), periwinkle shells, fish (*Elopssenegalensis*), orange crab (*Cardisoma armatum*) and black crab (*Callinectes amnicola*) shows that Zn across the stations was below the WHO acceptable limits of 3mg/kg. *Cardisoma armatum*, *Callinectes amnicola* and periwinkle shells were above WHO acceptable limits. *Callinectes amnicola* recorded the highest values of 5mg/kg.

Table 1: Concentrations of Heavy Metals in Waste Water

Stations	Zn (mg/L)	Ni (mg/L)	Mn(mg/L)	Pb (mg/L)	Fe (mg/L)	Cd (mg/L)
1	0.002±0.0	0.108±0.02	0.001±0.0	0.317±0.05	3.176±0.06	0.193±0.01
2	0.028±0.01	0.112±0.01	0.019±0.0	0.213±0.06	3.369±1.41	0.146±0.03
3	0.008±0.02	0.862±0.02	0.745±0.08	0.118±0.01	1.843±0.06	0.217±0.03
4	1.35±0.02	0.162±0.02	0.823±0.02	0.323±0.08	4.755±1.23	0.196±0.04
5	0.057±0.0	0.023±0.01	0.983±0.04	0.343±0.04	5.106±1.83	0.239±0.06
6	0.056±0.0	0.836±0.02	0.02±0.0	0.405±0.07	1.128±0.08	0.216±0.08
7	0.042±0.0	0.674±0.01	0.75±0.02	1.422±0.06	2.772±0.06	0.122±0.09
8	0.054±0.0	0.548±0.03	0.82±0.01	1.21±0.09	2.603±1.41	0.058±0.01
Mean	0.199±0.01	0.416±0.03	0.52±0.02	0.544±0.07	0.419±0.09	0.173±0.07

Table 2: Concentrations of Heavy Metals in Sediments

Stations	Zn (mg/L)	Ni (mg/L)	Mn (mg/L)	Pb (mg/L	Fe (mg/L)	Cd (mg/L)
1	1.843±0.04	0.128±0.06	0.098±0.0	0.428±0.03	64.543±4.64	0.152±0.01
2	1.704±0.04	0.086±0.07	0.023±0.0	0.432±0.02	68.59±2.41	0.116±0.04
3	1.549±0.08	0.432±0.08	0.415±0.04	0.275±0.0	76.457±8.63	0.127±0.03
4	1.53±0.06	0.173±0.04	0.663±0.06	0.182±0.02	79.267±7.41	0.219±0.02
5	1.158±0.05	0.103±0.04	0.028±0.01	0.576±0.04	56.928±9.21	0.233±0.04
6	0.204±0.03	0.745±0.06	0.024±0.01	0.451±0.03	21.495±4.12	0.211±0.08
7	0.22±0.01	0.543±0.06	0.42±0.01	0.527±0.0	94.048±6.13	0.074±0.01
8	0.98±0.01	0.029±0.01	0.66±0.01	0.438±0.0	90.367±7.98	0.042±0.01
Mean	1.149±0.03	0.279±0.06	0.291±0.03	0.414±0.03	68.962±5.87	0.147±0.03

Table 3: Concentrations of Heavy Metals in Periwinkle, Shells, Fish, and Crabs

Faunas	Zn (mg/L)	Ni (mg/L)	Mn (mg/L)	Pb (mg/L)	Fe (mg/L)	Cd (mg/L)
Periwinkle	2.43±0.08	3.086±0.06	1.632±0.03	2.083±1.41	1.853±0.09	0.484±0.03
Shells	3.2±0.06	2.43±0.07	2.23±0.04	1.483±0.09	3.012±0.08	0.332±0.08
Orange Crab	4.06±0.18	3.08±0.06	1.26±0.06	2.112±0.08	0.392±0.06	0.284±0.04
Fish	2.128±0.09	2.042±0.14	1.984±0.6	2.118±0.18	0.747±0.09	0.043±0.02
Black Crab	5.12±0.08	4.605±1.41	3.601±0.06	3.043±0.06	2.107±1.23	0.323±0.08

Nickel (Ni) is the most oxidized form of nitrogen compounds. It is generally found in surface and ground water, because it is the end product of aerobic breakdown of organic nitrogenous matter. The nitrate is not a direct toxicant but it could cause health hazard when converted to nitrite, the results shows that Ni levels in waste water, sediments, and the fauna were all above 0.07mg/L which is WHO acceptable limits with sediment quality guidelines.

Manganese (Mn) levels in waste water were above WHO acceptable limits of 0.20mg/L in the stations except 1, 2 and 6 which were below acceptable limits. Mn levels in sediments were above the WHO acceptable limits. Mn levels in periwinkle, shells, fish, orange crab and black crab were above the WHO acceptable limits. Pb concentrations in water ranges from 0.118±0.01mg/L to 1.422±0.06mg/L. Pb in sediments ranges from 0.182±0.02 to 0.576±0.04 mg/kg. In fauna periwinkle shells has the lowest concentration of 1.483±0.09mg/kg while black crab has the highest concentration of 3.043±0.06mg/kg. This result is worrisome because it exceeded the WHO standards with sediment quality guidelines of 0.01mg/L. The WHO limit of Pb in fauna is 1.7mg/kg. However, all the fauna species exceeded 1.7mg/kg except the periwinkle shells with a concentration of 1.483±0.09mg/kg. The high levels of Pb causes damage to the nervous connection, blood and brain disorder, most especially in young children. Other symptoms of acute Pb poisoning are headache, irritability and abdominal pain (Elinge*et al.*, 2013). Iron (Fe) exists in significant amounts in soil and rocks, principally in insoluble forms. It occurs naturally in ground formations which can give rise to more soluble forms. Fe concentrations in water, sediments and faunas all exceeded WHO standard and with sediment quality guideline of 0.30mg/kg. Fe concentrations in the sediments across the stations have high concentrations ranging from 21.495±4.12mg/kg at station 6 to 94.048±6.13mg/kg at station 7. Biologically Fe is the most important nutrient for most living creatures as it is a cofactor for many vital proteins and enzymes (Jaishankar *et al.*, 2014). Fe has been reported by Nwachukwu *et al.* (2014) to constitute a human health damage leading to hemochromatosis whose signs include fatigue and eventually heart disease, liver complications and diabetes. Cadmium (Cd) is an extremely toxic heavy metal even at low concentrations. It occurs naturally in rocks and soils from where it reaches ground water or surface water. The concentrations of Cd in water, sediment and faunas across all the stations exceeded the limit of 0.003mg/L recommended by WHO with sediment quality guidelines. This excess Cd if taken has damaging effect on human health. It is associated with cancer, hypertension, cardiovascular diseases as well as affecting the functionality of the kidney (Udousoro and Austin, 2019).

EDXRF Characterization of Waste Toner Samples: The elemental compositions of the three waste toner samples are presented in Fig. 8 to 10 and Table 4 to 6. Sample 001 has Fe_20_3 in the highest percentage of 35.4%, sample 002 has ZnO in the highest percentage of 15.1% and sample 003 has Fe_2O_3 in the highest percentage of 30.58%.

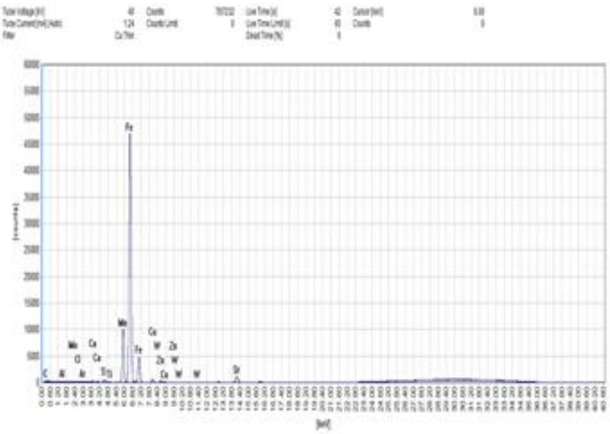

Fig.8: EDXRF Analysis for Waste Toner Sample 001

Table 4: EDXRF Elemental Compositions of Waste Toner Sample 001

Element	Name	Concentration (%)	Peak (cps/mA)
Fe_2O_3	Ferric Oxide	35.4	92216
MnO	Manganese (ii) oxide	20.56	75182
SiO_2	Silicon dioxide	10.04	463
SO_3	Sulfur trioxide	3.48	1784
CaO	Calcium oxide	3.61	2498
SnO_2	Tin(IV)oxide	1.23	5
ZnO	Zinc oxide	1.12	990

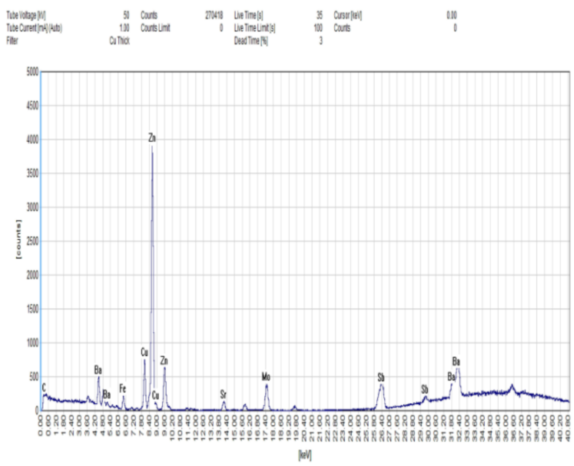

Fig 9: EDXRF Analysis for Waste Toner Sample 002

The chemical composition differences in the three (3) samples of toners were presented in Fig. 8 to 10 and Table 4 to 6. The results shows the presence of iron, titanium, silicon, manganese, sulphur, calcium, tin, zinc and cerium oxides with varying concentrations. Nanomaterials such as titanium oxide and pyrogenated silica are often used for better adhesion on inkjet ink glossy paper surfaces. Fe_2O_3 in sample 001 and sample 003 showed the highest percentage of 35.4% and 30.58% respectively. ZnO showed the highest percentage of 15.1% in sample 002. MnO in sample 001 also shows a high percentage of 20.56%. These results were similar to the Findings of

Fernandez *et al.* (2022) which found the presence of iron, titanium and silicon oxides, common in toners.

Table 5: EDXRF Elemental Compositions of Waste Toner Sample 002

Element	Name	Concentration (%)	Peak (cps/mA)
Fe_2O_3	Ferric Oxide	0.2	776
MnO	Manganese(ii)oxide	0.13	588
SiO_2	Silicon dioxide	4.52	347
SO_3	Sulfur trioxide	0.5	543
CaO	Calcium oxide	2.45	2244
ZnO	Zinc oxide	15.1	17181
Tio_2	Titanium dioxide	2.55	5710
CeO_2	Cerium dioxide	2.32	54
SnO_2	Tin(IV)oxide	1.21	2

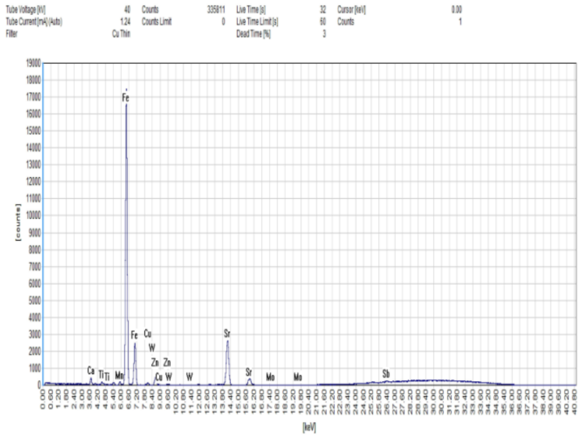

Fig 10: EDXRF Analysis for Waste Toner Sample 003

Conclusion: Results from the evaluation of heavy metals concentrations of sediments, water and fauna of waste toner laden drainage in the study area found pH levels to be within WHO set limits in both waste water and sediments. Nitrate levels were below WHO set limits. In contrast, Phosphate, EC and TDS were above the WHO permissible limits. Heavy metals content of waste water and sediments found Zn to be below WHO permissible limits. Ni, Mn, Pb, Fe and Cd were all above WHO limits. Zn, Ni, Mn, Pb, Fe and Cd were all above WHO limits in periwinkle, shells, fish, orange crab and black crab. EDXRF characterization of waste toner shows Fe_20_3 and ZnO in the highest percentage among other elements observed which are carcinogenic to human health.

Declaration of Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data are available upon request from the first author or corresponding author or any of the authors.

REFERENCES

APHA (1998). Standard methods for the examination of water and waste water (20th ed). American PublicHealth Association, Washington, DC. USA, p 77. DOI: https:doi.org/10.2105/SMWW.2882.035

Aremu, M; Majabi, G; Oko, J; Opaluwa, O; Gav, B; Osinfade, B (2014). Physicochemical analyses ofdifferent sources of drinking water in Okene Local government area of Kogi state, Nigeria. *Civ. Env. Res.* 6(5), 143-150. https://www.researchgate.net/publication/316547538

Assis, ACA; Barbosa, MF; Nabais, JMV; Custódio, AF; Tropecelo, P (2012). Diamond cell Fourier transform infrared spectroscopy transmittance analysis of black toners on questioned documents. *Foren. Sci. Intl*, 214, 59-66. DOI: https://doi.org/10.1016/j.forsciint.2011.07.019

Aydemir, C; Ozsoy, SA; (2020). Environmental impact of printing ink and printing process. *J. Grap. Eng. Des.* 11, 11–17. DOI: http://doi.org/10.24867/JGED-2020-2-011

Babar, S; Gavade, N; Shinde, H; Gore, A; Mahajan, P; Lee, KH; Bhuse, V; Garadkar, K; (2019). An innovative transformation of waste toner powder into magnetic g-C3N4 -Fe2O3 photocatalyst: Sustainable e-waste management. *J. Env. Chem.*

Eng. 7(10), 30-41. DOI: http://doi.org/10.1016/j.jece.2019.103041

Chukwu-Okeah, GO (2012) Predicting channel morphology from hydraulic parameters ofChinda Creek, Ogbogoro Rivers State. An unpublished M.sc Thesis, Depart of Geography and Environmental Management, University of Port Harcourt.

Edori, OS; Kpee, F (2016). Physicochemical and heavy metal assessment of water samples fromboreholes near some abattoirs in Port Harcourt, Rivers State, Nigeria. *American J. Chem. Sci*. 14(3), 1-8. DOI: http://doi.org/10.9734/ACSJ/2016/22525

Elinge, C. M; Itodo, AU; Peni, IJ; Birnin-Yauri, UA; Mbongo, AN (2013). Assessment of heavy metals concentrations in borehole waters in Aliero Community of Kebbi State. *Adv. App. Sci. Res.* 2, 279-282. DOI: http://doi.org/10.9734/ACSJ/2016/22525

Ewers, U; Nowak, D (2006). Health hazard caused by emission of laser printers and copiers. *Air Qual. Contl.* 66(5),203-210.

Fernández, B; Ayala, J; Del Valle, E; Martínez-Blanco, D; Castañón, AM Menéndez-Aguado, JM (2022). Recycling of waste toner powder as adsorbent to remove aqueous heavy metals. *Mat.* 15, 4150- 4174.

Golterman, HL; Clymo, RS; Ohnstad, MAM (1978). Methods for physical and chemical analysis of fresh water. 2nd.Billing and Sons limited Great Britain. p45.

Gray, NF (2020). Water Technology: an introduction for environmental scientists and Engineers, 7th ed.Arnold Publishers, London. p17.

Jaishankar, CP; Ollor, OA; Agi, VN; Azike, CA (2014). Assessment of physicochemical and bacteriological qualities of borehole water sources in Gokana local government area, Rivers state, Nigeria. *Intl. J. Patho. Res.* 3(3-4), 1-8. DOI: https://doi.org/10.9734/IJPR/2019/v3i3-430100

Krishnaraj, C; Vaira-Vignesh, R; (2015). Characterization of hybrid black toner using the parameters waste toner and nano phase carbon. *J. Eng. App. Sci.* 10(14), 6135-6139. https://www.researchgate.net/publication/283126299

Nakadate, T; Yamano, Y; Yamauchi, T; Okubo, S; Nagashima, D (2018). Assessing the chronic respiratory health risk associated with inhalation exposure to powdered toner for printing in actual working conditions: A cohort study on occupationally exposed workers over 10 years. *BMJ Open*, 8(2), 22-49. DOI: https://doi.org/10.1136/bmjopen-2018-022049

Nwachukwu, NM; Obodo, GA; Okonkwo, NA; Onwukeme, VI (2014). Physicochemical assessment of borehole waters in Ovim, Isiukwuato LGA, Abia State, Nigeria. *J. App. Chem*. 7(10), 31-33. DOI: http://doi.org/10.9790/5736-071013133.

Parthasarathy, M (2021). Challenges and emerging trends in toner waste recycling: A review. *Recycling*, 6(57), 1-14. DOI: http://doi.org/10.3390/recycling6030057.

Pirela, SV; Martin, J; Bello, D; Demokritou, P (2017). Nanoparticle exposures from nano-enabled toner-based printing equipment and human health: State of science and future research needs. *Crit. Rev. Toxic.* 47, 678–704. DOI: http://doi.org/10.1080/10408444.2017.1318354.

Udousoro, I; Austin, SI; (2019). Levels of some selected heavy metals in groundwater in Ebubucommunity, Eleme, Rivers state, Nigeria. *J. Earth Envir. Sci. Res.* 1(2), 1-5. DOI: http://doi.org/10.47363/JEESR/2019(1)111.

Vučinić, A; Vujević, D; Mujkić, K; Novak, M (2013). Recycling of waste toner in the Republic of Croatia–an environmentally friendly approach. *Chem. Eng. Trans*. 34, 121- 126. DOI: http://doi.org/10.3303/CET1334021

World Health Organization (WHO) (2011). Guidelines for Drinking-Water Quality. 4th Edition, World Health Organization, Geneva. p45.

Yordanova, D; Angelova, S; Dombalov, I (2019). Utilization options for waste toner powder. *Intl. Sci. J. Environ. Sci.* 8, 140-144. http://environment.scientific-journal.com/articles/3/23.pdf