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Full Length Research Paper

Temporal variation of SO$_2$ and NO$_2$ concentration around Parichha Thermal Power Plant, India

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The present study was based on Monthly variation of ambient air pollution in the village located within a radius of 3 km from the Parichhna thermal power plant (Jhansi, India). Parichha thermal power plant consumes annually 3.4 million tons of coal and the annual production capacity of the plant is 2.78 billion KWh. The thermal power plant uses approximately 10,000 tons of coal and emits large amount of air pollutants like fly ash, sulphur dioxide and oxides of nitrogen. Results revealed that the range of gaseous pollutants showed slight variation within the sampling dates during the four months under study. Although the average monthly concentration SO$_2$ (21±2.88 µg/m^3) and NO$_2$ (44±5.10 µg/m^3) was within the permissible limits given for industrial and residential areas, however, they are toxic on long term basis both for human health and nearby agricultural fields. The concentration of the SO$_2$ ranged between 17 to 28 µg/m^3, while the concentration of NO$_2$ ranged between 34 to 51 µg/m^3, during the study period. It is important to note that the values of the pollutants reported are after all the mitigative measures and preventive control equipments installed and working in the thermal Power plant. It has also been revealed that concentration of both gases was found to be consistently higher in the morning hours (8.00 to 10.00 h) compared to afternoon hours (12.00 to 14.00 h) throughout the study period.

Key words: Thermal power plants, pollution, coal, sulphur dioxide, nitrogen dioxide

INTRODUCTION

Thermal power plants are major sources of air pollution. Three major air pollutants emitted from these plants are Sulphur dioxide (SO$_2$), Sulphur trioxide (SO$_3$), Oxides of nitrogen (NO$_2$, NO$_3$) and Suspended Particulate Matter (SPM). The amount of pollutants emitted from any power plant depends upon the type of the fuel used, burning method and type of control equipment. These pollutants settle in ambient air. Coal is re-emerging as the dominant fuel for power generation in various power plants (Patel and Patel, 2006). In India, coal is the only natural resource and fossil fuel available in abundance for different large and small scale industries. Consequently, it is used widely as fuel for thermal power plants producing electricity and also as a thermal energy source (Mishra, 2004). In India, power generation has increased greatly in recent years to meet the demand of the increasing population (Jamil et al., 2009). The capacity of power generation has increased tremendously from

1362 MW in 1947 to 147,403 MW in 2008. India has installed capacity for electricity generation to about 90,000 MW, of which more than 70% is produced by coal based thermal power plants. Coal is the only fossil fuel available in abundance; hence its usage will keep growing for another 2 to 3 decades at least, till there is an improvement in renewable energy sources. Availability of coal in India is of poor quality such as petcock, lignite, bituminous etc., used in power plants in which the percentage of sulphur have 6.0, 4.0 and 3.8%, respectively; also with very high ash content and low calorific value. It has been found that metallurgical industry like steel plants use good quality coal but the coal supplied to thermal power plants is of the worst quality.

A number of the coal mines are owned by private companies and they do not wish to invest on quality improvement (Mishra, 2004). The thermal power plants during the combustion of coal emits mainly carbon dioxide (CO_2), sulphur oxides (SO_x), nitrogen oxides (NO_x), chlorofluorocarbon (CFC), other trace gases and airborne inorganic particulates such as fly ash and suspended particulate matter. The two important emissions of thermal power plants that have been taken under consideration for the present study are SO_x and NO_x.

SO_x

Sulphur dioxide is one of the main products released from the combustion of sulphur containing compounds in most energy fuels having significant environmental concern. The term SO_x is a generic term describing emissions of SO_2 and SO_3. It is predictable that just about 93% of the global SO_2 emissions are emitted in the northern hemisphere and the left over 7% are emitted in the southern hemisphere (WHO, 1979). The utmost anthropogenic sources of SO_2 consequence is from the burning of fossil fuels and from the smelting sulphide ores (Weil and Sandler, 1997). Presently SO_2 is the main issue pertaining to air pollution problems in developing countries, where it contributes both to urban pollution and to regional acid depositions (Cofala et al., 2004). Among man-made sources, fuel combustion (coal) in stationary sources accounts for 74%, industries 22% and transportation 2% of the total SO_x (De, 2012). A significant feature of SO_2 is that once it is emitted into the atmosphere it can be converted through complex oxidation reactions into fine particulate sulfate and removed from the atmosphere by wet or dry deposition (De, 2012; Skinder et al., 2014). SO_2 can be oxidized in the atmosphere to form sulphate aerosols that contribute to acid deposition (Holleman and Wiberg, 2001). Thus elevated level of SO_4^{2-} concentrations in rain water are due to strong SO_2 emissions from coal fired thermal power plants (Demirak, 2007).

NO_x

This represents composite atmospheric gases, nitric oxide (NO), and nitrogen dioxide (NO_2), which are primarily involved in air pollution. Nitric oxide (NO) is a colourless, odourless gas, but NO_2 has a reddish-brown colour and pungent suffocating odour (De, 2012). The formation of NO is favoured at high temperature, usually attained during much combustion process involving air (1210 to 1763°C). The second reaction is also favoured at temperatures of about 1100°C, but the amount of NO_2 formed is usually less than 0.5% of the total NO_x at 1100°C. It is also formed by photolytic reaction; further man-made sources annually release 5×10^7 tons of NO_x (De, 2012). The NO_2 levels depend mainly on chemical reactions and not on direct emissions (Mayer, 1999). It is considered that coal-fired power plants and vehicles are the nation's largest sources of nitrogen oxides and NO_x produced in high temperature combustion processes (Memon, 2000; Emberson et al., 2001; Skinder et al., 2014).

NO_x is emitted from a variety of natural and anthropogenic sources (Al-Khalaf, 2006). Nitric oxide (NO) is by far the most important nitrogen containing species emitted into the atmosphere on a mass basis from human activities involving motor traffic, brick kilns and combustion in thermal power stations, in homes or industrial processes (Williams, 2000; Kumar and Joseph, 2006; Ali and Athar, 2006; Skinder et al., 2014). NO_x levels were found to be stabilized in residential and industrial zones but increased alarmingly at commercial zones representing higher traffic activities (Goyal et al., 2006). Moreover, NO_x concentration has been found to be at its peak during late hours of the day due to high traffic density of public and commercial vehicles (Jain and Saxena, 2002). NO_2 levels were also higher in the post monsoon season followed by winter and pre-monsoon seasons (Goyal et al., 2006).

A chemical reaction in atmosphere converts primary pollutants into secondary air pollutants. Sulfur dioxide and nitrogen dioxide goes under oxidation process and gets converted to particulate sulfate and particulate nitrates and are important features of urban air photochemistry. The rates for the formation of sulfate and nitrates in the atmosphere through conversion mechanisms are of considerable interest. It is because the conversion rates are important factors in controlling the concentrations of NO_2 and SO_2. Thus, concentration of gases decreases on temporary basis as these are transformed into secondary products. Moreover, the rate of the conversion of nitrogen oxides to nitrate affects ozone formation and ultimate fate of the nitrogen oxides in the atmosphere. The environmental effects of these secondary pollutants are associated with acidification of precipitation, visibility reduction and its deleterious effects on human health (Khoder, 2002; Skinder et al., 2014).

MATERIALS AND METHODS

Study site

The present study was carried out around Parichha thermal power station. It is situated in Jhansi district of Uttar Pradesh, India. Jhansi district lies in the Bundelkhand region. Jhansi has an area of 45.22 sq Km and a population of about 4.70 million, situated at a height of about 255 m above mean sea level (asl). Jhansi district lies between 25° 27'4"N to 25° 28'4"N latitude and 77° 38' 28"E to 77° 40' 12"E longitude in the semi arid region of the country. The power station is owned by the central government and is a coal fired station located near the National highway on the northern bank of Betwa river in Jhansi district. The power station is surrounded by villages such as Badagawn, Goramachiya, Chirgawn etc., and as per latest census report Parichha has a total population of around 2000. The average annual rainfall ranged between 800 to 930 mm in summer, furthermore, humidity during morning hours was 40 to 50% and for the rest of the day 15 to 20%. The maximum temperature during summer is 45°C and the minimum temperature is 25°C. While in winter, maximum temperature is 23°C and the minimum temperature is 4°C. It has limited vegetative cover and most of the land is used for agricultural practices.

Estimation of gaseous pollutants

Gaseous pollutants (SO_2 and NO_2) samplings were carried out every fortnightly. The gaseous pollutants were absorbed in appropriate absorbents prepared and placed in the impingers. A handy air sampler (model, PEM-HAS IB) was employed for collecting the gaseous pollutants. This model has a set of two borosilicate glass impingers (35 ml) to collect two different gaseous pollutants separately at a time. The flow rate of the air was adjusted at 1.5 L per minute (LPM). On each sampling date the instrument was ran twice for two hours between 8.00 to 10.00 h and 12.00 to 14.00 h. The impingers were covered by ice while in operation: transportation and storage of collected samples in the laboratory before the analysis. All the samples were analyzed within 3 h of the collection of the samples.

Determination of sulphur dioxide in air

The method for measuring SO_2 was adapted from West and Gaeke (1956). In this method, air-exposed samples are treated in a solution of potassium tetrachloro-mercurate (TCM). A dichlorosulphitomercurate complex is formed, which subsequently reacts with pararosaniline and formaldehyde to form the intensely coloured pararosaniline methylsulphonic acid. The absorbance of the coloured solution was measured with spectrophotometer at 560 nm, and the concentration of SO_2 was determined based on a calibration curve.

Determination of nitrogen dioxide in the atmosphere

The principle of NO_2 measurement in atmospheric samples was described by Jacob and Hochheiser (1958). Ambient nitrogen dioxide (NO_2) is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion (NO_2^-) produced during sampling is determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide, and N-(1-naphthyl)-ethylenediamine di-hydrochloride (NEDA) and measuring the absorbance of the highly colored azo-dye at 540 nm.

RESULTS AND DISCUSSION

Monthly variation of ambient air pollution in the village located within a radius of 3 km from the Parichhna thermal power plant has been presented in the Table 1. Results revealed that the range of gaseous pollutants showed slight variation within the sampling dates during the four months under study. Sulphur in coal cannot be destroyed; it can only be converted from one form to another. During the combustion process, sulphur reacts with oxygen and formed SO_2 and SO_3 (Buecker, 2006; Patel and Patel, 2006). The average monthly concentration of SO_2 (21 ± 2.88 µg/m^3) and NO_2 (44 ± 5.10 µg/m^3) was within the permissible limits given for industrial and residential areas, Table 2. The concentration of the SO_2 ranged between 17 to 28 µg/m^3. While the concentration of NO_2 ranged between 34 to 51 µg/m^3. Although, the reported values of SO_2 and NO_2 lie within the limits, however, they are toxic on long term basis. It is important to note that the values of the pollutants reported are even after all the mitigative measures and preventive control equipments installed and working in the thermal power plant. It is considered that coal fired power plants and vehicles are the nation's largest source of nitrogen oxides (NO_x) and is produced in high temperature combustion processes (Memon, 2000; Emberson et al., 2001). While Sulphur dioxide is a prime pollutant which is released directly to the atmosphere from domestic and industrial processes, particularly those using petroleum and coal combustion (Wellburn, 1998; Emberson et al., 2001).

A temporal variation in SO_2 and NO_2 concentration was observed in all the sampling dates shown in Figures 1 and 2. Concentration of both gases was found to be consistently higher in the morning hours (8.00 to 10.00 h) throughout the study period compared to afternoon hours (12.00 to 14.00 h). The concentration of SO_2 during 8.00 to 10.00 h ranged between 19 µg/m^3 (15th April) to 28 µg/m^3 (15th March). Corresponding concentration of SO_2 on the same sampling dates during 12.00 to 14.00 h ranged between 17 µg/m^3 (15th April and 14th May) and 25 µg/m^3 (15th March).

Similarly, the concentration of NO_2 during 8.00 to 10.00 h ranged between 42 µg/m^3 (30th June) to 52 µg/m^3 (29th May). Consequent concentration of NO_2 on the same sampling dates during 12.00 to 14.00 h ranged between 36 µg/m^3 (30th June) and 45 µg/m^3 (15th March). Results also revealed that concentrations of SO_2 were lower than the NO_2 as shown in the Figure 3. These results are in consonance with the results of Cerón-Bretón et al. (2013).

The present study shows that the concentration of gases (SO_2 and NO_2) were found to be consistently higher in the morning hours throughout the study period compared to afternoon hours, it is because as the temperature increases, photochemical reactions transform NO_2 into secondary air pollutants which may lead to reduction of NO_2 in the afternoon hours

Table 1. Levels of SO_2 (µg/m^3) and NO_2 (µg/m^3) around Parichha Thermal Power Plant (India).

Sampling Date	Time (h)	Concentration of gases (µg/m^3)	
		SO$_2$	NO$_2$
15th March	08.00-10.00	28	51
	12.00-14.00	25	47
31st March	08.00-10.00	24	48
	12.00-14.00	22	41
15th April	08.00-10.00	19	39
	12.00-14.00	17	34
30th April	08.00-10.00	23	50
	12.00-14.00	18	45
14th May	08.00-10.00	21	49
	12.00-14.00	17	38
29th May	08.00-10.00	24	52
	12.00-14.00	18	45
14th June	08.00-10.00	22	49
	12.00-14.00	19	37
30th June	08.00-10.00	25	42
	12.00-14.00	18	36
Average monthly mean (µg/m^3)		21 (±2.88)*	44 (±5.10)*

*Standard deviation.

Table 2. National ambient air quality standards (NAAQS), CPCB, 2009.

Pollutants	Time weighted average	Concentration in ambient air	
		Industrial, residential, rural and other areas	Ecologically sensitive area (Notified by Central Government)
Sulphur dioxide (SO$_2$), µg/m^3	Annual *	50	20
	24 h **	80	80
Nitrogen dioxide (NO$_2$), µg/m^3	Annual *	40	30
	24 h **	80	80

*Annual Arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.**24 hourly or 8 hourly or 1 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

(Finlayson-Pitts and Pitts, 1993) as it receives solar radiations and the ozone is produced (Tang, 2009; Elampari et al., 2010). It has also been discussed that temperature has also significant effect on SO$_2$ concentrations (Salam et al., 2008). Due to the increasing temperature photochemical activities increase and also in the presence of ozone concentration (formed due to NO$_x$), which increase the oxidation of SO$_2$ and its conversion rate to sulfate (Spicer, 1986; Khoder, 1997; 2002).

Temporal variation of SO$_2$ and NO$_2$ concentration during the day, tally with the activities producing this pollutant such as thermal power plants; although the main source of SO$_2$ and NO$_2$ are thermal power plants, there are other sources as traffic flow, burning of agricultural biomass and other domestic or residential

Figure 1. Time-series and bimonthly variation for SO₂ concentrations during the sampling period around Parichha Thermal Power Plant in the Year 2008.
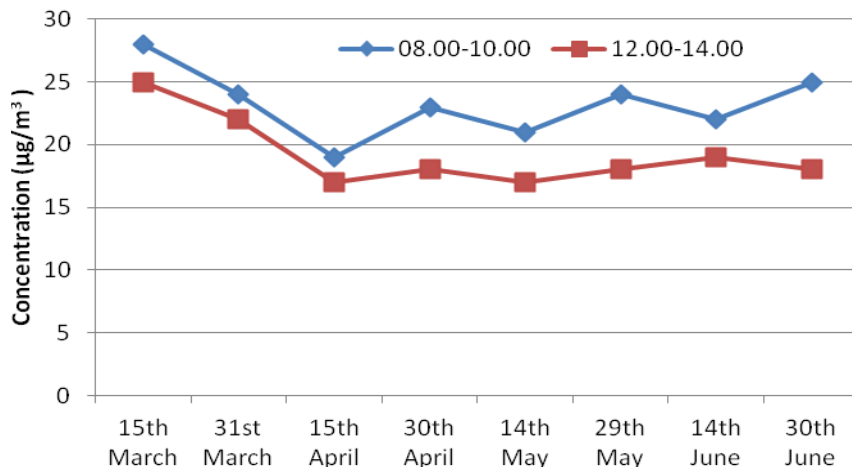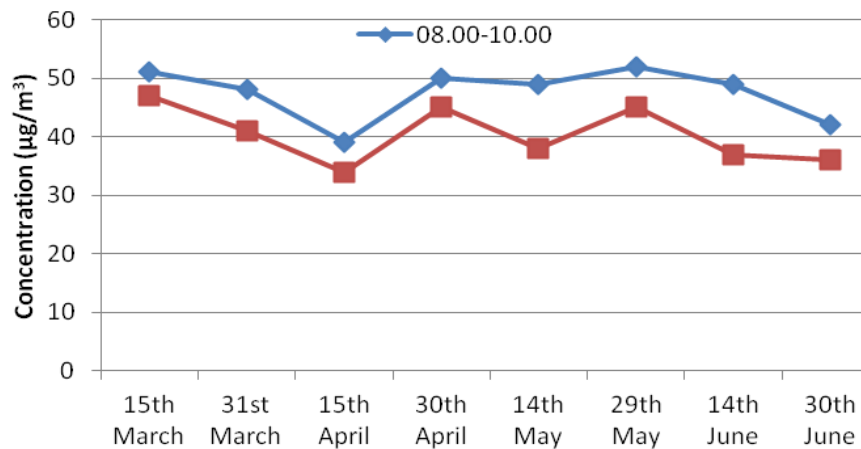
Figure 2. Time-series and bimonthly variation for NO₂ concentrations during the sampling period around Parichha Thermal Power Plant in the Year 2008.
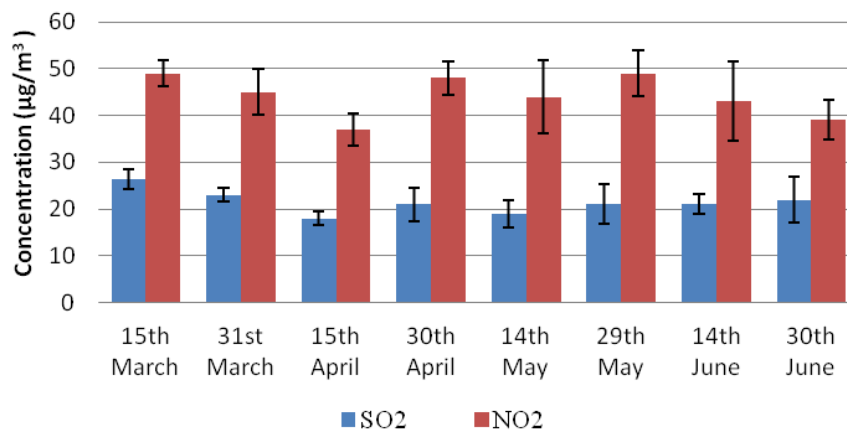
Figure 3. Comparison of SO₂ and NO₂ concentrations around Parichha Thermal Power Plant in the Year 2008.

activities. The results revealed that the values of SO_2 (within the vicinity of Parichha Thermal Power Plant) were lower than the concentration of NO_2; this variation might be attributed largely due to the proximity of the sampling site to the National High Way connecting Jhansi and Kanpur. The selected sampling sites were located just a few 100 m from the National High Way as the thermal power plant is located nearer to this highway. It is the fact that vehicular emissions contribute more NO_2 than SO_2 (Williams, 2000; Jackson, 2005a; Kumar and Joseph, 2006; Ali and Athar, 2006). Similarly, the concentration of SO_2 from motor vehicles is very low as compared to stationary sources (Williams, 2000). Thus this pattern is consistent with the observed temporal variation of NO_2 and SO_2 in the current study.

Due to continuous and long lasting emission of SO_2 and NO_2, which are the principal pollutants of coal based power plants, affecting surrounding structures, buildings, monuments of historic importance and metallic structures very badly due to corrosive reactions (Acid rain). Renowned example of this is the victimized Taj Mahal in the city of Agra which is being deteriorated due to these toxic gases (Butler et al., 2002; Dene, 2002; Pokale, 2012). Health effects caused by exposure to high levels of SO_2 include breathing problems, respiratory illness, changes in the lung's defenses and worsening respiratory and cardiovascular diseases (Skinder et al., 2014). People with asthma or chronic lung or heart diseases are the most sensitive to SO_2 (Prasad et al., 2010). The coal fired Parichha Thermal Power Plant besides emitting gaseous pollutants also emits huge quantity of fly ash particles which are deposited on surrounding agricultural lands and consequently deteriorates the soil quality in addition to vegetation (Kumari, 2009).

Conclusion

The present study showing that the concentration of gases (SO_2 and NO_2) was found to be consistently higher in the morning hours throughout the study period compared to afternoon hours. This temporal variation of SO_2 and NO_2 concentration during the day, tally with the activities producing this pollutant such as thermal power plant, traffic flow, burning of agricultural biomass and other domestic or residential activities, and it is necessary to note that the values of the pollutants reported in this study are even after all the mitigative measures and preventive control equipments installed and working in the thermal Power plant. So the government agencies related to pollution control should keep this into consideration for the proper monitoring of air quality in the coal based power plants to prevent environment from degradation.

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Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

Bioaccumulation of some trace element (Zn, Fe, Pb and Cu) in the gills and tissues of *Clarias gariepinus* and *Oreochromis niloticus* in River Ogbese, Ondo State, Nigeria

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River Ogbese support many human activities (domestic, agricultural, fishing, industrial activities) leading to its extensive contamination and accumulation of heavy metals which can cause both environmental and public health hazard. In order to ascertain the quality of the river, a study was carried out to determine some trace element concentration (Zn, Fe, Pb and Cu) in gills and tissues of *Clarias gariepinus* and *Oreochromis niloticus*, being the most dominant fish species in the water body. Thus, ten samples each of *C. gariepinus* (21.0 – 37.4TL, 171.7 – 305.8 g) and *O. niloticus* (15.2 – 20.6 TL, 70.8 – 150.5 g) were collected from River Ogbese and the concentration of Zinc, Iron, Lead and Copper were analyzed both in the gills and the flesh using atomic absorption spectrophotometry (AAS). The study revealed that the highest concentration of iron was obtained in the gills and tissues of both fishes; *C. gariepinus* (gill - 6.70-4.23±0.72, tissue - 6.84 - 5.27±0.44) and *O. niloticus* (gill - 6.79 - 1.89±1.42, tissue - 5.83-4.27±0.58). The metal concentration occurred in the order Fe>Zn>Cu>Pb. In general, accumulation of the essential elements; Zn, Fe, Cu were higher than the non-essential elements; Pb. This could be due to the fact that these essential elements are naturally abundant in Nigeria soil. The bioaccumulation of zinc and lead are significant (P>0.05) in the tissues of both species while iron varies significantly (P>0.05) in their gills. There is no significant variation (P<0.05) observed among zinc, lead and copper accumulated in the gills of both species.

Key words: River Ogbese, heavy metals, *Clarias gariepinus* and *Oreochromis niloticus*.

INTRODUCTION

Metals such as Fe, Cu and Zn are generally regarded as essential trace metals in view of their valuable role for metabolic activities in organisms, other metals like Cd, Pb, Ni and Hg exhibit extreme toxicity even at trace levels (Merian, 1991; DWAF, 1996). However, it is of interest to note that most essential metals are toxic when supplied in concentrations in excess of the optimum levels. Tam and Wong (1995) stated that heavy metal contamination

in aquatic environments is of critical concern due to the toxicity of metals and their accumulation in aquatic habitats. River Ogbese is one of the prominent water body in Ondo State, Nigeria, the main uses of the river in the catchments include domestic, recreational (e.g. swimming) and fishing. Also, domestic, industrial and agricultural wastes are dumped into the river, as such causing contamination and accumulation of metals which could bio-accumulate in the aquatic biota. Among the aquatic fauna, fish is the most susceptible to heavy metal toxicants (Nwaedozie, 1998) and are more vulnerable to metal contamination than any other aquatic fauna. As a result, fishes are considered as better specimens for use in the investigation of pollutant loads than water samples because of the significant levels of metals they bioaccumulate.

Significant heavy metal levels were recorded in fishes of Warri River (Atuma and Egborge, 1986); Kolo creek, fish and shellfish of the Niger Delta (Kakulu et al., 1987); water, sediment and Tilapia zilli from Kolo creek, Ogbia, Bayelsa, (Ebenezer and Eremasi, 2012). Data provided by Agada (1994) show evidence of selected heavy metal contamination of *Chrysicthys nigrodigitatus* (catfish) and *Pseudotolithus elongatus* (Croaker) respectively. Also, Sani (2011) examined the concentration of heavy metal in tissues of Tilapia and Catfishes. Similarly, this study is undertaken to determine the concentration of heavy metal in gills and tissue of *Clarias gariepinus* and *Oreochromis niloticus* in River Ogbese. *C. gariepinus* and *O. niloticus* are of great commercial importance because they are widely consumed freshwater fish in Nigeria (Olaifa et al., 2004) and the most dominant species in the River. It is therefore a good choice to study their susceptibility to environmental contaminants, particularly the heavy metals so that the result can provide baseline data on the current pollution status of this river and to predict the safety of their consumption in the environment.

MATERIALS AND METHODS

Study area

River Ogbese lies between longtitude 5°26' and 6°34' and latitude 6°43'E and 7°17' E. The River runs through Ogbese town, a town which is about five kilometres from Akure, in Akure North Local Government Area of Ondo State, Nigeria. River Ogbese is one of the major perennial rivers in South Western Nigeria; it took its source from Awo Ekiti in Ekiti State. It flows for approximately 22 km from its source to meet River Ose which is 265 km long and discharges into the Atlantic Ocean through an intricate series of creeks and lagoons (Figure 1).

Samples collection

Fish samples were collected from fishermen in River Ogbese using gillnets which were set over-night. The fishes were transported to the laboratory in a picnic box with some quantity of water (from the river). Each fish was properly cleaned by rinsing with distilled water

to remove debris, planktons and other external adherent. The samples were then dried, wrapped in aluminium foil and then frozen at –10°C prior to analysis.

Sample preparation

The fish samples were defrosted for two hours and the scales were removed from the tilapia using a plastic knife. Catfish (*C. gariepinus*) and Tilapia (*O. niloticus*) were dissected to remove organs (tissue and gills) according to FAO methods cited by Dybem (1983). The fish parts were dried at 80°C for 2 h in Gallenkamp hot box oven and then blended in an electric moulienx blender. Approximately, 0.5 g each of sample was weighed and ashed at 550°C for 24 h in an electric muffle furnace. The ash was diluted in 5 ml of concentrated hydrochloric acid (HCl) and concentrated nitric acid (HNO_3) mixed at ratio 3:1. The diluents is left for some minutes for proper digestion in a beaker of 50 ml, distilled water was added to the diluents to make up to 100 ml in volumetric flask. This was then filtered into a conical flask with filter paper. The levels of heavy metals such as iron, copper, lead and zinc were determined using Shimadzu AA-680 Japan Atomic Absorption Spectrometer flame emission spectrometer fitted with GFA – 4B Graphite Furnace, according to AOAC (1995) and the results were given in milligram per litre (mg/L).

Data obtained from the experiments were analyzed and the results were expressed as mean ± S.D. The results were evaluated using Student's test and two way correlation. Values of $p < 0.005$ were considered statistically significant.

RESULTS AND DISCUSSION

The concentration of heavy metals; (Copper, Lead, Zinc and Iron) in the gills and tissues of *C. gariepinus* and *O. niloticus* from River Ogbese indicates a level of metal pollution. This may be attributed to the various human activities, such as discharge of untreated sewage and uses of industrial materials that contain metals or the ability of the sediment to act as sink (Olowu et al., 2010). The presence of these elements in both the gills and tissues of fish in the study area agrees with studies carried out in some water bodies in Nigeria as presented in Table 1. Hence, heavy metal contamination affect the aquatic life of fresh water fish, therefore, proper monitoring of the aquatic systems is of great importance since the continuous bioaccumulation of these metals will lead to health hazard of the consumer of these economically important fish species from the water body. The mean concentration of Zinc (Zn), Iron (Fe), Copper (Cu) and lead (Pb) obtained in the gills and tissues of the two fish species are presented in Tables 2 and 3. The result obtained from the determination of Zn, Fe, Cu and Pb in the gills of the two fish species are represented in Figure 1. For tissue, the results are represented in Figures 2 and 3

Concentration of trace element in the gills and tissue of *C. gariepinus*

Table 2 shows the concentration pattern of trace elements in *C. gariepinus*, following the order Fe<Zn<Cu<Pb. The
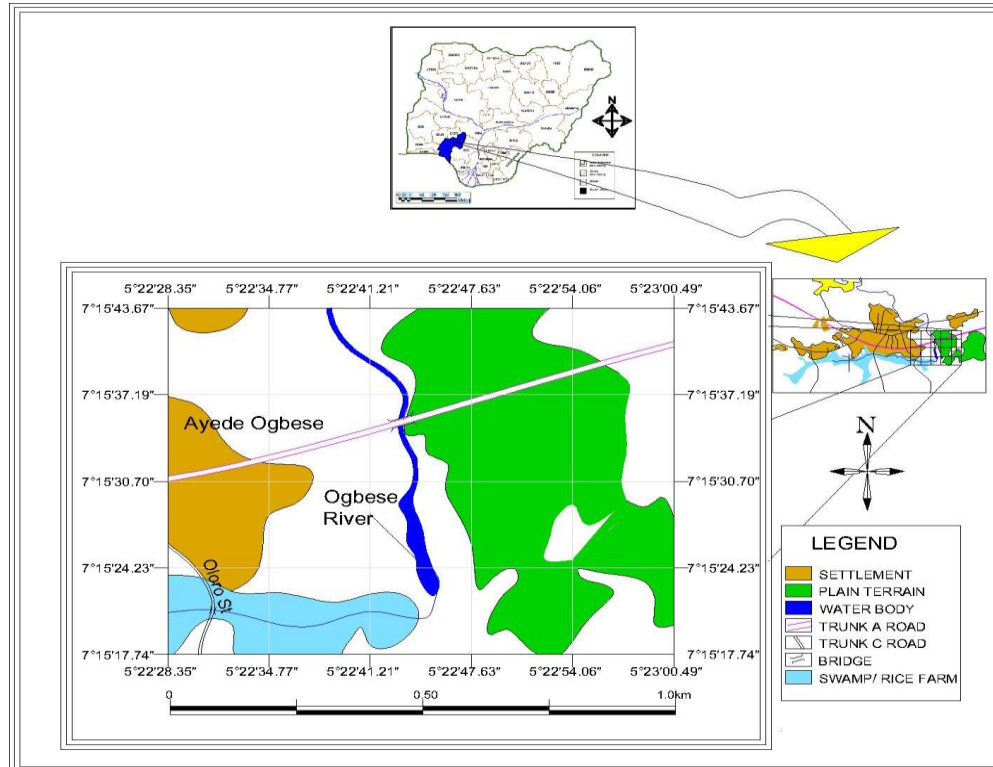
Figure 1. The map of River Ogbese.

result shows that Iron has the highest values in the tissue and gills of *C. gariepinus* (6.84±0.44 and 6.70±1.40). Although the concentration of iron was more in the tissue than the gills; an indication of bioaccumulation of Fe in the flesh of this species over time. Adeyeye and Ayoola (2012) revealed in their study of heavy metals concentration in some organs of *C. gariepinus* from Eko-Ende Dam, Ikirun, Nigeria, iron was the most abundant of all the metals considered. The result showed that the bioaccumulation of Zn in the tissue is more than that of the gills. The range of Zn was 2.84±0.28 and 1.44±0.37 in tissue and gills respectively. Thus, heavy metals when discharged into the river enter the food chain and accumulate into the fish body as observed during this study.

According to Allen-Gill and Martynov (1995), high levels of copper and zinc in fish muscles appear to be due to high levels of binding proteins in the muscles. Also, the high concentrations of iron and zinc in the fish parts could be associated to the fact that these metals are naturally abundant in Nigeria soils and since the source of metal depositories is the aquatic system (Olowu et al., 2010). The accumulation of iron is statistically significant in gills (>0.005) whereas zinc and lead vary significantly in the tissue. The concentration of copper in the tissue (1.68±0.23) is higher than the gills. This agrees with Sani (2011) who recorded highest copper concentration in the tissues of catfish than the gills and bones. On the

contrarily, Yilmaz et al. (2007) reported that in *Leuciscus cephalus* and *Lepornis gibbosus*, copper, cadmium, and cobalt accumulations were higher in the liver and gills than in the fish muscle. It is generally accepted that heavy metal uptake occurs mainly from water, food and sediment. However, the efficiency may differ in relation to ecological needs, metabolism and the contamination gradients of water, food and sediment, as well as other factors such as salinity, temperature and interacting agents (Pagenkopf, 1983).

The concentration of lead is higher in the gills (1.40±0.44) than the tissues (0.9±0.19) as agrees with Uzairu et al. (2009) in their study of the concentration levels of trace metals in fish and sediments from Kubani River, Northern Nigeria. However, the concentration of metals in gills reflects their concentration in water where the fish lives. Nevertheless, the presence of higher amounts of heavy metals in any parts of the body will definitely induce changes in biochemical metabolisms and other induced stresses.

Concentration of trace element in the gills and tissue of *O. niloticus*

The concentration pattern of trace elements in the gills and tissues of *O. niloticus* follows the order Fe>Cu>Zn>Pb. Iron has the highest values in the tissue

Table 1. Heavy metals concentration in fish (mg/kg) in studies from other locations in Nigeria.

Location/ Fish	Organ	Zn	Cu	Fe	Pb	Reference
Ogun River, Nigeria	Liver	19.75	4.70	--	3.40	Farombi et al. (2007)
(*Clarias gariepinus*)	Gill	20.35	4.55	--	2.40	
Kidney		5.00	--		3.35	
Heart		2.19	--		1.69	
Alau Dam, Maiduguri, Nigeria	Liver	0.52	0.44	0.40	0.40	Dimari et al. (2008)
(*Tilapia gallier)*	Gill	0.36	0.63	0.33	0.53	
Intestine		0.36	0.34	0.12		
Okumeshi River, Delta, Nig.	Liver	--	--	--	0.01	Ekeanyanwu et al. (2010)
(Tilapia)	Gill	--	--	--	<0.01	
Muscle		--	--		<0.01	
Kubani River, Zaria, Nigeria	Liver	49.56	19.31	--	0.28	Uzairu et al. (2009)
a. (*Clarias gariepinus*)	Gill	20.05	1.87	--	0.12	
Muscle		0.24	--		0.04	
b. (*Oreochromis niloticus*)	Liver	65.72	40.11	--	0.76	
Gill		5.32	--		0.24	
Muscle		1.15	--		0.02	
Lake Chad, Nigeria	Liver	0.54	0.52	0.34	0.32	Akan et al. (2009)
a. (*Tilapia zilli)*	Gill	0.33	0.45	0.28	0.03	
Kidney		0.31	0.15	0.01		
b. (*Clarias anguillaris*)	Liver	0.31	0.32	0.26	0.15	
Gill		0.32	0.24	0.10		
Kidney		0.21	0.12	0.02		
Henshaw Beach, Calabar, Nigeria	Liver	0.257	--	--	0.173	Edem et al. (2009)
(*Oreochromis niloticus*)	Gills	0.198	--	--	0.133	
(Group A: 29 cm size)		0.079	--	--	0.053	
Tiga Dam, Kano, Nig	Gill	-	0.00		2.30	Sani (2011)
(a) Tilapia	Muscle	-	0.11		2.00	
Gill		0.45	5.20			
(b) Catfish	Muscle		0.51		7.20	
Eko-Ende Dam, Ikirun, Nigeria						
(*Clarias gariepinus*)	Gill	1.45	0.68	11.64	ND	Adeyeye and Ayoola (2012)
Muscle		0.15	6.99	ND		
FAO/WHO Limits		40	30		0.5	FAO/WHO (1989)
IAEA – 407			3.28	146	0.12	Wyse et al. (2005)

and gills of *O. niloticus* (5.83±0.58 and 6.79±1.42 respectively). Although higher concentration was recorded in gills than the tissue which could be attributed to the fact that water always passes through mouth and gill when filtered, which agrees with the findings of Olowu et al. (2010). Dural et al. (2007) and Ploetz et al. (2007) reported highest levels of cadmium, lead, copper, zinc and iron in the liver and gills of fish species viz. *Sparus aurata, Dicentrachus labrax*, *Mugil cephalus* and *Scomberomorus cavalla*. The concentration of copper in the tissue of *O. niloticus* (4.46±1.48) is higher than the gills (1.44±0.12 and 2.86±0.51). This agrees with Sani

Table 2. Concentration of trace element in the gills and tissue of catfish (*C. gariepinus*).

Fish species	Zn			Fe			Pb			Cu		
	Max	Min	Std ±	Max	Min	Std±	Max	Min	Std±	Max	Min	Std±
Clarias gariepinus (tissue)	2.84	2.00	0.28	6.84	5.27	0.44	0.90	0.30	0.19	1.68	1.00	0.23
Clarias gariepinus (gills)	1.44	0.27	0.37	6.70	4.23	0.72	1.40	0.1	0.44	1.44	1.10	0.12

Table 3. Concentration of trace element in the tissue and gills of tilapia (*O. niloticus*).

Fish species	Zn			Fe			Pb			Cu		
	Max	Min	Std±	Max	Min	Std±	Max	Min	Std±	Max	Min	Std±
Oreochromis niloticus (tissue)	2.45	0.54	0.53	5.83	4.27	0.58	1.00	0.10	0.33	4.46	0.51	1.48
Oreochromis niloticus (gills)	1.87	0.40	0.35	6.79	1.89	1.42	1.50	0.00	0.45	2.86	1.20	0.51

Zinc (Zn) concentrations in gills of *Oreochromis niloticus* and *Clarias gariepinus*

Iron (Fe) concentration in the gills of *Clarias gariepinus* and *Oreochromis niloticus*

Lead (Pb) concentration in the gills of *Oreochromis niloticus* and *Clarias gariepinus*

Copper (Cu) concentration in *Oreochromis niloticus* and *Clarias gariepinus* gills
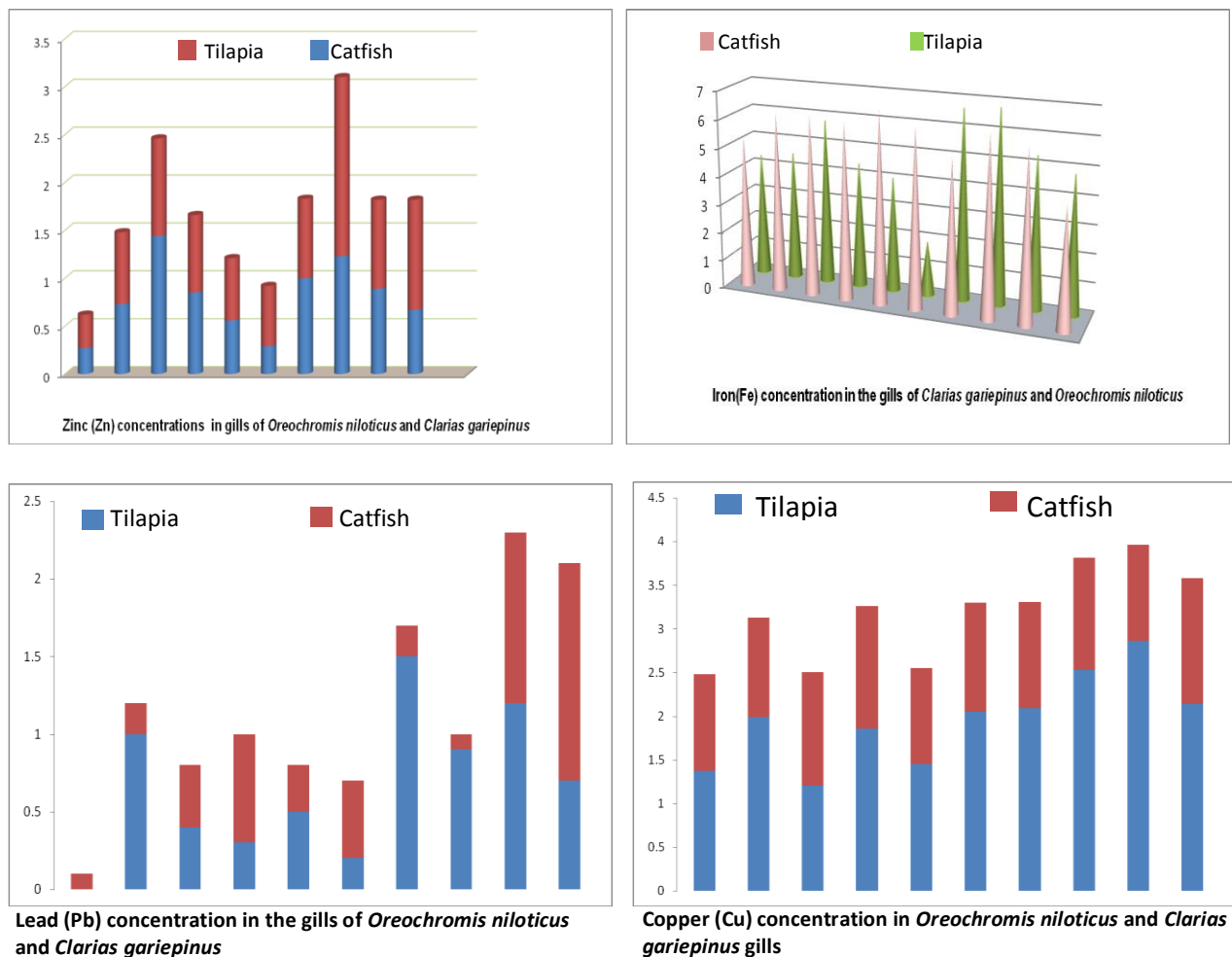
Figure 2. Concentration of trace element in gills of *O. niloticus* and *C. gariepinus*.

(2011) having the concentration of Cu in gills less than that of the tissue in tilapia. The high Cu concentration in the study exceeded the 1.5 uglg Cu/L allowable level in drinking water in Nigeria (FEPA, 1991). The Cu concentration in the gills and muscle tissues is comparable with the report of Ebenezer and Eremasi (2012). This is an indication that most Copper minerals are relatively insoluble. Naturally, Copper is often not a
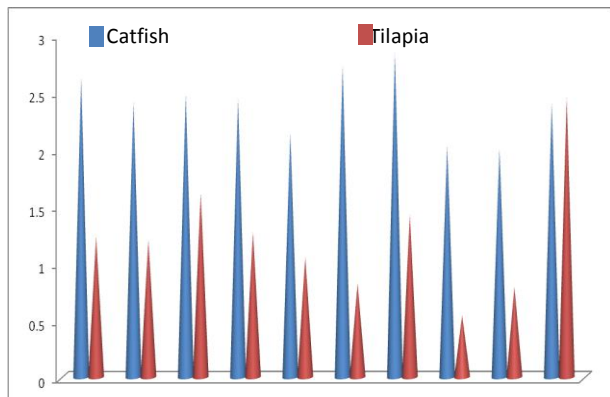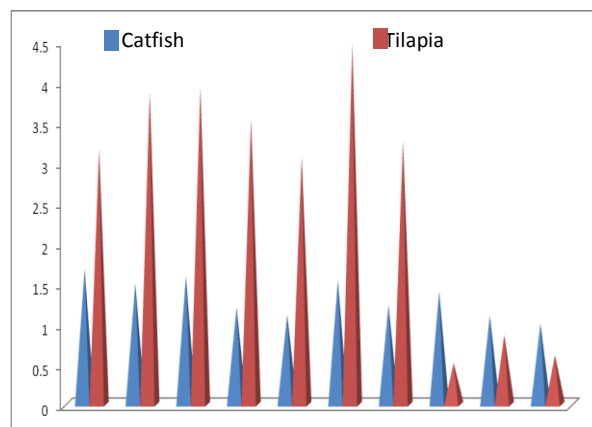
Zinc (Zn) concentration in *Clarias gariepinus* and *Oreochromis niloticus* tissues
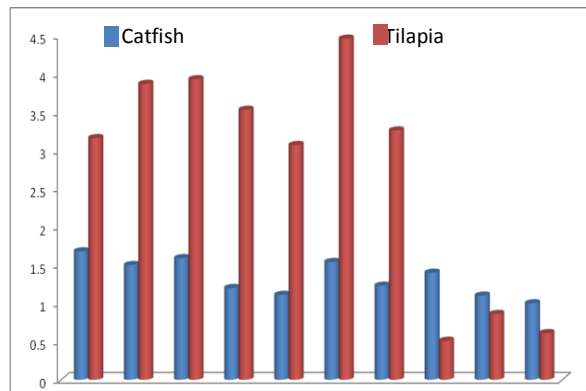
Iron (Fe) concentration in *Clarias gariepinus* and *Oreochromis niloticus* tissues
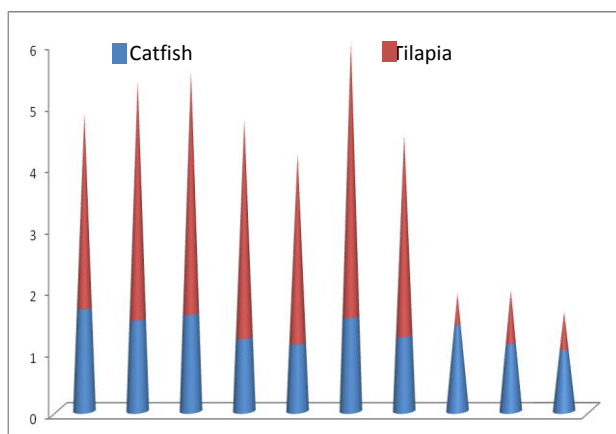
Lead (Pb) concentration in *Clarias gariepinus* and *Oreochromis niloticus* tissues

Copper (Cu) concentration in *Clarias gariepinus* and *Oreochromis niloticus* tissues

Figure 3. Concentration of trace element in tissue of *O. niloticus* and *C. gariepinus*.

threat to humans except when present at abnormally high values, where it causes anaemia, disorder of bones and connective tissues and liver damage. The toxicity depends upon the hardness and pH of the water. It is more toxic in soft water with low alkalinity (Taha, 2004). The Zn values range between 2.45±0.53 and 1.87±0.37 in tissue and gills respectively.

The result showed that the concentration of Zn in the tissue is more than that of the gills as shown in Figures 1 and 2. Alabaster and Lloyd (1980) stated that zinc has low toxicity to man, but relatively high toxicity to fish. The appreciable levels recorded in the *O. niloticus* in this study would therefore be a serious cause for concern.The accumulation of lead is higher in the gills of *O. niloticus* (1.50±0.45) than the tissue (1.0 ±0.33). The level of Pb recorded in this study is within the allowable limits of 2.0 mg/Pb/g. The higher level of Pb in the gills than in the muscle tissues indicated that the gill is the primary site for Pb uptake in fish. This observation is consistent with Yousalfzai and Shakoori (2008). There had been a strong

relationship between gill metal burden and toxicity (Playle et al., 1993; DiToro et al., 2001). The bioaccumulation of Pb by fish may create detrimental effects on fisheries resources and could constitute a considerably health hazard, to man. Lead reduces reproductive capacity (Wangboje and Oronsaye, 2001) while the consumption of the fish lead – polluted fishes by man interferes with heamoglobin synthesis. In severe cases; Pb poisoning may lead to encephalopathy anaemia, renal problems and death (Lawson, 1989).

Conflict of Interests

The author(s) have not declared any conflict of interests.

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