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Research Article

Point-effluent Discharge and River Recovery Potential: An Assessment of Spatio-Temporal Distribution of Heavy Metals in Water and Sediment from Upper Ogun River, Southwest-Nigeria

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ABSTRACT

Wastes are often discharged into surface water systems like rivers with little or no consideration for their assimilative capacities. In this study, we have investigated the pattern of river recovery for the upper river Ogun at varied points using six sampling stations of 250m interval i.e., upstream (ups 1, ups 2), dp (discharge point) and downstream (dst 1, dst 2 and dst 3) for 6-months across seasons. Samples analyzed for metals (Cd, Mn, Pb, Zn, Cu, Fe and Cr), in surface water and sediment showed a concentration gradient from the discharge point to downstream stations. All metals in sediment except Zn and Mn showed clear temporal patterns with higher concentrations in either dry season or rainy season. Discriminant function analysis (DFA) delineated sampling stations into least-polluted, intermediate-polluted and highest metal-polluted respectively. The classification of dst 3 alongside ups 1 and ups 2 suggests significant recovery 750m downstream from the discharge point. In general, although the river has experienced degradation, recovery to a condition close to its pre-disturbance state was observed.

Keywords: *effluent, habitat degradation, fluvial recovery potential, effluent discharge permits*

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INTRODUCTION

Unprecedented trends in global population growth and the increasing reliance on adjacent water bodies for the discharge of domestic and industrial wastewater currently constitute major distress to natural aquatic systems (Owokotomo *et al.*, 2020). The effects of human activities on the water quality of natural systems and the degree to which they disrupt the ecosystem are dependent on the ecological capacity of freshwater fluvial systems to recover and adjust to disturbances (Sedell *et al.*, 1990; Adeogun *et al.*, 2012). In the wake of widespread anthropogenic impacts, different countries have utilized information on river recovery to guide river management efforts (Dudgeon, 2005; Wu *et al.*, 2013), but this is scarcely documented in tropical climes (Fryirs and Brierley, 2000).

While the frequency of surface water impairment has raised concerns for ecological and human health, the extent of risks may not be accurately ascertained without a picture of the recovery capacity of the receiving environments (Beiras,

2018). Although the rate and extent of recovery are highly dependent on the nature and extent of disturbance and the inherent sensitivity of rivers (Gregory and Downs, 2008; Downs *et al.*, 2011) aspects of river recovery are driven by several factors including lithology, presence of riparian vegetation (Hartmann *et al.*, 2007; Owokotomo *et al.*, 2020) and water quality gradient along a river stretch (Agunwamba *et al.*, 2006; Longe and Omole, 2008; Adeogun *et al.*, 2011). In south-west Nigeria, sawmills and abattoirs are a common source of point effluent discharge into river systems (Adelegan, 2002; Adeogun *et al.*, 2011), with abattoir effluent containing metals from the soot of burned tyres, scrapings and washing of tyre-burned meat (Friday and Nwite, 2016), and sawmill leachates from wood-shavings containing metals from wood preservatives (Adeyeye *et al.*, 2018). In the light of knowledge gaps for recovery patterns of tropical fluvial systems, the objective of this study undertakes a catchment-scale investigation to examine river recovery of the upper reaches of river Ogun, receiving point effluent discharge from an abattoir and sawmill industry.

MATERIALS AND METHODS

Study area: Ogun River is one of two principal perennial rivers in the Ogun-Osun River Basin of Nigeria. The entire upper and lower Ogun River system is located within the south-western part of Nigeria (6° 26'N and 9° 10'N Lat; 2° 28'E and 4° 8'E Long). The upper Ogun River consists essentially of major tributaries from the Oyan and Ofiki river systems. It consists of wide ranges of savannah fringe lands from the Oke-Ogun area in the north and central parts, with rain forest covering the rest of the upper river basin southwards (Adeyemi *et al.*, 2020). In densely populated areas of the watershed, the river receives domestic input from bathing, washing and drinking (Fig. 1). It also serves as a point-source drain for organic wastes from abattoirs and sawmills along its river course (Adeogun *et al.*, 2011).

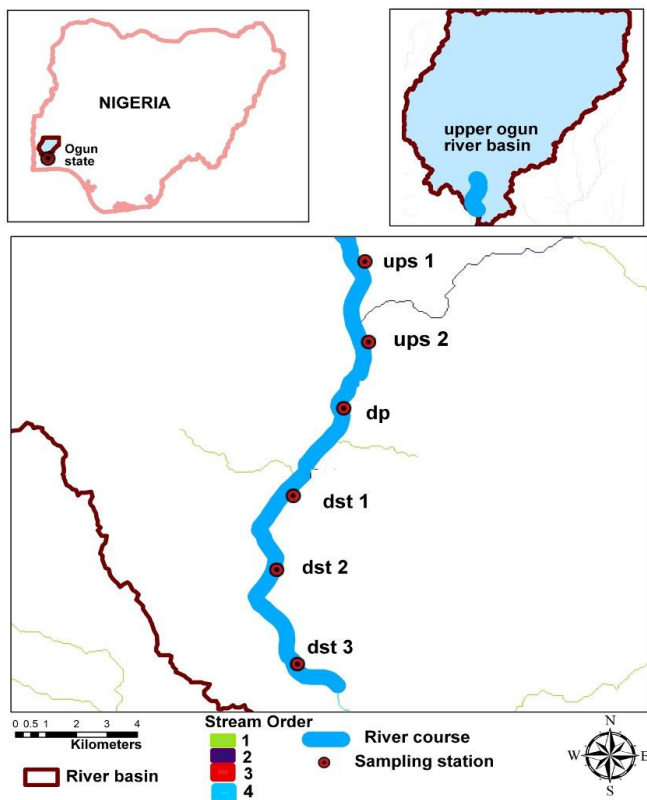


Figure 1: Map of upper Ogun River showing sampling stations and river connectivity: where ups=upstream, dp=discharge point, dst=downstream

Sampling Procedure: Bimonthly samples of surface-water and sediment samples were collected across the dry (February-March) and wet (April-July) seasons from a total of six stations. Upstream sample stations were ups 1 and ups 2 located before the point of discharge at a distance of 250 m apart while downstream (dst) were collected after the point of discharge at three different sampling locations i.e., at 250 m intervals from one another. The point-of-discharge indicates the station of effluent released into the river from an abattoir and sawmill facility.

Sample Analysis: The digested water and sediment samples were analyzed at the Central Research Laboratory of the University of Ibadan, Nigeria for Cd, Cr, Pb, Mn, Zn, Ni, Cu, Co and Fe, using an Atomic Absorption Spectrometer (Buck 97 Scientific AAS (210/211VGP)). Metal concentration in each digested sample was determined by comparing their absorbance with the aqueous calibration standard prepared from the stock standard solutions of the respective elements (APHA-AWWA-WEF, 2005). The stock solution used as standard reference material was purchased from Merck, Germany.

The efficiency of the optimized digestion procedure was checked by adding known concentrations of each metal in triplicate 0.5g samples. Samples were spiked with standard solutions prepared from the reference material of each metal and the percentage recoveries were calculated using the equation $I. R = [(Amount\ after\ spike - the\ amount\ before\ spike) / Amount\ added] \times 100\%$ (Ademoroti, 1996). The percentage recovery for all metals was not less than 87%.

Assessment of river recovery: Our primary focus is on river stretch relative to a notable occurrence of point-source pollution. Thus assessment was carried out using water quality gradient along the river stretch (Adeogun *et al.*, 2011). Limiting factors or explanatory variables for river recovery capacity i.e. the connectivity i.e. upstream-downstream linkage and position of reaches within a catchment (Fryirs and Brierley, 2000) and lithology (Olusola and Fashae, 2019) were used for this study. River connectivity typically describes the longitudinal, lateral, and vertical hydrological supplies within the river corridor and its watershed (Wohl, 2017). Hydrological profiling using Digital elevation models (DEM) for watershed analysis in ArcGIS version 10.3 (Owokotomo *et al.*, 2020), with two first-order streams supplying the downstream locations and a second-order stream supplying the upstream location portends little or no confounding factors to river recovery (Fig. 1). The lithology of the upper Ogun River system is defined by a pre-Cambrian basement complex that largely underlies the upper reaches (Olusola and Fashae, 2019).

Statistical Analysis: The total concentration of examined heavy metals in water was represented using mean plots with a 95% confidence limits error bar. Spatio-temporal variations of metals concentrations in sediment samples were presented as mean values and analyzed using contour plots. Discriminant function analysis (DFA) to discriminate between the quality of sampling stations using heavy metal levels in water and sediment was carried out. Statistica® version 8.0 (Statsoft. Inc, USA) and Minitab® version 14 were used for all analyses

RESULTS

Heavy metals in water: Given in Figures 2a-g are metal levels in water samples across stations. From a general overview, the lowest concentrations were observed at the upstream stations, the highest concentration at the point of discharge (dp) and a progressive decrease in concentration downstream (dst1-dst3).

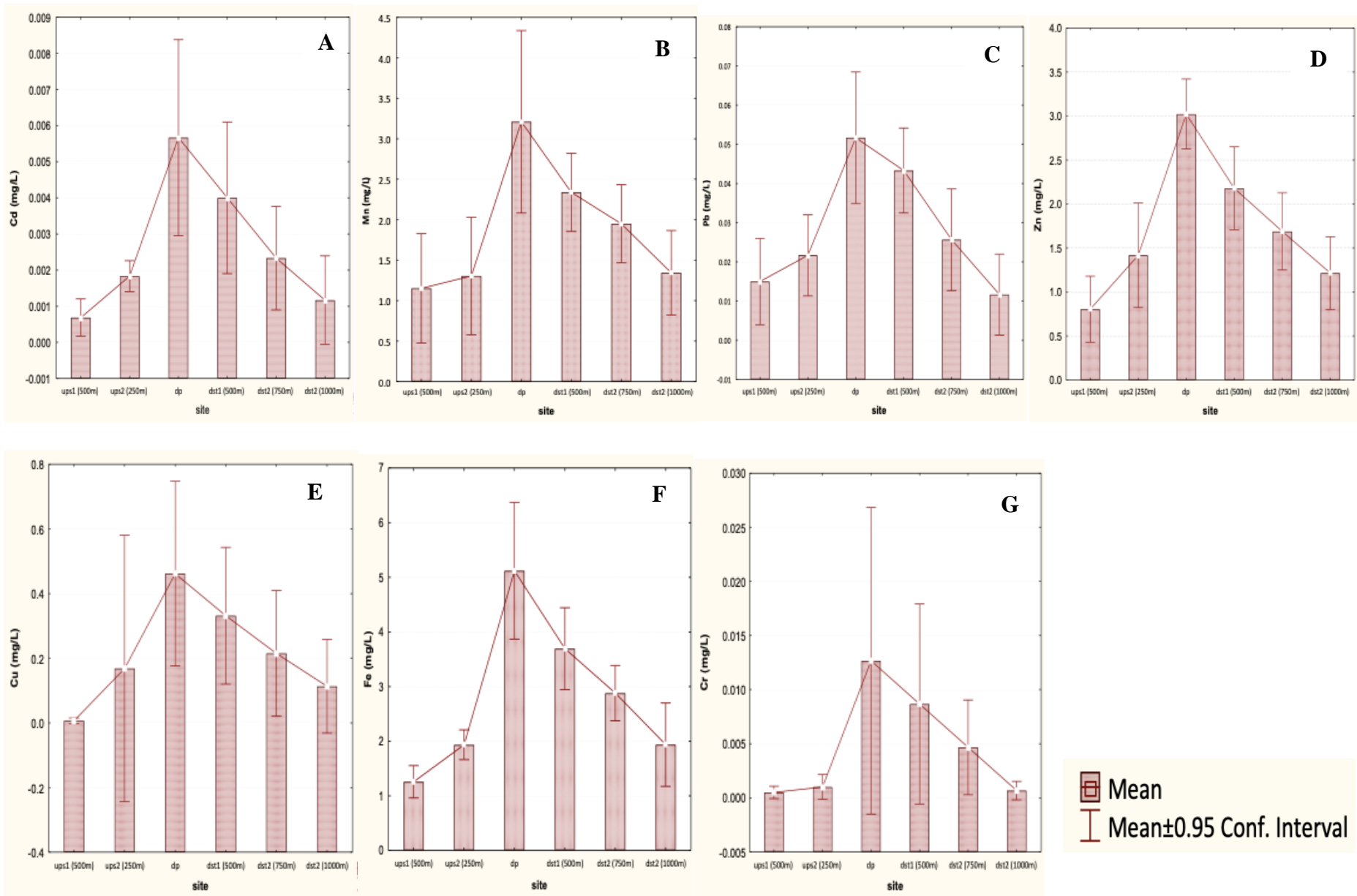


Figure 2a-g:

Levels of heavy metals in surface water samples from upper Ogun River, Southwest-Nigeria; a=Cd, b=Mn, c=Pb, d=Zn, e=Cu, f=Fe and g=C

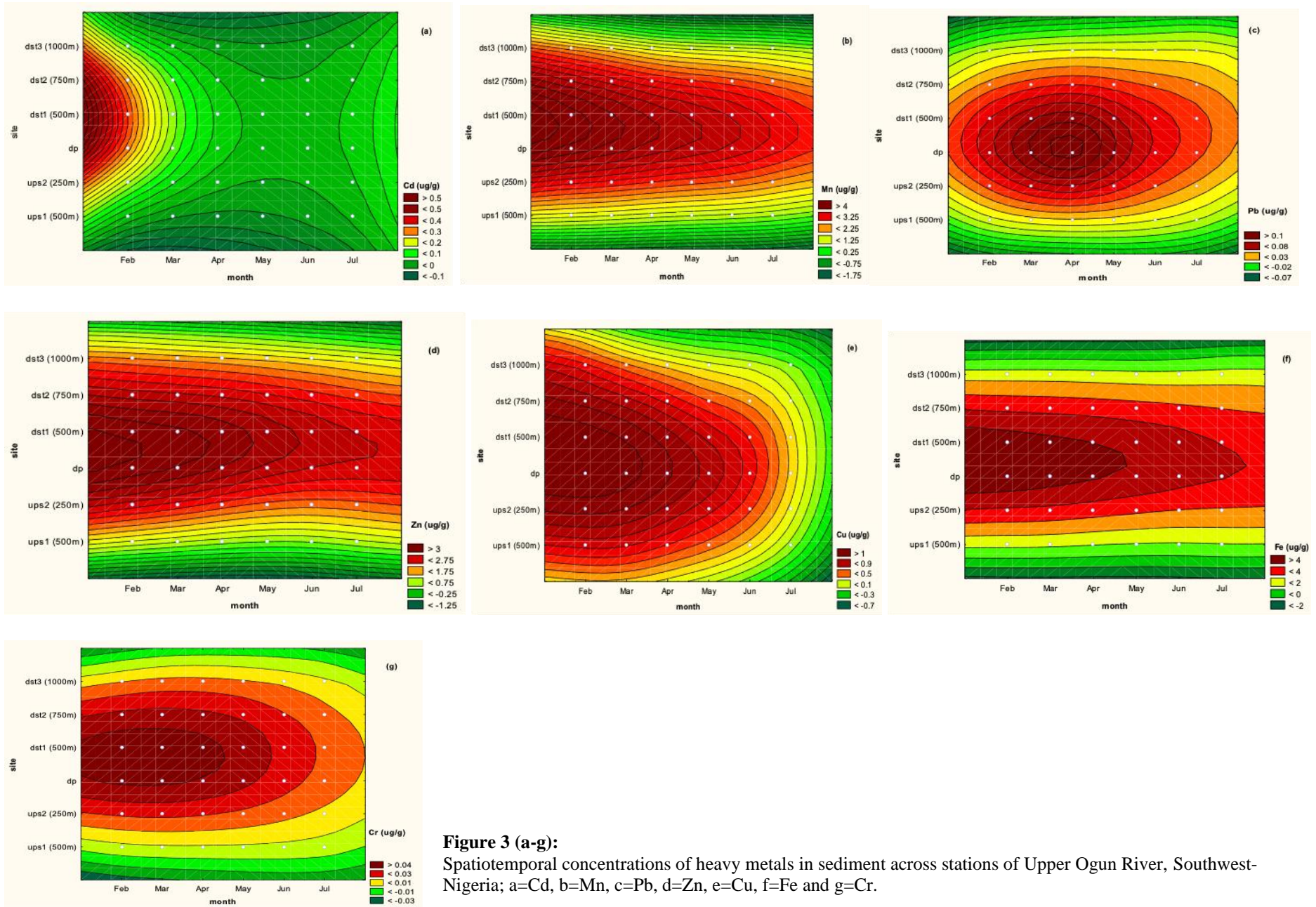


Figure 3 (a-g): Spatiotemporal concentrations of heavy metals in sediment across stations of Upper Ogun River, Southwest-Nigeria; a=Cd, b=Mn, c=Pb, d=Zn, e=Cu, f=Fe and g=Cr.

The lowest concentrations of Cd (0.0007-0.0018 mg/L) were detected in water samples upstream with the highest concentrations at the point of discharge (0.0057 mg/L). Lower concentrations in surface water were recorded at dst 1 (0.0040 mg/L), dst 2 (0.0023 mg/L) and dst 3 (0.0012 mg/L) compared to levels at the point of discharge (Fig. 2a). Similar trends were observed for Mn in surface water where the lowest values were recorded for ups 1 (1.15 mg/L) and ups 2 (1.31 mg/L) compared to point of discharge (3.21 mg/L) and downstream stations (dst 1=2.34 mg/L; dst 2=1.95 mg/L; dst 3= 1.34mg/L) (Fig. 2b). Lead in surface water from ups 1 (0.015mg/L) and ups 2 (0.022 mg/L) was significantly lower than values recorded at dp (0.052 mg/L) and dst 1 (0.043mg/L). Levels of Pb in dst 2 (0.025 mg/L) and dst 3 (0.012 mg/L) were not significantly different (Fig. 2c). The highest concentrations of Zn in surface water were recorded at dp (3.02 mg/L) and dst 1 (2.18 mg/L). Lower concentrations were recorded at ups 2 (1.42 mg/L), dst 2 (1.69 mg/L) and dst 3 (1.22 mg/L). The lowest concentrations were recorded at ups 1 (0.81 mg/L) (Fig. 2d).

Copper in surface water also showed the lowest concentrations at upstream stations i.e., ups 1 (0.07 mg/L) and ups 2 (0.168 mg/L). Highest concentration was recorded at dp (0.46 mg/L) with decreasing concentration gradient downstream i.e., dst 1 (0.33 mg/L), dst 2 (0.22 mg/L), dst 3 (0.11 mg/L) (Fig. 2e). Concentrations of Fe in surface water at dp (5.12 mg/L) was about 2 times more than levels measured upstream i.e., ups 1 (1.26 mg/L), ups 2 (1.94 mg/L). A decreasing concentration gradient in surface water was recorded for downstream stations i.e., dst 1 (3.70mg/L), dst 2 (2.88 mg/L), dst 3 (1.94 mg/L) (Fig. 2f). Significantly lower concentrations of Cr were recorded in surface water upstream i.e., ups 1(0.0005 mg/L), ups 2 (0.0010mg/L) compared to dp (0.0127mg/L). A concentration gradient was recorded in downstream stations i.e., dst 1 (0.0087 mg/L), dst 2 (0.0047 mg/L), dst 3 (0.0007 mg/L) with dst 3 values showing similar range to upstream values.

Heavy metals in sediments: The concentration of Cd in sediment showed significant spatial differences with lowest values recorded in sediments from ups 1 (0.1 mg/L) intermediate values at ups 2 and dst 3 (0.25 mg/L) and highest values between discharge point (dp) and dst 2 (0.43-0.60 mg/L) (Fig. 3a). Concentrations of Cd in sediments from ups 1 was relatively unchanged (0.1mg/L) while a steep gradient was recorded for other stations from the dry season (0.3-0.6 mg/L) to the rainy season (0.1 mg/L) (Fig. 3a). This trend clearly implicates abattoir and saw-mill activity as the source of Cd at the discharge point (dp) and not any point or diffuse source upstream (Fig. 3a). Manganese showed significant spatial variations with highest concentrations in sediments from dp (4.8 mg/L), dst 1 (4.5mg/L), dst 2 (4.0 mg/L), intermediate concentrations from ups 2 (0.28 mg/L), dst 3 (0.25 mg/L) and lowest sediment concentrations in ups 1 (0.14 mg/L), indicating no significant trend in Mn concentrations (Fig. 3b). Temporally, there was no significant trend in Mn concentrations. While this strongly implicates the contribution of industrial effluent in increased Mn concentrations in sediment, it also depicts that dilution during the rains did not contribute to the lowered levels of Mn downstream.

Significant spatial variations were also recorded for lead. The highest concentrations were recorded in sediments between ups 2 and dst 2 (0.04-0.10 mg/L) while the lowest concentrations were recorded at the distal regions ups 1 (0.02 mg/L) and dst 3 (0.023 mg/L). This spatial trend implicates industrial sources of lead into the river. Temporal trends showed the highest concentrations of lead in sediment (0.08-0.09 mg/L) at the transition between the dry season and rainy season (Fig. 3c). Zinc showed weak temporal trends with a consistently high concentration between ups 2 and dst 2 (2.23 – 3.20 mg/L) while ups 1 (0.08 mg/L) and dst 3 (1.23 mg/L) had lower concentrations in sediment (Fig 3d). Spatial variation in concentration of copper in sediment showed the highest concentrations of copper between ups 2 (0.8 mg/L) and dst 3 (0.5 mg/L). Slightly lower concentrations (0.4 mg/L) were recorded for ups 1.

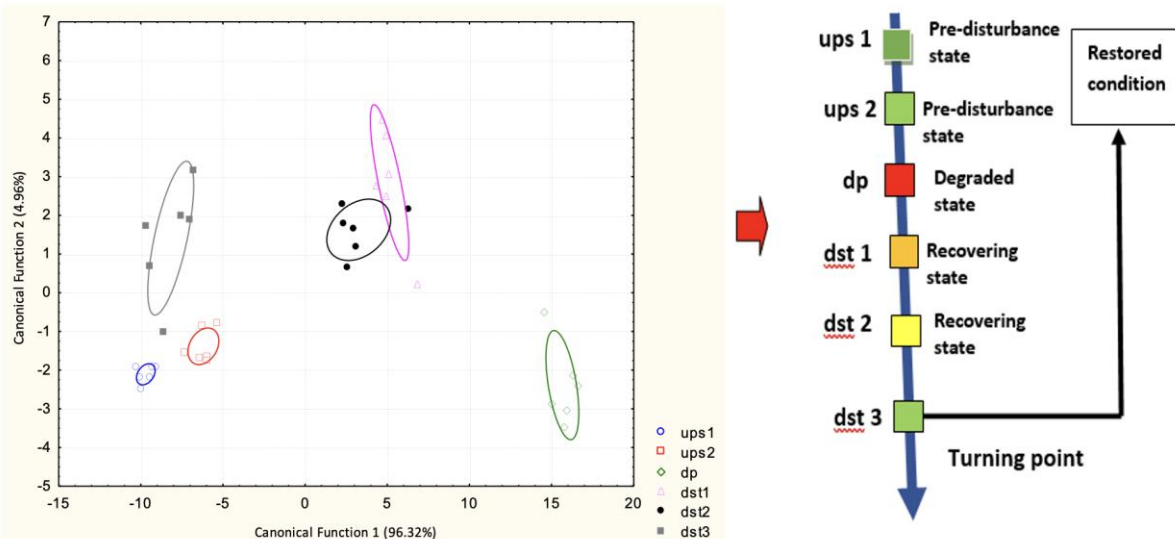


Figure 4: Discriminant scatter Plot and 95% Confidence ellipse of discriminant scores for sampling stations, and schematic depiction of Upper Ogun River recovery pathway .

Temporal variation showed a decrease in concentration across all sampling stations with progress from the dry (0.5-0.8 mg/L) season into the rainy season (0.12-0.25 mg/L) (Fig. 3e). Similarly, Fe in sediment showed weak temporal trends having a sustained high concentration between ups 2 and dst 2 (3.4 -4.22 mg/L) and lower concentrations at the distal stations i.e., ups 1 (1.67 mg/L) and dst 3 (1.82 mg/L) (Fig. 3f). Chromium showed significant spatial variations in sediment with highest concentrations between ups 2 and dst 2 (0.03-0.05mg/L) and lower concentrations at ups 1 (0.001 mg/L) and dst 3 (0.01 mg/L). The high concentration between ups 2 and dst 2 showed a downward concentration gradient with progress from the dry season (0.033 -0.04 mg/L) into the rainy season (0.026 mg/L) in July (Fig. 3g).

Discriminant analysis: Inferences for river recovery in the upper Ogun River: Figure 4 gives a graphical depiction of habitat quality via discriminant functions with a canonical plot depicting a categorization of pollution gradients into three groups (Fig. 4). The cluster representing the discharge point 'dp' represents the most polluted station, the second cluster consisting dst 1 and dst 2 i.e., downstream stations 1 and 2, represents the intermediate polluted group, while the third cluster consisting of ups 1, ups 2 and dst 3 represents relatively unpolluted/recovered stations of the river length (Fig. 4). Depictions from Figure 4 shows indicate that the upper Ogun River receiving abattoir and sawmill effluents attained a recovery akin to its pre-disturbed state.

DISCUSSION

The continuous discharge of wastewaters with associated contaminants of anthropogenic origin into inland freshwater aquatic ecosystems remains a serious issue of public health and societal concern in many developing countries in the tropics like Nigeria (Adeogun *et al.*, 2011). In this study, we have investigated the impact of point source industrial and domestic effluents discharge into the upper Ogun River, Nigeria. Our results showed a concentration gradient in metals levels for water and sediment samples collected from the discharge point to downstream stations indicating that complex mixtures of industrial and domestic effluent discharged into Ogun River produced a temporal and spatial impact on the water quality of the upper Ogun River. The spatial trends in metal gradients from the discharge point suggest that the natural capacity for a river for purification of polluted waters is a gradual process, so much that heavily polluted waters may traverse long distances downstream for days before attaining a significant degree of purification (Henry and Heinke, 2005).

In this study, samples analyzed for metals (Cd, Mn, Pb, Zn, Cu, Fe and Cr), in surface water and sediment showed a concentration gradient from the discharge point to downstream stations. All metals in sediment except Zn and Mn showed clear temporal patterns with higher concentrations in either dry season or rainy season. Discriminant function analysis (DFA) delineated sampling stations into least-polluted, intermediate- polluted and highest metal-polluted respectively. The classification of dst 3 alongside ups 1 and

ups 2 suggests significant recovery 750m downstream from the discharge point. In general, although the river has experienced degradation, recovery to a condition near its pre-disturbance state was observed.

The wide 95% confidence intervals (extreme high and low values over the study period) for levels of Cu in surface water at ups 2 suggests strong variability in values due to effects of the seasons which influence the remobilization of Cu from sediments into the overlying water column, or increased discharge from diffuse sources (Brooks *et al.*, 2007; Adeogun *et al.*, 2012). The wide confidence interval for Cr at the discharge point (dp) could be attributed to varied effluent quantity and metal concentrations discharged during the study period. Potential sources of metals from abattoir effluent into the river include soot of burned tyres and washing of tyre-singed meat (Friday and Nwite, 2016), and sawmill leachates from wood-shavings containing metals from wood preservatives (Adeyeye *et al.*, 2018). In general, the similarity of metal levels in surface water at downstream stations with upstream stations is indicative of environmental resilience and intact capacity for recovery (Garg and Garg, 1996).

It is notable that the upstream station ups 1 maintained a sustained low level of heavy metal contaminants compared to the polluted zone confirming its status as a suitable control station. The downstream station dst 3 most times showed metal concentration in sediments at levels comparable to the upstream station ups 1. This implies an occurrence of recovery about 750m downstream from the discharge point. A key inference from this observation is that active anthropogenic input and seasonal remobilization of metals from sediments of waste into aquatic systems accounted for a larger cause of metal load in the river while input from adjacent settlements and diffuse runoff from land use did not appear to have a strong influence on the pattern of river recovery downstream. Similar reports on recovery in upper reaches of river catchments due to minimal input from diffuse sources have been documented (Beiras, 2018). The river reaches located within the middle and lower parts of its catchments are notably vulnerable to the anthropogenic disturbances to the flow regime and the water quality (Pringle *et al.*, 2000). Although surface water is expected to recover from metal concentrations earlier followed by sediment (Clements *et al.*, 2010; Burton, 2018), the marked similarity in metal gradient between surface water and sediment from the discharge point downstream strongly suggests that surface water and sediment are recovering at the same pace or at close time intervals.

Inferences for river recovery in the upper Ogun River: The canonical plots show a graphical depiction of habitat quality via discriminant functions with a categorization of pollution gradients into three groups. The cluster representing the discharge point 'dp' represents the most polluted station, the second cluster consisting dst 1 and dst 2 i.e., downstream stations 1 and 2, represents the intermediate polluted group, while the third cluster consisting of ups 1, ups 2 and dst 3 represents relatively unpolluted/recovered stations of the river length. The smaller 95% confidence ellipse of the upstream stations i.e., ups 1 and ups 2 is indicative of lower dispersion of water quality values within those stations. On the other hand, the larger 95% confidence ellipse of the other stations

i.e., dp, dst 1, 2 and 3 indicates greater variability of values and input of a wider range of factors compared to the upstream stations. For the upstream stations, this feature is suggestive of the conserved water quality and quality of the stations despite the change in season; however, for the downstream stations, this readily suggests the presence of environmental disturbances. Further assessment of heavy metal in sediments across seasons showed that most of the heavy metals in sediment varied across seasons showing lower sediment concentrations with progress into the rainy season. Studies on the temporal and spatial variations of river water quality implicate increased water current or ionic redistribution processes during the rains (Bu *et al.*, 2010). The pollution gradient depicted by the discriminant analysis shows that there was a clear distinction in water and sediment quality of the station at the point discharge, compared to the downstream stations and finally the upstream stations (reference stations). From other studies, such a gradient is reflective of the potential of river systems to recover if a considerable length of its course remains significantly un-impacted (Longe and Omole, 2008). River recovery rarely reflects an orderly, progressive, and systematic process of adjustment, and two possible pathways for river recovery have been recommended depending on the cumulative impacts of various disturbances (Fryirs and Brierley, 2000). First, the river quality progressively improves till each reaches a turning point where it attains a condition akin to its pre-disturbed state; alternatively, in a situation where the river has been polluted alongside significant modifications of stream channel morphology, it is more likely that the river will not reach a turning point, rather, it will attain a different type of equilibrium (Fryirs, 2017). As such, if the degradation persists further down along the length of the river, regaining a fully restored condition downstream may be a difficult feat to achieve (Brierley and Fryirs, 2013). Depictions from the canonical plots of the discriminate analysis in this study indicate the upper Ogun River receiving abattoir and sawmill effluents attained a recovery akin to its pre-disturbed state.

The alignment of the upper Ogun River with the first recovery pathway (recovery towards its pre-disturbance state) strongly indicates that river morphology was not significantly tampered with, inherently suggesting that instream roughness and fine-grained sediments are critical for river purification and recovery were still intact (Dosskey *et al.*, 2010). Such a rugged substratum is traceable to the Precambrian lithology and underlying rock structure of the upper Ogun River basin. Lithology is a critical determinant of river morphology and by extension affects a significant aspect of its recovery capacity (Thomas, 2001; Harvey *et al.*, 2008; Olusola *et al.*, 2020). Besides, the dense rainforest vegetation distributed along the southward end of the upper Ogun River (Olusola *et al.*, 2020) could be a complementary factor to the protection of the watershed and the conferment of river resilience (Owokotomo *et al.*, 2020).

Implication for environmental enforcement: In Nigeria as in some other developing and developed economies, point-source control of pollution is authorized based on meeting emission standards and specific legislation on target priority substances, such as trace metals or persistent organics (POPs). Consideration of river recovery in a situation where tropical

ivers display profound temporal and spatial heterogeneity brings to bear, several ecological uncertainties that may arise in the face of authorized but unguided wastewater discharge. This requires that regulatory actions towards wastewater management and permits from discharging industries must balance a broad range of goals including ecological, environmental, and public health implications (Huang *et al.*, 2014).

In conclusion, the patterns of variability in metal concentrations upstream before the point discharge and downstream as highlighted by the discriminant analysis reveals an inherent trend and pathway towards ecological equilibrium. We allude this trend to the existence of an unbreached stress-handling capacity i.e., an appreciable level of resilience to a disturbance within the stretch of the upper Ogun River. We opine that information on the level of recovery potential can be used to determine the extent of intervention required to improve the condition of impacted rivers.

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