Elemental Total Nitrogen (TN): Total Phosphorus (TP) Ratios Influences On The Geological Metal Partitioning In Upstream River Kapsabet, Kenya.

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Abstract

Most aquatic environments normally undergo enrichment with nitrogen or phosphorus resulting in differences in the TN:TP ratios. Ideal TN:TP ratios may affect the overall functioning of the aquatic ecosystems. In this study, the overall impacts of TN:TP were related to the metal concentration along River Kapsabet. Water was collected using plastic bottles and Total nitrogen and total phosphorus analyzed. In addition levels of metals along the sites were analyzed using spectrophotometer. The concentration of TP increased from the upstream to the downstream sites while that of TN reduced from the upstream to the downstream resulting in consistent decline in the TN:TP ratio down the river profile. There were significant differences in the concentration of TN and TP among sites ($p < 0.05$). In water, the means and ranges in concentration of metals were: (μg/L): 0.24 (0.01-0.75) Pb, 0.07 (0.02-0.21) Cu, 2.78 (0.17-3.41) Fe and 0.32 (0.02-1.22) Zn. There was significant ($p < 0.05$) spatial distribution of metals along the river profile. In both water and sediments, site 3 and 4 contained significantly ($p < 0.05$) the highest concentrations of Pb, Fe and Zn associated with anthropogenic pollution. This study demonstrate gradient specific increase in total phosphorus along the river profile and associated reduction in total nitrogen resulting in the overall reduction in the TN:TP ratio along the river profile. All metals except Cu displayed increased concentration along the river profile and therefore indicate increased anthropogenic contribution to water enrichment with heavy metals. Yet, along the profile, there was an exponential increase in the concentration of essential metals with increased TN:TP ratio with no association between the TN:TP ratio and the essential Pb. These results indicate that application of the Redfield ratio (TN:TP) ratio may remedy the problem of heavy metal contamination in the aquatic ecosystems.

Key word: Geological metals, Metal partitioning, Total Nitrogen, Total Phosphorus

1.0 Introduction

Human activities have significantly increased the input of nitrogenous and phosphorus nutrients in freshwaters. Aquatic environments exhibit a huge range of total nutrient concentrations and a great variability in relationships between total nitrogen (TN) and total phosphorus (TP). P originates primarily from soil minerals and can accumulate to a substantial degree at sediments of lakes. On the other hand, N is unique among water nutrients, it originates from atmosphere as an inert gas, is closely tied to organic matter, exceptionally accumulates to a significant degree in lake sediments, and has a cycle either more complex than P (Wetzel, 1983). Enrichment of lotic ecosystems with nitrogen (N) or phosphorus (P) commonly stimulates primary production because N and P are often limiting resources to primary production (e.g., Dodds 2003). Basin geology is a variable that contributes to N and P availability for transport (e.g., Dahlgren, 1994; Gardner, 1990) and the physical environment, which partially determines watershed flow paths (basin slope, hydraulic conductivity fields, and many other factors). Similarly, human disturbance within a watershed enhances the mass of nutrients available and alters the transport pathways (drainage structures, pavement, and many others).

Stream water N:P ratios have been used to identify whether a lotic ecosystem has excess N or P relative to the Redfield ratio (N:P = 16:1 by atoms (Redfield, 1958), and is thus a rough indicator of N or P nutrient limitation (Schanz and Juon, 1983). Beyond use as an indicator of nutrient limitation, stream water N:P ratios have been shown to impact both the flora and fauna (Crosa et al., 2006). Stream water N:P ratios vary spatially (Green and Fritsen, 2006). Factors that influence spatial variation of N:P ratios include climate (Horne and Goldman, 1994), parent bedrock (Borchardt, 1996), watershed storage (Detenbeck et al., 2004) and anthropogenic nutrient enrichment (Turner et al., 2003).

Aquatic ecosystems in arid and tropical climates are more prone to low stream water N:P ratios (N:P < 16:1) than streams and lakes in more humid climates (Grimm and Fisher, 1986; Horne and Goldman, 1994). Horne and Goldman (1994) speculated that aquatic environment in the lakes in the tropics have low N:P ratios because vegetation is sparse, thus exposing P-rich soils to erosion. Their discussion of lakes, which is applicable to streams, theorizes that eroded soils enrich the lake with P, thus making N limit primary production. Grimm and Fisher (1986)

suggested that benthic sediments in arid streams may have a greater P exchange capacity than in mesic streams, thus causing greater stream water P concentrations relative to N. Detenbeck et al. (2004) found a statistical relationship between watershed storage and dissolved inorganic N:P ratios amongst 2nd and 3rd order streams. Turner et al. (2003) showed that on a global basis, high dissolved inorganic N:P ratios occur at high nitrate concentrations, and that nitrate concentrations.

Metal pollution is ubiquitous in the global environment and has drawn increasing attention due to a dramatic increase in anthropogenic heavy metals to the ecosystem through air, water and soils (Fang *et al.*, 2000; Adamo *et al.*, 2002; Lin and Kuo-Ming, 2003; Wilson and Pyatt, 2007; Khan *et al.*, 2008; Hang *et al.*, 2009). The problem has been aggravated by discharge of substances in the aquatic environments (Chen *et al.*, 1997; Chen *et al.*, 2006; Lin *et al.*, 2002). As is apparent, the fundamental influence that basin geology and human disturbance exert on streams is by serving as nutrient sources and forming the complex network of transport pathways. While N and P sources may explain N:P ratio variability, those sources must be connected to the stream via a transport pathway. However, the association with element stiochiometry on the metal fluxes in the aquatic environment is rarely studied Thus, this study determined the control of stream water N:P ratios on the metal levels in a stream with low levels of metal inputs.

2.0 Materials and methods

2.1 Study area and sampling sites

The study area was at Kapsabet River which is within Kapsabet town. There is ongoing construction of water treatment plant for Kapsabet municipality along this river. Water from this river is meant to serve the residents of the rapidly growing Kapsabet town. It is bounded by the latitudes; 34–36ºE, longitude; 0º03'−1º15'N and lies between 1134–2700 m above sea level with average slope of 4 per 1000. The region receives an average of 1350 mm/year of rain and is an important cereal and tea farming region of Kenya (Osano *et al*, 2002). Potential major sources of pollution for the Kapsabet River basin are the agricultural chemicals, urban effluents of Kapsabet, and from the tea farms. To increase production from the farms, commercial fertilizers and organic manure are used, which increase nutrients in the waterbody.

Four sampling sites were selected for this study based in the anthropogenic gradients of the catchment. The sites were S1, S2, S3 and S4 and their description are as provided. S_1; this is the remote point upstream Kapsabet River before the river enters the town. This point is expected to be the control point of this research since there will be no contributions from the runoff from the town and farming activities within town. S_2; this is a point closer to Eldoret –Kapsabet route and an entrance point of water into town. It will assist in monitoring of lead metal contamination from exhaust fumes and runoff from farms. The difference between S_1 and S2 shows pollution from the runoffs from the Eldoret–Kapsabet route, surrounding farms and town. S_3; this is a point where water leaves the town. It assisted in evaluating progressive contribution of runoffs from the town and farms around. S_4; this is a point which is approximately 300 M downstream after the river water has left the town. The difference between S_1 and S_4 will provide total contribution of town runoff and soil erosion to the river water.

2.2 Sample collection and analysis

Fieldwork consisted of collecting water samples at three pre-determined sites at each of the sampling stations. The river water samples were obtained using the Grab Technique using half litre metal free Van Dorn bottle. All water samples were drawn from about half meter (0.5 m) below the water surface at each of the two opposite sides of Kapsabet River. This depth was considered to represent a homogeneous water layer, free from riverbed sediment or atmospheric air interference. A total of 20 water samples were collected for this study, with 5 samples from each of the four sampling sites. The samples were then transferred poured into pre-washed half litre polythelene bottles. The bottles had been pre-washed by soaking in nitric and sulphuric acids solution of 1:1 volume ratio, washed in about 2L of tap water and rinsed three times in distilled water and dried prior to field work. While in the field the sampling bottles were rinsed several times with river water. Water samples were acidified to pH 2 with concentrated nitric acid according to APHA (1998). This treatment was necessary so as to prevent loss of ions, which are normally adsorbed on the walls of the sampling container. After the preliminary treatment, the samples were placed into an ice box and transported to laboratory for temporary storage in a refrigerator at 4°C before analysis.

Portions of the water samples were used to determine Total nitrogen (TN) by perfusaulphate digestion and Total phosphorus (TP) by the standard ascorbic acid method, after filtration of the sample through a 45-µm pore size membrane. The analyses were carried out at the Chemistry Water quality testing laboratory, following the standard analytical procedures detailed in APHA (1998).

2.3 Metal Analysis

Water samples were digested as a pre-requirement for spectrophotometer analysis so as to avoid interference from complexing organic matter (FAO, 1975). A combination of sulphuric acid and nitric acid digestion was used in this study (APHA, 1998). Samples were digested and concentrated on a hot plate from 100 ml to 25 ml for 3 hours. After digestion, the samples were cooled and then 2 ml of 30% hydrogen peroxide (H_2O_2) was added to each sample to oxidize any resistant organic matter (Reynolds and Thompson, 1970; Achoka 1998, Onyari *et al.*, 1991). After cooling to room temperature the digested samples were filtered into 125 ml polyethylene bottles through 0.45 μm nucleopore filter paper over a vacuum pump. The concentration of metals in a sample was determined by an Atomic Absorption Spectrophotometer Varian model AA 10/20. Prior to reading of the concentration of metals in the samples, at least two calibration standards were prepared for each metal. Each blank consisted of a mixture of 10 ml nitric acid, 10 ml sulphuric acid, 2 ml of 30% H_2O_2 and 25 ml of distilled water.

2.4 Statistical Analyses

All data collected were entered, organized and managed using EXCEL spreadsheet for Windows XP. Statistical analyses were performed with either a version of STATISTICA 6.0 (StatSoft, 2001) or GenStat 4.24 Release. Data collected were subjected to apriori test to determine the homoscedasticity (Michael and Douglas, 2004) before subjecting them to statistical analysis. The normality of the data distribution was checked by means of skewness and Kurtosis when performing analysis of variance. However, before conducting t-test, Levene's test on homogeneity of variance was conducted. Data on nutrients and analyzed metals were calculated as means ($\pm$ S.D) for each site on each sampling occasion. Mean differences among sites were analyzed using a one-way ANOVA. Where significant differences were discerned among attributes

analyzed by ANOVA, Duncans Multiples Range test (DMRT) was used to discriminate between the means (Michael and Douglas, 2004).

3. Results and Discussion

The concentration of total phosphorus and total nitrogen in water of River Kapsabet is shown in Fig. 2. Based on the figure, there were significant differences in the concentration of TN and TP among sites (One-Way ANOVA; $p < 0.05$). The concentration of TP increased from the upstream to the downstream sites while that of TN reduced from the upstream to the downstream. Therefore it appears that there is heavy use of phosphorus that elevated the concentration of TP along the sampling sites downstream. A survey of the sampling sites indicated that there was increased extensive use of fertilizers in the area than other sites such as S1 which has lower agricultural activities. Again due to the small nature of the river, most of the washing points along the river are located in this site and therefore likely to elevate the levels of TP in water. S3 and S4 also were at lower levels of elevations than other sites and therefore likely to receive a lot of non-point sources of inputs from other watershed into the water body, which is likely to elevate the amount of TP in the sampling site. Previous studies have established that total phosphorus is usually highly adsorbed into the soil and can be transported from the upper parts of the river catchments into the recipient water bodies and may account for the high total phosphorus concentration in local water bodies even if there is no evident point sources of pollution (Wetzel, 2005; Kalff, 2002). The continued decline of TN may be due to reduced use of fertilizers along the river channels or low levels of inputs of fertilizer from external sources.

The TN:TP ratio is provided in Fig. 3. There was a consistent decline in the TN:TP ratio down the river profile indicating either an increased TP or reduction in TN or combined reduction of TN and increasing TP. This results suggest that down along the river profile, increased anthropogenic activities are valuable sources of TP. It also appears that some of these activities may be responsible for volatilization of TN from the water body such as discharge of tea industry wastes which may convert the amount of available nitrogen to ammonia and nitrates through oxidative processes (Kalff, 2002).

The concentrations of the metals in most of the studied sites were low (Fig. 4). Spatial distribution of heavy metals in the soils showed consistent patterns of variations for all the metals

among the four stations except copper. All the four metals investigated displayed significant ($p <$ 0.05) differences among the sampling sites. Concentration of Pb, Fe and Zn increased along the river profile to be highest in sites S3 and S4 while the concentration of Cu decreased from the upstream to the downstream. The concentration of Pb, Fe and Zn in sites S3 and S4, which are all located near Kapsabet Town could be attributed to the enrichment of soils and water with the industrial discharge such as Chebut tea industry in addition to the urban effluent discharge from the area, which are similar to reported findings by Chen *et al.* (2005) and Adamo *et al.* (2005). The industrial discharge from the factory may contain traces of metals at low concentration(s), yet, continued deposition of effluents over the soil surface has been observed which increase the overall metals in the soils to levels that are beyond the threshold metal concentration. Accumulated metal deposition from the time the factory was built can cause immense problems of heavy metals in the soils surrounding the factory. The soils of this region are reported to be ultisols which are liable to accumulate metals at higher concentration than other soils found in Lake Victoria Basin (Mwamburi and Oloo, 1997; Mwamburi, 2003;). The decrease in the concentration of Cu may be associated with reduced geological contribution to Cu enrichment since Cu is normally found to be rich in areas that have low relative disturbances and may therefore be washed into the surrounding environment. This residual fraction contains naturally occurring minerals which may hold trace metals within their crystalline matrix; extractable copper is mainly associated with oxidizable phase, where it is likely to occur as organically complexed metal species. This behavior may be attributed to the high affinity of copper to humic substances, which are a fraction of natural organic matter and chemically very active in complexing such metals (Odum, 2008).

The relationships between TN:TP ratio is shown in Fig. 5. Based on the figure, there were marked exponential increase in the concentration of Cu, Zn and Fe but no significant relationships existed between TN:TP ratio and Pb. The observed exponential increase in these metals due to increase in TN:TP ratio, may due to their accumulation by the aquatic organisms in water which occur due to increased eutrophication of the aquatic ecosystem (Luoma and Rainbow, 2008). These essential metals are required for normal metabolic and cellular functions (Oduor, 2000) and will therefore be more readily accumulated in by the aquatic organisms in the waterbody and subsequently be transferred o the water column during deaths of these organisms. For Pb, which

is non essential metal, it was not being accumulated in water due to increased eutrophication probably because the aquatic flora and fauna did not require it for their metabolic functions and therefore no tendency to accumulate it.

4. CONCLUSION AND RECOMMENDATION

In conclusion, this study demonstrate gradient specific increase in total phosphorus along the river profile and associated reduction in total nitrogen resulting in the overall reduction in the TN:TP ratio along the river profile. All metals except Cu displayed increased concentration along the river profile and therefore indicate increased anthropogenic contribution to water enrichment with heavy metals. Yet, along the profile, there was an exponential increase in the concentration of essential metals with increased TN:TP ratio with no association between the TN:TP ratio and the essential Pb. These results indicate that application of the Redfield ratio (TN:TP) ratio may remedy the problem of heavy metal contamination in the aquatic ecosystems.

Recommendations

1. There should be collaboration between the government and communities staying closer to the river on the need to avoid pollution of the adjacent water body, since this will adversely affect the lives of aquatic organisms in the water bodies.

2. Nutrient reduction strategies should be used to control the excessive nutrients load into this river especially during rainy seasons. One such strategy could involve the construction of buffer zones to regulate the inflow of phosphates and nitrates

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Fig. 1: Map showing the location of Kapasabet River and the sampling sites

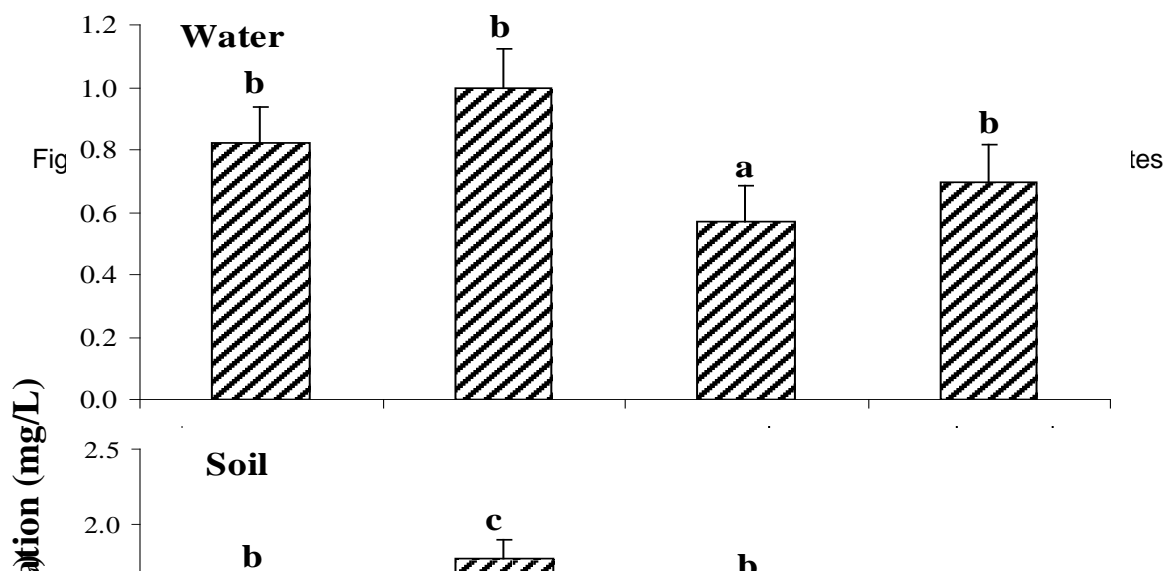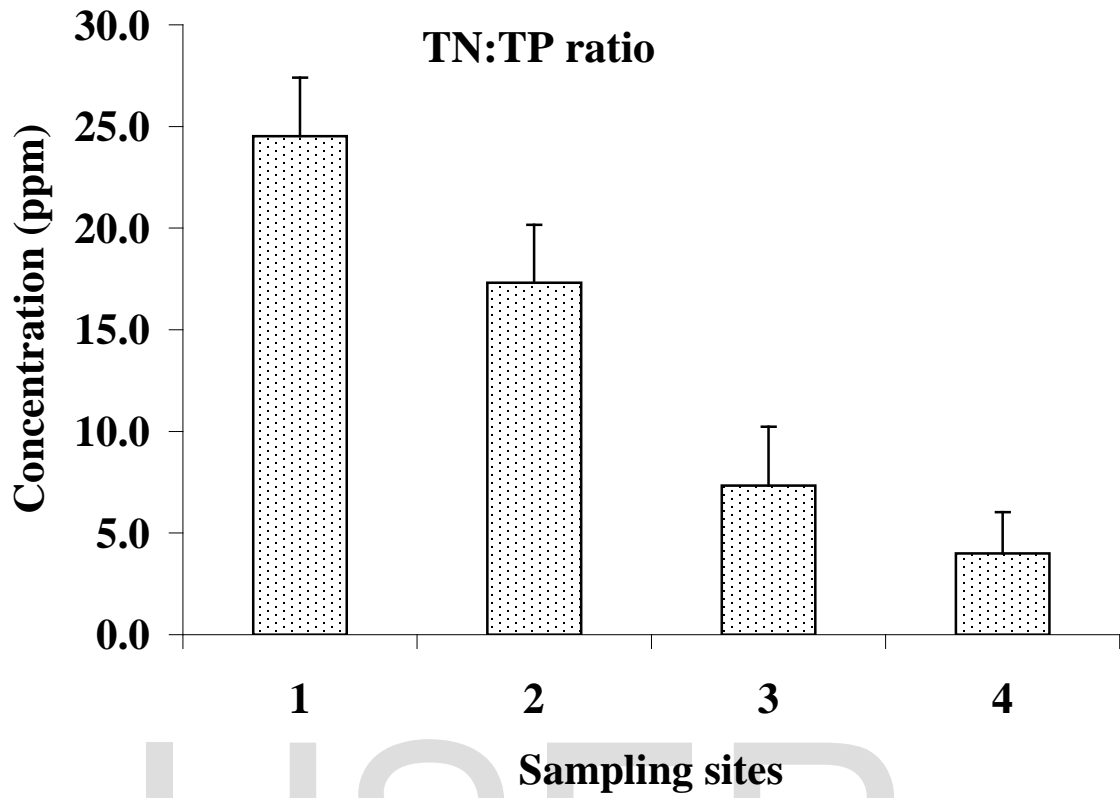Fig. 2. Concentration of total phosphorus along the four sampling sites in water, soils and sediment of Kapsabet River

Fig. 3. The TN:TP ratios of water 0n the sampling sites

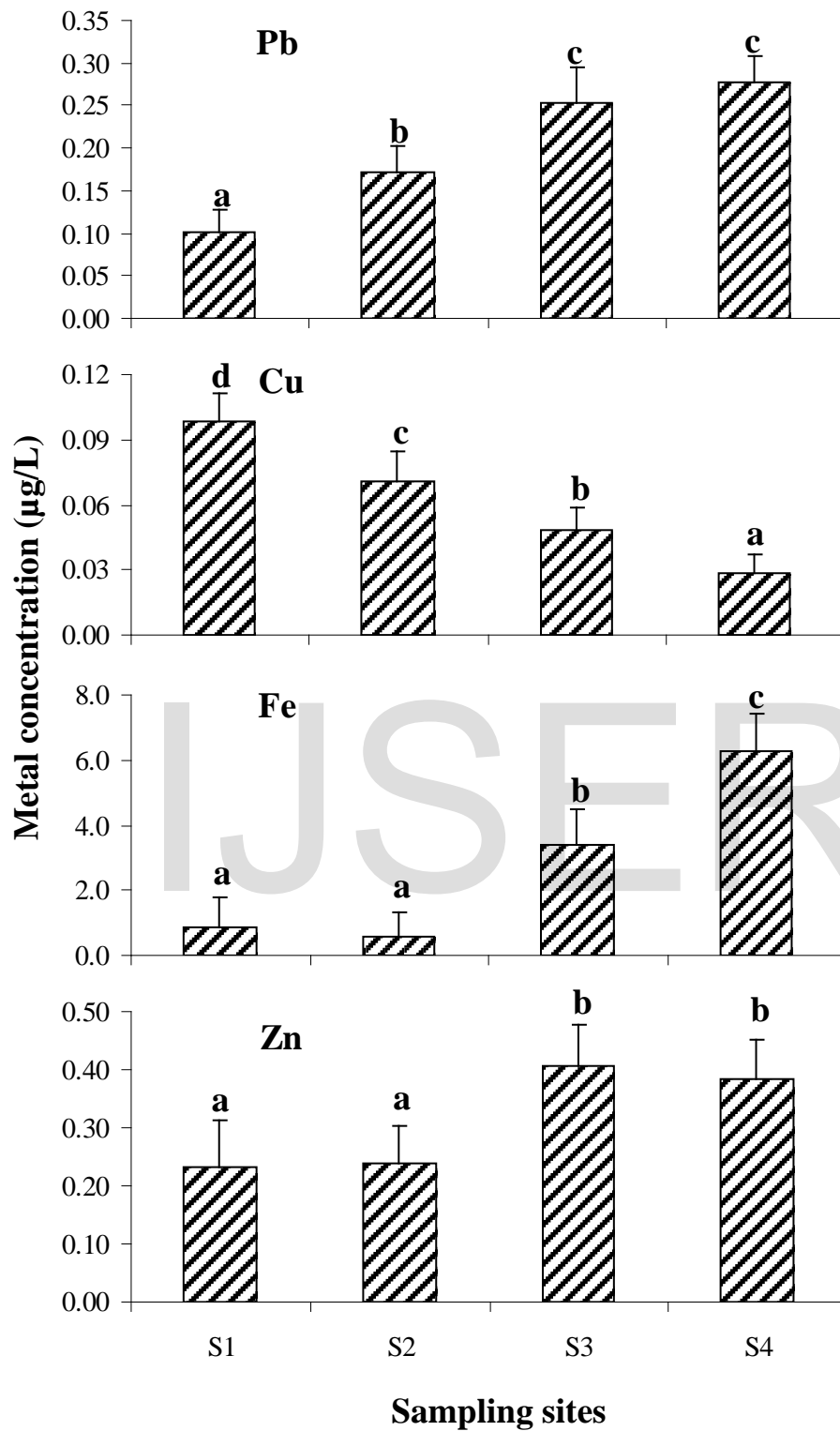Fig 4. Metal concentrations in water along the sampling sites

Fig. 5. Regression showing the relationships between TN:TP ratios and metals in water