Partitioning of iron and zinc in the catchment alluvial sediments of the River Gbako flood plains around Baddegi, central Bida basin, Nigeria

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Abstract
Partitioning of iron and zinc were studied in the alluvial sediments of the River Gbako floodplains around Baddegi using empirical formulas. The samples were cored from three pits (TR-1, TR-2, and TR-3). A study of the particle size distribution and geochemical analysis were performed. The particle size distribution results indicate that the sediments are sand dominated, having more than 50% sand with smaller percentages of clay and silt. Average partition coefficient values of Fe in the sediments are 1.02, 0.83, and 0.88, and for Zn 1.02, 0.95, and 0.83, for the TR-1, TR-2 and TR-3 sites, respectively. The average velocities of Fe mobilization in the sediments are 0.08 m/day, 0.07 m/day and 0.09 m/day for TR-1, TR-2 and TR-3, respectively, and for Zn mobilization are 0.07 m/day, 0.07 m/day and 0.09 m/day, for TR-1, TR-2 and TR-3, respectively. The metals are more preferentially partitioned in the sediments than the water percolating through them, which has an average hydraulic conductivity (K) of 4.2 m/day. The partition behavior of the metals is used to explain contaminant transportation in the alluvial sediments of the River Gbako floodplains around Baddegi and also explains the attenuation of pollutants and the process of natural groundwater purification within the shallow alluvial aquifers of these floodplains.

Index Terms: partition coefficient, hydraulic conductivity, alluvial sediments, floodplain, Nigeria

1. Introduction
1.1 The importance of trace metals
Trace metals occur naturally, and are important for characterizing both rocks and sediments. Certain anthropogenic factors may increase the concentration levels of trace metals, causing the sediments and/or groundwater to become toxic. The form and behavior of these metals in sediments can affect the geochemical processes of water/sediment interaction. Trace metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). Factors that may influence the form, concentration, and distribution of metal contaminants include sediment and groundwater chemistry, as well as local transport mechanisms. Some plants have a significant influence in retarding the mobility of metals introduced into sediments, and the idea of using metal-accumulating plants to remove heavy metals and other compounds was first introduced in 1983, but the concept has actually been implemented for the past 300 years on wastewater discharges. It is important to know the partition behaviour of metals, as this determines their availability and biodiversity. Sediments are the major sink for
heavy metals released into the environment by either anthropogenic or lithogenic processes.\textsuperscript{4} Heavy metal contamination of sediments may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated sediments, the food chain (sediments-plants-humans or sediments-plants-animals-humans), drinking of contaminated groundwater, reduction in food quality (safety and marketability) via phytotoxicity, reduction in the suitability of land for agricultural production leading to food insecurity, and land tenure problems.\textsuperscript{2,10} When sediments become contaminated with trace elements, the groundwater becomes a reservoir for them. Sediment/water interactions remain the only significant way of explaining the geochemical processes that determine if trace metals are mobile or immobile. Depending on their chemical properties, trace metals can be conservative and find their way into the groundwater system. Fertilizer application is one of the ways sediments can be enriched with trace elements. The application of such compounds enriches the sediments with potassium, calcium, chloride, nitrate and phosphate.\textsuperscript{12} When applied in excessive amounts on fields or improperly stored in stockpiles, inorganic fertilisers may lead to unacceptable or even toxic concentrations of chemical constituents in local, regional and even national groundwater systems.\textsuperscript{15} The aim of this research is to study the mobilization pattern of Fe and Zn in the alluvial sediments of the River Gbako floodplains around Baddegi, in Nigeria.

1.2 The study area
The study area is mainly low lying, and slopes towards the banks of the River Gbako. The flood plain of the river is extensive, with on average a uniform elevation across the study area. The average elevation in the area is 55 m above sea level, as calculated from a topographical map of the area. The area is mainly drained by the River Gbako, which is tributary to the River Kaduna. The temperature in this area is relatively high, between 33°C and 34°C throughout the season, which affects the rate of evaporation; in addition, intensive agricultural activities contribute to the evaporation.

2. Materials and methods

2.1 Sediment sampling and description
Samples were cored from three pits (TR-1: 0.3m deep, TR-2: 2.0m, and TR-3: 1.4m). The sediment samples were collected and macroscopically described at 0.1m intervals (TR-1) and 0.2m intervals (TR-2 and TR-3) from the surface to the bottom depth for each pit. All the samples were stored in polythene bags. Chemical analysis was done after the samples were processed.

2.1.2 Sieve analysis
Twenty (21) sediment samples were subjected to mechanical sieve analysis following the standard procedures.\textsuperscript{4}

2.2 Estimation of hydraulic conductivity, $K$
The hydraulic conductivity ($K$) was estimated from the sediment particle size distribution graph using an empirical formula.\textsuperscript{1} This formula is:

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K = C (d_{10})^2
\]  

where $K$ is the hydraulic conductivity in cm/sec, $C$ is a constant with units of (cm·sec)$^{-1}$, and $d_{10}$ is the grain diameter in centimetres, so that grains this size or smaller represent 10% of the sample mass. $C$ varies from about 40 to 150 for most sands. $C$ is at the low end of this range for fine, widely graded sands, and $C$ is near the high end of the range for coarse, narrowly graded sands.\textsuperscript{3}

2.3 Chemical analysis of sediments and groundwater
The collected samples as well as groundwater samples were subjected to laboratory chemical analysis. The sediments were processed by grinding in a mortar after drying them at room temperature for 48 hours. The samples were then digested and analysed with AAS for Fe and Zn. All the groundwater samples were analysed for major and minor elements and trace elements (Fe and Zn).

2.4 Partition coefficient values of Fe and Zn
An empirical formula was used to calculate partition coefficients of Fe and Zn. This
calculation involves dividing the concentration of the metals in the sediment samples cored from the three pits by the concentration of such metals in the groundwater samples from the pits. Thus, the partition coefficient is represented by the following formula:

$$D_i = \frac{C_i^{\text{solid}}}{C_i^{\text{liquid}}}$$  \hspace{1cm} (2)

where $D_i$ is the partition coefficient, $C_i^{\text{solid}}$ is the concentration of the element in sediment samples, and $C_i^{\text{liquid}}$ is the concentration of the element in groundwater samples. The velocity of Fe and Zn in the sediments was also determined using the equation below:

$$V = \frac{n}{n + (1-n)\frac{C_i^{\text{solid}}}{C_i^{\text{liquid}}}} V_{\text{liquid}}$$  \hspace{1cm} (3)

where $V$ is velocity of the metals in the solid (sediment or soil), $n$ is the porosity of the sediment, and $V_{\text{liquid}}$ is velocity of the water (the hydraulic conductivity).

3. Results and discussion
The results concerning the partition behaviour of Fe and Zn in the sediment samples are presented in Figures 1, 2 and 3, while the mobility of Fe and Zn in the sediments samples is illustrated in Figures 4, 5, and 6.

According to Raymond et al.\textsuperscript{3} sediments may become contaminated by the accumulation of heavy metals and metalloids through emissions from rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, application of fertilisers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition. Trace metals like Fe and Zn can be concentrated in sediments through adsorption and ion exchange processes.

The characteristic curves for the two metals (Fe, Zn,) with depth shows a similarity in the pattern of mobility through the sediment horizons. Heavy metals in the sediments due to anthropogenic sources tend to be more mobile, hence more bioavailable, than pedogenic or lithogenic ones.\textsuperscript{11,12} In TR-1, Fe and Zn partition similarly in the first two sampling intervals. However, at a depth of 0.3m the partition behaviours of Fe and Zn become inconsistent and varied. Zn can interrupt the activity in sediments, as it influences negatively the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter.\textsuperscript{13} Zinc occurs naturally in sediments (about 70 mg kg\textsuperscript{-1} in crustal rocks).\textsuperscript{7} Fe shows a lower partition coefficient value, indicating a possible decrease in the reactivity of
Fe with the sediments due to a change in the characteristic particle size of the sediments, which allows Fe to attain almost conservative status.

In TR-2, the pattern is quite irregular, providing a different pattern for the elements. The irregularities in the partition pattern may indicate the complex nature of the characteristic grain sizes of the sediments cored from the pits. Zn is less reactive at shallower depths of 0-1m, while Fe becomes less reactive at the deeper depth of 1.2m. This condition can explain the level of remixing in sediments within the active floodplains.

In TR-3, Fe has stable mobility behavior, maintaining the same partition coefficient values, in contrast with Zn which exhibits a sharp drop in the first horizon before stabilising to maintain a similar pattern.
Fe and Zn mobilities in the sediments (see \textit{Figures 4, 5 and 6}) are uniform, except in a few situations. In TR-1, a uniform mobility of Fe and Zn at 0.06m/sec is observed between 0.2-0.6m. The mobilities increase to 0.07m/sec and continue steadily at that level, showing preferential attachment to the sediments. In TR-2, Fe maintains a consistent mobility of 0.08m/sec throughout the sampling horizon, while Zn exhibits a slower mobility in the upper horizon before attaining the same rate as Fe at a depth of 0.4m. In TR-3, both Fe and Zn have the same mobility of 0.09m/sec throughout the sediments, which may be explained by the uniformity in the sediments’ grain sizes.

![Figure 4](image1.png)

\textit{Figure 4.} Velocity of Fe and Zn in sediment samples cored in TR-1.

![Figure 5](image2.png)

\textit{Figure 5.} Velocity of Fe and Zn in sediment samples cored in TR-2.

Generally, the influence of the grain size on the mobility of metals in the sediment horizons is significant, as revealed by the patterns of concentration levels of the trace metals with depth in the sediment horizons (see \textit{Figures 7, 8 and 9}). The principal factors controlling the mobility of the elements in the sediment horizons in the area are the particle size fractions, grain geometry, absorptive capacity and reactivity of the metals in the sediment. Under certain
conditions, metals added to sediments through the application of biosolids can leach downwards through the sediment profile, and can have the potential to contaminate groundwater.\textsuperscript{13} Sediments need to be protected from heavy metal contamination, and phytostabilization is advantageous because the disposal of hazardous material/biomass is not required, and it is very effective when rapid immobilization is needed to preserve the ground and surface waters.\textsuperscript{19} Phytostabilization, also referred to as in-place inactivation, is primarily concerned with the use of certain plants to immobilize soil, sediment and sludges.\textsuperscript{19}

![Figure 6. Velocity of Fe and Zn in sediment samples cored in TR-3.](image)

4. Conclusion
The partition behaviour of Fe and Zn in the floodplain sediments of the River Gbako have been studied to investigate their mobility and transport mechanisms. The transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are initially adsorbed by fast reactions, followed by slow adsorption reactions, and are therefore redistributed into different chemical forms with varying bioavailability, mobility, and toxicity. This distribution is believed to be controlled by reactions of heavy metals in soils such as mineral precipitation and dissolution, ion exchange, adsorption, and desorption, aqueous complexation, biological immobilization and mobilization.

References


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**Figure 7.** Fe and Zn in sediment samples cored in TR-1.
Figure 8. Fe and Zn in sediment samples cored in TR-2.

Figure 9. Fe and Zn in sediment samples cored in TR-3.