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Chemical speciation dynamics and bio-availability quantification of trace metals distribution in non-detrital sediments phase of Cross River Estuary, Nigeria

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Abstract
This study describes the chemical speciation of Hg, Cr, Co, Ni, V and Mn in non-detrital phase of surface sediments from Cross River Estuary of South East Niger Delta, Nigeria. The physicochemical properties like pH, electrical conductivity and reduction-oxidation potential of sediments from ten sampling points were investigated to determine the bio-available species of these trace metals as well as its toxicity. The total concentration of these trace metals were determined by means of Atomic Absorption Spectrophotometer (AAS). The results obtained revealed a mean concentration of the trace metals in the sequence of: Hg (0.01) mg/kg < Cr (0.098 ± 0.024) mg/kg < Co (0.204 ± 0.027) mg/kg < Ni (0.467 ± 0.0930) mg/kg < V (0.53 ± 0.069) mg/kg < Mn (1.40 ± 0.41) mg/kg. The pH, electrical conductivity and reduction-oxidation potential values of 5.15 ± 0.48, 120.11 ± 87.23 μScm^{-1} and 34.30 ± 13.78 mV, respectively revealed that the sediments were acidic and toxic in nature. This study is useful to investigate the complete impact of these trace metals in the environment.

Keywords: Trace metals, chemical speciation, bio-availability, non-detrital phase, toxicity, Niger Delta.

Introduction
The advancement of industrial activities globally has led to the geometric transportation of all sorts of materials forming sediments to nearby rivers, streams, estuaries, etc. Sediments are primarily detached soil particles transported by water, ice, wind, gravity and deposited at a new location [1]. The overall process of detachment, transportation and consolidation is called sedimentation [2]. Suspended solids also result from the detachment and transportation of mineral and organic particles by water and constitute a kind of sediments [3]. Sediment transport is critical to understanding how rivers work because it is the set of processes that operates between the flowing water and the channel boundary. Erosion includes the removal and transport of sediment (mainly from the interface) and deposition involves the transport and placement of sediment on the interface. Erosion and deposition are what form the channel of any alluvial river as well as the floodplain through which it operates. The amount and size of sediment moving through a river channel are determined by three fundamental controls: competence, capacity and sediment supply [4].

Non-detrital phase of sediment could be said to be the acid soluble phase (acetic acid) which exceeds the saturated stage in the silicate lattice in the sediment. This is available phase of trace metals to biota in aquatic environment, such that it's metal concentration affect life in the marine environment and further influences man through the food web [5].

Metals are considered to be trace in aquatic environment if present in concentration of 0.0001%-0.01% of total metal concentration in the aquatic environment [6]. These include; Fe, Cu, Zn, Cd, Pd, As, Ni, V, Cr, Mn, Hg, Co etc. Chemical speciation describes the composition (i.e., types and concentration of chemical compounds) of an aqueous solution [7]. The significance of chemical speciation to environmental science lies in its usefulness as a tool for the interpretation of chemo-dynamic properties and toxicity of chemical compounds [8, 9]. Chemical speciation depends, amongst other factors, on the composition of the system, pH, temperature, ionic strength (electrode potential and oxidation potential) and time [10]. Chemical speciation influences metal ions transport in soil and ground water and uptake by plants and microorganisms [9]. Therefore, we need to know the specie of the substance that is toxic, how much is sorbed (immobile) or dissolved (mobile).

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Bioavailability is the proportion of total metal ions that are available for participation into the biota (bioaccumulation). Total metal ions concentrations do not necessarily correspond to metal bioavailability but also of its chemical speciation [11]. For example sulphide mineral may be encapsulated in quartz or other chemically inert minerals and despite high concentration of mineral in sediments and soil containing this mineral, metals are not readily available for participation in the biota; associated environmental effects may be low [12, 13].

Clear evidence indicates that exposure to certain levels of these trace metals can result in significant human health and ecological risks most especially the formation of lung tumours and cancer as well as cell mutation to human beings through food chains from the aquatic environment [14, 15].

There may be some similarity between soils and sediments; it is risky to assume the behaviour of one particular element is the same in both systems. For example, the low complex stability of manganese may be the reason for the lack of information in literature on the specific behaviour of manganese in sediments. Plants can take up considerable amounts of manganese, and concentrations between 20 and 500µg/g in dry matter are typical [16]. Levels in excess of 500µg/g are probably toxic to many plants. Manganese toxicity to man has been well documented in the scientific literature. Almost all cases of manganese-caused diseases may be related to airborne. Elementary manganese is very toxic but Mn^{2+} is not toxic [17].

It is needful to study the chemo-dynamic properties because most toxic species are in form of free ions which are major players of potential risk in surface waters. The essence of this research work is to assess the potency of this river system to serve as suitable source of domestic (especially in its commercial treatment) water supply for the Niger Delta communities in its environment; to determine the extent of influence that the analysed trace metals have on biota in the aquatic environment and to provide a baseline information for trace metals deposition in the study area.

Materials and Methods
Geology/Geochemical Environment of Study Area
The Cross River originates from the hilly regions of the Northern Cross River State and flows through several town and villages before emptying into the Cross River. It receives water that drains through the crystalline basement rock of Oban Massif as well as the Odukpani formation. The river has shallow depth ranging from 1.0 m to 10.0 m at flood tide and about 8.0 m at ebb tide. Modern sediment dispersal systems regulated by the interaction of natural estuarine processes, man-induced processes and influx of sediment from multiple terrestrial sources are also evident.

The map of the river system is as shown in Figure 1, with the ten black dots indicating the sampling points along the river system.
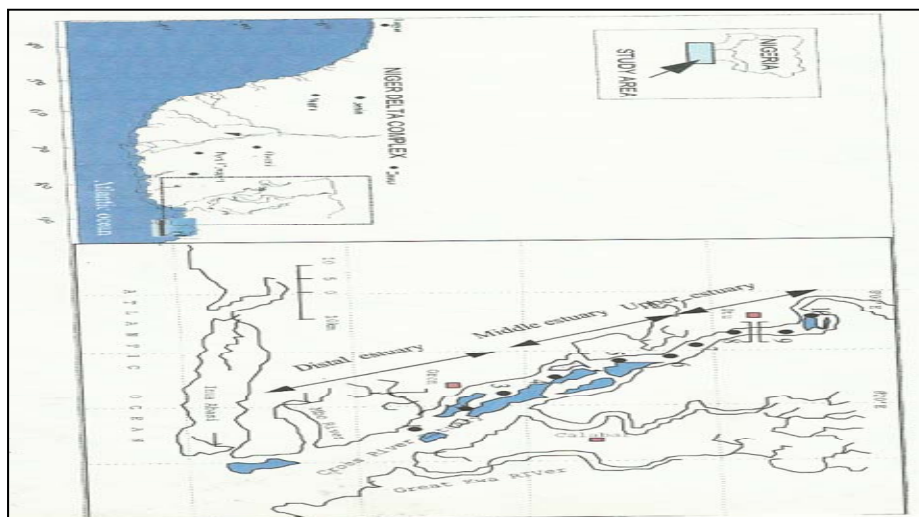

Fig 1: Map showing the Sample Locations in the Cross River Estuary

Data Collection and Laboratory Analyses
Van Veen grab sampler was used to collect about 100 g of the surface sediments from 10 different locations in order to create a composite sample for analysis. Collected samples were placed in a polyethylene vial, sealed and frozen for transport to the laboratory. Samples were measured for pH, redox potential (Eh) temperature and electrical conductivity.

The solution of samples was prepared and a digital pH meter (Orion Digital pH/mill-voltmeter 611) was used to obtain the pH of the sediments.

Measurement of pH
The pH meter utilizes a combined electrode of glass and calomel. The potential (EMF) of the electrode varies with the concentration of the hydrogen ion (H^+). Standard pH buffer tablets of pH 4.0 and 9.2 were used to prepare buffer solutions of specified pH, by transferring the content of a tablet of

specified pH into a 100 ml volumetric flask quantitatively and the solution diluted to make up the mark with distilled water. The electrode was cleaned with distilled water and immersed into a buffer solution of pH 7.0 and the displayed value adjusted with the calibration knob to 7.0. The electrode was cleaned again and immersed into buffer solution of 4.0; the displayed value was adjusted to 4.0 with the knob. The electrode was cleaned again and checked to confirm the pH with buffer solution of 9.2. The sediment samples (5.0 g) were measured into five beakers labelled according to sample location. Distilled water (50 ml) was added into each beaker and the lump of the sediment stirred to dissolve to homogenous slurry. Then the solution was allowed to attain room temperature and transferred to a clean beaker and the pH electrode was rinsed with distilled water before being immersed in the beaker and allowed to equilibrate. The pH

value of the sample was read up directly from the display of the pH meter and recorded [18].

Measurement of Electrical Conductivity

Electrical conductivity is the reciprocal of resistance of a unit volume of sample at specific temperature. A Thermo Orion Conductivity meter capable of measuring the desired range was used. Accurately 0.7459 ± 0.0002 g of anhydrous KCl was weighed and dissolved in distilled water then diluted to 1000 ml with distilled water in a volumetric flask, the conductivity meter electrode was put into the prepared 0.01 N KCl solution and the ON button pressed and followed by the CAL button until 1999 µS/cm was displayed on the meter. The electrode was rinsed with distilled water and the sample solution prepared for pH measurement, was used to test for electrical conductivity as the probe immersed into the sample solution then the result of conductivity was read directly as displayed on the metre in µS/cm and recorded [18].

Measurement of Oxidation Potential

The oxidation potential was measured using a digital Eh meter with its probe inserted into the prepared solution of the sediment samples and readings taken appropriately.

Measurement of the Amount of Trace Metals in Non-detrital Phase of Sediment Sample

The sediment samples were freeze-dried because of the present of Hg mercury which is included in the list of six investigated trace metals. Solutions of the dried samples were prepared using a 25% v/v acetic acid; this was because metals in the non-detrital phase (partition of the metals which are not locked up into the latticity of silicate in the sediment) were the interested metals for the analysis [5]. The concentration of trace metals was detected from the extracted or partitioned

sample solution using a Perkin Elmer A Analyst 200 Atomic Absorption Spectrometer (AAS), with the procedure carried out according to Loring and Rantala [19].

Result and Discussion

Table 1: Physicochemical Parameters of Sediment at Sampling Locations

Sample Location	pH	Eh (mV)	EC (µScm^{-1})
CR$_1$	4.57	46.00	61.60
CR$_2$	4.09	41.00	225.00
CR$_3$	5.50	20.00	47.50
CR$_4$	4.96	42.00	222.00
CR$_5$	5.00	38.00	205.00
CR$_6$	4.90	61.00	231.00
CR$_7$	5.31	29.00	67.00
CR$_8$	5.44	26.00	58.00
CR$_9$	5.67	16.00	39.00
CR$_{10}$	5.50	24.00	45.00
Mean S.D at 95% CL	5.15 ± 0.48	34.30 ± 13.78	120.11 ± 87.23

*CL means confidence level.

The physicochemical parameters shown in Table 1 are indicative of the liability as well as mobility of specified trace metals in the surface sediment. The variations in these properties in ascending order are as follows: CR$_2$ < CR$_1$ < CR$_6$ < CR$_4$ < CR$_5$ < CR$_7$ < CR$_8$ < CR$_3$ < CR$_{10}$ < CR$_9$ for pH values; CR$_9$ < CR$_3$ < CR$_{10}$ < CR$_8$ < CR$_7$ < CR$_5$ < CR$_2$ < CR$_4$ < CR$_1$ < CR$_6$ for redox potential values and CR$_9$ < CR$_{10}$ < CR$_3$ < CR$_8$ < CR$_1$ < CR$_7$ < CR$_5$ < CR$_4$ < CR$_2$ < CR$_6$ for electrical conductivity values. The results showed that pH is inversely proportional to redox potential and electrical conductivity values. The physicochemical properties are further illustrated in Figure 2.
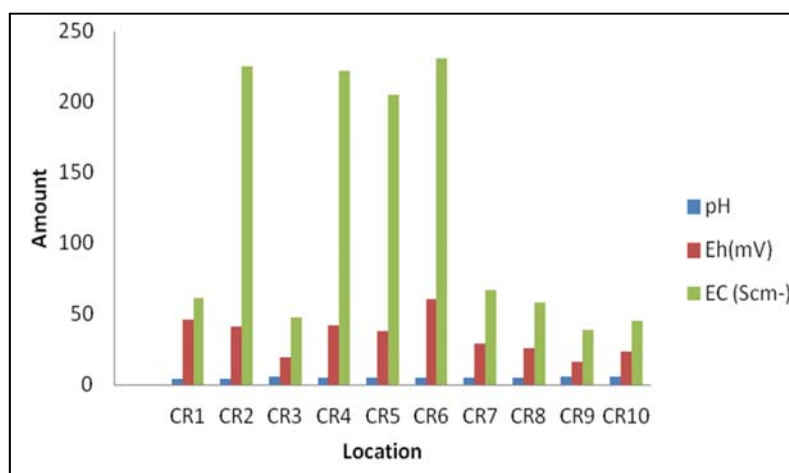

Fig 2: Physicochemical parameters of sediments at sampling station.

The mean pH value of 5.15 ± 0.48 is below the WHO permissible limit for fresh water which is between 6.5-8.0 [20]; this could be attributed to the reducing nature of the environment with a redox potential value of 34.30 ± 13.78mV

which could aid high microbial activities of reducing bacteria [21]. The mean value of electrical conductivity with 120.11 ± 87.23 µScm^{-1} reveals an excellent environment for aquatic organisms to inhabit [20, 22].

Table 2: Concentration of Trace metals in mg/kg across the ten Sampling Stations

Sample Code	Sample Coordinate	Cr	Co	Mn	Hg	Ni	V
CR$_1$	N4^0 43.961 E8^0 21.321	0.09	0.21	1.24	<0.01	0.42	0.52
CR$_2$	N4^0 46.531 E8^0 18.908	0.08	0.22	1.26	<0.01	0.46	0.54
CR$_3$	N4^0 46.927 E8^0 15.501	0.10	0.24	1.34	<0.01	0.47	0.69
CR$_4$	N4^0 52.615 E8^0 12.742	0.07	0.18	0.98	<0.01	0.38	0.45

CR$_5$	N4^0 56.879 E8^0 09.334	0.09	0.15	1.10	<0.01	0.32	0.47
CR$_6$	N5^0 00.437 E8^0 07.062	0.12	0.21	1.20	<0.01	0.40	0.52
CR$_7$	N5^0 04.318 E8^0 06.250	0.13	0.22	2.10	<0.01	0.62	0.49
CR$_8$	N5^0 04.318 E8^0 06.250	0.14	0.20	2.20	<0.01	0.59	0.60
CR$_9$	N5^0 12.726 E8^0 03.497	0.07	0.18	1.42	<0.01	0.49	0.52
CR$_{10}$	N5^0 12.258 E8^0 00.222	0.09	0.23	1.23	<0.01	0.52	0.53

The concentration of investigated trace metals as represented in Table 2 and Figure 3 are in the increasing order of: Hg (0.01) mg/kg < Cr (0.098 ± 0.024) mg/kg < Co (0.204 ± 0.027) mg/kg < Ni (0.467 ± 0.093) mg/kg < V (0.53 ± 0.069) mg/kg < Mn (1.40 ± 0.41) mg/kg. The concentration of these metals is lower than the WHO permissible values for surface water sediments and other International standards [23, 24].

This general assessment may not be comprehensive for assessing the level of toxicity of these trace metals. The chemical speciation and bioavailability of these metals give a comprehensive view of their level of toxicity in this environment. Chromium is available in +3 and +5 oxidation states in aquatic environments with the former being toxic and the latter not toxic, in oxidizing environments. Its +3 state could be easily oxidized to the +5 state and in neutral to slightly acidic environment it could be transported from sediments to water bodies (the toxic effects of this metal to biota in this environment may be more to water bodies than sediments). Cobalt is available in aquatic environment at +2 and +3 oxidation state which co-precipitates with Mn or Fe oxides in toxic condition and between pH 5 and 8 (this is expected of this environment). The total Nickel concentration is present in high amount, with the free available specie of +2 oxidation state which is liable and transported at pH > 6.5 and pH < 6.5, respectively. This shows that the available Ni specie in this environment may immensely affect biota as the pH of the environment encourages its mobility to the water body and in Figure 4, its active species are found plotted at the favourable oxidizing condition. Mercury in the aquatic sediment exist in the 0, +1 and +2 oxidation states, the 0 state is most toxic and is available in this environment as its only exist in reducing condition which is indicated in the Pourbaix diagram in Figure 4. The data for Pourbaix was obtained by using the Nernst and pH dependent equations expressed in equations 1 and 2:

$$Eh = E^0 - \frac{0.0591}{n}\log K \dots\dots\dots\dots\dots\dots\dots\dots 1$$
$$Eh = 1.52 - 0.0944\ pH \dots\dots\dots\dots\dots\dots\dots\dots 2$$

Manganese in acidic medium exist in the range of +1 to +7 oxidation state with +2 and +4 states being of greater important in aquatic environment, under oxidizing condition it does not exist as single ions (which is unlikely for this

environment). Vanadium has a stable oxidation state of +3, +4 and +5 in aqueous system with +4 and +5 oxidation states having a relatively low solubility unless in pH < 4.0 which is not typical for this environment.
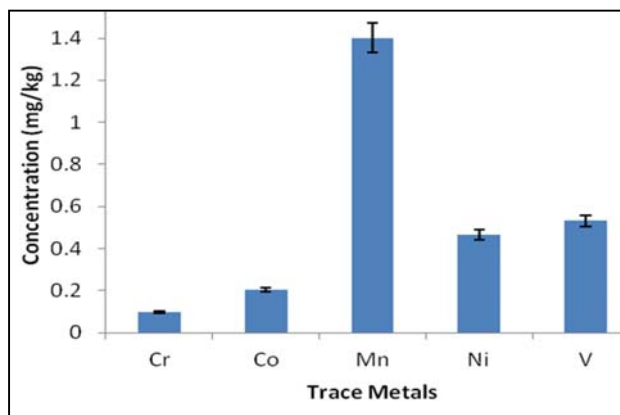

Fig 3: Mean concentration (mg/kg) of trace metals showing error bars
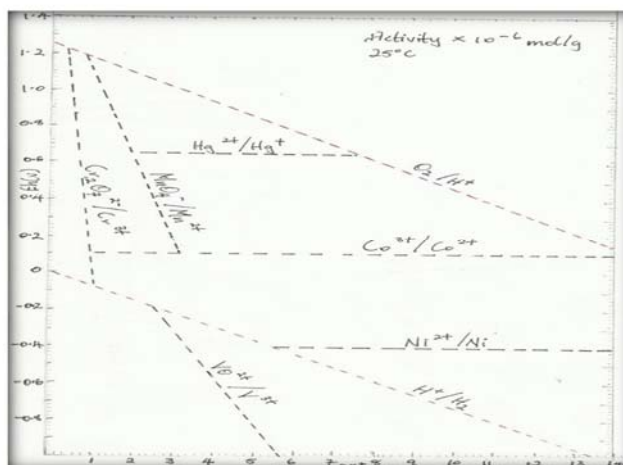

Fig 4: A Pourbaix diagram showing the bioavailability of trace metals at 25 ^{0}C

Table 3: Statistical Data of Trace Metals in Sediment Samples

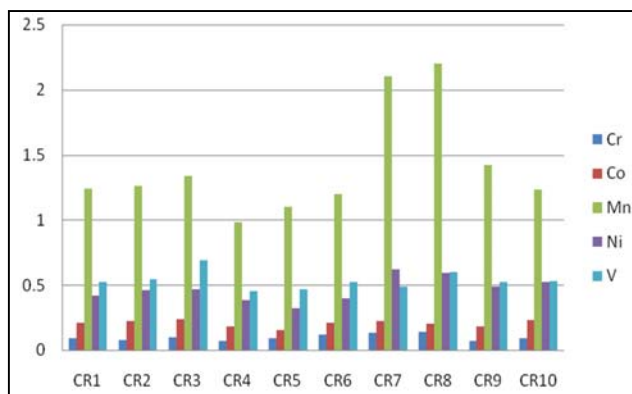| Trace Metal	Mean (mg/kg)	Range (mg/Kg)		Stand. dev. (mg/kg)
		Min	Max	
Cr	0.098	0.07	0.14	2.44×10^{-2}
Co	0.204	0.15	0.24	2.72×10^{-2}
Hg	< 0.01	< 0.01	< 0.01	< 0.01
Mn	1.401	0.98	2.20	4.10×10^{-1}
Ni	0.467	0.32	0.62	9.3×10^{-2}
V	0.533	0.45	0.69	6.87×0^{-2}

*Stand. Dev. means standard deviation

Fig 5: Mean concentration (mg/kg) of each trace metals at specified sampling location

Conclusion
The results of the physicochemical properties showed that pH is suitable for biota in this environment. EC, Eh and total trace metals concentrations are within permissible limits, although further investigations of the available trace metal species have proved that some free available species could pose some risk to biota and other applications. Chromium is expected in its highly toxic +3 oxidation and transported from sediment to the water environment. The effect of free available species of cobalt ions (+2 and +3) are suppressed by co-precipitation with the high amount of manganese at the favourable pH and redox potential values. The physicochemical properties of this environment favours the availability of the most toxic specie of nickel in both the sediment and water environment regardless of its low total concentration as detected in the sediment. Despite the extreme low amount of total concentration of mercury, its most toxic and available specie in the aquatic environment (Hg^o) is likely to be available as the physicochemical environment is favourable but the methylation of non-toxic +2 state to methylmercury which is more toxic than its natural zero state is not possible as the Eh-pH diagram shows Hg^{2+} in reducing environment depicting anaerobic condition (Matson, 2000). Although the amount of total Mn is relatively highest compared to any other detected trace metal in this environment, it does not pose any significant toxic effect to biota as its available specie Mn^{2+} is not toxic. The effects of vanadium in this system centres particularly on the +3 oxidation state as the other available species (+4 and +5) are only soluble at pH values less than 4. The management of these physicochemical properties could make the river system safe for domestic consumption or supply across communities located along the area.

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