FactSage Modelling of Pb and Ni Speciation in Surface Water from Woji Creek, Rivers State, Nigeria

Millicent U. Ibezim-Ezeani[1,2] and Owhonda C. Ihunwo[2*]

[1]Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323, Choba, Rivers State, Nigeria.
[2]Niger Delta Aqua Research Group, Department of Biochemistry and Chemistry Technology, School of Science Laboratory Technology, University of Port Harcourt, P.M.B. 5323, Choba, Rivers State, Nigeria.

Original Research Article

ABSTRACT

The present study is designed to use FactSage version 7.3 to simulate and predict the ionic speciation of lead (Pb) and nickel (Ni) in surface water sampled from Woji creek in Rivers State, Nigeria. Along the 3 km stretch (stations 1 to 5) of Woji creek, in-situ records were taken for temperature, pH and electrode potential (Eh); surface water samples to be assessed for Pb and Ni were collected in sterile bottles. Along the creek, surface water Eh is in the order: station 2 **>** station 4 **>** station 5 **>** station 3 = station 1, with mean value of Eh as 140 ± 20 mV. Surface water pH was close to neutral, and in line with: station 4 **>** station 2 **>** station 5 **>** station 1 **>** station 3; with 6.81 ± 0.13 as the mean value of pH. The trend of temperature values was recorded as: station 1 **>** station 2 = station 3 = station 4 **>** station 5; with the mean value deduced to be 25.6 ± 0.4. Mean concentration of Pb and Ni across the creek were 0.92 ± 0.27 mg/l and 0.46 ± 0.23 mg/l respectively. Pb species exists predominantly in the forms: $Pb_6(OH)_8{}^{4+}{}_{(aq)}$ (45%), $Pb_4(OH)_4{}^{4+}{}_{(aq)}$ (45%). Other forms of Pb present in the surface water are $PbO_{(s)}$ (5%), $PbO_{2(s)}$ (4%) and $Pb^{2+}{}_{(aq)}$ (1%). $NiO_{(s)}$ had the highest proportion of Ni in the surface water (67%), followed by $Ni(OH)_{2(s)}$ (30%) and $Ni^{2+}{}_{(aq)}$ (3%). The predicted metallic species could possibly be sorbet to particulates; thereby increase their chances of bioavailability and subsequent ingestion by fishes and other aquatic organisms. This will in turn influence their bioaccumulation via food chain and increase the tendency of risk impact on man and aquatic ecosystem.

Keywords: Heavy metal speciation; electrode potential; factsage; surface water; pourbaix diagram; woji creek.

1. INTRODUCTION

Physicochemical characteristics of surface water can affect the fate of heavy metals in the aquatic ecosystem. Disturbance of sediment leading to the resuspension of sedimentary materials can also aid in the production of heavy metal elements in the water column. Metals are either naturally occurring within species or complexes released from industrial and other anthropogenic activities [1].

The electrode potential (Eh), pH and temperature are parameters that can change the trace elements in sediment and water from one species to another; the changes in species can affect their rate and mode of mobility and absorption by biota. High turbidity and increased organic matter in aquatic systems can lead to adsorption of heavy metallic species to the particles in the water, thereby leading to an increased concentration of metal ions in the water column as compared to less turbid waters [2,3]. The distribution of heavy metals is thus, as a result of ion exchange, aqueous complexation, biological immobilization, mineral precipitation, and plant uptakes [4,5].

Assessing metal speciation in aquatic ecosystems is important in predicting the bioavailability of metals and providing reliable risk assessment strategies [6]. Lead is not considered an essential trace element, their NaCl infusion into the brackish ecosystem from the ocean increases the solubility of Pb, thus making the metal more mobile and bioavailable [7,8]. Pb form complexes with inorganic ligands such as chlorine (Cl^-) which are in high abundance when the tide pushes saline water upstream [9]. Lead and its compounds are generally toxic pollutants. Pb (II) salts and organic lead compounds are most harmful ecotoxicologically [10,11]. Ni is an essential trace element; Ni (II) has the ability to form complexes with adenine and certain L-amino acids such as aspartic acid, glutamic acid, asparagine, leucine, phenylalanine, and tryptophan [12]. However, a high concentration of Ni can cause toxicity [13]; Nickel sulphate, sulphides and oxides have been classified as human carcinogens and the elemental nickel as a possible carcinogenic metal [14].

The study of metal speciation in the environment is important in order to understand the potential fate and toxicity of a given metal; for this reason, several approaches have been developed over the years. For about 30 years, ion activity of metals has been studied as a means of assessing metal speciation [15,16]. In recent years, the use of predictive models (MINEQL+, WHAM, Visual MINTEQ and FactSage) have been applied to assess ion activity and metal speciation [17,18,19,20,21,22,23]. These models are based on chemical equilibrium constants, and are able to predict how water chemistry modifies different forms of the metals; and in some cases, for example, the Biotic ligand model predicts the subsequent changes in toxicity [24]. This study aims at using FactSage version 7.3 to simulate and predict the ionic speciation of Pb and Ni in surface water sampled from Woji creek in Rivers State, Nigeria.

2. MATERIALS AND METHODS

2.1 Study Area

The Obio/Akpor Local Government Area of Rivers State situated in the Niger Delta region of Nigeria is the location of Woji creek (study area). Some anthropogenic activities around the study area with the tendency to impact metallically on the environmental condition and physicochemistry of the creek include: traffic emissions, mechanic workshops, urban and industrial effluents discharge, market, construction and metallurgical works, scrap yard, entrepreneurial firms, sewage disposal, boat manufacturing and maintenance companies, etc. Relatively high level of metallic contaminants such as Pb and Ni metals were reported in investigation patterning to the creek [25]; and that these biologically indestructible heavy metals accumulate in the tissues of living organisms [26].

Five stations were mapped out along 3 km stretch of the creek for water sampling from June to September of 2018; and identified as: Station 1- 4°49'39.5"N 7°02'35.0"E, Station 2- 4°49'09.3"N 7°02'44.0"E, Station 3- 4°48'51.6"N 7°02'47.0"E, Station 4- 4°48'41.7"N 7°03'01.0"E and Station 5- 4°48'26.6"N 7°03'31.0"E (Fig. 1).

2.2 Sample Collection and Analysis

Five samples of water were collected transversely from both upstream to downstream and reverse flow; and mixed to form a composite sample representing each station [27]. The surface water samples were collected in sterilized plastic containers; and three drops of HNO_3 was added to act as preservative for the water samples [28,29]. In-situ records were taken for temperature, pH and Eh from the different sample station with the use of a multipurpose pH - 8424 portable pH/Eh/Temperature meter. This instrument has an accuracy of 0.01 for pH, ± 0.1% F·S ± 1 bit for Eh and ± 0.4°C for temperature. Water samples were analyzed by direct injection method for Pb (ASTM D3559) and Ni (ASTM D1886) [30]. The GBC SensAA Atomic Absorption spectrophotometer with detection limit of 0.001 ppm, and involves the use of a flame lamp for each metal analyzed.

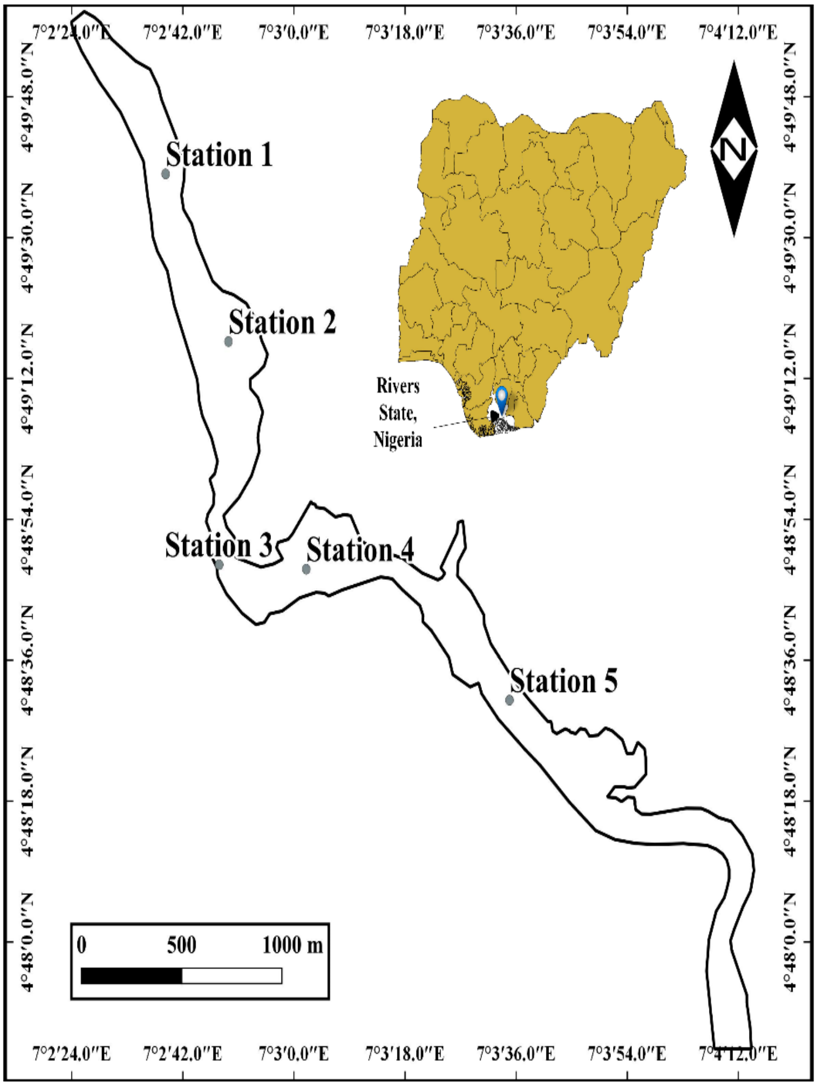

Fig. 1. Sketch of sample stations along the Woji creek of Rivers State, Nigeria

2.3 Quality Control and Quality Assessment

The accuracy of procedure for metal analysis with Atomic absorption spectroscopy was assessed using Certified Reference Materials for Pb and Ni standards; and the samples were analyzed in triplicate. The rate of recovery was assessed using the Matrix Spike (MS) process. This was generated by adding a known amount (a spike) of analyte to sample, testing the spiked sample, and determine if the added amount has been recovered. The recovery rate of the laboratory analytical method was assessed using water samples, to which a spiking solution was added. A spiking solution is a standard that is chosen for preparing MS; the concentration of the analyte in the spiking solution is usually 50 - 100 times higher than the concentration found in the unspiked sample. Percentage recovery for Pb and Ni were calculated as 98.7 and 98.9 % respectively.

2.4 Data Analysis

To create the predominance area diagram also known as a pourbaix diagram, FactSage Edu 7.3 software was used with the mean temperature of the surface water. FactSage is an integrated computing system in chemical thermodynamics and consists of a variety of information, database, calculation and manipulation modules that access various pure substances and solutions data [18]. The predominance area diagram identifies the species which is most dominant at the given temperature, while the species distribution diagram gives an estimate of the fraction or percentage of species existing at a specific pH and Eh.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characteristics of the Surface Water

Along the creek, the trend of surface water Eh (mV) is: 180 ± 30 (station 2) **>** 150 ± 20 (station 4) **>** 130 ± 22 (station 5) **>** 120 ± 16 (station 3) = 120 ± 15 (station 1), with mean value of Eh as 140 ± 20 mV (Fig. 2). Surface water pH was close to neutral, and in the order: 7.08 ± 0.6 (station 4) **>** 7.06 ± 0.3 (station 2) **>** 6.95 ± 0.3 (station 5) **>** 6.70 ± 0.4 (station 1) **>** 6.24 ± 0.6 (station 3); with 6.81 ± 0.13 as the mean value of pH (Fig. 3). The temperature values were in line with: 25.8 ± 0.5 (station 1) **>** 25.6 ± 0.4 (station 2) = 25.6 ± 0.4 (station 3) = 25.6 ± 0.2 (station 4) **>** 25.3 ± 0.3 (station 5); with the mean value deduced as 25.6 ± 0.4 (Fig. 4). pH levels across the creek are similar to those measured along the lower reaches of the Sambreiro River [31], and surface water in Ekerekana and Buguma creeks [32].

3.2 Heavy Metal Concentration and Speciation in Surface Water

3.2.1 Concentration of Pb and speciation in surface water

Concentration of Pb was highest in station 3 (1.33 ± 0.09 mg/l) and lowest in station 5 (0.54 ± 0.11 mg/l); mean concentration of Pb across the creek was 0.92 ± 0.27 mg/l (Fig. 5). Assessment of Pb concentration in Elechi creek which is also located in the Niger Delta region of Nigeria recorded concentrations that were below detectable limits (< 0.001) [33]. Concentrations of Pb across the creek also exceeded those measured in Elechi creek in 2012 [34].

As the pH values fluctuated across the creek, the pourbaix diagram (Fig. 6) showed that the Pb speciation also varied. In the creek, Pb species exists predominantly in the forms: $Pb_6(OH)_8^{4+}$ and $Pb_4(OH)_4^{4+}$ (Fig. 6); having proportions as: $Pb_6(OH)_8^{4+}{}_{(aq)}$ (45%), $Pb_4(OH)_4^{4+}{}_{(aq)}$ (45%), $PbO_{(s)}$ (5%), $PbO_{2(s)}$ (4%), $Pb^{2+}{}_{(aq)}$ (1%) (Fig. 7).

Under the stated environmental conditions in the surface water, Pb forms $Pb_6(OH)_8^{4+}$ and $Pb_4(OH)_4^{4+}$ species are forms of lead that exists in water with a slightly basic condition. This species of Pb can bind to finely dispersed suspensions in surface water, and this will lead to high retention periods in the water and transportation of the metals for a considerably long distance [35]. Although Pb and its compounds are generally toxic, Pb^{2+} salts and organic lead compounds are most harmful [10]. An excess of Pb can impair morphological and biochemical functions in plant tissue. It can also inhibit essential enzymatic activities required for the survival of the plant [36].

3.2.2 Concentration of Ni and speciation in surface water

Concentrations (mg/l) of Ni measured in surface water are as follows: station 1- 0.59 ± 0.12, station 2- 0.22 ± 0.09, station 3- 0.77 ± 0.11, station 4- 0.17 ± 0.09, and station 5- 0.54 ± 0.16 (Fig. 8). Mean concentration of Ni in the creek was calculated as 0.46 ± 0.23 mg/l. Mean concentration of Ni in a tropical manmade lake in Southwestern Nigeria was computed 0.08 ± 0.15 mg/l [37], this value is less than the values measured across Woji creek.

Pourbaix diagram for Ni at different pH and Eh across the creek revealed the presence of three species of Ni: $Ni^{2+}{}_{(aq)}$, $NiO_{(s)}$ and $NiOOH_{(s)}$ (Fig. 9). The proportion of species indicated that NiO(s) had the highest proportion of Ni in the surface water (67%), followed by NiOOH (30%) and Ni^{2+} (3%). $Ni(OH)_2$ and NiOOH are redox couple (Fig.10), hence can replace each other in the aquatic ecosystem depending on the presence or absence of protons in the ecosystem [38].

Nickel is one of 23 metal pollutants of great concern to the environment and human health [39], and it is an abundant element in the earth's crust (84 mg/l) [40,41]. However, due to anthropogenic activities, Ni is continuously added into the environment [42], leading to exposure of living organisms to increased concentrations of Ni, as well as an attendant increase in the risk of toxicity. In the environment, Ni is added through the combustion of fossil fuels and use of Ni compounds and alloys in industries such as steel as is found in Woji creek [25,43]. The most common state of Ni found in biological systems is Ni (II) [44].

The studied heavy metals exist in aqueous and solid phases; thus, giving the possibility of the metals in the solid form to adhere to particulates in the surface water [45]. Consequently, leading to the ingestion of metals adhered to suspended particles by fishes and other aquatic organisms; hence increasing the risk associated with bioavailability and bioaccumulation [46]. This could account for the high concentration of metals detected in different tissues of grey mullet sampled from Woji creek [26]. Metals bound to particulates in surface water also led to an increased ability for metal transport from the source of metal input to other reaches [47,48,49].

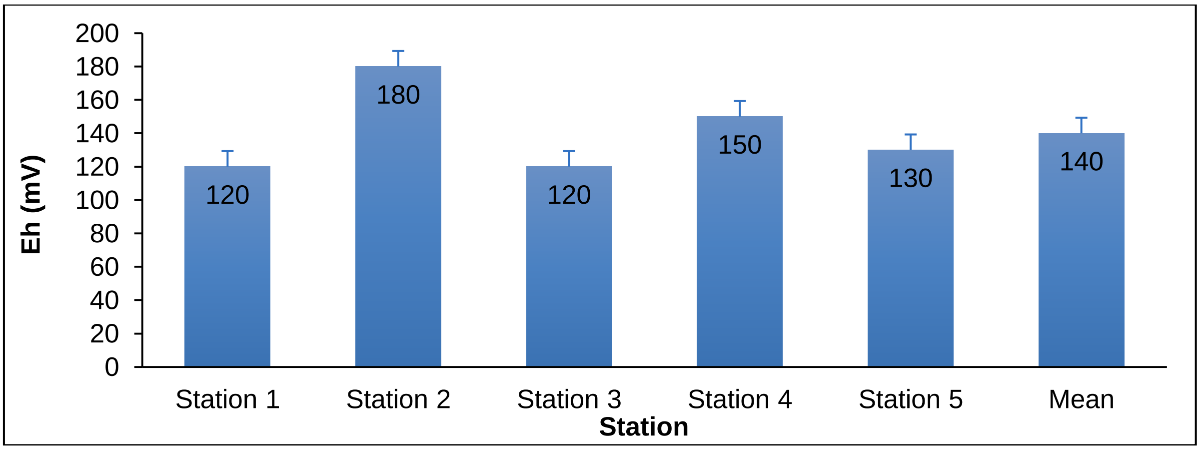

Fig. 2. Electrode potential at each station

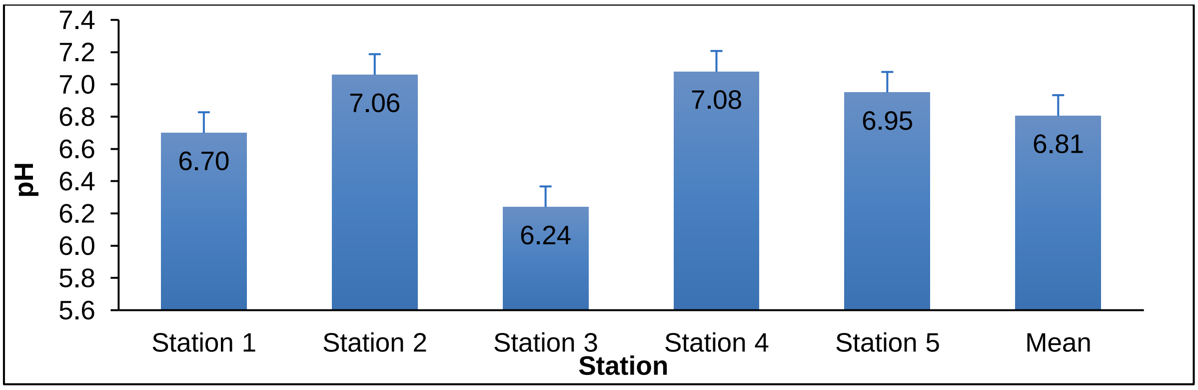

Fig. 3. pH at each station along the creek

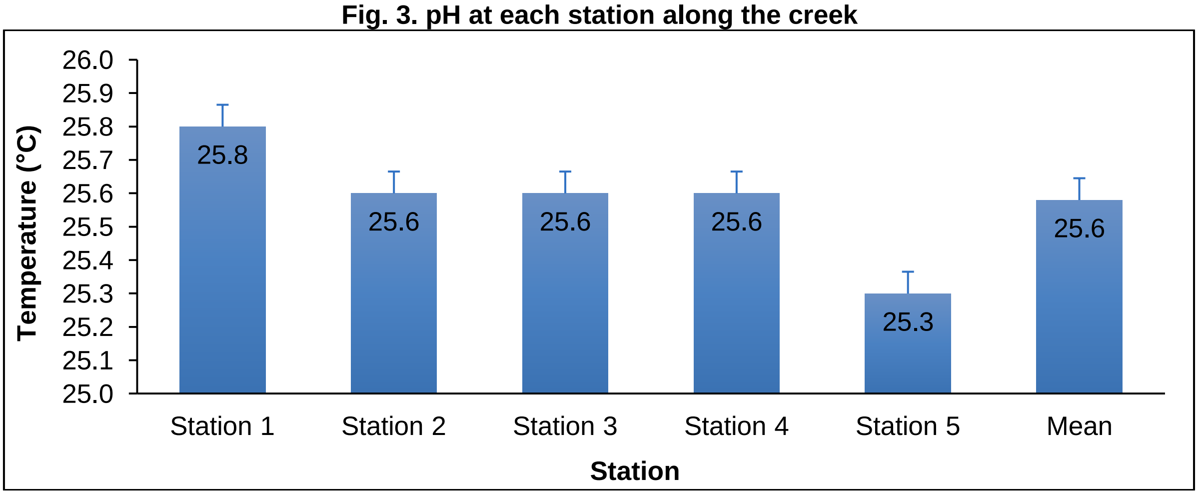

Fig. 4. Temperature (^oC) at each station

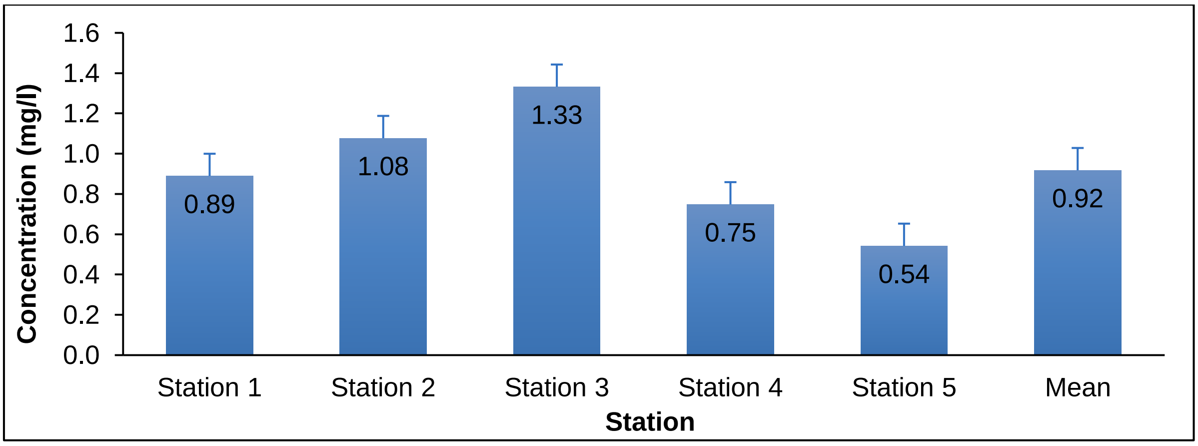

Fig. 5. Concentration of Pb across sample stations

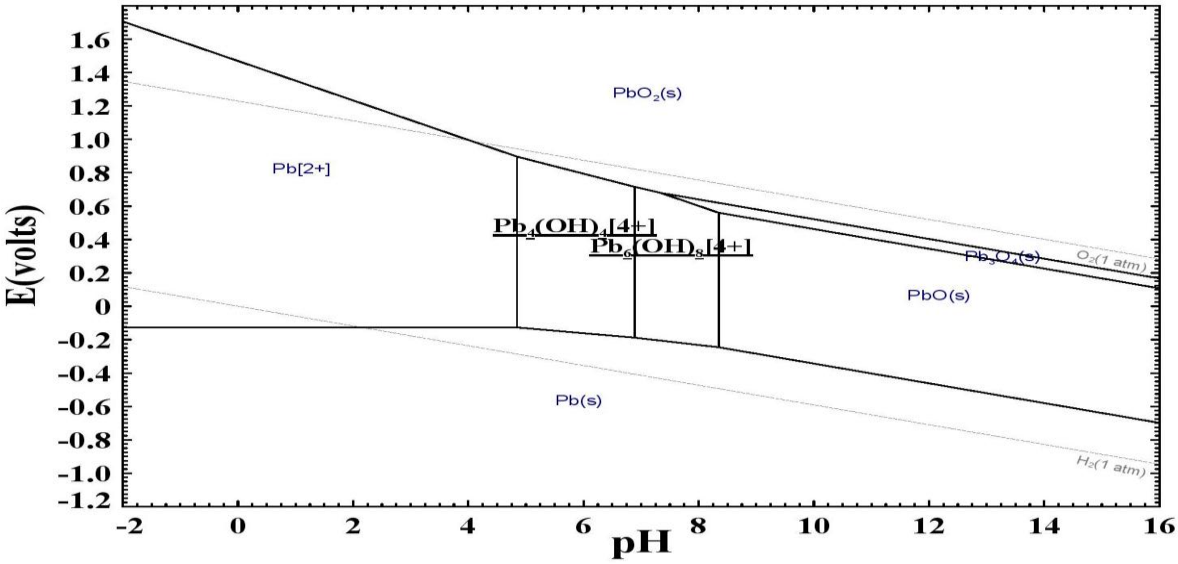

Fig. 6. Pourbaix diagram for Pb in the surface water

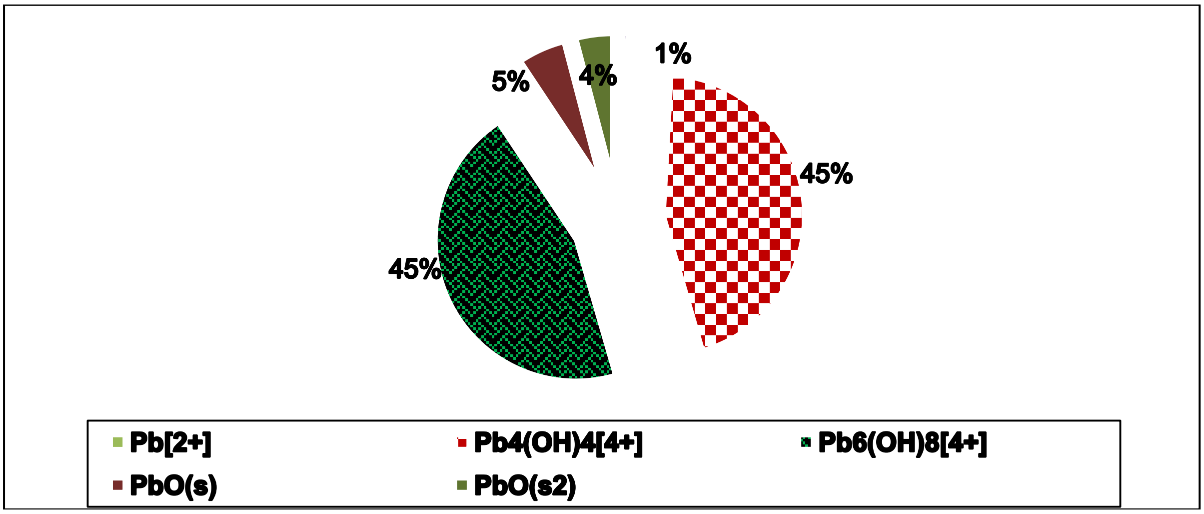

Fig. 7. Proportional plot of Pb species in surface water of Woji creek

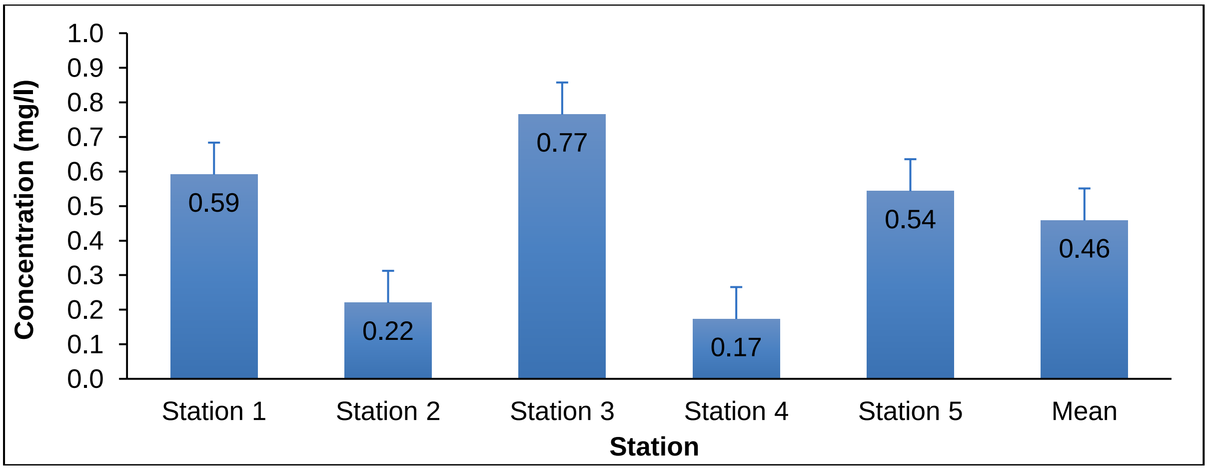

Fig. 8. Concentration of Ni across sample stations

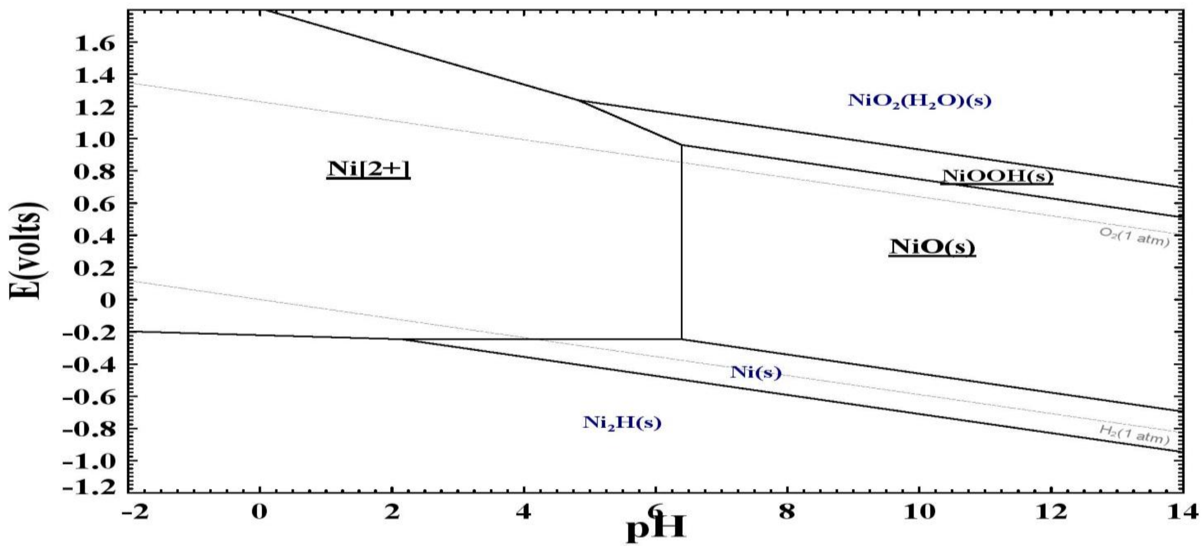

Fig. 9. Pourbaix diagram for Ni in the surface water

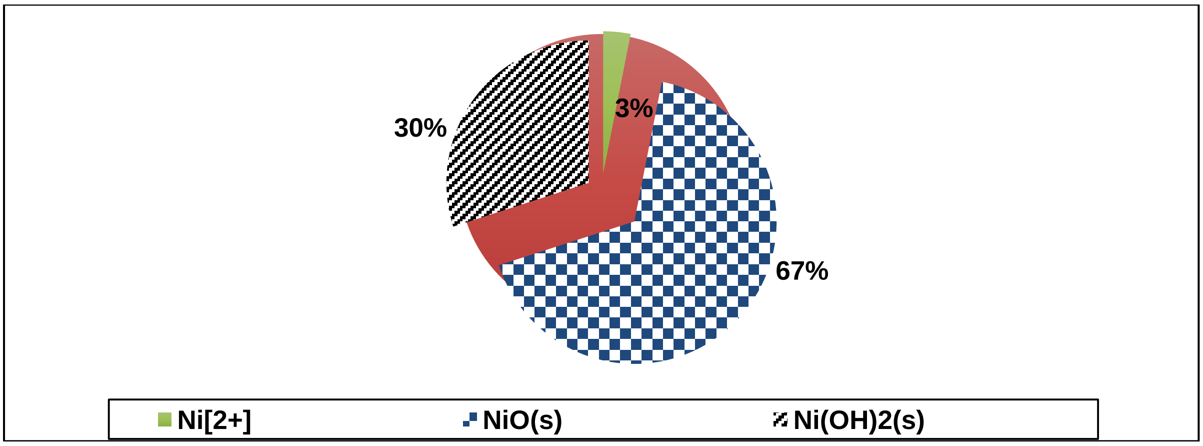

Fig. 10. Proportional plot of Ni species in surface water of Woji creek

4. CONCLUSION

In this study, the use of FactSage version 7.3 software together with in-situ pH, temperature and electrode potential was employed as a modelling tool to simulate the speciation of Pb and Ni metals in the surface water. Following simulation, Pb species exists predominantly in the forms: $Pb_6(OH)_8^{4+}$ (45%), $Pb_4(OH)_4^{4+}$ (45%). Other forms of Pb present in the surface water are PbO (5%), PbO_2 (4%) and Pb^{2+} (1%). NiO had the highest proportion of Ni in the surface water (67%), followed by $Ni(OH)_2$ (30%) and Ni^{2+} (3%). The predicted species can adhere to particulates in the water; this could facilitate the transport of the metallic species, and also increase their bioavailability and bioaccumulation. There is need therefore, for relevant environmental regulatory agencies to brace up to the task of ensuring proper monitoring of treatment of wastes and effluents to appropriate standards before their discharge into waterways.

ACKNOWLEDGEMENTS

The diligence applied by the field and laboratory personnel of Niger Delta Aqua Research Group, Prof. M. Horsfall Jnr (Dean, School of Science Laboratory Technology and University of Port Harcourt), Prof. PC. Mmom (Dean, Faculty of Social Science, University of Port Harcourt), Prof. AN. Dibofori-Orji (Dept. of Chemistry, Ignatius Ajuru University of Education, Port Harcourt, Nigeria), AR. Shahabinia (Groupe de Recherche Interuniversitaire en Limnologie, Departement des Sciences Biologiques, Universite du Quebeca Montreal) and Dr. MO. Onyema (Dept. of Pure and Industrial Chemistry, University of Port Harcourt) are highly appreciated. Also, the enabling support made possible by the paramount ruler (HRH Eze Amb. Sir Dr. EG. Ihunwo [JP. FCAI]) and indigenes of Woji community for the research is acknowledged with gratitude.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Housecroft CE, Sharpe AG. Inorganic chemistry. Pearson Prentice Hall, Essex, England; 2008.
2. Rugner H, Schwientek M, Egner M, Grathwohl P. Monitoring of event-based mobilization of hydrophobic pollutants in rivers: Calibration of turbidity as a proxy for particle facilitated transport in field and laboratory. Science of the Total Environment. 2014;490:191–198.
3. Yao H, Zhuang W, Qian Y, Xia B, Yang Y, Qian X. Estimating and predicting metal concentration using online turbidity values and water quality models in two rivers of the Taihu Basin, eastern China. PLOS One. 2016;11:0152491–0152491.
4. Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, et al. Remediation of heavy metal(loid)s contaminated soils - To mobilize or to immobilize? Journal of Hazardous Materials. 2014;266:141–166.
5. Ibezim-Ezeani MU, Ihunwo OC. Ecological risk assessment of Cd, Cr, Ni and Pb metals in Sambreiro river estuary sediment in the Niger Delta Region of Nigeria. International Journal of Environmental Analytical Chemistry; 2020. DOI: 10.1080/03067319.2020.1849669
6. Leeuwen HPV, Town RM, Buffle J, Rob FMJC, Davidson W, Puy J, et al. Critical review dynamic speciation analysis and bioavailability of metals in aquatic systems. Environmental Science and Technology. 2005;39:8545–8556.
7. Almaroai YA, Usman ARA, Ahmad M, Moon DH, Cho JS, Joo YK, et al. Effects of biochar, cow bone, and eggshell on Pb availability to maize in contaminated soil irrigated with saline water. Environmental Earth Science. 2014;71:1289–1296.
8. Usman ARA, Kuzyakov Y, Stahr K. Effect of immobilizing substances and salinity on heavy metals availability to wheat grown on sewage sludge-contaminated soil. Soil and Sediment Contamination: An International Journal. 2005;14(4):329–344.
9. Abbaspour A, Kalbasi M, Hajrasuliha S, Fotovat A. Effect of organic matter and salinity on ethylenediaminetetraacetic acid–extractable and solution species of cadmium and lead in three agricultural soils. Communications in Soil Science and Plant Analysis. 2008;39:983–1005.
10. Aitio A, Kiilunen M, Santonen T, Nordberg M. Handbook on the toxicology of metals. 4th ed.; 2015.
11. CRL EHN. Lead review; 2003.
12. Türkel N. Stability constants of mixed ligand complexes of nickel(II) with adenine and some amino acids. Bioinorganic Chemistry and Applications. 2015;374782.
13. Muñoz A, Costa M. Elucidating the mechanisms of nickel compound uptake: A

review of particulate and nano-nickel endocytosis and toxicity. Toxicology and Applied Pharmacology. 2012;260:1–16.

14. Zhou C, Vitiello V, Casals E, Puntes VF, Iamunno F, Pellegrini D, et al. Toxicity of nickel in the marine calanoid copepod Acartia tonsa: Nickel chloride versus nanoparticles. Aquatic Toxicology. 2016;170:1–12.
15. Paquin PR, Gorsuch JW, Apte S, Batley GE, Bowles KC, Campbell PGC, et al. The biotic ligand model: A historical overview. Comparative Biochemistry and Physiology Part C: Toxicology and Pharmacology. 2002;133:3–35.
16. Sunda WG, Tester PA, Huntsman SA. Effects of cupric and zinc ion activities on the survival and reproduction of marine copepods. Marine Biology. 1987;94:203–210.
17. Bale CW, Bélisle E, Chartrand P, Decterov SA, Eriksson G, Hack K, et al. Factsage thermochemical software and databases–Recent developments. Calphad. 2009;33:295–311.
18. Bale CW, Pelton AD, Thompson WT, Eriksson G, Hack K, Chartrand P, et al. FactSage. 2019;7:3.
19. Jones RT, Erwee MW. Simulation of ferro-alloy smelting in DC arc furnaces using pyrosim and factsage. Calphad. 2016;55:20–25.
20. Li C, Bai S, Ding Z, Yu P, Wen S. Visual MINTEQ model, ToF–SIMS, and XPS study of smithsonite surface sulfidation behavior: Zinc sulfide precipitation adsorption. Journal of the Taiwan Institute of Chemical Engineers. 2019;96:53–62.
21. Tipping E, Lofts S. Metal mixture toxicity to aquatic biota in laboratory experiments: Application of the WHAM-FTOX model. Aquatic Toxicology. 2013;142–143:114–122.
22. Tipping E, Stockdale A, Lofts S. Systematic analysis of freshwater metal toxicity with WHAM-FTOX. Aquatic Toxicology. 2019;212:128–137.
23. Zhang Y, Jiang J, Chen M. MINTEQ modeling for evaluating the leaching behavior of heavy metals in MSWI fly ash. Journal of Environtal Sciences. 2008;20(11):1398–1402.
24. Fernando Q. Metal speciation in environmental and biological systems. Environmental Health Perspective. 1995;103:13–16.
Available :https://doi.org/10.2307/3432004
25. Dibofori-Orji AN, Ihunwo O, Udo KS, Shahabinia AR, Onyema MO, Mmom PC. Spatial and temporal distribution and contamination assessment of heavy metal in woji creek. Environmental Research Communication. 2019;1:1–10.
26. Ihunwo OC, Dibofori-Orji AN, Olowo C, Ibezim-Ezeani MU. Distribution and risk assessment of some heavy metals in surface water, sediment and grey mullet (Mugil cephalus) from contaminated creek in woji, southern Nigeria. Marine Pollution Bulletin. 2020;154:111042.
Available:https://doi.org/10.1016/j.marpolbul.2020.111042
27. Patil GP. Composite sampling in: El-Shaarawi AH, Piegorsch WW. eds. Encyclopedia of environmetrics. John Wiley & Sons, Ltd, Chichester. 2002;387–391.
28. APHA. Metals by flame atomic absorption spectrometry, in: Arnold EG, Lenore SC, Andrew DE, Mary AHF. eds. Standard methods: For the examination of water and wastewater. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC 20005;1999.
29. ASTM. D1971-16: Standard practices for digestion of water samples for determination of metals by flame atomic absorption, graphite furnace atomic absorption, plasma emission spectroscopy, or plasma mass spectrometry. West Conshohocken, PA; 2016.
30. ASTM. Annual book of ASTM standards. American Society for Testing and Materials, West Conshohocken, PA; 2010.
31. Wokoma OAF, Njoku KU. Physical and chemical characteristics of the lower Sambreiro River, Niger Delta, Nigeria. Applied Science Reports. 2017;20(1):11–16.
32. Makinde O. Comparative assessment of physical and chemical characteristics of water in ekerekana and bugum creeks, Niger Delta Nigeria. Journal of Environment Protection and Sustainable Development. 2015;1(3):126–133.
33. Davies OA, Allison ME, Uyi HS. Bioaccumulation of heavy metals in water, sediment and periwinkle (Tympanotonus fuscatus var radula) from the Elechi Creek, Niger Delta. African Journal of Biotechnology. 2006;5(10):968–973.
34. Ojiesanmi AS, Ibe SN. Effects of pollution on vibrios in Woji river. Journal of Applied Sciences and Environmental Management. 2012;16(1):170–174.
35. Namieśnik J, Rabajczyk A. The speciation and physico-chemical forms of metals in

surface waters and sediments. Chemical Speciation and Bioavailability. 2010;22(1):1–24.
36. Pourrut B, Shahid M, Dumat C, Winterton P, Pinelli E. Lead uptake, toxicity, and detoxification in plants, in: Whitacre, D.M. ed. Reviews of environmental contamination and toxicology. Springer New York. 2011;113–136.
37. Ayoade AA, Nathaniel OG. Assessment of heavy metals contamination of surface water and sediment of a tropical manmande lake southwestern Nigeria. International Journal of Environment and Pollution Research. 2018;6(3):1–16.
38. Trafela Š, Zavašnik J, Šturm S, Rožman KŽ. Formation of a $Ni(OH)_2$/NiOOH active redox couple on nickel nanowires for formaldehyde detection in alkaline media. Electrochimica Acta. 2019;309:346–353.
39. Ahmad MSA, Ashraf M. Essential roles and hazardous effects of nickel in plants, in: Whitacre DM. ed. Reviews of environmental contamination and toxicology. Springer New York. 2011;125–167.
40. Rankin DWH. CRC handbook of chemistry and physics, in: Lide dr. ed. Crystallography Reviews. Taylor and Francis. 2009;223–224.
41. Muhammad BH, Shafaqat A, Aqeel A, Saadia H, Muhammad AF, Basharat A, et al. Morphological, physiological and biochemical responses of plants to nickel stress: A review. African Journal of Agricultural Research. 2013;8(17):1596–1602.
42. Kasprzak KS, Sunderman FW, Salnikow K. Nickel carcinogenesis. Mutation Research-Fundamental and Molecular Mechanisms of Mutagenesis. 2003;533:67–97.
43. Shahzad B, Tanveer M, Rehman A, Cheema SA, Fahad S, Rehman S, et al. Whether toxic or essential for plants and environment - A review. Plant Physiology and Biochemistry. 2018;132:641–651. Available:https://doi.org/10.1016/j.plaphy.2018.10.014
44. Denkhaus E, Salnikow K. Nickel essentiality, toxicity, and carcinogenicity. Critical Reviews in Oncology/Hematology. 2002;42:35–56.
45. Yao Q, Wang X, Jian H, Chen H, Yu Z. Behavior of suspended particles in the changjiang estuary: Size distribution and trace metal contamination. Marine Pollution Bulletin. 2016;103:159–167.
46. Boenigk J, Wiedlroither A, Pfandl K. Heavy metal toxicity and bioavailability of dissolved nutrients to a bacterivorous flagellate are linked to suspended particle physical properties. Aquatic Toxicology. 2005;71:249–259.
47. Balaban N, Laronne JB, Feinstein S, Vaisblat G. Dynamics of metals bound to suspended sediments in floods and on channel banks of the ephemeral Wadi Sekher, northern Negev desert, Israel. Catena. 2019;172:243–254.
48. Sharma P, Yadav P, Ghosh C, Singh B. Heavy metal capture from the suspended particulate matter by *Morus alba* and evidence of foliar uptake and translocation of PM associated zinc using radiotracer (65Zn). Chemosphere. 2020;126863.
49. Windom HL. Elemental composition of suspended particles across the southeastern continental shelf off the coast of north Florida and south Georgia: Provenance, transport, fate and implications to mid-outer shelf water column processes. Continental Shelf Research. 2019;178:27–40.