J. ENVIRONMENTAL SYSTEMS, Vol. 32(1) 27-36, 2005-2006

HYDROCARBON AND HEAVY METAL POLLUTION OF WATER AND SEDIMENTS OF CROSS RIVER AND AKWA IBOM COASTAL WATERS, NIGERIA

FLORA E. OLAIFA
University of Ibadan, Nigeria

ABSTRACT

A study was undertaken to determine the total hydrocarbon (THC) and heavy metal contents of water (surface: 0-15 cm and bottom: 2-13 m), sediments (intertidal and waterbed) in coastal areas of Cross River and Akwa Ibom States of Nigeria affected by a major oil spill in 1998. Water and sediment samples were collected in the dry (March and December) and wet (July and October) seasons between 1999 and 2002. Significant spatial variation ($p < 0.05$) was observed for THC and heavy metals. THC (mg/L) averaged 0.998 for surface and 0.827 for bottom water. All heavy metals of interest: chromium, copper, cadmium, lead, iron, manganese, zinc, and vanadium were present in samples and sediments contained significantly higher ($p < 0.05$) THC and heavy metals than water. Concentrations of THC in water and sediments exceeded World Health Organization's limits by an average of 0.9979 and 0.8269 mg/L in surface and bottom waters respectively.

INTRODUCTION

Accidental spills of petroleum and its products occur [1]. There were 5,334 spill incidents reported in Nigeria between 1976 and 1997 involving 2.8 million barrels of oil released onto land, swam estuaries, and coastal waters [2]. Materials discharged into coastal areas are found in the water column as well as sediments in open sea areas. Persistent hydrophobic contaminants have a strong affinity for fine-grained particles and consequently their sorption and settling into the

doi: 10.2190/ES.32.1.d
http://baywood.com

sediment is a major removal mechanism while river-borne particles and sediments act as carriers of contaminants and there are periods of re-suspension, transport and sedimentation [3].

MATERIALS AND METHODS

Nine sites on the Cross River, Calabar River (a tributary of the Cross River) and Ibeno coastline were studied. The study areas were located in both Akwa Ibom and Cross River States of Nigeria: Calabar River Estuary, Oron water channel, Ibaka water channel (also called Tom Short or Jamestown), James Island, Ikang water channel, Calabar River at Odukpani, the bridgehead at Ayadehe, Qua Iboe terminal at Ibeno and Ifeta, the reference location. These were labeled 1 to 9 respectively as shown in Figure 1.

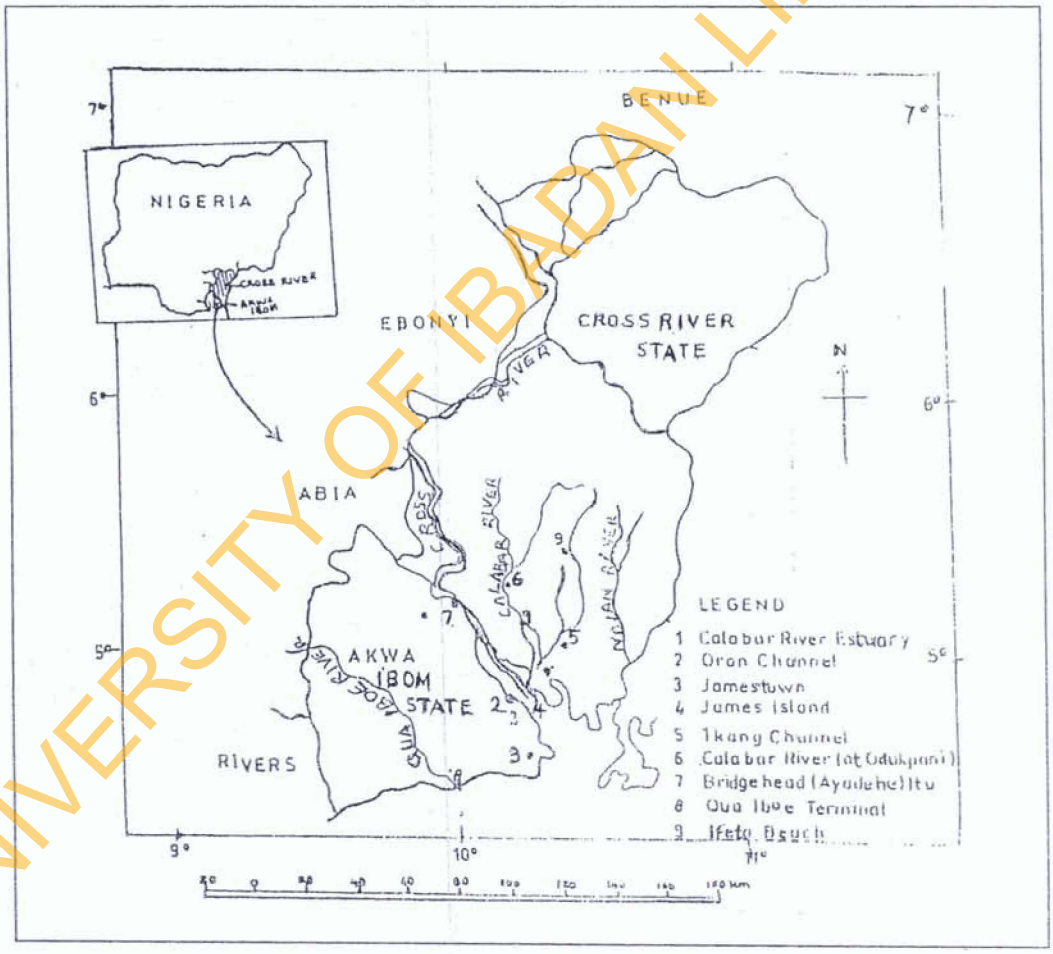

Figure 1. Map of Akwa Ibom and Cross River States showing the study locations.

The climate in the area is humid-tropical with 1300-3000 mm rainfall and 30°C mean annual temperature. Mangrove swamps and nypa palm forests are predominant. The soils are ferralitic in Akwa Ibom [4] and alluvial along coastal areas of Cross River valley [5].

Top and bottom water, intertidal and bottom sediments were sampled using water and sediment samplers [6].The water samples were emptied into all-glass and plastic bottles for hydrocarbon and heavy metal analyses respectively and refrigerated [7] while the top 3-5 cm of each grab sediment sample was sub-sampled and stored in clean aluminum foil for hydrocarbon analysis and a polythene bag for metal analysis. All samples were collected from the windward side of the boat to avoid contamination from the boat's engine, frozen to stop biological and chemical transformations, and then air-dried at room temperature for 48 hours.

Added to 250 ml of each water sample was 100 ml distilled n-hexane, then left to stand in a separatory funnel for 1 hour, and total hydrocarbon content quantified by gravimetric method. For sediment hydrocarbon, 19 air-dried sediment sample was extracted with redistilled n-hexane and the total hydrocarbon determined using Hach spectrophotometer model DR/300 at 430 nm. heavy metals, 1 g air-dried sediment sample was milled in a mortar, heated to reddish brown in a furnace, cooled and moistened with de-ionized water. Then 1 ml of 60% perchloric and 20 ml of 40% hydrofluoric acids were added and heated to dryness in a sand bath to approximately 180°C and cooled; 15 ml of 10% hydrochloric acid was added and heated in a closed crucible to dryness [8], and the concentration of metals in water and sediments determined using an atomic absorption spectrophotometer (AAS).

RESULTS

The mean total hydrocarbon contents of the surface and bottom waters during the dry and wet seasons were 1.34, 1.16 and 0.65, 0.50 mg/L respectively. The mean THC and heavy metal contents for water and sediments are shown in Figures 2 thru 5.

In surface water, a positive correlation ($p < 0.05$) was observed between water temperature and THC ($r = 0.70$); negative correlations between THC and pH ($r = -0.81$), TSS ($r = 0.80$), turbidity ($r = -0.93$), and salinity ($r = -0.81$). Simple linear regression was used to establish relationships for THC, chromium, and magnesium in water:

$$THC_w = 0.81 + 0.41\ Cr\ (R^2 = 0.26, Ra^2 = 0.22, SE = 0.4536, N = 18)$$

$$THC_w = 0.72 + 0.001\ mg\ (R^2 = 0.23, Ra^2 = 0.18, SE = 0.46303, N = 18)$$

Iron was the dominant metal in both rainy and dry seasons in water and intertidal sediments. Most waterbed sediments contained higher copper concentrations

Figure 2. Mean total hydrocarbon content (THC) of the water (mg/l).

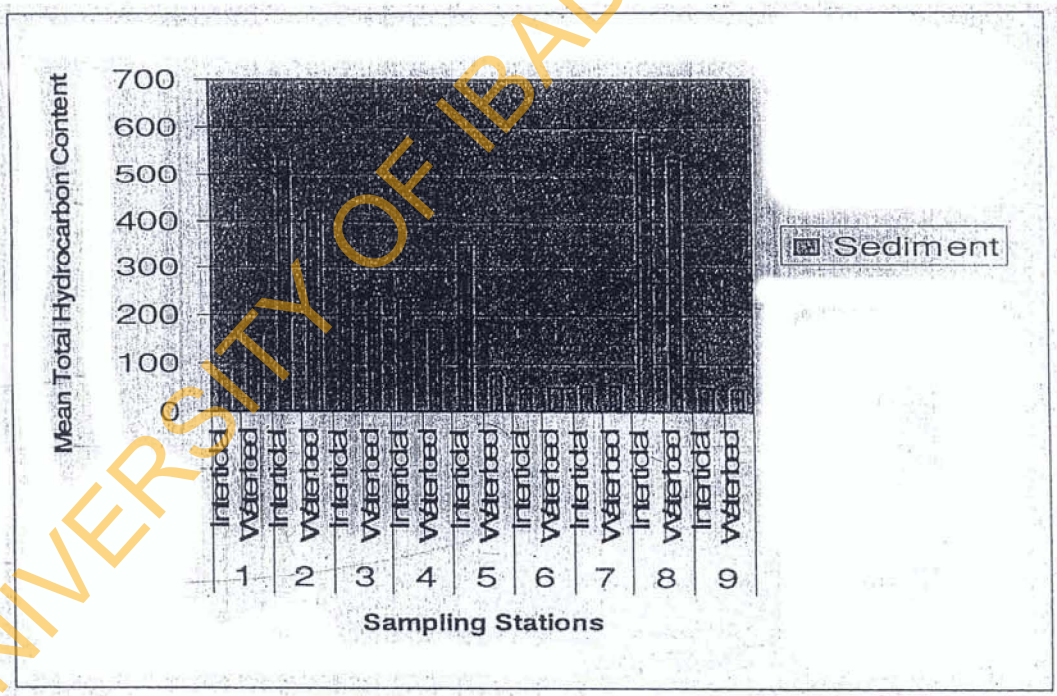

Figure 3. Mean sediment hydrocarbon content (Mg/L).

Figure 4. Mean sediment heavy metal content (ppm).

Figure 5. Heavy metal content of sediments (ppm)

in the rainy than dry seasons. The least abundant metal in sediment was cadmium and chromium in water.

DISCUSSION

The highest water THCs were obtained in the late dry season (March) and the least in the rainy season and these observations were lower than reported earlier few weeks after the spill [9]. During this study, no station recorded up to the recommended limit of 10 mg/L of THC in water [10] but concentrations were similar to pre-spill values [11]. The THC for the Cross River system before the spill of 1998 was 2.2 mg/l [12].

The fall in the observed levels of THC could be due to several factors like: the type of oil spilled (Class A: This class of crude oil is light, volatile, and generally flammable when fresh), tidal regime, and the period of sampling. There was a time lag between the spill and sampling. High THC values have been recorded at flood than ebb tide [13]. However during this study, some 8 (Qua Iboe terminal), 1 (Calabar River Estuary), and 2 (Oron water channel) recorded THC values greater than pre-spill values. This observation could have been due to the gradual degradation of tar balls buried in the sand and the lower THC levels observed in the rainy season could be due to dilution effect.

Heavy metals are defined as metals having densities greater than 5 g/cm^3. These are sources of metal toxicity as most organisms are ill-equipped to metabolize them in large concentrations [14]. The background levels of metals for African rivers were: Cadmium – 0.02, Lead – 3, Copper – 7.0, Zinc – 20, Manganese – 7, and Iron – 40 µg/ml [15] and coastal waters: Cd – 0.01, Pb – 0.03, Cu – 1.0, Zinc – 2.5, Mn – 0.4, and Fe – 2.0 µg/ml respectively [16]. Increased levels of heavy metals have been attributed to local pollution [17]. Chromium was present in excess of 0.05 mg/L allowed in drinking water at some stations. The observed concentrations of copper were lower than 5.8-600 µ/L recommended by USEPA [18], the Federal Environmental Protection Agency limits of < 1 mg/L [19] and the background concentration for rivers [20]. Copper had previously been recorded as 3.2 µg/l for Calabar River [21].

Many stations recorded higher concentrations of cadmium than FEPA recommended limits of < 1 mg/L and DPR limits of 0.01 mg/L Cd. Higher concentrations of lead were obtained in the dry than rainy seasons. This could have been due to a reduction in the water levels during the dry season thereby causing greater concentrations of pollutants to be recorded. This observation was similar to those of other workers [13, 22]. Vanadium is important as an indicator of petroleum pollution because oil is one of the major contributors of vanadium to the environment [23]. Nigerian Crude Oils contain 0.9-2.8 ppm of vanadium [24]. The mean vanadium content in ranged 1.125 and 2.25 ppm in surface and bottom waters and 3.58 to 4.32 ppm in intertidal and waterbed sediments respectively. Sediments varied within the study area and there were variations between intertidal and water

bed sediments at same locations. The sediment particle sizes obtained ranged from fine, medium, and coarse sand to mixtures of silt and clay. The sediment particle size directly influences the presence of pollutants. The dynamics, variability, and availability of pollutants like hydrocarbons and heavy metals depend mainly on sediments and its characteristics. Sediments made up mainly of silt/clay fractions retain more pollutants than sandy sediments [25]. The concentrations of heavy metals in sediment more than in water reflect the extent of impact by industrialization. The presence of heavy metals in sediments over the background levels indicated anthropogenic inputs [26].

Fe was the dominant metal in the sediments in both seasons and tended to depend on the silt/clay fraction. Higher concentrations of cadmium were recorded in all the stations than both the continental crust and unpolluted sediments for inland water, which could be due to greater inputs of cadmium into the environment through human activities like poor chemical use and disposal. Lower concentrations of copper, lead, manganese, and zinc were reported than present in unpolluted sediments, continental crust, the Niger Delta Area of Nigeria, and the Atlantic Coast. The concentrations of THC obtained during the dry season in sediments were higher than the values obtained fo the Niger Delta area [27]. The highest concentrations of THC were recorded close to oil activity sites (Station 8).

CONCLUSION

The sediment types and water quality varied with locations. Higher concentrations of THC and heavy metals were encountered in sediments than water. It was recommended that there should be regular monitoring and enforcement of environmental regulations. The release of heavy metals and oil into the environment should be controlled. There is a need to involve all stakeholders in environmental management, protection, and decision -making.

REFERENCES

1. Nigerian Environmental Study/Action Team, *Nigeria's Threatened Environment: A National Profile.* Nigerian Environmental Study/Action Team, Intec Printers Ltd., Ibadan, 1992.
2. W. F. Dublin-Green, J. N. Nwankwo, and D. O. Irechukwu, Effective Regulation and Management of HSE Issues in the Petroleum Industry, in *Nigeria SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production,* Caracas, Venezuela, June 7-10, 1998, Paper No. SPE 40/26,1998.
3. B. J. Eadie and J. A. Robins, The Role of Particulate Matter in the Movement of Contaminations in the Great Lakes, *Advanced Chemistry Series, 216,* pp. 319-364, 1987.
4. C. N. Obihara, The Acid Soils of Eastern Nigeria, *Nigerian Scientist, 1*:1, pp. 57-64, 1961.

5. S. W. Petters, Cross River State, in *Nigeria: Giant in the Tropics, Vol. 2, State Surveys,* R. K. Udoh and A. B. Mamman (eds.), Gabumo Publishing Co. Ltd., Lagos, Nigeria, pp. 51-136, 1993.
6. Van Veen, Onderzoek near het zandtransport von rivierren, *De Ingenieur, 48,* pp. 151-159, 1933.
7. UNESCO/WHO, Water Quality Survey, A Guide: Collection and Interpretation of Water Quality Data, prepared by IHD-WHO Working Group on Quality of Water, 1984.
8. H. H. Rump and K. Krist, *Laboratory Manual for Examination of Water, Wastewater and Soil,* Weinhem Verlag VCH, 190 pp., 1988.
9. F. E. Asuquo, O. R. Ogri, and E. S. Bassey, Distribution of Heavy Metals and Hydrocarbons in Coastal Water and Sediments of Cross River State, South Eastern Nigeria, *International Journal of Tropical Environment, 1*:2, pp. 229-242, 1999.
10. Department of Petroleum Resources, *Environmental Guidelines and Standards for the Petroleum Industry in Nigeria,* Department of Petroleum Resources, Ministry of Petroleum Resources, Lagos, p. 189, 1991.
11. E. S. Bassey and F. E. Asuquo, Seasonal Changes in the Water Quality of Ibeno Coastline, S. E. Nigeria, *International Journal of Tropical Environment, 2,* pp. 138-150, 1999.
12. Research Planning Institute, *Environmental Baseline Studies for the Establishment of Control Criteria and Standards Against Petroleum-Related Pollution in Nigeria,* R.P.I. Incorporated U.S.A. Final Report for NNPC; Lagos, Nigeria, pp. 118-127, 1985.
13. F. E. Asuquo, Physicochemical Characteristics and Anthropogenic Pollution of the Surface Waters of Calabar River, Nigeria, *Global Journal of Pure and Applied Science, 5*:4, pp. 595-600, 1999.
14. R. B. Clarke, C. Frid, and M. Atrill, *Marine Pollution* (4th Edition), Oxford University Press, New York, 1997.
15. J. D. Burton, Basic Properties and Processes in Estuarine Chemistry, in *Estuarine Chemistry,* J. D. Burton and P. S. Liss (eds.), Academic Press, London, p. 136, 1976.
16. J. M. Martin and M. Whitefield, The Significance of River Input of Chemical Elements to the Ocean, in *Trace Elements in Seawater,* C. S. Wond and E. Boyl (eds.), Plenum Press, New York, pp. 265-296, 1983.
17. C. L. Ndiokwere and V. P. Guinn, Determination of Some Toxic Trace Metals in Nigerian River and Harbour Water Samples by Neutron Activation Analysis, *Journal of Radiological Chemicals, 79,* pp. 147-151, 1983.
18. W. O. Odiete, *Environmental Physiology of Animals and Pollution,* Diversified Resources Limited, Lagos, Nigeria, pp. 220-246, 1999.
19. Federal Environmental Protection Agency, *Guidelines and Standards for Environmental Pollution Control in Nigeria,* pp. 1-238, 1991.
20. C. Biney, A. T. Amuzu, D. Calamari, N. Kaba, I. L. Mbome, H. Naeve, P. B. O. Ochumba, O. Osibanjo, V. Radegonde, and M. A. H. Saad, Review of Heavy Metals, in *Review of Pollution in the African Aquatic Environment,* D. Calamari and H. Naeve (eds.), Committee for Inland Fisheries of Africa (CIFA), *CIFA Technical Paper 25,* FAO, Rome, 1994.
21. S. E. Kakulu and O. Osibanjo, Pollution Studies of Nigerian Rivers: Trace Metal Levels of Surface Waters in the Niger Delta Area, *International Journal of Environmental Studies, 41,* pp. 287-292, 1992.

22. B. C. O. Okoye, Nutrients and Selected Chemical Analysis in Lagos Lagoon Surface Waters, *International Journal of Environmental Studies, 38,* pp. 131-136, 1991.
23. F. Khalaf, P. Litherathy, and V. Anderlini, Vanadium as a Tracer of Oil Pollution in the Sediments of Kuwait, *Hydrobiologia, 9,* pp. 147-154, The Hague, The Netherlands, 1982.
24. Eco-Consultancy Group, *Final Report on the Preliminary Studies of the Toxicity of Nigerian Crude Oils to Aquatic Organisms of the Coastal and Inland Waters of Nigeria,* Eco-Development Consultancy Group, Institute of Ecology, University of Ife, Ile-Ife, 1987.
25. U. Forstner, Accumulation Phases for Heavy Metals in Limnic Sediment, *Hydrobiologia, 9,* pp. 269-284, The Hague, The Netherlands, 1982.
26. E. U. U. Ntekim, S. J. Ekwere, and E. E. Ukpong, Heavy Metal Distribution in Sediments from Calabar River, South Eastern Nigeria, *Environmental Geology, 21,* pp. 237-241, 1993.
27. O. E. Adekanmbi, *Petroleum Hydrocarbons Pollution of Nigerian Waters and Sediments around Lagos and Niger Delta Areas of Nigeria,* Ph.D. thesis presented to the Faculty of Science, University of Ibadan, 1990.

Direct reprint requests to:

Prof. Flora E. Olaifa
Department of Wildlife and Fisheries Management
University of Ibadan
Nigeria
e-mail: floraolaifa@yahoo.com