An Evaluation of Heavy Metals Concentration in the Choba Section of the New Calabar River, Eastern Niger Delta

Nwankwoala H. O.*  
Department of Geology, University of Port Harcourt, Nigeria

Angaya Y. B.  
Department of Geology, University of Port Harcourt, Nigeria

Abstract: Assessment of heavy metals concentration in water and sediments of the Choba section of the New Calabar River, Eastern Niger Delta were carried out. Seven (7) river sediments and twelve (12) surface water samples were collected for the study. The heavy metals studied were: Mn, Pb, Zn, Fe, Cd, Cr, and Cu for in both river sediment and surface water. The World Health Organization (WHO) standards were used in evaluating Pollution Index (PI) of heavy metals in surface water. The Pollution Load Index (PLI) level of river sediments ranged from 5.12 – 33.26, with only PLI values <1 considered unpolluted. The other samples analyzed revealed high pollution levels, with Cu, Cr and Mn having moderate to considerable Contamination Factor levels, while the others were of low levels. For surface water, Pb and Zn had high Pollution Index values, with Pb having PI values ranging 10 – 211, with considerable contribution of pollutants from anthropogenic activities into the river. There is urgent need for regular monitoring of the Choba section of the River. The regulatory government agency responsible for protecting the environment should also pay adequate attention to this stretch of the river to avoid further contamination.

Keywords: Heavy metals; Sediments; Water pollution; New Calabar River; Choba; Eastern Niger Delta.

1. Introduction

Heavy metals are dangerous because they tend to accumulate. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down or extracted (metabolized). Heavy metals can enter the water supply by industrial or consumer waste or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and ground waters [1]. Although some heavy metals such as Manganese, iron, copper and zinc are essential micronutrients, other such as mercury, cadmium and lead are not required even in small amounts by any organisms [2]. Some heavy metals become a matter of concern because of their toxicity and tendency to accumulation in food chains. Fishes, mollusk or another aquatic life are located at the end of food chain may accumulate metals and pass them to the human being through food causing chronic or acute diseases [3]. Recent researchers have found that even low levels of mercury, cadmium, lead, aluminum and arsenic can cause a wide variety of health problems.

Heavy metals toxins contribute to a variety of adverse health effects. These exit over than 20 different heavy metals toxins that have impacts on human health and each toxin will produce different behavioural physiological and cognitive changes in an exposed individuals. The degree to which a system organ tissue or cell is affected by a heavy metal toxin depends not only on the toxin itself but also on the individuals degree of exposure to the toxin Förstner and Wittman [4]. The toxicity of heavy metals can be listed in order of decreasing toxicity as Hg>Cd>Cu>Zn>Ni>Pb>Cr>Al>Co. This is only approximate as the vulnerability of species to individual metals varies. Toxicity also varies according to the environmental conditions that control the chemical speciation of metals.

Because Water pollution is a significant problem and an essential natural resource for human life, there is need for assessment of the degree of contamination. More so, water is an important resource of developing economies and society in terms of agriculture, industry and various facilities [5]. Rivers not only supply water for human consumption but also receive wastewater discharge from all human activities. In the past two decades there have an increasing public awareness of the hazards exit from the contamination of the environment by toxic substances. Therefore in order to maintain the delicate relationship between human development and the quality of the environment, there is need for constant monitoring and evaluation of human activities in the Choba section of the New Calabar River that have the potential of altering the quality of the environment within which such activities occur. This is very necessary for risk assessment.

*Corresponding Author
1.1. The Study Area
The New Calabar River and its tributaries are all located in Rivers State. It is a low lying deltaic river which rises at approximately latitude 5°10’N and longitudes 6°50’E near Elele-Alimini and flows Southward for roughly 150km before its discharge into the Atlantic Ocean at about latitudes 4°20’N and longitudes 7°00’E [6]. It occupies a low relief region, ranging from 0-50m above sea level at the low zone, to 50-100 above sea level at its source. The soil of the river basin consists of clays, silt and sand, with high organic matter [7, 8]. The river is unidirectional in the upper reach and tidal in the lower reach. Its upstream reach is fresh water with tropical lowland and dense rainforest through secondary forest/farmland vegetation. The downstream reach is however brackish and consist of Mangrove swamp forest.

The Choba section of the New Calabar River is within Obio-Akpor Local Government Area alongside the Port Harcourt Local Government Area which forms the Port Harcourt Urban Area in Rivers State, Eastern Niger Delta, Nigeria. Rivers State is located in the South-South geopolitical zone of Nigeria and the eastern sector of the oil-rich Niger Delta region of the country. Port Harcourt doubles as the Capital City of Rivers State, and also the largest city in the State. The Port Harcourt urban area has a total population figure of 1, 382, 592 [9]. Obio-Akpor Local Government Area is one of the eight (8) Local Government Areas that forms the Greater Port Harcourt urban area, namely: Port Harcourt, Okrika, Obio-Akpor, Ikwerre, Oyigbo-Bolo, Tai and Eleme Local Government Areas respectively. As at 2012, the Greater Port Harcourt urban area had an estimated total population of 1,947,000 (Nigerian Administrative Division: City Population). This made it the 5th largest urban area in Nigeria; only after Lagos, Kano, Ibadan and Abuja. Port Harcourt has a tropical monsoon climate; having a lengthy and mostly heavy rainy seasons and very short dry seasons. December and January are the only months that truly qualify as dry season months, with December averaging 20mm of rain. The city’s heaviest precipitation is usually recorded in the month of September (averaging 367mm of rain). The average annual temperature value in the city is typically between 25°C - 28°C [10].

2. Methods of Study
Standard field sampling techniques were adopted for the sample collection exercise. The sampling exercise for the work was carried out on two different trips, which were weeks apart. The first sampling trip was aimed at obtaining sample from the effluent fallout point along the New Calabar River. The second sampling trip involved sampling both surface water and river sediment also along the New Calabar River. Due to the riverine nature of the sampling locations, transportation from one location to the next was achieved by the use of a paddling boat.

The sampling exercise for surface water and river sediment started off with sampling for river sediments first. This approach to sampling was adopted due to a time sensitive phenomena typical of that part of the New Calabar River. The New Calabar River, around the Choba bridge axis of the East-west road is usually in a regressive position at its banks in the early hours of the day. Towards noon, the level of water at the bank of the river starts rising, thereby flooding portions of its banks that were earlier exposed in the morning hours. As such, river sediment sampling at those sites were only possible in the early hours of the morning. Therefore, river sediment sampling was started with from take-off point (Choba Bridge, East-west Road), moving further towards and beyond the Dufil Prima Foods Plant. The sediments collected were a mixture of sandy, muddy and clayey sediments. It was at the farthest location of river sediment sampling that the surface water sampling was started with; moving upwards back towards the Choba Bridge, i.e. start-off point. Table 1 shows the coordinates and elevation of sampling locations while Figure 1 is Satellite imagery of study area.

The flow direction of the river influenced the decision to start sampling for surface water at the farthest location of sampling river sediment. The sampling of surface water from the farthest location, then moving up towards the take-off point ensures adherence to the best sampling technique for surface water. This choice ensured the movement of the boat while sampling was to guide against the flow direction of the river. This made sampling of surface water from an undisturbed flow, possible. Unstable parameters such as pH, temperature and electrical conductivity were determined in the field using pH meter, mercury thermometer and conductively meter respectively. Figure 2 shows the sampling locations. The locations of the boreholes were obtained with a handheld global positioning system (GPS). Fig. 3 is the Site of first river sediment sampling while Fig. 4 showed Fire ravaged vegetation in New Calabar River.

| Sample ID | GPS Coordinates | Elevation |
|-----------|-----------------|-----------|
| SD L₁     | N 04.89621° E 006.90061° | 1m        |
| SD L₂     | N 04.88980° E 006.89907° | 2m        |
| SD L₃     | N 04.88925° E 006.89564° | 4m        |
| SD L₄     | N 04.88671° E 006.89471° | 0m        |
| SD L₅     | N 04.88392° E 006.89209° | 4m        |
| SD L₆     | N 04.8752° 50.6° E 006° 53° 49.8° | 2m        |
| SD L₇     | N 04.86988° E 006.90355° | 3m        |

Table 1: GPS Coordinates and Elevation of sampling locations

![Figure 1](image1.png)

![Figure 2](image2.png)

![Figure 3](image3.png)

![Figure 4](image4.png)
| S/N | Sample ID | GPS Coordinates                  | Elevation |
|-----|-----------|----------------------------------|-----------|
| 1   | SW L₁     | N 04° 46’ 21.53” E 006° 54’19.8” | 3m        |
| 2   | SW L₂     | N 04° 46’ 23.78” E 006° 55’24.1” | 3m        |
| 3   | SW L₃     | N 04° 46’ 26.02” E 006° 56’49.8” | 3m        |
| 4   | SW L₄     | N 04° 46’ 28.26” E 006° 57’15.0” | 2m        |
| 5   | SW L₅     | N 04° 46’ 30.50” E 006° 58’30.2” | 2m        |
| 6   | SW L₆     | N 04° 46’ 32.75” E 006° 59’45.4” | 2m        |
| 7   | SW L₇     | N 04° 46’ 35.00” E 006° 00’00.0” | 2m        |
| 8   | SW L₈     | N 04° 46’ 37.25” E 006° 00’30.2” | 2m        |
| 9   | SW L₉     | N 04° 46’ 39.50” E 006° 01’00.0” | 2m        |
| 10  | SW L₁₀    | N 04° 46’ 41.75” E 006° 01’30.2” | 2m        |
| 11  | SW L₁₁    | N 04° 46’ 44.00” E 006° 02’00.0” | 2m        |
| 12  | SW L₁₂    | N 04° 46’ 46.25” E 006° 02’30.2” | 2m        |

**EFFLUENT FALL-OUT AREA**

| S/N | Sample ID | GPS Coordinates                  | Elevation |
|-----|-----------|----------------------------------|-----------|
| 1   | EF        | Latitude: 04° 53’ 18.2”          | 3m        |
|     |           | Longitude: 006° 53’ 48.8”        |           |

Note: RS= River Sediment, SW= Surface Water, EF= Effluent Fall-out area, L= Sampling Location

**Figure-1.** Satellite imagery of study area  
**Figure-2.** Map of study area showing sampling points

**Figure-3.** Site of first river sediment sampling  
**Figure-4.** Fire ravaged vegetation in New Calabar River

### 2.1. Calculation of Contamination Factor (CF); Pollution Load Index (PLI) and Geo-accumulation Index ($I_{geo}$)

**Contamination Factor (CF):**

$$CF = \frac{C_{metal}}{C_{background}}$$  \hspace{1cm} (1)

**Pollution Load Index (PLI):**

$$PLI = n \sqrt[\sum]{(CF_1 \times CF_2 \times CF_3 \ldots \times CF_n)}$$  \hspace{1cm} (2)
Where CF= Contamination Factor  
n= number of metals  
C<sub>background value</sub>= background value of metal  

An example of this type index is the pollution load index (PLI), which is based on the concentration factor (CF) of each metal [5]. PLI was calculated as the $m$th root of the product of the $m$ single indices. The pollution load index (PLI) provides a simple and comparative means for assessing the level of heavy metal pollution. Values of $PLI=1$ indicate heavy metal loads close to the background level, and values above 1 indicate pollution [11].

2.2. Index of Geo-accumulation  

An index of geo-accumulation ($I_{geo}$) was originally defined by Muller [12], in order to determine and define metal contamination in sediments [13], by comparing current concentrations with pre-industrial levels. It can be calculated by the following equation:

$$I_{geo} = \log_{2}(\frac{C_n}{1.5 B_n})$$  

($B_n$= Geochemical background, $C_n$ is the geochemical background concentration or reference value of the metal, Factor 1.5 is used because of possible variations in background values (allows for natural fluctuations) for a given metal in the environment as well as very small anthropogenic influences.

3. Results and Discussion

| Sample ID | Mn  | Fe  | Pb  | Zn  | Cr  | Cd  | Cu   |
|-----------|-----|-----|-----|-----|-----|-----|------|
| SD. L1    | 10.30 | 975.0 | 8.01 | 25.20 | 1.71 | 4.11 | 23.00 |
| SD. L2    | 7.88  | 218.0 | 7.42 | 21.40 | 1.93 | 7.50 | 14.10 |
| SD. L3    | 12.60 | 800.0 | 15.00 | 17.20 | 2.70 | 5.01 | 25.10 |
| SD. L4    | 8.10  | 873.0 | 6.04 | 27.10 | 1.83 | 5.01 | 21.30 |
| SD. L5    | 5.65  | 477.0 | 16.50 | 33.20 | 2.31 | 7.82 | 19.00 |
| SD. L6    | 7.38  | 564.0 | 14.50 | 31.10 | 2.12 | 4.91 | 15.30 |
| Minimum   | 5.65  | 218.0 | 6.04 | 17.20 | 1.71 | 4.11 | 13.60 |
| Maximum   | 12.60 | 975.0 | 16.50 | 33.20 | 2.70 | 7.82 | 25.10 |
| Mean      | 8.37  | 650.3 | 11.11 | 25.82 | 2.31 | 7.82 | 18.77 |
| DPR Standard (2002) | - | - | 35 | - | 20 | 100 | 0.3 |

Note: DPR = Department of Petroleum Resources  

| Sample ID | Mn  | Cr  | Pb  | Cd  | Fe  | Zn  |
|-----------|-----|-----|-----|-----|-----|-----|
| SW. L1    | 1.24 | 0.21 | 0.10 | <0.001 | 2.54 | 1.08 |
| SW. L2    | 1.55 | 0.01 | 1.09 | 0.01 | 3.60 | 2.53 |
| SW. L3    | 2.38 | 0.001 | 0.45 | 0.01 | 1.30 | 0.58 |
| SW. L4    | 2.01 | 0.05 | 1.87 | <0.001 | 4.16 | 1.10 |
| SW. L5    | 2.16 | <0.001 | 0.20 | 0.01 | 0.97 | 1.51 |
| SW. L6    | 1.85 | 0.65 | 2.00 | 0.03 | 2.43 | 1.24 |
| SW. L7    | 1.72 | 0.44 | 0.10 | <0.001 | 0.27 | 1.76 |
| SW. L8    | 1.53 | 0.03 | 1.30 | 0.08 | 0.90 | 1.80 |
| SW. L9    | 2.52 | 0.10 | 0.46 | <0.001 | 2.17 | 0.90 |
| SW. L10   | 1.36 | 0.07 | 1.55 | <0.001 | 3.40 | 1.21 |
| SW. L11   | 1.38 | <0.001 | 2.11 | <0.001 | 1.25 | 1.31 |
| SW. L12   | 1.20 | <0.001 | 1.12 | <0.001 | 1.01 | 1.26 |
| Maximum   | 1.20 | <0.001 | 0.10 | <0.001 | 0.27 | 0.58 |
| Mean      | 1.74 | 0.13 | 1.03 | 0.01 | 2.00 | 1.35 |
| WHO Limits (2011) | 0.4 | 0.05 | 0.01 | 0.003 | 3.00 | 3.00 |
Because the quality of the surface water only gives the momentary quality of the environment, the quality of the river sediment which gives a more definite detail of the quality of the environment is of more importance in interpreting changes in the quality of the environment. Results from sampling and analysis of the river sediment and surface water shows that the chemistry of the two varies distinctly from one location to the other and that certain locations could have been sites of localised pollution (Table 4). Table 5 shows the Pollution Index (P_I) values of sampled surface water while Table 6 shows the contamination factor values for river sediments.

### Table 4. Water quality according to pollution index value (Chinese Quality Standard Code for Groundwater - GB/T 14848-1993)

| Water Quality | Very good | Good | Moderate | Bad | Worst |
|---------------|-----------|------|----------|-----|-------|
| Pollution Index | <0.80 | 0.80-2.50 | 2.50-4.25 | 4.25-7.20 | >7.20 |

### Table 5. Pollution Index (P_I) values of sampled surface water

| Sample Locations | Mn | Cr | Pb | Cd | Fe | Zn |
|------------------|----|----|----|----|----|----|
| SW. L1           | 3.10 | 4.20 | 10.00 | 0.00 | 0.84 | 21.60 |
| SW. L2           | 3.80 | 0.20 | 109.00 | 3.30 | 1.20 | 50.60 |
| SW. L3           | 5.90 | 0.00 | 45.00 | 3.30 | 0.43 | 11.60 |
| SW. L4           | 5.00 | 1.00 | 187.00 | 0.00 | 1.30 | 22.00 |
| SW. L5           | 5.40 | 0.00 | 20.00 | 3.30 | 0.32 | 30.20 |
| SW. L6           | 4.60 | 13.00 | 200.00 | 10.00 | 0.81 | 24.80 |
| SW. L7           | 4.30 | 8.80 | 10.00 | 0.00 | 0.09 | 35.20 |
| SW. L8           | 3.80 | 0.00 | 130.00 | 26.60 | 0.30 | 36.00 |
| SW. L9           | 6.30 | 2.00 | 46.00 | 0.00 | 0.72 | 18.00 |
| SW. L10          | 3.40 | 1.40 | 155.00 | 0.00 | 1.10 | 24.20 |
| SW. L11          | 3.40 | 0.00 | 211.00 | 0.00 | 0.41 | 26.20 |
| SW. L12          | 3.00 | 0.00 | 112.00 | 0.00 | 0.33 | 25.20 |

### Table 6. Contamination factor values for river sediments

| Sample Locations | Mn | Fe | Pb | Zn | Cr | Cd | Cu |
|------------------|----|----|----|----|----|----|----|
| SD. L1           | 1.53 | 1.51 | 0.77 | 0.98 | 0.91 | 0.78 | 1.69 |
| SD. L2           | 1.17 | 0.33 | 0.72 | 0.83 | 1.03 | 1.43 | 1.04 |
| SD. L3           | 1.87 | 1.24 | 1.45 | 0.67 | 1.44 | 0.95 | 1.84 |
| SD. L4           | 1.20 | 1.35 | 0.58 | 1.05 | 0.97 | 0.95 | 1.56 |
| SD. L5           | 0.84 | 0.74 | 1.60 | 1.29 | 1.23 | 1.49 | 1.39 |
| SD. L6           | 1.09 | 0.87 | 1.40 | 1.21 | 1.13 | 0.94 | 1.12 |
| SD. L7           | 1.00 | 1.00 | 1.10 | 1.00 | 1.00 | 1.00 | 1.00 |

The heavy metal contamination factor in river sediments across all sampling locations were of low to moderate contamination levels. Majority of metals were however of moderate contamination factor levels. Based on the Pollution Load Index, all the sampled locations were found to be polluted; with locations 3 and 5 being the most polluted. Heavy metal concentrations in the surface water sample were objectionable when compared to the WHO permissible limits for drinking water. Those heavy metals are a great concern for the quality of fish consumed from the river. The pH reading for all the surface water samples were also found to be acidic like those of the river sediments; having pH values ranging from 5.6 - 6.2.

Because the quality of the surface water only gives the momentary quality of the environment, the quality of the river sediment which gives a more definite detail of the quality of the environment is of more importance in interpreting changes in the quality of the environment [15]. Results from sampling and analysis of the river sediment and surface water shows that the chemistry of the two varies distinctly from one location to the other and that certain locations could have been sites of localized pollution.

Chromium (Cr) pollution levels were slightly insignificant in most of the sampling locations, except for locations 6 and 7 which had pollution index values 13 and 8.8 respectively. Of all the heavy metals, Lead (Pb) recorded the most chronic levels of pollution across all the sampling locations; having pollution index values ranging 10 – 211. Next to Lead (Pb), Zinc (Zn) also recorded the chronic levels of pollution; ranging 11.6 – 50.6. On the other hand, Iron (Fe) recorded the least levels of pollution of all the other heavy metals, across all the sampling locations; recording 1.3 as its highest pollution index value. Cadmium (Cd) pollution index levels were insignificant in almost all the sampling locations; with locations 6 and 8 recording pollution index levels 10 and 26.6 respectively. Figure 5 shows heavy metals concentrations while Figure 6 is the plot of Iron (Fe) concentration in river sediments. Figure 7 shows Chromium (Cr) concentration plot in surface water and Figure 8 is the plot of Lead (Pb) concentration in surface water. Figure 9 is a plot of Cadmium (Cd) concentration in surface water while Figure 10 is Manganese (Mn) concentration plot in surface water.
Figure-5. Heavy metals concentrations

Figure-6. Plot of Iron (Fe) concentration in river sediments

Figure-7. Chromium (Cr) concentration plot in surface water.
Figure 8. Plot of Lead (Pb) concentration in surface water

Figure 9. Plot of Cadmium (Cd) concentration in surface water

Figure 10. Manganese (Mn) concentration plot in surface water
4. Conclusion

The heavy metal contamination factor in river sediments across all sampling locations were of low to moderate contamination levels. Majority of metals were however of moderate contamination factor levels. Based on the Pollution Load Index, all the sampled locations were found to be polluted. Heavy metal concentrations in the surface water sample were objectionable when compared to the WHO [14] permissible limits for drinking water. Heavy metal concentrations in the surface water sample were objectionable when compared to the W.H.O permissible limits for drinking water. The pH reading for all the surface water samples were also found to be acidic like those of the river sediments with pH values ranging from 5.6 - 6.2.

Because the quality of the surface water only gives the momentary quality of the environment, the quality of the river sediment which gives a more definite detail of the quality of the environment is of more importance in interpreting changes in the quality of the environment. Results from sampling and analysis of the river sediment and surface water shows that the chemistry of the two varies distinctly from one location to the other and that certain locations could have been sites of localized pollution.

This study therefore provides a complete sight on pollution levels and risks presented by heavy metals in water and sediment and offer reasonable evidence on interpreting changes in the quality of the environment. The continuous and/or periodical acquisition of data on the quality of the water bodies is essential for sustainable management of risk.

References

[1] Lenntech, 2005. "Heavy metals". [Online]. Rotterdam seweg, The Netherlands.
[2] Laws, E. A., 1945. Aquatic pollution, an introductory text. New York: John Wiley and Son, INC.
[3] Jörgensen, L. A. and Pedersen, B., 1994. "Trace metals in fish used for time trend analysis and as environmental indicators." Marine Pollution Bulletin, vol. 28, pp. 235-243.
[4] Förstner, U. and Wittman, G., 1981. Metal pollution in the aquatic environment. N. Y.: Springer Verlag, Berlin Heidelberg.
[5] Liu, W. H., Zhao, J. Z., and Ouyang, Z. Y., 2005. "Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China." Environment International, vol. 31, pp. 805-812.
[6] Francis, A. and Elenwo, U., 2012. "Aspects of the biology of trap caught chrysichthysnigrodigitatus (Lacepede: 1803) from the New Calabar River, Nigeria." International Journal of Fisheries and Aquaculture, vol. 4, pp. 99-104.
[7] Theodore, A. A. and Chikwuogwo, W. P., 2014. "Integrated risk assessment using chrysichthysnigrodigitatus: A case study of New Calabar River Basin." International Journal of Environment and Pollution Research, vol. 2, pp. 42-69.
[8] Nwankwoala, H. O., Angaya, Y. B., Amadi, A. N., and Ameh, I. M., 2017. "Contamination Risk Assessment of Physico-chemical and Heavy Metal Distribution in Water and Sediments of the Choba Section of the New Calabar River, Nigeria." Nigerian Journal of Engineering and Applied Sciences, vol. 4, pp. 15-24.
[9] National Population Commission (NPC), 2006. "National Demographic Census Data for Rivers State."
[10] Nwankwoala, H. O. and Ogbonna, V. A., 2017. "Water quality surveillance of boreholes around landfill site in Eligbolo-Eliozu, Obio/Akpor Local Government Area, Rivers State, Nigeria." Environ Risk Assess Remediation, vol. 1, pp. 44-49.
[11] Kwon, Y. T. and Lee, C. W., 1998. "Application of multiple ecological risk indices for the evaluation of heavy metal contamination in a coastal dredging area." The Science of the Total Environment, vol. 214, pp. 203-210.
[12] Muller, G., 1969. "Index of geo-accumulation in sediments of the Rhine River." Geology Journal, vol. 2, pp. 109-118.
[13] Banat, K. M., Howari, F. M., and Al-Hamada, A. A., 2005. "Heavy metals in urban soils of central Jordan: Should we worry about their environmental risks?" Environmental Research, vol. 97, pp. 258-273.
[14] WHO, 2011. Guidelines for Drinking-water Quality. 4th Edn. WHO Library Cataloguing-in-Publication Data. ISBN 978 92 4 1548151.
[15] Buccolieri, A., Buccolieri, G., and Cardellicchio, N., 2006. "Heavy metals in marine sediments of taranto gulf (Ionian Sea, Southern Italy)." Marine Chemistry, vol. 99, pp. 227-235.