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Part 2

Enrichment, contamination and geo-accumulation factors for assessing arsenic contamination in sediment of a Tropical Open Lagoon, Southwest Nigeria

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ABSTRACT

The presence of toxic heavy metals and metalloids in aquatic environments constitutes a major risk and there is an urgent need for continuous monitoring of such pollutants. This study assesses the concentrations of arsenic (As) in surface sediments from 15 locations on the Lagos Lagoon, Nigeria during the wet and dry seasons to determine the degree of contamination. The results showed that the mean total As concentration in sediment (2.44 mg kg\(^{-1}\) dry weight) did not exceed the Canadian Interim Sediment Quality Guideline (CISQG) value of 7.24 mg kg\(^{-1}\) dry weight during the wet and dry seasons. Based on the Sediment Quality Guidelines (SQGs) of the United States Environmental Protection Agency (USEPA) and ecological risk assessment using the enrichment factor (EF), contamination factor (CF) and geo-accumulation index (\(I_{geo}\)), the study’s results indicate two things: firstly, low to moderate and significant levels of enrichment from As; and secondly, low to moderate degree of contamination in Lagos Lagoon during the study period.

Keywords:
Arsenic
Sediment
Lagos Lagoon
Enrichment factor
Contamination factor
Geo-accumulation factor

1. Introduction

Arsenic (As) has emerged as an important worldwide problem due to the associated health risks and is now recognized as a notorious poison as well as a human carcinogenic and teratogenic agent (ATSDR, 2007; Ravenscroft et al., 2009). Unregulated human activities and industrial processes such as copper smelting, mining and coal burning contribute to high
levels of As in the environment. These high As levels from anthropogenic sources are usually associated with certain fertilizers, drugs, insecticides, wood preservatives, herbicides, pesticide application and other animal-feeding operations (Mandal and Suzuki, 2002). High concentrations of As in marine sediments can lead to acute and chronic toxicity in marine organisms via ingestion of particulate matter (As associated with particles), through membrane-facilitated transport or passive diffusion (As dissolved in water) (Bhattacharya et al., 2007). A recent study investigated the distributions of As and other metals such as iron (Fe) and manganese (Mn) in the sediments of two pristine areas (Crab and Spartina) in the Patos Lagoon Estuary, Brazil. It was reported that concentrations of As in sediments of Crab and Spartina areas ranged up to 33 mg kg⁻¹ and 24 mg kg⁻¹, respectively (Costa et al. 2016). Another study reported the concentration of As in sediments from Emet Stream, Turkey was 14.51–3317.1 mg kg⁻¹ (Benzer, 2016).

It has been reported that Lagos Lagoon contains elevated concentrations of heavy metals in environmental and biological media (Ajagbe et al., 2012; Chukwu, 2006; Ladigbolu and Balogun, 2011). A previous study reported that levels of heavy metals discharged into drains/canals/streams and subsequently into Lagos Lagoon were as follows: Fe – 161,718 kg, Mn – 205,989 kg, Co – 15,683 kg, Zn – 7026 kg, Cr – 5285 kg, Pb – 2259 kg, Ni – 6124 kg, Cd – 538 kg and Hg – 278 kg per annum (Oyewo, 1998). Ekaete et al. (2015) also reported that heavy metal concentrations in Lagos Lagoon sediments had the following ranges: Ni (Bdl-17.55 mg kg⁻¹), Mn (12.5-1180.25 mg kg⁻¹), Pb (Bdl-27.04 mg kg⁻¹), Zn (Bdl-543.33 mg kg⁻¹), Cu (Bdl-35.55 mg kg⁻¹), Cr (Bdl-220.53 mg kg⁻¹) and Fe (832.64-19722.80 mg kg⁻¹). Another recent analysis on the Lagos lagoon sediment extracts reported that they exhibit teratogenic, embryogenic, and genotoxic properties with some of the pollutants suspected of being potential human carcinogens (Sogbanmu et al., 2016). Despite the numerous pollution studies and sediment toxicity in Lagos Lagoon, reports focusing on As concentrations as a
major global concern are generally limited. Considering the increasing anthropogenic sources of coastal pollution and the previous report of Aderinola et al. (2009) which recorded As concentration in the sediment of Lagos lagoon as 0.083 mg kg\(^{-1}\), it is crucial to continuously monitor the As concentration alongside other contaminants in the sediments of Lagos Lagoon, Nigeria. The objective is to understand the current contamination scenario. Furthermore, although the assessments of drinking water and dietary exposure remain a major concern for As exposure, aquatic sediments as sinks represent a continuous exposure route for aquatic biota and this means that regular ecological risk assessments are required.

Ecological risk indices such as enrichment factor (EF), contamination factor (CF) and geo-accumulation index (I\(_{geo}\)) have been conveniently employed as diagnostic tools by a number of researchers (Abrahim and Parker, 2008; Likuku et al., 2013; Nowrouzi and Pourkhabbaz, 2014) for assessing the pollution status of metals (Pb, Cd, Ni, Fe, Cu, Mn, Co and Zn) contaminated sediments. The main objectives of this study are to assess the degree of As contamination in the sediments of Lagos Lagoon and the ecological risk associated with the obtained levels of As using the EF, CF and I\(_{geo}\).

2. Materials and methods

2.1. Site description and sediment sampling

Sampling was carried at Lagos Lagoon which is situated between latitudes 06\(^{0}\)26\(^{\prime}\) - 06\(^{0}\)36\(^{\prime}\)N and longitudes 003\(^{0}\)23\(^{\prime}\) - 003\(^{0}\)40\(^{\prime}\)E. It is an area where a wealth of human and transportation activities take place daily including unregulated discharge of effluents, sewage and solid wastes (Adeniyi et al., 2008; Nubi et al., 2008). The study area and sampling locations of sediments in Lagos lagoon are presented in Fig.1. Approximately 1 kg sediment samples were obtained using Van-Veen grab sampler during wet and dry seasons (n=45). Samples were sliced from the grab centre, using a plastic spoon to avoid contamination with the metallic part of the grab and placed in zip-lock plastic bags and placed in a cooler at 4\(^{0}\)C.
Then they were transported to the laboratory for further processing and analysis. The collection was done in three replicates during each sampling period.

2.2. Pre-treatment of samples, sample digestion and analysis

Sediments were air-dried for two to three weeks at room temperature. After drying, the samples were disaggregated and any visible remains of organisms and debris removed. The dried samples were then crushed in a mortar and passed through a 200µm sieve to normalize particle sizes. Crushed sediments were subsequently homogenized and ground to powder in a porcelain mortar for total As analysis. The processed sediment samples were thereafter transported under strict quarantine procedure for further processing to the laboratory located at the University of South Australia, Adelaide.

From the dried powdered sediment sample, approximately 0.25g was placed in Teflon vessels and 5ml aqua regia (HCl: HNO₃ at a ratio of 3:1) was added for digestion. These were allowed to stand in a fume cupboard overnight at room temperature for an initial digestion phase. Microwave digestion system (MARS 6, CEM) was used for the digestion of sediments following the procedure documented by Rahman et al. (2013). After digestion, sample solutions were cooled to room temperature, then transferred to a 50ml centrifuge tubes and made up to 50ml using Milli-Q water with a resistivity of 18.2 MΩ cm⁻¹ (ELGA Labpure). The solution was subsequently filtered (10 ml) using PTFE filters (0.45 µm, Agilent filters) with the aid of a syringe into plastic tubes for instrumental analysis.

An Agilent 7500ce (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS) was used to determine the amount of As in digested sediment samples. The detection limit of As in solution matrix of the ICP-MS was 0.1 µg l⁻¹.

2.3 Quality control and analysis of certified reference materials (CRMs)

Glassware and sample containers were cleaned with laboratory cleaning solution Decon 90. All reagents used were of analytical grade. A blank digest and certified reference
materials (CRM 2711, Montana soil) from the National Institute of Standards and Technology (NIST) served to verify the results of As in sediment. The CRM sample was digested after utilizing the same procedure as sediments and the results gave good recovery of up to 95%.

2.4. Statistical analysis

In this study, average of triplicate samples collected and analyzed for As in sediments were used to represent the data. All calculations were done utilizing Microsoft Excel 2010. Data of As in sediment were tested for normality and homogeneity using SPSS 21.0.

2.5. Contamination impact of As in sediments

The degree of contamination of As in sediments was evaluated using three ecological risk indices (EF, CF and Igeo). Moreover, in the absence of local sediment guideline values for the protection of aquatic life, data obtained for As in sediment were compared with the Sediment Quality Guidelines (SQGs) of the United States Environmental Protection Agency (USEPA) and Canadian Interim Sediment Quality Guideline (CISQG) (as adopted by several environmental regulators in Nigeria) to determine the degree of pollution caused by As (Buchman, 1999). Based on the SQGs proposed by USEPA (Giesy and Hoke, 1990), sediments may be categorized into three classes as non-polluted (< 3 mg kg⁻¹), moderately polluted (3- 8mg kg⁻¹and heavily polluted (>8mg kg⁻¹) for As, respectively.

2.5.1. Enrichment factor

The EF of metals is a useful indicator reflecting the status and degree of environmental contamination (Feng et al., 2004). The EF calculations compare each value with a given background level, either from the local site, using older deposits formed under similar conditions, but without anthropogenic impact, or from a regional or global average composition (Choi et al., 2012). The EF was calculated using the method proposed by (Sinex and Helz, 1981) with Fe as the element of normalization as follows:

\[
EF = \frac{(Me/Fe)_{sample}}{(Me/Fe)_{background}}
\]
Where (Me/Fe) sample is the ratio of As to Fe in the sample and (Me/Fe) is the ratio of As to Fe concentrations in the background. Iron was chosen as the reference element to normalize sediment As concentrations to alleviate the variations produced by heterogeneous sediments. This is because Fe is the most abundant naturally occurring and highly refractory metal and the levels of Fe were not generally influenced by anthropogenic sources.

2.5.2. Contamination factor

The level of contamination of sediments by As expressed in terms of CF was calculated as:

\[ CF = \frac{C_{m \text{ sample}}}{C_{m \text{ background}}} \]

Where, \( C_{m \text{ sample}} \) is the concentration of As in sediments

\( C_{m \text{ background}} \) is the background value of As equal to the average shale value (ASV) reported by (Turekian and Wedepohl, 1961).

1.5.3. The geo-accumulation index (I_{geo})

The I_{geo} compares current concentration of heavy metals with pre-industrial level. The I_{geo} values were calculated for As using the equation of Muller (1969):

\[ I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \]

Where:

\( C_n \) = measured concentration of As in the sediments

\( B_n \) = geochemical background value for As

The factor 1.5 is used to compensate for possible variations with respect to background lithological variations. Muller (1969) also proposed seven classes of the Igeo-accumulation index. Class 6 is an open class and comprises all values of the index higher than Class 5. I_{geo} of 6 indicates almost 100-fold enrichment above background value. In these computations, average shale value for As (13) by Turekian and Wedepohl (1961) was considered to be the background value for estimating I_{geo}.

3. Results and discussion

3.1. Concentrations of As in sediments
The analytical results of As in Montana soil indicate that the differences between certified (107.0 ± 5, mg kg$^{-1}$) and measured results (103.3 ± 0.6 mg kg$^{-1}$) were less than 5% (recovery 96.5%). Concentrations of As were found in the 0.27 - 7.97 mg kg$^{-1}$ range from Lagos Lagoon sediments (average: 2.38 and 2.47 mg kg$^{-1}$; median: 1.8 and 2.04 mg kg$^{-1}$ for wet and dry seasons, respectively). The observed mean contents of As revealed no consistent upward or downward trend. In fact, they fell within the acceptable limits of the (CISQG) value and probable effect levels (PELs) for As in marine/estuarine sediments of 7.24 mg kg$^{-1}$ and 41.6 mg kg$^{-1}$ dry weight, respectively. By comparing the mean or median concentrations of As in the sediments with the USEPA SQGs, the results indicate non-polluted sediments.

The spatio-temporal variations in As levels in sediments of Lagos Lagoon during the wet and dry seasons are presented in Fig. 1. Arsenic content in sediments in different sampling locations revealed no significant difference although irregular seasonal variations and sometimes relatively higher levels were also observed in sediments from the western axis (locations 2, 6 and 9) compared to locations 11-15. The dataset showed that concentrations of As in sediments followed normal distribution (chi-square statistics: 0.269, degree of freedom (df): 3 and p>0.05) while further statistical analysis using Bartlett’s test revealed that the normally distributed data was homogeneous (Bartlett’s statistics: 3.72, df: 3 and p>0.05). Similarly, lower levels were also obtained for Derwent Estuary surface sediments (Geocoastal, 2009), Manchar Lake, Pakistan (Arain et al., 2009) and Bangshi River, Bangladesh (Rahman et al., 2014). Compared with data reported in the literature, the present result was approximately 6 to 30 times lower than the levels reported by Oyekunle et al. (2012) for As in sediments from Ajawere River in Nigeria (12.38 ± 1.59 to 55.35 ± 4.29 mg kg$^{-1}$). Additionally, higher average concentrations of As have been reported for river sediments from Bangladesh in the range of 12 to 25 mg kg$^{-1}$ dry weight and 14–48 mg kg$^{-1}$ dry weight from Yellow River in China (Liu et al., 2009).
3.2 Risk associated with As in sediments

The results concerning the ecological risk indices for As in sediment of Lagos Lagoon are presented in Table 1. Generally, the results for EF with values ranging from 0.57 to 6.34 at stations 14 and 6, respectively, revealed low to moderate and significant levels of enrichment from As in Lagos Lagoon. Areas characterized by large amounts of human activity and traffic, entry points of river, sewage discharge points, solid waste dumps and wood logging activities on Lagos Lagoon (Adjoining Iddo, Makoko to Ogudu creek and Bariga) recorded significant enrichment during the period. From the evaluated CF, with mean values which varied from 0.09 (stations 1 and 3) – 0.41 (station 6), what is depicted is a low to moderate degree of contamination during the study period. Furthermore, the range of values obtained for the computed Igeo (Igeo < 0) for As suggest a potentially unpolluted ecosystem.

Comparative evaluation of the results of this study with International Sediment Quality Guidelines (ISQG) revealed that the mean concentrations of As in all stations during the wet and dry seasons were lower than threshold effect level (TEL), PEL, effects range low (ERL) and effects range median (ERM), and dry weight using the Screening Quick Reference Table (SQuiRT) (NOAA, 2009). Results of the mean concentrations of As in sediments of Lagos Lagoon evaluated against some international set standards did not exceed sediment quality guideline values. Based on a comparison with established ISQG values, sediments were not polluted with As and might not pose any immediate ecological risk (Table 2).

4. Conclusion

Lagos Lagoon was found to accumulate As in varying and sometimes very low but measurable concentrations throughout the study. Statistically, the concentrations of As in sediments were normally distributed throughout the analysis period. The SQGs, EF, CF and Igeo indicate that sediments were unpolluted to being moderately enriched by As. The present
study did not include the bioavailable forms of sediment-bound toxic metals, which could be included in future studies.

Acknowledgements

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References


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NOAA, 2009. SQUIRT, Screening Quick Reference Tables for Sediment, HYPERLINK.


Table 1
Risk associated with mean concentrations of As in sediments from Lagos Lagoon

<table>
<thead>
<tr>
<th>Station no.</th>
<th>EF</th>
<th>CF</th>
<th>Igeo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.28</td>
<td>0.09</td>
<td>-4.13</td>
</tr>
<tr>
<td>2</td>
<td>5.93*</td>
<td>0.27</td>
<td>-2.45</td>
</tr>
<tr>
<td>3</td>
<td>1.04</td>
<td>0.09</td>
<td>-4.10</td>
</tr>
<tr>
<td>4</td>
<td>1.89</td>
<td>0.14</td>
<td>-3.41</td>
</tr>
<tr>
<td>5</td>
<td>1.92</td>
<td>0.18</td>
<td>-3.09</td>
</tr>
<tr>
<td>6</td>
<td>6.34**</td>
<td>0.41</td>
<td>-1.86</td>
</tr>
<tr>
<td>7</td>
<td>0.59</td>
<td>0.23</td>
<td>-2.72</td>
</tr>
<tr>
<td>8</td>
<td>2.48</td>
<td>0.20</td>
<td>-2.94</td>
</tr>
<tr>
<td>9</td>
<td>3.52</td>
<td>0.28</td>
<td>-2.43</td>
</tr>
<tr>
<td>10</td>
<td>2.22</td>
<td>0.08</td>
<td>-4.19</td>
</tr>
<tr>
<td>11</td>
<td>0.80</td>
<td>0.04</td>
<td>-5.10</td>
</tr>
<tr>
<td>12</td>
<td>1.48</td>
<td>0.34</td>
<td>-2.14</td>
</tr>
<tr>
<td>13</td>
<td>1.23*</td>
<td>0.14</td>
<td>-3.45</td>
</tr>
<tr>
<td>14</td>
<td>0.57*</td>
<td>0.16</td>
<td>-3.23</td>
</tr>
<tr>
<td>15</td>
<td>1.14</td>
<td>0.17</td>
<td>-3.15</td>
</tr>
</tbody>
</table>

*EF < 2 (Depletion to mineral enrichment); **2 ≤ EF < 5 (Moderate enrichment); ***5 ≤ EF < 20 (Significant enrichment); CF < 1 (Low contamination); Igeo < 0 (Practically uncontaminated).

Table 2
Arsenic levels in the Lagos Lagoon sediment and comparison with International Sediment Quality Guidelines (ISQG)

<table>
<thead>
<tr>
<th>Arsenic levels</th>
<th>Wet Season concentration (mg/kg dry weight)</th>
<th>Dry Season (mg/kg dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0.27-7.97</td>
<td>0.47-5.47</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>2.38± 2.04</td>
<td>2.47± 1.47</td>
</tr>
<tr>
<td>Average shale value (ASV)#</td>
<td>13</td>
<td>0.3</td>
</tr>
<tr>
<td>*Threshold effect level (TEL)</td>
<td>7.24</td>
<td>7.24</td>
</tr>
<tr>
<td>*Effect range low (ERL)</td>
<td>8.24</td>
<td>8.24</td>
</tr>
<tr>
<td>*Probable effect level (PEL)</td>
<td>41.60</td>
<td>41.60</td>
</tr>
<tr>
<td>*Effect range median (ERM)</td>
<td>70.00</td>
<td>70.00</td>
</tr>
<tr>
<td>**Interim sediment quality Guideline (ISQG)</td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td>** ISQG (PEL)</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>

*PEL and TEL: Canadian Interim Sediment Quality Guideline (CISQG)  
**ISQG (PEL): Buchman (1999)  
#Background level of arsenic in the crust (ASV): Turekian and Wedepohl (1961)
Figure caption

Fig.1. Sampling area and spatio-temporal variations in As levels in sediments of Lagos Lagoon during the wet and dry seasons.