SPATIO-TEMPORAL VARIATION IN WATER QUALITY OF ORLE RIVER BASIN, SOUTH WEST NIGERIA

C.I. Ikhile
Department of Geography/Regional Planning, University of Benin, Benin City
E-mail: ikhilek@yahoo.com +2348037611689
and
K. A. Aderogba
Department of Geography, Tai Solarin University of Education, Ijebu-Ode
E-mail: kofoaderogba@yahoo.com +2348033125490

Abstract
The water quality of small streams in Auchi area of Edo State, S.W. Nigeria was investigated with a view to ascertaining the toxicity levels of the water and its impact on the human and ecosystems. The study was carried out at two weekly intervals for a period of eight months. The elements investigated include the major cations of Calcium (Ca\textsuperscript{++}), Magnesium (Mg\textsuperscript{++}), Sodium (Na\textsuperscript{+}), Potassium (K\textsuperscript{+}), and hydrogen-ion concentration (pH). Results indicated that Calcium (Ca\textsuperscript{++}), Sodium (Na\textsuperscript{+}) and hydrogen-ion concentration (pH) showed significant variation in the various rock types. Also Calcium (Ca\textsuperscript{++}), Sodium (Na\textsuperscript{+}) and Potassium (K\textsuperscript{+}) showed significant variation with pH. However, Sodium (Na\textsuperscript{+}), Potassium (K\textsuperscript{+}), Magnesium (Mg\textsuperscript{++}) and Hydrogen-ion concentration (pH) showed no definite pattern of variation. This paper focuses on this aspect of Orle River, thus giving baseline information on the temporal and spatial dynamics in the chemical attributes of the basin. This is necessary since the rivers form a major source of drinking water for the communities living within the area. At present, the natives treat the water with alum before use.

Keywords: Elements, calcium, magnesium, sodium, potassium.

Introduction
Although many different parameters may be considered when an aquatic ecosystem is assessed for its water quality and ecological integrity, one important chemical indicator is an analysis of the concentrations of the major cations Ca, Mg, Na, K, and Al. (Cronan, 2009). Each major cation has important biological functions, biogeochemical relationships, and ecological roles that influence the ability of an aquatic ecosystem to sustain life forms and active food webs. Concentrations of these ions in surface waters are determined by hydrologic factors and interactions among various source and sink processes such as atmospheric deposition, mineral weathering, ion exchange, microbial mineralization, biological assimilation, sedimentation, and geochemical precipitation reactions. In many surface waters, generation of acid neutralizing capacity is closely linked to the cycles of Ca, Mg, and Na, whereas cycling of the critical nutrient P may be strongly influenced by the biogeochemistry of Al. Despite wide variations in the concentrations of major cations in different surface water systems, several consistent chemical patterns have been observed. With the exception of locations affected by coastal marine aerosols, most surface waters contain mixtures of major cations ranked in the following order of abundance based on molar charge concentration: Ca > Mg > Na > K ≥ Al. However, acidified surface waters may experience elevated concentrations of Al, which pose a risk for sensitive aquatic biota. This work does not consider aluminium variation in the drainage basin.

The study area
The Orle River basin is located in the northern fringes of Edo State (6\textdegree 45’ N and 7\textdegree 0’ 5’N and 6\textdegree 0’ 00’ E and 6\textdegree 45’ E, Fig 1). It covers an area of 116 sq km. Detailed description of the geology has been given (Ikhile 1990, Ikhile and Akhionbare 2003 and Ikhile, 2009). The rivers take their sources from the area underlain by the Precambrian Basement Complex rocks in the northwestern fringes of the basin where the rocks are strongly folded. They consist of five subgroups (i) flaggy quartz-biotite and gnesis; (ii) the mica-schist; (iii) the quartz and the quartz-schist;
(iv) the metaconglomerates and (v) calc-gnesis and marble (Hockey et al, 1986). The flaggy quartz-biotite and gnesis is the strongest here, they resist weathering to some extent and result in more pronounced topography than the others. The mica-schists contain biotite-schist and muscovite-schist, they are usually found as small exposures in stream channels and are strongly weathered. Due to their very low resistance to weathering compared with other rock bodies in the area, deep, active erosion has exposed them and they have become fine-grained.

At the source of Orle River, outcrops of metaconglomerate abound. Quartz and biotite are the essential minerals, although calcite, green hornblend, tremolite-actinolite, diopside and feldspar are also present. Other rocks of importance here are calc-gnesses and marble which are found in the streams and rivers. The second geologic region consists of alluvial sands found mainly at Alegbete where the Orle River enters the geologic region. They resemble the Nsukka formation in age, lithology and environment of deposition. The fourth geologic region consists of alluvial sands found mainly at Alegbete where the Orle River enters the geologic region. They consist of mudstone/lignite sequence. They therefore resemble the Nsukka formation in age, lithology and environment of deposition. The fourth geologic region consists of alluvial sands found mainly at Alegbete where the Orle River enters the River Niger. They are rich in nutrients due to deposition, being derived from both the Precambrian Basement Complex and Sedimentary rocks.

The third geologic formation is the Tertiary Sedimentary. It covers the central and southeastern portion of the Orle River. The rocks belong to the Eocene-Paleocene epoch. The formation consists of Imo Shale group and a small portion of the Bende- Ameki group. They consist of mudstone/lignite sequence. They therefore resemble the Nsukka formation in age, lithology and environment of deposition. The fourth geologic region consists of alluvial sands found mainly at Alegbete where the Orle River enters the River Niger. They are rich in nutrients due to deposition, being derived from both the Precambrian Basement Complex and Sedimentary rocks.

The foregoing discussion of the geology of the study area reveals that:-

1. The quartz-biotite-schist and gnesis contain rocks such as schist and gnesis. The proportion of biotite and quartz in this rock band is usually higher. They confer resistance to weathering. Quartz (SiO\textsubscript{2}) is made up mainly of silica whilst biotite-K(Mg,Fe)\textsubscript{3} [(AlSi\textsubscript{3})O\textsubscript{10}].(OH)\textsubscript{2} contains among other minerals potassium, magnesium, iron, silica and water.

2. The mica-schists have low resistance to weathering and are such are heavily weathered. The main minerals are feldspars potash orthoclase and feldspars plagioclase abite – (KAl\textsubscript{3}Si\textsubscript{3}O\textsubscript{10}).(OH)\textsubscript{2} and biotite – (K(Mg,Fe))\textsubscript{3} Al\textsubscript{3}(AlSi\textsubscript{3})O\textsubscript{10}.(OH)\textsubscript{2}. This contains magnesium, iron, potassium, and aluminium among others.

3. The quartzite and quartz schists are made up of muscovite, KAl\textsubscript{3}(AlSi\textsubscript{3})O\textsubscript{10}.(OH)\textsubscript{2} and biotite – K(Mg,Fe), Al\textsubscript{3}(AlSi\textsubscript{3})O\textsubscript{10}.(OH)\textsubscript{2}. This contains magnesium, iron, potassium, and aluminium among others.

4. The metaconglomerate, calc-gnesis and marble contain hornblend (Ca, Na, Mg, Fe, Al)\textsubscript{7,8} [(AlSi\textsubscript{3})O\textsubscript{2}]O\textsubscript{10}.(OH)\textsubscript{2} and tremolite, diopside, and feldspars. Other common rocks in this group are plagioclase, sphene, zircon, epidote and magnetite. The sedimentary rocks also contain biotite and in some instances quartz.

The discussion above reveals that the minerals found in Orle River are those, which have been found by the World Health Organisation (1971), Prior et al (2002), Kuwar et al (2005) among others to affect the quality of river water. These minerals are released through surface water runoff to the streams. Some get to the stream later through underground water re-charge. These minerals affect the quality of the water body as the stream flows through these different geologic terrains.

The Orle River basin forms part of the Niger Drainage System. Orle River rises from the Igarra Hills in the North – West portion of the study area where its direction of flow is parallel to the Onyami River. It then made a right – angle turn to East and flows on in that direction until it enters the River Niger (Hockey et al, 1986). The significant tributaries are Edion, Echibu, Akagbe and Ojo rivers. The Edion river flows in its upper course in a similar direction as the Orle river. It joins Orle river east of Agbede. The Ojo river rises from the Igarra Hills in the North-Central part of the area and flows in a North-South direction and joins the Orle river at a downstream location. There are many tributaries of the rivers on the
Basement Complex Rocks than the Sedimentary rocks. Generally, the Basement Complex rocks are highly weathered, eroded and heavily washed by the rainfall and erosion incidences experienced in the area. Under these environmental conditions, erosion by tropical streams is feeble in some instances and strong on others depending on the rainfall regime in the area in that year. The dominant runoff process of Orle river basin is by means of surface runoff. This carries loose weathered products to the streams to affect the water quality.

**Sampling and analysis**

Water samples were collected at six different sites labeled 1 – 6 chosen from the Geological map of Orle River Basin (Fig 1). These are areas where the geology changes from one rock type to another and/or at major river junctions. These locations were chosen so as to find out the effect of the geological background over which the major rivers flow within the basin. The locations were regarded as the most representative of these particular geologic formations. The confluences were mainly two and were the most obvious locations to be chosen so as to compare the quality of the water from the individual rivers before joining with any other river. For example, River Edion joins Orle River at the first confluence. They are later joined by the Ojo River. The water samples were collected in the middle of the river close to the bottom in the upstream direction. The water samples were collected in the upstream direction from where the natives normally fetch water. This ensures that the effects of soap for washing, oil in plates and even feaces are excluded. It is usually in the downstream directions of any location that these activities are carried out. In any study involving the seasonal variation in water quality of this sort, the information should be gathered and the quality monitored for at least six consecutive months (WHO, 1971). Water samples were therefore collected fortnightly for 8 (eight) months beginning from November 1987 to June, 1988. A total of 336 samples were collected within this period of investigation.

Water samples were collected with colourless 4 litre plastic bottles fitted with plastic stoppers. A 4-litre quantity of water was regarded as sufficient to determine the various parameters investigated in this study. The bottles were all washed with Teepol solution and rinsed many times with distilled water, and subsequently with the water they were to contain. The concentration levels of Calcium (Ca$^{++}$), Magnesium (Mg$^{++}$), Sodium (Na$^{+}$) and Potassium (K$^{+}$) in the stream water samples were measured. The impact of environmental hydrogen-ion concentration (pH) on the water chemistry of the drainage basin was equally examined. Results of the analyses are presented on Tables 1-3 and Figures 2-6.
Figure 1: DRAINAGE AND GEOLOGY OF ORLERIVER BASIN
Results and discussion

The Spatio-temporal variation in the major cations and pH are measured:

(i) Between the seasons and
(ii) From source to mouth of the river catchment.

The values are presented as minimum, maximum and mean in the drainage basin.

Assessment of the variation between the seasons

Table 1: Seasonal Variation of Quality Parameters

<table>
<thead>
<tr>
<th>Seasons</th>
<th>pH</th>
<th>Ca++</th>
<th>Mg++</th>
<th>Na+</th>
<th>K+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Mean</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Dry</td>
<td>4.8</td>
<td>8.2</td>
<td>6.68</td>
<td>1.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Wet</td>
<td>5.8</td>
<td>7.4</td>
<td>6.88</td>
<td>1.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Source: Ikhile, (1990)

Hydrogen – ion Concentration (pH) (Table 1, Figure 2)

In Orle River Basin, generally the pH is higher in the raining season than the dry season. However, the lowest value of 4.8 was recorded in the dry season towards the end of March while the highest value of 8.2 was recorded in early December. The mean pH for the dry season was 6.68 while the wet season was 6.88. The variation in pH in the drainage basin is explainable in terms of vegetational decay and more influx into the basin during the rains (Ikhile, 2004). There is a greater variation pattern observed in dry season than the wet season (Figure 2).

Calcium (Ca++) Table 1, Figure 3]

Calcium is more abundant in the dry season than the wet season. The lowest value of 4.0mg/l was recorded in February and March while the highest value of 40.0 mg/l was recorded in the last weekend of December. The mean value of Calcium for the dry season was 9.78 mg/l while that of the rainy season was 9.39 mg/l. [Ikhile 2009] quoting
Imevbere [1970] has attributed the seasonal pattern of variation to the “effect be seen from the concentration of ions due to evaporation during the dry season and dilution due to flooding during the rainy season”. The variation in the dry season is more that the rainy season.

**Magnesium (Mg²⁺) (Table 1, Figure 4)**

Magnesium is more abundant in the dry season than the wet season. The minimum value of 1.2 mg/l was recorded in the second week of January and May while the maximum value of 9.6 mg/l was also recorded in January in the basin. The mean value for the dry season was 3.4 mg/l while the rainy season was 2.87 mg/l.

**Sodium (Na⁺) (Table 1, Figure 5)**
The values for sodium were generally higher in the dry season than in the rainy season. The results obtained are comparable with those obtained for an earlier work on the River Niger and its West Bank tributaries of Rivers Swashi and Kpan and for the Ikpoba and Owan Rivers in different studies (Imevbore (1970), Kadiri (1987) and Akhionbare (1998). The minimum value of 2.88 mg/l was recorded in May while the maximum value of 63 mg/l was recorded in February. The mean value for the dry season was 11.04 mg/l while the mean value for the rainy season was 5.94 mg/l. Sodium is a very mobile mineral which is washed out from the surrounding country rocks and can remain in the water during the dry season without being easily evaporated like Chloride (Ikhile, 2010). There is significant difference in Sodium content between the seasons at 0.05

Table 2: Seasonal variation in Sodium in Orle River Basin

<table>
<thead>
<tr>
<th>Seasons</th>
<th>Number of Samples</th>
<th>Mean</th>
<th>Standard error</th>
<th>Computed t-value</th>
<th>Degree of freedom (df)</th>
<th>Tabulated t-value (N-2) df</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>27</td>
<td>11.04</td>
<td>1.68</td>
<td>2.31</td>
<td>43</td>
<td>2.02</td>
<td>Significant at 0.05</td>
</tr>
<tr>
<td>Wet</td>
<td>17</td>
<td>5.94</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Ikhile (1990)

Potassium (K⁺) (Table 1, Figure 6)

Higher values were obtained for Potassium in the dry season than the rainy season. The minimum value of 1.52 mg/l was obtained in the last week of March and first week of April. The maximum value of 38 mg/l was obtained in the first week of December. There is a wider variation in the dry season (36.48 mg/l) than the rainy season (13.68 mg/l) whereas Imevbore (1970) noted very low level of Potassium in the River Niger which was attributed to influx from the white flood from July to September. The reverse is the case in the Orle River Basin. Similar results were obtained by Akhionbare (1998) for the Owan River.
Table 3: Variation of Chemical Quality Parameters in the Downstream Direction of Orle River

<table>
<thead>
<tr>
<th>Downstream Direction in Orle River</th>
<th>pH Min</th>
<th>pH Max</th>
<th>pH Mean</th>
<th>Ca(^{++}) Min</th>
<th>Ca(^{++}) Max</th>
<th>Ca(^{++}) Mean</th>
<th>Mg(^{++}) Min</th>
<th>Mg(^{++}) Max</th>
<th>Mg(^{++}) Mean</th>
<th>Na(^{+}) Min</th>
<th>Na(^{+}) Max</th>
<th>Na(^{+}) Mean</th>
<th>K(^{+}) Min</th>
<th>K(^{+}) Max</th>
<th>K(^{+}) Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>7.3</td>
<td>8.0</td>
<td>7.6</td>
<td>1.52</td>
<td>1.52</td>
<td>1.52</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>8.0</td>
<td>6.4</td>
<td>8.0</td>
<td>18.33</td>
<td>2.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Geology Change</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>First Confluence</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
<td>4.8</td>
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<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Second Confluence</td>
<td>5.1</td>
<td>4.0</td>
<td>4.58</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>5.7</td>
<td>4.2</td>
<td>4.2</td>
<td>8.25</td>
<td>2.4</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Potential for Hydrogen Concentration (pH) (Table 3, Figure 2)

The concentration of pH in the downstream direction of the drainage basin is quite varied. The minimum reading at the source during the study period was 7.3, while the maximum was 8.1 and mean was 7.68. This source region is in the Precambrian Basement Complex rock area where active weathering is taking place hence a tendency towards alkalinity with a lot of metallic ions in the river. (Ikhile, 2003, 2009). At the change in geology, there is a decrease. The minimum record here was 5.0 and the maximum was 7.5. The mean value was 6.76. At this location in the drainage
basin the influence of the Precambrian Basement Complex rocks seems to be reduced while the area is underlain with the Cretaceous sedimentary rocks and there is a lot of human activity of fertilizer applications and bush clearing and subsequent leaf litter decay which tended to influence the water towards acidity (Ikhile, 2004). The value at the first confluence is further reduced. The minimum record here was 4.8 while the maximum was 7.5 and the mean was 5.78. Here the values tended more towards acidity due to vegetational decay and more anthropogenic activities. At the second confluence, the minimum was 5.3 while the maximum was 8.2 and the mean was 6.7. At this location is the mouth of the river where it joins with the river Niger at Alegbete. Obviously, decaying vegetation and influx of wash-out and greater impact of dilution due to increased river volume is accountable for the result obtained. (Akhionbare, (1998), Ikhile, 2010).

**Calcium (Ca$^{++}$)**

The distribution of Calcium (Ca$^{++}$) in Orle River Basin in the downstream direction is large. There was a decrease in Calcium content in the downstream direction. The minimum value at the source was 6 mg/l, while the maximum is 40 mg/l with a range of 34 mg/l. The mean value is drainage basin is at Precambrian Basement Complex rock area where active weathering is taking place and the minerals are released in large quantities (Ikhile, 2004).

At the change in geology, the minimum value was 4 mg/l while the maximum 12 mg/l with a range of 8 mg/l and the mean is 9.50 mg/l. The Cretaceous sedimentary rock here does not seem to be releasing enough calcium ions into the river. At the first confluence, the minimum value is 4.0 mg/l, the maximum was 20.0 mg/l with a range of 16 mg/l. Here the river has been joined by a tributary of river Edion and the background rock formation is the Tertiary sedimentary rock. These background could have contributed to increase values obtained here compared with the Cretaceous sedimentary environment. Orle River, the minimum value recorded was 4.0 mg/l while the maximum was 26.0 mg/l with a range of 22 mg/l. The mean value was 8.25 Mg/l. There is a slight increase here in the general distribution compared with the first confluence. The effect of more water from Ojo river from the basement complex origin could have contributed to the slight increase of Calcium at the mouth of the river.

**Magnesium (Mg$^{++}$)**

Magnesium has no definite pattern of variation in the drainage basin. It however attains the highest value at the source which is at the Precambrian Basement Complex area. The minimum value attained here is 2.4 mg/l and the maximum is 9.6 mg/l with a range of 7.4 mg/l. The mean value is 3.50 mg/l. At the change in geology, the minimum value was 1.2 mg/l while the maximum was 1.6 mg/l with a range of 4.8 mg/l. The mean value is 2.7 mg/l. At the first confluence, the mean increased slightly to 2.73 mg/l while the minimum was 1.2 mg/l with the maximum being 3.6 mg/l with a range of 2.4 mg/l. At the second confluence, the minimum was 2.1 mg/l and the maximum was 4.8 mg/l with a range of 2.70 mg/l and a mean value of 3.06 mg/l. The values here are comparable with results obtained for other fresh water bodies (Ohagi, 1983, Akhionbare, 1998).

**Sodium (Na$^{+}$)**

There is no definite pattern of variation of sodium content of the river. It is however highest at the source which is an indication of sodium – ions being released from the bedrock of the river and the surrounding environment. The minimum value at the source was 8.0 mg/l while the maximum was 32.14mg/l with a range of 24.14 mg/l. The mean value was 16.25 mg/l. At the change in geology, the minimum value was 3.2 mg/l while the maximum was 63.0 mg/l and the range was 59.8 mg/l while the mean was 5.91mg/l. At the first confluence, the minimum value was 2.88 mg/l while the maximum value was 17.92 mg/l with a range of 15.08 mg/l and the mean was 7.13 mg/l. At the second confluence, the minimum value was 3.84 mg/l while the maximum value was 59.52 mg/l with a range of 55.68 mg/l and the mean was 9.3 mg/l. These results are similar to others obtained for rivers in the tropical environments (Ogbeibu, et al 1995).

**Potassium (K$^{+}$)**

Potassium (K$^{+}$) (Table 3, Figure 6)
Potassium increased at the source of Orle River, then reduced at the next two locations and increased again at the mouth. There is the possibility that the potassium released at the source is retained in the water by aquatic life and is not moved to the next location. The minimum value at the source was 1.52 mg/l the maximum was 15.2mg/l, while the range was 13.68mg/l. The mean at the source was 8.01 mg/l. At the change in geology, the minimum value was 1.52mg/l, the maximum was 9.28 mg/l while the mean was 4.4 mg/l. At the first confluence, the minimum value was 1.52 mg/l, the maximum value was 9.8 mg/l while the range was 8.28 mg/l and the mean was 4.1 mg/l. At the second confluence, the minimum value was 1.52 mg/l, the maximum value was 38.0 mg/l while the range was 36.4 mg/l and the mean was 5.73mg/l.

Conclusion

The Spatio-Temporal variation in Water Quality of Orle River Basin revealed that the major cations of Calcium (Ca$$^++$$), Sodium (Na$$^+$$) and hydrogen-ion concentration (pH) showed significant variation in the various rock types. Also Calcium (Ca$$^++$$), Sodium (Na$$^+$$) and Potassium (K$$^+$$) showed significant variation with pH. However, Sodium (Na$$^+$$), Potassium (K$$^+$$), Magnesium (Mg$$^{++}$$) and Hydrogen-ion concentration (pH) showed no definite pattern of variation.

Of the four major cations namely; Sodium, Potassium, Magnesium and Calcium, Calcium is the most abundant. The order of dominance of the major cations for the Orle River Basin is Ca > Na > K > Mg. This order agrees with earlier findings of Imevbere (1970), Kadiri (1987) Akhionbare (1998) and Ikhide (2003).There is significant difference in Sodium content between the seasons at 0.05

In the present state of the water, it is not fit for human consumption but needs to be subjected to treatment for human and industrial uses. The local people however use the water in its raw form.

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