Acidification Status of Surface Waters in the Niger Delta, Nigeria: A Review of Results and Predictions for the Future

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ABSTRACT

Acidification is the ongoing decrease in the pH of the earth's surface water systems and effects of increasing acidification calls for regular monitoring. The acidification status of regional-scale surface water bodies was studied using data from a relevant and related literature of rivers (15), creeks (7), streams (5) and lakes (4). Data from 2007 to 2016 were used for statistical trend analysis. Results indicate that all surface water bodies were slightly acidic with mean pH values of rivers (5.97), creeks (6.29), streams (5.67) and lakes (6.10). Causes of acidification were attributed to the formation of humic acid, increased acidic deposition occassioned by gas flaring, and waste disposal. Results also indicate a weak positive relationship between the mean pH values and the period of study. The fitted regression line of y = -0.0297x + 65769 was obtained. However, the relationship is not perfect as each individual year did not always show a pH increase relative to the previous year, and some years show greater changes than others. There is a clear warming trend indicative of the impacts of acidification and recovery process should be put in place.

Key words: Streams; lakes; creeks; acidification; acidic deposition; humic acid; river system

1. Introduction

Acidification is the ongoing decrease in the pH of the earth's water systems such as oceans, seas, rivers, streams, creeks, and lakes. Acidification of freshwaters as an environmental problem was first identified in Scandinavia during the early 1970s (Muniz, 1984). Today, lakes and streams in Central Europe, Scotland, Canada, and the United States are known to be acidified and many more are most susceptible to acidification (Lacroix and Knox, 2005). Between 1751 and 1994 surface ocean pH is estimated to have decreased from approximately 8.25 to 8.14, representing an increase of almost 30% in H^+ ion concentration in the world's oceans (Caldeira and Wickett, 2003).

Increasing acidity is thought to have a range of possibly harmful consequences, such as depressing metabolic rate and immune response in some organisms, and causing coral bleaching (Arubini, *et al*., 2008). Aside from the slowing and/or reversing of calcification, organisms may suffer other adverse effects, either indirectly through negative impacts on food resources, or directly as reproductive or physiological effects. For example, the elevated oceanic levels of CO_2 may produce CO_2-induced acidification of body fluids, known as hypercapnia. Also, increasing ocean acidity is believed to have a range of direct consequences. For example, increasing acidity has been observed to: reduce metabolic rates in jumbo squid (Kwok, 2003); depress the immune responses of blue mussels (Atkinson and Cuet, 2008); and make it harder for juvenile clownfish to tell apart the smells of non-predators and predators (Hannah, *et al.*, 2008), or hear the sounds of their predators (Hannah, *et al*., 2008). This is possibly because ocean acidification may alter the acoustic properties of seawater, allowing sound to propagate further, and increasing ocean noise.

The threats of acidification have also been reported to cause a decline in commercial fisheries, tourism industry and economy (Snyder, 2013).

Commercial fisheries are threatened because acidification harms calcifying organisms which form the base of the food webs. Food webs are considered simple, meaning there are few steps in the food chain from small organisms to larger predators. The effects on the calcifying organisms at the base of the food webs could potentially destroy fisheries. The value of fish caught from United States of America (USA) commercial fisheries in 2007 was valued at $3.8 billion and of that 73% was derived from calcifiers and their direct predators (Snyder, 2013). Several ocean goods and services are likely to be undermined by future ocean acidification potentially affecting the livelihoods of some 400 to 800 million people depending upon the emission scenario (Boncoeur and Alban, 2002). Acidification is not merely a threat but has significantly declined whole fish populations. In Scandinavia studies conducted on acidic water revealed that 15% of species populations had disappeared and that many more populations were limited in numbers or declining (Muniz, 1984). The rapid decrease or disappearance of marine life could also affect the diet of indigenous peoples.

Acidification monitoring programmes are in operation in five countries: Norway, Sweden, Finland, the United Kingdom (UK), and Ireland (Doney, 2012). A large number of studies on physico-chemical characteristics of rivers, streams, creeks and lakes have been conducted in the Niger Delta Area of Nigeria (Rim-Rukeh *et al*., 2007; Nduka *et al*., 2010; Ezekiel *et al.*, 2011; Uzoekwe and Achudume, 2011; Issa *et al.*, 2011; Puyate and Rim-Rukeh 2008; Rim-Rukeh and Agbozu, 2013). In all these academic publications, water quality status in relation to industrial and human activities is the focus. This review builds on the results of previous studies by examining the pH trends at 31 sites in the Niger Delta Area of Nigeria. Site trends are considered individually, but an attempt was made to identify general patterns of chemical change at the Regional scale and the extent to which human and industrial activities created the chemical change.

2. Materials and Methods

2.1 Study Area

The study area is the the Niger Delta region of Nigeria which is located within Latitude $5^{0}45^{1}$ – $6^{0}35^{1}$ and longitude $4^{0}50^{1}$ – $5^{0}15^{1}$ in the central part of Southern Nigeria. The area has a land mass covering some 70,000 square kilometers which accounts for about 8 percent of Nigeria's land mass (NDES, 2003). Geopolitically, the area comprises of all oil producing states of Abia, Akwa-Ibom, Bayelsa, Cross River, Delta, Edo, Imo, Ondo and Rivers (Fig.1).

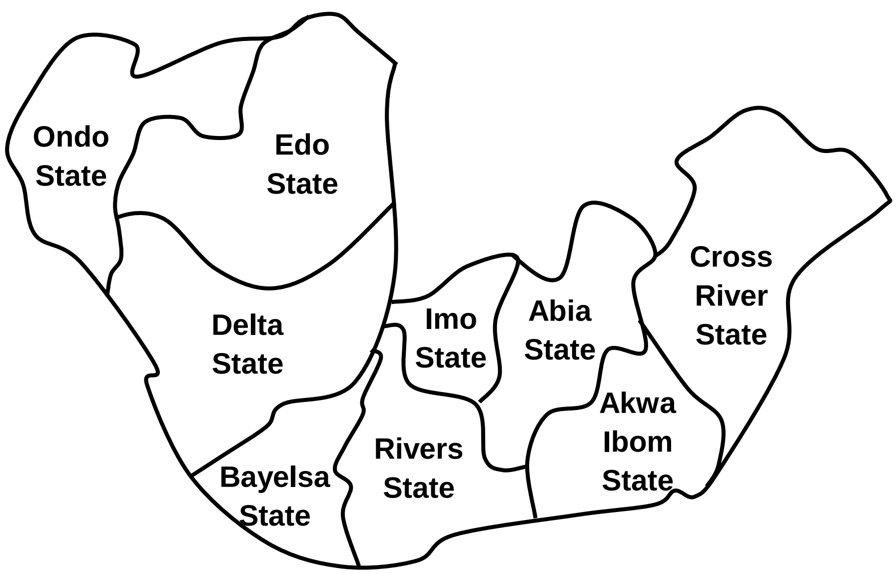

Fig. 1: Geopolitical map of the Niger Delta Area

The geology of the area is characterized by a vast flood plain built up by accumulation of sedimentary deposits washed down the Niger and Benue Rivers. The geology of the Niger Delta area has been extensively studied (Akpokodje, 1987 and Allen, 1965). The area is criss-crossed with numerous rivers, streams, tributaries, creeks and creeklets (Fig. 2). Within the survey area five main water body types were distinguished using the map criteria described in Table 1. The vegetation of the area is characterized by the presence of (i) sandy coastal, ridge barriers, brackish or saline mangrove forest; (ii) fresh water swamp forest and (ii) tropical rain forest. The area is the largest wetland in West Africa and one of the largest mangrove forests in the world (Darafeka, 2003).

Table 1: Summary of definitions of aquatic habitats used in the survey

Water body type	Definition
Lakes	A body of water >2 ha in area (Moss *et al.*, 1996).
Ponds	Water bodies between 25 m^2 and 2 ha in area which may be permanent or seasonal (Collinson *et al.*, 1995). Includes both man-made and natural water bodies.
Streams	Small lotic water bodies created mainly by natural processes.
Rivers	Larger lotic water bodies, created mainly by natural processes.
Creeks	Creek is a small to medium sized natural stream.

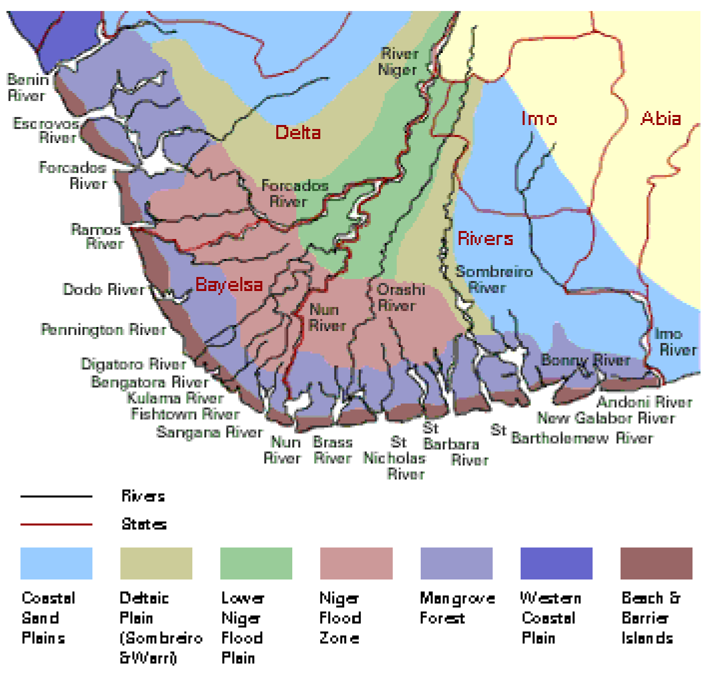

Fig. 2: River Systems in the Niger Delta, Nigeria

Previous study (Gobo, 1998) of the meteorology of the area reveals the average atmospheric temperature to be 25.5^0C in the rainy season and 30^0C in the dry season. The daily relative humidity values range from 55.5 percent in the dry season to 96.0 percent in the rainy season. Rainfall in the area averages 2500mm annually. The rainfall pattern shows two identifiable seasons; the rainy season (April to October) and the relatively short dry season (November to March).

The Niger Delta area is the home of the petroleum industry in Nigeria with distribution of oil fields. It is estimated that Nigeria earns over 90 percent of its foreign exchange and over 80 percent of government revenues from the petroleum (Okoko and Nna, 1998). Nigeria flares 17.2 billion m^3 of natural gas per year in conjunction with the exploration of crude oil in the Niger Delta (Ajugwo, 2013).

2.2 Materials and Methods

This review was conducted based on the survey of common empirical studies on the physico-chemical characteristics of surface water bodies (rivers, streams, creeks, lakes and ponds) in the Niger Delta Region of Nigeria. For the purpose of this review the pH parameter was extracted from the literature using ISI Web of Knowledge, SCOPUS and Google Scholar. Key items in the literature searches were: surface water body category (river, streams, lakes, creeks and ponds), stressor (acidification, and /land use change), and recovery process if any.

From this search I found huge numbers of the article abstract, which I read to determine which articles need to be included in the review of this paper. After reading through most of the articles, I found 31 papers relevant to the objectives of the review. Methodology of this review have been reported in literature (Feld *et al*., 2011; Taylor and Loftis, 1989)

3. Results and Discussion

Mean values of pH obtained for each surface water body system from individual pH measurements reported for each site is as presented in Table 2. Thirty one (31) surface water (rivers, streams creeks and lakes) were selected for analysis in this review.

Table 2: Mean pH values for rivers, streams, creeks, lakes and ponds surveyed during 2007 – 2016 in the Niger Delta Area.

S/N	Surface water (Rivers, Streams and Lakes)	Location of Surface water bodies (LGA/State)	Year of Study	Mean levels of pH values	References
1	Qua Iboe River	Ibeno/Akwa Ibom	2007	5.80	NNDC EMP Report (2007)
2	Apoi Creek	Southern Ijaw/Bayelsa	2007	6.90	Rim-Rukeh *et al*., (2007)
3	Osiama Creek	Southern Ijaw/Bayelsa	2007	6.51	Rim-Rukeh *et al*., (2007)
4	Brass River	Brass/Bayelsa	2007	6.41	Rim-Rukeh *et al*., (2007)
5	New Calabar River	Emuoha/Rivers	2007	6.10	Rim-Rukeh *et al*., (2007)
6	Warri River	Warri South/Delta	2008	6.16	Arimoro *et al*, (2008)
7	Dodo Creek	Southern Ijaw/Bayelsa	2008	6.00	Puyate and Rim-Rukeh (2008)
8	Olagoga Creek	Southern Ijaw/Bayelsa	2008	5.80	Puyate and Rim-Rukeh (2008)
9	Sangana River	Nimbe/Bayelsa	2008	6.00	Puyate and Rim-Rukeh (2008)
10	Forcados River	Burutu/Delta	2008	6.10	Puyate and Rim-Rukeh (2008)
11	Orashi River	Egbema/Rivers	2010	5.22	Nduka and Orisakw, (2010)

12	Ughwhe Stream	Isoko South/Delta	2010	5.32	Nduka and Orisakw, (2010)
13	Sombrieiro River	Degema/River State	2011	6.38	Ezekiel *et al*., (2011)
14	Ughoton Stream	Okpe/Delta	2011	6.14	Uzoekwe and Achudume, (2011)
15	Orogodo River	Ika South/Delta	2011	5.97	Issa *et al*., (2011)
16	Ethiope River	Sapele/Delta	2013	5.60	Rim-Rukeh and Agbozu, (2013a)
17	Osiomo River	Ologbo/Edo	2013	5.80	Rim-Rukeh and Agbozu, (2013a)
18	Jameison River	Ethiope West/Delta	2013	6.10	Rim-Rukeh and Agbozu, (2013a)
19	Andoni River	Opodo/Rivers	2013	5.64	Komi and Sikoki, (2013)
20	Ikpa River	Uyo/Akwa Ibom	2013	5.90	Bassey (2013)
21	Epie Creek	Yenagoa/Bayelsa	2013	5.90	Rim-Rukeh and Agbozu (2013b)
22	Imonite Creek	Adoni/ Rivers	2014	6.90	Iyama and Edori (2014)
23	Tenmako Lake	Southern Ijaw/Bayelsa	2014	5.10	Rim-Rukeh and Irerhievwie (2014)
24	Ikarama Lake	Yenagoa/Bayelsa	2014	5.90	Rim-Rukeh and Irerhievwie (2014)
25	Omoku Pond	Ethiope East/Delta	2014	6.60	Rim-Rukeh and Irerhievwie (2014)
26	Oguta Lake	Oguta/Imo	2014	6.80	Rim-Rukeh and Irerhievwie (2014)
27	Atochi Stream	Aniocha South/Delta	2016	5.80	Rim-Rukeh and Irerhievwie (2016)
28	Iyida Stream	Aniocha South/Delta	2016	5.90	Rim-Rukeh and Irerhievwie (2016)
29	Ijite Stream	Aniocha South/Delta	2016	5.20	Rim-Rukeh and Irerhievwie (2016)
30	Kolo Creek	Yenagoa/Bayelsa	2015	6.00	Eremasi *et al*., 2015
31	Itu River	Itu/Akwa Ibom	2016	6.35	Joseph *et al*., 2016

4.1 Status of Surface Water Acidification

pH is one of the most common water quality parameters tested in the volume of literature consulted probably because it affects many chemical and biological processes in the water. Low pH permits toxic elements and compounds to become mobile and available for uptake by aquatic plants and animals. Lower pH can produce conditions that are toxic to aquatic life, particularly to sensitive species like rainbow trout (KWW, 2001). The mean pH values of surface water samples ranged between 5.10 and 6.90 indicating a slightly acidic environment. Obtained results are consistent with the report of the Niger Delta swamp environment (RPI, 1995). However, this pH range is higher when compared with the pH values of some rivers in Canada that have values between 4.2 and 4.4 (Canadian Acid Rain Assessment, 1990).

Rim-Rukeh *et al*., 2007; Nduka *et al*., 2010; Ezekiel *et al.*, 2011; Uzoekwe and Achudume, 2011; Issa *et al*., 2011; Babalola, Hinmikaiye, and Ogundare, 2017; Puyate and Rim-Rukeh 2008; Rim-Rukeh and Agbozu, 2013b) have attributed the acidic pH in the surface water bodies to the formation of humic acid (HA) formed from decaying organic matter (leaves), which is consistent with the report of the Niger Delta swamp environment (RPI, 1995). Humic substances are formed by the microbial degradation of dead plant matter, such as lignin and charcoal (Ponomarenko and Anderson, 2001; Mao *et al*., 2012). Their presence in water may be due to their insolubility at acidic pH (MacCarthy, 2001). Humic acids are the major organic constituents of soil (humus), peat and coal and a major organic constituent of many upland streams, dystrophic lakes, and ocean water (Stevenson, 1994). It is produced by biodegradation of dead organic matter. It is not a single acid; rather, it is a complex mixture of many different acids containing carboxyl and phenolate groups so that the mixture behaves functionally as a dibasic acid or, occasionally, as a tribasic acid. Humic acids can form complexes with ions that are commonly found in the environment creating humic colloids. The contribution of humic acid to the acidic pH and its formation can be explained by three main theories: the lignin theory of Waksman (1932), the polyphenol theory, and the sugar-amine condensation theory of Maillard (1911) (Stvenson, 1994; Tan, 2014).

Efe (2011), Komi and Sikoki, (2013), Onianwa *et al*, 2002; Omoleomo *et al*; 2008 have attributed the acidification of Niger Delta surface water system to the formation of acidic substances occasioned by incidence of gas flaring. Acidic precipitation or depositions occurs where major emission of SO_2, CO_2, and NOx from human activities such as burning fossil fuels, and other anthropogenic activities. Oxides of sulphur and nitrogen get absorbed by rainwater and get chemically converted to tetraoxosulphate VI acid (H_2SO_4) and trioxonitrate V acid (HNO_3) respectively. Flaring is the controlled burning of the natural gas associated with oil production. These studies have clearly shown that gas-flaring constitutes a major source of water pollution in the oil producing region of Eastern Niger Delta. Gas flaring is a serious contributor to acid-rain, the impacts of which are already being felt in the Niger Delta region in terms of vegetation damage, corrosion and caving-in of roofing sheets, acidification of surface water bodies and death of aquatic lives. Similarly, World Bank, (2004), ascertained that gas flaring in Niger Delta had contributed more greenhouse gases to the atmosphere more than all other sources in Sub-Saharan Africa Combined.

NDDC, 2007; Rim-Rukeh and Irerhievwie 2005b, Puyate and Rim-Rukeh, 2008; Issa *et al*., 2011 have also attributed the acidic pH of the surface water bodies in the region to human activities such as, washing of cars, washing of clothes, dredging of sand, livestock introduction into the catchment; use of nitrogen fertiliser; increased efficiency of drainage etc. For example, Rim-Rukeh and Irerhievwie 2005b attributed the acidic pH in the studied water bodies to the presence of substances such as hydrocyanic acid that may have entered the water during the fermentation and washing of cassava. Water bodies receiving untreated cassava water have been reported to be highly acidic, sometimes with pH as low as 2.6 (Zualiya and Muzondo, 1993).

Rim-Rukeh and Agbozu, 2013b have also attributed acidification of Niger Delta surface water systems to the disposal of urban solid waste into these water bodies which is a common occurrence in Nigeria. In a study of 26 rivers on the western side of Nigeria, primarily in the industrialized oil production areas, found that pollution by solid waste contributed to acidification. The mean pH for the 26 rivers was 6.52 (Osibanjo and Ajayi, 1981). Impact of urban waste water discharge on water quality of Gomti river in Lucknow especially on lowering of pH has been extensively studied by Tripathi *et al*. (2006). They have reported that as soon as the river enters the city the water quality deteriorates with lower values of biochemical oxygen demand (BOD) and lower pH values. Ogun River of southwest Nigeria has been studied extensively for water quality parameters. It has been found that deterioration in river water quality could be attributed to urban run-off, discharge of untreated sewage, industrial effluents and run-off from agricultural fields. The most important factor determining water quality of Ogun River was found to be rainfall which was reflected in high variation in water quality parameters especially pH during rainy season and dry periods of the year (Jaji *et al*., 2007).

Although increasing dissolution of atmospheric CO_2 into rivers was not mentioned in the literature consulted other workers have attributed lowers pH values of surface water bodies to enhanced dissolution of atmospheric CO_2 (Pearson and Palmer, 2000; Feely *et al*., 2008; Beaufort *et al*., 2011). Based on a series of studies, six scenarios were formulated for the net surface of water – air fluxes of CO_2. They are (i) sinking or balance of atmospheric CO_2 to surface water under sunlight, and emission or balance of CO_2 to the atmosphere during the night; (ii) emission or balance of CO_2 to the atmosphere during daytime, and sinking or balance of atmospheric CO_2 to surface water during the night; (iii) emission or balance of seawater CO_2 to the atmosphere during both day and night; (iv) sinking or balance of atmospheric CO_2 to surface water during both day and night; (v) sinking or source or balance of atmospheric CO_2 to surface water during the warm period; and (vi) emission or sinking or balance of surface water CO_2 to the atmosphere during the cold period.

4.2 Trend Analysis of Surface Water Acidification

Understanding the trends in the levels of acidification in surface water is important not only because of its role in the global carbon cycle, but also because changes can affect surface water pH and acid neutralizing capacity. pH values of 31 surface water bodies have been obtained over a period of 2007 – 2016. A trend analysis of the mean pH values was carried out by using correlation coefficient and regression analysis. Graphical illustration of measured pH over these periods is as depicted in Figure 3. Within the study period the pH values shows a coefficient of determination (R^2) of 0.0359 which means that 3.59% of the observed increase of pH corresponds to increase of time and a correlation coefficient (r) of 0.189 indicating a weak positive correlation between the variables (Wilks, 1995).

Figure 3 suggests that as time increases, pH increases but the relationship is not perfect—it seems that knowledge of the variables does not suffice for an entirely accurate prediction about pH. Despite the non-linearity, between pH and time, there is a clear warming trend.

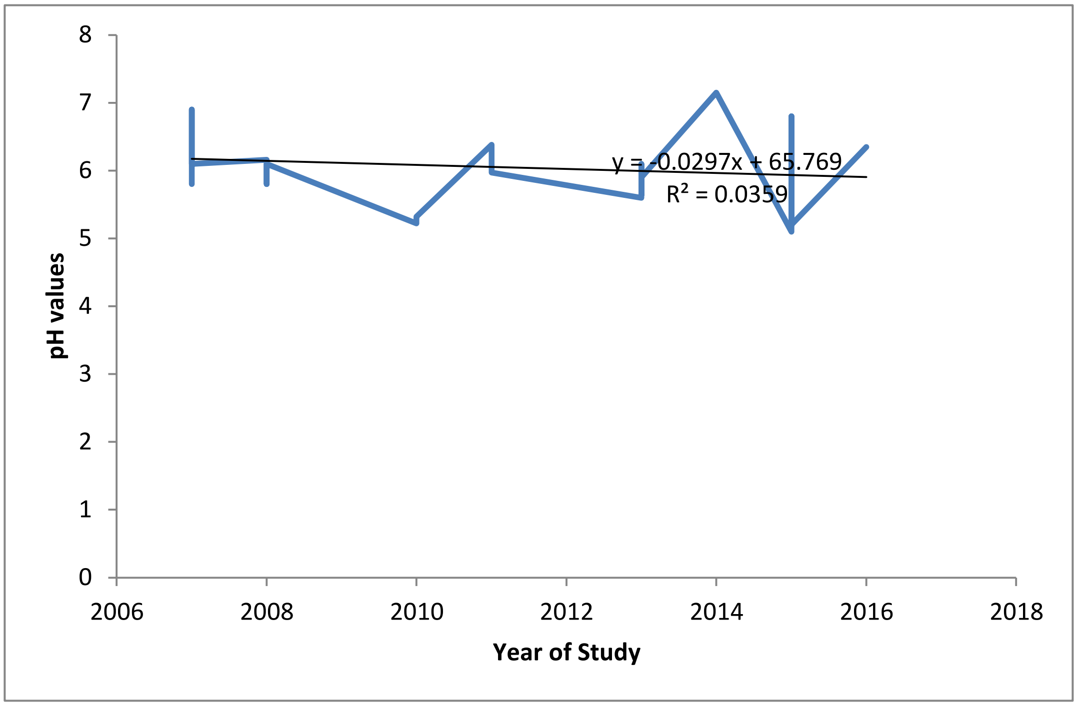

Fig. 3: Variation of pH over the period of 2007 - 2016

4.3 Comparative pH of Surface water bodies

Data summarising the chemical characteristics of the four main water body types are given in Table 4. As a whole, the water bodies were circum-neutral to slightly acidity pH values. The pH values followed the trend Creeks > Lakes > Rivers > Streams.

Table 4: Mean pH values of the surface water bodies

Surface water body types	Mean pH
Rivers	5.97
Creeks	6.29
Streams	5.67
Lakes	6.10

4.4 Implications of the study

On the basis of the current findings, a number of preliminary observations can be made on the implications of the outcome of this review.

First, it is worth emphasizing that all water body types are slightly acidic and lowering pH values have the potential to impart the functioning of the aquatic ecosystems. This finding has significant practical implications for water body monitoring and protection in catchments. Such findings reinforce the importance of understanding the contributing sources to the acidity. The results of this review suggest the importance of regular monitoring of such freshwater ecosystems. Most European countries now have river, stream and sometimes lake monitoring programmes (Moss *et al*., 1996).

More positively, the lower pH values of the water bodies shown by the current review suggest that there may be a range of opportunities for recovery from acidity. A number of studies have confirmed the recovery process of most European Rivers (Forsius *et al*., 2003; Jefferies *et al*., 1995). This should stimulate the interest of scientists and regulators for the purpose of pursuing gas flare reduction policy.

Finally, it is important to recognise that the current work has inherent limitations; it is a study of a geo-political zone that was anthropogenically impacted, not semi-natural, and the information collected relates only to pH. To protect the freshwater environment requires more data and greater understanding.

5.0 Conclusion

All 31 surface water bodies were found to be acidic occasioned by both natural process of humic acid formation due to the decomposition of organic matter and by anthropogenic activities (urban solid waste disposal). The possible entry of industrial effluents such as gas flaring contributed to the high levels of acid rain forming substances. If the current rate of natural gas flaring, increase vehicular emissions and rapid industrialization continues, then the Niger Delta area of Nigeria could experience high levels of acidification of surface water bodies in the near future. It is important therefore to examine possibilities such as adequate monitoring and trend observation as a safeguard for the future.

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