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Geochemical Characterisation of Wetland Soil Waters of Mpu, Enugu State, Southeastern Nigeria

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Abstract

Mpu of Enugu State southeastern Nigeria is underlain by Awgu and Mpu Formations. Awgu Formation consists mainly of black, micaceous, fissile and carbonaceous shales that contain traces of pyrites and carbonate minerals while Mpu Formation is made up of conglomerates, lignites, sandstones and ironstones. The three wetlands used for this study are situated in Awgu Formation. Six pits, each measuring 1m in depth were dug in the wetlands, two per wetland. Waters that drained into each of the pits were sampled for major element chemical characterization. Results from the analysis revealed that the waters are alkaline. Only one sample showed a pH value less than 7 while the range for the rest is 7.2-7.7. Total dissolved solids ranges from 187.2mg/L to 404.95mg/L. Calcium (Ca^{2+})ranges from 0.03mg/L to 0.47mg/L. Potassium (K^{+}) ranges from 0.93mg/L to 10.21mg/L while sodium (Na^{+}) which is the dominant cation ranges from 6.06mg/L to 26.54mg/L. Chloride (CL^{-}) ranges from 108mg/L to 162mg/L while bicarbonate (HCO_3^{-}) varies from15.25mg/L to 61mg/L. Sulphates (SO_4^{2-}) varies from 13.66mg/L to 114.5mg/L. The samples all have high concentrations of nitrates (NO_3^{-}). The range is 72.54 mg/L to 393.24mg/L. Iron (Fe^{2+}) is also in excess. The range is 2.66mg/L to 20.02mg/L. Analysis for heavy metals like lead and cadmium turned up 0.00mg/L. The soil water chemistry of the wetlands have shown that the wetlands have strong buffering processes that change the acidic soils to alkaline soil water. Previous studies of natural water from the Awgu Formation indicate that they have high concentration of lead and cadmium but at the wetlands, these heavy metals have been effectively removed from solution. The low solute concentrations are also an indication of the effectiveness of the wetlands in positively modifying the composition of polluted water but the excess nitrates are due to fertilizer application on the wetlands.

Keywords: water, Mpu; wetlands; heavy metals; buffering

A. Introduction:

A wetland is any piece of land that is saturated with water so that it remains wet or water logged for significant part of the year. As an ecosystem they have unique hydrological, vegetative and pedological characteristics that make them very productive. Wetlands have become very useful to environmentalist all over the world. Some of the benefits of wetlands include: provision of habitats for a wide variety of plants and animals ; provision of filtration functions by the removal of pollutants from water; flood and erosion control; provision of fertile lands for rice farming; use for fish farming; irrigation e.t.c.

Some of the excellent works on wetlands include that of Richardson and Vepraskas (2001) who discussed extensively on the unique geochemical characteristics of wetland soils. Reddy and Delaune (2008) outlined the scientific principles that govern the biogeochemistry of wetlands while Kadlec and Wallace (2009) provided extensive insights on how wetlands can be used to de-contaminate polluted water. The history of the Ramsar convention which sought to provide an international protocol for the use of wetlands is given by Mathews (2013). In Nigeria, Chukwu et al (2009) wrote that the use of wetlands for agriculture began in northern Nigeria where they have been used extensively for the cultivation of onions, tomatoes, garden eggs and pepper. In southeastern Nigeria, wetlands are used for rice cultivation, sugar cane, cocoyam and even fish ponds. Southeastern Nigeria has up to 22,859km^2 of wetlands spread across Anambra, Imo, Cross River, Enugu, Rivers, Akwa-Ibom and Ebonyi states of Nigeria (Chukwu et al,2009). The wetlands of southeastern Nigeria occur primarily as flood plains of rivers like Niger, Anambra, Cross River, Imo, Ebonyi and their tributaries. Further inland, wetlands occur as upland depressions or valley bottoms. This is the case in Enugu and Ebonyi states. The study area (Mpu) is one of the inland-based wetlands in southeastern Nigeria. Chukwu (2007), Umoh (2008) and Chukwu et al- (2009) have worked on the chemistry and pedology of wetlands in southeastern Nigeria. Their work have helped to highlight the important charactertics of wetlands with respect to soil types and biodiversity. Ozoko (2014) showed that natural waters in the shale aquifers of Awgu Formation have elevated geogenic concentrations of lead, cadmium, and arsenic. Awgu Formation is the parent rock of the wetland soils. The aim of this study is to characterize the geochemistry of wetland waters in the wetlands at Mpu in Enugu state, southeastern Nigeria.

B. The Study Area:

Location: Mpu is an important rural community in Aninri local government of Enugu State, Nigeria with a population of about 42,547 people. It is bounded by latitudes 5^0 59' N and 6^0 04'N and longitudes of 7^0 38'E and 7^0 43'E with an areal extent of 86km^2. Mpu has long been considered as an important agricultural community that use wetlands for farming of rice and cassava.

Topography and Drainage

The most outstanding topographic feature at Mpu is the Mpu hills which has been described by Ojoh(1992); Umeji(2002) and Nwajide(2013) as Mpu Formation. Apart from this hill which is about 150 meters above sea level, the rest of the topography is low-lying. The study area is drained by the Ivo river and its tributaries. Ivo river is a major tributary of the Cross River.

Climate and Vegetation

The climate of Mpu and environs is hot and humid with a mean annual rainfall of 1700mm/year. (Ofomata, 1991). It has two seasons, a dry season that runs from November to early April and rainy season spanning from March to October. The hottest months are February and March which also coincide with lowest static water levels. The normal temperature range for the area is 18^{o}C (Dec/Jan) to 37.7^{0}C. (March).

Geology

Two geologic formations underline the study area. (See figure 1).The oldest is Awgu Formation (Coniacian). It consists of black, carbonaceous shales. In some outcrops it is interbedded with mud stones. These shales designated as unit A are usually fissile, micaeous and are known to contain traces of pyrite and carbonate minerals. In the study area, it dips 7^0 -8^0 S E. It is unconformably overlain by unit B, named as Mpu Formation by Umeji (2002) and Nwajide (2013). The contact between the formations has conglomerates, lignites and iron stones. Mpu Formation (Late Maastritchian) is represented by the Mpu Hills mark the stratigraphic boundary between the Asu River group and Ezeaku group of formations. Mpu Formation consists of sandstones that display fining upwards sequence in the beds. The sandstone has clay inclusions Dips are about 70 in the western direction.

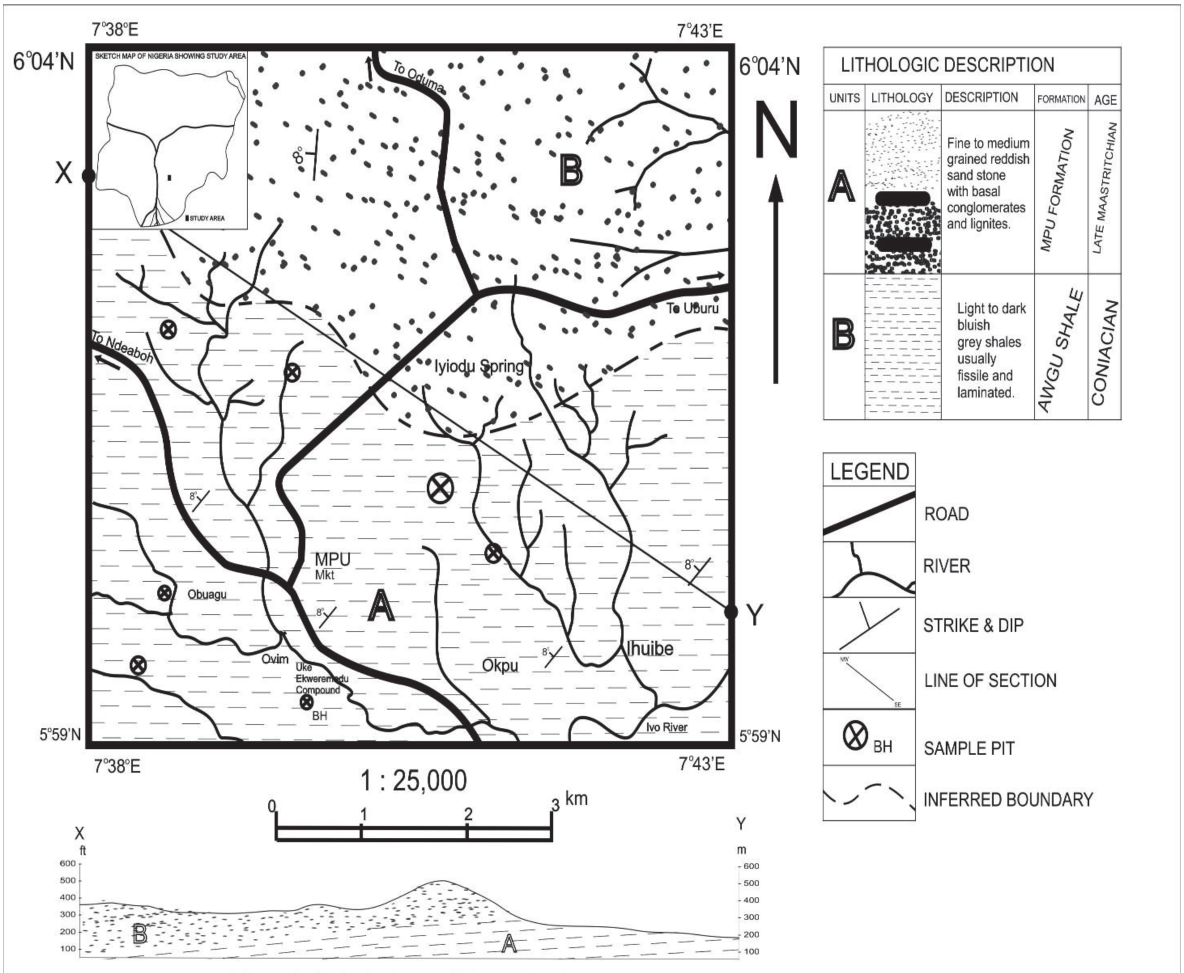

Figure 1: Geological map of Mpu and environs.

Wetland Characteristics

Three wetlands designated as wetland I, wetland II and wetland III were delineated for the purpose of investigation. Wetlands I measures 1.7km by 0.9 km and is located along Mpu –Uburu road while wetland II is 2.4km long and 1.6km wide. It is near Senator Ikekweremadu's house along the Mpu –Ohaozara road. Wetland III is located along Mpu-Ndeaboh road and measures 2.1km by 0.8km. Figure 2 shows the location of the wetlands in the study area and that the three wetlands (I, II and III) are all underlain by unit A (ie shales of Awgu Formation). The map also indicates that the wetlands are hydraulically connected to the tributaries of the Ivo River.

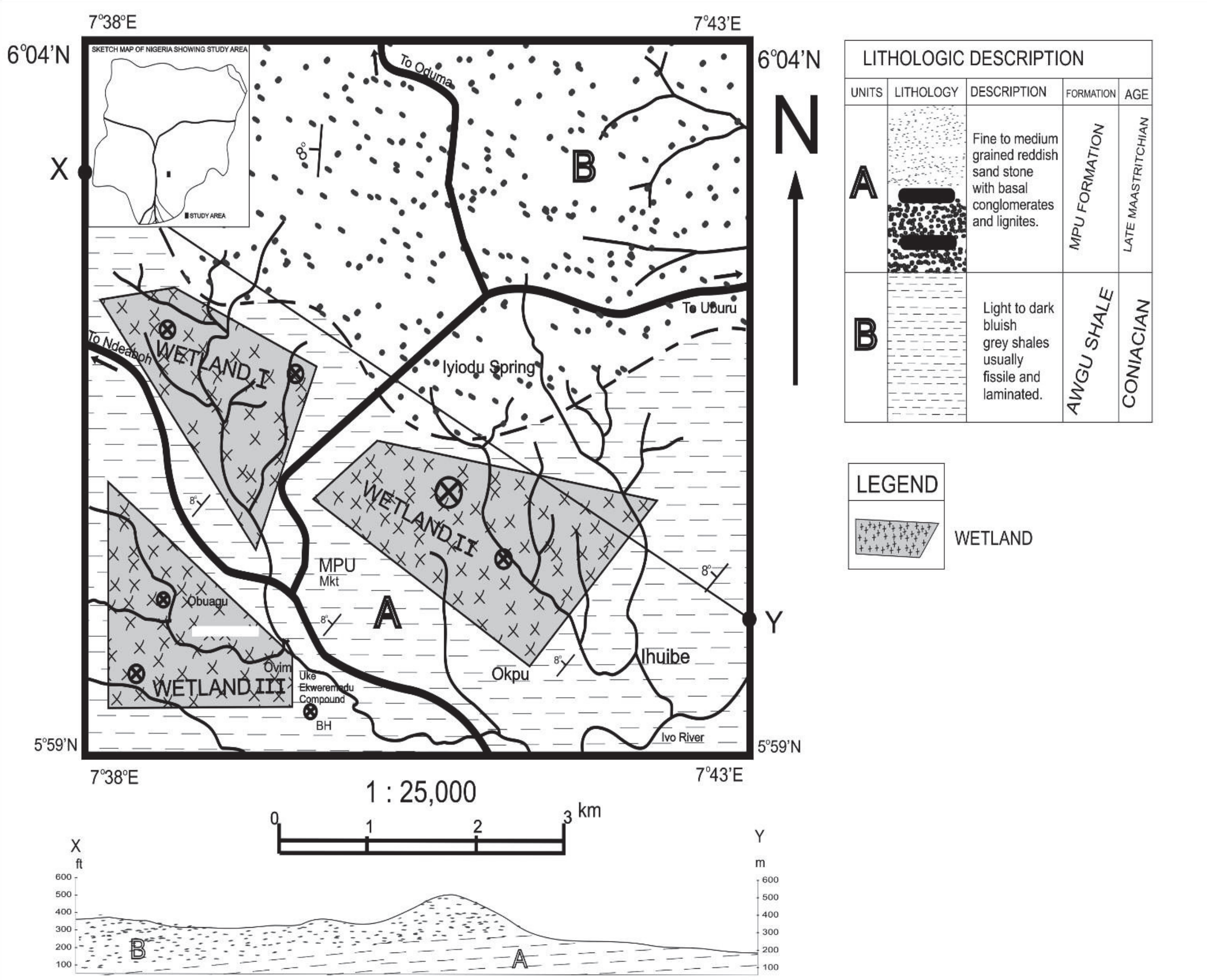

Figure 2: Map of Mpu showing the location of the wetlands.

Evaluation of the biodiversity in the wetlands show that mole crickets, earthworms, adult dragons flies and damsel flies are very common. Common plants species in the wetlands include rushes, sedges, water lilies and common reeds. The soils in all three wetlands are dark and greyish brown in colour at top but at depth, they are greyish black. They have a plastic consistency when they are moist and display poor drainage characteristics. Chukwu et al (2009), classified these soils as Typic Dystropepts under the suborder Tropets. Chukwu (2007) carried out the chemical analysis of the soils (Table 1).

Table1: Chemistry of Soils in Mpu (Modified from Chukwu, 2007)

Parameter	Sample 1	Sample 2
pH	4.88	5.13
pH(kcl)	4.16	3.19
Total N(%)	0.04	0.14
Organic matter	2.19	0.41
Available P(mg/kg)	4.80	2.75
½ Ca^{2+} cmol/kg	3.76	1.10
$1/2Mg^{2+}$ cmol/kg	1.98	1.73
K^+ cmol/kg	0.34	0.33
Na^+ cmol/kg	0.20	0.12
EA cmol/kg	6.00	7.80
CEC cmol/kg	13.5	9.5
Base Saturation (%)	46.5	34.5

From the table above, the soils developed over the three wetlands are clearly acidic with pH ≤ 5. They have low values of N and organic matter. Values for phosphorus are a little more significant but still low. This is indicative of low nutrient loading. Calcium varies from 1.10 cmol/kg to 3.76cmol/kg while magnesium ranges from 1.73 cmol/kg in sample 2 to 1.98 cmol/kg. Sodium levels in the soils are low and C.E.C (cation exchange capacity) value is also a little low (< 15cmol/kg). The general chemical composition is therefore an acid soil with low nutrient characteristics. Table 2 shows the size properties from the different wetlands in terms of their sand, silt and clay fractions.

Table 2: Size Properties of Mpu Wetland Soils

Sample No	% Sand	% Silt	% Clay	Soil Type	Wetland
1	47	16	37	Sandy Clay	I
2	22	17	61	Clay	
3	21	16	63	Clay	II
4	19	19	62	Clay	
5	20	42	38	Silt Clay	III
6	28	18	54	Clay	

Wetland I has a predominantly a sandy population that varies from 22% - 47%; silt (16%-17%) and clay from 37%-61%, which are representative of clay to sandy clay soil. Wetland II has clay sized particles as the dominant sizes but wetland III ranges from clay to silt clay. Wetland II has between 62%-63% of clay while Wetland III has between 38%-54% of the clay.

C. MATERIALS AND METHODS

Six holes were dug in the wetlands. Two holes in each wetland. Each hole was 1m deep. The aim was to create a hole into which water from the wetland could drain. The holes were rapidly filled with water in every case. The holes were dug in the month of August 2014. In all holes, samples of water were collected in new plastic containers of 1l capacity. The sampling protocol was achieved by rinsing each container with the wetland water before sampling. Parameters such as pH, temperature, taste, electrical conductivity and total dissolved solids were measured in the field with Hanna multi parameter water quality meter (Hi 98303). Samples were also acidified to pH <2 with concentrated Nitric acid (HNO3) for AAS analysis at the laboratory. The samples were analyzed with atomic absorption spectrophotometer for determination of the concentration of major cations and heavy metals. The anions were determined with methods prescribed by American Public Health Association (Clesceri et al, (1998)

Table 3: Chemistry of Wetland Soil Waters at Mpu

Wetland	Sample	pH	Temp. °C	Electrical Cond. µ^s/cm	Total Dissolved Solids mg/L	Calcium mg/L	Magnesium mg/L	Potassium mg/L	Sodium mg/L	Manganese mg/L	Iron mg/L	Phosphate mg/L	Chloride mg/L	Carbonate mg/L	Bicarbonate mg/L	Sulphate mg/L	Nitrate mg/L	Lead mg/L	Cadmium mg/L
Wetland I	Sample 1	6.2	28	382	248.30	0.00	0.05	1.86	8.26	0.10	8.24	0.043	162.00	3.00	15.25	13.66	293.96	0.00	0.00
	Sample 2	7.2	29	363	235.95	0.70	0.47	10.21	26.54	0.11	25.52	6.010	126.00		45.75	16.79	177.15	0.00	0.00
Wetland II	Sample 3	7.6	30	623	404.95	0.31	0.15	3.67	7.18	0.10	13.74	0.158	144.00	3.00	15.25	20.33	242.20	0.00	0.00
	Sample 4	7.4	28	326	211.90	0.22	0.11	1.75	6.06	0.13	8.34	0.022	144.00		30.50	114.51	398.24	0.00	0.00
Wetland III	Sample 5	7.2	26	313	203.45	0.52	0.33	1.72	8.33	0.00	6.04	0.012	108.00		30.50	14.17	167.67	0.00	0.00
	Sample 6	7.7	29	288	187.20	0.10	0.03	0.93	6.25	0.00	2.66	0.019	144.00	3.00	61.00	35.40	72.54	0.00	0.00

D. RESULTS AND DISCUSSION

The results of the chemical analyses of the wetland water samples are given in table 3. The pH range is from 6.2 to 7. The values of electrical conductivity range from 288 μs/cm to 623μs/cm which translates to a TDS (total dissolved solids) range of 187.2mg/l to 404.95mg/l. Calcium (Ca^{2+}) varies from 0.00mg/l in wetland I to 0.70mg/l also in wetland I while magnesium (Mg^{2+}) ranges from 0.03mg/l in wetland II to 0.47mg/l in wetland I. Potassium (K^{+}) varies from 0.03mg/l in wetland III to 21mg/l in wetland I while sodium, Na^{+} ranges from 6.06mg/l in wetland II to 26.5 4mg/l in wetland I. Manganese (Mn^{2+}) has very low values (from 0.00mg/l to 0.13mg/l). All the samples have excess iron (from 2.66mg/l in wetland III) to 25.62mg/l in wetland I. Chloride (Cl^{-}) ranges from 108mg/l in wetland III to 162mg/l in wetland I. Carbonates are small (only 3.00mg/l in 3 samples) while bicarbonates range from 15.25mg/l in wetland II to 61.0mg/l in wetland III. Sulphates, $SO4^{2-}$ varies from 13.66mg/l in wetland I to 114.51mg/l in wetland II. All the waters showed high concentration values for nitrates which range from 72.54mg/l in wetland III to 398.24mg/l in wetland II while phosphates range from

0.012mg/l in wetland III to 6.010mg/l in wetland I. The test for the presence of heavy metals like lead and cadmium turned up 0.00mg/l (zero) values.

From the foregoing, the wetland soil waters are virtually alkaline. Only 1 sample in wetland I showed a slightly acidic pH value of 6.8. The rest of the soil waters are alkaline in nature. Chukwu (2007) had already confirmed that the soil pH is less than 5. This means that the wetland has a strong buffering effect on the soil chemistry. The wetland soil waters have high values in alkali metals like sodium (Na^+) and Potassium (K^+) but low values in the alkali earth metals like Calcium (Ca^{2+}) and Magnesium (Mg^{2+}). The hydrogeochemical species of the waters is Na^+ - Cl^-type.

The excess Nitrate concentration (between 72.54-398.24mg/L) suggests contamination of all the wetlands by fertilizers. The wetlands are used for farming. The high values of Fe^{3+} (from 2.66mg/l to 25.62mg/l) may be responsible for the reddish brown colour of the top soil. Once the waters reach the surface, they change to Fe^{3+} because of the combination with oxygen. Kadlec and Wallace (2009) has extensively documented the use of wetlands for the treatment of contaminated water. According to them, wetlands have a great ability to convert most common pollutants like lead to harmless by-products. Ozoko (2014) has documented the occurrence of elevated concentrations of heavy metals in shales of Awgu Formation. These are the rocks that form the parent material for the wetland soils. The shales of Awgu Formation are known to have high concentrations of arsenic, Lead and Cadmium. It is interesting therefore to observe that in the wetlands of Mpu which are underlain by Awgu Formation, no traces of Lead or Cadmium could be detected.

In southeastern Nigeria, the study of wetlands is just beginning. This study provides great hope that wetlands, whether natural or constructed may be applied in solving the great problem of acid mine drainage plaguing the Enugu Coal Fields and in cleaning up industrial wastes of Enugu Metroplex. This study has highlighted how the wetland is able to change soil pH from acidic to alkaline levels and to deal with geogenic contamination of Awgu Formation waters by heavy metals.

E. CONCLUSION

The wetlands of Mpu are underlain by shales of Awgu Formation. Chemical characterization of the wetland water samples indicate strong buffering effects that change soil pH from acid alkaline. The water is the Na^{+}- Cl^- type. Excess nitrate levels indicate contamination by fertilizers. The waters seem able to neutralize the presence of Lead and Cadmium which are known to be occurring in the parent rock aquifer which occurs nearby. This indicates that wetlands – whether natural or constructed will be useful options for treatment of acid mine drainage in the Enugu Coal Fields elsewhere in the State.

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