Iron and Manganese Assessment in Surface and Under Profile Sediment of Water Dam and His Under-Catchment Area: Case of Okpara dam in Benin, West Africa

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ABSTRACT: Iron and manganese concentrations vary highly and seasonally into the water of Okpara dam. Their values were related the geochemistry of the under-catchment area and its bank. Almost all soil and rock in high degradation state sampled on the catchment and bank of this dam show – concentrations' values less or too higher than the sampled sediments in which concern iron and manganese. Iron is steal the most abundant metal whatever it is the soil or - rock analyzed. The dam bank rock metal profile showed a metal leaching more from the top to down profile. The under-profile sediment shows iron diffusion from the most anoxic layer to the less anoxic layers. The underground waters sampled from the catchment have express acidic behavior despite the neutral pH state of rivers water. The same acidity remains more in the sediment. Manganese is more concentrated (0.25 to 4.54 mg/L) in underground waters than iron (less than 2 mg/l). The sediment of the dam is the probable source of water column iron and manganese provider through physic-biogeochemical processes.

Cite this paper as: TOMÈTIN, LAS; AVAHOUNLIN, FR; TOPANOU, KN; BAWA, LM; MAMA, D (2023). Iron and Manganese assessment in surface and under profile sediment of water dam and his under-catchment area: case of Okpara dam in Benin, West Africa. *J. Appl. Sci. Environ. Manage.* 27 (2) 191-196

The water industry has a great challenge to produce water in quantity and high quality and at a cheaper cost. Due to the complicated geographical position of some regions, various surface water sources are treated for human consumption. Groundwater constitute 22 % of the soft water reserves and represent approximately 1000 billion m³ (Cardot, 1999). These water sources are generally of excellent physicochemical and bacteriological qualities. Nevertheless, the nature of crossed rock strongly influences the mineralization of groundwater. The surface water is divided into running and stored waters (stagnant). They are generally rich in dissolved gas, organic matters and suspended matters (SM), such as plankton. They are very sensitive to the mineral and organic pollution due to nitrate and pesticide which coming from agricultural law land where there are used as fertilizer by the mean of run-off. Okpara dam, built on an affluent of the Ouémé River called Okpara located at the North-East of Benin with 450 kilometers from Cotonou constitutes a very

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significant source of supply drinking water to almost all the population of Parakou; one of the greatest towns in Benin. The under catchment pouring reserve upstream is located at the East of the town of Parakou and has been studied in some previous papers (Tometin et al., 2013, 2014). This surface water is polluted by eutrophication of the dam (Tometin, 2015). Otherwise, the concentrations of iron and manganese are influenced by season. Iron, and in a lesser extent manganese, are the most abundant metallic elements in the earth crust. They can be found in water from the lixiviated undergrounds and industrial pollution. They can cause esthetic and organoleptic damages. The shortage of Fe causes anemia, while its prolonged consumption in water may lead to a liver disease called haermosiderosis (Iyengar and Gopar-Ayengar, 1988). Several literatures are available in which concern the removal of iron and Mn from raw water. This technique consumes a high quantity of potassium permanganate during water treatment from Okpara dam. What are furthermore, the origins of iron and manganese, and their mobility in the dam? So the problem statement is what kind of relationship between water plans and metallic ions (Fe, Mn) in the interface water-sediments? So that to contribute in understanding of this problematic.

MATERIALS AND METHODS

Okpara, the under catchment pouring of reserve is located between 9° 16' and 9° 58' of Northern latitude and 23° 6' and 3° 05' of East on longitude. It's cover mainly the districts of Perere in the East, Nikki in the North-East, N'dali in the West, Tchaourou in the South and a small part of the common of Bembereke in North (Figure 1).

Sampling: Water, soils, rock and sediment samples were collected from different points in August (raining season) and February (dry season) on the under-catchment (Figure 2) to check the variation in the quality of iron and manganese in the water. A total of 24 samples of water have been taken. The coordinate's points of all sites of sampling are projected on the map of (Figure 2).

Sample collection and processing: Water samples were collected in 0.5L polyvinyl chloride plastic containers. Electrical conductivity and the pH of the samples were measured. According to Afnor NF T 90-006 (Afnor II, 1997) by using of pH-meter/Oxi WTW 340i and dissolved oxygen by the electrochemical method in situ on situ. The turbidity, the color and the SM were measured by using HACH colorimeter. Iron concentration was determined by using the orthophenanthroline method and measured at 510 nm wavelengths. About manganese concentration, it was

determined according to the potassium periodate acidic oxidation method at 525 nm wavelength. A JENWAY spectrophotometer model 6305 is used for the absorbencies measurement.

Fig 1: Okpara catchment located

Fig 2: Geo-referred situation of the sampling points on the under-catchment.

The iron and manganese analysis methods are based on the standards of French Normalization Association (AFNOR) of the water quality, Tome3 (1997). After samples were, drying, the sediment samples are sieved

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using a nylon sieve mesh (2 mm) according to the Afnor standard X31-101 (Afnor, 1994). Dry Weight (DW 40°C) was determined by drying to constant weight at 40°C according to the French standard X 31-102 (Afnor, 1994). On the solids samples we determined the pH according to 1/2.5 dry sediment/water ratio (Guévara-Riban *et al.*, 2004). For iron and manganese total concentration determination, 0.25g of sample is placed in a furnace for organic matter calcinations at 450°C during 3h. The total digestion of sediments and soil was performed by aqua regia consisting in an addiction of 5 mL hydrofluoric acid (48%) and 1ml hydrochloric per acid (70%) on 0.25g of sediment or soil on a hotplate. The dry residue was recovered by 3.75mL of hydrochloric acid (38%) and 1.25 mL nitric acid (65%) and completed in a 100 mL graduated flask for Iron and manganese determination according to the same method for water sample after a consequent and adequate pH adjustment for iron. A portable X-Ray Fluorescence spectrophotometer (Scientific Thermo Analyzer XL3t Niton) was used to access the soils, rock and sediment metals after organic matter destruction at 450°C for 3 hours. This is a field portable analytical method, particularly useful for the analysis of initial exposure samples assessment or for applications where laboratory analysis is impractical. Additionally, the method is non-destructive; samples analyzed in the field can later be analyzed in a laboratory. The method is applicable to all elemental lead forms, including lead fume, and all other aerosols containing lead (Niosh, 1994).

RESULTS AND DISCUSSION

The underground's water pH 's are acidic (Table 1) compeer to the surface waters in rain season and remain like this in dry season but with less acidic character. The sediment pH has an acidic pH despite the basic state of the soil origin.

The acidity of water showed by its pH could be attributed to the soil crossed nature from the moment that the underground waters mineralization is strongly influenced by the nature of the crossed rock across physic-geochemical process (Edmunds and Smedley, 1996). The sediment pH has an acidic pH despite the basic state of the soil origin.

This characteristic reflects the tropical ferralitic and sandy-clay nature of the catchment area on which over studies show that the soil has an acid pH despite the basic nature of its composition (Faure, 1968; Volkoff, 1965). According to some hypotheses the presence of organic carbon and of humic acid in soil could probably indicate the origin of the acidity.
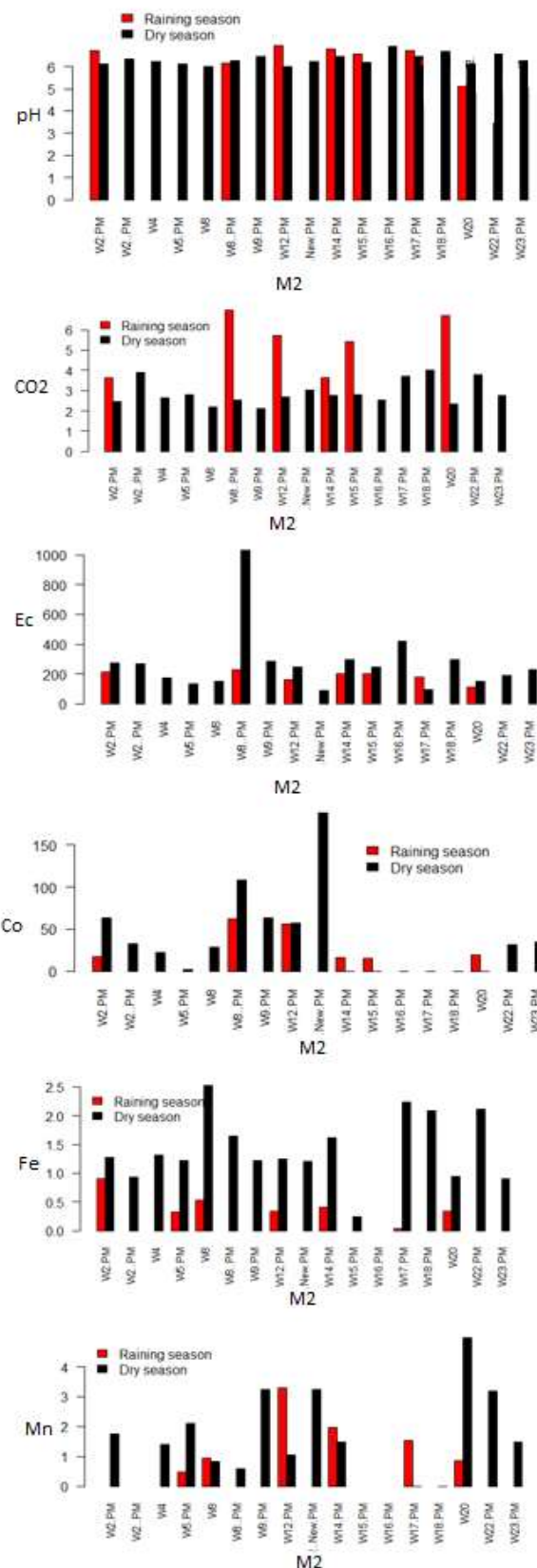

Fig 3: Underground waters from under-catchment analyses

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Table 1: Metals exploration of the under-catchment soils, sediments and rock by XRF.

Localizations	Description	Fe (mg/g)	Mn (ppm)	Ti (mg/g)	K (mg/g)
Biro	Soil	55.5 ± 0.3	1066 ± 60	12.1 ± 0.15	8.42 ± 0.23
Road bank (Biro)	Soil	103.9 ± 0.45	604 ± 0.056	5.09± 0.10	11.3 ± 0.03
Tebo	Red and fr. lat. rock	277.9 ± 0.8	359 ± 83	6.15 ± 0.17	6.9 ± 0.3
Tebo (river bank)	Red and lat. rock	623.4 ± 1.45	1550 ± 163	4.07 ± 0.18	1.76 ± 0.23
Perere	Wight sand + lat.	55.5 ± 0.3	669 ± 54	0.77 ± 0.04	1.4 ± 0.1
Biro-Perere	Red Soil	45.1 ± 0.3	363 ± 40	6.88±0.12	25.9 ± 0.4
Bridge (Biro-Perere)	Sediment	36.9 ± 0.2	450 ± 40	9.56 ± 0.12	26.6 ± 0.4
Perere	Red and fr. lat. rock	240.6 ± 0.8	3029 ± 253	5.35 ± 0.12	3.07 ± 0.18
Perere	Red and fr. lat. rock	140.2 ± 0.5	2443 ± 93	6.07 ± 0.15	3.37 ± 0.20
Gbegourou	Green fr. lat. rock	5.21± 0.071	9438 ± 730	2.57 ± 0.05	5.52 ± 0.11
Okpara dam: E.bk P-20	Lat. rock	17 ± 0.15	304 ± 32	7.92 ± 0.09	10.7 ± 0.2
Okpara dam: E.bk P-40	Lat. rock	49.7 ± 0.25	978 ± 0.06	8.43 ± 0.12	8.88 ± 0.22
Okpara dam: E.bk P-60	Lat. rock	227.3 ± 0.7	941 ± 86	6.40 ± 0.16	5.68 ± 0.25

Also the amphoteric character of iron combine with the basic soil nature from its composition could lead the iron to react as an acidic component. Organic matter oxidation could produce acid compound in water presence, but in the case of the underground waters we project it for future studies. The sediments of the dam have expressed more the same behaviors and have expressed an acidic pH than the soils from its under-catchment area. Added to physic-geochemical process we have some bio activities which occurred in the sediment by modulating physicochemical reaction like redox reactions, bioturbation and biodegradation process (Reynoldson, 1987; Reible *et al*., 1996).

Salinity of waters have been check during our work. All the sampled points have salinity lower than 1 µg/L except at SONEB Perere station where we noted respectively in first time (August) a well (open-cast) and in second time (February) a well with motor pump function respective values of 0.20 mg/L and 0.30 mg/L. The salted well is built in granitic rock. The result obtained is confirmed by very high recorded contents of chloride ion which is respectively 162.00 and 213.22 mg/L. Those values are strongly correlated with high TDS values (respectively 511 and 584) and Conductivity (respectively 912 µS/cm and 1031 µS/cm). The other points record chloride concentrations lower than 23 mg/L with average value of 6.57 mg/L out of 21 underground waters samples collected except the sampling point located in the market of Biro (33.52 mg/L). The high chloride values could be relative to a chemical (use of sodium hypochlorite) treatment plan of this well by "Societé National des Eaux du Bénin" (SONEB). Benin National Society of water treatment (BNSW). The calcium ions concentration (mg/L) and the color (PTCo) of water show clearly possible distinction of underground waters [(13.94 to 27.82) mg/L and (16 to 62) PTCo] to surface waters [(1.47 to 13.26) mg/L and (228 to 37400) PTCo]. This was observed in rainy season just as the SM and Turbidity. Suspended Matter are responsible of water turbidity; and are various such

as silt, clay, organic and inorganic matter (in small particles), made of soluble colored organic matter, plankton and other micro-organisms (APHAs, 1989). In the underground waters (Figure 3) iron concentrations' values obtained are less than 1 mg/L the ones of August but high in February and reach 2.53 mg/L. The manganese amount (Table 1) is important. The underground waters around Tèbo, Alafiarou, Winra, Douroubé expressed a high manganese values ranging from 2 mg/L to 5 mg/L. Values of iron remain weak to enrich the high amount of iron crossed in Okpara dam. Iron is the most abundant metal in the sediments of Okpara dam where average levels can reach 48.52 mg/g of sediment (Figure 3) in this study for the under profile sediments (June 2012) and 63.10 mg/g for surface sediments. For the surface sediment (December 2010) the percentage of organic matter (result not presented here) varies from 21.48% to 28.3% with an average of 24.62%. If this result is integrated into the sediment; the iron values 63.10 mg/g will become 47.57 mg/L not far from 42.11 mg/g found for sediment sampled in the same dam by Zogo (2010). This observation makes possible the used of portable X-Ray Fluorescence spectrophotometer XL3t Niton for quick metal assessment in front of great samples amount and difficult laboratory process for metals assessment. The Iron enrichment is due to the regional geological context of the dam. Many soil and rock in high degradation state sampled on the catchment and the dam bank presented iron (respectively) manganese values less or too higher (17 mg/g to 623 mg/g respectively 304 ppm to 978 ppm) (Table 4) than the sampled sediment from the dam (22 mg/g to 76 mg/g for iron) (Figure 3). Indeed, during his studies in 1993, Le Barbé showed that the geology of the soils of the dam gives it the nature of a soil rich in Iron. The same study showed that the soil of this region is more or less hydromorphic, the bedrock is formed by the red sandy clay, and it is topped by the horizon of clay and ferric accumulation leaching out of the upper horizon. This phenomenon is observable on

the dam bank lateritic soil which profile indicated more metal leaching in the first centimeters (17 mg/g for iron, 304 ppm for manganese at 20cm) than the deeper (227mg/g and 941 ppm for manganese at 60 cm). The river bank is then a probable source of iron and manganese in the dam. In contrast to Figure 3 we noted that the deeper sediments (80 cm to 150 cm) are less rich in iron than the latter sediments (0 cm to 80 cm). This fact indicated according to Boust *et al.* (1999) that iron is in diffusion process from the most anoxic layer to the less anoxic layers. The dam sediment is then the probable source of water column iron and manganese according to physicochemical and biogeochemical conditions (pH, redox potential, organic matter, bacteriological activity). At Sontou, the higher amount of manganese could probably due to the new coring soil and the great used of this well. The soil may contain high amount of manganese, and this metal has an easy ability to be dissolved and depleted from rock. Bloundi (2005) notes positive correlations between manganese and SM, phosphates and ammonium, and negative correlations with nitrates, dissolved oxygen and the pH in surface waters. Indeed, Ouddane *et al.,* (1992) showed that the concentrations of dissolved zinc and manganese decrease with an increase of the salinity. The all underground and surface waters salinity is less than 0.001 mg/L. Our underground waters also have a capability of calcite dissolution. In the reducing medium, the iron and manganese oxides are reduced and dissolved. This followed by metals departure from different compartments (more anoxic layer) of the sediment such as the organic matter, clay and especially the sulphides to the water column (less anoxic layer) (Tack, 1996; Boust *et al.*, 1999). According to Boust *et al.* (1999), reduced iron and manganese will be found in dissolved form Fe (II) and Mn (II) in porous water. Reducing medium will support the solubilization of the metal species (oxides) and then increase or decrease the mobility of the metallic trace elements which diffuse from the sediments to the water surface layer (Blanchard, 2000).

*Conclusion***:** Iron and manganese, concentrations vary highly and seasonally into the Okpara water dam. Their amount is related to the under-catchment area and its bank geochemistry. Many soil and rock in high degradation state sampled on the catchment and the dam bank presented iron and manganese values less or too higher than the sampled sediment from the dam. Iron steal the most abundant metal whatever is the analyzed soil or rock. The dam bank rock metal profile showed a metal leaching more from the top to down profile. The under-profile sediment indicated iron diffusion from the most anoxic layer towards the less anoxic layers. The dam sediment and his bank are the

probable provider sources in iron and manganese to water column across physic-biogeochemical process.

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