

*Full Length Research Paper***Influence of suspended matters on iron and manganese presence in the Okpara Water Dam (Benin, West Africa)****Tomètin A. S. Lyde^{1*}, Mama Daouda^{1,2}, Sagbo Etienne¹, Fatombi K. Jacques³, Aminou W. Taofiki³ and Bawa L. Moctar⁴**

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Received 19 July, 2013; Accepted 16 January, 2014

Iron and manganese, which their concentrations are seasonally high in the Okpara Water Dam, have a high mobility links to suspended matters (SM). The presence of the water plants constitutes SM retention support within the water column. The anthropoid disturbances caused by the fishermen activities constitute a factor of sediments renewing in the suspension. Solid (>0.45 µm)-liquid (< 0.45 µm) fractionation has been carried out and enabled us to observe that SM are responsible for iron content for more than 10 to 98% and for Manganese content about 23 to 93% filtration removes from 10 to 98% of the colloidal iron which is related to filtrated SM. The phosphorus constitutes a combined factor of the iron mobility in the dam. We have noticed in the top water layers a high proportion (low repartition coefficient) of dissolved (and colloids) iron respectively. The iron retained by SM is more concentrated in the middle of the water column than anywhere. The west side of the dam is identified as a manganese enrichment source. The manganese ion concentration influences positively on pH ($r = 0.57$), conductivity ($r = 0.78$), color ($r = 0.66$), and SM ($r = 0.66$) after decantation. Furthermore, the iron concentration is negatively influenced by the pH ($r = -0.52$) and positively by the TDS ($r = 0.51$) after filtration. A pre-filtration or a pre-decantation could reduce the quantity of chemicals used during water treatment.

Key words: Iron, manganese, suspended matters (SM), surface water, fractionation, mobility.

INTRODUCTION

Okpara Dam water constitutes a very significant source of supply drinking water of population of Parakou in the north of Benin. This water is polluted, that pollution can be observe through the eutrophication of the dam (Zogo, 2010). Otherwise, the concentration of iron and

manganese are influenced by season. Iron, and in a lesser extent, manganese, are the most abundant metallic elements in the earth's crust. It had been shown that both iron and manganese found in water coming from the lixiviated grounds and industrial pollution. These elements

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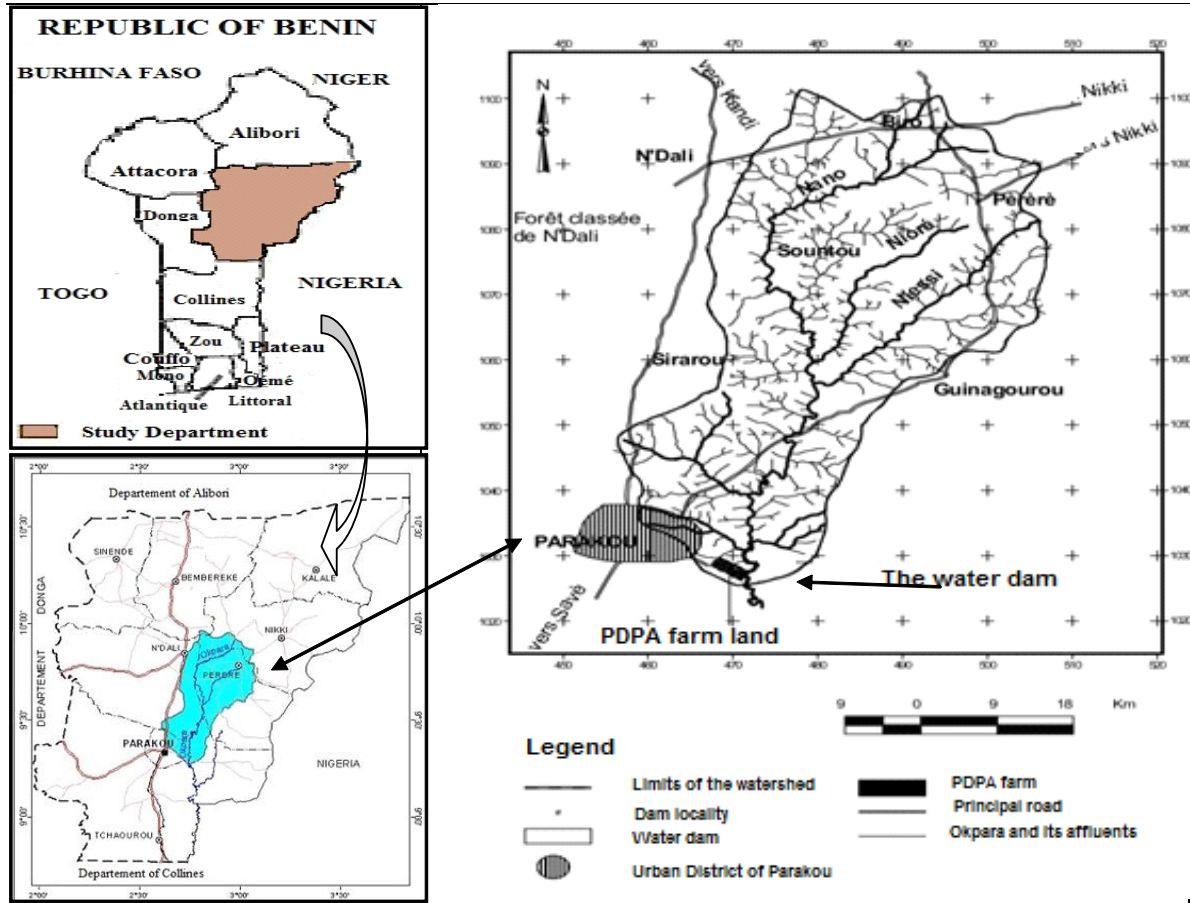


Figure 1. Localization of Benin, Parakou's town and hydrographic system in the under catchment of Okpara's Dam. Source: CENATEL (2003).

do not damage human health or environment. But they cause esthetic and organoleptic damages. Iron and manganese are found in surface or underground water. Removal of iron and manganese from Okpara raw water has been highlight through some studies (Zogo, 2010). This technique consumes a high quantity of potassium permanganate. Furthermore, the origins of iron and manganese, and their transfer in the water column remained not understood. The objective of this study consists of determining the mobility of iron and manganese along the water column across solid-liquid fractionation in raw water.

MATERIALS AND METHODS

Context

This study is focused on Okpara water dam built on an affluent of the Ouémé River called Okpara to supply the town of Parakou (located at the North-East of Benin with 450 kilometers from Cotonou) in drinking water. The dam under catchment is located at the East of the town of Parakou and has been studied in some previous papers. This pouring under catchment of reserve located between 9° 16' and 9° 58' of Northern latitude and 23° 6' and 3° 05'

of East on longitude, covers mainly the districts of Pèrère in the East, Nikki in the North-East, N'dali in the West, Tchaurou in the South and a small part of the Commune of Bembèrèké in North (Figure 1).

Analysis methods and testing

Water samples were carried out from five sampling points in December 2011 (D), April 2012 (A) and in June (2012) (Figure 2).

Two samples sites (N1, N2) were more focused. Raw water samples were taken 20 cm from the surface and from 1.5 m depth to 6.5 m in 1.5 L polyvinyl chloride (PVC) plastic containers the day of the tests. The samples were identified as follows: Sampling level in the water column profiles "surfaces (S); middle (M) and bottom depth (P) "followed by the etiquette of the sampling point (N) and period" as indicated in the Table 1. Example: The water sample taken from the surface of water at the research point N1 in April is identified as follows "S-N1-A". Filtration: Samples of raw water were filtered in an erlenmeyer by using a 0.45 µm pore size Durex folded filter paper. Decantation: A portion of the raw sample water was left for decantation in anoxic condition during one to two days, and some physic-chemical parameters were determined. The difference between the total solids in suspension and the non-decantable solids in suspension gives the concentration of decantable solids in suspension. SM are responsible of water turbidity; these SM are various such as silt, clay, organic and inorganic matter in small



Figure 2. Localization of the sampling points in station on the reserve of Okpara.

Table 1. Geo-referred situation of the sampling stations on the reserve.

Sampling points	Localization	Water column depth	Period
N1	N 09° 17' 08.88" E 002°43'58.67"	2.5 m to 4 m	(A) ; (Jn)
N2	N 09° 17' 02.06" E 002° 43'58.66"	6 m to 7.5 m	(D) ; (A) ; (Jn)
N3	N 09° 17' 02.04" E 002° 43'58.57"	2 m to 3.5 m	(A)
N4	N 09° 16' 58.25 E 002° 44'00.00"	4 m to 6.5 m	(Jn)
N5	N 09° 17' 15.89" E 002° 43'43.25"	0.2 m to 0.5 m	(A) ; (Jn)

particles, made up of soluble colored organic matter, plankton and other micro-organisms (American Public Health Association, 1989). Electric conductivity, the total dissolved solids (TDS) and the pH of the samples were measured using a Waterproof pH-meter. The turbidity, the color and the SM were measured by using a HACH colorimeter. The total iron and manganese content were measured; also dissolved and colloidal iron and manganese content were also determined in the raw, filtrated and decanted water samples. Iron concentration was determined by using the orthophenanthroline method and measure at 510 nm wavelength. Manganese concentration was determined according to the potassium periodate acidic oxidation method at 525 nm wavelength. A JENWAY spectrophotometer model 6305 was used for the absorbencies measurement. The iron and manganese analysis methods were

based to the standards of the French Standardization Association (AFNOR) of the water quality, Tome3 (1997).

Statistical analyses were performed on SPSS 16.0 software.

RESULTS

According to Figure 3, the suspended matters are well eliminated after filtration and decantation. This condition is favourable to the measurement of the true color. Filtration allowed more SM removal than decantation. The pH of these raw water samples reveals an acid

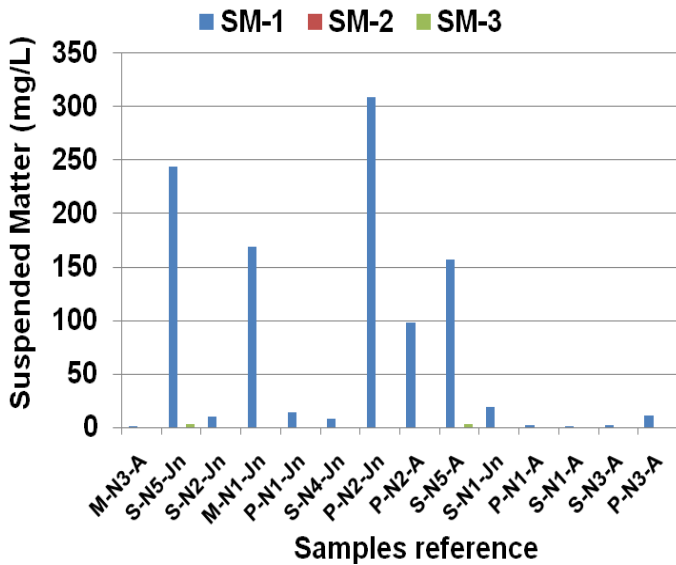


Figure 3. Suspended matter of each sample before filtration (SM-1), after filtration (SM-2) and after decantation (SM-3).

character higher from the surface to the bottom of water column (Figure 4). For these waters, there is an average value of all the points which is about 6.51 for raw waters, 6.62 after filtration and 7.56 after one to two days of decantation in anoxic condition. Thus there is an average variation of one unit of pH. All the collected water samples have pH increasing during their storage to a basic pH ranging between 7 and 8.5. The pH is one of the factors (other than the potential redox) which has a strong influence on the behavior of oligo-elements in the external environment. For example, the reduction in the pH of one unit can lead to an increase of more than one order of magnitude in the concentration of certain metals like aluminum, beryllium (Edmunds and Smedley, 1996). The Metals and metalloids concentrations in the oxy-anions form increase in the aqueous phases when the pH increases (Bonnet, 2000).

Two types of surface water's colors can be measured. One type is the apparent color taking into account the SM (Coul-1) and the second type which is true color measured after SM removal by centrifugation or filtration (Coul-2). We observed according to Figure 5 that whatever is the sampling point, the elimination of SM is always accompanied by the reduction of the color. This fact can be explained by the inorganic matter contribution (sand, clay, etc), and the presence of organic matter and other renewed mineral matters (iron and manganese) in the suspension carried by the surface water during rainy season. The samples taken in the bottom, points N1, N2, N3 and surface in April at point N5 are less suitable for color elimination after filtration or decantation because they presented color values more than 55 color unities.

We have also observed on Figure 6, a light increase of conductivity following the SM removal. This increase

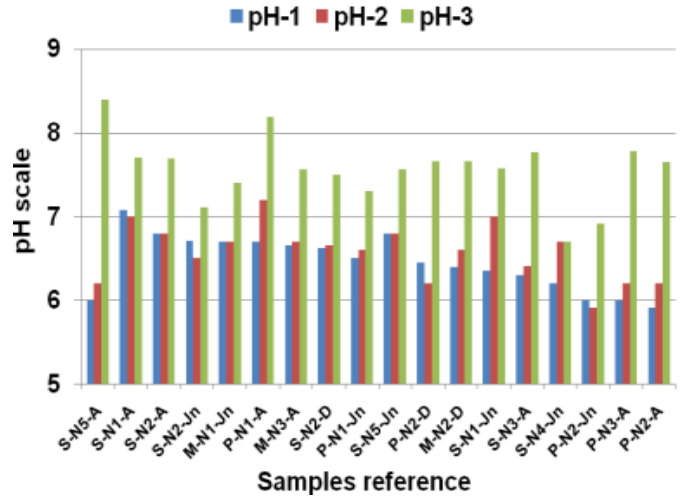


Figure 4. Samples pH values before filtration (pH-1), after filtration (pH-2) and after decantation (pH-3).

varies from 1 to 17 $\mu\text{S}/\text{cm}$ except in the point (N5) for the two distinct periods April and June. Water samples from point (5) presented higher conductivity ($>100 \mu\text{S}/\text{cm}$) which decreases after filtration. We could think about a precipitation reaction of the dissolved ions or their adsorptions on eliminated SM. According to Graeme and Jameson (1999), ventilation during filtration can also lead to the flocculation of the iron particles, by linking bubble to particle, which can more concentrate the particles in the flocks and give a better turbidity reduction after filtration (Bécher et al., 2007). In these conditions, waters which have high conductivity with strong rate of TDS will be unbalanced and one will observe the decrease of TDS which also involve a conductivity reduction. On the other hand the decantation process of samples from point N5 show conductivity increase with value around $485 \mu\text{S}/\text{cm}$. Phenomena after decantation process at point N5 are the same, with less values for points N1 and N2 water samples.

Figure 8 reveals that the turbidity of raw water samples varies from 13 to 885 NTU which are results like the values found on the surface water by Hector (2006) which varies from 1.8 to 1948 NTU. The rate of turbidity elimination after filtration is 10 to 94%. December water samples have lowest turbidities and vary from 13 NTU on the surface and 80 NTU in the bottom (4 m) with the rate of turbidity elimination after filtration around 46 to 80%. For waters which turbidities are lower than 100 NTU, the turbidity elimination tends to be 100% after the decantation. The rate of turbidity elimination after decantation is a function of initial turbidity (before and after SM elimination turbidity correlation $r = 0.76$). In dry season where there is no movement of the water the reduction of turbidity by the sedimentation of the suspended matter (SM) must be observed. However, the presence of the water plants, combined with the daily

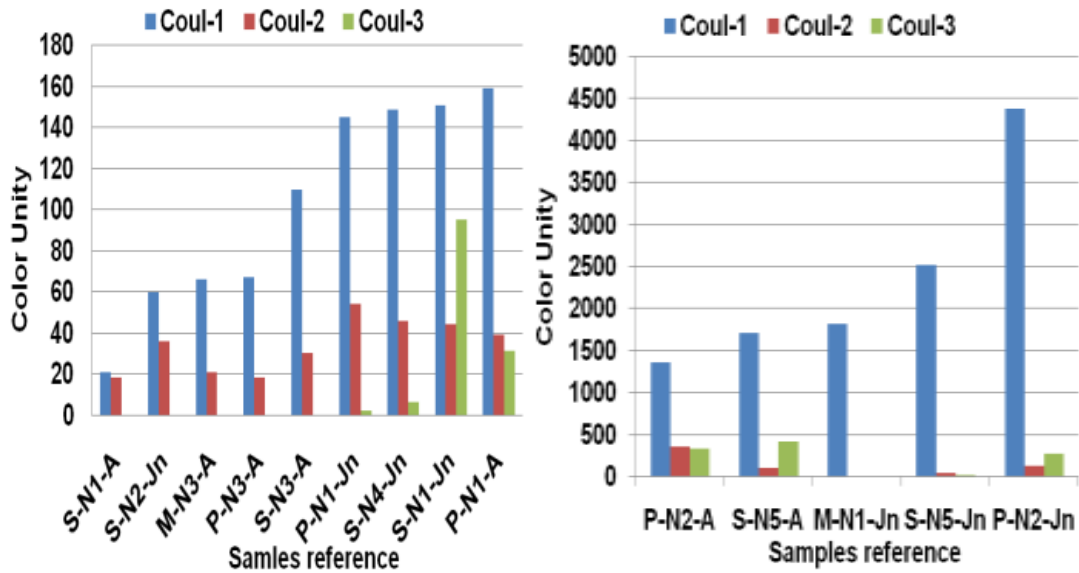


Figure 5. Samples color before filtration (Coul-1), after filtration (Coul-2) and after decantation (Coul-3).

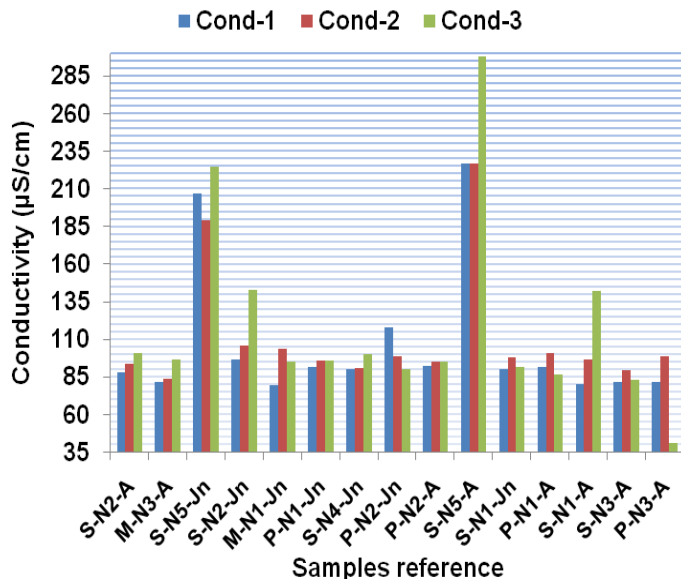


Figure 6. Samples conductivity before filtration (Cond-1), after filtration (Cond-2) and after decantation Cond-3).

impact of fishermen' activities are not favorable to the decantation process *in-situ*. The biological perturbation of the sediment is also a permanent factor of exchange of SM between sediment and water column (Santschi et al., 1997).

Figure 9 reveals that the manganese concentration decreases after filtration and this is more significant after the decantation except the point N5 where we observe the contrary phenomenon. The great values of concentrations are recorded in June (Jn) and more in the

water samples taken on the surface. The water samples taken in April thus present the greatest manganese concentrations after filtration; the dissolved form of manganese has significant values and this in the middle and the bottom of the water column. Less than 50% of manganese is eliminated in this point but this is not observed with other samples. The measured manganese concentrations in the point N5 water samples are higher than the results obtained by Zogo (2010) on the waters dam whatever is the season. One measured values are about the double of Zogo results. This sampling point (N5) on Figure 2 represented a water collecting point coming from the rivers located in the districts of Eastern of Parakou town, the water treatment plant of "Soneb", the agro-pastoral farm (Figure 1). This point N5 thus represented a source of manganese which enriches the reserve water.

We deduced from the obtained iron values presented on Figure 10 that the content of particular iron varies from 5 to 78% of the total iron content. The ratio between metal fixed by SM and dissolved metal corresponding to the partition coefficient (Kd) allowing the distribution between the dissolved and colloidal form and the particular form. Weak values of Kd indicate a strong contribution of dissolved metals to their total concentration (Vignati, 2004). For analyzed water samples, Kd is very high and varies between 1 and 70 with an average value around 17. According to the work of Valérie (2009) Kd measured for metallic traces elements vary typically in range of 1 to 3 for a given metal according to the sites. Kd is often considered as a site - specific parameter at a given time (Fournier-Bidoz and Garnier-Laplace, 1994). For that, we cannot expect a sufficient reproductibility of the partition coefficient

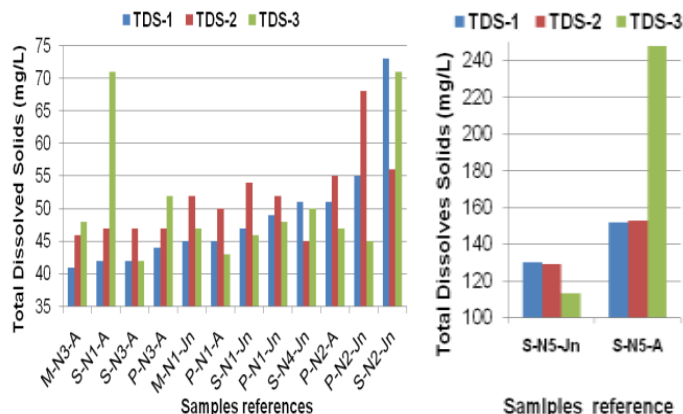


Figure 7. Samples total dissolved solids (TDS) before filtration (TDS-1), after filtration (TDS-2) and after decantation (TDS-3).

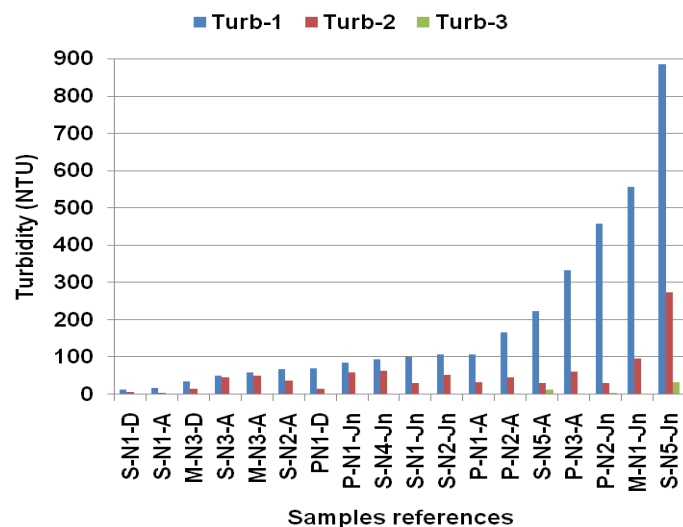


Figure 8. Samples turbidities before filtration (Color-1), after filtration (Turb-2) and after decantation (Turb-3).

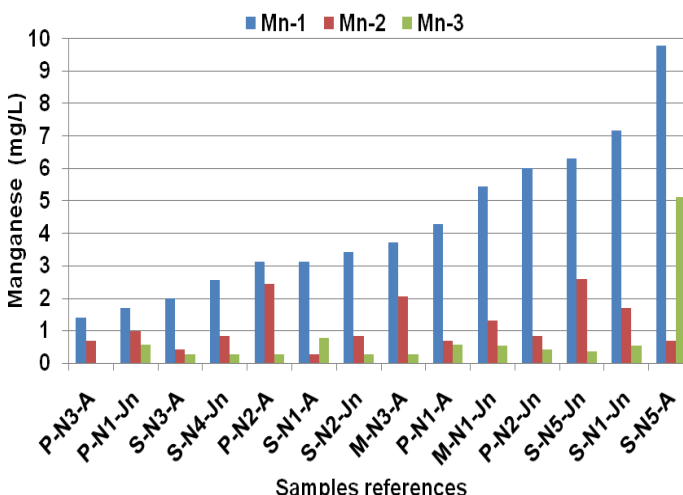


Figure 9. Manganese concentration of the samples before filtration (Mn-1), after filtration (Mn-2) and after decantation (Mn-3).

(Kd) value. The water samples taken on the surface (S) presented the weaker Kd and are less concentrated in dissolves and colloidal iron (< 5mg/L) than those of the bottom (P) from 5 to 30 mg/l whatever in December, April or June. SM contained iron in range of 53 to 99% in the water column. After filtration, all the collected water samples present lower values than 5 mg/L of iron, with an average around 0.96 mg/L in the surface layer and 2.57 mg/L in the bottom waters.

DISCUSSION

The main goal of a drinking water station production is to provide high quality water with a cheaper cost for the consumer. The various water quality parameters included such as turbidity, color, pH, SM, iron, manganese, relied on the water treatment process. To achieve the desired goal, each water treatment will ensure a good water quality and use high qualified human resources (Valentine, 2000).

Correlations are often established between turbidity, suspended matter, total solids and color. Analyzed water turbidity and to a lesser extent the color of analyzed water have show high decrease after filtration or the decantation and this is conform to result found by Zogo et al. (2011) which show that the rates of elimination of turbidity are higher at pH 6.50 and 40 mg/L of aluminum sulphate on the level of water of Okpara. After intense rains, there is SM increase with a good decantation. SM is strongly concentrated at the bottom of the water column from 2 to 310 than surfaces from 1 to 20. Simple filtration does not allow a correct elimination of the color and turbidity in the case of Okpara water in any season and any sampling point. The elimination of the color and turbidity by simple filtration is weak, probably because of the presence high content of iron and manganese seasonally. This weak turbidity elimination could be due to the TDS because (Figure 7), the turbidity of raw water can also be reinforced by the presence of inorganic solids like metallic oxides and hydroxides (iron or manganese) and biological organisms like the seaweed, the zooplankton and the filamentous bacteria or in cluster (Foley, 1980). The manganese ion concentration influences positively on pH (r = 0.57), conductivity (r = 0.78), color (r = 0.66), and SM (r = 0.66) after decantation. After decantation dissolved manganese form is strongly positively correlated (r = 0.72) with TDS-2 and, in contrast of results before filtration (r = 0.07) and after decantation (r = -0.15)

.This observation point out the particular forms of manganese in which concern their natural removal from water samples with the environment physic-chemical condition afferent. Furthermore, the iron concentration is influenced by the pH and in a less proportion by the TDS.

The average measured pH observed is 6.51. Zogo et al. (2011) has used the same pH value for pre-chlorination followed coagulation-flocculation to reach 50

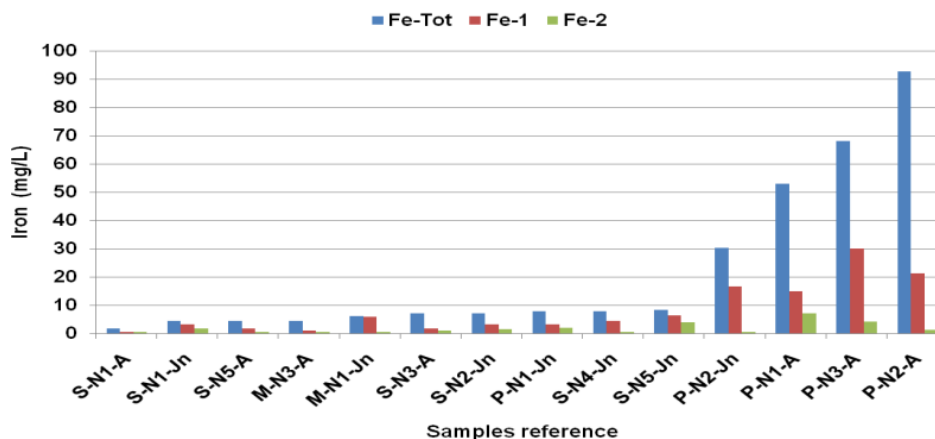


Figure 10. Total iron concentration (Fe-Tot); dissolved and colloidal iron before filtration (Fe-1) and after filtration (Fe-2).

to 95% of iron removal or 20 to 45% of manganese. The initial iron concentration variable was between 8.00 and 35.00 mg/L and an initial manganese concentration in range of 1.00 to 4.00 mg/L for experiences carried out by Zogo. The fact that we have observed a little increase in the pH after filtration and decantation, can be explained by an oxidation or a reduction of organic matters rate in the presence of the humic acids. Kedziorek and Bourg (1996) also showed that the humic substance presence could increase the pH; cation metals react then like anions (Bonnet, 2000). According to Soetaert et al. (2007) reoxidation by oxygen and the reduction of manganese and iron oxides tends to increase the pH. In addition, certain geochemical processes as the dissolution of calcite involve a consumption of hydronium ions (H_3O^+) and thus increase the pH. This can also justify in certain cases the increase of TDS after decantation.

In the reducing medium, the iron and manganese oxides are reduced and dissolved. This followed by a departure of the heavy metals from the different compartments of the sediment such as the organic matter, clay and especially the sulphides to the water column (Tack et al., 1996). This phenomenon appears observable in the deep layer of water column where Zogo (2010) observed high contents of organic matter. Filtration has eliminated 10 to 98% of colloidal iron which is related to SM filtrated. There would thus exist in water samples an important adsorbed iron. Because of their small size, the colloidal particles have specific surfaces

(report/ratio surfaces/mass) significant ($> 10 m^2.g^{-1}$) and can thus represent adsorbent or absorbent form for the chemical elements in general and the metallic elements in particular (Citeau, 2004). According to IUPAC (1997), the colloids are molecules or polymolecular particles dispersed in a medium and having, at least in a direction, a dimension ranging between 1 nm and 1 μm . if the lower limit is considered without ambiguity around 1 nm (Lead et al., 1997),

determination of the higher limit seems more complex. It can vary, according to authors, from 0.2 to 0.5 μm (Singhal et al., 2006), and can even reach 1 μm (Lead and Wilkinson, 2006). Then a part of the colloids could be eliminated with the SM.

After filtration, the content of iron dissolved and colloidal in water varied from 0.41 to 7.10 mg/L. Physical treatment like filtration has thus a beneficial effect in terms of the reduction of chemical quantity to carry out the treatment without a pre-filtration of these water samples. The iron form in the surface layer of the Okpara Dam water in dissolved and colloidal which that is combined more with SM, and this could explain the weak rate of variation of the iron content related to SM after the filtration of surface water. The iron concentration is negatively influenced by the pH ($r = -0.52$) and positively by the TDS ($r = 0.51$) after filtration. In the absence of oxygen and nitrates, metallic oxides are the most powerful oxidants and are reduced in the anoxic area. According to Audry (2003) the redox species of metals which have more than one oxidation step in natural water have different mobility, solubility, toxicities and reactivity. According to Boust et al. (1999), reduced iron and manganese will be found in dissolved form Fe (II) and Mn (II) in porous water. In this form, they can either (i) diffuse towards the oxic layers or re-oxidize into oxides or (ii) precipitate, if the products of solubility are reached, with the chemical species produced by the degradation of the organic matter (sulphides, phosphates, carbonates). Manganese precipitates in carbonate salts form $MnCO_3$ (rhodochrosite), iron precipitates under carbonates salts form $FeCO_3$ (siderite) and salts of monosulphurs FeS (mackinawite) (Boust et al., 1999). In fact the form of precipitated iron and manganese will be higher in the presence of phosphate ions which are mainly present in Okpara water (Zogo et al., 2011). The anoxia and acidity in the sediments are favorable with the dissolution of oxidize-hydroxylated forms. Thus, certain metals, like Fe,

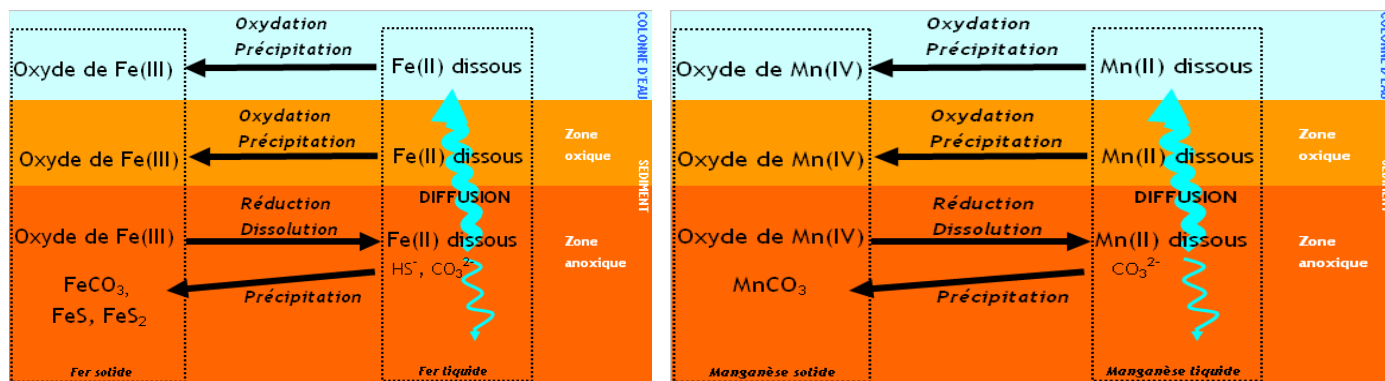


Figure 11. Behavior of iron and manganese in the sedimentary area of the rivers. (Boust et al., 1999).

Mn and Cr are more movable in their reduced form. The work archived by Zogo (2010) has show that the surface water layer in a given sampling point of the reserve of Okpara presented 10% of oxidized form (Fe III) against 90% of particular form iron with a total concentration of 2.015 mg/l. The redox conditions can increase or decrease the quantities of oxyhydroxydes and sulphides adsorbed (Lions, 2004). Reducing media 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).

The work achieved by Zogo (2010) concluded indeed that the splitting up related to the use of the grounds of under catchment area of the dam for intensive cotton culture and other food products accompanied by significant quantities of artificial fertilizers using are probably at the base of the imbalance observed on the level of this water ecosystem.

The work made possible to identify in the reserve of Okpara six macrophytes species and to count eighteen microphytes species. Moreover, according to trophic levels' based on the chlorophyll a contents (OECD, 1982), with a concentration sometimes higher than chlorophyll 25,00 µg/l has and the level of development of the macrophytes in the stopping of Okpara, this reserve can be classified in the category of the eutrophic lakes'. The amount of ortho-phosphorus could reached 30 mg/L in the surface water then.

Phosphorus measured in the bottom water (Tomètin et al., 2013) showed that the total phosphorus could reach to 191 mg/L at station N1 and 397 mg/L at station N2. Also the sediment constitutes a source of phosphorus renewed for the water column. Then the high phosphorus amount in the water and sediment under different forms (mobility) could be control by the iron and manganese. The fraction of phosphates related to iron is very sensitive to the variations of the sediments redox potential. When the redox potential is lower than 200 mV (ESH), a fraction of Fe^{3+} available to the level of the sediments is reduced in Fe^{2+} . Gomez et al. (1999) show

that this value of potential redox is variable according to the pH of the sediments, to the presence of organic ligands and to porous water salinity. Phosphorus is thus likely to be salted out in the water column when the interface water-sediment becomes anoxic (Gomez et al., 1999) by various mechanisms of diffusion of interstitial water (Enell and Löfgren, 1988). In anoxic conditions on the surface of the sediments, it formation of iron hydroxide will thus not have there as the straight lines part of the Figure 11 indicates it and thus not of fixing of the phosphorus which is thus released in great quantity in the water column. In oxic conditions on the surface of the sediments, there are however two possible cases: the phosphorus diffuse of the sediment (anoxic) towards the interface water sediment (oxic), where it is trapped the iron hydroxide which is excellent adsorbing phosphorus in the presence of oxygene dissolved (Figure 12).

Conclusion

Iron and manganese, present in Okpara Dam water have various concentrations according to the season. Their contents and mobility are tied in the major part; with SM quantities are strongly retained more by the water plants. The colloidal SM is the major factor of iron high amount in the water middle and bottom column. The high amount of phosphate in the water column constitutes a factor of iron and manganese precipitation which migrate from the top to the water bottom. Also, these naturals' factors can be added to the anthropological activities which increase the exchange between sediments and water column. SM constituted a major vector of the mobility of iron and manganese within the water column. After decantation or SM removal from the water sample, the pH of this water varies from 6.51 to 7.62. The organic matter decomposition in the sediments and the water column maintains the water column acidity favorable to the increase of the dissolved forms which migrate towards the water surface layer under free form to be oxidized or engaged as ionic or colloid forms, tied with SM which

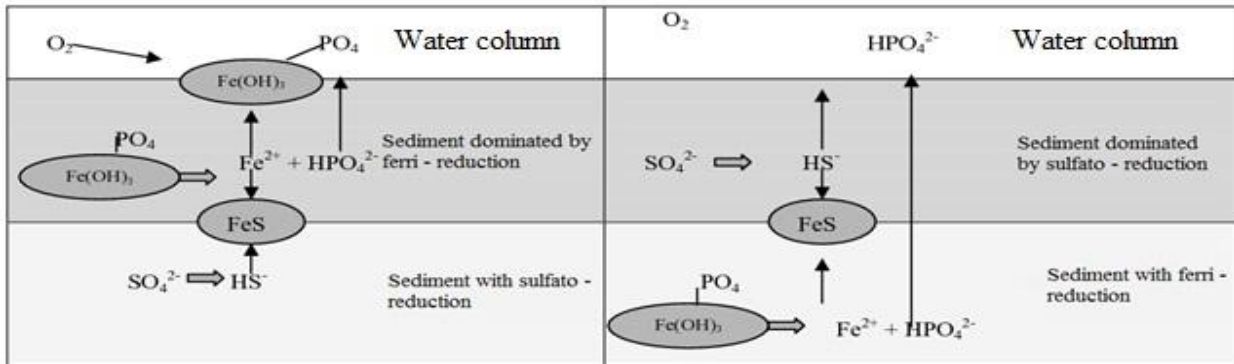


Figure 12. Diagrammatic representation of two possible mobility cases of phosphorus at water sediment interface in oxic conditions. The simple arrows represent flows of diffusion and the double arrows represent the chemical reactions (according to Matthiesen et al., 1998).

concentration increases from the surface to the bottom of the water column. Iron concentration along the water column strongly dependent on the organic matter responsible of the humic acids and the water acidic pH. Organic matter is the fundamental component of the SM. A probable source of manganese enrichment of the dam water is located at the point N5 where one river supplies water to the dam. The high concentration of manganese can be provided by total solid quantity of this river.

Physical treatment like pre-filtration has a beneficial effect in terms of chemical quantity reduction to carry out the treatment without a pre-filtration of these water samples. The fractionation and the speciation of iron and manganese in the water column and the sediments are new concept of control and treatment efficiency of Okpara Dam water.

ACKNOWLEDGEMENTS

The author extend their thanks to the Ministry of the Higher Education and Scientific Research of the Benin Republic for its financial grant, and Mrs. Chrysostome Montcho and Martial Dossou for technical assistance in the water analysis laboratory (Parakou Hydraulic General Direction) where some analyses were carried out immediately after sampling process. They acknowledge the useful comments and suggestions of the anonymous reviewers.

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