Scientific Research

Study of the Sediments of the Dam of Okpara (Benin): Physico-Chemical Characterization and Speciation of Iron and Manganese

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ABSTRACT

Iron and Manganese contents and parameters including pH, conductivity, and organic matter contents were determined in the sediments of the Okpara dam in Northern Benin. Fifteen samples were collected during a one-month period and analysed in laboratory using the method of sequential extraction of Tessier. The analyses indicated that sediments contained high concentrations in reducible fraction of Iron and relatively high contents of exchangeable fraction, acidhydrolysable fraction and residual fraction of Manganese. The findings of this study confirmed the hypotheses that the metal contents of the sediments were relatively high and varied according to the geochemical phases.

Keywords: Sediments; Iron, Manganese; Geochemical Phases; Pollution

1. Introduction

The diagnostic study of the situation of the Okpara dam, led by the Coordination Team of the Local Water Partnership of Borgou-Alibori in 2007 revealed the existence of serious threats to the safeguarding of this river and the dam, as well as to secure drinking water supplied to the population of Parakou. The major threats included continuous stranding of the river, pollution by municipal solid waste, wastewater, chemical fertilizers, erosion, invasion by plants, land conflicts and deforestation.

This situation is alarming that Okpara constitutes the single source of drinking water for the population in the region especially for the town of Parakou.

Several studies [1-3] showed that the human and industrial activities added to the increase of populations in African countries and particularly in Benin, generated many environmental problems; they involved a rapid increase of various pollutants such as heavy metals in lagoons, rivers, lakes which also received urban wastewater. This also applied to the river of Kpara.

Indeed, the Beninese Society of Electricity and Water (SBEE), company in charge of the production and the distribution of water and electricity in Benin reported that in the early 90s, consumers of the drinking water coming from the treatment station provided by the Okpara dam, started complaining about the organoleptic quality of the water in particular a change in color: sometimes reddish, sometimes brownish. The multiple physicochemical analyses carried out revealed that the phenomenon was due to the presence of Manganese in the treated water. To look deeper into the phenomenon, the central laboratory of this company conducted several analyses at various levels: from the surface of water towards the bottom. The studies undertaken showed that the Iron and Manganese ions were highly concentrated down at the bottom. Elsewhere, the results of this dam's water characterization work carried out over four years by Zogo D., Soclo H., Bawa M. and Gbaguidi M [4] between the time period (2006-2010) revealed that between June and January of each year, the raw water became particularly rich in Iron and Manganese. The enrichment of the water in these metals was due to the depletion of oxygen in the water since at the closure of cofferdams, the water-atmosphere exchange surface became almost motionless. The author, in addition, noted that, the works of treatment of water currently in place at the station of

Parakou were not designed to eliminate the high concentrations of Iron and Manganese in Okpara during low water period. The metals strongly contributed to the deterioration of the organoleptic quality of the water; hence the need to get rid of them before the drinking water is supplied for consumption.

The speciation of a chemical element corresponded to its distribution between the various physicochemical species presented in the environment to assess their relative importance.

Whether in soil, sediment or aquatic systems, the fate and the bioavailability of Metal Elements Traces (ETM) are related to their speciation. The risk posed by the ETM in soils depends on their ability to migrate from the solid phase to the soil solution where they can be available for crops. The speciation of metals related to the various fixing phases of soil thus was most widely studied. Various approaches were tested in order to carry out this speciation. The most usual have long been the methods of operational and functional fractionation even if in recent years the physical speciation methods have rapidly developed.

Operational fractionation consists of the successive use of various reagents in order to specifically extract the metals fixed to a given compartment of soil (organic matter, Iron oxides, manganese or aluminum, carbonates, sulphides etc.) and to assess its stock. However, these extractants lack of specificity [5,6] and the ETM thus are not really characterized by the elements of the soil to which they are linked but rather by the reagent used to extract them. That is why we talk of operational fractionation. The procedure of operational fractionation most known was developed by Tessier, A., Campbell, P.G.C., Bisson, M. [7]. Five phases are highlighted: exchangeable, oxydable, acid-soluble, reducible and residual. Since, so many other protocols of operational fractionation have been developed [8].

Functional fractionation consists in characterizing the trace metallic element (ETM) of the soil according to their "function" in the soil. They are made with a single extractant (dilute acids, organic complexants, salt works solutions etc.) supposed to simulate the physicochemical conditions of the soil. The most current example is the determination of the availability of the ETM for crops (bioavailability). This type of fractionation is also used to evaluate the variation of mobility and bioavailability of metals in a soil after a treatment such as, a contribution of station of purification mud. But it can also be used to assess the effectiveness of a rehabilitation of polluted soils by traces of metals [9,10]. Recently, in a harmonization care, a diagram of extraction was proposed by the Community Office of Reference Community Office of Reference (BCR) [11], aiming to appreciate the fraction of bioavailable metal. The quantity of metal extracted is

supposed to be representative of the quantities likely to pass in the solution of the soil and thus to be potentially bioavailable. Both types of fractionation involve reaching thermodynamic balance what limits their effectiveness. Indeed, it is generally accepted that balance is not often reached under natural conditions and that the kinetics of dissociation of complexes can be a significant parameter [12,13]. The concentration of free metal (good indicator of bioavailability according to the FIAM [14] in the soil solution, as in aquatic systems, results from a dynamic equilibrium in which the formation and dissociation of complexes in solution take place continuously. To properly estimate the amount of bioavailable metals in solution, it is necessary to obtain information on the kinetics of dissociation of the complex, *i.e.* to consider their lability/unstability. But in the case of soils especially, given the stocks of metals in presence, it is important to take into account the contribution of metals fixed to the solid fixing soil compartments and transfer speed of metal fixed to the soil solution.

Finally, from a kinetic point of view, there are at least two stages limiting potentially the transfer of metals from soils to crops: 1) the dissociation of the labile complexes in the solution of the soil at the solution/roots interface and 2) the extraction of metals from the solid phase of the soil towards the solution of the soil.

The objective of the study is to determine within the sediments the various possible combinations of Iron and Manganese which cause the enrichment of the water in these pollutants. The study aims at testing the hypotheses that the metal contents of the sediments are relatively high and vary according to the geochemical phases.

2. Material and Methods

2.1. Study Area

The town of Parakou is located between 09°21'N and 02°36'E (**Figure 1**) in the North-East of Benin, at 450 km from Cotonou, the economic capital of Benin, at an average altitude of 350 m and covering an area of 441 km^2 (www.villeparakou.bj). It is limited in the North by the commune of N'Dali, in the South, the East and the West by the commune of Tchaourou. It runs along a ridge that rises up to 390 m altitude and separates the Ouémé basin in the West from the one of Okpara in the East. The study area is based on a Precambrian crystalline peneplain and cristallophylienne made of granite and gneiss that can store water reserves only after deterioration [15].

The Dam of Okpara is built on the river of the same name, which represents one of the two principal tributaries of the river Ouémé of Benin. It is established in the district of Kika at Tchaourou and is at a distance of 12.3 km to the water treatment company of SONEB in Parakou. The catchment area of Okpara is composed of a
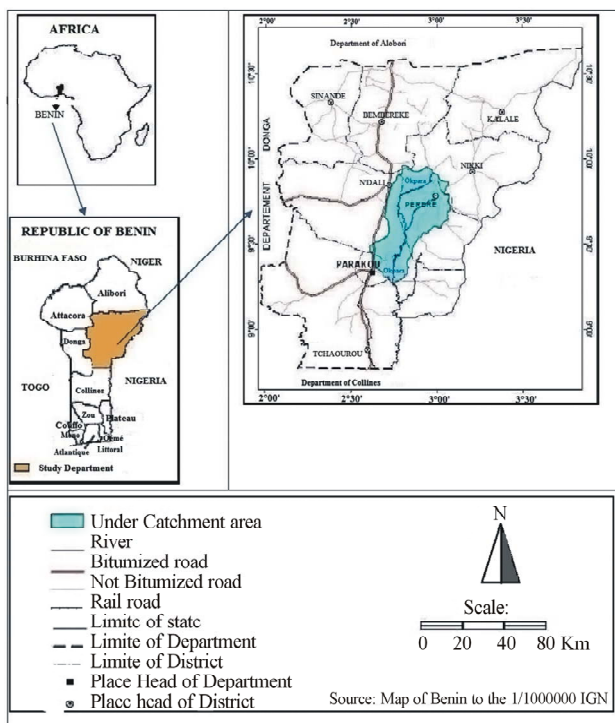
Figure 1. Location of the study area: Parakou, the Okpara dam in northern Benin in West Africa (source: CENATEL, 2003).

crystalline peneplain comprising with hard rock hills. Its area is of 2070 km² and covers completely or partially five communes of the department of Borgou namely Tchaourou, N'Dali, Pèrèrè, Nikki and Parakou. The climate is soudanian with an alternation of rainy season (May-October) and a dry season (November-April). The average annual rainfall is about 1200 mm. Temperatures vary between 18°C (December-January) with 38°C (March-April). The main soil types found in the catchment area are mainly tropical ferruginous soils, lateritic soils, sandy clay soils and granite-gneiss soils. The dam was initiated by the Dahoméenne Society of Kénafe (SODAK) in 1969 to meet the water needs related to the production of Kénafe, especially for washing the fibers. It was assigned to the Benin Electric Power Corporation (SBEE) in 1975 to feed the people of the city of Parakou in drinking water (PNE-Benin, DG-Eau, SONEB, in December 2008), (www.villeparakou.bj).

2.2. Sampling Techniques

Five sampling stations were selected based on their accessibility and proximity of emissions. Fifteen sediment samples were collected in the dam Okpara on board of a boat and with a Heckman bucket at the following depths 5cm, 10, 20, 30, 40 ... 140, 150 cm from the water surface. The samples were stored, since the boat to the laboratory in a portable cooler at 4°C. In the laboratory

we made the removal of stones and plant debris using a mesh of 2 mm diameter size. Wet sediments are sieved through a sieve of 63 μm in diameter and dried in an oven at 90°C. The sediments have been subsequently treated through several analyzes including determination of heavy metals and chemical parameters measuring (pH, conductivity, organic matter etc.).

The physico-chemical parameters (pH, conductivity) were measured using a multi-parameter in situ of the type Combo by HANNA. Chemical analyses were performed in the laboratory. The analytical method for the speciation of Iron and Manganese is that of Tessier *et al.*, [7] based on the sequential extraction of different splits (exchangeable, acid-soluble, reducible, oxidizable and residual). In addition, digestion of sediments was performed, using a microwave oven, by mixing strong acids: $HF-HNO_3-HClO_4$ in (4-5-1) ml [16] proportions. The evaluation of the content of Iron and Manganese in each split has been performed by molecular absorption spectroscopy.

2.3. Sequential Extraction Protocol

The protocol used for the extraction is summarised in **Figure 2**.

3. Results and Discussion

For each studied parameter, we draw the curve of evolution of the calculated contents' average.
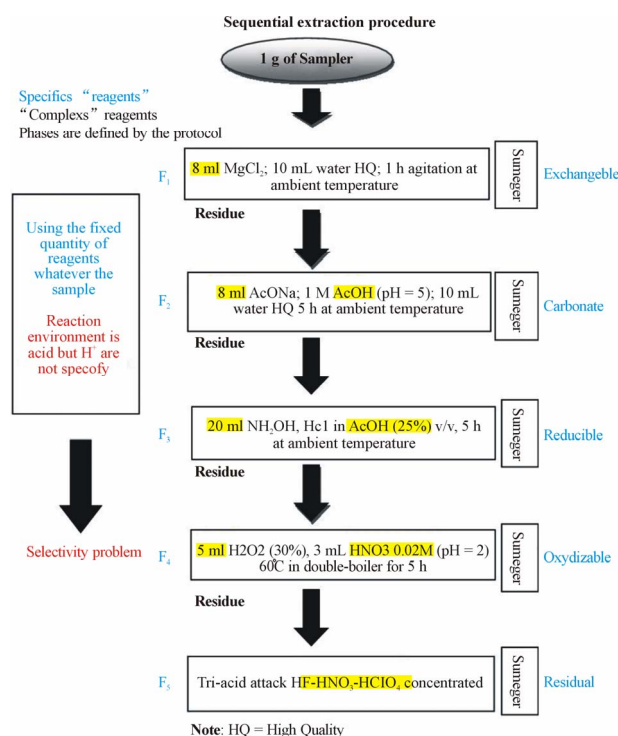

Figure 2. Diagramm of sequential extraction of tessier (1979).

3.1. Physico-Chemical Characteristics of Sediments

3.1.1. The pH of the Sediments

The pH of the sediments in the dam is at an average value of 6.49 indicating that the sediments of the dam are slightly acid (**Figure 3**). This characteristic reflects the tropical ferralitic and sandy-clay nature of the dam.

3.1.2. The Conductivity of the Sediments

The conductivity on an average value of about 126.15 µS/cm (**Figure 4**), it rises to significant peaks at points S_3 (228 µS/cm) and S_{10} (298 µS/cm). This increase could be due to the fact that the dam sediments are rich in monovalent and divalent ions, which come from various domestic and industrial wastes.

3.1.3. Organic Matter (OM)

The organic matter contents observed are decreasing from surface sediments to those of depth showing that the studied sediments are fairly loaded with OM (**Figure 5**). This result can result from the influence of waste water loaded with organic matter. These contents are probably due to significant leaching by rainwater and the return of irrigation water from agricultural land rich in organic substances that are in the vicinity of the dam.
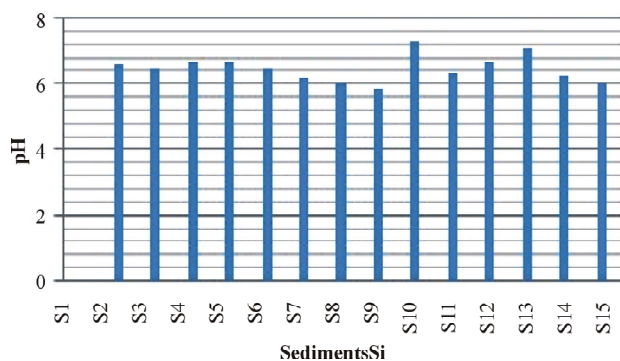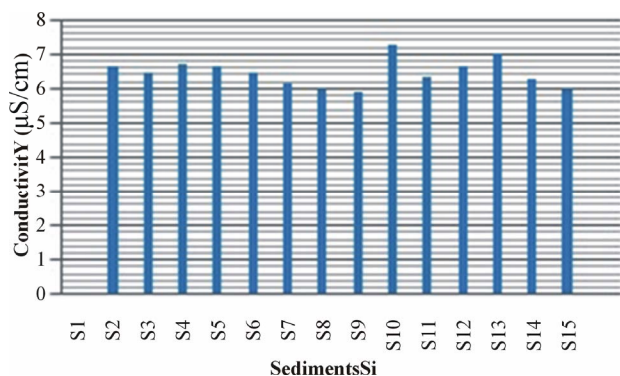

Figure 3. Spatial variation of sediment pH.

Figure 4. Spatial variation of the conductivity of the sediments.

3.2. Analysis of Metals in the Sediments of the Okpara Dam

3.2.1. Iron

Iron is the most abundant metal in the sediments of the dam of Okpara where average levels can reach 14365.026 µg/g (**Table 1**). The enrichment in Iron is due to the regional geological context of the dam. Indeed, during his studies in 1993 the BARBE [17] showed that the geology of the soils of the dam gives it the nature of a soil rich in the metal 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 a horizon of clay and ferric accumulation leaching out of the upper horizon.

Moreover, the presence of Iron in the sediments of the station is usual, since the latter is essentially due partly to the structure of silicates which are of the main components of the sediments [18].

Table 1 shows the distribution of Iron in the different geochemical phases, of the extracts of sediment of the dam of Okpara. It shows that in the sediments of the Okpara, Iron is unevenly distributed in the different geochemical phases of the sediments. It is linked at 65.20%, to metal oxides or reducible fraction, what confirms that the environment is anoxic or reducing. It is also linked to the residual fraction at a proportion of 19.90%, this, be-
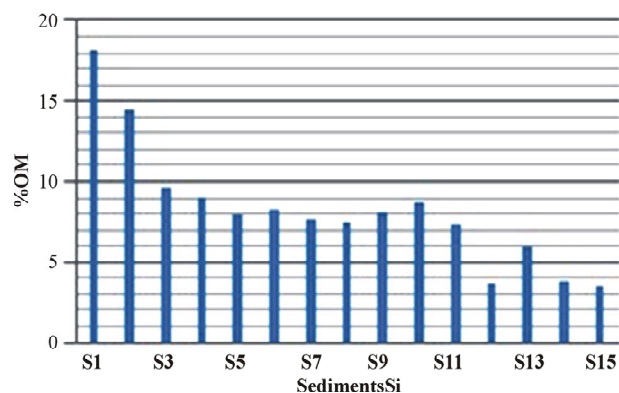

Figure 5. Spatial Variation of the Organic matter.

Table 1. Results of sequential extractions, mass and percentage of Iron.

Iron chemical forms	Iron Concentration (µg/g)	Percentage (%)
Exchangeable Iron (F_1)	198.600	1.38
Acid-soluble Iron (F_2)	510.874	3.55
Reducible Iron (F_3)	9368.700	65.2
Oxydizable Iron (F_4)	1430.201	9.95
Residual Iron (F_5)	2859.65	19.90
Total Fe	14365.026	100

cause the soils of the dam are composed of crystalline clay particles, crystalline minerals and stable network and that manganese is related to the resistant particles during oxidation. The proportion 9.95% observed about the Iron linked to the organic matter is due to anthropogenic pollution originating from sewage, and municipal waste discharge. Moreover, the Iron has a low affinity for carbonates (3.55%).

3.2.2. Manganese

The average manganese content of station 1 studied is 213 mg/g (**Table 2**). This is probably due to the leaching of the soils around the dam that are rich of manganese. The average variation of manganese in the sediments is very irregular and does not seem to be related only to discharges from the agglomeration of Parakou. This result would be due to domestic waste, agricultural leaching and other activities (mechanical garages, industry of vehicles surface treatment with paint, oil distribution stations, one textile industry and one concrete pipes manufacture industry). The same observations were made by Halima B. Bouih *et al*. [18], during their studies on "trace metal contamination in the sediments of Lake Fouarat" in Morocco.

Table 2 also indicates the unequal distribution of manganese in geochemical phases, of the extracts of sediment of the dam of Okpara. Indeed, Manganese is presented in exchangeable form with a proportion of 32.12%. We also observed that this paradoxically Manganese, Iron, detain high affinity to carbonates. By cons, it has an affinity for oxides (13.61%) comparable to that of Iron. It is also presented in the residual fraction with a high proportion (25.77%) and this is due to the nature of the soil of the dam that is composed of crystalline clay particles, stable network crystalline minerals and to the fact that Manganese is related to these particles resistant to oxidation.

4. Conclusion

The results obtained in this work allowed us to make an evaluation of metal contamination of sediments in the

Table 2. Results of sequential extractions; Mn mass and %.

Chimicals Forms of Manganese	Concentration de Mn (µg/g)	percentage (%)
Exchangeable Mn (F_1)	68.601	32.121
Acid-soluble Mn (F_2)	52.647	24.650
Reducible Mn (F_3)	29.062	13.607
Oxydizable Mn (F_4)	8.210	3.844
Residual Mn (F_5)	55.052	25.775
Total Mn	213.573	100

dam of Okpara. The physico-chemical analysis of the sediments showed that the dam was experiencing significant organic pollution vividly noticed in sediments. The concentrations of metals found in the sediments were very high, and one could say that the retention of Okpara was heavily polluted by trace metal elements from different origins. In fact, human activities, wastewater, storm water and those leaching from agricultural lands were among others, responsible for the heavy pollution. The color of the water often observed at the dam could be justified by the high concentrations of the Metal Trace Elements studied. Besides, the fragmentation related to land use in the catchment area of the dam for the intensive cultivation of cotton and other food product with the spraying of large quantity of chemical fertilizers were probably the causes of the lack of balance notice in this aquatic ecosystem.

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