ejpmr, *2017,4(9), 86-93.*

SJIF Impact Factor 4.161

EUROPEAN JOURNAL OF PHARMACEUTICAL
AND MEDICAL RESEARCH
www.ejpmr.com

Research Article
ISSN 2394-3211
EJPMR

ASSESSMENT OF THE DEGREE OF POLLUTION OF HEAVY METALS FROM INTERSTITIAL WATERS AND SURFACE WATER SEDIMENTS: EXAMPLE OF THE UBANGUI RIVER IN BANGUI.

***E. Foto, N. Poumayé, O. Allahdin, B.S. Gonidanga, O. Biteman Mobili and J. Mabingui**

UNESCO Chair, Lavoisier Hydrosciences Laboratory, Faculty of Sciences, University of Bangui, BP 908 BANGUI (Central African Republic).
*UNESCO Chair, Laboratory, Faculty of Sciences University of Bangui, BP 908 BANGUI (Central African Republic).

***Corresponding Author: Dr. E. Foto**
UNESCO Chair, Laboratory, Faculty of Sciences University of Bangui, BP 908 BANGUI (Central African Republic).

Article Received on 26/07/2017 **Article Revised on 06/07/2017** **Article Accepted on 16/08/2017**

ABSTRACT

This study consists of assessing the degree of waters pollution of the UBANGUI River by the heavy metals (trace elements) contained in the sediments taken from different sites. The first results present a global approach to sediment composition as well as the interstitial waters of the UBANGUI River in Bangui, to clarify its nature. Two sampling strategies were followed: 1) seasonal monitoring of the suspended particle concentration in water; 2) the use of DET (Diffusive Equilibrium in Thin Film) technique to characterize the sediments sampled. This approach was used to determine trace element concentrations in order to predict possible remobilization of these elements in the river water used for human consumption.

KEYWORDS: Sediments, trace metal, DET, UBANGUI, Pollution.

INTRODUCTION

The UBANGUI is the main river that serves as a waterway in the Central African Republic. In order to evaluate its potential contamination by certain chemical elements, particularly heavy metals, we have been interested in characterizing sediments that are fine particles that have been transported and then deposited over time and able to transit Water column. This study not only enriches the information on a possible remobilization of these pollutants been in the sediments but also highlighted the environmental problems related to the management of the freshwater sediments in tropical zones.

2 - MATERIALS AND METHODS

2.1- Materials

Sediment samples were analyzed using the DET (Diffusion Equilibrium in Thin Film) method described as follows: The DET technique is based on obtaining a balance between a hydrogel consisting of agarose and an aqueous solution (supernatant water or interstitial water).

This balance, which is obtained by diffusion of the species through the membrane (cellulose acetate filter) and the gel, is reached within a few hours depending on the nature of the medium and the thickness of the gel. The latter is then cut out, eluted in an aqueous phase and the eluate is analyzed, which finally makes it possible to calculate the concentrations of species present in the aqueous starting solution. This gel, the pore size of which is of the order of 20 nm, allows the dosage of the total dissolved fraction comprising the labile part but also some organic complexes.

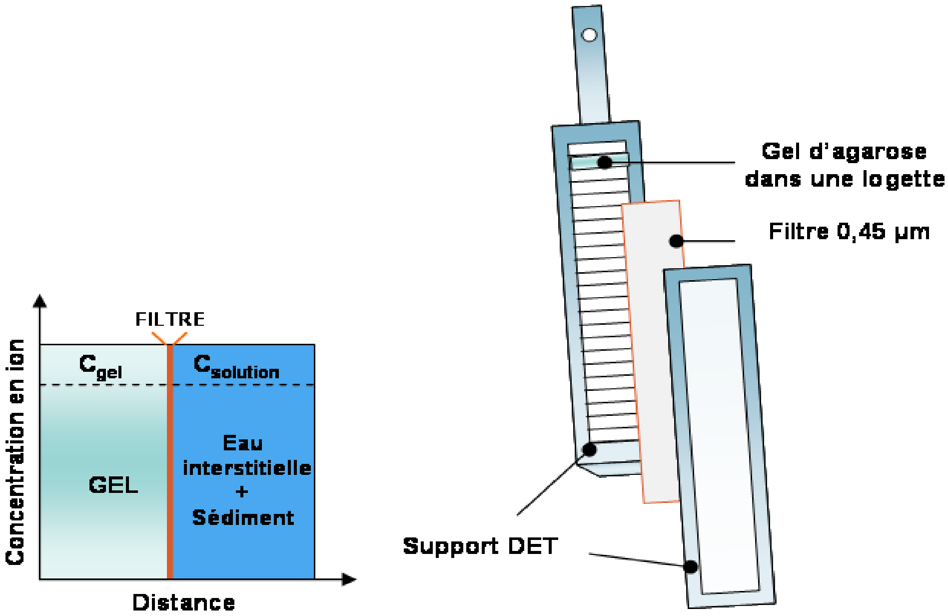

Figure 1: Principle of DET technique and support (for sediment) of agarose gels used for the study of supernatant water and interstitial water.

To avoid diffusion into the gel, a new type of support has been designed with compartments to eliminate this phenomenon of diffusion. The polyacrylamide gel initially was has also replaced by an agarose gel which is easier to handle and can be poured directly into the stalls.

This gel is prepared from a 1.5% agarose (PROLABO) aqueous solution by mixing the predetermined agarose mass with ultra-pure (MilliQ) water brought to 80°C. in a water bath. This solution gels by cooling below 36°C. To dispose of this gel on the DET probe, it is sufficient to reheat the solution, previously prepared, in a bain-marie. This last, clear solution is distributed using a pipette in the various stalls of the support (75 cubicles of 25µL distributed over a height of 15 cm) making sure that there is no freeze- Gel between the various compartments. When gelation is reached, a membrane made of cellulose acetate (Ø = 0.45 µm) is deposited on the surface of the compartments in order to avoid contact between the gel and the sediment particles.

Before deployment in sediment, this DET probe is immersed for 24 hours in a 0.01 mol / L NaCl solution and continuously purged with dinitrogen in order to remove the dissolved oxygen present in the gel. This makes it possible to avoid possible oxidations of reduced species (in particular Fe^{2+} and Mn^{2+}) present in sediments and interstitial waters during insertion of the probe.

In addition, when deployed, the probe should not remain in contact with air oxygen for more than 15 s (Davison et al., 1994).

After removing the protective membrane, the gel in each compartment is lightly removed, weighed (about 25 µg) and then placed in a 1.5 ml tube containing 1 ml of a Suprapur molar nitric acid solution. The samples are then analyzed by ICP - MS.

2.2 Total Sediment Attack Protocol

- Acidic attack

Weigh 0.2 g of sediment, add 10 ml of HF and 5 ml of HNO_3 and then heat to 110°C for 48 hours. Allow to evaporate for 2 hours, add 3 ml HNO_3 + 6 ml HCl heat 24h at 120°C. After evaporating, add again 10 ml of milliQ water and then heat for one hour at 100°C; After cooling, filtered at 45µ and then stored in the scintillation vials.

2.3 Alkaline fusion

200 mg of crushed solid are placed in a platinum crucible, and heated gradually to 450°C. for 1 hour, then held at this temperature for 3 hours. The crucible is cooled to room temperature. 200 mg of lithium tetraborate (Li_2BO_7) and 800 mg of lithium metaborate (LiB_4O_2) are added to this crucible and then heated to 1000-1100°C for 10 min to obtain a total melting of the mixture. After cooling, the resulting residue was dissolved in 200 ml of a 0.5M nitric acid solution. The concentration of the ions in the resulting solution is determined by ICP-AES (coupled induced plasma - atomic emission spectroscopy, Varian pro axial View model).

2.4 Principle of operation of the AES – ICP

This technique allows determining concentrations of trace elements in samples. It is a multi-elementary method. Atomic emission uses the property of atoms to pass from a higher energy level to a lower level by emitting spectral wavelength lines characteristic of an element (Battistel, 1997). This technique therefore relies on the measurement of this energy emitted in the form of a light ray at a specific wavelength, by an atom that goes from an excited state to a lesser state. The excitation of the element is due to its atomization, that is to say its dissociation into atom (M) or free ion. It is considered that the light intensity measured is proportional to the concentration of the element to be increased.

2.5 Principle of analysis by MEB / EDS

The ESEM scanning electron microscope, QUANTA 200 FEI, was used to observe and photograph the surface of sand grains. The elemental analysis of the surface of the support was carried out before adsorption of the dyes using the ESEM / EDS technique (ESEM, Quanta-200-FEI) and controlled by the QUANTA-400 software. For some ESEM analyzes, samples were previously coated with a thin carbon film to avoid the influence of load effects during ESEM analysis. The EDS measurements were carried out at 20 KV under high vacuum at 1 torr, and the maximum pulse output was set at 20 kpps. In the ESEM / EDS analyzes, the surface areas of the target sand grains ranged from 0.5 to 3.5 mm2. Micro-observations along different sections Transverse sand samples rich in iron, aluminum, titanium, etc.

3 - RESULTS AND DISCUSSIONS

3.1- Evolution of suspended materials

We have followed the evolution of suspended matter (SS) in the water of the Ubangi river at several sites in order to assess its variation. The figure shows a high rate of suspended matter during the high water period due to runoff.

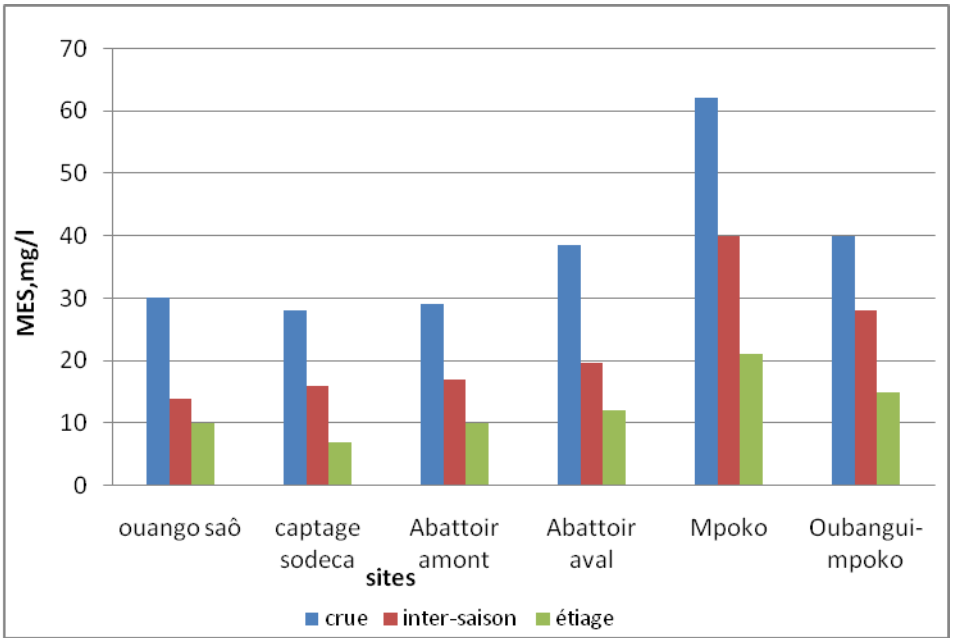

Figure 3: Seasonal variation of suspended matter in water.

3.2 - Chemical characterization of sediments

We are interested in sediments that are likely to exchange pollutants with water. We first carried out an analysis of sediments taken from the UBANGUI using the alkaline fusion technique. This method of dissolving by melting the sample (in a platinum crucible with a mixture of lithium tetraborate (200mg) and lithium metaborate (800mg) at 1100°C. and then dissolved in 0.5M nitric acid) Analysis of the major elements. The very loaded matrix of the resulting solution does not allow for the determination of the minor elements.

The results of analysis of 3 samples of sand and the average contents expressed as oxides are shown in Table 3.1.

Table 3.1: Analysis of 3 sediments (and average analysis) of UBANGUI after alkaline fusion.

sample, % in masse	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	CaO	K_2O	TiO_2
1	92.09	2.38	2.88	0.03	0.15	0.14	0.15	0.53	0.73
2	94.41	1.6	1.82	<ld	0.13	<ld	0.13	0.53	0.18
3	94.17	1.55	2.88	<ld	<ld	<ld	<ld	0.44	0.13
average	93.6±1.3	2.5±0.6	2.5±0.6					0.50±0.05	0.35±0.33

The sediments are mainly made up of quartz about 93.6% and a small proportion of clay and iron compounds (illite or iron oxide).

We obtained an X-ray diffraction spectrum of the sediment fraction obtained after clay enrichment by decantation and removal of the supernatant fraction of less than 2 μm.

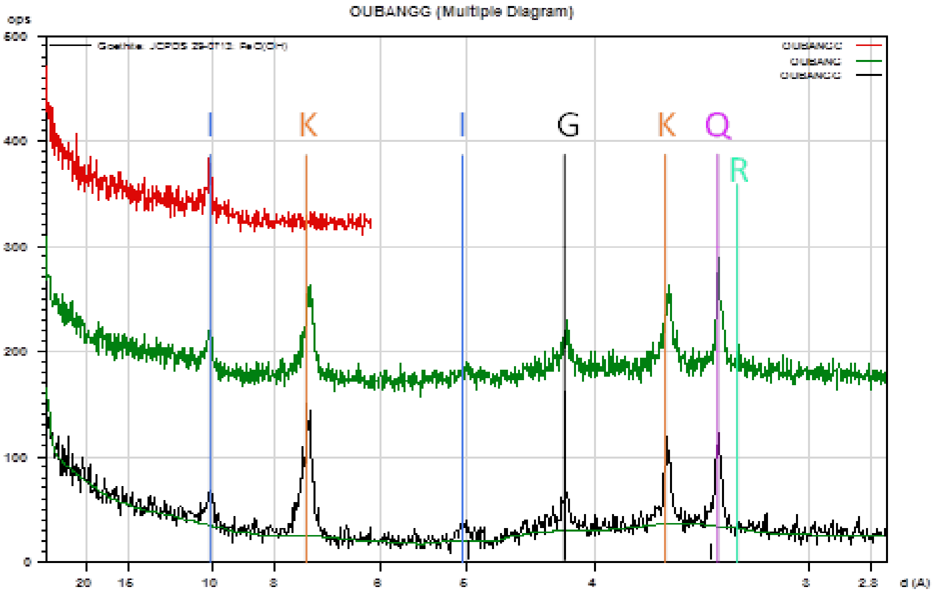

Figure 4 RX diffractogram of clay fraction <2µm (black: sand, green, glycol treatment, red: heated 490°C) (I = illite, K = kaolinite, G = goethite, Q = quartz, R = rutile).

The X-ray diffractogram shows that:-the clay consists mainly of illite and kaolinite. Infacts, the lines corresponding to kaolinite disappear by heating to 490°C. because of the transformation of this mineral into amorphous metakaolinite on X-rays; And the line attributed to illite is not modified by glycol treatment (Holtzapffel, 1985).

- the very low presence of rutile in agreement with the presence of titanium (Table 3.2).

The line corresponding to this weak compound is observable only after heating.- the presence of goethite, an oxide of iron. It may, however, be supposed that some of the iron is bound to the clays. In order to verify this hypothesis, we carried out a "Scanning Electron Microscope" (SEM) study coupled with an "Energy dispersive spectrometry" (EDS) system on sediment grains from the UBANGUI River (Figure 5):

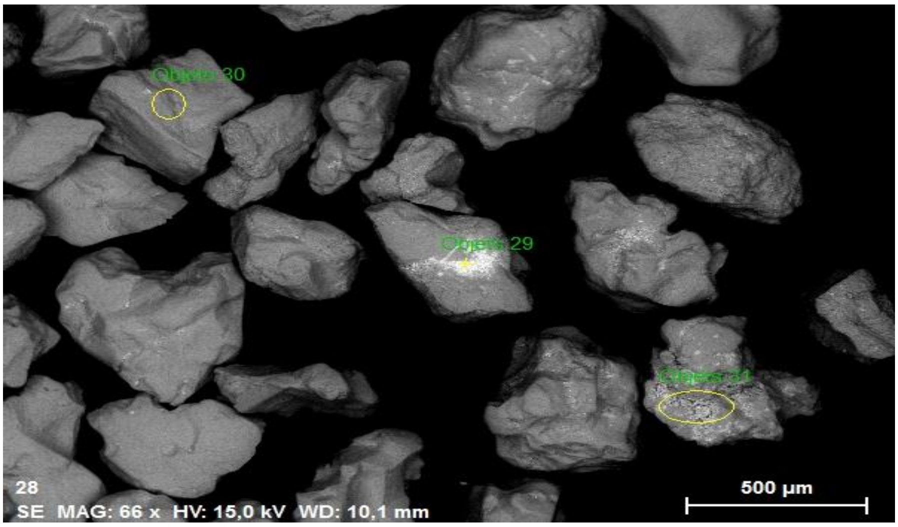

Figure 5: SEM image of sediments of the UBANGUI River.

The concentration of atoms % on the surface of 3 zones referenced (29, 30, 31) in Figure. 5 measured by the EDS system is shown in Table 3.2.

Table 3.2 Atomic percentages of various major elements at the grain surface in zones 29, 30, 31 (see Figure 5).

% atom	Oxygèn	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
zone 29	46.2	0.95	0.69	5.93	17.13	0.06	0.31	0.15	0.35	28.23
zone 30	53.4	0.46	0.29	2.74	40.59	40.99	0.21	0.1	0.06	1.67
zone 31	44.8	0.02	0.14	6.78	32.99	0.33	0.31	0.14	0.2	14.28

It may be noted that:
- white areas (29) are characteristic of "heavy" elements such as iron. The proportion of iron is higher, however, with a small proportion of aluminum. It may be supposed that the surface is composed of iron oxide and a lesser proportion of clay.
- The area at point 30 consists mainly of quartz.

The zone at point 31 could consist of iron oxide and clays such as: illite (K, H_3O) (Al, Mg, $Fe)_2$ (Si, $Al)_4$,O_{10} [$(OH)_2$ H_2O)] and / or kaolinite $Al_2Si_2O_5$ $(OH)_4$. In accordance with the X-ray diffraction spectrum.

Not knowing the exact atomic stoichiometric of the Illite present in our sediments, it is difficult to calculate the proportion of each component.

Nevertheless, it can be assumed that the high proportion of iron with regard to aluminum is in favor of iron oxide. In fact, if the proportion of illite in clays is 25%, the quantity of iron liable to enter into the constitution of illite is negligible with respect to iron oxide.

After studying the major constituents, we evaluated the trace elements in the collected sediments:
- upstream, downstream and near the water catchment area by the water treatment plant.
- Upstream and downstream of the slaughterhouse (abattoir).

The complete attack of the sediment was carried out using a mixture of hydrofluoric, nitric and hydrochloric acids and then the resulting solution was analyzed by ICP-AES after dilution. This total etching method makes it possible to remove the silicon in the form of gaseous H_2 SiF_6 acid and thus avoids the presence of a large matrix during the assay.

Table 3.3: Analysis of "minor" components of UBANGUI sediment grains, * (analyzes carried out by the European Institute of the Environment of Bordeaux).

Eléments, µg/g	upstream captage	Captage Sodeca	downstream Captage	upstream Abattoir *	Downstream Abattoir*	Référence
Al	9291	8357	2698			
Ca	8357	990.7	756	214	214	
Cr	22	17	24	29	16	25
Cu	6	6	7	28	23	22
Fe	9647	7219	13132	5530	12900	
K	2814	3213	1788	830	420	
Mg	343	335	123	120	180	
Na	1265	1434	1140			
Ni	5	5	10	11	3.2	23
Mn				2050	118	
Cd				<0.4	<0.4	0.33
Pb	8	7	6	82	47	25
Hg				0.036	0.037	0.094
Phosphore				734	204	
Zn	18	16	30	79	25	80
MO				22000	18000	
NTK				500	300	
Rapport MO/NTK				44	60	

The MO / NTK (organic carbon / organic nitrogen) ratio in the sediments collected near the slaughterhouse shows that humic acids are stable and difficult to biodegrade. A comparison of pollutant concentrations with the geochemical background of large rivers such as the St. Lawrence River in Canada before industrialization (criteria for assessing the quality of freshwater sediments (pre-industrial area 2007) and for nickel (Saulnier and Gagnon, 1996) shows that these sediments can be considered relatively unpolluted, except for lead in the vicinity of the slaughterhouse, possibly due to local pollution. It can be noted that the sediments near the catchment area are part of the less polluted and that this zone of catchment of water to supply the city was well chosen as suggested previously.

3.3 - Characterization of pore water

In order to study a possible remobilization of the pollutants contained in the interstitial sediments, we used the TEDs (Diffusion Equilibrium in Thin film) technique proposed by Zhang and Davidson (1994) commonly used in the laboratory of the University of Lille. The technique is described above. The gels were prepared in the laboratory in Lille and then immersed in a sealed plastic bag containing oxygen-free Milli-Q water. The probe connected to a small anchor was driven into the sediment by a diver and left for 24 hours and then removed and placed in its oxygen-free bag.

It was then cut as quickly as possible in the laboratory of Bangui in slices of 0.2 cm. Each slice placed in a small container was eluted in 1 cm 3 of a 1M nitric acid solution and returned for ICP-MS analysis after dilution.

Captage area

The catchment area is very disturbed due to the large suction of the water (about 1200m3 / day). Periodically, this area is manually dredged by moving the sediments to make a small channel to avoid clogging of the pumps. The concentrations are therefore fairly homogeneous in the first 4 centimeters.

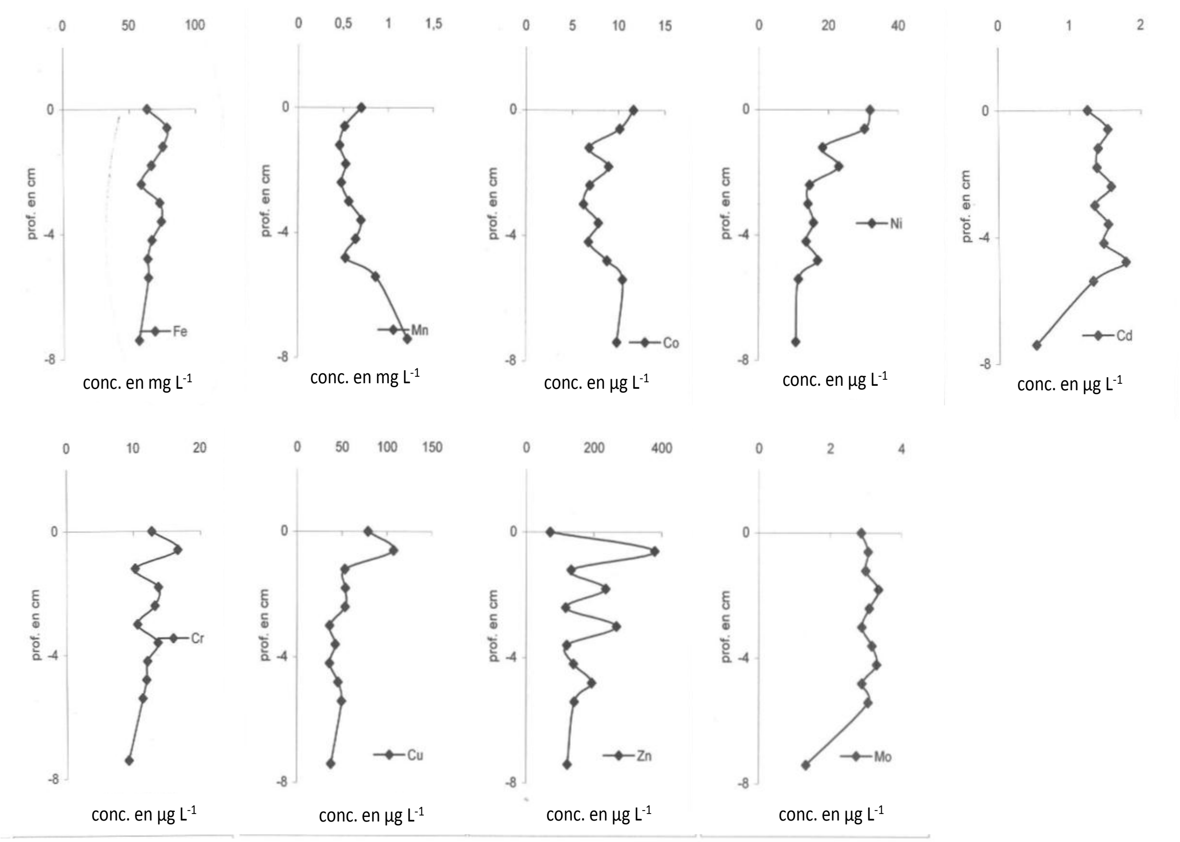

Figure 6: Concentration profiles of dissolved species in interstitial waters from DETs in sediments near the catchment area.

However, it can be noted that the concentrations observed in pore waters are higher than those found in surface waters. Interpretation of the concentration profiles in the sediments near the catchment area is difficult due to the disturbance of the water by the large catchment of water (1200 m^3 / h by 3 pumps of 400 m^3).

The increase in the metal content of interstitial waters in relation to river waters varies by a factor of between 50 and 100 for most metals, except about 150 times for manganese and nearly a factor of 1000 for the iron. This increase in the concentrations of the different species on the surface of the sediment results from (bio) geochemical phenomena (known as early diagenesis in the sediment: reduction by bacteria of oxides of manganese (II) and iron (II) in ions Manganese and ferrous metals and the release of the associated metals

The concentrations of iron and manganese very little in the sediment slices between 0 and 5 cm Between 6 and 8 cm the manganese concentration increases or the medium becomes more reducing and the reduction of Sulfates to sulphide begins.

- a reduction of soluble molybdates in insoluble molybdenum (II) waters and therefore a decrease in Mo concentration (L. Lesven 2008, Y. Gao, 2009).

Precipitation of iron into sulphide.

High levels of metal ions in pore waters can cause point pollution during manual sediment removal. It is necessary to mitigate this risk, due to the low volume of pore water compared to that of the water collected by the pumps.

We placed a second DET in the UBANGUI, not far from the Abattoir, where some of the discharges are eliminated towards the UBANGUI. The surface observed levels are higher than those found in the waters due to a slight agitation of the surface layer of the sediment when the DET penetrates into the sediment or an initiation of reduction of the oxides of iron and manganese. This hypothesis is supported by the decrease of molybdenum at the surface. Remind that molybdenum dissolved in molybdate form can be reduced in insoluble Mo (II) sediments.

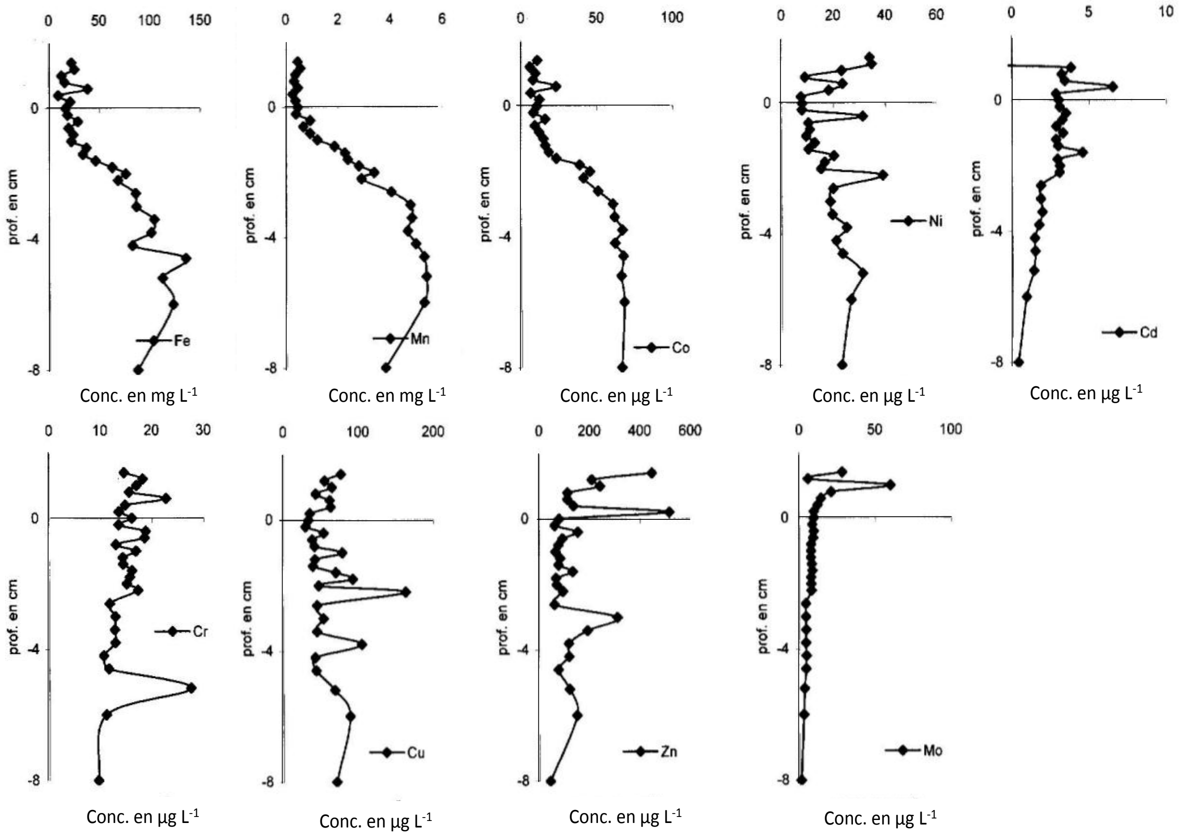

Figure 7 Concentration profiles of dissolved species in interstitial waters from DETs in sediments near slaughterhouse discharge.

The profiles of the interstitial waters obtained have an identical appearance to that found in the sediments of the rivers of the Nord Pas de Calais, although the iron and manganese values are much higher.

Since the soils are ferralitic, it can be assumed that the quantity of organic matter is much closer to the slaughterhouse and the bacterial activity is more intense. The iron and manganese contents are higher than near the catchment area. The temperature facilitates the reduction and solubility of the iron. Reduction of iron and manganese oxides to dissolved iron (II) and Mn (II) salts takes place as early as the 1 cm sedimentary section, resulting in the release of chromium and nickel. The Cu, Cd, Cr and Pb contents very little with some fluctuations due to the heterogeneity of the sediment or the presence of local microniches.

4- CONCLUSION

Chemical characterization showed no metallic pollution. Nevertheless, more information is needed to better understand the effects of chemical contaminants on the aquatic environment and to better assess sediment quality. The speciation and the distribution of trace metals in pore waters and sediment particles were assessed through of an experimental techniques. The results presented here fill some of the important knowledge gaps related to the nature of the Ubangi sediments.

5 – ACKNOWLEDGMENTS

The authors are also grateful to the French Embassy in Bangui, Nord Pas-de-Calais Region, Nord Pas-de-Calais Water Agency, UNESCO, University of Lille1, University of Bangui; the authors would like to thank Ludovic Leven, Romain Descamps and the European Institute of the Environment of Bordeaux for their technical assistance.

BIBLIOGRAPHICAL REFERENCES

1. Adeline Charriau, Ludovic Lesven, Yue Gao, Martine Leermakers, Willy Baeyens, et al. 2010, Trace metal behaviour in riverine sediments: role of organic matter and sulphides. Applied Geochemistry, Elsevier, 26(1): 80-90.

2. Billon, G., Ouddane, B., Recourt, P., Boughriet, A., 2002. Depth Variability and some Geochemical Characteristics of Fe, Mn, Ca, Mg, Sr, S, P, Cd and Zn in Anoxic Sediments from Authie Bay (Northern France). Estuar. Coast. Shelf. S. 55: 167-181.
3. Billon, G., Ouddane, B., Laureyns, J., Boughriet, A., 2003. Analytical and thermodynamic approaches to the mineralogical and compositional studies on anoxic sediments. J. Soil. Sediment. 3: 180-187.
4. Béranger S., Guérin V., Picot G., 2006. CAPHEINE: Caractérisation des phénomènes de transfert en zone insaturée des éléments traces Tome III, CNRSSP/06/07. 202 p.
5. Callède, J., Boulvert, Y. & Thiébaux, J. P., 1992. Le bassin de l’Oubangui. Coll. Monographies Hydrologiques, Orstom, Paris.
6. Chiang, W.H., 2005. 3D-groundwater modeling with PMWIN: a stimulation system for modeling flow and transport processes. Springer.
7. Critères por l’évaluation de la qualité des sediments au Québec et cadres d’application IBSN 978-0-662-08296-5.
8. Davidson, W. and Zhang, H. In situ speciation measurements of trace components in natural waters using thin films gels, 1994; Nature 367: 546 – 548.
9. Lesven, L., Gao, Y., Billon, G., Leermakers, M., Ouddane, B., Fischer, J.C., Baeyens, W., 2008. Early diagenetic processes aspects controlling the mobility of dissolved trace metals in three riverine sediment columns. Sci. Total Environ. 407: 447-459.
10. Yayer J., 1951. Caractéristiques hydrographiques de l’Oubangui. Rapport de mission. Service Commun d’Entretien des Voies Navigables, Bangui (RCA), 106 p.144.
11. Zhang, H. and W. Davidson., 1995. Performance Characteristics of Diffusion Gradients in Thin films for the in situ measurement of trace metals in aqueous solution. Analytical Chemistry, 67(19): 3391-3400.
12. Zheng, C. 1990. Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion and Chemical Reaction of Contaminants in Groundwater Systems By S.S. Papadopulos & Associates, Inc.
13. Seyler, P., Elbaz- Poulichet, F, 1996. Biogéochimique contrôle sur la variabilité temporelle des concentrations en éléments traces dans la rivière Oubangui.
14. Shouliang Zhang., 2011. Mineralogy, morphology, and textural relationships in coatings on quartz grains in sediments in a quartz-sand aquifer. Journal of contaminant hydrology, 124: 57-67.
15. Sondag, F. A. Laraque & C. Riandey, 1993. Chimie des eaux du fleuve Congo à Brazzaville et de l’Oubangui a Bangui. Grands Bassins Fluviaux, Paris, 22-24 novembre.
16. Critères pour l’évaluation de la qualité des sediments au Québec et cadres d’application IBSN 978-0-662-08296-5.
17. Holtzapfel, T., 1985. Les minéraux argileux: préparation, analyse diffractiométrique et détermination, Société Géologique du Nord publication n°12,13.