

Diagnosis of Lead Pollution of Surface Waters of a River: Case of the Djiri River in the Republic of Congo

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Abstract

This research work deals with the physico-chemical analysis of the surface water of the Djiri river with the aim of preventing the population against possible water pollution.

The analysis of the samples collected in the Djiri river revealed the presence of lead in these waters at levels exceeding the WHO guideline values: an average annual pollution (0.93 mg / l) which is visibly above the WHO guideline value (0.01mg / l).

The in situ data of the Djiri river revealed a significant drop in flow between the period 2016 characterized by a divergence index of 0.82344 thus highlighting a hydrological situation for which the actors of national hydrology will absolutely have to implement measures. Remedial mechanisms to protect this river against possible disappearance.

Keywords: metallic pollution, water quality standards, indicators and degree of pollution

1. Introduction

The Djiri river is located in the 8th arrondissement of Brazzaville, with a flow of 25 m³/s, it flows into the Congo river. The demographic growth of the city of Brazzaville has pushed many populations to occupy plots of land over the past ten years and to live in the Djiri district, so all around the Djiri river are dwellings where Socioeconomic activities are carried out.

The riparian populations use the waters of the Djiri for various uses:

- Swimming;
- Laundry;
- Washing up;
- Food washing.

An electric steelworks is erected 1km from the Djiri bridge (1st exit). It is likely to release toxic particles into the waters of the Djiri River that can cause damage to the environment in general and to human health in particular.

This work is part of the protection of the water ecosystem and the health risk coverage of neighboring populations.

Indeed, the problem of water pollution is closely linked to that of water quality and requires special attention in the Congo as in most developing countries; the faster a diagnosis of poor quality of water for use is made, the quicker the means can be implemented to provide solutions to cover health and environmental risks.

During this study, we estimated the physico-chemical and metallic quality of Djiri's surface water from two sampling points: Djiri Station (Upstream Point) and Old Djiri Manianga Bridge (Downstream Point).

Twelve months of sampling and physicochemical analyzes have made it possible to demonstrate overall the pollutant nature of lead, the relative values of which for the monthly in situ measurement excess are strictly positive

and consequently of the values of the pollution index strictly higher than the unit characterizing an exceeding of the WHO guide values for this metal (WHO standards, 2006). Lead is a point source of pollution.

2. Materials and Methodologies

2.1 Materials

The reagents, hardware and software requirements necessary for the implementation of the sampling process, physico-chemical analyzes and analysis of the data resulting from the physico-chemical characterization of the water are summarized in Table 7:

Table 1. Equipment, Product and Software for the acquisition of data from physico-chemical analyzes of water

| N° | Product/Software | Material type | Goal |
|----|--------------------|--------------------|---|
| 1 | Precision scale | | Mass measurement in other words the concentration of sand, suspended matter, dry residue and empty beaker |
| 2 | PH meter | Measuring device | Automatic in situ pH measurement of water |
| 3 | Conductivity meter | | Determination of the in situ electrical conductivity of water |
| 4 | Spectrometer | | Determination of the concentrations of elements dissolved in a given sample |
| 5 | Sieve | | Filtering the samples in their raw state and collecting the sand before any other handling |
| 6 | GPS | | Acquisition of the geographical coordinates of the sampling points |
| 7 | Plastic Bottles | Sampling Equipment | Water withdrawal from the river |
| 8 | MapInfo | Software | Realization of the GIS |
| 9 | MS EXCEL 2016 | | Realization of statistical data aggregates |
| 10 | XLSTAT | | Data analysis |
| 11 | MS ACCESS 2016 | | Realization of the database |
| 12 | Chemical Product | Chemical Reagents | To assess the levels of chemical species in water (Copper, Lead, Chromium, Iron, etc.) |

Source: Field data (Physico-chemical Analysis Laboratory, IRSEN).

Table 1 summarizes the chemicals, hardware and software allowing the acquisition of physico-chemical analysis data and data to be estimated from the algorithms for predicting experimental data.

2.2 Methodologies

2.2.1 Location of Sampling Points

The study takes place on the Djiri river and two sampling points were chosen based on their accessibility for sampling on the Djiri river (Table 5.1). The geographic coordinates of the upstream (S1) and downstream (S2) points are shown in Table 2.

Table 2. Geographic coordinates of points

| SITES | POSITION | LONGITUDE DECIMAL DEGREES | IN LATITUDE DECIMAL DEGREES |
|-------|------------|------------------------------|-----------------------------------|
| S1 | UPSTREAM | 15,3123 | -4,1475 |
| S2 | DOWNSTREAM | 15,4445 | -4,1615 |

S1: Old Djiri Bridge 1st Exit (Station)

S2: Old Djiri Bridge 2nd Exit

The upstream point (S1) is located 1km away from the electric steelworks.

All samples were taken over 12 months between May 2016 and December 2017 at two points (Upstream and Downstream) chosen because of their accessibility and their proximity to the target industrial site.

2.2.2 Physico-Chemical Analysis Methodology

During our study and using plastic bottles of 1.5l liter capacity, washed and rinsed beforehand with demineralized water, the sample is taken by immersing the bottle 25 cm from the free surface. The water samples, taken, are transported to the laboratory immediately for analysis. 20 physico-chemical parameters were measured to characterize the environment studied between May 2016 and December 2017.

Samples of the water to be analyzed were taken in plastic bottles in areas where water is not stagnant at the upstream point and downstream point from the plant chosen for the study.

Monthly water samples are taken from two selected points on the Djiri River:

- Djiri station (Near Old Djiri Bridge 1st North Exit);
- Manianga (Djiri Bridge 2nd North Exit).

The old Djiri bridge taken as the point of origin.

- Frequency: one sample per month and per sampling point
- Physico-chemical analyzes at the IRSEN Analysis Laboratory: for the identification of pollutants:
- Concentration of sand by sifting through a 0.0065mm sieve
- Material in suspension by filtration through a 0.45 micrometer filter
- Dry residue by evaporation at 105 ° C in an oven
- Ion concentration by a direct spectrometer and palintest.

Sampling marks the starting point of the process of acquiring experimental data;

Sampling consists of carrying out a series of water samples from the Djiri river once a month at each point chosen in order to carry out physicochemical analyzes leading to the qualitative state of the waters of the Djiri; These physico-chemical analyzes will take place in the IRSEN's physico-chemical analysis laboratory;

The protocol adopted for the analysis of the samples is spectrophotometry and the spectrophotometric analysis is based on the following parameters:

PH, T°C, CE, Ca²⁺, Mg²⁺, K⁺, TAC, NH₄⁺, Cu²⁺, Al³⁺, Mn²⁺, SO₄²⁻, PO₄³⁻, Fe^{tot}, NO₃⁻, Cr, Cl⁻, Sand, Suspended matter, Dry residue.

The principle of this protocol is described as follows:

For each parameter, the sample is calibrated i.e. the measurement of the wavelength of each parameter in the sample is determined;

With the 10 ml water cuvettes, add the reagents (crush the reagent tablets and mix with 10 ml of water);

The mixture obtained by putting together the crushed pellets and 10 ml of water, is placed in a direct spectrophotometer and the measurements immediately appear on the screen of the spectrophotometer.

Table 3. Codes used for the physico-chemical and metallic parameters evaluated

| SYMBOL | DESIGNATION |
|-------------------------------|--------------------------------|
| Al ³⁺ | Aluminium |
| Ca ²⁺ | Calcium |
| CE | electrical conductivity |
| Cl ⁻ | chlorine |
| Cr | Chromium |
| Cu ²⁺ | Copper |
| Fe ^{tot} | Total iron |
| K ⁺ | Potassium |
| MES | Suspended matter |
| Mg ²⁺ | Magnesium |
| Mn ²⁺ | Manganese |
| NH ₄ ⁺ | Ammonium |
| NO ₃ ⁻ | Nitrate |
| Pb ²⁺ | Lead |
| PH | Hydrogen potential |
| po ₄ ³⁻ | Phosphate |
| RS | Dry residue |
| sables | Sand |
| SO ₄ ²⁻ | Sulfate |
| T°C | Temperature in degrees Celcius |
| TAC | Full alkalimetric titer |

2.2.3 Metallic Pollution Assessment Methodology

-Determination of the in situ measurement excess Δ_C between the downstream point and the upstream point for each physico-chemical, chemical or metallic parameter at each point and at each moment:

$$\Delta_C = \text{Measured}_{\text{Downstream}} - \text{Measured}_{\text{Upstream}} \quad (1)$$

-**Indice de Pollution IP** pour chaque paramètre en chaque point et à chaque instant:

$$\text{IP} = \frac{\Delta_C}{\text{GuideValue}} \quad (2)$$

If $\text{IP} > 1$ Then the OMS guide value has been exceeded for the parameter analyzed otherwise no exceedance is observed.

- **Pollution degree** for each parameter at each point and at each moment:

Pollution degree for each parameter at each point and at each moment:

$$\text{D}^\circ\text{P} = \text{Measured}_{\text{Downstream}} - \text{Guide}_{\text{GuidValue}} \quad (3)$$

If $\text{D}^\circ\text{P} > \text{Measured}_{\text{Upstream}}$ Then there is pollution otherwise no pollution observed.

-**Evaluation of the metal flux:**

The flux is defined as the mass of the pollutant flowing over a surface in one year, it is expressed in tonnes per year.

$$\text{Metallic}_{\text{Flux}} = 31.536 * \text{Average}_{\text{DailyFlux}} * \text{Over}_{\text{measurement}} \quad (4)$$

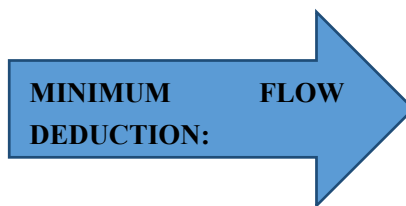
Minimum metal Flux:

If $\text{IP} > 1$ then $\Delta_C > \text{WHO}_{\text{GuideValue}}$

THE FOLLOWING INEQUALITY IS OBTAINED:

$$Average_{DailyFlux} * \Delta_C > Average_{DailyFlux} * WHO_{GuideValue}$$

$$Minimum_{metallicFlux} = Average_{DailyFlow} * WHO_{GuideValue} \quad (5)$$



The minimum flux is the flux corresponding to a pollutant concentration equivalent to the WHO guideline value.

3. Results and Discussion

3.1 Results

3.1.1 Characterization of the Waters of the Djiri River

The physico-chemical analyzes of the samples collected enabled the following results to be obtained:

Table 4. Summary of downstream observations [MG/L]

| DOWNSTREAM | | | | | | | | | | | | |
|-------------------------------|-------------|-------|-------|-------|-------|-------|-------|------|------|------|-------|------|
| Physico | TIME[Month] | | | | | | | | | | | |
| Chemical | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Parameter | | | | | | | | | | | | |
| Al ³⁺ | 0,001 | 0,03 | 0,12 | 1,75 | 0,08 | 0,8 | 0,9 | 0,9 | 0,7 | 0,9 | 0,9 | 0,13 |
| Ca ²⁺ | 9 | 15 | 18 | 21 | 16 | 12 | 13 | 10 | 12 | 13 | 12 | 16 |
| CE | 7,58 | 7,17 | 8,14 | 9,1 | 8 | 8 | 10,2 | 8,22 | 9,33 | 10,1 | 6,4 | 5,99 |
| Cl ⁻ | 8,4 | 2,02 | 3 | 2,11 | 2,97 | 1,7 | 2,32 | 2 | 2,25 | 3,08 | 3,67 | 4,18 |
| Cr | 2,05 | 0,08 | 0,09 | 0,15 | 0,09 | 0,08 | 0,09 | 0,09 | 0,06 | 0,08 | 0,06 | 0,07 |
| Cu ²⁺ | 0,3 | 0,9 | 0,17 | 0,21 | 0,15 | 0,9 | 0,1 | 0,11 | 0,8 | 0,9 | 0,8 | 0,11 |
| Fe ^{tot} | 4,1 | 0,016 | 0,022 | 0,022 | 0,026 | 0,014 | 0,018 | 0,01 | 0,09 | 0,01 | 0,08 | 0,09 |
| K ⁺ | 3,7 | 4,2 | 4,1 | 4,7 | 4 | 2,9 | 2,8 | 2,7 | 3,4 | 2 | 1,8 | 2 |
| MES | 8,4 | 13,25 | 18,08 | 24,7 | 22,08 | 9,13 | 7,22 | 13 | 14,4 | 13,3 | 10,22 | 12,2 |
| Mg ²⁺ | 11 | 11 | 13 | 11 | 12 | 10 | 10 | 10 | 14 | 12 | 11 | 11 |
| Mn ²⁺ | 1,77 | 1,7 | 1,76 | 2,01 | 1,81 | 1,15 | 2,18 | 1,12 | 0,99 | 1,66 | 0,98 | 0,98 |
| NH ₄ ⁺ | 0,002 | 0,09 | 0,18 | 0,19 | 0,08 | 0,1 | 0,12 | 0,9 | 0,09 | 0,08 | 0,06 | 0,09 |
| NO ₃ ⁻ | 0,06 | 2,86 | 3,04 | 3,75 | 3,07 | 3,02 | 2,99 | 4,44 | 6,07 | 6,22 | 8,55 | 9,76 |
| Pb ²⁺ | 2,8 | 0,77 | 1,07 | 1,13 | 0,62 | 0,9 | 0,27 | 0,5 | 0,8 | 0,73 | 0,9 | 0,83 |
| PH | 5,16 | 6,73 | 6,15 | 6,22 | 6,08 | 6,17 | 6,22 | 6,19 | 6,08 | 6,18 | 6,32 | 6,24 |
| po ₄ ³⁻ | 0,01 | 0,3 | 0,28 | 0,28 | 0,22 | 0,16 | 0,2 | 0,19 | 0,13 | 0,14 | 0,13 | 0,15 |
| RS | 0,62 | 31 | 37,5 | 40,2 | 37,5 | 20,4 | 18,9 | 25,6 | 28,4 | 35 | 39,2 | 42,9 |
| sables | 5,78 | 2,12 | 9,7 | 10,6 | 9,7 | 2,13 | 3,01 | 7,55 | 11,5 | 15,7 | 13,7 | 16,4 |
| SO ₄ ²⁻ | 0,14 | 21 | 25 | 27 | 9,3 | 18 | 29 | 13 | 10 | 13 | 12 | 17 |
| T°C | 28,2 | 28,2 | 27,7 | 27 | 27 | 27,8 | 27,9 | 27 | 27 | 26,8 | 26,8 | 26,4 |
| TAC | 179 | 199 | 201 | 187 | 187 | 150 | 158 | 110 | 99 | 99 | 94 | 101 |

Table 4 illustrates a summary of in situ measurements resulting from sampling carried out on the Djiri river at the downstream point;

Table 5. Summary of upstream observations[MG/L]

| UPSTREAM | | | | | | | | | | | | |
|-------------------------------|------------|------|-------|-------|------|-------|------|------|-------|------|------|------|
| Physico | TIME[MG/L] | | | | | | | | | | | |
| Chemical | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Parameter | | | | | | | | | | | | |
| Al ³⁺ | 0,001 | 0,01 | 0,9 | 1,2 | 0,06 | 0,6 | 0,7 | 0,5 | 0,5 | 0,8 | 0,7 | 0,1 |
| Ca ²⁺ | 4 | 40 | 14 | 16 | 6 | 10 | 11 | 9 | 11 | 10 | 11 | 14 |
| CE | 7,12 | 9,14 | 9,4 | 11,2 | 9,75 | 7,7 | 8,4 | 7,18 | 8,88 | 9,05 | 4,18 | 4,7 |
| Cl ⁻ | 4,5 | 2,26 | 1,8 | 1,87 | 1,3 | 1 | 2,1 | 17 | 2,1 | 1,75 | 2,11 | 3,44 |
| Cr | 1,6 | 0,06 | 0,08 | 0,09 | 0,09 | 0,06 | 0,08 | 0,05 | 0,04 | 0,06 | 0,05 | 0,06 |
| Cu ²⁺ | 0,3 | 0,6 | 0,15 | 0,17 | 0,9 | 0,8 | 0,9 | 0,6 | 0,5 | 0,6 | 0,6 | 0,8 |
| Fe ^{tot} | 2,5 | 0,1 | 0,016 | 0,021 | 0,08 | 0,012 | 0,01 | 0,09 | 0,08 | 0,07 | 0,06 | 0,09 |
| K ⁺ | 6 | 2,1 | 3,9 | 3,5 | 44 | 2,2 | 2,7 | 2,1 | 3 | 1,9 | 1,2 | 1,8 |
| MES | 4,5 | 14,9 | 13 | 15,2 | 2,76 | 9 | 11,1 | 10,9 | 11,14 | 10,5 | 8,44 | 11 |
| Mg ²⁺ | 7 | 9 | 10 | 9 | 10 | 8 | 9 | 8 | 10 | 12 | 8 | 9 |
| Mn ²⁺ | 1,64 | 0,75 | 1,55 | 1,17 | 1,17 | 1,1 | 2,14 | 1,07 | 0,97 | 0,98 | 0,95 | 0,82 |
| NH ₄ ⁺ | 0,42 | 0,04 | 0,09 | 0,12 | 0,48 | 0,07 | 0,06 | 0,08 | 0,07 | 0,06 | 0,05 | 0,07 |
| NO ₃ ⁻ | 0,04 | 3,18 | 2,77 | 3,14 | 3,7 | 2,05 | 4,17 | 3,18 | 4,6 | 4,51 | 5,01 | 8,96 |
| Pb ²⁺ | 1,42 | 0,36 | 0,8 | 0,83 | 0,44 | 0,5 | 0,17 | 0,3 | 0,7 | 0,6 | 0,5 | 0,7 |
| PH | 5,14 | 5,75 | 6,05 | 6,7 | 5,4 | 6,04 | 6,13 | 6,17 | 5,97 | 6 | 6,25 | 6,17 |
| po ₄ ³⁻ | 0,01 | 0,17 | 0,16 | 0,28 | 0,18 | 0,14 | 0,18 | 0,16 | 0,1 | 0,8 | 0,5 | 0,17 |
| RS | 0,45 | 33,1 | 23,3 | 37,7 | 28,7 | 20 | 27 | 22,9 | 25,7 | 30,1 | 33,7 | 41 |
| sables | 9,91 | 5,5 | 8,2 | 9,12 | 4,79 | 7,4 | 8,04 | 7,12 | 9,18 | 8,5 | 10 | 15 |
| SO ₄ ²⁻ | 0,13 | 3,12 | 20 | 23 | 8,4 | 13 | 8,75 | 11 | 9 | 11 | 10 | 14 |
| T°C | 28,4 | 28 | 27,9 | 27,2 | 26,4 | 27 | 27,4 | 26,2 | 26,7 | 26,9 | 26,4 | 26,1 |
| TAC | 95 | 187 | 175 | 122 | 95 | 100 | 105 | 99 | 97 | 88 | 84 | 92 |

Table 5 illustrates a summary of the in situ measurements resulting from the sampling carried out on the Djiri river at the upstream point.

Table 6. Extreme and average values of upstream in situ measurements[MG/L]

| UPSTREAM | | | |
|-------------------------------|-----------|-----------|---------------|
| Physico | | | |
| Chemical | | | |
| Parameter | MIN[MG/L] | MAX[MG/L] | AVERAGE[MG/L] |
| Al ³⁺ | 0,001 | 1,2 | 0,505916667 |
| Ca ²⁺ | 4 | 40 | 13 |
| CE | 4,18 | 11,2 | 8,058333333 |
| Cl ⁻ | 1 | 17 | 3,435833333 |
| Cr | 0,04 | 1,6 | 0,193333333 |
| Cu ²⁺ | 0,15 | 0,9 | 0,576666667 |
| Fe ^{tot} | 0,01 | 2,5 | 0,26075 |
| K ⁺ | 1,2 | 44 | 6,2 |
| MES | 2,76 | 15,2 | 10,203333333 |
| Mg ²⁺ | 7 | 12 | 9,083333333 |
| Mn ²⁺ | 0,75 | 2,14 | 1,1925 |
| NH ₄ ⁺ | 0,04 | 0,48 | 0,134166667 |
| NO ³⁻ | 0,04 | 8,96 | 3,775833333 |
| Pb ²⁺ | 0,17 | 1,42 | 0,61 |
| PH | 5,14 | 6,7 | 5,980833333 |
| po ₄ ³⁻ | 0,01 | 0,8 | 0,2375 |
| RS | 0,45 | 41 | 26,970833333 |
| sables | 4,79 | 15 | 8,563333333 |
| SO ₄ ²⁻ | 0,13 | 23 | 10,95 |
| T°C | 26,1 | 28,4 | 27,05 |
| TAC | 84 | 187 | 111,5833333 |

Table 6 presents the extreme and average values of the upstream observations:

- The PH oscillates between 5.14 and 6.7, which means that the studied medium is acidic (PH <7);
- The electrical conductivity EC oscillates between 4.18 μS / cm and 11.2 μS / cm therefore EC <100 μS / cm which implies low mineralization of the water and does not promote the movement of electrical charges in the water, in particular ions Pb²⁺;
- The temperature fluctuates between 26.1 ° C and 28.4 ° C;
- The lead content varies between 0.17 mg / l and 1.42 mg / l.

Table 7. Extreme and average values of downstream in situ measurements [MG/L]

| DOWNSTREAM | | | |
|-------------------------------|------------------|------------------|----------------------|
| Physico | | | |
| Chemical | | | |
| Parameter | MIN[MG/L] | MAX[MG/L] | AVERAGE[MG/L] |
| Al ³⁺ | 0,001 | 1,75 | 0,600916667 |
| Ca ²⁺ | 9 | 21 | 13,91666667 |
| CE | 5,99 | 10,2 | 8,185833333 |
| Cl ⁻ | 1,7 | 8,4 | 3,141666667 |
| Cr | 0,06 | 2,05 | 0,249166667 |
| Cu ²⁺ | 0,1 | 0,9 | 0,454166667 |
| Fe ^{tot} | 0,01 | 4,1 | 0,374833333 |
| K ⁺ | 1,8 | 4,7 | 3,191666667 |
| MES | 7,22 | 24,7 | 13,83166667 |
| Mg ²⁺ | 10 | 14 | 11,33333333 |
| Mn ²⁺ | 0,98 | 2,18 | 1,509166667 |
| NH ₄ ⁺ | 0,002 | 0,9 | 0,165166667 |
| NO ₃ ⁻ | 0,06 | 9,76 | 4,485833333 |
| Pb ²⁺ | 0,27 | 2,8 | 0,943333333 |
| PH | 5,16 | 6,73 | 6,145 |
| po ₄ ³⁻ | 0,01 | 0,3 | 0,1825 |
| RS | 0,62 | 42,9 | 29,76833333 |
| sables | 2,12 | 16,4 | 8,990833333 |
| SO ₄ ²⁻ | 0,14 | 29 | 16,20333333 |
| T°C | 26,4 | 28,2 | 27,31666667 |
| TAC | 94 | 201 | 147 |

Table 7 shows extreme and mean values of downstream observations:

- The PH oscillates between 5.16 and 6.73, which means that the studied medium is acidic (PH <7);
- The electrical conductivity EC oscillates between 5.99 μS / cm and 10.7 μS / cm, therefore EC <100 μS / cm which implies a low mineralization of the water and does not promote the movement of electrical charges in the water, in particular ions Pb²⁺;
- The temperature oscillates between 26.4 ° C and 28.2 ° C;
- The lead content varies between 0.27 mg / l and 2.8 mg / l.

3.1.2 Water Pollution Assessment

- Spatial variation of experimental measurement

Table 8. Measurement excess between the upstream point and the downstream point

| Over measurement | [MG/L] | | | | | | | | | | | |
|-------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Physico-Chemical | TIME[Month] | | | | | | | | | | | |
| Parameter | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Al ³⁺ | 0 | 0,02 | -0,78 | 0,55 | 0,02 | 0,2 | 0,2 | 0,4 | 0,2 | 0,1 | 0,2 | 0,03 |
| Ca ²⁺ | 5 | -25 | 4 | 5 | 10 | 2 | 2 | 1 | 1 | 3 | 1 | 2 |
| CE | 0,46 | -1,97 | -1,26 | -2,1 | -1,75 | 0,3 | 1,8 | 1,04 | 0,45 | 1,05 | 2,22 | 1,29 |
| Cl ⁻ | 3,9 | -0,24 | 1,2 | 0,24 | 1,67 | 0,7 | 0,22 | -15 | 0,15 | 1,33 | 1,56 | 0,74 |
| Cr | 0,45 | 0,02 | 0,01 | 0,06 | 0 | 0,02 | 0,01 | 0,04 | 0,02 | 0,02 | 0,01 | 0,01 |
| Cu ²⁺ | 0 | 0,3 | 0,02 | 0,04 | -0,75 | 0,1 | -0,8 | -0,49 | 0,3 | 0,3 | 0,2 | -0,69 |
| Fe ^{tot} | 1,6 | -0,08 | 0,006 | 0,001 | -0,054 | 0,002 | 0,008 | -0,08 | 0,01 | -0,06 | 0,02 | 0 |
| K ⁺ | -2,3 | 2,1 | 0,2 | 1,2 | -40 | 0,7 | 0,1 | 0,6 | 0,4 | 0,1 | 0,6 | 0,2 |
| MES | 3,9 | -1,65 | 5,08 | 9,5 | 19,32 | 0,13 | -3,88 | 2,1 | 3,26 | 2,8 | 1,78 | 1,2 |
| Mg²⁺ | 4 | 2 | 3 | 2 | 2 | 2 | 1 | 2 | 4 | 0 | 3 | 2 |
| Mn²⁺ | 0,13 | 0,95 | 0,21 | 0,84 | 0,64 | 0,05 | 0,04 | 0,05 | 0,02 | 0,68 | 0,03 | 0,16 |
| NH ₄ ⁺ | -0,42 | 0,05 | 0,09 | 0,07 | -0,4 | 0,03 | 0,06 | 0,82 | 0,02 | 0,02 | 0,01 | 0,02 |
| NO ₃ ⁻ | 0,02 | -0,32 | 0,27 | 0,61 | -0,63 | 0,97 | -1,18 | 1,26 | 1,47 | 1,71 | 3,54 | 0,8 |
| Pb²⁺ | 1,38 | 0,41 | 0,27 | 0,3 | 0,18 | 0,4 | 0,1 | 0,2 | 0,1 | 0,13 | 0,4 | 0,13 |
| PH | 0,02 | 0,98 | 0,1 | -0,48 | 0,68 | 0,13 | 0,09 | 0,02 | 0,11 | 0,18 | 0,07 | 0,07 |
| po ₄ ³⁻ | 0 | 0,13 | 0,12 | 0 | 0,04 | 0,02 | 0,02 | 0,03 | 0,03 | -0,66 | -0,37 | -0,02 |
| RS | 0,17 | -2,1 | 14,2 | 2,5 | 8,8 | 0,4 | -8,1 | 2,7 | 2,7 | 4,9 | 5,5 | 1,9 |
| sables | -4,13 | -3,38 | 1,5 | 1,48 | 4,91 | -5,27 | -5,03 | 0,43 | 2,32 | 7,2 | 3,7 | 1,4 |
| SO ₄ ²⁻ | 0,01 | 17,88 | 5 | 4 | 0,9 | 5 | 20,25 | 2 | 1 | 2 | 2 | 3 |
| T°C | -0,2 | 0,2 | -0,2 | -0,2 | 0,6 | 0,8 | 0,5 | 0,8 | 0,3 | -0,1 | 0,4 | 0,3 |
| TAC | 84 | 12 | 26 | 65 | 92 | 50 | 53 | 11 | 2 | 11 | 10 | 9 |

Source: Physico-chemical analysis laboratory, IRSEN.

Table 8 illustrates the in situ measurement differences between the downstream point and the upstream point. It emerges from this illustration that three parameters have strictly positive measurement deviations on all the measurements: lead, magnesium and manganese.

- Metal Pollution Index

Applying the method described in 3.2.2 gives results listed in the following table:

Table 9. Determination of the pollution index

| Mg²⁺ | Mn²⁺ | Pb²⁺ | WHO Guide Value | WHO Guide Value | IP-Mn | IP-Pb |
|------------------------|------------------------|------------------------|------------------------|------------------------|--------------|--------------|
| [MG/L] | [MG/L] | [MG/L] | Mn[mg/l] | OMS du Pb[mg/l] | | |
| 4 | 0,13 | 1,38 | 0,4 | 0,01 | 0,325 | 138 |
| 2 | 0,95 | 0,41 | 0,4 | 0,01 | 2,375 | 41 |
| 3 | 0,21 | 0,27 | 0,4 | 0,01 | 0,525 | 27 |
| 2 | 0,84 | 0,3 | 0,4 | 0,01 | 2,1 | 30 |
| 2 | 0,64 | 0,18 | 0,4 | 0,01 | 1,6 | 18 |
| 2 | 0,05 | 0,4 | 0,4 | 0,01 | 0,125 | 40 |
| 1 | 0,04 | 0,1 | 0,4 | 0,01 | 0,1 | 10 |
| 2 | 0,05 | 0,2 | 0,4 | 0,01 | 0,125 | 20 |
| 4 | 0,02 | 0,1 | 0,4 | 0,01 | 0,05 | 10 |
| 0 | 0,68 | 0,13 | 0,4 | 0,01 | 1,7 | 13 |
| 3 | 0,03 | 0,4 | 0,4 | 0,01 | 0,075 | 40 |
| 2 | 0,16 | 0,13 | 0,4 | 0,01 | 0,4 | 13 |

The 2006 WHO standards do not define a guide value for magnesium because it is considered a trace element.

Table 9 indicates that only lead has pollution indices strictly greater than unity at all times and implies as the choice of pollutant to follow: Lead.

- Determination of the Pollution Index, Pollution Degree on Lead.

The results on the assessment of water pollution come from the application of the assessment method adopted in 3.2.2. The result of this evaluation is that only lead has a pollution index strictly greater than unity, a degree of pollution (pollution indicator) above the experimental measurement upstream and a metal flow transported above the flow. Medium at all times.

Table 10. Determination of the pollution index, pollution degree

| TIME | DOWNSTREAM | UPSTREAM | WHO Guide | Average Excess | Pollution | Pollution | Observation |
|----------------|-------------------|-----------------|---------------------|-----------------------|------------------|------------------|--------------------|
| [Month] | MEASURE | MEASURE | Value OMS Pb | measurement | Index | degree | |
| | [MG/L] | [MG/L] | [MG/L] | [MG/L] | | [MG/L] | |
| 1 | 2,8 | 1,42 | 0,01 | 1,38 | 138 | 2,79 | Pollution |
| 2 | 0,77 | 0,36 | 0,01 | 0,41 | 41 | 0,76 | Pollution |
| 3 | 1,07 | 0,8 | 0,01 | 0,27 | 27 | 1,06 | Pollution |
| 4 | 1,13 | 0,83 | 0,01 | 0,3 | 30 | 1,12 | Pollution |
| 5 | 0,62 | 0,44 | 0,01 | 0,18 | 18 | 0,61 | Pollution |
| LEAD | 0,9 | 0,5 | 0,01 | 0,4 | 40 | 0,89 | Pollution |
| 7 | 0,27 | 0,17 | 0,01 | 0,1 | 10 | 0,26 | Pollution |
| 8 | 0,5 | 0,3 | 0,01 | 0,2 | 20 | 0,49 | Pollution |
| 9 | 0,8 | 0,7 | 0,01 | 0,1 | 10 | 0,79 | Pollution |
| 10 | 0,73 | 0,6 | 0,01 | 0,13 | 13 | 0,72 | Pollution |
| 11 | 0,9 | 0,5 | 0,01 | 0,4 | 40 | 0,89 | Pollution |
| 12 | 0,83 | 0,7 | 0,01 | 0,13 | 13 | 0,82 | Pollution |
| | | | | | Average | | |
| | | | | | Pollution | 0,93333 | |
| | | | | | Degree | | |

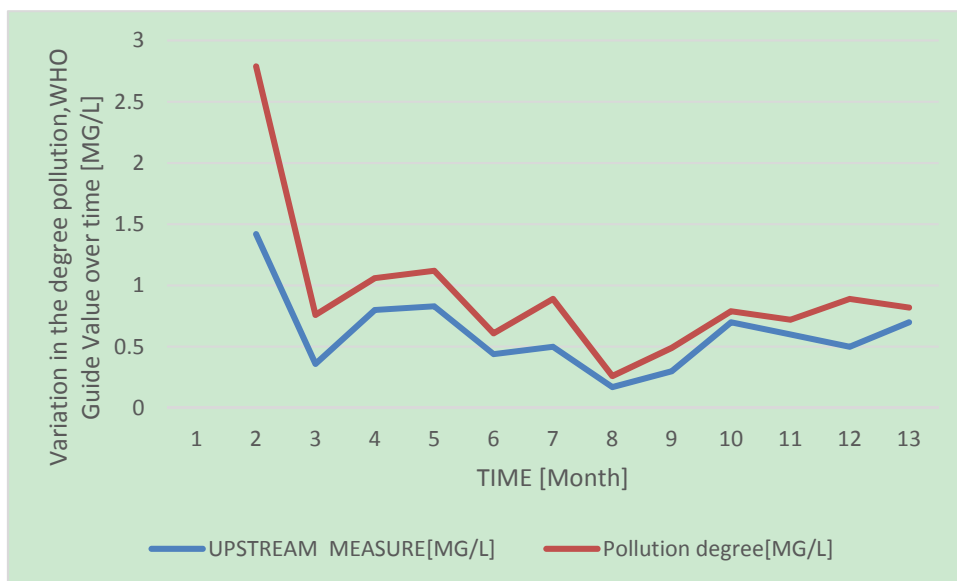


Figure 1. Comparison of pollution degree and measurement upstream of the river

Table 10 presents, on the one hand, pollution indices above the WHO guide value for lead and, on the other hand, pollution degrees above in situ measurements downstream, which indicates water pollution with lead.

- Seasonal variation of experimental measurement

Table 11. Seasonal measure excess

| | SEASON | | | WHO Guide | |
|--------------------------------|--------|---------|-----------|-----------|-------------|
| | SP | SS | Variation | Value | OBSERVATION |
| AVERAGE DOWNSTREAM MEASUREMENT | 1,2875 | 0,77125 | 0,51625 | 0,01 | overtaking |
| | SEASON | | | WHO Guide | |
| | SP | SS | Variation | Value | OBSERVATION |
| AVERAGE UPSTREAM MEASUREMENT | 0,765 | 0,5325 | 0,2325 | 0,01 | overtaking |

Seasonally, there are variations in the average measurement between the rainy season and the dry season upstream and downstream, indicating the pollution is more evident in the rainy season than in the dry season.

SS: Rainy season

SP: Dry season.

- Flux variation

Table 12. Determination of flux

| TIME | AVERAGE | METAL | WHO Guide | Average Measurement | MINIMUM |
|---------------|------------|-------------|-----------|---------------------|---------|
| | DAILY FLOW | FLUX | Value | Excess | FLUX |
| 1 | 20,76 | 903,4685568 | 0,01 | 1,38 | 0,2076 |
| 2 | 20,7 | 267,646032 | 0,01 | 0,41 | 0,207 |
| 3 | 20,73 | 176,5101456 | 0,01 | 0,27 | 0,2073 |
| 4 | 20,52 | 194,135616 | 0,01 | 0,3 | 0,2052 |
| LEAD 5 | 20,73 | 117,6734304 | 0,01 | 0,18 | 0,2073 |
| 6 | 20,73 | 261,496512 | 0,01 | 0,4 | 0,2073 |
| 7 | 20,71 | 65,311056 | 0,01 | 0,1 | 0,2071 |
| 8 | 20,73 | 130,748256 | 0,01 | 0,2 | 0,2073 |
| 9 | 20,73 | 65,374128 | 0,01 | 0,1 | 0,2073 |
| 10 | 20,71 | 84,9043728 | 0,01 | 0,13 | 0,2071 |
| 11 | 20,7 | 261,11808 | 0,01 | 0,4 | 0,207 |
| 12 | 20,7 | 84,863376 | 0,01 | 0,13 | 0,207 |

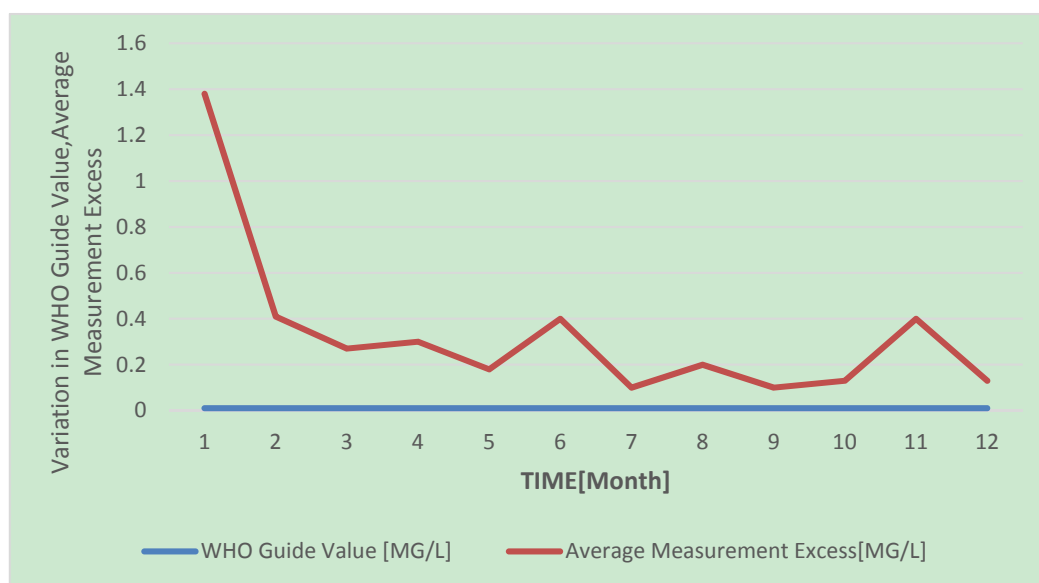


Figure 2. Comparison of in situ measurement excess vs WHO guideline value

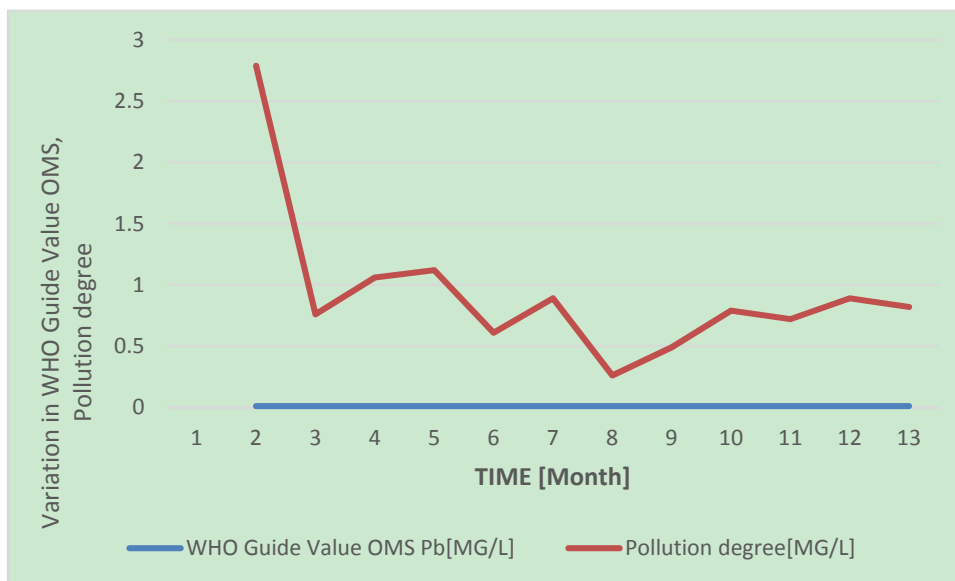


Figure 3. WHO guide value vs Pollution Degree comparison graph

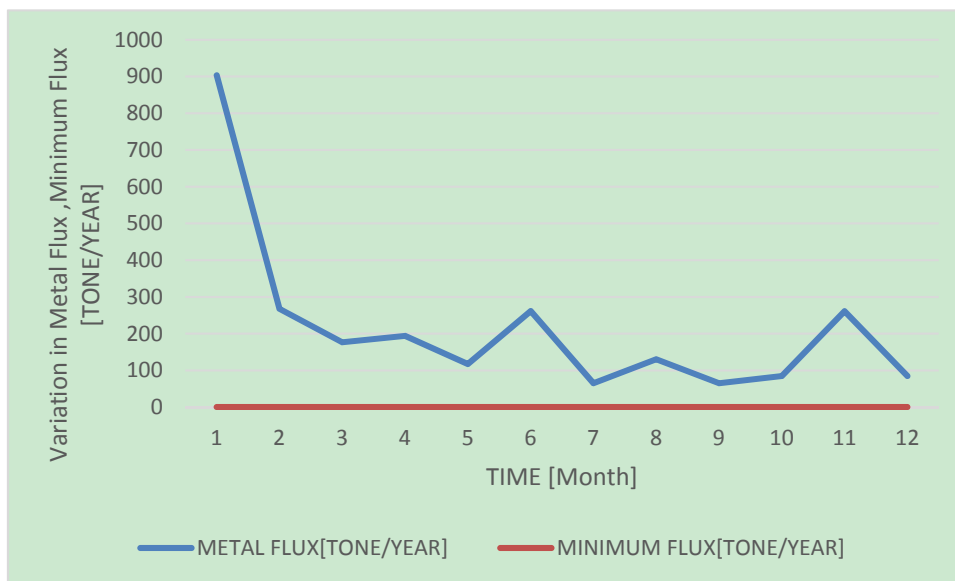


Figure 4. METAL FLUX vs MINIMUM FLUX comparison graph

Table 12 shows that the variations in measurements and lead flow between the downstream and upstream of the river are respectively above the WHO guide value and the average flow as illustrated in figures 1,2 and 3.

The quantity of pollutant transported is above the minimum quantity of the identified pollutant (figure 4) and this confirms the result of figure 3.

3.2 Discussion

Analysis of data from the physicochemistry of surface water from the Djiri River revealed for these waters a temperature ranging from 26.1 ° C to 28.4 ° C, an electrical conductivity ranging between 4.18 and 11.2, a pH ranging between 5.14 and 6.7.

The pH values observed imply a pH <7 and therefore an acidic environment and this increases the risk of the presence of lead in a more toxic ionic form (IBGE, 2005).

The electrical conductivity values observed indicate a low mineralization of the water compared to the conductivity of natural water which is between 50 and 1500µS/cm and this does not promote the movement of electric charges,

in particular metal ions (lead) which are in principle good conductors of electricity and this induces their accumulation in water;

The methodology used in our study for estimating the metal pollution indices of the surface water of the Djiri river as described in sub-paragraph 3.1.2 makes it possible to verify both that the pollution index (PI) is strictly greater than unity, this implies that the excess measurement is strictly greater than the WHO guide value and consequently the degree of pollution is above the measurement in situ upstream of the river;

It therefore emerges from this pollution assessment that only lead gives, at all times and at each sampling point, monthly in situ measurement surpluses above the WHO standard for water potability, this implies a source of lead metal pollution between downstream and upstream of the river.

As the geology of the basin is essentially made up of sands, the existence of a source of lead emissions other than the electric steelworks which is installed upstream of the river 1 km from the upstream sampling point is excluded.

Also, the seasonal analysis of the average excess measurement on lead shows upstream and downstream variations exceeding the WHO guide value applied and indicating that during the rainy season water runoff, the use of debris from Scrap metal recycled in the study area to compensate for landslides contributes more to pollution of the waters of the Djiri river than in the dry season (Table 11): 1.28 mg / l in the rainy season against 0.77 mg / l in the downstream dry season, i.e. a variation of 0.51 mg / l and 0.76 mg / l in the wet season and 0.53 mg / l in the upstream dry season, i.e. a variation of 0.23 mg / l.

The results of our study in terms of the diagnosis of metal pollution are in line with those of other studies of metal pollution of water carried out in other rivers around the world and in particular:

-the study of pollution by heavy metals and metalloids (Nadem et al, 2015) and which highlighted the pollution by lead on certain stations (lead content exceeding the admissible standards) of the waters of the estuary of Bou Regreg (Atlantic coast, Morocco), pollution of an anthropogenic nature, with high pollution indices. In fact, exceeding the WHO guide value at certain stations implies, in the case of our study, strictly positive in situ measurement excess and pollution degrees above the downstream in situ measurements;

-the study on the contribution to the analytical study of pollutants (in particular of heavy metal type) in the waters of the Chari river during its crossing of the city of N'Djamena (Nambatingar Ngaram, 2011) shows pollution by the Lead (lead content exceeding acceptable standards) of anthropogenic nature in the waters of the Chari River; the values at each sampling point exceed the WHO admissible standard (0.01 mg / l), which is consistent with the results of our study in term of point lead concentration and reflects excess measurements between downstream and upstream that are strictly positive thus implying pollution degrees above in situ measurements downstream;

-The study of the quality of surface water and its impact on the environment in the Wilaya of Skikda (Mohamed Zine BELHADJ, 2017) in Algeria revealed the significant presence of toxic metallic trace elements in the water, in particular Lead levels found in these surface waters exceed the WHO acceptable standard, thus testifying to water contamination; the results of our study also reveal the exceedances at each sampling point of the WHO admissible standard and confirm, through the indices and the estimated degree of pollution, values showing lead contamination of the waters of the Djiri river;

- Assessment of the risks of pollution by heavy metals (Hg, Cd, Pb, Co, Ni, Zn) of the waters and sediments of the Konkouré river estuary in the Republic of Guinea (Gbago ONIVOGUI et al., 2013) a found on some stations levels of metallic trace elements, in particular lead, exceeding WHO standards in terms of concentration at the time and at the point of sampling and this describes the same scenario observed in the results of our study because at all points and at the time of sampling, the in situ lead measurement exceeds the admissible WHO standard;

-The Contribution to the study of the physico-chemical analysis and the metallic contamination of seawater from the coast of Agadir in southern Morocco (Chaouay et al., 2016) revealed a contamination of the water lead (lead concentration exceeding the WHO standard) testifying in certain areas of pollutant discharges in the watershed justifying the existence of industrial sites; the results of our study are in line with those obtained from this study cited in terms of exceeding the WHO admissible standard observed in our study on the lead concentrations at each point during the sampling time.

-The study entitled "Contribution of the physico-chemical analysis to the evaluation of the metallic contamination of seawater on the coast of Agadir, 2016 (South of Morocco)" showed that the metallic contents in the seawater show significant variations depending on the areas and seasons of sampling, i.e levels exceeding the acceptable metal contents of the WHO, our study has revealed a seasonal variation in water pollution by lead.

4. Conclusion

The physico-chemical analyzes carried out on all the samples taken from the Djiri River have revealed a source of lead contamination in the water.

This contamination is linked to the presence of an industrial installation located 1km from the selected sampling point upstream of the Djiri watershed, in particular the point located on the old bridge over the Djiri river (Djiri station).

This study is a prelude to the design and production of a tool for valuing hydrological data which will be equipped with the following features:

- Storage of sampling data and physico-chemical analyzes of water;
- Management of hydrometric stations (gauging data, control of stations)
- Support for the scale for monitoring the flows of rivers;
- Have the physico-chemical state of a river at a given period;
- Monitor water pollutants in general;
- Integration of environmental water standards into the system.

This work perspective will greatly contribute to the establishment of a national observatory of hydrological data from rivers with a view to facilitating analyzes related to water quality in order to provide the necessary explanation in the face of the resurgence of water pathologies observed in these watercourses.

5. Recommendation

The study recommends that it is essential to set up and apply a mechanism for monitoring the quality of water in rivers at the national level.

Good quality water, that is to say water that meets WHO drinking water standards, will ensure the good health of those who use it.

To guarantee the protection of watercourses or that of the population against possible pollution, the operability of the monitoring of the water quality of watercourses is required of the bodies responsible for issues of protection of water ecosystems. Thus, to ensure the coverage of water pollution risks and ensure the good health of the populations, it is advisable to conceptualize and implement the hydrological data observatory in order to make available the analysis data of water quality and alert from time to time on any exceptions highlighted to make possible corrections.

Recognition

Les auteurs remercient avec gratitude les agents du laboratoire d'analyses physico-chimique de l'Institut de Recherche en Sciences Exactes et Naturelles, les chercheurs de la Formation Doctorale en Géosciences de la Faculté des Sciences et Techniques de l'Université Marien NGOUABI, pour leur immense contribution.

Data availability

The data used to support the conclusions of this study are included in the article.

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