Characterization of Sediments and Surface Waters of the Oued Guigou Watershed

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Abstract: The Oued Guigou catchment area is the upper part of the Oued Sebou and represents 52% of the Haut Sebou catchment area. It is part of an original morphostructural context between the Middle Atlasic Cause to the north and the Middle Atlas folded to the south. Sampling campaigns on surface water and sediment provide details of heavy metal contents. The results of the analyses revealed that the levels of certain heavy metals are below relative standards and that others were below detection limits but do not raise any ecological concerns. The high content of certain metals (Cr,Ni) has a natural origin and outweighs the anthropogenic origin. These fluctuations are spatial in nature (upstream to downstream).

Keywords: Surface water, sediments, physico-chemistry, heavy metals, Oued Guigou

1. Introduction

Like the majority of Mediterranean waterways, Morocco’s waterways are subject to various natural and anthropogenic disturbances (industrial and urban discharges, agricultural pressure, water pumping, dams, regulation, etc.). It is certain that population growth, which is the first cause of the increase in demand for water for human activities, will increase the constraints on this resource. In addition, natural factors, such as drought or geological constraints, affect the supply and distribution of drinking water. This study will be devoted to a qualitative characterization of the surface sediments and surface waters of the Guigou watershed.

2. Study Area

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The Oued Guigou watershed is the upstream portion of the Oued Sebou watershed. On a large scale, it is a basin in the Mediterranean area, between parallels 33°00′N and 33°40′N and extends between the elliptical 4°10′W and 5°10′W meridians. The Oued Guigou has a length of 155.50 km. It is one of the main tributaries of the hydrological network of the Oued Sebou watershed located upstream of the Haut Sebou watershed. It is born in the Middle Atlas at the Zad Pass (Figure 1). The Oued Guigou watershed covers an area of 3084 km² in a South-West/North-East direction and a perimeter of 428.80 km, or 52% of the Haut Sebou watershed. Its compactness index is 2.16, an average slope of 10.38.

As regards the geological framework, the study area is straddled between the Middle Atlas folded to the east and the Middle Atlasic Causse to the west. The Middle Atlasic Causse represented by the Ifrane causses, of Azrou and Guigou and of the liasic lands to the west of the accident North Middle Atlasic, topped with volcanic domes. The Middle Atlasic Causse shows in the study area, a tabular morphostructure developed in the dolomites of Lias, corrugated by a flexible tectonics with large radius of curvature and affected by some accidents in the North-West. It is topped with volcanic domes which are at the origin of the great basaltic effusions of the Guigou plain (Figure 2).
The Guigou watershed is characterized by a semi-arid Mediterranean climate influenced by the frequency of the foehn current. The winter is relatively wet and very cold with snowy precipitation and a hot and dry summer. Winter temperatures can be as high as -10°C and as high as 38°C for summer temperatures; precipitation has the same characteristics, they are of the order of 96.2 mm in winter and of 63.7 mm in summer with thunderstorms accompanied by showers more concentrated in the spatio-temporal plane, with a large diurnal-nocturnal amplitude. The drainage system in the Guigou basin is better developed on the right bank than on the left. The Drainage System is 726 km long and the Drainage Density is 0.23 km⁻¹ (Figure 3).

2.1 Sampling and Analysis

The selection of sampling sites was made taking into account the lithological diversity of the basin as well as the distribution of anthropogenic activities, 9 samples were made along the oued Guigou. Concerning surface waters Two campaigns were carried out in November 2012 (16/11/2012) and June 2014 (1/06/2014), 10 sampling sites were selected approximately along Oued Guigou, water samples were taken in 1.5 litre bottles and transported in a cooler at a temperature of approximately 4°C. (Rodier J, 2009)

Sedimentary samples were collected over three periods: 16/11/2012, 01/06/2014 and 29/04/2015 to determine sediment geochemistry.

Particular attention was paid throughout this stage to the packaging of samples. The sediment is stored in plastic bags up to the ICP-AES analysis laboratory of the CNRST. If storage is required for a certain period of time, the samples have been put in the freezer to avoid any further development.

The physico-chemical study of the waters concerned the determination of the temperature of pH, dissolved oxygen and salinity in situ and the analysis of chlorides (cl⁻), nitrates, ammonium ion nitrates and sulphates, these analyses were carried out at the CNRST laboratory in Rabat.

The study of heavy metal contamination of surface waters in the Guigou wadi watershed covered the following elements: cr, cd, ni, zn, fe, cu, pb. These analyses were carried out at the CNRST laboratory in Rabat by ICP-AES.

3. Results and Discussions

3.1 Surface water quality

Physico-chemical parameters

Water temperature plays an important role in modifying chemical, physical and biological reactions. It is recognized that changes in temperature fade beyond 3 m of depth, and that groundwater temperature is invariable during the year (Petit & Erpicum, 1987). An initial reading of the measured results (Figure 5) shows temporal variations in temperature between the November 2012 season and June 2015 and April 2014. The temperature of the water fluctuates between 8.6°C in autumn and it undergoes quite remarkable rises in spring and especially in summer which reaches 25°C. It is deduced that the warming of the temperature is due to the seasonal variations of the temperatures.
pH  

(pH, hydrogen potential) measures the H-ion concentration of water. It thus translates the balance between acid and base on a logarithmic scale of 0 to 14. This parameter conditions a large number of physico-chemical balances. Hydrogen potential values range from 6 to 8.5 in natural waters (Chapman et al. 1996). The results obtained during the winter period confirm the above standards, since the pH of the water at the various sites is between 7.73 and 8.89 and tend to be basic. In June, the pH of the waters of Oued Guigou fluctuates between 6.79 and 9 with the exception of the Ait salah site or it exceeds 9. These results can be explained by the effect of evaporation which increases at the site. The basic character of the waters is reinforced towards the downstream. This is explained by the presence of calcareous and marnocalcar terrains crossed by the Guigou. The change in pH = 6.79 which is due to the amount of organic matter that is concentrated at this station (Figure 6).

Electrical conductivity  

Conductivity is one of the ways to validate physicochemical analyses of water. Indeed, contrasts measured on a medium make it possible to detect pollution, mixing or infiltration zones. It is also used to assess the amount of salts dissolved in water (Pescod, 1985; Rodier, 1984). According to Chapman and Kinstach (1996), freshwater conductivity is less than 1000 µs/cm. Oued Guigou surface waters are weakly mineralized with values between 230 µs/cm and 552 µs/cm (Figure 7). These waters belong to the layer of the pleated Middle Atlas, characterized by the outcrop of the limestones and dolomites of the Jurassic. Recalling that dolomite is a carbonate sedimentary rock composed of at least 50% dolomite, that is to say a double carbonate of calcium and magnesium of chemical composition C₃Mg(CO₃)₂ and therefore a low metal content which are, for most very good electricity conductors in addition to the passage of water in the basalt area.

TDS  

It measures the total ion content of water, so it presents the sum of the anion and cation concentrations in water. It is generally the result of the lithological nature of the catchment area and the introduction of organic and mineral matter into the streams by stormwater. The total dissolved load (TDS), does not have any particular seasonal influence and varies between the period of April 2015 and the other two sampling campaigns. In addition, the Ait salah station located downstream of the basin has a total dissolved load three times higher than that recorded upstream of Guigou (Figure 8).

The nutrients are:  

Nutrients were below detection except for sulphate ion from evaporative rocks, sulphated organic matter, waste (WHO standard is 500 mg/l, for CEC is 250 mg/l)

The sulphates  

The values of this parameter in the test waters are highly variable and range from 14.03 mg/L to 237.74 mg/L (Figure 9).
9) from upstream to downstream; This content begins with low concentrations at the S1 site level but then becomes very high at the S2 site level. This content can be explained by a natural addition to the impact of agricultural fertilizer pollution.

The sulphate content at site S3 and S4 is very low. There is a strong activity of sulfatoreductive bacteria which transform sulphates into hydrogen sulphides which volatilize in air, or precipitate as an insoluble salt or incorporated into living organisms.

The resumption of an increase in the S5 content, particularly in S6 and S7, thus showing a natural contribution from the drainage of the outcrops of the Triassic rich in evaporates, as well as contamination by domestic effluents from Almis Guigou. Average sulphate concentrations are recorded at sites S8 and S9, reflecting a natural input in addition to an impact from agricultural pollution from the Oued Atchane tributary.

The Nitrates
Nitrates generally result from the decomposition of nitrogen organic matter by bacterial oxidation of nitrites and thus represent the ultimate product of nitrification. They also come from the leaching of minerals from rocks and soils. They have the most abundant form in natural streams. According to some authors such as Chapman and Kimstash (1996), nitrate levels in the natural environment rarely exceed 0.45 mg/l. Higher values imply the introduction into the river of domestic and industrial effluents or fertilisers used in agriculture, which can lead to very high levels exceeding hundreds of mg/l.

Nitrate levels along the Guigou wadi show high values in locations (S2, S5 & S6, Figure 9), reflecting the impacts of agricultural pollution. The nitrification process is intense under the effect of the oxygenation of the water knowing that the period is winter.

The nitrites
Nitrites are obtained by bacterial oxidation of ammonium ions during the nitrification process. The metastable nature of nitrites explains the existence of nitrites at low concentrations in nature, since they rapidly transform into nitrates under favourable conditions.

Levels in unpolluted water range from 0.03 to 3 mg/l but are generally well below 3 mg/l (Chapman and Kimstash 1996).

The origin of nitrites is varied according to the conditions of the environment and the feeding areas. Nitrosation on the one hand and the reduction of nitrates on the other are essential sources, but pollution from domestic and industrial effluents and leaching from agricultural land treated with nitrate fertilisers can lead to a high level of nitrite in natural waters. In Guigou wadi waters the concentration of nitrites is very low at all sampled sites (Figure 9).

Ammonium ion
Ammonium is the product of the final reduction of nitrogenous organic substances and inorganic matter in water and soil. It also comes from the excretion of living organisms and the reduction and biodegradation of waste, without neglecting domestic, agricultural and industrial inputs.

The ammonium ion concentrations at the stations studied are below 0.1 mg/L, these very low to zero levels suggest that this element does not pose a pollution risk to the surface waters of Oued Guigou.

Heavy metals in surface waters
In our study, we limited ourselves to the determination of six elements: Cd, Cr, Pb, Cu, Fe and Zn because these metals end up at very low concentrations but their ecological and health impacts can be significant. The Guigou wadi contains trace elements at very low levels (0.01 mg/l) (Figure 10)

The iron content of the 2012 season is very low (0.02 mg/l) at all sampled sites. For the 2014 campaign, concentrations above the international and Moroccan standard (0.2mg/l) are recorded at some sites such as (S3, S4 & S8, Figure 10). The highest concentration is detected at site S3, and this can be explained by a natural contribution and by important agricultural activities or by a remobilization of iron.

The only maximum concentration of zinc is detected at site S2 (0.25 mg/l) (Figure, 10), which can be explained by leaching of agricultural fertilizers and natural intake.
The results of the analyses of the sites sampled in 2014 show high levels of aluminum that exceed the aluminum level proposed by the WHO (0.2 mg/l), especially in sites that are not directly exposed to anthropogenic pollution. The peak concentration of aluminum is recorded at sites S3 and S4 (Figure.10) that are upstream of pollution sources, leaving a natural origin for this metal in addition to the impact of environmental conditions, especially pH. Aluminum concentrations were low at other sites during both campaigns. This can be explained by the fact that aluminum and its oxides remain inert in wild or sanitary landfills.

**Heavy metals in sediments**

Concentrations of heavy metals in the sediments of the Guigou wadi and its tributaries are found to be below relative standards and do not result. The high content of certain metals is the natural origin which prevails over the anthropogenic origin. The highest levels for iron are recorded at the sites (S9, S5, S8, Figure. 11). The high concentrations of iron in site S9 can be explained by a natural origin since it is located in a mountainous area, almost unaffected by pollution sources. Iron is abundant in rocks in the form of silicates, oxides and hydroxides, carbonates and sulphides. Site S5 is likely a result of natural causes or sources of pollution.

The results of the analyses of Zinc in the surface sediments collected along Oued Guigou show that the levels of this element vary in the same way at all sites during the three seasons except the S7 site during the flood period (Figure. 11).

This value can be explained by the impact of household waste discharged near this point. It is noted that all samples have levels that are lower than the mean natural zinc content in the soil.

Zinc levels are minimal at the different sites, which explains the low impact of natural intake. Manganese has levels in the study area ranging from 0.5 mg/l to 5 mg/l (Figure. 11). The probable origin of manganese at these sites can be explained by a natural contribution, especially at site S9, in a mountainous area away from any form of pollution.

Lead levels in Guigou wadi surface sediments range from 0.01 mg/l to 0.68 mg/l. The highest value is at stations S7 and S8 during the April 2015 campaign, these two peaks are sites exposed to agricultural pollution or urban effluents in addition to a natural stream. The 2014 season has very low or zero values compared with the November 2012 values but these values remain much lower than the levels that can tolerate sediment.

The results of the analyses concerning copper in the surface sediments collected from the various sampling sites in the catchment area studied show low values during the three campaigns with some net fluctuation, especially at stations S7 and S8. The natural origin may be the main source of these copper concentrations which remain as even below the tolerable average.

Nickel does not generally form insoluble precipitates in soils and therefore Ni retention is controlled by the precipitation mechanisms of secondary solid phases and adsorption. Nickel adsorbs to clays, iron and manganese oxides and organic matter. Formation of Ni complexes with organic and inorganic ligands

Chromium is rarely found naturally in its elementary form. It is found in magmatic (or igneous) rocks where it easily replaces iron, which has an ionic ray close to that of Cr(III). Ultrabasic rocks (dunites, serpentinites, peridotites) are the richest in chromium, where this element comes mainly from chromite (Fecr 2 O4(s)). The average chromium content in the Earth’s crust would be between 100 and 200 mg/kg. Chromium exists in two states of valence in soils, trivalent chromium, Cr(III) and hexavalent chromium, Cr(VI) (year and author). Cadmium levels are moderately represented at the Oued Guigou basin.

4. **Conclusion**

The quality of Guigou wadi surface water depends on the lithology drained by this stream. As well as the significant influence of local agricultural activity on the banks of this river.

5. However, the levels observed for most physical and chemical parameters do not exceed the Moroccan surface water quality standard presented (Moroccan Standards, Morocco Official Bulletin 5062, Rabat 2002). The comparison of the physico-chemical contamination of the Guigou wadi with other Moroccan (Sebou and Bounaim) and global (Seine) rivers shows that the latter remains within the tolerable limits in relation to the low socioeconomic development the region and the towns and villages on the river basin of the Oued Guigou.

Monitoring the evolution of the physico-chemical parameters of the surface waters of the Guigou river basin shows that the levels observed for most of the physico-not exceed the Moroccan surface water quality standard submitted.

Admittedly some major elements have high contents, notably Calcium and Magnesium, which would be attributed to the geological nature of the sites crossed. The content of some heavy metals was found to be lower than the relative...
standards, with the exception of Fe, which would be caused by natural origin than anthropogenic intake. In general, the physico-chemical quality of the waters of the Oued Guigou is considered globally good to poor quality, with the exception of a few points showing significant bacterial contamination and high concentrations of nitrates and phosphates.

The concentrations of metals in the sediments of Oued Guigou and these main tributaries are below the relevant standards, and the refore do not raise any ecological concerns. The high content of certain heavy metals (Fe, Mn, Cu) their natural origin which outweighs the anthropogenic origin. On the other hand, the low level of dangerous heavy metals (Ag, Hg, Cd) for public health was below the detection limit.

References
