Metallic trace elements contained in the sediments of Dayet Er-Roumi Lake (Morocco)

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Abstract. The contamination of aquatic ecosystems with metals remains a serious environmental problem of growing concern. Sediments are often studied as reservoirs or wells for many chemical pollutants. They are micropollutant traps; they also indicate the watercourse's historical pollution, lagoons, and lakes...Lake Dayet Er-Roumi (SIBE) is the only permanent natural lake in the Khemisset region (Morocco); this wetland is affected by several forms of pollution that are mainly linked to human activities (agricultural, domestic, industrial, etc.). The objective of our study is to contribute, through qualitative and quantitative analysis, to the assessment of lake sediment pollution by Spatio-temporal monitoring of certain toxic heavy metals such as Mn, Zn, Cr, Cd. These sediments are collected on the level of the lake's surface; the concentration of heavy metals was measured by microwave plasma atomic emission spectroscope (MP-AES). Metal analyses carried out at three measuring points during the winter season reveal a high concentration of Zn, Cr, and Mn at all stations during the winter season, which far exceeds the recommended standards, with a low level of Cd. The contamination factor "FC" and the degree of contamination "DC" reveal polymetallic contaminations dominated by two elements, zinc, and Chromium, which are the most worrying. These results clearly show that lake Dayet Er-Roumi is polluted; strategies to limit the lake's pollution must be implemented to avoid several ecological problems (fish mortality, etc.).

1 Introduction

Aquatic ecosystems cover 70% of the planet's surface. Pollution now threatens them because of human activities [1], particularly urbanization and industrialization... Among the many compounds emitted by human activities, heavy metals are one of the major pollution sources. These inorganic chemicals are being released into the environment as a result of human activities. Whether it is a specific spot of this environment (industrial and urban effluents, etc.) or a diffused one (runoff, dry and wet atmospheric deposition, etc.), These inorganic chemicals can penetrate aquatic ecosystems and integrate into the particle phase. These particles can settle on the bottom materials, where contaminants can accumulate over time [2]. Therefore Sediments can act in the long term as a reservoir of chemicals for the aquatic environment and organisms that inhabit the sediments or have direct contact with bottom materials. Since the sediment is a dynamic and essential compartment in aquatic ecosystems and plays an essential role for many animals and plants as a habitat or a nesting site, the exposure to certain substances contained in sediments could have a serious health risk to these organisms and also lead to critical or even dangerous situations affecting the ecological balance, and leading to the dysfunction of the trophic chain (low biodiversity, etc.) [3].

For many years, the metallic contamination of surface sediments (Mn, Ni, Cr, Cr, Cu, Zn, Pb, etc.) has attracted researchers' attention from very different horizons. It is one of the most threatening pollution aspects in aquatic environments. According to Forstner and Wittman (1981) [4], a significant fraction of heavy metals in the aquatic environment is reversibly associated with surface sediments, providing access to a more or less complete record of the state of contamination in aquatic environments. Therefore assessment of heavy metal concentrations in an aquatic system and their effect on organisms is essential.

As for other countries in the world, Morocco also does not escape the scourge of pollution. The Lake Dayet Er Roumi (Site of Biological and Ecological Interest) is the only permanent natural lake in the Khmisset region; it plays a significant socio-economic and ecological role, But this Daya has experienced fluctuations in its state, linked to climatic hazards on the onehand, and anthropic activities on the other.

Several studies [5] and [6] have shown that the water of Lake Dayet Er-Roumi is very polluted; they found strong mineralization (a high salinity, with a dominance of chlorides) and significant metallic pollution (Al, Mn,

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and Pb ...) which reflects the direct influences of human activity (intensive and uncontrolled use of phytosanitary products, wastewater, domestic waste ...) on the ecological quality of the lake. A complete diagnosis of the current pollution situation is essential to safeguard this ecosystem. Our work's perspective consists of assessing the degree of pollution, evaluating the metal quality of the lake's sediment during the winter season of the year 2019, and studying human activities' impact on the quality of the lake.

2 Material and Methods

2.1 Study area study

Dayet Er-Roumi Lake (33°45'N 06°12'W) is located 15 km southwest of Khémisset, situated in three rural communes: Ait Ouribel, Ait Ouahi, and Ait Houderrane. It is characterized by a semi-arid climate with a maximum summer temperature of 38°C, a minimum winter temperature of 7°C, and a middling rainy regime. It also has a 2 km long and a 400 m to 700 m width, with an area of about 90 ha and a maximum depth of 13.5 m in the center (according to the National Center for Information Exchange on Biodiversity of Morocco [7]), This lake is fed by groundwater and two tributaries (Fig. 1).

2.2 Samples

The choice of sampling sites has been made according to the juxtaposed activities; in total, there are five sampling stations (S1-S5), the three points in the lake (S1-S3) are representing the areas that are more likely to be affected by human activities (housing, hotel, etc.) and the other two points (the red sampling stations) are the stations where sampling is complex because there are plants and stones

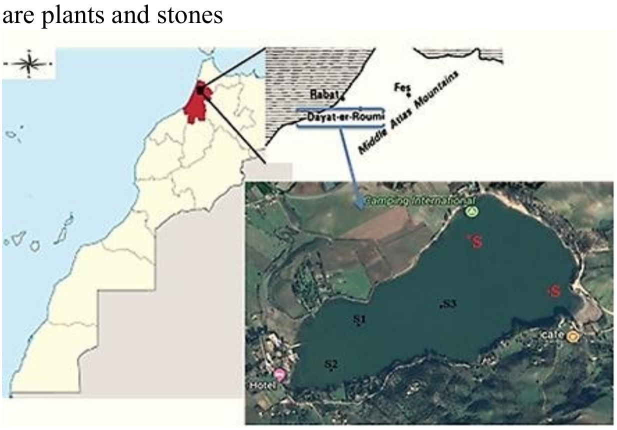

Fig.1. Study area and location of sampling stations.

2.3 Sample preparation and analysis

Sediment samples are collected on the surface layer of the lake using an Ekman bucket. The samples are transferred to clean plastic bags and then transported to a cooler (4°C). In the laboratory, these samples were dried in an oven for 24 hours at 80°C and sieved to obtain a powder with a diameter of ≤ 63 µm that has been stored in well-closed plastic vials to protect them against humidity. The vials were then stored in a cabinet in the dark and a cool place (20°C) until digestion. The method used for this digestion is total decomposition [8], 0.2g dry sediment samples were collected and placed in

Teflon tubes were previously washed with acid. For hot digestion, 5 ml of nitric acid, 2 ml of hydrogen peroxide, and 2 ml of hydrofluoric acid were placed in each tube and were put in a microwave oven at a temperature of 190°c for 45 min. after digestion of the samples, a 10 mL boric acid solution was added to the contents of thetubes, the final volume was reduced to 50 ml. The metals were measured by Microwave Plasma Atomic Emission Spectrometer (MP-AES). The validity of the analytical methods was verified by internal control and by an external control using an inter-calibration exercise [9].

2.4 Statistical Analysis

For a better results interpretation, we relied on statistical analysis, a calculation of Contamination factor "FC" and a Degree of contamination (DC). Metals are mainly associated with sediment particles (clays, carbonates, iron oxides and hydroxides, organic matter, etc.); it is, therefore, necessary to express the concentrations of metals according to a parameter related to the nature of the sediment.

2.4.1 Contamination factor "FC":

This normalization consists in expressing the ratio of the content of a given substance compared to that of the normalizing factor (We have used the crustal concentrations of Wedephol [10] and Pekey [11] as reference values (UCC-Upper Continental Crus)), allows defining the contamination factor "FC" of a given trace element in the sediment. This contamination factor is expressed by the following formula: $FC=Cx/Bg$

Cx: concentration measured for an element x, Bgx: Background for an element x

Contamination classes are defined for FC [12], [13] [14]: $FC < 1$ (absence to low contamination),

$1 \leq FC < 3$ (moderate contamination), $3 \leq FC < 6$ (significant contamination), $6 \leq FC$ (very high contamination).

2.4.2 Degree of contamination (DC):

Allows the estimation of a priori polymetallic contamination for each sampling point. It is the sum of the FC; it is calculated according to the following formula (Hakanson 1980): $DC=\sum FC$

This index is associated with 4 quality classes [12]: $DC < 6$ (low contamination),

$6 \leq DC < 12$ (moderate contamination), $12 \leq DC < 24$ (significant contamination), $24 \leq DC$ (very high contamination).

3 Results and discussion

3.1 Metallic contamination of sediments

The three Figures reveal the existence of metallic contamination characterized by significant Spatiotemporal variability. The highest average concentrations are those of Mn (1232.5 mg / kg) followed by Zn (993.94 mg / g) and Cr (102.424 mg / kg).

Concerning the heavy metal manganese (Fig.2), significant levels were recorded. The manganese concentrations vary between 1232.5 mg / kg and 684.96 mg/kg. The maximal concentration (1232.5 mg/kg) was observed at station 1, which indicates an anthropogenic activity (uncontrolled use of fertilizers and pesticides). The values recorded largely exceed the recommended standards [15] and [16]. These results show the vulnerability of the lake to extreme pollution.

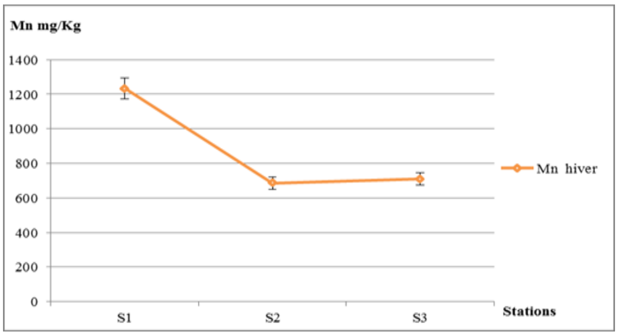

Fig.2. Spatio-temporal variation of Mn.

According to Figure 3, Zinc values reveal significant concentrations over the winter seasons; it varies between 993.94 mg/kg and 196.514 mg/kg; the maximal values were recorded during the winter at station 2. The high concentration of zinc is associated mainly with anthropogenic activities (agriculture, domestic waste, etc.). Our results show that the average zinc concentration far exceeds the recommended standards [15] and [16]. These high concentrations can have adverse effects on the aquatic environment.

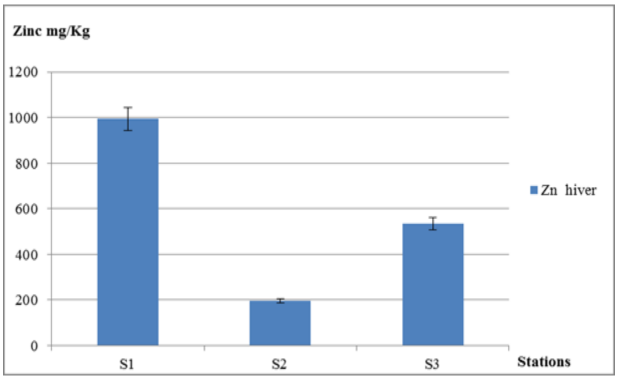

Fig.3. Spatio-temporal variation of Zn.

Chromium concentrations range from 102.75 mg/kg to 58.424 mg/kg (Fig.4). The monitoring at all stations reveals high concentrations during the winter season, particularly Station 3 is reaching a high concentration of 102.75 mg/kg and exceeds recommended standards [15] and [16]. This high concentration is likely due to the leaching of agricultural land showing the intense anthropogenic activity in the region and its impact on lake sediment quality.

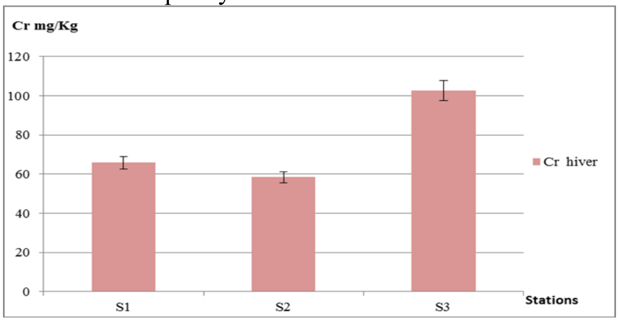

Fig.4. Spatio-temporal variation of Cr.

According to the results, we conclude that the sediments of lake Dayet Er-Roumi are polluted, the concentration of Mn, Zn, and Cr is very high in all measuring stations and vastly exceed the standards [15] and [16], this suggests that a significant part of these heavy metals may come from the inputs used, such as chemical fertilizers, pesticides (insecticides, fungicides, etc.), and may also come from domestic waste and landfills, etc. For Nickel, the concentrations at the stations studied are deficient and almost negligible. All concentrations recorded during the winter season at all stations are not detected (below the detection limit) by MP-AES.

3.2 Index and degree of sediment contamination

In order to have a quantitative idea of the sediments, additional analyses are carried out. The index approach also makes it possible to predict the extent of sediment pollution and identify priority polluted sites. It is found that the FC-Mn and FC-Cr are greater than 1 ($1 \leq$ FC-Mn < 3), which reflects an enrichment by these elements with moderate contamination. For the FC-Zn, the sediments of all sampling sites have FC greater than 6 ($6 \leq$ FC) except station 3, reflecting enrichment or even contamination by this element, which is considered extremely toxic to wildlife. The FC calculation shows that the lake's sediments are highly contaminated by the metals studied (Table 1).

For DC, the analysis of the results reveals polymetallic contamination dominated by two or more elements. The averages DC exceed the maximum class threshold defined by Hakanson (1980), indicating significant contamination for all stations with an average DC of 14.87; this value indicates significant polymetallic contamination (Table 1).

4 Conclusion

Overall, it appears that the levels of ETM show Manganese, Chrome, and zinc enrichment. This inventory reflects the direct influences of anthropogenic inputs. The various contamination indices calculated revealed situations of concern for several stations and several ETMs. Cases of polymetallic contamination dominated by two or more elements have been recorded (Zinc and Cr being the most worrying). All analyses show significant concentrations in the sediment. However, if the concentrations recorded do not give rise to immediate concern and cannot cause acute toxicity, it should be stressed that the eco-toxicological risk lies in the cumulative nature of heavy metals involved in bioaccumulation and bioamplification phenomena. Heavy metals can thus accumulate in low doses in various organs and reach the toxic threshold by altering either metabolic reactions in individuals or by causing demoecological disturbances in the populations of the affected ecosystems.

Table1. Contamination factor (FC) and degrees of contamination (DC) of the sites studied.

	Manganese mg/kg	Zinc mg/kg	Chromemg/kg	Facteur of Contamination "FC"			Degree ofContamination "DC"
				Fc Mn	Fc Zn	Fc Cr	
S1	1232.56	993.942	65.8225	2.338	19.112	1.880	23.33
S2	684.96	196.514	58.4245	1.299	3.7791	1.669	6.7471
S3	709.442	534.543	102.757	1.346	10.279	2.936	14.561
Average	875.656	574.999	75.668	1.661	11.057	2.162	14.87

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