# Determination of Some Heavy Metal Pollutants in Sediments of the Seybouse River in Annaba, Algeria

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Source: Air, Soil and Water Research, 5(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/ASWR.S10081

Air, Soil and Water Research

ORIGINAL RESEARCH

# Determination of Some Heavy Metal Pollutants in Sediments of the Seybouse River in Annaba, Algeria

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**Abstract:** This study was conducted in order to fight against pollution of the environment. The study concerns river sediment of the Seybouse River in northeastern Algeria. Northeastern Algeria is known for its various industries (steel, fertilizer, metal processing, etc), and the sediment deposited by the Seybouse River, is probably polluted by heavy metals.

For this study, we used two protocols of digestion of sediments, the first, using a mixture of hydrofluoric acid and perchloric acid, and the second, using aqua regia. The comparison of these two protocols will help us to find the best solubilization and thus facilitate the extraction and determination of heavy metals in sediment.

Before determining the concentration of some heavy metals (Fe, Zn, Mn, Sn, Ni, Cr, Pb and Cu), we first analyzed parameters of sediments such as pH and organic matter. We used atomic absorption spectrometry (AAS) to measure these heavy metals. The functional groups characteristic of organic matter and particularly clays were identified by infrared spectroscopy.

The average concentrations of metals exceeded acceptable standards for sediment pollution with heavy metals. Maximum concentrations in mg/kg respectively of the elements studied (Fe, Zn, Mn, Sn, Ni, Cr, Pb and Cu) were, respectively, 2460.20 ± 74.8; 1140.65 ± 38.2; 3.60 ± 1.2; 1.20 ± 0.5; 16.80 ± 2.6; 9.50 ± 3.2; 476.31 ± 21.6 and 145.15 ± 35.2. These results clearly show that the sediments deposited by the Seybouse River are heavily polluted.

**Keywords:** heavy metals, Seybouse River, sediments, atomic absorption spectrometry (AAS), infrared spectroscopy (FTIR)

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*Air, Soil and Water Research* 2012:5 91–101

doi: 10.4137/ASWR.S10081

This article is available from http://www.la-press.com.

## Introduction

The Seybouse River Basin extends over an area of 6.471 km$^2$, is located in the northeastern part of Algeria, and has a permanent population of approximately 1.3 million inhabitants (Fig. 1). The river basin lies within the territories of Wilayas of Guelma, El-Taref (near Drean), and Annaba.

The river basin is bordered in the north by the Mediterranean Sea, in the south by the Wilaya of Souk-Ahras, in the west by Edough Massif, Lake Fetzara, and in the east by Mafragh oued.

The effluents are torrential with irregular contours and longitudinal tension. The river passes through depressions of the Seybouse containing alluvium. This allows the regulation of a large amount of winter precipitation received by the chain of mountains. When the river reaches the plain of Annaba, it loses its energy and leaves behind a large load of sediment. Geomorphological characteristics of the plain are the gently sloping barrier of sand dunes and areas prone to flooding to allow the river to flow easily into the Mediterranean Sea.[1–3]

In recent decades, industrial liquid wastes have caused many problems for the environment. The heavy metals from wastewater are for the most dangerous when they manage to contaminate the sediment. The pollution of the Seybouse River by heavy metals in the vicinity of industrial facilities in the region of Annaba has been frequently reported in the literature.[4–6] The hydrogeological context of the region of Annaba could provide favorable conditions for the migration of pollutants into groundwater. There has been little research on the soils of the rivers of the industrial area of Annaba.

The origin of this pollution is related to social development. Urbanization in the region over the past 30 years has produced a considerable loss of agricultural soils and urban green space. Urbanization has also resulted in heavy traffic and, in particular, increases in various types of industry, such as steel, food processing, and chemical.

Most of the Seybouse River and its tributary Meboudja are characterized as excessively polluted mainly due to the intense industrial activity in the river basin. The planned development of wastewater collection and treatment systems should greatly contribute to reducing pollution of sediments.

The presence of chemical and microbiological contaminants in sediments requires a control of quantity and quality of sludge polluted rivers.[7,8] Studies have shown that the solubility of heavy metals depends on properties such as soil type, pH, texture, organic matter content, etc.[9,10]

The objective of this study was to evaluate the concentrations of metals in river sediments of the Seybouse River in the industrial area of Annaba. In addition, this study has been conducted to compare the concentration of heavy metals associated with sediment samples using two protocols of digestion. In addition, the determination of pH and organic matter content will help us to the mechanism by which exchange of metals in sediments.

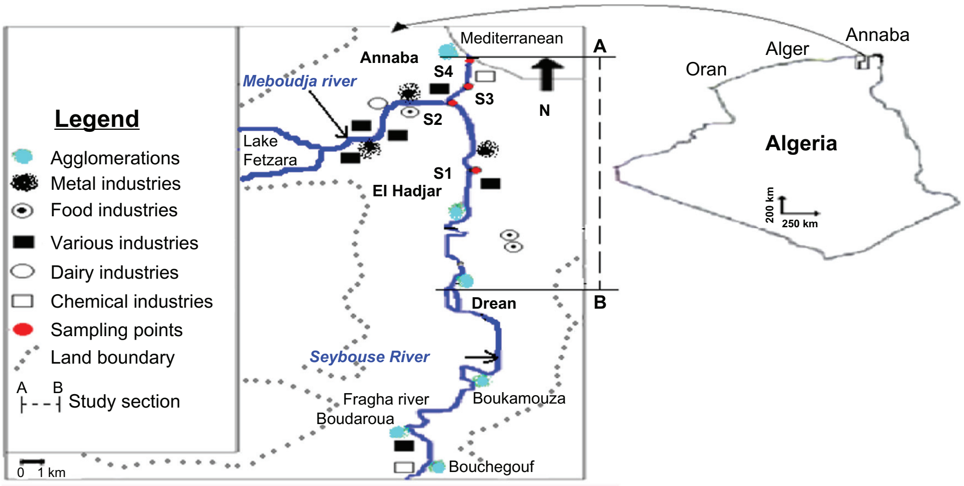

**Figure 1.** The map of studied area and sampling points.[4,6]

## Materials and Methods

### Study area

The Seybouse River lies northeast of Algeria. It stretches south to the end of the Saharan Atlas, then heads north ending in the littoral of Annaba and flowing into the Mediterranean Sea (Fig. 1). It spreads over a distance of 240 km, passing through the territories of the wilaya of Souk-Ahras, Guelma, Annaba and El-Tarf. Overall, the river extends over the administrative boundaries of 68 municipalities located in 7 wilayas. Its water resources are vital for sustaining economic activities in the region. The river runs through the plain Seybouse Annaba to join Meboudja River in the industrial zone. This ensures the emptying of Lake Fedzara.

The lake of Fedzara is the only significant aquatic ecosystem in the region and recently acquired official protection status through the Ramsar Convention. The dimensions of lake are 1917 km from west to east and 13 km from north to south, and the lake water is characterized by high salinity.[4,5]

Industrial activities are very important in the region and are mostly concentrated around the city of Annaba. The most important industries are: iron and steel complex of d'El Hadjar (ArcelorMittal), dairy products (Orelait), metal processing (SN-Metal) and phosphate fertilizer complex (Fertial).

There is increased competition among water uses along the river. Overall, agriculture consumes more than 70% of the available water, while the domestic and industrial sector utilizes the remaining 30%. With regard to ground water, nearly two-thirds are used for irrigation and one-third is for domestic and industrial use.

Land degradation is becoming a serious problem in the area, and erosion is the main cause for siltation problems in storage reservoirs. Furthermore, the Seybouse River receives significant pollution loads from many cities and industries.

Work conducted in our laboratory has shown that the waters of the Seybouse River and its tributary Meboudja contain a series of heavy metals. The solubility of heavy metals is strongly influenced by the pH and $E_H$ of the water. Cations can precipitate in the sediments.[4–6] Sediment contamination by heavy metals has become an issue of growing concern for the environment. Such contamination is often caused by human activities.

The formation of the aquifer system of the plain of Annaba (Fig. 2) consists of Mio-Pliocene sediments.[11] This is an alteration of sandy clay, where there are seven tanks of varying importance (Gaud),[11] the main ones being the shallow aquifer and gravel. The first is contained in sandy clay formations including sand lenses. Compact gray clays constitute the bedrock. These lenses are more common near the Seybouse River and at the periphery of Numidian sandstone. The groundwater is generally free, except in some points of their captivity in levels of clays.

From the hydrogeological point of view, the river flows through depressions containing an alluvial water table.[12] These formations distinguish two aquifers (Fig. 2), which communicate through the Oued Meboudja, the superficial aquifer of Annaba and the alluvial aquifer of high terraces.[13]

### Sampling and treatment

The samples were taken at different points in the Seybouse River downstream area of industrial liquid waste from the region of Annaba. These points, denoted S1 to S4 (Fig. 1), are at varying distances from each other: S1 to S2 are approximately 2.5 kilometers apart, S2 to S3, approximately 2 kilometers, and S3 to S4, approximately 4 km. S1: sediment near the steel plant of El Hadjar (ArcelorMittal); S2: sediments near rivers Seybouse and Meboudja; S3: Sediment near the industrial zone of Meboudja where there are small and medium enterprises and S4: sediment near the phosphate fertilizer complex.

Sediment samples were collected at 1 meter from the shore of the Seybouse River at a depth of 50 cm, avoiding the introduction of vegetation. Four samples of 0.5 kg were collected from an area of approximately 1 $m^2$ (using a stainless steel scoop) along the Seybouse River at sites S1, S2, S3 and

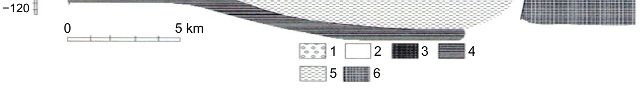

**Figure 2.** Hydrogeology of the Seybouse River.
**Notes:** (A to B) (1) Pebbles and gravels, (2) sand, (3) numidian clay, (4) cenomannian marl and marly limestone, (5) plio-quaternary destrital clays, (6) metamorphic formations.

S4 in November 2011 (Fig. 1). Sixteen samples were collected in polypropylene containers (1 kg), carefully closed to avoid any contact with air. The samples were stored, where necessary, at a temperature of 4 °C to prevent bacterial activity that could modify their properties. For sample preparation analysis, we used the NF X31-101 in order to have a representative fraction of the raw sample for the experiments. The samples were dried in an electric furnace at a temperature of 40 °C until the mass became constant. They were then homogenized having been previously ground and sieved through sieves of stainless steel ≤ 2 mm mesh. Therefore, all analyses were conducted using samples prepared in this way.

## Determination pH and organic matter in sediments

The determination of the total organic matter content was performed after dry combustion according to the NF ISO 10694: The method is based on the transformation dioxide ($CO_2$) from the total carbon present in the sample. The carbon is oxidised to $CO_2$ by heating the sediment to at least 900 °C in a flow of oxygen-containing gas. The amount of $CO_2$ released is then measured by gravimetry.

The pH of the sediment is an important parameter for the existence of a phase; its speciation and toxicity depend on the pH of the sediments. We used the method described by NF X31-103. The procedure of the method is the balancing of an ion mass of 10 g of sediment. We added 25 mL of doubly distilled water twice, stirred with a magnetic stirrer for 60 minutes at an ambient temperature of 22 °C ± 2 °C. The suspension obtained was left to stand for 2 hours protected from the air. We then measured the pH using a pH meter.

## Extraction of sediments

The extractions of sediments were performed on fractions of size ≤ 2 mm to ensure homogeneity of the samples. The large particles of debris and gravel are removed.

Methods of sequential extraction of metals in sediment samples are widely described in the literature,[14–17] and have been the subject of much criticism. For our study, we selected two extraction systems described below: one using a mixture of hydrofluoric and perchloric acids and the other using aqua regia. We determined using each the mean levels in mg/kg of metals in the four samples from each of the sites, S1, S2, S3 and S4.

### Hydrofluoric-perchloric acids

The metal contents were determined according to the PR NF ISO 14869-1 standard,[18] that is, 0.5 g dried sediment was moistened with 4 mL of doubly distilled water in Teflon beakers and 10 mL of hydrofluoric (HF) and 3 mL of perchloric ($HClO_4$) acids were added to the sediment. The mixture was let to settle for 12 hours. The beaker was the heated at 150 °C during 2 h and then evaporated to near dryness. Digests were diluted after filtration (0.45 μm filter) to 100 mL with a 2% chlorhydric acid (HCl).

### Aqua regia

Nitric and hydrochloric acids were used for the mineralization of the residual fraction of sediment.[14–16] For this work, we used the French standard NF X31-415, ISO 11466. A 1.0 g sample of soil was treated with 15 mL HCl and 5 mL $HNO_3$ and kept at room temperature for 24 hours. The sample was then heated in a sand bath on a hot plate to 50 °C for 5 hours and then refluxed at 130 °C for 3 hours. The samples were filtered, washed with doubly distilled water, and placed in 50 mL volumetric flasks. In addition to the total concentrations, metals were partially extracted from fine fractions of sediment. Twenty grams of dry fine fraction were put in contact with 50 mL of distilled water and shaken at room temperature (25 °C) for 2 hours. The extract was filtered and acidified at 1% with nitric acid.

## Results and Discussion

Heavy metals in sediments are not fixed permanently; the three parameters which influence the mobility of heavy metals are: organic matter, soil texture and pH of the mixture. They also change their speciation and, consequently, their mobility.

Table 1 indicates that there is a direct correlation between pH and organic matter content. At points S1 and S2, the pH is 5.50 and 6.10 with an organic matter content of 4.60% and 5.30% respectively. This is explained mainly by the acidic liquid waste from the steel industry in El Hadjar. The samples from point S3 are basic (pH 7.80) containing 8.60% organic matter. The samples from point S4 are close to neutral (pH = 7.20) with 3.60% organic matter. Sediment point S4 is far from the industrial area

**Table 1.** pH and organic matter (average of 3 measures) in the sediment of the Seybouse River in November 2011.

| Samples | S1 | S2 | S3 | S4 |
|---|---|---|---|---|
| pH | 5.50 (±0.1) | 6.10 (±0.1) | 7.80 (±0.1) | 7.20 (±0.1) |
| Organic matter in percent | 4.60 (±0.4) | 5.30 (±0.3) | 8.60 (±0.5) | 3.60 (±0.2) |

**Note:** Values in parentheses are standard deviations.

Meboudja, at about 4 km, and close to the release of phosphate fertilizer complex (manufacture of nitric acid and ammonia).

The effect of pH on the adsorption of metals has been particularly studied. The results of Table 1 show an increase in pH from the points S1 to S4, which may contribute to the adsorption of the metal reducible fraction of sediment (iron oxides and manganese) after exchange of metal cations with $H^+$ on some sites surface.

The evolution of levels of organic matter is not important and depends on the industrial waste sector. The highest value obtained in point S3 was near the industrial area of Meboudja (Fig. 1). The lowest value (3.60%) was at point S4 near the coast, which is due to the sea, which removes organic debris, and also to the sediment texture (coarse sand), which, in general, fixes little organic matter.

The organic material is composed of carbonyl functional groups such as phenolic, amine, etc. Therefore, the surface charge of organic matter is always negative, varies in intensity depending on the pH of the medium, and comes from the dissociation of functional groups. The organic material consists of carbonyl functional groups such as phenol and amine. Groups of R-COOH and R-OH contribute most to the acidic nature of the organic material. Indeed, all the metallic elements easily combined with organic matter and can form organometallic complexes. Their presence and their activity depends on the chemical nature of sediments.

In effect, all the metallic elements readily combine with organic matter to form organometallic complexes. Their presence and activity depend on the chemical nature (geochemistry) of the geological components.

## Determination of heavy metals in sediments

Total concentrations of heavy metals (Fe, Zn, Mn, Sn, Ni, Cr, Pb and Cu) were analyzed using atomic absorption spectrometer (Shimadzu Corp., Japan, AA-6200) with a system double beam, equipped with hollow cathode lamps. The spectral range extends at least from 180 to 900 nm.

Quality control was based on the use of standard metal solutions and duplicate analysis (for the fraction soluble in water). Condition standards for the determination of metals are presented in Table 2. The metal standard solutions purchased from Merck, Titrisols, and company were used to validate the analytical method. The blank and standards used for calibration were tested periodically.

The determination of the metals studied was carried out by atomic absorption spectrometry using an air-acetylene flame. The experimental conditions of assays are presented in Table 2.

**Table 2.** Conditions for determination by AAS.[4,6,19]

| Element | Wavelength (nm) | Supply current of the hollow cathode lamp (mA) | Nature of flame | Flow of test solution (l/min) | Atomization (°C) | Rec. Sens. (ppm) | Det. Lim. (ppm) |
|---|---|---|---|---|---|---|---|
| Fe | 248.3 | 8 | Air/$C_2$ $H_2$ lean | 2 | 2450 | 0.05 | 0.006 |
| Zn | 213.9 | 10 | Air/$C_2$ $H_2$ lean | 2 | 2750 | 0.01 | 0.008 |
| Mn | 279.5 | 10 | Air/$C_2$ $H_2$ stoichiometric | 2,2 | 2800 | 0.02 | 0.015 |
| Sn | 224.6 | 10 | Air/$C_2$ $H_2$ luminous | 2 | 2850 | 0.3 | 0.01 |
| Ni | 232.0 | 10 | Air/$C_2$ $H_2$ lean | 1,8 | 2850 | 0.04 | 0.002 |
| Cr | 357.9 | 8 | Air/$C_2$ $H_2$ rich | 1,8 | 2850 | 0.04 | 0.004 |
| Pb | 217.0 | 8 | Air/$C_2$ $H_2$ lean | 1,8 | 2450 | 0.008 | 0.001 |
| Cu | 324.8 | 8 | Air/$C_2$ $H_2$ lean | 1,8 | 2850 | 0.04 | 0.004 |

The study of interference during the analysis of elements was performed. No serious interference in air-acetylene flame was found for zinc. During the analysis of nickel, high concentrations of iron and chromium may increase the nickel signal. At doses of manganese, silicon depresses the signal and this effect is overcome by the incorporation of 0.2% of calcium chloride in samples and standards. The total chromium requires the elimination of the interference of total iron by adding a solution of ammonium chloride to 2 g/L in samples and standards. Finally, for the determination of iron, depression by silicon is reduced by the addition of 0.2% of calcium chloride.[4,6,19] Our results highlight relatively large amounts of Fe, Zn, Mn, Sn, Ni, Cr, Pb and Cu, which require dilutions of sediment samples.

The mean concentrations of Fe, Zn, Mn, Sn, Ni, Cr, Pb and Cu in various sampling points are represented by Figure 3.

## Statistical analysis

Levels (mean ± standard deviation) of metals in sediments from the Seybouse River are presented in Table 3. The two extraction methods were performed on the same samples. Analysis of metals was carried out over several days. Each metal was determined in samples (average of 4 measures). Next, we determined the mean, standard deviation (SD) and relative standard deviation (RSD). The statistical calculation (Table 3) shows that in general the results found by the two extraction methods were similar; however, the extraction with the mixture using hydrofluoric-perchloric acids generally have better repeatability (SD [a] $<$ SD [b]) and good precision and reproducibility (RSD [a] $<$ RSD [b]). The comparison of two variances using the Fischer-Snedecor law shows that F (calculated) $<$ F (Table). The value of the table: F (Table) = 9.28; $P = 0.95$ and $\alpha = 0.05$, for a number of measurements ($n = 4$). The difference between the accuracy of method a and method b is not significant. It is therefore possible to use either method.

To obtain the best conditions in an environmental study, it was necessary to compare the levels of metal clay sediments from different regions.[20–23] Table 4 summarizes some comparative data.

Iron is an essential element that can be toxic at high concentrations; it was among the most abundant

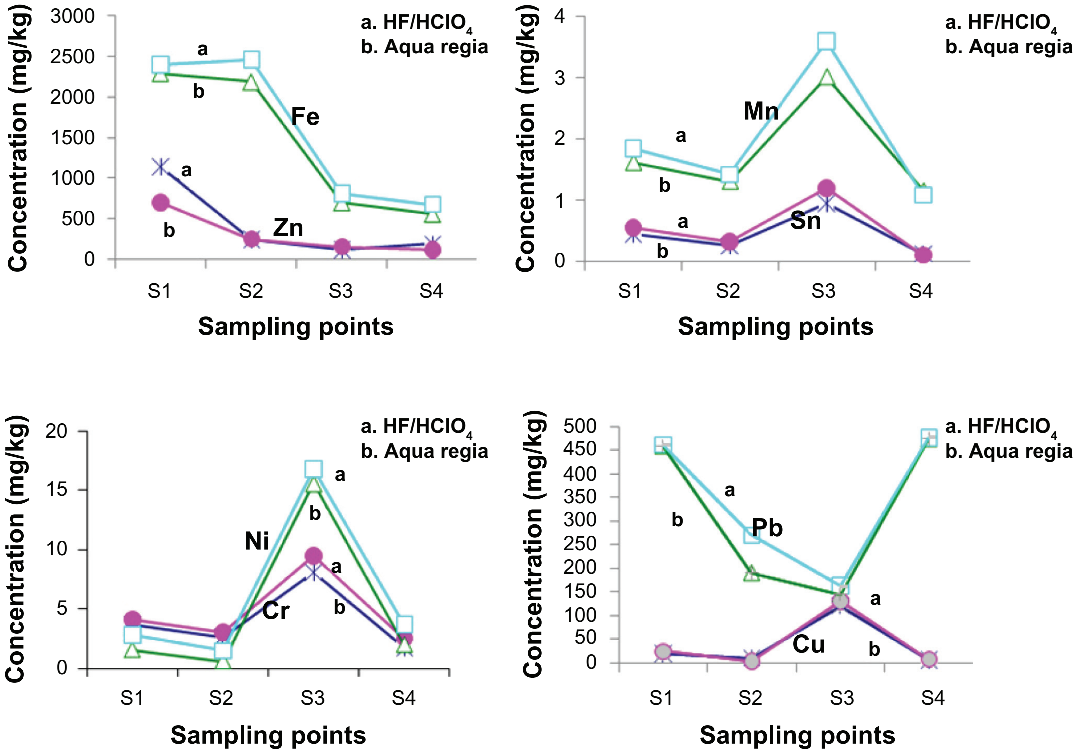

**Figure 3.** Concentration of metals in sediments samples from four sites in the industrial region of Annaba, Algeria.

**Table 3.** Heavy metal contents in mg/kg (average of 4 measures) in the sediment of the Seybouse River (Fig. 1), November 2011.

| | **S1** | | | | **S2** | | | | **S3** | | | | **S4** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Mean ± SD[a]** | **RSD (%)** | **Mean ± SD[b]** | **RSD (%)** | **Mean ± SD[a]** | **RSD (%)** | **Mean ± SD[b]** | **RSD (%)** | **Mean ± SD[a]** | **RSD (%)** | **Mean ± SD[b]** | **RSD (%)** | **Mean ± SD[a]** | **RSD (%)** | **Mean ± SD[b]** | **RSD (%)** |
| Fe | 2400.80 ± 72.1 | 3.00 | 2295.20 ± 87.4 | 3.80 | 2460.20 ± 74.8 | 3.00 | 2188.40± 65.1 | 2.97 | 808.10 ± 64.4 | 7.97 | 808.10 ± 67.9 | 8.40 | 675.0 ± 49.4 | 7.32 | 675.00 ± 49.6 | 7.34 |
| Zn | 1140.65 ± 38.2 | 3.35 | 702.10 ± 27.5 | 3.91 | 250.20 ± 30.6 | 3.35 | 250.20 ± 33.7 | 13.47 | 155.10 ± 9.1 | 5.86 | 155.10 ± 10.8 | 6.96 | 190.2 ± 8.3 | 4.36 | 113.50 ± 6.9 | 6.08 |
| Mn | 1.85 ± 0.7 | 37.83 | 1.85 ± 1.1 | 59.46 | 1.42 ± 0.8 | 37.83 | 1.42 ± 0.9 | 63.38 | 3.60 ± 1.2 | 33.33 | 3.02 ± 1.5 | 49.67 | 1.08 ± 0.7 | 64.81 | 1.08 ± 0.8 | 74.07 |
| Sn | 0.55 ± 0.2 | 36.36 | 0.55 ± 0.2 | 36.36 | 0.32 ± 0.1 | 36.36 | 0.32 ± 0.1 | 31.25 | 1.20 ± 0.5 | 41.66 | 0.95 ± 0.3 | 31.57 | 0.10 ± 0.06 | 60.00 | 0.10 ± 0.06 | 60.00 |
| Ni | 2.80 ± 1.2 | 42.85 | 1.55 ± 1.0 | 64.51 | 3.05 ± 1.4 | 42.85 | 1.50 ± 0.7 | 46.66 | 16.80 ± 2.6 | 15.47 | 15.60 ± 3.2 | 20.51 | 3.70 ± 1.8 | 48.64 | 2.00 ± 0.7 | 35.00 |
| Cr | 4.10 ± 2.4 | 58.53 | 4.10 ± 2.6 | 63.41 | 3.05 ± 2.1 | 58.53 | 3.05 ± 2.7 | 88.52 | 9.50 ± 3.2 | 33.68 | 8.10 ± 3.5 | 43.20 | 3.70 ± 2.8 | 75.67 | 2.00 ± 0.9 | 45.00 |
| Pb | 460.50 ± 16.7 | 3.62 | 458.20 ± 18.9 | 4.12 | 270.20 ± 15.3 | 3.62 | 190.30 ± 17.6 | 9.24 | 162.55 ± 18.4 | 11.32 | 145.15 ± 20.1 | 13.84 | 476.31 ± 21.6 | 4.53 | 476.31 ± 25.1 | 5.27 |
| Cu | 24.80 ± 7.2 | 29.03 | 20.12 ± 5.5 | 27.36 | 10.44 ± 4.9 | 29.03 | 3.66 ± 1.7 | 46.45 | 131.05 ± 33.4 | 25.48 | 145.15 ± 35.2 | 24.25 | 8.10 ± 3.3 | 40.74 | 6.33 ± 2.7 | 42.65 |

**Notes:** [a]Digestion with Hydrofluoric-perchloric; [b]digestion with aqua regia.
**Abbreviations:** SD, standard deviations; RSD, relative standard deviations.

elements in the sediments analyzed. The maximum average content of about 2460.20 mg/kg in the sample S1, represents almost twice the value of a natural, uncontaminated sediment (Table 4). Its concentration was below the levels found in sediments of the Rhine, the Seine estuary and the lower Loukkos River in Morocco. In the sample S4 it did not exceed 675.00 mg/kg, while in the S3 and S4 points, levels were below 808.10 and 675.0 mg/kg. The longitudinal profile (Fig. 1) shows that the iron content decreases with increasing distance from the industrial area of El Hajar and the ArcelorMittal steel complex.

Zn is an essential element at low concentrations but causes a high acute toxicity levels. The maximum content of zinc found in sediments of the Seybouse River show was 1140.65 mg/kg recorded in the sample S1, while in the sample S4, the content did not exceed 113.50 mg/kg.

Comparing the different levels found in the samples and the levels of natural sediments (Table 4) shows that the concentrations found in all samples greatly exceeded the natural levels. This reflects that there is an medium contamination. The longitudinal profile shows that the highest content was found in the sample S1. This is related to various industrial, agricultural and liquid discharges. At high concentrations, Mn is harmful to the environment. Mn concentrations found in the sample S3 showed a maximum value of 3.60 mg/kg eight times lower Mn concentrations found in the sediments of the estuary of the River Loukkos Morocco. The presence of this element in the studied sediments is not tolerated.

Sn is a metal highly toxic to all living organisms. The amount of Sn ranged from 0.10 mg/kg at point S4 to 1.20 mg/kg at point S3. The accumulation of this element in the sediment over time causes a risk of contamination. Its presence is attributed to emissions of industrial facilities at Meboudja (Fig. 1) from metals (stripping, tinning, etc).

Ni is a highly toxic element even at low levels. The levels of Ni found in the different samples showed maximum values of 16.80 mg/kg at point S3. This concentration causes a toxic risk to environments. The minimum concentration of Cr found in sediments at Seybouse Riverat point S2 was 1.50 mg/kg. This element presents a risk of pollution, especially to point S3. As with Sn, Ni content comes from the transformations of metals (pickling, tinning, etc).

**Table 4.** Concentrations of heavy metals in various types of sediment in mg/kg.

| Nature of the sediments | Fe | Zn | Mn | Sn | Ni | Cr | Pb | Cu |
|---|---|---|---|---|---|---|---|---|
| Unpolluted sediment[20] | 13200 | 44,3 | – | – | – | – | – | 16,6 |
| Sediment of the Rhine (Germany)[21] | 32300 | 115 | – | – | – | – | 30 | 51 |
| Sediments of Seine (France)[22] | – | 80 | – | – | 17 | 50 | 25 | 15 |
| Estuary down Loukkos (Morocco)[23] | | | | | | | | |
| Mean (±SD), maximum values | 29290<br>(±8,81) | 130,13<br>(±15,35) | – | – | – | 83.23<br>(±29,50) | 97.23<br>(±41,68) | 23,03<br>(±7,71) |
| Our study<br>Mean (±SD), maximum values | 2460.20<br>(±74.8)<br>(S1) | 1140.65<br>(±38.2)<br>(S1) | 3.60<br>(±1.2)<br>(S3) | 1.20<br>(±0.5)<br>(S3) | 16.80<br>(±2.6)<br>(S3) | 9.50<br>(±3.2)<br>(S3) | 476.31<br>(±21.6)<br>(S4) | 145.15<br>(±35.2)<br>(S3) |

Cr is very harmful to living organisms. The hexavalent form of Cr is the most toxic. The maximum concentration of Cr found in sediments at Seybouse Riverat point S3 was 9.50 mg/kg. The minimum level was 2.00 mg/kg at point S4. This level represents less than eight times the values found in sediments of the estuary lower Loukkos River in Morocco and less than five times the levels of sediments from the Seine (Table 4). Despite its relatively low level in the different samples of Seybouse River, it represents a danger to the industrial region of Annaba (Fig. 1). This content comes from liquid discharges from the steel processing industry surface treatment workshops. This content has harmful effects on the environment.

Pb is a toxic metal generally present in small quantities. In effect, the levels found in sediments at point S4 were the order of 476.31 mg/kg. This amount exceeds by nearly five times that of lower estuary of the Loukkos River, which is in the range of 97.23 mg/kg. It is about twenty times the levels found in sediments of the Seine and the Rhine (Table 4). We consider that the sediments of the Seybouse River are highly polluted by Pb. This is linked with rural and urban industrial centers, the large releases from steel plants, canning, fumes from foundries and incinerators, the exhaust gases of vehicles, and so on.

Cu is an essential element for all living organisms but is toxic at high levels. Concentrations of copper detected in the samples (S3) show a maximum value which is the order of 145.15 mg/kg. This exceeds by about seven times the levels found in sediments of the estuary lower Loukkos River in Morocco. Unpolluted sediments have a content of 16.6 mg/kg. Compared with sediments of the Seine and the Rhine (Table 4), we can say that the sediments in S3 are considered polluted by Cu. The presence of this element in sediments is derived from liquid discharges from industrial sites in the area of Meboudja.

Maximum average concentrations of the metals analyzed can be classified according to their relative abundance in sediments (Fig. 3) as follow: Fe > Zn > Pb > Cu > Ni > Cr > Mn > Sn. Several parameters influence this order: sediment composition (clay, organic matter, carbonate, etc), the nature of pollution, the sources of pollution (anthropogenic activity or natural), and so on. These values decrease as one moves toward the coast (point S4) of Annaba. There is no doubt that the very high concentrations of certain metals found in the sediments analyzed are the result of industrial and urban pollution. Air pollution caused by different factors contributes significantly to these results.

## Infrared spectra of sediments

Infrared measurements were made with a Shimadzu FTIR-8400S-(EC) infrared spectrophotometer. Spectra of sediment samples were obtained using special discs of potassium bromide (KBr) kept in a dry atmosphere.

Figure 4 shows the FTIR spectra of sediment samples S1, S2, S3 and S4. The study of the IR spectra is based on many studies.[24–28] The peak at 3620 $\text{cm}^{-1}$ (samples S1, S2 and S3) is assigned to OH groups (alcohols, phenols, organic acids). An intense band at 3420 $\text{cm}^{-1}$ present in all samples corresponding to the elongation of the molecular water adsorbed by the inorganic material or by the KBr pellet. A less intense peak 2509 $\text{cm}^{-1}$ is typical of calcite (samples S3 and S4). The two peaks of low intensity at 2345 $\text{cm}^{-1}$ and 2364 $\text{cm}^{-1}$ (samples S1, S2 and S3) correspond to P–H vibrations from phosphorus.

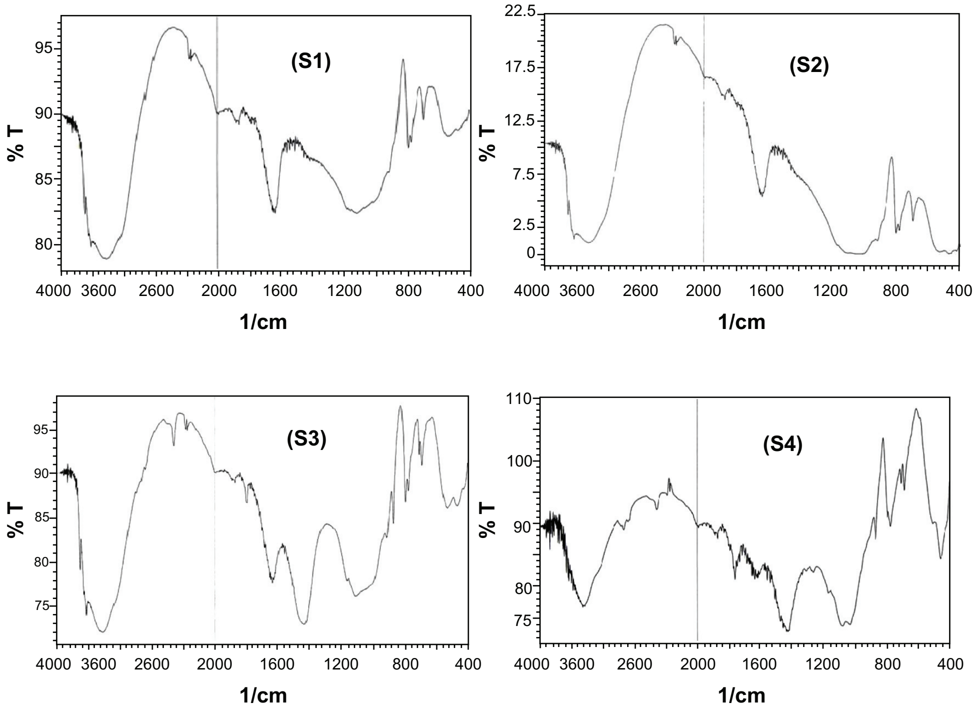

**Figure 4.** Infrared spectra (FTIR) of sediment samples in the Seybouse River at a depth of 50 cm and granulometry ≤ 2 mm.

A band around 1630 $cm^{-1}$ (all samples) is attributed to olefinic and aromatic C=C, C=O groups. Between 100 and 1100 $cm^{-1}$, two peaks of high intensities, centers at 1070 $cm^{-1}$ and 1036 $cm^{-1}$ are assigned to $PO_4^{-3}$ (sample S3 and S4). We also note a characteristic frequency of deformation of Al—OH at a little intense peak at 914.20 $cm^{-1}$ (all samples). Stretching of C—S appears at 690 $cm^{-1}$ (all samples). An absorption band corresponding to two peaks around 480 $cm^{-1}$ and 560 $cm^{-1}$, which are attributed to $Si—O—Al^{IV}$ and $Si—O—Mg^{IV}$. It should be noted that there is a series of bands between 900 and 500 $cm^{-1}$ which are detectable in the spectrum of $H_2Si_2O_5$ hydrated silica. This absorption is attributable to Si—O vibrations of quartz and minerals clays found in the spectrum of the humin. The study of the IR spectra shows that the samples are analyzed for mineral composition and organic. This is confirmed by the different spectra by the absorbances at about 3620 $cm^{-1}$ and 3697 $cm^{-1}$ (Si—OH vibrations) which also correspond to the vibrations bands of quartz and clays (illite, chlorite and kaolite). In contrast, samples S1, S2 and S3, S4 are very similar for all absorption bands with some differences in intensity. This result indicates that they have the same basic chemical structure and are characterized by the appearance of an intense band between 1430 and 1440 $cm^{-1}$ that may correspond to vibrations of $CH_2$ and $CH_3$ bonds. The spectra confirm the presence of bonds particularly characterizing clay type sediment.

The studied elements can accumulate in surface sediments containing organic matter and clays. The existence of functional groups, carbonyl (C=O), alcoholic (OH), carboxylic (COOH etc) can cause complexation of metal cations. The surface of clay has variable loads due to the presence of hydroxyl groups of silanol (—SiOH) and aluminol (—AlOH).[29,30]

The medium pH and organic matter can cause heavy metal mobility. Sediment collected at points S2 and S3 had a pH greather than 6, which can promote the complexation of metals. On the other hand, a pH greater than 5 and a soil with organic matter content of at least 5% favor the accumulation of lead. Adsorb metals in soil according to mechanisms of cation exchange in acid and chemosorption under the influence of organic ligands in alkaline medium.[31]

Copper is fixed preferentially to iron oxides, manganese, clays and organic matter at high pH.[32] Chromium VI is extensively converted to trivalent chromium in soils and sediments under anaerobic conditions and low pH ($pH < 5$). In the sediments analyzed, the predominant form was chromium VI.

Work showed that at pH ≤ 6, Fe, Cu, Zn and Pb were less mobile than Cr and did not migrate thoroughlyin soil. Heavy metals can be partially desorbed by other competing ions in water when their concentration is sufficient. Second, the metals are selectively adsorbed, iron hydroxides binds preferentially Zn, Cu, Pb, Hg, and Cr, while aluminum hydroxide prefer Cu, Ni, Co, Cr, Mo, and clays binds Zn, Cu and Pb.[6]

## Conclusion

The results obtained in this work have allowed us to evaluate the degree of metal contamination of sediments in the Seybouse River. Preliminary work on the different sediment samples allowed us to determine the pH and the rate of organic matter. Digestion of sediment samples using two protocols of digestion is efficient for determination of heavy metals. The results of assays are reproductible by AAS.

This study showed that, at a depth of 50 cm in clay-like sediment, heavy metals were found in the following maximum concentrations (mg/kg): Fe (2460.20 ± 74.8), Zn (1140.65 ± 38.2); Mn (3.60 ± 1.2), Sn (1.20 ± 0.5), Ni (16.80 ± 2.6), Cr (9.50 ± 3.2), Pb (476.31 ± 21.6) and Cu (145.15 ± 35.2). These elements tend to accumulate in sediments containing (8.60%) organic matter and pH = 7.80. Organic matter and pH of the medium can cause heavy metal mobility. Sediment collected at points S2 and S3 have a pH greater than 6, which can promote the complexation of metals. On the other hand, a pH greater than 5 and an organic matter content of less than 5%, favor the accumulation of lead. In sediments analyzed, the predominant form was chromium VI. Metals can adsorb in sediment according to mechanisms of cation exchange in acid and alkali chemosorption. However, the metals studied tend to contaminate the broad agricultural plain region of Annaba because of pollution by agrochemicals, industrial effluents and domestic sewage.

## Author Contributions

Conceived and designed the experiments: AL, AH, MA. Analysed the data: AL. Wrote the first draft of the manuscript: AL. Contributed to the writing of the manuscript: AL, AH. Agree with manuscript results and conclusions: AL, AH, MA. Jointly developed the structure and arguments for the paper: AL, AH, MA. Made critical revisions and approved final version: AL, AH, MA. All authors reviewed and approved of the final manuscript.

## Funding

Author(s) disclose no funding sources.

## Competing Interests

Author(s) disclose no potential conflicts of interest.

## Disclosures and Ethics

As a requirement of publication author(s) have provided to the publisher signed confirmation of compliance with legal and ethical obligations including but not limited to the following: authorship and contributorship, conflicts of interest, privacy and confidentiality and (where applicable) protection of human and animal research subjects. The authors have read and confirmed their agreement with the ICMJE authorship and conflict of interest criteria. The authors have also confirmed that this article is unique and not under consideration or published in any other publication, and that they have permission from rights holders to reproduce any copyrighted material. Any disclosures are made in this section. The external blind peer reviewers report no conflicts of interest.

## References

1. General Campaign of Geophysics. Prospection géophysique de la plaine alluviale de l'Oued Seybouse et ses affluents: région de Guelma. General Campaign of Geophysics. Nartional Agency for the Protection of the Environnement, Algeria. Rapp interne. 1971.
2. Djabri L, Hani A, Mania J, Messadi D. Etude des caractéristiques d'une nappe côtière de l'Est algérien (cas de la nappe alluviale de Guelma-Bouchegouf-Annaba). *Hidrogeologia*. 1994;10:13–29.
3. Djabri L, Hani A, Laouar, Mania R, Mudry J, Louhi A. Potential pollution of groundwater in the valley of Seybouse River, north-eastern Algeria. *J Environ Geol*. 2003;44(6):738–44.
4. Louhi A, Ali-Mokhnache S, Djabri L, Gheid A, Messadi A. Pollution des Oueds Meboudja et Seybouse dans la zone industrielle de Annaba (Nord-Est Algérien). Partie I: Utilisation de la spectroscopie d'absorption atomique avec flamme. *J Soc Alger Chim*. 1998;8(1):45–55.
5. Debièche TH. Evolution de la qualité des eaux (salinité, azote et métaux lourds) sous l'effet de la pollution saline, agricole et industrielle. Application à la basse plaine de la Seybouse Nord-est Algérien. [Thèse de doctorat.]:Université de Franche-Comté; Besançon, France; 2002.
6. Messadi A, Louhi A, Ali-Mokhnache S, Zenati N. Utilisation des spectroscopies d'absorption et d'émission atomique pour le contrôle de la pollution minérale des Oueds Meboudja et Seybouse dans la zone industrielle de Annaba (Nord-Est Algérien). *Cahiers de l'Association Scientifique Européenne pour l'Eau et la Santé*. 2001;6(1):41–8.
7. CEC-Commission of the European Communities. Council directive (86/278/EEC) on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Official Journal of the European Communities*. 1986;181:6–12.
8. New Zealand Department of Health. *Public Health Guidelines for the Safe Use of Sewage Effluent and Sewage Sludge on Land*. Wellington, New Zealand: New Zealand Department of Health; 1992.

9. McBride M, Sauvé S, Hendershot W. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *Eur J Soil Sci*. 1997;48:337–46.
10. Kouame IK, Gone DL, Savane I, et al. Mobilité relative des métaux lourds issus de la décharge d'Akouédo et risque de contamination de la nappe du Continental Terminal (Abidjan—Côte d'Ivoire). *Afrique Science*. 2006; 2(1):39–56.
11. Gaud B. *Etude hydrologique du système dee Annaba-Bouteldja. Synthèse des connaissances et recherche des conditions de modélisation*. Annaba, Algeria: Rapport ANRH; 1975.
12. Djabri L. *Mécanismes de la pollution et vulnérabilité des eaux de la Seybouse. Origines géologiques industrielles, agricoles et urbaines* [dissertation]. Annaba, Algeria: Université de Annaba; 1996.
13. Hani A. *Analyse méthodologique de la structure et des processus anthropiques: application aux ressources en eau d'un bassin côtier méditerranéen* [dissertation]. Annaba, Algeria: Université de Annaba; 2003.
14. Lin Z. Mobilization and retention of heavy metals in mill-tailings from Garpenberg sulfide mines, Sweden. *Sci Total Environ*. 1997;198:13–31.
15. Thöming J, Calmano W. Applicability of single and sequential extractions of assessing the potential mobility of heavy metals in contaminated soils. *Acta Hydrochim Hydrobiol*. 1998;26:338–43.
16. Prudent P, Massiani C, Thomas O. Evolution of heavy metal species in leachates and in the solid phase during composting of municipal solid wastes. In: Vernet JP, editor. *Environmental Contamination*. Amsterdam, The Netherlands: Elsevier; 1993:187–216.
17. Analytical Methods Committee, *Analyst (London)*. 1959;84:214.
18. NF ISO 14869-1. *Qualité du sol-Mise en solution pour la détermination des teneurs élémentaires totales-Partie* 1*: mise en solution par l'acide fluorhydrique et l'acide perchlorique* (Indice de Classement X-31-428-1). La Plaine Saint-Denis, France: AFNOR Groupe; 2001.
19. Price WJ. *Spectrochemical Analysis by Atomic Absorption*. Chichester, England: Wiley Heyden Ltd; 1983.
20. Nicolaidou A, Nott JA. Metal in sediment, seagrass and gasteropods near a nickel smelter in Greece: possible interactions. *Mar Pollut Bull*. 1998; 36(5):360–5.
21. Forstner U, Mûller G. Heavy metal accumulation in river sediments, a response to environment pollution. *Geofrum*. 1973;14:53–62.
22. Meybeck M, de Marsily G, Fustec É. La Seine en son bassin: fonctionnement écologique d'un système fluvial anthropisé. Paris: Elsevier; 1998.
23. El Morhit M. *Hydrochimie, éléments traces métalliques et indices ecotoxicologiques sur les différentes composantes d un écosystème estuarien (bas Loukkos-Maroc)* [dissertation]. Rabat, Maroc: Université Mohammed V—AGDAL; 2009.
24. Van Der Marel R, Bentelspacher H. *Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures*. Amsterdam, The Netherlands: Elseevier; 1996.
25. Gerasimowisz WV, Byler DM. Carbon-13 CPMAS NMR and FTIR spectroscopic studies of humic acids. *Soil Sci*. 1985;139:270–8.
26. Hernandez MT, Moreno JI, Costa F, Gonzalez-vila FJ, Frund R. Structural features of humic acid-like substances from sewage sludge. *Soil Sci*. 1990; 149:63–8.
27. Amir S, Hafidi M, Merlina G, Hamdi H, Revel JC. Elemental analysis, FTIR, 13C-NMR of humic acids from sewage sludge composting. *Agronomie*. 2004;24:13–8.
28. Cross AD. *Introduction to Practical Infra-red Spectroscopy*. London, UK: Butterworths; 1964.
29. Kalt A, Wey R. Composés interfoliaires d'une silice hydratée cristallisée. *Bull Gr Fr Argiles*. 1968;20:205–14.
30. Mortland M M, Shaobai S and Boyd S.A. 1986. Clay- organic complexes as adsorbents for phenol and chloro- phenols: Clays & Clay Minerals 34, 581–5.
31. Pichard A, Bisson M, Diderich R, et al. Zinc et ses dérivés. Verneuil-en-Halatte, France: INERIS; 2005:62. Fiche de données toxicologiques et environnementales des substances chimiques DRC-01-25590-00DF259.
32. Baker DE, Senft JP, *Cooper-heavy metal in soils*, Blackies academic and professional, London (UK), 1995;8:224–43.