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ARTICLE

Ecological Assessment of Physicochemical Pollution of Wadi Sebou (Gharb, Morocco)

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ABSTRACT

In Morocco, hydrological and hydrobiological surveys of wadis, river and stream are rare. In this research, we plan to attempt to characterize the physico-chemistry of surface waters of sixteen stations sampled at the level of the Sebou basin during the period 2013–2023. The diagnosis showed that this natural watercourse is highly enriched in oceanic salts. A large fluctuation in the chemical nature of the waters was recorded, as well as electrical conductivity (EC), which oscillates between 629 and 22,766 µS/cm. Hydrogen Potential ranges from 8.01 to 8.79 while remaining basic. Nitrate (NO3$^-$) concentrations range from a maximum of 886.9 mg/l to a minimum of 0.24 mg/l. Similarly, the ammonium concentration varies from 0.04 to 15.34 mg/l. It was also noted that the waters were very rich in chloride ions (860.27 to 145.55 mg/l), in sodium Na+ ion (51 to 2,530 mg/l), in sulfate ions SO4-- (441.4 to 37.62 mg/l), in calcium ions Ca2+ (97.6 to 1,072.8 mg/l) and in magnesium ions Mg2+ (631.2 to 17.28 mg/l) which explains the high hardness of these waters. The concentrations of potassium ions (K+) range from 2.54 to 17.55 mg/l. The high alkalinity is due to the high concentrations of bicarbonate ions (75.64 to 362.34 mg/l). Our study concludes that the waters of the Sebou remain below the irrigation threshold authorized by Moroccan law when moving away from its Atlantic estuary. They are

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too degraded and we suggest that urban and industrial wastewater be pre-treated as a priority to reduce pollution of the natural environment.

Keywords: Watercourse; Physicochemistry; Norme; Quality; Sebou; Kenitra; Morocco.

1. Introduction

Morocco owes its significant water resources to four main factors: altitude, latitude, climate and nature of the rocks. The first three of these, closely combined, make it a relatively well-watered country, except in the pre-Saharan and Saharan regions.

Thanks to its favourable geographical position in the North of Africa, morocco remains in most of its territory, a state with an essentially semi-arid climate. Apart from the North-West region and the summit of the Atlas, rainfall remains low in Morocco, compared to the countries bordering the North of the Mediterranean (Portugal, Spain, France, Italy, etc.).

The alternation of periods of heavy rainfall and severe drought, which can last for several years, marks the climatic and hydrological regimes of morocco. Indeed, recent rainfall statistics and those covering several centuries indicate that the Moroccan territory has always undergone cycles of drought followed by rainy years. Average annual precipitation varies from 500 to 2,000 mm in the wettest area of the North-West, to less than 100 mm in the arid areas of southern Morocco [1]. Average rainfall in Morocco is lower compared to other Mediterranean countries such as Spain (636 mm/year), Portugal (854 mm/year), France (867 mm/year) and Italy (832 mm/year).

In a normal year, total rainfall throughout the territory is estimated in an average year at approximately 150 billion cubic meters per year, of which 121 billion go to evaporation and approximately 29 billion to total surface and underground flow [2].

In winter, a layer of snow forms on the high mountains of the Rif, the middle Atlas and the high Atlas, sometimes very thick. Consequently, we find ourselves in the presence of three large water towers, with capacities all the greater since these high massifs are partly covered by enormous limestone masses containing large water tables. The sources from these rocks reinforce, in fact, the upper course of many rivers: Ras-El-Ma in Chaouen, Aîn-Sebou, source of the Oum-Er-Rbia, etc.

Morocco's water resources are limited. Renewable water resources are estimated at 29 billion m^3 / year, are a little more than 1000 m^3 / inhab / year. The resources that can be mobilized do not exceed 21 billion m^3 / year, or in 1996, 830 m^3 / inhab / year and 411 m^3 / inhab / year in 2020 according to the projections of the General Directorate of Hydraulics [2,3].

They are, moreover, subject to extreme cyclical variations, episodic drought cycles. Water, already scarce, is also subject to the continuous increase in needs, due to the rapid evolution of the population, the improvement of the standard of living, industrial development and the extension of irrigated agriculture. These pressures on water resources are accompanied by a growing and increasingly serious deterioration in their quality due to various pollutant discharges, such as domestic and industrial wastewater.

Our environment is increasingly being reworked by man, to the point that there is practically no longer any truly natural environment in our country. Whether it is to make waste outlets or waterways, we have considerably disrupted the ecological balance of our waterways.

Two groups of pollution can be distinguished: Physical pollution (mechanical and thermal pollution) and chemical pollution (mineral-dominated and organic-dominated pollution).

Ecosystem assessment must be approached by taking into consideration two aspects: first, the natural characteristics of the waters (major elements) and then their degree of pollution.

Chemical analysis methods, now very sophisticated and often expensive, generally make it possible to measure the nature and extent of the contamination. These analyses are sometimes very complex due to the diversity of contaminants present, not to mention their possible degradation or transformation products. Chemical analysis therefore remains essential for identifying pollutants and the limits of variations in their contents.

We will focus here mainly on the study of pollution by urban and agricultural wastewater. Industrial pollution can have direct toxicity, eliminating most animals which can therefore no longer serve as indicators [4].

The objective of our investigations is to diagnose the physical and chemical quality of the watercourses of the Gharb plain. This organic and mineral pollutant measurement of the Sebou raw water consists of pH, electrical conductivity, Sodium, Chloride, Sulphate, Calcium, Magnesium, Potassium, Carbonate, Bicarbonate, Hydrometric Title, Ammonium and Nitrates analyses.

2. Materials and Method

2.1. Study Area

Long considered inexhaustible, water resources are currently becoming a source of concern for man. Indeed, the latter consumes large quantities for his domestic, industrial and agricultural needs. He therefore needs water in quantity and quality, particularly when it comes to his food. Man has therefore sought to evaluate what water quality was, and he has come up against a problem of definition. Meybeck and Helmer state that it is difficult to give a simple definition of water quality because of the wide choice of variables that can describe the state of this water [5]: in fact, quality can be expressed through a combination of concentration of inorganic or organic substances, but also through the composition and state of aquatic living beings.

However, these analytical techniques do not make it possible to assess the effects of the presence of contaminants on living organisms or on the health of the ecosystem, such as biotic indices.

The first methods, called physicochemical, attempt to give values to different variables concerning hydrology (speed, flow, water level, etc.), general parameters (temperature, conductivity, dissolved oxygen, etc.), nutrients (nitrogen compounds, phosphorus compounds, etc.), organic matter (total organic carbon, COD, BOD5, etc.), and other variables [6,7].

The second methods, called biological, are based on the following phenomenon [8]: in response to environmental factors, animals and plants group together in associations or biocenoses. When a disturbance occurs, it causes a change in the species composition. This change is therefore a biological indicator of water pollution. Verneaux specifies that this biological modification simultaneously involves a structural modification of the initial population, an appearance and proliferation of species that are elective of particular conditions and a more or less rapid disappearance of all or part of the initial population [9].

Biological methods are classified into three hierarchical levels [10]:

* molecular level. Biochemical and ecotoxicological methods at the cellular level;

* organism and population level. Ethological methods;

* community level. Biocenotic method aimed at revealing changes in the structures of these communities.

Water quality is classified according to its physical, chemical, biological and organoleptic characteristics. Also classified according to its common uses. In addition, non-potable water for human consumption can be used for watering plants, or for aquaculture or for cooling factory machines [2,11,12].

The rational use of the water reserves of the Sebou River is at the heart of the concerns of regional managers in order to opt for an equitable strategy which values this resource at its own value and would make it possible to meet the challenge of the growing demand for quality water.

The Sebou wadi and its waterways occupy an area of 34,000 km2. It flows for about 600 kilometers, from its source in the Mountains to Mehdia-Kénitra where it empties into the Atlantic Ocean. It thus creates an estuary 35 km long. The rise of salt water from the ocean is stopped at the hill dam located just at the entrance to the city of Sidi Allal Tazi [13].

Indeed, the Sebou wadi is the site of numerous discharges of pollutants from various sources. The Sebou plain is an important region of Morocco thanks to its agricultural and industrial activities, but it suffers more pollution. The existence of several agricultural fields in the Gharb plain in addition to the variety of its factories (tanneries, sugar factories, paper mills, oil mills, breweries, dairies, cheese factories, canneries, cellars) and the wastewater outlets of the main towns of the plain (Fès, Meknes, Mechraa BelKsiri, DarGueddari, AllalTazi, Kénitra), without excluding the illegal dumping of household waste which also proves to be a degradation source of the Sebou waters healthiness.

Rivers then leave the mountain ranges. Some flow into the atlantic ocean (Loukkos, Sebou, Bou-Regreg, Oum-er-Rbia, Tensift, Draà, Saqia-Hamra), others into the Mediterranean Sea (Martil, Laou, Moulouya, etc.). In the end, many of them only end up at a pre-Saharan confluence or are lost in the desert sands (**Table 1**; **Figures 1**, **2**).

Table 1. Statistical Data on the Rivers of Morocco.

Name of Basin	Area (Km2)	Flow (MCM)	Exploitable potential (MCM/year)
Loukkos, Tangier, and Mediterranean coastal	12,805	3,600	190
Moulouya, Figuig, Kert Isley Kiss	76,664	1,610	512
Sebou	40,000	5,560	1300
Bouregreg and Chaouia	20,470	850	120
Oum er-Rbia and el Jadida Safi	48,070	3,315	405
Tensift and Ksob Igouzoulen	24,800	800	520
Souss Massa Draa	126,480	1,444	691
Guir Ziz Rheris	58,841	626	313
Sakia el Hamra and Oued Eddahab	302,725	390	16
Total	710,855	18,195	4,067

Figure 1. Map of the Hydrographic Network of Morocco.

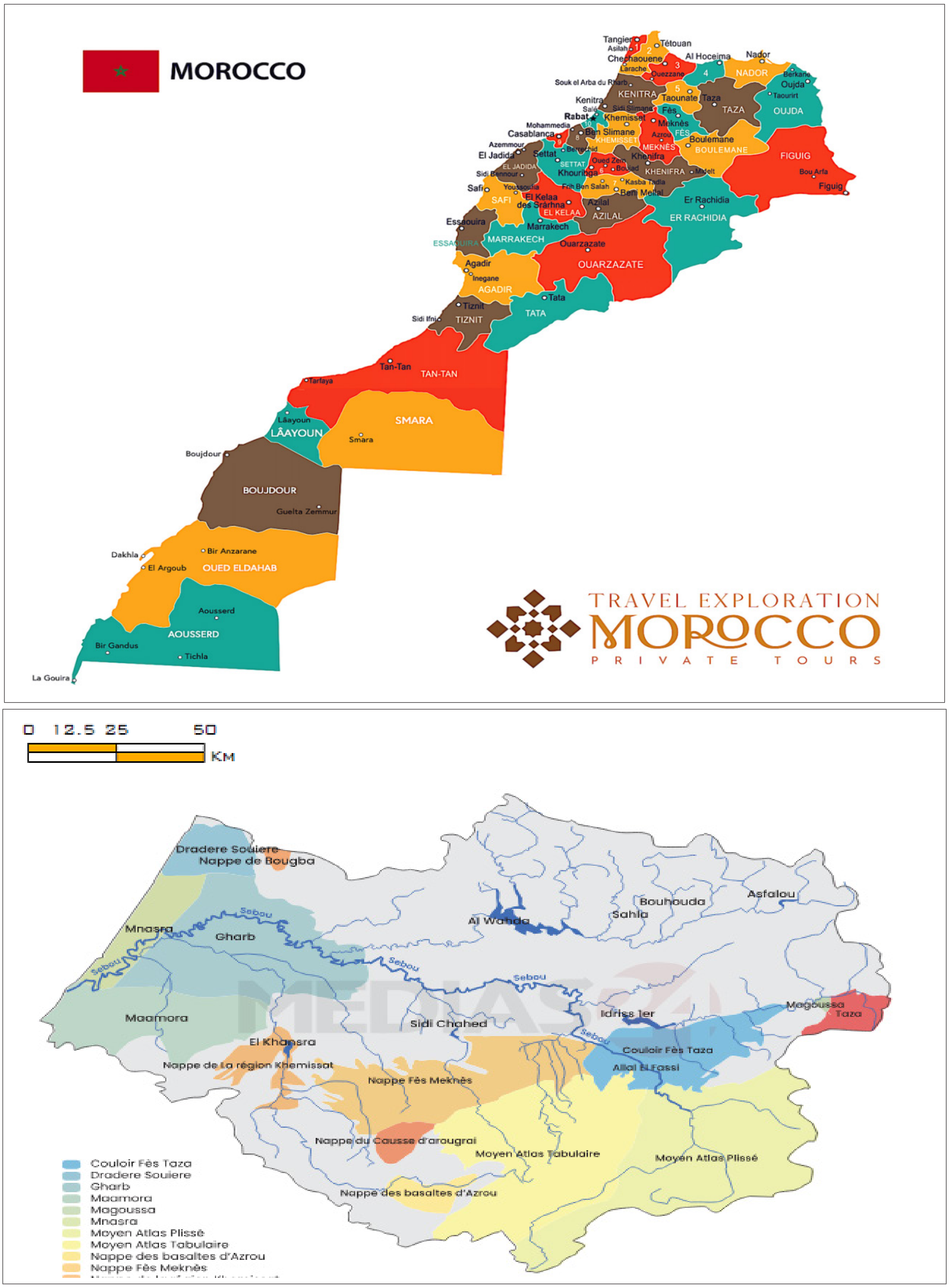

Figure 2. Geographical Location of the Sampling Waters Stations from River at Gharb Morocco.

The Sebou Plain forms a basin between the Rif Atlas Mountains to the northeast and the Atlantic Ocean to the west, with a surface area approaching 38,380 km^2. It is the largest basin in Morocco and currently has a total population of approximately 6 million inhabitants [14].

The Gharb region, with its agricultural and industrial potential, is very productive and contributes honorably to Morocco's gross domestic product. Basin is of the Mediterranean type with a predominance of semi-arid to sub-humid and humid bioclimatic stages. The most important industries in the region are of agri-food nature: sugar refineries, leather goods, oil mills, tanneries, dairies and cheese factories.

Taking a water sample is a delicate operation that must be carried out with the greatest care; it guarantees the quality of the analyses and their significance. In general, the sample must be pure and significant, and must not alter the physical and chemical properties of the watercourses (Colour, pH, O2, EC, etc.) [14]. Also, the instruments for taking water samples must be subject to special handling. The type of bottles (glass or plastic) will depend on the analyses targeted and applied to the sampled water. Instantaneous water sampling is the widely recommended technique. Bottles should be filled without agitating the water and avoiding gas bubbles [15,16].

2.2. Water Sampling

One-litre plastic bottles were used, first rinsed with distilled water and then in the field with local water. The samples were taken at 16 stations in sites where water was running during the period 2013–2014 and completed on 2018–2023. They are filled in total immersion, without air bubbles, to limit as much as possible the alteration and the subsequent variation of the samples. The collected water samples were transported at 4°C in portable coolers to the analysis laboratory. Furthermore, from one sampling to another, the measurements were carried out at exactly the same time and in the same place for the same site.

2.3. Water Analysis

In this study, the analyses are: pH, electrical conductivity, Calcium, Magnesium, Sodium, Potassium, Carbonate, Bicarbonate, Chlorides, Sulfates, Ammonium, Nitrates and hydrometric titer.

2.3.1. PH Measurement

PH measurements are carried out directly in the field on the Sebou wadi using a portable field pH meter type Hanna HI-8424. The pH of a solution expresses its hydrogen ion concentration, using a logarithmic notation: $\text{pH} = -\log[\text{H+}]$.

This notation expresses the real or ionic acidity of a solution; that is, the quantity of free H+ ions in the solution. The pH is therefore a function of the degree of dissociation:

at equilibrium $[\text{H+}][\text{OH}^-] = 10^{-14}$

at neutral pH $[\text{H+}] = [\text{OH}^-] = 10^{-7}$ or $\text{pH} = -\log[\text{H+}] = 7$

at acidic pH $[\text{H+}] > 10^{-7} > [\text{OH}^-]$ or $\text{pH} < 7$

at basic pH $[\text{H+}] < 10^{-7} < [\text{OH}^-]$ or $\text{pH} > 7$.

The measurement must be carried out on site at the time of sample collection so as not to modify the ionic balances as a result of transport or prolonged storage. In the case of poorly buffered water samples, the pH should be determined without the sample being exposed to air.

The pH is measured also on site using a portable pH meter or using the multi-parameter analyzer (HANNA HI 8314 and CONSORT C-835 portable pH meter and WTW2006 benchtop pH meter).

2.3.2. Electrical Conductivity Measurement

The electrical conductivity of water represents its ability to conduct an electric current. It is the conductance (inverse of the resistance) of a column of water between two metal electrodes. It is a function of the total concentration of ions, their mobility, their valence, their relative concentration and the temperature.

The unit of conductivity is the siemens per meter (S/m), but in the case of water we generally use the microsiemens per centimeter (µS/cm) or the mmho/cm. By multiplying the conductivity by an arbitrary factor which is equal to 0.64, we obtain an estimate of the total weight of dissolved salts or TDS (Total Dissolved Salts).

Conductivity measurement is based on the Wheatstone bridge principle, which measures the resistance R (in Ohms) of a water column of section S (in square centimeters) and length L (in centimeters) between 2 platinum electrodes (or those covered with platinum black) in parallel. Knowing the resistance R, the electrical resistivity (in ohms centimeters) is deduced using the formula: r = R x S /L.

The relationship between resistivity and conductivity at a given temperature is as follows:

Conductivity (µ s/cm) = 1,000,000 / Resistivity (Ω x cm).

The reference temperature at which the measurement results are expressed is 20°C.

The sample must be protected to prevent gains or losses of dissolved gas and protected from ambient air containing ammonia or acid gases, in polyethylene bottles with airtight caps. The measurement will preferably be carried out "in situ" using a portable conductivity meter (Consort C831 meter, WTW 325i, Consort C535 portable) or upon receipt of the sample at the laboratory (Consort C835 benchtop and C833).

Electrical conductivity (EC) was measured directly on site on the Sebou River by a Hanna Instrument HI-2300 and WTW325i and Consort 2535 conductivity meter.

2.3.3. Dosage of Calcium and Magnesium

Ca++ and Mg++ ions were measured by complexation with ethylenediaminetetraacetic in the presence of Eriochrome black T.

To 10 ml of the sample, add 2 ml of buffer solution so as to have pH = 10 (check if necessary, with a drop on indicator paper) and 4 – 6 drops of Eriochrome black indicators T.

Titrate with complexon III N/50 (using a 1/20 burette) until the wine-red colour disappears and a pure blue tint appears. Proceed slowly to the end of the change. By this dosage, we obtain the sum Ca + Mg, i.e., n ml.

Calcium Dosage

To 10 ml of the sample to be titrated, add approximately 40 ml of H2O, 2 ml of NaH 40% = 40 ml of NaOH 2% so as to obtain pH = 12 and a small quantity of the Patton Etreeder indicator mixture (at the end of a lanceolate spatula). The colour should be clearly pink; otherwise, check the pH.

Titrate with complexon III N/50 until blue. When you are not used to the change, it may be useful to compare with a control. By this assay, you obtain Ca Or n' ml.

The complexon gives complexes with many metal cations which Possibly the dosage of calcium and magnesium. In some cases it may be necessary to add potassium cyanide (2 ml, 1 in 1000 solution) to avoid interference from heavy metals (Cu, Ni, Co, Zn, etc.).

Determine the exact titer of complexon III N/50 by a dosage of the standard solution of Ca, following the method described above:

−10 ml of standard solution Ca N/50. Or V ml.

− 2 ml of NaOH 40%.

Indicators of Eriochrome T. 3 drops. (Preferably sharper change)

Titrate with complexon III N/50 or V' ml.

Carry out at least 2 successive dosages. (The difference between the titrations carried out with the two indicators: patton and Eriochrome black must be less than 0.05 ml).

The results are expressed in milliequivalents per Liter:

Ca meq / l = n' ml x N x 1000/10

Mg meq / 1 = (n – n') x N x 1000 /10

2. Magnesium Determination

Determination of calcium ions by a solution of disodium salt of Ethylene Diamine Tetra-Acetic acid (EDTA) at a pH between 12 and 13. Calcone carboxylic acid, which forms a red complex with calcium, is used as an indicator. Magnesium is precipitated in the form of hydroxide and does not interfere during the determination. At the equivalent point the indicator turns light blue.

Determination of calcium and magnesium ions by a solution of disodium salt of ethylene diamine tetra-acetic acid at a pH = 10. Eriochrome T black which forms a red complex with calcium and magnesium is used as an indicator. At the equivalent point the indicator turns greenish blue.

EDTA Solution titrated = 0.01 mol/l. Dissolve 3.725 g of disodium salt of Ethylene-Diamine Tetra-Acetic acid ($C_{10}H_4N_2O_8Na_2$.2H2O) in water and dilute to 1000 ml in a graduated flask. Store the EDTA solution in a brown bottle.

40% sodium hydroxide; Dissolve 400g of NaOH in 500 ml of distilled water after cooling dilute in a graduated flask to 1000 ml.

Buffer solution: Dissolve 16.9 grams of ammonium chloride (NH4Cl) in 143 ml of concentrated ammonium hydroxide (NH4OH) and dilute to 250 ml with distilled water.

Eriochrome Black T; Carefully mix 0.5 grams of Eriochrome Black T and 4.5 grams of hydroxylamine hydrochloride in 100 ml of 95° Ethyl alcohol.

Calcium standard solution N/10; Place 5.0044 grams of $CaCO_3$, dried at 105°C, in 20 ml of 18% hydrochloric acid and dilute to 1000 ml with distilled water.

operating mode:

Calcium ion determination: Introduce 20 ml of the sample into a 250 ml Erlenmeyer flask. add 1 ml of sodium hydroxide solution and about 0.2 g of the calcone carboxylic acid indicator. If the pH remains below 12, add the amount of sodium hydroxide solution necessary to bring the pH between 12 and 13. Shake and immediately dose with the EDTA solution while continuing to shake. Pour slowly at the end of the dosage. The change is reached when the colour becomes clearly blue. The colour should no longer change with the addition of an additional drop of the EDTA solution.

Determination of magnesium and calcium ions: Introduce 20 ml of the sample into a 250 ml Erlenmeyer flask. Add 2 ml of the buffer solution and 3 drops of the Eriochrome Black T indicator. The solution should turn dark red or purple, and its pH should be 10 ± 0.1. If the pH is less than 10, add the necessary amount of buffer. Dose immediately using the EDTA solution while stirring constantly. Pour quickly at the beginning of the dosage and then pour slowly at the end. Add the EDTA solution drop by drop as soon as the colour of the solution begins to change from red and violet to blue. The final turning point is reached when the last red shade disappears. The colour should no longer change by adding an additional drop of EDTA.

Expression of the results:

V1 = Volume of the EDTA solution used for the Ca determination.

V2 = Volume of the EDTA solution used for the Ca and Mg determination.

VE = Volume of the sample.

C = the concentration, expressed in mole/l, of the EDTA solution.

The calcium concentration Ca++ expressed in mg/l is given by the formula:

$c(Ca^{++}) = V1 * C * 1000 * 40.08 / VE$

The magnesium concentration Mg++ expressed in mg/L is given by the formula:

$c(Mg^{++}) = (V2 – V1)* C * 1000 * 24.32 / VE$

2.3.4. Chloride Cl^- Measurement

Chloride determinations using silver nitrate, accompanied by potassium chromate. Chloride dosage is carried out using the Mohr method (AFNOR T90-014). The specific colour of the water, the presence of sulphites and phosphates hinder the determination. Clarify turbid water by adding a solution of alum or potash, stir, decant and neutralise. Alkaline water is neutralised with a few drops of diluted sulphuric acid in the presence of phenolphthalein. Acidic waste water is neutralised with soda in the presence of heliantine. Sulphurous waste water is brought to the boil and neutralised while reducing water is treated with a few drops of hot perhydrol. Chlorides are determined in a neutral medium using a standardised solution of silver nitrate (0.02N) in the presence of potassium chromate (10%). The end of the reaction is indicated by the appearance of the brick red colour characteristic of silver chromate.

2.3.5. Determination of Sulfates

Sulfate determination by colorimetry. Sulfate ions will be precipitated by barium chloride and hydrochloric acid into barium sulfates. The precipitate is stabilized using a stabilizing agent. The colorimetric measurement of the test solution is carried out at a wavelength of 420 nm before determining the concentration using a calibration curve.

Preparation of the standard sulfates solution: 500 mg / l Dissolve 0.9062 g of K_2SO_4, dried in an oven at (105 °) in 1000 ml of distilled water.

Preparation of the buffer solution: Dissolve 24 g of Na Cl in distilled water, add 2 ml of conc. HCl and make up to 100 ml with distilled water.

Preparation of the glycerol solution: Mixture of 25 ml of glycerol and 75 ml of ethyl alcohol.

Also provide powdered barium chloride for analysis. Spectrocolorimeter type Pharmacy NOVASPEC II [17–20].

Preparation of the Calibration Curve

In a series of 25 ml graduated flasks, prepare a calibration control whose concentrations surround the range of concentrations of solutions to be measured, operating as an example, according to the indications in **Table 2**.

Take 2 to 5 ml of water sample in 25 ml graduated flasks.

Add 0.5 ml of glycerol + 5 ml of buffer solution + 10 ml of distilled water.

Weigh 0.5 g of barium chloride. Make up to 25 ml with distilled water.

Stir, leave the sample for 10 min.

Pass it through the colorimeter at a wavelength of 420 nm.

Calculate the concentration using the following formula. C = L / slope (the slope is determined from the calibration curve).

C: concentration of sulfates in meq/l.

L: the reading displayed by the colorimeter.

Slope: Calculate the sulfate calibration curve.

Table 2. Calibration Curve Solution Concentrations.

Vials	Standard Solution (ml)	Buffer Solution (ml)	Glycerol Solution (ml)	Barium Chlorides (g)	Distilled Waters	Concentration SO_4^- (mg/l)
Control	0	0.2	0.4	0.25	Complete at 25 ml	0
1	0.4	0.2	0.4	0.25		0.07
2	0.8	0.2	0.4	0.25		0.16
3	1.2	0.2	0.4	0.25		0.24
4	1.6	0.2	0.4	0.25		0.33
5	2.0	0.2	0.4	0.25		0.41

2.3.6. Determination of Nitrates and Ammoniums

Determination of Kjeldahl nitrogen NTK by the AFNOR 1999 NF EN 25663 method

Nitrogen can be present in polluted waters in many valence states:

- Reduced form: this is organic and ammoniacal nitrogen (N-NH4+);
- Molecular form: this is dissolved nitrogen (N2);
- Oxidized form: this is nitrous nitrogen (N-$NO2^{-}$) and nitric nitrogen (N-$NO3^{-}$).

This method allows the transformation into ammonium of compounds of biological origin (proteins, peptides, amino acids) but not that of nitrogen compounds of industrial origin (oximes, hydrazine, semicarbazone, etc.). The same applies to nitrites and nitrates. To determine the latter, perform a reduction in an alkaline medium. Kjeldahl nitrogen corresponds to the sum of organic amino compounds and ammonium. Organic nitrogen is obtained by difference.

Dosage of $NO3^{-}$ and NH4+ by distillation with two catalysts: magnesium oxide and DEVARDA alloy. Ammoniums and nitrates were recovered by boric acid and finally determined by H2S04.

2.3.7. Determination of Carbonates ($CO3^{-}$) and Bicarbonates ($HCO3^{-}$)

Determination of carbonates and bicarbonates by a 0.02 N sulfuric acid solution under the coloured indicators phenolphthalein and bromocresol green. For 0.02 N sulfuric acid. Make a dilution from a 0.1 N titrisol.

Phenolphthalein. Dissolve 0.1 gram of phenolphthalein in 100 ml of 95 ° ethanol.

Introduce the sample into a 250 ml Erlenmeyer flask first. Then add two drops of phenolphthalein. If the solution remains colourless, this indicates that the carbonates ($CO32^{-}$) do not excite in the solution but if the solution becomes pink, in this case we titrate with 0.02 N H2 SO4 until the solution becomes colourless. In a second step, add 2 drops of bromocresol green in the same Erlenmeyer flask (the solution becomes blue) titrate the bicarbonates ($HCO3^{-}$) with a 0.02 N H2SO4 solution. At the turning point, the colour changes from blue to yellow.

V = Volume of H2SO4 required to neutralize $HCO3^{-}$ in the absence of CO_32^{-}

V 1 = Volume of H2SO4 required to neutralize CO_32^{-}

V 2 = Volume of H2SO4 required to neutralize $HCO3^{-}$ in the presence of CO_32^{-}

In the absence of carbonates CO_32^{-}

meq / l $HCO3^-$ = V * 0.02 * 1000/10

In the presence of carbonates CO_32^-

The first acidity of the ions CO_32^-

meq / l CO_32^- = V1 * 0.02 * 2 * 1000 /10

The second acidity of the ions $HCO3^-$ is:

meq / l $HCO3^-$ = (V2 –V 1) * 0.02 * 1000 /10

2.3.8. Determination of Sodium and Potassium

Determination of sodium and potassium by flame photometer. Atomization of the element sought (possibly after dilution of the sample) in the flame of a photometer. Determination, at wavelengths 589.0 nm for sodium and 766.5 for potassium, of the ion concentration of the element sought by the direct method of determination using a calibration curve.

All reagents must be of recognized analytical quality. During the analysis and for the preparation of reagents, use only good quality distilled water.

Sodium standard solution:

Dissolve 2.542 grams of (Na Cl) sodium chloride, previously dried in an oven at 110° C, in water and dilute to 1000 ml; 1 ml of this solution contains 1 mg of sodium.

Potassium standard solution:

Dissolve 1.907 g of potassium chloride (K Cl), previously dried in an oven at 110 ° C, in distilled water and dilute to 1000 ml; 1 ml of this solution contains 1.00 Mg of potassium.

Preparation of the calibration curve solutions:

Prepare, at the time of use, from standard solutions at least 4 calibration solutions covering the range of concentrations to be determined for the element considered.

meq /l Na+ 0 – 0.2 – 0.4 – 0.6 – 0.8 – and 1.00 meq

meq /l K+ 0 – 0.1 – 0.2 – 0.3 – 0.4 – 0.5 meq.

Reading samples:

Before taking measurements, adjust the instrument according to the manufacturer's instructions.

Plot a calibration curve (concentration in meq/l as a function of the reading) by measuring the standard solutions and adjusting the zero of the instruments with distilled water. The calibration curve must be, or close to, a straight line.

Take the measurement on the test portion of the sample by adjusting the minimum and maximum concentrations of the standards while fixing the position of the Na and K filter according to the element to be measured.

Calculate the concentrations of the samples analyzed from the concentrations obtained for the dosing solutions, taking into account any dilutions.

Express the final results in meq/l.

2.3.9. Title Hydrometric or Total Hardness

Total water hardness is a measure of the calcium and magnesium in the water. These two elements combine to form calcium carbonate.

Hard water is water that weakens the normal working of soap by depositing salts of fatty acids (the fatty acid is the active substance in soap). The sedimentation charge in normal water is often calcium and magnesium ions. Water hardness can be temporary due to bicarbonate ions (and can be removed by boiling). Permanent hardness is due to the

presence of other anions such as chloride, sulphate, carbonate and nitrate of calcium and magnesium ions. Water hardness is usually expressed as the concentration of calcium carbonate in the water in ppm. In some countries, minimum levels of calcium are advised (the minimum level for calcium is 20 mg/l). The main problem with a high total water hardness level is that deposits can form in the pipes and make them less effective. If the water is too hard, it can also cause a decrease in the effectiveness of soaps and detergents, and affect the taste of the water. The method used to estimate the total hardness of water is the method of estimating the concentration of calcium and magnesium ions in the composition of complex compounds with EDTA, where the calcium and magnesium ions interact with EDTA at a rate of 1:1 in the presence of the appropriate reagent and the appropriate pH. At pH 12, the calcium ion can be estimated alone in the presence of the Murexide detector. Both ions (calcium and magnesium) can be estimated in the presence of the Eriochrome Black T detector at pH 10.

Prepare 250 ml of 0.05 M EDTA solution.

To quantify the calcium ion alone, 50 ml of the water sample is placed in an Erlenmeyer flask with a small amount of Murexide, then about 10 drops of potassium hydroxide (concentration 20%) are added to reach pH = 12. This can be confirmed by pH paper. We perform a titration with EDTA solution until the crimson red turns purple. We record the volume of EDTA, repeat the experiment twice and record the results in a table. We call the average volume in this case V1.

To quantify calcium and magnesium ions, put 50 ml of water sample in an Erlenmeyer flask with a small amount of Eriochrome T black. Then add about 8 drops of buffer solution (ammonium hydroxide + ammonium chloride) to reach pH = 10, this can be checked by pH paper. We perform a titration with EDTA solution until the red turns blue. We record the EDTA volume. The experiment was repeated twice and the results were recorded in a table. We call the average volume in this case V2.

Calcium concentration (ppm) = 0.05 * V1 * Atomic weight of Ca * 20

Magnesium concentration (ppm) = 0.05 * (V2 − V1) * Atomic weight of Mg * 20

Hardness (CaCO3 ppm) = 0.05 * V2 * Molecular weight of CaC03 * 20

TH is the hydrotimetric title of water, that is to say the rate that measures its mineralization or its concentration in mineral salts, namely potassium, magnesium and calcium. The TH of water tells us precisely its level of limestone. Knowing the TH of water therefore allows us to know its degree of hardness, which is linked to the composition of the soils of each region.

The hydrotimetric title is measured in French degrees, the symbol of which is °F. In concrete terms, 1°Fcorresponds to 4 mg/l of calcium or 10 mg/l of calcium carbonate (the cause of scale deposits).

TH between 0 and 10°F ⟹ very soft water
TH between 10 and 20°F ⟹ soft water
TH between 20 and 30°F ⟹ medium hard water
TH between 30 and 40°F ⟹ hard water
TH at 40°F ⟹ very hard water

3. Results

The measurement of the degradation of the Sebou quality was made through the determination of several indicators and physical and chemical elements dissolved in its waters. Using the conclusions of our work which will contribute to enriching the databases accumulated on the Sebou basin, we will be able to specify the level of its degradation thanks to the analyses carried out during our stay at the Laboratory of the Regional Office for Agricultural Development of Gharb Kenitra.

We can deduce (**Tables 3** and **4**; **Figures 3–9**) that the Sebou basin suffers from countless categories of pollution coming from nature (flooding, dissolution of rocky substrates, sea salts), agriculture, industries and urban effluents.

Table 3. Physicochemical Data (Anions) of Raw Water from the Lower Sebou River.

Stations	**pH**	**$NO3^{-}$ mg/l**	**CL^{-} mg/l**	**$SO4^{-}$ mg/l**	**$HCO3^{-}$ mg/l**	**$CO3^{-}$ mg/l**
S1	8.62	9.3	213	314.64	233.02	12
S2	8.65	10.42	161.88	159.18	214.72	18
S3	8.39	0.24	202.35	150.25	213.5	6
S4	8.46	17.11	154.78	141.18	275.72	0
S5	8	63.36	243.53	181.94	246.44	0
S6	8.12	20.58	202.35	151.62	362.34	0
S7	8.69	86.92	248.5	183.59	241.56	21.6
S8	8.33	188.6	385.53	258.32	323.3	13.2
S9	8.49	827.9	230.4	106.7	75.64	0
S10	8.24	2692	860.27	113.1	122	0
S11	8.4	260.8	269.09	37.62	100.04	0
S12	8.31	886.9	476.41	276.57	84.18	0
S13	8.79	94.6	461.31	359.29	246.44	49.2
S14	8.21	162.2	397.7	441.4	178.12	42
S15	8.73	59.9	304.59	248.5	241.56	18
S16	8.33	693.8	145.55	54.04	108.58	0

Table 4. Physicochemical Data (Cations) of Raw Water from the Sebou River.

Stations	Ca++ mg/l	Mg++ mg/l	K+ mg/l	Na+ mg/l	NH4+ mg/l	TH mg/l	CE µS/cm
S1	97.6	89.04	6.44	1,240	0.18	6.15	1,190
S2	118	46.56	6.24	1,270	0.43	4.89	1,120
S3	126.4	59.52	2.54	1,560	0.04	5.72	1,240
S4	166.4	17.76	5.27	1,360	0.68	4.9	1,160
S5	150.8	44.4	4.29	1,820	0.22	5.62	1,430
S6	169.2	68.64	9.56	1,330	0.18	7.09	1,400
S7	148.4	51.36	4.68	1,470	0.68	5.85	1,490
S8	220.4	111.6	12.48	1,840	0.5	10.16	2,370
S9	217.6	17.28	3.71	51	0.68	6.16	629
S10	914.4	631.2	5.07	140	1.76	49.16	15,820
S11	148.4	26.64	6.63	190	15.34	4.82	11,960
S12	314.8	39.36	17.55	390	0.54	9.51	22,766
S13	170.8	124.08	9.75	2,530	2.66	9.44	2,200
S14	1,072.8	74.88	15.99	150	1.26	57.94	16,700
S15	144.8	94.08	7.41	400	1.29	7.54	1,660
S16	174	99.36	2.73	120	1.51	8.49	880

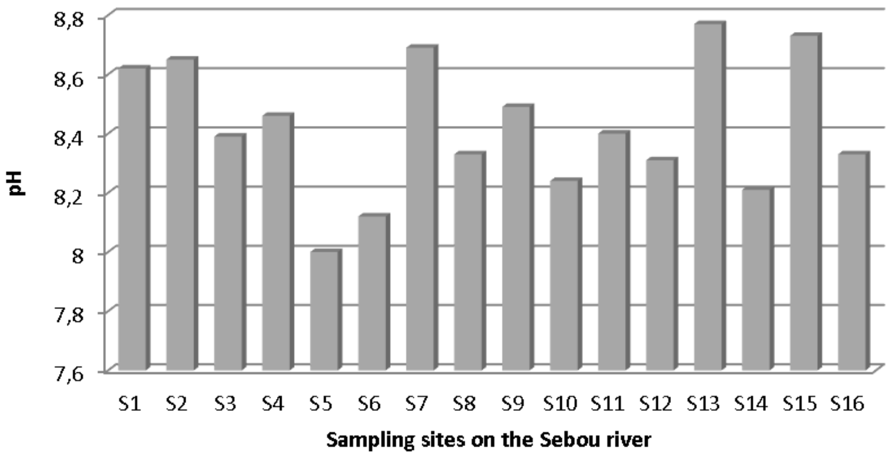

Figure 3. PH Variations Depending on the Sampling Stations on the Sebou River.

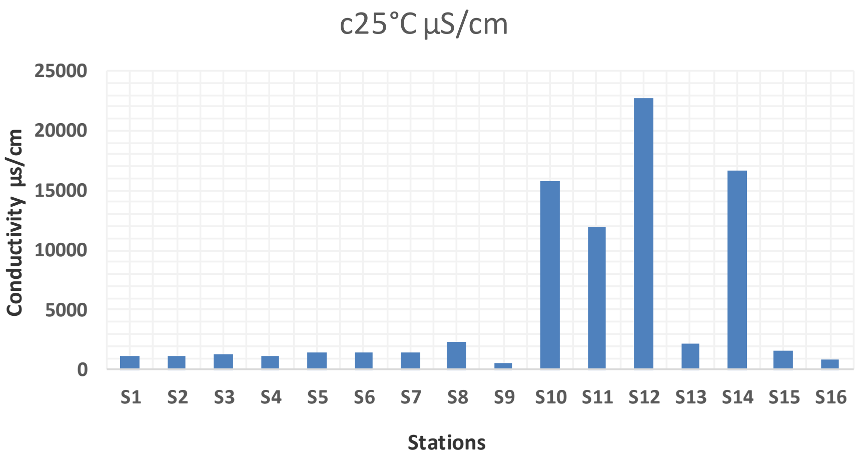

Figure 4. Variations in Conductivity According to Water Intake Sites on the Sebou.

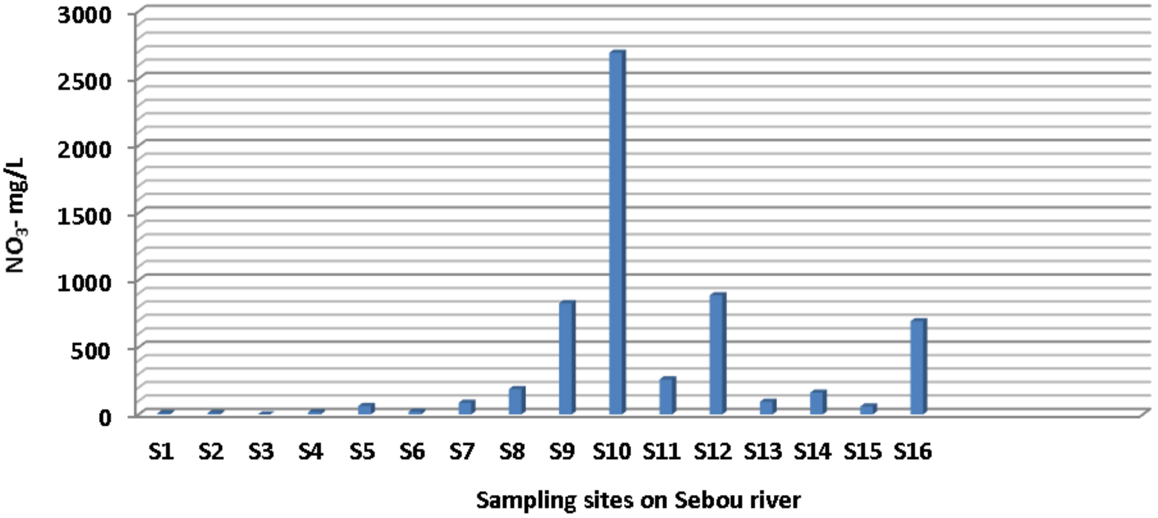

Figure 5. Spatial Evolution of Nitrate Content in Raw Water from the Sebou Basin.

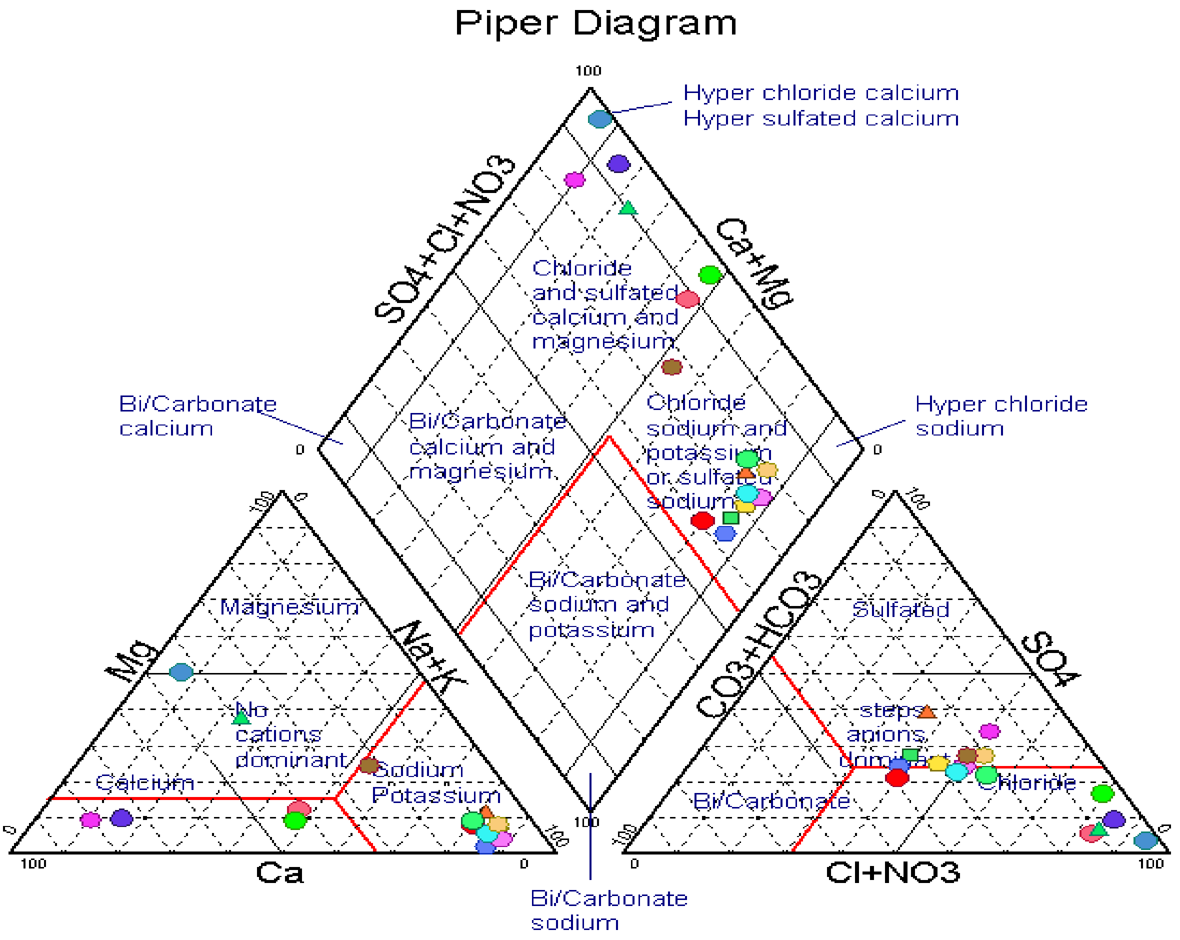

Figure 6. Projection into the Piper Diagram of the Waters Hydrochemistry of Sebou Basin.

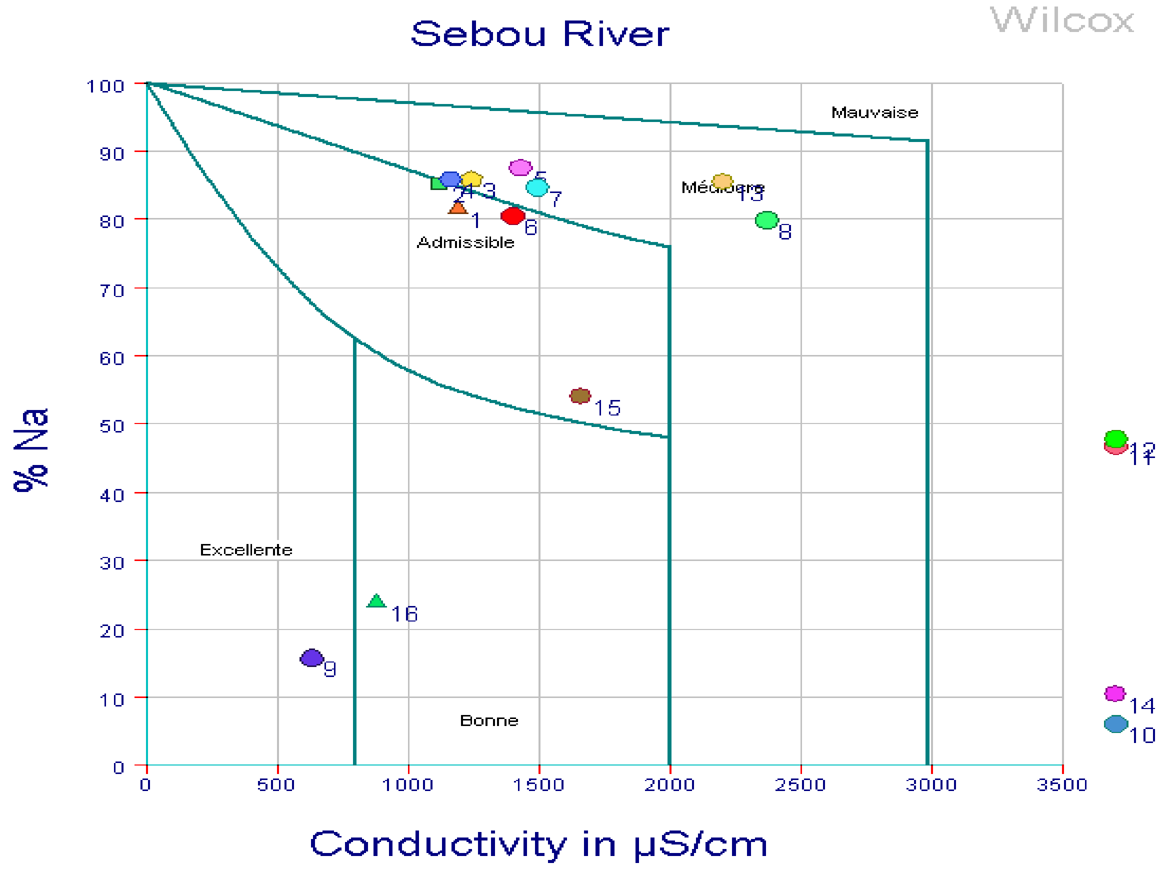

Figure 7. Projection of the Sebou Water Quality in Wilcox Diagram.

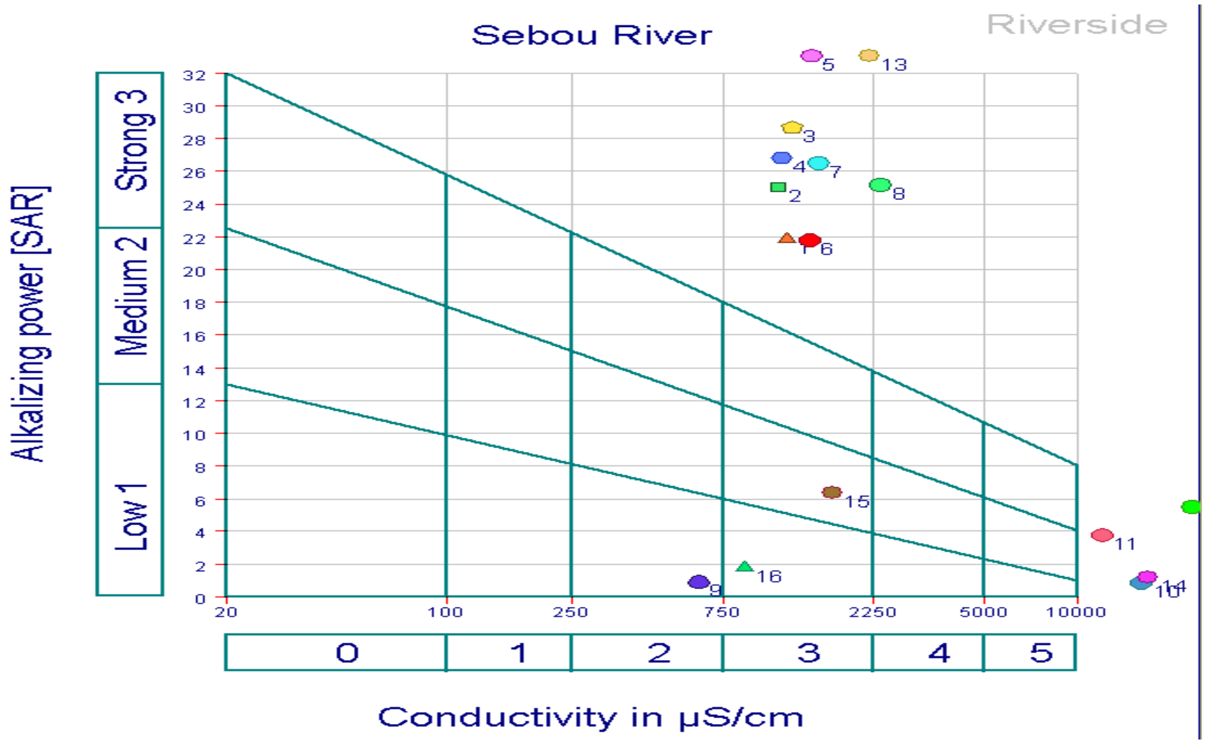

Figure 8. Diagram of the Alkalinity Classes of Raw Water from the Sebou Basin.

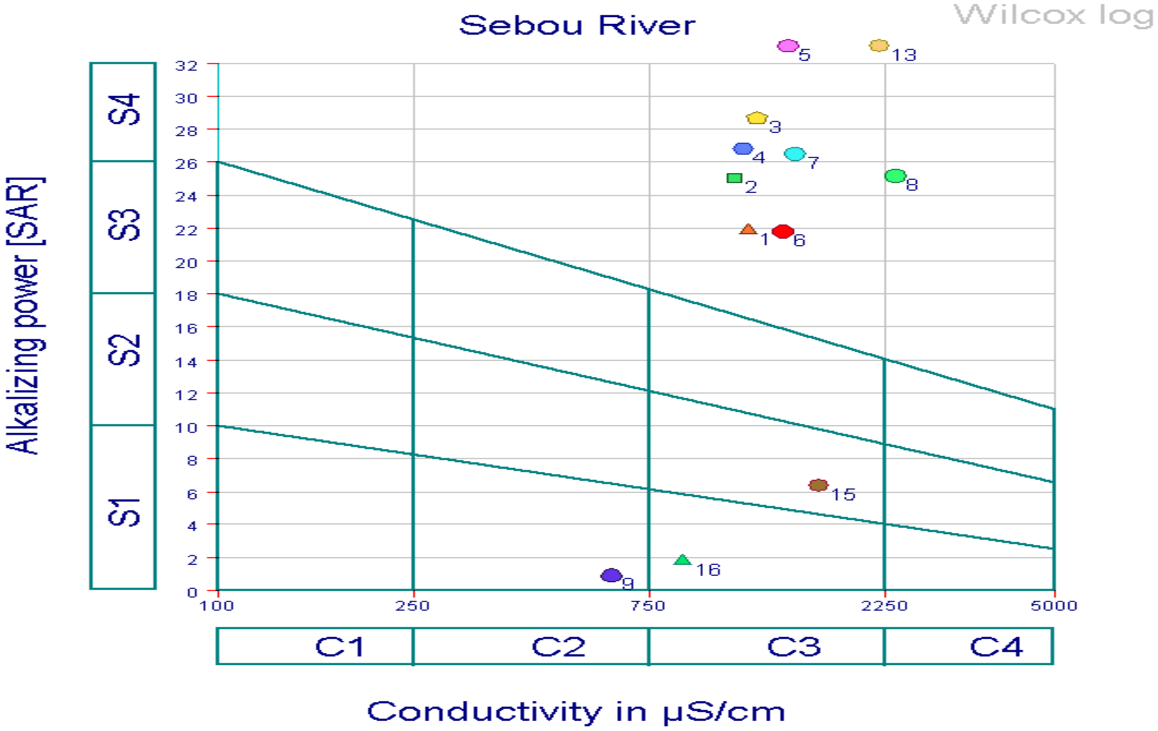

Figure 9. Diagram of the Alkalinity Classes of the Sebou Waters.

The climate regime of the Gharb plain is Mediterranean, rainy in winter and warmer in summer. The hydrogen potential does not change significantly and the waters are slightly alkaline, varying from 8 to 8.77 (**Tables 3** and **5**, **Figure 3**) following their crossing of the limestone and marl-limestone terrains constituting the major bed of the Sebou River.

Salinity closely follows the levels of dissolved salts and ions (Na+, K+, Cl^-) (**Tables 3**, **4** and **5**; **Figure 4**). It results in particular from the leaching of the crossed limestone terrains and sea spray. In addition, the electrical conductivity synonymous with salinity (**Figure 4**) oscillates between 629 and 22766 µS/cm with an average of 5250 µS/cm above the Moroccan irrigation threshold (>2700 µS/cm) [21–23].

The average pH is 8.42. The hydrogen potential is slightly basic but remains within irrigation standards. The ammonium content ranges from 0.04 to 15.3 mg/L. Regarding the quality of surface water, 65% of the water is of poor quality and 35% of good quality. It was also noted that the concentrations of Cl^- ions have a minimum of 145.55 mg/L and a maximum of 860.27 mg/L.

As for the concentrations of sulfate ions $SO4^-$, they range from 37.62 to 441.4 mg/l. Similarly, the concentrations of bicarbonate ions vary from 75.64 to 362.34 mg/l. These concentrations are compatible with the standards for agriculture. The concentrations of calcium ions Ca++ vary from 1072.8 to 97.6 mg/l with an average of 272.17 mg/l.

As for the magnesium Mg++ concentrations, they range from 17.28 to 631.20 mg/l with an average of 99.73 mg/l. These values obtained are in accordance with Moroccan standards. The concentrations of sodium ions in water vary from 51 to 2530 mg/l with an average of 991.33 mg/l. The concentrations of potassium ions in surface water vary from 2.54 to 17.55 mg/l and an average of 7.52 mg/l.

Concerning nitrate levels (**Figure 5**), the average is 379.66 mg/l and the concentrations vary between 0.24 and 2692 mg/l and show the impacts of nitrogen fertilizers used in agriculture, as well as wastewater and leachates from illegal dumps [24–30].

Concerning the hydrometric title (**Table 5**), the average is 12.71 mg/L and the HT varies from 4.82 to 57.94 mg/L and clearly reflects the pollution of pedological origin of alkaline-earth soils and rocks likely to precipitate in the form of calcareous incrustations [24–30].

The hardness of the water or its TH varies from 1°F to 14.5°F with an average of 4.5°F. The Sebou is known for having very calcareous water.

Figure 6 indicates that overall the waters are calcic hyperchlorinated and calcic hypersulfated. The waters are loaded with sulphates, calcium, magnesium or even sodium and potassium [31,32].

Furthermore, the projection of physicochemical data in the Wilcox diagram (**Figure 7**) and Log Wilcox (**Figure 8**), classifies the waters of the Sebou as mediocre or bad but rarely good. The waters are bad by the alkalizing power of the Na+ ions (Sodium Adsorption Ratio). They belong to the C3S3 and C4S4 groups (**Figure 9**) and are unsuitable for irrigation [33,34].

Intense agricultural activities on lands adjacent to the river banks clearly impact the waters of the Sebou basin through high levels of nitrogen and sulfates which reach the watercourse through erosion and drainage of nitrogen and phosphate fertilizers and phytosanitary pesticides [29,35].

The upstream-downstream evolution of the physicochemical indicators reflects the degraded quality of the water in sodium chloride due to the rise in depth of the waters of the Atlantic Sea.

This study concludes that the water level of the Lower Sebou is poor but this research is still incomplete and needs to be deepened by analyses of trace elements, pesticides and hydrocarbons to prepare the scientific and technical foundations for managers [3, 36–39].

Table 5. Statistical Analysis of the Physicochemical Results of the Sebou Waters

Statistics	Nb. Observations	Minimum	Maximum	1st Quartile	Median	3rd Quartile	Mean	Variance (n−1)	Standard Deviation (n−1)
pH	16	8.01	8.79	8.29	8.39	8.63	8.42	0.05	0.22
CE µS/cm	16	629	22,760	1,182	1,460	4767	5250	5,168,589	7,189
NH4+ mg/l	16	0.04	15.3	0.3	0.6	1.3	1.7	13.6	3.6
NO3^{-} mg/l	16	0.24	2,692.0	19.71	90.76	369.05	379.66	469,921	685
CL^{-} mg/l	16	145.55	860.27	202.35	246.01	388.57	309.83	32,578	180
SO4^{-} mg/l	16	37.62	441.40	134.16	170.56	262.88	198.62	12,189	110
HCO3^{-} mg/l	16	75.64	362.34	118.64	223.87	246.44	204.19	7337	85.65
CO3^{-} mg/l	16	0.00	49.20	0.00	3.00	18.00	11.25	241	15.55
Ca++ mg/l	16	97.60	1,072.80	147.50	167.80	218.30	272.17	82,648	287.48
Mg++ mg/l	16	17.28	631.20	43.14	64.08	95.40	99.73	21,151	145.43
K+ mg/l	16	2.54	17.55	4.58	6.34	9.61	7.52	20	4.48
Na+ mg/l	16	51.00	2,530.00	180.00	1,255.00	1,492.50	991.33	609,766	780.87
TH mg/l	16	4.82	57.94	5.69	6.62	9.45	12.71	259.62	16.11

4. Conclusions

Moroccan rivers and streams have been the subject of very few hydrobiological and hydrogeological surveys. In this research, we propose to describe the physico-chemistry of the watercourses of 16 stations in the Sebou basin during the years 2013–2014 and 2018–2023. The physicochemical characterization of the Sebou waters showed that this river is too polluted by mineral salts.

Thus, for electrical conductivity (EC), we note a wide fluctuation in the ionic content of the waters from 629 to 22766 µS/cm. The diagnosis of the Sebou waters showed that this watercourse has a normally low electrical conductivity, but near its mouth on the Atlantic Ocean, it reaches peaks. The waters are highly enriched in mineral salts at the estuary.

The average pH fluctuates between 8.01 and 8.79. The pH is slightly basic but remains acceptable according to the Moroccan thresholds for irrigation. Chloride concentrations were also observed to vary from 145.55 to 860.27 mg/l. The ammonium content ranges from 0.04 to 15.34 mg/l. The nitrate concentrations range from 0.24 to 886.9 mg/l. Nitrate concentrations generally vary from 0.24 to 10.42 to 17.11 and 20.58 mg/l for the first stations far from the urban agglomeration of Kenitra. On the other hand, for the stations receiving wastewater effluents and leachates from the illegal dump, nitrate concentrations increase enormously to 886 and 2692 mg/l.

In addition, the $SO4^-$ ion concentrations vary from 37.62 to 441.4 mg/l. The bicarbonate contents vary from 75.64 to 362.34 mg/l and these concentrations are compatible with agricultural standards. The Ca++ contents vary between 97.6 and 1072.8 mg/l. As for the magnesium ion Mg2+ contents, they range between 17.28 and 631.2 mg/l and these values found are in accordance with agricultural standards. The sodium ion contents in water vary between 51 and 2530 mg/l, while the potassium concentrations vary from 2.54 to 17.55 mg/l.

The water of the Sebou is very hard. The hardness of the water or its TH, is explained by its multiple courses in the rocky subsoils, during which it is loaded, more or less depending on the regions and the nature of these soils, with magnesium and limestone. If regions have soft water like the North of the country, the Gharb is known for having very calcareous groundwater. It is desirable to measure the water hardness regularly, because its limestone content can vary over time.

We conclude, from this first hydrobiological investigation, that the waters of the Sebou are too loaded with mineral salts but remain below the thresholds set by the irrigation standards of Morocco. The waters of the Sebou are quite degraded and we demand adequate treatment of all urban and industrial effluents to stop the nuisances suffered by the receiving environment and avoid the waste of this natural water so coveted and prized.

Author Contributions

Conceptualization, D.B.; methodology, D.B., E.M.H., F.S. and B.A.D.; software, E.J. and L.I.; validation, D.B. and E.M.H.; formal analysis, E.H.; investigation, M.M.; resources, D.B.; data curation, F.K.; writing—original draft preparation, E.M.H., H.T. and D.B.; writing—review and editing, M.M., H.K. and D.B.; visualization, E.H.; supervision, D.B.; project administration, D.B. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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