PROCEEDINGS BOOK
12th ICEEE–2021
"Global Environmental Development & Sustainability: Research, Engineering & Management"
November 18 – 19, 2021 RKK – Óbuda University, Budapest, Hungary
ISBN: 978-963-449-256-6 www.iceee.hu

URBAN AND INDUSTRIAL SURFACE WATER POLLUTION AND THEIR IMPACTS ON THE ENVIRONMENT. CONSTANTINE CITY CASE STUDY. NORTH-EAST OF ALGERIA

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Abstract: *The study area is located in Constantine, at the North-East of Algeria; it regards the segments of wadi Rhumel and its branch wadi Boumerzoug. It is characterized by a semi-arid climate. This work focused on the assessment of the physical-chemical quality and the level of contamination by hydrocarbons (oils and greases) and metallic trace elements (TMEs) (As, Cd, Cu, Fe, Ni and Zn). 14 samples were collected spread the wadi, and were analyzed. Results show the order of abundance of the cations in the majority of the samples is: Na> Ca> Mg> K. The concentrations ranking is: Na (66.812-396.493 mg/l), Ca (90.11-96.66 mg/l), Mg (18.96-30.52 mg/l), K (9.494-13.988 mg/l). For TMEs, the analyses showed relatively high concentrations. The abundance ranking in most elements is: As >Fe > Cd > Ni > Zn > Cu. The concentrations ranking is: As (1.316-0.436 mg/l), Fe (0.119-0.170 mg/l), Cd (0.054-0.099 mg/l), Ni (0.007-0.043mg/l), Zn (0-0.08 mg/l), Cu (0.008-0.016 mg/l). All analysis shows oils and greases concentrations are extremely high (88.2-390.6 mg/l). The correlation matrix and the PCA between all metal elements reflect the signature of anthropogenic and domestic inputs at the same time. The SEQ-Water: qualifies very poor quality according As and Cd contents, good to fair for Ni and good quality for Cu and Zn. This situation reveals a direct influence of anthropogenic inputs conveyed by the wadis. Oils and greases, their contents are found to be very high and reflect an intense uncontrolled activity linked to the use of hydrocarbons and derivatives.*

Keywords*: Anthropogenic, contamination, oils and greases, SEQ-Water, TME, wadi Rhumel, wadiBoumerzoug.*

INTRODUCTION

The phenomenon of oil pollution is a major concern for those involved in the protection of the environment, health and the economy. This pollution can have a direct or indirect impact on human health and the balance of ecosystems, both marine and continental. Service stations are a major source of urban pollution, which is why they are the subject of this study. The operation of this type of activity represents a potential source of nuisance (traffic, noise, atmospheric pollution, soil and water pollution) for the immediate neighborhood, but also for the environment in general. The phenomenon of pollution from service stations can be divided into two categories: on the one hand, chronic pollution lasts for a long time and is most often due to the corrosion of tanks and underground pipes. On the other hand, accidental pollution due to oil spills when filling station storage or fuel distribution or even during engine maintenance operations [1]. This state of affairs prompted us to initiate this study to assess the state of health of watercourses following these types of activities. Several approaches are used to assess the degree of contamination of water, among these approaches a field survey to determine the different pollutants and another in the laboratory to quantify these pollutants and assess the degree of contamination and several studies have been made [2, 3, 4 and 5]. The study area is located in the North East of Algeria and concerns the segments Rhumel and Bouerzoug Wadis which passes through the city of Constantine and its immediate surroundings. The objective of this study is the assessment and quantify the physico-chemical quality and the level of contamination by hydrocarbons (oil and grease) and metallic trace elements (TME) (Cd, Cu, Ni, Fe, Zn and As) that were discharged into the waters of the main wadis in the study area. Samples were taken from the main Rhumel and Boumerzoug rivers and their tributaries.

Geological and hydrogeological settings

The study region is located in the North-East of Algeria, part of the Tell Constantinois and belongs to the Kebir-Rhumel watershed. It covers the city of Constantine and its periphery (Figure 1). It is bordered on the North and South by parallels 36°35'N to 36°10'N and on the East and West by meridians 6° 25'E to 6°45'E. The city of Constantine and its periphery is part of the external zones of the Maghrebids, allochthonous domain, a relatively complicated geology, of an essentially detrital lithological nature, characterized by an essentially rocky relief and a poor vegetal cover, and are drained by a relatively dense hydrographic network. The Rhumel is the main river and the Boumerzoug its main tributary. The hydroclimatological study allowed us to conclude that the study area is characterized by a semi-arid climate with influences, a sub-humid regime in the North and a semi-arid regime in the South. The annual average precipitation is 477.34mm, with the month rainiest is February (70.18mm) and the driest month is July (2.11mm). Average annual temperatures are around 16.24°C. As for the thermal regime, we have two very distinct seasons: a hot and dry season and another cold and humid. Since our study took place at this time of year (September 2020), our analytical results would be largely influenced by the dryness of the campaign.
The largest and most harmful industrial discharges are located within a radius of 20 km around the city of Constantine; these are the discharges (partly treated) from the mechanical construction industries of Oued Hamimime and Ain Smara, as well as those generated by the textile and dairy units of Constantine (Chaabet Rsas), by the tobacco complex and the hydrocarbon depotat El Khroub, by the El Hamma B cement plant [4], by the building materials units, and other PMI in Didouche Mourad,the discharge of Bardo crafts from brassware, their receiving environment is the Wadi Rhumel and its main tributary the Boumerzoug, which functions as real open sewers.

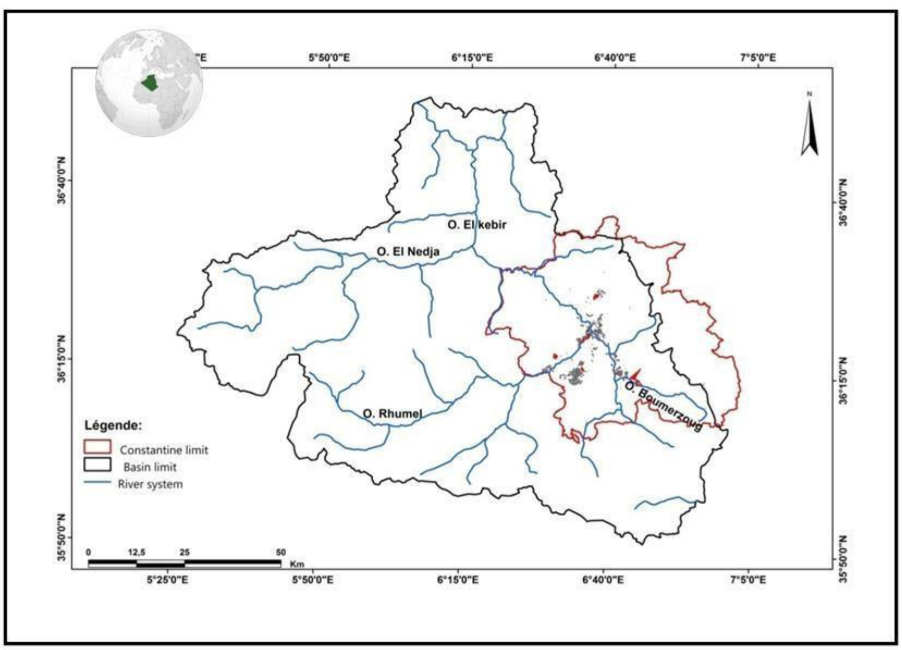

Figure 1. The study area situation

MATERIALS AND METHODS

Sampling and analysis: The samples analyzed were collected at the 14 stations, spread over five rivers, namely the wadis Rhumel, Boumerzoug, El Barda, Hamimime and Ziad. The sampling campaign took place in September (September 1st to 2 nd, 2020). The stations have been chosen so as to integrate as much as possible the influence of certain areas, by placing themselves upstream and downstream of them. The selection criteria for our stations were based on the proximity to the three industrial zones: Palma, Boumerzoug and Khroub upstream and downstream of these (Figure 2); but also in relation to the service stations which are located near the wadis and which are liable to discharge their discharges directly into the latter. The samples were taken from bottles rinsed beforehand with distilled waterand also with the water sample to be taken, stored in the laboratory at a temperature of 4°C [6].

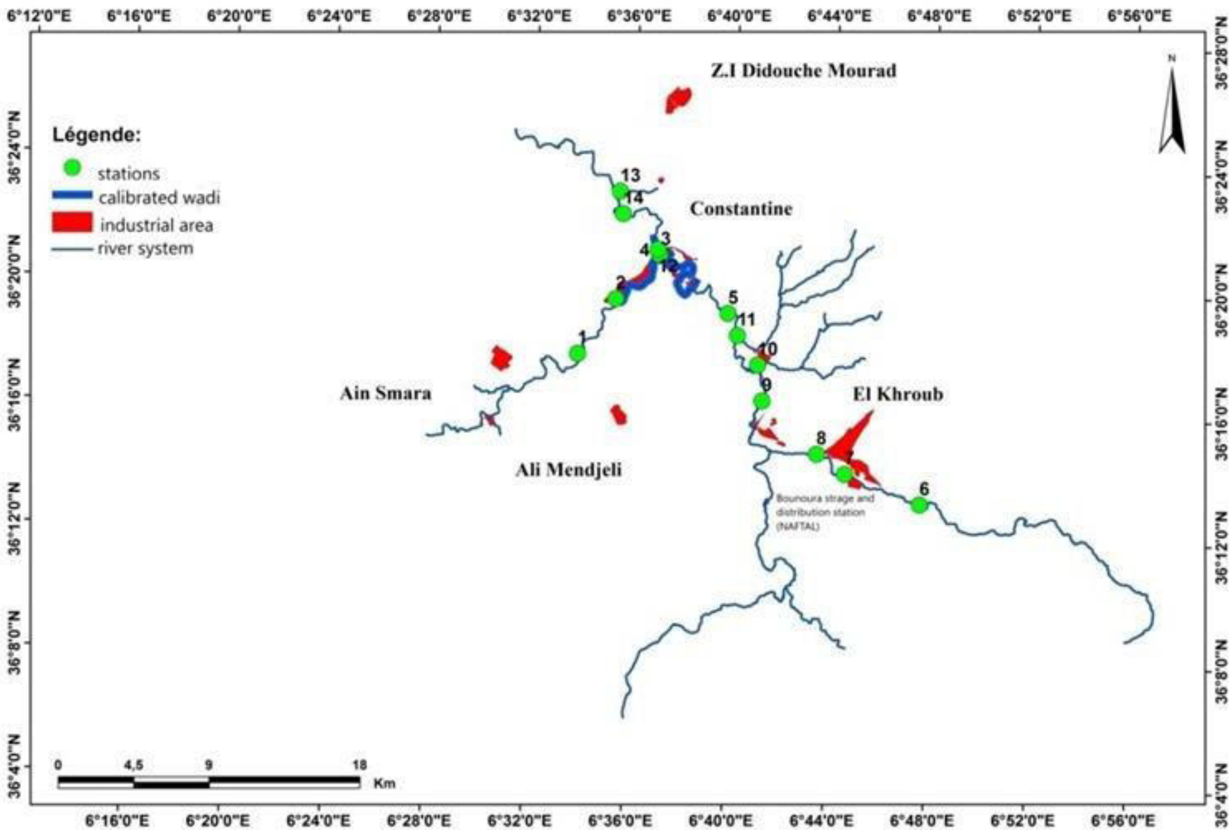

Figure 2. Different stations localization

Electrical conductivity and temperature are measured using an in-situ field conductivity meter where the thermometer is included in it. The results are expressed successively in µS/cm and in °C. The pH is taken with a model electrometric pH meter (pH-meter E520 Metrohm Herisau), in the laboratory, by immersingthe electrode in water approximately 6 to 8cm from the surface. The pH meter is calibrated with a solution of distilled water. The determination of ETMs (Cd, Cu, Ni, Fe, Zn and As) and of the major elements (Ca, K, Na, and Mg)were carried out by Flame Atomic Absorption Spectrophotometry (AAS) of the Perkin Elmer A Analyst type.200.The BOD5 is measured using a BOD meter type BSB-Controller Modell 1020T, for 164ml of sample, three NaOH capsules are added, and incubation for 5 days in the dark, the result is multiplied by a factor of 10 in mg/l. Nitrites are measured by DR/2000 spectrophotometer;

Finally, for the determination of the concentration of oils and greases is carried out mainly in three stages: acidification with HCl (pH>4), then extraction with hexane, then drying with (NaSO4), they are determined by gravimetry.

STATISTICAL ANALYSIS AND GRAPHICAL PRESENTATION

Principal component analysis (PCA): The Principal component analyses (PCA) are multivariate statistical techniques commonly used by scientists on hydrochemistry to classify water samples [7, 8]. These techniques allowed the exploration of the multivariate data holding several variables. The compliance of these parameters by the mean principal component analysis (PCA) is inspected by the Kaiser-Meyer-Olkin (KMO) and Bartlett sphericity tests applied to all the data. KMO was> 0.5 and Bartlett's sphericity shows that $\chi 2$ (observed) is greater than $\chi 2$ (critical) at 105 degrees of freedom, indicating that our analysis results are suitable for PCA. The relationships between the analyzed elements were tested using the Pearson coefficient. The results of all the physico-chemical analysis are shown in the next table (Table 1):

Table 1. statistics of physico-chemical characteristics and trace metal concentration

	CE µS/cm	Ca	Mg	Na	K	Fe	Cu	Zn	Ni	As	Cd	DBO5	O.G
Min	1582	90.11	18.96	66.81	9.49	0.119	0.008	0	0.007	0.436	0.054	6	88.2
Mean	1928.86	92.69	24.08	208.09	12.14	0.14	0.013	0.036	0.025	0.977	0.07	8.5	313.3
Median	1915.5	92.95	23.97	191.78	12.12	0.136	0.013	0.03	0.024	1.059	0.065	9	334.8
Max	2280	96.66	30.51	396.49	13.98	0.17	0.016	0.08	0.043	1.316	0.099	11	390.2
Std.Dev	165.32	2.23	3.34	118.21	1.359	0.017	0.002	0.028	0.010	0.272	0.01	1.454	83.78

RESULTS AND DISCUSSION

The pH values measured at the stations revealed a slightly alkaline pH, while the temperatures of the rivers vary little, and are mainly a function of that of the air. For conductivity, this parameter essentially depends on the presence and concentration of major elements. In general, the EC values are a little high, varying between 1582 and 2280µS/cm; this is due to industrial and urban discharges as well as to the nature of the terrain crossed.

For the major elements, the concentrations vary from one element to another; they increase upstream to downstream of industrial zones and towns. The order of abundance of cations at most stations is as follows: Na> Ca> Mg> K (Figure 3).

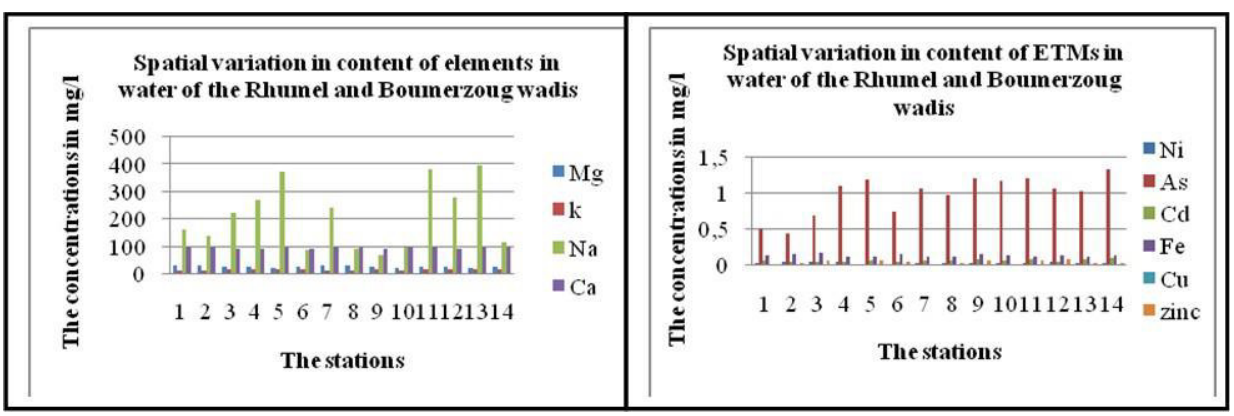

Figure 3. Spatial variation of chemical elements in the study area

The contents of Ca (90-96.66mg/l), Mg (18.96-30.51mg/l), and Na (66.81-396.49mg/l), the highest values are observed downstream of the city of Constantine (city collectors) and near industrial zones, Rhumel, Boumerzoug, Bounouara, Bardo, and finally O. Ziad (downstream of the Bekira activity zone) influenced by untreated domestic and industrial effluents. The concentrations of BOD5 observed in the various stations in the study area reflect not only the impact of the agglomerations, but also the agricultural and livestock activities developed in the upstream part of Boumerzoug Wadi. The concentration of oils and greases are extremely high, greatly exceeding the recommended standards this is due to the uncontrolled discharges which discharge directly into the wadis without undergoing primary treatment, adding to this the washing of the soil by the runoff water which leads to the pollution of surface water and deep water when there is infiltration. The service stations have a huge influence on the quality of the rivers in the study area in terms of oils and greases; the hydrocarbon industries company (NAFTAL) could be a significant contribution of these materials illustrated by high levels (390.6mg/l) (Figure 4) downstream of this industry.

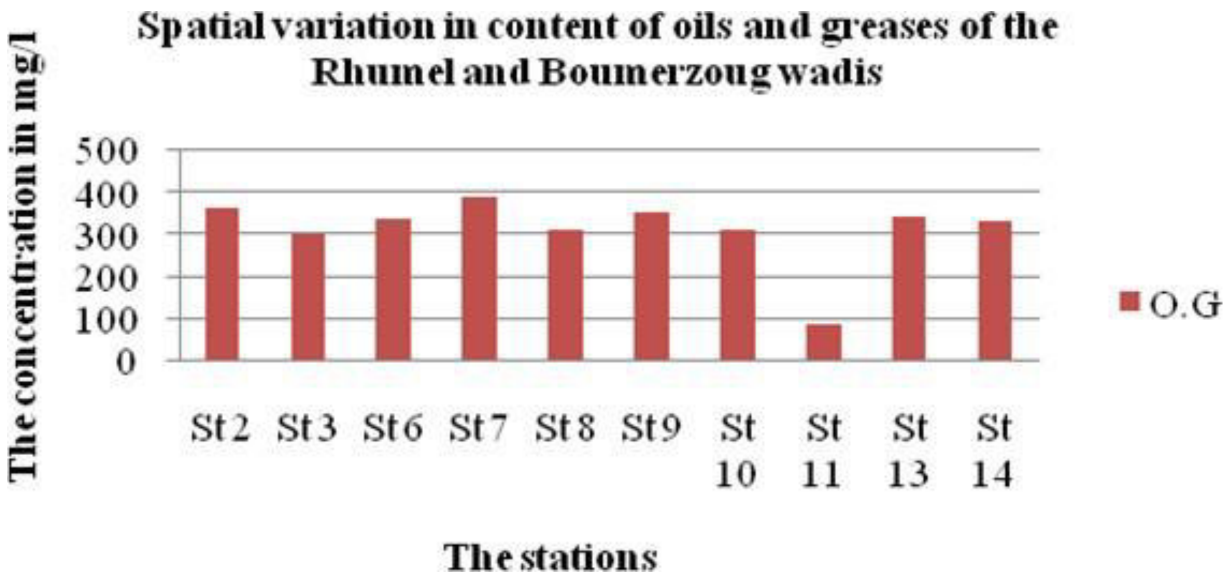

Figure 4. Spatial variation of oils and greases in the study area

For metallic trace elements, analysis showed relatively high concentrations of TME. The order of abundance in most elements is as follows: As> Fe> Cd> Ni> Zn> Cu (Fig.3). The Zn (0-0.008 mg/l) and Cu (0.008-0.016mg/l) contents are the lowest compared to other ETMs, but they remain quite high from a pollution point of view. The coexistence of the two elements in the same samples taken stipulates a common origin. They reach waterways either directly in urban effluents (the major source of which is corrosion of pipes for Cu), industrial and discharges from artisanal activities not connected to the sanitation network, or in a diffuse manner through runoff water especially those of riverbank soils cultivated for Zn (fertilizers and pesticides).
The concentrations of Fe (0.119-0.165mg/l), they increase upstream and downstream influenced by industrial discharges, the primary source of pollution of this element, but also domestic discharges.
Arsenic (0.436-1.316 mg/l), Cadmium (0.054-0.099mg/l), and Nickel (0.007-0.054mg/l), represent very high levels. Their concentrations increase from upstream to downstream especially along the Boumerzoug Wadiwhere the mechanical industries of O. Hamimime are located and the deposits of Rhumel Wadi, crafts, tannery, ceramics and the pharmaceutical industries. Small and medium-sized farms (PMEA) are developing along the Boumerzoug Wadi which can be a source of contamination (fertilizers and pesticides). Road traffic can be a source of contamination, as the samples are located not far from the road (runoff water). The greatest concentrations are downstream from the city of Constantine at El Menia, the point where all pollutants converge, as this site receives all of the surface runoff from Boumerzoug and Rhumel. The correlation matrix reveals that some variables are significantly correlated with each other. Thus, pH is negatively correlated with EC (r = -0.647), Zn (r = -0.564) and K (r = 0.509), and is positively very strongly correlated with NO2 (r = 0.836). The EC is positively correlated with K (r = 0.568), BOD5 (r = 0.680) and Zn (r = 0.577). Mg is negatively correlated with K (r = -0.582), the same for Na with Fe (r = -0.616). K, on the other hand, is positively correlated with BOD5 (r = 0.562) and Zn (r = 0.640). The latter is positively correlated with BOD5 (r = 0.622). Cu is negatively correlated with Ni (r = -0.560), positively with As (r = 0.604) and Cd (r = 0.779). A principal component analysis (PCA) performed from data performed on a data matrix consisting of 14 samples for a total of 15 parameters shows that there is a broad relationship between these variables.

The main factor 1 comprises 27.28% of the total variance and has the high loads in pH, EC, K, BOD5, NO2 and Zn. This factor indicates that the EC is highly influenced by anthropogenic activity directly related to wastewater discharges. The main factor 2 contains 24.23% of the total variance and indicates high loads of metallic trace elements: As, Cd, Fe and Cu. Given the wide use of these elements in industry, this factor could indicate the signature of the industrial origin of this pollution.
The main factor 3 has 14.22% of the total variance and is related to Na, which in other places does not show such an influence which prompts us to question its possible origin. In addition, the projection of the water parameters of the fourteen sampling stations on the main plane (axes 1-2) (Figure 5) which covers 51.51% of the total information, makes it possible to detect a very dispersed total structure, which is normal for a period of low water limited by the inflow of water from climatic origin. However, this structure shows similarities and dissimilarities between the water parameters and between the stations. This representation indicates a structure dominated by the detachment of stations St5, St6, St9 and St11 which project from the positive side of axis 1 showing the highest contents of CE, BOD5, K and Zn. A second group is formed by NO2 and pH which contribute to the formation of axis 1 on the negative side reported to stations St4 and St8. This factor load, which represents 27.28% of the total variance, indicates that axis 1 is that of domestic waste.
Stations St10, St13 and St14 stand out on the positive side of axis 2, absorbing much of the information provided by this axis and marked by the high contents of As, Cd, Cu and Na. Finally, a last group is placed on the negative side of axis 2 formed by stations St1, St2, St3 and St12 dominated by the highest contents of Fe, Ni, Mg and Temperature. Axis 2 is undoubtedly the signature anthropogenic activity dominated by industrial waste. Station St7 which projects on the negative side of axis 1, standing out from the group, thus showing the highest levels of oils and greases.

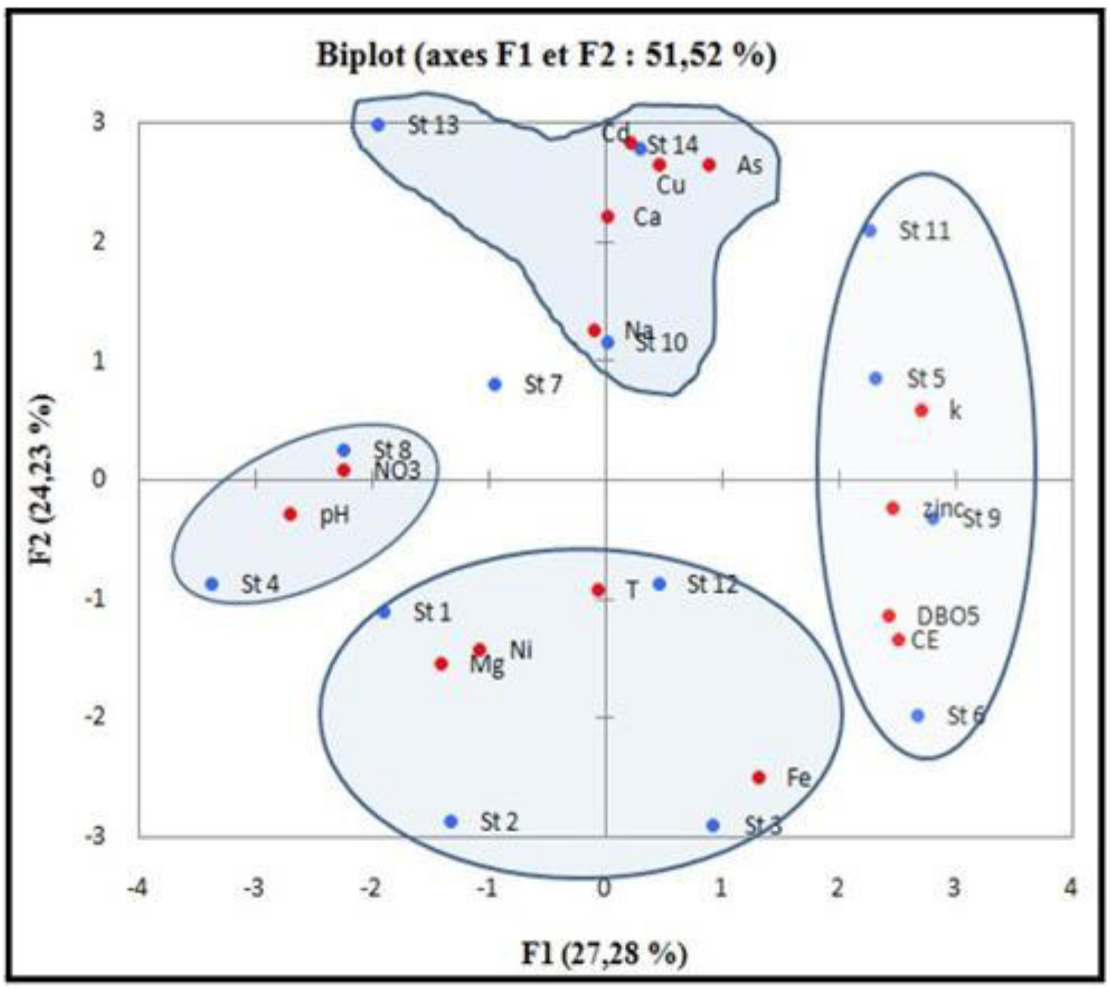

Figure 5. PCA of water parameters and projection of withdrawals

Table 2. The water quality of the 14 stations in the study area

Oueds	stations	T°C	pH	CE	As	Cd	Cu	Ni	Zn	NO_2	H.G
Oued Rhumel (Be.Co)	1	Light green	Blue	Blue	Red	Red	Green	Yellow	Blue	Red	
	2	Yellow	Blue	Blue	Red	Red	Green	Yellow	Light green	Red	Red
	4	Red	Yellow	Blue	Red	Red	Green	Yellow	Blue	Red	
Oued Bmerzoug	3	Red	Blue	Blue	Red	Red	Green	Yellow	Light green	Red	Red
	5	Red	Blue	Blue	Red	Red	Green	Green	Light green	Red	
	6	Orange	Blue	Blue	Red	Red	Green	Green	Green	Red	Red
	7	Red	Blue	Blue	Red	Red	Green	Green	Blue	Red	Red
	8	Orange	Blue	Blue	Red	Red	Green	Green	Green	Red	Red
	9	Yellow	Blue	Blue	Red	Red	Green	Yellow	Green	Red	Red
	10	Yellow	Blue	Blue	Red	Red	Green	Green	Blue	Blue	Red
	11	Yellow	Blue	Blue	Red	Red	Green	Yellow	Green	Red	Red
Oued Rhumel (Af.Co)	12	Yellow	Blue	Blue	Red	Red	Green	Yellow	Green	Red	
	13	Yellow	Blue	Blue	Red	Red	Green	Green	Green	Red	Red
	14	Yellow	Blue	Blue	Red	Red	Green	Yellow	Green	Red	Red

(Be.Co) : Rhumel Wadi before the confluence
(Af.Co) : Rhumel Wadi after the confluence

Blue: Very good; Green: Good; Yellow: Fair; Orange: Bad; Red: Very bad

CONCLUSIONS AND RECOMMENDATIONS

According to the analysis carried out, it appears that industrial and urban discharges are responsible for a degradation of the physico-chemical quality of the waters of the Boumerzoug and Rhumel wadi, this pollution seems to have both a domestic and industrial origin linked to the discharge of untreated wastewater which flows directly into rivers.
However, the industries present in the study sector also have their share of responsibility for the degradation of the quality of these waters. The same is true for the metallic trace elements which seem to be present with relatively high concentrations, in particular for the Arsenic and Cadmium, which remains worrying, which make the quality of the water poor, as well as for oils and greases which are considered as hazardous waste. Although the number of elements analyzed is reduced, the wastewater of the city of Constantine remains overloaded with pollutants and constitutes a serious problem for the Beni Haroun dam, especially in the absence of a fully functioning wastewater treatment and purification station (WWTP).
So it becomes imperative to set up a monitoring and control program for the various sources of pollution and their effect on humans and the environment, by forcing these industries to equip themselves with a system for treating their discharges, as well as recycling and recovery of waste if necessary.

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