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ASSESSMENT OF GROUNDWATER POLLUTION BY HEAVY METALS IN THE INDUSTRIAL ZONE OF SKIKDA

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Pumped groundwater volumes have been estimated at 52 hm^3 per year with 12hm^3 per year being abstracted from oil installation industry in Skikda city, situated in the north east of Algeria. Large industrial demands of groundwater have caused prejudicial effect on alluvial aquifer through aquifer depletion and moreover by contamination of aquatic ecosystems. An environmental assessment was carried out on water resources collected from boreholes and river, the aim was to assess heavy metal contamination in water close to our industrial area. Indeed, 20 water samples were collected in December 2021, including surface water and groundwater. results reveal that Safsaf river presents an alkaline pH (7.49), a high conductivity which reached 10620 us/cm exceeding the WHO limit fixed at 2500 us/cm, dissolved oxygen reaching up to 5.21 mg/l, and a maximum BOD_5 of 140 mg/l, this load exceeded WHO standards fixed at 25 mg/l. cadmium concentrations measured at 1.48mg/l as a maximum load which exceed WHO standards fixed at 0.05 mg/l, zinc concentrations show a large peak of 9.3 mg/l, when WHO standards limits it at 3 mg/l in water and arsenic was measured at 1.05 mg/l*, greatly exceeding WHO standards fixed at 0.01mg/l. this high concentration of heavy metals may be of industrial origin, as the river flows through the industrial zone, or anthropic, as Safsaf passes through the entire city of Skikda. On the other hand, groundwater results indicate the presence of cadmium ranged from 0.005 to 5.09 mg/l and largely exceed WHO standards about only 0.003 mg/l.* high concentration could be due to anthropogenic and industrial discharge. *Also, presence of a high concentration of Zn ranged from 0.325 to 7.21 mg/l and largely exceed WHO standards about only 3 mg/l. and which has practically the same sources of pollution as surface water*

Keywords: *groundwater, contamination, Skikda, heavy metal, WHO.*

INTRODUCTION

Any increase in production activity results in an increase in waste, and if there is no destruction, recycling, there is pollution (Faurie et al., 2003).The problem of water pollution undoubtedly represents one of the most worrying aspects of environmental degradation by contemporary technological civilisation (Ramade, 2005). Pollutant discharges can profoundly modify the physico-chemical components of the receiving aquatic environments as well as the biocenoses populating these environments (Pesson, 1980).

Our work consists in carrying out an evaluation of water pollution by heavy metals in the industrial zone of Skikda, which is located in a region that receives daily sewage, domestic waste and effluents from the zone.

Our objective is therefore to determine the degree of contamination and the fate of heavy metals (As, Zn, Cd) in these waters.

MATERIALS AND METHODS

In July 2018 to March 2022, three water sampling campaigns were carried out in the surroundings and inside the industrial zone of Skikda (25) stations were selected, (10) samples from the surroundings of the zone, (3) samples from inside the zone, (4) samples from the refinery effluents, and one sample from the sea water. The pH, electrical conductivity (δ), temperature (T) and dissolved oxygen (DO) were measured *in situ* using a multi-parameter suitcase. All water samples were stored in a cooler, transported to the laboratory. However, prior to storage, these samples were filtered and then stored in a refrigerator at a temperature not exceeding 4°C. Samples for the determination of heavy metals were acidified until their pH was below 2 and then stored in a refrigerator until the day of the ICP reading. The determination of calcium, magnesium and chloride ions was done by the titrimetric method. Sulphates and nitrates were determined by spectrophotometry, sodium and potassium by flame photometry (Rodier, 1996).

STATISTICAL ANALYSIS AND GRAPHICAL PRESENTATION

The temperature values of the water vary between 21.2 and 14.8°C; they are not dependent on the season. The pH values of the stations vary between 7.42 and 9.2; these values exceed the irrigation standard according to FAO (6.50<pH<8.40), and from 6.5 to 8 for the WHO standard. In fact, the pH of the site is alkaline; this alkalinity is related to the lithology of the region which is presented by the predominance of carbonate formations. The electrical conductivity ranging between 334 and 62200 µs/cm, whose minimum content is recorded downstream of Wadi Safsaf (O1), while the highest value is recorded at the level of the P9 All the values measured exceed the WHO irrigation standard (70-300 µs/cm), as well as the FAO standard (700µs/cm). Dissolved oxygen levels vary from a minimum value of 5% to a maximum value of 30%. These values generally exceed the irrigation standards defined by the FAO and the WHO standards, which range from 70 to 90%, but the E2 effluent is extremely low in oxygen, at 4.2%, due to the high pollution load it carries.
From Table 1, it can be seen that calcium ions are in close concentration in the different stations, with calcium contents varying between 250 and 421 mg/l. These contents are classified in the range of 0.5 to 0.5 mg/l. These levels exceed the FAO irrigation standard (200 mg /l). Magnesium contents vary between 13.44 and 40.22 mg/l, with the lowest content recorded in the middle of oued Safsaf (P5) while the highest value is recorded at the upstream end of the wadi (P4).

Table1: physico-chemical parameters analysed in the water

	$N0_3$	NO_2	NH_4	SO_4
p1	0,558	0	0	11,62
p2	2,659	0	0	236,33
p3	3,7	0,01	0,02	294,62
p4	1,6	0,02	0,06	187,59
p5	0,3	0	0	186,5
p6	0,809	0	0,07	268,92
p7	1,52	0	0,16	88,11
p8	2,987	0	0,67	382,88
p9	2,77	0	0,16	294,5
p10	3	0,01	0,02	279,39
p11	1,09	0	0,13	172,49
p12	6,58	0,01	0,37	258
p13	0,79	0	0,13	271,7
p14	9,12	0,01	0,37	325,84

p15	0,79	0,01	0,07	256,66
p16	1,55	0,02	0	173,74
p17	2,25	0,08	0	13,96
p18	2,6	0,15	0	97
p19	3,3	1,02	0,08	193,5
p20	0,8	1,14	0	133,28

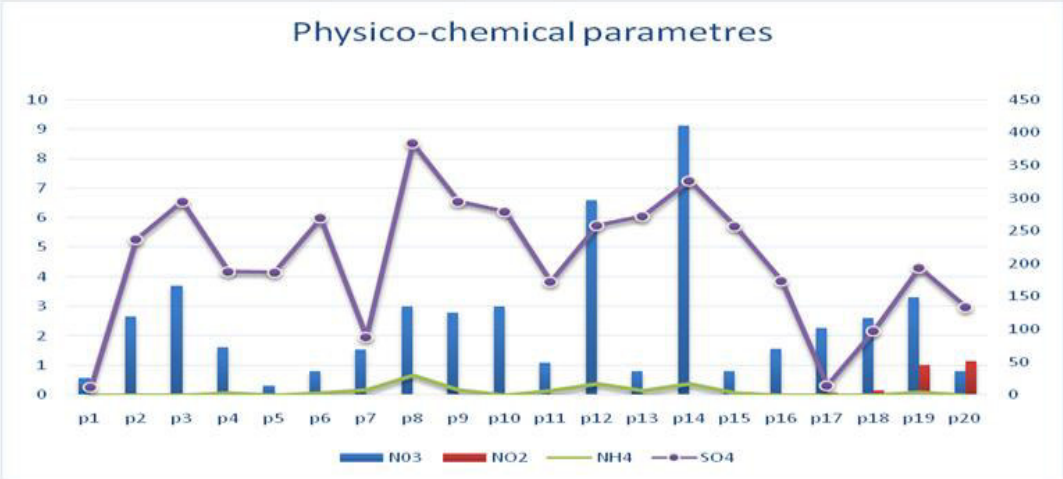

Figure 1. Graph of physic-chemical parameters

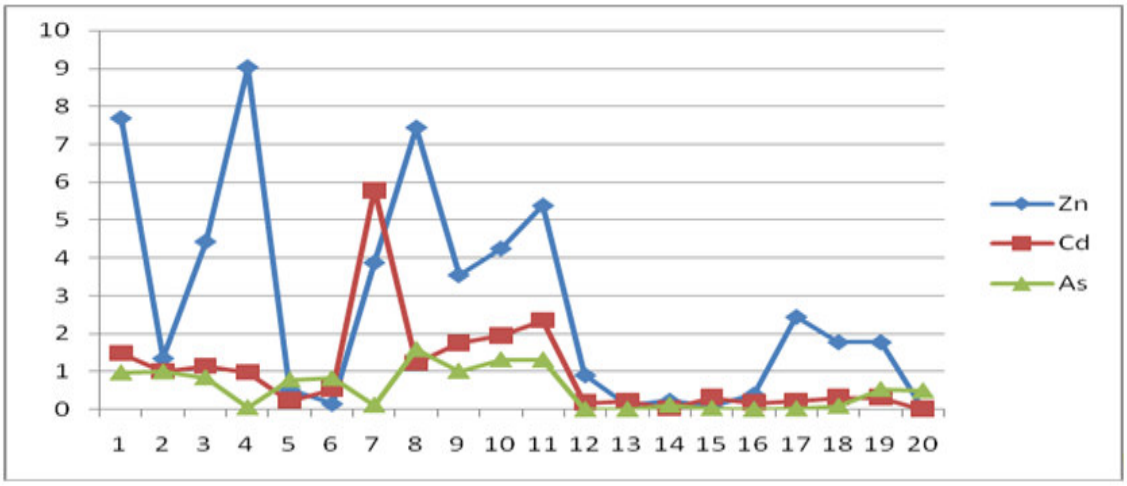

Figure 2. Graph of heavy metal parameters

RESULTS AND DISCUSSION

All points sampled show concentrations above the FAO standard (150 mg/l). The Ca+2 and Mg+2 ions come mainly from the dissolution of carbonate formations (limestone, dolomite, magnesite, etc.). The sodium and potassium contents show a great difference from one station to another; an average sodium concentration is around 200 mg/l.

The potassium content of the three stations studied ranges from 12 to 236 mg/l. The distribution of chloride concentrations in the water of Wadi Safsaf varies between 50 mg/l at station P6 and 380 mg/l at station P1. The totality of the measured water points have concentrations higher than the irrigation standard fixed by the FAO at 350mg/l, and 250 mg/l according to the WHO.

The levels of sulphates found in the water of Wadi Safsaf oscillate between 20mg/l at the station (P5) and (P9) and 792 at the station (P12). The values obtained for nitrates are 12mg/l and 299mg/l respectively for station (P7) and station (P11).
Copper levels in the different stations of oued safsaf vary between a minimum value of 2.3 mg/L recorded in the effluent station (O1) and the maximum value of 8.7 mg/L at the station (P3). Cadmium levels are above the European (0.150 mg/L) and WHO (3 mg/L) standards. The minimum value of zinc is recorded in the station (P12) downstream of the wadi of the order of 0.12mg/L.
Generally, zinc and copper levels are low in the natural surface waters of Wadi Safsaf because the aquatic environment is dynamic and the mobility of chemical elements and heavy metals is greater. In addition, the high rainfall recorded in the region, on average 1000 mm/year, contributes to the dilution process of the concentrations in the water. It should be noted that as the pH of the water is mostly alkaline (above 9), this alkaline environment favours the hydrolysis of Zn 2+ and therefore, the decrease of its content in the aqueous phase (Burnol et al.2006). The threshold of toxicity of this trace element in irrigation water of the WHO is fixed at 10 µg/L. In our study, the surface waters of oued safsaf in the Skikda region have concentrations ranging from 125.8 µg/L to 160.2 µg/L. These concentrations are quite high and exceed the above-mentioned standards. Cadmium can be released into water through natural weathering processes, discharges from industrial facilities or wastewater treatment plants, atmospheric deposition, leaching from landfills or soil or phosphate fertilizers (ATSDR, 2012). At the study site, these high concentrations could be due either to geogenic factors that favour the release of cadmium into water, related to the geological nature of the terrain, mainly the presence of carbonate formations and probably basement formations, or to anthropogenic discharges. On the site of the industrial estate, the combustion of fossil fuels and road transport may contribute small amounts of cadmium.

CONCLUSIONS AND RECOMMENDATIONS

Spatial variations of physico-chemical parameters, major elements and heavy metals in groundwater in the different sampling stations showed that: Wadi Safsaf water has an alkaline pH, a very high conductivity. A high concentration of heavy metals (Zn, Cd, As) in wadi water, as well as groundwater seems to be affected, except that we report a high contamination of these waters by cadmium which is found concentrated and exceeds the required standards, However, it has been established that for all the sampling TMEs carried out, a metallic contamination in the soil (Cd, Zn and As). Our results may lead to consider the contamination status of surface and groundwater. A temporal follow-up is recommended, other compartments (sediments, atmosphere) and other MTE such as iron, lead, mercury should complete our impact study.

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