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Hydric pollution assessment generated through the petrochemical industrial zone in the Skikda region (North-East Algeria)

Wafa Tahar[1], Lyamine Mezedjri[1,2] & Ali Tahar[1]

[1]Laboratory of Plant Biology and Environment, Department of Biology, Faculty of Science, Badji Mokhtar University, Annaba 23000, Algeria; email: thrwafaz@gmail.com
[2]Department of Biology, Faculty of Sciences, University of August 20, 55, Skikda 21000 Algeria; email: mezedjri.lyamine@gmail.com

ABSTRACT In this study, we carried out a diagnosis of the quality of the wastewater discharged from the Skikda industrial zone, compared with three control points, in the natural environment. The study has been conducted over two consecutive years and on a regular basis, monitoring 10 selected stations and 19 characteristics, giving a total of 4,560 analyses. The measurements show a very pronounced degradation of the quality of the wastewater of the 7 selected complexes with accentuated chemical and hydrocarbon pollution. The statistical approach adopted allows us to group the stations studied into 5 homogeneous groups, with a similarity level of 96.84%. This approach provides some information on the industrial activity influence in the Gulf of Skikda on the immediate environment (Oued Saf-Saf and Mediterranean Sea) with consequences and impacts on environmental quality in the region.

KEY WORDS Pollution, petrochemical industry, residuary waters, statistical analysis, gulf of Skikda.

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INTRODUCTION

The first industrial activities in the region were limited to pottery and glass manufacturing. The chemical activity as it is currently conceived appeared at the beginning of the XIXth century with the textile industry and the treatment of wool (Bliefert & Perraud, 2001). Nowadays, as part of the Algerian development strategy, an important industrial facility located directly at the coastal fringe discharges effluents straight into the natural environment.

Quite recently, considerable public and political awareness has been paid to the negative effects of industrial pollution that, mostly, are only visible today (Rodier, 2005; Bliefert & Perraud, 2001). Such awareness has resulted, at the national level, in adopting regulations for protecting the environment, among others the Coastal Law, as well as the decree relating to industrial liquid waste regulation and legislation relating to environmental protection in the context of sustainable development (JORA, 2002, 2003, 2006). In that context, particular attention was paid to wastewater released from industrial facilities, in the total absence of analytical data, knowledge of the impact of industrial activity in the Gulf of Skikda on water resources and marine fauna and flora remained poorly understood.

The present work, which is part of PRFU (Research Projects Training-University) research project, code F01620090020, for a period of three years, is concerned with the identification of the physico-chemical pollution in this region during a period of 24 months, between August 2017 and July 2019. The purpose of this paper is to carry out a diagnosis and an inventory of fixtures.

MATERIAL AND METHODS

Study area

The Gulf of Skikda (Fig. 1) is characterized by a coastal line of 142 km and a fishing area of 3,068 km^2 (ISTPM, 1982), representing 4.69% of the total national fishing area. It has an important fishery resource exploited by three fishing ports: in fact, the different resource assessment campaigns indicate an estimated stock of about 18,000 t of biomass of which 6,000 t constitute the exploitable reserves (ISTPM,1982; Djabali, 1988; ERH, 1996; Refes et al., 2011).

Located at the bottom of the gulf, Skikda region is one of the most densely populated areas on the Algerian coast with a population of more than 800,000 inhabitants. The Skikda Industrial Zone is located east of the city and covers an area of 1,200 ha (Fig. 1; Table 1). It groups together a number of specialized units in the transport, refining and processing of hydrocarbons. These activities generate considerable amounts of effluent either discharged directly into the sea or via a coastal river, the Saf-Saf Ouadi (Fig. 1), bordering the Industrial Zone westward over a 6 km length at an average flow rate of 390 l/s (SCI, 1989).

Locally, the Gulf Sailing Directions of Skikda provide indications about the existence of an eastward directed general current reaching 1 to 2.5 knots, as well as a current of 0.5 to 1.5 knots circulating closer to the coast. This secondary current, however, does not appear to enter the Gulf of Skikda on the west side.

Marine water circulation in this gulf (Millot, 1987) formed a part from the general circulation system over the western Mediterranean Sea, which controls and conditions biological, hydrological, chemical, muddy, etc. factors. Such circulation emerges along with the penetration of modified Atlantic water (MAW) which enters the Algerian basin around 0° E in the form of a narrow vein of

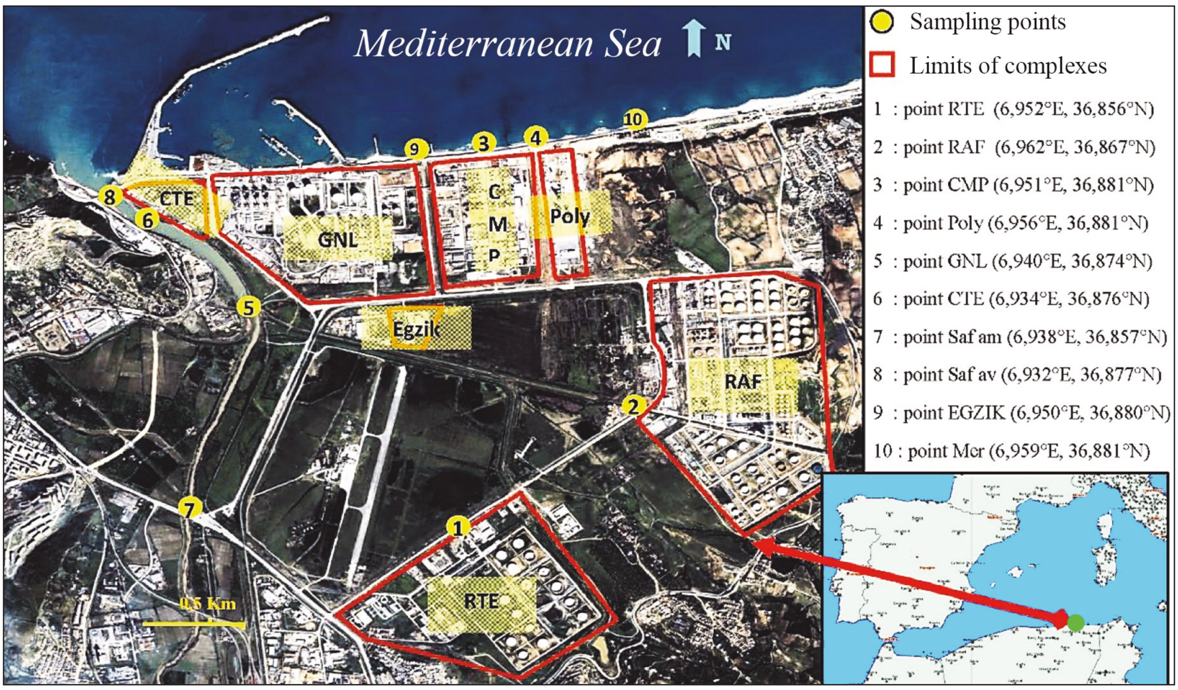

Figure 1. Location map of the Gulf of Skikda and study area with sampling points.
Source: QuickBird satellite image (modified), February 2003.

N°	Code	Designation	Observation
1	RTE	Hydrocarbon transport and storage complex	Water treatment plant absent
2	RAF	Skikda Refinery	Present functional water treatment plant
3	CMP	Plastics Complex	Water treatment plant present, out of order
4	Poly	High density polyethylene complex	Present functional water treatment plant
5	GNL	Liquefied Natural Gas Complex	Water treatment plant absent
6	CTE	Skikda Thermal Power Plant	Water treatment plant absent
7	SAF AM	Control point at the level of Wadi Saf- Saf upstream of its passage through the industrial zone of Skikda	None
8	SAF AV	Control point at the level of Wadi Saf- Saf at the mouth downstream of its passage through the industrial zone of Skikda	None
9	EGZIK	Industrial Zone Management Complex	Water treatment plant absent
10	Mer	Control point at sea level west of the industrial zone of Skikda	None

Table 1. Sampling points in the study area descriptions.

current, and sweeps along the Algerian coasts to the east. Around 1° or 2° E, it becomes unstable and meanders and then cyclonic and anticyclonic eddies appear, drifting eastward at a speed of 10 km/d. These anticyclonic currents evolve and reach diameters of 100 to 200 km, associated with "upwellings" with all the consequences on biological productivity (good phytoplanktonic and halieutic development). A circulation slowdown is observed around 5° E and 6° E. Due to unstable phenomena, the eddies move away from the Algerian coasts during a period of 1 to 2 months to return to the west. The Algerian basin thus constitutes a reservoir that feeds the northern basin of the western Mediterranean Sea (Millot, 1993).

Sampling and Analytical Methods

When it is a question of studying chemical substances, whose variations are unknown at a site, Quevauviller (2001) recommends an optimal number of five samples per year for four consecutive years, whereas Algerian texts recommend one sample per quarter for two years (JORA, 2006). As far as we are concerned, and taking into account the industrial activities diversity in the Skikda Industrial Zone and the complex nature of the discharged water, we opted for simple and independent random sampling of 10 stations (Fig. 1). This kind of sampling has the advantage to be representative the population studied, estimators are unbiased and ensure error independence as well as straightforward implementation of statistical methods. Sampling is instantaneous in accordance with the recommendations of Rodier (2005) and Prichard (1995). They were carried out over 24 months (between August 2008 and July 2010), i.e. one sample per month and per station. The physico-chemical characteristics measured in the collected wastewater are temperature, pH, conductivity, salinity, hardness (TDS), redox power (rH), dissolved oxygen and oxygen saturation rate.

These parameters were measured *in situ* using WTW type 197-S soil probes (AFNOR, 1979). In the laboratory, the biochemical oxygen demand (BOD5) obtained using the WTW OxiTop®Control 12 device (AFNOR, 1979), turbidity measured using a JENWAY turbidimeter ref 6035 (AFNOR, 1979), chloride ion concentrations obtained by volumetric method after silver nitrate titration (ASTM, 2004; AFNOR, 1979; Rodier, 2005), nitrates, nitrites and phosphates measured with a UV/visible spectrophotometer (AFNOR, 1979; ASTM, 2004), total hydrocarbons (CxHy) were measured gravimetrically (Rodier, 2005). Organic elements are represented by four metals: iron, copper and lead, measured with an atomic absorption spectrophotometer reference D2576 (ASTM, 2004), and mercury, measured with a reference mercury meter D3223 (ASTM, 2004). The choice of these four parameters is related to the types of activities in the industrial zone of Skikda.

In order to better identify the problems and nuisances generated by the Skikda industrial zone, we carried out regular monitoring of the liquid discharges (at the outflow-natural environment interface) of the seven complexes shown in Fig. 1 and Table 1, to which we associated three control stations: in the Wadi Saf-Saf upstream of the ZIK (station 7), a point downstream in the mouth of the Wadi Saf-Saf after its passage through the ZIK (station 8) and finally a point on the coastline, east of the industrial zone (station 10). The latter point isn't protected by the harbor breakwater and therefore it is influenced by the important currents prevailing in the gulf. These are currents affected by north-northwest winds for 3 quarters per year, which means it can inform us on the eventual diffusion of pollutants.

Statistical data analysis

The data collected represents 4560 samples. We first calculated the basic statistical parameters for each characteristic and then compared the stations to each other for each of the 19 variables using the ANOVA (Analysis of Variance) classification criteria (Dagnelie, 2006).

Finally, we classified the 10 stations into homogeneous groups. The search for homogeneous groups or classes of stations can also be done by hierarchical classification. Several methods are proposed by Dagnelie (1986) to achieve this goal. However, we will only use the one proposed by Bouroche & Saporata (1980) and which has been taken up by Dagnelie (1970, 2006) and Palm (2000), whose algorithm is programmed in the MINITAB software (Anonymous, 2011). By this method, similarity or divergence between stations can be determined and a distribution into homogeneous groups or classes is obtained. This is an agglomerative hierarchical method that uses the simple link procedure and the square distance of Pearson (Bouroche & Saporata, 1980; Dagnelie, 1986; Huberty, 1994; Anonymous, 2011).

The MINITAB 16 data analysis and processing software was used to perform all calculations.

RESULTS AND DISCUSSION

Initially, the data description provided at each of the 19 characteristics measured during our study, coupled with a comparative survey of the results obtained with Algerian texts (JORA, 2006), permitted us obtaining key mean values recorded at each station (Table 2).

Data interpretation, in the light of collected information from Algerian literature and legislation (AFNOR, 1979; Kruk, 1998; Bliefert & Perraud, 2001; Quevauviller, 2001; ASTM, 2004; Rodier, 2005; JORA, 2006), offers the indications set out below.

Station 1 (RTE): hydrocarbon storage complex

The water discharged from this hydrocarbon transport and storage complex (RTE) has a relatively high temperature, a slightly acidic pH and a relatively low level of dissolved oxygen saturation.

These are turbid and highly mineralized waters.

Their biochemical oxygen demand is high.

Hydrocarbons, always present in large quantities, are a threat to aquatic species.

The nitrate ions concentrations (up to 25 mg/l, but with an average value of 3.2 mg/ l) and phosphates (4.7 mg/l on average) are not particularly high. Metals are quite abundant, especially lead (up to 0.2 mg/l) and iron (up to 16 mg/l - 5.5 mg/l on average).

Station → Variables	1 (RTE) Moy.	ET	2 (RAF) Moy.	ET	3 (CMP) Moy.	ET	4 (Poly) Moy.	ET	5 (GNL) Moy.	ET
Temp. °C	19.95	5.47	25.60	6.62	25.50	3.69	23.1	3.59	26.78	3.36
Turbidity NTU	56.10	22.77	49.40	38.38	4.8	7.25	2.0	1.1	2.03	1.07
pH -	6.70	0.51	7.34	0.88	8.0	0.65	7.7	0.42	7.59	0.53
Cond. µS/cm	5490	5025	1034	665	55135	4884	56546	710.0	54680	11768
Salinity -	2.91	3.02	0.31	0.36	37.40	0.37	37.2	0.71	35.80	7.66
TDS mg/l	5400	4955	1018	756	54426	6469	54663	2526	54431	11728
rH -	18.68	28.87	-21.70	52.20	-63.1	37.74	-42.3	24.6	-33.88	31.93
O_2 mg/l	4.09	1.89	3.87	1.698	5.2	0.90	5.8	0.75	5.29	0.95
O_2 % %	43.07	14.93	44.76	13.79	63.9	7.84	66.4	5.83	66.09	9.59
DBO_5 mg/l	27.45	23.75	79.55	30.91	7.0	7.48	7.8	8.69	8.57	8.98
Cl^- mg/l	3239	495	565.1	247	21231	920.0	21977	3360	24183	2009
NO_3^- mg/l	3.24	6.60	1.18	3.321	2.7	6.64	2.8	6.82	0.58	2.42
NO_2^- mg/l	0.18	0.39	0.00	0.00	0.4	1.23	0.4	1.26	0.00	0.00
PO_4^{3-} mg/l	4.71	2.83	3.32	2.011	0.40	0.16	0.4	0.230	0.283	0.247
C_xH_y mg/l	258.0	1069.0	112.8	328.3	5.5	19.21	7.4	23.25	0.30	0.979
Fe mg/l	5.52	3.72	3.17	7.12	0.40	0.43	0.4	0.39	0.487	0.507
Cu mg/l	0.01	0.010	0.02	0.063	0.0	0.04	0.0	0.01	0.011	0.021
Pb mg/l	0.02	0.040	0.02	0.037	0.0	0.04	0.0	0.03	0.025	0.042
Hg mg/l	0.01	0.010	0.00	0.005	0.0	0.0	0.0	0.02	0.001	0.003

Station → Variables	6 (CTE) Moy.	ET	7 (Saf am) Moy.	ET	8 (Saf am) Moy.	ET	9 (EGZIG) Moy.	ET	10 (Mer) Moy.	ET
Temp. °C	24.67	4.21	18.49	4.78	24.50	3.85	21.8	5.32	20.2	4.15
Turbidity NTU	1.51	0.71	59.02	48.56	20.17	20.89	7.7	13.36	3.4	2.43
pH -	7.77	0.84	7.46	0.36	7.48	0.44	7.6	0.48	7.7	0.46
Cond. µS/cm	51872	120350	1493.9	355.6	50727	6471	18542	8926	55846	2375
Salinity -	36.84	0.44	0.69	0.53	33.46	4.55	13.2	8.27	37.1	0.44
TDS mg/l	49885	114370	1471.1	324.3	49700	6689	17800	8628	54504	3442
rH -	-38.22	27.52	-43.6	101.6	-29.93	24.8	-39.1	28.55	-38.6	26.18
O_2 mg/l	5.49	1.14	4.630	1.63	5.46	0.92	5.1	1.74	6.1	0.99
O_2 % %	66.51	11.84	46.61	13.99	65.0	7.14	56.5	17.66	66.1	5.52
DBO_5 mg/l	10.94	10.76	24.17	14.84	10.6	14.1	20.9	17.12	8.9	10.09
Cl^- mg/l	24000	3772	637	322	21338	1371	10566	5895	22186	1875
NO_3^- mg/l	2.81	6.82	23.68	27.92	1.17	3.32	3.8	6.97	0.0	0.0
NO_2^- mg/l	0.43	1.26	2.62	2.97	0.0	0.0	0.5	1.32	0.0	0.0
PO_4^{3-} mg/l	0.323	0.227	3.2	2.002	0.424	0.218	1.9	0.83	0.4	0.22
C_xH_y mg/l	1.15	2.52	12.50	49.90	24.4	76.5	2.0	5.31	83.3	345.8
Fe mg/l	0.477	0.465	2.43	4.616	0.686	0.675	4.3	18.75	0.7	0.8
Cu mg/l	0.032	0.081	0.01	0.009	0.009	0.013	0.0	0.01	0.0	0.03
Pb mg/l	0.017	0.034	0.02	0.053	0.034	0.065	0.0	0.03	0.0	0.08
Hg mg/l	0.001	0.003	0.09	0.308	0.004	0.01	0.0	0.0	0.0	0.000

Table 2. Means and standard deviations' values for the data collected across the 10 stations (Mean: mean; SD: standard deviation) over all 24 months. Yellow boxes: elements at concentrations that do not comply with the texts in force (JORA, 2006) (tab. III), with effects on the trophic chain and biodiversity. Blue boxes: concentrations in conformity, but not without effect on the trophic chain. Orange box: concentration largely out of range, likely to have very serious effects on human health and the environment.

Discharged water from the RTE is polluted and is extremely disadvantageous concerning proper aquatic life development.

Station 2 (RAF): Refinery

Discharged waters are mostly very hot, poor in oxygen, acidic, with a strong mineralization.

BOD5 demonstrates the polluted aspect of these waters, with high turbidity and low nitrate and nitrite values.

Hydrocarbons are always present in the water at high levels, which proves the purification system inefficiency.

Variations in metal levels are significant, for iron, mercury and lead in particular, which is explained through corrosion and facility obsolescence, giving these waters a distinct toxicity.

Chlorides and phosphates are present at high levels with all the consequences on the receiving environment.

Station 3 (CMP): plastics complexes

The water discharged by this complex is very hot, basic, well oxygenated with a very strong mineralization and an important turbidity.

BOD5 shows an accentuated chemical pollution of these waters and high nitrate and nitrite values during summer.

Frequent hydrocarbon traces can be found as a result both of the use of hydrocarbons as a raw material and of an out-of-service purification system.

Variations in metals are small. It can be seen that the change in the production process (replacement of the mercury cathode electrolysis process by anion exchange membrane electrolysis process for production optimization and environmental protection), carried out at the chlorine-soda unit, is very efficient. It has eliminated the problem of the presence of mercury in this complex.

Chloride values are very high, which indicates chlorine pollution (Chlorine is produced by salt electrolysis. It is used as a base material for the production of vinyl chloride monomer VCM).

Station 4 (Poly): Polyethylene complex

Waters are warm, neutral to basic pH, well oxygenated, with a strong mineralization.

BOD5 and chlorides show a high chemical pollution and significant values of nitrates and nitrites during the summer (respectively they reach 25 mg/l and 5 mg/l).

Hydrocarbons traces are found despite an operational purification system presence.

Variations in metals are small. Therefore, the discharged waters by this complex present a chemical pollution, degraded in nature and dangerous to the proper marine organism development.

Station 5 (LNG): liquefied natural gas complex

Discharged water coming from this complex is very hot, neutral to basic pH, well oxygenated, with a very strong mineralization.

BOD5, conductivity, TDS and chlorides show a clear chemical pollution of these waters.

Hydrocarbons are absent in these discharges.

Metal variations are small, with problematic mercury levels (up to 0.001 mg/l). Consequently, the water discharged by this complex presents a pronounced chemical pollution, inappropriate to a good aquatic life development.

Station 6 (CTE): thermal power plant

The discharged waters are very hot, with a basic pH that can sometimes reach a pH = 11, presenting a good oxygenation with a very strong mineralization.

BOD5, conductivity, TDS and chlorides show a pronounced chemical pollution of these waters and high nitrate and nitrite values especially in summer (NO_3^-= 25 mg/l and NO_2^-=5 mg/l).

The variations in metals are small, except for lead, which can present a potential risk for the proper development of certain marine organisms (it reaches 0.1 mg/l).

Therefore, the discharged water by this complex presents a significant chemical pollution.

Station 7 (Saf am): Ouadi Saf-Saf Upstream the industrial zone

The waters of the Ouadi Saf-Saf are characterized by a pH which varies according to the seasons, the oxygenation is a function of the temperature and thus of the seasons (strong oxygenation in winter and the opposite in summer). These waters are disturbed by large quantities of suspended matter.

BOD5 demonstrates the relatively good health of this watercourse before it passes through the industrial zone of Skikda, but it does not exclude the presence of organic pollution, which is confirmed by the presence of significant quantities of nitrates and nitrites especially in summer.

There are frequent traces of hydrocarbons and worrying values of mercury. The values of the other metals are in conformity with the texts in force, but lead is another problematic factor (it reaches values of the order of 0.21 mg/l).

Chloride values correspond to natural conditions. Those of phosphates are relatively high, related to agricultural activities.

Upstream of its passage through the industrial zone of Skikda, it is free of any chemical pollution, except that which is related to agricultural activity and the food industry. Indeed, the wadi Saf-Saf crosses vast lands, on which nitrogenous and phosphate fertilizers are used. In addition, agri-food industries (poultry breeding batteries, canning factories, pasta production, dairies, etc.) have settled on its banks.

Station 8 (Saf av): Wadi Saf-Saf downstream of the industrial zone

The waters flowing through the mouth of the Wadi Saf-Saf are very hot, relatively basic, well oxygenated, with strong mineralization and high turbidity.

BOD5 shows an accentuated chemical pollution of these waters.

Average values are recorded in the order of 24 mg/l of hydrocarbons (but values can reach 322 mg/l in the case of pipe or crude oil storage tank explosion accidents, which are still rare).

The variations of around 0.001 mg/l for mercury and up to0.3 mg/l for lead are recorded.

Chloride values are very high and can reach 23.2 g/l, which confirms the chemical pollution.

So, we can say that the waters of the mouth of Wadi Saf-Saf present an accentuated chemical pollution. They show a radical change in comparison with the waters of this wadi upstream.

Station 9 (EGZIK): management complex

The waters discharged by the Skikda industrial zone management complex are very hot, basic, well oxygenated, turbid and sometimes with strong mineralization.

BOD5 shows an accentuated chemical pollution of these waters and high nitrate and nitrite values during the summer.

There are frequent traces of hydrocarbons.

The variations of metals are marked, especially for iron which can reach 92.3 mg/l and lead which can reach 0.1 mg/l.

Chloride values are very high, which confirms the infiltration from the sea and from the neighboring complexes (CMP, Poly, LNG).

Therefore, the water discharged by the Skikda industrial zone management company is of polluted nature.

Station 10 (Sea)

Based on the findings on the control point (Mer), it can be concluded that:

The sea water in this control station is basic, very well oxygenated with strong mineralization and moderately turbid.

BOD5 shows either chemical pollution or a self-purification system establishment in these waters. The latter hypothesis is supported by the absence of nitrates and nitrites during the period of our study.

Frequent hydrocarbons traces are observed, sometimes with very high contents that can reach 1550 mg/l. Metals show slight variations. Trace values of mercury, iron and lead are sometimes detected, which are signs of the surrounding industrial activity's influence (CMP plastic complex, high-density polyethylene complex and the management company of the Skikda EGZIK Industrial Zone).

Very high chloride values comparing to the chloride contents in natural Mediterranean Sea water (19g/l), allowing us to consider pollution by chlorine (brines discharged, excess chlorine discharged by the chlorine-soda unit of the CMP complex and treatment of industrial installations and pipelines against marine organisms, by chlorine salts neighboring complexes).

We can therefore affirm from the witness point (Sea) at sea level east of Skikda industrial zone there is chemical pollution.

Finally, data description for each of the 19 measured characteristics during the 24 months and for all the 10 stations, combined with Algerian texts (JORA, 2006), revealed the state of the art of wastewater quality collected at each station. The obtained results demonstrate a very pronounced degradation over these waters and a significant chemical pollution, except at station 7 (Saf-Saf, upstream of the industrial zone) upstream, which is characterized by relatively normal river water, apart from mercury, which presents abnormally high values. These exceptional mercury values may be related to the presence of an upstream mercury deposit. These results are similar to those obtained by Mezedjri et al. (2007).

On the other hand, using Student's test (t) (Mezedjri, 2008), using annual averages for 2005, 2006 and 2007 for each of the 19 measured characteristics, in every station, gives important information on the variations in the wastewater quality collected in any station. Indeed, this test shows that the wastewater remains unchanged and consistent over time (the water quality for all the variables measured does not show any significant difference between years over time). This proves in fact that water pollution has settled over time. Consequently, a comparison between stations is necessary to highlight the differences as well as the similarities between the stations studied.

The results of means comparisons between the 10 stations, according to the analysis of variance test with 1 classification criterion, on each of the 19 variables measured over the 2 years are given in Table 4.

This table shows a very highly significant differences existence (rejection threshold: 0.1% error) between the 10 stations for the every following variables: T, S, pH, O2%, O2 mg/l, rH, conductivity, TDS, turbidity, BOD5, NO3-, NO2-, Cl- and PO43, just significant differences (1%error) between the stations for the mean iron contents and finally, non-significant differences (> 5% error) between the 10 stations for each of the variables Cu, Pb, Hg and CxHy.

The significant differences observed are related to the diversity of each complex's activity, the different water types (process or cooling water) discharged and the specific characteristics of each environment (marine or fresh water) (Bliefert & Perraud, 2001).

For heavy metals (Cu, Hg, Pb) and total hydrocarbons (CxHy), although there are no significant differences between the 10 stations, this does not mean that the values recorded for these variables are insignificant; rather, quite the contrary, some values, such as those for total hydrocarbons, are very high. This non-difference is owed to the diffusion of these metals and hydrocarbons in the considerable quantities of discharged water, and also to the different variations of these chemical variables in the natural environment (absorption by living organisms, com-

N°	PARAMETERS	UNIT	VALUES LIMITS	VALUE TOLERANCES OLD BOUNDARIES INSTALLATIONS
1	Temperature	°C	30	30
2	Turbidity	NTU	5	5
3	pH	-	6.5 - 8.5	6.5 - 8.5
4	phosphates	mg/l	10	15
5	BOD5	mg/l	35	40
6	Total hydrocarbons	mg/l	10	15
7	Iron	mg/l	3	5
8	Copper	mg/l	0.5	1
9	Lead	mg/l	0.5	0.75
10	Mercury	mg/l	0.01	0.05
11	Total Nitrogen	mg/l	20	25

Table 3. Limit values for industrial liquid effluent discharge parameters (JORA, 2006).

Variables	F_{obs}	p
T °C	8.900	0.000 ***
S ‰	427.90	0.000 ***
PH	8.74	0.000 ***
O_2%	17.57	0.000 ***
O_2 mg/l	6.87	0.000 ***
rH mV	5.36	0.000 ***
Condi µS/cm	326.40	0.000 ***
TDS mg/l	304.53	0.000 ***
Turbi NTU	43.33	0.000 ***
DBO_5 mg/l	27.90	0.000 ***
NO_3^- mg/l	7.88	0.000 ***
NO_2^- mg/l	6.83	0.000 ***
C_xH_y mg/l	0.96	0.476 ns
Hg mg/l	1.29	0.249 ns
Fe mg/l	1.92	0.050 *
Cu mg/l	1.17	0.315 ns
Pb mg/l	0.80	0.613 ns
Cl^- mg/l	100.55	0. 000 ***
PO_4^{3-} mg/l	13.83	0. 000 ***

Table 4. Results of analyses of univariate variance obtained for each 19 variables measured on the 10 stations over 24 months.

bination with other elements more complex to detect, evaporation or precipitation) (Bliefert & Peraud, 2001; Quevauviller, 2001; Rodier, 2005).

All these results confirm those previously obtained by the ANOVA test over a period of one year and for 14 physico-chemical characteristics (Mezedjri et al., 2007).

Concerning the variables where the analysis on variance test has rejected equality of means (for which the ANOVA test gives significant differences), the question then arises of looking for similarities, or in other words, looking for groups of means or stations that are likely to be homogeneous.

Numerical classification methods' use, as a variance analysis complement, is uncommon (Dagnelie, 2006). The bibliography concerning this approach is relatively limited (Cox & Cowpertwait, 1992; El Kherrak, 1993; Bautista et al., 1997; Dirienzo et al., 2002). These medium grouping methods are very numerous and diverse. Nevertheless, it is fortunate that, as far as the medium classification, obtained results are overall not very dependent on the applied methods (Dagnelie, 2006).

The 10 sampling stations grouping according to the physico-chemical of the analyzed waters quality, by means of a dendrogram using the Pearson simple link and square distance and for a minimum similarity level of 96.84%, allows to distinguish five distinct homogeneous groups as in Fig. 2.

A first group limited to the control point at the Saf-Saf wadi upstream of its passage through the industrial zone of Skikda Saf am (station 7). This point is characterized by fresh river water, exempt from any industrial chemical pollution though not free of problems.

A second group limited to the RTE point (station 1), which is a hydrocarbon storage and transport complex and whose liquid discharges are composed solely of maintenance and equipment cleaning water.

A third group related to the RAF point (station 2), which is characterized by water discharges from the hydrocarbon refining process.

A fourth group concerns the Egzik point (station 9), whose wastewater studied comes from the collection of current consumption water and rainwater.

This wastewater, which has a certain amount of chemical pollution from neighboring facilities, also contains substances of everyday use (detergents, cleaning products, water for daily consumption, etc.).

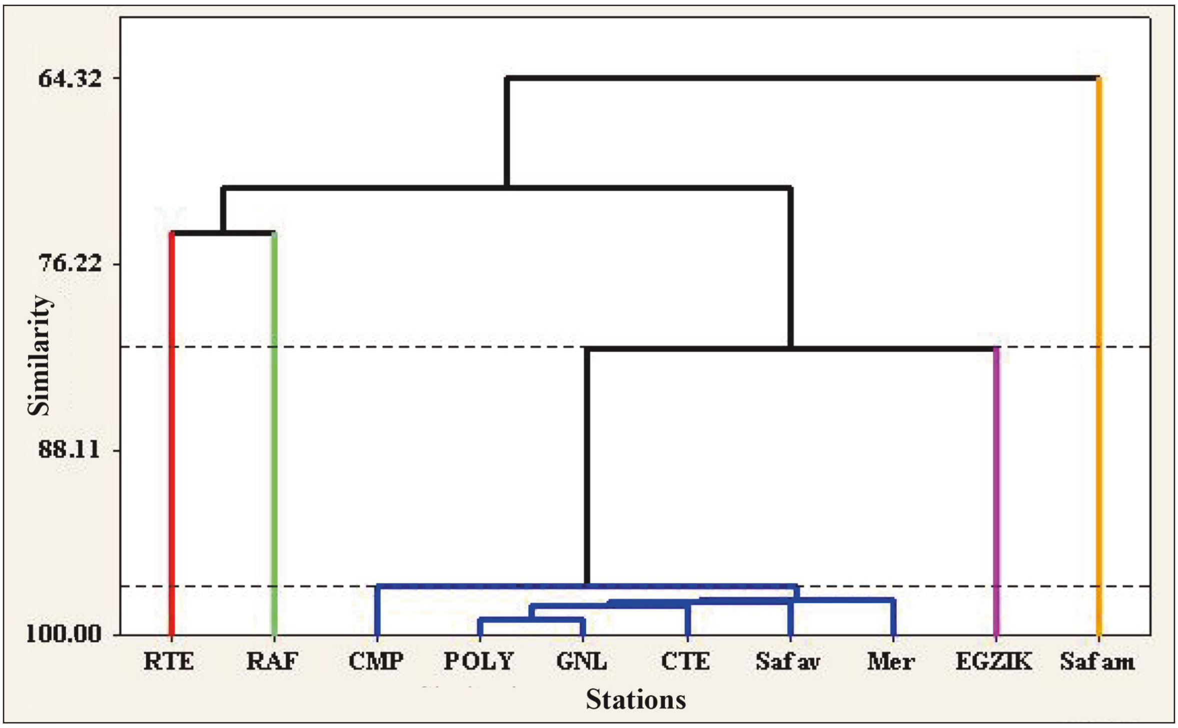

Figure 3. Dendrogram with single link and square distance from Pearson.

Finally, the last group, with a similarity level of 96.84%, is made up of the Sea (station 10), Saf av (station 8) and the CMP (station 3), Poly (station 4), LNG (station 5) and CTE (station 6) complexes, whose liquid discharges are made up of process and cooling water, having undergone intense chemical treatments (demineralization and desalination of drinking water and sea water, both used, anti-scaling and anti-marine organism treatment with biocides such as copper salts, chlorine, etc.). In this group, we notice the important influence of the CTE and LNG complexes (Fig. 2) on theSaf-Saf wadi: at the mouth, the water quality is completely different from that of the control point upstream of the industrial zone (Saf am) and close to that of the water discharged by the two neighboring CTE and LNG units. In the same way, we observe a rapprochement of the physico-chemical quality between the Sea control point and that of the CMP and Poly complexes which discharge directly into this natural environment.

A swimming water survey of the Skikda coastline (data not yet published) confirms a certain physico-chemical parameters constancy (14 parameters out of the 19 studied during this study), as one moves eastwards towards the bay, not only in space but also in time. Over a one-year period, the swimming waters, analyzed through appropriate statistical analysis, demonstrate the same physico-chemical quality in all the stations studied.

As a result, instead of a decrease or negative gradient in pollution as soon as one heads east, a certain constancy in pollutant concentrations is observed, regardless the presence of important sea currents in the region (see above). We can therefore say that pollution not only settles in time (Mezedjri et al. 2007), but also settles in space (the entire surrounding region is contaminated), with all the possible consequences and impacts on the marine fauna and flora of the region (fishing and spawning area), on the fishing sector, tourism (seaside area) and human health.

CONCLUSIONS

Generally speaking, data collected shows that wastewater from the seven complexes is polluted. All the petrochemical complexes have chemical pollution except for the refinery (RAF) and the terminal (RTE), which have oil pollution. On the other hand, the two chosen control points, Saf av and Mer, also present a sensitive chemical pollution, and it is even noted that the quality of the water of the wadi Saf-Saf (at the level of the third control point) changes completely after its passage through the industrial zone of Skikda. All these indications show the inefficiency of the adopted purification system (in most of the situations, the results obtained are not in conformity with the laws in force) at the level of the 7 complexes studied.

On the other hand, as far as metals are concerned, their variations are limited at all stations except for iron, which can sometimes have very high grades. In the same sense, the change in the production process of the plastics complex (CMP) has led to the elimination of mercury (used in the production of plastics) in the wastewater of this complex.

The use of the generalized linear model or the analysis of variance with a fixed model ANOVA classification criterion, for the data set obtained, shows very highly significant differences between stations, for all the physico-chemical variables studied, with the exception of total hydrocarbons and metals which show no significant difference. However, this absence of significant differences does not exclude the possibility that these variables may have dangerous and harmful levels for marine organisms.

The hierarchical analysis of the observations or the classification of the sites according to the physico-chemical quality of the waters allows, on the one hand, to group the 10 stations into 5 distinct groups and, on the other hand, to highlight the influence of liquid discharges from the petrochemical zone of Skikda and its impact on the immediate environment (the Wadi Saf-Saf and the sea). The results obtained (water quality almost unchanged during the two years of our investigation in the 10 stations and important quantities of waste water discharged) combined with the dominant currents in the region, show consequently the influence of the discharges from the industrial zone on the surrounding area.

This influence can have important repercussions on the marine fauna and flora in the eastern region of the Gulf of Skikda, through the disappearance of certain sensitive and fragile species (changes in temperature, salinity, pH, etc.) and the installation of more resistant opportunistic species, because generally the greater the reduction of a habitat, the more the species associated with this habitat are threatened (Attrill & Power, 2002 in Refes et al., 2011).

According to Klingler (2007), it is possible that in the future there will be a pronounced reorganization of ecosystems with encounters between species that were not previously in contact, which will lead to new interspecific competitions for resources.

Finally, these effects on the environment (water and sediment) could rapidly have repercussions, not only on the fauna and flora, but also on socio-economic activities (fishing and aquaculture, seawater desalination, tourism, etc.).

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