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Study of the Quality of the Industrial Residuary Waters, Rejected in the Gulf of Skikda (Algeria)

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Abstract: During the period spreading from August 2005 to July 2006, we achieved a comparative survey between the quality of waters rejected by the industrial zone of Skikda and the quality of waters appropriated on three witnesses' sites in a natural habitat. The survey has been done on a period of 12 months and carry on 10 stations with a total withdrawal of 120 samples and a frequency of 1680 different analyses achieved. The results of univariate and multivariate statistical analyses show, the existence of significant differences between the 10 studied stations for all physicochemical characteristic studied, and the absence of significant differences for the four inorganic elements (metals). The classification of the 10 stations in homogeneous groups with single linkage and squared Pearson Distance gives a dendrogram with 4 homogeneous groups of stations to the level of similarity of 85,48%.

Key words: Residuary waters, environment quality, statistical tests ANOVA, MANOVA, dendrogram

INTRODUCTION

In Algeria we noted, during these last years an awareness of public and policies on the negative effect of the industrial pollution and more especially of the residuary waters rejected by the industrial factories. This awareness succeed, in Algeria, by the adoption by the political authorities of regulations to protect the environment, among them the coastal law (JORA, 2002), the decree relative to the regulation of the industrial liquid garbage (JORA, 1993) and the law relative to the protection of the environment in the setting of the lasting development (JORA, 2003).

In spite of the development of the techniques of treatments and retraining of waste waters, as well as the processes of desalination of the sea water, at the same time we note an extension of the reasons of massive and varied pollutions, with all consequences on the environment quality.

The notion of residuary waters includes waters of various origins (Rodier, 1998). In this classification we recover wastewaters of urban, industrial and agricultural origins. In the region of Skikda (Algerian East coasts) an important industrial device is implanted (electric energy production, natural gas, petrochemistry, production of plastic and hydrocarbons transportation and refinement) that is located directly on the coastal fringe. This important device rejects these sewages directly in the gulf of Skikda (Mediterranean Sea). This last is characterized by an inshore line of 142-km long and a surface of fishing of 3068 km^2, it represent 4,69% of the total national fishing surface. The gulf of Skikda has a non negligible piscatorial resource (I.S.P.T.M., 1982). Indeed the different companions of resource assessment let appear an evaluation of the stock to about 18000 tons of biomass, which 6000 tons constitute the exploitable reserves (I.S.P.T.M., 1982; Djabali, 1988; E.R.H., 1996). Therefore, the impact of industrial activity in the gulf of Skikda on marine fauna and flora remains unrecognized. Also with a total absence of analytic data on the quality of residuary waters rejected in the marine environment, this type of work comes like a necessity and a source of information on the quality of waters rejected by the industrial zone of Skikda and its impact on the gulf's aquatic environment. The present study is the result of collaboration between academics, industrials represented by the enterprise of management of industrial zone of Skikda and the environment authorities of department of Skikda.

Our first objective is to realize a comparison between the qualities of the liquid dismissals of the different components of the industrial zone of Skikda with some witnesses point's in the receiving environment. Our second objective is to provide a reliable and exploitable data base for decision-makers and industrials in order to work to attenuate the pressures exercised by this activity on natural habitat.

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Fig. 1: Card of situation of survey zone and sampling points. Quickbird satellite Picture, February 2003: 1cm = 0,5 km

MATERIALS AND METHODS

Presentation of the survey zone: The industrial activity is especially intense in the department of Skikda, and especially in its chief place.

The industrial zone of Skikda (ZIK) has been created March 3, 1984, it is located at the East of the city of Skikda with a surface of 1200 ha (Fig. 1). It regroups several specialized units in transportation, refinement and transformation of the hydrocarbons. All this concentration of activities generates a hydric and atmospheric nuisance. In this research we will limit ourselves to the liquid dismissals. These dismissals are either, rejected directly in the sea or by the slant of Saf-saf wadi that it also succeeded thereafter in the sea. Saf-saf is a river that borders the (ZIK) by the West on a length of 6 km, its middle width is of about twenty meters with a debit of 569 $m^3 s^{-8}$ (Fig. 1).

To better surround the problems and the nuisances generated by the industrial zone of Skikda (ZIK), we conducted a regular control of liquid dismissals of the seven complexes that compose (ZIK), compared with three witnesses stations [the sea to the East of (ZIK) (Mer)(10), the Saf-saf wadi upstream before its passage by (ZIK) (Saf am)(7) and a station downstream in the mouth of the Saf-saf wadi with the sea (Saf av) (8)] (Fig. 1). The Table 1 gives the features of the seven bigger complexes of the (ZIK).

Sampling and analytic methods: Considering the diversity of the industrial activities and of the complex nature of waters rejected in the (ZIK), we opted for a simple hazardous sampling (Prichard, 1995) with instantaneous withdrawals (Rodier, 1998). The frequency recommended by the Algerian texts is a withdrawal per quarter (JORA, 1993). When it is about studying the chemical sub-stances whose variations are underestimated on a site, the optimal number and the frequency of sampling are of five samples per year during 4 years (Quevauviller, 2001). The present work is achieved on ten stations (Fig.1) during the period August 2005 to July 2006, either a sample per month and by station. The physicochemical characteristics measured in the residuary waters are: the temperature (T°), the saltiness (S‰), the (pH), the reducing power (rH), the toughness (TDS), the conductivity (χ), the dissolved oxygen (O_2) and the oxygen saturation rate (O_2%). All these features are measured by means of land probes of WTW type 197-S. The Biochemical Oxygen Demand (BOD_5) by means of the WTW (OxiTop®Control 12) device. The turbidity (turbi) is measured by a JENWAY turbidimetre ref 6035. The inorganic features are represented by four metals. The iron (Fe), the copper (Cu) and lead (Pb) are measured by means of a spectrophotometer to flame references D2576 (ASTM, 1974). The mercury (Hg) is measured by means of a mercurimetre references D3223 (ASTM, 1974). The choice of these four elements is strictly bound to the types of activities that are in the (ZIK).

Table 1: Description of the seven complexes of the industrial zone of skikda (ZIK)

Code	Designation	Production	Industrial waters	Observation
1 RTE	Eastern transport	Hydrocarbons and natural gas transport [9].	- Process 75m^3/d	Treatment station absent
2 RAF	Oil refinery	Hydrocarbons refinement [9].	- Process 5712 m^3/d	
			- Cooling 336000 m^3/d	Treatment station present
3 CMP	Plastics complex	PVC, VCM, polyethylene, ethylene, chlorine sodium carbonate, hydrochloric acid, chlorite of sodium and water distilled [9].	- Process 244480,8 m^3/d	
			- Cooling 157800 m^3/d	Treatment station present
4 Poly	High density polyethylene plant.	High density polyethylene [10].	- Process 0,3 m^3/T of product	Treatment station present
5 GNL	Liquefied natural gas complex	Natural gas, ethane, propane, butane and naphtha [9].	- Process 1440 m^3/d	
			- Cooling 150000 m^3/d (sea water) and 1500 m^3/d (closed circuit)	Treatment station absent
6 CTE	Thermal power station	Electricity [9].	- Process 180000 m^3/year	Treatment station absent
9 EGZIK	Industrial area management company	Management of the industrial zone [10].	collection of all waters servant of the industrial zone	Treatment station absent

Statistical analyses of data: The collected data by stations constitute a matrix of dimension 12×14 = 168. The analysis of the data has been done for the set of the 10 stations. First of all, we calculated the basis statistical parameters for every characteristic, and then we compared the stations between them for each of the 14 variables by mean of univariate Analysis of Variance test (ANOVA) (Daghrlie, 2000).

After what we compared, between them, all stations while taking in consideration the set of the 14 studied features by mean of multivariate analysis of variance test (MANOVA) (Daghrlie, 2000; Palm, 2000).

Finally we have with the help of method with Single Linkage and squared Pearson Distance classified the 10 stations in homogeneous groups (Dagnelie, 2000; Palm, 2000; X, 2003).

All calculations have been executed with the software of statistical analysis and treatment of data (MINITAB 14) (X, 2003).

RESULTS AND DISCUSSION

The Table 2 presents the results of the description of data for each of the 14 measured features during the 12 months for each of the 10 stations.

The results of univariate Analysis of Variance test (ANOVA) presented in the Table 3, shows that significant differences exist between the stations for all physicochemical variables. These differences are bound to the nature of the activity in every complex and to the features of every middle (Bliefert and Perraud, 2001) (sea water or soft water). whereas for the heavy metals (Fe, Cu, Hg, Pb) there is no significant differences existing between the 10 stations, it is due to the diffusion of these metals in the important quantities of waters rejected and also to the different variations of these inorganic variables in the natural habitat (absorption by the living organisms, combination with other elements more complex to detect, evaporation or precipitation) (Rodier, 1998; Quevauviller, 2001; Bliefert and Parreud, 2000).

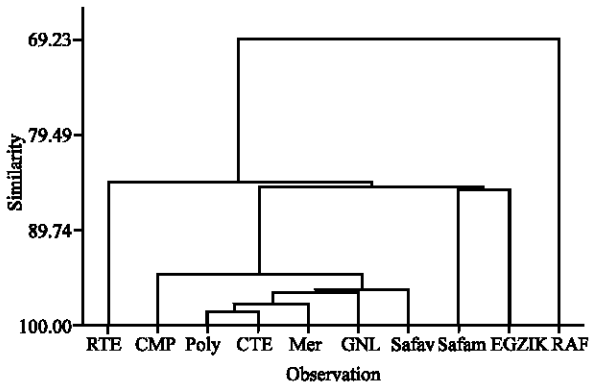

Fig. 2: Dendrogram with single linkage and squared pearson distance

The test of MANOVA and whose results represent in, the Table 4 for the physicochemical variables and the Table 5 for metals, confirms the results of ANOVA. The tests of Wilk's, Lawley-Hotelling and Pillai's succeed to the same results (Huberty, 1994). In the case of the physicochemical characteristics Table 4 significant differences exist between the 10 stations, whereas for the inorganic elements Table 5 we note no statistical differences between the 10 stations.

These conclusions confirm the results gotten by Mézédjri and Tahar (2006), at the time of a preliminary study, on the variations of metals (Fe, Cu, Pb and Hg) in the Saf-saf Wadi and the sea water in the gulf of Skikda, between March and June 2005 and that concluded to the non-existence of significant differences between the three chosen stations.

The regrouping of the 10 stations according to the physicochemical quality of waters analyzed, by means of a dendrogram with Single Linkage and squared Pearson Distance gives to the level of similarity of 85,48% (Fig. 2), four distinct homogeneous groups of stations. The first group consists of (RAF) point, characterized by water dismissals of hydrocarbons refinement process. The second group consists of (RTE) point, that is a complex of

Table 2: Statistical parameters of basis: mean (m) and Standard Error of the average (SE) for the 10 stations.

	Station									
	1 RTE		2 RAF		3 CMP		4 Poly		5 GNL	
Variables	m	SE	m	SE	m	SE	m	SE	m	SE
T (°C)	19.31	1.65	24.68	2.06	24.67	1.09	21.99	1.08	26.41	1.15
S (‰)	1.967	0.736	0.433	0.142	37.417	0.125	36.958	0.264	34.11	3.11
PH	6.759	0.190	7.507	0.343	8.105	0.174	7.747	0.123	7.673	0.166
O2 (%)	47.41	4.44	46.55	4.61	65.18	2.99	68.54	1.48	68.30	3.61
O2 (mg L^{-1})	4.797	0.608	4.127	0.550	5.542	0.308	6.144	0.227	5.605	0.340
rH (mV)	17.0	10.6	-31.6	20.4	-67.4	10.3	-44.75	7.21	-36.9	10.3
(mS cm^{-1})	4.00	1.26	1.197	0.264	55.17	1.75	56.533	0.281	52.23	4.77
TDS (mg L^{-1})	4.01	1.30	1.185	0.304	54.14	2.36	55.017	0.739	52.05	4.75
Turbi (NTU)	67.37	4.82	41.4	10.2	5.07	2.49	2.350	0.369	2.492	0.312
BOD5 (mg L^{-1})	29.81	9.50	63.18	8.16	5.70	1.78	5.91	2.09	6.73	2.03
Hg (p.p.m)	0.0064	0.0033	0.0020	0.0016	0.0015	0.0008	0.0058	0.0053	0.0013	0.0010
Fe (p.p.m)	5.92	1.22	2.047	0.457	0.398	0.127	0.421	0.123	0.436	0.152
Cu (p.p.m)	0.0076	0.0027	0.0324	0.0255	0.0292	0.0154	0.0123	0.0043	0.0178	0.0083
Pb (p.p.m)	0.0056	0.0030	0.0038	0.0038	0.0174	0.0079	0.0134	0.0063	0.0182	0.0085
	Station									
	6 RTE		7 RAF		8 CMP		9 Poly		10 GNL	
Variables	m	SE	m	SE	m	SE	m	SE	m	SE
T (°C)	23.09	1.11	17.81	1.39	23.33	1.08	20.82	1.50	19.64	1.27
S (‰)	36.942	0.135	0.750	0.210	31.80	1.64	9.47	2.73	36.958	0.0988
pH	7.880	0.314	7.444	0.116	7.467	0.125	7.666	0.163	7.668	0.138
O2 (%)	67.85	4.45	53.42	4.10	69.33	1.60	62.88	6.16	68.82	1.31
O2 (mg L^{-1})	5.808	0.395	5.471	0.470	6.065	0.193	5.715	0.578	6.573	0.287
rH (mV)	-36.08	7.91	-20.17	6.30	-27.75	6.71	-40.92	9.59	-38.00	7.68
(mS cm^{-1})	52.75	3.78	13.752	0.0874	47.90	2.25	12.71	1.82	55.433	0.953
TDS (mg L^{-1})	51.33	3.59	13.753	0.0909	47.36	2.41	12.06	1.62	54.55	1.26
Turbi (NTU)	1.763	0.248	62.2	15.4	18.54	6.45	10.13	5.28	2.817	0.735
BOD5 (mg L^{-1})	11.25	3.34	15.96	3.33	7.45	2.13	22.23	4.62	6.36	2.00
Hg (p.p.m)	0.0014	0.0011	0.1159	0.0991	0.0056	0.0033	0.0014	0.0007	0.0021	0.0013
Fe (p.p.m)	0.441	0.132	3.87	1.79	0.657	0.166	8.17	7.65	0.479	0.113
Cu (p.p.m)	0.0532	0.0316	0.0083	0.0030	0.0111	0.0045	0.0052	0.0027	0.0189	0.0105
Pb (p.p.m)	0.0075	0.0054	0.0051	0.0043	0.0156	0.0080	0.0101	0.0072	0.053	0.0280

Table 3: Results of the univariate analysis of the variance ANOVA

N°	variables	F_{obs}	P
1	T (°C)	4.01	0.000 ***
2	S (‰)	141.69	0.000 ***
3	pH	3.13	0.002 **
4	O_2 (%)	2.74	0.006 **
5	O_2 (mg L^{-1})	5.81	0.000 ***
6	rH (mV)	4.21	0.000 ***
7	χ (mS cm^{-1})	125.75	0.000 ***
8	TDS (mg L^{-1})	116.28	0.000 ***
9	Turbi (NTU)	15.20	0.000 ***
10	DBO5 (mg L^{-1})	14.69	0.000 ***
11	Hg (p.p.m)	1.29	0.249 ns
12	Fe (p.p.m)	1.23	0.286 ns
13	Cu (p.p.m)	1.04	0.412 ns
14	Pb (p.p.m)	1.81	0.074 ns

$p>\alpha = 0.05$: (ns) no significant, $p = \alpha = 0,01$: (**) significant, $p = \alpha = 0.001$: (***) significant

Table 4: Results of the test of MANOVA done on the characteristic physicochemical

Critère	Statistique test	F_{obs}	P
Wilk's	0.01305	6.923	0.000 ***
Lawley-Hotelling	18.05765	19.908	0.000 ***
Pillai's	2.16644	3.456	0.000 ***

$p = \alpha = 0.001$: (***) significant

Table 5: Results of the test of MANOVA done on the inorganic elements

Critère	Statistique test	F approx	P
Wilk's	0.66517	1.286	0.130 ns
Lawley-Hotelling	0.43580	1.277	0.136 ns
Pillai's	0.38228	1.292	0.125 ns

$p>\alpha = 0.05$: (ns) no significant

hydrocarbons Storage and transportation and whose dismissals are constituted by waters of maintains and cleaning of machines. The third group is composed by one witness point (Saf am) of which is composed by soft waters of rivers and by (EGZIK) point, characterized by the drainage of the current consumption and pluvial waters. Finally the fourth group with a level of similarity of 94,48% composed by the witnesses points (Mer and Safav) and the complexes (CMP, CTE, Poly and GNL) whose liquid dismissals are composed by waters of cooling and intense chemical treatments (demineralization and desalination of water). In this group we notice the important influence of the complexes (CTE and GNL) (Fig. 1) on Saf-saf, to the mouth we get a water quality close to the one rejected by the two previous units. In the same way, we observe closeness, of the physicochemical quality, between the witness point (Mer) and the one of the complexes (CMP and Poly) that pours directly in this natural habitat Fig. 1.

CONCLUSION

The present work has for object a comparative survey between the quality of waters rejected by the industrial zone of Skikda and three witnesses' sites in the gulf of Skikda.

The use of the univariate analysis of variance ANOVA, permitted to deduct significant differences between the stations, for the set of the 10 physico-chemical features, and an absence of significant differences for the four studied inorganic elements (metals and heavy metals). The use of the multivariate analysis of variance MANOVA confirms the results of the ANOVA.

The stations classification according to the physicochemical quality of the studied waters, permits on the one hand, to regroup the 10 stations in 4 distinct homogeneous groups, and on the other hand to notice the influence of the liquid dismissals of the petrochemical zone of Skikda on the natural habitat.

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