

Determination of the Sea Waters Quality of Arzew-Algeria Gulf

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Abstract

This work consists of assessing the degree of pollution caused by wastewater near the gulf of Arzew-Algeria. This study is based on the analysis of the physicochemical parameters, the parameters indicating pollution and the determination of heavy metals (Pb, Zn, Cd, Fr, Cr, Ni) on seawater samples taken from the site. Four companions of seasonal sampling were carried out during the year 2015. The results obtained show significant values in physicochemical parameters, pollution indicator parameters and heavy metal content in seawater samples. The results of the pollution indicator parameters show the presence of important pollution at the site studied. The results obtained are far superior to the Algerian standards defined.

It is clear from the determination of heavy metals that the site under investigation shows a slight contamination by metals. The absence of treatment and the long-term exposure to these discharges will lead to severe metal pollution in seawater.

Keywords: Arzew; Marine pollution; Physicochemical parameters; Pollution indicators; Heavy metals

Introduction

Every year, pollution is gaining ground. Even beaches allowed for swimming are not totally clean. Water is one of the essential elements for most large industrial enterprises. After being used, most of this wastewater is returned to the environment. As it is usually loaded with organic matter, it becomes a major source of pollution for the environment that receives it [1]. The study of the content of heavy metals (Pb, Zn, Cd, Fe, Cr and Ni) in polluted superficial sea waters and sediments in the Gulf of Arzew shows that these levels vary with harvest and season.

The Algerian coast would undoubtedly deserve a little more attention from public authorities and citizens or from the 487 beaches on the Algerian coast, 213 are prohibited to bathing, the majority of which are closed because of pollution. In recent years, several industries have been active in Arzew. There are mainly chemical and petrochemical industries. These industries, like all human activities, produce various effluents and waste. Untreated effluent is discharged into the sea. The large slabs of petrochemicals presented along the coast off the industrial poles of Arzew and Bethioua, causing adverse effects on marine fauna and flora. Estimated quantities of more than 20,000 tons of petrochemicals are illegally dumped by foreign oil tankers and LNG tankers into the waters of these two ports linked to the industrial complexes of Arzew and Bethioua. In this study, we will show the impact of effluent discharges on aquatic receptor. For this, we measured the main parameters of this pollution.

Several authors Boutiba et al. [2], Samir [3] have shown a growing pollution throughout the Algerian coast, especially in the coastal areas of large cities like the Oran coast. The pollution of marine ecosystems by hydrocarbons has been a concern for national governments and the international community for many years. According to the results obtained by Laama [4], Sahnoun et al. [5], Remili and Kerfouf [6] concerning the analysis of sea water samples taken at different locations are summarized in the following Table 1.

Selection and Description of Study Area

The industrial zone of Arzew was realized in 1970 east of Oran. By virtue of its strategic geographical position, its existing infrastructure

accentuates more by the important urban-industrial development of the establishment of the industrial zone which was originally conceived as a factor of spatial planning policy and unfortunately, not ensure socio-economic development in a harmonious way. The cities of gulf (Arzew, Bethioua and Ain-bia) are characterized by a problem specific to the presence of complexes that gives it an industrial function. The industrial zone of Arzew is one of the three most important industrial of the country.

This industrial zone covers a total area of 961.69 ha (Figure 1) and allows the establishment of 15 production units and 17 service units.

Materials and Methods of Analysis

The coastline of the Arzew gulf is increasingly attacked today by various forms of nuisance due to industrial activity and massive urbanization, resulting in an ever-increasing extent of pollution from domestic and Industrial development. The coastal fringe is increasing wastewater discharge without any treatment, causing biological and physicochemical contamination of marine waters [6,7]. This coastal fringe is experiencing a galloping population expansion accompanied by anarchic urbanization and intense port associated with various industrial activities, which have consequences for the coastal environment [8].

In our study, we carried out 4 season sampling companions (Figure 2), the 1st on winter (January), the 2nd during the spring (April), the 3rd on summer (July) and the last on autumn (October).

To take a sample, I used a glass bottle, to keep it sterilized, to introduce it under the surface of the water to 15-30 cm below the level

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LAAMA. 2009			SAHNOUN. 2010				REMILI. 2009	
Port of Algiers			Industrial area of Arzew				Wastewater discharged at the level of the coast of the city of Oran	
	S1	S2		S1	S2	S3	Cd (mg/L)	0.52
MES (mg/L)	83	152	DCO (mg/L)	530	900	585	Pb (mg/L)	0.23
DBO5 (mg/L)	23.3	16.7	DBO5 (mg/mL)	220	360	250	Zn (mg/L)	0.61

Table 1: Various studies on the analysis of sea water samples.



Figure 1: View of the Arzew gulf with the industrial zone and the various ports.



Figure 2: Different sampling stations.

of the water then to remove the cap to fill the Bottle to avoid any kind of contamination of the sample.

Seawater samples taken at different sites are preserved in polyethylene bottles with capacities ranging from 250 ml to 1 liter, previously washed with distilled water and transported at low temperatures 4°C in portable coolers. The conservation of the water samples was done

according to the guide for the preservation and handling of samples according to ISO 5667/3. The temperature of the water is measured in situ using a two-way oximetry (type WTW OXI 96), pH and electrical conductivity are measured using a pH meter of type (WTW 525). For the determination of the BOD₅, the OxiTop is used; COD (COD-type meter WTW) was used. The MES was quantified by filtration

(circular WHATMAN filters with a 47 mm diameter and a porosity of 0.45 μm) is determined according to the AFNOR standard (T90-105). The determination of the traces of metals is carried out by atomic emission spectroscopy with plasma coupled by induction according to standard NF EN ISO 11885.

The analytical methods used are described by [9]. The analyzes were carried out at the Physico-chemical, Materials, Catalysis and Environment laboratory within the USTO's university.

Results and Discussion

All results are grouped in Table 2.

Physical parameters

Temperature (T): The mean values of the temperature recorded in the sea water of the studied sites vary between 12°C and 21°C. According to the results, we note that the sea water temperature at the site level is within the norm (below 30°C) which is considered as the limit value of direct rejection in the receiving environment [10].

pH: The pH is an important parameter which represents the degree of ionization of the medium studied; it gives us an indication on the level of the pollution of the water. It should be strictly monitored during the sampling period. The average of pH values recorded in sea water ranged from 6.8 to 8.3. The results obtained remain in the global standards which recommend a pH of the discharges comprised between 6.5 and 8.5.

Dissolved oxygen: Dissolved oxygen is a very useful parameter to indicate the quality of the water; it is considered one of the parameters most sensitive to pollution. Its value gives information on the state of water pollution. The dissolved oxygen analyzes performed on seawater samples ranged from 4.3 mg/L to 10.5 mg/L.

Conductivity: The recorded salinity of the raw effluent oscillates at an average of 36000 μS/cm. This salinity is mainly linked to the discharge of wastewater. The values recorded are relatively high, which can cause aggressive problems in the pipes. Beyond 3000 μS/cm,

the conditions are unfavorable for a normal ecological balance. For the samples of seawater analyzed, the results obtained reveal averages varying between 34933,33 μS/cm and 38433,33 μS/cm. The results obtained show that the electrical conductivity is very high in seawater. The conductivity of seawater is very high due to the high concentration of dissolved salts because it makes it possible to evaluate the total load in electrolytes of water. Conductivity gives an idea of the mineralization of water and is therefore a good marker of the origin of water. Indeed, the measurement of the conductivity makes it possible to appreciate the quantity of the dissolved salts in the water, and therefore of its mineralization. The electrical conductivity depends on the loads of endogenous and exogenous organic matter generating salts after decomposition and mineralization and also with the phenomenon of evaporation which concentrates these salts in water; it also varies according to the geological substrate traversed.

Suspended matter: The suspended matter represents all the mineral and organic particles contained in the waters. High levels of suspended solids can be considered a form of pollution [7]. The results obtained during our study reveal very high concentrations. For the samples obtained, the mean values recorded ranged from 294 mg/L to 3062 mg/L. The results obtained during our study show that the concentrations of the suspended solids in all the samples analyzed far exceed the national standards defined (35 mg/L). These concentrations are probably caused by the boats emptying, sewage and urban domestic waste that are rich in colloidal matter of mineral or organic origin.

Chemical parameters

Chemical oxygen demand (COD): The COD monitoring of seawater shows very high values which far exceed the limits allowed by the national standard (120 mg/L) and international of direct discharges. Indeed, the COD values range between 460.8 and 4944 mg/L with an average of 1600 mg/L.

Biochemical oxygen demand for 5 days (BOD₅): Monitoring of BOD₅ follows that of COD with lower values. It oscillates between 207.57 mg/L and 2001.62 mg/L with an average of 582.93 mg/L. These

Parameter	Norms	Range of results	
		MIN	MAX
Temperature °C	30	12	21
pH	6.5-8.5	6.8	8.29
Dissolved Oxygen (mg/L)	-	4.3	10.5
Conductivity (μS/cm)	3 000	34933.33	38433.33
Suspended Matter SM (mg/L)	35	294	3062
Chemical Oxygen Demand COD (mg/L)	120	460.8	4944
Biochemical Oxygen Demand BOD ₅ (mg/L)	40	207.57	2001.62
Total Hydrocarbons (HCT) (mg/L)	10	9.2	11.3
Organic Matter (mg/L)	-	15.83	71
Total Phosphorus (mg/L)	2	0.15	3.46
Nitrogen Kjeldahl Total (NTK) (mg/L)	30	16	21.4
Nitrate (mg/L)	50	1.66	2.66
Nitrite (mg/L)	-	0.02	0.05
Ammonium (mg/L)	-	0.21	4.54
Lead	1(mg/l)	0.003 μg/L	0.24 μg/L
Zinc	5 (mg/l)		0.66 μg/L
Cadmium	0.2(mg/l)	0.14 μg/L	8.58 μg/L
Iron (mg/L)	1	0.056	0.28
chrome (mg/L)	0.1	0.005	0.024
Nickel (mg/L)	5	0.019	0.033

Table 2: Results and norms of seawater physicochemical parameters of the Arzew gulf.

values also exceed 2 to 20 the permissible standard (40 mg/L) for direct discharge.

Biodegradability ratio COD/BOD The ratio of biodegradability allows us to assess the derivability of organic matter. The ratio of biodegradability concerns the COD/BOD₅ ratio which serves to specify the degree of biodegradability of the organic matter at the sites studied. The results of this ratio are all between 2.5 and 4 so the sites studied are highly biodegradable.

Total hydrocarbons (HCT): The values obtained for HCT stay near to the norm (10 mg/L). Values fluctuated from 9.2 mg/L to 11.3 mg/L with an average of 10.22 mg/L.

Organic matter: Average values of organic matter in seawater range from 15.83 mg/L to 71 mg/L. The results obtained allow us to observe the variations of the organic matter during the period of study. MO concentrations increased throughout the winter season and decreased in the spring. The increase in organic matter content at study sites is due to the high levels of organic matter discharged into the environment. This high organic matter content is explained by the pollutant load carried by the anthropogenic coastal discharges of the waste water discharged at the sites studied.

Total phosphorus: Analysis of total phosphorus in the samples collected revealed very high concentrations. The mean values obtained are between 0.15 mg/L and 3.46 mg/L. Compared to the Algerian limits set at 2 mg/L, the phosphorus contents found are well above the defined standard. Much of the organic phosphorus also comes from wastes of protein metabolism and its elimination as phosphates in the urine by man and the rest comes mainly from detergents. Phosphorus has an important role in the eutrophication of the marine environment because too much phosphorus can accelerate it. An excessive phosphorus intake can also create favorable conditions for the development of cyanobacteria water flows, especially when the surface water temperature is relatively high and there is a lack of dissolved oxygen.

Nitrogen kjeldahl total (NTK): In practice, Nitrogen Kjeldahl is an indicator of environmental pollution and its monitoring makes it possible to monitor the evolution of contamination. In our case, the amplitude of NTK variations during the study remains low. Values range from 16 mg/L to 21.40 mg/L and are more or less within the permitted standard (30 mg/L).

Nutrient Salts

The nitrate: Nitrates represent only one of the many forms of nitrogen present in water, while in general constituting the most abundant form of mineral nitrogen. Analysis of the nitrate content at sea level revealed concentrations between 2.66 mg/L and 1.66 mg/L, compared to the Algerian limits set at 50 mg/L, the nitrate contents recorded remain very inferior. As a result, the waters studied are not subject to a risk of nitrate pollution.

The nitrite: Average concentrations of nitrite in seawater range from 0.02 mg/L to 0.05 mg/L. The low concentrations of nitrites found in the waters studied could be explained by the fact that the nitrite ion (NO_2^-) is an intermediate between ammonium and nitrates and is unstable in the presence of oxygen, whose concentration is generally much lower than that of the two forms which are related to it, nitrate ions and ammonium. For the seawater samples analyzed, the results show a continuous decrease of nitrite at the site studied throughout the four study seasons, a decrease in winter and then a stabilization of the

concentration in spring, we note that despite the High levels of nitrite; The nitrates always remain in surplus. This is obviously the reflection of a massive and continuous supply of nitrates or a possible nitrification of ammoniacal nitrogen.

Ammonium: Results from ammonium analysis in seawater samples show concentrations ranging from 0.21 mg/L to 4.54 mg/L. The ammonium ion, NH_4^+ , is the reduced form of nitrogen. It comes mainly from the decomposition of natural proteins contained in phytoplankton and microorganisms. It may also come from the supply of purified urban effluents or industrial discharges. It is found in natural waters at concentrations ranging from 0.1 mg/L to more than 10 mg/L. The amount of ammonium in the sea water increased in winter and decreased in the spring. The high levels of ammonium can be explained by the enrichment of these sites in this nitrogen compound, which results from the discharges of domestic and industrial wastewater, besides the bacterial decomposition of organic nitrogen compounds, the bacterial mechanism called ammonification. Urban ammonium releases can cause a significant increase in the concentrations of this element in the receiving environment, this reduced form of mineral nitrogen, which can lead to the consumption of dissolved oxygen in this medium during its oxidation. Prove to be toxic.

Determination of heavy metals

The lead: The determination of lead in water samples gives information on the content of this metal in the sea. Average concentrations range from 0.003 $\mu\text{g/L}$ to 0.24 $\mu\text{g/L}$. By comparing our results with the Algerian standard of 1 mg/L defined by the OJ [10], we find that the site studied is far from being polluted by lead.

The zinc: The mean values of zinc found in samples of seawater range from 0.14 $\mu\text{g/L}$ to 0.66 $\mu\text{g/L}$. The sets the zinc content in liquid effluents at 5 mg/L, so our results are still below the norm [10].

The cadmium: Cadmium is a relatively rare metal in nature. Its stability in water is a function of pH and oxidation-reduction potential. Its origin, from an industrial point of view, is related to plastics, engine oils, batteries and in products of thermal stability. For pH above 8, cadmium precipitates with carbonates. When mixing sewage with seawater, cadmium forms very stable complexes with chlorides. Cadmium does not degrade in the environment, but physical and chemical processes can alter its mobility, bioavailability and residence time in different environments. In aquatic environments, the mobility and bioavailability of cadmium increases when pH, hardness, suspended solids concentration and salinity are low and oxidation-reduction potential is high [11]. The mean values of cadmium recorded in the studied water fluctuate between 0.24 $\mu\text{g/L}$ and 8.58 $\mu\text{g/L}$. According to the standards defined by the OJ [10] which fix the cadmium content in liquid effluents at 5 mg/L, our results are much lower than this standard, so there is no cadmium pollution at the D study.

Iron, chrome and nickel: The results show that the values of total metal pollution (iron, chromium, nickel) show negligible variations between the different sampling campaigns. The iron concentrations of the analyzed water ranged from 0.056 mg/L to 0.28 mg/L with an average of 0.122 mg/L. The chromium concentration shows that the extreme values of 0.005 mg/L and 0.024 mg/L with an average concentration of 0.012 mg/L. The recorded nickel values range from 0.019 mg/L to 0.033 mg/L with an average value of 0.026 mg/L [12].

Conclusion

Marine pollution from sewage is a serious problem in the Mediterranean Sea, especially in riparian countries in the process of industrialization like Algeria. With the absence of stations and sewage treatment systems in these countries, wastewater is discharged into the sea without any prior treatment, leading to degradation of the sanitary quality of coastal waters and disruption of marine ecosystems. This work deals with an assessment of the state of marine pollution along the Arzew golf course.

Space-temporal monitoring of several physicochemical tracers has given us the image of a relatively intense pollution which results in a large organic and mineral load. The results of the pollution indicator parameters reveal that the site studied is over the month polluted by the wastewater discharged. Analysis of nutrient salts shows the richness of the site studied in nutrients imported by wastewater discharges.

The determination of heavy metals indicates the presence of slight pollution by lead, zinc, cadmium, iron, chromium and nickel. The long-term exposure to these releases will increase the metal content that can alter aquatic life. However, we find that the impact of the releases studied is relatively moderate. However, continuous exposure can degrade the marine ecosystem and affect wildlife and marine life. These results show the need for prior treatment of raw wastewater, biological treatment should be considered to improve their quality to the required standards and to meet the expectations of the public authorities with regard to protection of the environment and human health.

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