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Impact of urban and industrial effluents on the coastal marine environment in Oran, Algeria

A. Tayeb [a,b], M.R. Chellali [b,c,d,*], A. Hamou [b], S. Debbah [e]

[a] Head of Health, Safety and Environment Department, Sonatrach GL2Z Arzew, Oran, Algeria
[b] Laboratory of Environmental Science and Material Studies, Faculty of Exact and Applied Sciences, University of Oran 1-Ahmed Benbella, Oran, Algeria
[c] Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology, Paulinska 16, 917 24 Trnava, Slovakia
[d] Institute of Materials Physics, University of Muenster, 48149 Muenster, Germany
[e] Biotechnology and Industrial Safety Engineer, Sonatrach Arzew, Oran, Algeria

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ABSTRACT

In Algeria most of the urban waste water is dumped without treatment into the Sea. It is tremendously important to assess the consequences of organic matter rich sewage on marine ecosystem. In this study we investigated the effects of industrial and urban sewage on the dissolved oxygen (O_2), chemical oxygen demand (COD), biochemical oxygen demands (BOD_5), pH, salinity, electrical conductivity (EC), Metal element (Hg, Pb, Cu, Ni, Cr, Cd), petroleum hydrocarbons (HC), oil and grease (OG) in Bay of Oran, Algeria. A ten-year follow-up research showed that the concentrations of oil and grease released into the bionetwork are of higher ecological impact and this needs to be given the desired consideration. Information on bathing water quality revealed that the most beaches in Oran are under the national environmental standard limit.

Due to rapid industrial expansion and population growth in coastal cities, a tremendous amount of heavily domestic and industrial effluents have become increasingly evident, causing a serious health, economic and environmental problems (Baron et al., 1982; Daniel et al., 2002). Usually, most of littoral developing countries discharge their communal sewages into the sea before being treated by sewage treatment plant (STP) (Walle et al., 1993; Vallega, 1995). Wastewater mishandling in the Mediterranean countries can be attributed in large to unsuitable technology, pathetic organizations, absence of governmental determination, and insufficient funding (Massouda et al., 2003). Furthermore, the international transportation manufactory is responsible for the carriage of approximately 90% of world trade, contributing to a substantial oil and chemical pollution (Albakjaji, 2012). With only 0.7% of the entire surface area of the world's oceans, the Mediterranean concentrates 25% and 30% of the globe and oil traffics, respectively (Rømer et al., 1998). Approximately 500 million tones are transported annually in the Mediterranean region. The maximum amount of these ejections can be estimated at 1.2 million tons per year (Marchand, 2002). This means, that more than 300,000 tons of oil are lost or discharged annually into the sea, caused mainly by hydrocarbon residues during operational discharge, degassing, deballasting and tank washing (Mendelsohn and Fidell, 1979). Depending on the amount of pollutants and local protocols; physical, chemical and biological analysis could be used (Fisk et al., 2001).

The rate of oxygen demand are often used to predict the impact of an effluent discharged on receiving bodies such as river, lake and sea (Sawyer et al., 2003). Nowadays, the most common factors used to determine the concentration of organic matter in wastewater are the chemical oxygen demand (COD), and the biochemical oxygen demand (BOD_5). COD is standard method to measure amount of chemicals pollution in the water that can be oxidized (Russell, 2006). BOD_5 is a regular analysis that delivers information about the organic strength in waste stream. The amount of oxygen consumed in a sample within a five-day period at 20 °C. The heavy metal content in wastewater have also been a major interest to the Scientists as these toxic elements toxic could cause severe health and environmental impact (Sponza, 2002; Duker et al., 2005). Most of the heavy metals with elements such as Cadmium (Cd), Lead (Pb), Manganese (Mn), Copper (Cu), Zinc (Zn), Chromium (Cr), Mercury (Hg), As (Arsenic), Iron (Fe) and Nickel (Ni) are important for living organisms but required only at quite low concentrations (Akpoveta et al., 2010). The most common techniques used to evaluate the trace metals in ecological waters such as

* Corresponding author at: Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology, Paulinska 16, 917 24 Trnava, Slovakia.
E-mail addresses: atayeb@avl.sonatrach.dz (A. Tayeb), m_chel01@uni-muenster.de (M.R. Chellali).

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energy dispersive X-ray fluorescence (XRF) spectrometry (Lau and Ho, 1993; Eksperiandova et al., 2002), atomization atomic absorption spectrometry (ETAAS) (Huang et al., 1999; Lin et al., 2001), inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Tepe et al., 1998; Rao et al., 2002), and neutron activation analysis (NAA) (Zecca et al., 2001) are high cost controlled devices. High performance liquid chromatography (HPLC) technique was effectively used for multielement measurement (Cardellicchio et al., 1999; Ding et al., 2000; Li et al., 2002). However the system still expensive and time-consuming process. Moreover, UV–Vis spectrophotometry technique (Safavi and Abdollahi, 2001; Ghasemi and Niazi, 2001), is very hard to use due to the separation problems of overlapping absorption spectra during the analysis. Due to its simplicity and lower cost, Flame atomic absorption spectrometry (FAAS) is one of the most widely used methods for determination of trace elements with significant accuracy (Scaccia, 1999; Chen and Teo, 2001).

The aim of the present study was to measure the impact of pollution on the marine ecosystem, bathing water and human health, by application of atomic absorption spectrometry. Series of analyzes on domestic and industrial wasted water discharged into the Mediterranean Sea have been completed at the coastal line of Oran in Algeria. This knowledge will allow administrators to improve a more realistic policy for waste management and the prevention of water contamination founded on joint efforts by local governments, companies, and residents.

Algeria is an African country having a coastal territory of about 1600 km long Mediterranean Sea. The Bay of Oran is located between the Andalouses coast in the west and industrial gulf of Arzew in the east (Leclaire, 1972). With 783,000 inhabitants, and 124 km coastline, the city of Oran increased from provincial capital to a rank of Mediterranean metropolis.

The east region of Arzew is well known for oil, gas, refining and petrochemical industries (see Fig. 1a). The first large-scale Liquefaction Natural Gas (LNG) plant in the world started began functioning in 1964 when LNG was transported from Arzew, Algeria to Canvey Island, with initial production capacity of 2560 metric tons/day of LNG. The area is surrounded by urban concentration of about 148,782 inhabitants, counting 12,454 susceptible residents (e.g., individual $\geqslant$ 65 years of age, or children less than 6 years old). The industrial platform is spread over an area of 2500 ha (hectare). Approximately 900 ha are reserved for the petrochemical manufacturers, 400 ha are kept for pipeline in the technical corridor, as well as cables between different units and oil/gas gates. The pole consists of a large number of hydrocarbon and petrochemical plants, Liquefaction Natural Gas/LNG (GL1Z, GL2Z, GL3Z, and GL4Z: non-operating since 2010) (Wooler, 1975; Woolcott, 1987; Sun et al., 2012; Xu et al., 2014), Liquefied Petroleum Gas/LPG (GP1Z and GP2Z) a Refinery RA1Z (Mercier, 1966), three units of Ammonia and Nitrogen Fertilizers production (Fertial, Al Djazaïria Al Omania LilAsmida (AOA), and Sorfert) (BAT, 2000), Methanol synthesis CP1Z, Electricity generation plant, and Seawater desalination system. On the other hand, the western region is touristic destination, famous for its beaches, hotels, landscapes, mountains and small villages. The lack of industrial activities has greatly contributed to the preservation of biodiversity in the west region. Generally, more than 90 million m^3 of unprocessed wastewaters are liquidated annually by the city of Oran. The gulf constitutes a major receiving area for unwanted water in Oran (see Fig. 1b).

A quantitative and qualitative inventory was realized on marine pollution between tracks of Andalouses, and Mers El Hadjadj, generated by the human activities. Samples were collected during the period 2013–2014, from coastal sites located at the three regions (East, west, and center) of Oran. The industrial effluent were assembled from different representative units by a state-owned Oil and Gas Company (SONATRACH group) in Arzew. Polyethylene or borosilicate glass containers were used to collect the effluent water. Prior each use, the storage bottles were carefully washed according to specified procedures (American Public Health Association, 2005). Physicochemical Studies for pH, temperature, conductivity, salinity, Ammonium Nitrate, Phosphorus content, Suspended Solids (SS), Dissolved Oxygen (DO), BOD_5 and COD values, using techniques and methods reported in the literature (Rainwater and Thatcher, 1960; Brown et al., 1970; Hem, 1985). The gas chromatographic (GC) analysis has been used for the determination of hydrocarbon (HC) petrochemical samples. The oil and grease (OG) samples determination was completed using an infrared spectrometer. The measurements of heavy metals Pb, Ni, Cu, Fe, Zn and Mn in the water, were performed using the PerkinElmer AAnalyst 100 atomic absorption Spectrometry (AAS), located at SONATRACH group. The calibration curves were set independently for all the metals by running different concentrations of standard solutions.

The analysis were done in collaborations between Sonatrach laboratories, Normal Superior School of Technical Education Oran (Le Laboratoire de recherche en Technologie de l'Environnement), University of Science and Technology Oran (Faculty of Industrial Chemistry), and university of Oran 1 (Laboratory of Environmental science and Material studies).

1. East Coast of Oran

The ten-year follow-up analyses including, biological oxygen demand and chemical oxygen demand parameters of industrial pollution as well as urban domestic sewage, are presented graphically in Fig. 2. The COD and BOD_5 values were frequently above the national standard thresholds (black dashed line) 120 mg/l, and 40 mg/l, respectively, mainly due to the presence of organic matter in the effluent, caused by dysfunction or lack of wastewater treatment, and de-oiling plants (Shon et al., 2005; Krasner et al.,

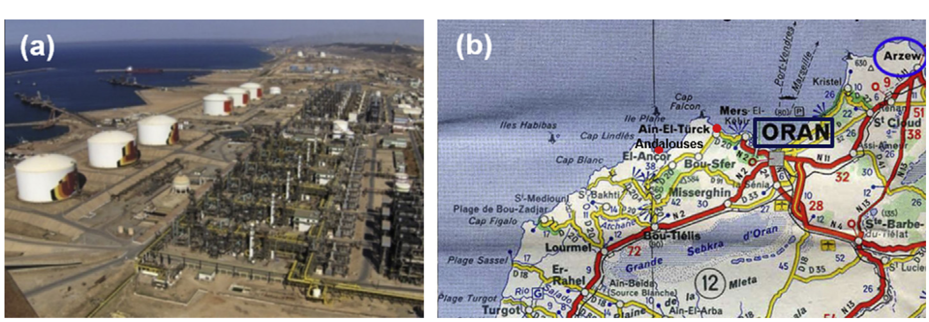

Fig. 1. Locations – Arzew Industrial Area (a) and Gulf of Oran (b).

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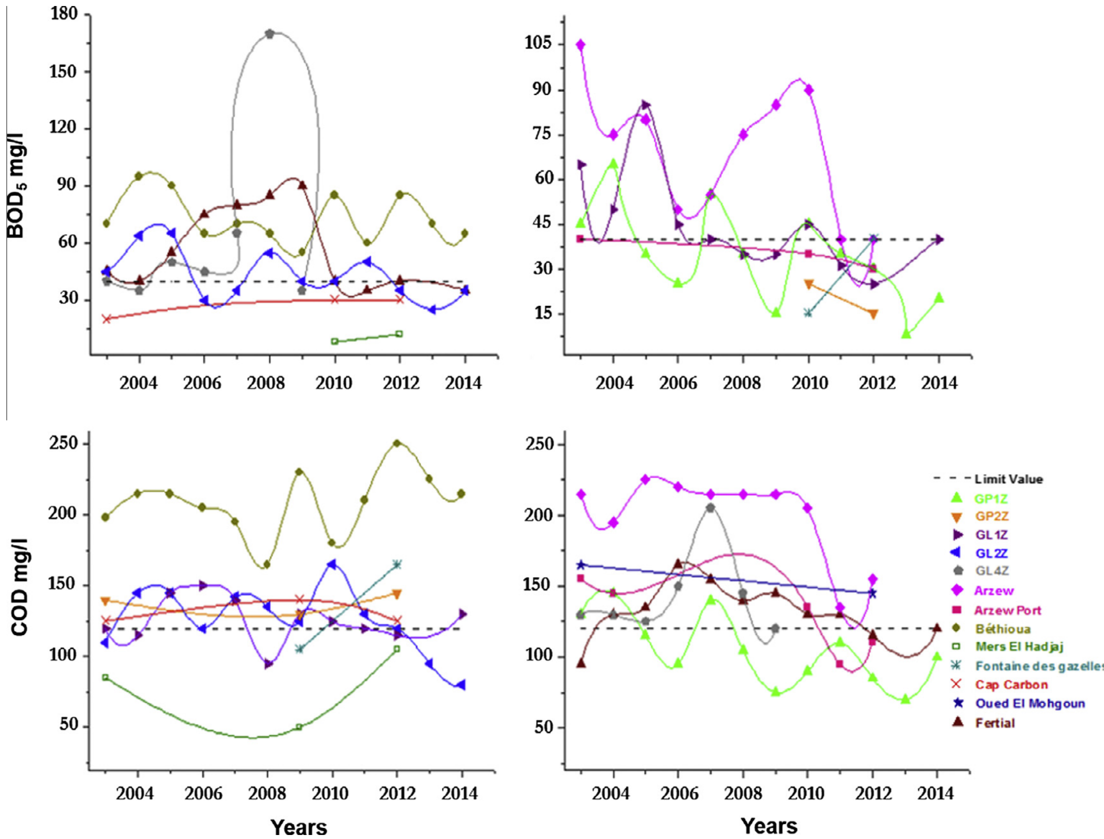

Fig. 2. Plots of BOD_5 and COD in the Bay of Arzew since 2003.

2009). However the most common measures done in 2014 meet generally standards and discharge requirements, with COD/BOD ratio varies between 2 and 3. This shows a good biodegradability of the ecosystem during the last period.

The excessive levels of Suspended Solids (SS) into water can have harmful impacts on the physical, chemical and biological properties of the ecosystem. Results in Fig. 3, show that SS levels are mostly below the national limit. In fact, some suspended solids were settle down into sediment to the bottom of the body of water, while others kept suspended, during the collection process. The average size of suspended solids was approximately 2 μm establish in the water column. Each particle less than 2 μm (average filter size) is ruminated as dissolved solid. The highest SS content were observed to be maximum in Bethioua and Arzew having values of 72 and 75 mg/l respectively. Generally related to the chemical and offshore activities in the region, though bacteria and algae may also involve to the solids concentration (Langland and Cronin, 2003; Devlin and Brodie, 2005).

Presence of nitrogen and phosphorus in wastewater effluents are clearly seen in Fig. 4a and b. Recently, the phosphorus and nitrate levels are well beyond standard safety thresholds set by the Algerian Environmental Protection Agency. However, few years ago phosphorus and nitrates abundance supported the growth of algae and aquatic plants in the area. As consequence, oxygen concentrations that aquatic species need to survive has been decreased in the water, causing damage in the Bay (Truchot and Duhamel-Jouve, 1980; Frederiksen and Glud, 2006). Pollution of water is almost due to waste produced from municipalities, industrial complex, as well as Nitrogenous fertilizers and Phosphorus exploited in the agriculture sector in the region (Ahlgren et al., 2008; Boels et al., 2012). Furthermore, detergents products that contain poly-phosphorus can be also a major source of phosphorus (Manachini and Fortina, 1998). A city of 100,000 inhabitants, and unequipped with a STP, rejects a daily average of two tons of detergents. Exceeding the standard thresholds for nitrates and phosphorus in Bethioua and Arzew discharges, are mainly due to the lack of treatment plants for urban wastewater. A project to build a STP in Bethioua, with processing capacity of 14,000 m^3/day is under construction.

Fig. 5a and b shows that industrial waste discharge are contaminated by oil, grease (OG) and petroleum hydrocarbons (HC) in the region of Arzew. Lately, the amounts of oil discharged are more or less stable, and below the national limit values in Algeria, which are 20 mg/l, and 25 mg/l, for HC, and OG, respectively. However, accidental peak of 41 mg/l has been recorded during the year of 2003 in Arzew. Likewise, two other peaks were noticed in June

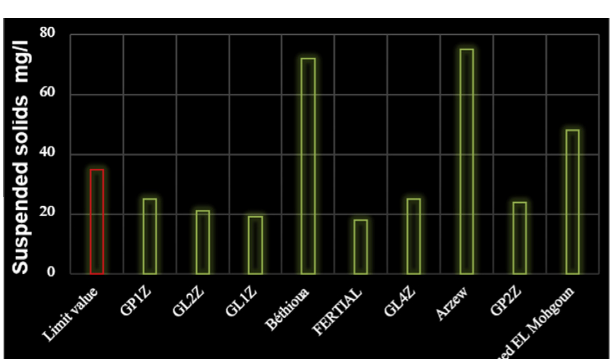

Fig. 3. Levels of Suspended Solids (SS) discharged into the Bay of Arzew recorded in 2014.

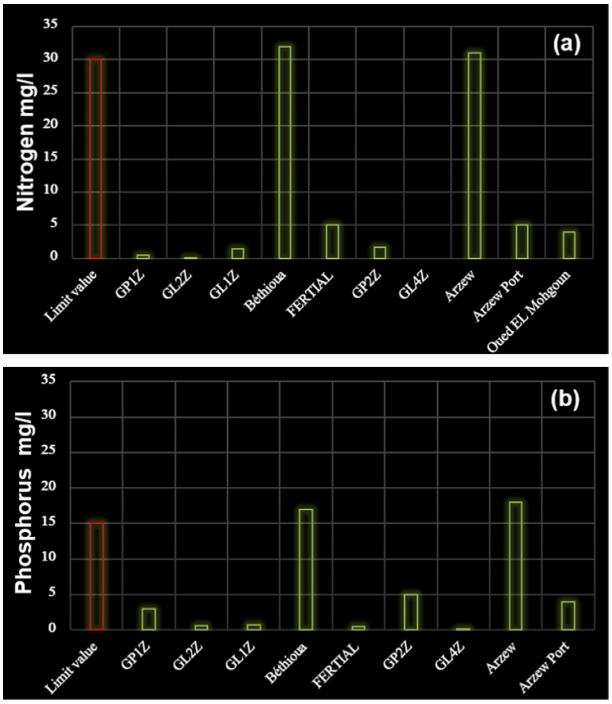

Fig. 4. Levels of Nitrogen (a) and Phosphorus (b) discharged into the Bay of Arzew recorded in 2014.

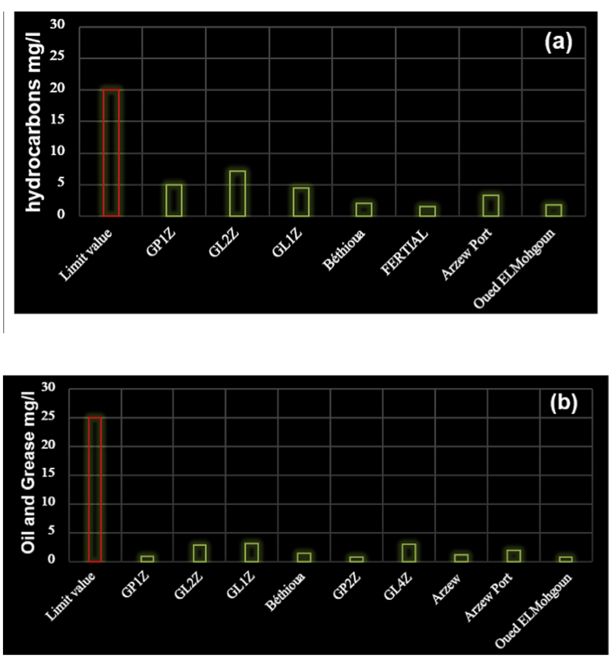

Fig. 5. Industrial waste of hydrocarbons (a) and oil and grease (b) discharged into the Bay of Arzew recorded in 2014.

2012 and April 2014 at the port of Bethioua. The presence of hydrocarbons were due to the voluntary and illegal deballasting operations of vessels near our coast, even with the presence of prohibited international regulations (Boyle, 1985; McConnell and Gold, 1991). Generally, Oils and Hydrocarbons rates in LPG, and LNG plants in Algeria, are usually below regulatory thresholds.

Nevertheless, the absence of an external control via qualitative monitoring stations in marine waters, is in favor of polluters. Also, the lack of de-oiling and malfunction of some stations, harm

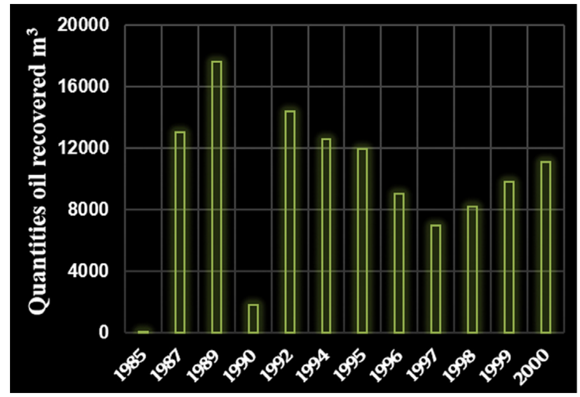

Fig. 6. The total amount of oil being recovered in Algeria (1985–2000).

strongly the aquatic ecosystem in the region. Fig. 6 shows the total amount of used oil being recovered in Algeria.

During the calendar years 1985–2000, an annual volume of approximately 97,016 m^3 was recovered in the country. This quantity is less than 50% of the used oil estimated to be available for collection. Algerian used oil recovery strives for the delivery of wasted oil with other purchaser and this also seems to be the case in the European Union. During year 1999, it was evaluated that 28% of total capacity of used oil was predisposed unlawfully (Monier and Labouze, 2001).

Important arsenic levels have also been detected at Bethioua site in Arzew. The arsenic detected is may be a result of natural geochemical processes, because of its natural presence in most of rocks in the region. Geochemical investigations are likely recommended. Investigations by atomic absorption spectroscopy showed that the marine environment of the region is polluted by heavy metals, originally from land based activities (industrial plants), and shipping (summarized in Table 1).

Although, concentrations of heavy metals such as Hg, Pb, Cu, Ni, Cr, and Cd are mainly found as trace elements, this presence threatens the marine biotope, and contributes to the disproportion of ecosystem in the region. Pollutants such as heavy metals and oils, could reduce the rate of photosynthesis and increase respiration rate of aquatic organisms. As result the bio-toxicity, eutrophication will be increase in marine environment (Zeng et al., 2015). Chemical and biological corrosion (seaweeds, etc.) are also possible, depending on material systems, and environmental area (De Belie et al., 2004; Nielsen et al., 2006).

Analyses of cooling water discharged from petrochemical and gas processing plant showed that temperatures are below the limit thresholds. Even though the GP1Z station is the only one who reached 35 °C, it was very rare to exceed regulatory limit during the heatwaves period. Water temperature is vital because many physical, chemical and biological processes are meaningfully influenced. In order to avoid exposing the aquatic life system to

Table 1
Marine analysis carried out at distance more 30 m from coasts.

Heavy metals (mg/l)	Limit value	GP1Z	GP2Z	GL1Z	GL2Z	GL4Z
OG	20	3.22	2	1.38	1.09	1.32
HC	10	3.25	9.78	4.07	2.48	3.48
Hg	10	0.001	0.001	0.001	0.001	0.001
Pb	1	0.002	0.0045	0.004	0.003	0.0045
Cu	3	0.001	0.001	0.001	0.001	0.001
Zn	5	0.113	0.338	0.107	0.347	0.341
Ni	5	0.0011	0.0023	0.002	0.0014	0.001
Cr	3	0.0012	0.0038	0.0031	0.0015	0.0071

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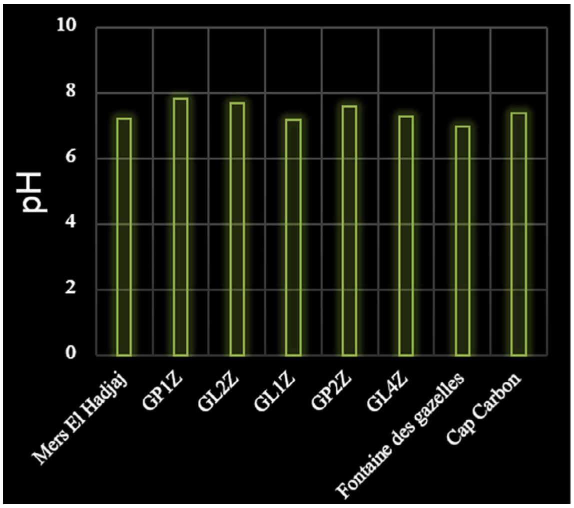

Fig. 7. pH ranges.

excessive temperature, Sour water produced by steam stripping hydrocarbon fractions in Arzew refineries, are cooled prior being released to wastewater. Generally, pH ranges in Arzew industrial zone and beaches such "Cap Carbone", "Fontaine des gazelles" were neutral and up to standard (see Fig. 7).

2. Central Coast of Oran

The physicochemical measurements of bathing water achieved in Casino, Mers El Hadjadj, Ain Franin, and Ain Defla beaches are summarized in Table 2. Temperatures observed during 2013 indicate a strong seasonal variations. A decrease in temperature from September to February there with a minimum value in in winter, variant between 7 and 11 °C, and an increase from March to June with a maximum variation between 24 and 27 °C, recorded from Jun to August. Measurements were similar to the results obtained in the literature (Guibot, 1987). In fact, temperature is an essential parameter to control surface trade intensity and sea-air circumstances in marine science (Šolić et al., 1999; Chevaldonne and Lejeusney, 2003; Schifano et al., 2013).

Salinity closes to the coast was ranged between 36 g/l and 37 g/l, usually linked with variations in local rainfall and temperatures. It could be seen that salinity decreases slightly in the summer period. This fluctuation can be explained by the contribution of surrounding rivers in the region, whose effects the surface salinity (Hatje et al., 2003; You et al., 2010; Cañedo-Argüellesa et al., 2013). It should be noted that the salinity is very important for the preservation of the marine organisms (Bianchia and Morrib, 2000; Dunlopa et al., 2008). In fact, the capacity of water to permit an electrical current is measured by conductivity, mostly affected by the occurrence of inorganic dissolved solids (+ and − ions) in marine. As shown in Table 2, conductivity values are between 48 and 57 mS/cm. This means that the dissolved oxygen content is very good. The ability of sea can be also affected by temperature: the warmer the water, the higher the conductivity. The pH ranges were neutral for all measured samples. Chlorides (Cl^-) is an inert tracer element representing information on physical progressions particularly evaporation happening through recharge and time-dependent flow. Therefore, the measured Cl^- concentration range from 18.4 to 19.8 mg/l, which is rather low compared to normal limit. A very similar pattern of evolution is seen for sulfate with value around 1 mg/l. Both sulfate and chloride in the measured water may be partly resultant from the concentration of aerosols. Furthermore phosphorus and nitrates were present, but much lower than the standard thresholds, with values of 10 mg/l, and 2 mg/l, respectively. The concentrations of heavy metals such as copper and iron were found as traces in the bathing water. The results show that these beaches are not polluted. A thorough study of marine fauna and flora of this area is likely suggested.

Table 2
Results of the analysis of bathing water companion Oran center, 2013.

Physicochemical parameters	Dhaliss beach	Casino beach	Aïn Defla beach	Ain Franin beach
T (°C)	17–11/Winter		24–27/Summer	
pH	7–7.3	7–7.3	7.1–7.3	7–7.2
Conductivity (mS/cm)	48–57	42–51	48–56	45–56
Salinity (g/l)	36.3	36.3	36.2	36.7
Dissolved oxygen (%)	102–111	101–118	105 –118	105–153
PO_4^{-3} (mg/l)	⩽0.6	⩽0.6	⩽0.6	⩽0.6
P_20_5 (mg/l)	⩽0.5	⩽0.5	⩽0.5	⩽0.5
NO_2 (mg/l)	⩽0.2	⩽0.2	⩽0.2	⩽0.2
NO_3 (mg/l)	⩽10	⩽10	⩽10	⩽10
NH_4^+ (mg/l)	1–10	1–10	1–10	1–10
Phosphorus (mg/l)	0.2–1	0.5–1	0.2–1	0.5–1.5
Sulfate (mg/l)	1.1	1.1	1.05	1
Chloride (mg/l)	18.4	19.8	18.5	19.5
Copper (mg/l)	0.213	0.2881	0.013	0.0023
Zinc (mg/l)	0.0011	0.015	0.013	0.0023

3. West Coast of Oran

In order to protect species and biotopes system, industrial activities are absolutely forbidden in the west region of Oran. The only sources of marine pollution are urban effluents discharged into the sea. Measurements done around this area, are summarized in Table 3. Results showed that the pH remains neutral in most beaches. Temperature varies as function of season, and the salinity reached 37 g/l. The amount of dissolved oxygen varies between 113% and 129%. Consistently levels of dissolved oxygen are greatest for a healthy environment. The heavy metal content, especially copper, zinc and iron were very low, and below the standard thresholds. In addition, Nitrates and Phosphorus were under the statutory threshold limit. We can conclude that the bathing water in Paradis, Beau-Sejour, and Bousfer beaches, have a low index of marine pollution.

4. West-Central Coast of Oran

Measurements done on the beaches of Petit Port, Kristel, Beaux-Sejour, and Andalouses, as well as the port of Oran, showed much higher concentrations than standard limits, sometimes with values even greater than 270 mg/l, and 140 mg/l, for COD and BOD_5, respectively (see Fig. 8a and b).

Similarly, Nitrates, and Phosphorus concentrations in Petit Port, Kristel, Beaux-Sejour, and Andalouses beaches were around 80 mg/l and 32 mg/l, respectively, which are also high. Only suspended solids, and potential hydrogen rates of hydrocarbons, and oils were standard. The rate of total hydrocarbons measured were reasonable and less than 0.5 mg/l for all samples. The average concentrations of heavy metals were (<20, 0.2, 3, 5, 1 and 10), for (Cd, Cu, Zn, Ni, Pb and Ni) respectively. Low level of heavy metals have leaded to serious health effects in the region such acute poisoning (Nriagu, 1988; Bia et al., 2006), Health risks (Khan et al., 2008; Singh et al., 2010), and paraphernalia of heavy metals have been well known and acknowledged since past years (Hayes, 1997; Järup, 2003). This abnormality is due to the lack of treatment plants of urban waste water (STP), especially in the region of Ain El Turk (Petit Port, Kristel, Beaux-Sejour), which has about 35,687 inhabitants. In order to improve the urban waste water treatment

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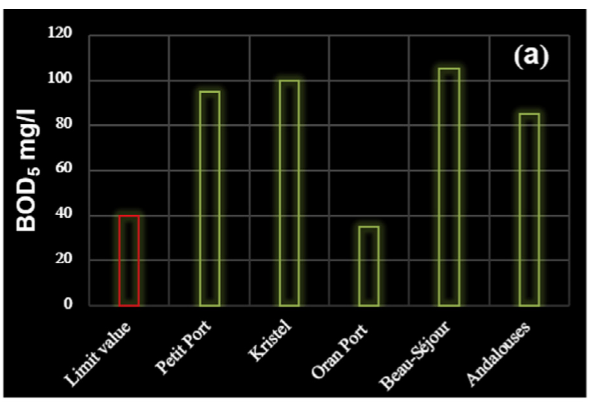
Table 3
Qualitative analysis of bathing water west Oran in 2013.

Physicochemical parameters	Paradis beach	Beau-Sejour beach	Coralez beach	Bousfer beach	Andalouses beach
T (°C) winter/summer	7–10/20–23	7–11/19–24	7–12/19–24	7–11/20–24	8–11/20–23
pH	7–7.3	7–7.3	7.1–7.3	7–7.6	7–7.5
Conductivity (mS/cm)	48–57	42–51	45–56	43–56	48–55
Salinity (g/l)	35–37	34.8–37	35–37	35–37	34.4–37
Dissolved oxygen (%)	129	120	121	120	113
PO_4^{-3} (mg/l)	⩽0.6	⩽0.6	⩽0.6	⩽0.6	⩽0.6
P_2O_5 (mg/l)	⩽0.5	⩽0.5	⩽0.5	⩽0.5	⩽0.5
NO_2 (mg/l)	0.02–1	0.02–1	0.02–1	0.02–1.6	0.02–1
NO_3 (mg/l)	⩽10	⩽10	⩽10	⩽5	⩽5
NH_4^+ (mg/l)	1–10	1–10	1–10	1–10	1–10
Phosphorus (mg/l)	0.5	0.5	0.5	0.6	0.4
Sulfate (mg/l)	1–3	1–3	1–3	1–3	1–3
Chloride (mg/l)	19.5	19.7	18.9	21.1	19.5
Copper (mg/l)	0.021	0.018	0.016	0.014	–
Zinc (mg/l)	0.001	0.015	0.013	0.002	–



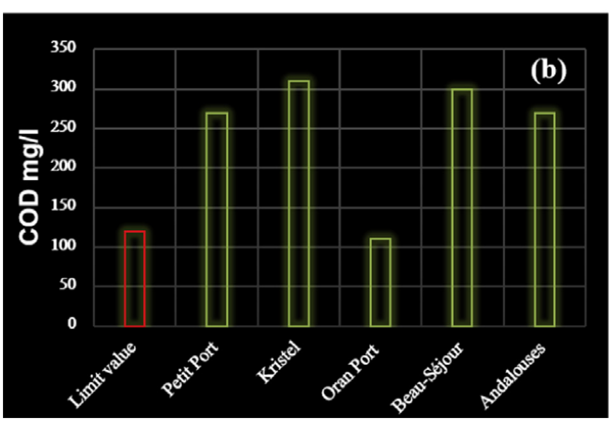


Fig. 8. Plots of BOD_5 (a) and COD (b), discharged in the beaches of Oran recorded in 2014.

in the city, the storm drainage system will be independent from public and health networks. Slaughterhouses and dairies will be recovered, and treated outside municipal STPs. The project will be very favorable to the marine ecological balance in the region.

Our study showed that urban waste in the region of Oran is under the standard limit, causing a significant marine pollution. Most pollutants were found in Kristel, Beaux-Sejour, and Andalouses beaches in the central-Western region, as well as Arzew and Bethioua areas in the East of Oran. On the other hand, Oran's coastal territory, are subject to illegal deballasting and degassing from ships activities, sourced from petrochemical and gas port in Arzew. An important Arsenic content were observed for some samples in the industrial zone of Arzew. This can be also explained by natural geochemistry of the region. The results obtained by the atomic absorption spectroscopic analysis shows that the concentrations of heavy metals in these releases are found as traces elements. The presence of phosphorus and ammonium nitrate observed, is due to sanitary sewer overflows, the lack and malfunctioning, sewage treatment plants. The inefficiency and the untreated sewage discharged from densely populated urban has contributed to deterioration in the marine biota of the region. Increasing levels of pollution in coastal region has harshly harm the biodiversity of the marine system. Most of pollutants found its way to the food chain and may effect in bioaccumulation of toxic substances and pathogenic microorganisms in addible sea-food sorts.

To overcome this pollution, we recommend allowing the construction of sewage treatment plant urban sanitary water for the region of Ain El Türck and Arzew. It would also be wise to develop an air observing system and detection of illegal discharges into the Algerian Mediterranean Sea with the cooperation of neighboring countries. An installation of a release monitoring station to sea and ports in Oran is more than necessary. This will contribute to the development of risk mapping for better management of shipping, oil pollution, as well as preservation of the marine ecosystem of the Mediterranean.

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