*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2013.869661

52 (2014) 2309–2314
February

Taylor & Francis
Taylor & Francis Group

# Characterization and treatment of contaminated marine sediments for reuse

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Received 18 December 2012; Accepted 21 November 2013

ABSTRACT

The development of human activities remains an almost constant threat to the marine environment. The marine environment is assaulted in many different ways: tourism; increasing urbanization in coastal areas; waste and pollutants that are discharged directly by atmospheric pollution, which causes the surface deposition of toxic gas and dust; industrial waste (wastewater emission); the use of pesticides in agriculture; and so. Our study investigated the pollution in an industrial zone, and urban and industrial discharges dumped into the sea without any environmental consciousness. We established a matrix of treatment, whether chemical or biological, in order to eliminate the heavy metals and degrade pollution in marine sediments, especially polycyclic aromatic hydrocarbons, for the recovery and reuse of these sediments in other areas.

*Keywords:* Marine environment; Liquid effluents; Heavy metals; HAP; Sediment treatment

## 1. Introduction

Although marine pollution is considered to be a global problem, the risk may be greater in some areas than others. One of these areas is the Mediterranean Sea because the sea is almost closed or semi-closed [1] and the rate of change of the water is in the order of 80 years. The contaminants of concern for the marine environment are those that show persistence in the environment, an ability to be transported over long distances, a tendency for bioaccumulation and toxicity vis-à-vis non-target organisms [2]. The Gulf of Arzew is located between the west Carbon Cap and east Pointe Salamander. The continental shelf in this area has a very steep slope at the foot of djebels Ourousse and Sicioum (near Cap Ferrat and Cap Carbon) [3]. Contamination of aquatic environments by metallic elements and their organometallic derivatives is anthropogenic [4]; these compounds are present in the marine environment at very low concentrations, called the trace and ultra trace in the order of 10 ng/L or lower, but are still able to induce adverse biological effects to marine flora and fauna [5] (Fig. 1).

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*Presented at the 6th International Conference on Water Resources in Mediterranean Basin (WATMED6), 10–12 October 2012, Sousse, Tunisia*


Fig. 1. Localization of the west of Algeria (Google Wikipedia Algeria map).

## 2. Location of sampling points

In order to assess the pollution level of coastal Oran, several samples were taken from different coastal areas, namely Ain El Turk (El Aoun) (P1), the port of Oran (P2), Kristel (P3), the Gulf of Arzew (P4), and Mers El Hadjaj (P5), as shown in Fig. 2 [6].

The coastline of Oran is a set of landform shapes which depend directly or indirectly on the sea's movement. It includes the coastline with beaches and cliffs, different from one area to another. The Gulf of Oran is in the central part of the coast of Oran and opens west to east and it is bounded on 30 km of uplands and draws a half circumference on the regular meadows from Cape Falcon to Cape of Aiguille [7]. It is between the Bay of Andalusia and the Gulf of Arzew. Gulf of Arzew is located between the west Carbon Cap and the peak of east Salamander. The continental shelf in this area has a very steep slope at

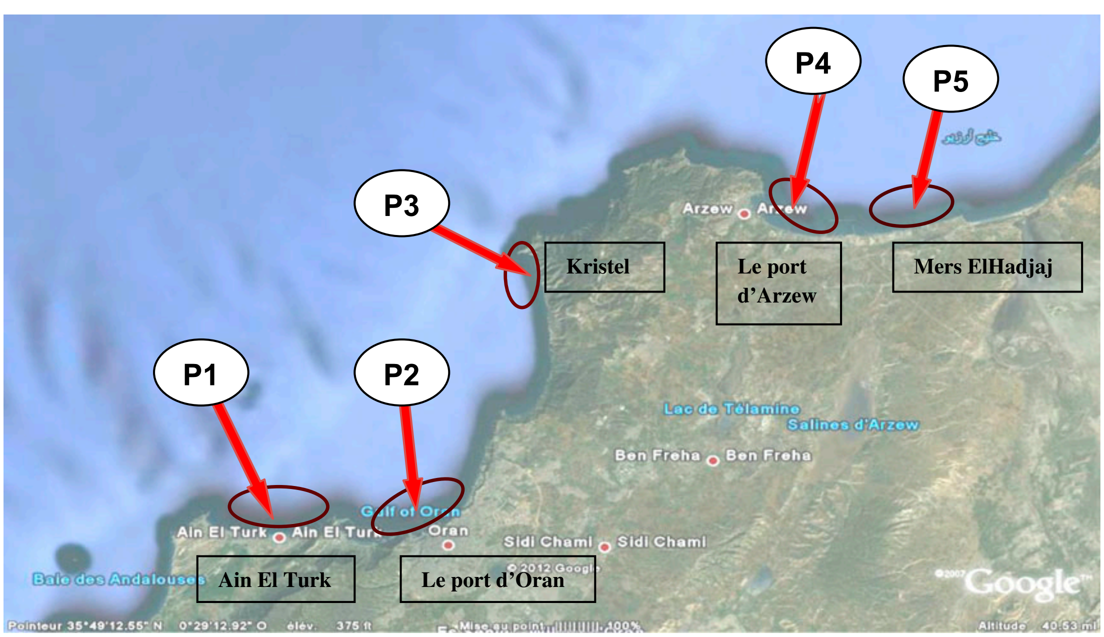


Fig. 2. The points of sampling sediment and polluted surface waters along the coast of Oran (Google map).

the foot of djebels Ourousse and Sicioum (near Cap Ferrat and Cap Carbon) [8].

## 3. Materials and methods

### 3.1. Sampling

Sampling of surface-waters-polluted marine sediments was carried out along the coast for three follow-up dates on the various points mentioned above.

### 3.2. Principle of work

Our work was divided into two parts.

#### 3.2.1. Analysis and characterization

This part has been devoted to: the determination of physico-chemical indicators of pollution in seawater-polluted surface such as the pH, $DOB_5$, COD, TSS, and total nitrogen phosphates [TKN]; the determination of organic pollutants from hydrocarbons in sediments from different sampling sites; and at the end, the determination of trace metals, such as Fe, Cu, Zn, Ni, Pb, and Cd possibly in surface seawater and sediments [9]. The use of detection devices such as atomic absorption spectrometry for trace metals and gas chromatography mass spectrometry GC/MS for the detection of polycyclic aromatic hydrocarbons [PAHs] was indispensable for the realization of this study.

#### 3.2.2. Treatment and recovery

- *Physico-chemical treatment:* This type of treatment is based on physico-chemical interactions (adsorption/desorption, oxidation/reduction, and ion exchange) to destroy, alter, or immobilize contaminants [10] (Table 1).
- *Biological Treatment:* It consists of introducing micro-organisms (bacteria and fungi) which are able to destroy or remove organic micropollutants or accelerate the process of natural decomposition of organic contaminants [11].

Table 1
Advantages and disadvantages of the different treatments

| Advantages | Disadvantages and limitations |
|---|---|
| By extraction | |
| • Handles different types of contaminants<br>• No problem of gas emission into the atmosphere | • Need to collect and treat waste solutions washing or extraction |
| By leaching | |
| • Sediment contaminated with organic<br>• Sediment grained<br>• Control of air emissions | • Odor<br>• Costly<br>• Slow<br>• Heavy implement |
| By flotation | |
| • Technology driven mining industry<br>• Focus inorganic contaminants (copper, zinc, etc) and organic (PAH, PCB, etc) Granulometry of 0.2-0.005 mm<br>• Low energy requirements | • Agent packaging may be necessary<br>• Depends on size, very effective for clays |

Table 2
Average values of physico-chemical parameters of the five withdrawals of surface polluted water

| Parameters | ECH | | | | | Standards [mg/l] |
|---|---|---|---|---|---|---|
| | ECH01 | ECH02 | ECH03 | ECH04 | ECH05 | |
| T° | 22.5 | 21.3 | 22.1 | 21.1 | 20.3 | 30 |
| pH | 8.22 | 8.01 | 8.02 | 7.38 | 8.25 | 5.5 |
| $BOD_5$ [mg/l] | 17.3 | 16.3 | 18.4 | 23.6 | 12.8 | 40 |
| COD [mg/l] | 1913 | 1,564 | 1,740 | 625 | 1,781 | 120 |
| Suspended solids [MES] [mg/l] | 1,010 | 923 | 990 | 842 | 1,413 | 30 |
| Total nitrogen [NTK] [mg/l] | 4.54 | 7.00 | 10.32 | 17.60 | 10.21 | 40 |
| Phosphates [mg/l] | 0.382 | 0.370 | 0.414 | 12.62 | 0.652 | 2 |

Table 3
Average values of the amount of heavy metals in the five withdrawals of sediments

| | SD | | | | | |
|---|---|---|---|---|---|---|
| Metals [mg/l] | SD01 | SD02 | SD03 | SD04 | SD05 | Standards [mg/l] |
| Iron | 8.672 | 3.421 | 5.22 | 4.50 | 9.41 | 05 |
| Copper | 2.613 | 4.321 | 3.765 | 3.15 | 5.432 | 03 |
| Zinc | 7.432 | 0.076 | 6.723 | 7.25 | 8.341 | 05 |
| Nickel | 2.44 | 3.761 | 1.732 | 2.062 | 2.576 | 01 |
| Lead | 8.41 | 7.67 | 9.21 | 0.95 | 1.221 | 01 |
| Cadmium | 0.432 | 0.224 | 0.844 | 1.15 | 0.127 | 0.2 |

Table 4
Average values of the amount of heavy metals in the filtrates of the five withdrawals of the sediments

| | ECH | | | | | |
|---|---|---|---|---|---|---|
| Metals [mg/l] | ECH01 | ECH02 | ECH03 | ECH04 | ECH05 | Standards [mg/l] |
| Iron | 0.843 | 1.221 | 0.875 | 0.419 | 0.127 | 05 |
| Copper | 0.0027 | 0.076 | 0.245 | 0.142 | 0.0536 | 03 |
| Zinc | 0.943 | 0.632 | 0.451 | 1.112 | 2.311 | 05 |
| Nickel | 0.941 | 0.0431 | 0.0487 | 0.132 | 0.194 | 01 |
| Lead | 0.437 | 1.222 | 1.476 | 0.223 | 0.023 | 01 |
| Cadmium | 0.041 | 0.0578 | 0.0731 | 0.132 | 0.0037 | 0.2 |

These micro-organisms weaken the chemical bonds of PCBs, organic contaminants, PAHs, or pesticides, and transform them into less harmful substances, such as carbon dioxide, methane, and inorganic salts. This process requires conditions of temperature, aeration, and nutrition support for the activity of micro-organisms [12]. In this context, our work was done by choosing the right method (matrix), a combination of physico-chemical method and biological method for subsequent treatment to improve outcome.

## 4. Results and discussion

### *4.1. Physico-chemical analyses*

See Table 2.

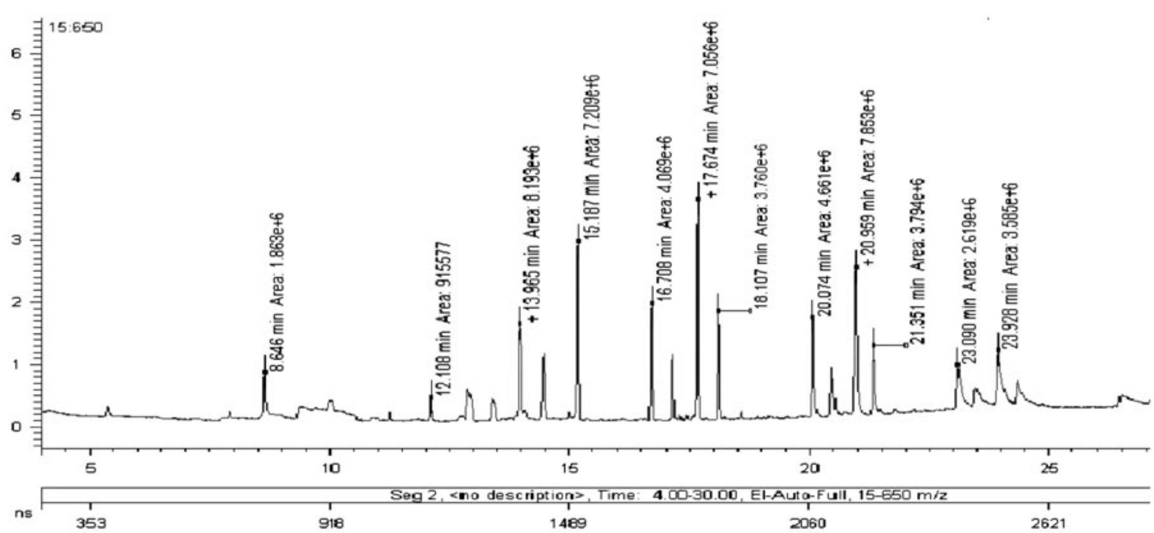


Fig. 3. Spectrum spectrophotometer in gas chromatography mass GC/MS sediment at Arzew (P4).

Table 5
Pollutants and their probabilities of occurrence in the sediments of the area of Arzew (P4)

| Compounds | Retention time [min] | Chemical formulas | Probability of occurrence [%] |
|---|---|---|---|
| Tri methyl ethyl-2,4,6-phenol | 15.979 | $C_{15}H_{24}O$ | – |
| 4,6-di (1-1-dimethyl ethyl)-2 methyl phenol | | | |
| 2,4-bis (1,1 dimethyl ethyl)-6-methyl phenol | | | |
| 6-methyl-2,2-di-tert-butyl-phenol | | | |
| 2,4-di-tert-butyl-6-methyl phenol | | | |
| diphenylamine | 17.880 | $C_{12}H_{11}N$ | – |
| 1H-indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl | 19.103 | $C_{18}H_{20}$ | – |
| Aniline benzene | | | |
| Phenylamino | | | |
| Aniline, N-phenyl-benzene | | | |
| N-phénylbenzeneamine | | | |
| Pentadecanoic acid, 14-methyl-methyl ester | 21.757 | $C_{17}H_{34}O_2$ | – |
| Fluoranthène1,2 -(1,8-naphthalenediyl)-benzene | 24.440 | $C_{16}H_{10}$ | 44.36 |
| 1,2 - (1,8-Naphthalene) benzene | | | |
| Benzofluorene | | | |
| Idryle | | | |
| 1,2-(1,8-naphthylene) benzene | | | |
| pyrene | | | |
| Beta-pyrene | | | |
| Benzo-phenanthrene | 24.450 | $C_{18}H_{12}$ | 35.75 |

### 4.2. Analysis of metals

The analysis results show that there is a persistence of metals such as iron, zinc, copper, nickel, lead, and cadmium in filtrates of the sediments (Tables 3 and 4).

### 4.3. PAH analysis

We conducted analysis of PAHs in sediment of the Arzew zone (Industrial Zone P4) (Fig. 3 and Table 5).

## 5. Conclusion

Wastewater discharge in Algeria, if not controlled, may accelerate coastal pollution, with serious damage to the economy (tourism, fishing, etc.) and the health of the population. The problem of water pollution requires a treatment to prevent polluted effluents from causing the total destruction of aquatic ecosystems. The presence of heavy metals in sediments is important. With the increase of urbanization and socioeconomic activities [13], the rate of heavy metals will only increase, and wastewater discharges through a system of adequate sewage are necessary if we want to maintain a balance in the aquatic ecosystem of the Gulf of Arzew. The protection of coastal marine zone of Arzew demands from industrial units located in the area the establishment and operation of system wastewater treatment appropriate to their type of rejection. This is the same for urban waste of the city [14]. The valuation of sediment is an interesting solution that fits into the philosophy of sustainable development for both the clearance of materials affecting the port activity and exploitation of these resources (sediment) in several areas in accordance with all environmental criteria [15]. The choice of the value chain is essentially guided by the technical, economic, environmental, and regulatory requirements.

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