Arab J Sci Eng (2011) 36:573–580
DOI 10.1007/s13369-011-0052-x

RESEARCH ARTICLE - EARTH SCIENCES

E. F. Derradji · F. Benmeziane · A. Maoui · H. Bousnoubra · N. Kherici

Evaluation of Salinity, Organic and Metal Pollution in Groundwater of the Mafragh Watershed, NE Algeria

Received: 12 May 2009 / Revised: 5 February 2010 / Accepted: 23 May 2010 / Published online: 21 June 2011

Abstract This study was conducted in northeast Algeria along the Tunisian border. The principal goal of this study was to characterize the groundwater quality of the Mafragh Watershed and the space variation. Hydrochemical analyses of salinity (Cl, SO_4), organic pollution (BOD_5, dissolved oxygen DO) and dissolved metals (Fe, Cu, Zn) were conducted at 22 stations located in the proximity of the Kebir East and Bounamoussa rivers, which constitute the Mafragh Watershed. Sampling was conducted during the end of the high-water period (May 2007). This study revealed a DO content of 5 mg/l, as well as high BOD_5 (40 mg/l), Cl (400 mg/l) and SO_4 (250 mg/l) values. Conversely, metals did not show high concentrations, with Fe ranging from 0.01 to 0.032 mg/l, and Cu and Zn being near the detection limit.

Keywords Watershed · Salinity · Organic pollution · Metal pollution

الخلاصة
لقد أجري هذا البحث على الحدود التونسية في الجزء الشمالى الشرقى من الجزائر. الهدف الرئيسي للعمل هو تحديد خصائص المياه الجوفية ونوعية المياه لحوض المفرغ مع تنوع الفضاء. وقد أريت التحليلات الكيميائية التي تتكون في قياس الملوحة (Cl، SO_4)، والتلوث العضوي (BOD_5، والأوكسجين الذائب DO)، والمعادن (الحديد، النحاس، الزنك) في 22 محطة تقع في المناطق القريبة من النهرين الرئيسيين : الكبير الشرقي و بوناموسى المكونين لحوض المفرغ. وأخذت العينات وحللت خلال نهاية فترة ارتفاع المياه (مايو 2007). وهذه الدراسة سجلت (5 مغ / لتر)كتركيز الأوكسجين الذائب (DO)، كما لوحظ ارتفاع قيم BOD_5 (40 مغم/لتر)،Cl (400 مغ / لتر)، وSO_4 (250مغم/لتر). على العكس من ذلك، لم تظهر المعادن تراكيز عالية من الحديد تتراوح من 0.01 الى 0.032 مغم/لتر، النحاس والزنك بالقرب من حد الإكتشاف.

E. F. Derradji (✉) · H. Bousnoubra · N. Kherici
Geology Laboratory, Department of Geology, Faculty of Earth Sciences, University of Annaba, P.O. Box No. 12, Annaba 23000, Algeria
E-mail: derradji_d@yahoo.fr

F. Benmeziane
Department of Agronomy, University of El Tarf, P.O. Box No. 73, El-Tarf 36000, Algeria

A. Maoui
Department of Biology, Faculty of Sciences, University of Guelma, Guelma 24000, Algeria

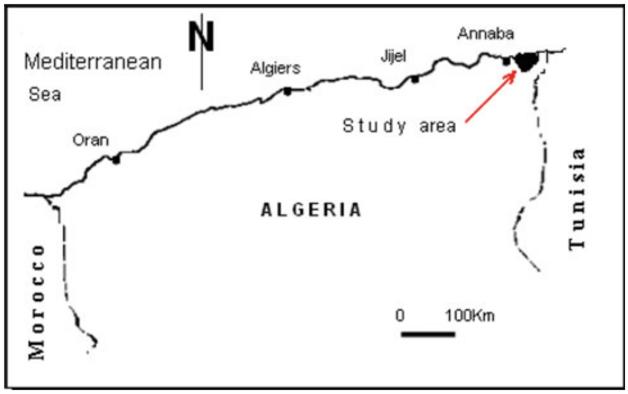


Fig. 1 Geographic situation of the study area

1 Introduction

1.1 Location

The Mafragh Watershed is located in the northeast part of Algeria and is drained by the Bounamoussa River in the west and the Kebir East River in the east. These rivers join the sea *via* a single outlet known as the Mafragh River. This watershed extends from 7°45′ to 8°45′ E and from 36°20′ to 36°55′ N. The watershed is bound in the north by the Mediterranean Sea, in the south by the Souk Ahras Mountains, in the east by the El Kala wetlands near the border of Tunisia, and in the west by the Seybouse Watershed (Fig. 1). The watershed considered in the present study covers an overall area of 2,915 km^2.

1.2 Climate and Precipitation

Analysis of the climatic data for a period of over 30 years revealed that the study area is characterized by a Mediterranean climate with a long wet season (from September to May) with a mean precipitation of 134.49 mm measured at Ain Assel Station, and a mean air temperature of 12.26°C measured at Salines Station. The region is also characterized by a dry, hot season from April until August, during which time there is a mean precipitation of 2.69 mm at Salines Station and a mean air temperature of 23.64°C at Ain Assel Station. The study area also has an annual average precipitation of approximately 794.32 mm and temperature of 17.63°C based on data collected at Ain Assel Station [1].

2 Geological and Hydrogeological Setting

The studied region belongs to the geological northeast Algerian tell and contains geological formations dating from the Tertiary to the Quaternary period. This unit extends from Constantine Province to the Algero-Tunisian border [2] and is composed of sedimentary formations from the Oligocen age with inferior Burdigalian (sandstone, clays, marls) and Quaternary deposits, some of which are of marine origin (alluvial deposits, beach sandstone) while others were formed by continental sedimentation (sandstone, red clays, dunes, Quaternary alluvial deposits).

Moreover, an unconfined dune aquifer is located in Bouteldja Province. The Dunar Massif of Bouteldja is formed by wind sands that are 20–120 m thick, often with clay intercalations in the lenses (Fig. 2). The Dunar Massif forms an unconfined water table with a clay and sandstone substratum that is impermeable and semi impermeable [3]. Atmospheric precipitation, the Righia and Oum Agareb marshes, streams from favorable slopes of the Numidian formations and tributaries of the Kebir East River supply the water table. The Dunar Massif of Bouteldja is characterized by a permeability that varies from zero in zones composed of clay and red sand passages to 6×10^{-4} m/s in white sand formations. The measured transmissivity of the Dunar Massif ranges from 5×10^{-4} to 1.3×10^{-2} m^2/s.

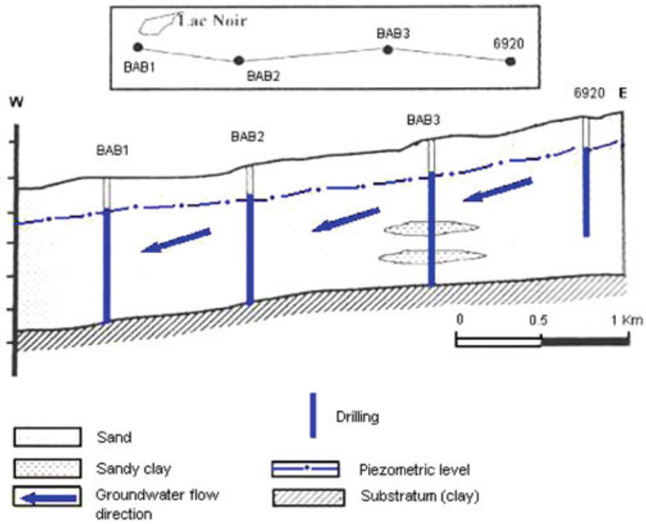


Fig. 2 Hydrogeological cup of the unconfined dune aquifer

The confined deep aquifer of Bouteldja and El Tarf extends from east to west, with a marly substratum and a clay roof. The reservoir is formed by rollers and gravels. The thickness of this aquifer varies between 4 and 15 m according to the morphology of the marly substratum. This aquifer has been tapped by drilling (in its major part) and by wells (in its superficial part). These installations are in continual exploitation.

The Bouteldja Aquifer has a clay substratum composed of gravels, rollers and sands resulting from the Numidian complex, with marl passages. The entire aquifer is surmounted by a muddy-clay layer that constitutes the roof of the confined aquifer. The thickness of the aquifer ranges from 50 to 150 m. According to Gaud [4], the transmissivity ranges from 10^{-3} to 2×10^{-3} m^2/s.

These aquifers play an important role in the drinking water supply for the local population. Potential local sources of contamination included anthropogenic sources, such as direct industrial or sewage discharge into the groundwater and local contamination of wells. In addition, polluted stormwater can infiltrate the aquifer directly through the soil or transport potential contaminants to streams and groundwater. Once in the rivers, these pollutants can also reach the groundwater *via* the river–aquifer interface. The directions of water flow shown in Fig. 2 are not related to the distance from the rivers or potential sources of contamination.

3 Materials and Methods

3.1 Sampling and Analysis

The hydrochemical analysis was based on 22 sampling sites (Fig. 3). Samples were collected from drinking water wells in the proximity of the Kebir East and Bounamoussa, which are the two principal rivers in the Mafragh Watershed. Samples were collected into new polyethylene flasks that had been rinsed two or three times with the water to be analyzed. The flasks were filled until overflowing and closed underwater to minimize aeration. All flasks were carefully labelled and numbered prior to transport.

Organic pollution was determined based on the dissolved oxygen (DO) and biological oxygen demand at 5 days (BOD_5). The BOD_5 is the difference between the water oxygen rate measured immediately after sampling and that measured after an incubation period of 5 days at a temperature of 20°C [5]. The oxygen biological consumption of water (i.e. the dissolved oxygen) was measured with a probe, and the SO_4^{-2}, Cl^-, Fe, Cu, and Zn were measured according to Rodier [5].

Dissolved oxygen was analyzed with a selective probe (Reference: Multi 340i/SET, German mark (WTW) and BOD_5 was measured using a BOD meter (Reference: OxiTop, German mark (WTW).

Sampling was conducted during the high-water period (May 2007) and analyzed in the central laboratory of ASMIDAL and (D.R.A.) at Annaba (east of Algeria).

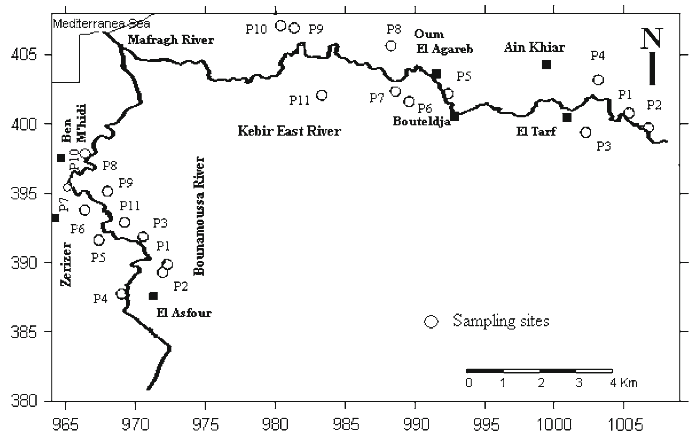


Fig. 3 Map of sampling sites

Table 1 Guidelines for drinking-water quality [7]

Parameters of pollution	Guidelines for drinking-water quality [7]
SO_4	250 mg/l
Cl	200 mg/l
BOD_5	3 mg/l
Dissolved oxygen (DO)	No health-based guideline value is recommended
Zn	100 μg/l
Fe	300 μg/l
Cu	50 μg/l

4 Results and Discussion

The study area is well known for its agricultural and industrial activities, and is characterized by several forms of pollution of surface water and groundwater. Chemical analyses highlight the cause and effect relationship between the sea and the aquifer and the river and the aquifer. Because the wells were located on agricultural land, fertilizer was a possible source of local well contamination.

4.1 Organic Pollution

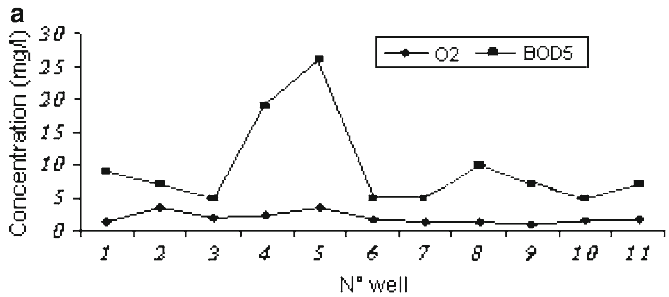
BOD_5 represents the biological activity of organic matter, with a high value indicating polluted water. The BOD_5 corresponds to the oxygen used by bacteria to destroy or degrade the biodegradable organic matter present in the water [6] over 5 days. The presence of dissolved oxygen in superficial waters plays an important role in the maintenance of the aquatic life. In rivers and lakes, DO values greater than 10 mg/l are desired; however, high DO levels in groundwater may be an indication of surface waters rapidly entering the system (Table 1).

4.1.1 BOD_5

The BOD_5 values are presented in Fig. 4a (Bounamoussa area, $n = 11$) and Fig. 4b (Kebir East area, $n = 11$). The groundwater samples had a mean BOD_5 of 5 mg/l (samples 3, 6, 7 and 10) to 25 mg/l (sample 5) for the Bounamoussa area and 5 mg/l (samples 1, 5) to 40 mg/l (sample 10) for the Kebir East area; these values are higher than the criteria established by the WHO (Table 1) of 3 mg/l. This indicates that there is significant biological activity associated with the organic matter in the water at the sampling sites and that organic matter is being discharged into the rivers from wastewater.

4.1.2 Dissolved Oxygen (DO)

The DO levels ranged from 1.0 mg/l (stations 1, 7, 8 and 9) to 4 mg/l (station 5) for the Bounamoussa area (Fig. 4a) and from 1 mg/l (sites 3 and 5) to 4.8 mg/l (sites 1, 8, 9) for the Kebir East area (Fig. 4b). Regions



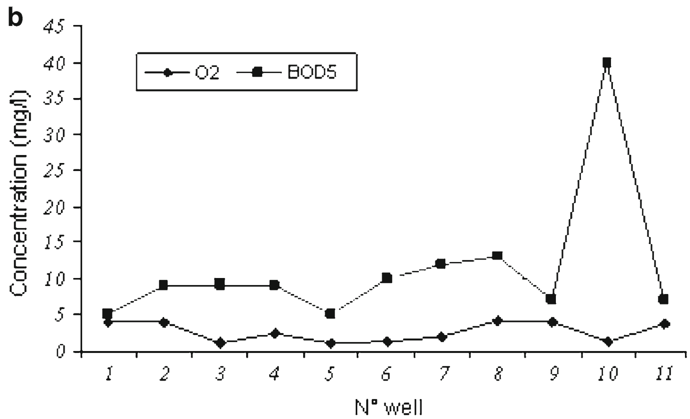


Fig. 4 **a** Concentration of BOD_5 and dissolved oxygen in the Bounamoussa area. **b** Concentration of BOD_5 and dissolved oxygen in the Kebir East area

characterized by DO values raging from 2 to 5 mg/l contain areas of avoidance by fauna, while regions with less than 2 mg/l are subject to mass mortalities as a result of anoxia.

4.2 Salinity (Chloride and Sulfate)

The presence of salt formations in soils (at surface or depth) may cause numerous environmental problems, including rapid erosion, regional uplift and subsidence, slope movements, sinkhole activity, and changes in the surface and underground hydrology [8] (Fig. 5a, b).

Chlorides are a combination of chlorine with another element or compound. The purification of water using hypochlorites containing cyanides is a low cost process that is frequently used. For example, domestic water is disinfected with chlorine. However, the level of chlorine in drinking water must be less than 0.3 mg/l [9], or else it can also act like an oxidizer. Additionally, the excessive presence of sodium chloride in water can have adverse effects on elderly people suffering from renal and cardiovascular diseases [10]. Moreover, high levels of chlorides in water can have harmful effects on the growth of crops [11]. The presence of sulfates in water is related to the dissolution of the gypseous formations as a result of anthropogenic activities such as pasturage. The results obtained in this study were compared with the water quality standards established by the WHO [7] and are shown in Table 1.

As shown in Fig. 5a, b, maximum values of Cl (600 mg/l) and SO_4 (450 mg/l) were observed at stations 8 and 9, respectively. The minimum values of Cl and SO_4 (100 mg/l) were observed at stations 1 and 2.

Generally, the allowed concentration of chlorides is less than 200 mg/l [7]; however, this level was exceeded in certain areas in the present study. Chlorides have an atmospheric origin in the northern Bounamoussa area and north-west Kebir East area, where the rains are saturated with sea water.

The contribution is remarkable on the graph, which clearly shows that the concentrations increase in areas near the sea and decrease in El Asfour and El Tarf, which are far from the ocean, indicating the effects of the sea on the chloride concentration. The observed increase in chlorides was also due to the geological characteristics of the region (chemical washing).

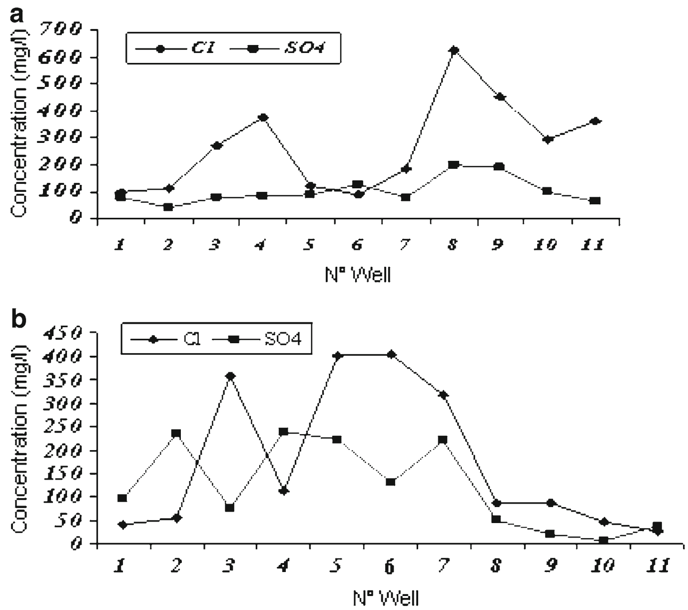


Fig. 5 **a** Concentration of Cl and SO_4 in the Bounamoussa area. **b** Concentration of Cl and SO_4 in the Kebir East area

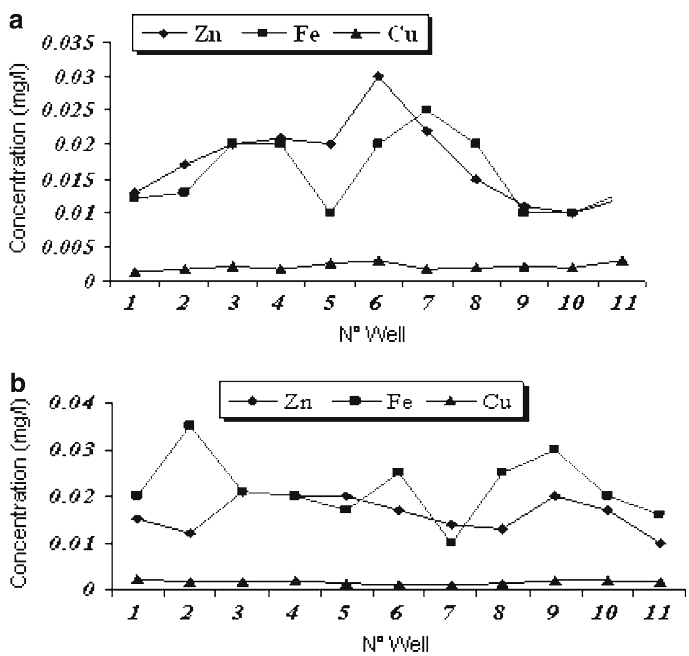


Fig. 6 **a** Concentration of Fe, Cu and Zn in the Bounamoussa area. **b** Concentration of Fe, Cu and Zn in the Kebir East area

A high sulfate concentration was observed in the Ain Khiar area as a result of washing of the geological formations (sand, clay and sandstone). The climatic conditions, especially droughts by evapotranspiration, are another source of increasing minerals concentration.

4.3 Metal Pollution

Iron is present as ores in nature (Fig. 6a, b). Iron oxidation plays a major role in lentic ecosystems and aquifers that contain iron.

Copper is present in nature in the form of native, oxidized or sulfurized ores. In air, copper overlaps with a thin layer of basic carbon. In metallurgy, copper is used in many alloys including brass (copper, zinc), bronze (copper, tin), and nickel-silver (copper, nickel, zinc). Additionally, copper is widely used in wiring and electronics due to its good conductivity. Biologically, copper plays an important role in various metabolic systems as a coenzyme of metalloproteinase, as well as in haemoglobin synthesis. Apart from industrial pollution or agricultural treatments, this metal usually comes from corrosion of distribution piping (0.5–1 mg/l), or more rarely as the residue of algae treatments using copper salts [12].

Although zinc is an oligoelement that is essential to many living organisms, it also is toxic to a wide variety of aquatic organisms in levels as low as several mg/l [13]. Specifically, zinc inhibits photosynthesis and causes various tissue lesions, particularly in fish. The principal causes of zinc pollution are the corrosion of water drains as well as zinc roofs. In addition, zinc pollution can also be caused by pesticides used in agricultural areas, as well as metallurgy and soap factories.

Metal concentrations (Fe, Cu, Zn) in water are generally low (<1 mg/l); however, these concentrations are much higher in aquatic systems located close to areas influenced by anthropogenic activities, especially industrial activities. The metal concentrations observed in the present study are shown in Fig. 6a, b.

4.3.1 Iron

The iron concentrations ranged from 0.01 to 0.025 mg/l for the Bounamoussa area and 0.01 to 0.032 mg/l for the Kebir East area. These levels were likely due to the period of sampling (flood period). During this period, there is increased water flow and dissolved oxygen (DO), which causes a redox reaction that influences the chemical state of iron.

4.3.2 Copper

The copper levels observed in the present study were below the limit of detection (0.005 mg/l). These findings indicate that there is no copper pollution in the studied area.

4.3.3 Zinc

The Zn contents ranged from 0.01 to 0.021 mg/l, and were generally lower than the allowed standards (0.8 mg/l). The concentrations were found to be stable in the El Tarf area until the Bouteldja zone (0.02 mg/l), but in the El Asfour area until the Bordj Hamaoui area the contents ranged from 0.01 to 0.031 mg/l.

5 Conclusions

In the present study, high concentrations of some abiotic parameters were observed. The factors that influenced the water quality varied and included the following: effluents, which bring water containing significant concentrations of mineral salt during the low water period, multiple wastewater streams from the towns of El Tarf, Righia, Bouteldja and Ben M'hidi, industrial wastes (tomato factories in Bouteldja, Ben M'hidi), agricultural runoff (fertilizer), topography and changing of slopes during runoff. The study area included a coastal zone in which lithology, climate, and geography (sea presence) influence salinity in the water table. The Mediterranean Sea, which influences the salinity of groundwater *via* its invasion and interaction with sea-aquifers, can generate an increase in salinity. Thus, the sodic-chlorinated chemical facies of water, specifically, the presence of sulfated-sodic, bicarbonated-calcic, and chlorinated-calcic facies, are dominant influencing factors for two rivers (Bounamoussa and Kebir East) and groundwater wells. Climatic conditions, especially droughts, are another factor leading to increased salinity. Overall, the drinking water must be controlled before use when its quality has deteriorated. Future studies should be conducted to identify nutrients that can serve as indicators of potential sources of high BOD water.

References

1. Derradji, E.F.: Quantitative and qualitative identification of the water resources in the area of Annaba—El Tarf (North-eastern of Algeria). Es Sciences Thesis, 200 pp. University of Annaba, Algeria, (2004) (in French)

2. Vila, J.M.: The alpine range of Eastern Algerian and the borders Algerian-Tunisian. Es Sciences Thesis, University of Pierre and Marie Curie, Paris VI, pp. 282–296 (1980) (in French)
3. Kherici, N.: Vulnerability to chemical pollution of superposed watertables groundwater system in industrial and agricultural area (Annaba - Mafragh) NE Algeria. Es Sciences Thesis, University of Annaba, Algeria, p. 170 (1993) (in French)
4. Gaud, B.: Synthesis of knowledge and research for modeling: hydrogeological study of the Annaba-Bouteldja aquifer system. National Agency of des Hydrous Resources, Annaba, Algeria, p. 151 (1979) (in French)
5. Rodier, J.: Analysis of water, 8th edn. Dunod, Paris, pp. 1383 (1996) (in French)
6. Derradji, E.F.; Bousnoubra, H.; Kherici, N.; Romeo, M.; Caruba, R.: Impact of organic pollution on the superficial waters in the North-East of Algeria. Sécheresse **18**(1), 73–80 (2007) (in French)
7. WHO: Guidelines for drinking-water quality, 3rd edn incorporating first and second addenda. Recommendations, vol. 1, p. 515. WHO, Geneva (2008)
8. Lucha, P.; Cardona, F.; Gutiérrez, F.; Guerrero, J.: Natural and human-induced dissolution and subsidence processes in the salt outcrop of the Cardona Diapir (NE Spain). Environ. Geol. **53**, 1023–1035 (2008)
9. AFNOR: French Agency of Standardization, Water-methods of tests, Paris La Défense (1995) (in French)
10. Pozet, N.; Hadj-Aissa, A.; Labeeuw, M.; Monnerot, P.; Zech P.: Influence of the water composition on the renal function. Practical review of nutrition, vol. 7. Dietecom (1993) (in French)
11. Durand, J.H.: Irrigable soils. French academic press, Paris (1983) (in French)
12. Lauwerys, R.: Industrial toxicology and professional intoxications, 3rd edn. Masson, Paris (1992) (in French)
13. Roméo, M.: Toxicology of heavy metals in the marine environment. Oceanis **17**(4), 383–402 (1991) (in French)