

Evaluating the Impact of Oil Waste Pollution on Irrigation Water Quality in Jalo, Libya

Santiago López-Mendoza¹, Victoria Gutiérrez-Ortega², Manuel J. Ferreira³, Sofia Rodrigues-Pereira⁴, Fernando Navarro-Santos⁵
Javier Torres-Pérez⁶, Marta Ruiz-Delgado⁷, Tiago A. Silva⁸, Pedro A. Matos⁹, Antonio García-López¹⁰

^{1,2,3,4,7} Biology, University Ibn Tofail, Kenitra, Morocco

⁵Geology, University Benghazi, Libya.

⁶Laboratory of Gestion et Managment, University Benghazi, Libya.

⁸Society Arabic Gulf of Oil, Champ Nafora, Gallo, Libya.

⁹Society of Development, Sabha, Libya

¹⁰Academic attached of Ambassy Libya, in Rabat- Maroc.

Abstract— The petrochemicals wastes and pollutants are dumped without treatment in the environment, lakes and soil in Libya. The objective of our present research is to study the impact of waste from crude oil extraction on the environment of the Libyan region of Ajdabiya. The monitored physicochemical indicators are: Temperature, pH, electrical conductivity (CE), TDS, Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Salinity, Total Hardness (TH). The mineralization faithfully follows the rates of dissolved salts. The electrical conductivity varies from 7880 to 46700 $\mu S/cm$ and far exceeds the Libyan irrigation standards ($>2700 \mu S/cm$). Concerning the nitrate their contents range from 230 to 1210 mg/L and clearly reflect the crude oil pollution origin. The Piper diagram and Wilcox-Riverside projections shows that the waters associated with crude oil have a chloride-sodium and potassium or sulphated sodic and slightly bicarbonated sodium or potassium facies. Moreover, the hydrophysico chemical plot shows that the quality of this water is poor and above all a degraded quality.

Keywords— Agriculture, Irrigation, Hydrochemistry, Pollution, Ajdabiya, Libya.

I. INTRODUCTION

Oil is a natural resource that is an important resource for many countries in the Gulf, Africa, Asia and America [1-2]. Unfortunately the history of oil in the African region is fraught with problems identified by the Extractive Industries Assessment Report (EIR) which has highlighted social and environmental problems [3-4]. Several marine, coastal and continental ecosystems have been damaged by oil activities around the world and especially Libyan cities, such as the city of Ajdabiya [5-8].

Our work evaluates the degree and the modalities of pollution generated by the waste of oil in Jalo-Libya. Thus, to provide decision-makers with scientific and technical support to initiate a continuous decision-making dynamic aimed at protecting the environment and waters for irrigation that is vital for the whole country.

Indeed, the present study proposes to validate a physicochemical monitoring [9-11] intended to describe and evaluate the nature, the quality and quantity of pollutants generated by the oil extraction in the Libyan region of Jalo. In fact, the waters associated with the oil production are highly polluted and have an environmental impact on groundwater, surface water and oceans. We will also look for ways to reduce their consequences [12-13].

II. MATERIAL AND METHODS

2.1 Field of study

Ajdabiya is the capital of Al Wahat district, located in north-eastern Libya. It is located about 160 km south of Benghazi, on the coastal highway leading to Tripoli in the Gulf of Sirte. It was from 2001 to 2007 the capital of the district of the same name, Ajdabiya which has about 76968 inhabitants (**Fig.1**) [14].

2.2 Water sampling and analysis

For all sampling area (**Tab.1**), the parameters studied and the methods used are as follows:

*Temperature (T °C) is measured on site by a thermometer probe;

*The pH was measured directly after sample collection using a Model 3310 pH meter;

*The electrical conductivity of the water samples was measured directly after sample collection using a Conductimeter Model Consort. Electrical conductivity EC is expressed in ds / m or $\mu\text{s} / \text{cm}$ at 25 °C;

*Total Dissolved Solute TDS in mg / L and Salinity in g / L ;

*Estimate of calcium and magnesium (Ca^{+2} , Mg^{+2}). Calcium and magnesium ions were estimated by plating the EDTA solution, which is a stable compound with calcium and magnesium ions using the Eriochrome black T reagent, Murexid [15-16] ;

*Determination of chloride (Cl^-). Chlorides are measured by the method of Mohr (AFNOR T90-014). The chlorinated water samples were calibrated with 0.014M silver nitrate using potassium chromate as a reagent in a neutral or alkaline medium [17].

*Determination of sulfates SO_4^{2-} . The method used was based on the fact that the sulfate ions are deposited in the 1: 1 HCl acid medium in the presence of barium chloride due to the formation of barium sulfate in the form of single crystals of barium sulfate. Absorption can be measured by UV. V is Spectrophotometer [18];

*Determination of carbonate and bicarbonate (HCO_3^- , CO_3^{2-}). Carbonates and bicarbonates were estimated by the concentration of HCL (0.05 N) [19] ;

*Determination of sodium and potassium (Na^+ , K^+). Each element was estimated to have distinct radii when excited by a flame (photovoltaic) using a flame photometer [20].

*Total hardness TH, calcium or magnesium hardness, alkalinity, bicarbonate and carbonates are measured by volumetric method of hydrochloric acid (0.05N) titration method (AFNOR T90-036).



FIGURE 1: MAP OF THE STUDY AREA AJDABIYA-JALO, LIBYA

TABLE 1

GEOLOCATION OF WATER SAMPLING STATIONS ASSOCIATED WITH CRUDE OIL IN AJDABIYA-JALO.

Stations	Latitude	Longitude		Stations	Latitude	Longitude
Well 2	27°51'18.12"N	21°56'49.03"E		Well SEP	28°59'44.44"N	21°34'29.73"E
Well 3	27°10'52.51"N	21°34'55.18"E		Well 249	28°59'12.19"N	21°22'32.48"E
Well 4	27°47'56.12"N	20°31'54.67"E		Well 256	28°45'50.37"N	22°12'26.00"E
Well 5	29°10'45.26"N	21°17'56.09"E		Well D44	29°15'50.42"N	19°12'27.11"E
Well 6	28°59'44.44"N	21°34'29.73"E		Well G128	28°56'47.46"N	19°42'23.98"E
Well 7	28°59'12.19"N	21°22'32.48"E		Well G144	29°50'29.70"N	19°46'38.06"E
Well 8	28°45'50.37"N	22°12'26.00"E		Well G36	30°20'30.24"N	19°35'34.61"E
Well 9	29°15'50.42"N	19°12'27.11"E		Well tank	30°45'44.17"N	20°14'22.06"E
Well 10	28°56'47.46"N	19°42'23.98"E		Well S1	27°51'18.12"N	21°56'49.03"E
Well 11	29°50'29.70"N	19°46'38.06"E		Well S2	27°10'52.51"N	21°34'55.18"E
Well 12	30°20'30.24"N	19°35'34.61"E		Well S3	27°47'56.12"N	20°31'54.67"E
Well 13	30°45'44.17"N	20°14'22.06"E		Well S4	29°10'45.26"N	21°17'56.09"E



FIGURE 2: SPREADING AND STORAGE AREAS FOR CRUDE OIL WASTE IN LIBYA

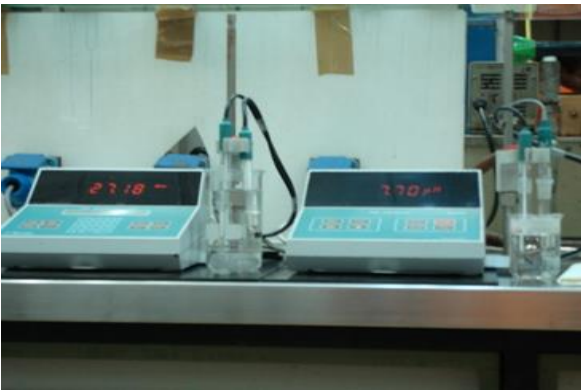


FIGURE 3: METHODS OF ASSAYING AND ANALYZING PETROLEUM WASTE

III. RESULT AND DISCUSSION

In the initial production of oil fields, the oil is not associated with water, but after a period of production, begins the emergence of water with oil extracted. The amount of water is gradually increased due to the upward water creep and in the final phase of the field operation, the proportion of produced water can reach 90% and more [25-26].

In the tanks, there is always water that is below the tank is the water associated with the oil. The water that accompanies the oil is characterized by a huge amount of dissolved mineral salts. It is salt water; see very salty ranging from a few hundred thousand to more than 600000 ppm. The salinity varies in Libya from 25 to 117,5 g/L and comes from a salt-laden oil of 25000 to 117500 mg / L (**Tab. 3**). Nitrates (234 to 609 mg / L); sulphates (278 to 2609 mg/L); Total Hardness (572 to 9820 mg / L) are present at levels exceeding acceptable standards [27].

TABLE 2
DESCRIPTIVE STATISTICS OF PHYSICOCHEMICAL CRUDE OIL WASTE OF AJDABIYA.

Variables	Observations	Minimum	Maximum	Mean	Standard deviation
T°C	42	21	46	33,3714	6,71
pH	42	6,2	7,96	7,2195	0,41
CE µS/cm	42	12654	66925	36855,5476	19135
TDS mg/L	42	8225	48432	24075,0952	12649
TH mg/L	42	572	9820	4095,9762	2435
Na ⁺ mg/L	42	723	37320	9941,3786	10894
Mg ²⁺ mg/L	42	219	1009	622,5048	208
Ca ²⁺ mg/L	42	464	5820	1894,0714	1434
K ⁺ mg/L	42	19,5	1140	403,3238	373
CL ⁻ mg/L	42	2800	70421	27537,1667	17119
SO ₄ ²⁻ mg/L	42	278	2609	1238,2333	640
NO ₃ ⁻ mg/L	42	234	609	402,1190	108
HCO ₃ ⁻ mg/L	42	410	6561	799,1024	923
CaCO ₃ mg/l	42	28,8	4032	1829,5262	1121
Salinity g/L	42	25	117,50	76,1429	19

The pH does not show significant variations and the waters are generally acidic to slightly basic ranging between 5.57 and 7.86 (**Tab.2**) following their contamination by petroleum residues.

The electrical conductivity is measured in µs / cm and varied from 12654 and 66925 µs/cm (**Tab.2**). When pure water is free of salts, bases and acids, it increases the electrical conductivity in the water [15]. This fact makes it possible to introduce the quantity of salts into the water. Any water has an electrical conductivity, but the removal of the ionic concentration of the water decreases its conductivity.

The Total dissolved solutes (TDS) is an important indicator of the suitability of water for various uses. The more soluble salts, the less soluble is water. If the water contains less than 1 mg / liter, the water is unacceptable and this water is not valid. For many uses, the concentration of dissolved salts in water varies considerably from one region to another [28]. In water polluted by oil it varies from 8225 and 48432 mg/L and is far from norms.

Total Hardness TH varied from 572 to 9820 mg/L and is linked to calcium and magnesium concentrations.

Calcium and magnesium with bicarbonate and carbonate and sulphate or silica components are insulation materials for heat in boilers and in household and industrial appliances. But combined with fatty acid ions give undesirable deposits lead to distortion of basins and walls in bathrooms and toilets. The high level of magnesium also causes intestinal diarrhea, especially for new users who do not know this water.

Chlorides with a concentration greater than 100 mg / L for salt water, lead to physiological complications and various diseases. The food industry usually requires less than 250 mg / L and the textile, paper and synthetic rubber industries require less than 100 mg / L of chloride. With 2800 and 70421 mg / L of chlorides the waters associated with oil exceed the norms of

agricultural irrigation. Sulphates also combine with calcium to be an adhesive that limits the thermal conductivity in the tubes. Therefore, it is prohibited for certain industries such as sulphate level higher than 250 mg / L. The sulphate level of 500 mg / L or more gives the water a bitter taste. Water containing more than 1000 mg / L of sulphates causes damage to physical health. The waters studied had between 278 and 2609 mg / L of sulphates and are widely polluted. Bicarbonate when heated with water vapor gives carbon dioxide and carbonate and the latter combines with alkaline earth elements and the head of calcium and magnesium and forms a crust composed of Calcium and magnesium carbonate leads to reduced thermal conductivity through the walls of the conduction tubes and reduces the flow of fluid in these tubes and sometimes clogged completely. For many industries, the level of carbonate, bicarbonate or alkalinity is generally high. Concerning the nitrate contents (**Tab.2**), the values oscillate between 234 mg / L and 609 mg/L and clearly reflect a nitrogen pollution of petroleum origin [27].

The Piper diagram (**Fig.4**) shows that globally the waters associated with petroleum have a chloric sodium facies and potassium or sulphated sodium and slightly bicarbonated sodium or potassium. Moreover, the projection of hydrophysicochemical data in the Wilcox diagram and Riversade (**Fig.4**), shows that the water quality associated with Ajdabiya Libya oil is poor and above all a deteriorated quality at because of the alkalizing power of sodium (SAR). These waters are classified in group C4S4 and outside this grid and are unfit for irrigation.

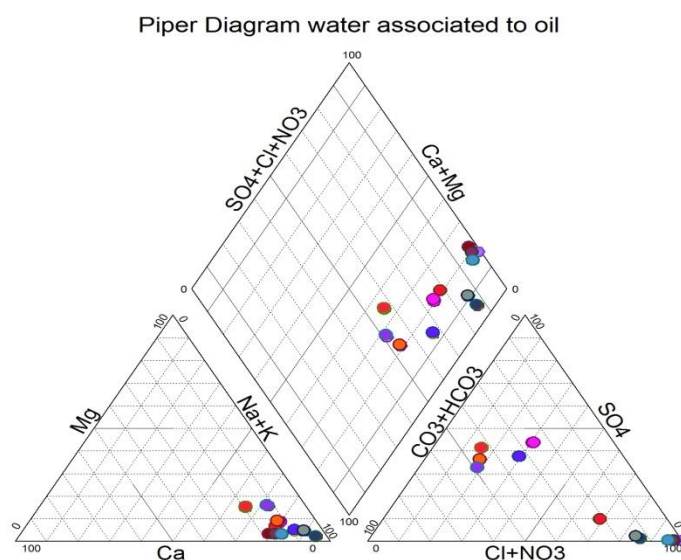


FIGURE 4: HYDROCHEMICAL FACIES OF WATER ASSOCIATED TO CRUDE OIL IN AJDABIYA, LIBYA

IV. CONCLUSION

All water studies and research have identified water needs in light of Libya's population increase, which is expected to reach about 14 million by 2025. Total freshwater resources are around 4.5 billion cubic meters and the total needs of this population are about 7.6 billion. The expected deficit is about 1.3 billion cubic meters. To compensate for this deficit, groundwater resources must be studied and rationalized. This study has explore and analyze water resources in order to assess their quality and validity [33]. Clouds are not well distributed and precipitation is random [34].

Large-scale oil pollution has led to a deterioration of water quality. In addition to increased salinity of the waters due to several factors such as the intrusion of salt water from layers carrying salt water to fresh rolling classes or the entry of seawater or salt water to proximity. The water associated with oil "or" productive water "is estimated at 44 million barrels of water a day, assuming an average rate of four million barrels of water per million barrels of oil, with a production rate of only 11 million barrels a day.

In conclusion of this study it is proposed to develop WWTPs for the treatment of water produced with the extraction of oil and its purification and re-injection into waterways. Thus, further reduce the amount of metal ions present in the treated water and the removal of metal ions and also reduce sulphate ions, nitrates, salinity and electrical conductivity [36-39].

Most countries already involved in offshore oil development have developed their own laws and standards at national and regional level. Instead of presenting final policy recommendations, we prefer to put in place tools and build a strong normative, regulatory and legal framework to protect the environment in Libya.

REFERENCES

- [1] F.C Waddans, 1980. The Libyan oil industry. Croom Helm, London. 338p.
- [2] J Gurney, 1996. Libya; the political economy of oil. Oxford Institute of Energy Studies. Oxford University Press: 24Ip. p.203-206.
- [3] T.H Moller, Molloy, F.C., H.M. Thomas, 2002. Oil spill Risks and the State of Preparedness in the Regional Seas. Discussion paper of the International Tanker Owners Pollution Federation Limited, London, UK. 9p.
- [4] UNEP, 2002. Africa Environment Outlook: Past Present and Future Perspectives. UNEP, 400p.
- [5] J.H Teas, Lessard, R.R., Canevari, G.P., Brown, C.D., Glenn, R., 1993. Saving oiled mangroves using a new non-dispersing shoreline cleaner. In: Proceedings, Conference on Assessment of Ecological Impacts of Oil Spills. American Institute of Biological Sciences, Washington, D.C., pp. 147-151.
- [6] M.B Baegi, H.S Assaf, and K.M Hangari, 1991. Al Awaynat surface uranium mineralisation - a new approach to its origin. Third Symposium on the Geology of Libya, vol. 7 (eds. M.J. Salem and M.T. Busrewil and A.M. Ben Ashour), Elsevier, Amsterdam, p. 2619-2626.
- [7] P Stanislav, 1999. Environmental impact of the offshore oil and gas industry, EcoMonitor Publishing East Northport, N.Y. 425p.
- [8] NRC, 2002. National Research Council of the National Academies. Oil in the Sea III. Inputs, Fates and Effects, The National Academies Press, Washington D.C. 265 pp.
- [9] A., Ibada. Ph.D. Evaluations de la Salubrité Microbiologique et Physicochimique et de la pollution des Eaux de la Nappe Murzuq (Sabha - Libye). Université Ibn Tofail, Faculté des Sciences Kénitra Maroc, 2014.
- [10] A Ibada, M.F Abosith, A Alemad, K El Kharrim, D Belghyti, "Physicochemical quality of murzuq groundwater Sabha – Libya" WIT Water and society, Vol 178, WIT Press, 2013, ISSN 1743-3541, doi. 10.2495/WS130191.
- [11] A Ibada. et al., 2014 : Evaluation physicochimique des eaux souterraines de la nappe Murzuq Sabha, Libye. Journées Méditerranéennes des Systèmes d'Information de l'eau. WIS 189, 19-21 Mars 2014 Rabat Maroc.
- [12] Québec, 2003: Centre d'expertise en analyse environnementale du Québec MA. 408-IdePet 1.0 *Identification des produits pétroliers*, 2003, p.10-22.
- [13] Metrohm, 2012 : Analyse pétrochimique, l'assurance qualité des produits pétroliers, Mise en page Ecknauer + Schoch ASW, imprimé en Suisse par Metrohm AG, CH-9100 Herisau 8.000.5080FR – 2012-11.
- [14] O Salem. Management of Shared Groundwater Basins in Libya. In, Policies and strategic options for water management in the Islamic countries. Symposium, Tehran, Islamic Republic of Iran, 15-16 dec. 2003, UNESCO, pp.89-97. IHP-IV Series on Groundwater n°73.
- [15] J Rodier. L'analyse de l'eau: eaux naturelles, eaux résiduaires, eau de mer : physico-chimie, bactériologie et biologie », Ed. Dunod, Paris, France, 8, 1996. p1383.
- [16] J Rodier et C Graude. détermination de la dureté dans les eaux par la méthode au complexon III. Bull. Institut hygiène du Maroc, (1952), N.S. XII, (3-4), 275.
- [17] APHA, AWWA, et WEF, (1998), Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association et Water Environment Federation, 20^e edition.
- [18] J Rodier: L'analyse de l'eau : Eaux naturelle, eaux résiduaires, eaux de mer, 7^{ème} Edition, Dénod, 1986. Paris, p.1383.
- [19] A Alemad, M Nagi, A Ibada, R Nasser, Alwathaf Y., Elrhaouat O., Elkharrim K., Babaqi A., Belghyti D., (2013): The impact of sana'a solid waste on the quality of groundwater in Yemen, 2nd International Conference on Water and Society, 4 - 6 September 2013, New Forest, UK, PaperDOI: 10.2495/WS130151.
- [20] D Belghyti, Daifi H, Alemad A, Elkharrim K, Elmarkhi M, Souidi Y, Benelharkati F, Joti B, Elmoukrifi Z, Ibada A, Azami-Idrissi Y, Baroud S, Elkhayyat F, Elrhaouat O, SadeK S, Y. Taboz, H. Sbai, R. Naser, H. Chigger & N. Groundwater management for sustainable production of drinking water quality in Maâmora. Water and Society II 241. WIT Transactions on Ecology and The Environment, Vol 178, © 2014 WIT Press. www.witpress.com, ISSN 1743-3541.
- [21] J Beens et U.A.T Brinkman: The role of gas chromatography in compositional analyses in the petroleum industry. TrAC, Trends in Analytical Chemistry, 19:260– 275, 2000.
- [22] M Rondon. PhD Influence de la formulation physico-chimique et des propriétés interfaciales sur la stabilité des émulsions asphaltènes-eau-huile. Application à la déshydratation du pétrole, Université, 2006.
- [23] J Laxalde. Analyse des produits lourds du pétrole par spectroscopie vibrationnelle. HAL Id. 2012.
- [24] N Jaffrezic-Renault 2003 : développements analytiques: micro capteurs électrochimiques pour le suivi in-situ des contaminants, Laboratoire IFOS, Ecole Centrale de Lyon, 69134 ECULLY Cedex (France) Reçu le, 06 Janvier 2003, Accepté le 16 Mai 2003.
- [25] E & P Forum/ UNEP technical Publication, (1997). *Environmental Management in oil & gas. Exploration and Production: An overview of issues and management approaches. UNEP IE/PAC Technical Report 37.*
- [26] A FUTYAN, and AH. JAWZI. The hydrocarbon habitat of the oil and gas fields of North Africa with emphasis on the Siit Basin. First Symposium on the Sedimentary Basins of Libya, Geology of the Sirt Basin, vol. 2. (eds. M.J. Salem., A.S. El-Hawat and A.M. Sbata), Elsevier, Amsterdam, 1996. p. 287-308.
- [27] H Abouzeid et A Outair. Les Nitrates dans les eaux, 7ème Congrès Mondial des ressources en eau, Rabat, Maroc, 13-18 Mai 1991, Volume 2.

- [28] FAO. Comparing water requirements for agricultural production in the Libyan Jamahiriya and twenty other countries. Rome, 2004.
- [29] CSS, Committee Standards and Standard, Department of Environment- Morocco, Folds back, 1994.
- [30] MEM, « Moroccan Standards, official Bulletin of Morocco, » Ministry of Environment of Morocco, n° 5062. 2002, Rabat.
- [31] IAEA. Regional Shared Aquifer Diagnostic Analysis For the Nubian Sandstone Aquifer System, Second Draft Report, International Atomic Energy Agency Vienna, Austria, 24 September 2010.
- [32] I Merdrignac, D. Espinat. Physicochemical characterization of petroleum fractions: the state of the art. Oil & Gas Science and Technology - Rev.IFP, 62(1): 7–32, 2007.
- [33] Organisation mondiale de la santé (OMS), (1984). Directives de qualité pour l'eau de boisson. Vol. 2. Critères de santé et autre information justificative. Genève.
- [34] World Health Organization (WHO), (eds). Guideline for Drinking Water Quality, Health Criteria and Other Supporting Information: 2nd Edition, Vol.2, Geneva, pp. 940-949, 2004.
- [35] Salem O. et Pallas P., 2002. The Nubian Sandstone Aquifer System (NSAS), In, Appelgren B. (ed.). Managing Shared Aquifer Resources in Africa (ISARM Africa), Proceedings of the International Workshop, Tripoli (Libya), 2-4 June 2002. Paris, UNESCO, pp. 19-21. IHP-VI, Series on Groundwater n°8.
- [36] D Mara. Guidelines for the safe use of wastewater and excreta in Agriculture and Aquaculture: Measures for public health protection, World Health Organization, Geneva, 1989, 187p.
- [37] UNESCO. 1972. Étude des ressources en eau du Sahara septentrional. Nappe de la Djeffara. Projet ERESS. Unesco presse, 2002. Eau: les ressources cachées de l'Afrique [en ligne]. Paris, UNESCO. Communiqué de presse N° 2002-35. Disponible sur Internet, http://portal.unesco.org/fr/ev.phpURL_ID=3026&URL_DO=DO_TOPIC&URL_SECTION=201.html.
- [38] UNESCO, 2006, Ressources en eaux et gestion des aquifères transfrontaliers de l'Afrique du nord et du sahel: Paris.
- [39] UNESCO, *Vers une Gestion Concertée des Systèmes Aquifères Transfrontaliers. Constat Préliminaire Partie I*: Académie de l'Eau, BRGM, OIEau, UNESCO, Paris, Août 2011.