Groundwater contamination by nitrates, salinity and pesticides: case of the unconfined aquifer of Triffa Plain (Eastern Morocco)

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Abstract: Located at the North-eastern part of Morocco the plain of Triffa is under a semi-arid climate. The water resources in this zone are rather fragile and influenced by a highly irregular rainfall distribution, both in time (annual and inter-annual distribution) and in space with an yearly average which does not exceed 240 mm.

In the Triffa plain the impact of anthropogenic activity on the groundwater resources is reflected both by: a) the decrease in the piezometric level due to the over exploitation and droughts; and b) the deterioration of the chemical quality of water. Currently, this situation is felt mainly by the farmers.

The unconfined aquifer is under stress due to increase of the pollution rate, especially nitrates, that are above the WHO standards, and

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salinity. Organochlorine pesticides are ubiquitous and persistent organic pollutants used widely in agriculture. Due to extensive use in agriculture, organic environment contaminants such as HCH, DDT, DDD along organochlorine pesticides are distributed globally by transport through air and water. Pesticides such as aldrin, lindane, heptachlor, have also been detected and are indicators showing the need to reduce the pressure on groundwater quality by informing and training farmers on the use of fertilizer and pesticides.

Riassunto: Situata nella parte nord est del Marocco la pianura di Triffa è caratterizzata da un clima semiarido. Le risorse idriche della zona sono piuttosto "fragili" e influenzate da una distribuzione della piovosità altamente irregolare, sia nel periodo (annuale o intra-annuale) che nello spazio, con una media annuale che non supera i 240 mm.

Nella pianura di Triffa l'impatto delle attività antropiche sulle risorse delle acque sotterranee si riflette sia attraverso a) un abbassamento del livello piezometrico dovuto al sovrasfruttamento e alla siccità, b) il deterioramento della qualità chimica delle acque. Attualmente questa situazione si fa sentire a causa delle fattorie.

L'acquifero non confinato è sotto stress a causa dell'incremento del tasso di inquinamento, specialmente di nitrati, che sono al di sopra del WHO standard, e per la salinità. I pesticidi con organoclorine sono ovunque e inquinanti organici sono usati ampiamente in agricoltura. A causa dell'uso estensivo in agricoltura i contaminanti organici dell'ambiente come HCH, DDT, DDD, per i pesticidi con organoclorine sono distribuiti globalmente a causa del trasporto attraverso l'aria e l'acqua. Pesticidi come aldrin, lindane, heptachlor sono stati individuati e sono indicatori che mostrano il bisogno di ridurre la pressione sulla qualità delle acque attraverso l'informazione e l'istruzione degli agricoltori sul corretto uso dei fertilizzanti e dei pesticidi

Introduction

Water resouces are considered as a first priority by the Moroccan national strategy. The economy of the country is mainly based on agriculture, which is reflected on water use. Not surprisingly, irrigation is responsible for 90% of water consumption in Morocco, thus water resources management is a fundamental variable the present and the future of Morocco, regardless of climate change.

The Triffa plain, located in the NE Morocco, not far from the Mediterranean coast, is an important agricultural area (36 060 Ha) with 33% of fruit plantations (citrus), 24% of cereals, 13% of industrial crops, 7% of fodder farming and 3% of various agriculture (Fig. 1). Irrigation is essential due to the semi-arid climate conditions, with rainfall being dominated by a strong variability both in space and time, often resulting in water scarcity. Water demand is high for agriculture and for drinking water supply. Unfortunately, in recent years it is perceived a quantitative and qualitative deterioration of groundwater resources.

The Triffa plain is characterized by two aquifers; a shallow unconfined in the plio-quaternary layers, generally with poor groundwater quality and a deep Liasic carbonate with good groundwater (Zarhloule et al 2009).

Excessive use of pesticides and groundwater for the agriculture may lead to contamination of ground waters of the unconfined aquifer by drift, vertical drainage and leaching. The groundwater contamination in Triffa plain may cause a continuous human exposure since it represents the most important source of drinking water supply.

This survey highlights the water stress as well as the water contamination by the nitrates, the salinity and the presence of the pesticides

The objectives of this survey is to identify the influence if the hu-

man activity on the groundwater resources due to intense agricultural activity and uncontrolled use of fertilizers, pesticides). For this purpose, 700 wells have been inventoried and 251 have been selected for the acquirement of data such as: water table, TDS, major's elements, nitrates and pesticides. The sampling was conducted in 2007

Data acquisition and processing

The sampled sites in this study include observation wells, springs and wells for irrigation. Water samples were collected from 251 existing wells (Fig. 1). Choice of the wells to sample (Fig. 1) was based on the following criteria: i) spatial distribution, to ensure appropriate coverage of the aquifer; ii) location of the wells with respect to regional groundwater flow direction; and iii) location of the wells with respect to the main agricultural areas..

For the pesticides 15 wells were selected in an area with uncontrolled fertilizer use associated to intensive agricultural systems (Citrus, vegetables, cereals and various tree crops) (Fig 1, Table 1).

Samples were taken from each well and stored in 500 ml polyethylene bottles. One of the bottles was acidified with HCl (pH < 2) for

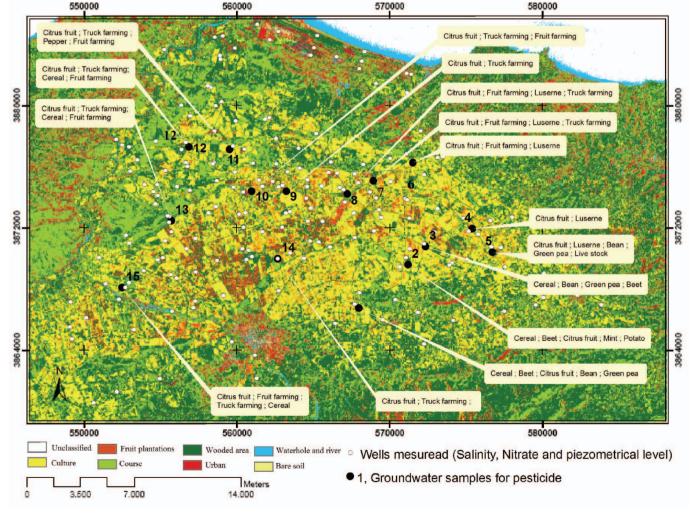


Fig. 1:Land use map (modified after Hormony Mairess. 2011) with the measured and pesticides sampled wells

determination of cations and the other was cooled to $+4^{\circ}$ C or lower and kept unacidified for anion analyses. Unstable hydrochemical parameters including water temperature, pH and EC were measured in-situ using portable pH meter, and electric conductivity meter that had been calibrated before use.

Major and some Nitrate elements were analysed at the hydrogeochemistry laboratory of Moroccan office of Phosphates where the Cations were analyzed by ICP-MS spectrophotometry, Cloride and Bicarbonate were analyzed by volumetric methods, Sulfates by gravimetric methods and the Nitrates by AFNOR methods. As for pesticides, the organochlorides residues were analysed with a Gas Phase Chromatograph (Varian Star 3400), equipped with an electron capture detector (63 Ni). Three groups of organochlorine pesticides in addition to HCB and endosulfan were sought: DDT and its metabolites, hexachloricyclohexane (HCH) and its isomers and cyclopentadiene (aldrin, dieldrin, endrin, heptachlor and heptachlor epoxide).

Resutts and Discussion

Study area and aquifer structure

The Triffa plain is situated at the North-Eastern part of Morocco (Fig.2) with 750 km² surface area. It is limited by Ouled Mansour hills in the North, Beni Snassen Mountains and Cherra river in the South and respectively in the East and the West by Kiss river and. Moulouya river. The plain constitutes a vast synclinal depression formed by secondary and quaternary geological formations. The plain is characterized by two types of aquifers; the Liasic limestone and dolomites host a confined aquifer that are the origin of the ther-

mal water in the region and an unconfined aquifer in the Quaternary heterogeneous layer system.

A flexure (Fig. 2) running approximatelly E-W, divides the unconfined aquifer in two distinct parts. North of the flexure (Fig. 3) the unconfined aquifer is composed by villafranchian limestone, while south of it the aquifer is formed by Quaternary layers composed mainly by silt and conglomerate overlying the Villafranchian limestone. The transmissivity coefficient in the south of the flexure varies between 10^{-2} and $5 \ 10^{-3} \ m^2/s$ for the Quaternary layers and 2.10^{-4} and $4.10^{-5} \ m^2/s$ for the Villafranchian layers. The substratum is formed by marls dating from the Pliocene.

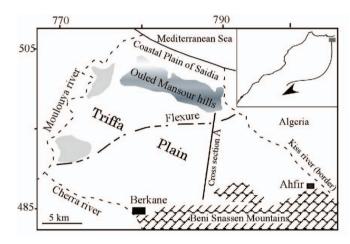


Fig. 2: Study area

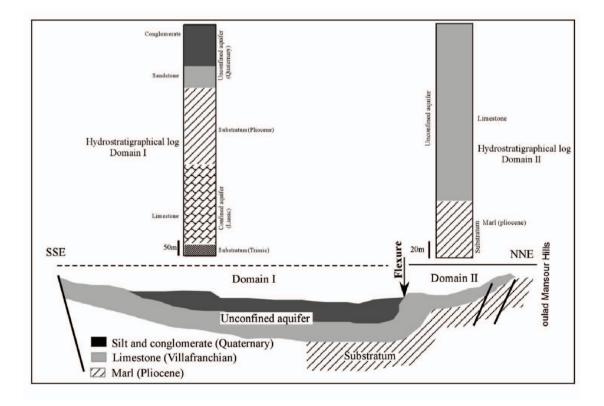


Fig. 3:N-S cross section

The climate in this area is in general semi-arid. The total rainfall does not exceed 327 mm/year, being concentrated between January and April. The mean yearly temperature is 17.40° C, but season-al variability is high, with a mean minimum of 11 °C and a mean maximum of 25 °C. The average annual evapotranspiration is about 300mm/ year. Water budgets estimate an infiltration rate of 14% of the precipitation.

The overall volume of water extraction for irrigation from the unconfined aquifer is approximately estimated at 55.17 Mm³/year in 2004, and the returns of irrigation water are the main source of groundwater recharge of the unconfined aquifer, they represent 30 to 55 Mm³/year from pump irrigation, 140 Mm³/year from water irrigation dam, and 5-10 Mm³/year from irrigation: by springs. These returns of irrigation water will influence the chemical quality of water

The hydrogeologic conditions of the triffa plain were addressed previously by several researchers. A.El Mandour (1989) studied the geology and hydrogeology of unconfined aquifer of the area. A modelling groundwater flow of the aquifer was conducted by H.El Idrysy and F. De Smedt (2006). Boughriba et al (2006), Zarhloule et al (2009) covered the Nord of the plain in a study of the hydrochemical identification and salinity problem of groundwater.

The piezometric study was undertaken so as to monitor and to highlight the main changes of the evolution of piezometric level from 1961 until 2007 (Figs 4a-d). The direction of the groundwater flow is generally from the South to the North and the majority arrives in the central part of the plain, where the drainage system and most of the pumping wells are situated. Here, the groundwater flow seems to slow down and gradually change direction to the north-west, where it drains to the Charraa and Moulouya river

Also from 1961 to 2007, the figures (4) show that the piezometric level decreases in the central part of the plain due to groundwater pumping, which resulted during 2007 in a change of flow direction in the northern part of the aquifer (Fig. 4d).

Hydrochemistry and pesticides

The leaching of large amounts of nitrate and pesticides from agricultural fields is a serious problem. The occurrence in groundwater of high salinity values, high nitrate and high pesticides is described in many regions in Morocco (Laftouhi et al., 2003; El Bakouri et al., 2008; Saâdi et al., 1999; Fakir et al., 2001; Boughriba et al., 2006; Zarhloule et al., 2009) and in the word (Morvan et al., 2006; Hildenbrandt et al., 2008; Batista et al., 2002; Cerejeira et al., 2003; Soutter and Musy, 1998; Baran et al., 2007; Bijay-Singh et al., 1995; Andrade and Stigter, 2009; Papadopoulou et al., 2004; Matin et al., 1998; Sankararamakrichna et al., 2005; Worrall and Kolpin, 2004).

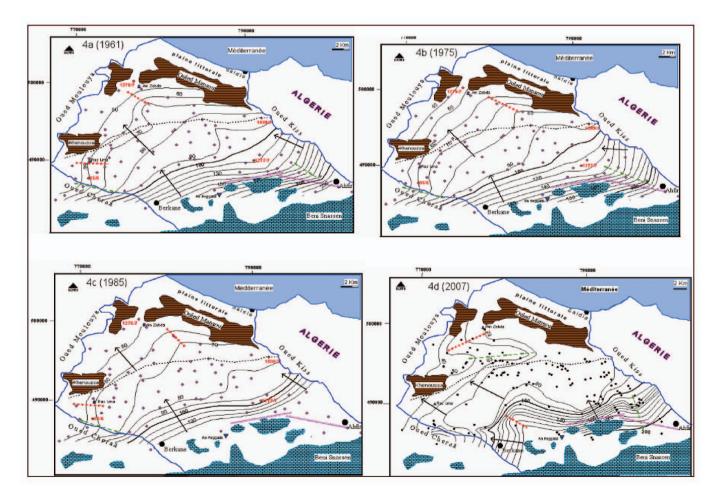


Fig. 4 (a-d): Average groundwater heads of the unconfined aquifer (from 1961 to 2007)

Salinity

TDS map (Fig. 5) shows that the values vary between 0.6 and 10 g / l. The areas of high TDS are located in the south of the Ouled Mansour hills (Marl) and in the south and the north par of the flexure. In addition to the lithological nature of the reservoir, the intensive irrigation within the south and the north areas of the flexure may contribute to an enhanced mineralization.

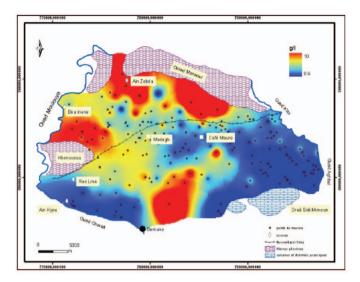


Fig. 5: *Map of TDS (mg/l)*

Nitrate

Nitrate levels in the unconfined aquifer are situated between 2 and 153 mg/l (Fig.6). 40% of the tested wells present a high concentration more than 50 mg/l.

High concentrations of nitrates are mainly located in the northwestern and south-western of the flexure where the concentration is more than 150mg/l. Comparing the nitrate contamination map with the piezometric map suggests that the nitrate contamination occurs mainly in areas of shallow water depths or/and in areas where the soil is permeable. The high concentrations of nitrates are due to the

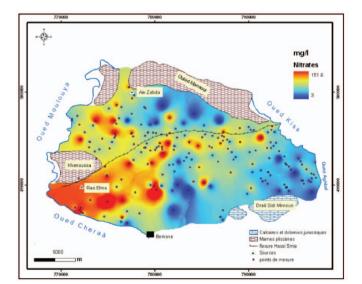


Fig. 6: Map of Nitrates (mg/l)

intensive irrigated agriculture and of the excessive application and repeated of mineral and organic fertilizer often in excess to what is recommended (Zarhloule et al, 2009).

Regarding land use, groundwater contamination by nitrate associated with vegetable cultivation fields

Pesticides

The surveys conducted of farmers and companies have shown that chemical control at the plain of Triffa is provided by approximately 60 active matters belonging to 10 chemical groups with 62% of insecticides, 25% of fungicides, 10% of herbicides and 3% of acaricides. The total annual used in Triffa plain is about 1000 t/year.

Pesticides analyzed are those used by farmers in the region and as the region is a border area with Algeria where the informal trade is highly developed, other unauthorized pesticides such as DDT was also analyzed.

For pesticides and according to a farm use survey, 15 wells have been selected (Fig. 1), and 14 elements have been analyzed (Table. 1). The chromatographic analysis showed the presence of six organochlorine chemicals elements in samples with equal to close value to the qualifying standard and about 25% of wells sampled were contaminated by at least one active matter (Table 1).

The results of pesticides (Table 1 and Figure 7) show that six elements have been detected in four wells (W2.W5.W10 and W12). The W5 contains the aldrine, endosulfan sulfat, lindane and DDT with $0.03\mu g/l$ for each element. For W2, the water contains Aldrine and Lindan, for W10, the water contains endosulfat and Dieldrine and for W12 shows the only the presence of Lindane.

For each element, the concentration in the unconfined aquifer is low or even tolerable, but their summation is a major problem for human health. According to FAO / UNEP (1991), all uses of aldrin are prohibited. The patterns of regulatory measures are:

a) high toxicity of the substance;

b) Persistence of the substance (particularly in temperate regions)c) bioaccumulation of residues of the substance in the food chain.

Also, for other elements that its use was banned because of damage to wildlife, such as DDT and DDD still available in black-market (contraband) between Algeria and Morocco.

This type of observation is one of the main problems in the interpretation of test results because the long-term cumulative effects of all these products on health are still poorly understood.

The origine of the pesticides in the unconfined aquifer of Triffa, It's due to the type of agriculture (cultivation of herbaceous plants), no controlled use of the pesticides in those areas and also to dismissal of waste waters.

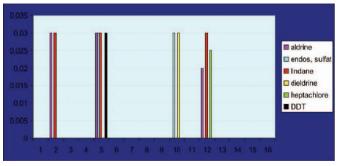


Fig. 7: Pesticides diagram

Tab. 1: concentration of pesticides in ground water samples ($\mu g/l$)

¥1	Aldrine	Endosulfan, sulfat < 0.02	<i>Lindane</i>	Dieldrine	Endrine	Hepta chlore	< 0.02	< 0.02	< 0.02	Endosufan, 1 < 0.02	Ū	-		Endrine, aldh < 0.02
W1	< 0,01 <mark>0,03</mark>	< 0,02 < 0,02	< 0,02 <mark>0,03</mark>	< 0,01 < 0,01	< 0,02 < 0,02		< 0,02 < 0,02	< 0,02 < 0,02 < 0,02 < 0,02		< 0,02 < 0,02				
W3	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02		< 0,02		< 0,02	< 0,02 < 0,02
W4	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	02	02 < 0,02		< 0,02	< 0,02 < 0,02
W5	0,03	0,03	0,03	< 0,01	< 0,02	< 0,02	0,03	< 0,02	< 0,02	,02	,02 < 0,02		< 0,02	< 0,02 < 0,02
W6	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	٨	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
W7	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	٨	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
8M	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	٨	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
6M	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	Λ	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
W10	< 0,01	0,03	< 0,02	0,03	< 0,02	< 0,02	< 0,02	< 0,02	^	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
W11	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	,02	,02 < 0,02		< 0,02	< 0,02 < 0,02
W12	0,02	< 0,02	0,03	< 0,01	< 0,02	0,025	< 0,02	< 0,02	^	< 0,02),02 < 0,02		< 0,02	< 0,02 < 0,02
W13	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	٨	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
W14	< 0,02	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	^	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
W15	< 0,01	< 0,02	< 0,02	< 0,01	< 0,02	< 0,02	< 0,02	< 0,02	^	< 0,02	0,02 < 0,02		< 0,02	< 0,02 < 0,02
W16	< 0,01	< 0,02	< 0.02	< 0.01	< N N 2	< 0.02	< N N2	< 0.02	^		-			

Conclusion

Overall this study has allowed us to demonstrate contamination of groundwater in the plain Triffa due to agricultural intensification afflicting the region. The study of nitrate pollution has shown that 40% of wells tested with levels above the standard for drinking water set at 50 mg NO₃ / 1 by WHO. The values recorded in this study proved very disturbing. In effect this pollution has a direct danger to human louse.

Chromatographic analysis of 15 groundwater wells identified significant contamination by organochlorines and bioaccumulation of these chemicals at low doses could have very negative health consequences for the long term consumer and the environment. Ultimately, it seems clear in any event that sustainable agriculture is essential to protection of the environment; developments will be conducted simultaneously in the interests of agriculture

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