J. Mater. Environ. Sci. 5 (S1) (2014) 2151- 2155
ISSN : 2028-2508
CODEN: JMESCN
MPE14

Impact of agricultural practices on groundwater quality: Case of Gharb region-Morocco

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Received 7 Dec 2013, Revised 16 July 2014, Accepted 17 July 2014
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Abstract
Fertilizer and pesticide use due to agricultural activities is the most sensitive cause of groundwater contamination. Research in the Mnasra area on district in the coastal zone of Gharb plain in northwest Morocco sought to determine spatial and temporal variability of groundwater nitrate (NO^-_3) and pesticide concentrations in 2012. The monitoring has focused on shallow groundwater near agricultural fields (9 locations). Total of 36 groundwater samples were collected (March, April, May and September) and analyzed for NO^-_3 concentrations by ionic chromatography and pesticides residues by accelerated solvent extraction (ASE). For all groundwater samples, NO^-_3 concentrations were exceeding the critical value of 50 mg.L^{-1}. Three pesticides benalaxyl, chlorpyrifos and cypermethrin have been followed. No pesticide molecules were detected, what can be explained by the low quantity applied of these compounds in the area, the use of foliar spray products or the degradation of molecules on the top soil before reaching the groundwater.

Keywords: Mnasra, groundwater, nitrate, pesticide, contamination

1.Introduction
Agricultural activities increase nitrate and pesticide loading groundwater is a worldwide problem. Nitrate leaching is a common issue in most agricultural regions of the world, especially where the crops with high water and nitrogen requirements tend to increase potential risk of nitrate pollution to the groundwater [1, 2, 3]. The environmental effects include a decline in biodiversity, eutrophication of ecosystems and surface waters further diffuse nitrate pollution of groundwater. For pesticide, it has been estimated that less than 0.1% of the product applied to crops actually reaches the target pest; the rest enters the environment gratuitously, contaminating soil, water and air, where it can poison or otherwise adversely affect nontarget organisms [4]. The presence of pesticides in groundwater has been documented in several monitoring programs and numerous investigations [5, 6]. Nevertheless, in Morocco very few data about pesticide groundwater monitoring is found.
Gharb region is the largest agriculture area in Morocco. This region is well known by industrial crops: such as sugar beet, sugar cane, in addition to conventional crops such as cereals, and vegetables culture due to the appropriate climate and soil properties. Hence, the use of fertilizers and pesticides is a mandatory requirement to increase crop production and limit the plant diseases. Generally, the economic effects of increased production have been very positive; however, the ecological effects are not always as positive. This study investigates the impact of agricultural activities on groundwater nitrate and pesticide pollution in Gharb region for the year 2012.

2. Materials and methods

2.1. Study areas, sampling and storage

The surface area of Gharb is of 600 Km^2. The region is dominated by sandy and clayey soils. The climate is Mediterranean with annual precipitations ranging between 480 and 600 mm, and the average temperature is 27°C in summer and 13°C in winter (Office Régional de Mise en Valeur Agricole du Gharb). Thirty six water samples were collected from 9 wells (d<16 m depth) installed in 9 sites allocated on the coastal zone Mnasra of Gharb the northwest of Morocco (Fig.1). Water samples were collected in 1 L clean plastic bottles and stored in the freezer (-20°C) until their analysis. Three pesticides have been followed: benalaxyl, chlorpyrifos and cypermethrin.

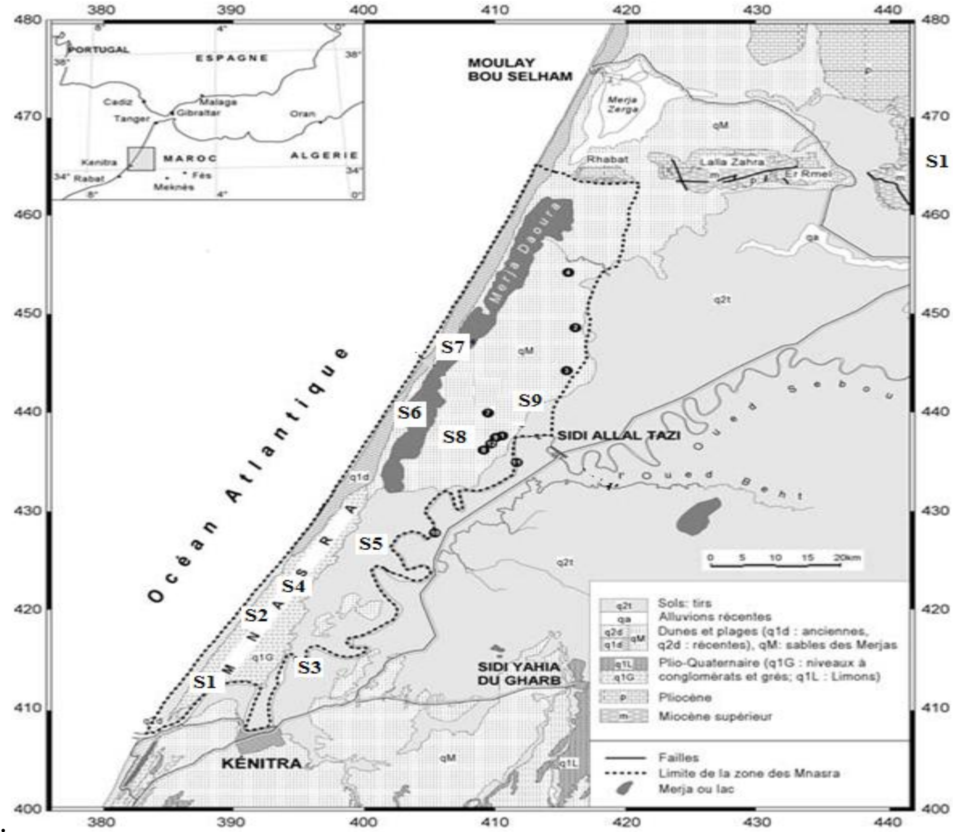

Fig.1 Location of the study sites and monitoring wells. The study site is an agricultural area that includes rural villages.

2.2. Materials

All the reagents and solvents used were of analytical grade. Pesticide standards ordered from Fluka- France were used. Working standard solutions were made by diluting these stock standards and mixtures of standards of different concentrations were used in most cases for the screening of the pesticide residues.

2.3. Techniques

2.3.1. Ionic chromatography

Two (2) mL of each sample were filtered through 0.45 μm polytetrafluoroethylene (PTFE) membrane, and were diluted 10-folds in order to avoid column obstruction. Then, nitrate analysis was carried out using ion chromatography Dionex ICS-3000 equipped with an AS11HC column (250 × 4 mm, i.d.) and conductometric detector. The mobile phase was KOH (25 mM) and flow rate was 1.3 $mL.min^{-1}$. Method limit quantification was 100 $\mu g.L^{-1}$.

2.3.2. Accelerated Solvent Extraction (ASE)

Solid-phase extraction step was initially carried out using an automated device J.T. Baker.Inc (USA) using Envi-C18 cartridges (12 mL, 2000 mg). The cartridges were preconditioned with 2 × 1 mL acetonitril and 2 × 1 mL MilliQ water.

The 400 mL water samples passed through the SPE cartridges. After vacuum drying for 80 min, the SPE cartridges were eluted with 2 × 2 mL methanol and completed till 5 mL and analyzed by HPLC.

2.3.3. Liquid Chromatography HPLC

Analysis of the water samples was carried out by high performance liquid chromatography (Ultimate 3000, Dionex) with a diode array detector operated at 210 nm. Separation was achieved with a kinetex C18 column (100 × 4.6 mm i.d., 2.6 µm particle sizes). The temperature of the column was 30°C. The mobile phase was water: acetonitrile (20:80, v/v) from 0 to 1 min, (90:10, v/v) from 1 to 10 min, (90:10, v/v) from 10 to 11 min and (20:80, v/v) from 11 to 13 min. The flow rate was 1 $mL.min^{-1}$.

The mean recoveries obtained were 79.7 ± 2.1% for benalaxyl, 29.5 ± 8% for chlorpyrifos and 61.8 ± 9.7% for cypermethrin. The limits of quantification achieved were 0.02; 0.04; 0.04 $µm.L^{-1}$ for benalaxyl, chlorpyrifos and cypermethrin respectively.

3. Results and discussion

3.1. Agricultural activities for the year 2012

Table 1 summarizes the main figures revealed by our survey related to crops encountered, trade name of fertilizers, trade pesticide products and their molecules and the quantity applied of active ingredient. Vegetable and leguminous cultures are the mean crops encountered. The sandy nature of soil and the Mediterranean climate are the favorable condition for this kind of crop. The most fertilizer used by farms is ammonitrate 33.5% with a rate of 24 N $Kg.ha^{-1}$ per application. Livestock manure is also used, mainly cattle and poultry one. The quantity applied is up to 33 $tons.ha^{-1}$ per year. For pesticide, farmers tend to change the product each time, in order to have an efficient treatment for crop disease and better rate of production. Due to the laboratory equipment, benalaxyl, chlorpyrifos and cypermethrin are the three monitored pesticides in groundwater samples.

Table 1: Characteristics of the 9 studied agriculture fields localized on the coastal part of Gharb area

Fields	Crops	Fertilizers	Pesticide products	Pesticide molecules	Q.A.A.I
F1	Navy Bean	Nitrate 33.5%	Antracol	Propineb	1.75
F2	Water melon	Nitrate 33.5%	Likeroate	Dimethoat	0.3
F3	Maize -Navy bean	Nitrate 33.5%	Mancofill	Mancozeb	1.6
F4	Peanut	Nitrate 33.5%	-	-	-
F5	Carrot-Navy bean Peanut- Pepper	Nitrate 33.5%	Dithan M45 Antracol	Mancozeb Propineb	2.6 1.75
F6	Banana	Teca fulvique	Gramoxon Nemathorin	Paraquat Fosthaizate	0.6 2 g/foot
F7	Peanut- Sunflower	-	-	-	-
F8	Banana- Navy bean	Amino 84+	Tarique Dursban 4	Cypermethrin Chlorpyrifos	0.21 0.24
F9	Cabbage-Eggplant- Navy bean	Nitrate 46%	Galben	Benalaxyl Mancozeb	0.24 1.16

3.2. Nitrate concentration

Table 2 shows the different nitrate amount analyzed in 39 water samples. All samples exceed widely the limit 50 $mg.L^{-1}$ fixed by the World Health Organization (WHO). Only 4 samples were below the norm. 2012 was a cold year, especially from December to March which was characterized by a frozen period. Crops installed in this period were lost, which led the farmers to reinstall new ones. It was noticed that the excessive use of nitrogen fertilizers was very common in the production of vegetables, fruits and industrial crops. Many farmers applied much more nitrogen than the mean value. Fertilizer applications were so high that they depressed plant growth and yields, making the amount of non-absorbed nitrogen even higher [7]. The results demonstrated that nitrate concentration was high during the spring period. The sampling of April has done during a rainfall day. Similar results were found by Rutkoviene et al. [8] who reported higher nitrate concentration in the water of shallow wells in March-July, and lower in September-February period. The authors explain that spring precipitation could carry the pollutants to deeper layers of the soil and then to groundwater. Jun et al. [9] demonstrate the relationship between precipitation and the water level fluctuation. They indicate that well locations and surface water applications also should be considered while interpreting the groundwater level changes.

Table 2: Concentration of nitrate ($mg.L^{-1}$) found in the well water samples during the period of the study

Wells	March	April	May	September
W1	87	130	72	68
W2	152	158	138	118
W3	94	181	112	93
W4	94	86	96	116
W5	109	162	95	94
W6	59	185	74	64
W7	13	64	19	11
W8	118	199	169	109
W9	267	234	116	13

Another parameter that could influence nitrate values is soil nature. The coastal location of the fields could also explain the high nitrate values. Indeed, Levallois et al. [10] confirm that intensive potato culture on sandy soil could have serious impacts on the quality of groundwater. Besides, large amounts of nitrate accumulated in the vegetable soils and the shallow groundwater was heavily contaminated by nitrate-N in areas with intensive agricultural practices. In fact, Ju et al.[11] find that groundwater in shallow wells (<15 m depth) was heavily contaminated in the greenhouse vegetable production area, due to the nitrate leaching where total N inputs were much higher than crop requirements.

3.3. Pesticide residues

Our results reveal an absence of the three pesticide molecules studied. Their concentrations were lower than the detection limit in all water samples. This result could be due to the low applied quantity of pesticides; 0.24, 0.24 and 0.21 $Kg.ha^{-1}$ per application respectively as shown in table 1. Also it can be explained by the minimal use of these products in the region. In practice, the farmers tend to use foliar spray products and change it during the same crop cycle, which reduces the risk of groundwater contamination. Indeed, Leistra et al. [12] reveal that volatilization was estimated to be the dominant process in the decline of chlorpyrifos from the leaf surfaces: from 63% to 66% of the dosage during daylight hours. Winter et al. [13] indicate that pesticide which are slightly soluble in water, may attach to soil particles instead of remaining in solution; by consequence they are less likely to be found in the groundwater. In fact, chlorpyrifos and cypermethrin present a very weak water solubility of 1.05 and 0.009 $mg.L^{-1}$ respectively. Degradation of molecules before reaching groundwater appears as another factor explaining the no detection of those molecules. Patakioutas et al. [14] find that cultivation of potatoes decreased the half-life of benalaxyl from 26.7 to 12.6 days. Youcel et al. [15] report in a laboratory study that for subsurface soils, chlorpyrifos degraded rapidly in the 0-14 days stage and that in general, it appears that the time required for 50% loss of chlorpyrifos is approximately 10 days in a 0-15 cm and 40-60 cm clayey sandy soil. Whereas, Rani et al. [16] report that both insecticides chlorpyrifos and cypermethrin was found in the top 10-cm layer, chlorpyriphos was found distributed in the soil up to a depth of 35 cm and cypermethrin remained up to 15 cm. their results indicate that the low mobility of both the insecticides under saturated moisture condition and hence may not contaminate groundwater.

Conclusion

Total of 36 groundwater samples were collected during the crop year 2012. Samples were analyzed for NO^{-}_{3} concentrations by ionic chromatography and pesticides residues by accelerated solvent extraction (ASE). For all groundwater samples, NO^{-}_{3} concentrations were exceeding the critical 50 $mg.L^{-1}$. Three pesticides benalaxyl, chlorpyrifos and cypermethrin have been followed. No pesticide molecules were detected, what can be explained by the low quantity applied of these compounds in the area, the use of foliar spray products or the degradation of molecules on the top soil before reaching the groundwater.

Agricultural groundwater pollution by nitrate is a serious problem that has a negative impact on both environment and human health. To maintain yield increase and minimize nitrate pollution of the ground waters, management practices for N-fertilizer should be disseminated and applied an excessive fertilizer application prevented. To meet water-quality standards and criteria, concerned institutes and local agencies need to determine the amount of contaminant movement to surface waters so they can issue permits and control discharges of waste.

Acknowledgements
The authors would like to thank CNRST – Morocco for the scholarship, IAV Hassan II and ORMVAG for the technical support and farms for their great cooperation.

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