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ORIGINAL ARTICLES

Determination of pesticides, Nitrates and Nitrites level in Groundwater of Akkar plain in Northen Lebanon

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ABSTRACT

To estimate the environmental risk posed by the use of pesticides is a major problem, which involves the identification, characterization, quantification and knowledge of the fate of these compounds in the environment. Their impact is directly related to their concentration and toxicity, control of reliable analytical methods is a necessity. The relative risk of contamination of drinking water by organic residues increased from time to time, in this context, the objective of this work is to build a general idea as an initiative for a further study to evaluate the quality of groundwater in Akkar region.
The water quality is evaluated by studying:

- The level of chemical pollution presented by the concentrations of nitrate, nitrite, ammonium and ortho-phosphate ions by colorimetric methods.
- The level of micropollution by measuring the concentration of residues of pesticides G.C./E.C.D. and L.C./U.V.-visible.

The level of disastrous pollution is reflected by the analysis of nitrate, nitrite and pesticide residues in water, used for direct human consumption without prior treatment, to reduce the risk accompanying pollution especially for sites Zennad Sheikh (the amount of pesticides 29.75 p.p.b., the concentrations of nitrate and nitrite are respectively 145.76 mg / L and 1.86 mg / L), Tall Bibi (the amount of pesticides 13.3 p.p.b., the concentrations of nitrate and nitrite are respectively 135.17 mg / L and 0.45 mg / L), and Har*et al* Jdideh (the amount of pesticides 12.36 p.p.b., the concentrations of nitrate and nitrite are respectively 99.88 mg / L and 0.71 mg / L). There are sites in the study area that show amazing results in lack of proper monitoring national and local awareness of the risks associated with the intensive use of fertilizers and pesticides. For all sites the chemical analyzes of water for ammonium meet the standards value and contain a concentration of less than 0.5 mg / L and non worrying values for ortho phosphate. The results of this study increase the need and importance of surveillance and control of pesticide residues and other pollutants to be carried out continuously and more specialized.

Key words: Groundwater, Contamination, Pesticides, Nitrates, Nitrites.

Introduction

The contamination of surface water and groundwater by chemical pollutants and micropollutants is a recurring problem faced by managers of water system. (Bouman *et al*., 2002; Levet *et al*., 2008). However in the absence of alternative control method applicable to large scale quickly, the use of chemicals in agriculture is expected to continue for several more decades.

The agriculture irrigates the environmental compartments by pesticides (insecticides, herbicides and fungicides ...) and chemical nutrients (nitrates, nitrites, ammonium, phosphates ...). All these products are used extensively for the highest yields, without regard to the surrounding environment or considering the impact of this heavy use on human health and ecological effects (Levario-Carillo *et al*., 2004; Meyer *et al*., 2003; Viel *et al*., 1998).

The absence of data on the level of pesticides and nutrients in northern Lebanon groundwater guide us to take in hand the problem of groundwater pollution in the Akkar plain, which is the second agricultural region of the country. This aquifer characterized by high vulnerability to pollution (Halawani *et al*. 1999; Hatoum, 2007) is the only water resource for consumption and irrigation of the most residences in Akkar.

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Materials and Methods

The sampling strategy adopted in the context of this work was based on a spatial coverage of an entire agricultural system during the month of May 2011, Nine sampling sites on two areas (coastal and interior) were selected taking into account some cultures consuming pesticides and the influence of the position of cultivated areas from wells. Their locations are shown on the map (Figure 1) (1:Al Arida, 2:Sheikh Zennab, 3:Kob*et al* Chamra, 4: Har*et al* Jedideh, 5: Qaabrine, 6: Al Knayseh, 7: Massaoudieh, 8: Tall Bibi, 9: Semmakiyeh).

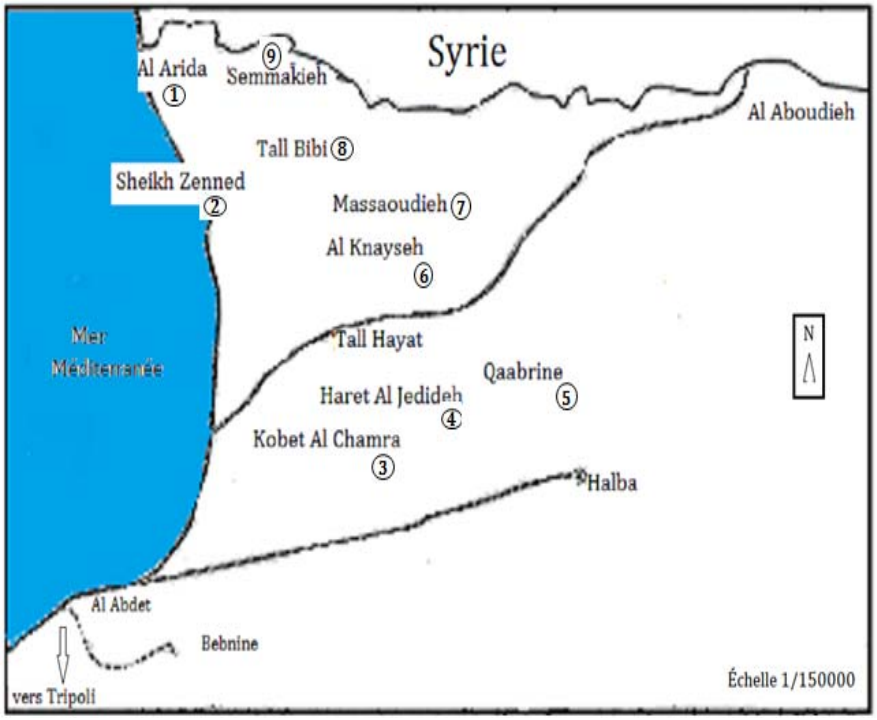


Fig. 1: Location of the sampling sites at Akkar plain

The analysis of nitrate and nitrite were carried out with reference to AFNOR methods 1990.

The analysis of pesticide residues is resumed by the following steps:

1- The Liquid-liquid extraction (Abe *et al*., 2010).

By mixing and stirring 1.0 L of water with 50 ml of dichloromethane for 15 minutes and 5 minutes decantation, obtain the extract residue (organic phase) is obtained. Three successive liquid-liquid extractions are performed; the extracts are combined and evaporated using a rotary evaporator by adding acetonitrile to obtain about 10 ml final volume after evaporation in order to ensure the absence of dichloromethane. The next stage of evaporation is done under nitrogen atmosphere to reach a final volume of 1 ml and use it for injection. The recovery rate is determined using the method of positive and negative control; it is above 70% for all target compounds (Akerbolm, 1995).

2- Identification and Quantification

Depending on the type of pesticide, we used:

- The gas chromatography Agilent technology type (Tranchant *et al*., 1995) equipped with an electron capture detector characterized by capillary chromatographic column with a length of 30 m, a diameter of 0.25 mm and 0.25 micrometer thickness. The carrier gas was high purity nitrogen, flow 1mL/min and the injection is carried out in splitless mode with an injection volume of 1 µl. Its initial temperature is 230 ° C and the detector is 300 °C.

-The liquid chromatography Agilent Technologies coupled to a UV/visible detector and characterized by C18 column 100 mm long, 3 micrometers inner diameter, mobile phase was an acetonitrile / water (ratio v / v respectively 70% / 30%) at a rate of 0.1 ml/mn and an injection volume 5µl, the wavelength is set at 230 nm as a value average (Palma *et al*., 2004; Khim-Heang and Corvi, 1998).

J. Appl. Sci. Res., 8(8): 4663-4667, 2012

Results and Discussion

Study of chemical contamination by nitrates and nitrites.

Regarding the results of this study, it was find that the nitrate content for all samples are higher than the allowable limit of water for human consumption (50mg/L), two of nine samples only meet the standard value of 0.1 mg / L nitrite. The high concentrations observed, especially for sites 1. 2, 4 and 8, have double exceeded the nitrate and nitrite standards, and this can be explained by the intensive use of fertilizers and the decreased ability of soil degradation (Figure 2).

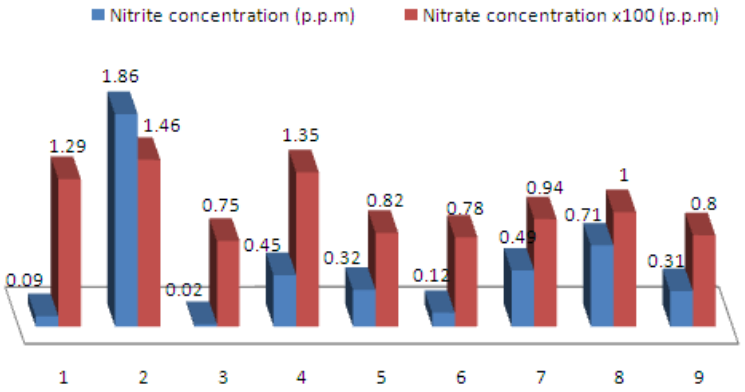


Fig. 2: The concentrations of nitrate and nitrite in each studied site

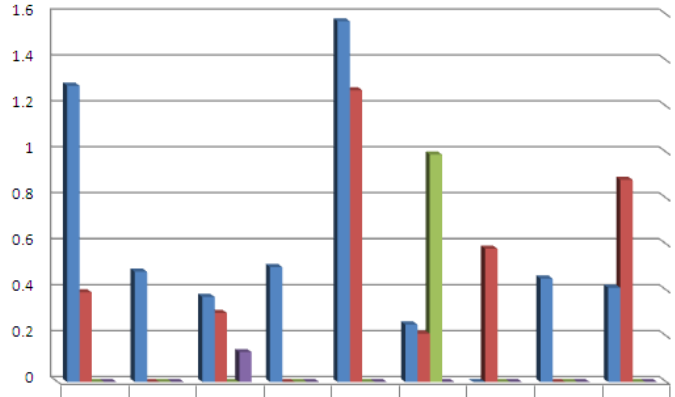
Study in pesticide residue contamination:

For each sample's site, it was tried to quantify the 11 pesticides identified using the two chromatographic methods, however, it must be noted that these 11 pesticides do not summarize all pesticides used in the study area. The analysis of samples shows that approximately all sites are affected by three types of pesticides at least and this confirms that those areas we are faced with the risk of pesticide toxicity.

The Directive 80/778/EEC of 15th July 1980 on the quality of water intended for human consumption set for pesticides, a maximum allowable concentration of 0.1 p.p.b. For each substance and a value of 0.5 p.p.b. for total substances.

For the pesticides studied by G.C./E.C.D. we summarize that:

- The trifluralin is the most popular and its highest concentration is detected for the site number 5 (1.57 p.p.b.).
- The highest concentration of penconazole was observed for site 5 (1.27 p.p.b.).
- The presence of dimethoate for the site 6 with a concentration 0.99 p.p.b.
- The-cyhalothrin comes with an acceptable concentration 0.13 p.p.b. for site 3 (figure 3).



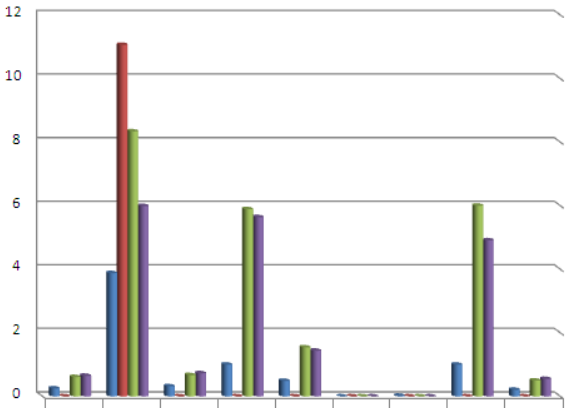
	1	2	3	4	5	6	7	8	9
Trifluralin	1.29	0.48	0.37	0.5	1.57	0.25	0	0.45	0.41
Penconazole	0.39	0	0.3	0	1.27	0.21	0.58	0	0.88
Dimethoate	0	0	0	0	0	0.99	0	0	0
Cyhalothrin	0	0	0.13	0	0	0	0	0	0

Fig. 3: The concentrations of the pesticides detected by G.C. in each studied site (p.p.b.)

As regards pesticides studied by H.P.L.C.-U.V./visible:

-The presence of kresoxim-methyl is in almost all sites (except site 6) with concentrations between 0.02 and 3.88 p.p.b., the latter is observed for site 2.

- A value alarming pyrimethanil for site 2 (11.06 p.p.b.).
- High levels of abamectin, méthalaxyl are observed especially for sites 2, 4 and 8 (Figure 4).



	1	2	3	4	5	6	7	8	9
Kresoxim methyl	0.25	3.88	0.32	1	0.49	0	0.02	1	0.21
Pyrimethanil	0	11.06	0	0	0	0	0	0	0
Methalaxyl	0.61	8.34	0.67	5.89	1.54	0	0	6	0.5
Abamectine	0.65	5.99	0.73	5.64	1.44	0	0	4.91	0.55

Fig. 4: The concentrations of pesticides detected by L.C. in each studied site (p.p.b.)

These results are alarming with regard to the recommendations on the quality of water intended for human consumption especially for sites 2, 4 and 8.

By grouping the pesticides detected at each site by type, it was observed that fungicides and insecticides are the most common pesticides detected and this can be explained by the nature of the most widespread crop in the region of Akkar, which is potato.

Conclusion:

By comparing the amount of pesticides detected in each site and the concentrations of nitrate and nitrite, there is some correlations between the two types of chemical pollution (nitrate and nitrite) and micropollutants (in pesticides), especially the sites 2, 4, 8 for which it was observed the highest concentrations in the three pollutants.

In this study, the results show the presence of chemical contamination (mineral and organic) in almost all sites, which may meet certain levels certainly scary especially sites 2, 4 and 8.

During this study, it was found sometimes a situation of widespread contamination with the simultaneous presence of several pesticides on the same site and exceeded the standard for pesticides, nitrate and nitrite in drinking water. This type of observation is one of the main issues raised in the interpretation of analytical results for the cumulative effects of long-term all of these products on health are still poorly understood.

The results of our chemical analysis show that the groundwater is not necessarily good, in contrast to the traditional belief which assumes that the ground water rid of contaminants during its infiltration into the groundwater. The power of retention by the soil micro is linked to the chemical nature of the latter, the soil type and depth of groundwater. The reality is that the ground delays the groundwater contamination but does not eliminate it!

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