academicJournals

Vol. 8(31), pp. 4269-4279, 15 August, 2013
DOI: 10.5897/AJAR12.1706
ISSN 1991-637X ©2013 Academic Journals
http://www.academicjournals.org/AJAR

African Journal of Agricultural Research

Full Length Research Paper

Pesticides occurrence in groundwater sources of Mouzaïa (Algeria)

Hafida Lebik and Hamid Ait-amar

[1]Laboratoire des Sciences de Génie des Procédés Industriels, Algeria.
[2]Faculté de Génie Mécanique et de Génie des Procédés, USTHB, BP 32, El Alia, 16111 Algeria.

Accepted 30 May, 2013

Mitidja Plain, located in the North of Algeria, is considered as the most important agricultural area of Algeria, where pesticides are widely used. This study assesses pesticides occurrence in the groundwater beneath Mouzaïa situated in the west of Mitidja. In 6 selected sampling points, 5 pesticides belonging to different chemical families: oganophosphorus (Malathion, Parathion), organochlorines (DDT and Aldrine) and triazines (simazine); were analyzed using GC-MS techniques preceded by liquid-liquid extraction (LLE) or solid phase extraction (SPE). To identify the subject in its environmental setting, analysis of physicochemical parameters in groundwater and soil samples from study area were also carried out. Results of analysis of those parameters demonstrated the good quality of water and soil samples only rates of phosphates in soil were high up to 300 ppm due probably to fertilizers use. Aldrin, Simazine, and Parathion weren't detected in groundwater samples due to the low use of these pesticides in the study area; whereas DDT, even if it's banned for use in Algeria for years, was detected in one sample which demonstrates its high persistence in the environment. Malathion which was detected in all groundwater samples reached high concentrations that reached 0.96 µg/L, exceeding the current drinking water quality limits established by the World Health Organization (WHO).

Key words: Solid phase extraction, groundwater, physicochemical parameters, pesticides.

INTRODUCTION

The development of organic chemistry that began in the 1940s, introduced a new era of synthetic pesticides that became the largest spectrum of industrial chemicals used in modern society. Today, we count more than 900 active ingredients (Ware and Whitacre, 2004) which enter in the composition of thousands of pesticides products, mainly used in agriculture; to control insects, diseases, weeds and other pests. However, even if pesticides' use is an essential tool in increasing productivity, enhancing quality, protecting livestock, and fighting vector diseases; there are now evidences that these products do create risk to man and his environment.

Each year, pesticides contribute to an estimated 26 million human poisonings and 220,000 deaths worldwide (Pimentel and Pimentel, 2008). In Algeria, pesticides poisoning came into second position after drugs in the causes of acute intoxications (Mokrani, 2005). Although chronic effects of pesticides exposure on human health are less readily identifiable, a wealth research conducted in this context (Krieger et al., 2010; WHO, 2008; MDRGF, 2008; Sténuit and Van Hammée, 2008; Cox C, 2006; Pretty, 2005; Sanborn et al., 2004; Solomon et al., 2000) found a signification association between pesticides exposure and many health problems including: cancer, neurological damage, reproductive and developmental hazards, immunotoxicity and endocrine disruption.

Despite their widespread application, only a small amount of the pesticides used actually reaches their targets.

*Corresponding author. E-mail: lebikhafida@yahoo.com, hait-amar@usthb.dz.

About 3% of herbicides and insecticides do so (Fedorov et al., 2004); the rest is lost; falling on non-targeted organisms or transported into different environmental matrices. In addition many pesticides eventually end up in groundwater, which represent; if we eliminate the polar ice caps, the source of 98% of total fresh water (Alvarez and Illman, 2006). Major concerns about groundwater contamination with pesticides are that about one-half of the human population obtains its water from wells and once groundwater is contaminated, the pesticide residues remain for long periods of time. Not only are there extremely few microbes present in groundwater to degrade the pesticides, but the groundwater recharge rate is less than 1% per year (Pimentel, 2005). Thus, assessing pesticides occurrence in groundwater is necessary to preserve its quality.

Pesticides are one of the main contaminants the most detected in groundwater. In the US where we use pesticides the most in the world (Alvarez and Illman, 2006), According to the USGS (United States Geological Survey) report about the program of national assessment of pesticides in streams and groundwater; published in 2007, more than half of the shallow wells sampled, and 33% of the deeper wells, contained at least one pesticide (USGS, 2007). In France, a study carried out by IFEN (the Environment French Institute) showed that pesticides contaminated 61% of samples in which 27% exceeded the standards of drinking water (IFEN, 2006). Similar results have been reported in different studies conducted in many countries: India (Sankararamakrishnan et al., 2005; Singh, 2001), Turkey (Aydin and Yurdun, 1999), Australia (Kennedy et al., 1998), Morocco (El Bakouri et al., 2008).

In Algeria, there is no systemic assessment of the occurrence of pesticides in the different environmental compartments. So, there are only two studies conducted in Algiers that treat this subject and they revealed that, the pesticides residues exceeded the maximum level in drinking water (maximum level is 0.1 µg/L for each substance and 0.5 µg/L for the sum of all pesticides) respectively 30% (Bouziani, 2008) and 50% (Moussaoui et al., 2005) of groundwater samples. Considering this, and knowing that 30,000 tones of pesticides, according to the Algerian Environmental Protection Association (2009) are used every year, and the fact that Algerian farmers tend to overdose the pesticides in the treatment mixture or increase the number of treatments (Afrique Agriculture, 2004), the situation may be alarming.

This study investigates the presence of selected pesticides in groundwater beneath Mouzaïa; an agricultural zone situated in The Mitidja Plain, in the north of Algeria. The fate of pesticides once introduced into the environment and the risk of their leaching into groundwater are influenced by many processes and multiple factors, including not only pesticide properties, but also soil properties (structure, organic matter, clay content, etc.), site hydrological processes (rainfall, permeability, etc.) and agricultural practices (time and frequency of application, irrigation, type of crops, etc.) (Arias-Estévez et al., 2008; Van Der Werf and Zimmer, 1998). For these reasons, the selection of the study area is an important criterion in the investigation of the presence of pesticides in groundwater.

MATERIALS AND METHODS

Presentation of the study area

The study area is the municipality of Mouzaïa which is located in the Mitidja plain, considered as the most important plain of the north of Algeria with a total surface of 1450 km² (Belaïdi and Rebhaoui, 2005). It is characterized by a Mediterranean climate with an average annual rainfall estimated between 650 to 1000 mm per year (Lounis et al., 2011), fertile lands, abundant groundwater resources (with an annually extracted flow of 272 hm^3 (Belaïdi and Rebhaoui, 2005) and reach surface water. It's the pivot of the agriculture of the whole region.

Mouzaïa is a high agricultural activity zone counting over 301 farms, where 90% own at least one well (Imache et al., 2007). The most cultures practiced in it are, respectively, citrus fruits 38%, arboriculture 17%, cereals 27%, wheat /vegetables as rotational culture 11%, crops 6% and at last vine 1% (Imache et al., 2006). It covers an area of 5625.04 ha corresponding to about 65% of the total surface of the perimeter of the Mitidja West Slice1 (Imache et al., 2006) where it belongs too.

Today, because of the irrational use of the aquifer, the Mitidja is subject to an overexploitation causing the reduction of groundwater level. Other problems, just as alarming threat also the quality of this resource like nitrates pollution, hydrocarbons and marine water intrusion (Belaïdi and Rebhaoui, 2005). Due to these reasons, a probable groundwater contamination by pesticides in these areas is suspected. Since there is no studies carried out in the region treating this subject, it was decided to initiate a first study of its kind which investigates the presence of pesticides in Mouzaïa groundwater.

Sampling strategy

Six important sites situated at the Mouzaïa ground water table (MO-1, MO-2, MO-3, W063-470, W063-332 and W041-1768), were selected to take samples (Figure 1), considering different factors: (a) the repartition in the study area (The first three located in exploitations inside the zone while the others are in the borders near the streams where there is a great exchange groundwater/surface water), (b) The type of culture practiced in the exploitations; there's Citrus fruits in MO-1, vegetables in MO-2, and Arboriculture in MO-3, (c) The network established by The National Agency of Hydraulics Resources (ANRH) for the monitoring of the Mitidja water resources which includes three among the six points (W063-470, W063-332 and W041-1768).

The campaign of sampling conducted by the ANRH in the same region revealed that others pollutants concentrations were the highest during the autumn and the spring periods because of the groundwater recharge (Belaïdi and Rebhaoui, 2005). Adopting the same strategy, water samples were collected in November 2010 corresponding to the autumn time in Algeria. Soil samples were also collected from (MO-1, MO-2, MO-3, and W063-470) for assessing soil physicochemical properties.

For each sampling point, triple water samples were collected, in 1 L borosilicate glass bottles cleaned thoroughly and rinsed with the extracting solvent just before use, instantaneously from the wells and stored at 4°C in the dark. Then extraction and analysis were carried out within a period not exceeding the 6 days after sampling. Before analysis, the samples were filtered through membrane filter with pores size of 0.2 µm and diameter of 47 mm to remove sand and debris.

Soil was sampled adopting a diagonal plan which consists in taking samples every 10 m, while walking diagonally through the field. Subsamples thus obtained were mixed proportionally to get the final sample called 'the composed sample' that would allow having reliable results.

The samples were taken from the upper 20th centimeters of the soil. From one point to other, the procedure was as systematically as possible, in order to reproduce the same conditions of sampling. To preserve their proportionality, the elementary samples were collected in polyethylene boxes of the same volume. Particulars zones were avoided during sampling, to have a representative samples. At the end of the sampling procedure, the composed sample of a total weight of 2 kg obtained by mixing the elementary samples, was put in polyethylene bags hermetically closed, conserved at the temperature of 4°C and conduct, within the 24 h of sampling, to the sciences laboratory of soil belonging to The Algerian Agronomic Research Institute (INRA), where they were tasted for pH, conductivity, $CaCO_3$, phosphates, carbon, and mater organic.

Physicochemical analysis

In order to evaluate the global quality of groundwater, physicochemical parameters were also evaluated in soil and water samples.

Water analysis

Temperature, pH, conductivity, turbidity, and other elements indicator of pollution as nitrates, phosphates and dissolved oxygen analysis were performed in water samples.

The pH was measured *in-situ* with a digital pH-meter of EUTECH Instruments *(*Ecoscan pH5) according to NF T 90-008. This apparatus has also a probe for measuring temperatures. Conductivity assessment was performed by means of HANNAH Instruments EC 214 conductivity meters according ISO 7888 method. For the turbidity, a turbidimeter of Merck Turbiquant 1500T apparatus based on nephelometric method was used according to AFNOR NF EN 27027 method. *In-situ*, WYW OXI 330i oxygen meter was used for the measuring of dissolved oxygen according to ISO 5814 method.

Nitrates detection was monitored with a spectrophotometric method (ISO 7890-3) based on sulfosalicyclic acid, by absorbance measurements on HACH Lange, series DR 2800 at 420 nm. Whereas, phosphates measurements were performed, using the same apparatus, and according to NF EN 1189 method, by absorption in the presence of ammonium molybdate, at 700 nm.

Soil analysis

The soil analysis from 4 samples (MO-1, MO-2, MO-3, W063-470) concerns the carbon determination with the ANNE method (NFX 31-109), where the sample is oxidized by potassium bichromate in sulfuric medium; the total carbonates using Bernard calcimeter (NF-ISO-10693), it's based on the characteristic reaction of calcium carbonates in the presence of hydrochloric acid; the conductivity of the soil was determined by the analysis of cations and anions in aqueous extract where the rate of dilution of soil is 1/10; the pH was measured by electrometric apparatus using a dilution rate soil/water of 1/2.5; the digestible phosphorus is determined by the Olsen method (NF ISO 11263).

Pesticides analysis

Chemicals and reagents

All reagents were of analytical grade. Solvents of chromatographic purity were purchased from SIGMA-ALDRICH (Seelze, Germany). For SPE, 1 g C-18 SPE (Solid Phase Extraction) cartridges types CHROMABOND were obtained from (MACHERY NAGEL, Germany). Analytical certified standards were acquired from SIGMA-ALDRICH (Seelze, Germany) and SUPELCO Analytical (Bellefont, PA, USA). The purity of all reference standards was greater than 95%.These standards were used to prepare individual pesticide stock solutions at 500 mg/L in acetone. Primary dilution standard solution (PDS) of 0.5 ppm and 0.5 ppb were prepared from stock standard solutions and pure hexane or ethyl acetates according to the extraction solvent used for each compound. Working solutions were prepared by mixing appropriate volumes of the PDS to obtain final concentrations at the range of 0.01-10µg/L. Each time 2 types of working solutions were prepared: one contains PDS of Organochlorines pesticides (OCs) to be analyzed and the other contains PDS of OPs and triazines pesticides to be analyzed.

Sample preparation

OCs and OPs/triazines pesticides were analyzed conforming to the directives of the AFNOR published respectively, in NF EN ISO 6468 February1997 and EN ISO 11369 August 1997 (AFNOR, 2001), the recommendations of the American Public Health Association (Clesceri et al., 1999) and the EPA instructions (Lawrence, 1996).

Organochlorine pesticides (OCs)

1 L water sample was extracted by dichloromethane and hexane as described below. In the first cycle, the sample was extracted with 100ml dichloromethane by shaking vigorously the mixture in separatory funnel for 5 min before allowing the layers to separate for at least 1 h. Then, the organic phase was recovered while the aqueous phase was extracted again with 100 ml of hexane in the separatory funnel. A last cycle of extraction was performed on the aqueous phase by 100 ml of hexane. All organic phases were combined dried by anhydrous sodium sulfate (previously dried in the oven for 4 h at 400°C and cooled, first at 200°C, then, at ambient temperature), and concentrated to 1.5 ml by a rotary evaporator HAHN Vapor (HS-2005V-N) under a gentle stream of Nitrogen for GC determination.

Organophosphorus pesticides and triazines

1 L water sample was extracted by 1g C-18 SPE cartridges types CHROMABOND, after pH verification and neutralization, if necessary. The cartridge was connected to a vacuum manifold system (MACHERY NAGEL, Germany) where it was conditioned with 10 ml of ethyl acetate dried and rinsed by 5 times their volume (5 × 6 ml) , consecutively, with methanol and deionized water. The whole volume of water sample was loaded through the column at a flow rate of 5 ml/min and dried under Nitrogen throw.

Afterwards, pesticides were eluted using 10 ml of Methanol-Ethyl Acetates (50:50, v:v). The final volume was taken to dryness under Nitrogen stream till 1.5 ml for gas chromatography (GC) determination.

Apparatus and chromatographic conditions

All experiments were performed on Agilent - 6800 plus GC coupled

Table 1. Results of physicochemical analysis of soil samples.

Identification	pH	Conductivity (dS/m)	$CaCO_3$ (%)	Phosphate (ppm)	Carbon (%)	Organic matter (%)
MO-1	7.39	0.24	2.80	150	1.64	2.83
MO-2	8.07	0.26	12.00	60	1.43	2.47
MO-3	8.00	0.24	6.00	150	1.64	2.83
W063-470	7.54	0.25	8.80	300	1.95	3.35

to Agilent MSD-5973 Mass Spectrometry detector (Agilent Technology, USA) system. The quadrupole mass spectrometer was operated in electron impact ionization (EI) mode at 70 eV. The transfer line was set up at 280°C. The source and the quadrupole were at 230 and 150°C, respectively. A sample volume of 2.5 µl was injected in splitless mode with a 7683 BAgilent auto sampler. HP-5MS, 30 m × 0.32 mm Di, 0.25 µm particle size capillary column was used. The carrier gas was ultra pure helium with 1.2 ml/min flow rate. Measurements in the GC-MS were performed in the Single-Ion Monitoring (SIM) mode. For the acquisition and the data treatment MSD-ChemStation D.01.02.16 software was used.

For OCs analysis, injection temperature was 250°C and the following temperature program was used: 100°C for 1min increased to 170°C at 15°C/min and maintained for 3 min, then to 270°C at 15°C/min maintained for 7 min.

For OPs and triazines analysis, injection temperature was 280°C and the following temperature program was used: 90°C for 4 min increased at 10°C/min to 150°C, then at 5°C/min to 240°C and maintained for 1.5 min. Finally at 15°C/min to 280°C and maintained for 10 min.

Identification, quantification and recovery studies

Multi residue method was used for the analysis, thus, the identification of the target pesticides was carried out by searching in the appropriate retention time windows obtained by the injection of the standard solution which contains the compounds to be analyzed. The confirmation of a previously identified compound was established by the database of MSD-ChemStation.

The samples quantification was carried out by injecting working solutions of pesticides at different concentrations to perform calibration curves. From these calibration curves the accuracy of the analyzed compound in the sample solution was calculated. The linearity of the calibration curves was studied using peak area. The Selectivity was monitored by running control blank samples in each calibration.

The appraisal of analytical results, for the pesticides quantified, was performed by assessing the rate of recovery. For this purpose blank water samples were spiked with the target analytes dissolved in acetone, at a low concentrations level. The fortified sample obtained is then extracted and analyzed in accordance with the specified method.

RESULTS AND DISCUSSION

Selection of the pesticides to analyze

In Algeria, more than 400 pesticides products (DPVCT, 2007) are authorized for sale and most of them are used in huge quantities, especially, in the agricultural regions. Investigating the presence of all those pesticides in Mouzaïa groundwater is impossible in view of the price of the chromatographic analysis. Considering these conditions, another approach was adopted based on the chromatographic analysis in mode SCAN used as a primary detection method.

Samples have been collected from the water of different sampling points and mixed proportionally to constitute two composed samples; one sample was treated by LLE and injected using SCAN mode in the same conditions of analysis of OCs pesticides; whereas the other sample was subject to SPE and injected in the same conditions of analysis of OPs and Triazines pesticides using SCAN mode. For the two samples, the presence of residues in water samples wasn’t established for any of pesticides compounds. These results are justified by the fact that the residues investigated are at trace levels and the presence of interferences may make the identification of these residues from full scan spectral data very hard to establish. So the use of selected ion monitoring (SIM) technique provides lower detection limits (Hollandmass, 1990), however this technique is applicable for specified compounds which requires the selection of pesticides to analyze first.

Adopting another strategyfield investigations were conducted in the site during 3 years (2008 to 2010). The result of these investigations shows that OPs pesticides are the most chemical used in Mouzaïa (Figures 2 and 3). A list of priority pesticides for Mouzaïa was established based on these results and taking into count the agricultural profile of the sampling zone, the historic of pesticides use, the chemical proprieties of those compounds and their leaching probability and finally the most commonly detected pesticides in groundwater. At the end, 5 pesticides were selected for the study; OCs pesticides (DDT, Aldrin), OPs (Malathion, Parathion) and Triazines (Simazine).

Results of physicochemical parameters analysis

In soil

Results of physicochemical parameters analysis in soil, resumed in Table 1 showed that, low salinity and low total carbonates rates are detected for all samples while phosphorus levels are high. The pH is an important parameter that influences the solubility of nutrients,

Table 2. Results of physicochemical analysis of water samples.

Identification	T (°C)	pH	Dissolved oxygen (mg/L)	Conductivity (µS/cm)	Turbidity (N.T.U)
MO-1	23.30	7.39	5.78	473	0.65
MO-2	23.08	7.59	5.71	449	0.04
MO-3	22.60	7.66	5.46	395	0.28
W041-1768	20.60	7.94	6.46	1012	0.04
W063-470	21.40	7.68	6.20	1001	0.01
W063-332	22.70	7.52	6.30	700	0.01

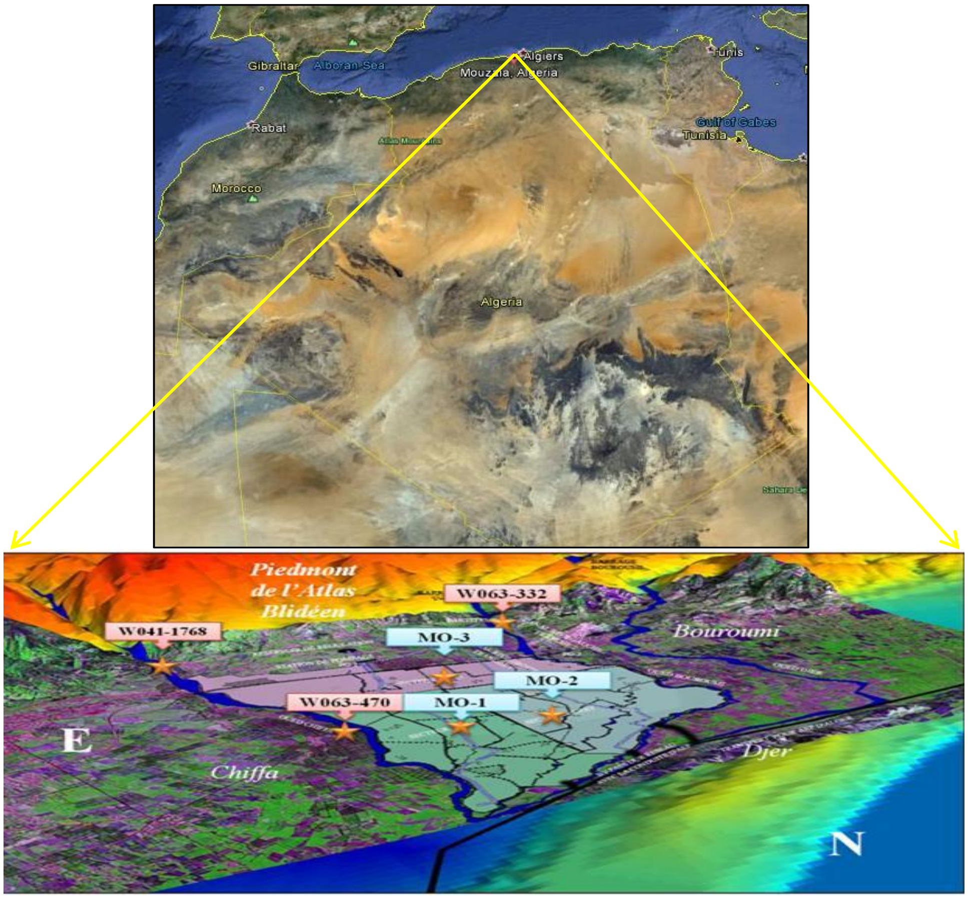

Figure 1. Location of sampling sites in Mouzaïa, North Algeria (ENSA).

activity of microorganism and absorption balance (Wauchope et al., 2001). Soils from MO-1 and W063-470 are slightly alkaline whereas the others are alkaline. The organic matter represents an important fraction of soil since the rate of pesticide leaching in soil decreases with increasing organic matter (Van der Werf, 1996). In this study, soil samples indicate an acceptable content of organic matter with an average amount of 2.87%. The transfer of pollutant into groundwater is also function of the permeability, the more soil permeability is important, the more speed of pollutant transfer is significant. Mitidja Plain is characterized by permeability of unsaturated zone at the range of 10^{-4} to 10^{-9} m/s.

In water

Table 2 resume results of physicochemical analysis in water. Water's temperature governs solubility in particularly gases'; it is directly related to waterorigins (Boeglin, 2009). Samples in this study were taken from groundwater; given the fact that, they were protected underground; their temperature was stable (20.6 to 23.3°C) and not affected by climatic conditions.

pH of natural waters is directly related to the nature of the lands crossed. Hard water has high pH whereas siliceous lands or soils poor in calcareous have pH in the order of 7 and sometimes less In this study, pH samples varies between 7.39 and 7.94, and even if these waters present a slightly alkaline character, they are within the limits of the guidelines values advocated by the European directive which gives as a guide level a variation of 6.5 to 8.5 (Rejsek, 2002). Dissolved oxygen concentrations went from 5.46 to 6.6 mg/L; this is the case of deep waters which contain, in most cases, only a few milligrams per liter of dissolved oxygen.

Conductivity measurements allow evaluating the overall mineralization of water; it is a parameter that depends on the geology of the lands in contact with water. Generally, the mineralization increases with the depth. Different types of facies can be distinguished according to geological origin *(*Boeglin, 2009*)*. For MO-1, MO-2, MO-3 and W063-332 conductivity is, respectively, 473, 449, 395 and 700 µS/cm. These values situated between 200 and 700 µS/cm, are characteristic of waters of the Jurassic and Cretaceous, synonyms of an average mineralization. For the others: W041-1768 and W063-470, the conductivity is respectively equal to 1012 and 1001 µS/cm, which means values between 1000 and 1500 µS/cm characteristic of the Triassic, synonym of high mineralization.

Turbidity of water is due to the presence of suspended solids dispersed in colloidal state such us clay, silts, and organic matter *(*Boeglin, 2009). Low turbidity (0.01 to 0.65 NTU) was observed for all samples.

Naturally occurrence of nitrates in waters is largely associated with the mineralization and oxidation of Nitrogen; they are not absorbed by soil so there is a probable risk of migration to water table. Agricultural activity plays an important role in the process of enrichment of water by nitrates; it's the main source of groundwater pollution *(*Huang et al., 2010*)*.

In Algeria, nitrates are the most common contaminants found in groundwater. During the analysis campaign conducted by the National Agency of Hydraulic Resources (NAHR) in the Mitidja plain during 2007, nitrates were detected at levels that reached 200 mg/L (NAHR Report, 2007) exceeding the standard value of drinking water in Algeria fixed at 50 mg/L NO_3^-. In this study, the detected concentrations were between 11.85 and 34.88 mg/L (Figure 4). This improvement in water quality may be explained by the decrease in use of fertilizer in the region due to severe Algerian laws on traffic and purchase of chemical fertilizers considered as the main source of nitrate in groundwater *(*García-Galán et al., 2010; Razowska-Jaworek and Sadurski, 2005*)*.

Furthermore, these low levels of nitrates can be explained by land use in the study area which is dominated by arboriculture considered less water pollutant comparing to vegetable crops large consumer of fertilizers and therefore most likely to pollute ground water *(*Andrade and Stigter, 2009).

Orthophosphates in soil and water result from the decomposition of organic matter and the leaching of fertilizers used in agriculture. They can also come from industrial activity, detergents and domestic wastewater *(*Bremond and Perrodon, 1979), cite in assessing ground water quality in the irrigated plain of Triffa north-east Morocco, 2008). It must be noted that, low levels of orthophosphates were detected for all water samples and do not exceed 4.43×10^{-3} mg/L (Figure 5). These concentrations are far from the value of 0.5 mg/L, beyond which pollution of natural water by phosphates can be suspected *(*Rejsek, 2002).

The main reason for these low concentrations of phosphates can be explained by the fact that these latter, being fixed to the ground, have little mobility *(*Lerner and Harris, 2009*)*. This is confirmed by high levels of phosphates in the soils samples analyzed. However, an excessive enrichment of soil in phosphates leads to his migration into groundwater. Crops fertilization, principal source of phosphorus *(*Banton and Bangoy, 1997*)*, was low in the study area, so the risk of water pollution by this source has been eliminated; although pesticides may also contribute to this form of pollution *(*Rejsek, 2002).

Results of pesticides analysis

In order to obtain retention times of each target molecule, standard solutions of 500ppm were injected in SIM mode according to the established analytical chromatographic method. Table 3 shows the resume ions quantifications for each analyzed compound and the retention time obtained.

Calibrations curves were performed by injecting working solutions of pesticides at different concentrations. Good linearity of the response was found for all pesticides at concentrations within the tested interval, with good linearity: linear coefficient reaching 0.997. Detection limit (DL) estimated using S/N ratio 1:3, is found to be 0.1 µg/L for Malathion and DDT; 0.01 µg/L for Aldrin, Simazine and Parathion. Among the molecules analyzed neither Aldrin nor Simazine and Parathion were detected in the six samples.

Aldrin

Aldrin is a molecule strongly adsorbed in the soil, particularly by organic matter. In the study area, the average percentage of soil organic matter was 2.87%. This content is likely to fix Aldrin to the soil, and thus, facilitate its oxidation to Dieldrin which is very stable in soil *(*Khan, 1980*)*. In addition, Aldrin is resistant to leaching *(*Canada, 1995*)* if it is not applied in large

Table 3. Quantifications Ions researched and retentions times obtained.

Molecule	Target ions quantifications	Retention times obtained (min)
Aldrin	263, 265, 293	11.238
DDT	235, 237, 165, 199	13.806
Simazine	201, 186, 203	14.856
Malathion	125, 127, 173	18.407
Parathion	291, 139, 261	18.721

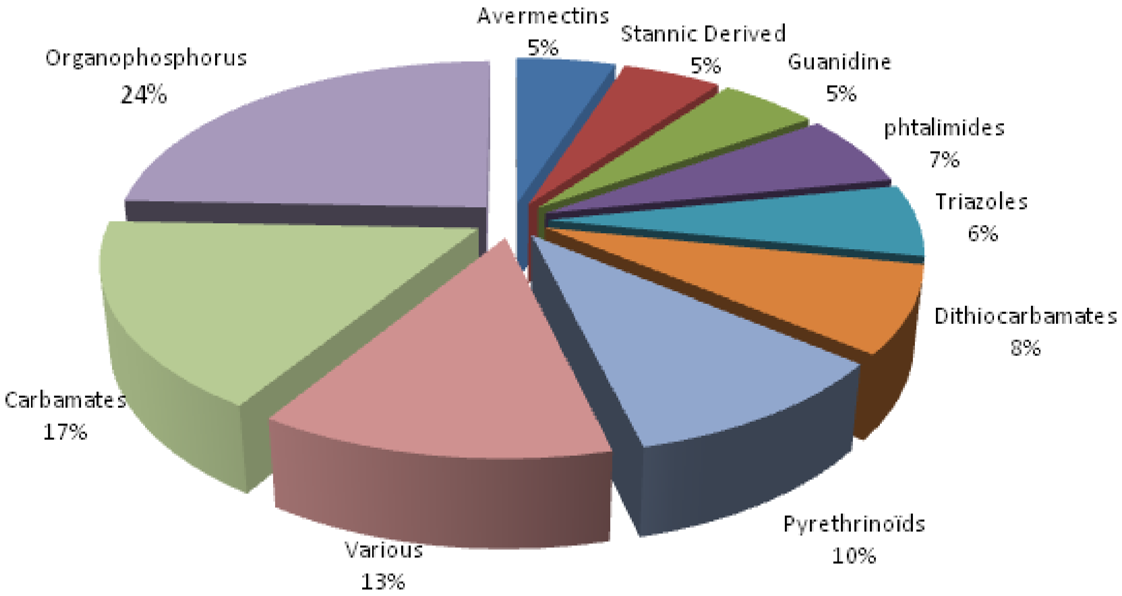

Figure 2. Chemical families of the pesticides used in Mouzaïa.

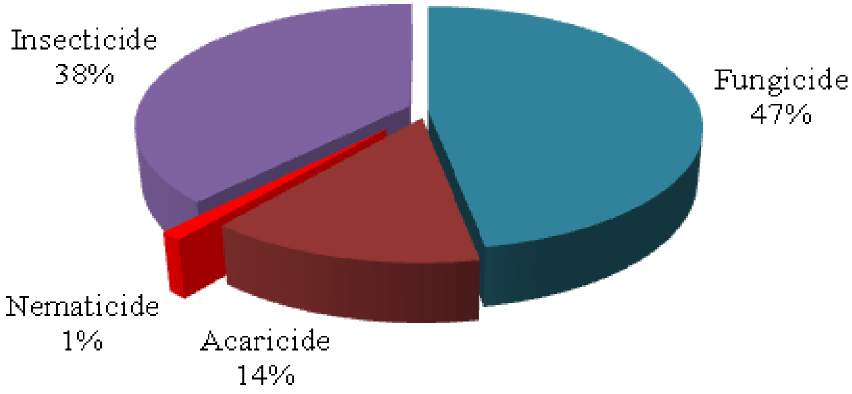

Figure 3. Repartition of Pesticides categories used in Mouzaïa.

quantities, which results in a low risk of groundwater contamination, explaining its absence in our samples.

Simazine

According to field studies, herbicides in general and Simazine, in particular, are not used in the study area. So its absence in groundwater samples is quite expected.

DDT

Even if DDT is banned for use in Algeria for several

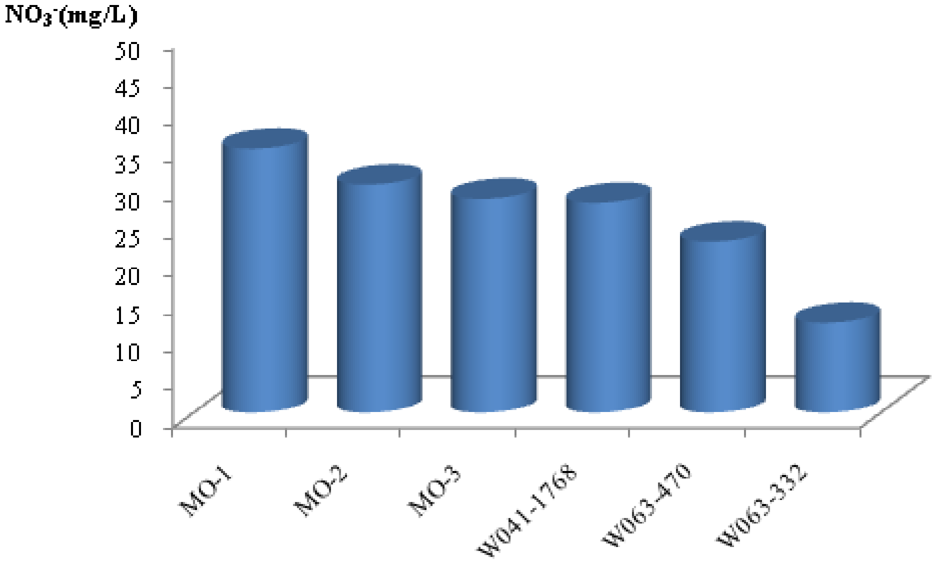

Figure 4. Results of nitrates assessments in groundwater samples.

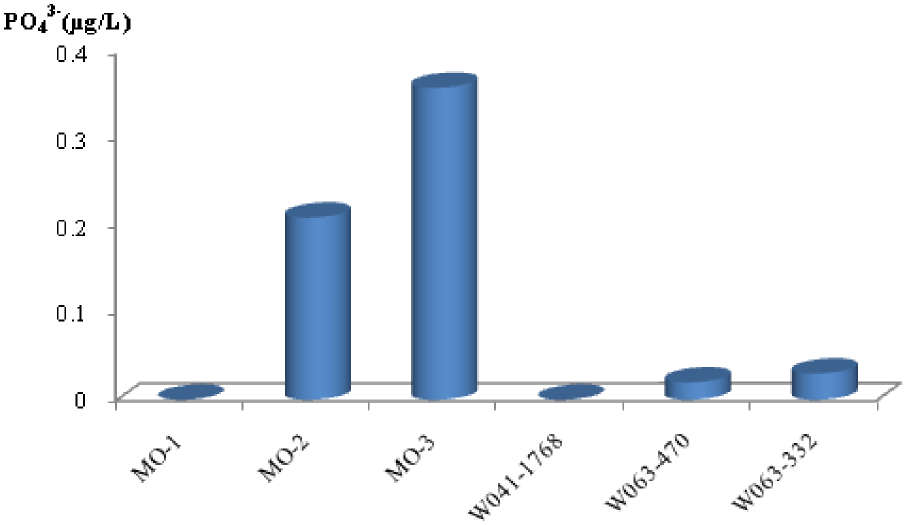

Figure 5. Results of orthophosphates assessments in groundwater samples.

years, it was detected in MO-2 (Figure 6). The presence of this element, illustrates its high stability in the environment, due to its properties: persistence and high lipid solubility.

Parathion

This is considered as a pesticide with low leaching risk (GUS = 0.2) *(*Andrade and Stigter, 2009*)*, so we do not expect to find it in groundwater. However, in areas where this pesticide is applied in large quantities, the situation is different and his occurrence into groundwater may be possible.

Malathion

While Malathion wasn't detected in the two locations (W041-1768, MO-3), his presence in water samples have been observed for three analysis points W063-332, W063-470, and MO-2 with high concentrations equal to 0.73, 0.75 and 0.96 µg/L, respectively. These values are alarming toward groundwater quality, reaching levels 10

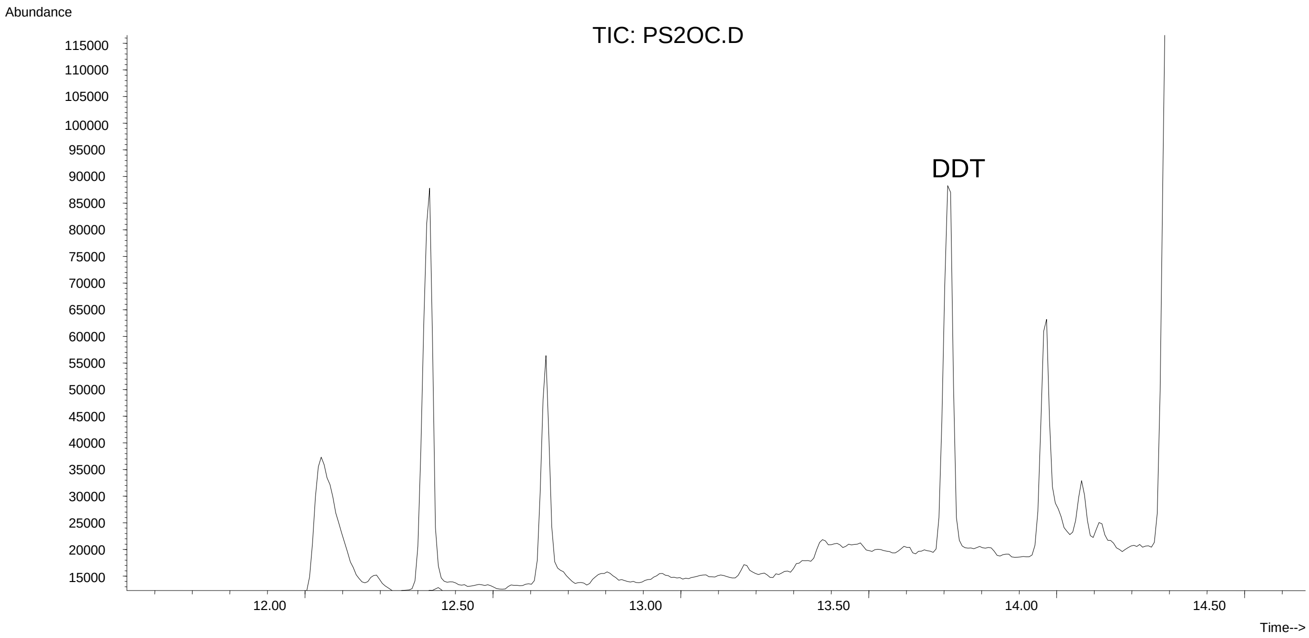

Figure 6. DDT Peak detected in MO-2.

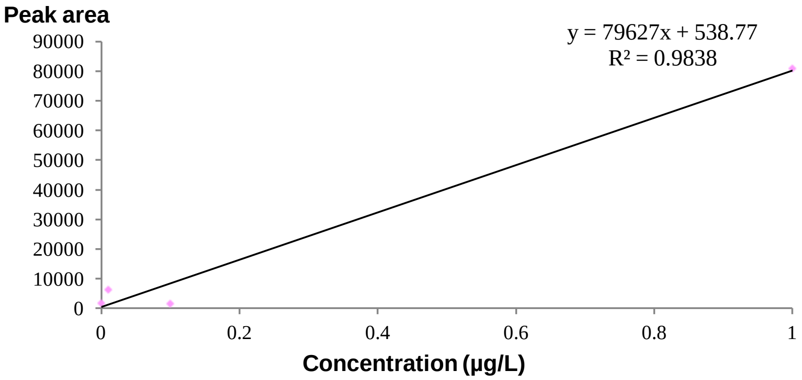

Figure 7. Aqueous calibration curve.

times higher than the guideline values recommended by WHO for the maximum concentration of each compound (0.1 µg/L), and twice those recommended for the total amount of pesticides residue (0.5 µg/L). Malathion was also detected in MO-1. Looking at soil properties and water table characteristic, groundwater in the study area appears to be well protected against contamination; So Malathion presence in such a large quantity in water samples is probably due to its intensive use in Algeria.

Recovery studies

The quality of the all procedure of extraction was verified by processing recovery study for the Malathion, the only pesticide quantified in water samples. For this purpose, aqueous calibration curve has been established by fortifying pure water with aqueous solutions of Malathion prepared previously by diluting Stock Solutions in Acetone. The fortified samples thus obtained were extracted and analyzed in the same conditions as the samples. Aqueous Calibration curve was then determined and recovery rate for the Malathion (T_{Rm}), was calculated, value of 97.08% was obtained (Figure 7).

Conclusion

Although physicochemical analysis indicate the goodquality of samples either in soil or water; results of pesticides analysis showed that, Malathion was detected in all groundwater samples of Mouzaïa and the concentrations found reached high values exceeding the current drinking water quality limits established by the WHO. The presence of this compound could be attributed to the intense agricultural activity in the study area associated with the large use of Organophosphorus pesticides especially after Organochlorines pesticides have been banned for use in Algeria. The analysis results also revealed that, pesticides not used in the study area such as herbicides (simazine) weren't detected in the analyzed groundwater samples. Aldrin considered as POP and banned for use in Algeria for years wasn't detected in samples due probably to its strong capacity of adsorption into soil particularly with the presence of organic matter at 2.87%. A same result was found for Parathion whereas DDT was detected in one sample.

In Algeria, more than 400 pesticide products with different physicochemical properties are authorized for use. It must be pointed out that, this work represents a first approach to study pesticides groundwater pollution in Mouzaïa; it was limited to only few pesticides which are either commonly used in Mouzaïa region or found frequently in groundwater samples; it was also restricted to only few sampling locations during one analysis campaign. However, results found in this study would be a useful tool to carry out more detailed monitoring research on different seasons with a wider spectrum of pesticides to get a clear baseline data for the entire Mouzaïa region. Finally, it should be noted that, these results helped us to raise farmers from the region awareness on pesticide use to minimize the impact of the agricultural activity on the environment.

ACKNOWLEDGMENTS

This study would not have been accomplished without the help of Mr CHEHAT Foued, General Manager of the Algerian National Agricultural Research Institute (INRAA). The authors are indebted to Mr Meklati Brahim, Chief of Research of Physicochemical Analyses Centre (CRAPC) and Mr Boumechhour Abdenour from the same organism for there technical support; they also wish to thank Mr Hartani Tarik from the High National School of Agronomy (ENSA) for his precious help.

REFERENCES

AFNOR (Association Française de Normalisation) (2001). Qualité de l'eau AFNOR, Tome 2: Normes et réglementation « environnement ».6th Edition. Pesticides and PCB's. AFNOR.

Afrique Agriculture (2004). Protection: Un secteur dynamique qui s'expose au Phytosem. Afrique Agriculture /Agrieconomics. Novembre 2004, pp. 18-31.

Alvarez PJJ, Illman WA (2006). Bioremediation and Natural Attenuation: Process Fundamentals and Mathematical Models. John Wiley & Sons Inc. P. 614. Andrade AIASS, Stigter TY (2009). Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use. Agric. Water Manag. 96:1751-1765.

Arias-Estévez M, López-Periago E, Martínez-Carballo E, Simal-Gándara J, Mejuto JC, García-Río L (2008). Review: The Mobility and Degradation of Pesticides in Soils and the Pollution of Groundwater Resources. Agric. Ecosyst. Environ. 123:247-260.

Aydin A, Yurdun T (1999). Residues of Organochlorine Pesticides in Water Sources of Istanbul. Kluwer Academic Publishers. Urban Groundwater Pollution in Turkey: Water Air Soil Poll. 111:385-398.

Banton O, Bangoy LM (1997). Hydrogéologie: Multiscience environnementale des eaux souterraines. Presses de l'Université du Québec/ AUPELF. P. 436.

Belaïdi M, Rebhaoui H (2005). Annuaire hydrogéologique de la nappe de la Mitidja. ANRH (Agence National des Ressources Hydrauliques) DRC-Soumâa (Blida).

Boeglin JC (2009). Contrôle des eaux douces et de consommation humaine. Ed. Techniques de l'ingénieur, P. 4210.

Bouziani M (2008). L'usage immodéré des pesticides: De graves conséquences sanitaires.*http://www.santetropicale.com/SANTEMAG/algerie/index.htm*

Bremond R, Perrodon C (1979). Paramètres de la qualité des eaux. Ministère de l'environnement Paris, p. 259. cite in. Assessing ground water quality in the irrigated plain of Triffa (north-east Morocco). Agric. Water Manag. 95:133-142.

Clesceri LS, Greenberg AE, Eaton AD (1999). Standard Methods for the Examination of Water and Wastewater. 20th Ed. American Public Health Association-American Water Works Association-Water Environment Federation. P. 2671.

Cox C (2006). Ten Reasons not to Use Pesticides. J. Pestic. Reform. 26(2):10-12.

DPVCT (2007). Direction de la Protection des Végétaux et des Contrôles Techniques. Index des produits phytosanitaires à usage agricole. Ministère de l'agriculture et du développement rural (Algérie).

El Bakouri H, Ouassini A, Morillo J, Usero J (2008). Pesticides in ground Water beneath Loukkos Perimeter, Northwest Morocco. J. Hydrol. 348:270-278.

ENSA (2007/2008). Ecole Nationale Supérieure Agronomique, Rapport rentrant dans le cadre du projet SIRMA (Systèmes IRrigués au MAghreb). Disponible sur: *www.eau-sirma.net*. Not cited in the work.

Fedorov LA, Yablokov AV (2004). Pesticides – The Chemical Weapon that Kills Life. Pensoft Publishers: Bulgaria. P. 137.

García-Galán MJ, Garrido T, Fraile J, Ginebreda A, Díaz-Cruz MS, Barceló D (2010). Simultaneous occurrence of nitrates and sulfonamide antibiotics in two ground water bodies of Catalonia (Spain). J. Hydrol. 383:93-101.

Hollandmass PT (1990). Spectrometric Determination of Pesticide Residues. Pure &App/. Chem. (IUPAC). 62(2):317-336.

Huang J, Xu J, Liu X, Liu J, Wang L (2010). Spatial distribution pattern analysis of groundwater nitrate Nitrogen pollution in Shandong intensive farming regions of China using neural network method. Mathematical and Computer Modelling, doi: 10.1016/j.mcm. 2010. 11. 027

IFEN (2006). (Institut Français de l'Environnement): Trégouët, B., Nirascou, F. Les pesticides dans les eaux : Données 2003 et 2004. IFEN 5:40.

Imache A, Chabaca M, Merabet B, Hartani T, Djebbara M, Bouarfa S, Kuper M, Le Grusse P, Le Goulven P (2006). Demandes en eau des exploitations agricoles du périmètre irrigué de la Mitidja ouest (Algérie), 2ème atelier régional scientifique et technique du projet SIRMA, Marrakech 29, 30 et 31 mai 2006.

Imache A, Le Goulven P, Bouarfa S, Chabaca M (2007). Evolutions de la demande en eau agricole dans la plaine irriguée de la Mitidja, Algérie. M., Kuper, A., Zaïri, (éditeurs scientifiques) 2008. Economies d'eau en systèmes irrigués au Maghreb. Actes du Troisième Atelier régional du projet SIRMA, Nabeul, Tunisie. 4-7 juin 2007.

Kennedy IR, Baskaran S, Sánchez-Bayo F (1998). Pesticides in Soil, Water and Produce: Analysis Environmental Monitoring and Remediation. CRC for Sustainable Cotton Production Department of Agricultural Chemistry and Soil Science the University of Sydney. P. 88.

Khan SU (1980). Pesticides in the Soil Environment, Vol.5: Fundamental Aspects of Pollution Control and Environmental Science.

Elsevier Sci. Pub. Company. P. 247.

Krieger R, Doull J, Hemmen JV, Hodgson E, Maibach H, Reiter L, Ritter L, Ross J, Slikker W, Vega H (2010). Hayes Handbook of Pesticide Toxicology, Third Edition, Volume 1, Academic Press

L'Association Algérienne pour la Protection de l'Environnement, citein, Le Quotidien d'Oran, (2009).

Lawrence KH (1996). Compilation of EPA's Sampling and Analysis Methods. Library of Congress Cataloging-in-Publication Data. Boca Raton: CRC Press LLC. P. 1716.

Lerner DN, Harris B (2009). The relationship between land use, groundwater resources and quality. Land Use Policy. 26S:S265–S273.

Lounis A, Hartani T, Aidaoui A, Sellam F (2011). Qualité des eaux souterraines dans la Mitidja : Enjeux liés à l'intensification agricole (Cas du basin versant de Sidi Rached). Ground Water Conférences sur la gestion des ressources en eau souterraine Orléans - France (14-16 Mars 2011).

MDRGF: Mouvement pour le Droit et le Respect des Générations Futures, (2008). Dossier pesticides.http://www.mdrgf.org/archive.html

Mokrani K (2005). Favorisées par la commercialisation anarchique des produits à usage domestique, les intoxications par pesticides, un problème de santé publique. J. La Tribune (Algeria), editionof 20 November 2005.

Moussaoui KM, Boussahel R, Tchoulak Y, Haouchine O, Benmami M, Dalachi N (2005). Utilisation, Evaluation, et impacts des pesticides en Algérie, Laboratoire des Sciences et Techniques de l 'Environnement: Ecole Nationale Polytechnique.

Pimentel D (2005). Environmental and Economic Costs of the Application of Pesticides Primarily In the United States, Environment, Development and Sustainability. 7:229-252.

Pimentel D, Pimentel MH (2008). Food, Energy and Society.3d Ed. CRC Press: Taylor and Francis Group, LLC. P. 402.

Pretty J (2005). The Pesticide Detox: towards a more sustainable agriculture. Earth Scan.

Razowska-Jaworek L, Sadurski A (2005). Nitrates in Ground Water: Selected Papers From the European Meeting of the International Association of Hydrogeologists, Wisla, Poland, 4-7 June 2002 Selected Papers On Hydrogeology 5. Taylor & Francis Routledge.

Rejsek F (2002). Analyse des eaux : aspects réglementaires et techniques. Centre régional de documentation pédagogique d'Aquitaine.

Sanborn M, Cole D, Kerr K, Vakil C, Bassil K, Sanin LH (2004). Pesticides Literature Review. The Ontario College of Family Physicians: *www.ocfp.on.ca*.

Sankararamakrishnan N, Sharma AK, Sanghi R (2005). Organochlorine and Organophosphorous Pesticide Residues in Groundwater and Surface Waters of Kanpur, Uttar Pradesh, India. Environ. Int. 31:113-120.

Canada (1995). Santé de l'environnement et du milieu de travail, L'aldrine et la dieldrine. http://www.hc-sc.gc.ca/ewh-semt/index-fra.php.

Singh RP (2001). Comparison of Organochlorine Pesticide Levels in Soil and Groundwater of Agra, India. Bull. Environ. Contam. Toxicol. 67:126–1322001, Springer-Verlag New York Inc.

Solomon G, Ogunseitan OA, Kirsch J (2000). Pesticides and Human Health: A Resource for Health Care Professionals. Physicians for Social Responsibility and Californians for Pesticide Reform. www.igc.org/cpr.

Sténuit J, Van Hammée ML (2008). Aperçu sur l'épidémiologie des pesticides. *mdrgf@wanadoo.fr*

USGS (2007). (U.S. Geological Survey) Gilliom RJ, Barbash JE, Crawford CG, Hamilton PA, Martin JD, Nakagaki N, Nowell LH, Scott JC, Stackelberg PE, Thelin GP, Wolock DM. Pesticides in the Nation's Streams and Ground Water, 1992–2001: The Quality of Our Nation's Waters. Circular 1291, U.S. Geological Survey, Reston, Virginia: 2006. Revised February 15, 2007. http://www.usgs.gov

Van der Werf HMG (1996). Assessing the Impact of Pesticides on the Environment. Agric. Ecosyst. Environ. 60:81-96.

Van Der Werf HMG, Zimmer C (1998). An Indicator of Pesticide Environmental Impact Based On A Fuzzy Expert System Chemosphere. 36(10):2225-2249.

Ware G, Whitacre D (2004). The Pesticide Book. 6th Ed. Meister Pro Information Resources.

Wauchope RD, Yeh S, Linders JBH, Kloskowski R, Tanaka K, Katayama A, Kördel W, Lane M, Unsworth J (2001). Pesticide Soil Sorption Parameters: Theory, Measurement, Uses, Limitations and Reliability. Poster Presented At the IUPAC Congress/General Assembly, July 2001.

WHO (2008). Pesticides: Children's Health and the Environment, www.who.org