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Evaluation of Organochlorine Pesticide Residues in Undergroundwater of the Mostaganem Region, Algeria

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Abstract

At the same time as their beneficial effects in the defense of the cultures and the protection of the harvests, organochlorinated pesticides express their fatal effects on the human and environmental health on the quiet. Harmful effects quickly established with certain proofs by the scientists.

The objective of our study is to estimate the level of subterranean contamination of waters of the groundwater of Mostaganem province by organochlorinated pesticides. So, very successful analytical techniques are essential for their identification and quantification. In This work we have ends in the development of a method of analysis multiresidus of organochlorinated pesticides in waters of well by chromatography in gas phase coupled with the mass spectrometry.

The use of this instrument in the field of the analysis of the residues of pesticides is considered the most adapted because of these impressive performances in terms of selectivity and sensibility after a stage of extraction of our samples on solid phase (SPE).

All in all 07 OCP(oraganochlorine pesticides) was detected in almost all the samples in variable contents (0.00215 – 0.49856 µg. L^{-1}) among which three exceeded the maximal limits of residues (MRLs) fixed by European directives. Other samples are necessary to estimate better the levels of contamination of underground waters by organochlorinated pesticides.

Keywords

Organochlorinated pesticides; Underground waters; Contamination; Multiresidus; GC/MS; SPE

Introduction

The prodigious expansion of the chemical industry in the 20^{th} century changed deeply and irreversibly the production and consumption patterns in both regions technologically and economically more advanced than in less affluent regions of the planet. In particular, mass production and widespread use of chemicals in agriculture, in particular mineral fertilizers and phytosanitary products, have othe intensification of agriculture with a dramatic increase in crop yields.

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Among the chemicals the most used in our current environment are without a doubt pesticides and related products. Pesticides (insecticides, raticides, fungicides and herbicides) are chemical compounds with properties toxicology, whose first intensive use (DDT) goes back to the Second World War World. Indeed, organochlorine pesticides (OCP), considered among the organic pollutant the most toxic and persistent (POP's), have been massively used all over the world as contact insecticides and to a lesser extent as fungicides and acaricides. In addition to their beneficial effects in crop protection and protection of, organochlorine pesticides mutely express their adverse effects on health.

human and environmental issues. Harmful effects quickly established with clear evidence by scientists [1-3]. This has led to more or less harsh regulations aimed at restricting their use or their total prohibition. It is within this framework that a whole arsenal of legality has been developed to bring it into line with our country's commitments and the international conventions to which it has acceded [4].

The misuse of pesticides in the agricultural sector in Algeria during the 1960s and 70 generated large unused stocks across the national territory that are stored in an anarchic and diffuse manner without taking into account the risks to the health of people and the environment, in particular water resources. This threat of degradation of the quality of these resources and groundwater, more vulnerable [5].

Lack of a water quality control body and laboratories specializing in the control of water pollution by these micro-pollutants as well as the absence of preventive measures necessary to reduce the risk of their leaching to groundwater, contributes to the deterioration of the environment and human health in the medium and long term.

The Chemical Inventory carried out in 2003 recorded a total of 1,731 tonnes of products of all types, of which 197.3 tonnes are classified as POPs of which 191 tonnes are DDT (96.8%) located mainly in Mostaganem region (180 tons) [5].

Analyzes of water samples taken from the Staoueli area (Algiers) have shown that in more than 30% of the samples the concentration of certain molecules organochlorines (lindane, Heptachlor, 2,4 DDT and 4,4 DDT, 2,DDE (dichlorodiphenyldichloroethylene) and 4,4 DDE) exceeds the guide values recommended by World Health Organisation WHO [6]. However, there is no information on the residues of OCP in the groundwater of western Algeria.

Mostaganem aquifer has always provided water, industry, agriculture and the drinking water supply of the city of Mostaganem and the neighboring agglomerations. However, the quality of this resource has deteriorated considerably, particularly over the last three decades (Figure 1).

Materials and Methods

Characterization of the study area

The borough of Mostaganem is located on the west coast of the country; it has a Seaside of 124 km. The chief place of the wilaya is located 365 km to the west of the capital Algiers and 80 km east of Oran. It covers an area of 2269 km².

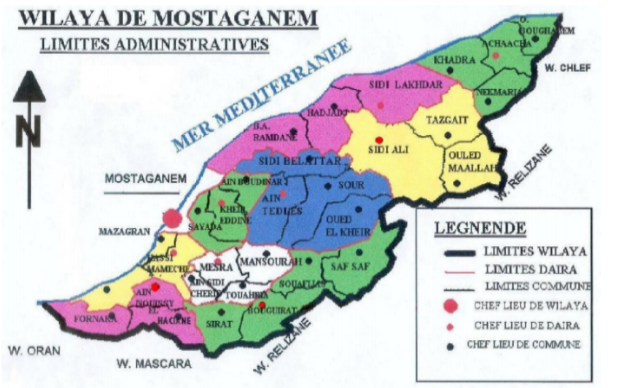

Figure 1: Administrative boundaries and map of the wilaya of Mostaganem.

At the end of 2010, the Wilaya of Mostaganem had a population of 768,942 with a density of 339 inhabitants (HAB) / km2, the estimates at 31/12/2014 show a population of 821,049 inhabitants, i.e. a density of land occupancy of 362 HAB / km². (Official portal of the wilaya of Mostaganem, 2016).The diversity of the wilaya of Mostaganem allows it to possess enormous potentialities particularly in terms of "Agricultural land". Its overall agricultural area is estimated at 177,310 units of this area, 132,268 ha (74%) represents 33,900 ha (25%) benefit from irrigation .region has succeeded in increasing and varying its agricultural production (potatoes, vegetables, cereals, fruit trees), thanks to the extension of cultivable areas of the use of modern techniques, subsidized fertilizers, and the drip irrigation system. Rainfall is medium to low with values between 350 and 500 mm and mobilization capacity, is also very low due to the lack of equipment and hydraulic works. Also, the number of sites favorable to the construction of dams is virtually nil. As a result, the surface water resources available for D.W.S (Drinking Water Supply) and for industry are non-existent. The water available for the wilaya of Mostaganem is mainly underground according to the data from the wilaya monograph:

- The number of boreholes operated is 91.
- Total mobilizable volume: 617 l / s.
- Total sustainable exploitation: 22.76 hm3/ year of which
- Drinking Water Supply: 22.32 hm^3/ year
- Industry: 0.44 hm^3/ year

The data mentioned highlight the lack of water resources in the wilaya of Mostaganem.

Sampling

Water sampling was carried out from different wells. They were collected in one-liter bottles of amber that have been previously cleaned and washed with water deionized and then rinsed with nitric acid (HNO_3) at 10% followed by several rinses with water purified. The wells sampled were equipped with pumps; the sampling was carried out in the morning. Before being filled to the edge, the flasks were still rinsed with water to the samples were then numbered and stored at + 4°C in a cooler along the transport. Sample processing and dosing were carried out at laboratory of toxicology of the University Hospital of Oran within a period not exceeding 48 hours.

Chemicals and instrumentation

The solvents used for the extraction hexane, Acétate d'éthyle, methanol and acetone were obtained from Merck (LC grade). The standards for the pesticides chosen for the study were obtained from RESTEK®.Ultra-pure water with a resistivity of 18.2 Ω (Produced by a water-producing apparatus ultra pure PURELAB®) Ultra Q used to prepare spiked samples and as a solvent for SPE extraction. Analyses were conducted in laboratorie of pharmacology and toxicology of Oran hospital.

Chromatographic analysis

- The pesticide residues were analyzed by gas chromatography (GC) using a Perkin Elmer Clarus® 680 and quadrupole mass spectrometer Perkin Elmer Clarus® SQ8T. A capillary column Varian Rxi Sil MS (RESTEK®) 30 m × 0.25 mm × 0.25μm film thickness fused silica was used for the chromatographic separation of fipronil and Supelco SPB-35 30 m × 0.25 mm × 0.25 μm was used for the chromatographic separation of OCPs. hélium was ed as the carrier gas.The GC conditions used are presented in Table 1.
- Capillary column of brand Rxi Sil MS of the mark RESTEK® of 30 m length, and of 0.25 mm inside diameter. The stationary phase consists of 5% phenyl and 95diméthyl-polysioxane. Libraries: Wiley®2011 + Pfelger®ver1-pesticides + NIST®2011.

Analytical procedure

Solid Phase extraction followed by gas chromatographic detection was optimized and used for the determination organochlorated pesitids residues. Before use, SPE cartridge C18 ODS were conditioned successively with 10 ml of actate ethyl and10 of methanol and after with 20 mL of ultra-pure water. Water samples (1000 mL) were loaded under vacuum at flow rate of 10 mL min^{-1}. After sample loading, cartridges were dried under vacuum for 10 min ans 10 mn under nitrogen flux. After elution with 6 mL of of ethyl acetate and 6 ml of methanol the collected extracts were evaporated to dryness under a gentle stream of nitrogen and redissolved in 1000 μL acetone. Then, GC/MS analysis was performed as described in Section 2.4. The mass spectrum of each compound was characterized in full-scan mode and selected-ion-monitoring mode was used for all quantitative measurementsThe final spectrometric conditions are given in Table 2. Retention times, m/z ratios, and limits of detection used for quantitative purposes are given in Table 3. The limit of detection (LoD) for these compound derived by use of A signal-to- noise ratio

Table 1: The final chromatographic conditions used are

-Column 5SIL-MS | -Flow rate of helium: 1 mL / min

-Injection in splitless mode (2) | -Injection volume: 3 μL

-Injection temperature: 280°C

Oven program:

Landing (° C / min)	**Temperature (° C)**	**Hold Time (mn) (°C /mn)**
0	50	2
8	280	0
Palier (°C /mn)	**Température (°C)**	**Temps de maintien (mn)**
0	50	2
8	280	0

Table 2: The final spectrometric conditions retained.

Ionization mode: positive electro-ionization
Transfer line temperature: 280°C
Ionization temperature: 220°C
SIR mode: see Table 2
Inter scan delay: 0.03

Table 3: Retention times, m/z ratios, and limits of detection of OCPs by gas Chromatography, limts of détection, limits of quantification.

Pesticide	Quantification Ions	Identification Ions	Retention times (min)	Interval of Tr in SIR mode	LoD 10-3(ppb)	LoQ 10-3(ppb)
Lindane	181	181 ; 183 ; 109	20,21	[20,10-20,30]	2.14	7.15
Alachlor	160	45 ; 160 :188	21,89	[21,75-22,05]	1.31	4.38
Métolachlor	162	162 ; 238 ; 45	22.80	[22,60-23,00]	0.96	319
Heptachlor Epoxyde	81	81 ; 353 ; 355	23,87	[23,70-24,00]	0.70	2.33
Endrine	81	81 ; 79 ; 263	25,87	[25,70-26,00]	2.41	8.03
Endrine Aldehyde	67	67 ; 345 ; 250	26,45	[26,30-26,60]	19.73	65.75
Endrine Kétone	67	67 ; 317 ; 315	28,06	[27,90-28,20]	31.99	106.62

1:3. Blanks were performed for each batch experiment to monitor possible contamination. No compound were found in blank samples.

Results and Discussion

In total we analyzed 5 samples of groundwater:

- The identification of POC in groundwater was done according to the time retention and the specific ions of each molecule.
- Quantification was performed by the calibration method with matrix matching

In this study, organochlorine pesticides were analyzed by GC / MS; The applied to the analysis of our groundwater samples, has been validated in the analytical conditions described above. In terms of accuracy, repeatability, linearity and limits of detection and quantification meet the defined standards. Moreover, they are generally similar to those reported in the littérature Table 4.

This method allowed us to estimate residues of organochlorine pesticides in some water samples, which are far from negligible.In the study area, contamination levels of well water samples are high in relation to the WHO pesticide residue the European Union (EU) which are 0.1 µg / L for a substance.

The measured values showed a worrying pollution of the water table at the level of the majority of sampling sites. The levels of residues of organochlorine pesticides are variable from one site to another. Of the 5 wells surveyed, concentrations of: 0.318; 0.277; 0.112 and 0.199 ppb (µg / L) of Endrin Aldehyde were revealed in 4 wells and concentrations of 0.227; 0.238 and 0.498 ppb (µg / L) of Endrin in 3 wells. These results exceed the MRLs of 0.1 µg / l per substance. The levels of Heptachlor Epoxide have exceeded the MRLs (0.03 µg / l) with concentrations of 0.210 and 0.306 ppb (µg / L) in 2 wells.

Endrin Ketone was detected in only one sample, Lindane and Alachlor present in three samples, whereas Metolachlorse finds in all samples. The latter did not demonstrate that the MRLs were exceeded.

This can be explained by the fact that most applied or stored pesticides enter in contact with water by runoff from the treated surfaces, leaching during infiltrations or by atmospheric deposition, wet or dry. The contamination of underground water depends essentially on the properties of the pesticide, the characteristics of the soil, weather condition but also the distance from the application site to the water source. Her spatial and temporal distribution is a function of patterns of exploitation of land and pesticides used. In addition, many pesticides end up in water underground, and their degradation products may remain for several years. In In addition, organochlorine pesticides are generally characterized by their which predisposes them to stay long in the soil where they have a less important to adsorb on the particles. Thus, it is only in can be detected in quantities in groundwater, such as seems to be the case in our study area where these products have been widely used in the Algerian west for several years, mainly in the fight against pests of the crops, namely the vine.

The high persistence of these active substances, which was associated with their effectiveness, is now the origin of their total ban on agriculture because of the toxic risks to health humans and the environment. Thus, the phenomenon of diffuse water pollution underground is a real danger in Africa in general, and in all major cities African countries in particular [7].

In the cultivated area of Mostaganem, it is difficult to characterize finely and spatially the current state of diffuse pollution of aquifers. However, despite the limitations, we have contributed to the assessment of the contamination of the underground environment; our work provides an initial estimate of water quality the level of contamination, it could also serve as a basis for a further analysis of causality in subsequent work.

The results of our study coincide with those reported in other studies assessment of water contamination in Africa.

Mawussi detected the presence of DDT (0.11 and 0.15 µg / L), aldrin (0.07 µg / L), endrin (0.13 µg / L), heptachlor (0.33 µg / L), heptachlor epoxide (0.09 µg / L), α endosulfan (0.29-0.32 µg / L) and β endosulfan (0.25-0.40 µg / L) in the waters of the Anié, Mono andof wells in Adeta in Togo [8]. In the same register, another study carried outby Edoh in 1991 in the city of Lomé, revealed that tap water and wells serving as drinking water and / or watering vegetable crops levels of residues of aldrin, dieldrin and heptachlor 43 times higher than those standards of the European Union and WHO [9]. Mwevura found concentrations of residues of organochlorine pesticides which oscillated between 0.1 and 0.39 µg / L for DDT, 0.08 and 0.45µg / L for DDE, 0.21 and 2.49 µg / L for the dieldrin and 0.2 µg / L for lindane in the coastal zone of Dar es Salaam [10].

Organochlorine residues were detected by Nwankwoala and Osibanjo in the superficial cells of Ibadan in Nigeria at various

Table 4: GC / MS Sample Analysis Results.

Pesticide		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	MRLs
Lindane	Area (mAu)	68	38	57	22.5	10.50	0.1
	[C] ppb (ug/L)	0.00732	0.00332	0.00585	0.00126	0.00039	
Alachlor	Area (mAu)	59	68.5	40	24	1	0.1
	[C] ppb (ug/L)	0.00369	0.00446	0.00215	0.00086	0.001	
Metolachlor	Area (mAu)	238.5	230	111	204	148	0.1
	[C] ppb (ug/L)	0.00827	0.00812	0.00601	0.00766	0.00667	
Heptachlor Epoxyde	Area (mAu)	126.50	2861	92.50	4238.50	65	0.03
	[C] ppb (ug/L)	0.0175	0.210	0.0151	0.306	0.0132	
Endrine	Area (mAu)	1941.50	1997	545.5	1037	3303	0.1
	[C] ppb (ug/L)	0.227	2.3878	0.0499	0.0478	0.498	
EndrineAldehyde	Area (mAu)	4200.50	3740.50	1877	2856	1677.50	0.1
	[C] ppb (ug/L)	0.318	0.277	0.112	0.199	0.0950	
EndrineKetone	Area (mAu)	116	266	67,50	341,50	208,50	0.1
	[C] ppb (ug/L)	0.0256	0.0187	0.0399	0.0410	0.00174	

concentrations: dieldrin (0.018-0.657 μg / L), lindane (0.007-0.297 μg / L), heptachlor (0.004-0.202 μg / L), aldrin (0.04 μg / L), endosulfan (0.43 μg / L) and total DDT (1.266 μg / L) [11]. Cissé et al. detected residues of lindane (0.22 μg / L), α-endosulfan (1.26 μg / L) and of β-endosulfan (1.84 μg / L) in groundwater in Senegal in the area of Niayes in Dakar [12].

In Ghana, Ntow (2005) detected epoxy heptachlor in the rivers of Akumadan, Afrensu, Bosumpon and Anyinatase in the Ofinso district at residual values averages below 0.1 μg.L-1L [13]. Heptachlor was detected in well in Senegal at 3.43 μg L-1 [12].

In South Africa, Fatoki and Awofolu reported concentrations of pesticides organochlorines ranging from 5.5 to 210 ng / L in the waters of East London Harbor which receives effluents and from 5.7 to 450 ng / L in the waters of the Buffalo River crossing agricultural areas [14].

In Kenya, the average residual concentrations of DDT, DDD, DDE, lindane, heptachlor And Aldrin in the waters of Lake Nakuru were 1.09; 6.89; 0.90; 1.33; 3.85 and 4.54 μg / L [15].

These sufficiently high residue levels may raise concerns about impacts on the health of populations consuming the contaminated waters given their long-term intrinsic toxicity causing various pathologies and other disorders physiological disorders (neurological disorders, malformations, decreased fertility, hormonal and immune responses) [16-18]. Indeed, according to our investigations with farmers and phytosanitary products in the region, we found that these substances were, in the majority of cases, not in conformity with the Agricultural Practices. These bad practices have led to harmful to man and his environment. This situation makes it necessary to monitoring of environmental contamination in this region hydraulic, faunistic and floristic resources. The data from monitoring should enable policy-makers to take corrective action for a strict application of the regulation allowing the products to be switched off and persistent organic pollutants.

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