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Groundwater Contamination by Pesticides and Metals Elements in Agricultural areas of the Northwest of Morocco and Health hazard

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Abstract : *This study aims to investigate the pesticide residues and metal elements in 39 wells located in the agricultural area of the northwest of Morocco. Results showed the presence of lead, chromium, selenium, copper, manganese, iron and zinc at different levels, with negligible mercury and nickel below detection limits. However, selenium and iron values exceeded the international regulation levels in 64 % and 15.4 % of samples, respectively. Organochlorine and dichlorodiphenyltrichloroethane (DDT) pesticides are found in all water samples, where their concentrations are ranged between 2 ng L^{-1} and 8 ng L^{-1}, while organophosphorine, carbamate and other organochlorines pesticides are below detection limits. The daily intake of selenium (22.62 µg per day) was lower than that of the international standards (6 - 21 µg per day). The concentrations of DDT in studied samples are over the permissible limits of international standards for drinking water.*

Keywords: Contamination, *Pesticide residues, Metals, Groundwater.*

I. Introduction

For several years, the increasing of water resource deficit has contributed to the degradation of its quality, As indicated by the World Health Organization [1], the degradation of the water quality becomes a serious problem for public health, Shortage of drinking water worldwide is becoming very acute nowadays [2]. This problem required the Moroccan authorities to pay attention on the water preservation along with efforts made for development and the management of water resources. For this, the Green Moroccan Plan (GMP) attempts to improve the agricultural production and to develop a new specialization that could be the most suitable for agriculture, taking into account the climate and water actual state. However, any improvement requires an increased recourse to the use of fertilizers and pesticides to get the agriculture yields better and fight against parasites (herbicides, insecticides, fungicides). At present, about one million hectares of the irrigated zones are annually treated with pesticides [3], that becomes a source of contamination in soil and groundwater.

The studied area, the northwest of Morocco, has a major rivers as a hydrous system (Sebou, Rdom,...). The geology is characterized by surface outcrops of limestone and Sandstone Mountains of Jurassic limestone hills surrounded by Miocene marls, which constitute the major part of the landscape [4]. The agriculture is the main activity in this zone, favored by a good weather conditions and the fertilizing soils. This region is considered at 0.4 % of the country with a superficies of 281.000 hectares (1.2 % of useful national agricultural) [5]. However, the presence of pesticides and some metal heavy metals in the environment in this region can affect the water quality and consequently is a major issue for ecosystems and human health.

For this approach, the main objective is to determine the water quality stemming from this region by analyzing certain toxic pesticides and metal elements, by using chromatography and atomic absorption techniques respectively, establishing the cause of contamination and the associated health risks that may be hazardous for the population.

II. Materals And Methodes

Groundwater samples from 39 wells were collected from the Northwest of Morocco, covering a total area of 1100 km^2 (Fig. 1). For metals analysis, samples were put directly from wells using a propylene container tied to a polyethylene rope, in polyethylene tubes (50 ml) that contain 0.5 ml of nitric acid (Merck, 65% with high purity). For pesticides analysis, the samples were collected with a glass sampler and transferred to amber glass bottles that were previously washed and decontaminated [6]. Samples were placed at low temperature (4°C) using portable coolers. The average of the depth of recorded wells extended from 6 to 100 meters. For each well, information on the location, the frequency of use, the mode and the nature of the treatment are taken into account. The sampled waters of the selected wells were taken from a 1L compound rural community of more than 300 houses for drinking, cleaning and irrigation activities.

The metal contents such as Pb, Cd, Cu, Ni, Cr, Mn, As, Se and Hg are determined directly by Atomic Absorption Spectrophotometer with Graphite Furnace (AAS-GF) type Varian, 240, Zeeman. Iron and zinc are measured by flame AAS, type Varian Spectrophotometer with an Atomic Absorption Flame (SAAF) type Varian, 240 Fast Sequential. All analyses were performed in triplicate and experimental errors were found below 5% RSD with the comparative accuracy. The analytic method validity is verified by the intern control with various standards (national council of research in Canada: BCSS-1) and by external control with the exercises of intercalibration [7].

The limits of detection (LODs), defined as the lowest concentration level that can be determined to be statistically different from blank (99% confidence) of each metal ion were as As (0.02 μg L-1) Cd (0.004 μg L-1), Pb (0.002 μg L-1), Cr (0.002 μg L-1), Cu (0.002 μg L-1), Hg (0.01 μg L-1), Fe (5 μg L-1), Ni (0.002 μg L-1), Zn (3 μg L-1), Al (0.05 μg L-1), Mn (0.002 μg L-1), Se (0.01 μg L-1).

For pesticide analyses, three liquid-liquid extractions with hexane were successively performed on 1 L of water from each well. These extracts were combined and concentrated using a rotary evaporator until 100 μL and then adjusted to 1 ml with hexane [8]. Organochlorine (yHCH, HCH, Heptachlor, Heptachlor epoxide, Aldrin, Endrin,TCB, Aroclor, DDE, DDD, Chlordane, Endosulfan, DDT) and organophosphorine pesticides (dichlorvos, TBP, Sulfotep, Dimethoate, Methylchlorpyrifos, methyl parathion, malathion, fenitrothion, chlorpyrifos, parathion, Ethion) were separated and quantified by gas chromatography (GC), VARIAN CP3380, that is equipped with electron capture detectors (^{63}Ni) and a capillary column ''nonpolar'' CP-Sil 8 CB 30mx0.25mmx0.25μm (5% dimethylpolisiloxane). The Determination of carbamate pesticides (Methomyl, Oxamyl, arbofuran, Carbaryl, Aldicarb, bendiocarb) was realized by LC-Chromatography, (Shimadzu) coupled with array iodine detector (DAD). A Column C18 (HS-5HCODS, 5μm), of 25 cm in length and interior diameter of 3.2 mm has been used. The mobile phase was mixed with acetonitrile -water mixture (80/20, v/v) according to a flow rate of 1 ml min^{-1}.

For calculation of the mean recovery of the used method, water samples were prepared with standard solutions of pesticides (2.5 mg L^{-1} to 5 mg L^{-1}), and the obtained recovery for all solutions was checked between 75 and 80 %.

III. Results And Discutions

It is generally accepted that the toxic species in each well is dependent on the various agriculture activities and clays as complexing agents. Table 1 gathers the obtained results for metal elements in 39 wells, which are very significant ($P<0.001$).

The majority of trace metals, arsenic, cadmium, chromium, copper, manganese, mercury, nickel, lead, iron and zinc are present at concentrations far below international standards of water drinking. Only selenium and iron have exceeded international standards respectively 10 µg/l and 300 µg/l. Indeed, selenium shows an overshoot of 64% in the wells tested with a minimum value of 0.21μg/l and maximum of 83.98 mg/l. For iron 15.4% of wells exceeded this standard with a minimum value of 5μg/l and maximum 627μg/ l.

In the absence of any anthropological source of these elements, the presence of these two elements make us suggest a natural origin (soil geochemistry) [9]. Indeed, a similar study in the region of the Essonne in France showed the natural origin of these elements in groundwater [10].

Assuming a daily consumption of 1.5 l water for each individual and an average content of selenium in the range of 15.08 µg/l, the daily individual average would be 22.62µg/day. Compared to food, water is an important source of selenium in the region. In France, the daily intakes of selenium were determined at values ranging between 40 and 50 mg [11].

With the exception of dichlorodipheniltrichloroethane (DDT) found in the trace state (from 0.002 mg L^{-1} to 0.008 mg L^{-1}, organophosphorine, carbamate and organochlorine pesticides in all analyzed wells were below the detection limit. The limits of individual substances are of ≤0.1μg L^{-1} and ≤ 0.5 μg L^{-1} for organophosphorine and carbamate, respectively. Assuming that the daily consumption of water for each individual is 1.5 L and the average of Se content is a 15.08 μg L^{-1}, the daily individual average in the element would be a 22.62 µg per day. Compared to food, water is an important source of selenium in the studied area. The daily consumptions of selenium in France were between 40 and 50 µg per day [12]. However, the recommended dietary selenium is 55 µg per day, that's considered as sufficient concentration [13]. The high concentration of iron has no health risks, but its presence in the analyzed waters with a high quantity may have some secondary effects principally related to the flavor and the color of water. However the presence of DDT, even with a very low concentration means a recent use, which is related to a fraudulent agricultural use or an anti-vectorial treatment that entrain wells and/or groundwaters pollution if no decision was taken in this direction. Indeed, the low values of the identified DDT can be related to their chemical behavior with the associated soils.

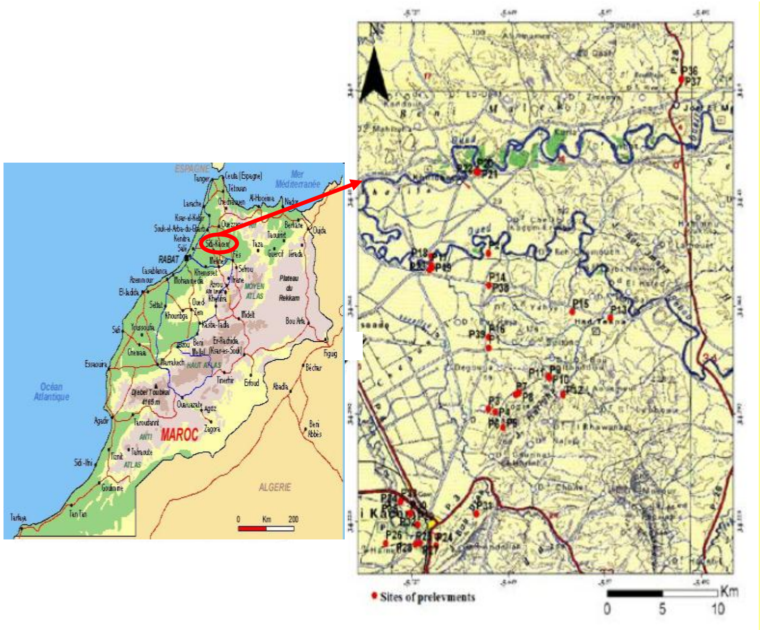

Figure 1: Location of sampled wells (in red).

Table 1: Metal content (in µg L^{-1}) in 39 wells.

Samples (µg L^{-1})	Pb	Cr	Cd	Se	Hg	Cu	Al	Mn	As	Zn	Fe	Ni
P1	7.25	<0.002	0.3	8.62	<0.01	5.23	65.12	7.42	1.57	197	9.00	<0.002
P2	<0.002	1.25	<0.004	0.61	<0.01	<0.002	91.15	9.80	<0.02	<3.00	<5.00	<0.002
P3	<0.002	0.7	<0.004	0.21	<0.01	<0.002	81.12	9.40	<0.02	<3.00	<5.00	<0.002
P4	<0.002	0.80	<0.004	0.38	<0.01	1.4	75.83	25.60	1.70	11.00	<5.00	<0.002
P5	9.1	<0.002	0.02	16.56	<0.01	1.12	170.47	17.24	2.91	<3.00	78.00	<0.002
P6	7.53	<0.002	0.12	8.57	<0.01	1.14	58.78	11.63	2.87	<3.00	62.00	<0.002
P7	7.04	<0.002	0.23	17.12	<0.01	2.5	123.32	37.15	<0.02	<3.00	<5.00	<0.002
P8	12.30	<0.002	0.19	12.1	<0.01	3.1	118.35	7.35	2.53	<3.00	<5.00	<0.002
P9	5.31	4.20	0.16	8.53	<0.01	6.53	231.16	6.34	1.5	<3.00	54.00	<0.002
P10	14.23	< 0.002	0.25	12.87	<0.01	5.1	167.25	4.79	1.12	<3.00	<5.00	<0.002
P11	8.01	< 0.002	0.03	17.67	<0.01	3.2	113.04	2.75	0.76	<3.00	<5.00	<0.002
P12	3.07	5.65	0.66	5.7	<0.01	2.00	235	7.24	0.67	74.00	306	<0.002
P13	13.07	<0.002	0.68	16.15	<0.01	8.71	43.05	5.01	3.25	<3.00	<5.00	<0.002
P14	<0.002	0.83	0.11	2.36	<0.01	1.20	27.8	2.80	0.31	<3.00	<5.00	<0.002
P15	8.14	<0.002	0.08	48.1	<0.01	3.00	28.57	6.36	0.53	10	<5.00	<0.002
P16	23.02	5.10	0.05	83.98	<0.01	2.00	31.52	4.00	2.8	<3.00	<5.00	<0.002
P17	7.03	5.27	<0.004	12.35	<0.01	6.10	67.53	5.12	<0.02	<3.00	<5.00	<0.002
P18	5.31	4.62	<0.004	13.51	<0.01	8.67	376	198.51	<0.02	<3.00	<5.00	<0.002
P19	5.12	3.65	0.10	16.52	<0.01	9.31	125.31	6.73	1.93	<3.00	<5.00	<0.002
P20	3.27	6.74	<0.004	3.45	<0.01	1.00	49.18	96.23	1.54	<3.00	121.00	<0.002
P21	4.25	8.37	<0.004	8.35	<0.01	2.00	37.67	9.56	<0.02	<3.00	93.00	<0.002
P22	5.73	7.62	2.52	9.12	<0.01	7.35	35.91	<0.002	<0.02	<3.00	<5.00	<0.002
P23	4.12	1.23	0.03	11.35	<0.01	7.92	36.23	2.05	1.03	<3.00	<5.00	<0.002
P24	<0.002	3.31	0.1	3.12	<0.01	1.00	60.03	4.7	<0.02	<3,00	<5.00	<0.002
P25	<0.002	1.02	0.02	22.9	<0.01	1.00	35.8	4.4	<0.02	<3.00	<5.00	<0.002
P26	0.38	1.66	<0.004	19.2	<0.01	1.00	33.06	11.00	<0.02	<3.00	91.00	<0.002
P27	<0.002	1.63	0.04	23.8	<0.01	1.00	36.7	5.60	<0.02	<3.00	72.00	<0.002

P28	0.29	2.88	0.12	32.8	<0.01	3.00	38.7	3.50	<0.02	33.00	57.00	<0.002
P29	2.32	0.64	0.10	16.34	<0.01	7.12	112.73	1.20	1.50	76.50	64.00	<0.002
P30	1.10	1.23	0.04	18.5	<0.01	1.30	92.00	4.20	4.04	824	573	<0.002
P31	6.54	1.76	0.03	11.48	<0.01	1.00	81.33	2.60	0.27	<3.00	321	<0.002
P32	<0.002	0.92	0.10	24.4	<0.01	<0.002	67.54	3.80	0.04	<3.00	412	<0.002
P33	12.71	<0.002	0.11	17.13	<0.01	3.20	38.76	19.30	4.11	<3.00	627	<0.002
P34	13.45	<0.002	0.09	35.7	<0.01	4.60	58.47	15.20	<0.02	<3.00	578	<0.002
P35	<0.002	0.65	0.10	15.17	<0.01	1.30	29.2	2.20	<0.02	<3.00	<5.00	<0.002
P36	1.42	4.09	0.03	64.58	<0.01	2.10	45.14	4.60	<0.02	7.00	7.00	<0.002
P37	<0.002	2.35	0.05	19.30	<0.01	1.00	28.86	3.00	<0.02	<3.00	<5.00	<0.002
P38	4.03	4.11	0.16	3.00	<0.01	1.00	88.56	7.50	3.29	<3.00	<5.00	<0.002
P39	<0.002	5.91	0.40	3.39	<0.01	<0.002	60.14	5.00	0.23	18.00	<5.00	<0.002
S.I(µg l^{-1})	25.0	50.0	5.00	10.0	1.00	2000	200	500	10.00	3000	300	20.00

S.I**:** System International

IV. Conclusion

For a few decades, organochlorines have generally posed a significant risk related to their persistence in the environment [14]. The consumption of water containing small amounts of the pesticide is a real health chronic risk factor for populations. They can accumulate in human bodies mainly in the adipose tissue , the liver and muscles [15].

The metal assessment of groundwater shows a significant presence of Se in over 50% of selected wells in the region. The same observation is noted for Fe. Consequently, the geochemical characteristics of groundwater flow must be taken into the consideration in programs of drinking water supply and the health risk. No organophosphorine and carbamate pesticides are present in the analyzed waters, but a very low content of organochlorine particularly DDT. Nevertheless, the daily uses of these water resources by autochthonous population raises questions on the presence of some toxic substances particularly Se et DDT encourages (obliges) the local Moroccan authorities and managers to make serious decisions in favor pollutions of this region.

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