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Assessment of the use of agrochemical products in agriculture on the coastal area of Oualidia, Morocco

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Abstract
This work aims to identify cultural practices in the area of Oualidia and identify the types of agrochemicals from a survey of agriculture in the region. With nine types of anti-cotyledons herbicides and 5 anti-grass herbicides were listed. Also, three types of nematicides belonging to two different families are used to prevent against the RNK. Only "Nemasol" is intended to treat the bare ground. For insecticides, the most used are seven in number and are essentially specific for vegetable crops. For fungicides, they are five of them. The classification of 30 pesticides identified in Oualidia allow to distinguish that 6% of highly hazardous pesticides are classified (FD) represented by the nematicides, 20% are moderately hazardous (R) represented by fungicides and insecticides, 60% are slightly Hazardous (LD) mainly represented by herbicides. Herbicides and pesticides are found at lower risk of use because 73.3% and 20% LD are unknown as with acute danger, only an herbicide "Illoxan EC 36" which is recognised MD. The estimated flow of pesticides into the coastal aquifer has been studied based on seven differentiated active ingredients according to the survey as the most frequently used. The classification of active substances according to their toxicity aims to understand its toxicity of pesticides containing it. The study of risk factors for different active ingredients has detected three substances with great potential for groundwater contamination: Fenamiphos content in "Nemacur" Methomyl content in "Lannate and Salvador" and 2.4 D in content anti-cotyledons herbicides, despite a rapid hydrolysis in water.

Keywords: Weed control, Phytosanitary survey, pesticides, Oualidia area, Morocco

1. Introduction
The consumption of pesticides used in modern agriculture exceeds several tens of thousands of tones in many countries of the world [1]. The use of pesticides is causing a major problem at the interface of agriculture and preservation of water resources. Water pollution by nutrients, pesticides and sediment is a major problem in agricultural watersheds [2]. Pesticides are the first products on the list of the pollutants, which international organizations give a special attention, because of their diverse uses and inevitable direct exposures of natural resources, peoples and animals to these products. In Morocco, pesticides are increasingly used and comprehensive studies on the impact of pesticides on humans and the environment, although very rare, have shown potential water contamination, food and soil. According to the Moroccan Ministry of Environment, there are 6,4 10^6 kg of insecticides that have been used for the campaign 2004-2005. These insecticides are used proportionately (quantitatively) as fungicides and herbicides. The average annual rate of pesticide used is reported at about 12 10^6kg and the majority of users of these products are misguided [3]. Almost 50% of the national consumption of pesticides related to vegetables and citrus. Also, in the area of Oualidia agricultural productivity is mainly focused on market gardening, which justifies the intensification of the phytochemicals control in this area [4].

The objective of this work is to conduct a phytotechnical survey among farmers, primarily to identify the intensity of chemical control. It also provides information on the most commonly used pesticides and helping to establish a database on the distribution of pesticides in the area of Oualidia and their actual use in agriculture.

2. Materials and Methods

2.1. Study area

The survey is conducted on Douars "DOUAR BAKIR" "DOUAR OULAD LHLAL" in the region of Oualidia. Thereof, are most representative in terms of agricultural areas and human intensity. This region is characterized by the existence of the lagoon of Oualidia, which is located on the Atlantic Ocean. This lagoon is 7 10^3 m long on average and 0,5 10^3 m wide, giving a total area of 3,5 10^6 m^2 [5]. The area is part of the Doukkala territory of the region. The frequency of survey farmers is 49% owned including 42% belong ‘’Douar OuladLhlal’’ and 58% in ‘’DouarBakir’’. Agriculture in the Douars is the family type. Thus, the number of people surveyed is representative. From the total cultivated land, one farmer type for each field to avoid redundancy in our results.

2.2. Survey methodology

The questionnaire covers three aspects: the first concerns the use of pesticides, period and frequency of treatment, the second concerns the use of chemical fertilizers, period and annual frequency. The third part includes the results of laboratory analyses obtained for each good water. Fresh fruits of *Malus domestica* were bought from King Fahd University of Petroleum and Minerals (KFUPM) commercial shopping center. They were thoroughly washed thrice with double distilled water, sliced into pieces, dried in a hot air oven at 343,15^{o}K for 24h and then crushed into powder using a grinder (Joya, 16-002). An intense brown color *Malus domestica* extract was obtained after mixing 10g of the fruit powder in 200 mL double distilled water and then boiling it for10 min in a hot plate. The residue was separated by filtration through Whatman filter paper. The filtrate obtained was stored in a refrigerator for further use.

The scientific tool proposed in this study to assess the impact of the use of chemicals in coastal agriculture is the classification of different pesticides identified in the region according to their degree of toxicity established according to lethal dose 50 (LD50) as specified by the World Health Organization [6] with four classes showed in (Tab.1) This is to determine the high-risk chemicals and offer similar efficacy to other initiatives, but to lesser or other consequences recent biological methods.

For herbicides, the selectivity criterion is also taken into account in order to classify these chemical herbicides and estimate their impact on the environment. Herbicides are called selective when used under normal conditions of use, they meet some cultures and can fight only against some weeds of these cultures [7].

Table 1 :WHO classification of pesticides [8] and ranking INERIS of pesticides

Classification Hazardous level	**Level name**	**LD50 level in rats (mg / kg body weight)**			
		Oral Route	**Dermal Route**	**Classes of toxicity**	**Classes of toxicity limits according to ADI (mg / kg bodyweight)**
Ia	excrement dangerous (ED)	< 5	< 50	A	*****ADI< 0,0001
Ib	highly dangerous (FD)	mai-50	50 - 200	B	0,0001 <ADI<0,001
II	moderately dangerous (MD)	50 – 2000	200 - 2000	C	0,001 <ADI< 0,01
III	slightly hazardous (LD)	> 2000		D	0,01 <ADI< 0,1
U	Not known as having acute hazard (ND)	5000 or more		E	0,1 <ADI

ADI: Acceptable Daily Intake

3. Results and discussion

3.1.Use of pesticides in the area of Oualidia

The synthesis of well-dispersed, single, structurally flower-like silver nanoparticles was accomplished via a one-pot reaction involving the reduction of silver salt using the aqueous extract of red apple fruit. UV–vis absorption spectrum of the solution showed the surface Plasmon resonance derived from the silver nanoparticles at around 409 - 448 nm. The reaction parameters viz. concentration of silver salt, aqueous extract and reaction time were optimized for maximum yield of silver nanoparticles.

3.1.1. *Use of herbicides*

The table (2) shows the main herbicides and recommended by the Regional Office of Agricultural Development of Doukkala (ORMVAD) and how to use them according to the guidelines of the national health and food safety office (ONSSA).There are six of the nine anticotyledons herbicides are compounds of active ingredient: 2,4-D in different proportions and one of anti-grass ILLOXANE 36 EC. The compound 2,4-D included in the composition of the majority of herbicides used by agriculture in the region is classified by WHO as Class II, hence the importance of farmers to the rational use of such herbicides.

According to Fried (2008), quoted by Boudjedjou (2010), the flora of a plot is composite with at least ten major species (before weeding) with very different behaviors. It is usually impossible to control all species of a weed community with a single active ingredient: it takes at least herbicide active material and a broadleaf herbicide active ingredient. Hence the justification for the use of more than one herbicide by the same farmer [9, 10, 11].

A study in Morocco by Bouhache (2000) demonstrated once more the impact of weed on the growth and development of the culture [12]. Weeds limit the yield potential of wheat in an arid region because they increase evapotranspiration. The more weeding operation is early, more culture sees early water and soil and agricultural elements promote better-made inputs (fertilizers, irrigation, pesticides ...), it limits the effect of competition exerted by weeds on cereal crops [13]. Thus, weed control is considered an essential tool to increase efficiency and improve the quality of the harvested product [14].

In Morocco, cereal crops are more dependent on herbicides, weeds since many associated with it. In a companion sampling conducted in 1999 on corn in the Doukkala region of Morocco, fifteen broadleaf weeds that are 75%, were inventoried. To thwart the escape of these weeds, farmers rely mainly on chemical control through the use of herbicides as “Agroxone, Printazol 75” and 2.4 D (dichlorophenoxyacetic acid) against broadleaf weeds, ‘’Grasp Illoxan 604’’ and ‘’36 EC’’ against grasses [15]. Herbicides: “PrintazolIlloxan 75” and “36 EC” are used, which is revealed by the survey.

Another working by INRA (2010) that listed the bad end of cycle control in cereal fields in the Doukkala region conducted 22 species with a dominance of canary grass (Phalaris Brachystachys) (75%) followed of field bindweed (*Convolvulus arvensis*) (66%) and wild oat (Avenasterilis) (59%).

A study by Culhavi (2010) aimed to provide a comparison of the 15 effective chemical means to fight against the problems associated with species *Convolvulus Arvensis L.* in winter wheat [16]. This study demonstrated the efficacy of chemical control by “DIALEN SUPER 464 SL” against weeds and specifically field bindweed (field bindweed) found in wheat crops especially winter with a controlled rate can reach more than 90% by using a concentration of 0.9 10^{-3} m^3 / 10^4 m^2. While in the same study treatment with the herbicide Mustang at a concentration of 10^{-3} $m^3/10^4$ m^2 in the same plot yielded a return of 65.75%. However, herbicides “DIALEN SUPER SL 464” and Mustang were very selective for the cultivar grown winter wheat and have not caused any visible symptoms of phytotoxicity [17].

An experiment was conducted in northern Sudan during the 2009/10 and 2010/2011 seasons to assess the efficacy and selectivity of ‘’Pallas OD” against weeds in wheat. The results showed high selectivity of the herbicide “Pallas OD” with a decrease of the dry weight of weeds from 95% to 99%. To control broadleaf weeds treatment efficiency reached 80% - 94% and for grass control treatment effectiveness 95% to 100%. This study highlighted the efficient and safe use for weed control herbicide “Pallas OD” with a concentration of 10^{-6}kg (active ingredient) / m^2[18].

Regarding the use of the herbicide “Chevalier”, a field test of two years was conducted in 2010-2011 in the experimental field plot of the Department of Culture, Agricultural College of Baghdad University to test effect of different rate (350, 530 and 760 mg.m-2) sorghum residues, alone or in combination with 50% (150 $mg.ha^{-1}$) of the recommended ‘’Chevalier’’ herbicide rate with a check sorghum and weeds without residues. The application of the herbicide Chevalier at 50% in plots amended with sorghum residues at 350 mg m-2 levels have resulted in a return similar to that label with herbicide rate treatment. Thus, the integration of sorghum

residues 0,35 10^{-3}kg m^{-2} with a lower rate of “Knight Herbicide” can provide adequate weed control without compromising performance. Which could be used as a management approach feasible and environmentally sound bad weeds in wheat fields [19]. As another research, has demonstrated the effectiveness of tribenuron-methyl and bifenox to control weeds in wheat, where the use of “Granstar 75 DF (75% tribenuron-methyl) [20].
Culture development stages are critical to the decisions taken by the Technical Management cereal. Herbicide applications must be between the stages 2-3 leaves and be tillering, and that nitrogen tillering, stem elongation and flowering, while the fight against disease is most important stages and heading upstream. The Doukkala including the province of Oualidia is recognized by its large production in market gardening. Controlling weeds in vegetable gardening, in turn, requires different strategies for different groups of crops, especially depending on the installation of the culture mode [21]. Many studies conducted so far and affirm the effectiveness of chemical treatments of weed control compared to weeding by hand [22] [23].
Chemical control is the most effective method of struggle against weeds, especially using herbicides increasingly specific that do not affect them at a profit crops. However, the most reasonable are to opt for repression or suppression of the use of herbicides, to their impact on the cultural environment, which can be translated among others, uniformity of plant communities in favor of tolerant species and a decrease in species richness [24].
The continuous use of the same herbicide products inevitably leads to flora selections, that is to say, often mono-specific stands, consisting of species on which the active ingredients are not effective. Sometimes we talk about flora inversion. These new populations can be mastered only if one modifies weeding techniques or at least if it diversifies the products used by choosing other chemical families that have other sites of action [25].
In the context of our study, three of the herbicides used in the area of Oualidia and identified according to the survey are recognized very selective, Pallas OD, DIALEN SUPER SL 464 and Mustang. These herbicides are respectively effective for the weed control: 95% to 99%, 90% and 65.75%.

Table 2 : List of Anti-cotyledon and anti-grass herbicides [9, 10]

Herbicides	**Active Ingredient**	**Quantity in 10^4 m^2**	**Period of use**
GRANSTAR 75 DF	Tribenuron-methyle (75%)	12.5 10^{-3} kg	From Stage [1]3Ftillering, bolting to flowering,
HARMONY EXTRA	50% Thifensulfuron-methyl + 25%Tribenuron - methyl	20 10^{-3} kg	
MUSTANG 306 SE	2,4-D + Florasulman	0,6 10^{-3} m^3	
PRINTAZOL 75	330 kg/m^3 2,4-D+ 285 kg/m^3 2,4-MCPA + 56 kg/m^3 2,6-MCPA	10^{-3} m^3	[2]FT
DIALEN SUPER 464 SL	2,4-D + Dicamba -	0,75 10^{-3} m^3	flowering stage until Maturity
	(Dimethyl-ammonium)		
MENJEL 24 EC	2,4-D -ester butylglycol	2 10^{-3} m^3	
AURORA PLUS 70 WG	Carfentrazone-ethyl	0,3 kg	
	+ 2,4-D		
AGROXONE F	240 kg/m^3 2,4-D+ 240 kg/m^3 2,4-MCPA	1,25 10^{-3} m^3	[2]FT
DERBY 175 CC	100 kg/m^3 Flumetsulam +	0,05 10^{-3} m^3	[2]FT
	75 kg/m^3 Florasulam		

anti-grass herbicides			
PALLAS 45 OD*	Proxsulam + Cloquintocet-mexyl (Safner)	$0,5\ 10^{-3}\ m^3$	From the stage (1) 3F to the stage tillering until elongation to flowering
ILLOXANE 36 EC	360 g/l Dichlofop Methyl	$2,5\ 10^{-3}\ m^3$	(1) 3F, (3) DT
HUSSAR OF*	64 g/l de Fenoxaprop-P-ethyl + 8 g/l d'Iodosulfuron methyl sodium + 24 g/l de Mefenpyr-diethyl	$10^{-3}\ m^3$	
CHEVALIER*	30 g/kg Mesosulfuron sodium + 30 g/kg Iodosulfuron	0,330 kg	
	sodium + 90g/kg Mefenpyr diethyl (Safener)		
ATLANTIS*	30 g/Kg Mesosulfuron-methyl + 9 g/Kg Iodosulfuronmethyl	0,500 kg	
	+ 90 g/Kg Mefenpyr-diethyl (safner)		
(1) 3F= 3 sheets (seedling) up to tillering(2) FT= in tillering to early bolting			
(3) DT= Start Tallage(*) : Also used in the fight against parasites broadleaf			

1.2. *Using of nematicides*

According to our survey, the most feared pathogens by farmers are nematodes which have caused the antecedent epidemics that have marked the study area. The survey identified two types of crop treatments for prevention against these plant pests: treatment of bare soil before seed precaution against soil-borne diseases that can affect the root system of plants and treatment in the early stages of development seeds.

There are 55 species identified of parasitic nematodes plant roots (Root Knot Nematodes = RKN). The kinds *Meloidogyne Arenaria M.* incognita and *M. Javanica* pathogens are involved in 90% of infections of plants caused by nematodes in the world [26, 27, 28]. Unlike most species of *Meloidogyne*, they are an extremely polyphagous pest with a wide host range, up to 3000 plant species of which most commercial crops. Nematodes are a real threat to farmers, especially for tomato and pepper crops that are most vulnerable to these pathogenic agents.

A parasitic plant diseases surveillance study caused by RNK conducted in Morocco, for Janati [29, 30] highlighted the major implication of four genres: *M. javanica*, *M. incognita* and *M.arenaria*, respectively 60; 29; 7 and 3%. The main infections were detected all along the Atlantic coast. This distribution is probably due to the types of vegetation resistant to high salinity soils which characterize those areas, and which constitute a favorable reservoir for these parasites [31].

Other surveillance studies followed to thwart the invasion of RNK in coastal areas. In 1983, an international project against nematodes and specifically the kind *Meloidogyne spp.* was conducted in several countries. This study detected the presence of the genus *M. javanica* in tomato crops, eggplant and cucumber in our study. In the same area, *M. javanica* was observed on several crops under plastic greenhouse and field, especially tomato, eggplant, melon, and on weeds. *M. incognita was* observed on pepper and carnation greenhouse and open field tomato [32, 33].

It is important to remember that nematodes are microorganisms that breathe and move easily by sliding in the water film surrounding soil particles. So, porous moist soil is very favorable to their development. Their activity is also influenced by temperature, with an optimum around 293,15 °K. Although nematodes are more numerous in the 10 to 15 cm of the soil, their distribution is very heterogeneous [34].

The treatment of nematodes in the region is mainly chemical. There are two major classes of nematicides: fumigant and no fumigant nematicides. Currently, the majority belong to the nematicides of no fumigant group. Nematicides no fumigant are all organophosphates and carbamates. In contrast to fumigant, these chemicals are highly dependent on initial mixing with the soil and the local redistribution dissolved in soil water [35]. Nematicides most used as reported by farmers and "Nemasol Nemacur".

“Nemacur” is a nematicide fenamiphos of the family, used for the treatment of crops that marketed in two forms in Morocco:
- "Nemacur 240 CS" to the ground tomato or banana crops. The optimal dose is 0,02$10^{-4}$ m^3 / m^2 for tomatoes and 0,040 $10^{-4}m^3/m^2$ for the banana.
- "Nemacur 10 G" for ground citrus crops, tomatoes, and melons. Optimal dosages for each culture were respectively 30 10^{-4} kg / m^2, 50 10^{-4} kg / m^2 , 50 10^{-4} kg /m^2.

The active substance metam sodium, also used for the treatment of bare soil, provides the nematicide effect of “Nemasol 510”. The effective dose is 0,6-1 10^{-4} m^3/ m2. After treatment of the bare ground, the second treatment with nematicides "Nemacur CS 240" and "10 Nemacur G" is scheduled every 15 days, accompanies all the thrust period until maturation of crops.

3.1.3. Use of insecticides

The results of the study showed that farmers use six insecticides: Salvador, Takumi 20 WDG, Proclaim 05 SG, Supermethrine and Lannate 25 WP. The principal enemies are Whitefly and Noctuelles (Tab.3). The use of insecticides is as varied in the region with few cities are defined in our survey indicating the active ingredient, the manual and target cultures [36].

The insecticide "Cypermethrin" contains a cyanide group in the molecule and can be included in the group of type II pyrethroids [37]. Pyrethroids are the insecticides, the most often used in agricultural, veterinary and domestic. Indeed, they represent more than half the global market for insecticides and are widely used in Africa [38], because of their great effectiveness against insects and low acute toxicity in humans and in many animal species [39]. They are biodegradable and photo-oxidizable[40].

Before any poisoning, a pyrethroid insecticide, check its exact composition in search of a solvent such as ethylene glycol. Indeed, the solvent may have a more serious toxic potential that the insecticide itself [41]. Methomyl, methyl or N [[(methylamino) carbonyl] oxy] ethanimidothioate is an anticholinesterase carbamate marketed since 1976 under the name Lannate [42]. With organophosphate insecticides, carbamates have gradually replaced the organochlorine insecticides because they have important properties. Moreover, they are not persistent in the environment and are not bio-accumulate in the food chain [43]. Proclaim Insecticide SG 05 is composed of an active material "Emamectin benzoate". “Lannate 25 WP” is an insecticide containing Methomyl, belonging to the family of carbamates, and broad-spectrum [44]. The optimum concentrations differ by type of agriculture as shown in (Tab.3).

3.1.4. Using fungicides

According to the survey, unlike other types of treatment, the fight against plant parasitic fungi, arouses a big interest to farmers, probably depends on the frequency of infections with these pathogens.

The products used are based on sulfur as "soufrano", "soufravit WG 80" (80% sulfur) and “sulfur triturated afepasa DP 98.5" (98.50% sulfur). The pathogen is referred mildew parasite of tomato crops. The optimum dose is 30 10^{-4}kg / m^2. When sulfur is 98.5% and 500 g / hl when the sulfur is 80%. We also find other types of products as "Impact RM" which is a fungicidal compound of 117,5kg/m^3 flutriafol and 0,250 kg/l carbendazim. It has an action both preventive on major foliar diseases of cereals and mainly wheat (Septoria, yellow and brown rusts, powdery mildew, Fusarium, Rot pays, blight and Rynchosporioses). However, for septoria, other fungicides carbendazim, have proven more effective. The optimum dose is 10^{-7} m^3 / m^2[45].

There are two types of use of methomyl either powder or solubilized in ethanol. The lethal dose of the fungicide contained Methomyl is 12-15 mg / kg [46].

3.2. Classification of pesticides listed in the region of the Oualidia

The toxicity of pesticides is assessed according WHO classification that is directly related to the oral LD50 and / or skin in rats (Tab.1). The use of nematicides is the one that represents the greatest risk. The results obtained are shown in (Tab.4), as, three products are used which are rated highly both dangerous. This is because of their contents of active substance "fenamiphos" ranked highly hazardous by the WHO. "Nemacur CS 240" contains 240 kg / m^3 and Nemacur 10 G contains 10%. Fungicides and insecticides are coming in second place.

Also, the products used are classified mildly to moderately dangerous. Fungicides and insecticides classified moderately hazardous contain the active substance "methomyl" classified as highly dangerous by the WHO. Herbicides are pesticides with lower toxic effects on crops, as most herbicides are classified Slightly hazardous, unless the product "Illoxan 36 EC" which is recognized Moderately hazardous, this is due to the presence of the active substance 'Diclofop methyl "in high concentration (360 kg/ m^3), and the LD50 for rats orally is 563 to 693 mg.kg-1.

Table 3 : Using of principal insecticides

Insecticides		**Active ingredient**	**Crop**	**Enemies**	**Optimal dose**
Salvador	Salvador 24 SL	Methomyl	Tomatoes, eggplant and peppers	Whitefly, Noctuelles, aphids	0,00015-0.00025 m^3/ m^3
	Salvador 25 WP			Whitefly, Noctuelles, aphids, moths, codling moth and leafminer	1,80-2 Kg/ m^3
Takumi 20 WDG		Flubendiamide	Tomatoes	Leafminer (*Tutaabsoluta*)	0,50 Kg/ m^3
Proclaim 05 SG		Emamectin benzoate	Cucumber, alfalfa, bell pepper, tomato	Noctuelles	0,25 10^{-4} Kg/ m^2
Supermethrine	Supermethrine 10	Cypermethrine	Tomato	Noctuelles	0,0006 m^3/ m^3
	Supermethrine 25		Zucchini and bell pepper		0,0003 m^3/m^3
Lannate 25 WP		Methomyl	Eggplant, peppers, tomatoes	Whitefly,Noctuelles, aphids	0,0015-0,0025 m^3 / m^3

The determination of the oral and dermal LD50 in rats for various pesticides used is based on the consultation of the product information sheets provided on the internet by the various producing companies and also based on several published works. Lack of information or research on the toxicity of certain products, brings in search of the toxicity of the active molecule contained in the pesticide, to be precise [47]. The chemical identity of diclofop-methyl is "Propanoic acid, 2- [4- (2,4-dichlorophenoxy) phenoxy] -, methyl ester" [48].

3.3. Estimation of pesticides flows into the coastal aquifer

According to the survey, seven active ingredients considered have been identified as frequently used. Based on their toxicity, "methomyl and fenamiphos" are highly dangerous (Ib), "Emamectin benzoate; cypermethrin and 2.4-D "are hazardous Moderately (II) and" flubendiamide and diclofop-methyl "are slightly hazardous (III).

3.3.1. Emamectin benzoate

The active substance 'Emamectin benzoate "enters into the composition of insecticides macrolide [49]. The active substance "Emamectin benzoate" is resistant to microbial degradation (174 days half-life) and hydrolysis (193-day half-life). However, the main route of dissipation of primary environment "Emamectin benzoate" should be photolysis on the ground (5-day half-life) [50].

The pathway of degradation Emamectin benzoate was studied in four soils in dark aerobic conditions at 293,15 °K or 298,15 °K (in soil). Under these conditions of moderate exposures, Emamectin revealed a high persistence in soil (half-life (DT50) = 25.2 to 414 days) in which it was transformed into a number of metabolites. The recommendation for the allowable concentration of the active substance 'Emamectin benzoate "in water is not specified. "Emamectin benzoate" has a potential to be adsorbed to particulate matter in surface and be closely related to marine sediments seen its low or even its non-mobility [51].

3.3.2. 2,4-Dichlorophenoxyacetic Acid (2,4-D)

The active substance usually contained in the herbicide is "2,4-D". According to the US Agency for Environmental Protection (USAEP), "The toxicity of 2,4-D depends on its chemical forms, including salts, esters and acid form. 2,4-D typically has low toxicity for the human. In Environmental degradation will be fast in sediments (half-life <1 day) and photo-oxidation (half-life of 1 day) and average ultraviolet photolysis in water (half-life of 2- 4 days). Also, 2,4-D amine salts and esters are not persistent in the environment and there is no evidence that the bio concentration of 2,4-D occurs through the food chain [52]. Therefore, the persistence of the anion of 2,4-D is a major concern because 2,4-D residues may reach groundwater by leaching through the soil strata, for its power high leaching. The 2,4-dichlorophenoxyacetic acid is a hydrophilic compound which tends to remain in the water and does not adsorb on the soil.

Table 4 : Classification of the main pesticide identified

Pesticides	Type	DL 50 Dermal (mg/Kg)	DL50 Dermal (mg/Kg)	Ranking INERIS	Ranking WHO
NEMACUR 240 CS	Nematicide	200 - 500	> 400 < 2000	A	Ib
NEMACUR 10 G		25	>2000	A	Ib
NEMASOL 510		896	>2000	C	III
PRINTAZOL 75	Herbicide	1200	ND*	C	III
MENJEL 24 EC		850	2000	C	III
AURORA PLUS 70 WG		>5000	>4000	C	III
GRANSTAR 75 DF		5000	2000	C	III
HARMONY EXTRA		> 5000	> 5000	C	U
MUSTANG 306 SE		> 2000	> 2000	C	III
PRINTAZOL 75		962	>4000	C	III
DIALEN SUPER 464 SL		> 942	> 2000	C	III
AGROXONE F		765	2000	C	III
DERBY 175 CC		> 2000	> 2000	C	III
PALLAS 45 OD (Pyroxsulam)		> 2000	ND*	C	III
ILLOXANE 36 EC		563-693	2000	C	II
HUSSAR OF*		> 3150	> 5000	C	III
CHEVALIER*		ND	> 5000	C	U
ATLANTIS*		> 4000	> 5000	C	U
SALVADOR 24 SL	Insecticide	170	ND*	A	II
SALVADOR 25 WP		136	ND*	A	II
TAKUMI 20 WDG		> 2000	> 2000	C	III
PROCLAIM 05 SG		> 2000	> 2000	C	III
SUPERMETHRINE		187 - 326	1600	C	II
CORAGEN		> 5000	> 5000	C	U
SOUFRANO	Fungicide	>2000	>2000	C	III
SOUFRAVIT 80 WG		>2000	>2000	C	III
SOUFRE TRITURE AFEPASA 98,5 DP		>2000	>2000	C	III
IMPACT RM		5500	> 2260	C	III
LANNATE 25 WP		117	>1000	A	II
LANNATE 20 L		170	> 1000	A	II
ND* : No Identified					

The absorption of 2.4-D by plants, and possibly more organic matter and microbial activity in the fertile agricultural soils may limit the infiltration of 2,4-D residues to groundwater. The compound is relatively mobile, due to rate and types of applications [53]. This approves once again that herbicides are plant protection products with less toxic effects on crops**.**

3.3.2. Methomyl

According to our survey, the active substance "methomyl" is the most frequently used in the area of Oualidia which, belongs to the chemical group of carbamates. The insecticidal composition "SALVADOR" and fungicide "LANNATE" are both contain methomyl**.** The chemical formulation of methomyl is "S-methyl N-(methyl carbamoyloxy). The thioacetimidate". Adsorption of methomyl to soil particles is low to moderate. Soil microbes rapidly degrade Methomyl [54]. The dissipation half-life in soil is methomyl reportedly three to six weeks [55]. Under aerobic conditions, the methomyl has a 30-45-day half-life in the soil and especially degrades into carbon dioxide. It is relatively stable to hydrolysis in the soil under neutral and acidic conditions. Under basic conditions, it degrades over a 30-day half-life. Under anaerobic conditions, total degradation takes 8 days. In one experiment, hydrolysis half of methomyl in solutions at pH 6.0, 7.0 and 8.0 take 54, 38 and 20 weeks, respectively. In pure water, the half-life of hydrolysis was estimated to be 262 days. Methomyl is unlikely to bioconcentrate in aquatic systems [56].

3.3.4. Fenamiphos

The active substance "fenamiphos" belongs to the chemical group to organophosphate nematicide effect. The chemical nomenclature international (ISO) of "Fenamiphos" is 3-iodo-N'-(2-mesyl-1,1-dimethylethyl) -N- {4-[1,2,2,2-tetrafluoro-1-(trifluoro-methyl)ethyl]-o-tolyl} phthalamide (International Union of Pure and Applied Chemistry [IUPAC]). Acute flubendiamide is low.

The decrease in bioavailability, due to strong sorption soils, is cited as a major cause of the prolonged persistence of certain biodegradable pesticides in soil [57].To approve the importance of bioavailability of pesticides to accelerate the biodegradation phenomenon, a study was conducted by Singh (2003) showed that the pesticide "Fenamiphos" strongly absorbed on an organically seems to be readily available for the exceptionally rapid degradation by the soil bacterium *Brevibacterium sp* with a hydrolysis rate of 77% [58].The dissipation half-life of nematicide "Nemacur" in water is 602 days at pH= 7. The contamination of water sources by nematicides can occur by two main routes. The first is a simple to contamination by spills or washing equipment, which occur in / or near water sources. The second, less obvious, is the soil from leaching into groundwater. Fenamiphos has great potential for groundwater contamination [59].

3.3.5. Flubendiamide

The active substance "Flubendiamide" represents a new class of insecticides with a very high activity against a broad spectrum of lepidopteran pests of crops [60]. According to a recent study, the "Flubendiamide" normal field dose ($1.0\text{-}2.510^{-4}$ kg / m^2) would not pose a threat to soil enzymes [61). In addition, "Flubendiamide" is very mobile in soil, which supports the choice "Flubendiamide" as an active substance having a respectful environment with the least ecotoxicity and low bioaccumulation [62].However, do not overlook its high toxicity for certain marine organisms.

In 2011, a study by Kumar Das and Mukherjee on Flubendiamide degradation by hydrolysis in water and photolysis in soil found that the dissipation in water was faster at pH 4.0 (half-life time of 250.8 days), moderate to pH 9.2 (half-life time is 273.6 days) and long at pH 7 (half-life time is 301 days. Thus, generally "flubendiamide "is considered stable to hydrolysis at pH 4.0 and 9.2 [63]. It is also highly persistent in soil and aquatic environments (Tab.5). However, a low risk was shown in the exposure assessment of surface water flubendiamide [64].

3.3.6 Cypermethrin

The active substance "cypermethrin" ranks among the oldest synthetic pyrethroids (first synthesis in 1974). This pesticide is highly toxic to bees and highly toxic for fish and freshwater invertebrates. The acute contact LD50 of 0,023 mg / bee. The LC50 (96 hours) for Cypermethrin in rainbow trout is 0.0082 mg / L, and bluegill is 0.0018 mg / L. The acute LC50 Daphnia, a small crustacean freshwater is 0.0002 mg / L. Recent research shows that it has a high potential to bioaccumulate in the tissues of aquatic organisms [65].

Cypermethrin is moderately persistent in the environment and is degraded by a combination of abiotic transformations and biotransformation. It resists hydrolysis in neutral medium and acid but alkaline hydrolysis. Cypermethrin has a moderate persistence in soil. Its half-life is two months. It is slightly persistent in water with a half-life of 9 days under aerobic conditions and 17 days under anaerobic conditions. As Cypermethrin is insoluble in water and has a strong tendency to adsorb to soil particles. It is, therefore, unlikely to result in contamination of underground waters [66].

3.3.7 Diclofop-methyl

The active substance "diclofop-methyl" enters the herbicide composition of the family aryloxyphenoxypro-pionate, chemical nomenclature is propionic acid, 2- [4- (2,4-dichlorophenoxy) phenoxy] -, methyl ester. The laboratory experimentation, as diclofop-methyl was stable in acidic solutions and near neutral for at least 15 days.However, diclofop-methyl is rapidly dissipated into natural water systems and suspended on the ground, with a half-life of fewer than 4 days. This was explained by the important role of the suspended organic matter and metal ions in accelerating the hydrolysis of this herbicide. Other studies have shown that the graminicide activity of diclofop-methyl was affected by rising temperatures beyond 301,15 °K and water stress. It is classified as a restricted use pesticide (RUP) by EPA must have the word of warning "danger" printed on the product label. Diclofop-methyl is not expected to be found in drinking water. In addition, "diclofop-methyl" is known for its toxicity to aquatic organisms, the active substance is highly toxic to fish. The recommendation for water quality for diclofop-methyl for the protection of aquatic life is 6.1 mg / L [67].

The insoluble active ingredients belong to the chemical group of pyrethroids and the chemical group of Anthranilic Diamides and therefore not liable to pollute the ground water that the chemical group of Anthranilic Diamides are the most persistent. However, we note that the active substances belonging to the chemical group of organophosphates and the chemical group of Phenoxyacetic Acid are highly soluble in water. Thus, nematicides fenamiphos containing the active substance has a large potential for groundwater contamination (Tab.5). The active ingredients in herbicides extras in (Tab.5), and the chemical group composed of some insecticides pyrethroids that are less persistent [68].

In addition, because of its high solubility in water and its half-life in soil (33 days), methomyl may have a potential for contamination of groundwater [69]. From the results of various research works, it has been found that substances having a high solubility in water can contaminate groundwater, namely fenamiphos and 2.4 D, despite hydrolysis in the fast enough water which is 10 and 78 days respectively. From (Tab.5), the most resistant to hydrolysis substances with a duration which exceeds one year, respectively Flubendiamide, Methomyl and Emamectin benzoate [70].

Table 5 : Active substances considered extremely dangerous to moderately dangerous

Active substance	**Type**	**Chemical group**	**Classification (7)**	**Solubility in water (mg/l) at 293,15 °K**	**Hydrolysis in water per (j) at pH 7**	**Persistence by days (j)**
Fenamiphos	Nematicide	Organophosphorus	Ib	400	10	120 à 122
Flubendiamide	Insecticide	Anthranilic diamide	III	0,03	602	1000
Emamectin benzoate		macrocyclic lactone (macrolides)	II	93	386	50,4
Cypermethrin		Pyrethroids	II	0,01	18 to 34	14 21
Methomyl	Insecticide Fungicide	Carbamates	Ib	58	532	66
Diclofop-methyl	Herbicide	Aryloxyphenoxypropionate	III	50	62	10 to 30
2,4-Dichlorophenoxy-acetic Acid (2,4-D)		Phenoxyacetic Acid	II	500 to 900	78	2 to 10

Conclusions

The phytosanitary survey in Oualidia and specifically in "Douar Bakir" and "Douar Oulad Lhlal" revealed the use of 30 pesticides any kind confused, dominated by herbicides. The widespread use of herbicides to control weeds and the increase of crop productivity in modern agriculture exerts a threat important on economically.

According to the analysis of the survey results, herbicides are pesticides with lower toxic effects on crops, as most herbicides are classified slightly hazardous. The survey showed that in the area of chemical control against the weeds anticotyledons is dominated by the active ingredient 2,4-D that enters the composition 66.66% of the herbicides used. This active ingredient has the advantage of rapidly degrade in the environment. For against, it is

highly soluble in water and must not reach the ground water. It is recommended to limit the use of such herbicides in agricultural land or groundwater level of irrigation wells is low.
However, pesticides that pose the greatest risk to the environment and essentially water sources are nematicides and pesticides containing active substance "methomyl". If organophosphate nematicides are not used responsibly, they could have a serious impact on humans, animals, the environment and agriculture sustainability. This is mainly due to their content of active substance "Fenamiphos" ranked highly toxic by the WHO and with great potential for contamination of groundwater by infiltration even its high solubility in water. Hence, the need to introduce other physical and biological methods to fight against RNK as solarization, biofumigation and the use of biologic nematicide in effect, namely certain mycelia (*Paecilomyces lilacinus* strain) and bacterial species (Agrobacterium radiobacter K 84 Bacillus subtilis IBE 711, Pseudomonas chlororaphis).
The active substance "metomyl" returns both in the composition of insecticides and fungicides, ranked highly toxic by the WHO. The active substance "methomyl" because of its high solubility in water and its high resistance to hydrolysis with a duration, which exceeds one year, has great potential for groundwater contamination.
We recommend, the use of pesticides must be controlled and progressively replaced by non-chemical control methods, attention to economic gain should not be done depends on the safety of groundwater and lagoon. The risks in case of excessive pesticide use - defined as before - according to their different physicochemical characteristics, user manual, concentration and duration of treatment. Also, according to the soil texture and the types of crops. Pesticides used by spraying, with a high risk of contamination of surface water and exceptionally in this study, the waters of the lagoon by the release of aerosols formed in association with the water vapor that condenses during the heat wave or morning dew.
As a precaution, avoid spreading pesticides in rainy days because the waters facilitate the mobilization of water-soluble active substances and resistant to hydrolysis, or by trickling up the lagoon or infiltration to groundwater water. Fortunately, this infiltration to groundwater occurs over a long period and may be thwarted by the action of microorganisms that play a significant role in the biodegradation of certain pesticides or pesticide residues that are sensitive to it. The investigation conducted has determined certain active substances in high toxicity to aquatic organisms.

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