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Research Article

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Pesticides for agricultural use in the province of Ben Slimane, Morocco: Inventory, toxicity and physicochemical quality of groundwater

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ABSTRACT

The study of the inventory of pesticides qualitatively and quantitatively and the quality monitoring of subterranean waters of BEN SLIMANE's province by the analysis of some physico-chemical parameters make us to release some interactions between agricultural pesticides and environment. Inquiries realized in the zone of study, allowed the inventory of 63 pesticides agricultural use marketed, among which 21 Insecticides, 9 Weed-killers and 33 Fungicides with a total of 57 active Materials. The use of pesticides with agricultural use in the zone of study and the comparison of their degree of toxicity with the international standards, allowed us to raise certain risks bound to these substances, particularly the phytosanitary products the active materials of which belong to the classes Ib and II which represent a potential risk on the various components of the ecosystem and which require a follow-up in the future in the various components to know METHOMYL, DELTAMETHRINE, CYPERMETHRIN, THIACLOPRID, IMIDACLOPRID, TAU-FLUVALINATE, DIMETHOATE, BIFENTHRINE, 2,4-D. The physico-chemical quality subterranean waters of the zone of study respects the Moroccan standard, except the conductivity in 4 municipality OULAD LOUTA, MELLILA, FDALATE and SIDI BETACHE who and exceeded the standard because of the effect of the geologic nature on the quality of waters.

Keywords: Inventory, Pesticide, Impact, water, groundwater, toxicity, Ben Slimane

INTRODUCTION

In Morocco, approximately 300-350 active substances are allowed and enter into the composition of more than 1000 trade specialties, including more than 80% approved for agricultural use [1].

Despite pesticides are approved they are not quite safe, if an adjuvant is considered to be inactive; it can become toxic depending on the manner of use. The aim of this work is to conduct investigations in BEN SLIMANE province whose purpose is to prospect points of sale of pesticides in the province in order to characterize; inventory and study places of final destination of the products sold. Define pesticides used for principal crops in the study area and establish toxicity of active contents sheets products used to define the impacts of pesticides on the different components of the ecosystem (environment, health...).

Parallel to this inventory a physicochemical study was conducted at the level of any point located in the area of inquiry, which aims to have an idea about the quality of the groundwater water.

EXPERIMENTAL SECTION

General presentation of the study area:

The BEN SLIMANE Province is located between the administrative capital RABAT and CASABLANCA metropolis with an area of 276 000 ha = 2760 km^2 and a population of 233 123 inhabitants (2014) [2].

Land in the study area:

Agriculture

Agriculture is the most dominant activity in the Province's economy. The useful agricultural Surface (S.A.U) accounts for 55.8% of the land area of the Province is approximately 133.920 ha (3.767 irrigated Ha, 130.153 bour) spread over 14.033 farms. The rest are occupied by the forests with 23.7% (56.988 ha). The course and uncultivated land represent 20% (49.119 ha) [2].

Major crops

Grain farming represents the main activity of rain fed agriculture in the province with 61% of the useful agricultural Surface. Legumes, fodder and industrial crops represent respectively 9%, 8% and 1.4%. The distributions of these crops as well as average yields of the five latest companions are reported in the table below [2]:

| Emocios | Area (ha) | | Yield | (Qx/ha) | Production (Qx) | | |
|------------------|-----------|-----------|-------|-----------|-----------------|-----------|--|
| Species | Bour | Irrigated | Bour | Irrigated | Bour | Irrigated | |
| CEREALS | 81850 | - | 16.5 | - | 1.342.550 | - | |
| Durum wheat | 21.500 | - | 17 | - | 366.100 | - | |
| Common wheat | 46.550 | - | 16.7 | - | 781.150 | - | |
| Barley | 9.350 | - | 15 | - | 140.550 | - | |
| Corn | 750 | - | 18 | - | 13.750 | - | |
| Oats grain | 3.700 | - | 11 | - | 41.000 | - | |
| FODDER | 11.080 | 445 | 43 | 2.625 | 476.440 | 116.812 | |
| Oats | 8.250 | - | 29,6 | - | 244.200 | - | |
| Barley oven. | 2.830 | - | 77 | - | 217.910 | - | |
| Alfalfa | - | 20 | - | 250 | - | 500 | |
| Corn furnace. | - | 400 | - | 400 | - | 160.000 | |
| Ryegrass | - | 10 | - | 200 | - | 2.000 | |
| Other | - | 15 | - | 200 | - | 3.000 | |
| LEGUMES | 12.150 | - | 9.6 | - | 117.550 | - | |
| Bean | 2.850 | - | 11 | - | 32.050 | - | |
| Pea | 2.550 | - | 11 | - | 28.650 | - | |
| Lens | 3.650 | - | 8 | - | 29.950 | - | |
| Chickpea | 2.650 | - | 9 | - | 23.850 | - | |
| Dry beans | | - | 7 | - | 3.150 | - | |
| INDUSTRIAL CROPS | 830 | - | 9 | - | 7.800 | - | |
| Sunflower | 300 | - | 10 | - | 3.000 | - | |
| Sorghum | 230 | - | 7 | - | 1.650 | - | |
| Lupin | 300 | - | 10,5 | - | 3.150 | - | |

Table 1: The main crops in the study area (Source: Directorate Provincial agricultural of BEN SLIMANE)

Hydrology of the area:

Surface water resources

The BEN SLIMANE Province contains a large number of points of superficial water, sources and the (temporary and permanent) rivers which are used for irrigation and drinking water of the centres and douars[2].

Course of surface waters:

Table 2: The course of surface waters in the study area (Source: Directorate Provincial agricultural of BEN SLIMANE)

| Oued Maleh | 59.00 km in length |
|---------------|--------------------|
| Oued N'fifikh | 54.00 km in length |
| Oued Arrimen | 22.50 km in length |
| Oued cherrat | 21.50 km in length |
| Oued Ghbar | 15,00 km in length |
| Oued Bouznika | 15.00 km in length |
| Oued Hassar | 14.00 km in length |
| Oued Sikouk | 6.00 km in length |

Groundwater resources

It are very limited at the level of BEN SLIMANE Province the lithological nature of land existing, very low permeable and very poorly fed because of relatively abundant siltcovers which impede the infiltration of meteoric water and conversely promote surface runoff.

The investigations on the ground:

Several surveys were conducted in the area of study to agricultural use pesticide. These investigations have requested significant movements on the ground and contacts very close with farmers and traders (dealers) of the plant protection products.

The specifications developed for this purpose is structured along the following lines:

- Trade name
- Active ingredient
- Supplier and its place
- Culture destination
- Rate of application

During these investigations in the area, we prospected places of sale of pesticides in the region characterize an inventory of study places of final destination of the products sold and do a partial monitoring of the quality of groundwater.

Total 5 resellers of plant protection products have been identified in the survey area(table 3).

Table 3: Information about resellers of plant protection products

| Seller | Name and first name | Place | Activity | Phone | Workforce |
|----------|---------------------|----------|---------------------------------------|----------------|--------------|
| Seller 1 | IDAMIA Brahim | Skhirat | Distribution of agricultural supplies | 05 37 74 21 72 | 10 employees |
| Seller 2 | IDAMIA Said | Skhirat | Distribution of agricultural supplies | 06 61 56 78 66 | 3 employees |
| Seller 3 | HAKIM Abdelah | Skhirat | Distribution of agricultural supplies | 06 18 15 17 00 | 5 employees |
| Seller 4 | MOHA Karim | Bouznika | Distribution of agricultural supplies | 06 61 77 48 99 | 3 employees |
| Seller 5 | BAIT Redouan | Bouznika | Distribution of agricultural supplies | 05 37 87 90 00 | 2 employees |

The quality of groundwater:

Sampling points

Sampling Points were selected in 15 municipalities in the Province of BEN SLIMANE. These samples were divided according to the types of crops in the study area.

The study was conducted on 15 water samples from 15 wells in rural areas in the 15 municipalities of BEN SLIMANE during the period of April 2015. A water sampling was conducted in each well.

RESULTS AND DISCUSSION

Studies of physicochemical parameters of the underground waters of the study area:

All of the results of physicochemical analyses of 15 municipalities in the Province of BEN SLIMANE are represented in table 5. Their analysis will be based on the Moroccan standard [3]

| Place of sampling | Temperature (° C) | pН | Conductivity (µS/Cm) | Salinity (g/L) |
|-------------------|-------------------|------|----------------------|----------------|
| CHERRAT | 19,2 | 7,06 | 2400 | 1,1 |
| MOUALIN ELGHABA | 21,6 | 7,2 | 1683 | 0,7 |
| AIN TIZGHA | 15,2 | 7,52 | 1499 | 0,5 |
| EL MANSOURIA | 21 | 7,33 | 1905 | 0,8 |
| ZIAIDA | 21,3 | 7,71 | 889 | 0,2 |
| MELLILA | 19,3 | 7,2 | 4400 | 2,3 |
| OULAD TOULAA | 22,5 | 7,4 | 1170 | 0,3 |
| OULAD LOUTA | 20,1 | 7,33 | 3440 | 0,7 |
| BIR ENNASR | 21,2 | 7,6 | 826 | 0,2 |
| BOUZNIKA | 19 | 7 | 2300 | 1,2 |
| OULED MALEK | 22 | 7,4 | 1100 | 0,2 |
| MOUALINE OUED | 21,4 | 7,2 | 1160 | 0,3 |
| FDALATE | 20 | 7,2 | 3000 | 0,6 |
| AHLAF | 20 | 7,3 | 900 | 0,3 |
| SIDI BETACHE | 19 | 7,1 | 4000 | 2,2 |

Table 4: Features 15 Commons in-situ physicochemical

Temperature

The results of the temperature of the 15 communes are represented in figure 3.

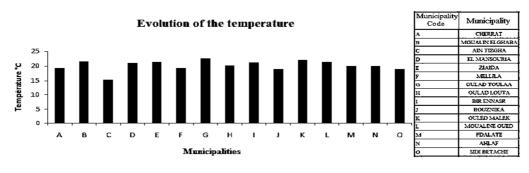
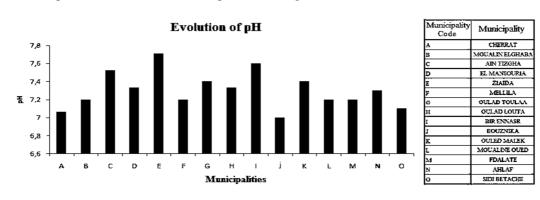


Figure 1: Evolution of the temperature

Note that maximum Temperature is 22.5 $^{\circ}$ C and the minimum temperature is 15.2 $^{\circ}$ C. These temperatures are acceptable according to the Moroccan standard [3].

This temperature variation is related to the depth of the well, more the well is deep minimum temperature is important and vice versa.



Influence of pH

The results of the pH of the 15 communes are represented in figure 4.



Generally the measured pH values are neutral. They are between 7 as Minimum and 7.71 as Maximum, so they are in the majority of groundwater level. Its values are in the field of the Moroccan standard between 6.5 < pH < 8, 5. These waters are well buffered [3].

Study of conductivity of water

The results of the conductivity of the 15 communes are represented in figure 5.

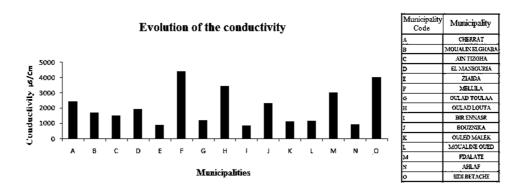


Figure 3: Evolution of the conductivity

Note that Commons MELLILA (4400 μ S/Cm), OULAD LOUTA (3440 μ S/Cm), FDALATE (3000 μ S/Cm) and SIDI BETACHE (4000 μ S/Cm) exceeded the Moroccan standard which is 2700 μ S [3].

Moreover the evolution of this setting highlights the role of the effect of the geology on the quality of the water.

This influence is visible at the level of the pit where mineralization is higher in relation to leaching of land surrounding (clayey and sandy terrain).

Inventory of pesticides to agricultural use in the study area:

With surveys of farmers and the Direction provincial of the Agriculture of BEN SLIMANE allowed us noted that most farmers purchase plant protection products at five retailers in the communes of SKHIRAT and BOUZNIKA.

Inventory of pesticides for agricultural and commercial use in the study area

Surveys conducted in the study area, helped inventory of 63 pesticides agricultural marketed. The main elements of this inventory are as follows:

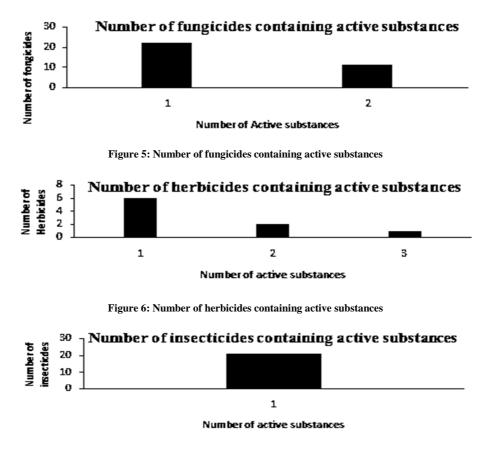
- 21 insecticides, 9 Herbicides and 33 fungicides with a total of 57 active substances.

The main elements of this inventory



Figure 4: Elements of the inventory

Analysis of the products and their active substances by categories can be:





On 33 fungicides 11 fungicides contain 2 active ingredients and 22 fungicides with 1 ingredient active.

On 9 Herbicides 2 Herbicides contain 2 active ingredients, Herbicides 1 which contains 3 active ingredient and 6 Herbicides with 1 active ingredient.

21 insecticides contain 1 active ingredient.

Major pesticides identified according to risk and toxicological classification:

As reported the danger according to the World Health Organization (WHO) means the degree of risk to health (risk of a single or multiple exposure over a relatively short time) for classifying ecotoxicological and toxicological, the classification of the world Organization of health which was adopted is based on the danger that can constitute a pesticide on human and animal health.

Case of Insecticides-Acaricides

Table 6: Table represents the classification of insecticides-acaricides according to their risk and toxicological

| The Active ingredient | Insecticides | Dermal LD50 (mg/KG) | Oral LD50 (mg/KG) | Solubility in water | WHO | Chemical family |
|-----------------------|-----------------|---------------------------|----------------------|---------------------|-----|-------------------|
| DELTAMETHRINE | DECIS EXPERT | > 2000 | 87 | 0,005 mg/L | II | PYRETHROID |
| | SICO-FLUXX | | | | | |
| CYPRENETHRINE | ARRIVO 25 EC | > 2000 | 287 | 9 μg/L | II | PYRETHROID |
| | VITATHRINE | | | | | - |
| THIACHLOPRID | CALYPSO 480 SC | > 2000 | 836 (M); 444 (M) | 184 mg/L | II | NICOTINOIDE |
| IMIDACLOPRID | CONFIDOR 200 OD | > 5000 | 131 (M); 506 (F) | 601 mg/L | II | NITROGUANIDINE |
| SPIRODICLOFEN | ENVIDOR | > 2000 | > 2500 | 190 µg/L | III | TETRONIC ACID |
| GLYPHOSATE | SPEED | > 2000 | > 2000 | 10,5 g/L | III | AMINO ACID |
| METHOMYL | LANNATE 25 WP | > 1000 | 20 (M); 28 (F) | 58 g/L | Ib | CARBAMATE |
| ABAMECTINE | VALMEC | 330 | 10 | nn sol | III | AVERMECTIN |
| ADAMECTINE | TINA | 330 | 10 | IIII SOI | | |
| FENAZAQUIM | PRIDE 200 SC | > 5000 | 134 | 130 µg/L | П | QUINAZOLINE |
| | | | | | п | DERIVATIVES |
| TAU-FLUVALINATE | MARVIK 2F | > 2000 | 282 (M); 261 (F) | 1,03 µg/L | II | PYRETHROID |
| ALPHACYPERMETHRINE | CONCORD 100 EC | > 2000 | 57 | 3,97 µg/L | Π | PYRETHROID |
| TEBUFENPYRAD | MASAI | > 2000 | 320 | 2,4 mg/L | III | PYRAZOLAMIDE |
| PYRIDABEN | NEXTER 10 SC | > 2000 | 435 (M); 358 (F) | 12 µg/L | III | PYRIDAZONE |
| PROPAGITE | OMITE 570 EW | 4000 | 2800 | 632 mg/L | III | |
| DIMETHOATE | PERFEKHION | > 2000 | 245 | 39,8 g/L | П | ORGANO-PHOSPHORUS |
| BIFENTHRINE | TALSTAR | > 2000 | 54,5 (M) ; 186,1 (F) | < 0,001 mg/L | П | PYRETHROID |

Case of Herbicides

Table 7: Table represents the classification of Herbicides according to their risk and toxicological

| The Active ingredient | Herbicides | Dermal LD50 (mg/KG) | Oral LD50 (mg/KG) | Solubility in water | WHO | Chemical family |
|----------------------------|---|------------------------|----------------------|---------------------|-----|-----------------|
| 2,4 – D | AL FAHD MIX YEDESTER 225 U 46 COMBI FLUID 6 | > 2000 | 764 | 34 g/L | Π | ARYLOXYACIDE |
| 2,4 - MCPA | U 46 COMBI FLUID 6 AL FAHD MIX | >1000 | 700 | | III | |
| FORMASULFRON | MAISTER OD | > 2000 | > 5000 | 37 mg/L | III | SULFONYLUREE |
| IODO SULFRON-METHYL-SODIUM | MAISTER OD | > 2000 | 2678 | 25g/L | III | UREA |
| ISOXADIFEN-RTHYL | MAISTER OD | > 2000 | 1611 | 1,06 mg/L | III | |
| BENTAZONE | BASARGAN | > 5000 | 1800 | 570 mg/L | III | THIADIAZIME |
| DIMETHERAMIDE | INTEGRITY | > 2000 | 371 | 1,45 g/L | III | CHLOROACETAMIDE |
| PENDIMETHALINE | PROWL | > 2000 | > 5000 | 0,33 mg/L | III | DINITROANILINE |
| NICOSUFLURON | NICOSH 750 WG | > 2000 | > 5000 | 7,5 g/L | III | SUFLONYLUREE |
| GLYPHOSATE | ROUNF UP | > 2000 | > 2000 | 10,5 g/L | III | ACIDE AMINE |

Case of fungicides

| The Active ingredient | Fungicides | Dermal LD50 (mg/KG) | Oral LD50 (mg/KG) | Solubility in water | WHO | Chemical family |
|-----------------------|---|---------------------------|-------------------------|---------------------------|-----|------------------|
| THIRAME | THIRAMIC BASULTRA | > 2000 | 3700 (M) ; 1800 (F) | 0,0165g/L | III | CARBAMATE |
| CHLOROTHALONIL | BAKALA CLORTOSIP | > 2000 | > 5000 | 0,81mg/L | III | ISOPHTALOMITRILE |
| BUPIRIMATE | NIMROD 25 EC | | 4000 | 13,06mg/L | III | PYRIMIDINE |
| DIFENOCONAZOLE | PRIORITOP DIFCOR 250 EC SCORE 250 EC | 2010 | 1453 | 15mg/L | III | TRIAZOLE |
| BOSCALIDE | COLLIS SC SIGNUM WG | > 2000 | > 5000 | 4,64mg/L | III | CARBOXIME |
| KRESOXIM-METHYL | COLLIS SC ALLERGO | > 2000 | > 5000 | 2mg/L | Ш | STROBILURIME |
| PROPINEBE | ANTRACOL COMBI ANTRACOL 70 WP | > 5000 | > 5000 | < 0,01g/L | III | CARBAMATE EDBC |
| OXYCHLORURE DE CUIVRE | FLARE GOLD | > 2000 | 1862 | < 0,312 mg/L | III | MINERAL |
| METALAXYL-M | FLARE GOLD RIDOMIL GOLD MZ 68 WC | > 2000 | 953 (M) ; 375 (F) | 26g/L | III | PHENYLAMIDE |
| MANCOZEBE | AGRIZEB 80 WP ACROBAT TURBO ZM RIDOMIL GOLD MZ 68 WC | > 2000 | > 5000 | 2 - 20mg/L | III | CARBAMATE EDBC |
| PROPAMOCARBE | PROPLANT CONSENTO | > 2000 | > 2000 | 500g/L | III | CARBAMATE |
| HEXACONAZOLE | HEXA 5 SC | | | | | |
| AZOXYSTROBINE | ZEBRA 320 SC PRIORITOP | > 2000 | > 5000 | 6,7mg/L | III | STROBILURIME |
| PENCONAZOLE | TOPAS 100 EC | > 3000 | 2125 | 0,073mg/L | III | TRIAZOLE |
| MYCLOBUTANIL | SYSTHANE 240 EC | > 2000 | 1600 (M); 2290 (F) | 132mg/L | Ш | TRIAZOLE |
| DIMETHOMORPHE | ACROBAT CABRIO DUO ORVEGO | > 2000 | > 5000 | 0,0107g/L | III | ACIDE ANNAMIQUE |
| EPOXICONAZOLE | ALLERGO OPERA MAX | > 2000 | > 5000 | 8,4mg/L | III | TRIAZOLE |
| BOCALID | BELLIS WG | > 2000 | > 5000 | 4,64mg/L | III | CARBOXIME |
| PYRACLOSTROBINE | BELLIS WG OPERA MAX SIGNUM WG CABRIO DUO | > 2000 | > 5000 | 1,9mg/L | III | STROBILURIME |
| SOUFRE MOUILLABLE | KUMULUS DF | > 2000 | > 2000 | 63µg/L | III | MINERAL |
| AMETOCTRADINE | OVERGO | > 2000 | > 2000 | 0,23mg/L | III | UNSPECIFIED |
| TEBUCONAZOLE | ZEBRA 320 SC KING 250 EW | > 2000 | 1700 | 36mg/L | III | TRIAZOLE |
| PHOSETHYL ALUMINIUM | ALIETTE FLASH | > 2000 | 5800 | 120g/L | III | |
| CYMOXANIL | ANTRACOL COURBI | > 2000 | 960 | 780mg/L | III | UNSPECIFIED |
| FENAMIDONE | CONSENTO | > 2000 | > 5000 | 7,8mg/L | III | IMIDAZOLINE |
| TRIFLOXYSTROBINE | FLURT | > 2000 | > 5000 | 0,62mg/L | III | STROBILURIME |
| CYCLOXYDINE | FOCUS ULTRA | > 2000 | 4420 | 40mg/L | III | CYCLOHEXANEDIONE |

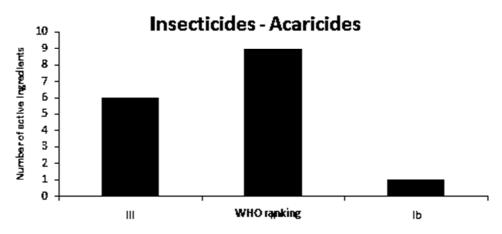


Figure 8: Number of active ingredients in each ranking for (WHO) for insecticides and acaricides

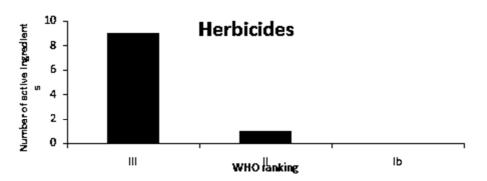


Figure 9: Number of active ingredients in each ranking for (WHO) for herbicides

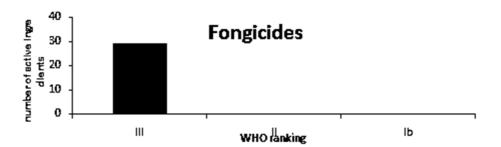


Figure 10: Number of active ingredients in each ranking for (WHO) for fungicides

The insecticides used in the study area contain a most dangerous active substance (class Ib), 9 of moderately dangerous substances (class II) and 6 slightly hazardous substances.

For herbicides are poorly used in the study area, there are 9 slightly dangerous active substances (class III) and 1 moderately dangerous substance (class II).

In addition, fungicides despite their high number, they contain class III which is slightly dangerous products [4].

Toxicity of active substances identified in the study area:

The list of compounds identified as the most toxic during the inventory of pesticides for use in agriculture is represented by 9 active substances: Methomyl, deltamethrin, Cypermethrin, Thiacloprid, Imidacloprid, Tau-fluvalinate,Dimethoate, Bifenthrin, 2,4-d.

After the study of the toxicity of its active ingredients there is that the effects on the various components of the ecosystem are:

• For mammals including man:

Acute toxicity: very toxic waterway oral and ocular and moderately toxic by inhalation, irritating to eyes

Long-term toxicity: neurologic effects, lose weight, stimulation of the nervous system

- Toxicity to non-target species:
- Toxic to non-target fish or Daphnia, bird and bee oral or bioaccumulation species.
- The behaviour in environmental fate:

Risk of contamination of groundwater and surface water by leaching and runoff, great half-life and poorly soluble in water and degraded by biodegradation, hydrolysis or photolysis and absorbed by sediment.

Pesticides are designed to kill "pests", but some pesticides can also have adverse effects on the components of the ecosystem. The likelihood of suffering adverse effects depends on the type of pesticide and other chemicals it contains, the duration and the frequency of exposure.

Some adverse health effects due to exposure to a pesticide can be felt immediately. Some symptoms may occur several hours after exposure. Other effects may occur after several years, for example cancer.

Some symptoms due to exposure to a pesticide shall cease at the end of the exhibition. Others may take some time to disappear. People regularly exposed to pesticides, long term health effects are more worrying.

CONCLUSION

This research allowed us to make a study of pesticide inventory in BEN SLIMANE province and also to control the quality of groundwater, to analyze some physicochemical parameters to clear interactions between agricultural use pesticide and environment.

Inventory has found 63 agricultural pesticides marketed, including 21 Insecticides, 9 Herbicides and fungicides 33 with a total of 57 active substances, which belongs to the different level of toxicity report by the World Health Organization. Hence it has noted certain risks related to these substances (active substances), particularly plant protection products whose active substances belong to class Ib and II which represent a potential hazard on the various components of the ecosystem and requiring a follow-up in the future in the various components of the ecosystem come water, soil, plant and animal information METHOMYL, DELTAMETHRIN, CYPERMETHRIN, THIACLOPRID, TAU-FLUVALINATE, DIMETHOATE, IMIDACLOPRID, BIFENTHRIN, 2,4-d that on a great impact on mammals including humans, toxicity to non-target such as Daphnia, birds, bees fish species, and also a great impact on the environment where there is a great persistence and leaching potential, therefore a contamination of surface and groundwater.

Acknowledgements

It is essential to deepen the study and gather more information on the quality of groundwater in the province and particularly the level of contamination of these ecosystems by elements particularly traces the heavy metals and pesticides and to study the risks associated with their presence, because the inhabitants of the province of BEN SLIMANE rely mainly on groundwater for water.

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