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Comparative Study of the Mobility of Malathion, Attamix and Thiodan as Obsolete Pesticides in Colombian Soil

Rosalina González Forero
La Salle University
Colombia

1. Introduction

The organizations responsible for carrying out control and surveillance of pesticides in Colombia stored large quantities of them many years ago. They didn't know exactly the impact generated in that storage, but for the nature of the pesticides it is highly possible the incorporation of these hazardous substances in the soil, due the mobility throughout the leaching of the residue. This study worked with soils of the Colombian Agricultural Institute (ICA) because it is the organization in charge of the management of pesticides in Colombia. The research identified the mobility process by leaching of waste from the obsolete pesticides Thiodan, Attamix and Malathion, which according to previous researches (Duarte and Guerrero 2006 & Gonzalez 2011) these chemicals were stored in large quantities and the containers were deteriorated by weathering conditions.
In the investigation was simulated a spill at two concentrations: Event 1 (non diluted or commercial presentation), and Event 2 (agricultural recommended doses). Measures of the concentrations of leach pesticides at different depths into the soil (10, 17 and 25 cm) were determined using gas chromatography. The soils studied were taken from two sources Mosquera and Villavicencio branches of ICA.

2. Pesticides[1]

Malathion 57% EC: Malathion is an organophosphate insecticide that inhibits cholinesterase from insects. It is used worldwide to control a wide range of crop pests and control campaigns insect vectors that transmit diseases to humans: mosquitoes, bedbugs and mosquitoes. It is a brownish-yellow liquid that smells like garlic. (Proficol 2008), (ATSDR, 2008)
Molecular Formula: $C_{10}H_{19}O_6PS_2$
Molecular Weight: 330.36
Active ingredient: Malathion S1, 2-di (etoxycarbonil) ethyl O, O-dimetilfosforoditioato, 604 g per liter of formulation to 20 oC.
Attamix: Its active ingredient is Chlorpyrifos. Also the pesticide is known as Dursban 23, which belongs to the family of pesticides, insecticides and organophosphates. It is white

[1]This study was developed also by Ricardo Campos as a Co-Author (Faculty Member at La Salle University) and the research was funded by La Salle University

crystal like solid and strong aroma. In the United States, Attamix is used for residential use and it was allowed until 2000 when it was restricted by the United States Environmental Protection Agency (U.S. EPA). (ATSDR, 1997)
Molecular Formula: $C_9H_{11}Cl_3NO_3PS$

Chemical Name: O, O – diethyl O – (3,5,6 – trichloro – 2.Pyridinyl) phosphorothioate

Thiodan E.C.: Is a pesticide that smells like turpentine, but it does not burn. It is used to control insects on crops and non-food grocery, and as a wood preservative.

Chemical Name: 6,7,8,910,10 – hexachloro – 1, 5,5 a, 6,9,9 a – hexahydro – 6, 9 – methane – 2,4,3 – benzodioxatiepin – 3 – Oxia

3. Leaching and mobility tests

Leaching is defined as the removal of a substance in a solid phase by a liquid phase which is in contact with it. The determination of the toxic characteristics of waste depends on the analytical method and therefore cannot generalize results if they have not established criteria for evaluating mobility of toxic compounds by experimental analysis.
The factors or variables that limit the leaching method to make related to hazardous waste are given by:

- Surface area of waste
- Nature of the fluid extractor
- Value leachate / waste

From the variables mentioned above have been developed leaching tests classified according to the renewal of the exhaust fluid into two categories: the extraction tests and dynamic tests. The extraction tests were used in this research.

3.1 Mobility tests of a residue

The mobility test of a residue simulates infiltration conditions in the environment (soil). In the test: the waste infiltrates the soil and it can reacts with the components of that environment, causing public health risks due to environmental pollutants it absorbs; or do not react, but to infiltrate in large numbers so that the scope of such sources of groundwater. The methodology used for the mobility test was the procedure of the Colombian Institute Agustin Codazzi (IGAC) because it has a Reference Laboratories in this field in Colombia. It implies:

1. Sampling of the soil object of study.
2. Selection of specific method of sampling for the study. For the present study the sampling method can be seen in Figure 1. The method used was zig-zag due the number of samples to analyze at the laboratory.
3. Making a stripping of topsoil covering the ground.

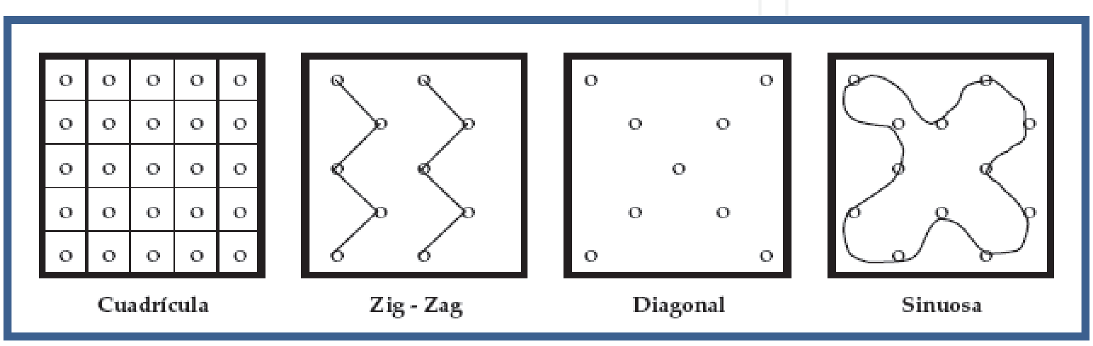

Fig. 1. Methodologies for soil sampling, Source. Codazzi. 2005.

3.2 Sampling for Mobility Analysis

To analyze the mobility, blocks of soil were taken from the fields of ICA. The soil block's dimensions were 25x25x25 cm. This height of the blocks was determined with a leaching test with water. In this test was spilled 1000 ml of water to calculate the deepest length.
The next set of pictures in figure 2 shows the process to take the samples of soils.

Fig. 2. Soil Sampling.

3.3 Experimental Units

The areas of those units, according to the heights determined in the field test for the assembly were: 25 x 25 cm, and a maximum depth of 25 cm with a free margin of 3 cm. All had the same dimensions and were evaluated at three different depths, being able to observe the behavior of the insecticide into the soil. The units were made in acrylic material to observe the movement of the pesticide. The lower surface was perforated for the collection of the leaching material. Figure 3 shows the experimental units.

Fig. 3. Experimental Units.

4. Simulated spill of the insecticide

As was mentioned in the previous section was performed spills for each of the events: Event 1 (non diluted or commercial presentation), and Event 2 (agricultural recommended doses). For each depth were spilled different volumes. They were obtained according to pilot tests to collect representative volumes. Below are the photographs of spills, as well as tables 1 to 6, which have the volumes applied and volumes collected after the spills for each pesticide.

Fig. 4. Spill.

4.1 Malathion

Sample Height (cm)	Volume Applied (ml)	Volume Obtained (ml)
25	1000	32.8
25	1000	42.4
25	1000	54.5
17	680	45.6
17	680	73.4
17	680	58.7
10	400	51.4
10	400	46.8
10	400	68.1

Table 1. Event 1

Sample Height (cm)	Volume Applied (ml)	Volume Obtained (ml)
25	1000	48.6
25	1000	43.4
25	1000	63.7
17	680	72.4
17	680	64.2
17	680	56.6
10	400	76.5
10	400	70.4
10	400	62.8

Table 2. Event 2

4.2 Attamix

Sample Height (cm)	Volume Applied (ml)	Volume Obtained (ml)
10	1002	35,2
10	1002	9,5
10	1002	14,7
17	1003,4	21,5
17	1003,4	20,5
17	1003,4	16,8

Table 3. Event 1

Sample Height (cm)	Volume Applied (ml)	Volume Obtained (ml)
10	1002	43,3
10	1002	-
10	1002	20,5
17	1003,4	47,5
17	1003,4	-
17	1003,4	48,5

Table 4. Event 2

4.3 Thiodan

Sample Height (cm)	Volume Applied (ml)	Volume Obtained (ml)
25	400	142
25	400	152.5
25	400	115
17	680	95
17	680	45
17	680	92
10	1000	100
10	1000	18
10	1000	110

Table 5. Event 1

Sample Height (cm)	Volume Applied (ml)	Volume Obtained (ml)
25	400.8	110
25	400.8	46.5
25	400.8	98
17	681.36	200
17	681.36	177
17	681.36	164
10	1002	184
10	1002	240
10	1002	201

Table 6. Event 2

5. Initial concentrations

5.1 Malathion

The maximum concentration at which the insecticide is in the market is 650000 mg/L For the second event, was taken as the concentration the agricultural use specifications provided by the supplier, which was 604 mg/L.

5.2 Attamix

The commercial concentration of the pesticide had a value of 480000 mg/L. The concentration used for the second event was 960 mg/L of active ingredient chlorpyrifos.

5.3 Thiodan

The first event had a concentration of 350000 mg/L. The second event had as the concentration the value provided by the supplier as 0.7 mg/L.

6. Extraction

For all the samples obtained it was used a liquid - liquid extraction to isolate the pesticide from the samples and analyzed by gas chromatography. The methodology used was the described in the EPA 3510C method adjusted to the conditions of the Environmental Engineering Laboratory at the University of La Salle. The technique uses the dichloromethane (CH_2Cl_2) as a solvent and the process is characterized by separating the active ingredient of impurities and water content. To carry out the procedure first was stabilized the solution at pH 7.0 with sodium hydroxide; then, the solution was mixed with three portions of 90 ml of dichloromethane and the extract was separate in a gravity separation funnel. The figure 5 presents the extraction procedure:

Fig. 5. Extraction

6.1 Gas chromatography

The following chromatographic conditions were established for the analysis of the pesticides:
Injection volume: 2.0 mL (splitless mode)
Injector temperature: 280 ° C
Detector temperature: 280 ° C
Carrier gas, nitrogen at a constant flow of 1.0 mL / min.
Fuel Gas: Air: 300 mL / min.

Hydrogen: 30 mL / min
Make up gas: helium: 35 mL / min.
Oven temperature: 140 ° C start for 1 min. then a gradient of 20 ° C / min. 220 ° C and a stay at this temperature for 2 min. then again performed a gradient of temperature at 5 ° C / min. to 280 ° C with a stay at this temperature for 5 min. for a total analysis time of 24 min.

7. Results

The next tables present the results obtained from the chromatography analysis:

7.1 Malathion

Event	Height (cm)	$\overline{X}$ Concentration (mg/L)
1	25	581475
1	17	600825
1	10	615600
2	25	439.66
2	17	452
2	10	466

Table 7. Malathion Results

According to the above table, were constructed Figures 6 and 7; each of them corresponding to events 1 and 2. The correlation shows that the concentration decreases in proportion to the height of soil analyzed. The soil has a greater retention of material than the liquid phase, which implies that the impact will be much more evident in the solid phase than in the liquid. On the other hand the concentrations are quite high.

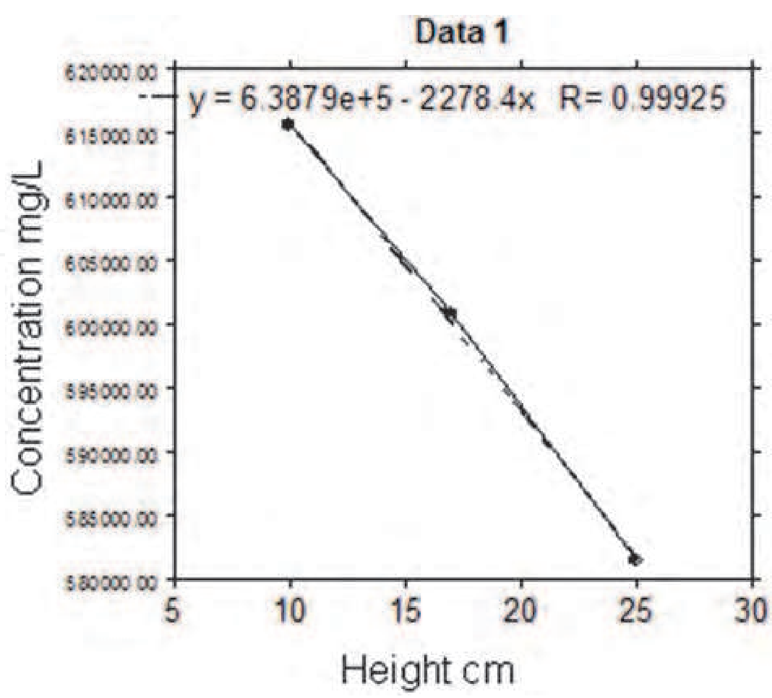

Fig. 6. Event 1

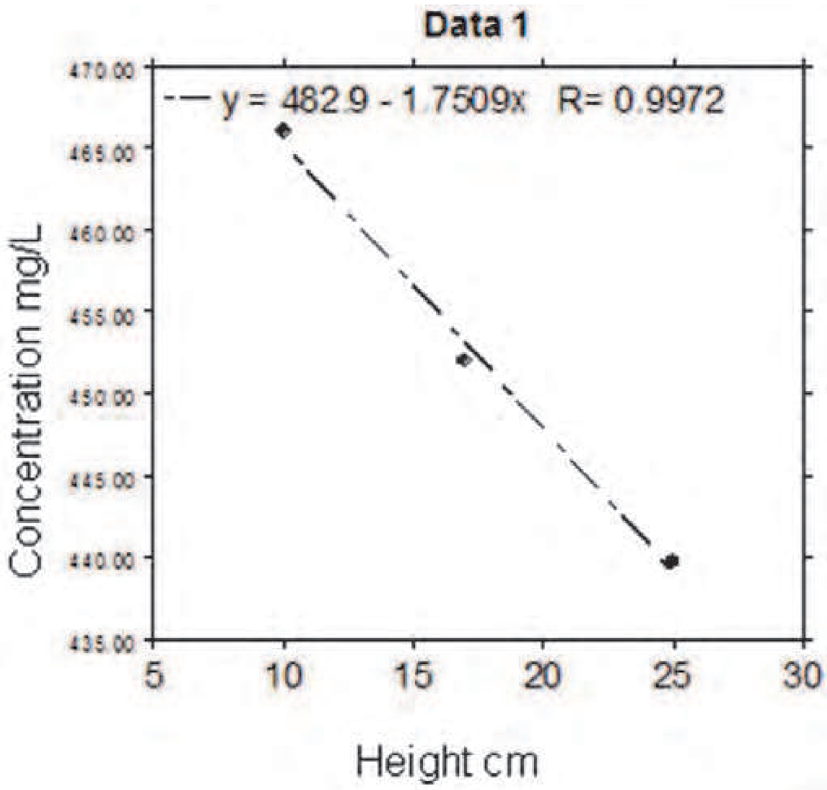

Fig. 7. Event 2

It is observed from the previous graphs that the degree of change in concentration of the pesticide in function to soil depth is significant. The graphs shows that the soil does not catch the pesticide enough. It means the pesticide has the ability to attack the biota present and generating highly toxic levels. For example, the LD50 is 1470 mg / kg oral rat, which implies that the current dose of stroke, 1 (one) liter of pesticide spilled, may die 600 rats of 600 g in weight. In the case of an adult rabbit weighing 4 kg, Malathion, which has a dermal LD50 of 5428, 28 animals die. Since the biotic point view these data have a strong importance.

7.2 Attamix

Event	Height (cm)	$\overline{X}$ Concentration (mg/L)
1	17	32.67
1	10	21.58
2	17	17.82
2	10	14.31

Table 8. Attamix Results

According to the above table were constructed the Figures 8 and 9, each corresponding to the different events. The concentration increases as the depth of soil sampled, quite contrary to the previous case. But the concentration is pretty low compared each event.

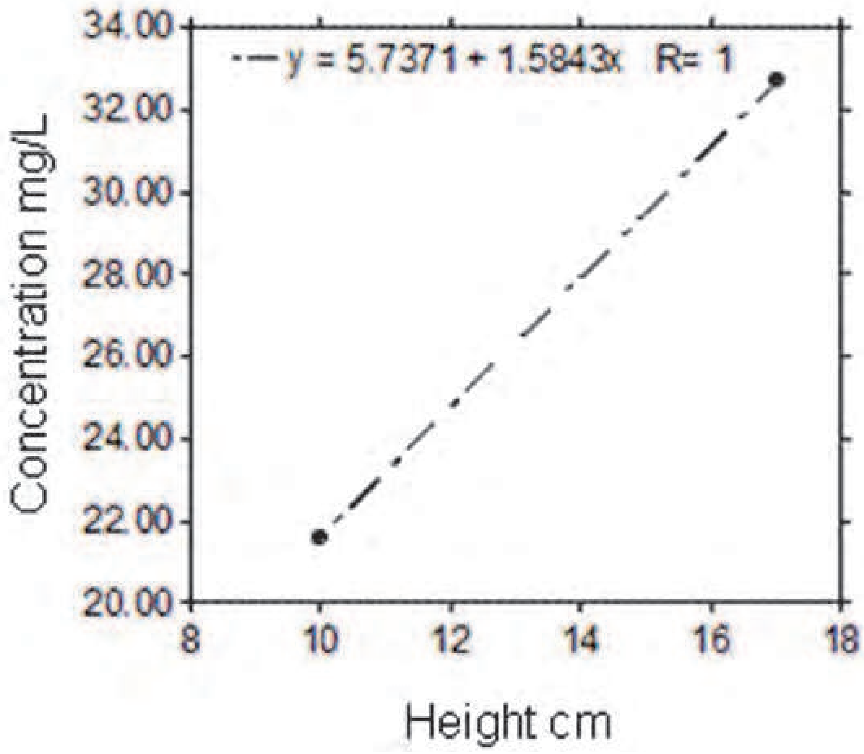

Fig. 8. Event 1

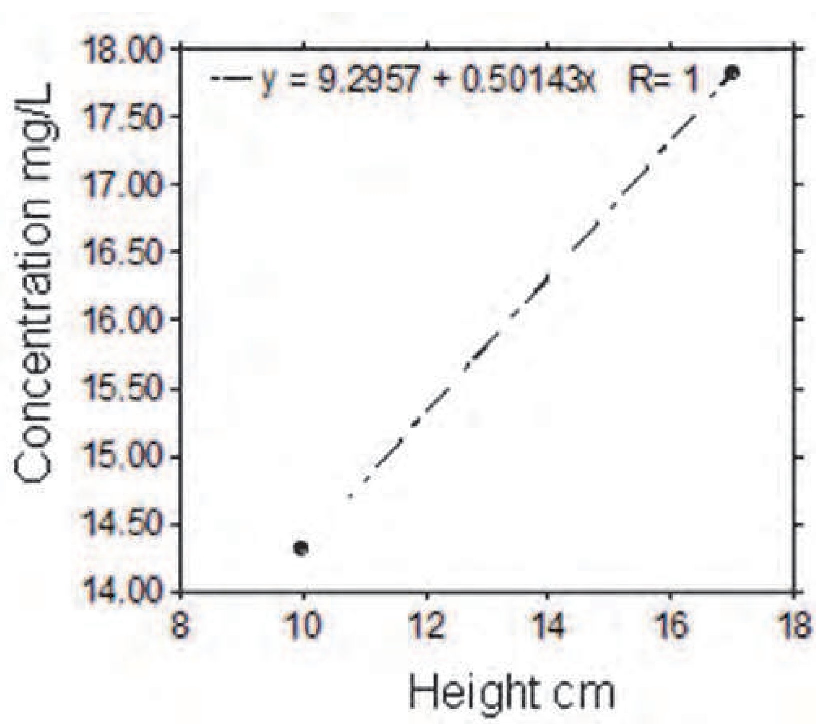

Fig. 9. Event 2

It is observed that the change in concentration of pesticide from events in function to soil depth is not significant. This suggests that the pesticide is highly related to soil because the pure pesticide leaching concentration is only almost twice as high concentration of diluted pesticide. According to its data sheet, this pesticide is highly toxic to aquatic organisms (LC50/EC50 <0.1 m/l in most sensitive species). The concentrations obtained by these two events generate mortality. For terrestrial organisms, where the pesticide is held, the first event with an approximately concentration of 900000 mg/L, the product is highly toxic to birds based on a diet (LC50 between 50 and 500 mg/L), causing their death.

7.3 Thiodan

Event	Height (cm)	$\overline{X}$ Concentration α-endosulfan (mg/L)	$\overline{X}$ Concentration β- endosulfan (mg/L)
1	25	63.3	39.10
1	17	45.9	24.93
1	10	30.9	13.6
2	25	5.29	4.3
2	17	11.11	6.84
2	10	19.88	12.02

Table 9. Thiodan Results

Thiodan has as active ingredients the- and β- endosulfan. According to the above table were constructed figures 10 and 11. The coefficients show that the concentration increases in the first event in proportion to the height of soil analyzed, meaning that deepens as the ground has been a greater release of material, which implies that the impact will be much more evident in the liquid phase in the solid, which implies an impact on water resources.

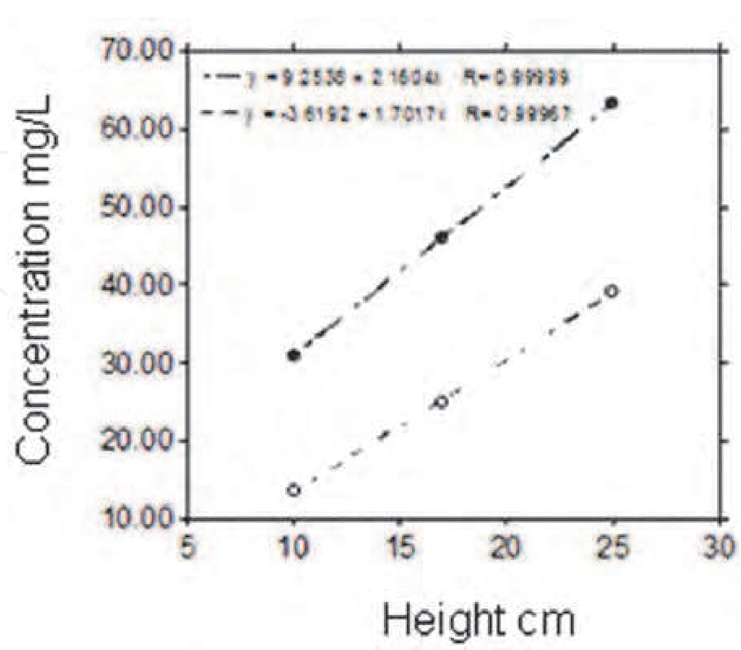

Fig. 10. Event 1. Black circle α- Transparent circle β-

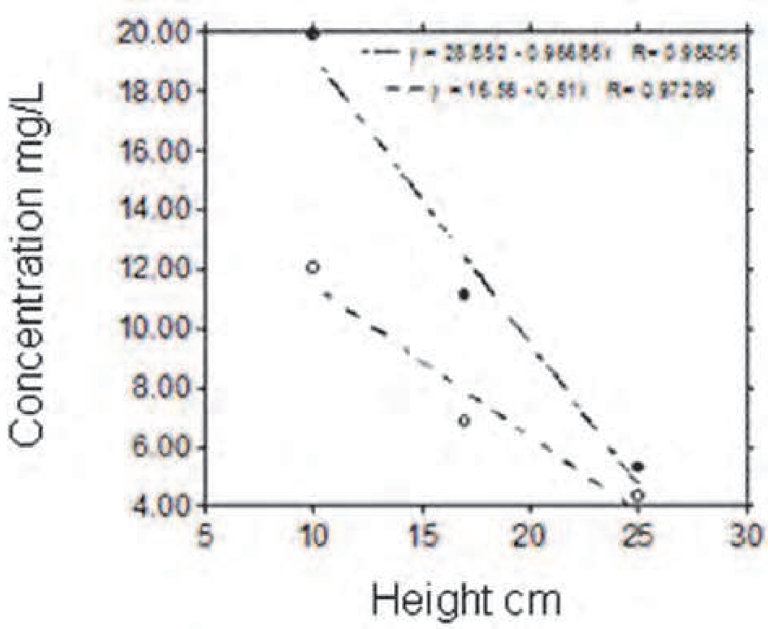

Fig. 11. Event 2. Black circle α- Transparent circle β-

The data from the second event presents a different phenomenon; it means that when the pesticide has more water content will favor retention is the solid phase as it delves into the less leach field.

Taking into account the concentration values reported in the leachate and the datasheet of the material, the lethal dose for biomarkers is 10 mg/kg. This indicates that all concentrations exceed the limits, except for the 25 cm diluted, so evidence that the potential risk of material, which in fact is prohibited in its entirety.

When is compared the leachate concentration with the initial concentration; is observed that the effect will be macro on soil because the material will be deposited into the soil. But the portion of leach is highly toxic yet.

8. Conclusions

Was evaluated the mobility of pesticide residues (Malathion, Thiodan And Attamix) in soils of the properties of ICA Mosquera and Villavicencio. For Malathion was found that the concentration decreases in proportion to the depth of the soil analyzed. It implies that the impact will be much more evident in the solid phase than in the liquid phase. The degree of change in concentration of the pesticide in function of the soil depth is representative, because the soil is not enough to catch all of the pesticide and it attacked the biota generating highly toxic levels.

In the case of Attamix the concentration increases as soil depth increases in a contrary way as the Malathion. But the retention of the pesticide is higher than from Malathion. It means that the leaching concentration is very lower than the initial concentration.

Were established concentrations of organochlorine and organophosphorus pesticides in the leachate showing differences between them. For the first event, Malathion about 600,000 mg/L, 28 mg/L for Attamix and 50 mg/L for Thiodan. For the second event 450 mg/L for Malathion, Attamix 15 mg/L and Thiodan and 10 mg/L. This indicates that Malathion is easily leached, while Attamix is preferably on the soil, as well as Thiodan.

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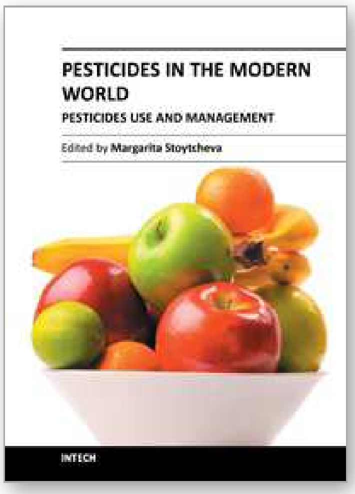

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This book brings together issues on pesticides and biopesticides use with the related subjects of pesticides management and sustainable development. It contains 24 chapters organized in three sections. The first book section supplies an overview on the current use of pesticides, on the regulatory status, on the levels of contamination, on the pesticides management options, and on some techniques of pesticides application, reporting data collected from all over the world. Second section is devoted to the advances in the evolving field of biopesticides, providing actual information on the regulation of the plant protection products from natural origin in the European Union. It reports data associated with the application of neem pesticides, wood pyrolysis liquids and bacillus-based products. The third book section covers various aspects of pesticides management practices in concert with pesticides degradation and contaminated sites remediation technologies, supporting the environmental sustainability.