Food and Environment Safety - Journal of Faculty of Food Engineering, Ştefan cel MareUniversity - Suceava
Volume XI, Issue 2 – 2012

STUDIES REGARDING SOIL QUALITY AND ITS IMPACT ON ENVIRONMENT

***Camelia POPA**[1]

[1]Ştefan cel Mare University of Suceava, Faculty of Food Engineering, 13
Universităţii Street, 720229, Suceava, Romania,
e-mail: cameliamai_2010@yahoo.com
*Corresponding author
Received 25 March 2012, accepted 11 May 2012

Abstract: *The purpose of this study is to make an analysis of the soil form the area of Agricultural Research and Development Resort Suceava, regard the content of pesticide and a risk assessment of their environmental threats. After analyzing the sample harvested from this area there were identified qualitative and quantitative the acid 2,4D and the Florasulam, compounds of the pesticide called Mustang, post emergent pesticide, used previous years in combating weeds with broad leaf from cereal crops. Studies have revealed that emphasizes the fact that samples taken from soil surface have higher concentrations both in Florasulam and 2,4D than harvested from depth, because along with the leaching of pesticides and under the action of micro-organisms in the soil, their concentration decreases.2,4D has remained in the ground less than the Florasulam which, under the action of micro-organisms or soil passes into hydroxylated derivative compound with similar structure to florasulam but with persistence and accumulation in soil.*

Keywords: *environment, pesticide, mustang*

1. Introduction

Soil, through his position, nature and her role, is a product of interaction between biotic and abiotic environment, representing a live organism, where an intense life takes place and a certain ecological equilibrium has established. Soil, through their properties of maintaining and develop life, to regenerate, filter the pollutants, absorb and transform them. If the air and water represent vectors of pollutants transmissions, soil represents the environment of accumulating them. The principal chemical process that takes place in soil is alteration. Soil physic-chemical conditions of alteration depend on chemical constituents that reach the soil. They can come from atmosphere, lithosphere, biosphere or chemical reactions of alteration nature which can take place on chemical, biochemical or biological way [1]. Soil, naturally, presents the capacity of defense and auto-build which annihilate the natural pollutant factor, exceeded capacities, undetectable in our days because of pollution [2]. With industrial development, population growth and their needs, soil degradation has taken on worrying. Ways through which the soil pollution are many and complex but they all lead to degradation by the penetration of elements from outside [3]. A special case in the pollution of soils is the pollution with pesticides. Their time of waiting in the soil depends on the nature of the soil as well as the link with the biodegradability [4]. Pesticides from the

soils go into the vegetal life and then into the animal life, in the end being accumulated in the body's fatty tissue. Due to the high degree of persistence and toxicity, pesticides have taken the name of organic polluted polluters (POP). Soil fertility and the ability to auto generate is provided by the activity of micro-organisms and mezofauna [5]. The behavior of pesticides in soils is dictated by physical factors, chemical and biologic processes such as absorption- desorption, chemical degradation, volatile, leaching, absorption by plants. The geographic position of the city of Suceava specific climate, are decisive factors in affecting the soils by natural ways: rain, storms, frost, snowstorm, massive snow fall. On all these, the atrophic factor is added also. Suceava county occupies a distinct place in the Romanian economy because of diversity and in some cases because of the abundance of its natural resources.

Over 52% of the county's surface belongs to the forests found, respectively aprox. 7% of the country surface, in the underground there can be found deposits of manganese, copper ores, sulphur, barite, salt, natural gas, mineral, uranium ore, and aprox. 42% of the surface is represented by arable land, the majority being located along the valleys of Siret,Moldova and Suceava [6].

Representative industries in the county are: timber industry, developed in direct correlation with forests fond surface; pulp and paper industry, represented by one of the largest company in the country in this domain, SC "AMBRO" S.A Suceava; the food industry, which develops in direct correlation with the County, because agriculture is based mainly on the processing of animal products (meat, milk),light industry, represented by clothing companies and knitwear, leather and footwear, machine building industry, represented by companies that produce tools and bearings; mining in the county, represented by exploiting and processing of ore (ores, cuprifere, polimetalic, uranifere, manganese salt), industry in decline over the past decade [6]. All these activities have led to the impairment of the quality of soil ground by: storage for waste wood chips, waste from domestic, mining etc.; soil pollution by waste and waste from food processing industry; accidental overflow pollution by oil products, chemicals used in technological flows; pollution with pesticides; massive deforestation which lead to the emergence or accentuation of slip phenomena-erosion, acidifications, etc.

The resort of Agricultural Research and development is individualized by climate conditions, characterized by specific restrictions, non-uniformity of thermal-water regime of the failure to excess-and by a wide variety of soil types, from low fertility soils with up to those with good fertility. The consequence of this ecological diversity, along with the need to diversify-related, research in response to solve the main problems of agriculture in the Suceava Plateau [7]. The land on which the cores were taken from the soil type mold was grown in 2010 – 2011 with wheat. To combat the weed has been used a herbicide, Mustang ". The pesticide MUSTANG is part of the herbicides class and was produced in the USA by the company Dow Agro Sciences LLC in 2007. Is used in weeding wide leaf crops of grain. For effective weed control (over 95%) should be applied in the early stages of vegetation. The recommended rate is 0,4-0,6 l/ha, diluted in 200-400 l water/ha; Active substance: 6,25 g/l florasulam + 300 g/l 2,4-D [8].

Environmental risk:Florasulamis a very mobile compound, not persistent in soil, airy, is a fast biodegrade in derivative analogue 5-OH-XDE-570, which in turn is much harder to biodegradable CO2. Florasulam is not significantly degraded by abiotic processes. Easily degrade in aquatic

systems, where also the derivative hidroxilat is bio-transforming. This derivative 5-OH-XDE-570 is much more mobile in the ground than the original compound, florasulam. Persistence and accumulation of the derivative is more variable than that of florasulam, indicating that it can persist in the lowerpedogenetic layers. Data submitted indicates that florasulamul has a very low potential for bioaccumulation in aquatic organisms. With reference to the risk of contamination of groundwater by florasulam has shown that it can take place, but in a lesser extent due to biodegradation under the action of the micro-organisms, but the potential for derivative analogue, infiltration is greater due to its solubility in water but it's slower. 2,4-D acid has reduced persistence in soils. The half-life in soil is more than 7 days. Micro-organisms in the soil are primarily responsible for its demise. In aquatic environments, microorganisms degrade slightly 2, 4-D acid. Despite short time,half life in soil and aquatic environments, the chemical has been detected in the groundwater in Canada and at least five other States.

2. Experimental

Sampling to a depth of 5 cm, is aimed at identification of pollutants and the impact on the soil surface, and taking samples from 25-30 cm depth, you can determine the degree of accumulation of pollutants in the layer being plowed, and the maximum concentration of agricultural plant roots [10]. 8 soil samples were taken randomly, choose from 4 points at depths of 5 to 25 cm. for sampling methodology was followed, in accordance with order no 184/97 A.N.P.M. [11]:

1) Vegetation has been completely removed from the area sampling;

2) A sampling instrument was used for assuring a sufficient volume of the sample for analysis;

3) Sampling was carried out at two different depths ranging from 5 to 25-30 cm from the soil surface.

Once collected, the soil samples were labeled by numbering the $I_{1,\ 2}$ to $III_{1,2}$ immediately transported to the laboratory in order to be prepared to perform qualitative analysis.

Determination of pH: ISO 10390:2005 (12). The pH value of aqueous suspension of determined in soil is an analytical index easily obtainable, which characterizes the reaction of the soil and the acid-basic properties of soil-water system. In an aqueous suspension or alkaline soil, at equilibrium, the H + ions are distributed between the solid and liquid phase. Taking into account the variation of soil pH values, both in site and in aqueous suspensions of varying concentrations (in the solid phase) where the measurements are taken, the definition of soil pH has a conventional, depending on values and soil/water system where the measurements are taken. In the present case there has been a ground/water ratio 1:100 the mass/volume. After soil samples were dried, they were mojarated, homogenized and from each sample were weighed on a glass plate, 1 g of the ground and were dissolved in 100 ml of distilled water in Erlenmayer glasses. It has shaken off the solution and it was left for 1 h to sediment and filtered on the filter paper. For measuring pH meter was used 11 d portable HACH HQ.

Determination of pesticides in soil: in order to determine the presence of pesticides in soil samples taken, i.e. their determination, they were first prepared, weighted and then order a few rounds: drying in the Memmert oven at 105^{o}C at a constant weight, shredding, sieving. The next stage was to pesticides in soil extraction

with light petroleum to SOXHLET, evaporation to dryness and retrieve residue in 5 ml of acetonitrile and undergo analysis by high-performance liquid chromatography (HPLC) performance. Contents in acid and 2,4-D in the samples thus processed florasulam is determined by high pressure liquid chromatography, reverse phase, using water as the mobile phase and acetonitrile, acidified with acetic acid in the following terms: analysis: 280nm wavelength; the ambient temperature; injection volume: 20 µl; working pressure: 150-180 barr; the gradient according to table 1 [13].

Table 1
Composition of mobile phase (gradient)

Nr.	Time (min)	Mobile Phase A (%)	Mobile Phase B (%)
1	0	95	5
2	9	95	5
3	17	50	50
4	40	50	50

* A – sour water (1% acetic acid); B – sour acetonitrile (1% acetic acid).

The analyses were performed on a liquid chromatograph type Schimadzu. The concentration of the acid 2,4-D were calculated using the standard method, using external relationship 1.

$$C(\%) = \frac{A_p \cdot \frac{g_{Eacid}}{25}}{A_E \cdot \frac{g_p}{5}} \cdot 100 \qquad (1)$$

where:

A_p– surface of 2,4D acid peak from sample chromatogram

g_{Eacid}– grams of 2,4D acid standard

A_E – surface of 2,4D acid peak from standard chromatogram;

g_p– the amount of soil taken in the work (g);

25 – standard dilution;

5 – sample dilution.

3. Summaries and discussions

Measuring the pH of the aqueous extract 1/100 for the 6 soil samples is observed that the samples taken from the soil surface (5 cm) have more acidic pH compared to those taken from deep, respectively 25 cm. Results are shown in Table 2.

Table 2
Soil acidity for 8 samples harvested from different points and depths

No.	Analysed samples	The value of pH	Soil acidity
1.	Sample no. I_1	6,27	Slightly acid
2.	Sample no. I_2	6,44	Slightly acid
3.	Sample no. II_1	5,10	Moderately acid
4.	Sample no. II_2	6,13	Slightly acid
5.	Sample no. III_1	5,94	Moderately acid
6.	Sample no. III_2	6,11	Slightly acid

*I_1- surface sample (5cm); I_2 – depth sample (25cm).

For the extraction of pesticides were used each (approximately) 40 g of dry soil to constant weight at a temperature of 105 ^{0}C, which were subjected to Soxhlet extraction with each 200 ml petroleum ether.The extract was evaporated to dryness on water bath, was taken in 5 ml acetonitrile and analysed by liquid chromatography using the method of section 2. To identify the components were utilized certified reference materials. After analysing soil samples by HPLC were qualitative identified 2, 4-D acid and florasulam with appropriate retention times, as can be seen in the chromatograms presented in Figs. 1 and 2. The order of elution is florasulam, 2, 4-D acid.

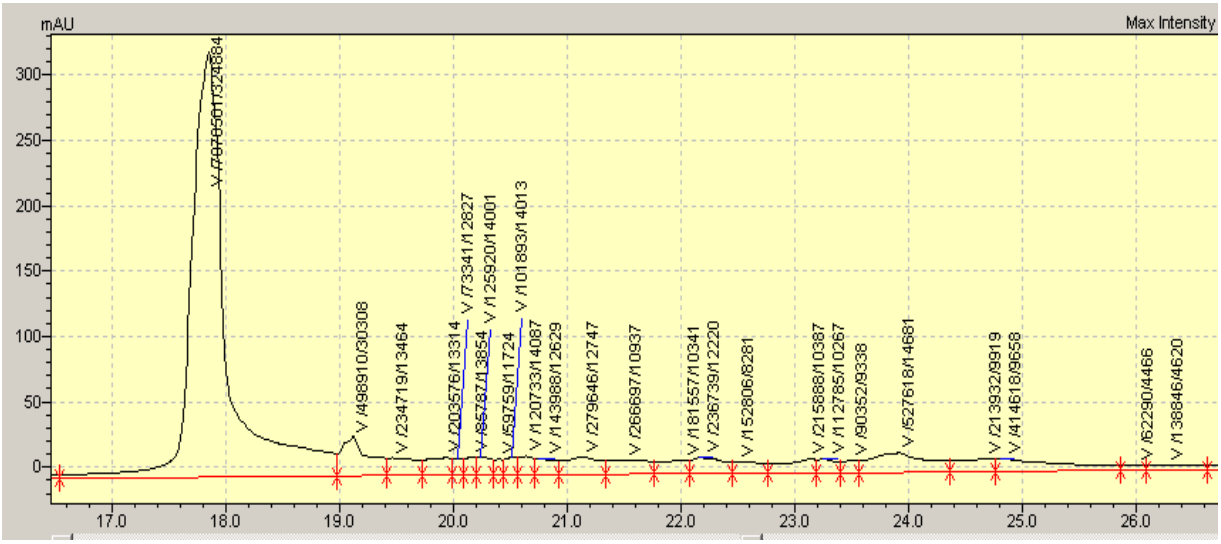

Figure1. Chromatogram of soil sample III_2.

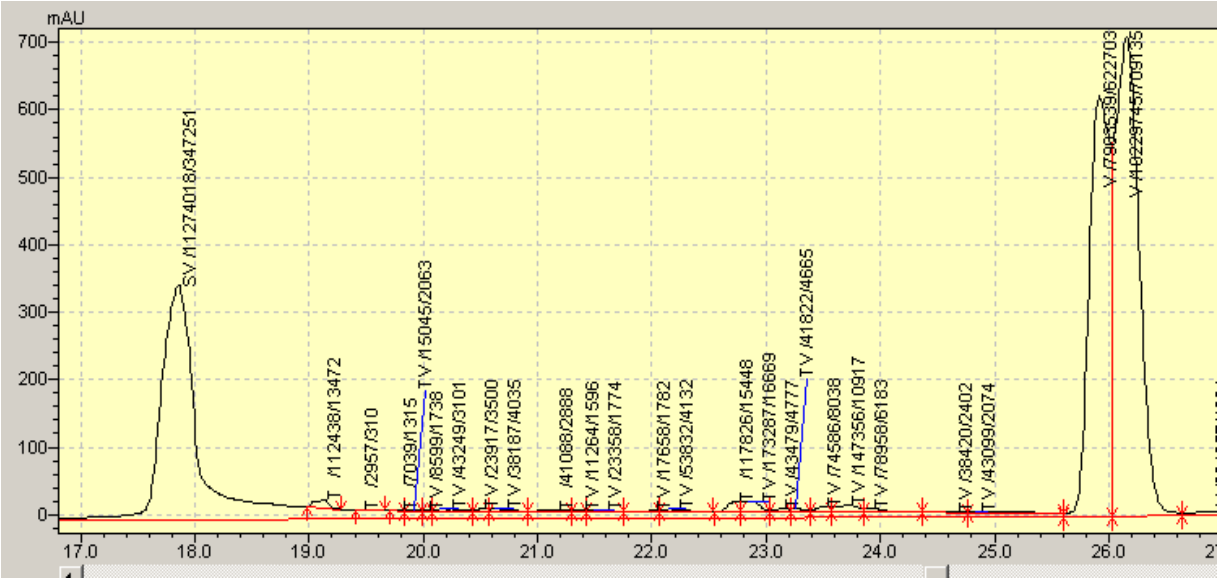

Figure 2. Chromatogram of soil sample III$_2$enriched with acid 2,4D.

It can be seen that the peak of florasulam is not pure, it has a shoulder. This tells us that florasulam goes in chromatogram together with a component with a very similar structure and polarity, i.e. hydroxylated derivative of florasulam. Literature data indicates that hydroxylated derivative is formed in soil from florasulam, under the action of microorganisms. The results of analysis of the 6 samples are shown in Table 3. From the results obtained in this study, results the following conclusions:

- the samples collected from the surface of the soil 5 cm, have concentrations in both the 2,4-D acid and florasulam greater than those harvested from deep (25 cm), which means that with the leaching of pesticides, soil micro-organisms under the influence they lost in their concentration;

- samples taken from soil surface have higher concentrations in the Florasulam than in 2, 4D acid, according to the studies of literature [8] which affirm that Florasulam in soil is greater than 2, 4D acid, the latter being more easily biodegradable, with a half-life of 7 days, compared to florasulam, that once in the form of derived analogue persists long periods of time.

Results obtained to determine the pH of come in support of above affirmations; namely, samples of the surface have pH more acidic than depth, in other words, a content to 2, 4D above to the surface.

Although the concentration of product in florasulam, conditioner is 50 times less than 2, 4D acid, its concentration in the soil is often 100 times greater. Degradation of florasulam is lower net depravity 2, 4D acid.

Table 3
The concentration of acid 2, 4-D and florasulam obtained from calculations

Analysed samples	Components	Retention time	Peak Area	Sample mass	Dilution	2,4-D Acid Concentration (µg /kg)	Florasulam Concentration (µg /kg)
Sample No. I_1	Florasulam	17.85	12412004.50	43.05	5		52.54
	2,4DAcid	25.99	6849.80	43.05	5	$2.97216 \cdot 10^{-2}$	
Sample No. I_2	Florasulam	17.85	7642256.10	43.36	5		38.82
	2,4DAcid	25.18	7645567.90	43.36	5	32.939272	
Sample No. II_1	Florasulam	17.85	7116538.80	44.58	5		29.78
	2,4DAcid	24.69	169714.90	44.53	5	0.711843	
Sample No. II_2	Florasulam	17.86	7411629.30	45.83	5		29.26
	2,4DAcid	25.70	58269.30	45.83	5	0.237484	
Sample No. III_1	Florasulam	17.81	10648238.30	44.84	5		43.856
	2,4DAcid	25.98	75269.30	44.84	5	0.313531	
Sample No. III_2	Florasulam	17.84	7070500.00	44.87	5		28.376
	2,4DAcid	26.01	62289.90	44.87	5	0.259295	

4. Conclusions

Following the experimental measurements demonstrated the presence of components of Mustang herbicide in collected soil samples. Have been identified active substances in herbicide (Florasulam acid and 2,4-D acid) emphasizing at the same time and concentration.

Florasulam is an extremely mobile compound, do not persist in the soil airy and well under the action of micro-organisms in the soil, the derivative is biodegrade in the compound with analogue structure, similar to that of florasulam. Persistence and accumulation of the derivative product is significantly different from that of florasulam, indicating that it can persist long into the lower pedogenetice layers. With reference to the risk of contamination of groundwater by florasulam, it was found that this can take place, but in a lesser extent due to biodegradation under the action of the micro-organisms, but for the derivative product (analogue), potential flow is higher due to its solubility in water but also to his slower metabolism.

2,4-D acid has much less persistence in soils, also thanks to the action of micro-organisms present in the ground, given the half-life of less than 7 days. Concentrations of 2,4D acid are quite small ranging between 2.97216 · 10-2 µg/kg and 32.939272 µg/kg compared with those of florasulam

28.372416-52.546237 mg/kg mg/kg Although the concentration of product in florasulam, conditioner is 50 times less than 2,4D acid, its concentration in the soil is often 100 times greater. Degradation of florasulam acid is net lower depravity 2,4D acid.

In general, due to the high degree of persistence and toxicity, pesticides have been referred to as persistent organic pollutants (POPs). POPs are chemicals that persist in the environment, bioaccumulated in living organisms and runs the risk of causing adverse effects on the environment and even human health.

Several studies concerning the pesticides widely used have already demonstrated that their application leads to changes in soil nutrient levels and changes in the activity of microbial diversity in soil and/or genetic soil structure. Accordingly, disorders of microbial communities that ensure more soil-friendly key processes, such as the degradation of organic matter and nutrient cycle, could influence the proper fertilization soil and sustainable agricultural productivity.

Excessive use of the extensive and often even inadequate synthesis of pesticides, constitute the main source of pollution, with serious risks for human health and also led to a new type of which jeopardizes the rationale for their use, namely the emergence and development of species tolerant of harmful pesticides. The immediate trend now was to increase the rates charged to offset the decline in the efficacy of pesticides.

In the case of the using pesticides there are attacked not only the species to be destroyed (pests), as well as many other species that are required for soil fertilization. Only 3% of the pesticides used to secure. Sometimes, under the action of pesticides is the inhibition of certain groups of micro-organisms and on the other hand, the development of others. Thus, the microbial balance is not altered, resulting in a even stimulating micro-organisms.

Remaining of pesticides in soil depends on the type of link between them and the ground but in particular the biodegradability of pesticides. Up to 80% of pesticides are adsorbed by humus, a fact which, due to the persistence in the soil increases much.

5. References

[1]. LUPAŞCU G., JIGĂU G., VÂRLAN M., General Pedology, Junimea Publishing, Iaşi, (1998)
[2]. COJOCARU I, Sources, processes and products for remediation, Junimea Publishing, Iaşi, (1995)
[3]. PUIU Ş. Pedology, Ceres Publishing, Bucureşti, (1980)
[4]. ARIAS-ESTE´VEZ M. et al., The mobility and degradation of pesticides in soils and the pollution of groundwater resources, *Agriculture Ecosystems & Environment - AGR ECOSYST ENVIRON*, 123 (4), 247-260, (2008)
[5]. STOIAN L., An alternative: Biological agriculture, *Hortus*, 4, (1996)
[6]. National Environmental Protection Agency Suceava – Report on the state of the Suceava environment in 2010: on-line at http://www.mmediu.ro/legislatie/substante_pericul oase.html
[7]. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA), Pesticide Fact Sheet: Florasulam Washington, D.C. 20460, Office of prevention, pesticides and toxic substances: on-line at: www.epa.gov/opprd001.com
[8]. United States Environmental Protection Agency (US EPA), – 2,4-D RED FACTS: on-line at www.epa.gov/oppsrrd1/reds.com
[9]. PAPACOSTEA P., Soil Biology, Scientific and Encyclopedic Publishing, Bucharest, (1976)
[10]. http://apmdj.anpm.ro/legislations
[11]. ISO 10390:2005, Soil quality. Determination of pH. Standardization Association of Romania, Bucharest, Romania.
[12]. POPA C. et al., Invention patent. Methode for determinind the content of de 2, 4-dichlorphenol, dicllorphenoxi acetic acids and 3,6 diclhor-2 metoxibenzoic acid (1994)