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STUDIES ON THE CONTENT OF METALS AND PESTICIDES IN FRUIT GROWING AREAS AND THEIR ECOTOXICOLOGICAL IMPACT

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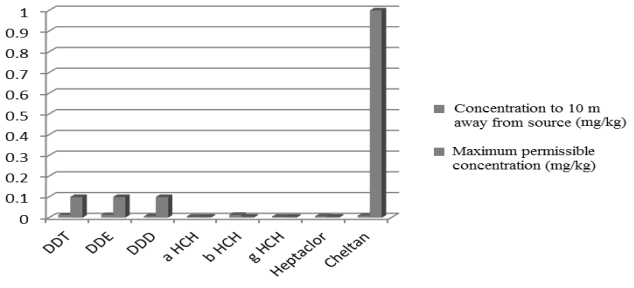
The selected substances have a high degree of toxicity. Their toxic effects pose serious risks to human health through the effects of consecutive mutations and genotoxic exposure to pesticides of organic origin, which may lead to the emergence of cancer in various tissues and organs. Atomic absorption spectroscopy was proposed for the determination of metals in water samples collected from two different points before and after the plants treatment (spraying fruit trees). The results obtained using the spectrometer reveal a high content of Fe and Pb in samples collected from the waters of the River Dâmbovița. The values of concentrations is higher than the maximum permissible limits of iron (about 10 times), and lead (2 times). The results obtained for the assay of metals were correlated with the determination of pesticides using HPLC. Many pesticides are known to have a high metal content; accordingly, the concentration of Pb in water in agroecosystems can be attributed to this type of treatment with pesticides.



INTRODUCTION

Worldwide science and practice in the field of protection of the environment and human health were faced with a group of chemicals – pesticides – that are scattered everywhere, have a strong toxicity, are persistent chemical compounds and have properties to carry long distances and accumulate in organisms. Under certain conditions, the permissible doses for these substances are exceeded, administered or absorbed by the animal or plant capable of producing through their deterioration action incompatible with the proper functioning of the pests. In general, mankind cannot stop using their poisonous necessary in some ecosystem, especially in agriculture.[1] People are part of a complex ecosystem with a large number of species of plants and animals directly affected by the use of pesticides.[2] Any decline of a species causes an imbalance of the ecosystem with unpredictable effects in the long run over the human. The use of pesticides caused the death of some species and also changes in behavior and physiology effects on wildlife. Pesticides are spread in the environment on the entire planet. Through rain, pesticides are leaking into rivers, immerse in water underground and lead to the accumulation of chemicals in water rates, killing the natural ecosystem and water pollutant. Also, there were studied the effects of the pesticides on fish, as since they are an important source of fat for human nutrition. Lipids are high in fatty acids which are

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essential for the human cardiovascular system. Infants and children are especially susceptible to the toxic action of pesticides causing health hazards.[3] Organophosphate Pesticides and Carbamate Pesticides affect the nervous system by disrupting the enzyme that regulates acetylcholine, a neurotransmitter. Therefore DDT and chlordane were prohibited from trading.

Many studies have shown an increased risk of cancer (leukemia, breast, pancreas, liver, prostate, skin),[5] Parkinson's disease,[6] dermatitis, birth defects, fetal death,[7] depresia,[8] and malaria. [9] These substances are used as chemical or biological agent.[10] The pesticides including insecticides, fungicides, herbicides, moluscide, acaricides, rodenticides.[11,12] After the chemical structure, the pesticides are classified in insecticide families, such as organochlorines, organophosphates, and carbamates. Organochlorine hydrocarbons (*e.g.* DDT) could be classified into dichlorodiphenylethanes, cyclodiene compounds and hexachlorocyclohexanes. Their toxicities vary greatly, but they have been phased out because of their persistence and potential to bioaccumulation.[13] Pesticides can be classified based upon their biological mechanism function or application method. A systemic pesticide moves inside a plant following absorption by the plant. At present, research continues in order to obtain pesticides with much less adverse effects to the health of the environment. Among the measures for maintaining the health of the soil and water, it is recommended the application of the laws in force on the protection of water quality and soil, and to avoid, as far as possible treatments with pesticides or rationalization of their use. Pesticides represent one of the causes of water pollution, pesticides and some persistent organic pollutants contributing to soil contamination. In addition, pesticide use reduces biodiversity, threatens endangered species,[14] reduces nitrogen fixation,[15] contributes to pollinator decline[16] and destroys habitat (especially for birds).[17]

European Union (EU) established a Community framework for sustainable use of pesticides. The proposed measures relate in particular to improve the monitoring, training and information to users, and specific measures for the use of these substances. Member States shall take all measures necessary to promoting low pest management of pesticides, including integrated pest management and agriculture organic, in accordance with Regulation (EC) no. 834/2007 of 28 June 2007 on production and labeling of organic products.[18]

EXPERIMENTAL

Materials

In the study of metals content samples of abiotic nature – 23 soil samples (adjacent to an intensive plantations of fruit trees), 8 samples of water – from surface water sources in the plantation of fruit trees and 7 wells samples in the village where the plantation of fruit trees were considered. For the determination of pesticide residues in the soil were collected 57 samples of soil at 40 cm deep, at distances of 1, 10, and 100m from the ground.

Methods

Atomic absorption spectrometry based on a series of relationships and notions that apply to analysis within the international system of quality ISO 17025 analytical data\/IUPAC-1992 was used.

To be able to correlate the level of metals with that of pesticides used in phytotherapeutic treatments the HPLC was employed for pesticides assay. Many pesticides are known to have a high metal content. Influence of pesticides bioaccumulation potential was investigated about biotic samples taken from snails of the species *Galba truncatula* (12 samples), which is a species of air-breathing freshwater snail, an aquatic pulmonate gastropod mollusk in the family *Lymnaeidae.*[1]

RESULTS AND DISCUSSION

Before and after spraying plantations 4 with pesticides water samples were collected from two different points on the Dâmbovița River to determine the heavy metals. As a result of investigations of spectrometric were obtained values that indicate the presence of metal residue in samples. Metal key values or content of existing metal are shown in Table 1.

The results obtained using the spectrometer reveals a high content of Fe and Pb in water samples taken from surface waters and fountains, which is higher than the maximum extent permissible in case the iron – about 10 times – and in the case of lead – about two times.

Many pesticides are known to have a high content in Bps, so the concentration of Pb in water can be placed on the treatment with pesticides in agroecosystems. It can be seen that there is no significant change in parameter values following administration of toxic chemical treatments, but can easily be observed that the water in this area is contaminated. Prolonged exposure, caused by the intensive use of phytotherapeutic treatments, has led to the accumulation of some metals in the water, as it is shown in Figs. 1 and 2. Some metals are ecotoxicological substances, their presence in the environment being quantitatively influenced by natural causes or human. Expanding on a human activity has contributed to the creation of the global cycle of metals, which may be described as anthropogenic enrichment factors (FAI). Human activity is responsible for the majority of global movements of cadmium, lead, zinc, mercury.

Table 1

The metal content of the water samples collected in the Dâmbovița River

Atomic number	Metal symbol	Average lot I (before splashing)	Average lot II (before splashing)	Average lot I (after splashing)	Average lot II (after splashing)	Maximum permissible limits
		ppm				
13	Al	11.80	10.90	14.92	12.54	200
14	Si	11.80	9.00	8.97	10.08	-
20	Ca	2970.00	2538.00	1964.41	2182.68	-
24	Cr	22.60	18.20	24.66	22.02	100
25	Mn	313.60	308.00	308.92	363.44	-
26	Fe	1000.00	872.00	836.60	1020.24	100
28	Ni	84.70	65.10	58.72	71.61	100
29	Cu	17.55	16.20	23.90	20.09	30
30	Zn	22.40	19.40	17.40	22.31	50
48	Cd	2.20	2.20	2.19	1.83	5
82	Pb	16.95	16.20	14.72	18.63	10

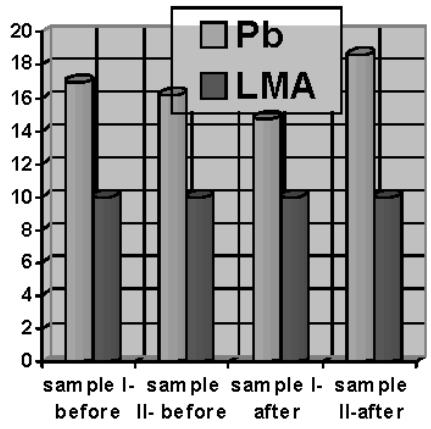

Fig. 1 – Content of Pb (ppm) in water samples.

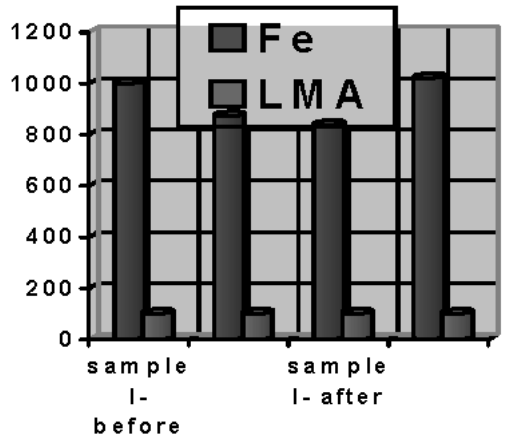

Fig. 2 – Content of Fe (ppm) in water samples.

An important characteristic of Fe, Cu, and other transition metals with variable valences is to participate in electron transfer reactions. The electron-transfer reactions involve the participation of oxygen, which can lead to the production of toxic oxidant, mechanism of toxicity that can be considered very important to animals and plants. The best known are oxidant anion (O2-) peroxide and hydroxyl radical (OH), both causing cell destruction. These items cause various harmful effects on the organisms that come into contact. Cadmium 5mg\/dm³ of water produce disorders of the kidneys and bone fractures. Toxic effects are achieved by the construction of the metal cell macromolecular compounds, as well as joining with, Pb, Hg and As at sulfhydryl groups of proteins. In the past, is called heavy metals. The term heavy metal, was the word equivalent for metals that are environmental pollutants. In order for a metal to be considered heavy, this must have a density greater than water for five times. However, heavy metal has been placed through a classification scheme considering their chemistry more important than their relative density. This assessment is more logical because certain non-heavy metals may be important environmental pollutants. For example, aluminum is a metal with the relative density of only 1.5 higher than water. However, he is a major pollutant in acid Lakes, where it becomes soluble and is toxic to fauna. Brood fish in particular is very sensitive to poisoning. Aluminum is also important in Alzheimer's disease in humans and can be stored in the CNS (central nervous system). Aluminum can cause adverse effects on the human nervous system and of animals. The absorption of aluminum can cause anemia, osteomalacy (soft bones or that break easily because of deep disorders in the metabolism of phosphorus and calcium in the bone mass) and infarct.[13] The metals

are non-degradable chemicals, which means that they cannot be separated into less toxic components. Detoxifying contaminated organisms is done by attaching a metal ion to a protein, called metaltionine (about covalent bonds with the sulfur). This complex is stored in intracellular inclusions (insoluble forms) for storage or to be excreted. Chronic exposure to lead in small doses is associated with increased blood pressure and there is a direct correlation between plasma concentration of lead and blood pressure level with brain vessel and cardio vessel disease. Some studies have reported the Association of chronic exposure to lead EKG changes or an increased incidence of peripheral artery disease in people chronically exposed to cadmium and lead.

For the determination of pesticide residues in the soil were collected 57 samples of soil, at 40 cm deep, and at distances of 1, 10, and 100 m from the plantation. Samples of the soil from ground in the first group at distances of 10 m (in 20% of cases) contained substances organochlorines as shown in Table 2. The results showed more than 12% of the samples containing DDT, and 10% samples containing HCH, in quantities significantly higher than CMA (maximum permissible concentration). In other words, in many of the samples collected were recorded significant levels of pesticide residues from category organochlorines.

The content of the residues of DDT and HCH has exceeded the CMA in 3-6% of the samples. The layer of soil collected contained in each of the three samples the following pesticide residues: b-HCH, DDT, DDE, cheltan and heptachlor, but on the plantation the content of pesticides is less: DDE from 0.002 up to 0.096mg\/kg; heptachlor and cheltan from 0.006 to 0.018, and 0.085 mg\/kg, respectively (Fig. 3).

Table 2

Concentrations of the organochlorines in soil samples

Organochlorines	Distance from source		Maximum permissible concentration (CMA)
	1m	10 m	
1.DDT	5.95 mg/kg	0.012 mg/kg	0.1mg/kg
2.DDE	0.282 mg/kg	0.013 mg/kg	0.1mg/kg
3.DDD	7.893 mg/kg	0.006 mg/kg	0.1mg/kg
4.a HCH	0.042 mg/kg	0.005 mg/kg	0.05 mg/kg
5.b HCH	0.246 mg/kg	0.0135 mg/kg	0.05 mg/kg
6.g HCH	0.013 mg/kg	0.005 mg/kg	0.05 mg/kg
7. Heptaclor	0.204 mg/kg	0.006 mg/kg	0.05 mg/kg
8. Cheltan	1.923 mg/kg	0.009 mg/kg	1.0 mg/kg

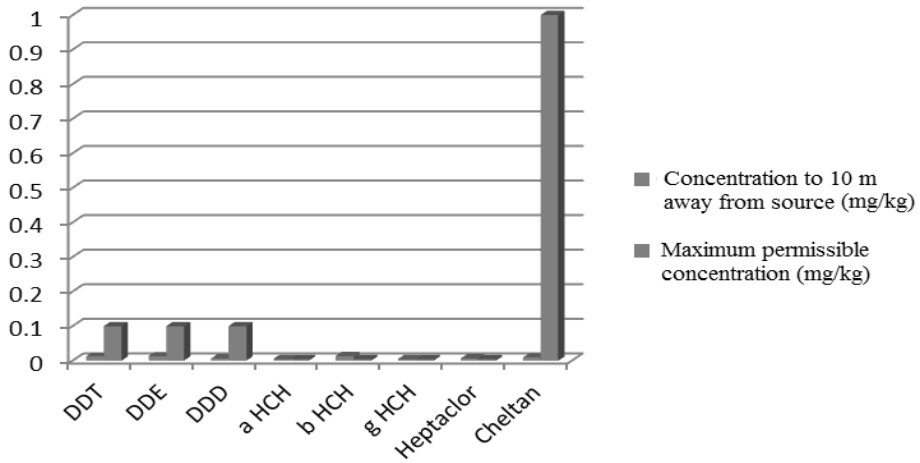

Fig. 3 – The concentration of pesticides organochlorines at 10 m distance of plantation.

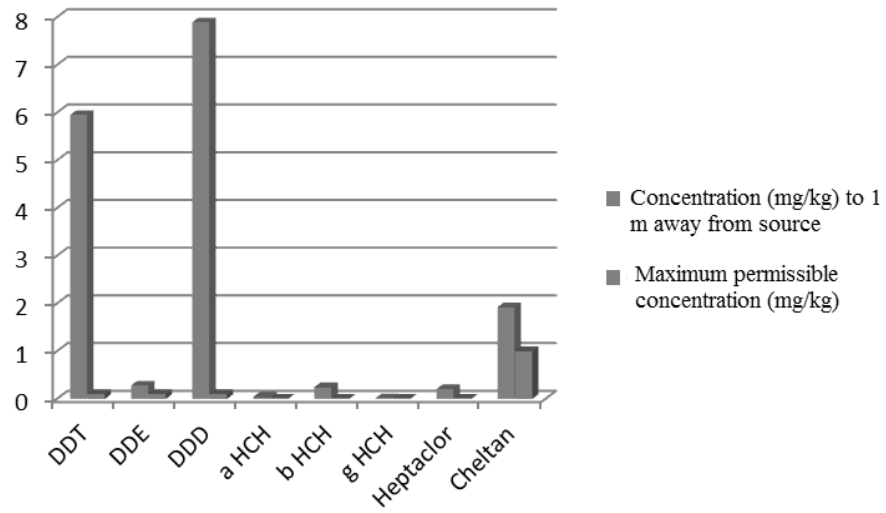

Fig. 4 – The concentration of pesticides organoclorurate at 1 m distance of plantation.

86% of soil samples were collected at a distance of 1 m and 10 m, and 14% of samples were collected at the distance of 100 m from the intensive plantation of trees contain pesticide residues belonging to the group of organochlorines. Residues of β-HCH isomer (59% of investigations), heptachlor (62% of cases), cheltan (48% of cases) and DDT metabolite 2,4-DDT (46% of cases) were found in the samples.

Residues bigger than the CMA in the soil (0.1 mg/kg) DDT and HCH have been detected in 21% of the samples. About 11% of samples contained residues of atrazine and simazine in the amount not higher than CMA (Fig. 4).

The certain results were obtained in the water samples collected from wells around the plantation (at distance to 50-200 m). For the water in the fountains near the plantation, 45% of samples contained residues of b-HCH (0.0007-0.0012mg/dm^3), 38%-g-HCH (0.0002-0.0004 mg/dm^3) and heptachlor (0.0002-0.0007mg/dm^3); CMA-0.002-0.001mg/dm^3. For the water in the fountains of the village: 52% of samples contained residues of DDT (0.0003-0.001, CMA-0.002mg/dm^3) and cheltan (0.0005mg/dm^3, CMA-0.02mg/dm^3).

In 2 of the 3 samples collected from surface water were found residues of b-HCH (0.006-0.005mg/dm^3).

At present, the risk to the health of the population and the quality of the ambient factors associated with pollution are not estimated. The intensity of soil pollution with POP is not known, and the volume of investigations in this area is very limited. Due to low water solubility and absorption into the soil, sustainable organochlorines have the particularity to keep a long time layer from the surface of the soil. Study of the migration of pesticides in soil organochlorines demonstrates that spreads in their substance.

Results of the study denote the need to elaboration of complex measures aimed at preventing the negative impact of pesticides on the environmental and human health. In terms of living organisms, pesticides have been highlighted in a species of gastropods whose biotope is plantation, using lipid extracts from *Galba truncatula*. Pesticides and heavy metals are persistent and nonbiodegradable and they can be in the food chain bioaccumulation plant-soil-food or water-water-food organisms. As a result, their presence in large amount represents a potential danger for health and for the environment after all, as a result of their extreme toxicity. For these reasons their concentration monitoring plays an important role. The toxic effects depend on the nature, strength, strength of body and the presence of other contaminants.

For highlighting the effects of DDT were used populations of snails of the species *Galba truncatula* collected from different regions of the Dâmbovița River basin. The snails have a high nutritional value and also because of the feeding way are considered valuable for bioindicators pesticides present in the aquatic environment. The following results were obtained for the concentration of pesticides based on organochlorines in the tissues of snails in Voineşti area (Table 3).

Table 3

The concentration of organochlorines found in the tissues of snails in the Voineşti area

Organochlorines	Concentration ppm	Maximum permissible concentration (mg/kg)	Time of retention
1. γ HCH	0.1343	2	1.46
2.β HCH	0.4620	0.1	1.85
3. op. DDE	0.0659	-	3.10
4. op. DDD	0.0007	-	4.69
5. pp. DDD	0.0022	-	6.19
6. pp DDT	0.0012	1	7.37

Table 4

The concentration of organochlorines found in the tissues of snails in the Manesti area

Organochlorines	Concentration ppm	Maximum permissible concentration (mg/kg)	Time of retention
1. γ HCH	0.2493	2	1.52
2.β HCH	2.7449	0.1	1.93
3. op. DDE	0.0120	-	3.37
4. op. DDD	0.0285	-	3.97
5. pp. DDD	0.1342	-	6.25
6. pp DDT	0.0823	1	7.11

These data show an increase in the concentration of β-HCH pesticides over the limit allowed. Hexachlorcyclohexane (HCH) are refined products, which include in particular HCH Isomer γ-(gamma-hexachlorocyclohexane) in commercial product Lindane. These are produced with properties similar to other organoclorurate insecticides, having a higher solubility in water (7mg/L). Emulsified concentrates of HCH were used for agricultural pest control, etc. The LD50 of these organoclorurate is between 60-250 mg/kg, which determined that HCH to be moderately toxic.

The results from Table 4 show an increase in the concentration of β-HCH over the allowed limit, in the Manesti area. Pollution of these bodies is due to the fact that in successful plantation, there is a high concentration of pesticides. The snails are bodies biofilter sparing small particles of pollutants present in the rainwater that washes the soil and the presence of their plantation in their body that a contamination of the environment. The concentration of pesticides organochlorines between 2004-2009 years demonstrate a massive reduction of the maximum values measured in water and sediments. Organisms have a significant reduction in concentrations being three times as compared with the amounts in 2004-2009.

CONCLUSIONS

In the study it was found that the values of chemical parameters (indicators) were different in the two moments of the trial. This indicates that after chemical treatments were applied in agroecosystems in the aquatic environment of Dâmbovița River occurs contamination with pesticides. As a result of the long use of plant-health treatments, potentially toxic metals, shown above, are induced in the ground water and adjacent crops.[19] Certain metals have greater concentrations than the acceptable limits, which indicates an accumulation of chronic effects on the agricultural ecosystem. Such is the case with lead and iron, which have a presence beyond normality, this is an average of 16.75 ppm Pb (lot I-before splashing), 16.20 ppm Pb (lot II-before splashing), 14.72 ppm Pb (lot I-after splashing), 18.63 ppm Pb (lot II-after splashing).

Pesticide use raises a number of environmental concerns. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water and soil.[16] Alternatives to pesticides are available and include methods of cultivation, use of biological pest controls (such as pheromones and microbial pesticides), genetic engineering, and methods of interfering with insect breeding.[14] Another measure refers to good practice in the use of pesticides which should include several levels of use, which shall not exceed the highest doses authorized or which must be applied in such a way as to leave a residue as small as possible. Also, for the neutralization of pesticides and metals to be viable, this process must be selective, to act

quickly and to convert them into less toxic intermediates compounds, biodegradable, or ideally, in inorganic CO2, H2O, NH3, etc.

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