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Mira M. Pucarević, Petar Đ. Sekulić

Institute of Field and Vegetable Crops Novi Sad,
Maksima Gorkog 30, Serbia and Montenegro

POLYCYCLIC AROMATIC HYDROCARBONS AND PESTICIDES IN SOIL OF VOJVODINA

ABSTRACT: The paper deals with several groups of compounds that represent the most frequent pollutants of soil in the world. The paper also reviews results of long-term studies conducted at the Institute of Field and Vegetable Crops in Novi Sad on the residues of pesticides and polycyclic aromatic hydrocarbons (PAHs) in the soil of the Vojvodina Province. The analyzed samples have been found to contain residues of persistent pesticides and their metabolites: lindane and its metabolites 6,20 μg/kg, alachlor 3,56 μg/kg, aldrin 2,3 μg/kg, heptachlor epoxide 0,99 μg/kg, chlordane 3,82 μg/kg, DDT and its metabolites 10,77 μg/kg, dieldrin 2,04 μg/kg, endrin 3,57 μg/kg and endrin aldehyde 1,36 μg/kg. Soil samples from Novi Sad municipality contained 53,69 μg/kg of DDT and its metabolites. The values of atrazine ranged from 0,0005 to 0,8 mg/kg. The values of PAHs were 6,64 mg/kg in industrial soil, 4,93 mg/kg in agricultural soil, and 4,55 mg/kg and 5,48 mg/kg in the Novi Sad municipality. The lowest value, 0.83 mg/kg, was found for nonagricultural/nonindustrial soils.

KEY WORDS: soil, pesticides, polycyclic aromatic hydrocarbons, PAHs

INTRODUCTION

As part of the environment, soil may contain many organic compounds of natural as well as anthropogenic origin. The concentrations and toxicity of organic compounds present in such complicated mixtures range very widely and depend also on possible interactions (synergies) among chemicals.

The development of instrumental analysis techniques and the lowering of the detection limit have made it possible to identify new organic compounds that are present in the soil in very low concentrations. The list of the most commonly studied soil pesticide pollutants has been expanded to include polychlorinated biphenyls (PCBs), alyphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs) and polychlorinated naphtalenes (PCNs). The continuous introduction of these persistent compounds into the environment has resulted in their accumulation. Depending on how strong the bond is, organic

compounds adsorbed on soil particles may migrate down to deeper soil layers and then to ground or surface waters, or they may remain in the surface layer of the soil and, in some cases, end up in plants. These compounds also bioaccumulate in fish and other aquatic organisms.

Polychlorinated naphtalenes (PCNs) are a group of 75 compounds with two condensed aromatic rings substituted with one to eight chlorine atoms. They were synthesized back in the 19th century and used as dielectrics under different names (Halovax (USA), Seekay (UK) or Nibren (Germany)). Some of these compounds have similar toxicity to that of dioxins. Polychlorinated naphtalenes are produced by the combustion of substances that contain chlorine, so the most common PCN source are waste incineration plants. They are also present in commercial PCB mixtures as by-products of synthesis (Yamashita et al. 2000). PCN quantities found in urban soils range from 0.1 μg/kg to 15.4 μg/kg, while those found in rural soils range between 0.1 μg/kg and 0.82 μg/kg (Krauss, 2003).

Polychlorinated biphenyls (PCBs) have similar uses and characteristics to PCNs and include a total of 209 compounds in which one to ten chlorine atoms are attached to the biphenyl nucleus (Facchetti, 1993). For the sake of simplicity, each of the 209 compounds (congeners) has been assigned a number from 1 to 209 (so-called Ballschmiter-Zell, or BZ, number). In Germany, seven congeners have been chosen as indicators of pollution by PCBs based on the frequency with which a particular congener appears in commercial PCB mixtures. Their BZ numbers are 28, 52, 101, 118, 138, 153 and 180. PCB concentrations are most oftren correlated with PCN ones, the ratio being 100:1 (Kannan et al., 2000). Commercial PCB mixtures go under a variety of names depending on the manufacturer (Arochlor, Chlorexol, Pyralene, Phenoclor, Clophen, Apirolio, Sovol, Delor, Kanechlor). They are used as dielectrics in transformers, hydraulic oils, pesticide synergists, in nonflammable coatings, and in the manufacture of ink and paper. Because of their widespread use, persistence and often improper disposal, PCBs can now be found in all parts of the ecosystem. The PCB content of Bangkok soils was found to be 0.1—1.2 μg/kg (Müller, 2001).

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 compounds made up of condensed benzene rings. They are a product of incomplete combustion of organic substances, coal, gas and wood. Because of their planar structure, these compounds have highly mutagenic and cancerogenic properties. PAH concentrations have often been studied in sediments obtained from ports and near roads. The average PAH content of forest, agricultural and urban soils has been found to 0.05, 0.07 and 1.10 mg/kg, respectively, while that of roadside dust has been determined to be 137 mg/kg (Ayaka et al. 1999). The total PAH content of Bangkok soils has been found to range from 47 to 140 μg/kg (Müller, 2001).

The source whose combustion produced PAHs can be determined by studying PAH residues in soil or some other matrix and by defining relationships among the PAHs concerned (Zou et al. 2003).

PCN, PCB and PAH concentrations in all soil types are interrelated and dependent on human activity. The highest concentrations are those found in

urban areas and gardens. Agricultural soil is polluted by PAHs via particles from the air. Also, the low-molecular-weight fraction of these compounds is more often found in agricultural soils than in urban ones because of greater evaporability and easier transport by air (K r a u s s, 2003).

Pesticides commonly used in plant protection form a large group of diverse compounds (there are 242 active ingredients currently registered in Serbia and Montenegro alone) that come into contact with the soil. Besides the compounds, the products of their decomposition can often be found as well (4,4'-DDT and 4,4'-DDE, 4,4'-DDD, glyphosate and AMPA, atrazine, desethylatrazine, desisopropylatrazins and different hydroxy derivatives of atrazine). DDT (which is no longer in use since the 70s) and its metabolites are very persistent compounds and as such can be found in soil in significant quantities years after they were last used.

The Institute of Field and Vegetable Crops in Novi Sad began monitoring the presence of pesticides (as the first major group of organic compounds) in the soil in 1991, when the Ministry of Science and Technology of the Republic of Serbia and the Fund for Soil Protection. Utilization, Improvement and Management of the Republic of Serbia financed the first such research project. In order to make the initial assessment of the status of soils in the Vojvodina Province, 1,600 soil samples were taken in total, 926 of which were analyzed for the presence of persistent pesticides (15 organochlorine and 4 triazine ones) and products of their degradation.

A study of PAHs was prompted by the NATO bombardment of Serbia and Montenegro that took place in 1999 in which large amounts of oil were set on fire at the Novi Sad oil refinery as a result of repeated bombing. In order to determine if any soil pollution occurred in the area as a result, soil from the Rimski Šančevi Experiment Field of the Institute of Field and Vegetable Crops was studied for the presence of PAHs.

As it is known that the highest PAH concentrations are found in urban areas and near roads, gardens in the city of Novi Sad were studied for PAH presence during 2000 and 2001. Almost all of these compounds were found to be present, especially in suburban areas and on the outskirts of the city, where conventional heating methods are the most common source of PAHs. The total PAH content was somewhat higher in 2001 than in 2000.

In soil studies conducted in 2001, which were financed by the Executive Council of the Vojvodina Province, 50 samples of agricultural soils of Vojvodina were investigated. In 2002, 11 additional samples of soils near industrial sites were studied.

MATERIALS AND METHODS

Pesticide extraction was done using supercritical extraction accompanied by gas chromatography (V e r e š b a r a n j i et al., 1993), while soil PAH extraction was performed by the US EPA 3540C and 3630C method. The extraction of 16 PAHs from the soil was carried out by a glass apparatus according to Soxhlet in the following manner: soil and sediment were extracted

with and 100 ml methylene-chloride for 24 hours. The extract was reduced to 2 ml and dissolved in cyclohexane to 5 ml volume. The resulting extract was purified on a silica gel column. PAHs were eluted from the silica gel column with 25 ml of methylene/pentane mixture (2:3), reduced till dry and dissolved for analysis in acetonitrile. The acetonitrile extract was analyzed by gas chromatography (HP1100) with peak identification using a diode array detector (DAD). The C-18 column was used with acetonitrile/water gradient.

RESULTS AND DISCUSSION

Pesticides

Table 1 shows the results of the study of organochlorine pesticide residues found in the 926 soil samples from the Vojvodina Province and 19 soil samples from the Novi Sad municipality. As we can see, the average contents determined in the study were much lower than those reported in the foreign and domestic literature, i.e. than the threshold values (Šovljanski et al. 1989), Table 2.

Tab. 1. Residues of pesticides and their metabolites in soils, μg/kg d.w.

Pesticide/metha-bolite	alfa-HCH	beta-HCH	Lindan	Alahlor	Heptahlor	Hlorpirifos	Aldrin	Heptahlor-epoksid	Hlordan	4,4-DDE	Dieldrin	4,4-DDD	Endrin-aldehid	4,4-DDT	Endrin
926 soil samples from Vojvodina Province, 1991															
Mean	0,99	1,09	4,12	3,56	n.d.	n.d.	2,3	0,99	3,82	2,59	2,04	2,47	1,36	5,71	3,57
Max.	16.4	47	48,12	0,02	n.d.	n.d.	96	48,91	109,5	105,2	96	120,5	68,78	302,1	248,05
Min.	0,29	0,01	0,55	467,7	n.d.	n.d.	0,01	0,15	0,02	0,29	0,01	0,01	0,01	1,4	0,01
19 soil samples from Novi Sad municipality, 2001. year															
Mean	0.22	0.20	6.61	1.91	n.d.	n.d.	3.08	n.d.	n.d.	25.2	7.58	4.09	7.53	24.4	n.d.
Max.	0.22	0.56	19.54	2.45	n.d.	n.d.	5.5	n.d.	n.d.	128.5	13.9	13.45	24.53	133.0	n.d.
Min.	0.22	0.15	0.83	1.3	n.d.	n.d.	0.61	n.d.	n.d.	0.55	1.24	0.36	0.95	0.56	n.d.

n. d. — not detected

The level of DDT and its metabolite was found to be higher in the urban soils of Novi Sad (19 samples, DDT + metabolites = 53.69 μg/kg) than in the agricultural soils (926 samples, DDT + metabolites = 10.77 μg/kg) (Table 1). This is probably a result of actions by uninformed individuals who continued to use DDT in their home gardens in excessive doses even after the substance was banned.

Tab. 2. Proposed maximum residue levels for DDT and Lindane in soil

Pesticide	Proposed MRL mg/kg
Lindane + metabolites	60
DDT + metabolites	100

Among the triazine herbicides that were studied, the most important were atrazine residues in the soil. Atrazine residues are analyzed on a regular basis at the Laboratory for Agroecology. Depending on precipitation and temperatures, the atrazine used for maize protection may be retained in the surface layer of the soil in a quantity phytotoxic to the following crop. The atrazine tests are necessary in droughty years and may prevent major losses. Table 3 shows the results of multiyear studies of atrazine residues in the soil. By comparing the results from Table 3 with the maximum tolerable levels for sensitive crops shown in Table 4, we can see that atrazine is very often present in our soils in phytotoxic concentrations.

Tab. 3. Atrazine residues content of soil

Year	Number of soil samples	Atrazine concentration
		mg/kg soil
1991	926	0.002—0.570
2000	4	0,03—0,08
2001	7	0,0005—0,018
2002	15	0,022—0,8

Tab. 4. Maximum residue levels for atrazine in soil for sensitive crops (Official Herald of RS 11, 239, 1990)

Crop	mg/kg soil
Alfalfa, rapeseed and sugarbeet	0.06—0.09
Oat, soybean, barley and cucumber	0.15—0.20
Sunflower	0.20—0.25
Wheat and rye	0.25—0.30
Potato, flax and onion	0.30—0.40
Brussels sprouts	1

Polycyclic aromatic hydrocarbons (PAHs)

The results of our study of PAH content at the Institute's experiment fields have been already published (P u c a r e v i ć et al., 2000). A total of 42 soil samples were studied. The average PAH content was 0.173 mg/kg, ranging from 0.056 to 1.022 mg/kg. Of the 16 PAHs analyzed in total, only four were found to be present — naphthalene, chrisene, fluorene and pyrene. The general conclusion was that no accumulation of by-products of combustion occurred at the Institute's fields due to favorable winds.

The results of the next PAH study are shown in Table 5. Analysed in the study was the PAH content of nonagricultural soils, soils in the municipality of Novi Sad (two-year results), and soils located near industrial facilities.

Tab. 5. Average total PAH content of the soil

Origin of soils	Year	Number of samples	Mean	Max.	Min.
			mg/kg		
Nonagricultural soils	2002	37	**0,83**	0,09	3,57
Urban soils of Novi Sad	2000	18	**4,55**	8,79	2,25
Agricultural soils	2001	50	**4,93**	7,89	1,85
Urban soils of Novi Sad	2001	19	**5,48**	8,26	2,44
Industrial soils	2002	11	**6,64**	37,05	0,89

The average PAH levels are presented in Table 5 in ascending order. As we can see, the levels of these compounds are the lowest in soils that are neither agricultural nor industrial. As the samples of nonagricultural soils were taken from nature reserves, where human activity is minimal, the PAH content of those soils was minimal as well. The agricultural soils (50 samples) tested in 2001 had more total PAHs than the soil from trial fields analyzed in 2000. This may have been a result of the use of agricultural machinery that requires large amounts of oil to run, but it also may have been due to the fact that the plots studied in 2001 were in closer proximity to roads. The results for the soils in the vicinity of industrial facilities indicate that industry is a major source of PAHs and that it contributes to soil pollution by these compounds. The highest PAH content among the industrial soils was found near an accumulator-manufacturing plant in Sombor.

Our study of soil PAH content continued as part of the national biotechnology program under the auspices of the Ministry of Science, Technology and Development of the Republic of Serbia as part of a project entitled *A Program of Soil Protection. Utilization and Management* lasting from 2000 to 2003. During the first year of research, agricultural soils of Vojvodina were studied. Table 6 shows the results of PAH content study for the purpose of characterization and management of soils to be used for the production of safe food.

Tab. 5. Average total PAH content in soil intended for safe food production

	Year	Area, ha	Number of samples	Mean	Max.	Min.
				mg/kg		
Potato	2002.	240	45	0,43	0,82	0,16
Vegetable crops		1200	199	0,50	1,23	0,16
Corn and wheat		370	159	0,51	0,70	0,36
Soybean and sunflower		316	49	0,40	0,70	0,35
MRL Guidelines for organic production, mg/kg soil Official herald of SRJ 51/2002				1		

The results of these studies showed that most of the soils were suitable for the production of safe food in accordance with organic production guidelines (Official herald of SRJ 51/2002). The only exceptions were three soil samples taken from sites near Novi Kneževac, which had increased total PAH levels.

CONCLUSION

— The levels of residues of persistent organochlorine pesticides and their metabolites found in the soil under study are such that they require no special measures to be taken

— The study of soil pesticide residues should be expanded to include study of the presence of new persistent compounds that are used in plant protection or in large quantities.

— The maximum atrazine concentrations found in the soil in our study were within the limits of phytotoxicity to sensitive crops, ranging from 0.0005 to 0.8 mg/kg.

— The level of DDT and its metabolite was found to be higher in the urban soils of Novi Sad (53.69 μg/kg) than in the agricultural soils (10.77 μg/kg).

— Total PAH content was lower in the nonagricultural soils (0.83 mg/kg) and higher in the urban soils (4.55 mg/kg and 5.48 mg/kg) and soils situated near industrial facilities and roads (6.64 mg/kg)

— Almost all of the PAHs tested for were found in the soils from the municipality of Novi Sad. In suburban areas and on the outskirts of the city, the PAH content was higher because of the use of conventional heating methods, which are the most common source of PAHs. The total PAH content was somewhat higher in 2001 than in 2000.

— The study of soil pesticide residues should be expanded to include study of the presence of PCBs, PCNs, PCDDs and PCDBs, since these compounds are present in the environment according to the literature.

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ПОЛИЦИКЛИЧНИ АРОМАТИЧНИ УГЉОВОДОНИЦИ И ПЕСТИЦИДИ У ЗЕМЉИШТУ ВОЈВОДИНЕ

Мира М. Пуцаревић, Петар Ђ. Секулић
Научни институт за ратарство и повртарство Нови Сад,
Максима Горког 30, Србија и Црна Гора

Резиме

Органска једињења која се могу наћи у земљишту приказана су у овом раду. Такође је приказан и део вишегодишњих испитивања садржаја остатака пестицида и полицикличних ароматичних угљоводоника у земљишту изведених у Институту за ратарство и повртарство у Новом Саду. Испитано земљиште са територије Војводине садржи остатке перзистентних пестицида и њихових метаболита: линдан заједно са метаболитима 6,20 μg/kg, алахлор 3,56 μg/kg, алдрин 2,3 μg/kg, хептахлор епоксид 0,99 μg/kg, хлордан 3,82 μg/kg, ДДТ заједно са метаболитима 10,77 μg/kg, диелдрин 2,04 μg/kg, ендрин 3,57 μg/kg и ендрин алдехид 1,36 μg/kg. Земљиште са територије општине Нови Сад садржи остатке DDT-а заједно са метаболитима у количини од 53,69 μg/kg. Током вишегодишњих испитивања садржаја атразина у земљишту нађене вредности су се кретале у опсегу од 0,0005 mg/kg до 0,8 mg/kg. Нађени садржај полицикличних ароматичних угљоводоника је у индустријском земљишту 6,64 mg/kg, у пољопривредном земљишту 4,93 mg/kg, у земљишту на територији општине Нови Сад 4,55 mg/kg и 5,48 mg/kg, док је садржај на непољопривредно/неиндустријском земљишту најнижи и износи 0,83 mg/kg.