EFFECT OF NOVI SAD OIL REFINERY BOMBARDMENT AND FIRES ON SOIL PROPERTIES IN VOJVODINA PROVINCE

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ABSTRACT

The bombing of the Novi Sad Oil Refinery in 1999 has lead to soil pollution by the products of burning oil and oil derivatives. These products were first carried by winds to the Rimski Sancevi Experiment Field of the Institute of Field and Vegetable Crops (located in the vicinity of the Novi Sad Oil Refinery), where they entered the soil via precipitation. Later, they spread to the city of Novi Sad, its vicinity, and the whole of the Vojvodina province, contaminating the soil. In the present study, we examined the extent to which this soil had been polluted. In 1999, we began to study the level of soil contamination at the Institute's Experiment Field at Rimski Sancevi. In 2000, we carried out the same kind of study in and around the city of Novi Sad, while in 2001 we expanded the study to the whole of Vojvodina. The studies' findings show that the soil reaction has not changed and that the levels of heavy metals in the soil have not excedeed the maximum tolerable concentration (MTC). The presence of PAHs at various concentrations was detected, however. This presence is a result of the fires at the Novi Sad Oil Refinery.

Key words: oil refinery, environment, bombing, fires, soil pollution

INTRODUCTION

The Novi Sad Oil Refinery was bombed in 1999 on four occasions. Over 100,000 tons of oil and oil derivatives are estimated to have burned up in the process. The burning of oil and oil derivatives released into the atmosphere significant amounts of nitrogenous and sulphureous oxides, which reacted with atmospheric water to produce nitrogenous and sulphureous acids. Improper burning of oil produced huge amounts of soot. This soot was the center of condensation for the other by-products of burning. From the point of view of soil pollution, particularly significant among these are polycyclic aromatic hydrocarbons, or PAHs.

In order to obtain a realistic picture of the wider impact of the Novi Sad Oil Refinery fires, several projects were conducted in the Vojvodina province in general and the Novi Sad area in particular to study the status of the soil.
We assumed that 100,000 t of oil containing an average of 84-85% C; 12-14% H; and 4-5% N, O and S (Djukanovic Mara 1991)[2] burned up in the fires. The generation of nitrogenous and sulfurous acids is shown in Figure 1.

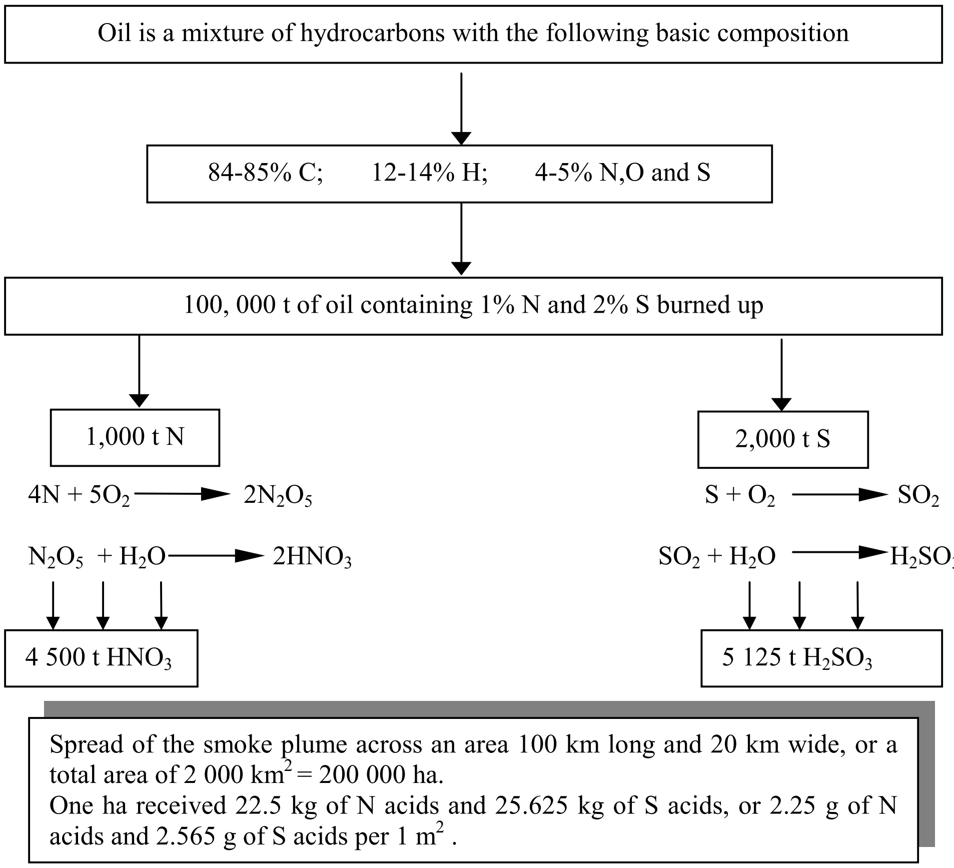

Figure 1. Amounts of N and S acids produced by the burning of 100,000 t of oil

MATERIALS AND METHODS

In 1999, right after the bombing ended, it became apparent that the rain that had been falling in abundance that year had a negative effect on the yields of wheat and other small grains at the Rimski Šančevi Experiment Field of the Institute of Field and Vegetable Crops in Novi Sad. It was therefore decided that a study be conducted to determine whether the effects of combustion by-products permanently damaged the soil. To do this, 42 2-m deep pedological profiles were opened and samples of pedogenetic horizons were taken from them. The profiles were probed down to 5 m depth in search of the first aquifier water. Those that were found to contain such water, 15 of them in total, were sampled. Another part of the study involved a control of feritlity of the Experiment Field's commercial plots, where samples were taken from the 0-30 cm layer on 2-4 ha. By taking 187 topsoil samples we wanted to obtain a detailed picture of all relevant soil properties. The samples were subjected to all physical and chemical analyses necessary for determining the soil type, subtype, variety and form as well as those aimed primarily at determining possible soil pollution. With this in mind, we determined total, potentially available and available levels of trace elements and heavy metals. Another segment of the study involved biological soil properties, including the abundance and enzymatic activity of certain microbial groups.

The next study was carried out in the Novi Sad area. In collaboration with the Novi Sad Agency for Urban Development, pedological profiles were opened at a total of 18 sites in the municipality of Novi Sad, covering every suburban community in the municipality as well as the city of Novi Sad itself. Two-meter deep profiles were opened on plots on which fruits and vegetables are grown. The soil samples were analyzed using the same methodology as in the case of the Institute's Experiment Field.

The plume of smoke containing soot, PAHs, and N and S oxides spread beyond the municipality of Novi Sad and over a sizeable area in the Vojvodina province. In cooperation with the Provincial Council of Vojvodina, researchers from the Novi Sad Institute took 50 samples from all over the province. When taking samples from the 0-30 cm layer, they made sure to include all soil types found in the province and to mirror their relative contribution to overall soil composition in Vojvodina. Using the same methodology as in the previous two studies, the samples were analyzed for all relevant parameters that might show conclusively whether the soil had been damaged and, if so, to what extent.

The soil was analyzed at the Institute's Laboratory for Agroecology, which is accredited to perform analyses of soil properties. The following basic chemical properties were determined: soil reaction, humus content, and the levels of free calcium carbonate. Also determined were the levels of basic biogenic elements — N, P and K. The methods we used are the official methods of the Yugoslav Soil Science Society (YSSS)[4]. The total, potentially available and available levels of trace elements (Cu, Fe, Mn, Zn) and heavy metals (Cd, Ni, Co, Cr, Pb) were determined. The total contents were determined in a solution after breaking down the soil using concentrated nitrogen acid and hydrogen peroxide (Alloway, 1995.)[2]. The potentially available contents were determined from an extract obtained using 1M HCl, while the available contents were measured by means of the EDTA extract. Using these solutions, trace elements and heavy metals were determined by atomic absorption spectrophotometry on an AAS Varian Spectra 600. PAH extraction was performed using the supercritical extractor Hewllet Packard Model 7680A. The resulting extracts were analyzed by liquid chromatography using HP 1100 with a Diode Array detector, which enabled the confirmation of the compound's identity based on the UV spectre. The PAH standards used in the study were manufactured by Supelco (Catalogue No. 48905).

RESULTS AND DISCUSSION

The 1999 soil study at Rimski Šančevi has shown the folowing:

The burning of oil and oil derivatives brought into existence huge amounts of N and S oxides and their acids.

Acid rains that fell on the Institute's Experimental Field and the province of Vojvodina have not changed the soil reaction but have lead to the scalding of young plants. (Table 1). Table 1 shows that the reaction of the chernozem variety on loess and loess-like sediments was either slightly acid, neutral or slightly alkaline.This was due to the presence of free $CaCO_3$ in the calcareous and calcareous gleyed varieties. The limeless and limelessly gleyed varieties had a stable reaction resulting not from the free $CaCO_3$ but from the dominant role of the Ca^{2+} ion in the adsorption complex and the soil's buffer capacity that enables to resist sudden changes of pH by substituting the Ca^{2+} from the adsorption complex with the H^+ ions from the soil solution.

Table 1. Soil reaction and free $CaCO_3$ content in the A horizon of the chernozem varieties at Rimski Šančevi

Variety	pH_{H2O}	pH_{KCl}	$CaCO_3$ (%)	Adsorbed Ca (mg equiv. /100g)	% contribution of Ca on ads. complex
Calcareous	7.68	6.86	3.85	22.96	90.05
Calcareous gleyed	7.76	6.92	2.39	23.12	89.50
Limeless	7.19	6.26	0.00	15.03	84.16
Limeless gleyed	7.06	6.19	0.11	17.65	83.17

- The oil refinery fires have not increased the soil level of any trace element or heavy metal at the Experimental Field. (Table 2). The contribition of the available form of a particular heavy metal to its total content depended on the metal, but pedogenesis had some influence too. The calcareous and calcareous gleyed varieties of chernozem had a significantly lower contribution of heavy metals than the limeless and limeless calcareous gleyed varieties. The reason for that was the effect of the environment's reaction on the chemical immobilization of heavy metals and the stabilization of complex organic compounds of heavy metals with humic acids. Further, the free $CaCO_3$ in the calcareous chernozem varieties also had a significant influence on the availability. Particularly noteworthy was Cd, where the limeless chernozem variety had an available Cd content that was equal to the total Cd content. The available Co and Ni contents were twice as high as those in the calcareous varieties. (Table 2).
- Of the total of 16 PAHs analyzed, four were found to be present in the soil.
- One of these four — chrysene — is cancerous[3, 9], while the rest are toxic.
- The mean total PAH content was 1.173 mg/kg (Table 3), which is above the lowest risk zone as prescribed by the US EPA. Still, even such a low PAH content affects the safety of the crop species grown in the area. Looking at the PAH content values we obtained and the US EPA's lowest risk zone (1993a)[8], we can see that the soil of the Rimski Sancevi Experiment Field is above this minimum risk zone. However, since the threshold value is 0,1 mg/kg, and the average content at the Experiment Field is 0.173 mg/kg, the excess is only very slight. After comparing the values from our study with those found in the literature, we can conclude that the presence of PAHs in our soil is minimal. However, even these minimal quantities found in certain parts of the Experiment Field can affect the safety of plant products, since any PAH presence, however small, has some

sort of effect. Therefore, it can be concluded that the Novi Sad Oil Refinery fires had a negative effect on the soil's natural properties when it comes to these organic pollutants.

Table 2. Heavy metal forms in the the chernozem varieties at Rimski Sancevi (mg/kg)

Element	MTC for HNO_3	Content mg/kg	Calcareous	Calcareous gleyed	Limeless	Limeless gleyed
Co	50	Total -HNO_3	14.38	14.62	14.39	15.21
		Pot. availableHCl	3.91	4.14	3.08	3.98
		Available EDTA	1.70	1.83	3.59	3.77
Pb	100	Total -HNO_3	29.07	29.76	28.72	32.65
		Pot. available HCl	14.20	14.22	11.71	13.65
		Available EDTA	5.44	5.49	7.50	7.56
Cd	2	Total -HNO_3	0.49	0.39	0.11	0.37
		Pot. available HCl	0.49	0.45	0.22	0.33
		Available EDTA	0.21	0.22	0.21	0.24
Ni	50	Total -HNO_3	34.75	36.25	36.39	37.88
		Pot. available HCl	9.66	9.80	8.40	9.45
		Available EDTA	3.29	3.52	6.76	6.65
Cr	100	Total HNO_3	69.70	94.41	43.21	103.07

Table 3. PAH content in 42 topsoil samples taken from the Rimski Sancevi Experiment Field (mg/kg of absolutely dry soil)

mg/kg of absolutely dry soil					
	Naphthalene	*Chrysene*	*Fluorene*	*Pyrene*	*Total*
Average	0.131	0.048	0.808	0.104	**0.173**
Minimum	0.056	0.032	0.808	0.104	**0.056**
Maximum	0.229	0.078	0.808	0.104	**1.022**
% of positive results	78.571	23.810	2.381	2.381	**78.571**
Standard deviation	0.048	0.015	0.000	0.000	**0.161**

- The study's findings showed that the PAHs had originated from burning oil and oil derivatives at the refinery, since the soil and profiles in which they were found are located away from the roads, which precludes the possibility that the PAHs had originated from car exhaust fumes.
- The levels of PAHs need to be further monitored in the profiles in which they were found in order to monitor the progress of PAH decomposition in the soil.

Our study of the level of soil contamination in and around Novi Sad carried out in 2000 has shown the following:

- Properties of different types of soil in the municipality of Novi Sad have been changed by human agency.
- These changes involved increased levels of potassium and, especially, phosphorus, which were a result of excessive fertilizer application. The most dramatic was the change in the levels of available phosphorus and potassium in the city of Novi Sad itself. The huge, toxic, amounts of phosphorus found at the Klisa, Sangaj, Salajka, Telep, and Adice sites were a result of excessive application of mineral NPK fertilizers. The remaining two sites had a high phosphorus content, which is necessary for growing vegetable crops. The soil levels of available potassium were optimally high, the only exception being the Sangaj site, where the available potassium content was close to being excessive to harmful. (Table 4).
- All this occurred typically in house gardens in Novi Sad itself, whereas the soil properties of plots in Greater Novi Sad remained close to their initial status (Table 4.). Apparently, there were significant differences in the levels of available phosphorus and potassium within the various soil types. The phosphorus content of the chernozem soils ranged between 7.53 mg/100g to 40.18 mg/100g, while the potassium content varied from 11.20mg/100g to 50mg/100g. The reason for this was not pedogenesis, or the process of soil formation, but the long-standing improper use of fertilizers (primarily mineral ones), which caused a significant decrease in the natural phosphorus and potassium levels relative to the typical available phosphorus and potassium contents of 15-20 mg/100g.
- The analyses of the trace element content (Cu, Fe, Mn and Zn) have shown that the levels of these elements are below the maximum tolerable concentration (MTC) except for the Zn content at the Sangaj site. In the first horizon, this content was above the MTC (311.57 mg/kg), while in the next one it was 49.73 mg/kg, which suggests that the Zn content has been increased by anthropogenic activity, i.e. that this is a case of minor pollution. Since the Zn content exceeds the MTC by only 4%, we do not consider this alarming. The available trace element contents as well as the levels of the macroelements P and K depended more on the location, i.e. the plot's owner. Thus, the Cu content ranged from 2.51 mg/kg to 39.35 mg/kg.The other trace elements also indicate that the process of pedogenesis is not at the present the dominant factor in determining their levels. What determines them instead is the method of utilization and fertilization. All of the trace elements under study were found to be at levels that enable normal plant growth and development. There are, however, significant differences in these levels that can only be explained by the differences in the method of fertilizer application on individual plots within the same soil type.

Table 4. Basic chemical properties of soil in and around Novi Sad

Site	Profile	Hori-zon	Depth (cm)	pH		$CaCO_3$
				KCl	H_2O	%
Futog	1					
Begeč	2	**Ap**	0-12	6,40	7,15	0,00
Stepanovićevo	3	**Ap**	0-25	7.41	7.88	7.21
Kovilj	4	**Ap**	0-15	6,30	6,80	0,00
Kisač	5	**Ap**	0-35	7,36	7,90	5,94
Budisava	6	**Ap**	0-16	6,28	7,10	0,00
Rumenka	7	**Ap**	0-30	6,50	7,00	0,00
S. Kamenica	8	**Ap**	0-20	7,09	7,87	3,79
Petrovaradin	9	**P**	0-20	7,23	7,87	8,01
Kać	10	**AP**	0-35	7,28	7,94	3,37
Čenej	11	**Ap**	0-24	6,69	7,49	0,00
NS Klisa	12	**Ap**	0-20	7,36	7,82	5,45
Veternik	13	**Ap**	0-14	6,88	7,58	0,67
NS Šangaj	14	**Ap**	0-25	6,82	7,50	9,37
NS Šalajka	15	**Ap**	0-18	6,79	7,27	8,74
NS Telep	16	**Ap**	0-10	7,18	7,83	7,03
NS Adice	17	**Ap**	0-20	7,06	7,42	0,62
NS Centar	18	**A**	0-10	7,38	7,82	16,95

Site	Profile	Humus	N	P_2O_5	K_2O
		%	%	mg/100 g	
Futog	1				
Begeč	2	0,91	0,06	14,99	11,20
Stepanovićevo	3	3.36	0.221	13.30	17.20
Kovilj	4	1,76	0,116	8,42	14,00
Kisač	5	3,32	0,219	40,18	50,00
Budisava	6	3,85	0,254	30,28	40,60
Rumenka	7	2,27	0,15	7,53	20,00
S. Kamenica	8	1,60	0,105	10,82	15,40
Petrovaradin	9	1,90	0,125	20,02	27,00
Kać	10	2,73	0,181	19,86	28,50
Čenej	11	3,17	0,209	19,32	20,00
NS Klisa	12	3,44	0,227	119,3	50,00
Veternik	13	1,84	0,121	47,60	18,00
NS Šangaj	14	5,71	0,377	121,0	34,00
NS Šalajka	15	4,17	0,276	190,9	68,00
NS Telep	16	2,35	0,155	174,6	29,00
NS Adice	17	1,90	0,125	166,4	39,00
NS Centar	18	5,83	0,385	35,20	55,00

Table 5. Levels of heavy metal forms in the topsoil in and around Novi Sad (mg/kg)

Site	Cd* HNO_3	Cd** HCl	Ni* HNO_3	Ni** HCl	Co* HNO_3	Co** HCl	Cr* HNO_3	Cr** HCl	Pb* HNO_3	Pb** HCl
Klisa	1.40	0.53	36.6	15.1	13.5	5.70	18.9	3.89	36.0	19.9
Veternik	1.11	0.20	28.4	7.7	9.8	3.93	14.9	4.66	22.1	11.2
Šangaj	1.69	1.03	43.9	17.6	15.3	4.91	22.4	7.03	92.2	72.1
Šalajka	1.37	0.69	44.6	19.1	11.2	4.89	17.4	8.98	37.4	37.0
Telep	1.07	0.47	27.2	10.3	10.5	4.14	12.2	2.22	34.0	25.9
Adice	1.21	0.35	27.0	6.4	10.8	3.99	19.3	3.29	24.5	15.6
NS Centar	2.15	1.12	61.2	28.1	18.4	7.70	18.3	4.75	69.2	58.9
Futog	0.97	0.19	27.52	4.9	11.0	2.8	12.4	2.32	19.7	10.1
Begeč	0.85	0.11	27.0	3.0	15.4	2.54	12.7	2.61	18.6	7.6
Stepanovićevo	1.58	0.61	32.5	11.4	14.8	5.39	11.0	1.20	28.9	21.4
Kovilj	1.22	0.11	22.7	4.53	10.9	3.24	4.6	0.58	24.2	10.20
Kisač	1.66	0.53	38.7	13.23	17.4	6.41	15.4	1.10	33.0	19.42
Budisava	1.20	0.18	37.7	10.54	18.5	5.29	15.0	2.66	28.0	16.36
Rumenka	1.41	0.17	37.4	9.31	15.0	3.82	18.7	2.00	30.1	14.32
S. Kamenica	1.39	0.35	73.9	11.82	23.3	6.49	55.2	5.22	34.5	17.14
Petrovaradin	1.37	0.92	37.0	24.42	16.3	10.15	15.3	6.82	32.1	25.63
Kać	1.24	0.32	42.1	11.76	19.6	6.90	28.5	2.32	29.7	16.98
Čenej	1.31	0.28	34.6	10.39	14.5	4.93	13.6	2.29	30.5	14.64
MTC	**2**		**50**		**50**		**100**		**100**	

* Total content, soil degraded by $_{cc}HNO_3$ and H_2O_2
** Potentially available content, soil extracted using 1M HCl

Table 6. Soil PAH content in and around Novi Sad (mg/kg of absolutely dry soil)

Sample name	Nafphtalene	Acenaphthylene	Phenanthrene	Acenaphthene	Fluorene	Anthracene	Fluoranthene	Pyrene	Benzo (a) antracene	Chrysene	Benzo (b) fluoranthene	Benzo (a) pyrene	Benzo (k) fluoranthene	Dibenzo (a,h) antracene	Benzo (g,h,i) perylene + Indeno(1,2,3-cd)-pyrene	**Sum 1-16**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15 + 16	
Futog	0.306	0.623	0.370	n.d.	n.d.	0.301	n.d.	0.645	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**2.245**
Begeč	0.274	0.267	0.374	n.d.	n.d.	0.271	0.129	0.522	0.665	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**2.502**
Stepanovićevo	0.305	0.273	0.182	n.d.	n.d.	0.275	n.d.	1.014	2.125	n.d.	n.d.	0.394	n.d.	1.120	1.055	**6.743**
Kovilj	0.302	0.282	0.488	n.d.	n.d.	0.427	n.d.	1.209	n.d.	n.d.	n.d.	0.260	n.d.	0.067	n.d.	**3.035**
Kisač	0.317	0.284	0.175	0.047	n.d.	0.301	0.130	0.927	2.731	n.d.	n.d.	0.258	n.d.	0.110	0.079	**5.359**
Budisava	0.297	0.255	0.256	0.070	n.d.	0.414	n.d.	0.703	0.971	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**2.966**
Rumenka	0.350	0.744	0.246	0.105	n.d.	0.574	n.d.	1.777	4.139	n.d.	n.d.	0.648	n.d.	0.058	0.145	**8.786**
Sremska K.	0.323	0.729	0.239	n.d.	n.d.	0.276	n.d.	1.330	0.075	n.d.	n.d.	0.497	n.d.	n.d.	n.d.	**3.469**
Petrovaradin	0.327	0.708	0.203	n.d.	n.d.	0.344	n.d.	1.613	1.608	0.065	n.d.	0.796	n.d.	0.053	0.203	**5.920**
Kać	0.378	0.281	0.279	n.d.	n.d.	0.616	n.d.	1.914	n.d.	n.d.	n.d.	0.325	n.d.	0.059	n.d.	**3.852**
Čenej	0.350	0.598	0.218	n.d.	n.d.	0.503	n.d.	1.157	n.d.	n.d.	n.d.	0.127	n.d.	n.d.	n.d.	**2.953**
Klisa	0.376	0.285	0.313	n.d.	n.d.	0.588	n.d.	1.929	n.d.	n.d.	n.d.	0.375	n.d.	n.d.	n.d.	**3.866**
Veternik	0.372	0.329	0.332	n.d.	n.d.	0.372	0.357	1.024	n.d.	0.099	n.d.	0.128	0.457	0.072	0.125	**3.667**
Šangaj	0.695	0.375	0.316	0.059	n.d.	0.353	n.d.	2.107	n.d.	n.d.	n.d.	0.777	n.d.	0.733	n.d.	**5.415**
Šalajka	0.374	0.678	0.476	0.058	n.d.	0.387	0.640	0.927	n.d.	0.083	0.746	0.132	0.371	n.d.	n.d.	**4.872**
Telep	0.375	0.148	0.748	n.d.	n.d.	0.358	0.432	1.248	1.915	0.086	0.259	0.227	0.440	0.098	0.241	**6.575**
Adice	0.340	0.630	0.600	n.d.	n.d.	0.301	n.d.	1.208	2.827	n.d.	n.d.	n.d.	0.543	0.084	n.d.	**6.533**
Novi Sad centar	0.386	0.490	0.386	n.d.	n.d.	0.087	n.d.	n.d.	1.544	n.d.	n.d.	0.087	n.d.	0.081	n.d.	**3.061**
n.d.- not detected																
Average	**0.358**	**0.443**	**0.345**	**0.068**	**0.000**	**0.375**	**0.338**	**1.250**	**1.860**	**0.083**	**0.503**	**0.359**	**0.453**	**0.230**	**0.308**	**4.546**
Maximum	**0.695**	**0.744**	**0.748**	**0.105**	**0.000**	**0.616**	**0.640**	**2.107**	**4.139**	**0.099**	**0.746**	**0.796**	**0.543**	**1.120**	**1.055**	**8.786**
Minimum	**0.274**	**0.148**	**0.175**	**0.047**	**0.000**	**0.087**	**0.129**	**0.522**	**0.075**	**0.065**	**0.259**	**0.087**	**0.371**	**0.053**	**0.079**	**2.245**

Table 7. Basic chemical properties of 50 representative soil samples (0-30 cm) from Vojvodina

SITE	Soil Type	pH 1M KCl	pH H2O	$CaCO_3$ (%)	Humus (%)	Total N (%)	Al-available P_2O_5 (mg/100g)	Al-available K_2O (mg/100g)
Horgoš	Arenosol	8.5	9.37	14.42	0.45	0.043	5.1	9
Gakovo	Chernozem	7.4	7.91	6.78	3.22	0.223	16.6	20
Maglić	Chernozem	7.31	8	8.94	3.04	0.224	27.3	23.5
Nadalj	Chernozem	7.22	7.93	7.84	4.2	0.261	36.5	27.66
Parage	Chernozem	7.26	7.93	3.83	3	0.226	16.9	24.5
Rimski Šančevi	Chernozem	7.29	7.97	1.7	2.61	0.186	19.3	27.5
Ruski Krstur	Chernozem	7.3	8.1	7.23	3.38	0.23	30.1	24
Srpski Miletić	Chernozem	7.25	7.85	2.55	2.6	0.226	18.9	22
Žabalj	Chernozem	6.83	7.43	0.85	2.82	0.194	12.2	27
Kula - Lipar	Chernozem	7.42	7.99	12.76	3.27	0.213	53.6	36
Srbobran	Chernozem	7.42	8.04	10.21	3.51	0.23	28.6	33
Aleksa Šantić	Chernozem	7.24	7.86	8.53	3.66	0.242	21.13	16
Tornjoš	Chernozem	7.38	7.97	5.51	3.88	0.262	18.3	18.5
Žednik	Chernozem	7.47	8.05	10.17	3.02	0.209	16.16	18
Bavanište	Chernozem	7.1	7.9	1.02	3.51	0.244	27.5	20
Crepaja	Chernozem	7.31	7.94	8.48	3.08	0.21	15.9	16.5
Begejci	Chernozem	7.2	7.92	3.83	3.37	0.237	34.8	38.5
Crna Bara - Čoka	Chernozem	7.21	7.84	1.7	2.86	0.206	135.6	44.5
Idvor	Chernozem	7.29	8	3.83	2.98	0.206	22.7	27.5
Kikinda	Chernozem	6.26	7.17	0	3.68	0.246	6.5	50
Zrenjanin	Chernozem	7.29	7.9	11.34	3.3	0.194	33.37	28.66
Kozjak	Chernozem	7.42	8.02	8.94	2.5	0.198	12.3	12.5
Padina	Chernozem	7.18	7.91	4.13	3.54	0.021	18.8	15.33
Deliblato	Chernozem	7.19	7.82	0.76	2.57	0.171	16.5	17.66
Rivica	Chernozem	6.31	7.27	0	2.09	0.166	7	23
Ruma – Irig	Chernozem	7.06	7.74	3.35	2.39	0.156	14.43	21.33
Šid	Chernozem	6.94	7.4	1.95	1.97	0.162	7.7	15.83
Indjija	Chernozem	7.36	8	5.09	2.95	0.204	15.6	19.5
Pećinci – Popinci	Chernozem	7.28	8.03	5.51	2.77	0.194	30	28
Sremska Mitrovica	Chernozem	7.16	7.96	6.78	3.03	0.216	26.4	20
Orlovat	Chernozem	7.27	7.9	3.4	3.06	0.219	30.7	28.5
Bačko Novo Selo	Fluvisol	7.48	7.9	10.21	1.45	0.108	21.5	11.5
Kać	Fluvisol	7.33	7.96	17.45	1.85	0.158	3.8	12
Obedska Bara	Fluvisol	5.61	6.6	0	2.11	0.152	16.9	22.5
Sanad	Fluvisol	7.47	8.2	0.43	2.6	0.189	131.5	70
Bečej	Humogley	6.76	7.62	0.68	2.9	0.193	34.66	27
B.Arandjelovo	Humogley	7.36	8.03	3.83	2.72	0.173	22.8	31
Vršacki Ritovi	Humogley	6.96	7.92	4.25	3.66	0.22	55.7	28.5
Bogojevo	Humogley	7.17	7.93	4.68	2.85	0.207	38.2	18
Torda	Humogley	6.46	7.47	0	3.23	0.236	3.3	28.5
Ilandža	Humogley	7.33	8.01	5.11	2.01	0.158	23	19
Rusko Selo	Humogley	5.62	6.69	0	3.73	0.27	4.9	47.5
Donji Tovarnik	Humogley	6.99	7.95	0.76	2.07	0.137	11	25
Petrovaradin	Kambisol	6.92	7.8	0.42	2.85	0.2	54.9	24.5
Vršac	Kambisol	5.34	6.54	0	1.79	0.081	20.8	29.33
Morović	Pseudoglej	5.37	6.56	0	2.04	0.161	15.7	18
Višnjićevo	Pseudoglej	4.74	6.03	0	2.29	0.163	3.1	19
Palić	Soloncak	7.44	8.1	5.02	2.24	0.168	29.9	22
Boka (Sokolac)	Solonjec	5.79	7	0	3.22	0.221	2.5	23.5
Kumane	Solonjec	6.18	7.54	0	2.97	0.184	7.2	22

Table 8. Total levels of trace elements and heavy metals in 50 soil samples in Vojvodina

SITE	Soil Type	Fe HNO_3	*Mn* HNO_3	Cu HNO_3	Zn HNO_3	Co HNO3	Pb HNO_3	Ni HNO_3	Cd HNO_3	Cr HNO_3
Horgoš	Arenosol	3898.0	112.4	4.83	11.03	3.13	32.10	19.47	0.68	6.87
Gakovo	Chernozem	20086.7	535.0	21.27	51.37	13.59	37.13	44.50	0.68	32.03
Maglić	Chernozem	25313.3	684.3	21.40	64.10	16.05	40.83	46.97	0.82	45.30
Nadalj	Chernozem	22633.3	636.3	22.24	65.47	12.26	36.49	38.47	0.29	46.60
Parage	Chernozem	26400.0	697.7	22.87	73.30	14.35	30.13	38.20	0.18	61.13
Rimski Šančevi	Chernozem	27560.0	619.7	24.03	72.43	11.59	30.20	34.77	0.19	63.43
Ruski Krstur	Chernozem	23860.0	636.0	21.23	61.97	14.60	34.93	40.00	0.25	45.07
Srpski Miletić	Chernozem	25733.3	648.3	22.17	66.20	12.75	27.33	37.23	0.28	58.20
Žabalj	Chernozem	28020.0	662.7	23.07	66.87	15.68	27.87	43.37	0.75	60.13
Kula - Lipar	Chernozem	24200.0	624.7	22.77	66.83	15.31	46.40	46.27	0.68	41.43
Srbobran	Chernozem	21573.3	561.7	26.80	57.43	12.78	42.77	41.87	0.22	34.33
Aleksa Šantić	Chernozem	19955.6	542.4	20.43	54.02	11.88	38.67	40.10	0.98	32.31
Tornjoš	Chernozem	16613.3	455.3	17.83	46.57	10.94	30.57	34.77	0.28	28.43
Żednik	Chernozem	17693.3	560.0	19.43	5.22	12.08	40.13	44.53	0.78	28.80
Bavanište	Chernozem	25006.7	556.3	21.37	67.23	13.23	26.67	49.50	0.48	90.03
Crepaja	Chernozem	23740.0	581.7	5.33	60.70	16.50	54.70	53.23	0.85	65.10
Begejci	Chernozem	22206.7	299.9	21.37	61.23	13.52	32.53	38.50	2.05	42.33
Crna Bara - Čoka	Chernozem	23746.7	639.7	26.67	104.00	11.85	31.83	39.83	1.55	57.63
Idvor	Chernozem	27293.3	668.7	23.23	67.60	10.49	24.00	40.63	0.05	82.77
Kikinda	Chernozem	31893.3	789.7	31.50	90.77	16.85	30.87	49.83	1.78	70.60
Zrenjanin	Chernozem	23904.4	553.4	20.48	61.40	11.01	44.82	46.17	0.52	56.64
Kozjak	Chernozem	23313.3	562.7	19.03	55.60	12.09	32.63	54.33	0.02	53.60
Padina	Chernozem	24200.0	627.6	21.54	62.64	9.91	26.42	40.82	0.00	73.43
Deliblato	Chernozem	21324.4	489.2	17.13	53.67	12.04	27.67	43.79	0.10	70.49
Rivica	Chernozem	29220.0	688.3	37.97	84.57	12.57	29.13	42.77	0.52	88.43
Ruma – Irig	Chernozem	27940.0	707.4	24.36	79.69	11.50	27.74	42.46	0.21	77.45
Šid	Chernozem	27086.7	653.1	21.70	72.21	13.94	26.61	40.42	0.23	80.31
Indjija	Chernozem	26686.7	656.0	21.27	70.03	12.92	36.17	43.47	0.00	91.30
Pećinci – Popinci	Chernozem	27306.7	529.7	23.03	68.23	12.97	34.83	68.63	0.63	177.67
S. Mitrovica	Chernozem	26866.7	516.3	23.50	65.70	10.86	36.53	46.47	0.50	111.67
Orlovat	Chernozem	26586.7	680.3	24.63	73.60	11.32	30.43	41.77	0.08	82.57
B. Novo Selo	Fluvisol	15813.3	330.0	33.13	59.73	13.44	37.23	38.07	0.95	19.27
Kać	Fluvisol	27573.3	597.0	34.93	136.87	18.62	77.07	51.60	1.45	36.40
SITE	**Soil Type**	**Fe HNO_3**	**Mn HNO_3**	**Cu HNO_3**	**Zn HNO_3**	**Co HNO_3**	**Pb HNO_3**	**Ni HNO_3**	**Cd HNO_3**	**Cr HNO_3**
Obedska Bara	Fluvisol	25493.3	583.7	22.87	87.23	15.38	32.70	44.33	0.00	105.10
Šanad	Fluvisol	22646.7	649.7	25.27	78.37	14.24	35.60	40.50	1.62	50.07
Bečej	Humogley	36448.9	793.6	38.13	123.56	17.26	36.47	50.67	0.41	80.40
B. Arandjelovo	Humogley	20453.3	546.0	20.33	64.57	10.74	30.73	33.20	1.38	42.17
Vršacki Ritovi	Humogley	29473.3	240.5	30.87	84.97	10.87	36.20	53.00	0.32	137.57
Bogojevo	Humogley	25893.3	296.0	32.67	97.00	12.98	40.37	37.93	0.42	61.73
Torda	Humogley	26860.0	334.3	26.77	70.17	14.30	30.53	44.13	1.55	59.33
Ilandža	Humogley	19760.0	287.0	23.83	60.90	8.82	28.67	40.40	0.00	75.27
Rusko Selo	Humogley	29453.3	329.3	31.63	92.20	14.92	30.23	48.13	1.42	65.17
Donji Tovarnik	Humogley	29506.7	350.3	28.03	110.13	13.06	33.30	56.27	0.17	131.23
Petrovaradin	Kambisol	27600.0	654.0	254.93	106.03	15.38	32.13	43.40	0.38	83.60
Vršac	Kambisol	31220.0	563.9	179.98	85.98	16.51	30.27	45.86	0.47	87.58
Morović	Pseudoglej	26346.7	603.7	19.37	88.87	10.67	26.97	36.27	0.00	82.47
ViSnjicevo	Pseudoglej	27713.3	465.3	21.73	71.10	11.87	27.53	36.87	0.30	86.70
Palic	Soloncak	7797.8	227.6	15.40	27.63	4.66	24.52	19.08	0.34	10.04
Boka - Sokolac	Solonjec	26453.3	363.0	25.97	125.53	7.84	23.30	34.83	0.00	82.27
Kumane	Solonjec	36080.0	851.3	32.47	93.07	21.05	36.80	48.07	1.65	79.03
MTC		**/**	**1000**	**100**	**300**	**50**	**100**	**50**	**2**	**100**

- Our analyses of heavy metals in profile samples indicate that their levels increase with depth, so that, for example, Cd content exceeds the MTC threshold at depths of around 50 cm and higher. The topsoil heavy metal content was found to be below the MTC (Table 5), except for the Ni content in downtown Novi Sad, which was 61.17 mg/kg, while the MTC for this element is 50 mg/kg. Since this soil is used for lawns, however, there is no danger of contaminating plant products used in the human diet. The potentially available Ni content was at the availability level of 46% of total Ni, which is almost identical to Ni availability in the other layers of deposol. An increased Ni content was also found in a rendzina soil at the Sremska Kamenica site. The Ni content in this location was increased throughout the profile down to 200 cm depth, which indicates that it is not a result of pollution but that it is of geochemical/natural origin.
- A total of 16 PAHs produced by the Novi Sad Oil Refinery fires were analyzed. Almost all of them were found to be present in the samples and their levels were found to be far above the lowest risk zone as prescribed by the US EPA[7,8] (Tab.6).
- The biological properties of the soil were not altered, which may have been a result of possible biological transformation PAHs and the neutralization of their harmful effects.

Results of the investigations in Vojvodina province (2001) are:

- It has shown that pedogenesis and the method of soil utilization decisively influence soil properties.
- The organic matter/humus content has been found to be on decline relative to the global study of soil fertility in Vojvodina carried out in 1992.
- The levels of potassium and phosphorus differed largely from soil type to soil type as well as within each soil type. This was a result of excessive fetilizer use in the previous 10 years (Table 7.).
- In most of the samples, the levels of trace elements and heavy metals were below the MTC as prescribed by the the Official Register of the Republic of Serbia 23/1994. Increased levels of copper were found in samples originating from vineyards, which was a result of using Cu sulfate as a fungicide (Table 8). The presence of heavy metals in the soil is springs from the original substrate the soil has formed on. Heavy metal levels exceeding the MTC may negatively affect yield levels, but they primarily influence the quality and safety of the plant product. Technological development has introduced heavy metals into the agroecosystem and has made possible the contamination of the soil and agricultural products. It is therefore essential to determine the status of heavy metals in the soil and establish whether the possible increased levels of a particular heavy metal are geochemical/natural or anthopogenic/pollutant in origin.
- Analysis of Co (Table 8), which is both a trace element and a heavy metal, has shown that the soils of the Vojvodina province have Co levels that are below the MTC and that the potentially available Co content is such that it provides the plants with sufficient amounts of this element.

  The Pb content was found to be below the MTC in all of the locations. The highest Pb content was recorded at the Kac site with its fluvisol soil. The study of the potentially available and available Pb indicates that this element is contained in readily degradable minerals and that the available Pb content is similar to that found in other soils, which means that this site is at no risk of possible pollution of plants and plant products with this heavy metal.

Ni content analyses (Table 8) have shown the Ni content at a total of seven sites (Crepaja — chernozem on Banat loess terrace; Kozjak — chernozem on Deliblato loess terrace; Pecinci-Popinci — chernozem on Srem loess terrace; Kac — fluvisol on aluvial terrace; Becej — humogley on aluvial terrace; VrSacki ritovi — humogley on aluvial terrace; and Donji Tovarnik — humogley on Srem loess terrace) to be above the MTC of 50 mg/kg as prescribed by the Official Register of the Republic of Serbia No.11 from the year 1990. Analysis of potentially available and available Ni contents suggests that they are not of anthropogenic character, i.e. that the increased Ni levels were not a result of pollution but they they are of geochemical origin instead, since these levels are the same or lower than the levels found in other locations.

Our study of total Cd content (Table 8.) shows that this content in the Begejci location (chernozem on Banat loess terrace) exceeds the MTC of 2 mg/kg. Similar levels were also recorded at Kikinda (1.78 mg/kg) and Kumane (1.65 mg/kg). The potentially available and available Cd contents turned out to be near the threshold of detectability by the method we used (atomic absorption spectrophotometry). In all of the locations, including Begejci, the available Cd levels of this element were such as to exclude the possibility of any form of contamination of plants and plant products by this element.

The study of Cr content (Table 8.) revealed this element to be above the MTC in the following locations: Pecinci-Popinci — chernozem on Srem loess terrace; VrSacki ritovi —humogley on aluvial terrace; and Donji Tovarnik — humogley on Srem loess terrace; Sremska Mitrovica — chernozem on Srem loess terrace; and Obedska Bara —fluvisol on aluvial terrace. The next step in the study was to determine the availability of these elements. The results have shown that the availability of Cr is the same as or lower than in other locations and soil types.

Our study of heavy metal content in 50 locations in Vojvodina has shown that the levels of these elements are primarily geochemical in origin, i.e. that the soils of Vojvodina are not polluted by heavy metals and that they are suitable for the production of safe food of good quality.

- Pesticide residue analyses were not performed because of heavy pesticide use in crop production at the time of sampling (April-May, 2001).
- Study of PAH presence is currently in progress.

CONCLUSION:

Based on our studies of soil as the ultimate destination of pollutants released and/or produced as a result of the bombing, we can see that we have carried out the initial portion of the necessary research. We consider this to be a good foundation for showing at future donor conferences that our country has the personnel, equipment and knowledge necessary for research in this field. The scope of our studies was directly proportional to the funds that were available. With additional funds at our disposal, we would be able to widen the scope of our research and study the overall status of soil in Vojvodina and conduct detailed studies of the various hot spots in the province, such as the vicinity of the Novi Sad refinery and the petrochemical complex near the town of Pancevo, parts of the FruSka Gora mountain, and so on.