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MOBILITY OF HEAVY METALS ORIGINATING FROM BOMBING OF INDUSTRIAL SITES IN SERBIA

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Abstract. The investigation has been carried out to: a) determine the content of metals in surface soil after the contamination by spilling oil and oil products (gasoline, diesel fuel) and burning them as a result of fires following the NATO air strikes of the "NIS Jugopetrol" fuel storages at Belgrade-Cukarica, Smederevo, Nis, Bor and Prahovo, and b) study a possible soil contamination with heavy metals after destruction of fuel storages because these data are scarce. The following elements: As, Pb, Hg, Cd, Ni, Zn, Cr and Cu were analysed, because of the known, or suspected importance of atmospheric impacts to their concentration in the soil. The purpose of this study was to develop information on environmental pollution of selected industrial sites and the potential degradation and/or migration of the constituents at such sites.

Keywords: fuel storage sites, heavy metals, soil pollution, atomic absorption spectrometer.

AIMS AND BACKGROUND

Crude oil represents a complex mixture of both organic and inorganic components. Trace metals are one group of elements amongst the inorganic component present in crudes. These elements have been found in different proportions in different crudes and consequently in the oil products. Frequently Ni and V are found in the largest concentrations in crude oil. Another metals such as Fe and Zn may be importantly present, too. Also, Zn additives are often used in lubricating oils. Unlike the organic components of the oils, heavy metals are neither thermally decomposable nor microbiologically degradable. It is expected that, upon extraction of the crude oil and accidental deposition on surface of surrounding soil and sediments, trace metals are incorporated in the soil and sediment load, increasing the background levels of metal content of the local soil and sediment.

During the period of NATO aggression (from March 1999 to June 1999) many of the fuel storages across Yugoslavia were bombed. Numbers of the storage tanks were directly hit and caught fire, while others were indirectly hit by debris. Significant quantities of oil and oil products were spilled out and burned. Consecutive

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soil pollution with heavy and inorganic metals either due to oil spill or airborne fallout from oil fires, can not be disregarded.

The purpose of this study was to develop information on environmental pollution of selected industrial sites and the potential degradation and/or migration of the constituents at such sites. The following elements: As, Pb, Hg, Cd, Ni, Zn, Cr and Cu were analysed taking into consideration their toxicity, presence in crude oil and oil products, and because of the known, or suspected importance of atmospheric impacts to their concentration in the soil, i.e. the main source of atmospheric copper pollution is the burning of fossil fuels[1]. As we were led to the assumption that the fuel storages sites could be the "hot spots" after the NATO bombing, in order to investigate those as potential ones, five locations were chosen: "NIS Jugopetrol" fuel storages at Belgrade-Cukarica, Smederevo, Nis, Bor and Prahovo. These locations present a threat to the environment because of a possible migration of contaminants during higher water levels.

DESCRIPTION OF THE LOCATIONS

The fuel storage Belgrade-Cukarica is located alongside Sava River and its tributary, Topcider River (see Fig. 1). It was composed of 4 tanks for gasoline (leaded and unleaded, capacity of 9400 m^3) and 4 diesel oil tanks (capacity of 1300—2500 m^3). The air strikes destroyed some tanks and pumping station. Almost all tanks had been empty when they were hit and no significant quantities of fuel were spilled and burned. As the soil at the site is very permeable, there is strong possibility that the spilled diesel reached the nearby rivers.

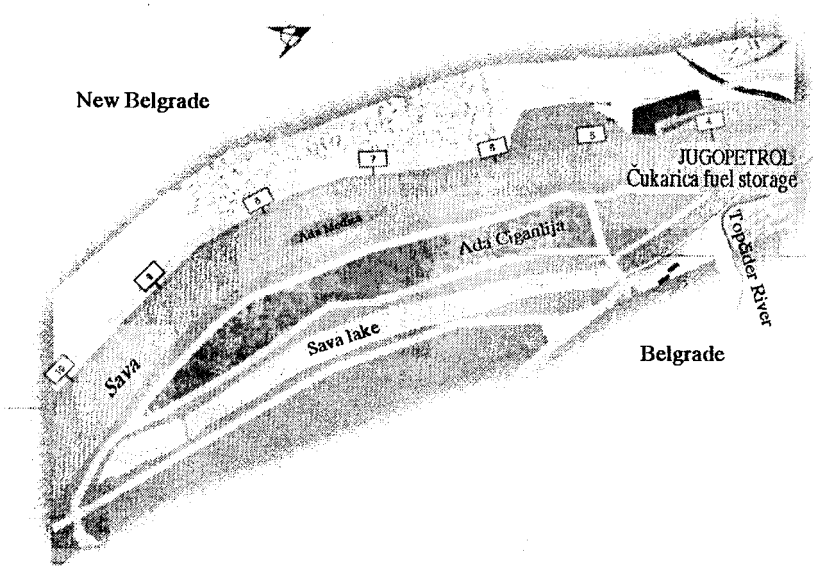

Fig. 1. Location of the fuel storage Belgrade-Cukarica

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The oil storage in Smederevo (15 storage tanks, 250 000 m^3 storage capacity) spreads over the area of 60 ha on the very bank of the Danube river (see Fig. 2). During the first attack, tanks were filled up to 10% of total capacity. About 25 000 t of crude oil and oil products were burned. Due to possible penetration of the toxic substances to soil, there is a danger of groundwater pollution. The contaminated area is 10 000 m^2, and surface of 3000 m^2 is the most polluted[2] to the depth of the soil about 4-12 cm.

The oil depot in Bor covers area of 5 ha with 8 storage tanks, which were completely destroyed during the air strikes. Fortunately, they were almost empty and "cleaned" before bombardment. The tanks had a very good environmental prevention[2]. At the moment of attack, only small amounts of fuel were stored in tanks (in pumping facilities, pipelines and tanks of 20-30 t), only minor fires occurred and there was no spilled oil.

In the area of Nis 5 oil storage tanks were situated. Both two main diesel oil tanks (5000 m^3) were hit during the bombing. A high percentage of the total content of oil was burned, and the other part of it was collected in a concrete embankment and conducted to an oil separator and re-injected into the system. It is possible according to FOCUS report[3] that during the fire heavy metals were released into the air.

Prahovo oil depot is situated on the bank of the Danube river, on the border between the Federal Republic Yugoslavia and Romania. It was advantageous that most of the 9 oil storage tanks were empty and others contained only small amounts of oil (2500 m^3 released) at the time of airstrikes. Some of the oil was burned, some was trapped on the site, but some had leaked into Danube River[4].

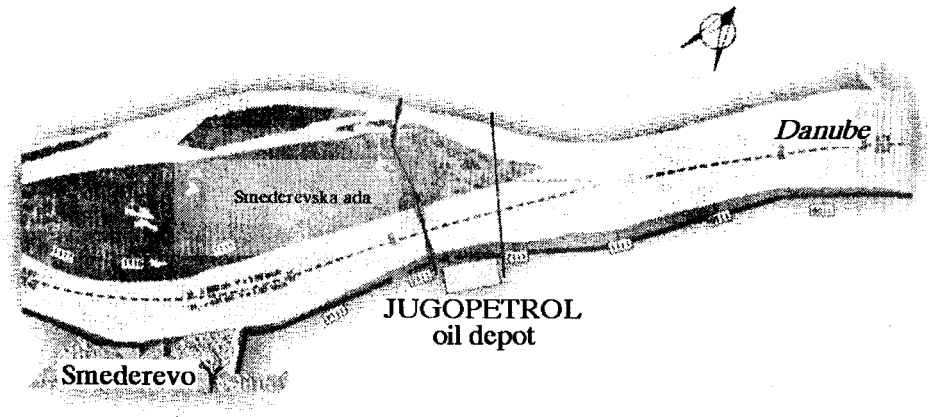

Fig. 2. Location of the fuel storage in Smederevo

EXPERIMENTAL

At the studied sites, within each location a few soil samples were taken from bomb craters and from the fields next to the oil depots on June 1999 and after 8 months when the some craters were levelled on March 2000. Soil sampling consisted of randomly taken shallow scoops of surface soil (0-5 cm in depth) and pooling them. The distance between the positions of taken samples as a usual, was 100 m, while in some instances it was 500 m (i.e., for Nis oil depot). Prior to analysis all samples were stored in polyethylene bags at temperature about 4°C to avoid changes in chemical composition. After air-drying at room temperature, sieving and mixing the sample, an aliquot of 10 g was weighed for analysis.

The soil fraction smaller than 2 mm was leached in 20% HCl at 110°C in a Soxhlet apparatus for an hour[5]. Samples were analysed for Cr, Pb, Cd, Zn, Ni, Cu and As by a Varian flame atomic absorption spectrometer type AA 20 plus. Hg was determined by the method of extraction in carbon tetrachloride using colorimetry[6]. The metal concentrations were deduced from calibration curves derived from standard solutions. The results were related to dry weight. The analytical detection limits were defined as 0.5 mg/kg for Pb, Ni, Zn and Hg, 0.3 mg/kg for Cr, 0.2 mg/kg for Cu, and 0.1 mg/kg of Cd and As.

RESULTS AND DISCUSSION

The ranges of each metal through the site location collected on June 1999 and on March 2000 are presented in Tables 1 and 2, respectively. The presence of heavy metals in surface soil of the damaged Oil Refinery Novi Sad[7] is compared with the data obtained for fuel storages (see Table 1). It must be emphasised that the total metal concentrations in surface soil at the Refinery site were obtained by complete digestion with aqua regia including hydrofluoric acid[8].

When the range of particular metal content is very wide, one or two orders of magnitude, the results do not obey normal statistical distribution. In that case, an objective situation across the studied location can not be presented with mean value for the content and standard deviation. Nevertheless, these values are shown for the purpose of revealing possible causes of this phenomenon.

Mercury contents were below the detection limit of 0.5 mg/kg. The used analytical procedure provides the results for selective extraction but not for the total metal content. Therefore, the applied method is uncommon for the determination of total metals in soil samples. The comparison of different digestion techniques for soil samples showed that the data obtained by the method used for Cd, Pb, Cu, Zn, Ni are always smaller than those determined by standardised aqua regia digestion procedure[9]. Due to the same reason, the comparison of the metal concentration at the studied fuel storage sites and the Oil Refinery Novi Sad is not on the equivalent basis, since different procedures were used for sample preparation.

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Table 1. Ranges of heavy metals contents, mean values and standard deviations (SD), in soil at fuel storage sites on June 1999, and the presence of heavy metals in surface soil (0-30 cm) of the Oil Refinery Novi Sad site[7] and in arable soil in Vojvodina[11] (mg/kg dry matter)

Location		As	Pb	Cd	Ni	Zn	Cr	Cu
Belgrade								
Cukarica	range	7.5-12.8	1.6-2.6	0.7-2.1	17.3-35.5	34.6-56.3	11.1-19.2	5.7-10.4
	mean (8)*	**9.9**	**2.1**	**1.4**	**25.7**	**46.2**	**15.1**	**7.9**
	±SD	1.6	0.3	0.5	6.5	7.6	2.6	1.5
Prahovo	range	8.9-9.8	16.4-75.2	1.1-2.0	22.4-28.5	23.5-120.1	9.8-23.0	4.8-22.6
	mean (8)	**9.2**	**32.6**	**1.6**	**24.4**	**58.4**	**14.1**	**9.0**
	±SD	0.3	19.5	0.4	2.6	30.1	4.5	5.8
Smederevo	range	8.9-10.0	6.2-15.4	1.0-3.0	142-238	151-268	11.1-19.1	26.3-51.4
	mean (8)	**9.4**	**10.7**	**2.0**	**194**	**204**	**15.0**	**38.7**
	±SD	0.4	3.3	0.6	33	40	2.6	8.1
Bor	range	10.2-10.3	18.7-41.3	1.2-1.6	16.7-22.2	85.3-126.5	12.9-21.4	95.5-135.7
	mean (4)	**10.3**	**30.6**	**1.4**	**19.5**	**105**	**17.1**	**112**
	±SD	0.1	9.5	0.1	2.5	18	3.6	18
Nis	range	10.0-10.6	42.7-436.3	1.1-1.3	26.7-53.4	86.5-128.5	39.6-51.8	15.5-21.1
	mean (6)	**10.3**	**137.9**	**1.2**	**40.2**	**108**	**44.7**	**17.9**
	±SD	0.7	148	0.1	9.1	15	4.5	2.0
Novi Sad	mean (5)	**5.18**	**83.68**	**4.25**	**84.96**	**61.36**	**45.24**	**26.8**
arable soil	mean (1600)	2.19	10.28	0.48	4.26	10.61	2.41	10.82

* Number of samples are indicated in parenthesis.

Table 2. Ranges of heavy metals contents in soil samples, mean values and standard deviations (SD) on March 2000 (mg/kg dry matter)

Location		As	Pb	Cd	Ni	Zn	Cr	Cu
Belgrade								
Cukarica	range	10.2-15.9	22.3-41.4	0.8-1.1	32.6-45.5	57.1-85.3	39.6-47.3	14.9-22.2
	mean (5)	**12.7**	**29.5**	**0.9**	**38.9**	**73.1**	**43.4**	**18.4**
	±SD	2.1	7.6	0.1	5.7	10.6	3.5	3.2
Prahovo	range	9.5-11.3	7.9-49.0	0.9-1.5	24.1-27.2	54.4-129	20.8-27.4	4.0-14.9
	mean (4)	**10.3**	**19.9**	**1.2**	**25.6**	**71.2**	**26.0**	**8.4**
	±SD	0.8	19.4	0.3	1.4	38.9	6.5	4.9
Smederevo	range	9.2-11.6	33.3-34.4	1.0-1.3	60.5-83.9	70.3-82.9	43.4-68.6	10.5-21.7
	mean (4)	**10.2**	**33.8**	**1.2**	**70.8**	**76.7**	**56.3**	**13.8**
	±SD	1.0	0.5	0.1	15.0	5.4	11.0	5.3
Bor	range	9.1-16.4	16.0-188.0	0.9-6.1	13.7-33.2	41.0-239.0	8.8-33.8	84.9-1168
	mean (4)	**11.8**	**66.5**	**2.4**	**20.4**	**103**	**18.5**	**433**
	±SD	3.1	82.1	2.4	9.2	86.5	10.7	502
Nis	range	9.5-11.2	23.7-270.0	0.9-1.2	34.7-199.0	65.4-176.0	32.8-119.0	13.3-16.6
	mean (4)	**10.1**	**85.3**	**1.0**	**78.3**	**104**	**58.3**	**14.8**
	±SD	0.7	123	0.1	80.7	52.3	40.6	1.7

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Also, the same finding was approved by the results of UNEP/UNCHS Balkan Task Force (BTF), Technical Industrial Sites Mission Report[2], for Bor oil depot. Our data for the studied metals are always lower than those determined by BTF using nitric and hydrofluoric acid for digestion. Therefore, our method is similar to the step sequential extraction procedure for determination of mobile metal quantity that usually represents small fraction of the total metal content[9].

In some instances, taking into consideration an individual spot at the Nis site (Table 1), the Pb content showed extremely high value of 436.3 mg/kg that can be attributed to a contamination by leaded gasoline (0.4 g/l tetraethyllead used for 95 octane number). Also, at the Bor oil depot site (Table 2), the content of Cu is significantly high (1168 mg/kg) resulting probably from the activities of the copper mine factory. This value is about 20 times higher than the average Cu content (55.3 μg/g) obtained in the study of Lorenz et al.[10] for 10 contaminated European soils. The concentration of Ni at almost all investigated sites in both sampling period can be considered high with respect to its average concentration reported[10] for polluted European soils of 25.6 μg/g.

Although the method used in this study gave results only for the mobile form of metals, the mean concentration of As at all studied fuel storage sites across Serbia (Belgrade, Prahovo, Smederevo, Bor, Nis) was about 2 times higher than its total content in soil at Novi Sad Oil Refinery site. As well as the content of mobile Pb at Nis site was higher than its total content in refinery surface soil. Taking into consideration the highest obtained concentration for Pb at the Nis site (436.3 μg/g), the one was about 5 times higher than the mean concentration of the soil at Novi Sad refinery site. The content of Ni at Smederevo oil depot site was 2.3 times higher than in Novi Sad refinery soil. Soil contamination with Zn at depots in Smederevo, Bor and Nis was much higher (2-3 times) than in the Refinery. Chromium was present at the same level at Nis and Novi Sad sites. Copper content was about 3-14 times higher at Bor site than in all others depots and Novi Sad Oil Refinery site.

The contents of each analysed metal within particular location in comparison with the average mean concentrations of Cd, Pb, Hg, As, Ni, Cr, Cu, Zn (in mg/kg) in arable soils with neutral pH reaction (0.48, 10.2, 0.01, 2.19, 2.4, 4.2, 10.8, 10.6, respectively) obtained by analysis of 1600 samples collected from representative sites distributed in a regular pattern across the Vojvodina Province[11] were always several times higher. It should be emphasised that the contents of metals in arable soils were determined by a technique different than that used in this investigation indicating possible variations in the obtained concentrations. Namely, the concentration of arsenic was determined with silver-diethyldithiocarbamate by spectrophotometry, mercury content was done by cold vapour atomic absorption spectrophotometry, while the other heavy metals were extracted by concentrated nitric acid and determined by atomic absorption spectrometry.

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Considering Tables 1 and 2, there is an apparent evidence for enhancement of almost all the investigated metals, particularly chromium in all studied locations. Within the chosen locations, increased concentrations of the metals were observed for Bor oil depot site on March 2000 (Table 2). On the other hand, for Smederevo oil storage it is evident a slight decrease of Zn, Ni, Cu and Cd while for Prahovo oil depot that could be said for Pb, Cd and Cu. An insignificant decrease of Cd content is observed at all studied locations except in Bor. Since Cd is a very mobile toxic metal, a danger exists because of its possible penetration from soil to groundwater and nearby rivers.

In the period from June 1999 to March 2000 it can be expected that various natural processes and anthropogenic emissions caused pronounced concentration gradient in the soils of the observed sites. This can be seen through the high values of the relative standard deviations (SD, %) of some metals analysed in March 2000 (Pb: 97.5% for Prahovo, 123% for Bor and 144% for Nis; Cd: 100% for Bor; Ni: 103% for Nis; Zn: 84% for Bor and 50% for Nis; Cd: 58% for Bor and 70% for Nis; Cu: 116% for Bor). In most cases increased relative standard deviations were related to increased metal concentrations.

Accumulation of some metals during investigated period (Table 2) indicates the necessity for a long-term recording of data in order to provide a realistic assessment of metals transport. In addition, further monitoring and analysis is required. These findings can be attributed to the contamination by NATO bombardment and partly by industrial activities at the investigated sites.

CONCLUSIONS

The content of metal within particular locations in two sampling periods (June 1999 and March 2000) demonstrated an increase with the time of investigation, i.e. accumulation of some metals is evident. Although, data were obtained by extraction procedure that usually gives lower values, they were almost significantly higher than those determined for arable soils and could be attributed to the contamination by NATO bombardment and partly by industrial activities at the investigated sites. Considering that the investigated sites are located in the vicinity of rivers, they present a threat to the environment because of a possible migration of contaminants during higher water levels. A long-term record of data is required to provide a realistic assessment of metal transport and the future environmental and health risks.

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