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Heavy Metal (As, Cd, Cu, Hg, Pb and Zn) Distribution in Topsoil Developed on Alluvial Sediments of the Drava and Sava Rivers in NW Croatia

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Key words: Geochemical mapping, Topsoil, Alluvial sediments, Heavy metals, NW Croatia.

Abstract

In the region of north-western Croatia (NWC) 328 topsoil samples were taken (from a depth of 0 to 25 cm). The composite samples were analyzed after near total decomposition (a hot acid mixture: $HClO_4$–HNO_3–HCl–HF at 200°C) by ICP–AES for As, Cd, Cu, Pb and Zn. Hg was analysed by cold vapour AAS. The following element concentration ranges were acquired: As 2–74 mg/kg (geometric mean 8 mg/kg), Cd 0.4–9.4 mg/kg (geometric mean 0.4 mg/kg), Cu 5–248 mg/kg (geometric mean 22 mg/kg), Hg 5–4,535 mg/t (geometric mean 55 mg/t), Pb 15–699 (geometric mean 32 mg/kg) and Zn 28–1,432 (geometric mean 82 mg/kg).

The analysis of the spatial distribution of heavy metals in NWC showed increased values of As, Cd, Hg and Pb at Mts. Žumberak, Medvednica, Ivanščica and Kalnik that originate mainly from natural sources (bedrock mineralizations and ore deposits). The Cu and Zn contents on Mt. Medvednica are only slightly less natural in origin. The high concentrations of copper on the slopes of Mts. Žumberak, Medvednica, Kalnik and in the NW part of Hrvatsko Zagorje are of anthropogenic origin and are related to wine-growing areas.

In the Sava River valley the average levels of Hg, Zn, As, Cd, and Pb are higher than the calculated baseline values (geochemical background) in the NWC while the Cu values are equal to the baseline values. The higher values of As, Cd, Pb, and (in part) Zn are for the most part of anthropogenic origin, and to a lesser extent of natural origin. The Hg in the topsoil has a strong anthropogenic influence caused by mining upstream (Litija) and by the city of Zagreb's urban area (fossil fuel combustion, traffic, electrolysis, diverse paints, pharmaceutical products, chlor-alkali industry and paper industry). The pedogenic profile shows that the content of Cd, Pb, Cu and Zn at a depth of 20 cm is almost half the content of the same elements found in the first two centimeters of the soil. At a depth of 60 cm, the concentrations are in the level of background values characteristic of the preindustrial era.

When compared to the calculated baseline values, the contents of As, Cd, Cu and Hg in the soils of the Drava River valley are higher, while the Pb and Zn contents are anomalous. According to permitted concentrations of heavy metals for ecological food production prescribed by Government regulations the contents of As, Pb and Zn in the topsoil on the Drava alluvial sediment are too high. The Cu concentrations are lower than the limit permitted by Government regulation. The higher contents of mercury, although under the limit prescribed by Government regulation, are an immediate consequence of fossil fuel combustion and traffic in the urban area of the city of Varaždin. Factor analysis and high correlation coefficients show a mutual connection of Pb, Zn and Cd (Pb and Zn r=0.96; Pb and Cd r=0.80; Zn and Cd r=0.84). These 3 heavy metals show high positive factor loadings on the first factor (F1) which accounts for more than 58% of the data variability. The flood waters of the Drava River were highly loaded with anthropogenic Pb, Zn and Cd mainly as a consequence of mining, smelting and flotation activities upstream in the Meža valley in the Republic of Slovenia and Austria. Also, they were additionally loaded with waste waters from upstream settlements. The soil profile shows that increasing depth results in the lowering of the Pb, Zn, Cd and As content reaching the background level of that area at 80 cm depth. This suggests that the alluvial sediments of the preindustrial era lay deeper.

1. INTRODUCTION

The Drava and Sava rivers with their tributaries are the main drainage rivers in northwestern Croatia (NWC) (Fig. 1). The big settlements, cities and industrial plants are located alongside their streams. From its spring source in Italy to the Croatian border, the river Drava flows through the Alps in a relatively narrow river valley. After Pohorje Mt. in eastern Slovenia it reaches the Pannonian Basin where it has excavated a relatively wide valley. The river frequently flooded in this area in the past. In spite of river banks built a few decades ago, it still floods in some of the lower parts along the river (KEREŠA, 2002).

The Sava River arises in the Alps in western Slovenia, and it flows through a relatively narrow valley to the Croatian border. After it reaches the southwest part the Pannonian Basin, the Sava River flows in a wide river valley, and it has been known to flood lately during high water levels. The last great flood in the Zagreb area happened in 1964, and some parts of the Sava River valley downstream from Zagreb occasionally flooded up until 1994.

In the Alps, the Sava and Drava Rivers drain mountain massifs which also contain mineralisation and mineral deposits. Exploitation of Pb and Zn ore deposits

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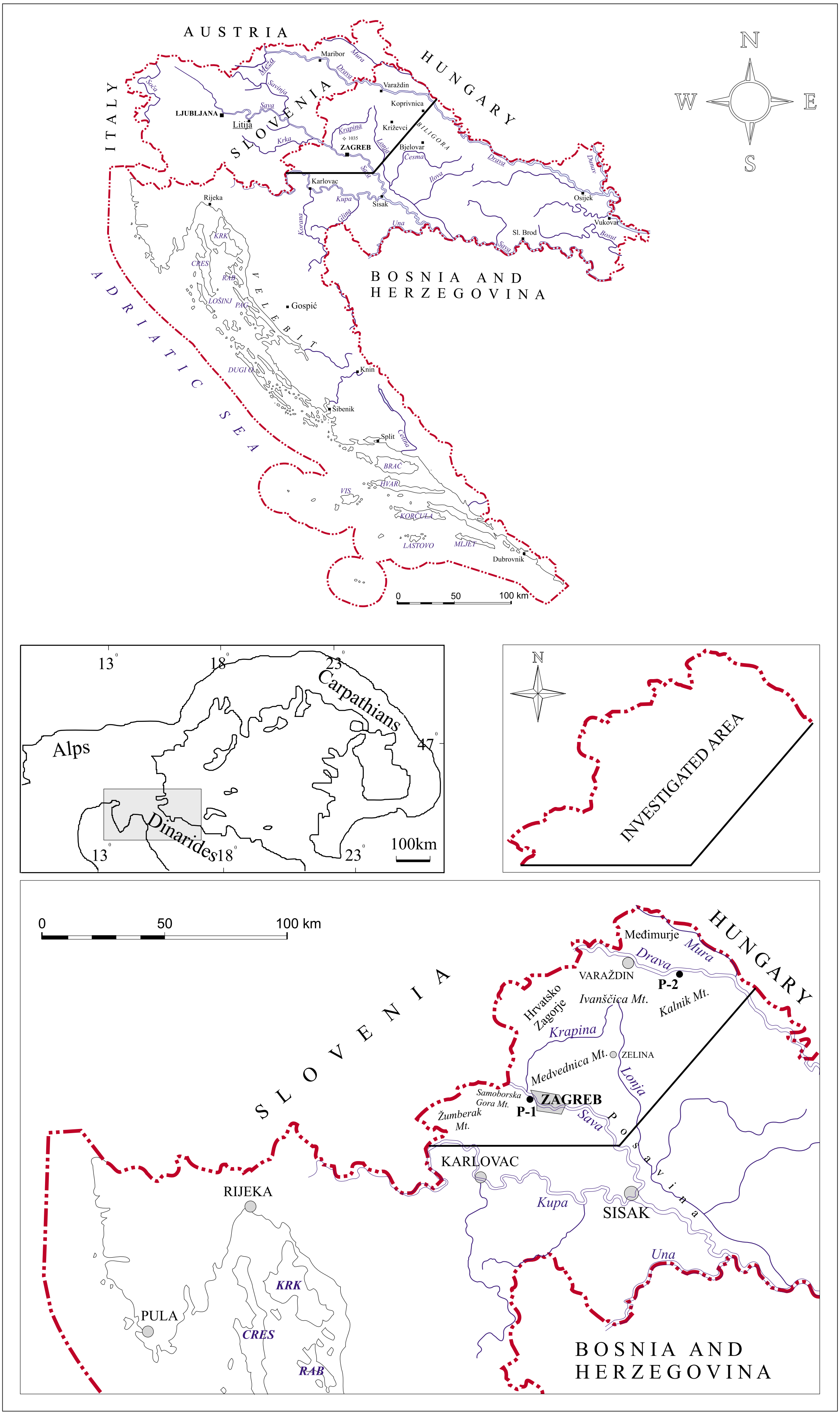

Fig. 1 Location map of investigated area with location of soil profiles P–1 (Sava River valley) and P–2 (Drava River valley).

in Austria and in the vicinity of Mežica in the eastern part of Karavanke Mt. (eastern Slovenia), are particularly interesting when considering the content of heavy metals in soils in the alluvial plain of the Drava River. These mining sites, along with mining waste dams and flotation devices were active until the last decade (ŠTRUCL, 1974; DROVENIK et al., 1980; SOUVENT, 1994). Three natural and one anthropogenic geochemical associations of Pb and Zn were found through geochemical investigation of soils, alluvial sediments and attic dust in the Mežica area (ŠAJN et al., 2000). The Meža River, which is a tributary of the Drava River, drains the ore-bearing area. The Sava alluvial sediments reflect the influence of Pb, Zn, Ba, and Hg ore deposits in the Litija region, Samoborska Gora Mt. and Medvednica Mt. areas (MLAKAR, 1994; ŠINKOVEC, 1971; NAMJESNIK et al., 1992).

The content of heavy metals in a soil depends on the primary mineral composition of the parent material from which the soil was generated, as well as on the pedogenic processes and on the subsequent input of these elements to the soil (by wind, rain, ice, water etc.). Heavy metals are most often bonded to clay minerals, micas, chlorite and Mn–Fe oxy-hydroxides. Feldspars can also have higher contents of Pb, Zn and Cu. The carriers of the greatest amounts of Cu and Zn can also be the main minerals of basic magmatic rocks (olivine, serpentine, pyroxene and amphibole). Sulphide mineralization and weathering zones above them can be the source of an increased content of Cu, Zn, As, Cd, Hg and Pb (ADRIANO, 1986; RÖSLER & LANGE, 1976; RUPPERT, 1991).

The concentration of heavy metals in soils also largely depends on the source of the parent material. Namely, the parent materials above the bedrock base have, as a rule, lower contents of these elements (with the exception of parent material in the weathering zones above ore deposits) than parent materials generated from fine grained alluvial sediments (the effect of over concentration through multiple redeposition of material in the river system) (MIKO et al., 2001).

Such natural, although relatively higher contents of heavy metals in soils above alluvial sediments, can in some regions be increased further due to anthropogenic input of these elements into the river system (waste waters from large settlements, waste disposal on the river coast, mining industry flotations), through atmospheric deposition of particles from urban sources (heating plants and other industry emission) and through the heavy traffic (SUTHERLAND & TOLOSA, 2001; FAKAYODE & OLU-OWOLABI, 2003).

The purpose of this paper is to show the connection of the higher contents of heavy metals in topsoil to the historical mining activities upstream from the studied area, also to the agricultural activities (agrochemicals), and to the atmospheric deposition of these elements onto the topsoil (traffic, industry and other urban emissions) on the basis of the spatial distribution of heavy metals in the topsoil of the fluvial plains of the Sava and Drava Rivers.

1.1. Geology

Drava River valley

Todays flowline of the Drava River is regulated through the building of dams and a few accumulation lakes, because of which there is no more flooding of larger areas outside the regulated streams. The Drava River valley consists of two terraces and a recent floodplain. The terrace sediments, that were the source rocks for the parent material for soil generation, were deposited during the Upper Pleistocene and Holocene. The terrace sediments consist of gravels, sands and of gravelly and silty sands. The gravel consists of quartz pebbles, metamorphic rocks, volcanics and subordinately of lithoclasts (cherts, breccia and carbonates). The sands consist of quartz (50–70%), feldspar (14–26%) muscovite (4–13%), rock fragments (1–3%) and carbonates (1–2%). A heavy mineral fraction (specific gravity >2.88) represents a relatively high percentage (11–38%, and up to 60% in some places) of the composition. The primary minerals of this fraction include garnet, epidote, amphibole, and to a lesser extent tourmaline, zircon, rutile, apatite, disthene, staurolite, chlorite and titanite (ŠIMUNIĆ et al., 1981; MARKOVIĆ & MIOČ, 1989; MIOČ & MARKOVIĆ, 1998). The river bed and floodplain sediments consist of sands, muds, gravels and gravelly sands. They are generated through resedimentation of older fluvial sediments, and therefore have a similar mineral composition to the older terrace sediments.

Sava River valley

The Sava River alluvial sediments are also deposited on two terraces and a fluvial plain. The age of the sediments is Upper Pleistocene and Holocene. The terrace sediments that comprise the greater part of the Sava River valley consist primarily of gravels and sands, and secondarily of sandy and silty clays. The gravel pebbles are for the most part carbonate, then sandstone, chert, quartzite, volcanics, metamorphites and quartz. The composition of the Sava River terrace pebbles differs completely from the composition of the Drava River pebbles. The sands of the Sava terraces consist of quartz, feldspar, muscovite and rock fragments. The content of quartz ranges from 64 to 88% and of the other components from 7 to 18%. The heavy mineral fraction consists of garnet, epidote, amphibole, pyroxene and subordinately of staurolite, disthene, rutile and titanite (ŠIKIĆ et al., 1979; BASCH, 1983). The composition of the heavy mineral fraction is similar to that of the Drava River sands.

The sediments of the floodplain areas and recent stream beds consist of coarse grained sandy–clayey silts, silty clays and thin layers of charcoal that were flooded in from Slovenian coalmines (BASCH, 1983).

The greater part of the light mineral fraction of these sediments consists of quartz (around 79%), and the heavy mineral fraction of epidote and garnet.

1.2. Pedology

Fluvisols (FL) are developed on younger fluvial sediments of the Drava River. Eutric Leptosols (Lpe) are developed on the line from the state border up to Varaždin, on the south side of the Drava River, on older terraces rich in gravels. Eutric Cambisols (Cme) prevail on the older terrace sediments on the north side of the Drava River. Eutric and Dystric Gleysols (Gle and GLd) are characteristic of the swampy parts of older alluvial terraces on the south side of Drava River valley east of Varaždin.

Fluvisols (FL) were developed on the fluvial sediments in the immediate vicinity of the Sava River flowline, similar to the Drava River. Eutric Cambisols (CMe) were found on terrace sediments north and south of the Sava River, on a line from the state border up to the southeast of Zagreb. Eutric and Dystric Gleysols (GLe and GLd) developed further to the southeast, where the sediments of the fluvial plain and terraces are fine grained and richer in ground and surface waters (FAO, 1990; BOGUNOVIĆ et al., 1996; MARTINOVIĆ, 1997; ŠPOLJAR, 1999).

2. MATERIALS AND METHODS

2.1. Sampling and sample preparation

For the purpose of the Geochemical map of the Republic of Croatia 328 topsoil samples (below A_{mo} or A_{oh} horizons) from NWC were collected in a quadratic grid 5x5 km. The initial gridpoint for the geochemical mapping in Croatia and Slovenia was located in Istria, Croatia (PIRC et al., 1991). The soil samples were taken at each sampling site from 5 shallow pits (0–25 cm depth) and one composite sample was prepared from each sample site. The detailed sampling procedure was given in Guidelines for the Geochemical Mapping of Croatia (HALAMIĆ et al., 2000[1]). These guidelines were based on previous works of PIRC et al. (1991), PROHIĆ et al. (1997, 1998), PEH & MIKO (1999[2]), HALAMIĆ & GALOVIĆ (1999[3]), and differ only slightly from the recommendation given by DARNLEY et al. (1995) and SALMINEN et al. (1998). The collected samples were air dried and sieved to pass the 63 μm screen.

2.2. Analytical methods, accuracy and precision

After sieving, a homogenized 2 g sample was near totally decomposed in a hot acid mixture $HClO_4$–HNO_3–HCl–HF at 200°C. The ICP–AES analyses were performed in ACME Laboratories in Vancouver (Canada) for As, Cd, Cu, Pb and Zn. Volatilization during fuming may result in some loss of As. The content of mercury was analysed with FAAS after aqua regia digestion.

Accuracy of the analyses was controlled with the aid of certified geological reference materials (USGS: GXR–2, GXR–5, and SJS–1). The accuracy for most elements analyzed in reference soil materials is in the range of ±15% of the certified values, except for Cd (±23%). The precision of the analyses was determined by repeated analysis of both certified reference samples and randomly selected soil samples (13 duplicated samples), the resulting coefficient of variation is, on average approximately 5% (HALAMIĆ & GALOVIĆ, 1999[3]).

2.3. Statistical treatment and graphic presentation

The evaluation of basic statistical parameters for all elements was performed, after $\log_{10}$ transformation, on the analytical data from the whole database for NWC (N=328) and separately for each river valley (Drava N=21, Sava N=18). These parameters are given in Tables 1, 3 and 7. Also the non-parametric distributions of each element are given as the 10th, 25th, 50th, 75th, 90th, 95th, 98th and 99th percentile values, which are present as elemental concentration distribution contour boundaries on the maps (Plates 1–6). The coefficents of correlation of each river valley are given in Tables 4 and 8. The R-mode factor analysis was used as a tool of data reduction, with the purpose of a clearer insight into the basic relationships among variables. It was performed separately for the data set of each river valley, with the aim to observe similarites of geochemical behaviour of the analysed elements and to allow a more straightforward insight into the structure of the data. The eigenvalue of factors and factor loadings are given in Tables 5, 6, 9 and 10.

All statistical analyses were performed with the STATISTICA software (Ver. 5.1). The single-element geochemical maps were produced with the SURFER mapping software (Ver. 7.0). Griding was performed by linear kriging (ISAAKS & SIRVASTAVA, 1989) with grid cell resolution of 2x2 km.

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[1] HALAMIĆ, J., MIKO, S., PEH, Z. & GALOVIĆ, L. (2000): Upute za izradu “Osnovne geokemijske karte Republike Hrvatske” [*Instructions for production of “The basic geochemical map of the Republic of Croatia”* – in Croatian].– Unpubl. report, Archive of the Institute of Geology, Zagreb, 51/2000, 22 p.

[2] PEH, Z. & MIKO, S. (1999): Geokemijski atlas srednje i južne Dalmacije [*Geochemical Atlas of Central and Southern Dalmatia* – in Croatian].– Institute of geology, Open file report, 115/1999, Zagreb, 102 p.

[3] HALAMIĆ, J. & GALOVIĆ, L. (1999): Geokemijske karte sjeverozapadne Hrvatske [*Geochemical Maps of Northwestern Croatia* – in Croatian].– Unpubl. report, Archive of the Institute of Geology, Zagreb, 72/99, 111 p.

	SLO (N=819) mean	NWC (N=328) mean	geo. mean	median	min.	max.	Stdv.
As (mg/kg)	<5	10	8	8	2	74	7.86
Cd (mg/kg)	0.5	0.5	0.4	0.2	<0.4	9.4	0.84
Cu (mg/kg)	23	25	22	22	5	248	20.19
Hg (mg/t)	160	94	55	60	5	4535	256.50
Pb (mg/kg)	34	39	32	29	15	699	54.26
Zn (mg/kg)	104	101	82	77	28	1432	123.24

Table 1 Basic statistical parameters for topsoil in Northwestern Croatia (NWC) (SLO = data for Slovenian soils from PIRC, 1993; ANDJELOV, 1994; ŠAJN et al., 2000; geo. mean = geometric mean; Stdv. = standard deviation).

3. RESULTS AND DISCUSSION

The basic statistical parameters (mean, geometric mean, median, maximum and minimum of the measured values and standard deviation) for NWC are given in Table 1. For comparison, the data for the Slovenian territory (PIRC, 1993; ANDJELOV, 1994; ŠAJN et al., 2000), have been added into that table. The statistical distribution of the elements is graphically represented as a single-element maps (Plates 1–6).

3.1. Northwestern Croatia (NWC)

Arsenic

The measured content of As in the topsoil of NWC varies from 1.8 to 74 mg/kg with a mean value of 10 mg/kg (Table 1). Concentrations above the recommended values (Table 2) were registered at individual locations on Mts. Žumberak, Medvednica, Kalnik and Ivanščica and in the Drava and Sava River valleys (Plate 1). Higher values at the first four locations are most likely a consequence of the bedrock composition or of mineral deposits, respectively. However, a higher concentration of As in the soils of the Međimurje region can also be a consequence of intensive agricultural activity (pesticides).

Cadmium

The Cd content in the soils of NWC varies from <0.4 (below detection limit) up to 9.4 mg/kg with a mean value of 0.5 mg/kg (Table 1). Around 56% of all measured values are below the detection limit. Half the value of the detection limit (0.2 mg/kg) was taken as a minimum value for statistical analysis of these samples. Over 95% of topsoil samples in NWC have a cadmium content lower than the maximum content prescribed by the law for agricultural soils (Table 2) (NARODNE NOVINE, 1992, 2001). Concentrations above the recommended values were registered on Mts. Žumberak, Ivanščica, Kalnik and in the Drava River valley (Plate 2). The anomalies on Mts. Žumberak, Ivanščica and Kalnik are of natural origin (mineralization) while the ones in the Drava River valley are for the most part a consequence of mining activities upstream.

Copper

The copper content in the NWC soils varies from 5 to 248 mg/kg with a mean value of 25 mg/kg (Table 1). The high concentrations of copper in the investigated area are mainly of anthropogenic origin in relation to agricultural activities, especially wine-growing (fungicides based on copper sulphate). These concentrations are a characteristic of the wine growing areas of Mts. Žumberak, Medvednica, Kalnik and in the western part of the Hrvatsko Zagorje region (Plate 3). The anomaly on Medvednica Mt. north of Zagreb (Plate 3) is however, the consequence of ore mineralization in that area.

Mercury

The mercury content ranges from <10 mg/t, which is the lowest detection value, up to 705 mg/t, with the exception of a very high concentration measured on top of Mt. Kalnik (4,535 mg/t) and has a mean value of 94 mg/t (Table 1). Only 1% of analysed samples from NWC have values below the detection limit. Relatively high values of Hg content were registered along the Sava River, on the Medvednica, Samoborska Gora, and Ivanščica Mts. and in the Zagreb and Varaždin city areas, but the values were significantly below the maximum allowed (Plate 4, Table 2; NARODNE NOVINE, 1992, 2001). High contents on Mts. Žumberak, Kalnik and Ivanščica are the consequence of ore mineralization, while the anomalies in soils developed on alluvial sediments and in urban areas are of anthropogenic origin.

Lead

The concentration of lead in NWC ranges from 15 to 385 mg/kg, with a mean value of 39 mg/kg (Table 1). Anomalous concentrations follow the course of the alpine Drava River and are in relation to its fluvial areas. Their origin could be both anthropogenic and natural. The relatively higher values on Mts. Žumberak, Medvednica, Kalnik and Ivanščica are a consequence of lead mineralization in that area (Plate 5). Other regions of NWC have Pb values significantly lower than the maximum values prescribed by law (Table 2).

	Light structure soils, skeletal soils and soils with a low humus content (NN 1992)	Heavier and heavy structure soils and soils with a high humus content (NN 1992)	Soils for the ecological agricultural production of plants (NN 2001)
As (mg/kg)	20	30	10
Cd (mg/kg)	1	2	0.8
Cu (mg/kg)	60	100	50
Hg (mg/kg)	1	2	0.8
Pb (mg/kg)	100	150	50
Zn (mg/kg)	200	300	150

Table 2 Prescribed concentrations of heavy metals in agricultural soils for normal and ecological production (NARODNE NOVINE, 1992, 2001) (analysed dry soil extracted by aqua regia).

Zinc

The measured values of Zn in NWC range from 28 to 1,432 mg/kg with a mean value of 101 mg/kg (Table 1). Around 10% of the samples have zinc concentrations higher than those legally allowed (>300 mg/kg) (NARODNE NOVINE, 1992). All these anomalies are in soils developed on alluvial sediments of the Drava River (Plate 6). Higher contents have been measured in samples from the Sava River valley, downstream from Zagreb, in the Lonja River valley, in the central part of the Krapina River flowline, and also in the valley of the Horvatska River in the Hrvatsko Zagorje region. These concentrations could also indicate anthropogenic dispersion of Zn in the environment. This is most visible in parts of Posavina with intense agriculture and an increased use of artificial fertilizers. Namely, some artificial fertilizers can contain up to 0.1% Zn (BREHLER & WEDEPOHL, 1972). Higher concentrations on Mts. Ivanščica and Kalnik and in the southeastern part of Samoborska Gora Mt. are probably a consequence of Zn mineralization, as in the case of Medvednica Mt.

The topsoil developed on Sava and Drava alluvial sediments has higher contents of these heavy metals than concentrations in the region of NWC (HALAMIĆ & GALOVIĆ, 1999[3], 2000[4]) or the concentrations in topsoil of the Republic of Slovenia (PIRC, 1993; ANDJELOV, 1994). Therefore their distribution is described in detail below.

3.2. Sava River valley

The basic statistical parameters for the topsoil of the Sava River valley are shown in Table 3. Compared with topsoil developed in the Drava River valley, the average content of almost all heavy metals in Sava valley topsoil is lower, with the exception of Hg (Tables 3 and 7).

The content of As, Cd, Hg and Pb in the Sava River valley is higher, the Cu content is lower and the Zn content is average when put in relation to the average content of heavy metals in normal soils worldwide. The average contents of Hg, Zn, As, Cd, and Pb are higher than calculated baseline contents (geochemical background) in topsoil of NWC. The Cu values are equal to the baseline values of this area. The geochemical background levels for the NWC were calculated with the aid of iterative 2σ-technique (MATSCHULLAT et al., 2000). The calculated values of heavy metals in the Sava River valley topsoil are below the limit prescribed by Government regulations for the ecological production of plants in Croatia (NARODNE NOVINE, 2001) (Table 2). The only exception is arsenic which is on the border of the legally prescribed value. Also, As, Cd, Cu, Pb and Zn show no relevant deviation from their average values, i.e. they do not show any anomalous values. There are two possible reasons for the higher contents of As, Cd, Pb and in part of Zn. Mainly it is a consequence of anthropogenic input into the soil through airborne distribution of the material (atmospheric deposition – combustion of fossil fuels, industry, traffic), or a reflection of the historical mining activities in the broader region surrounding Zagreb in the past (Mts. Samoborska Gora and Medvednica). The higher contents of heavy metals in soils of the fluvial valley downstream from Zagreb are related to more clay rich soils. The heavy metals were transported in suspension and then sedimented during floods that were relatively common in this area before the appropriate dams were built. A lesser part can be related to pollution through agrochemicals (pesticides etc.) (ROMIĆ & ROMIĆ, 2003).

The content of mercury in the Sava River valley topsoil shows higher, and in part anomalous values, when compared to the baseline values of NWC. The highest values were registered after the Sava Rivers' recourse into Croatia and in the Zagreb city area which indicates the anthropogenic origin of the mercury. The high content of Hg in the topsoil of the fluvial sediments after the Slovenian–Croatian border is mainly

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[4] HALAMIĆ, J. & GALOVIĆ, L. (2000): Geokemijske karte sjeverne Hrvatske [*Geochemical Maps of Northern Croatia* – in Croatian].– Unpubl. report, Archive of the Institute of Geology, Zagreb, 72/2000, 104 p.

	SAVA (N=18)					
	mean	**geo. mean**	**median**	**min.**	**max.**	**Stdv.**
As (mg/kg)	10	9	9	5	18	4.20
Cd (mg/kg)	0.5	0.4	0.5	0.2	0.8	0.19
Cu (mg/kg)	24	23	23	12	35	7.39
Hg (mg/t)	111	79	77	10	450	108.16
Pb (mg/kg)	34	33	34	18	58	11.12
Zn (mg/kg)	91	88	90	53	135	23.59

Table 3 Basic statistical parameters for topsoil in the Sava River valley (geo. mean = geometric mean).

	Cu	Pb	Zn	As	Cd	Hg
Cu	1					
Pb	0.66	1				
Zn	$\boxed{0.90}$	$\boxed{0.78}$	1			
As	0.47	0.39	0.47	1		
Cd	$\boxed{0.74}$	0.57	$\boxed{0.74}$	0.41	1	
Hg	0.43	0.62	0.46	0.30	$\boxed{0.73}$	1

Table 4 Correlation coefficients for topsoil in the Sava River valley (correlation significant at $p<0.05$).

Factor	Total	% of var.	Cumul.%
1	3.96	66.01	66.01
2	0.79	13.14	79.14
3	0.64	10.69	89.83

Table 5 Eigenvalues of factors for Sava River valley topsoils.

	Factor 1	Factor 2	Factor 3
Cu	0.20	0.24	0.90
Pb	0.48	0.13	0.70
Zn	0.24	0.21	0.92
As	0.14	0.96	0.25
Cd	0.60	0.20	0.59
Hg	0.96	0.11	0.22
Expl.Var.	1.69	1.09	2.61
Prop.Totl.	0.28	0.18	0.43

Table 6 Factor loadings for Sava River valley topsoils (varimax normalized; extraction: principal components; marked loadings are >0.5).

the consequence of industrial pollution of the Sava River, and to a lesser extent the Sutla and Krapina rivers, by waste waters. The pollution of the river Sava is caused by mining and smelting activities in Slovenia (Litija). Around 150 tons of Hg were excavated in Litija (MLAKAR, 1994). In the Zagreb city area, mercury emanates into the air mainly from industrial plants. Sources of airborne mercury are fossil fuel combustion, traffic, electrolysis, diverse paints, pharmaceutical products, chlor-alkali and paper industries (MIKO et al., 1992; PALINKAŠ et al., 1996). Research on the mercury content in urban soils along the city's main roads and its periphery, shows concentrations twice as high as background values (NAMJESNIK et al., 1992).

Pearson's product moment correlation coefficient shows strong correlations between Zn and Cu ($r=0.90$), Zn and Pb ($r=0.78$), Zn and Cd ($r=0.74$), Cu and Cd ($r=0.74$) and Hg and Cd ($r=0.73$) at $p<0.05$ (see Table 4). Arsenic shows no correlation to any of the heavy metals. Such high coefficients of correlation indicate the source of zinc, lead, copper and cadmium from the mining and smelter industry upstream. A lesser proportion of the mercury content is probably also from the same source, while the remaining bulk concentration could be a consequence of atmospheric pollution. This is also indicated by the results of factor analysis as shown in Tables 5 and 6. Mercury is grouped in the first factor that explains around 66% of the total variance. Arsenic is included in the second factor and shows no significant correlation to any of the other heavy metals, indicating that it originates from a different source. The higher concentrations in the western part of Zagreb are of anthropogenic origin (airborne mercury), while its origin in agricultural soils downstream form Zagreb could be a consequence of agricultural activities. Cu and Zn are grouped into the third factor which explains only around 10% of the total variance. Their origin could be related to mining and smelting activities in the mountain areas of Croatia around the Sava River valley (Mt. Samoborska Gora – Rude; Mt. Medvednica) and also Slovenia (Litija).

A pedogenic profile southwest of Zagreb was selected for detailed analysis on the basis of the spatial distribution of heavy metals in the fluvial sediments of the river Sava. The depth of the profile was 121 cm (Fig. 2). Seven samples were taken through the whole profile. The analysis showed that the surface horizon is enriched with As and also all other analysed heavy metals, as opposed to lower horizons. The Cd, Pb, Cu and Zn content at a depth of 20 cm is almost half the content of the same elements at a depth of 2 cm. The concentrations decrease with depth, and at 60 cm reach "background" values characteristic of the pre-industrial era. Only the As content slightly increases with depth and reaches its maximum at 60 cm. Baseline values are recorded at 90 cm (Fig. 2).

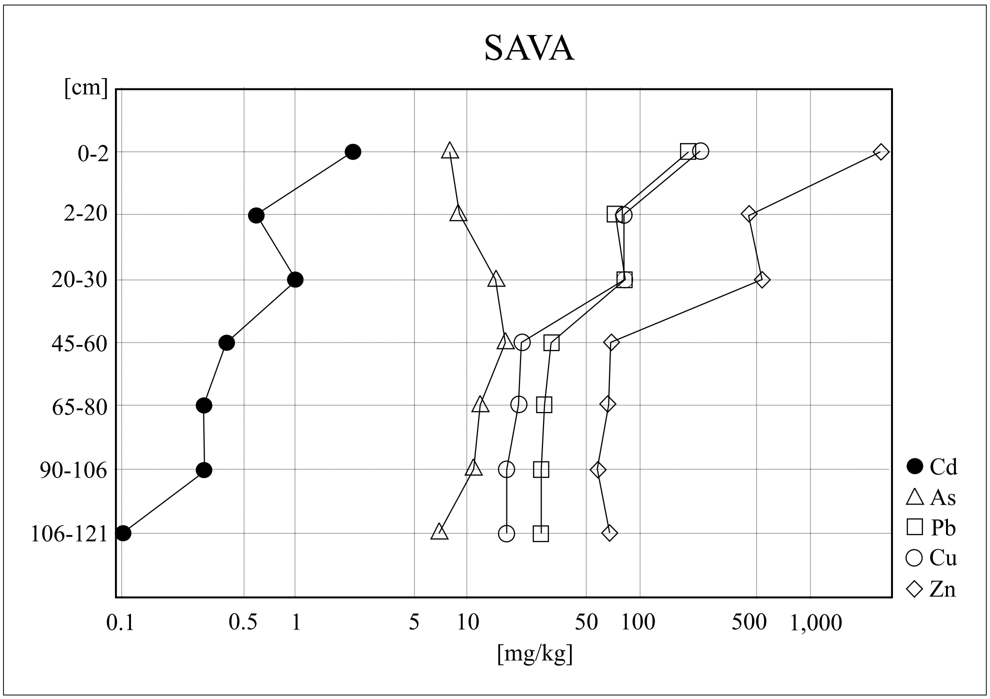

Fig. 2 Vertical distribution diagram of heavy metals in topsoil in Sava River valley – Profile P–1 (for location see Fig. 1).

3.3. Drava River valley

The topsoil developed on Drava alluvial sediments has higher concentrations of Pb, Zn and As in relation to the other investigated areas in NW Croatia (MIKO et al., 2001; HALAMIĆ & GALOVIĆ, 1999[3], 2000[4]). The basic statistical parameters for the analysed samples are given in Table 7.

The measured values of heavy metals in these soils are higher for As, Cd, and Hg, and anomalous for Pb and Zn, when related to the values acquired for the NWC region (Table 1). Only the Cu values are lower in relation to NWC (Tables 1 and 7). All the contents of heavy metals in soils of the Drava River valley are higher, while the lead and zinc values are anomalous when related to calculated baseline values. When comparing the measured contents in soils of the Drava River valley to the average global levels, it is obvious that the contents of As, Cd and Hg are higher and the Pb and Zn contents are significantly higher, while the Cu content is lower. According to permitted concentrations of heavy metals for ecological food production prescribed by the Croatian Government regulation (NARODNE NOVINE, 2001) the contents of As, Pb and Zn in topsoils on the Drava alluvial sediment are too high (Tables 2 and 7). However, different methods of sample preparation (total digestion vs. aqua regia, and <2 mm vs. 0.063 mm granulometric fraction) influenced certain differences in the measured contents.

The concentrations of copper in the Drava River valley are lower than those prescribed by Government regulation and show no correlation to any other elements (Table 8). Copper shows a high positive loading on the second factor (F2) which accounts for over 16% of the data variability. The increased contents of arsenic are in some places higher than those prescribed by Government regulation for the ecological production of food (Table 2), but are still lower than the anomalous values measured in topsoil that developed on the Drava River alluvial sediments. Similarly to Cu, As shows no direct correlation to any other heavy metal. The factor analysis shows high positive loadings of this element on the fourth factor (F4) (Table 10). Such a result indicates

	DRAVA (N=21)					
	mean	**geo. mean**	**median**	**min.**	**max.**	**Stdv.**
As (mg/kg)	12	9	11	2	28	8.10
Cd (mg/kg)	0.8	0.4	0.2	0.2	4.5	1.28
Cu (mg/kg)	26	25	26	14	48	8.81
Hg (mg/t)	77	56	55	25	470	116.20
Pb (mg/kg	76	49	41	22	382	109.07
Zn (mg/kg)	194	125	96	61	974	282.27

Table 7 Basic statistical parameters for topsoil in the Drava River valley (geo. mean = geometric mean).

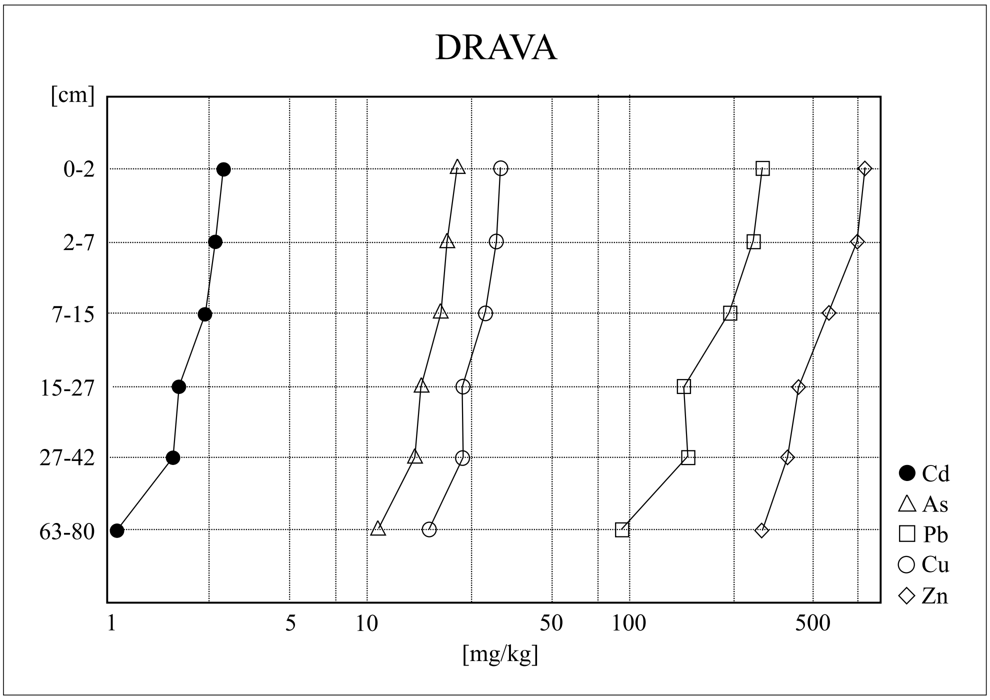

Fig. 3 Vertical distribution diagram of heavy metals in topsoil in Drava River valley – Profile P–2 (for location see Fig. 1).

a different source for both heavy metals. Increased values of As are found in intensively cultivated agricultural areas of the north bank of the river Drava (Plate 1). This indicates its anthropogenic origin in the soil. The higher contents of mercury, although under the limit prescribed by Government regulation, are an immediate consequence of fossil fuel combustion and traffic in the urban area of Varaždin. The factor analysis shows mercury grouping in the third factor (F3) which accounts for about 13% of the data variability (Table 10). Lead, zinc, and in part cadmium, from the Drava River valley topsoil have anomalous values over the limit prescribed by Government regulation for ecological agricultural production. The interrelation of these elements is showed by high correlation coefficients (Pb and Zn r=0.96; Pb and Cd r=0.80; Zn and Cd r=0.84 – Table 8) and by the results of factor analysis. These three heavy metals show high positive factor loadings on the first factor (F1) which accounts for more than 58% of the data variability (Tables 9 and 10). Since the marginal areas of the Drava River valley have no known natural polluters, the sources of the high values of heavy metals in this topsoil have to be searched for upstream. The flood waters of the Drava River were highly loaded with anthropogenic Pb, Zn and Cd as a consequence of mining, smelting and flotation activities upstream in the Meža River valley in the Republic of Slovenia (SOUVENT, 1994; ŠAJN et al., 2000) and Austria.

	Cu	Pb	Zn	As	Cd	Hg
Cu	1					
Pb	0.35	1				
Zn	0.37	0.96	1			
As	0.41	0.56	0.46	1		
Cd	0.20	0.80	0.84	0.38	1	
Hg	0.23	0.47	0.47	0.19	0.27	1

Table 8 Correlation coefficients for topsoils in the Drava River valley (correlation significant at p<0.05).

The soil profile shows that increasing depth results in the lowering of Pb, Zn, Cd and As content reaching the background level for that area at 80 cm depth. This suggests that the alluvial sediments of the pre-industrial era lay deeper and that the soil contamination with heavy metals continuously increases up to recent soil horizons (Fig. 3).

4. CONCLUSIONS

Spatial distribution of heavy metals in topsoils of NWC shows that the higher to anomalous values of Cu in NWC are, for the most part, related to winegrowing areas, that is, to the anthropogenic input of this metal into the topsoil. The anomalous values of As and Cd are mainly of natural origin (mineralization). Only some of the As anomalies are of anthropogenic origin (Međimurje region – agriculture), and anthropogenic Cd is related only to the Drava River fluvial valley. High contents of Hg on Mts. Kalnik and Ivanščica are of natural origin, whilst the source is of anthropogenic origin in the Zagreb and Varaždin city areas as well as in the Drava River valley.

Analysis of the spatial distribution of heavy metals in the Sava River valley showed no anomalous values of analysed heavy metals, with the exception of higher Hg contents in the Zagreb city area. The correlation

Factor	Total	% of var.	Cumul.%
1	3.48	58.07	58.07
2	0.96	16.04	74.11
3	0.82	13.63	87.75
4	0.54	9.03	96.78

Table 9 Eigenvalues of factors for Drava River valley topsoils.

	Factor 1	Factor 2	Factor 3	Factor 4
Cu	0.14	0.97	0.09	0.18
Pb	0.87	0.15	0.27	0.31
Zn	0.91	0.19	0.27	0.18
As	0.27	0.19	0.06	0.94
Cd	0.95	0.03	0.03	0.11
Hg	0.22	0.09	0.97	0.06
Expl.Var.	2.61	1.05	1.09	1.06
Prop.Totl.	0.43	0.17	0.18	0.18

Table 10 Factor loadings in topsoil of the Drava River valley (varimax normalized; extraction: principal components; marked loadings are >0.5).

coefficient indicates a significant correlation of Hg to Cd and Pb (r=0.73 and r=0.62 respectively) (Table 4). Cd has high correlations to Cu and Zn (r=0.74 and r=0.74 respectively) that are mostly a consequence of mining and smelting activities from upstream areas. The factor analysis showed grouping of mercury in the first factor that explains over 66% of the total variance. All this leads to the conclusion that only a small part of the Hg content in the Sava River valley topsoil is caused by upstream mining and smelting activities, and that a greater amount is caused by fossil fuel combustion and industrial plants from the Zagreb city area (airborne pollution) (NAMJESNIK et al., 1992).

The Drava River valley area has anomalous values of Pb, Zn and Cd when compared to the Sava River valley. As and Hg, show only local anomalous deviation from average values, while the Cu concentrations are within the normal range. These three elements showed no significant correlation to any other analysed heavy metals, which means that their source is different from the source of Pb, Zn and Cd. Higher contents of As were found in agricultural areas NE of Varaždin. They are probably a consequence of the treatment of these agricultural areas with agrochemicals (pesticides that contained As).

The anomaly of Hg is related to the Varaždin city area and is a result of the pollution of the topsoil through atmospheric deposition. Pb, Zn and Cd showed a significant correlation to one another (Table 8). These three elements were also grouped in the first factor (F1) (Table 10), characteristic of the anthropogenic input of these elements in the soil, and which also explains over 58% of the total variance. The soils of the Drava River valley generated from fluvial sediments that were in part naturally enriched with heavy metals (mineralization of Pb and Zn upstream in Austria and Slovenia). Furthermore, the river Drava flooded regularly until recently, carrying with it heavy metals that were washed down from Pb and Zn mines (mining waste dams, firm and liquid smelter waste, etc.). After flooding the heavy metals were washed out from the flood sediments and placed into the topsoil.

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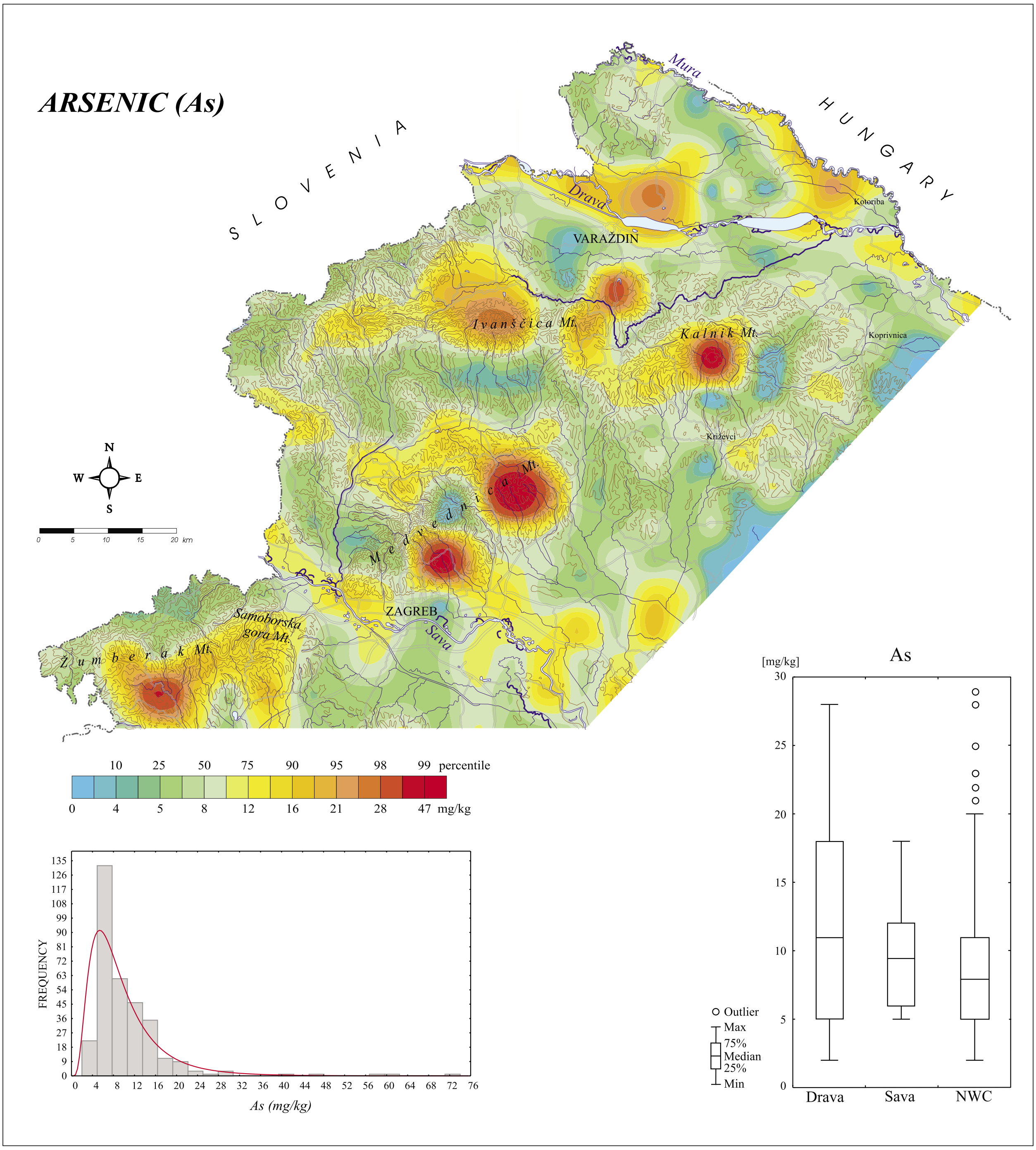

PLATE 1

Spatial distribution map of arsenic in topsoil of the north-western Croatia with box-whiskers diagram and histogram.

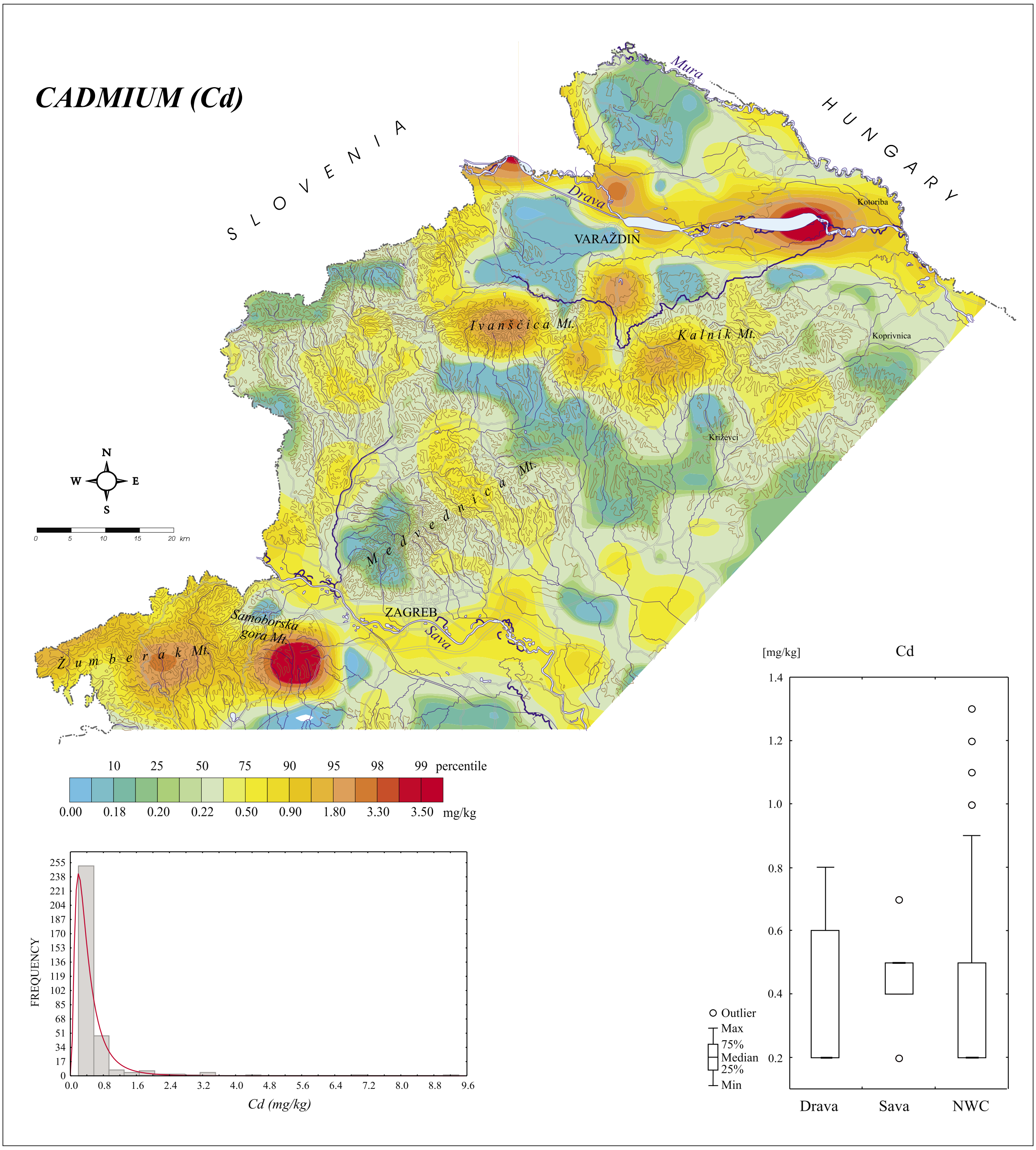

PLATE 2

Spatial distribution map of cadmium in topsoil of the north-western Croatia with box-whiskers diagram and histogram.

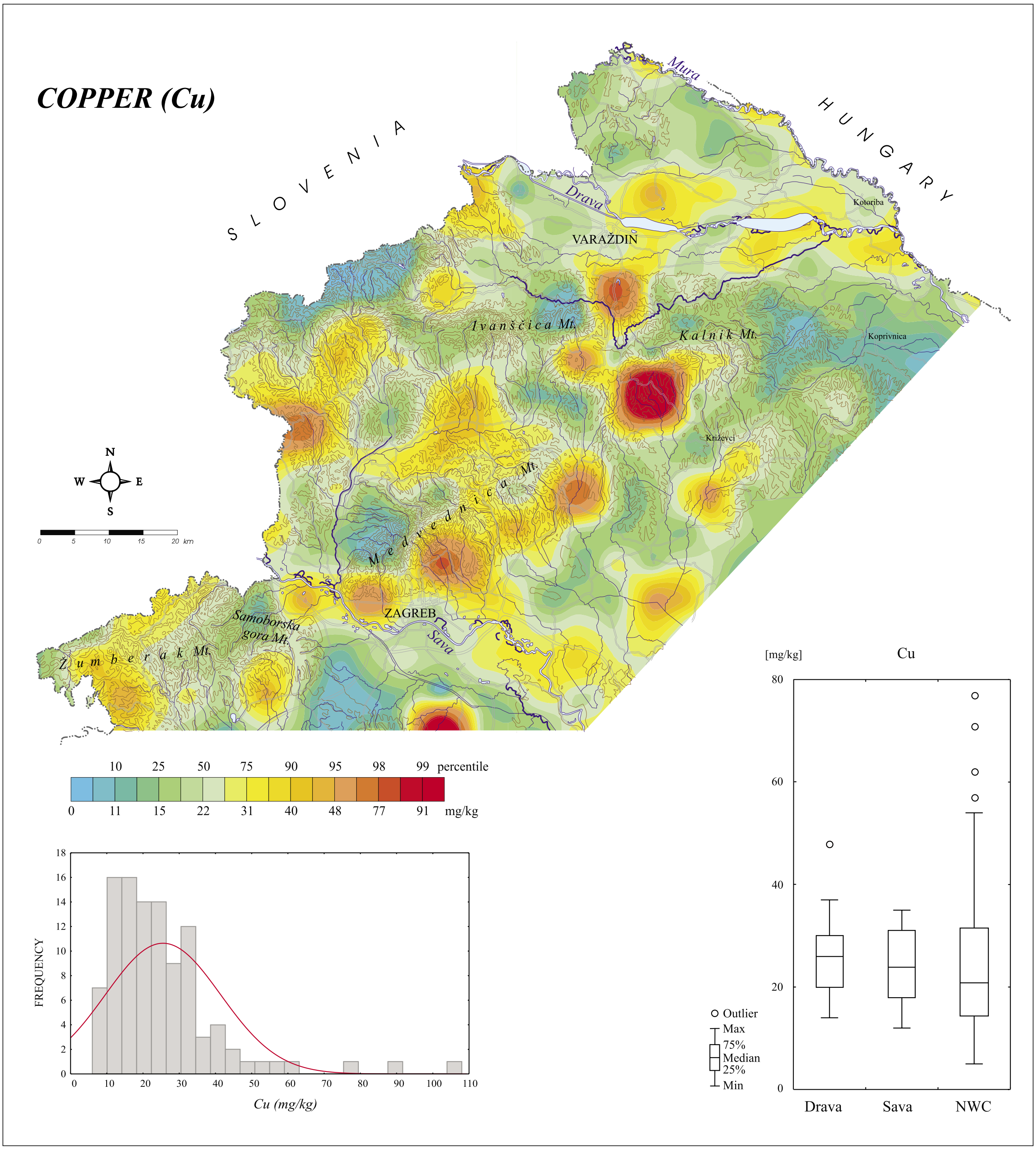

PLATE 3

Spatial distribution map of copper in topsoil of the north-western Croatia with box-whiskers diagram and histogram.

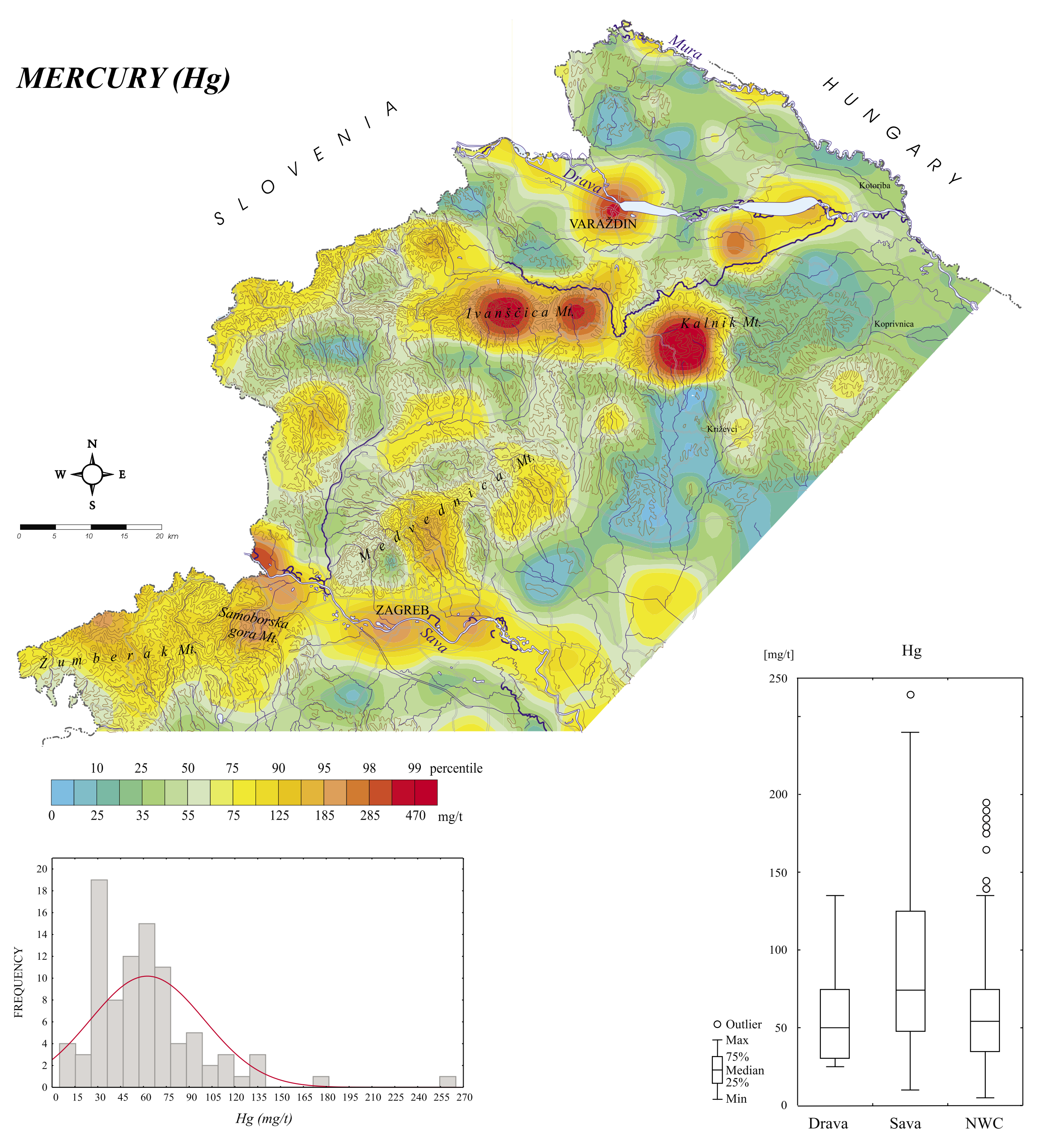

PLATE 4

Spatial distribution map of mercury in topsoil of the north-western Croatia with box-whiskers diagram and histogram.

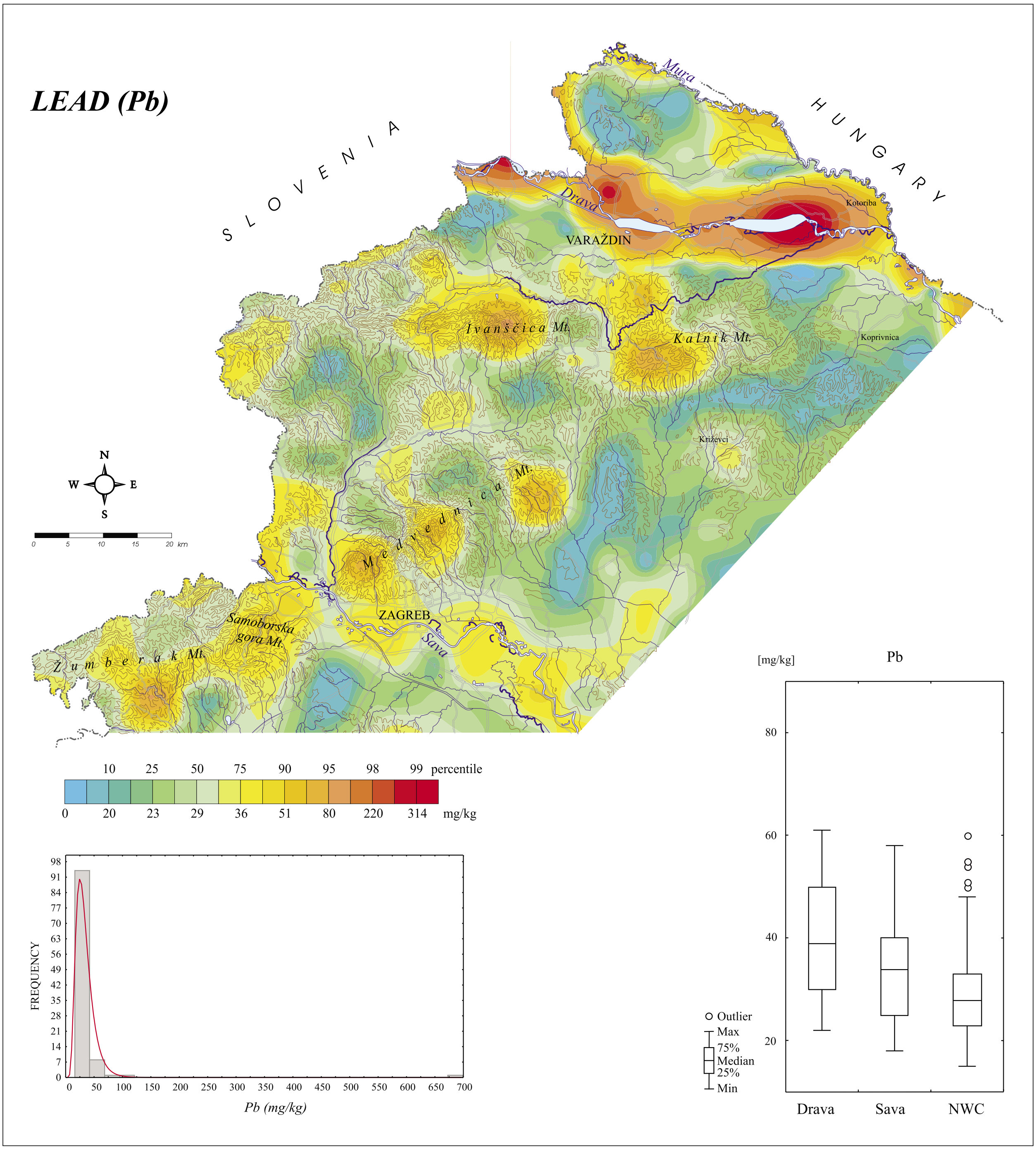

PLATE 5

Spatial distribution map of lead in topsoil of the north-western Croatia with box-whiskers diagram and histogram.

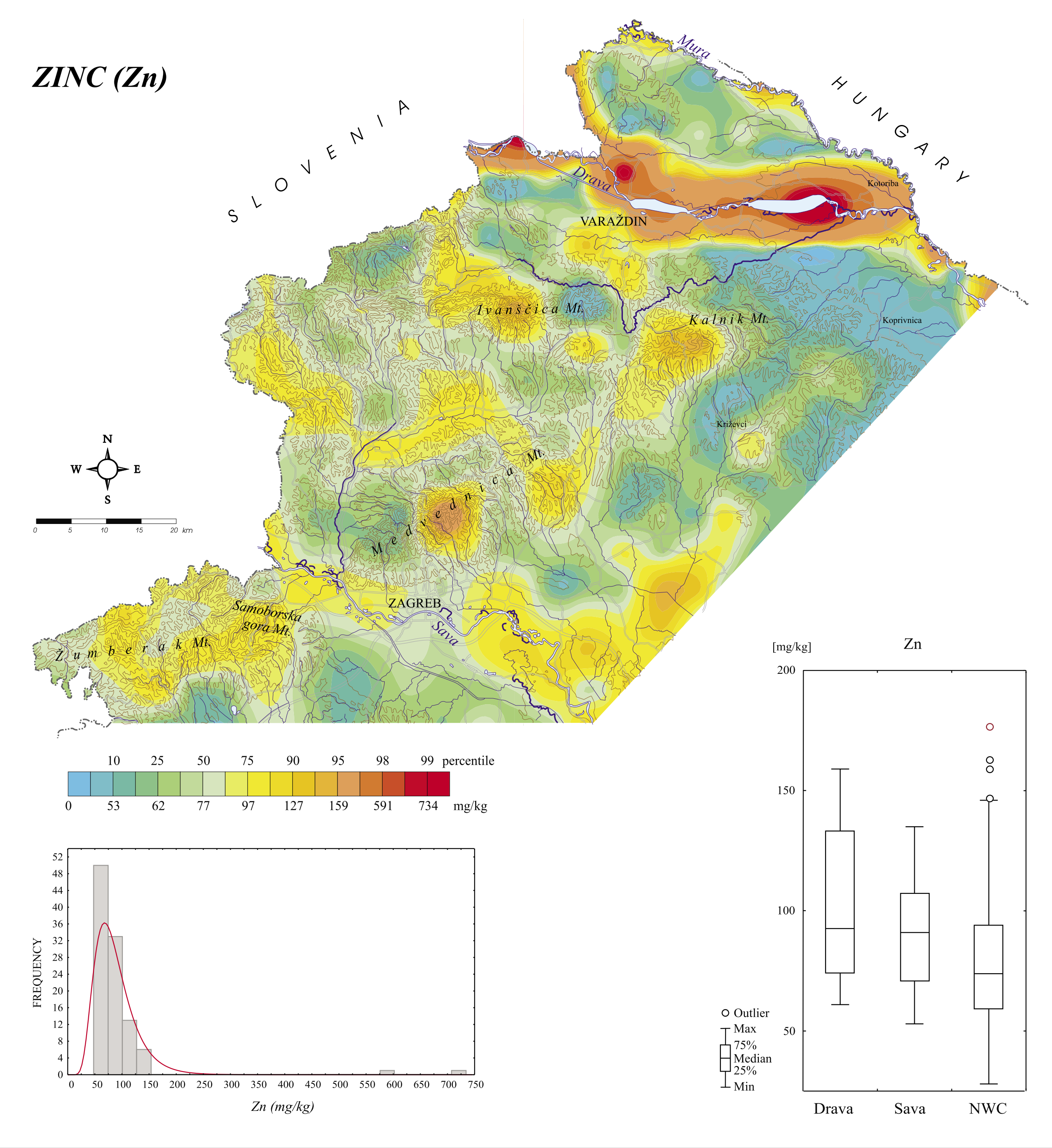

PLATE 6

Spatial distribution map of zinc in topsoil of the north-western Croatia with box-whiskers diagram and histogram.