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Geochemical Baseline Mapping of Soils Developed on Diverse Bedrock from Two Regions in Croatia

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Abstract

The comparison of contents and distribution maps for Al, As, Ba, Ca, Co, Cr, Cu, Fe, La, K, Na, Ni, Mg, Mn, P, Pb, Sc, Sr, Ti, Th, V, Y, Zn and Hg in the topsoil cover of two typical regions are given. One is a carbonate bedrock (karst) dominated region (southern Dalmatia) and the other a non-carbonate bedrock dominated region (NW Croatia). The results imply that the soils developed on carbonate bedrock have higher mean values of almost all elements excluding K, Na, Mg and Ba, which are lower in carbonate terrains. In comparison with the non-carbonate terrains, for the carbonate terrains the following elements have higher mean concentrations: Al, As, Co, Cu, Fe, La, Mn, Pb, Ni, Mn, Th, V, Cr, Zn, Zr and Nb, while Sr, P and Ti have similar contents. Approximately 4% of the sites can be considered as moderately enriched (polluted) in Pb, either from mining activities or airborne deposition. Only a limited number of sampling sites can be directly linked with mineralization. The derived factors are usually interpreted as associations of elements that imply a common source or behavior in regard to geogenic or anthropogenic influences. It was found that difference between the northwestern Croatia and southern Dalmatia is not expressed only by concentration differences but also by element associations. Five factor models accounting most of the data variability seemed appropriate to portray the geochemical variability within the topsoil of both regions.

1. INTRODUCTION

Soil is a vulnerable geological medium, which sustains the bulk of human activities including, among others, the food production as one of the most important. In the age of increasing pollution and devastation of human environment the soil protection deserves every respect and mindfulness, particularly because of its vital importance not only to the human beings but also for the sustenance of each facet of life on this planet as a whole. In order to trace the increasing human contribution to overall contamination of the planet, particularly by the chemical elements harmful to health, it is necessary to determine the natural content of major and trace elements in soils on the regional scale. Up to the present time there was no methodical research in our country as regards finding a solution to this burning worldwide problem. In due time, this work was animated and supported by the Ministry of Science under the project of Geochemical Map of The Republic of Croatia with the scope to detect a pollution problem on a regional scale and pinpoint some target areas in the country where adversities for its inhabitants threaten to become most pronounced.

Geochemical research has shown a much greater natural variability among almost all elements in soil, irrespective of the soil type, when contrasted to the stream sediment (REIMANN, 1988). This is a fact that allows reduction of sampling density, fitting it more appropriately into the regional scope of investigation which can be implemented successfully either on carbonate or non-carbonate geological bedrocks. Sampling design and analysis have been performed to be complement with recommendations issued by IGCP (DARNLEY et al., 1995) and FOREGS (SALMINEN et al., 1998), which classify soil into the first group of sample materials (regolith) with the widest geochemical applicability.

This paper is aimed to establish the geochemical baselines for a set of chemical elements in the two geographically separate parts of the country whose soils originated on different geological substrates: 1) on predominantly non-carbonate (non-karstic) terrains (northwestern Croatia); and 2) predominantly carbonate (karstic) terrains (southern Dalmatia). Geochemical baselines, or natural background concentrations for a particular element refer to the natural variability of its contents in the secondary (surficial) environment (soils, stream, overbank, floodplain or lake sediments). The geochemical baseline, which has been defined within the IGCP 360 project Global Geochemical Baselines, is of essential importance in environmental legislation, which prescribes limits for heavy metals in contaminated land and other surficial materials such as defined by environmental authorities. This is additionally complicated by regional geochemical data showing that natural background concentrations vary widely due to the

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differences in bedrock geology and the origin of the soil cover, as is the case in the Mediterranean region of Croatia. In the region of southern Dalmatia the geochemistry of the topsoil cover distinguishes between the two major environments; the southern Adriatic islands (Mljet, Korčula, Hvar, and Brač to some extent) and the mainland which consists of the two somewhat less pronounced environments: alluvial valleys-karst poljes and carbonate bedrock (PEH & MIKO, 1999).

2. GEOLOGY AND PEDOLOGY

The north-western part of Croatia (Žumberak Mt., Pokuplje, Posavina upstream of Sisak, Medvednica Mt., Hrvatsko Zagorje, Podravina to the east of Varaždin, and Međimurje) is bordered to the west and north by the Croatian-Slovenian borderline, to the south by the river Kupa, and to the east by the Gauss map Y coordinate line of 5612500 (approximately the line connecting the cities of Čakovec and Sisak). The southern Croatian territory is bounded to the west by the line extending from Split to the Peruča Lake. Its northern fringe is defined by the state boundary towards Bosnia and Herzegovina. To the east the area is narrowing against the Montenegro border at the cape of Oštra (Fig. 1).

The investigated territories belong to different geotectonic complexes. The northwestern Croatia fits into the Supradinaric palaeodynamic unit with elements of Alpine structures. This area is also known as the Inner Dinaride Belt (HERAK, 1986; HERAK et al., 1990). On the other side, recent tectonic setting of the southern Croatia is a consequence of the disintegration of carbonate platform areas, which resulted in the extended, highly elevated karstic terrain, also known as the Outer Dinarides. The complex geotectonic evolution of these belts is reflected in prevalence of "non-carbonate" lithology in NW Croatia, while its southern portions are built chiefly of carbonate sedimentary rocks.

In the former case a variety of rocks occurs ranging from Devonian (Silurian?) to Quaternary ages. The main bodies of the mountain ranges Žumberak, Medvednica, Kalnik, Ivanščica, and some other smaller ranges, which are a minor part of the whole region of NW Croatia, consist mainly of Palaeozoic and Mesozoic rocks (para-metamorphic rocks, ortho-metamorphic rocks, carbonate sedimentary rocks, igneous rocks and clastic sedimentary rocks). A major portion of this territory consists of Tertiary rocks (limestones, marls, clastites, igneous rocks) and Quaternary rocks (mostly alluvium sediments of the rivers Sava, Drava, Mura, Kupa, and their tributaries) (Fig. 2).

The geological setting of the southern part of Croatia area resulted from a vigorous tectonic activity since the Palaeozoic times. In its western part structures appear more compact, while to the east they display strong neotectonic faulting and partitioning into the minor blocks. Throughout the area limestones and dolomites prevail which, due to tectonics and later karstification, manifest various karstic phenomena. The clastic flysch-type sedimentary rocks, mostly marls, also occur, although in a rather limited quantity. The occurrence of other siliciclastic rocks, outside the flysch complex, is extremely rare and related only to the Palaeozoic tectonic windows far to the northwest. The stratigraphic sequence can be traced from the Palaeozoic to the Quaternary (Fig. 2).

The investigated areas are considerably contrasted not only by their geological settings but also in their climatic characteristics, which resulted in formation of the variety of soil types. Most soils in the northern part of Croatia (Fig. 3) are characterized by high moisture content as a consequence of high precipitation, flooding and high groundwater levels. Water can saturate the upper part of the horizon inducing the waterlogged conditions, which induce the development of hydro-morphic soils (ŠKORIĆ, 1986). In contrast, the southern parts of the country are covered by soils that are moistened only by the precipitation input, without additional saturation. Infiltration through the soil and into the ground is free and unimpeded.

The major area of the NW Croatia is covered by soils from the group of gleys such as eutric, mollic and calcic gleysols (ŠPOLJAR, 1999). These can be found in the valleys of the rivers (Sava, Drava, Mura, Sutla, Krapina, and Kupa). The second most frequent group of soils consists of stagnic and podzololuvisols, which cover the plains between Žumberak Mt., Vukomeričke Gorice and Zagreb as well as along the Sava River downstream to the town of Sisak. Besides, these soils are spread in the belt between the Sava river on the one side, and Ivanščica, Kalnik and Moslavačka Mountains on the other. The third major soil group, represents the mollic and calcaric fluvisols, particularly in the wide valleys of the Sava and Drava rivers immediately along their course. More rarely other types of soils occur, such as rendzic, mollic, umbric and dystric leptosols; eutric, dystric, humic and chromic cambisols; and albic, gleyic and chromic luvisols. About 2% of the collected samples belong to the urban areas of Zagreb, Sisak and Varaždin.

In contrast to the northern Croatia, the karst bedrock in the southern Dalmatia is dominantly covered by the coloured soils, terra rossa - chromic cambisols, which cover the largest part of the coastal terrain and most of the islands. The next important group of soils consists of rendzic and mollic leptosols, which can be traced in the highest mountain reaches of the Mosor, Biokovo and Dinara Mountains as well as on the most elevated areas of the island of Brač and the Pelješac peninsula. Besides, these soil types cover a narrow strip of the coastal area from Split eastward to Ploče. Minor patches of the territory are overlain by the more rare soil varieties such as aric anthrosols (Sinjsko Polje, the zone along the Neretva river, and portions of the islands of Brač, Hvar and Korčula), mollic and calcaric fluvisols

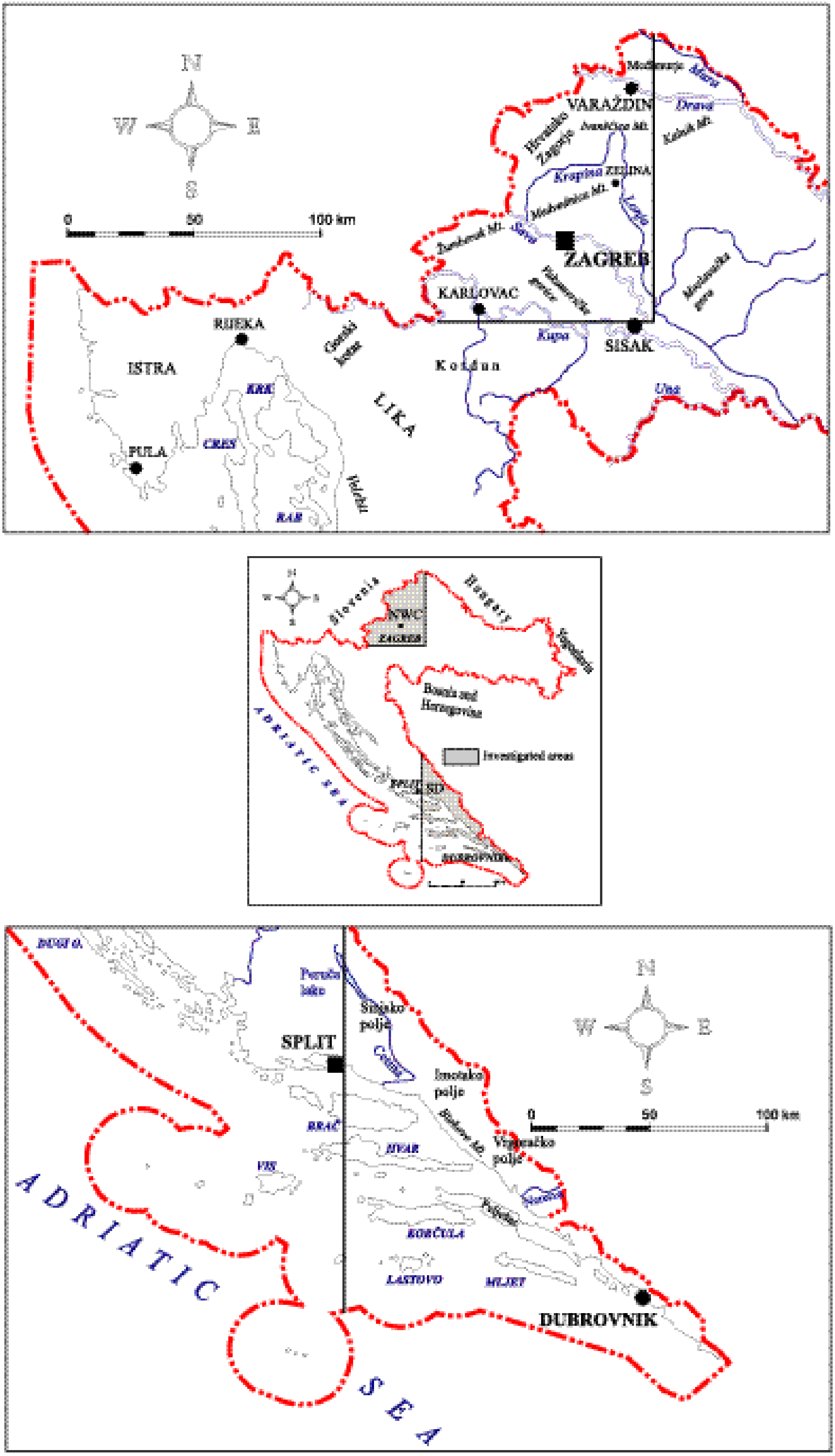

Fig. 1 Map of Croatia with location of studied areas (northwestern Croatia and southern Dalmatia).

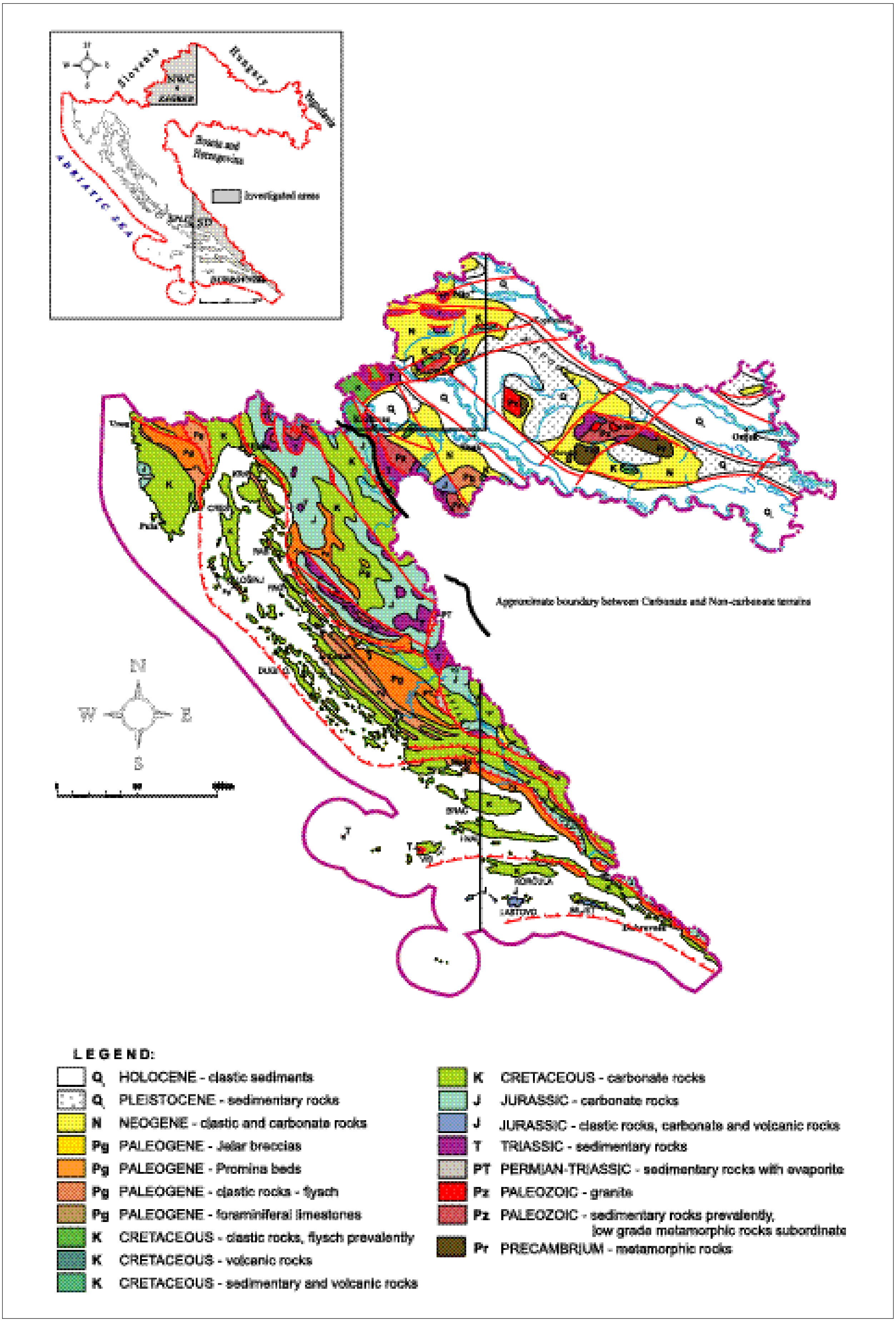

Fig. 2 Geological map of Croatia (VELIĆ & VELIĆ, 1993).

(Imotsko and Vrgoračko Polje together with the valley of Neretva), chromic luvisols (smaller area between the Imotsko and Sinjsko Polje); and fibric and terric histosols (the swampland along the Neretva River). Much of the soils on flysch bedrock, and more rarely, on carbonate terrains are anthropogenized and transformed into rigosols.

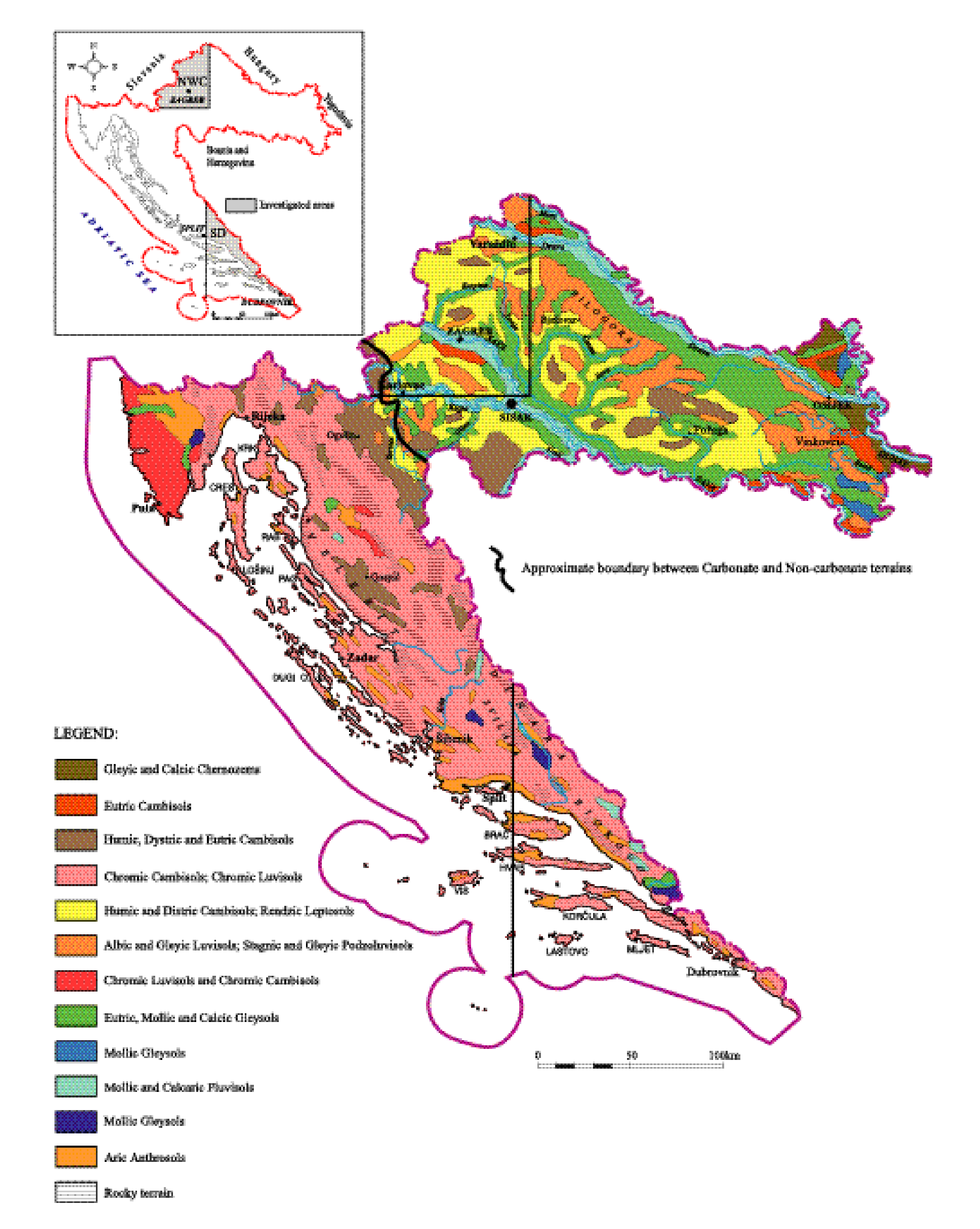

Fig. 3 The soil map of Croatia (modified from ŠKORIĆ, 1986).

3. MATERIALS AND METHODS

3.1. Sampling and sample preparation

Soil samples from coastal and inland terrains were collected at a density of 1 site/25 km^2 in a regular grid with the initial point of the grid for the whole country located in Istria near the city of Rovinj (PIRC et al., 1991). Detailed protocols of the sampling procedures to be applied for this region are given by PIRC et al. (1991), and PROHIĆ et al. (1997, 1998), as well as by MIKO et al. (1999), PEH & MIKO (1999), HALAMIĆ & GALOVIĆ (1999). All of the above protocols are summarized in the Guidelines for the Geochemical Mapping of Croatia (HALAMIĆ et al., 2000), which only slightly differ from the recommendations given by DARNLEY et al. (1995). The tolerated dislocation of sampling from the sampling cell nodes was 5%. In northwestern Croatia a total of 293 soil samples were collected which is equivalent to a surface of approximately 7,350 km^2, in southern Dalmatia 404 (225 on the 5x5 km grid and 179 on the 1x1 km grid) soil samples collected cover an approximate surface of 5,600 km^2 (Fig 1).

The soil samples were taken at each sampling site from 5 shallow pits (the Amo-mollic horizon, from the depth of 0 to 20 cm) and one composite sample was prepared from each sampling site.

3.2. Analytical procedures and quality assurance

The dry soil samples were sieved to pass 63μm screen and were analyzed after near total (a hot acid mixture: $HClO_4$-HNO_3-HCl-HF at 200°C) decomposition for 35 elements by ICP-AES in the ACME Labs in Vancouver. The following elements were analyzed: Ag, Al, As, Au, Ba, Bi, Be, Ca, Cd, Co, Cr, Cu, Fe, La, K, Na, Nb, Ni, Mg, Mn, Mo, P, Pb, Sc, Sb, Sn, Sr, Ti, Th, U, V, W, Y, Zn, and Zr. The analytical results for Ag, Au, Bi, Be, Mo, Sb, Sn, U and W were not used since more than 80% of the samples contained concentrations of these elements below the instrumental detection limits. Single element geochemical maps were constructed only for the remaining elements with concentrations above the detection limit (usually more than 90% of the analyzed samples).

Accuracy of analyses was controlled with the aid of certified geological reference materials, i.e. soils from the USGS; GXR-2, GXR 5, and SJS-1. The accuracy for most elements analyzed in reference soil materials is in the range of ±10 % of the certified values (PEH & MIKO, 1999; HALAMIĆ & GALOVIĆ, 1999). The precision of the analyses was determined by repeated analysis of both certified reference samples and randomly selected soil samples, the resulting coefficient of variation in average is approximately 5% (PEH & MIKO, 1999; HALAMIĆ & GALOVIĆ, 1999).

The field data and the chemical analyses are stored as a database, which besides the chemical data also contains 20 parameters that describe topographic, geologic, geomorphologic and pedologic features of the sampling sites and samples. All collected samples are preserved and stored for future use. The single-element geochemical maps were produced with the aid of the SURFER mapping software. Griding was performed by linear kriging (ISAAKS & SIRVASTAVA, 1989) with grid cell resolution of 2 x 2 km.

3.3. Evaluation of basic statistical parameters and multivariate statistics

The evaluation of basic statistical parameters for all elements was performed on the analytical data from the whole database. These parameters are given in Table 1, while others are displayed together with frequency distribution histograms presented on each individual map. Also the nonparametric 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. For decades both exploration and environmental geochemical studies frequently use R-mode factor analysis as a multivariate mathematical technique to reveal the underlying structure of a specific set of data (DAVIS, 1986). As such, it is commonly used as a tool of data reduction, with a purpose of clearer insight into the basic relationships among variables (R-mode), or among samples (Q-mode). A simply structured factor model, which contains only a few heavily loaded factors, is always indicative of the strong dependence among elements, and therefore as such, is used to compare the geochemistry of the studied regions. Factor analysis was performed for the data set of each region separately with the aim to observe similarites of geochemical behavior of the analyzed elements and to allow a more straithgfoward insight into the structure of the data. All statistical analyses were performed with the STATISTICA software.

4. RESULTS AND DISCUSSION

4.1. Element distributions

In the secondary environments the geochemical background varies regionally with the basic geology, as is indicated by the results of geochemical mapping performed in the Panonnian and the karst regions of Croatia. The results of the geochemical baseline mapping program together with the accompanying full data bases for NW Croatia and southern Dalmatia is summarized in atlases of single element maps (HALAMIĆ & GALOVIĆ, 1999; PEH & MIKO, 1999; MIKO et al., 2001). The summary statistics for Croatian soil geochemical data obtained so far during the geochemical mapping program is given in Table 1. For comparison

		NW Croatia	S Dalmatia		Croatia	Slovenia (ANDJELOV, 1994)
	# samples	median	median	median	mean	mean
Al (%)	1143	7.33	7.94	7.32	7.23	6.69
As (mg/kg)	984	14	14	12	14	8.17
Ba (mg/kg)	1151	330	279	326	345	371
Ca (%)	1153	1.24	2.29	1.41	3.77	2.58
Co (mg/kg)	1152	14	18	15	15	28
Cr (mg/kg)	1153	94	112	96	104	90
Cu (mg/kg)	1153	34	45	34	49	28
Fe (%)	1153	3.67	4.13	3.67	3.68	3.75
Hg (mg/kg)	293	60	-	60	94	-
K (%)	1024	1.21	1.21	1.36	1.34	1.23
La (mg/kg)	1151	49	50	43	45	31
Mg (%)	1152	0.68	0.82	0.75	1.09	1.35
Mn (mg/kg)	1153	780	1009	770	844	1044
Na (%)	1151	0.49	0.28	0.43	0.51	0.52
Ni (mg/kg)	1153	59	79	59	65	53
P (%)	1024	0.062	0.071	0.064	0.076	0.07
Pb (mg/kg)	1153	43	53	42	46	38
Sc (mg/kg)	1023	11	12	11	11	13
Sr (mg/kg)	1153	86	102	98	120	98
Th (mg/kg)	1024	13	17	13	14	11
Ti (%)	1153	0.40	0.41	0.41	0.39	0.38
V (mg/kg)	1153	118	143	117	125	118
Zn (mg/kg)	1153	91	109	94	101	113

Table 1 Summary statistics for the analyzed elements in topsoils from Croatia (data from Western Croatia from MIKO et al., 2001).

the mean concentrations of elements in Slovenian soil (ANDJELOV, 1994) are also presented since the data were obtained in the same manner (sampling and analytical procedures were the same). Also for a clearer insight a comparison of the distribution of both major and trace elements in the analyzed soils is given on box and whisker-plots in Figs. 4 (major elements) and 5 (trace elements). From the summary data in Table 1 it is visible that most of the elements (Al, As, Co, Cu, Fe, La, Pb, Ni, Mn, Th, V, Cr, Zn, Zr and Nb) have higher median values in soils developed on carbonate bedrock with the exception of Na, K, Fe and Ba, which have higher concentrations in soils of the northwestern part of Croatia. Sr, P, Mg, and Ti manifest a similar range of contents in both regions. The non-outlier ranges in Figs. 4 and 5 show that the trace elements have the largest variability of content in soils developed on carbonate bedrock in southern Dalmatia, while the variation in northwestern Croatia is far less expressed. The samples from western Croatia (the regions of Gorski Kotar, Lika and Kordun in general, MIKO et., al., 2001) have elements of a transition zone since the soils that are developed on the limestones on the Karlovac plateau are derived (as a result of aeolian transport) from material that originates from the northwestern Croatia. This is expressed by an intermediate variation between the other two geographically distant and geologically different regions. The relatively small variation in the content of trace elements in soils of northwestern Croatia is probably due to the relatively limited area that was sampled. The major elements (Fig. 4) in all regions show a similar degree of variation. A short description of the individual elements presented and corresponding geochemical maps is given in the text that follows.

Aluminium (Al)

Aluminium content in soils (Plates 1 & 2) is mainly controlled by the clay content, the parent lithology and the content of carbonates, which is best illustrated on the plot CaO vs. Al_2O_3 in Fig. 6. The data for western Croatia are given for comparison (MIKO et al., 2000, 2001).

Aluminum ranges from 1.46% to 10.84% with an arithmetic mean of 6.89% in northwestern Croatia whereas in southern Dalmatia its contents range from 0.82% to 14.04%. The lowest aluminum contents are found in soils that contain higher carbonate contents such as rendzinas on dolomites and limestones, soils developed on flysch bedrock and on carbonate rich

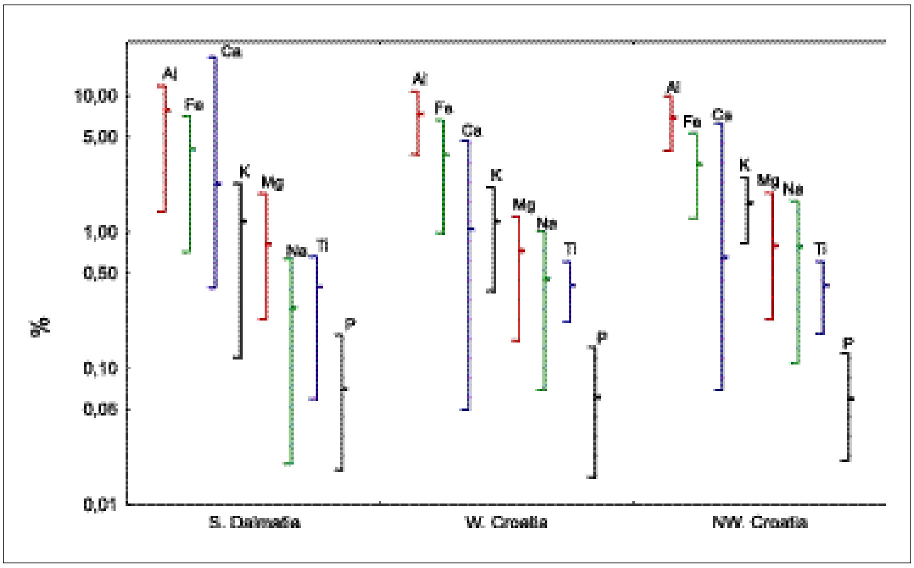

Fig. 4 Concentration ranges of major elements in soils from southern Dalmatia, western Croatia and northwestern Croatia, median; non-outlier minimum, non-outlier maximum (data for W Croatia from MIKO et al., 2000, 2001).

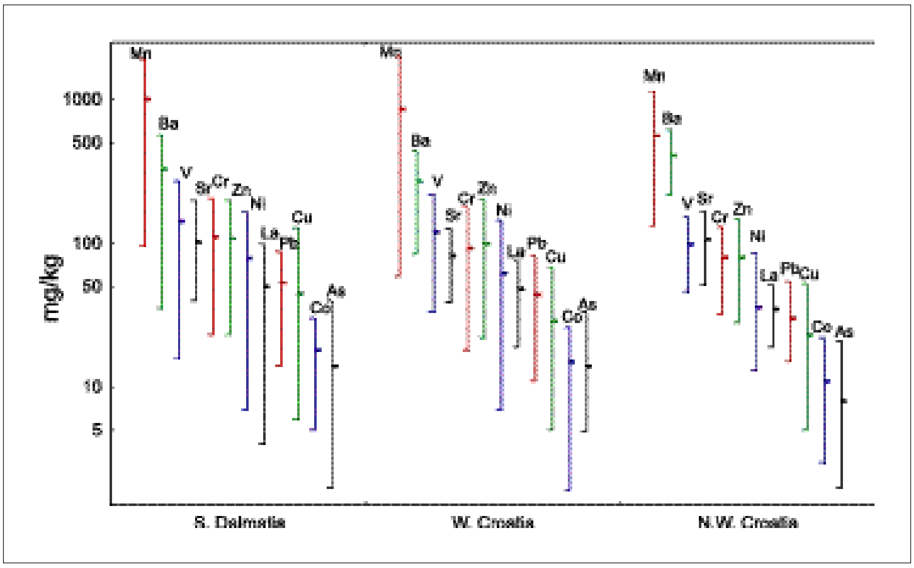

Fig. 5 Concentration ranges of minor and trace elements in soils from southern Dalmatia, western Croatia and northwestern Croatia, median; non-outlier minimum, non-outlier maximum (data for W Croatia from MIKO et al., 2000, 2001).

alluvium deposits along the Sava River near Zagreb, or in karst poljes which contain lacustrine sediments. Higher contents of Al are found in soils overlying magmatic and metamorphic rock complexes. In the region of southern Dalmatia the terra rossa soils regularly have more than 8% of Al as a consequence of high clay content, while the alluvial and marsh soils due to dilution by carbonates have concentrations lower than 6%. The effect of carbonate dilution is best viewed on the plot CaO vs. Al_2O_3 (Fig. 6).

Arsenic (As)

The distribution and contents of arsenic (Plates 3 & 4), which is considered a potentially toxic element, ranges in northern Croatia from 1.8 to 52.7 mg/kg with an average of 10 mg/kg. The soils developed on carbonate bedrock in southern Dalmatia have a similar range of contents but in average contain 16 mg/kg of As. In general there is a high correlation of As with the Al content in soils indicating that the clay content controls the As content in the soils. Therefore alluvial soils and soils derived from flysch have low contents of arsenic, while terra rossa has elevated concentrations of As. Although most of the high concentrations of As can be linked with the underlying lithology in areas of intensive agriculture (Međimurje), agrochemicals as a source cannot be excluded. In Žumberak Mt. the As can partly be derived from the sulphide mineralization that occurs in the region.

Barium (Ba)

The barium content (Plates 5 & 6) in the analyzed soils from both regions ranges from 40 to 3,000 mg/kg. Barium has a geochemical affiliation for potassium (Fig. 7), especially in feldspar, so the weathering products also retain this relationship. High concentrations of Ba were found in Žumberak Mt., where it is related to sulphide mineralization. In some parts of alluvial plains of the rivers Sava (near Sisak), Drava and Krapina the contents of Ba exceed 500 mg/kg. The mean Ba content of

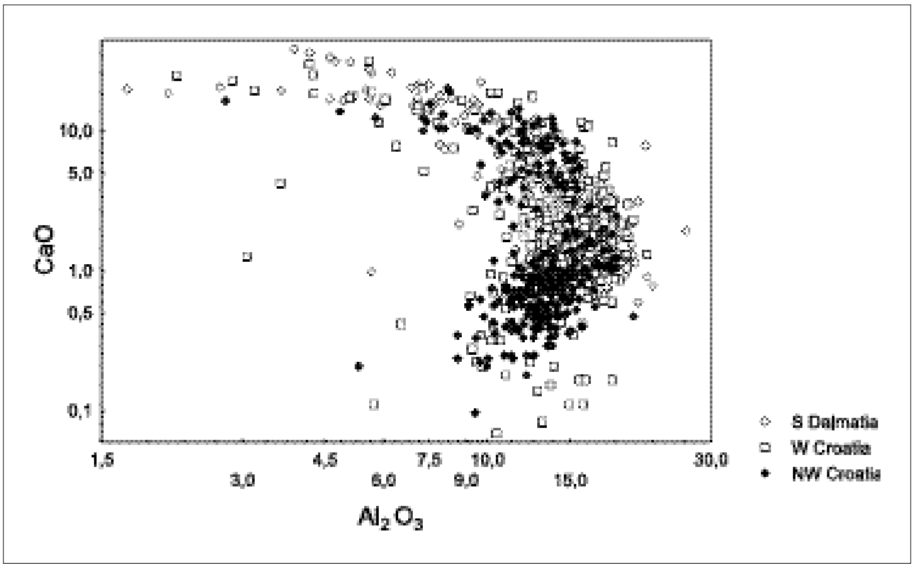

Fig. 6 The relationship between the contents of CaO and Al_2O_3 (data for W Croatia from MIKO et al., 2000, 2001).

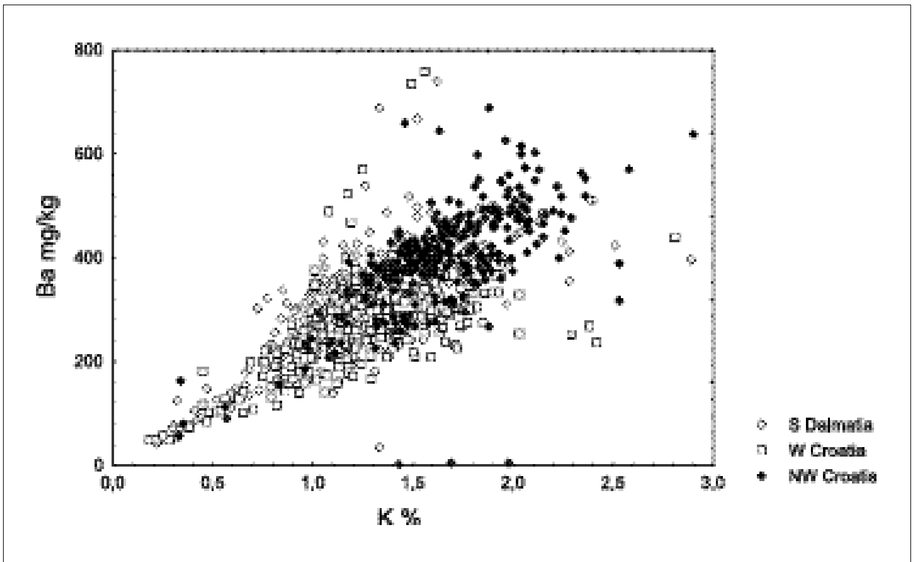

Fig. 7 The relationship between the contents of K and Ba (data for W Croatia from MIKO et al., 2000; 2001).

soils from the Pannonian part of Croatia is 424 mg/kg, whereas from southern Dalmatia is 324 mg/kg. Soils developed on carbonate clastic rocks and alluvial and marsh soils in the karst regions have Ba contents below 200 mg/kg, which also reflect the effect of carbonate dilution. The analysis of Ba data of soils (MIKO et al., 2000) for the Adriatic Islands Mljet, Korčula, Hvar and Brač indicate enrichment of this element, as do the recent sediments from the southern part of the Adriatic Sea (DOLENEC et al., 1998). Barium together with K and Na, seems to be the key element that determines the geochemical provinces in Croatia, which are the karst region, with low contents of these elements, the transition zone of the Karlovac plateau, and northwestern Croatia with high concentrations of Ba, K and Na.

Calcium (Ca)

Calcium (Plates 7 & 8) as a major element and nutrient ranges from 0.07 to 14.70% in northwestern Croatia, and from 0.39% to 35.09% in southern Dalmatia with mean concentrations of 2.08% and 6.02% respectively. The lowest concentrations of Ca were determined in soils developed on loess deposits and gleyic soils in northwestern Croatia and in southern Dalmatia in terra rossa and brown soils developed on limestones. Rendzinas developed on limestone, dolomite and flysch due to the large amount of fine carbonate detritus regularly contain more than 3% of Ca. The effect of dilution by carbonates is illustrated by the scatter plot CaO-Al_2O_3 in Fig. 6. High calcium contents characterize soils developed on floodplain sediments of the rivers Sava, Drava, Neretva and the karst poljes Imotsko Polje and Vrgoračko Polje that are also flooded in spring periods and whose floors contain lacustrine type of sediment.

Cobalt (Co)

The distribution of cobalt (Plates 9 & 10) is in high correlation with the distribution of Al, Fe and Mn, indicating the effects of coatings of iron and manganese hydroxides on clay mineral surfaces. The content of Co

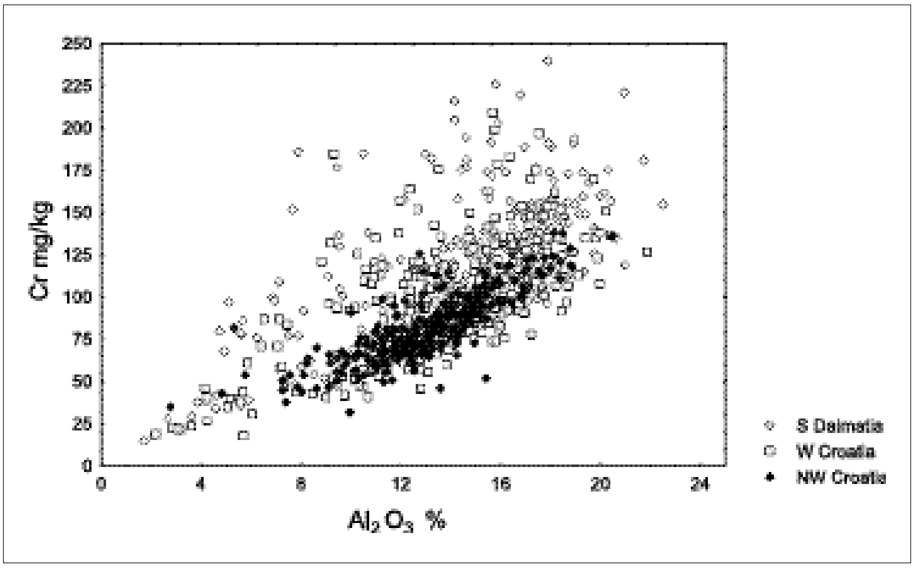

Fig. 8 The relationship between the contents of Cr and Al_2O_3 (data for W Croatia from MIKO et al., 2000, 2001).

ranges from 2 to 38 mg/kg in both regions and the mean contents in northern Croatia is 12 mg/kg and in southern Dalmatia 17 mg/kg. The highest contents of cobalt occur in terra rossa with high iron and manganese content in southern Dalmatia. In northern Croatia the high concentrations of cobalt are also controlled by bedrock lithology with elevated values in soils developed on basic and ultrabasic magmatic rocks as well as on Cretaceous flysch deposits.

Chromium (Cr)

The concentration of chromium (Plates 11 & 12) in soils ranges from 32 to 524 mg/kg with a mean value of 83 mg/kg in northwestern Croatia, whereas in southern Dalmatia range from 15 to 2,200 mg/kg with a mean value of 126 mg/kg. The higher (>83mg/kg) concentrations of Cr in fluvisols and gleys can be attributed to deposition on reducing geochemical barriers and high organic matter content in NW Croatia while the high anomalies of over 500 mg/kg near Zelina can be a consequence of chromite bearing ultramafic magmatic rocks and clastic rocks derived from older basic magmatic rocks. The highest concentrations of Cr in the karstic regions are confined to three general environments: to terra rossa soils which contain redeposited bauxite fragments (wider region of Sinjsko Polje and Imotski), the soils developed on Eocene flysch and the soils developed on Quaternary sands (Mljet Island and Korčula Island). Both the Eocene flysch and Quaternary sands are probably partly derived from basic or ultrabasic rocks. The influence of clays on Cr distribution is shown on the Cr vs. Al_2O_3 plot on Fig 8.

Copper (Cu)

The content of copper (Plates 13 & 14) in soils ranges from 5 to 248 mg/kg with a mean value of 26 mg/kg in northwestern Croatia, while in southern Dalmatia it ranges from 6 to 923 mg/kg, with the mean value of 67 mg/kg. Copper is a potential risk element and most of the elevated concentrations cannot be correlated with a certain soil type but more to agricultural activity especially the vicinity of vineyards (the application of pesticides based on copper sulphate). The anthropogenic influence on Cu distribution is shown on the Cu vs. Al_2O_3 plot on Fig. 9 indicating a divergence of data from the general Cu/Al trend.

Iron (Fe)

Iron content in soils (Plates 15 & 16) is mainly controlled by its clay content, the parent lithology and the content of carbonates just as in the case of Al. This link is stressed by high correlation (r=0.92, Tables 2 and 3) of the two elements and the similarity of distribution maps (see Plates 1 & 2). Iron contents range from 0.60% to 6.43%, with a mean value of 3.28% in northwestern Croatia while in southern Dalmatia its contents range from 0.43% to 35.0%, with a mean value of 3.94%. The lowest Fe concentrations, just as in the case of Al, are found in soils that contain higher carbonate contents such as rendzinas on dolomites and limestones, soils developed on flysch bedrock and on carbonate rich alluvium deposits along the Sava River near Zagreb, or in karst poljes which contain lacustrine sediments. In the region of southern Dalmatia the terra rossa soils regularly have the highest Fe contents >4.5%, while the alluvial and marsh soils due to dilution by carbonates have concentrations lower than 3%.

Lanthanum (La)

The La content in soils (Plates 17 & 18) seems to be mainly controlled by its clay content, and it correlates well with elements of geochemically similar behavior such as Th, and Sc (r=0.6). The correlation (r=0.45) with Al is rather low but the general trend indicates the importance of Al. The concentration of La in soils ranges from 9 to 54 mg/kg with a mean value of 34

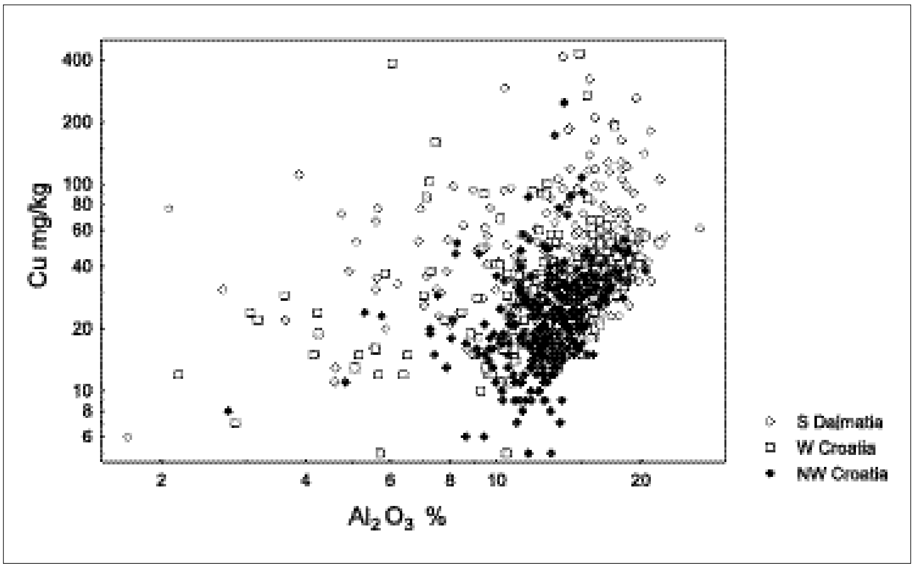

Fig. 9 The relationship between the contents of Cu and Al_2O_3 (data for W Croatia from MIKO et al., 2000, 2001).

mg/kg in NW Croatia, whereas in southern Dalmatia ranges from 4 to 109 mg/kg and the mean value of 48 mg/kg. The effect of dilution by carbonates is also evident in the distribution of this element; and the contents of La are highest in terra rossa and have mean values of 60 mg/kg which is similar to the values given by DURN (1996) for Istrian terra rossa.

Lead (Pb)

The concentration of lead (Plates 19 & 20) in soils ranges from 15 to 382 mg/kg with a mean value of 34 mg/kg in northwestern Croatia, whereas in southern Dalmatia range from 9 to 220 mg/kg and the calculated mean value is 52 mg/kg. There is a significant difference in the content of Pb in soils developed on carbonate terrain and those on non-carbonate terrains. In carbonate terrains the rendzina types of soil have higher than average contents (>60mg/kg). The effect of carbonate dilution is obvious in soils developed on clastic rocks and alluvial sediments which have low Pb contents ranging from 20 to 30 mg/kg. Higher contents of lead are also linked to higher altitudes; a similar distribution pattern impact is also encountered in mountain regions of western Croatia (MIKO et al., 2000, 2001). The anomalous lead concentrations in southern Dalmatia can be attributed partly to traffic but the influence of war activities at the beginning of the 1990s cannot be excluded. The anomalous lead concentrations were found in soils developed on the floodplain sediments of the Drava River. The source of the lead can be traced to the Pb-Zn mining regions (Mežica, Bleiburg) located in the upper coarse of the Drava River in neighbouring Slovenia and Austria. Most of the other areas in northwestern Croatia that display elevated contents of Pb can be mainly traced to past mining activities and Pb-Zn-ore occurrences; possible car traffic influences cannot be unequivocally recognized on a regional scale.

Potassium (K)

Potassium content in soils (Plates 21 & 22) ranges from 0.33% to 3.28%, with a mean value of 1.66% in northwestern Croatia, whereas in southern Dalmatia its contents range from 0.12% to 2.89%, with a mean value of 1.20%. The content of potassium in soils is besides Na and Ba the major element that discriminates the soils developed in the karst region and the soils from northwestern Croatia. In Fig 10, a S-N profile from the Adriatic coast (Lošinj and Cres Islands, through the regions of Gorski kotar to Međimurje in the north, shows a northward increasing trend in the content of these two elements. The increase is most evident to the north from the Sava River, which is also very similar with K distribution in Slovenian soils (ANDJELOV, 1994). In southern Dalmatia the highest K contents are present in terra rossa and soils developed on flysch, and in soils developed on the southern/southwestern parts of the islands Hvar, Korčula and Mljet. High K contents were also found in recent marine sediments (DOLENEC et al., 1998) in the region of these islands.

Sodium (Na)

The contents of the sodium (Plates 23 & 24) are higher in NW Croatia and range from 0.11% to 3.21%, with a mean value of 0.83%; in southern Dalmatia its contents range from 0.01% to 1.04%, with a mean value of 0.29%. The content of sodium together with Ba and K is the major element that discriminates the soils developed in the karst region and the soils from the Pannonian basin. Although the distribution pattern of sodium in soils (Plates 21 & 22) is similar to potassium in northwestern Croatia (a trend increase towards the north from the Sava River) there is an absence of significant correlation between the two elements (r=0.1), whereas in southern Dalmatia the correlation (Table 3) is significantly higher (r=0.63). The lowest concentrations of Na in the karst terrains are found in soils devel-

	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Th	Sr	V	Ca	P	La	Cr	Mg	Ba	Ti	Al	Na	K
Cu	1.00																				
Pb	0.05	1.00																			
Zn	0.12	0.96	1.00																		
Ni	0.34	0.12	0.14	1.00																	
Co	0.45	0.15	0.23	0.77	1.00																
Mn	0.26	0.16	0.18	0.34	0.53	1.00															
Fe	0.41	0.08	0.21	0.52	0.81	0.34	1.00														
As	0.28	0.24	0.24	0.41	0.44	0.24	0.37	1.00													
Th	0.19	0.02	0.06	0.24	0.37	0.04	0.46	-0.00	1.00												
Sr	0.19	0.04	0.08	0.10	0.08	0.17	-0.01	0.05	-0.09	1.00											
V	0.36	0.03	0.17	0.41	0.73	0.27	0.89	0.29	0.49	-0.05	1.00										
Ca	0.28	0.15	0.18	0.07	0.01	0.15	-0.15	0.16	-0.42	0.48	-0.29	1.00									
P	0.28	0.19	0.28	0.23	0.36	0.33	0.44	0.31	0.07	0.11	0.32	0.23	1.00								
La	0.05	-0.05	-0.04	0.09	0.18	0.08	0.24	-0.07	0.80	-0.07	0.34	-0.58	-0.03	1.00							
Cr	0.23	0.11	0.14	0.91	0.71	0.15	0.55	0.30	0.34	-0.04	0.48	-0.15	0.17	0.17	1.00						
Mg	0.09	0.25	0.27	0.01	-0.04	0.04	-0.11	0.19	-0.42	-0.00	-0.24	0.74	0.25	-0.59	-0.11	1.00					
Ba	0.07	0.14	0.20	0.08	0.18	0.08	0.24	0.02	0.20	-0.01	0.25	-0.17	0.13	0.17	0.15	-0.12	1.00				
Ti	-0.12	-0.07	-0.05	-0.12	0.06	-0.07	0.24	-0.13	0.31	-0.21	0.46	-0.71	-0.12	0.52	0.07	-0.62	0.22	1.00			
Al	0.26	0.00	0.13	0.35	0.61	0.14	0.83	0.14	0.66	-0.11	0.87	-0.40	0.26	0.47	0.47	-0.33	0.30	0.36	1.00		
Na	-0.25	0.00	-0.01	-0.28	-0.19	-0.10	-0.07	-0.16	-0.09	-0.08	0.02	-0.40	-0.16	0.23	-0.16	-0.28	0.02	0.63	-0.01	1.00	
K	0.24	0.04	0.08	0.24	0.41	0.12	0.51	0.02	0.50	0.03	0.43	-0.13	0.10	0.30	0.31	-0.14	0.31	-0.01	0.66	-0.10	1.00

Table 2 The correlation matrix for the geochemical soil data from northwestern Croatia (n=293).

oped on marls, while the highest accumulations are present in marsh sediments. In general the drained soils (developed on limestone) have the lowest Na contents in both regions. The highest concentrations of Na occur on soils developed on ortho-greenshists and spilitized basic rocks (Medvednica Mt.) in NW Croatia, these rocks seem to be an important source for Pliocene sediments that occur on the slopes of Mt. Medvednica, because the soils developed on these rocks have a similar distribution pattern as Ti (the correlation coefficient for NW Croatia is 0.62). Elevated Na contents are present in all soils that lie between the rivers Mura and Drava. The differences in contents of Na between the regions are presented in the Na vs. K plot in Fig. 11.

Magnesium (Mg)

Magnesium (Plates 25 & 26) as a major element and nutrient plays an important role in the chemistry of the

	Al	Fe	Ca	K	Mg	Na	Ti	P	Mn	Ba	V	Sr	Cr	Zn	Ni	La	Pb	Cu	Co	Th	As
Al	1.00																				
Fe	0.96	1.00																			
Ca	-0.83	-0.79	1.00																		
K	0.44	0.39	-0.51																		
Mg	-0.53	-0.54	0.38	-0.37	1.00																
Na	0.15	0.13	-0.31	0.69	-0.21	1.00															
Ti	0.90	0.93	-0.81	0.32	-0.53	0.11															
P	0.04	0.05	-0.09	0.01	-0.10	-0.08	-0.00	1.00													
Mn	0.59	0.64	-0.59	0.31	-0.50	0.11	0.62	0.26	1.00												
Ba	0.67	0.60	-0.64	0.64	-0.46	0.34	0.56	-0.01	0.51	1.00											
V	0.77	0.79	-0.62	0.21	-0.36	0.01	0.74	-0.04	0.50	0.44	1.00										
Sr	-0.50	-0.45	0.72	-0.19	-0.10	-0.13	-0.50	-0.04	-0.23	-0.32	-0.39	1.00									
Cr	0.64	0.74	-0.54	0.20	-0.48	0.11	0.69	0.11	0.56	0.30	0.62	-0.25	1.00								
Zn	0.48	0.51	-0.41	0.03	-0.32	-0.08	0.46	0.32	0.48	0.29	0.52	-0.27	0.46	1.00							
Ni	0.42	0.57	-0.34	0.15	-0.32	0.10	0.47	0.06	0.40	0.10	0.63	-0.10	0.73	0.46	1.00						
La	0.39	0.39	-0.35	0.10	-0.24	-0.02	0.43	0.02	0.29	0.24	0.31	-0.24	0.28	0.28	0.18	1.00					
Pb	0.61	0.59	-0.57	0.19	-0.29	-0.02	0.56	0.16	0.51	0.47	0.50	-0.35	0.35	0.47	0.20	0.23	1.00				
Cu	0.11	0.17	-0.03	-0.02	-0.06	0.08	0.18	0.04	0.12	-0.02	0.17	-0.01	0.18	0.27	0.30	0.13	0.10	1.00			
Co	0.70	0.81	-0.62	0.33	-0.52	0.15	0.77	0.10	0.76	0.41	0.64	-0.25	0.79	0.48	0.76	0.36	0.41	0.31	1.00		
Th	0.91	0.85	-0.78	0.38	-0.48	0.09	0.87	0.00	0.53	0.64	0.72	-0.50	0.51	0.43	0.27	0.43	0.59	0.10	0.60	1.00	
As	0.37	0.35	-0.33	0.22	-0.18	0.05	0.31	-0.08	0.22	0.29	0.43	-0.22	0.19	0.16	0.29	0.17	0.25	0.01	0.28	0.38	1.00

Table 3 The correlation matrix for the geochemical soil data from southern Dalmatia (n=404).

analyzed soils. Its contents range from 0.23 to 7.52% in northwestern Croatia and from 0.82% to 9.24% in southern Dalmatia, with mean concentrations of 1.44% and 1.19% respectively. The lowest concentrations of Mg were determined in soils developed on loess deposits and gleyic soils in northwestern Croatia and in southern Dalmatia in terra rossa and brown soils developed on limestones. Rendzinas developed on dolomite due to the large amount of fine dolomitic detritus regularly contain more than 1.5% of Mg. The scatter plot CaO-MgO (Fig. 12) shows the variation of these elements in the analyzed soils in accordance with their dolomite and calcite content (compositions of normative dolomite from EBENS & CONNOR, 1980). High magnesium contents characterize soils developed on floodplain sediments with abundant dolomite of the rivers Sava, Drava, and Neretva.

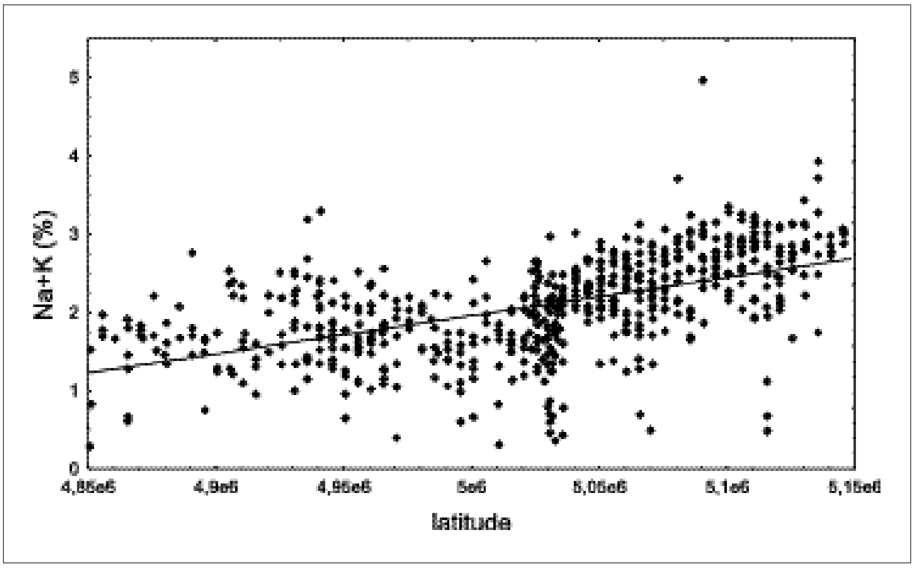

Fig. 10 The relationship between the contents of Na+K and latitude.

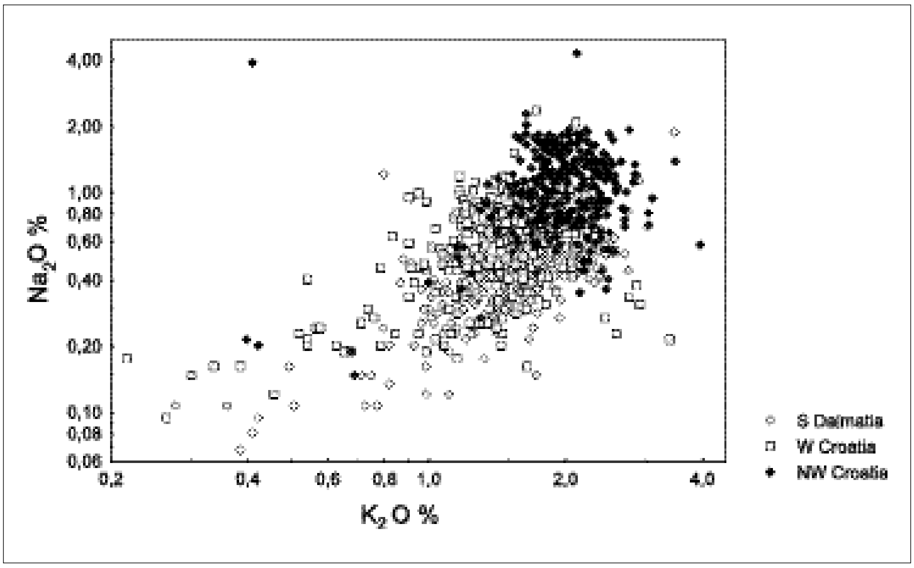

Fig. 11 The relationship between the contents of Na_2O and K_2O (data for W Croatia from MIKO et al., 2000, 2001).

Manganese (Mn)

The concentration of manganese (Plates 27 & 28) in soils ranges from 131 to 5,619 mg/kg with a mean value of 622 mg/kg in NW Croatia, and from 96 to 2,563 mg/kg in southern Dalmatia with the mean value of 971 mg/kg. In southern Dalmatia higher than 1,000 mg/kg concentrations of Mn occur in terra rossa, brown soils and rendzinas on limestones, as well as in soils developed on marls. The content of Mn in this region is lowest (<500 mg/kg) in soils, which are for some periods saturated with water and where mobilization of Mn in the soil profile is present. These are soils in large karst poljes and the floodplain of the Neretva River. Manganese hydroxides together with iron hydroxides play an important role in concentration of metals (McKENZIE, 1989) and in the case of soils developed on carbonate bedrock there is a high correlation of Mn with Co (r=0.76) while elements such as Cr, V, Ni, Pb and Zn are preferentially concentrated by iron oxides (for Mn r<0.5, for Fe r>0.5). In NW Croatia the highest concentrations of Mn are found in the eastern parts of Ivanščica Mt. and Kalnik Mt. probably as a reflection of Mn deposits and occurrences. The alluvial soils in the valleys of the Drava and Mura Rivers also have elevated contents of Mn.

Nickel (Ni)

The distribution of nickel (Plates 29 & 30) is similar to the distribution pattern of Co and is in high correlation with the distribution of Al, Fe and Mn, indicating the effect of coatings of iron and manganese hydroxides on clay mineral surfaces. The content of Ni ranges from 13 mg/kg to 427 mg/kg, with a mean value of 42 mg/kg in NW Croatia and in southern Dalmatia its contents range from 7 to 288 mg/kg, with a mean value of 84 mg/kg. The high concentrations near Zelina are a consequence of basic and ultrabasic magmatic bedrocks. These rocks are probably sources of Ni in alluvial soils that occur in floodplains of rivers (central northwestern Croatia) that drain this region. The highest concentrations of Ni in

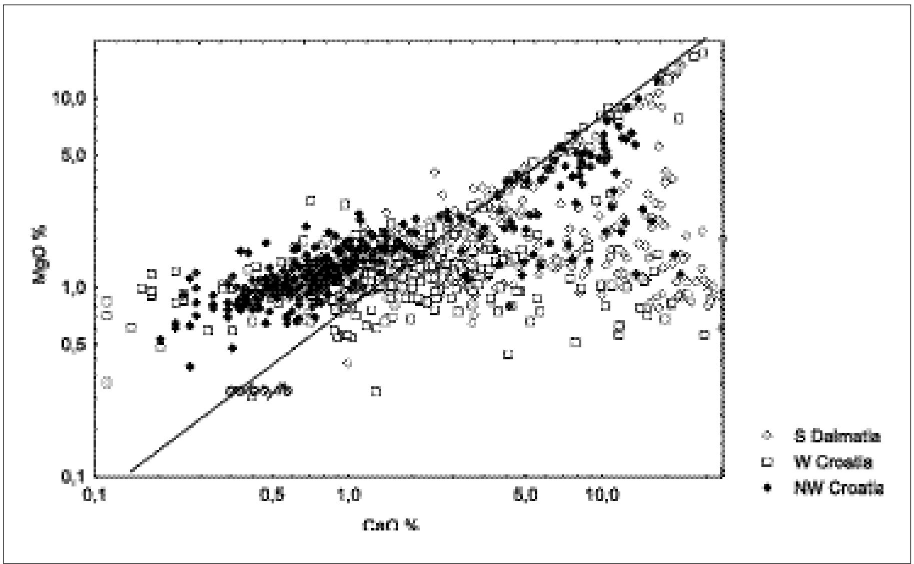

Fig. 12 The relationship between the contents of MgO and CaO. Dolomite = normative dolomite from EBENS & CONNOR, 1980) (data for W Croatia from MIKO et al., 2000, 2001).

the karstic regions are confined to three soil types, the terra rossa soils, the soils developed on Eocene flysch (the wider region of Dubrovnik) and the soils developed on Quaternary sands (Mljet Island and Korčula Island). Both the Eocene flysch sedimentary rocks and Quaternary sands are probably partly derived from weathering products of basic magmatic rocks.

Phosphorus (P)

Phosphorus (Plates 31 & 32) contents range from 0.02% to 0.19%, with a mean value of 0.064% in northwestern Croatia; in southern Dalmatia its contents range from 0.012% to 0.68%, with a mean value of 0.08%. The lowest concentrations of P are found in soils of the islands Korčula, Hvar and Mljet in southern Dalmatia. The type of soil seems to have little influence on the content of P in the karst region since the variation and means are similar for all soil types; only soils on flysch (sandstones and marls) have in general lower P contents (<0.06%). In NW Croatia there is also obvious correlation of P content and soil type but in general forest soils have the lowest (median = 0.04%) content and the arable soils the highest (median = 0.09%) content. The anthropogenic influence on the distribution of this nutrient is evident since highest concentrations are found in agricultural regions.

Scandium (Sc)

The Sc content in soils (Plates 33 & 34) is mainly controlled by its clay content, and it shows a high correlation with Al and Fe (r=0.9). Geochemically it is considered a conservative element similar to Al and is also often used for normalization procedures. The concentration of Sc in soils ranges from 2 to 18 mg/kg with a mean value of 9 mg/kg in NW Croatia, and in southern Dalmatia it ranges from 4 to 34 mg/kg, with the mean value of 12 mg/kg. The effect of dilution by carbonates is also evident in the distribution of this element; the contents of Sc are highest in terra rossa while the soils developed on marls and carbonate alluvial sediments have the lowest contents.

Strontium (Sr)

The distribution of strontium (Plates 35 & 36) is similar in some aspects to the distribution pattern of Ca. The dissimilarity occurs in soils developed on dolomite, since these soils contain high Ca contents but lack strontium whose concentrations are low in dolomite and alluvial sediments containing dolomite. The content of Sr ranges from 45 mg/kg to 1,090 mg/kg, with a mean value of 118 mg/kg in NW Croatia; in southern Dalmatia its contents range from 40 mg/kg to 476 mg/kg, with a mean value of 127 mg/kg. The high content of strontium is found in both regions in soils developed on Tertiary lacustrine marls, on flysch bedrock, soft limestones and in alluvial valleys in the karst regions that during flooding have features of intermittent lakes (Vrgoračko polje). Soils on dolomitic bedrock and terra rossa on limestone have low Sr contents (<90 mg/kg).

Titanium (Ti)

Titanium content (Plates 37 & 38) ranges from 0.08% to 1.09%, with a mean of 0.39% in northwestern Croatia, whereas in southern Dalmatia its content ranges from 0.05% to 0.87%, with a mean of 0.37%. The lowest Ti contents are found in soils that contain higher carbonate contents such as rendzinas on dolomites and limestones, soils developed on flysch bedrock and on carbonate rich alluvium deposits along the Sava River near Zagreb, or in karst poljes which contain lacustrine sediments. The high correlation (r=0.9) of Ti with Al and Fe in soils from southern Dalmatia (Table 3) is indicative of similar processes of enrichment. In soils from NW Croatia there is an absence of such relation-

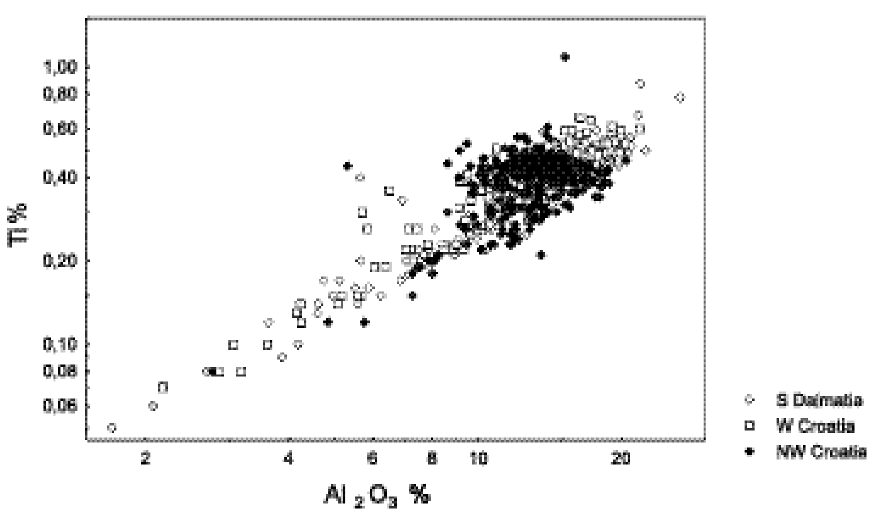

Fig. 13 The relationship between the contents of Ti and Al_2O_3 (data for W Croatia from MIKO et al., 2000, 2001).

ships (Al vs. Ti r=0.37; Fe vs. Ti r=0.24; Table 2), and the highest contents of Ti are confined to gleys developed on loess, and in marshlands.

The highest contents of Ti are found in soils overlying basic magmatic and ortho-greenschist metamorphic complexes on Medvednica Mt. The distribution differences between the karst region and the Pannonian region is illustrated on the plot Ti vs. Al_2O_3 in Fig. 13.

Thorium (Th)

The concentration of Th in soils (Plates 39 & 40) ranges from 2 to 17 mg/kg with a mean value of 11 mg/kg in NW Croatia, whereas in southern Dalmatia it ranges from 2 to 29 mg/kg, with the mean value of 16 mg/kg. The thorium content in soils has a high correlation with Al and Fe (r=0.8 in southern Dalmatia, r=0.7 in NW Croatia). The effect of dilution by carbonates is also evident in the distribution of this element, and the contents of Th are highest in terra rossa while the soils developed on marls and carbonate alluvial sediments have the lowest contents.

Vanadium (V)

The content of vanadium in the analyzed soils (Plates 41 & 42) ranges from 22 to 238 mg/kg, with a mean value of 101 mg/kg in NW Croatia; whereas in southern Dalmatia its contents range from 16 mg/kg to 386 mg/kg, with a mean value of 142 mg/kg. The distribution of V similar to the distribution patterns of Al and Fe (r=0.9) indicates the role played by coatings of iron hydroxides on clay mineral surfaces (SCHWERTMAN & TAYLOR, 1989). The highest contents of V similar to Ti are found in soils overlying basic magmatic and ortho-greenschist metamorphic rock complexes on Medvednica Mt. The highest concentrations of V in the karstic regions characterize the terra rossa, while soils developed on Eocene flysch (the wider region of Dubrovnik) and the soils developed on Quaternary sands (Mljet Island and Korčula Island) as well as alluvial (with carbonates) soils have low concentrations of vanadium.

Zinc (Zn)

The content of Zn (Plates 43 & 44) ranges from 28 mg/kg to 974 mg/kg, with a mean value of 92 mg/kg in NW Croatia; in southern Dalmatia its contents range from 16 to 491 mg/kg, with a mean value of 113 mg/kg. There is a significant difference in the behavior of Zn in soils developed on carbonate terrain and those on non-carbonate terrains. In carbonate terrains Zn is controlled by the clay content (Zn-Al correlation coefficient r= 0.48, Table 3) and higher contents are the characteristic of rendzina type of soils as well as of soils developed at higher altitudes (<140 mg/kg), which is similar to the distribution of Pb (r=0.47). The effect of carbonate dilution is obvious in soils developed on clastic rocks and alluvial sediments, which have low Zn contents (<75 mg/kg). Anomalous lead concentrations in NW Croatia are found in soils developed on the floodplain sediments of the Drava River. The sources of the Zn, as in the case of Pb (r=0.96, Table 2) can be traced to the Pb-Zn mining regions (Mežica, Bleiburg) located in the upper course of the Drava River in neighbouring Slovenia and Austria. Most of the other areas in northwestern Croatia that display elevated contents of Pb can be mainly traced to past mining activities and Pb-Zn ore occurrences, although other possible anthropogenic influences cannot be unequivocally recognized, especially in the lower course of the Sava River.

Mercury (Hg)

The content of mercury at this stage of investigation was determined only in soils from northwestern Croatia (Pl. 45). The Hg concentrations range from values below 10 μg/kg to 4,535 μg/kg, with a mean value of

94 μg/kg. The highest concentration of 4,535 μg/kg was measured in soils developed on limestone from a location on Kalnik Mt. The sources of this high Hg contents, as well as the high contents on the neighboring Ivanščica Mt. are probably a consequence of mineralization occurrences. Urban soils in general have higher Hg contents especially in the cities of Zagreb and Varaždin. High contents of Hg in urban soils of Zagreb were also determined by NAMJESNIK et al. (1992) and PALINKAŠ et al. (1996); in a study by MIKO et al. (1992) it was determined that the Hg is derived from fossil fuel consumption (coal). The elevated Hg contents in soils developed on the Sava River floodplain sediments is a consequence of material derived from the Litija mining region which produced 150 t of Hg from 1880 to 1965 (MLAKAR, 1993). The soils of the region of Samoborska gora Mt. (Rude) also contain elevated Hg contents as a response of base metal sulphide mining and occurrences of mineralization.

4.2. Geochemical associations and environmental applications

Geochemical baselines are principally useful for the determination of environmentally significant contents of elements for the evaluation of pollution sources. Since the variation of geology at a regional scale influences the geochemical background considerably the definition of these values must be performed in a correct manner. There are various approaches in use depending on the type of data, media, and analytical techniques (DARNLEY, 1995; SALMINEN & TARVAINEN, 1997; BODIŠ & RAPANT, 2000). The legislative approach uses the geochemical data for comparison with defined environmental thresholds as in the Netherlands (VAN LIENEN et al., 2000) or the intervention criteria in Italy as used by De VIVO et al. (1998). Today in Croatia only agricultural thresholds for ten potentially toxic elements (Pb, As, Cd, Co, Ni, Zn, Cu, Hg, Mo and Cr) (NARODNE NOVINE, 1992) exist which were derived from a small data set and compiled from regulations of other countries.

The human impact on soils can be also evaluated by calculation of enrichment factors (HASSAN & ISMAIL, 1993). The enrichment factor (EF) is the concentration ratio of an element in each individual sample ($C_{nsample}$) and the conservative element (usually Al, Ti, Sc) in the sample ($C_{cons.sample}$), in respect to same ratio of element and the conservative element in a reference material $C_{n\ ref.}/C_{cons.\ ref.}$ (FÖRSTNER & WITTMANN, 1981; LI, 1981):

$$EF = (C_{nsample}/C_{cons.sample}) \; / \; (C_{n\ ref.}/C_{cons.\ ref.})$$

The definition of the enrichment factor indicates that this parameter depends on the choice of reference element and the choice of reference material.

The influence of referent element choice upon the value of enrichment factor is discussed in papers of numerous authors, but Al is the commonest in use and its correlation with the clay content in sediments and soils, is well established (WINDOM et al., 1989; DURN et al., 1999) and has been quite frequently applied in the karst regions of Croatia (PROHIĆ et al., 1995, 1998; MIKO et al., 1999). According to the criteria of GOLCHERT et al. (1991) who distinguish three categories of the enrichment factors: EF≤2, 2<EF<10 and EF≥10, where EF lower than 2 indicates a natural variation of an element and those higher than 10 indicate severe pollution, MIKO et al. (2000) determined moderate (2<EF<10) Pb pollution of soils in Western Croatia as a consequence of acid rain deposition. The calculated enrichment factors for Pb for the whole data set show that 50 sampling sites have EFs higher than 2, of which 25 are situated in the region of Western Croatia and within the Risnjak national park, i.e. approximately 4% of the sites can be considered as moderately enriched (polluted) either from mining activities or airborne deposition. Only a limited number of sampling sites can be directly linked with mineralization. This calculation of Pb enrichment factors is based on the median values of Pb (42 mg/kg) and Al (7,32 %) for the whole data set as the reference material. Due to significant concentration differences of Pb in soils developed on carbonate bedrock (48 mg/kg) and non karstic terrain (30 mg/kg), an universal reference material for the whole territory of Croatia was found not to be appropriate in this case, since it would give an underestimate or overestimate of the EF as in the case of Pb (Fig. 14).

Statistical analysis has been frequently employed both in exploration geochemistry and environmental geochemistry for determination of baseline values and as a tool for distinguishing between geogenic and anthropogenic effect. Most frequently used are those techniques based on correlation coefficients such as cluster analysis and factor analysis. The later was applied by authors in the neighbouring countries (De VIVO et al., 1997; 1998a; ŠAJN et al., 1998) and in Croatian karst regions (PROHIĆ et al., 1997, 1998; MIKO et al., 2000). The derived factors are usually interpreted as associations of elements that imply a common source or behavior in regard to geogenic or anthropogenic influences. In our case, it was found that difference between the northwestern Croatia and southern Dalmatia is expressed not only by concentration differences but also by element associations.

Element associations in Southern Dalmatia

A five-factor model accounting for 74% of the data variability seemed appropriate to portray the geochemical variability within the topsoil in southern Dalmatia.

The Th, Al, Fe, Ti, (-Ca), V, Pb, Ba, Mn, and La factor (Table 4) accounts for 38% of the total data variability. The factor scores distribution patterns show the low values for soils developed in alluvial plains, dolomites and flysch bedrock (high concentrations of Ca), while the high values correspond to brown soils on

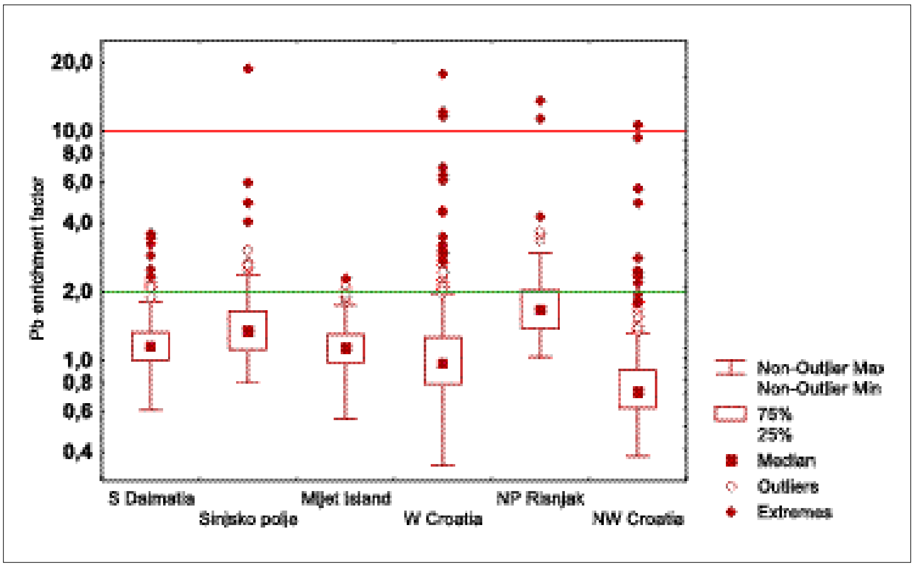

Fig. 14 The range of Pb enrichment factors in soils from different regions in Croatia.

limestone, and terra rossa. This element association is the major geogene association of soils developed on Croatian karst (PROHIĆ et al., 1998; MIKO et al., 1999, 2000) and can be termed as the clay factor.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Al	0.91				
Fe	0.87				
Ca	-0.81				
Ti	0.88				
Mn	0.56				
Ba	0.64	0.58			
V	0.76				
Th	0.93				
As	0.45				
La	0.48				
Pb	0.68			0.47	
K		0.88			
Na		0.91			
Cr		0.63			
Ni		0.84			
Cu		0.66			
Co		0.64			
P				0.87	
Altitude				0.54	
Zn			0.50		
Mg					-0.72
Sr				0.67	
Expl. Var	8.38	2.34	2.74	1.47	1.42
Prp. Totl	0.38	0.11	0.12	0.07	0.06

Table 4 Varimax rotated factor matrix for the topsoil geochemical data from southern Dalmatia (n= 404).

The most interesting association in a geogene sense is the K-Na-(Ba) factor (factor 2) with high scores associated with soils on the Adriatic islands of Mljet, Korčula and Hvar, and slightly lower values on the island of Brač and the Pelješac peninsula. High concentrations of the elements of factor 2 were also observed in surficial sediments from the southern part of the Adriatic Sea by DOLENEC et al. (1998). The association of elements and its spatial distribution implies an aeolian influence connected to the development of soils on mainly aeolian Quaternary sediments, whose source was probably the Po River plain; although some analysis of deeper profiles on the western part of Korčula Island have shown extremely high contents of Na, K, Ba, La, Sr and Th indicating tephra type of material deriving possibly from Italian volcanos (Vesuvius). A detailed mineralogical analysis is yet to prove this asumption.

Factor 3 with high loading for Cr, Ni, Co, and Cu is hard to interpret unequivocally because in some regions it might reflect possible bauxitic influence while in others, it reflects probably mafic components of weathered clastic materials (mainly flysch deposits and sands derived from these deposits - eastern parts of Korčula and Mljet islands). The association of elements (P, Zn, altitude and Pb) loaded on Factor 4 is interpreted as reflecting an anthropogenic source for Zn, P and Pb. This is very similar to the mountainous karst regions of western Croatia (Risnjak national park and the Velebit massif) where a similar distribution pattern is also present (MIKO et al., 2000, 2001). The high positive scores that correlate positively with altitude are interpreted as a consequence of acid rain deposition; a very similar association of elements is found in the mountainous regions of central Europe (MATSCHULLAT & BOZAU, 1996). Factor 5 (Sr, Mg) spatially corresponds to soils developed on lacustrine sediments in karst poljes and the marl deposits that surround the Sinj Polje.

Element associations in northwestern Croatia

The geochemical variability within the topsoil in northwestern Croatia can also be described by a five-factor model, which accounts for 71% of the data variability. Although there is some similarity in the element associations, there are also some significant differences and none of the element associations dominate. The weathering of basic magmatic rocks and ortho-greenschists seem to be an important supply of material for both older sedimentary rocks and recent soils in the region which resulted in a corresponding suite of elements comprising Ni, Cr, Co, Fe, V and As (Factor 1, Table 5). This factor accounts for 18% of the data variability, and is similar to factor 4 (Al, Th, K, La and Ba) with high factor scores related to eugleys (marsh soils). The factor 2 has high positive loadings for Mg and Ca and coincides with the dilution effect caused by the presence of dolomite in alluvial soils and rendzinas developed on dolomite. The negative loadings of Ti and Na on this factor is a result of dilution by the former elements and their common source. This factor accounts for 13% of the data variability. The Pb-Zn (Factor 3) association also accounts for 13% of the data variability and is a consequence of secondary dispersion from mining activities (floodplain of the Drava River) and sulphide ore occurrences in the mountainous regions. The pollution effects caused by human activities (besides mining) cannot be unequivocally deduced especially in the floodplain regions that are both urbanized (Zagreb, Karlovac and Varaždin) and have in the past been flooded by waters that drained various mining regions. Factor 5 (Mn, Cu, P and Sr) accounting for 10% of the total data variability, correlates especially well with arable soils and wine producing areas.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Ni	0.88				
Cr	0.87				
Co	0.82				
Fe	0.66				
V	0.58				
As	0.57				
Mg		0.59			
Ca		0.69			
Na		-0.79			
Ti		-0.90			
Zn			0.94		
Pb			0.96		
Al				0.75	
Th				0.84	
K				0.76	
La				0.67	
Ba				0.45	
Mn					0.58
Cu					0.53
P					0.57
Sr					0.60
Prp. Totl	**0.18**	**0.13**	**0.13**	**0.17**	**0.10**
Expl.Var	**3.88**	**2.85**	**2.87**	**3.63**	**2.13**

Table 5 Varimax rotated factor matrix for the topsoil geochemical data from northwestern Croatia (n= 293).

5. CONCLUSIONS

The results of geochemical baseline mapping performed in two different parts of the Croatia whose soils originated on different geological substrates, 1) predominantly non-carbonate terrains (northwestern Croatia) and 2) predominantly carbonate terrains (southern Dalmatia), show that Al, As, Co, Cu, Fe, La, Pb, Ni, Mn, Th, V, Cr, and Zn have higher median values in soils developed on carbonate bedrock, with the exception of Na, K, Fe and Ba, which have higher concentrations in soils of the Pannonian part of Croatia.

The relatively small variation in the content of trace elements in soils of northwestern Croatia is probably due to the relatively limited area that was sampled and was also confirmed by different element associations in the two regions.

The application of different techniques on the geochemical data set for the determination of environmentally significant contents of elements in order to evaluate the pollution sources must be in the future viewed in accordance with geological variability of Croatia. Since the variation of geology at a regional scale influences the geochemical background considerably the definition of these values in future will be assessed when geochemical mapping at this density is concluded for the whole country.

Acknowledgments

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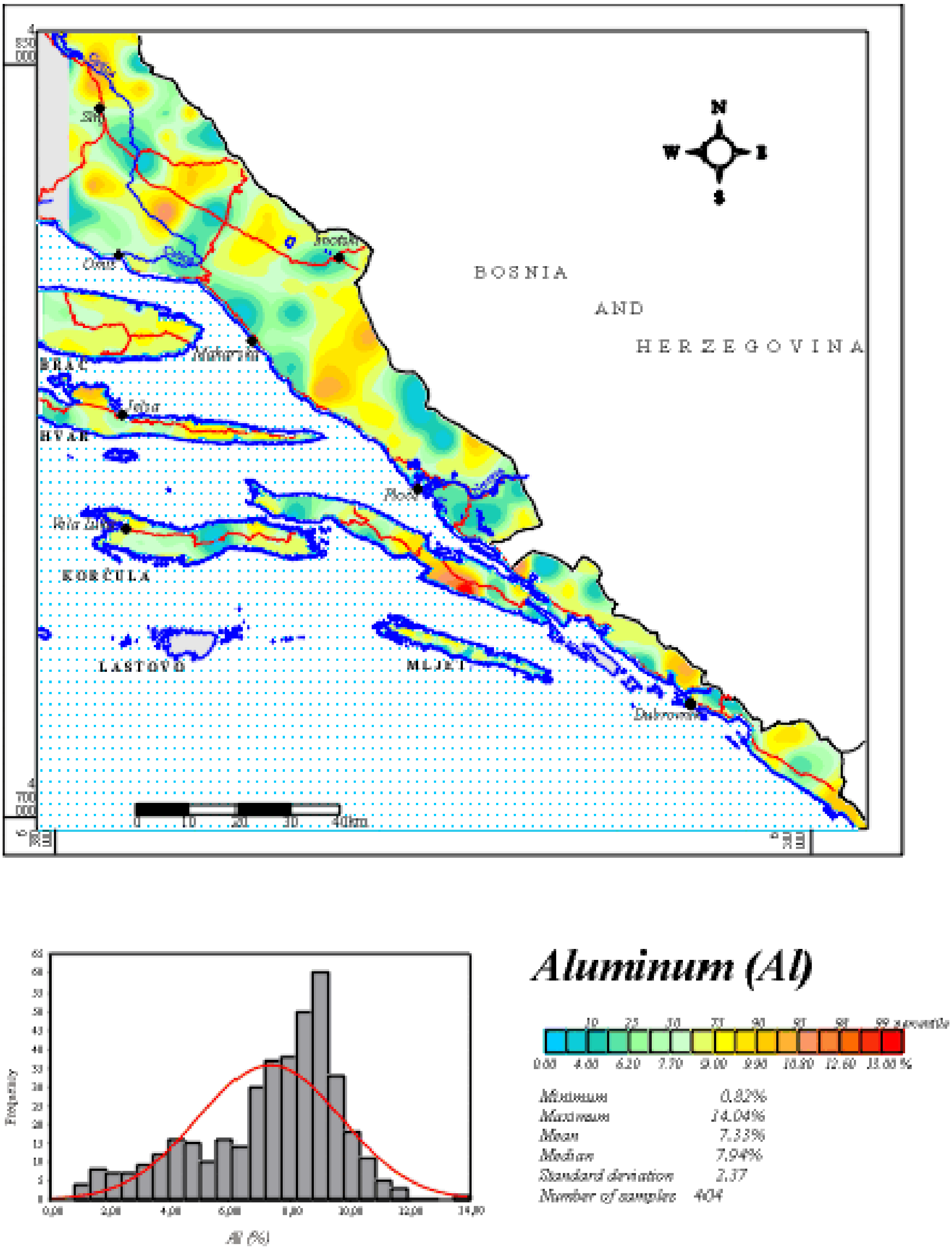


PLATE 1

The distribution of Al in soils from S Dalmatia.

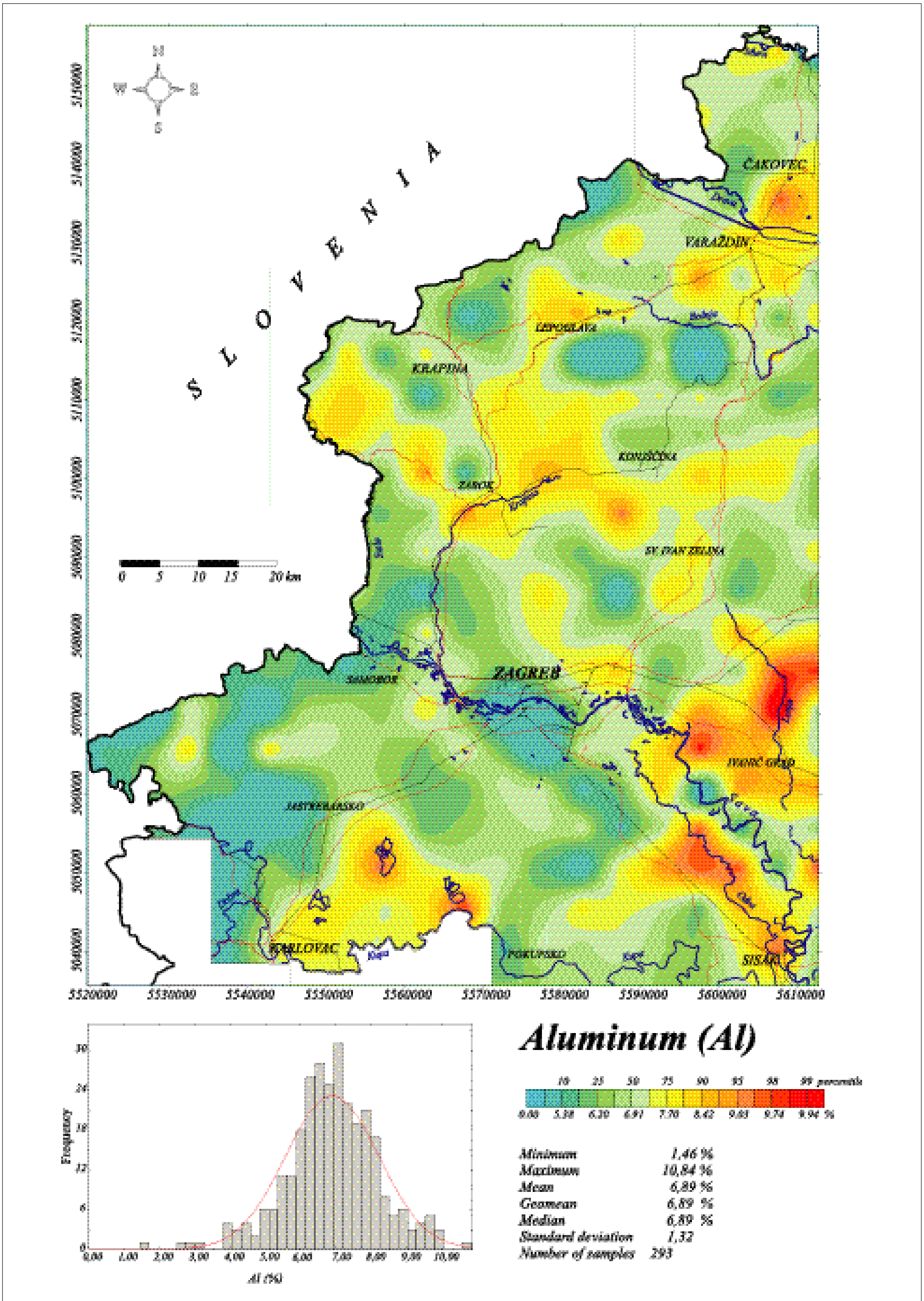


PLATE 2

The distribution of Al in soils from NW Croatia.

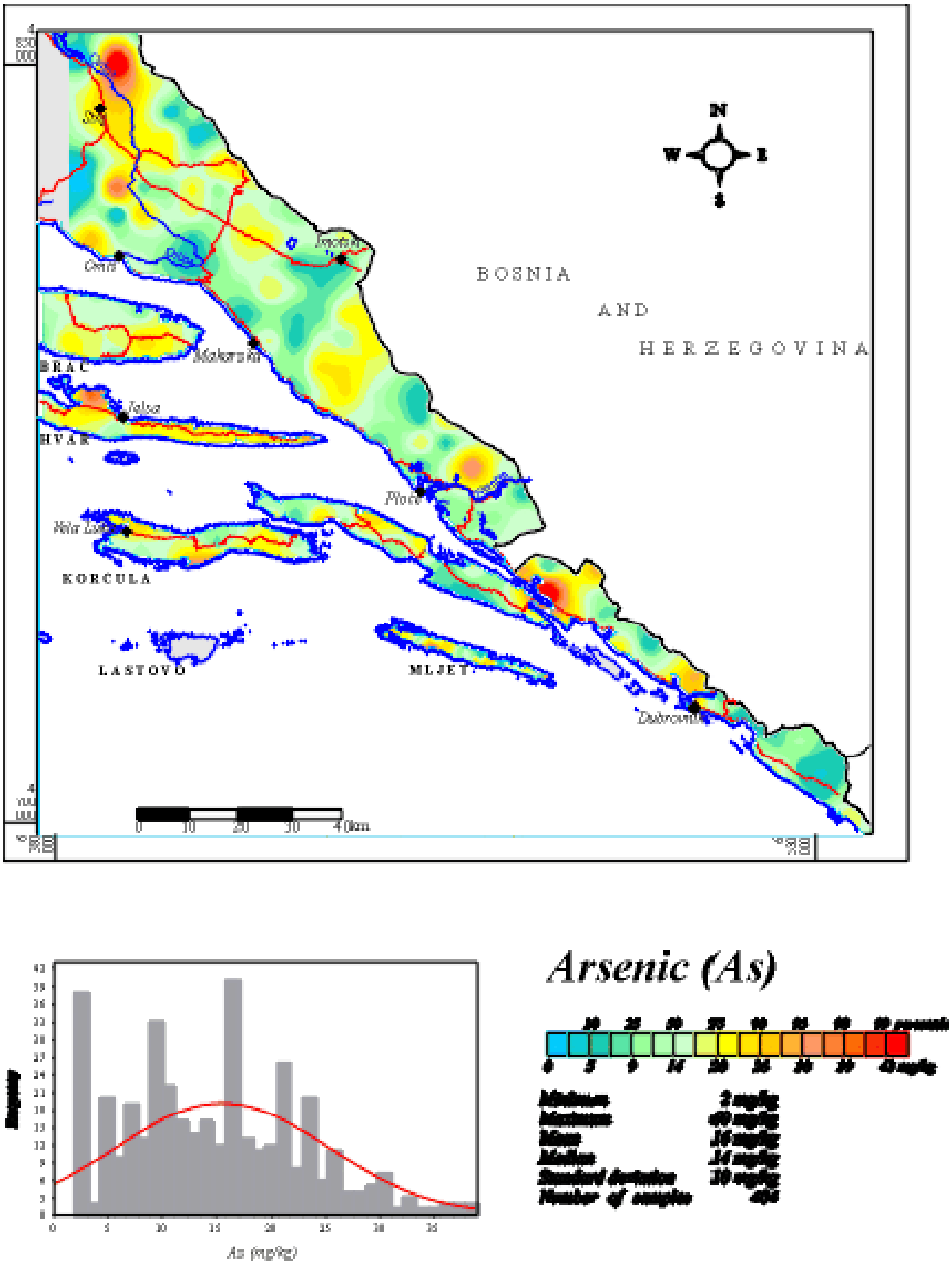


PLATE 3

The distribution of As in soils from S Dalmatia.

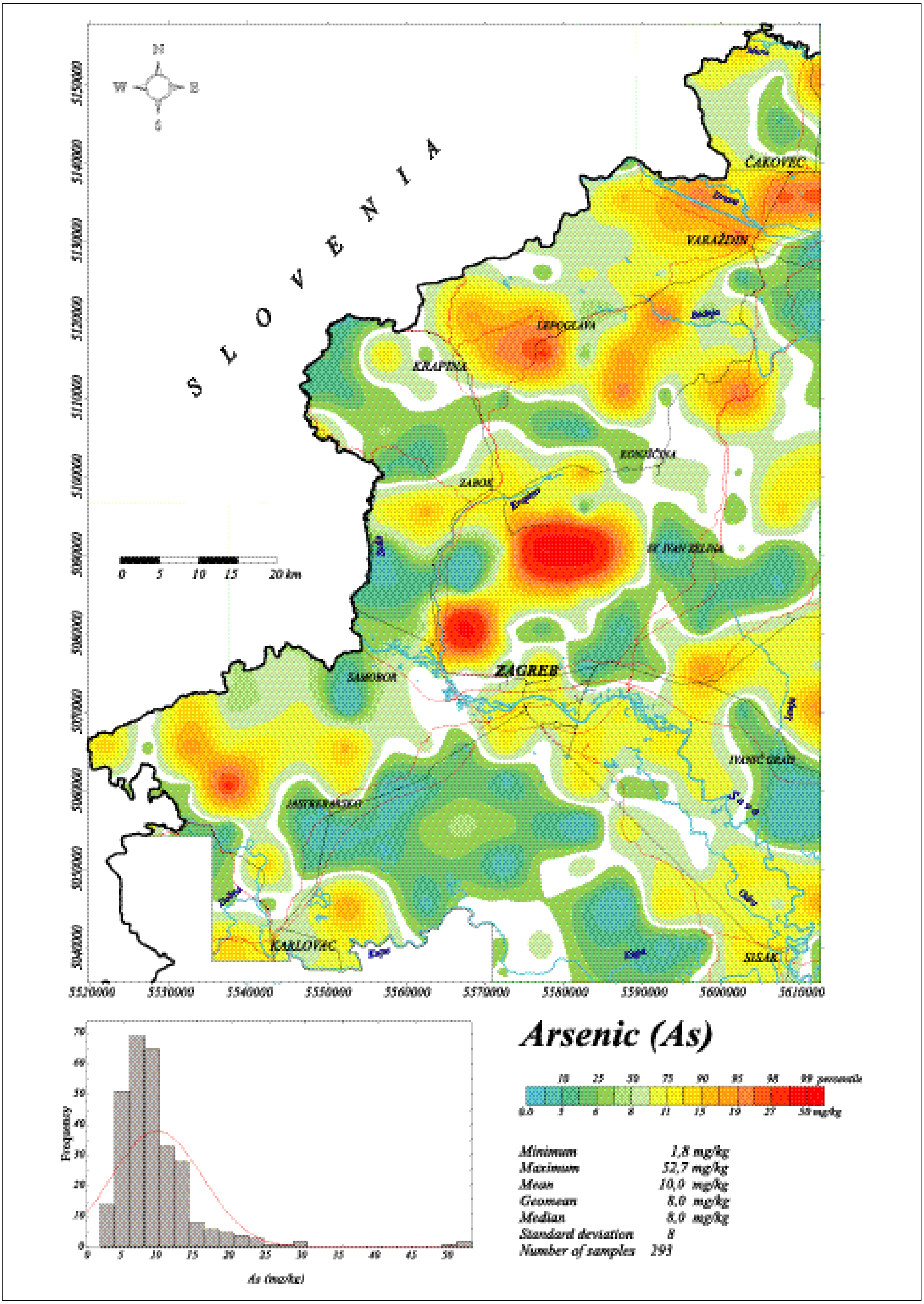
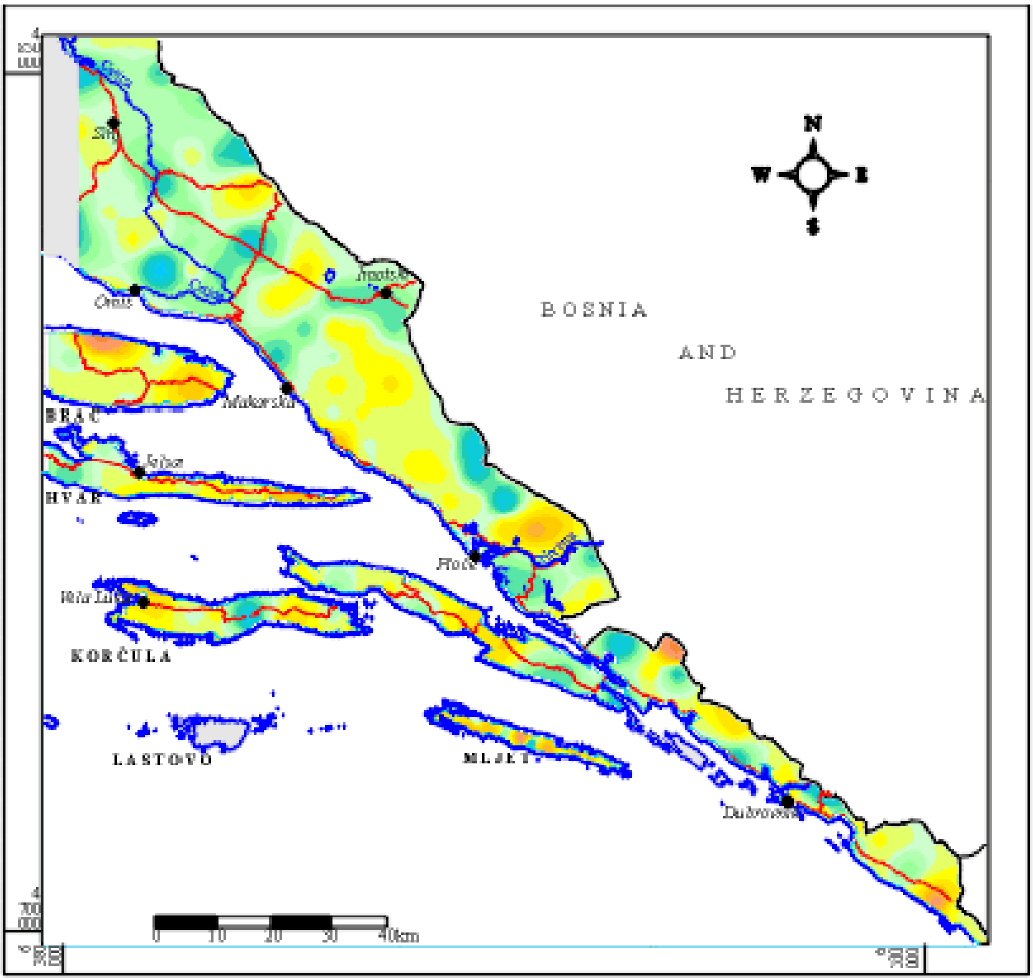
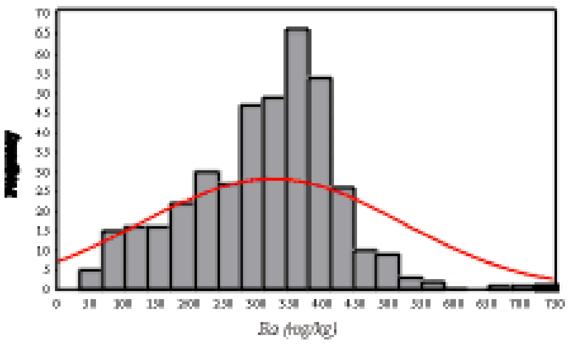


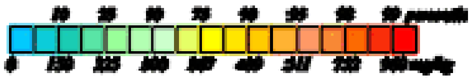
PLATE 4

The distribution of As in soils from NW Croatia.





Barium (Ba)



Minimum	35 mg/kg
Maximum	2610 mg/kg
Mean	324 mg/kg
Median	330 mg/kg
Standard deviation	195
Number of samples	404

PLATE 5

The distribution of Ba in soils from S Dalmatia.

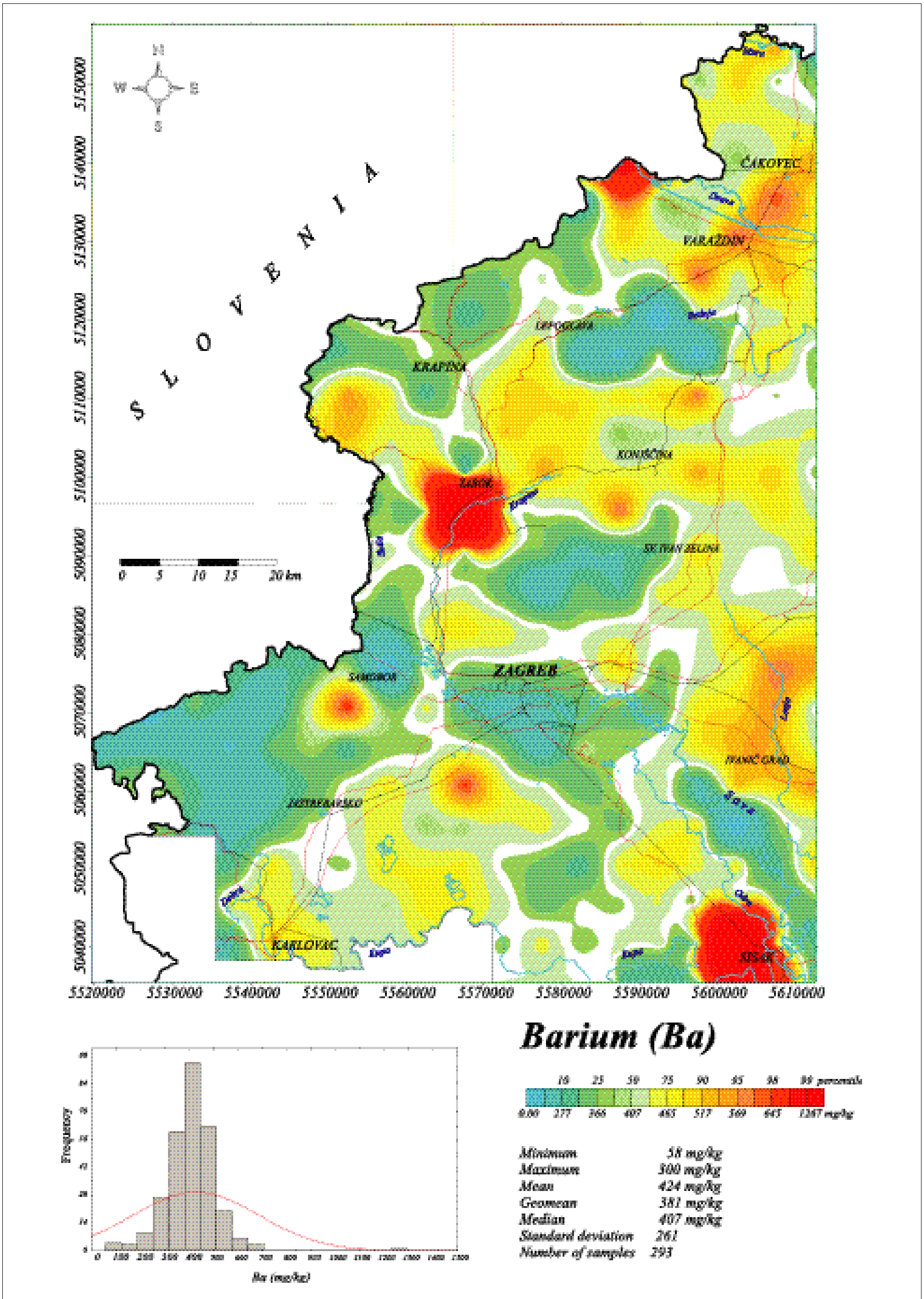


PLATE 6

The distribution of Ba in soils from NW Croatia.

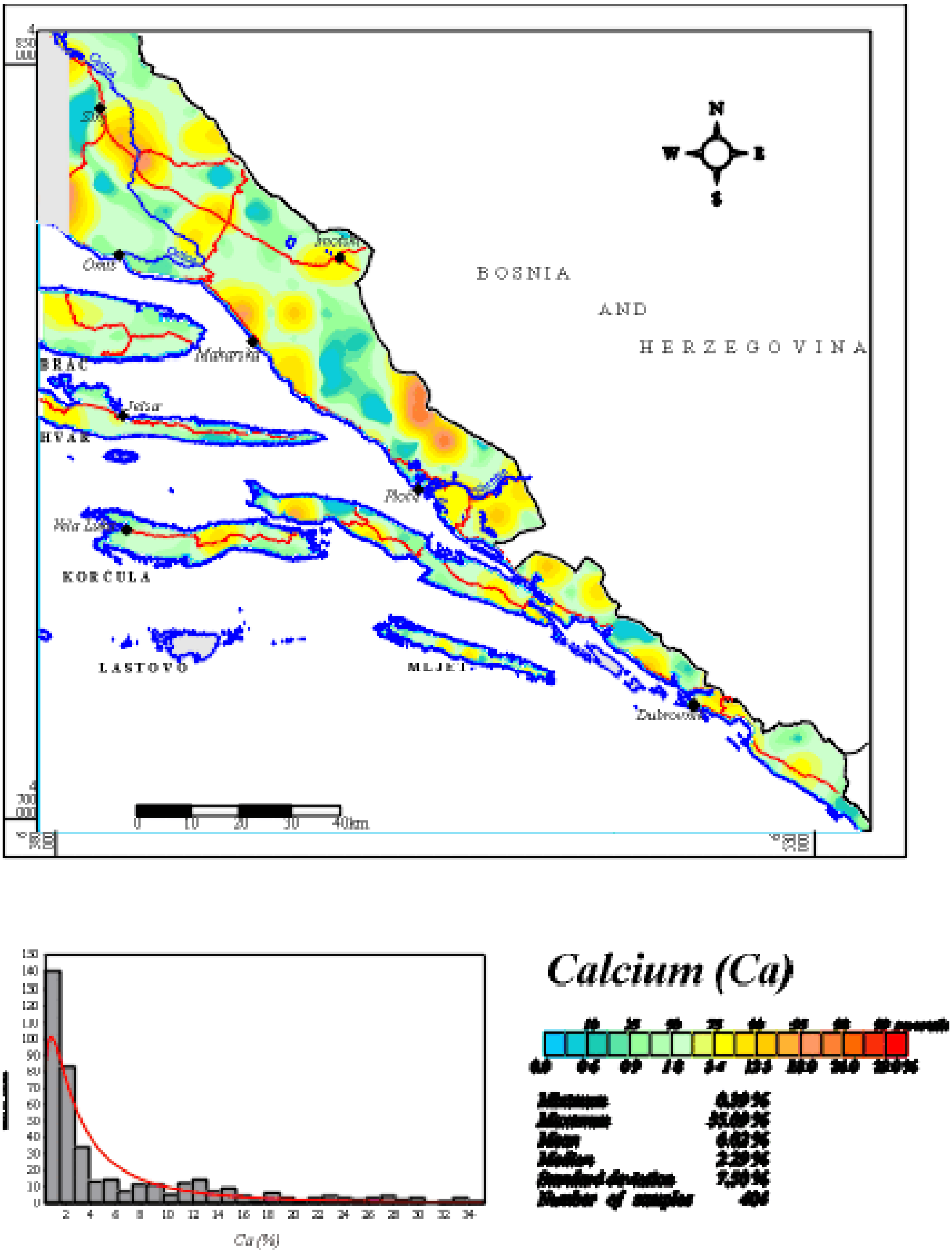


PLATE 7

The distribution of Ca in soils from S Dalmatia.

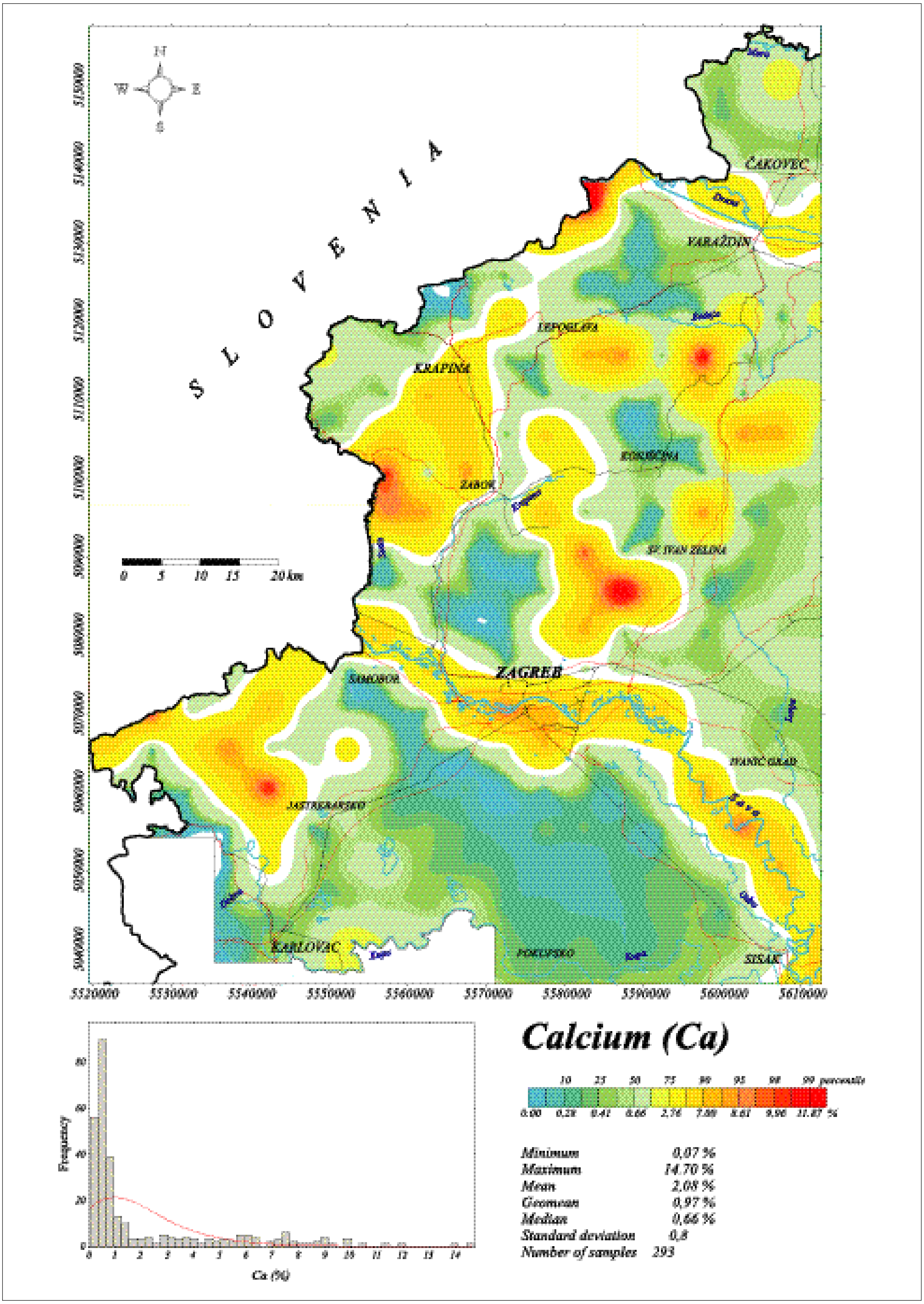


PLATE 8

The distribution of Ca in soils from NW Croatia.

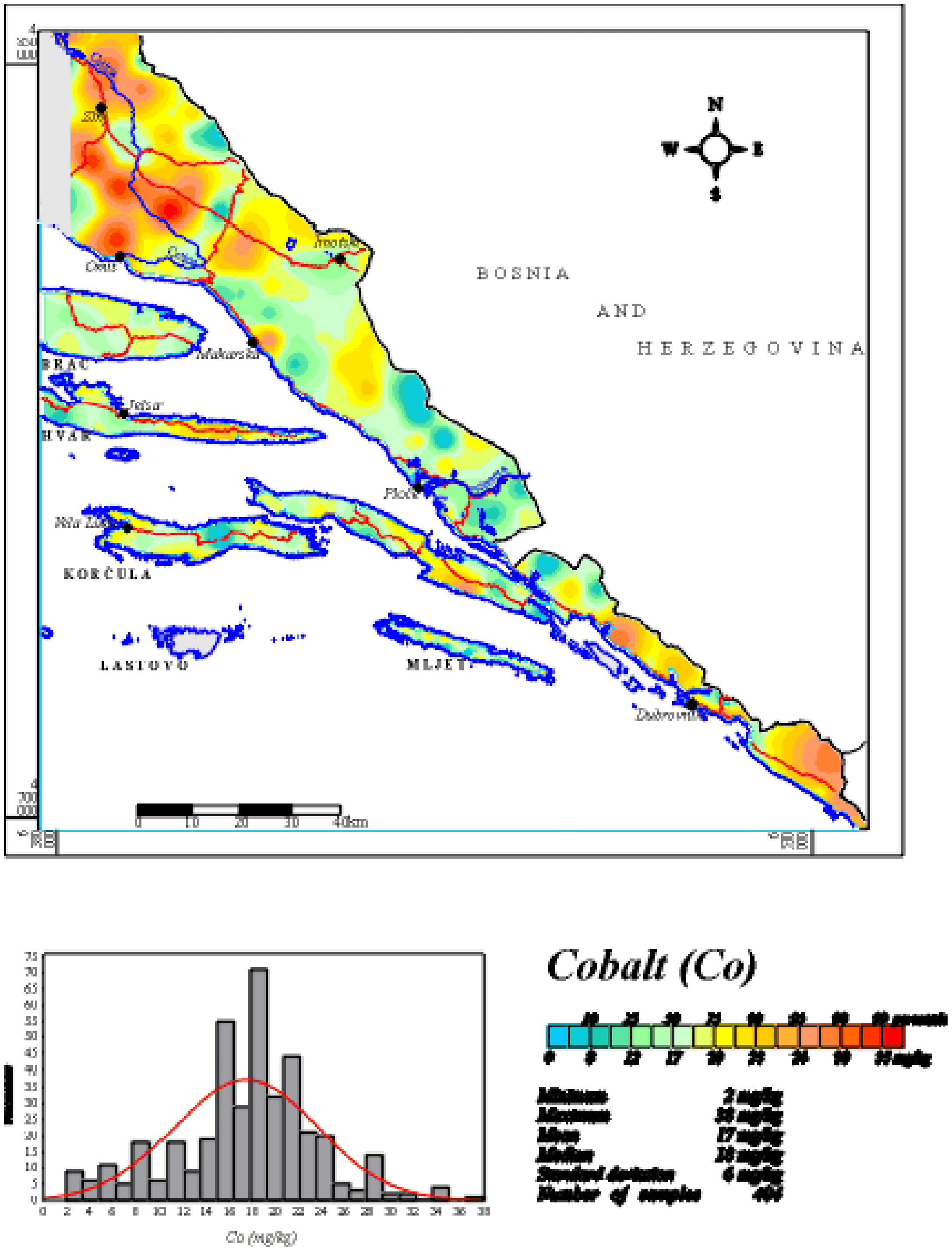


PLATE 9

The distribution of Co in soils from S Dalmatia.

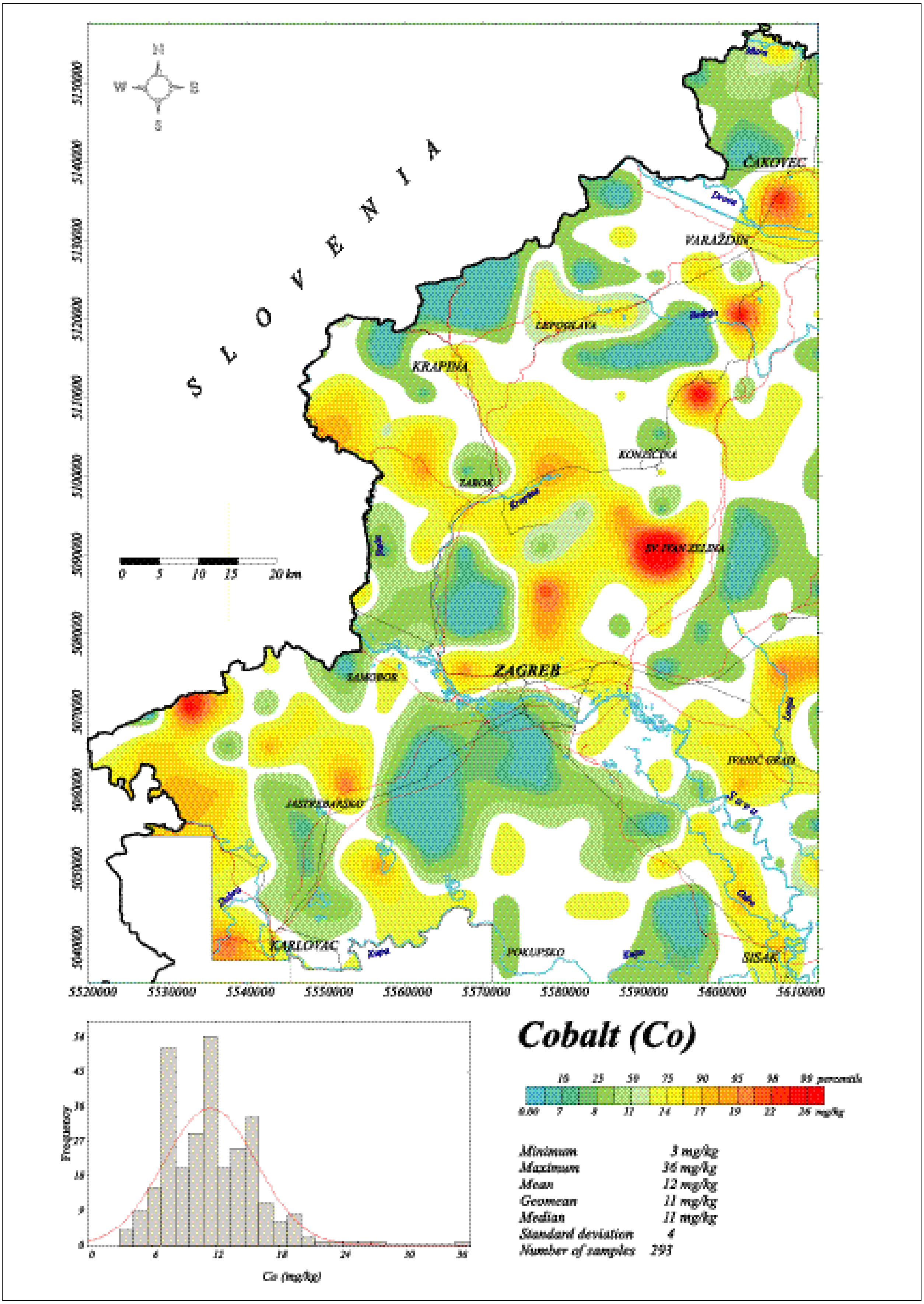


PLATE 10

The distribution of Co in soils from NW Croatia.

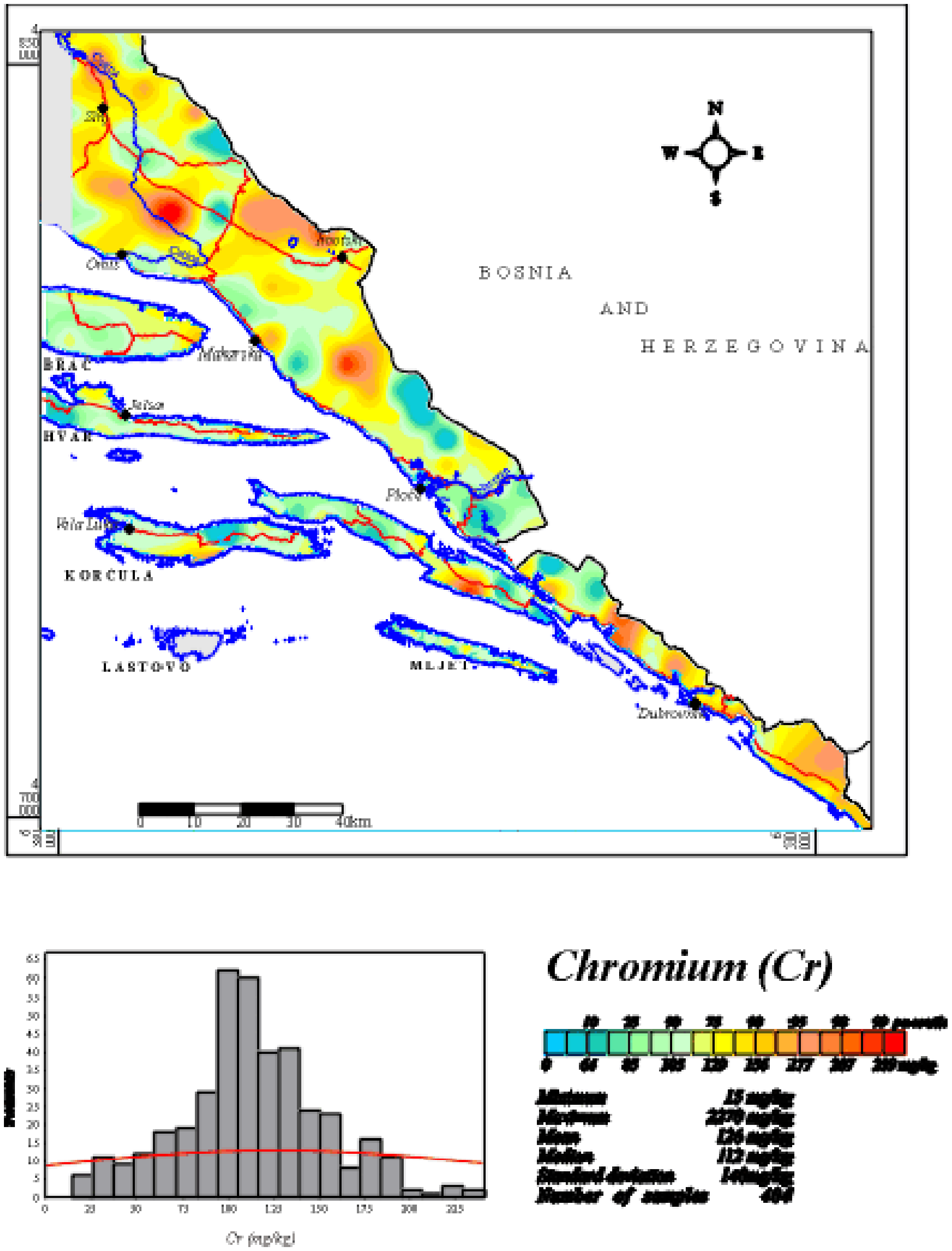


PLATE 11

The distribution of Cr in soils from S Dalmatia.

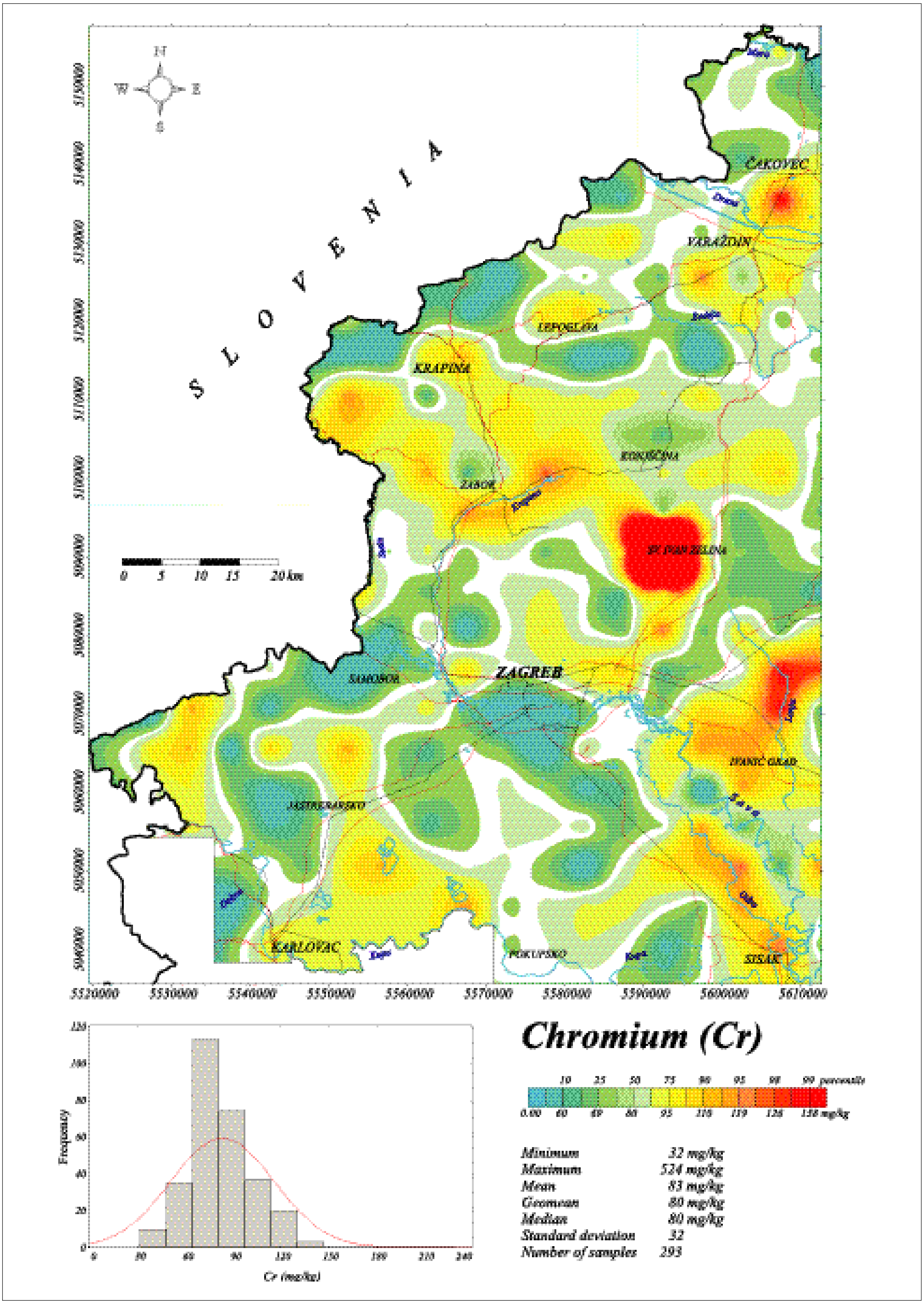


PLATE 12

The distribution of Cr in soils from NW Croatia.

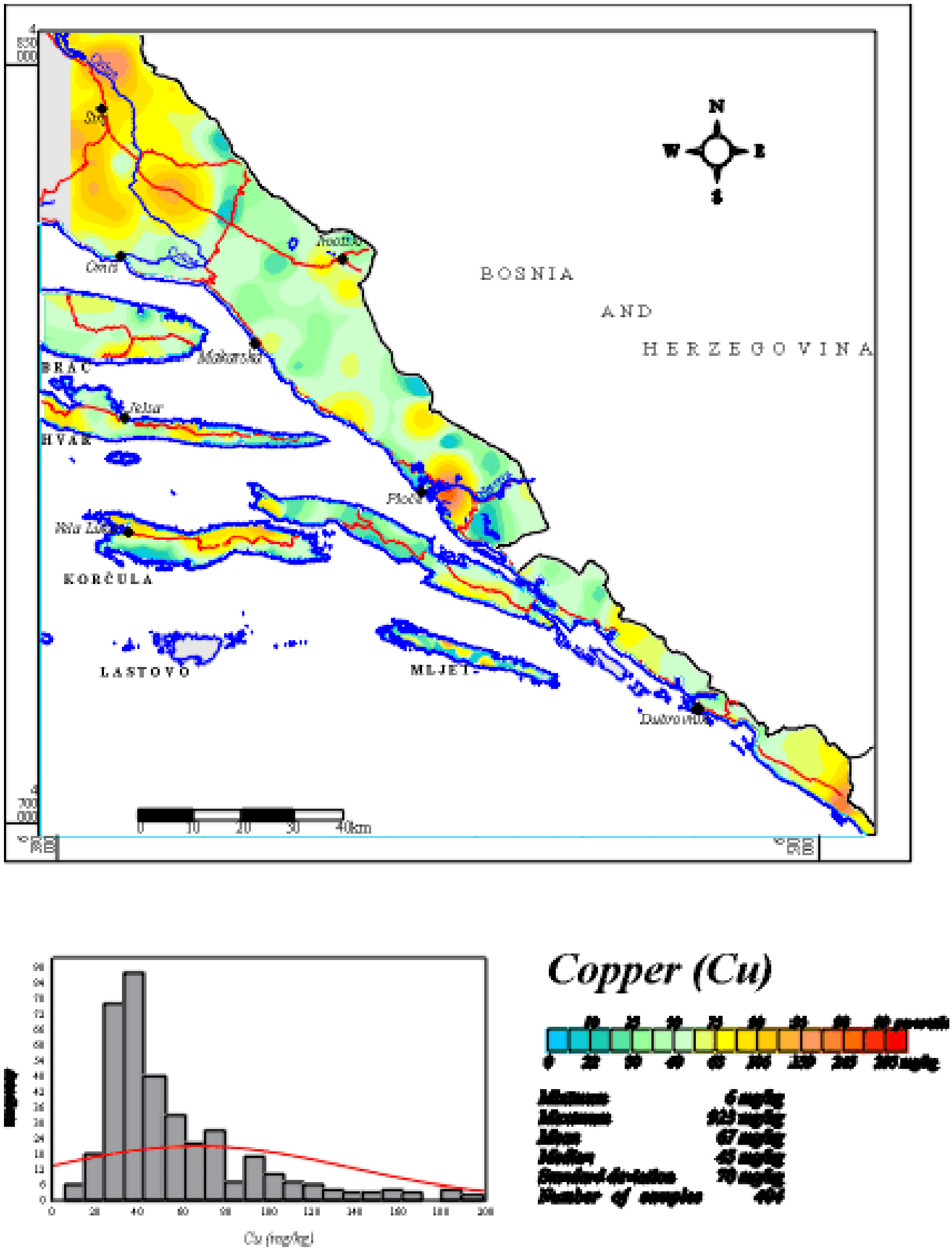


PLATE 13

The distribution of Cu in soils from S Dalmatia.

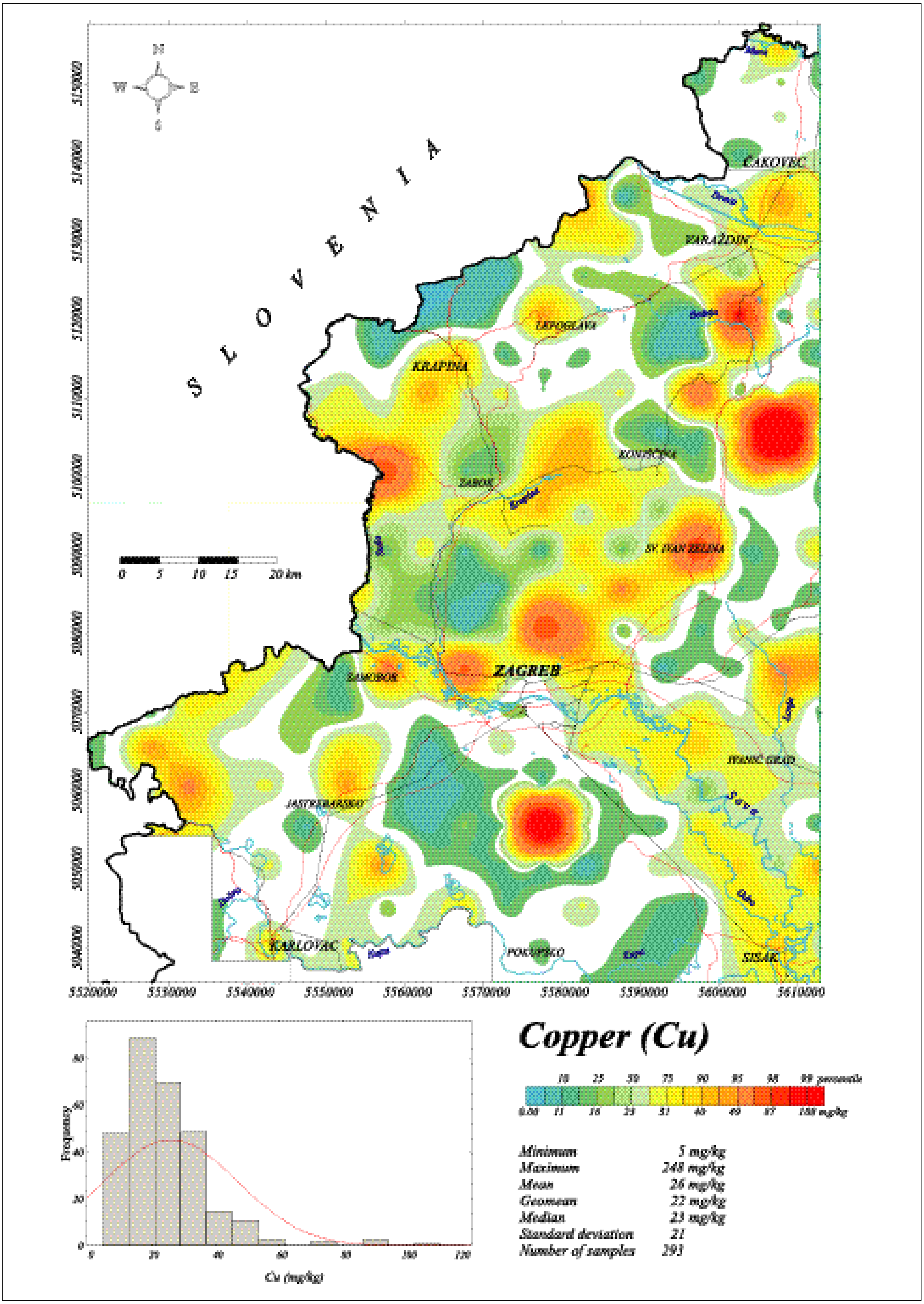
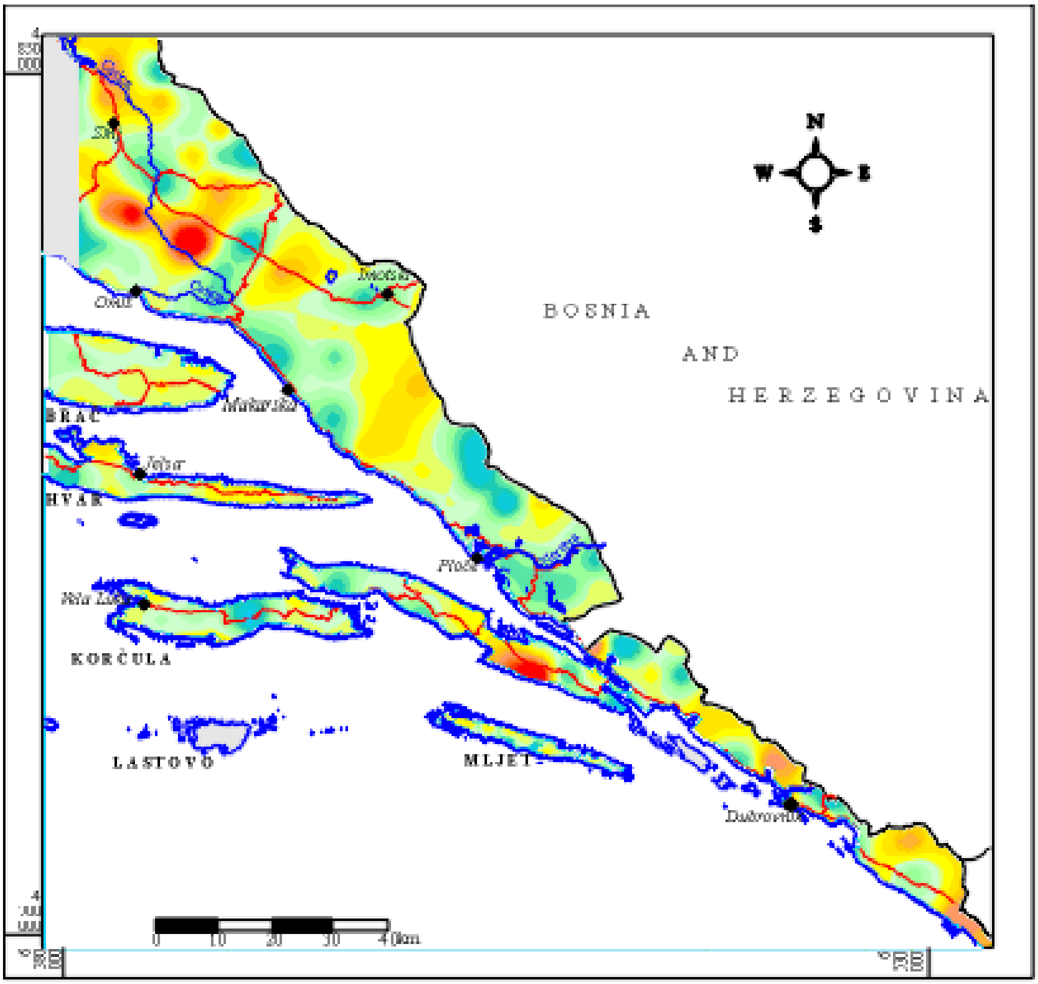


PLATE 14

The distribution of Cu in soils from NW Croatia.



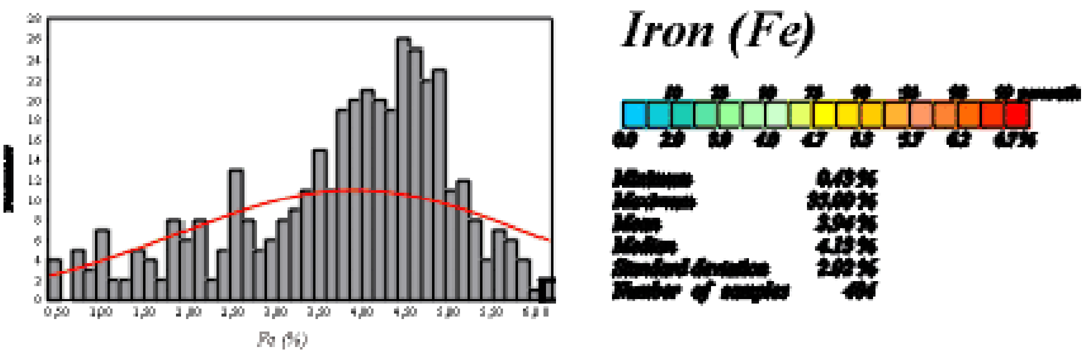


PLATE 15

The distribution of Fe in soils from S Dalmatia.

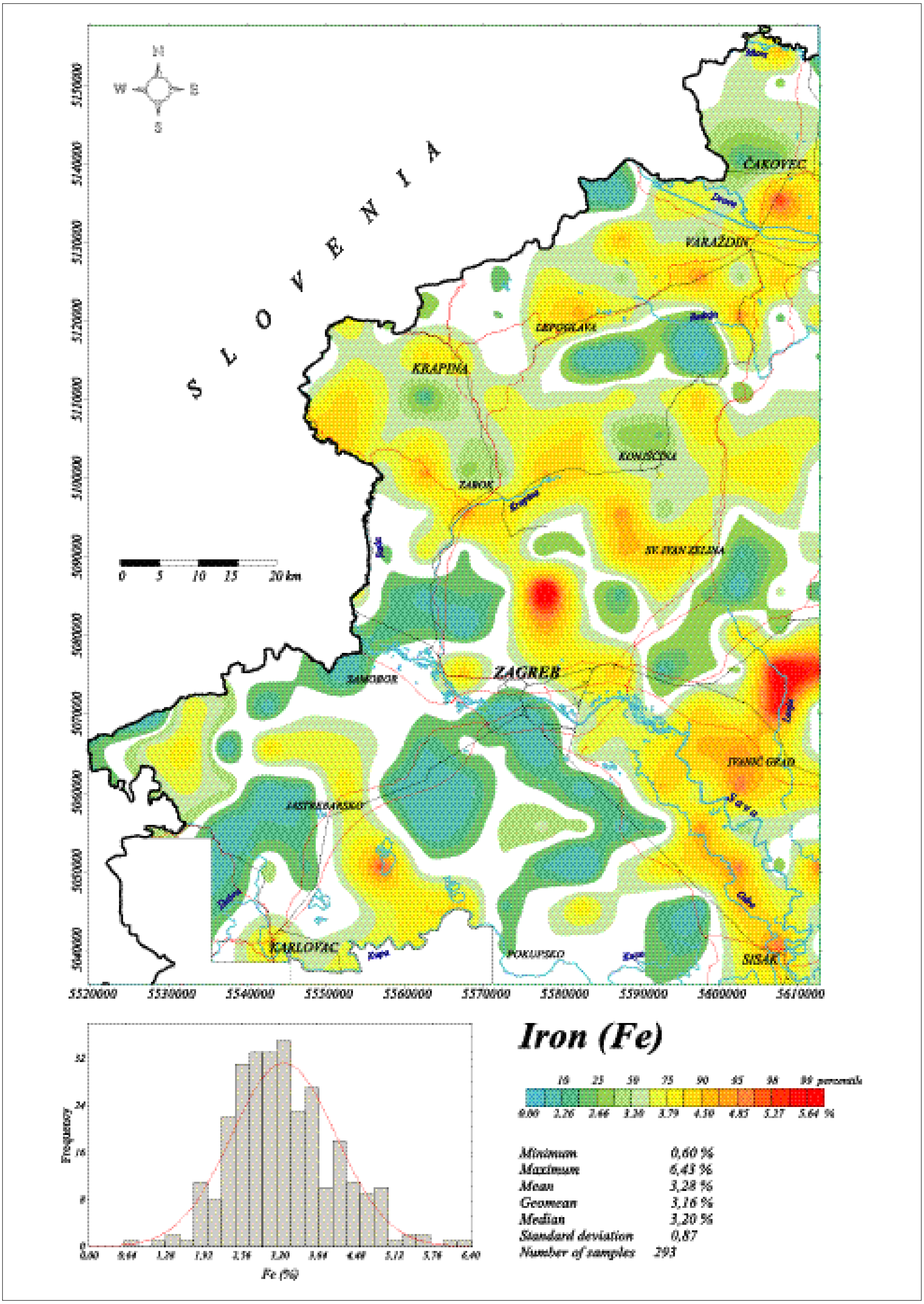


PLATE 16

The distribution of Fe in soils from NW Croatia.

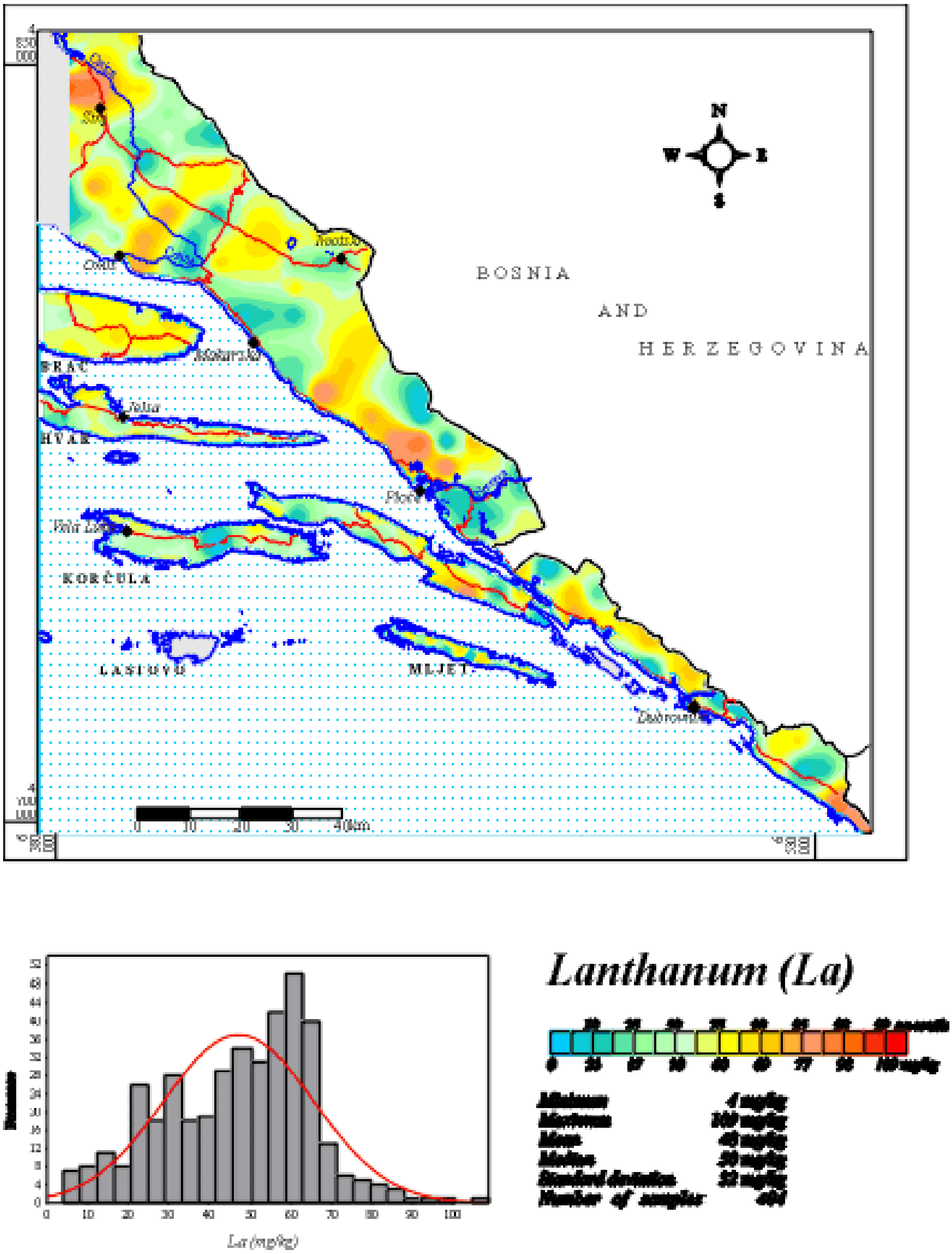


PLATE 17

The distribution of La in soils from S Dalmatia.

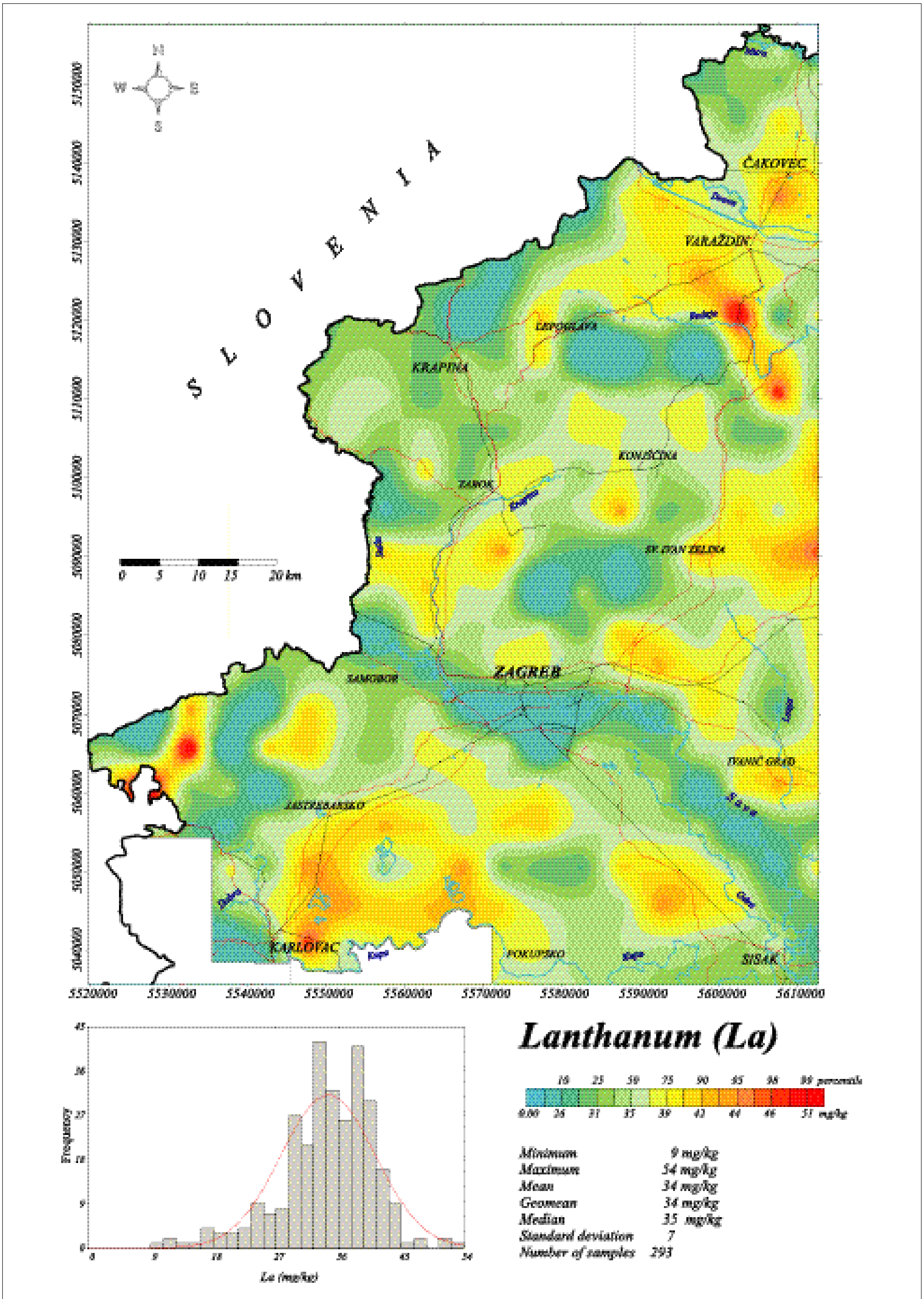


PLATE 18

The distribution of La in soils from NW Croatia.

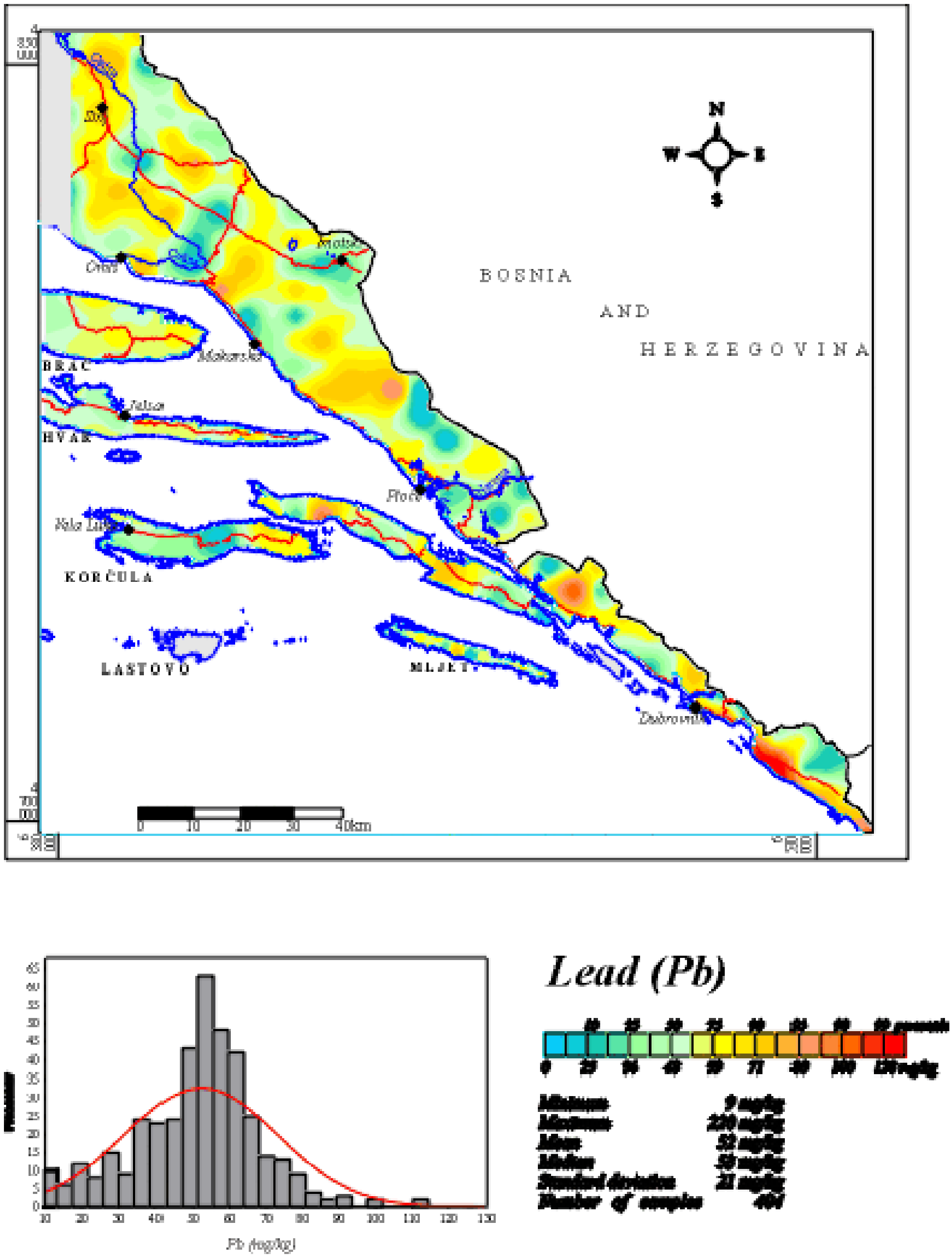


PLATE 19

The distribution of Pb in soils from S Dalmatia.

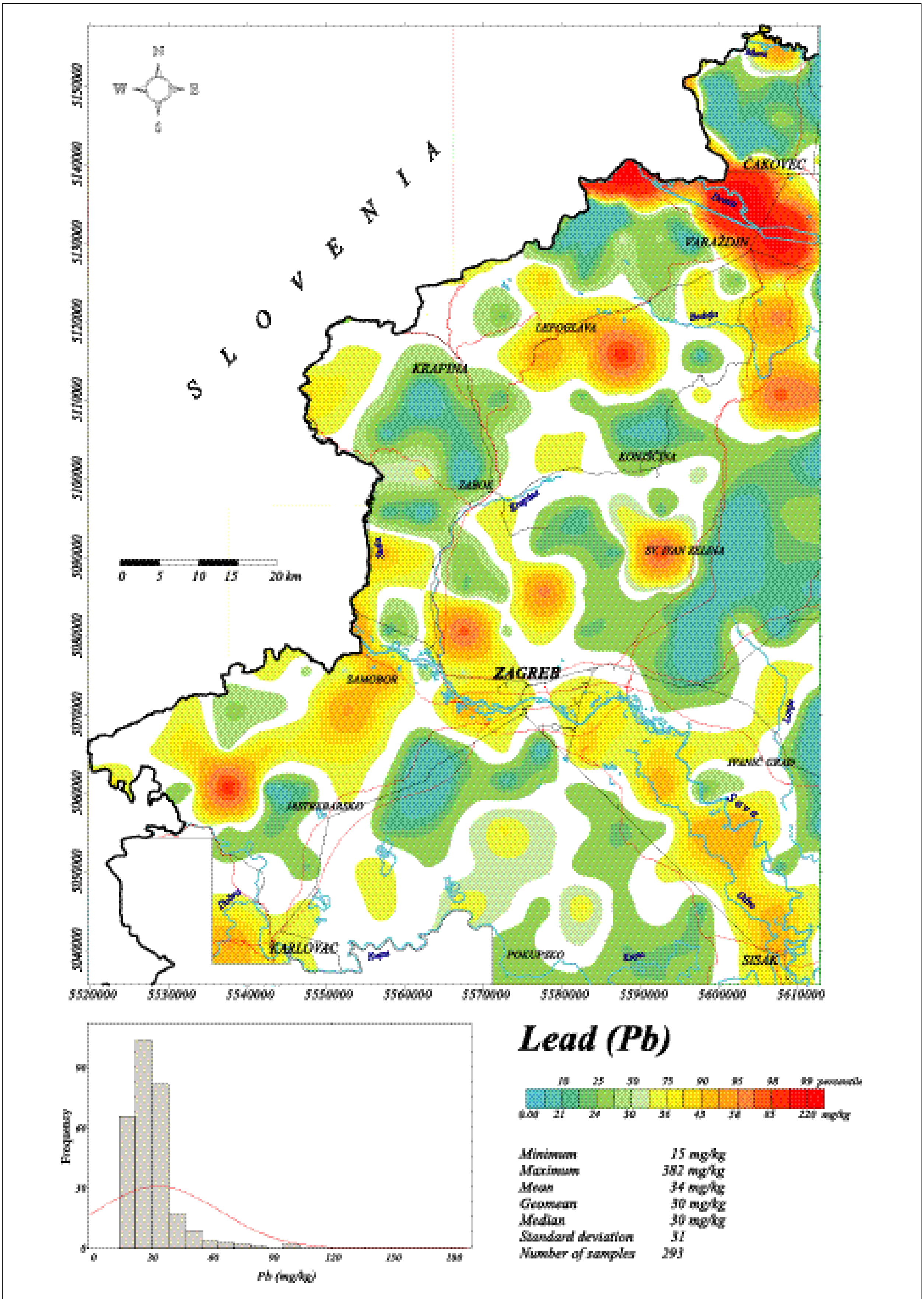


PLATE 20

The distribution of Pb in soils from NW Croatia.

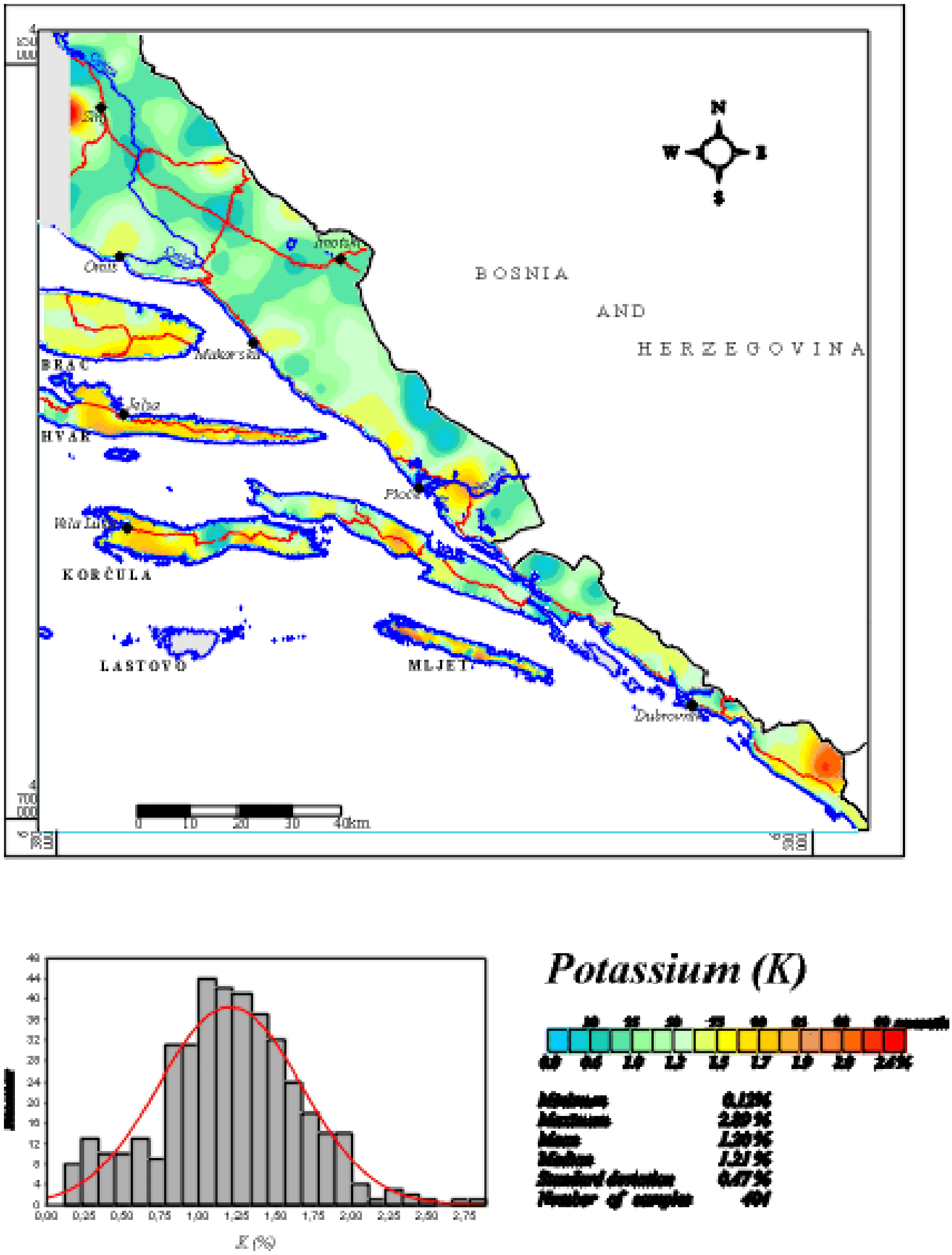


PLATE 21

The distribution of K in soils from S Dalmatia.

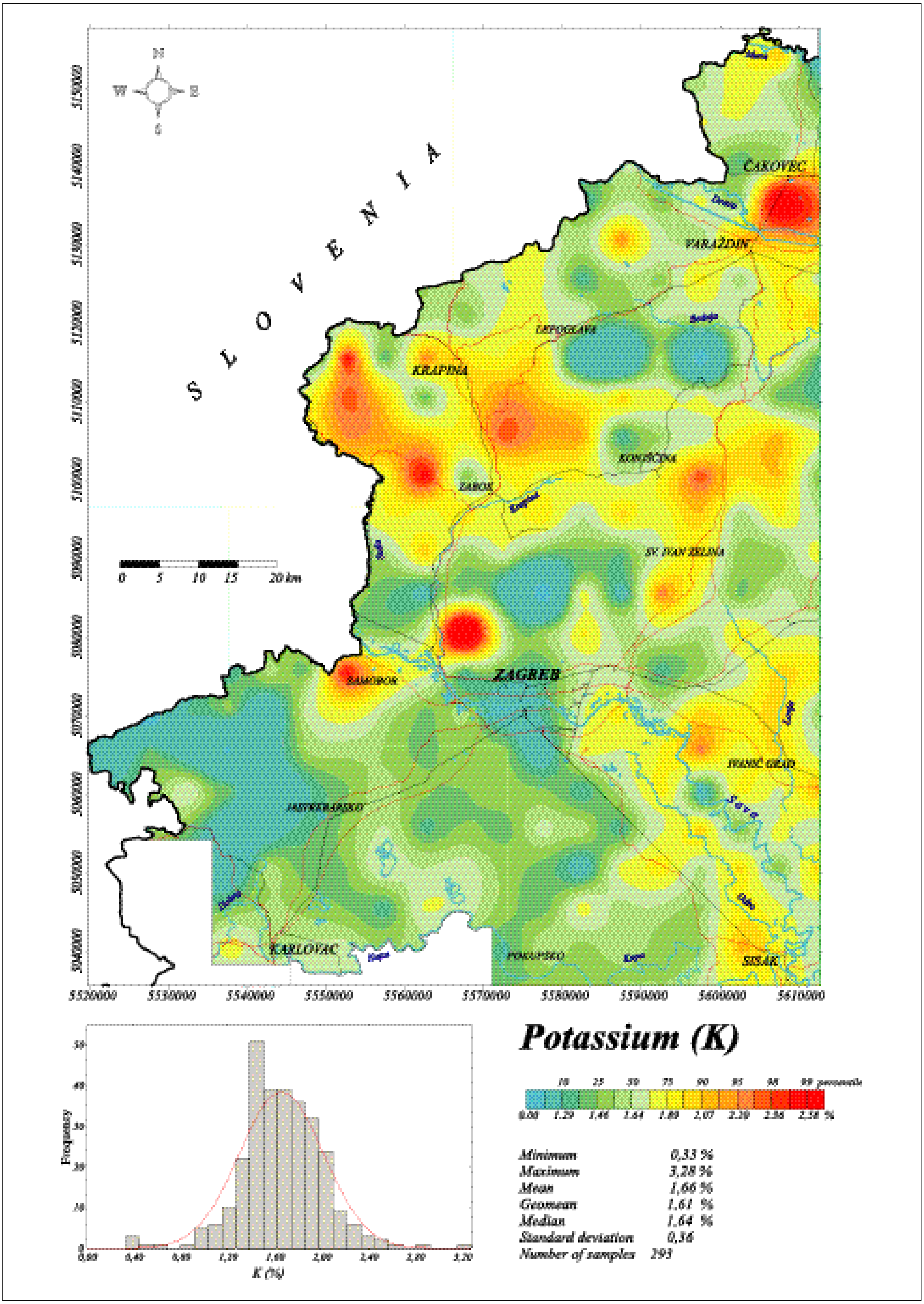


PLATE 22

The distribution of K in soils from NW Croatia.

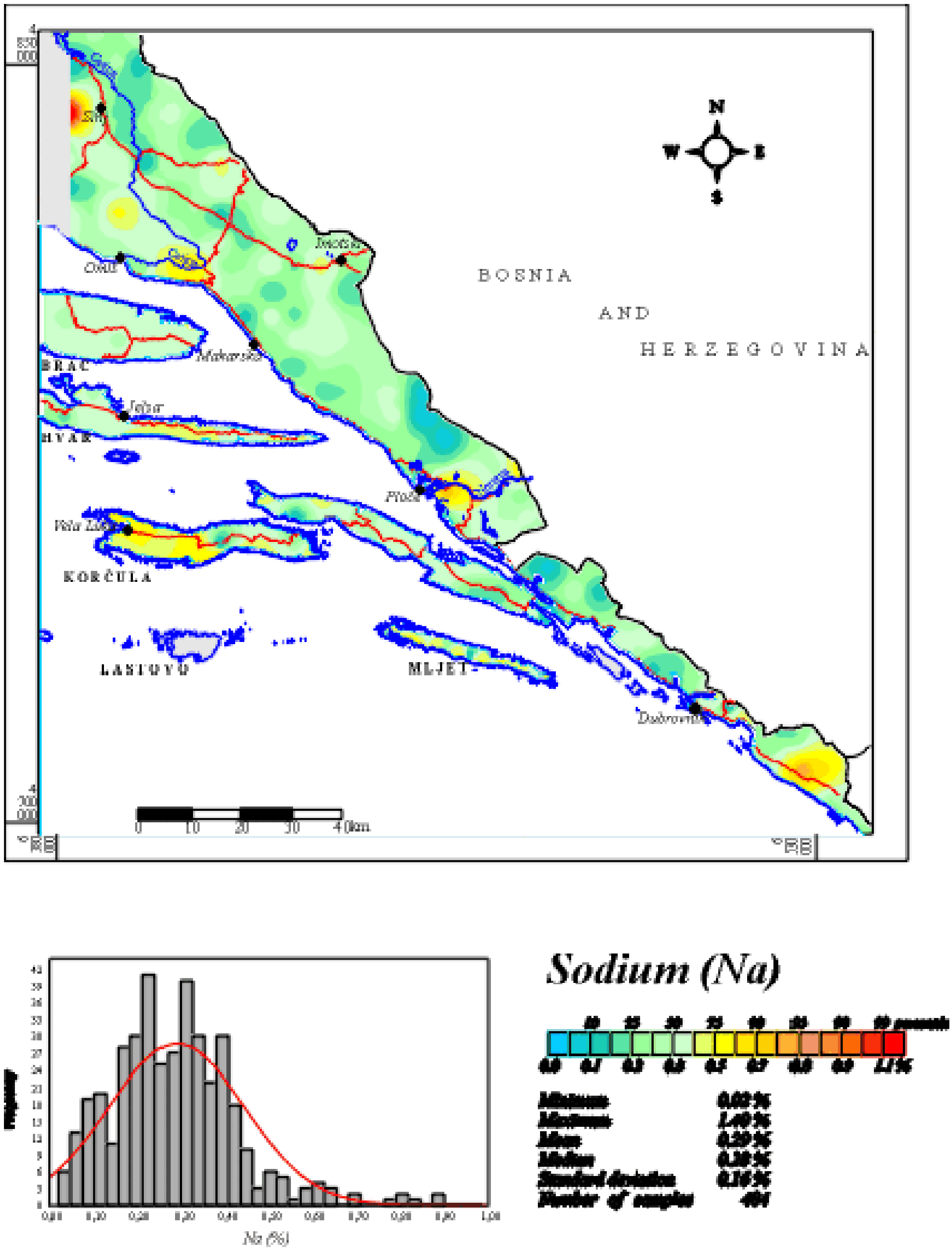


PLATE 23

The distribution of Na in soils from S Dalmatia.

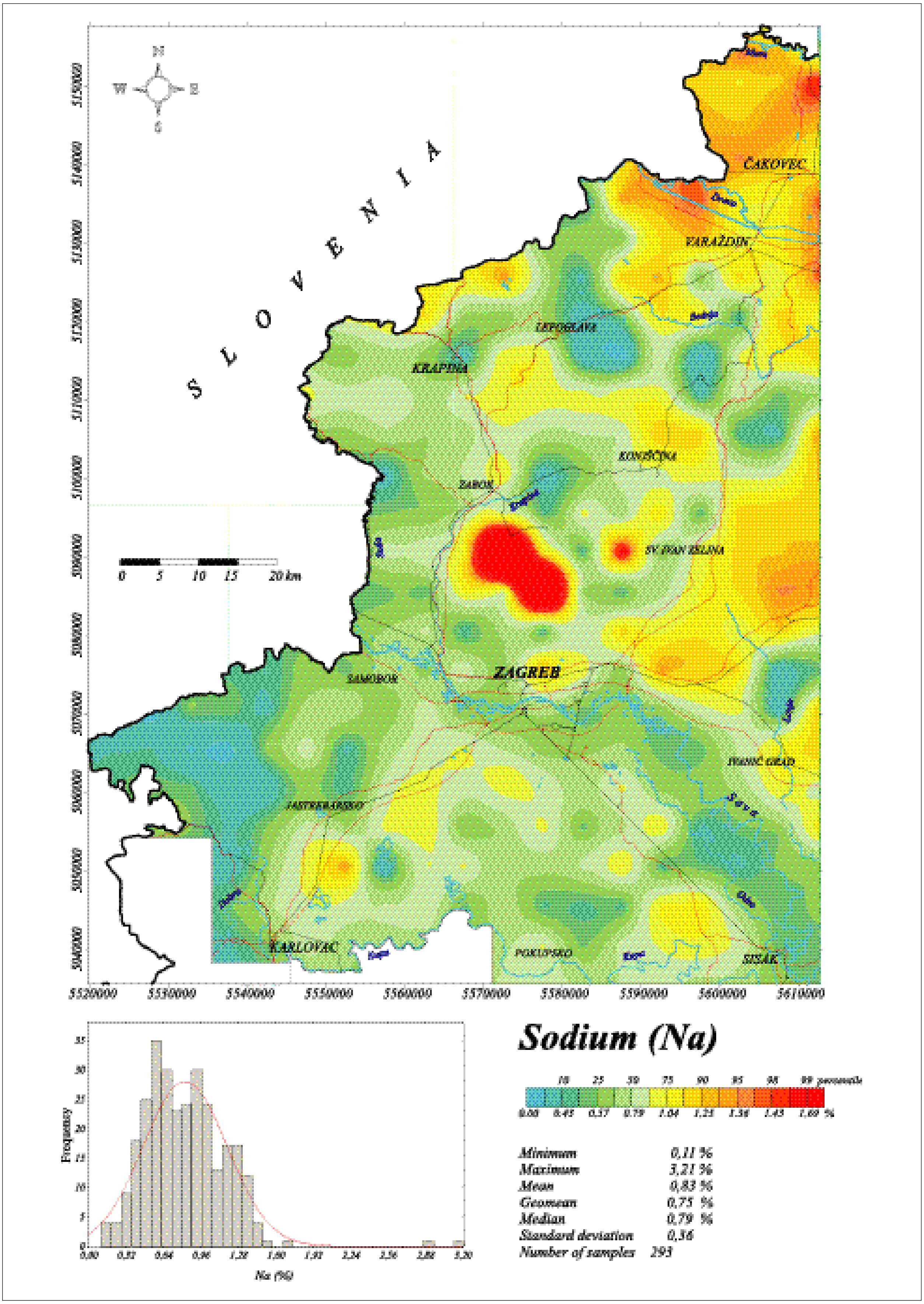
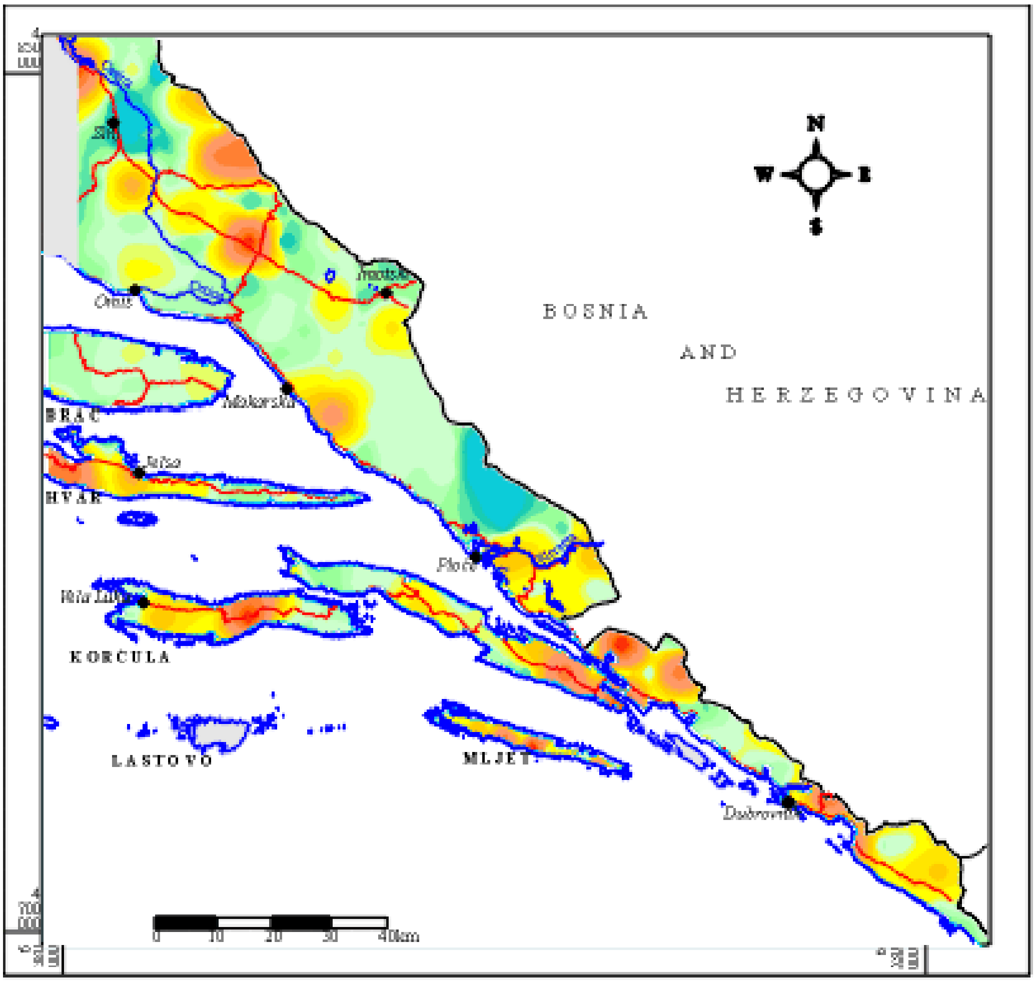


PLATE 24

The distribution of Na in soils from NW Croatia.



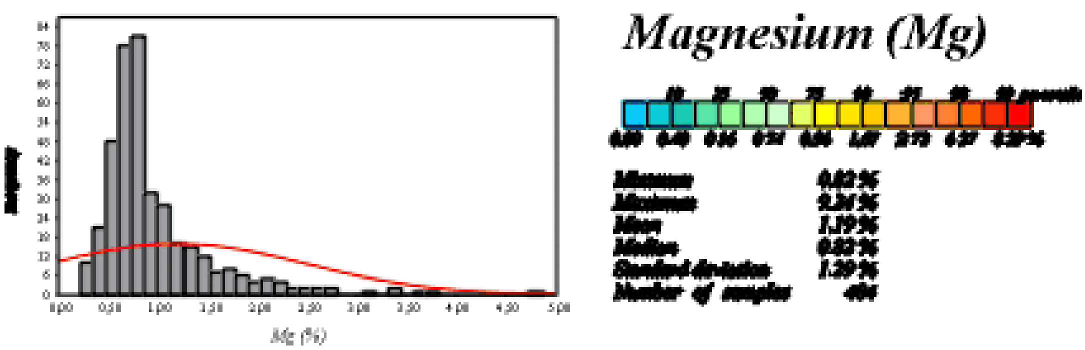


PLATE 25

The distribution of Mg in soils from S Dalmatia.

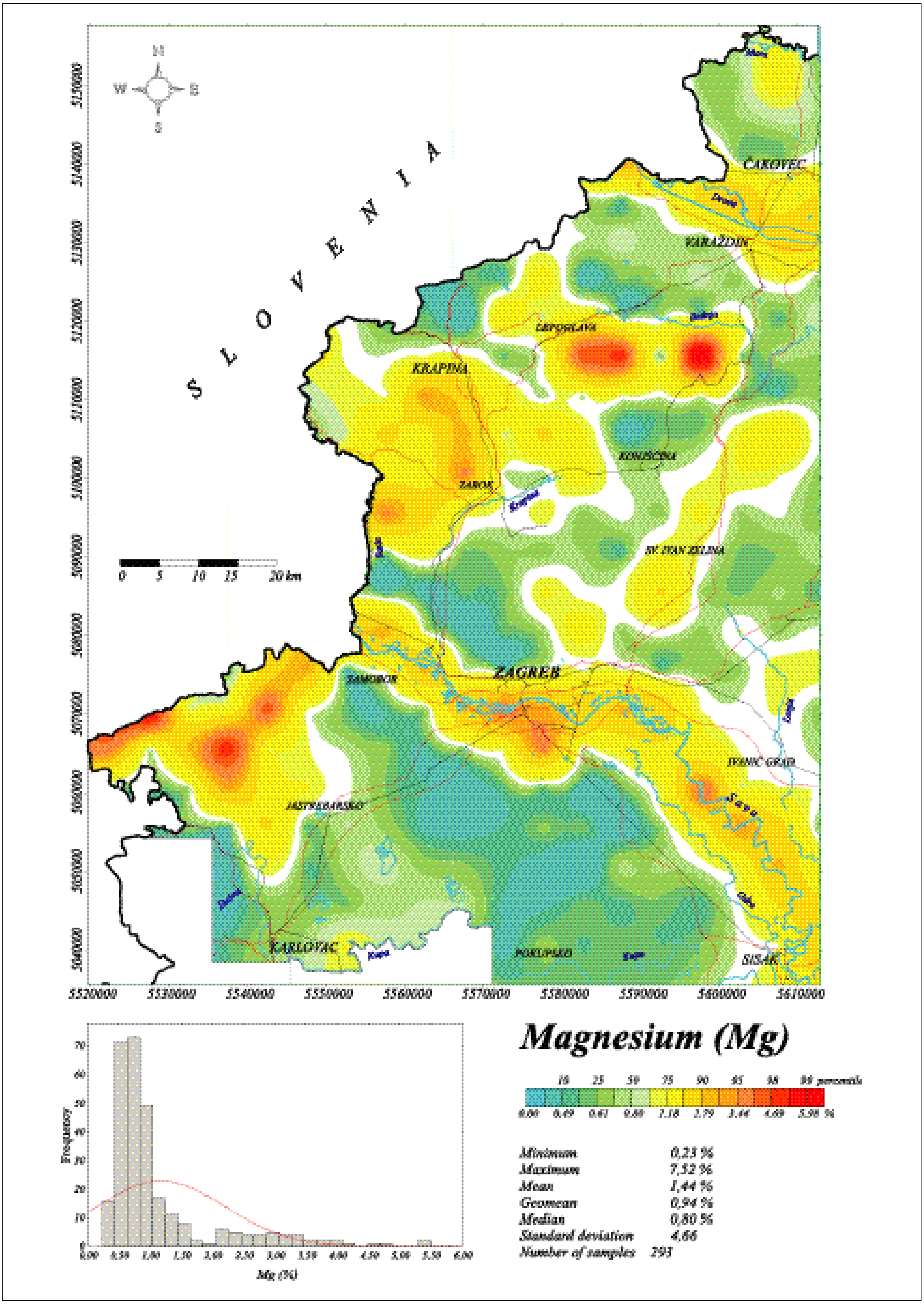
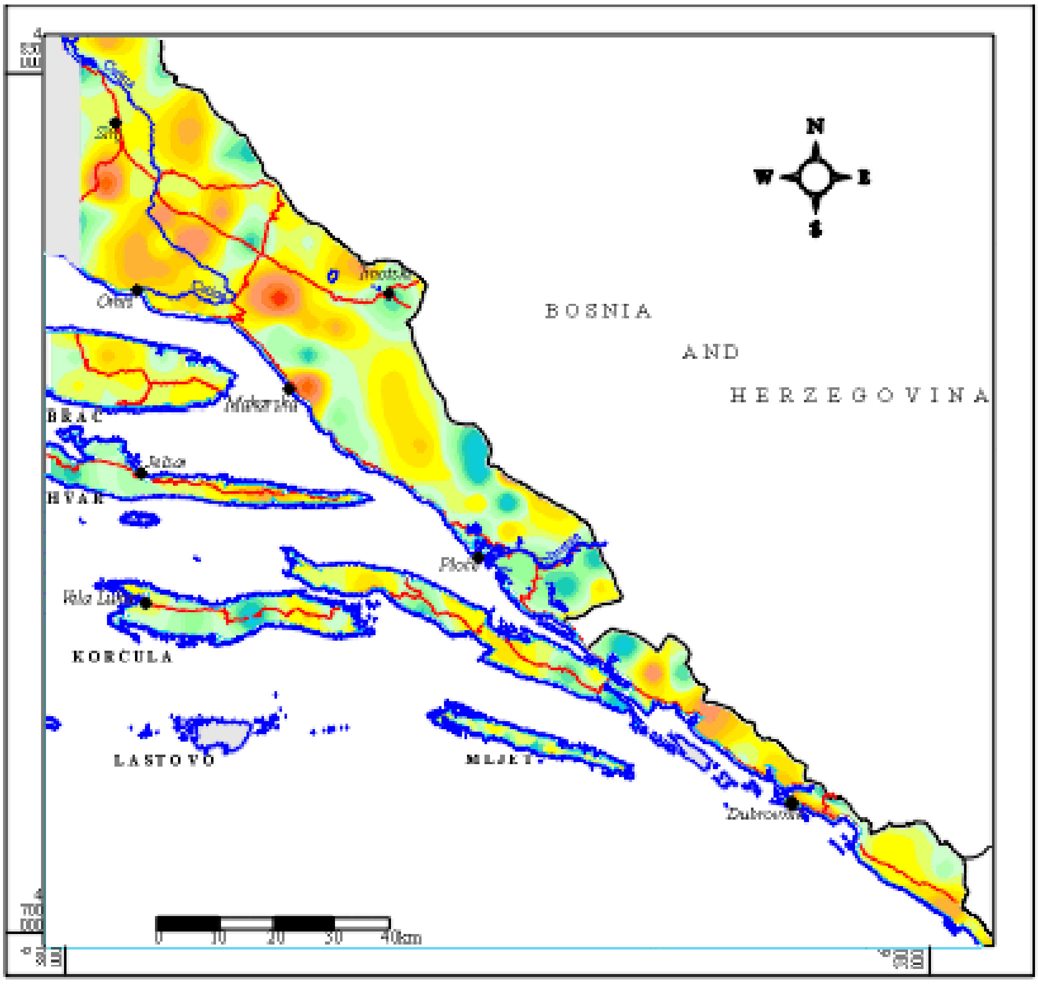


PLATE 26

The distribution of Mg in soils from NW Croatia.



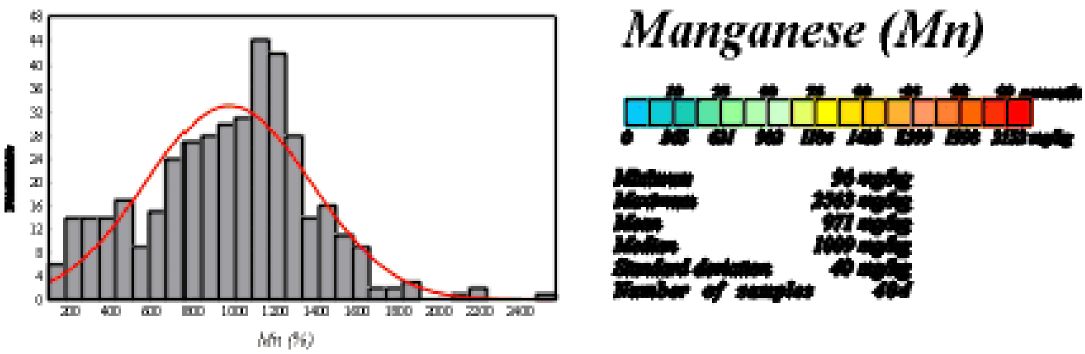


PLATE 27

The distribution of Mn in soils from S Dalmatia.

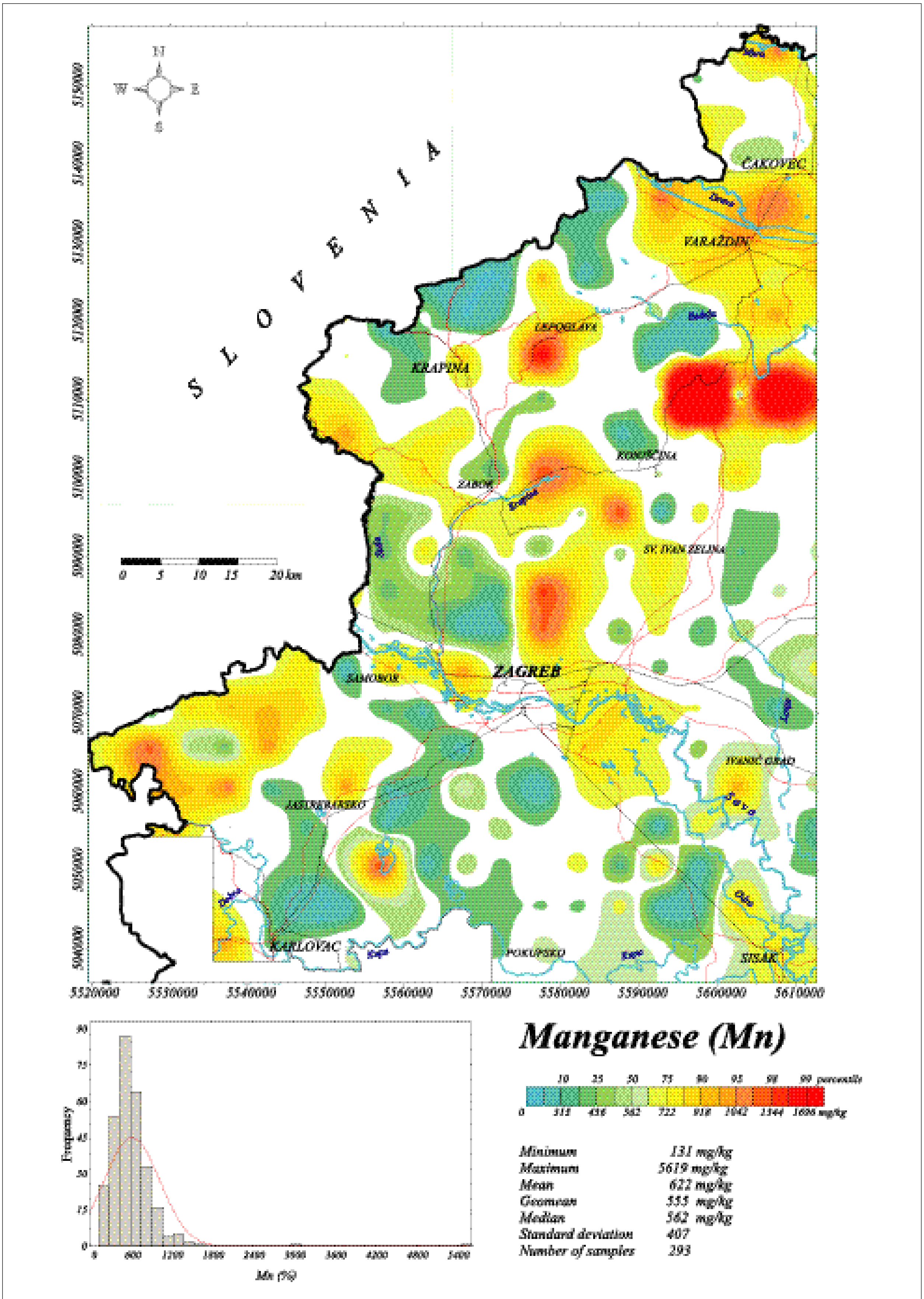


PLATE 28

The distribution of Mn in soils from NW Croatia.

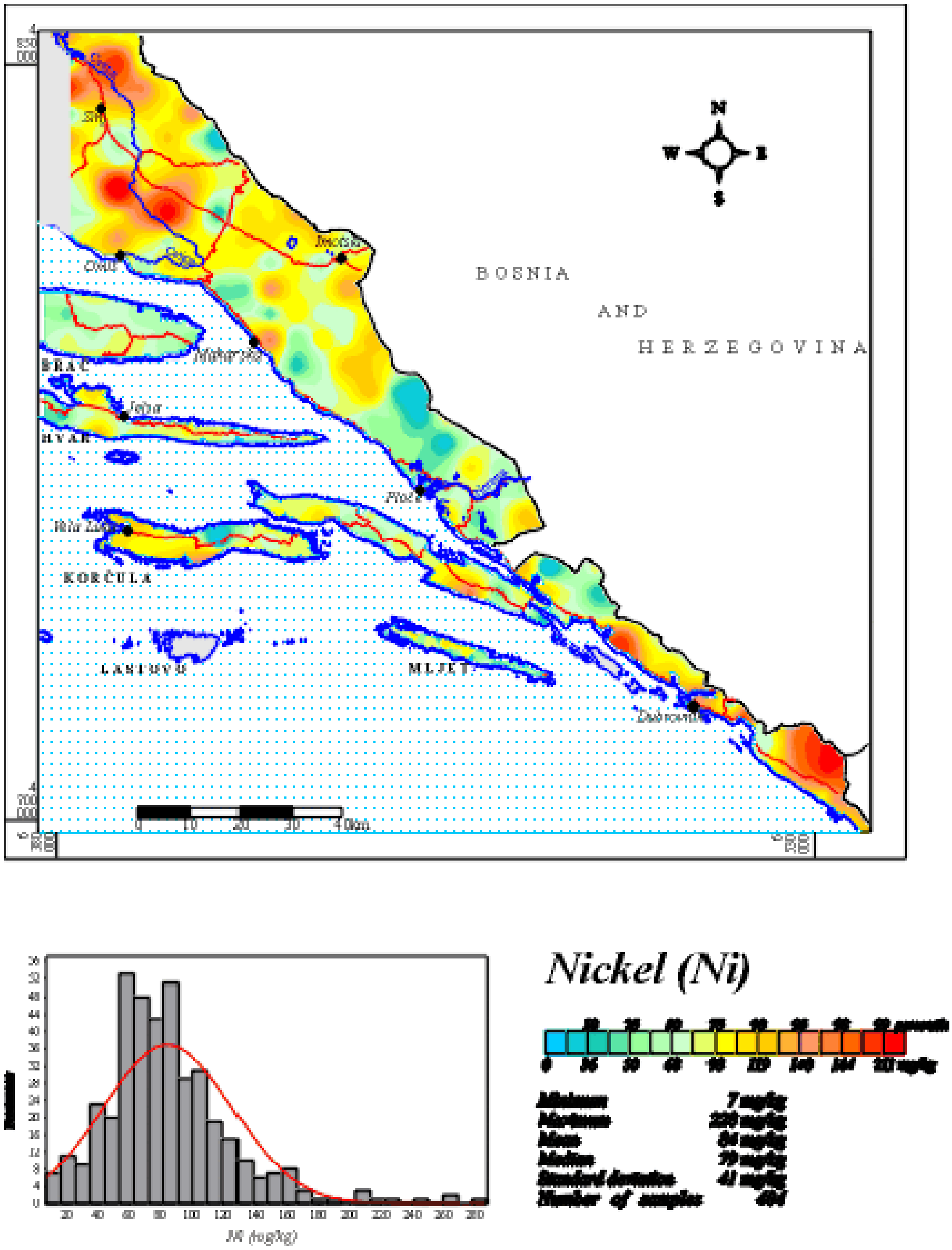


PLATE 29

The distribution of Ni in soils from S Dalmatia.

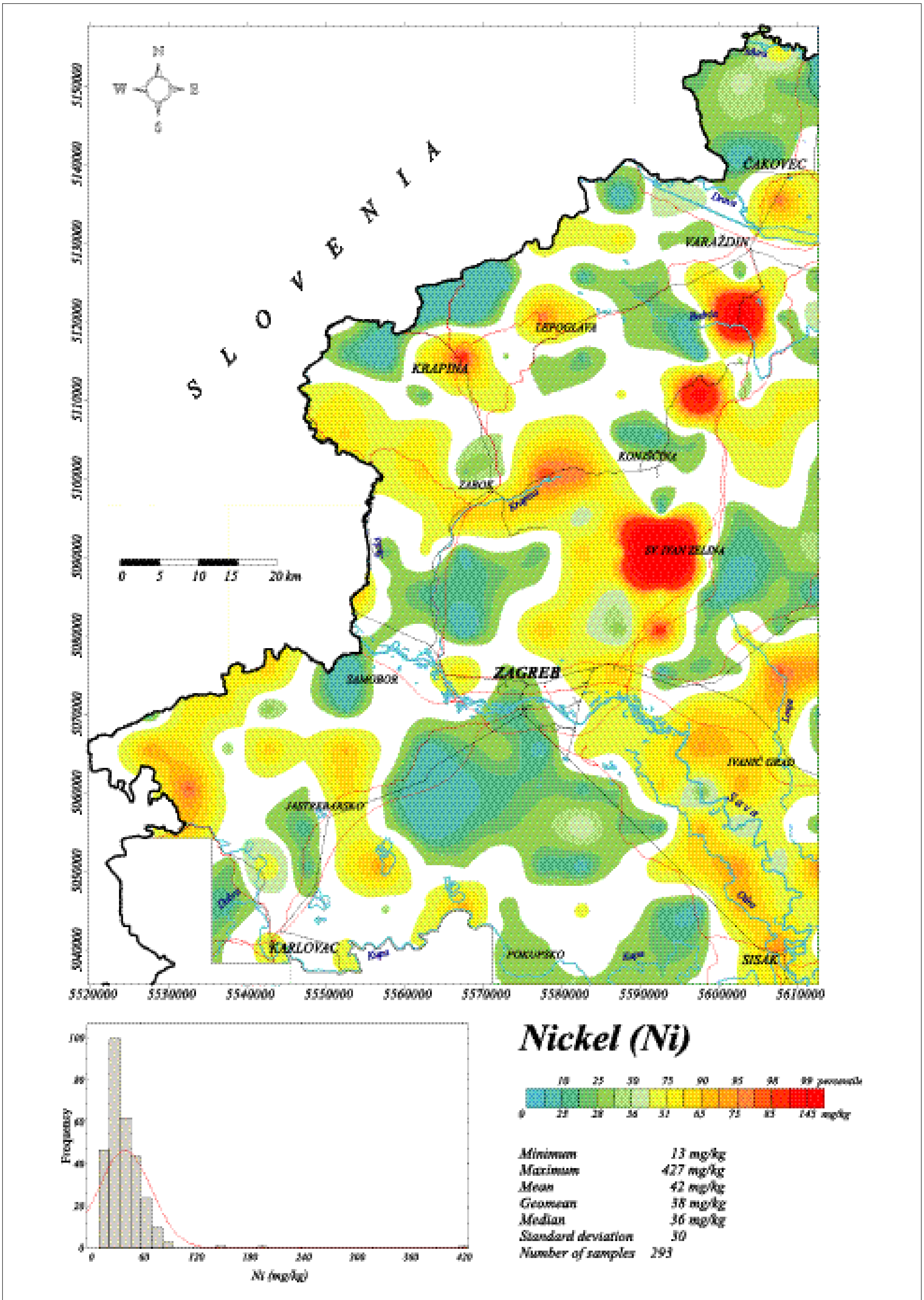
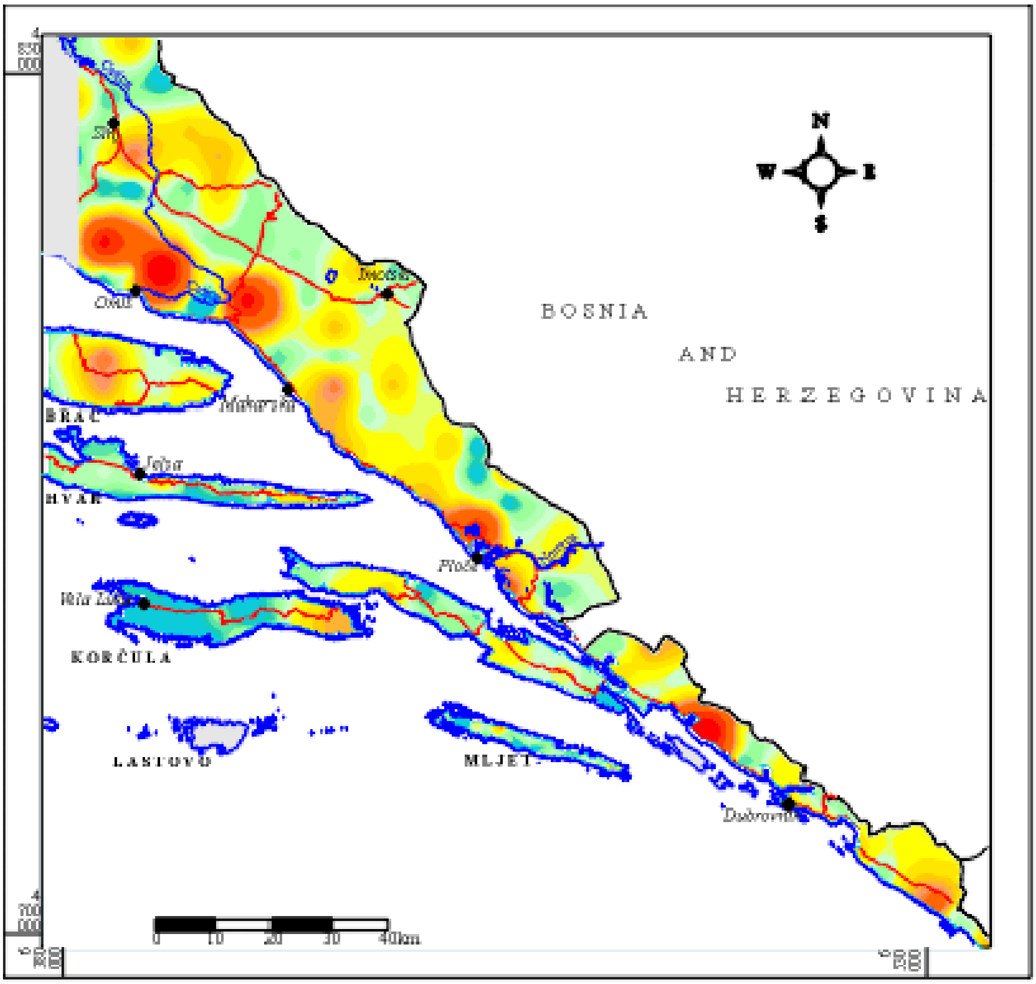


PLATE 30

The distribution of Ni in soils from NW Croatia.



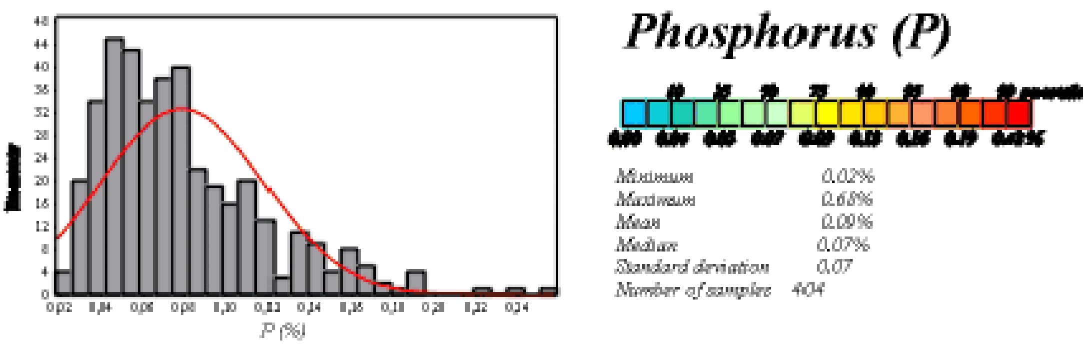


PLATE 31

The distribution of P in soils from S Dalmatia.

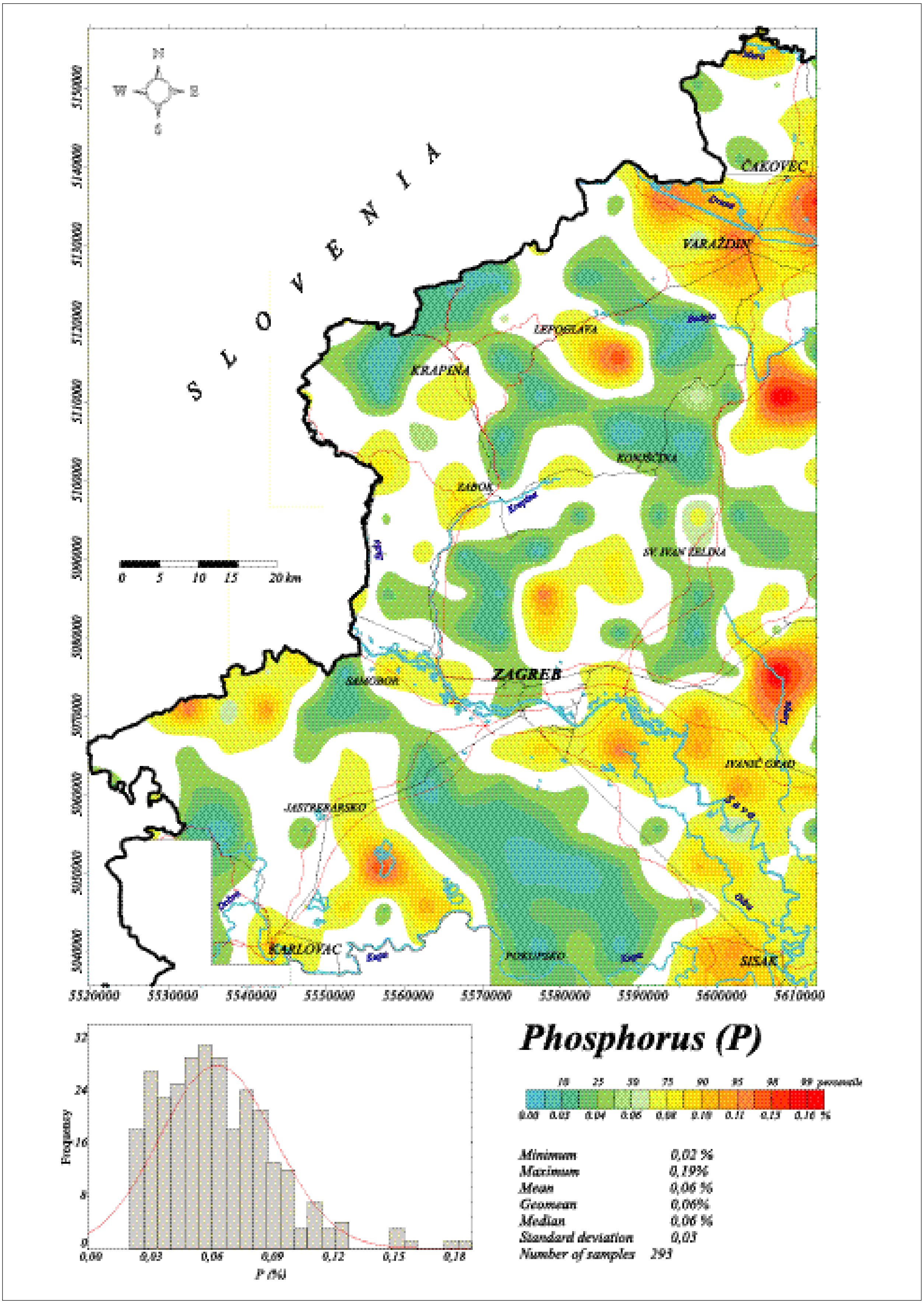
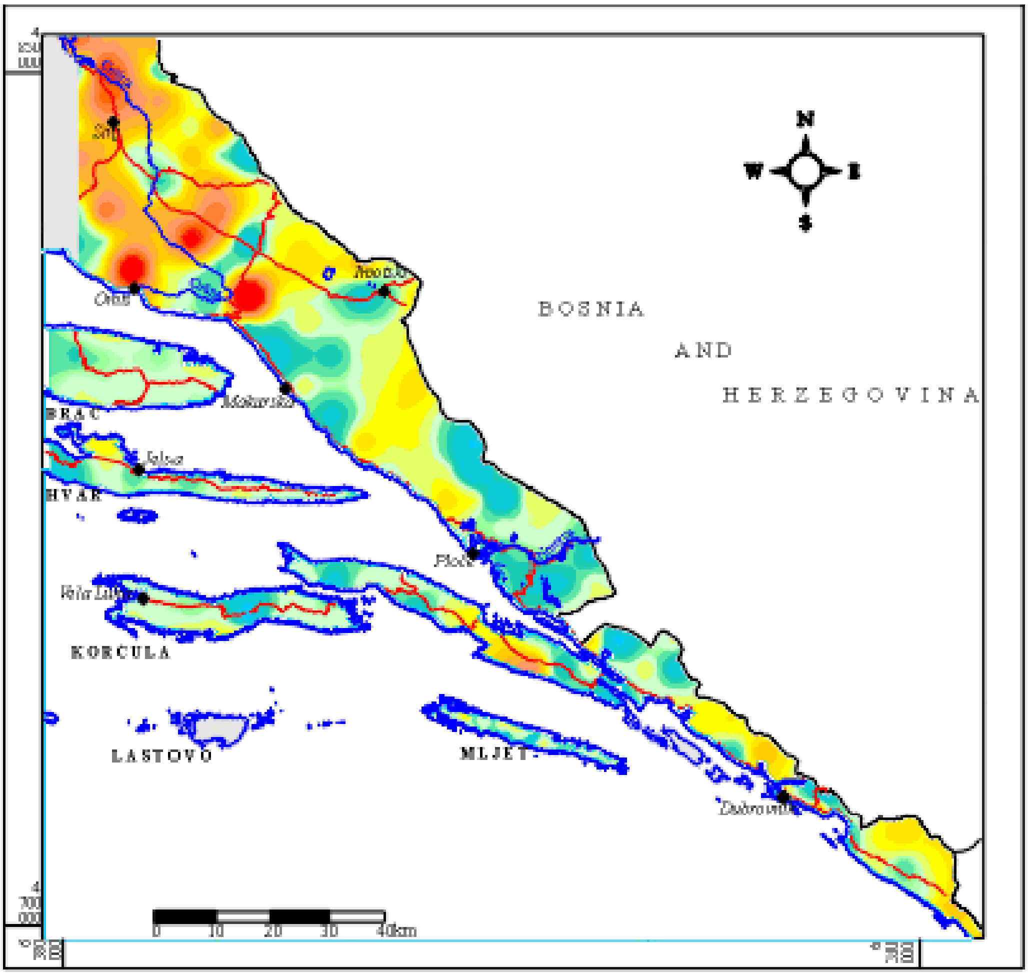
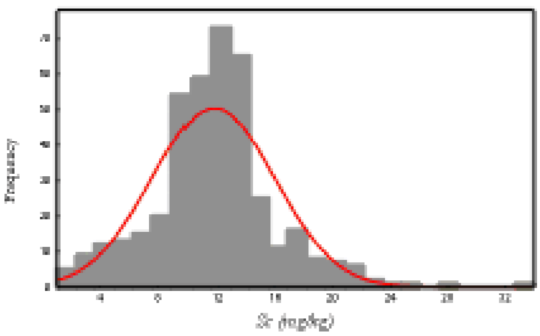


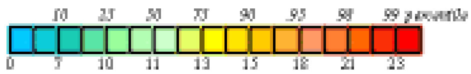
PLATE 32

The distribution of P in soils from NW Croatia.





Scandium (Sc)



Minimum	4 mg/kg
Maximum	34 mg/kg
Mean	12 mg/kg
Median	12 mg/kg
Standard deviation	1 mg/kg
Number of samples	404

PLATE 33

The distribution of Sc in soils from S Dalmatia.

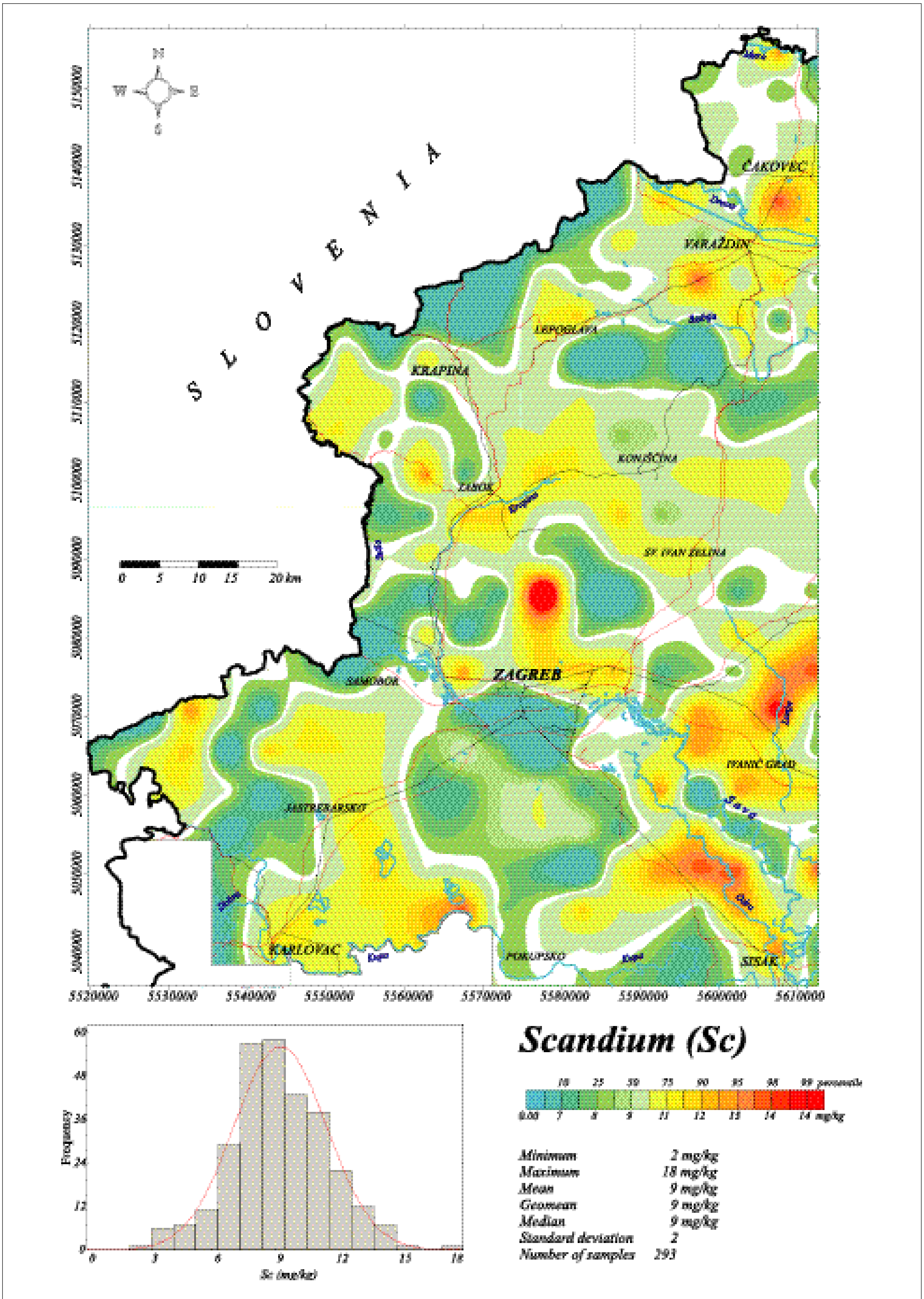


PLATE 34

The distribution of Sc in soils from NW Croatia.

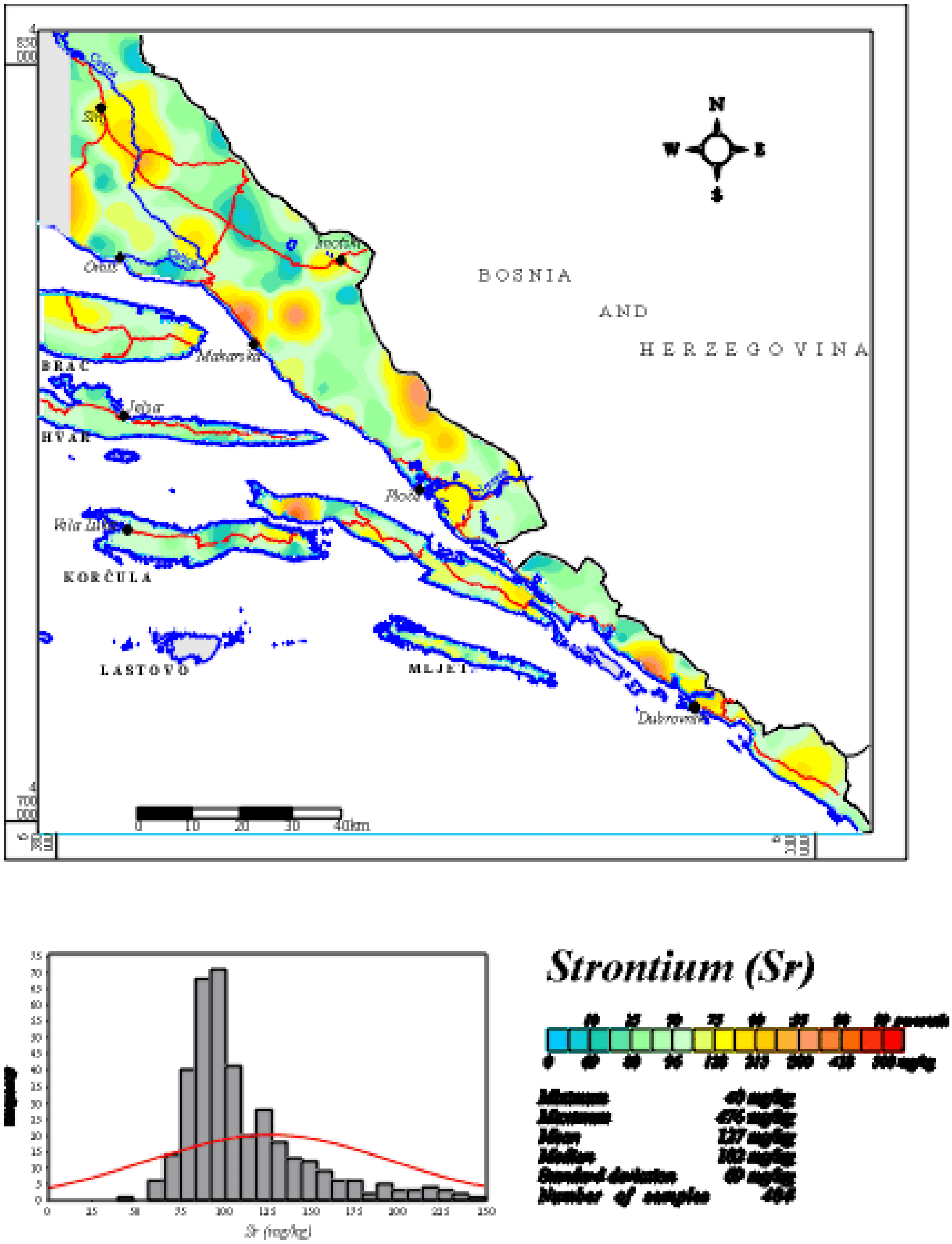


PLATE 35

The distribution of Sr in soils from S Dalmatia.

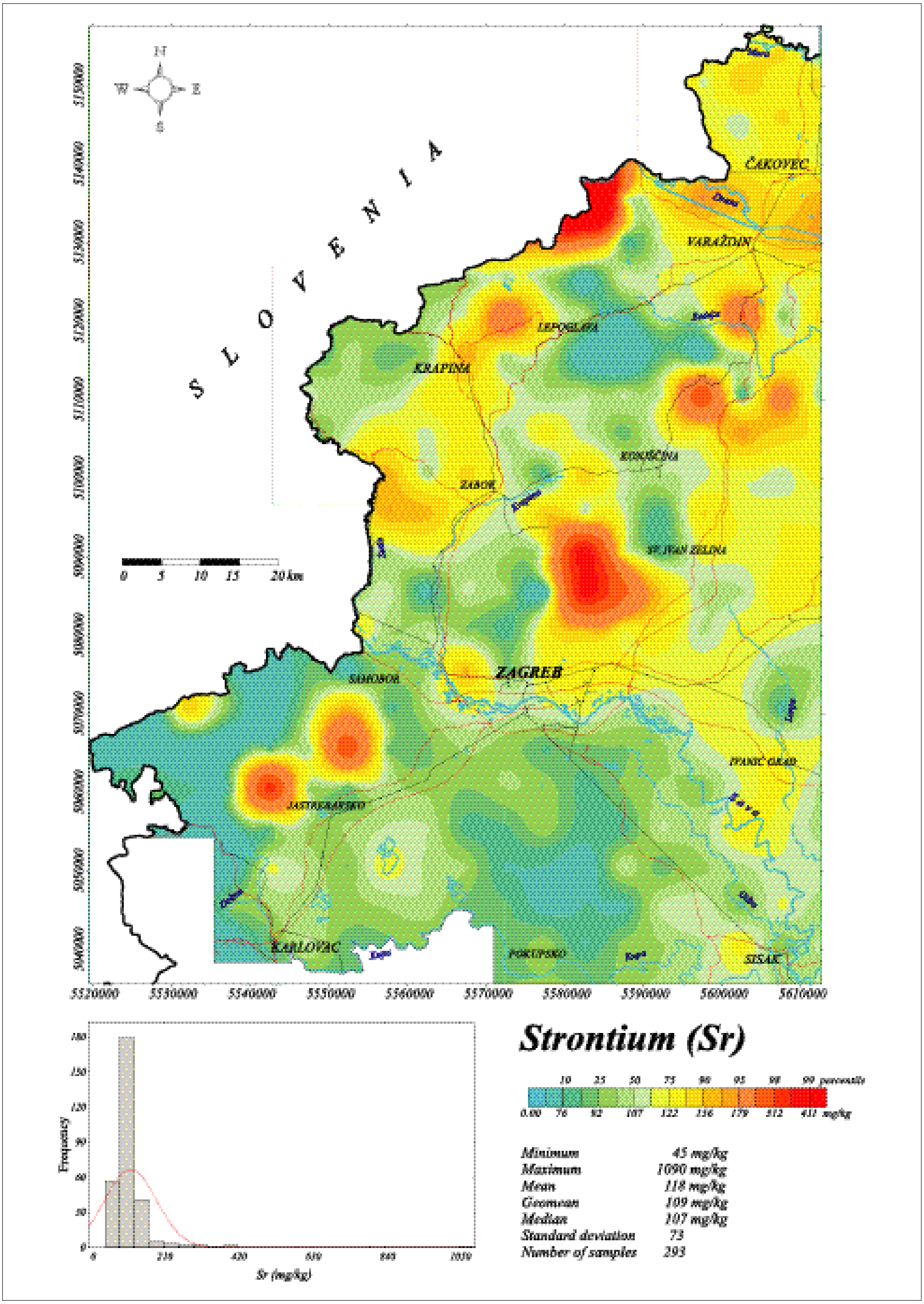


PLATE 36

The distribution of Sr in soils from NW Croatia.

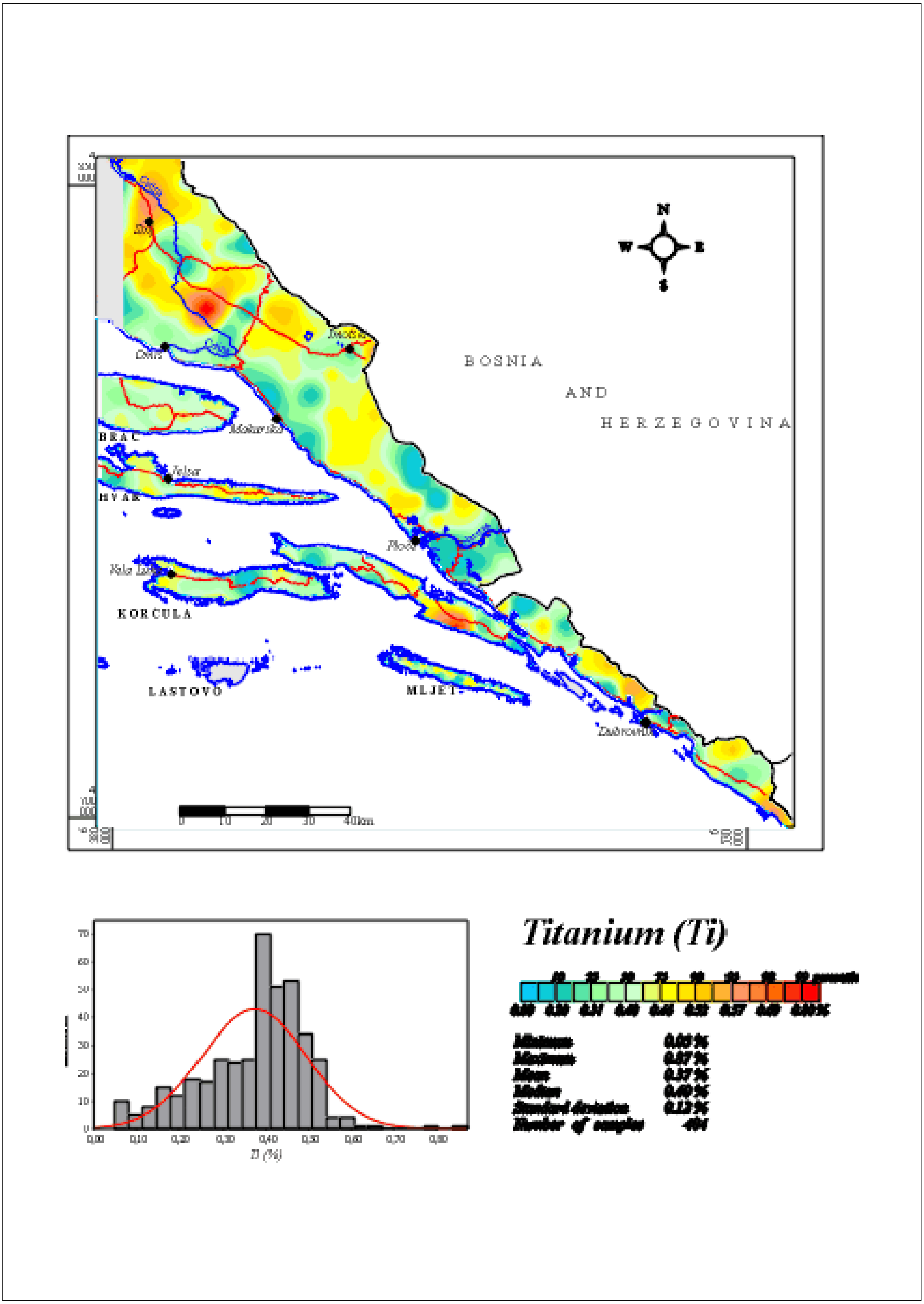


PLATE 37

The distribution of Ti in soils from S Dalmatia.

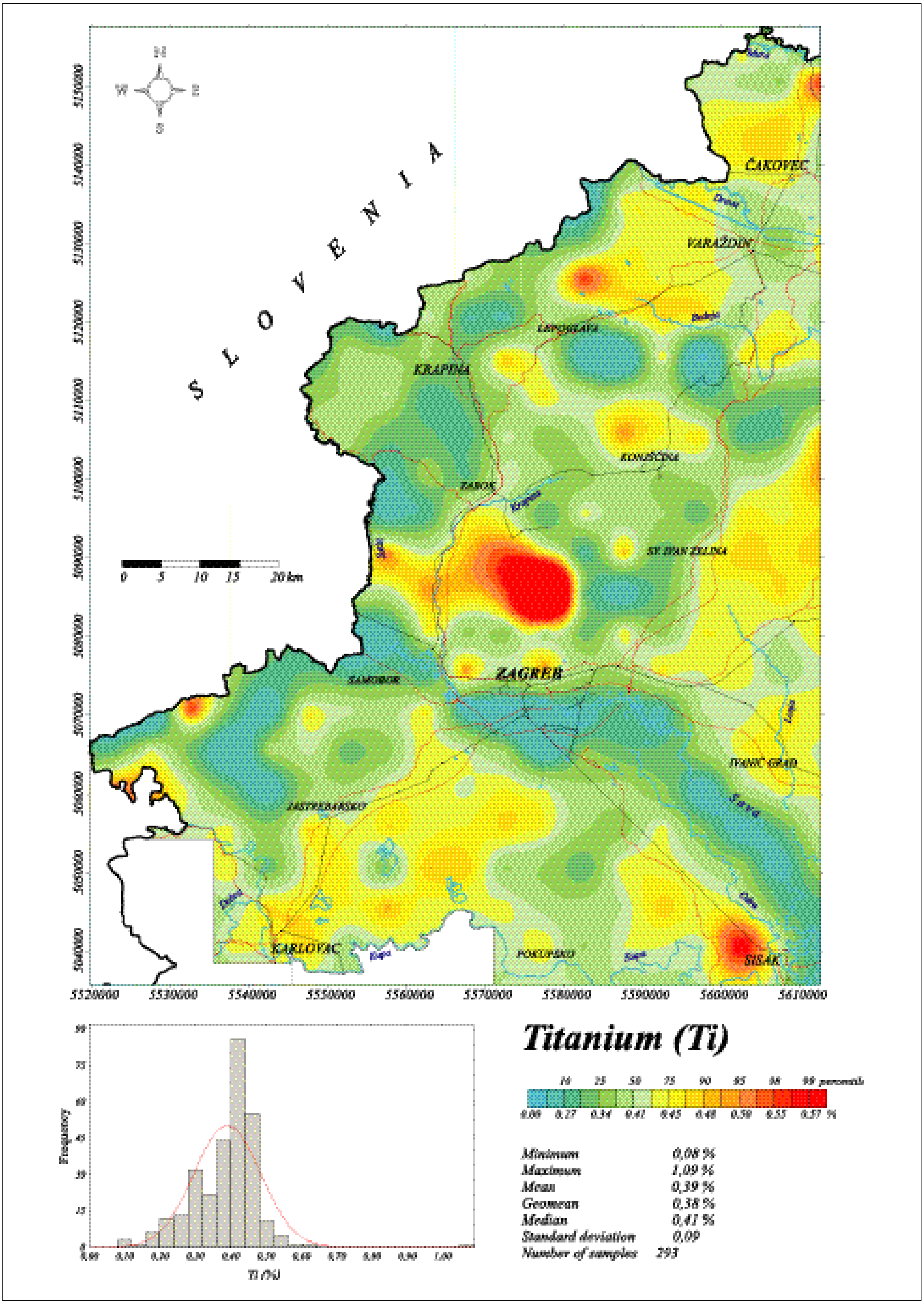


PLATE 38

The distribution of Ti in soils from NW Croatia.

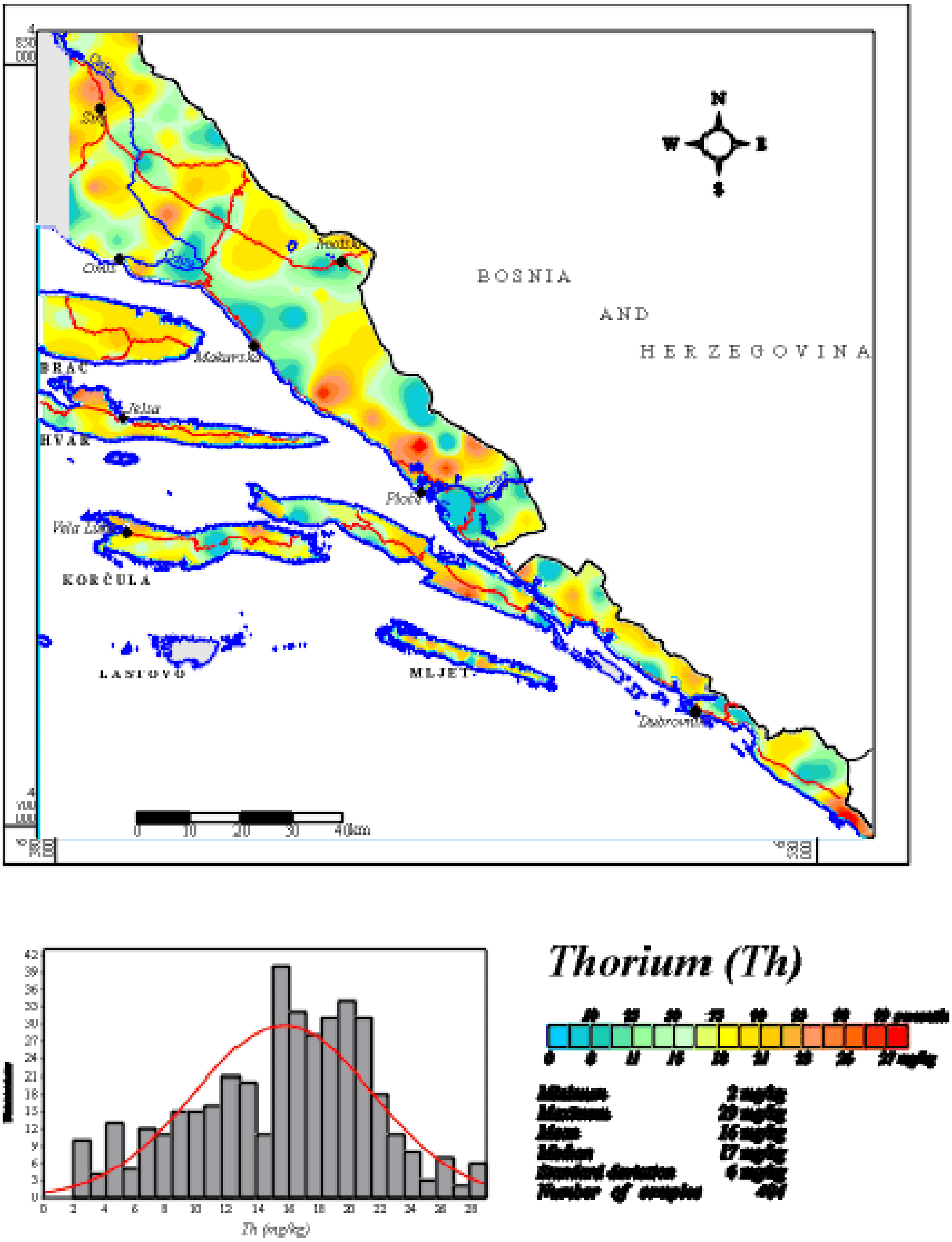


PLATE 39

The distribution of Th in soils from S Dalmatia.

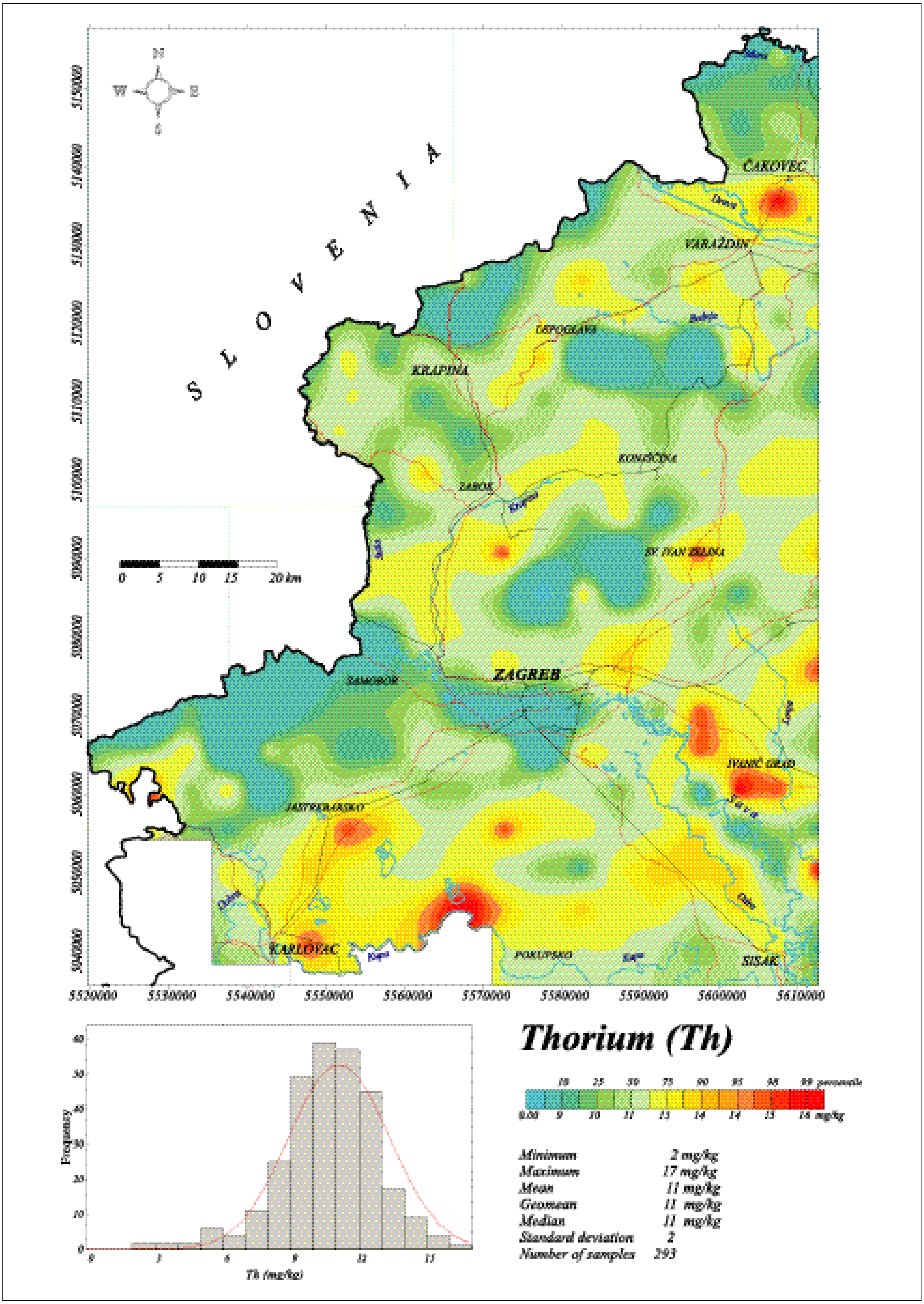
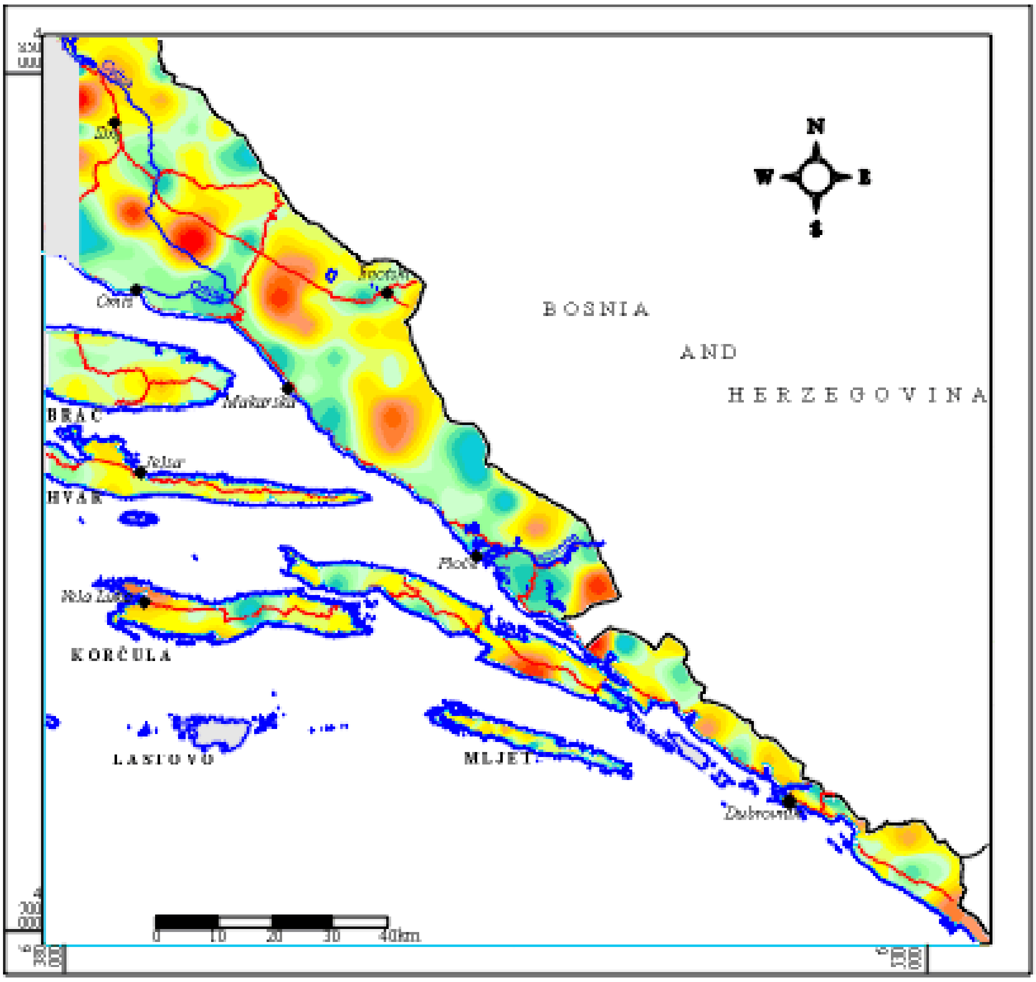


PLATE 40

The distribution of Th in soils from NW Croatia.



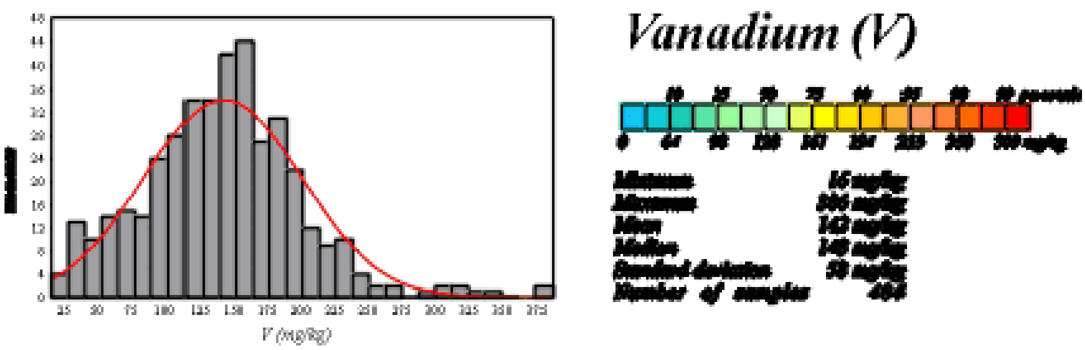


PLATE 41

The distribution of V in soils from S Dalmatia.

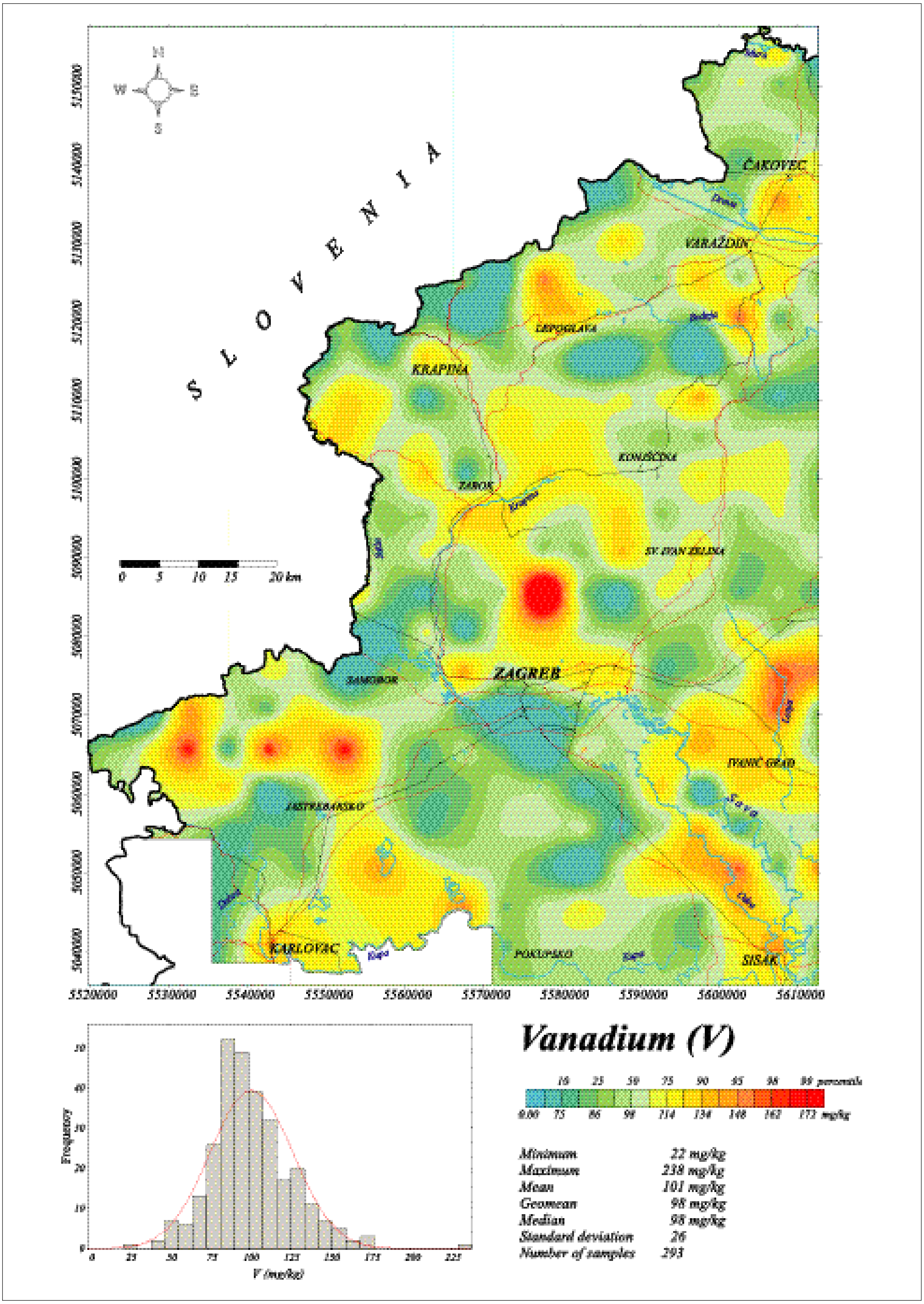


PLATE 42

The distribution of V in soils from NW Croatia.

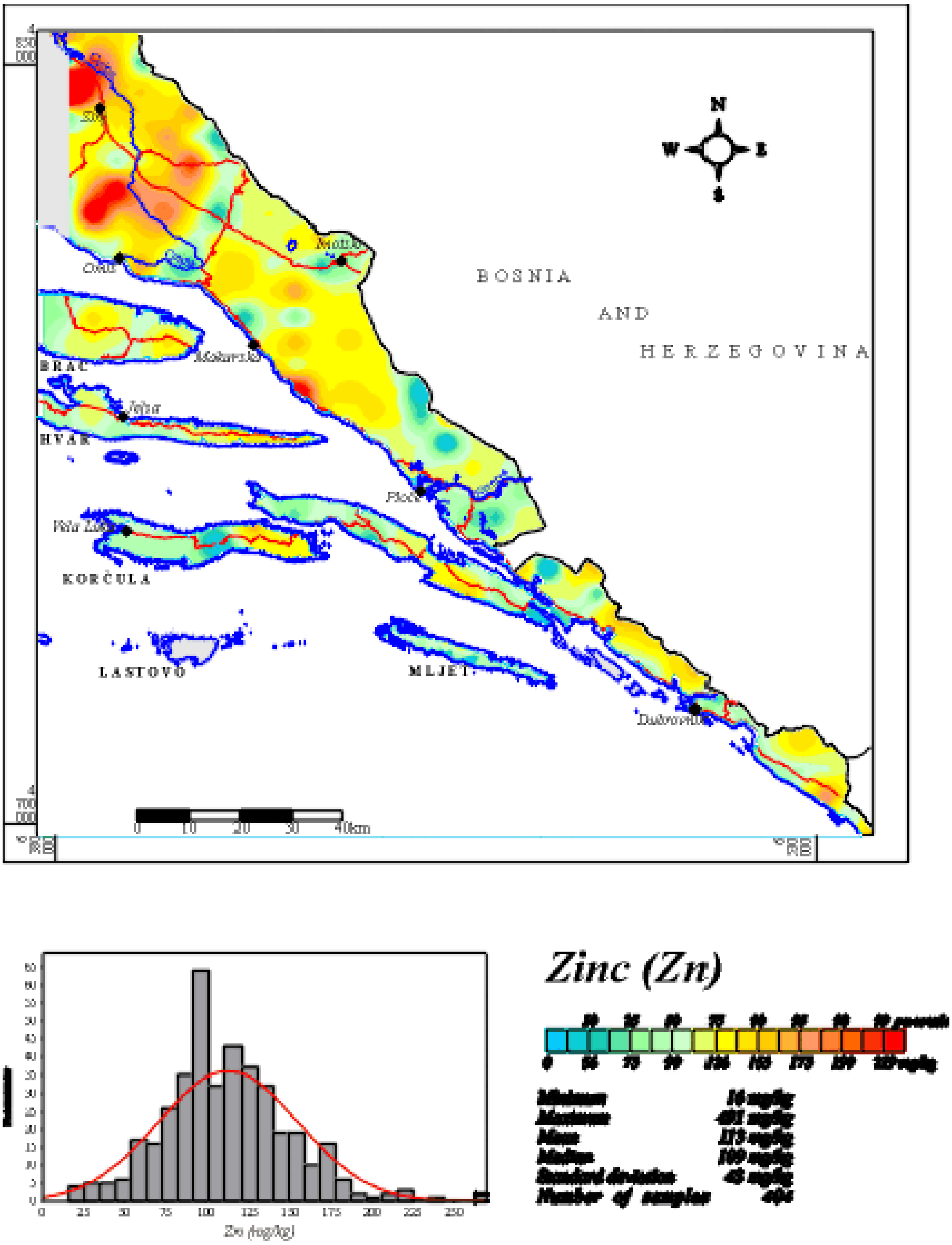


PLATE 43

The distribution of Zn in soils from S Dalmatia.

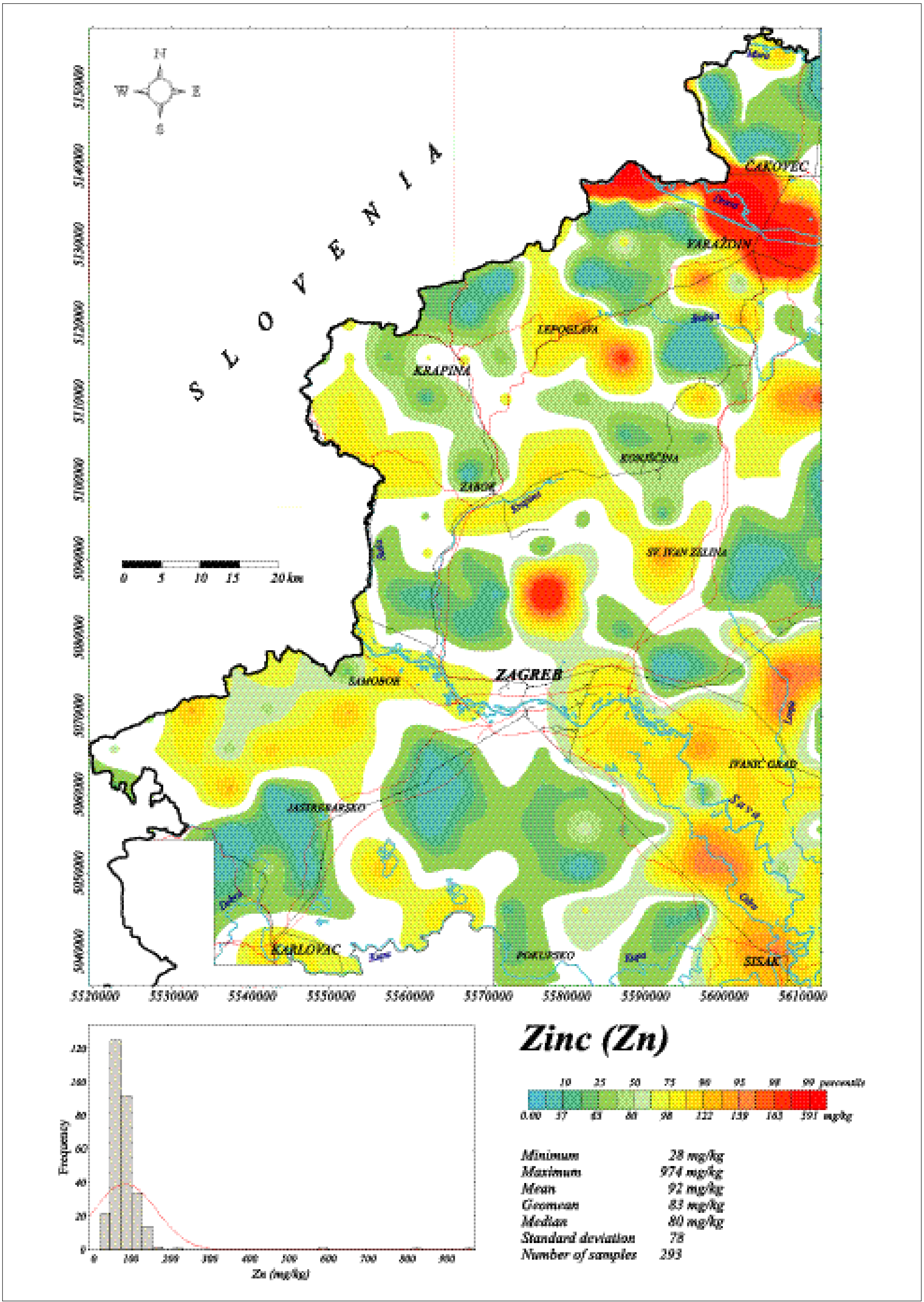


PLATE 44

The distribution of Zn in soils from NW Croatia.

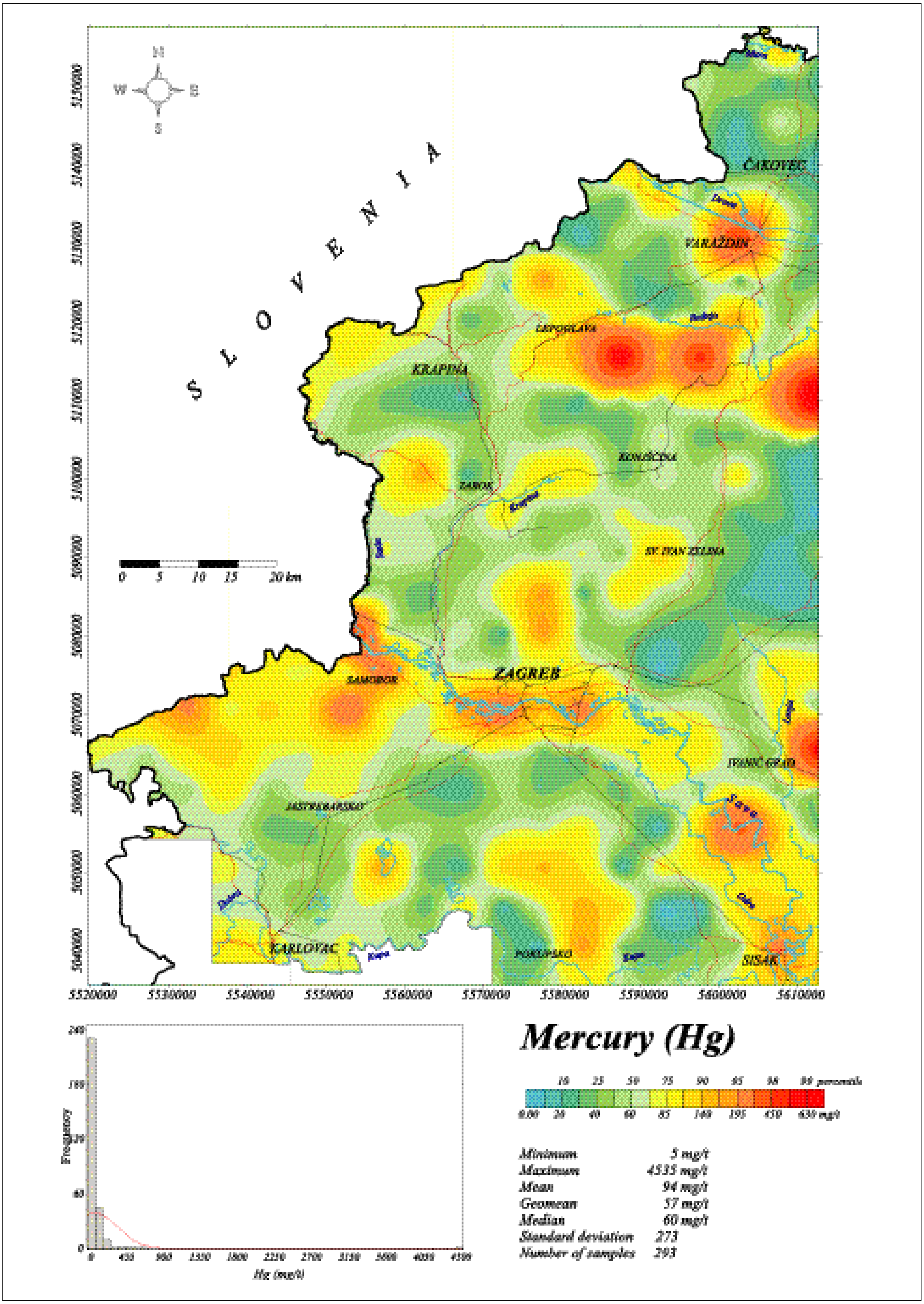


PLATE 45

The distribution of Hg in soils from NW Croatia.