
Trace Metals in Agricultural Soils of the Danube River Tributary Basins in Croatia

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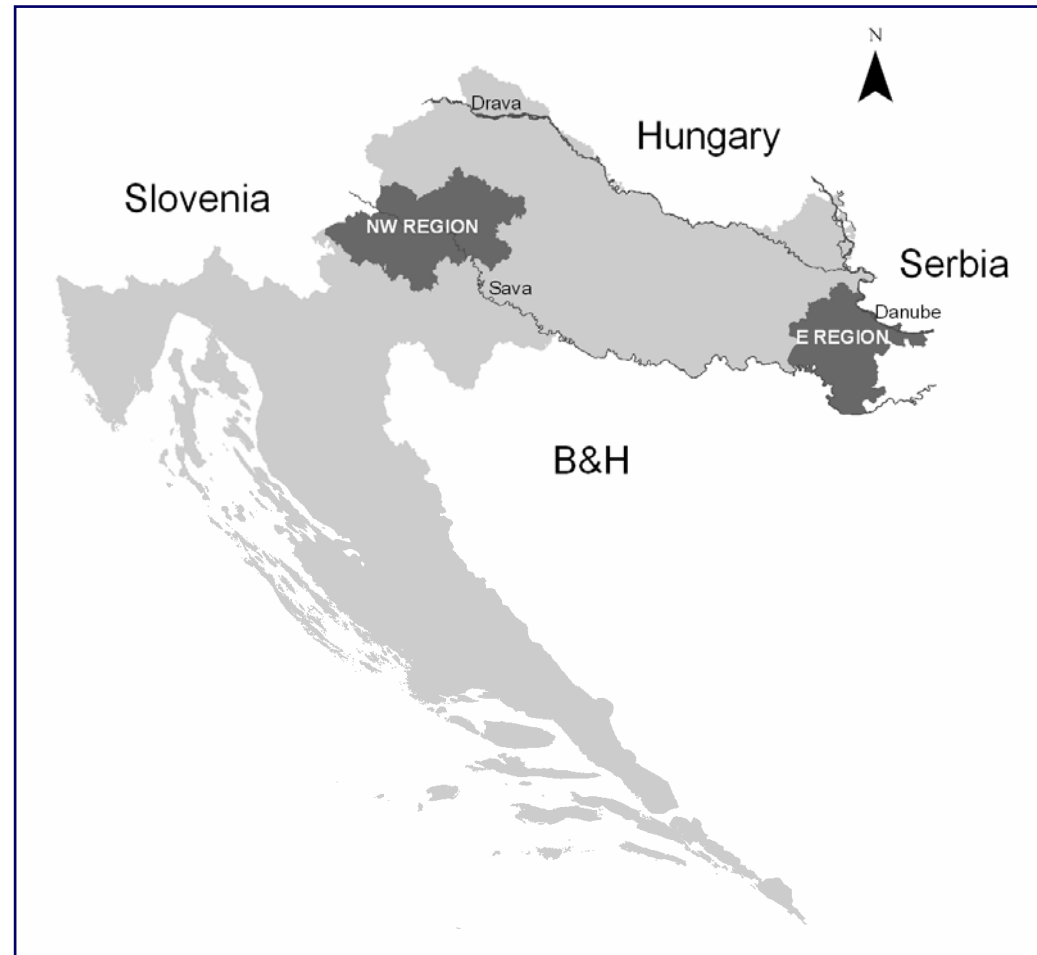
Danube River Tributary Basins

- ❑ consists of the Drava and Sava River basins
 - ❑ 62% of state territory
 - ❑ intensive agricultural production
 - ❑ industrial activities
 - ❑ growing municipal communities
 - ❑ potential sources of soil pollution
 - ❑ negative effects on soil functions and water quality
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- ❑ Soil quality and pollution level assessment

Study Areas

NW region

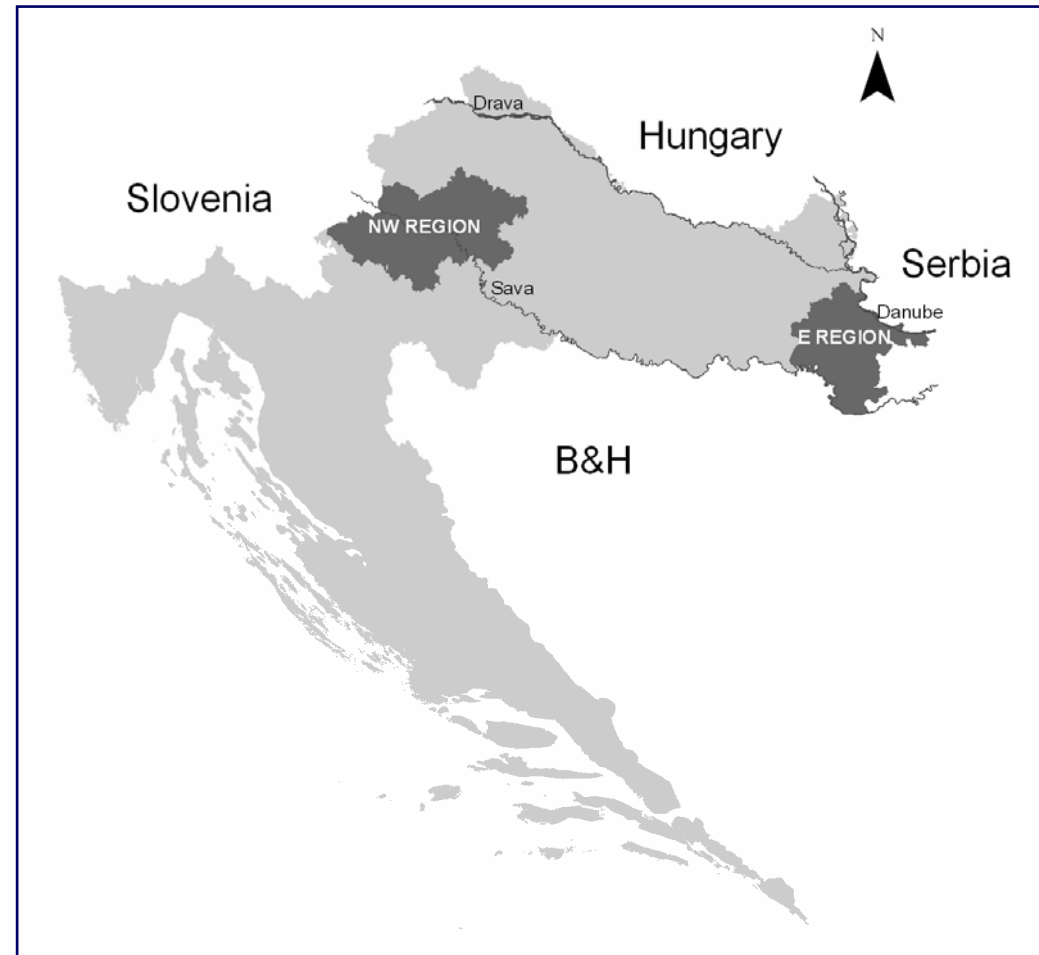
- ❑ City of Zagreb and the Zagreb County → western entry of the Sava River flow
- ❑ area of 3000 km²
- ❑ large variability in lithology, soil types and land use
- ❑ large alluvial plain bordered by a mountain range
- ❑ > 50% of land used for agriculture



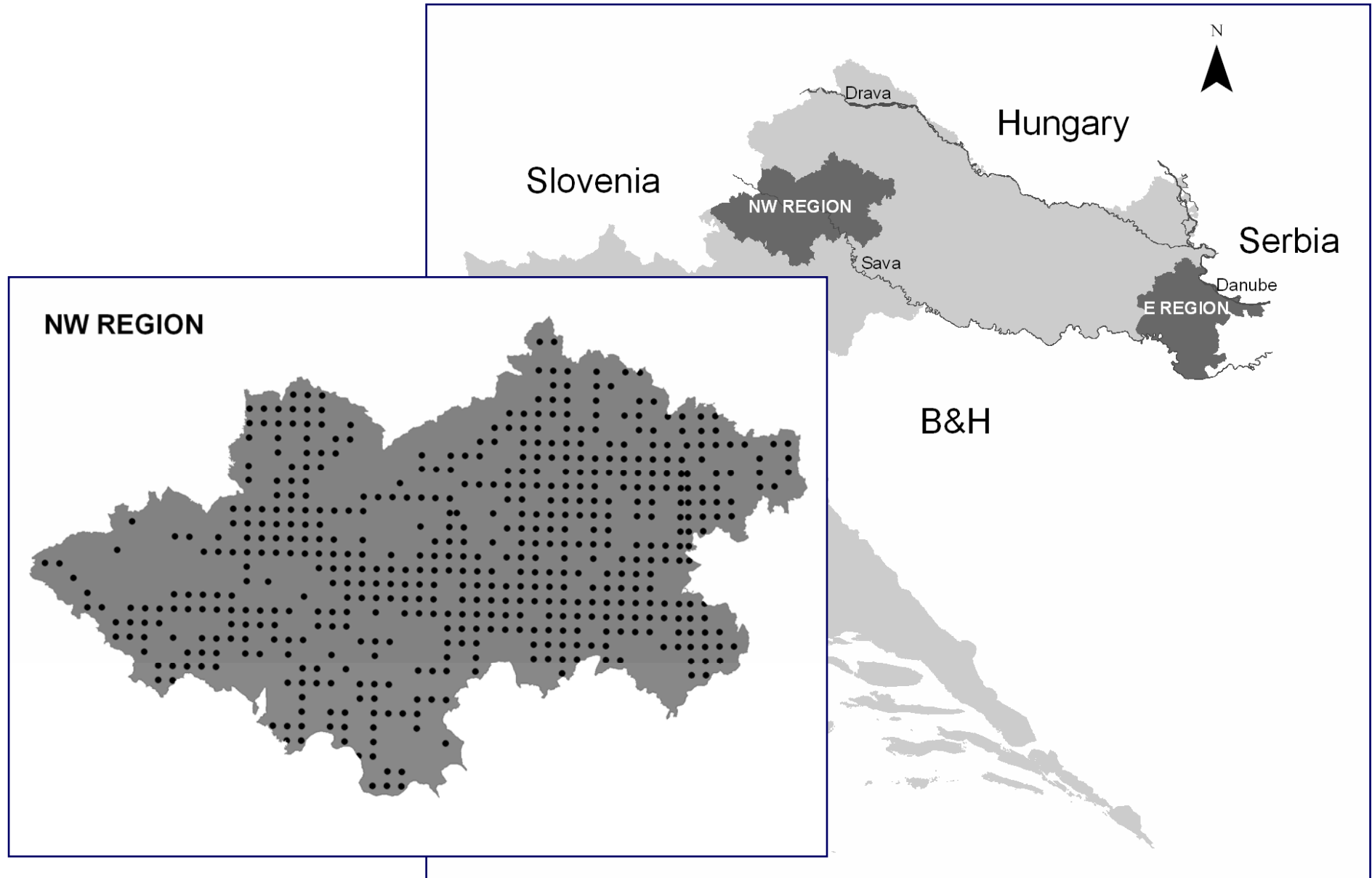
Study Areas

E region

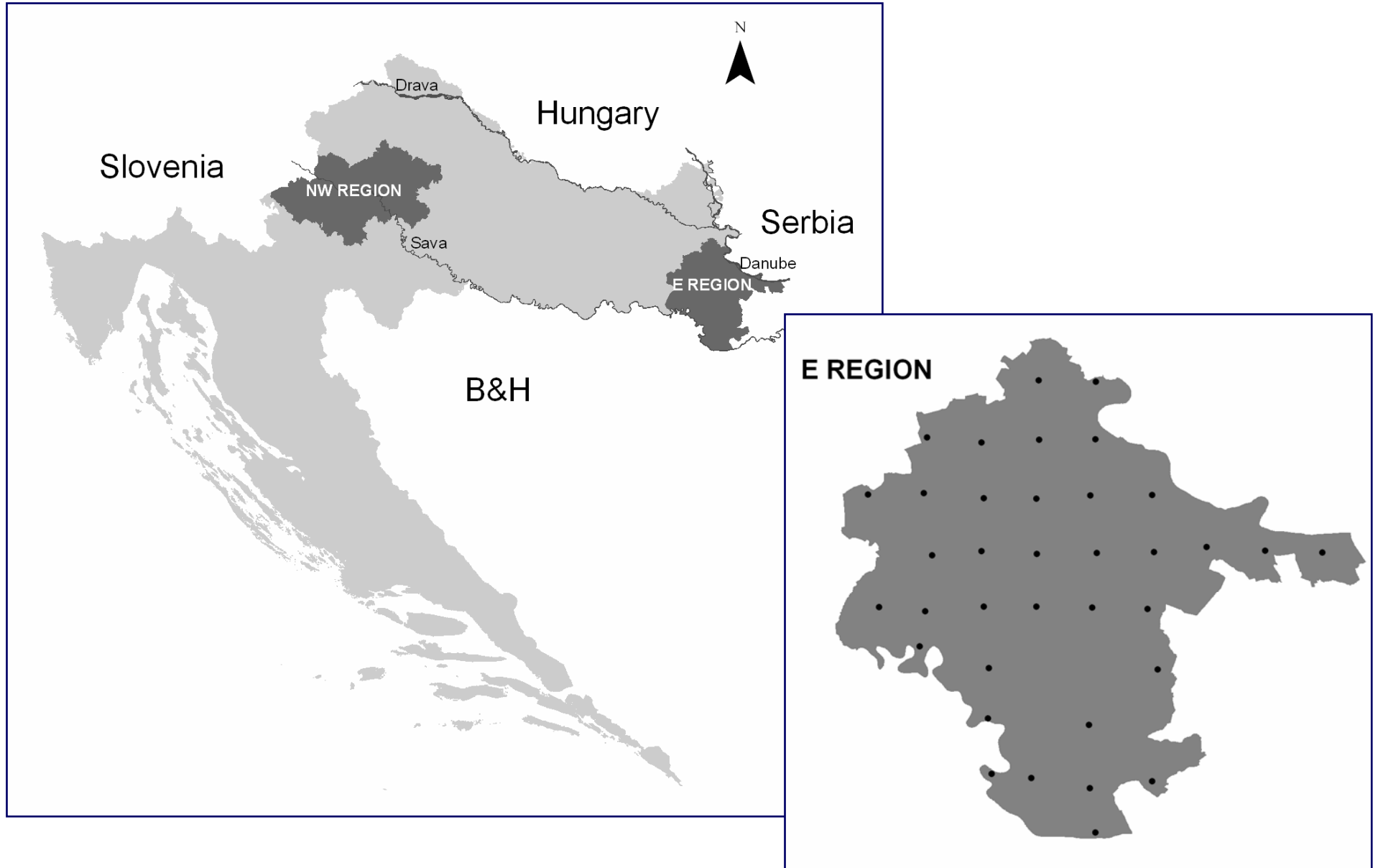
- ❑ Vukovarsko - Srijemska County
- ❑ eastern flow of the Sava River in Croatia
- ❑ area of 2448 km²
- ❑ low variability in lithology, soil types and land use
- ❑ large plateau bordered by Mt Fruska Gora and Mt Dilj
- ❑ > 60% of land used for agriculture



NW REGION: 536 topsoil (0-30 cm) samples collected
2-km sampling grid



E REGION: 36 topsoil (0-30 cm) samples collected
8-km sampling grid



Chemical analyses

- ❑ heavy metal concentrations in soil digest determined by ICP-OES after aqua regia extraction
- ❑ Hg content determined by CV AAS technique

Geospatial database built using ArcGIS

Statistical analyses

- ❑ summary statistics results compared with median values in Croatian soils and maximal permissible concentrations (MPC)
- ❑ interpolated maps generated by ArcGIS extension of Geostatistical Analyst

NW REGION

- ❑ background element concentrations lower than median element values in Croatian soils
- ❑ highest concentrations of Cd, Cr, Cu, Ni, Pb and Zn exceed MPC
- ❑ critical conditions recorded for Cu, Ni and Cr
- ❑ mean values for all samples lower than critical thresholds
- ❑ high values unevenly distributed

Variable	Mean	Median	SD	Min	Max	Skewness	Kurtosis	Croatian soils ^a	MPC ^b
pH	6.65	6.46	1.02	3.45	8.31	0	-1.28	-	-
OM (%)	4.47	3.94	2.05	0.91	14.1	1.36	2.41	-	-
Ca (g kg ⁻¹)	11.7	5.00	26.5	0.67	214	5.11	27.7	8.2	-
Cd (mg kg ⁻¹)	0.34	0.25	0.27	0.06	3.28	4.05	31.5	0.4	2
Co (mg kg ⁻¹)	11.1	11.1	3.26	2.74	27.0	0.92	3.04	13.0	-
Cr (mg kg ⁻¹)	54.0	51.2	16.1	11.5	122	0.73	1.24	88.2	120
Cu (mg kg ⁻¹)	40.1	22.1	77.5	3.64	641	5.24	29.9	25.4	120
Fe (g kg ⁻¹)	30.8	30.8	7.65	5.85	59.1	0.09	0.03	34.0	-
Mg (g kg ⁻¹)	8.07	6.66	5.15	2.67	36.6	3.04	10.6	7.2	-
Mn (mg kg ⁻¹)	595	548	292	146	4537	5.33	62.4	722	-
Ni (mg kg ⁻¹)	31.5	27.5	14.9	2.85	117	1.83	4.94	47.5	75
P (mg kg ⁻¹)	694	644	286	215	3023	2.56	12.8	670	-
Pb (mg kg ⁻¹)	21.6	18.2	15.7	1.00	216	6.73	65.2	33.0	150
S (mg kg ⁻¹)	355	299	222	47.7	2275	2.82	15.8	-	-
Zn (mg kg ⁻¹)	74.6	67.8	30.9	27.1	479	5.13	56.4	88.0	200

E REGION

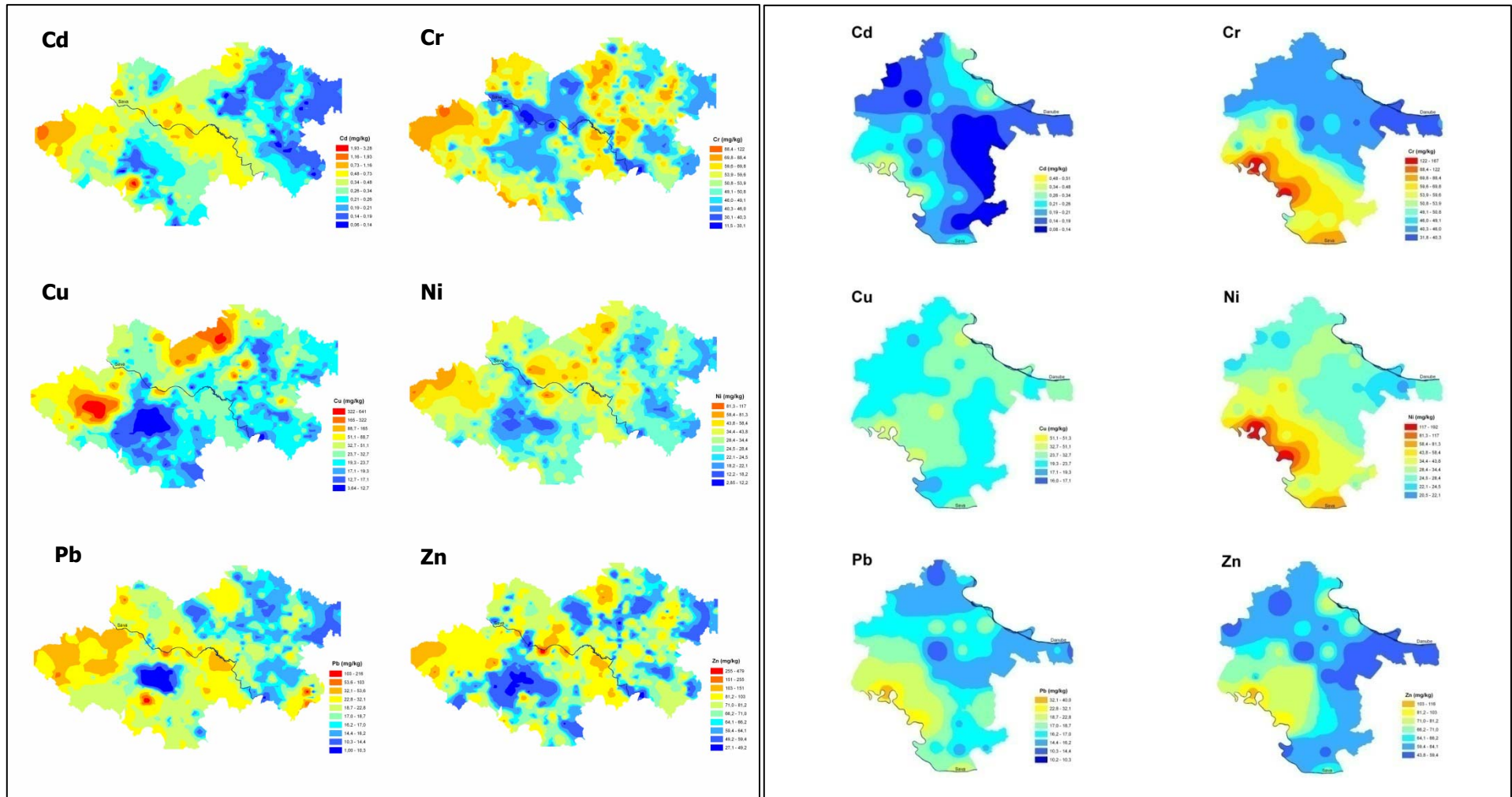
- ❑ background element concentrations lower than median element values in Croatian soils
- ❑ highest concentrations of Ni and Cr exceeded MPC
- ❑ maximum concentrations of all other elements do not exceed MPC
- ❑ median values for all samples lower than critical thresholds

Variable	Mean	Median	SD	Min	Max	Skewness	Kurtosis	Croatian soils ^a	MPC ^b
pH	7.12	7.50	0.93	5.16	8.22	-0.39	-1.37	-	-
OM (%)	2.42	2.21	0.87	1.14	5.22	1.20	1.85	-	-
Ca (g kg ⁻¹)	15.1	7.98	18.3	3.13	96.0	3.02	10.7	8.2	-
Cd (mg kg ⁻¹)	0.19	0.19	0.10	0.08	0.51	1.26	2.38	0.4	2
Co (mg kg ⁻¹)	12.6	12.1	2.84	8.60	23.4	2.83	9.42	13.0	-
Cr (mg kg ⁻¹)	53.4	45.5	27.1	31.8	167	3.37	11.6	88.2	120
Cu (mg kg ⁻¹)	24.6	22.7	7.88	16.1	51.3	1.83	3.34	25.4	120
Fe (g kg ⁻¹)	29.7	29.4	4.56	23.4	47.7	2.52	8.31	34.0	-
Mg (g kg ⁻¹)	8.87	8.04	3.50	5.19	21.3	1.71	3.57	7.2	-
Mn (mg kg ⁻¹)	699	738	227	324	1385	0.55	1.08	72.2	-
Ni (mg kg ⁻¹)	37.9	27.0	36.4	20.5	192	3.65	13.0	47.5	75
P (mg kg ⁻¹)	845	751	418	447	3019	4.24	21.8	670	-
Pb (mg kg ⁻¹)	17.5	16.5	4.97	10.2	40.0	3.36	13.5	33.0	150
S (mg kg ⁻¹)	212	206	62.6	132	388	1.06	1.03	-	-
Zn (mg kg ⁻¹)	64.7	61.5	13.8	43.8	116	2.09	5.71	88.0	200

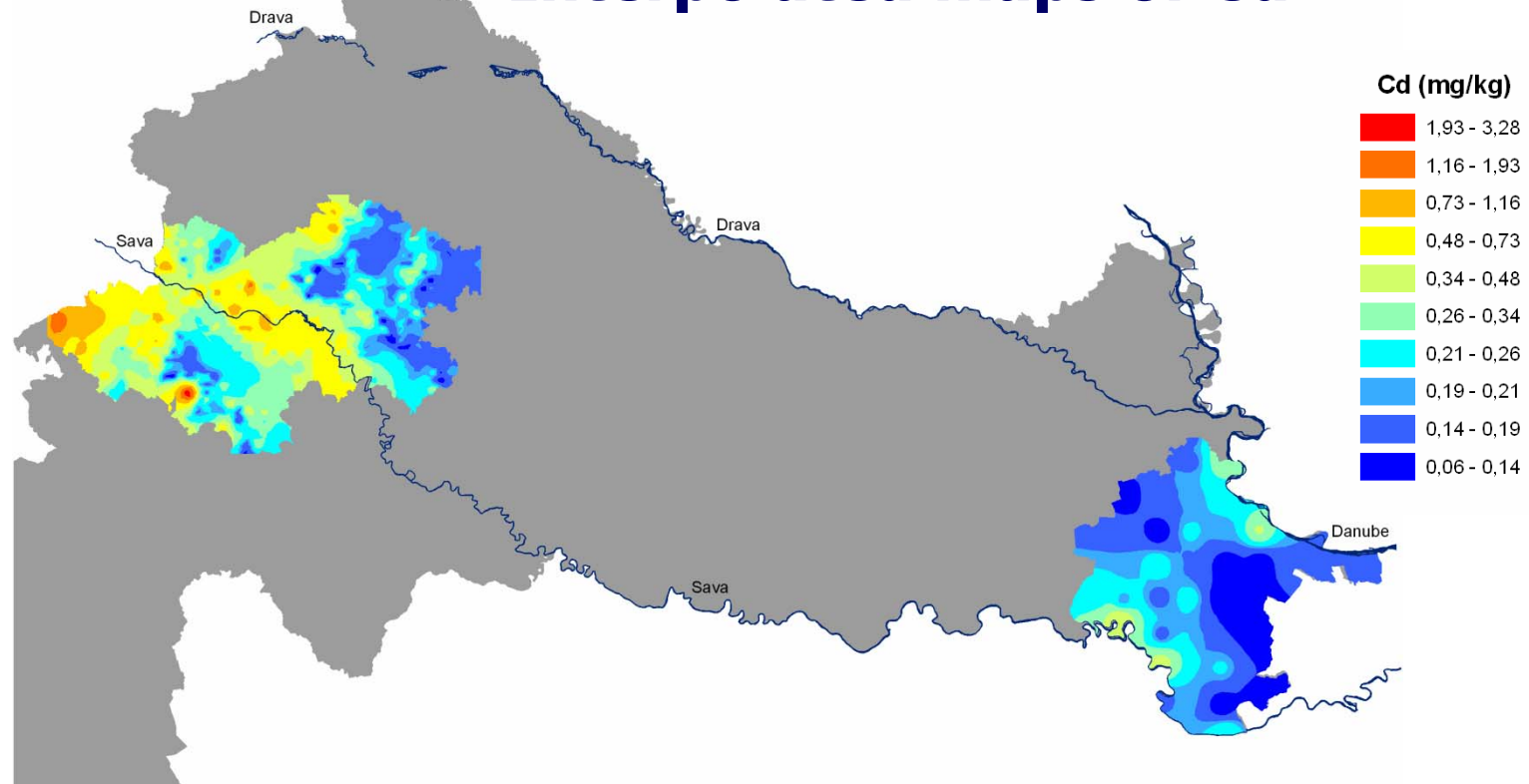
□ geochemical maps for both study areas produced for trace metals for which an MPC is prescribed (Cd, Cr, Cu, Ni, Pb and Zn)

NW REGION

E REGION

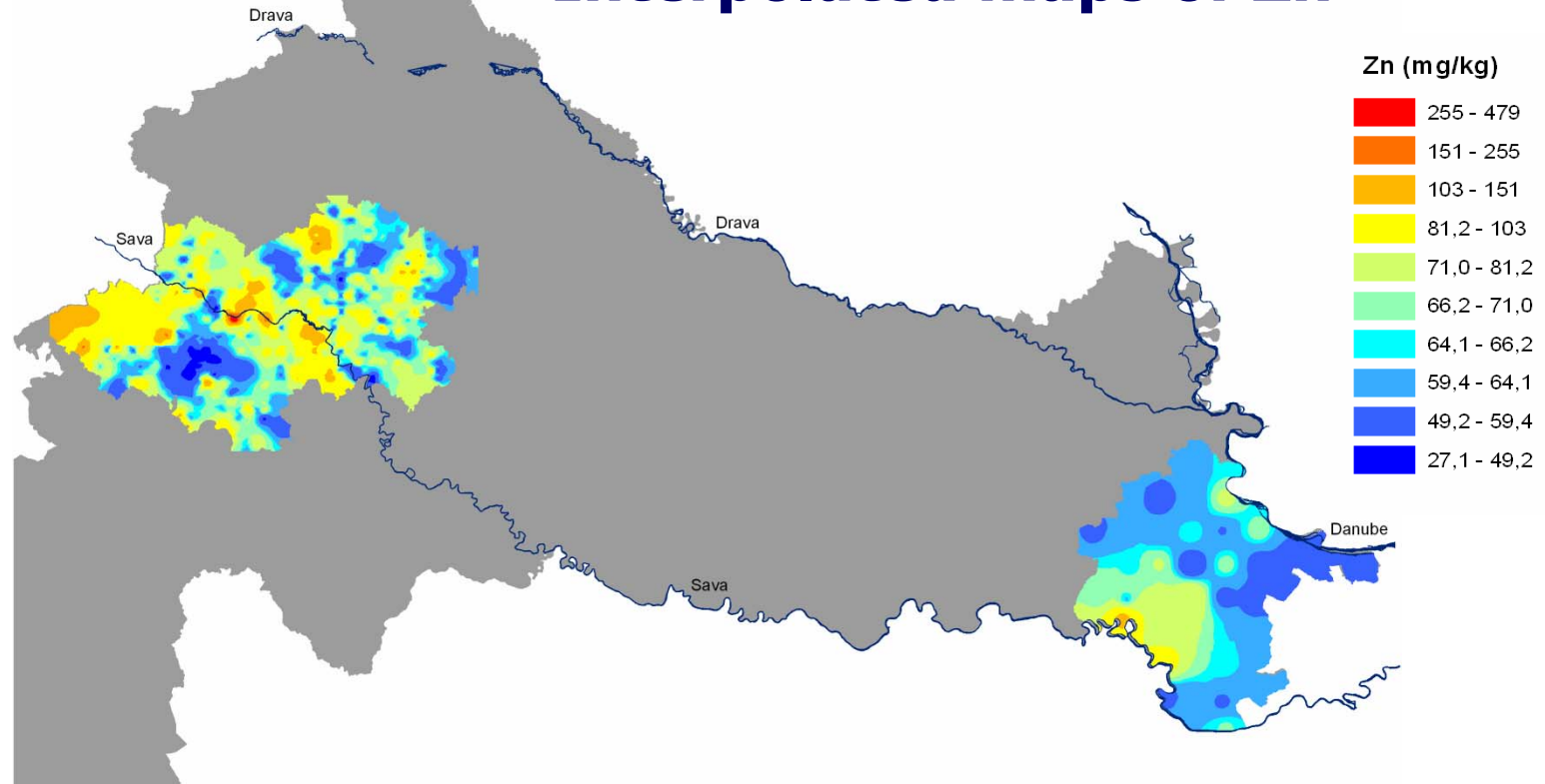


Interpolated maps of Cd



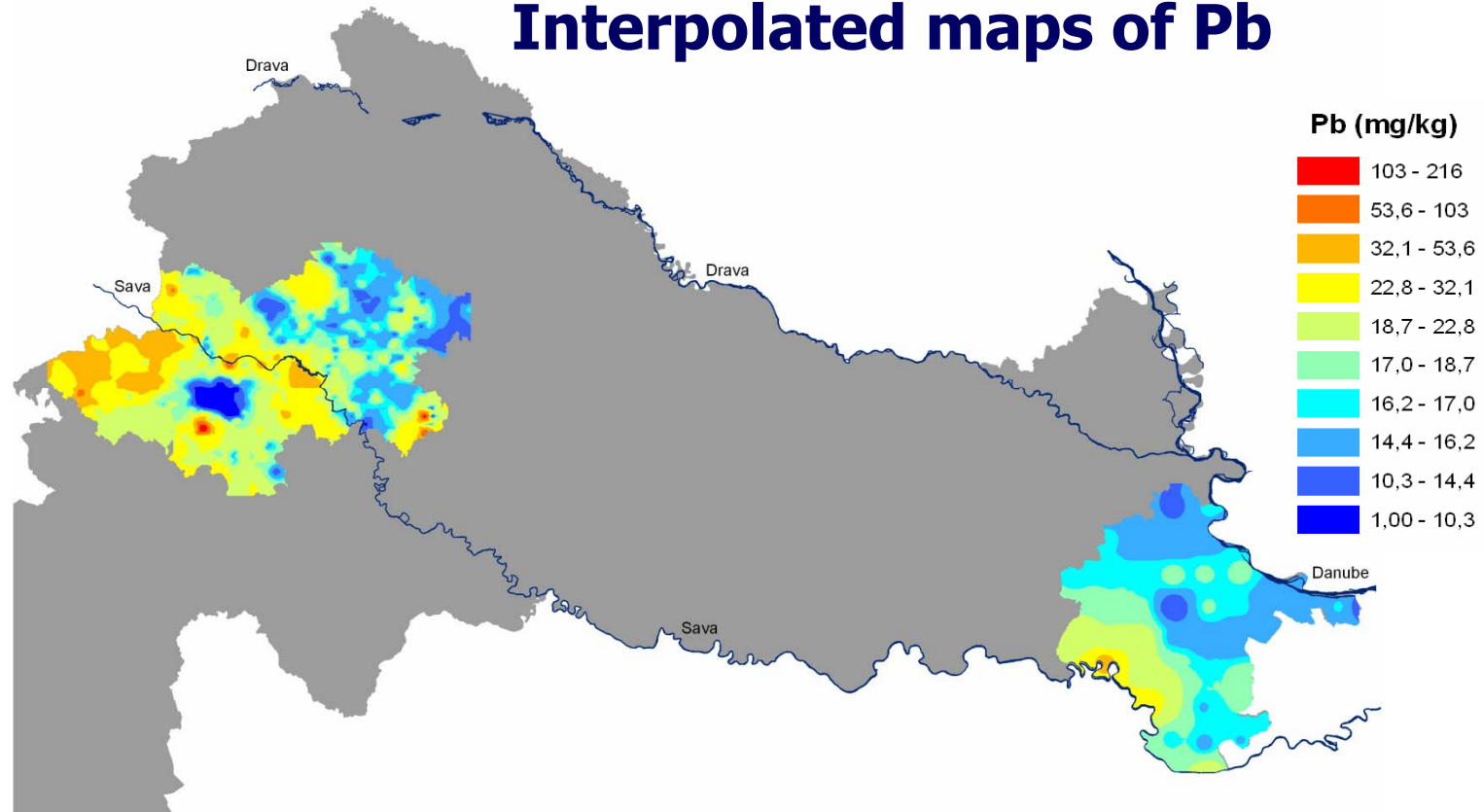
- ❑ Cd concentrations in soils exceeding 0.5 mg/kg → evidence of soil pollution from one of a number of possible sources
- ❑ increased Cd concentrations recorded in a narrow belt on floodplain sediments of the Sava and Danube River, and along the along the piedmont belt
- ❑ widespread distribution and high mobility of Cd → potential contaminant in a great number of natural environments

Interpolated maps of Zn



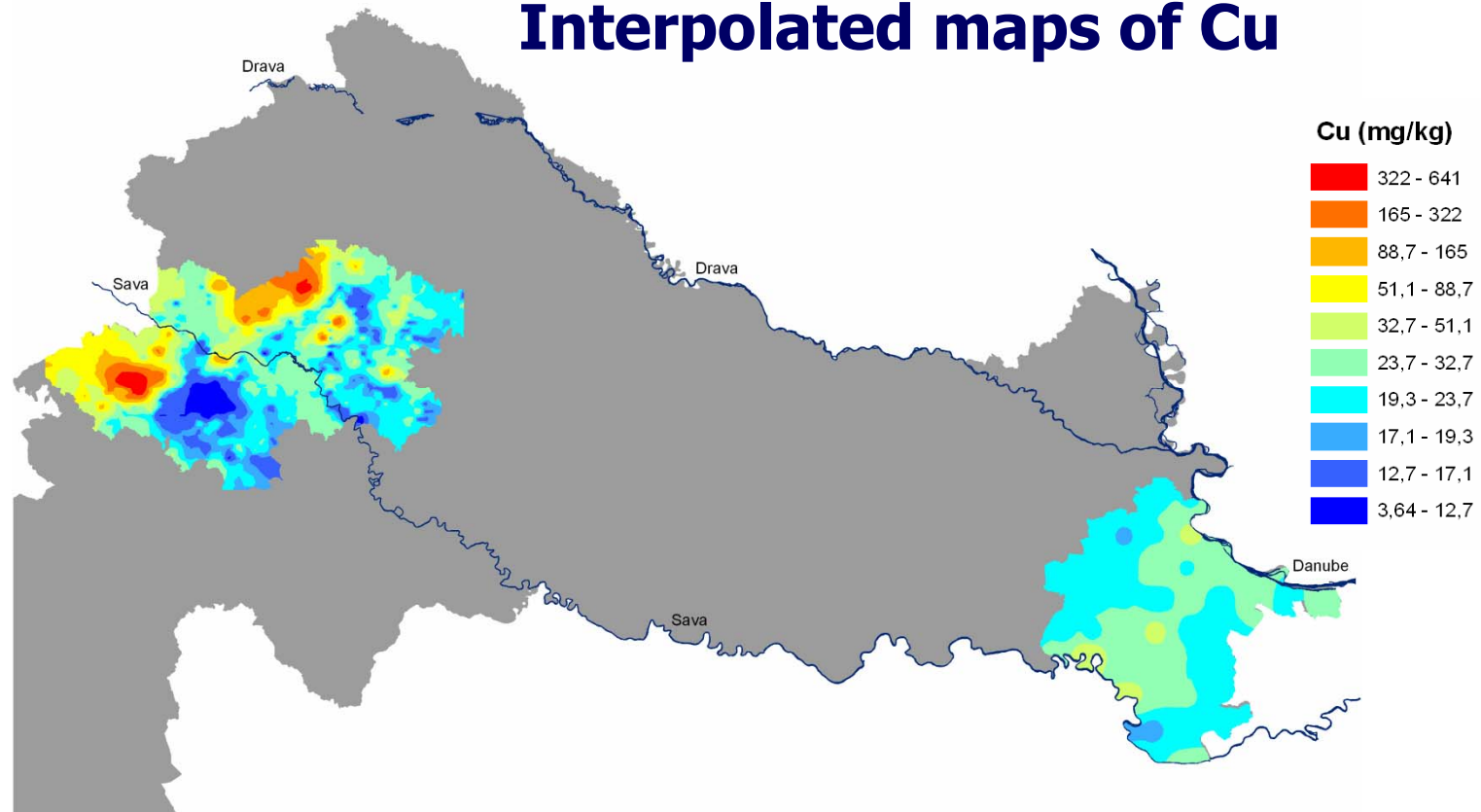
- ❑ highest contents of Ni, Cr and Zn adjacent to Mt Medvednica related to parent material
- ❑ high concentrations also occur on the Holocene fluvial deposits of the Sava River floodplain
- ❑ residual products of soil erosion and weathering of parent materials occurring in upstream areas transported by the river and released during flooding

Interpolated maps of Pb



- highest Pb contents recorded in the Sava River banks, which may be both anthropogenic or geogenic in origin
- its presence not attributable to erosion by surface water
- mining and industrial activities upstream of Zagreb, both in Croatia and Slovenia, influenced quality of the Sava River in the past
- pollutants released directly into the river, had been transported and released to the floodplain together with sediments

Interpolated maps of Cu



- ❑ Cu map related to land use rather than to geological background
- ❑ high values uniformly distributed along the piedmont belt
- ❑ above the alluvium in valleys of the Danube and Sava Rivers
- ❑ caused by vineyards, where the application of Cu-based fungicides resulted in Cu soil accumulation

Conclusions

- ❑ increased heavy metal concentrations are the result of superimposed processes
- ❑ compared with the Vukovarsko-Srijemska County, soil element concentrations in the Zagreb region have slightly increased median values, but several times higher ranges
- ❑ increased topsoil metal concentrations of these regions are both natural and anthropogenic in origin
- ❑ Ni, Cr, Zn, and Cd in alluvial deposits of the Sava River are the residual products of parent material weathering occurring in upstream areas, and are transported by the river and released during flooding

Conclusions

- ❑ besides Pb and Cu, Zn and Cd can also have anthropogenic sources of contamination mainly related to different types of agricultural land use, industry, heavy-traffic roads, airport and marshalling yards
- ❑ contamination risk highest in floodplain sediments
- ❑ floodplain soil properties:
 - exposed to changes
 - at higher risk caused by geogenic materials brought from upstream areas and even other countries

Thank you for your attention!

