Geologia Croatica	54/1	119 - 130	6 Figs.	4 Tabs.		ZAGREB 2001

Geochemical Comparison of Stream and Overbank Sediments: A Case Study from the Žumberak Region, Croatia

Zoran **PEH** and Slobodan **MIKO**

Key words: Geochemical mapping, Drainage basin approach, Stream sediment, Overbank sediment, Discriminant analysis, Žumberak, Croatia.

Abstract

Geochemical comparison between the stream and overbank sediments from low- to medium-order drainage basins is grounded on the presupposed statistical contradistinction of their locality-paired sample correlatives. Discriminant analysis differentiated the overbank from stream material mainly on account of higher content of most of the analyzed elements in the former vis-à-vis an otherwise common geochemical semblance. Only the carbonate material seems to be depleted in overbank sediment samples. Investigations also demonstrated that in the relatively non-contaminated area it may be more difficult to verify the supposed purity-contamination reciprocity between the investigated media, since the recent and prehistoric materials were not contrasted as regards their non-lithogenic components.

1. INTRODUCTION

Regional geochemical mapping makes use of various sample media which offer the general prospect either of finding a particular type of mineral deposit or, more commonly, of locating the presence of certain anthropogenic contaminants. Opinions on the particular advantages and drawbacks concerning different types of sample materials have been amply described (e.g. REIMANN, 1988; OTTESEN et al., 1989; MACKLIN et al., 1994; EDÉN & BJÖRKLUND, 1994; PULKKINEN & RISANEN, 1997; HUISMAN et al., 1997; SWENNEN & SLUYS, 1998; SWENNEN et al., 1998, and others). Yet, owing to the fact that all of these are not readily available in different parts of the globe, the general consensus has not been established hitherto, which is why the regional and local schemes of geochemical survey in various countries, and sometimes even in the same country, differ accordingly.

In Croatia, regional geochemical mapping is based upon soil as the primary sample medium. This is mainly due to the fact that soil is the only sample material available throughout the country, particularly when the southern, almost entirely carbonate terrains are considered. In the northern, Pannonian region, owing to the expansive drainage system, other sample materials, e.g. stream or overbank sediments, can be found in abundance. As a consequence, the question may arise whether stream sediment, or soil, or, perhaps some other type of regolith material, would be the most appropriate for sampling in order to detect the greatest variation among geochemical data. This is particularly of interest in areas where two distinctly different lithologies, such as carbonate and non-carbonate sedimentary rocks, associate in a complex way (as in the Žumberak region). It should be emphasized that soil sampling, when compared to the sampling of stream or overbank sediments, is based on an altogether different philosophy. The first approach is, as it were punctuated, with no strictly defined conjoined area of underlying bedrock influence, regardless of the chosen sample design. The second approach is area-related which increases the possibility of reflecting the surface lithology of the whole area upstream from the sampling site. Besides, when observing the drainage basin as a fundamental geomorphological unit (CHORLEY, 1969), it is certain that less bias would be inferred if one can deem it to be an area originated and embedded in the surrounding landscape by a set of natural processes pertaining not only to the strictly geomorphological but also to the geochemical domain. This is why many authors, especially from the northern, carbonate-free part of Europe, but also elsewhere in the world, applied, as a rule, the catchment basin analysis in their geochemical research (BONHAM-CARTER et al., 1987; CARRANZA & HALLE, 1997; ÓDOR et al., 1997, and others). Thus, the sampling of appropriate media in a catchment basin is rendered desirable wherever the landscape allows it, because their geochemical assemblage may elucidate the average composition of this unit area more faithfully than any of the soil sampling designs. This may be of particular value in the case of geochemical reconnaissance both in the regions suspected of mineralization or for possible pollution.

When reconnaissance geochemical surveys are carried out in low- to medium-order drainage basins, where both stream and overbank sediments are obtainable for sampling, it may not be obvious as to which of

Institute of Geology, Sachsova 2, HR-10000 Zagreb, Croatia.

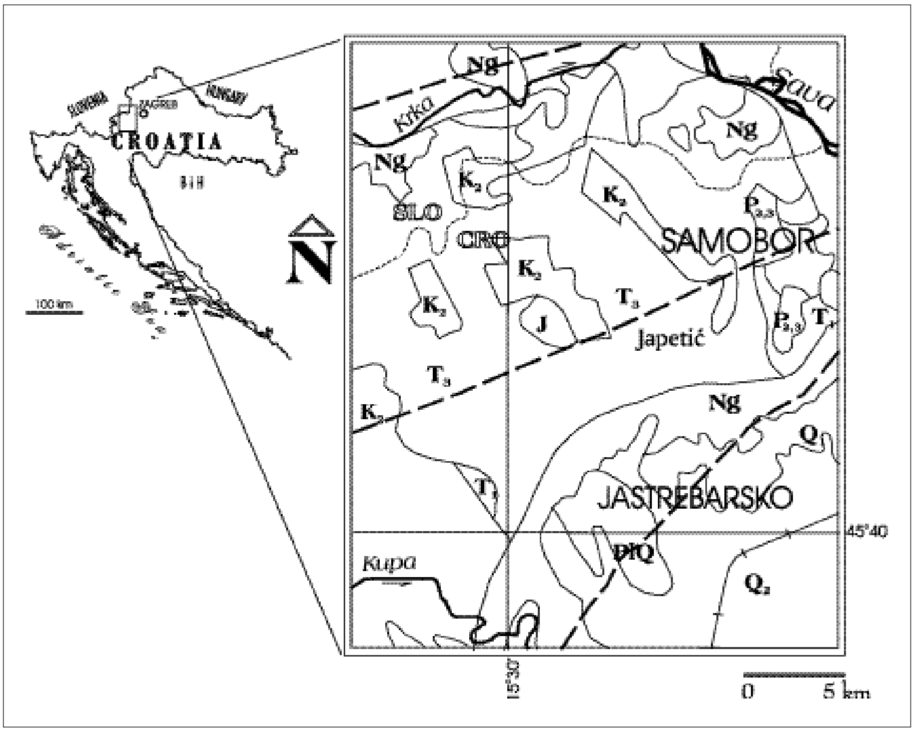

Fig. 1 Simplified geological map showing location of the study area (after BUKOVAC et al., 1983; ŠIKIĆ et al., 1978; PLENIČAR et al., 1976). Legend: Q_2) Holocene in general; Q_1) Pleistocene in general; PlQ) Plio-Quaternary: unconsolidated sediments; Ng) Neogene in general: clastic rocks; K_2) Upper Cretaceous: limestones, dolomites and flysch; J) Jurassic in general: predominantly limestones; T_3) Upper Triassic: predominantly dolomites; T_1) Lower Triassic: predominantly clastic rocks; $P_{2,3}$) Middle and Upper Permian: predominantly clastic rocks.

these media, or perhaps both, should be sampled in order to acquire the best geochemical information from the study area. Granted that processes having control over the mass movement within the catchment basin are common in both cases, one may suppose a subsequent similitude in their overall geochemical assemblage, with only a small variation in the data. Nevertheless, for practical consideration a time dimension should always be taken into account, especially in validating the anthropogenic versus natural contribution to the chemical content of alluvial materials. This is due to the fact that stream sediment represents an active material of recent origin which is temporarily suspended on a stream bed, while overbank sediment indicates alluvial regolith of earlier depositional cycle(s) produced as a result of extensive floods (OTTESEN et al., 1989). On this premise, a tacit assumption is made about the main difference in the geochemical composition between the two types of alluvial sediment. Namely, overbank sediment (except in its uppermost section) should represent an unpolluted, pristine medium when deposited in a natural, pre-industrial environment, while, on the other hand, stream sediment is expected to reflect every kind of recent contamination that may arise in the investigated area. Furthermore, geochemical variation resulting from potential mineralization within a catchment basin is supposedly detectable in both. Therefore, the immediate scope of the present study will be to explore the geochemical difference between these two sample media in an area with a well-known overall geological setting and expected, but minor, anthropogenic influence. It will hopefully shed some light on the possible advantages in utilization of one or, perhaps, both of these sample media in further low- to medium-density geochemical mapping of some target areas in Croatia.

2. DESCRIPTION OF THE STUDY AREA

Žumberak is a mountainous territory located to the west and in the immediate vicinity of the Croatian capital of Zagreb. To the north and west it is bordered by Slovenia, and to the south by the Kupa river, while its east and southwest portions gently dip towards the Karlovac depression (Fig. 1). The landscape combines the features of Dinaric, highly dissected, carbonate terrains abounding in various karstic phenomena such as sinkholes, together with Pannonian, mostly non-carbonate terrains of moderate relief and with a regular drainage network. The highest point in the area is the summit of Sveta Gera (1,160 m), while the surrounding valleys of the Sava, Krka and Kupa rivers with their terraces do not exceed altitudes of about 200 m.

2.1. Geological setting

The study area is geologically mapped at 1:100,000 scale and presented mostly on the sheet of Zagreb (ŠIKIĆ et al., 1978). Only a small portion falls within the sheets of Črnomelj (BUKOVAC et al., 1983) and Novo Mesto (PLENIČAR et al., 1976). Geotectonically, it belongs to the broad boundary zone between the Dinaric carbonate platform (Dinaricum) spreading to the southwest, and adjacent Inner Dinaride area (Supradinaricum) lying on the northeast (HERAK & BUKOVAC, 1988; HERAK, 1991). The geotectonic character is well reflected in the intricate tectonic and, particularly, lithological patterns.

The oldest rocks in the area are mostly clastic sedimentary rocks of Middle and Upper Permian age. These consist predominantly of sandstones, more rarely of conglomerates, shales and siltites. Apart from the clastic rocks, limestones and dolomites occur sporadically. The Early Triassic rocks are prevalently non-carbonate, mostly sandstones in their lower part with increasing portions of carbonate component toward the upper levels. Sedimentation was continuous until the Middle and Upper Triassic in predominantly carbonate facies. The Upper Triassic dolomites are the most significant lithological member of the series. Jurassic sedimentary rocks are almost entirely carbonate with limestones as a dominant member, while the overlying discordant Upper Cretaceous rocks consist of a thick flysch-type series which was deposited during the Cenomanian-Senonian period. The latter include predominantly calcareous and clayey marls and calcarenites which, together with the former, frame the margin of the Dinaric carbonate platform. Their contact with the surrounding Upper Triassic dolomites (Supradinaricum) is clearly tectonic, the nappe front frequently masked by vertical neotectonic faults (HERAK & BUKOVAC, 1988). Frequent tectonic activity with periodic changes of depositional environment during the Tertiary resulted in greater diversity of the clastic sedimentary facies. From Palaeocene to Pliocene, a variety of clastic sedimentary rocks were formed, mostly sandstones and marls. Carbonate clastic rocks predominate only through the Badenian. The transition into the Quaternary was marked by the onset of freshwater sedimentation with an extensive and thick series of lithofacially differentiated sediments - from gravel to clays. Plio-Quaternary sediments occupy a considerable part of the study area, particularly its lowered southern rim bordering the Karlovac depression. Quaternary deposits are represented almost entirely by the Holocene alluvial sediments of the local streams.

2.2. Mineral occurrences

Mineralization in the investigated area is related mostly to the layers or veins hosted in the fine-grained clastic Permian rocks. Apart from a number of scattered Fe, Pb, Zn, Cu, Au and Hg occurrences together with gypsum and barite, there is a small-scale siderite-haematite-sulphide ore deposit in the valley of Rudarska Gradna. Until the middle of the last century it had been mined extensively for iron for a few hundred years. The iron ore typically occurs in the form of a siderite layer of submarine sedimentary origin interstratified between the Palaeozoic sandstone beds (ŠINKOVEC, 1971; ŠIFTAR, 1989). The main ore body is accompanied by haematite lenses as well as with sulphide veins containing chalcopyrite and a barite-galena paragenesis. The latter occur invariably in the underlying sandstone strata, while the overlying sandstone series contains in its uppermost parts the thick (45 m) gypsum-anhydrite bed (ŠINKOVEC, 1971) which marks the border with the Triassic.

Small mineral occurrences of the same origin are widely disseminated through the Permian outcrops of the nearby valleys such as Lipovačka Gradna and Ludvić, as well as Okićnica. A different type of mineralization can be found in the western part of the investigated area. It appears as small remnants of sedimentary limonite deposits covering the Middle and Upper Triassic dolomite palaeosurface. A few such occurrences are strewn over the area of the Slapnica valley, north of Krašić.

2.3. Anthropogenic influence

The area of investigation is free from the immediate impact of great industrial or other sources of contamination. The nearest industrial center, the capital city of Zagreb, is more than 20 kilometres away to the east. Small cities such as Samobor, scattered on the perimeter of the investigated mountainous area, do not employ industries of great scale or pollution capacity.

There are, however, two known sources of human influence that may be observed in the local catchment areas. One can be ascribed to the bygone mining activities that may have left traces of increased concentrations of heavy metals such as Pb, Zn and Fe both in the stream and overbank sediments within some of the low-order catchments. The other can result from recent agricultural activity, generally viniculture, with anticipated increases in Cu (from bluestone) and P (from fertilizers). The former is restricted to the inner, mountainous part of the study area, while the latter can be found scattered over the wider zone of the southern slopes of Samoborsko gorje, particularly in the surroundings of Krašić and Jastrebarsko.

3. MATERIALS

3.1. Sampling

More than forty low- to medium-order drainage basins ranging in size from 0.65 to 122.94 km^2 were sampled, in a close-spaced sampling design covering the territory of approximately 600 km^2 (Fig. 2). For a closer inspection into the sources of geochemical variance between the stream and overbank sediments the paired samples of both media were regularly collected from the same sample site (within a few metres). This procedure necessarily excluded a number of smaller, dominantly mountainous drainage basins (mostly of the fourth order) from the analysis, where only stream samples were available for sampling. A total of 40 sites with both stream and overbank material have been sampled over the entire area (Table 1), a sampling density of approximately one sample per 15 square kilometers being thus defined.

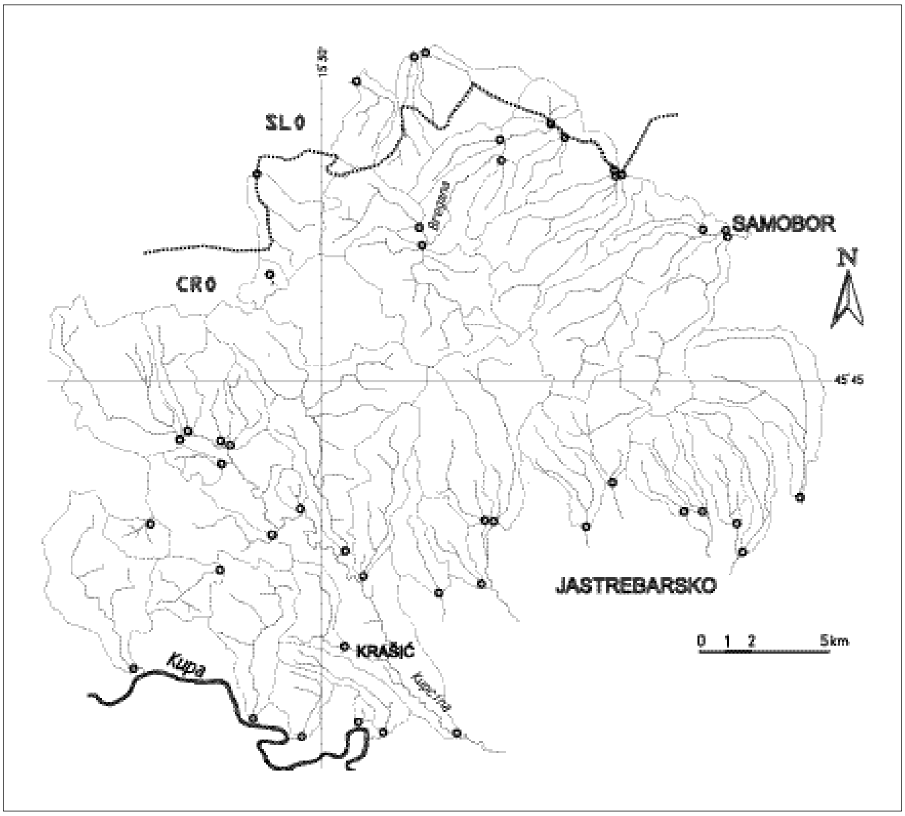

Fig. 2 Sample map.

The sample sites were selected at the basin outlets, sufficiently upstream from the confluence with higher or same order streams in order to avoid sampling the sediment that may result from mixing of material from the two channels during the flood flow. An active stream sediment, which represents the composite of the recently deposited bed load material, was collected from several spots (ordinarily 5-10 as recommended by SALMINEN et al., 1998) over a short channel stretch upstream of the selected site. Simultaneously, a single overbank sediment sample was taken from approximately the same point at the exposed area of either bank of a channel. The latter is composite material taken from the bank section ranging in height from 25 cm beneath the surface down to the water level (usually 0.5 to 2 m thick), while the first 25 cm of upper, near surface, horizon was avoided because of possible anthropogenic disturbance and pedogenesis. In both cases a quantity of about 3 kg of sediment was collected to yield enough representative material for sieving and analysis.

3.2. Sample preparation

Collected samples were air-dried (at <40°C) for approximately three months. After drying, the samples were disaggregated in a porcelain mortar, homogenized, and finally dry-sieved through stainless-steel screens to the fraction of <125 µm. This fraction was preferred because the highest concentration of most of elements, especially trace elements, occur in the fine-grained, usually from 63 to 125 µm size fraction (e.g. RHOADS & CAHILL, 1998). Also, different studies show that the <125 µm size fraction makes up more the 95% of the particles in most samples (SWENNEN et al., 1998).

3.3. Analytical methods

Analytical work was performed at the ACME Analytical Laboratories in Vancouver, Canada, where samples were subjected to multi-acid digestion ICP analysis, and geochemical Hg analysis by flameless AA. A total of 36 elements were thus analyzed with Au, Be, Bi, Mo, U and W invariably, and Ag, Sb, Sn and Cd mostly having concentrations below the detection limit. Elements such as Th, Y, Nb and Sc were measured slightly above the threshold, so that all of these were omitted at the outset from further considerations.

4. STATISTICAL ANALYSIS

4.1. Univariate statistics and data transformation

A set of 22 elements was used in statistical analysis. Eight major and 14 minor and trace elements were selected as predictor variables in the process of discrimination. Table 2 displays the summary statistics of the analytical data including the skewness coefficient as a measure of normality. Due to the fact that a number of variables in both groups show highly positively skewed

Case	Sample	Drainage basin	Order	Catchment	Area (km^2)
1	41	Ludvić	4	Sava	4.41
2	194	Orejovec	4	Kupa	5.25
3	196	Piroški potok (SLO)	4	Krka	6.03
4	197	Skradnja (SLO)	4	Krka	5.07
5	214	Fučanski jarak	4	Sava	2.81
6	221	Velika draga	4	Sava	2.99
7	349	Jaševnica	4	Kupa	12.02
8	351	Ponornica 351	4	Krka?	1.01
9	354	Ponornica 354	4	Kupa?	2.86
10	366	Vorbaščica	4	Kupa	4.56
11	371	potok 371	4	Kupa	0.65
12	19	Škrobotnik	5	Sava	8.79
13	21	Breganica	5	Sava	11.21
14	42	Lipovačka g.	5	Sava	26.00
15	43	Rudarska g.	5	Sava	15.48
16	178	Reka	5	Kupa	9.19
17	187	Okićnica	5	Kupa	19.11
18	190	Potok 190	5	Kupa	3.15
19	198	Sušica (SLO)	5	Krka	9.79
20	275	Bregana	5	Sava	14.52
21	276	Rakovac	5	Sava	8.39
22	328	Žumberačka reka	5	Kupa	15.96
23	331	Sušica	5	Krka	8.51
24	333	Suvaja	5	Kupa	22.91
25	334	Potok	5	Kupa	5.44
26	335	Svilnica	5	Kupa	3.63
27	337	Ponikva	5	Kupa	6.46
28	338	Slapnica	5	Kupa	16.25
29	339	Puškarov jarak	5	Kupa	9.77
30	340	Brebrovac	5	Kupa	5.69
31	342	Stiska	5	Kupa	11.43
32	343	Malunja	5	Kupa	6.87
33	344	Gonjeva	5	Kupa	8.11
34	345	Kamenica	5	Kupa	17.23
35	346	Bukovica	5	Kupa	12.25
36	347	Slatinek	5	Kupa	4.33
37	368	Stiper	5	Kupa	5.72
38	370	Selna	5	Kupa	5.32
39	18	Bregana	6	Sava	57.40
40	72	Kupčina	6	Kupa	122.94

Table 1 General data describing the sample sites.

frequency distributions, transformation must have been carried out for most of the minor and trace elements such as Hg, Pb, Cu, Sr, Ba, As, Zn and Cr, but also for some major elements such as Ti and P. The process of conventional log- and ln-transformation was applied separately for each group, but in some cases (Ni for example) the results were poorer than original distributions. In such instances the variables were left natural (the total data set can be requested from the authors).

4.2. Basic principles of discriminant analysis

Geochemical variation between the two investigated sample media, already "known" to be geochemically separable, can be thoroughly investigated by the use of multivariate discriminant analysis. Thus, the two-group (K=2) problem is introduced which presents the simplest case with a solitary discriminant function as a basis for separation. In analysis these groups are labelled STREAM or OVERBANK, respectively. The discrimination procedure revolves generally around how to compute a linear combination of original (predictor) variables that will best distinguish between the groups. This is achieved by both maximizing the ratio of between-group in comparison to within-group variability and generating the smallest misclassification errors (DILLON & GOLDSTEIN, 1984; DAVIS, 1986; ROCK, 1988). The latter is also enhanced by limiting

	STREAM			OVERBANK		
	Mean	St.D.	Skew.	Mean	St.D.	Skew.
Fe (%)	1.55	0.67	0.17	2.25	0.86	0.83
Ca (%)	9.56	4.90	-0.20	7.10	4.16	0.11
Mg (%)	3.28	2.50	0.45	2.67	2.12	0.89
Ti (%)	0.22	0.13	2.48	0.25	0.07	-0.17
Al (%)	2.94	1.20	0.00	4.18	1.22	0.19
Na (%)	0.36	0.15	0.72	0.41	0.11	0.51
K (%)	0.80	0.35	0.33	1.08	0.41	1.40
P (%)	0.05	0.02	1.76	0.04	0.01	0.89
Cu (ppm)	21.63	18.10	3.89	41.55	101.33	6.19
Pb (ppm)	42.43	149.09	6.29	25.7	20.11	3.41
Zn (ppm)	47.23	21.17	1.70	56.28	24.92	2.94
Ni (ppm)	27.93	17.08	1.20	40.23	19.78	1.25
Co (ppm)	9.25	5.14	0.60	13.00	5.81	0.30
Mn (ppm)	757.13	509.10	0.73	847.65	590.75	1.12
As (ppm)	8.08	3.75	1.77	9.76	7.24	2.95
Sr (ppm)	118.83	100.56	2.68	128.20	127.61	3.06
V (ppm)	49.25	18.37	0.32	70.10	19.26	0.15
La (ppm)	19.15	8.51	0.05	25.60	7.78	-0.38
Cr (ppm)	47.68	24.66	1.53	58.80	19.70	0.46
Ba (ppm)	195.03	118.46	2.63	337.93	589.20	6.09
Zr (ppm)	24.6	11.73	0.26	33.68	11.63	0.10
Hg (ppb)	62.63	139.00	6.10	363.48	1831.75	6.31

Table 2 Univariate statistics (mean, standard deviation and skewness) of major, minor and trace elements in the stream and overbank sediment samples of the Žumberak region.

the size of both groups at an approximately equal number of objects so that the optimal cutting score is placed exactly between their centroids. Graphically, the calculated discriminant function portrays a new axis along which the groups are maximally set apart. Finally, according to variables with the most prominent discriminant loadings, geological meaning could be attached to the axis. Thus it can be labelled with regard to a specific gechemical process which is liable for separation between the groups. Other measures for determining the individual contribution of predictor variables, such as the standardized coefficients, may be often fairly misleading as they are more subject to instability caused by intercorrelations between discriminatory variables (DILLON & GOLDSTEIN, 1984).

5. RESULTS

The results of the two-group discriminant analysis are briefly summarized in Table 3. Owing to data standardization the optimal cutting score for the two groups of equal abundance (40) has a zero value, with the group centroids placed at equal distance from the cutting point along either side of the discriminant axis. On the value of the test statistics the difference in the separation of the STREAM and OVERBANK centroids can be judged as statistically significant, although a few samples in both groups appear to be more loosely scattered about their means. Accuracy of the discrimination procedure can be inspected from the classification matrix (Table 4). 69 samples out of total of 80 in the data set are correctly classified on the basis of their geochemical composition, which makes 86 percent for the combined population of both groups. As can be seen from the Table 4, the unequal classification efficiency of the two groups shows that these are asymmetrically discriminated. Better results are achieved with the STREAM group having only three misclassified samples (7.5 percent incorrect), while OVERBANK shows much more asymmetry with 20 percent of inaccurately classified samples. This asymmetry, however, does not diminish the efficacy of discrimination between the two sample media, particularly considering the problems of multivariate normality (ROCK, 1988). Despite the recommended normalization procedures of observed data, some variables still tend to be distributed differently in both groups, which results in unequal dispersion of predicted groups.

When the significance of a particular subset of elements in the general discrimination scheme is considered, it is evident that in spite of the apparently bipolar nature of the discriminant function, the accent is heavily placed on the positive pole (Fig. 4), where the bulk of the analyzed elements are loaded. The axis weighs V, Al, Fe, Zr and La against essentially a single element - Ca, which is obviously a reflection of the inverse relationship between the aluminosilicate and carbonate component in the two sample media. Owing to their low discriminant loadings, other elements add little to

Number of variables in model (p)	22
Number of groups (K)	2
Number of functions (K-1)	1
Number of cases (n_1, n_2)	40, 40
approximate F ratio (degrees of freedom)	4.04 (22, 57)
p-level	0.000008
Canonical R	0.78
Average R value for STREAM (centroid), R_1	-1.23
Average R value for OVERBANK (centroid), R_2	1.23
Mahalanobis distance D^2	6.23

Table 3 Compositional differences between STREAM and OVERBANK sediments.

OBSERVED GROUP	PREDICTED GROUP STREAM (p=0.5)	OVERBANK (p=0.5)	% correct	Total
STREAM	37	3	92.50	40
OVERBANK	8	32	80.00	40
Total	**45**	**35**	**86.25**	**80**

Table 4 Classification matrix.

the geochemical distinction between STREAM and OVERBANK. This is particularly evident with some major and minor elements such as Mg, Na, Ti, P, but also Mn and Sr.

6. DISCUSSION

Comparison between the classification results represented by the plot of all samples (Fig. 3) against the plot of variable contributions (Fig. 4) along the discriminant axis offers insight into the geochemical relationship between the groups. There is an immediate impact of stream and overbank sediments differing primarily in the relative abundance of a bulk of analyzed elements, as only Ca (and disregarding Mg and P) can be found increased in the stream samples. This can be interpreted in two ways: either as an indication of the predominantly carbonate character of the active stream sediment in the investigated catchment basins, or (not excluding the first), that material composing the overbank samples contains greater concentrations of elements with a higher natural variability and considerably higher metal contents (particularly V, Al and Fe). The latter can be of interest in further investigations for possible anomalies concerning mineralization or contamination in the study area.

The main reason for the shift to the increase of Ca in the stream sediments can be sought from two sources. One is probably due to the dominant carbonate lithology in most of the sampled drainage basins - over two-thirds of their area is underlain by dolomite and limestone. However, having in mind that we are dealing here with the present-day stream bed material, it cannot, naturally, represent the whole catchment area but is limited only to a portion which is exposed to recent fluvial erosion (OTTESEN et al., 1989). Most obviously, the central part of the Žumberak, undergoing vigorous tectonic uplift (PRELOGOVIĆ, 1969), provides an ample source of carbonate material which is eroded from the bedrock in the deeply cut valleys (such as Bregana, for example) and feeds the sample sites at the basin outlets. Regional tectonic influence is of particular importance because it represents a clear-cut example that a tacit assumption of equal erosion through the whole drainage basin may not be true (ROSE et al., 1979). The lower parts of the sampled drainage basins, especially in the southeast part of the studied area (the catchment of the Kupa river) are distinguished by the processes of aggradation or, at least, by the greatly reduced capacity for erosion due to the low channel gradients. Of no lesser significance is that their stream channels, particularly those of higher order (fifth and sixth), run mostly through non-carbonate (Neogene clastic) rocks, highlighting the contrast between "alien", more carbonate, recent material in the stream bed and adjacent overbank.

The other reason for the higher content of Ca in the stream samples as contrasted with its overbank counterpart is of a geochemical nature and still more emphasizes their recentness. During the short depositional history of the stream sediment, the friable Ca and Mg minerals from dolomite and limestone were subjected mostly to physical weathering which resulted primarily in the finer grain size of clastic particles downstream. Chemical weathering contributes little to the loss of carbonate material via running water and out of the system (which also includes the riverplain), especially in the Žumberak streams which are weakly alkaline (pH = 7-8). On the other hand, most of the dissolved material

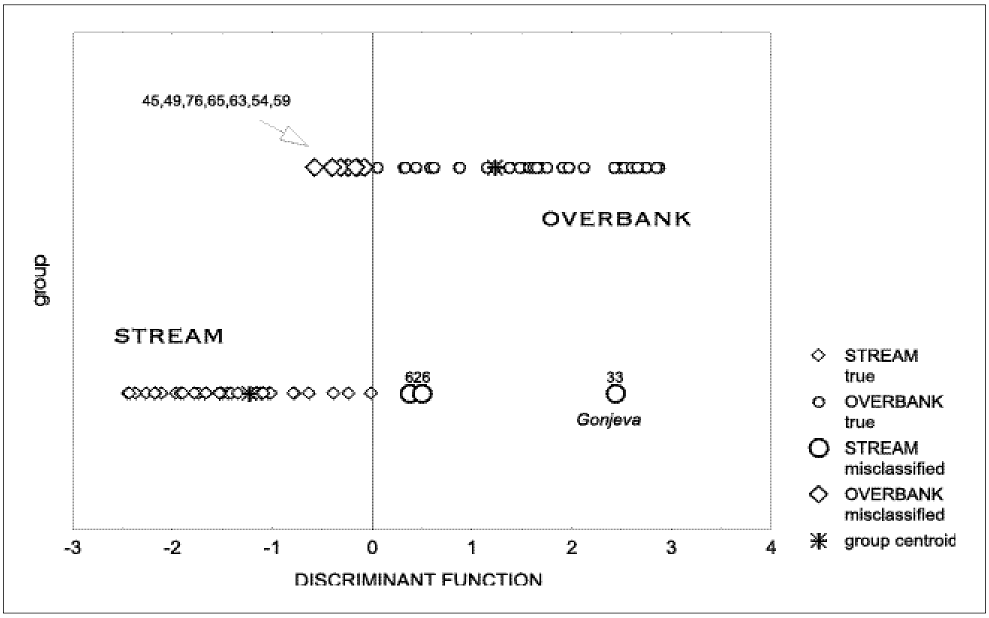

Fig. 3 Plot of discriminant scores (DS) (projection of samples onto discriminant function line).

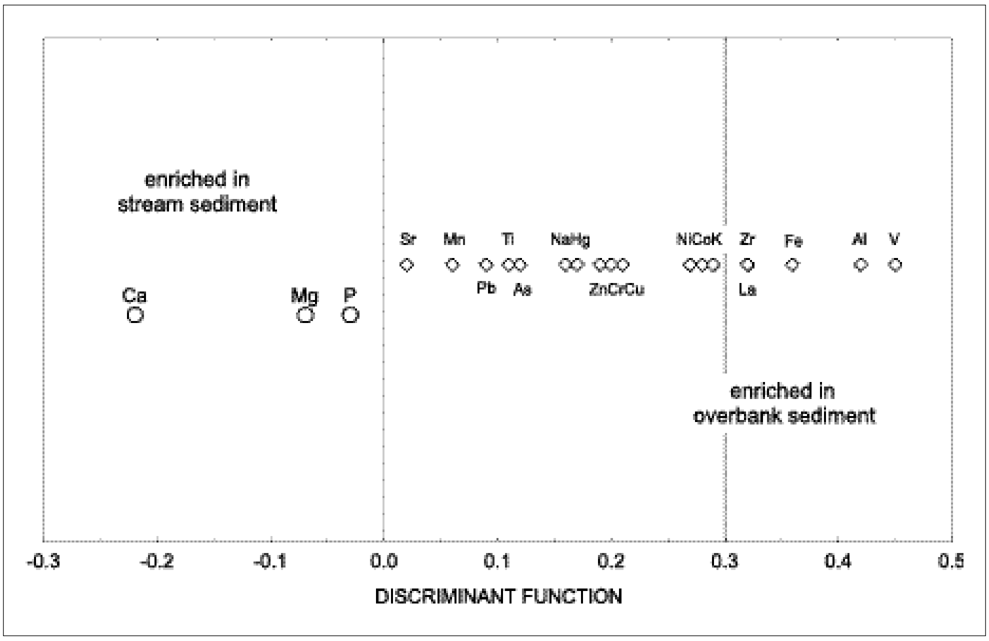

Fig. 4 Plot of discriminant loadings (projection of variables onto discriminant function line).

in the streams comes from solution by groundwater (EASTERBROOK, 1969). This is the process, perhaps, that accounts for most of the lack of Ca and Mg in overbank sediment over the study area, namely, decalcification of the previously deposited alluvium due to fluctuating hydrological conditions in the area. The dissolution of carbonate minerals in the overbank sediment is induced by the raising of the groundwater level which creates periodic waterlogged conditions with a significant decrease in pH in the upper part of the overbank profile (BERG & LOCH, 1998). In the two-group discrimination model it is reflected the other way round, that is, through the increasing carbonate component in the STREAM group.

The second indication distinguishing the two sample media, as seen in Fig. 4, is related to the greater deficiency of analyzed elements in the stream sediment. Lower overall concentrations in this material have been generally observed earlier (e.g. REIMANN, 1987; SWENNEN et al., 1998), and can be accounted for the fact that much of the element contents (V, Al and Fe in particular in this case) are dispersed in the finer fraction (silt-clay) which is winnowed out leaving the stream sediment coarser and "depleted". Apart from being accordingly attenuated, this material is also fairly nonhomogeneous as can be seen from the asymetrically shaped histogram of discriminant scores (DS) for STREAM (Fig. 5a).

In contradistinction to its stream counterpart, the overbank sediment appears to have a higher "natural" background, much on account of its longer depositional history which supplied it with a mixture of geochemical

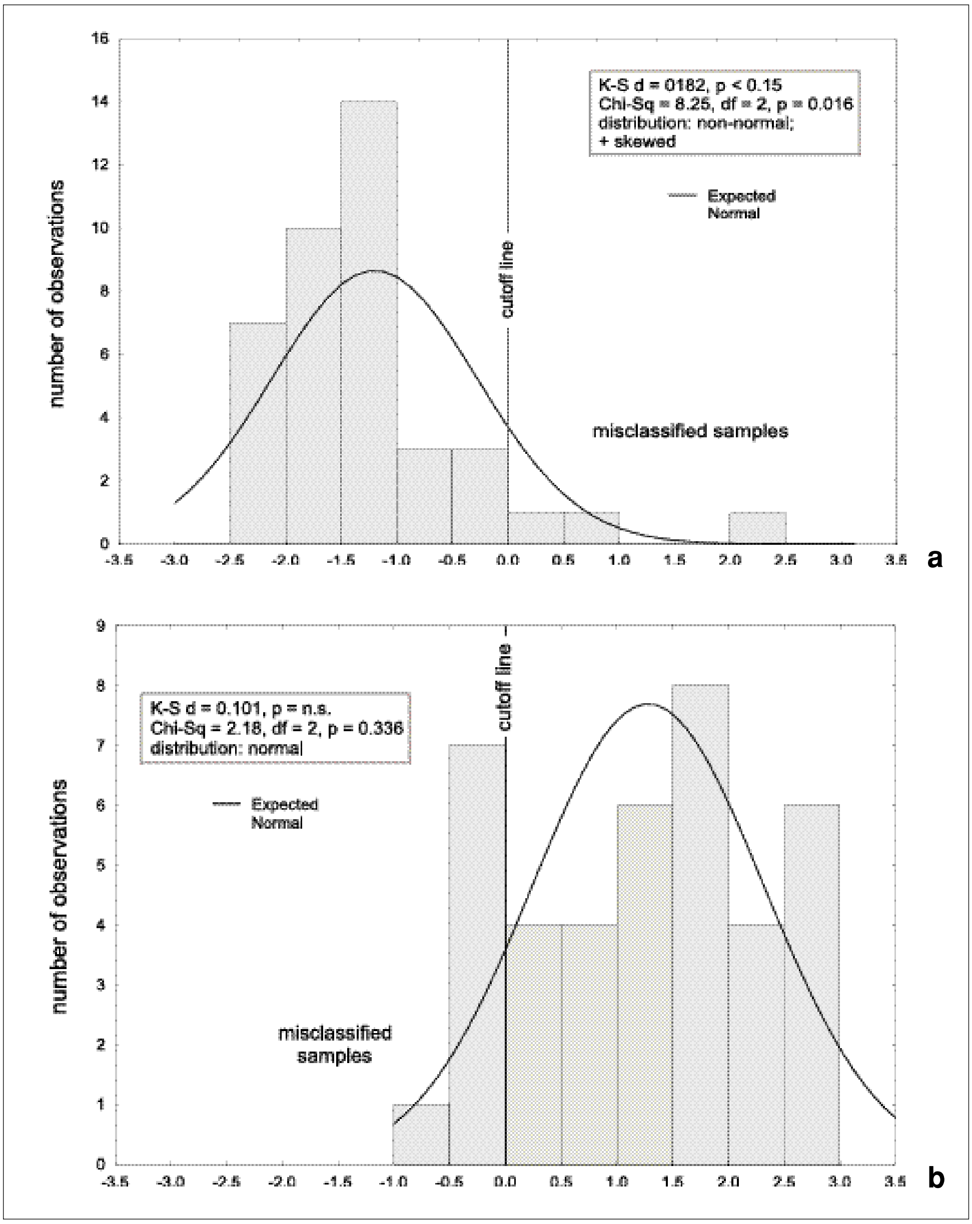

Fig. 5 a) Histogram of discriminant scores for STREAM; b) Histogram of discriminant scores for OVERBANK.

and mineralogical characteristics that embrace the whole drainage area upstream from the sample site. This is particularly important with respect to the distribution of heavy metals and trace elements in both sample media (originating either from ore mineralization or man-made pollution) because, as can be seen from Fig. 4, there is no preferential distribution pattern.

Apart from the relative abundance of non-carbonate components in the overbank sediment, a much greater geochemical homogeneity of precipitated material (analyzed as a composite sample) can also be expected. This is clearly shown by the normally distributed discriminant scores for OVERBANK (Fig. 5b). The more uniform dispersion of chemical elements through overbank samples affects the boundary between OVERBANK and STREAM groups making it a little unilaterally diffuse. As a result, more overbank samples with lower element concentrations are lost to the other group showing more affinity with the stream sediment. The cohesion of the STREAM group can be deemed considerable as only three samples bear more similarity with adjoiningly sampled overbank. This is obvious from closer inspection into the areal distribution of discriminant scores for both groups (Figs. 6a and b). Excluding the eastern borders of the studied area, where the overbank composition clearly conforms with entirely non-carbonate bedrock, it may be hard to locate an uninterrupted section with a greater agglomeration of drainage basins containing highly discriminated overbank samples (DS>1), despite attempting to relate them with the underlying bedrock. Conversely, the stream sediment characteristics are much more perceptible on the terrain as the pertinent basins are scattered almost evenly all over the study area (DS<-1) with only a minor clustering along its southern and northern fringes: stream sediment samples in the southwest are almost indistiguish-

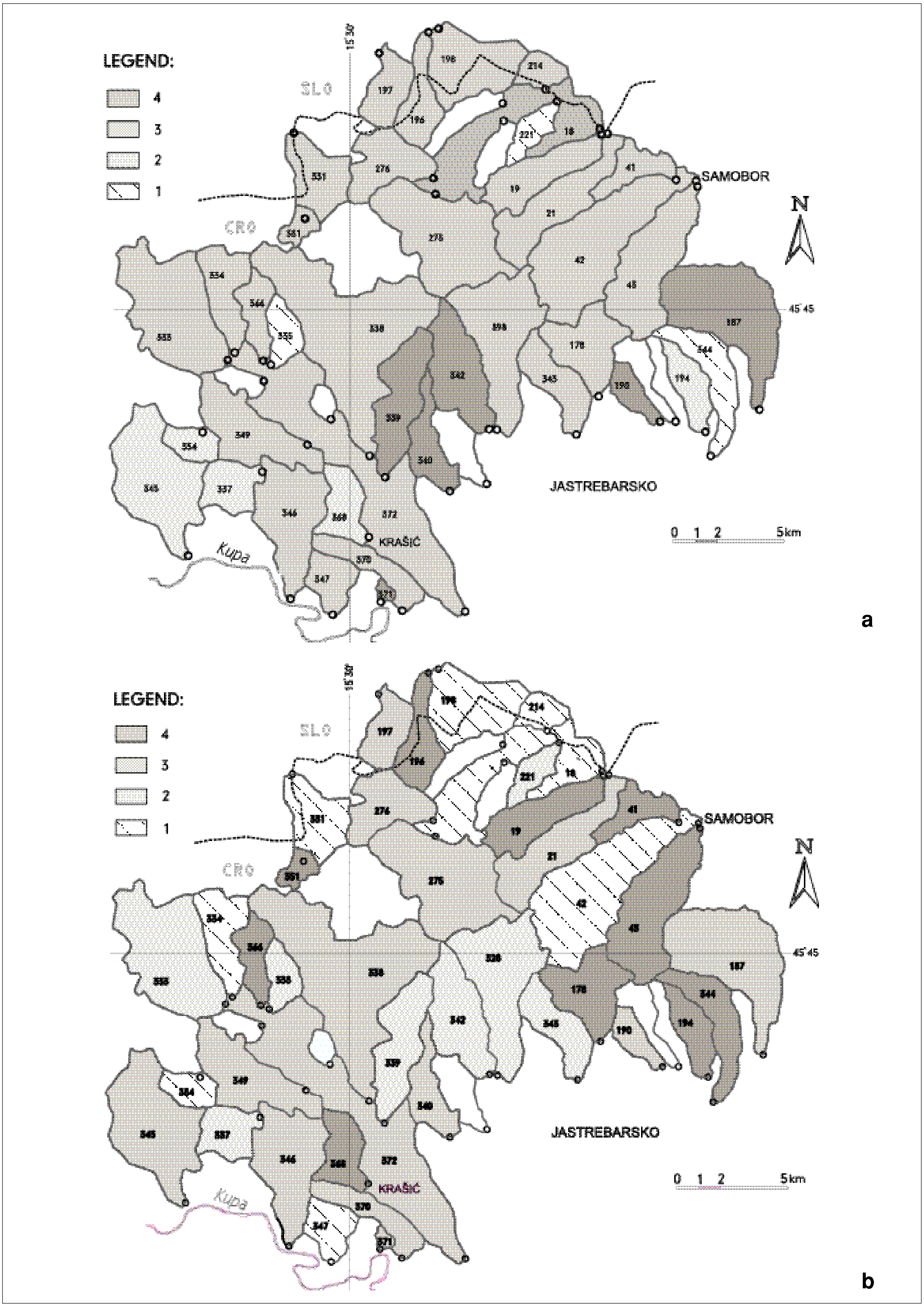

Fig. 6 a) Map displaying the areal dispersion of discriminant scores for STREAM. Legend: 1) misclassified samples (DS>0); 2) weakly separated samples (-1<DS<0); 3) well separated samples (-2<DS<-1); 4) extremely separated samples (DS<-2). b) Map displaying the areal dispersion of discriminant scores for OVERBANK. Legend: 1) misclassified samples (DS<0); 2) weakly separated samples (0<DS<1); 3) well separated samples (1<DS<2); 4) extremely separated samples (DS>2).

able from the adjacent overbank (-1<DS<0) which obviously concurs with the underlying Senonian flysch, mostly marls, producing a weak geochemical contrast between the two sample media. The basins in the central south are best discriminated probably due to the share of contrasted lithologies - their upper parts draining the carbonate, almost entirely dolomitic bedrock, while the lower portions overly the Neogene, essentially non-carbonate terrain, which enhances the contrast; the basins in the south-east and the north conform with the foregoing picture with one noticeable distinction. There is but one stream sediment sample that not only deviates markedly from its own group (more than two standard deviations) but is, moreover, placed among the most prominent members of the other group. Such a misclassification (sample 344-Gonjeva, Fig. 3), provided that the sampling procedure was correctly carried out, is ultimately due the causes other than regular erosion-aggradation processes in the vicinity of the sample site (the fifth-order drainage basin of Gonjeva, which is the tribute of the Kupa river). It is assumed that the nature of drainage basin processes that brought about the discussed differences between STREAM and OVERBANK groups cannot differ greatly over small area of the few tens of kilometres across. Actually, such a case is probably induced by poor geomechanical properties of the bank material, having an impact on the slope stability at the sampling site or upstream. The bank failure might have been triggered by hydrogeological causes, probably by rainfall, somewhere along a two-metre high levee, the slump being resedimented downstream as fine-grained bedload. Another cause is possibly lateral erosion and reworking of the overbank material due to the slight meandering of the Gonjeva channel at the sampling location. The process of stream downcutting through its own alluvium in view of tectonics may be ruled out on account of the absence of similar anomalies in the nearby drainage basins (190, 194). Besides, the lower part of the Gonjeva stream runs through the Karlovac depression which is currently undergoing a stage of steady tectonic subsidence (VELIĆ, 1983).

7. CONCLUSION

Geochemical comparison of the low- to medium-order stream and overbank sediments based on the direct contrast between locality-paired samples was conducted to elucidate the possible differences in natural geochemical variation in both media. Of particular interest was spotting the disposition of a subset of elements for a specific medium explainable in terms of either mineral ore occurrences or anthropogenic influences (mostly municipal) in the investigated drainage basins. This would help narrow the focus of interest onto the medium with better availability to sampling, as well as lesser problems of interpretation.

The media comparison was performed using two-group discriminant analysis which allowed the best insight into the group structuring and differences caused by the selective contribution of predictor variables. The results can be summarized as follows:

a) STREAM and OVERBANK are well separated groups with 86.25% correctly classified samples (only 11 out of 80 are misclassified).

b) The total element content is much more uniformly dispersed in the overbank material, obviously as a result of recurrent flooding and mixing during its depositional history.

c) The geochemical difference between the sample media is conveyed almost entirely by the higher content of the greatest part of analyzed elements in the overbank sediment.

d) Overbank sediment is depleted in carbonate material (Ca, Mg), perhaps due to decalcification.

e) Vanadium is the trace element with the highest discrimination potential, increased in overbank sediment.

f) There is no apparent preference of heavy metals and trace elements with regards to either sample medium - evidence of mineralization and pollution is screened by the reciprocal “abundance-scarcity” relationship between the media.

Concerning the fact that the investigated catchment basins are of an order that almost invariably supplies both media with sample material, one can draw a fairly resolute choice between these, at least on regional level, on account of the clues inferred above. In comparison to its stream correlate the overbank sediment seems to be more convenient for sampling, especially by reason of its higher natural geochemical variability on the background of an otherwise common geochemical semblance. In a relatively low-polluted area, such as the investigated Žumberak region, an active stream sediment, which is a sample medium of recent origin, is not capable of indicating the presence of pollutants in contrast to its presumably pristine, pre-industrial overbank associate. More so since the mineral ore occurrences can be detected regularly in both recent and earlier sedimented material.

8. REFERENCES

BERG van den, G.A. & LOCH, J.P.G. (1998): Decalcification of soils in wetlands subject to fluctuating hydrological conditions.- In: BERG van den, G.A. (ed): Geochemical Behaviour of Heavy Metals in a Sedimentation Area of the Rivers Rhine and Meuse. Geologia Utraiectina, 163, 21-39, Utrecht.

BONHAM-CARTER, G.F., ROGER, P.J & ELLWOOD, D.J. (1987): Catchment basin analysis applied to surficial geochemical data, Cobequid Highlands, Nova Scotia.- J. Geochem. Explor., 29, 259-278.

BUKOVAC, J., ŠUŠNJAR, M., POLJAK, M. & ČAKALO, M. (1983): Osnovna geološka karta SFRJ, 1:100.000, list Črnomelj, L33-91 (Basic geological map of SFRJ, 1:100.000, The Črnomelj sheet).- Geološki zavod Zagreb and Geološki zavod Ljubljana (1972-1983), Savezni geološki zavod, Beograd.

CARRANZA, E.J.M. & HALE, M. (1997): A catchment basin approach to the analysis of reconnaissance geochemical-geological data from Albay Province, Philippines.- J. Geochem. Explor., 60, 157-171.

CHORLEY, R.J. (1969): The drainage basin as the fundamental geomorphic unit.- In: CHORLEY, R.J. (ed.): Water, Earth and Man. Methuen and Co., London, 72-99.

DAVIS, J.C. (1986): Statistics and data analysis in geology.- 2nd ed., John Wiley & Sons, New York, 646 p.

DILLON, W.R. & GOLDSTEIN, M. (1984): Multivariate analysis: methods and applications.- John Wiley & Sons, New York, 575 p.

EASTERBROOK, D.J. (1969): Principles of geomorphology.- McGraw-Hill, New York, 462 p.

EDÉN, P. & BJÖRKLUND, A. (1994): Ultra-low density sampling of overbank sediment in Fenoscandia.- J. Geochem. Explor., 51, 265-289.

HAWKES, H.E. (1976): The downstream dillution of stream sediment anomalies.- J. Geochem. Explor., 6, 345-358.

HERAK, M (1991): Dinaridi: Mobilistički osvrt na genezu i strukturu (Dinarides: mobilistic view of the genesis and structure).- Acta geologica, 21/2 (Prir. istraž., 63), 35-117 (1-83), Zagreb.

HERAK & BUKOVAC, I. (1988): The tectonic window of Duralije in Žumberak Mt.- Geol. vjesnik, 41, 231-236.

HUISMAN, D.J., VERMUELEN, F.J.H., BAKER, J., VELDKAMP, A., KROONENBERG, S.B. & KLAVER, G.Th. (1997): A geological interpretation of heavy metal concentrations in soils and sediments in the southern Netherlands.- J. Geochem. Explor., 59, 163-174.

MACKLIN, M.G., RIDGWAY, J., PASSMORE, D.G. & RUMSBY, B.T. (1994): The use of overbank sediment for geochemical mapping and contamination assessment: results from selected English and Welsh floodplains.- Appl. Geochem., 9, 689-700.

ÓDOR, L., HORVÁTH, I. & FÜGEDI, U. (1997): Low-density geochemical mapping in Hungary.- J. Geochem. Explor., 60, 55-66.

OTTESEN, R.T., BOGEN, J., BØLVIKEN, B. & VOLDEN, T. (1989): Overbank sediment: a representative sample medium for regional geochemical mapping.- J. Geochem. Explor., 32, 257-277.

PLENIČAR, M., PREMRU, U. & HERAK, M. (1976): Osnovna geološka karta SFRJ, 1:100.000, list Novo Mesto, L33-79 (Basic geological map of SFRJ, 100.000, The Novo Mesto sheet).- Geološki zavod Ljubljana (1963-1969), Savezni geološki zavod, Beograd.

PULKKINEN, E. & RISANEN, K. (1997): A geochemical investigation on overbank sediments in the Inari area, northern Finnish Lapland.- J. Geochem. Explor., 59, 11-26.

REIMANN, C. (1988): Comparison of stream sediment and soil sampling for regional exploration in the Eastern Alps, Austria.- J. Geochem. Explor., 31, 75-85.

RHOADS, B.L & CAHILL, R.A. (1999): Geomorphological assessment of sediment contamination in an urban stream system.- Appl. Geochem., 14, 459-483.

ROCK, N.M.S (1988): Numerical geology.- Lecture Notes in Earth Sciences, Vol. 18, Springer-Verlag, Berlin - Heidelberg - New York - London - Paris - Tokyo, 427 p.

ROSE, A.W., HAWKES, H.E. & WEBB, J.S (1979): Geochemistry in mineral exploration.- 2nd ed., Academic Press, London, 657 p.

SALMINEN, R., TARVAINEN, T., DEMETRIADES, A., DURIS, M., FORDYCE, F.M., GREGORAUSKIENE, V., KAHELIN, H., KIVISILLA, J., KLAVER, G., KLIN, H., LARSON, J.O., LIS, J., LOCUTURA, J., MARSINA, K., MJARTANOVA, H., MOUVET, C., O'CONNOR, P., ODOR, L., OTTONELLO, G., PAUKOLA, T., PLANT, J.A., REIMANN, C., SCHERMANN, O., SIEWERS, U., STEENFELT, A., VAN der SLUYS, J., de VIVO, B. & WILIAMS, L. (1998): FOREGS Geochemical Mapping Field Manual. Geological Survey of Finland, 36 p., Espoo.

SWAN, A.R.H. & SANDILANDS, M (1995): Introduction to geological data analysis.- Blackwell Science Ltd., Oxford, London, 442 p.

SWENNEN, R. & VAN der SLUYS, J. (1998): Zn, Pb, Cu and As distribution patterns in overbank and medium-order steam sediment samples: their use in exploration and environmental geochemistry.- J. Geochem. Explor., 65, 27-45.

SWENNEN, R., van der SLUYS, J. & BRUSSELMANS, A. (1998): Geochemistry of overbank and high-order stream sediments in Belgium and Luxembourg: a way to asses environmental pollution.- J. Geochem. Explor., 62, 67-79.

ŠIFTAR, D. (1989): Starost evaporita i porijeklo sulfata u Rudama kraj Zagreba (The age of evaporites and the origin of sulfate at Rude near Zagreb).- Geol. vjesnik, 42, 59-64.

ŠIKIĆ K., BASCH, O. & ŠIMUNIĆ, A. (1978): Osnovna geološka karta SFRJ, 1:100.000, list Zagreb, L38-80 (Basic geological map of SFRJ, 1:100.000, The Zagreb sheet).- Institut za geološka istraživanja, Zagreb (1972), Savezni geološki zavod, Beograd.

ŠINKOVEC, B. (1971): Geologija ležišta željezne i bakrene rude u Rudama kraj Samobora (Geology of the iron and copper ore deposit at Rude near Samobor).- Geol. vjesnik, 24, 165-181.

VELIĆ, J. (1983): Akceleracija vertikalnih tektonskih pokreta tijekom neogena i kvartara u zapadnom dijelu Savske depresije (The Neotectonic relations and development of the western part of the Sava River depression).- Geol. vjesnik, 36, 225-265.

Manuscript received February 2, 2000.

Revised manuscript accepted April 23, 2001.