

# Geochemical and Statistical Methods in the Evaluation of Trace Elements Contamination: an Application on Canal Sediments

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## Abstract

The contamination levels of V, Cr, Ni, Cu, Zn, Cd, and Pb in canal sediments (Danube alluvial formation) were assessed to evaluate environmental quality and potential contamination. Results indicate that silicates and oxides (Fe and Mn) are important for binding investigated elements (Cr, Zn, Cd, Ni, V Pb, and Cu). The values of calculated enrichment factors indicate that the investigated locations includes minor to moderate enrichment of sediment with Cr, V, Cu, Pb, Cd, Ni, and Zn, except for one location where sediment is severely enriched with Zn. Factor analysis shows two main anthropogenic sources:

- Cr, Zn, Cd, Ni, V, and Pb are mainly derived from industrial sources and,
- Cu and Pb are mainly derived from other local contamination sources combined with traffic sources.

With increasing distance from the Refinery, the anthropogenic impacts of the metal content were lower and geochemical control of the contents of the element became dominant, which indicate the influence of the refinery on the metal pollution in the sediments.

**Keywords:** contamination, trace elements, enrichment factors, Danube alluvial sediment, factor analysis

## Introduction

Assessing the content of potentially harmful trace elements in the soils and sediments is imperative in order to evaluate the potential risk of their contamination. Many trace elements are often problematic environmental pollutants, with well-known toxic effects on living systems [1, 2]. These pollutants could be transferred to humans via ingestion, dermal contact, or breathing [3]. In the Indicative List of the main pollutants in water (Directive 2000/60/EC – Annex 8 [4]), the metals and their compounds are given. Council Directive 86/278/EEC [5] emphasizes that soil analysis should cover the following elements Cd, Cu, Ni,

Pb, Zn, Hg, and Cr. The origin of metals that accumulate in sediments is partly from natural sources through the weathering of rocks and partly arising from a variety of human activities, including mining, smelting, electroplating, and chemical manufacturing plants, as well as domestic discharges, shipping, and boating activities [6]. In urban areas, various stationary and mobile sources release large quantities of trace elements into the atmosphere and soil, exceeding the natural emissions rates [7-9]. It is widely recognized that industrial activities have considerably enhanced the atmospheric emission and subsequent deposition of several elements, including many trace metals. Karageorgis et al. [10] have reported that metals are also encountered in petroleum fuel mixtures in the form of salts of carboxylic acids, or as porphyrin chelates. Apart from V and Ni, which

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predominantly occur at the highest content in crude oil and residual fuel oils, As, Fe, Mn, Mo, Zn are also encountered [10]. Since various human activities may cause contamination with trace elements, many researchers have indicated the need for a better understanding of soil contamination [7]. Contamination of urban soils and sediments with heavy metals can also cause groundwater contamination, because metals in the polluted soils tend to be more mobile than those of unpolluted ones [11]. In order to assess sediment contamination, many researchers employed the use of method geochemical normalization and calculation enrichment factors (EFs). EFs are commonly used as a means of identifying and quantifying human interference with global element cycles [10]. In geochemical studies, the normalization of elemental content using an immobile element is common practice for correcting grain-size effects and dilution by sedimentary phases such as carbonates and silica. This simple way of data processing may also reveal possible sediment enrichment in trace metals. Currently, Al is the most frequently used geochemical normalizer in sediments, assuming that Al is held exclusively in terrigenous aluminosilicates [10].

This paper presents the continuation of research of trace element contamination on the investigated location. The major objectives of this study is to assess potential contamination and identify the different sources that contribute to trace element content in alluvial sediments, by:

1. determining element content in sediment,
2. analysis distribution of total metal content by location,
3. defining of depth profiles of metal content,
4. determining of background contents and calculation of enrichment factor, and
5. applying Factor Analysis to normalized contents of metals.

Contents of Cu, Cr, Zn, Pb, Cd, Ni, V, and Al were determined in investigated sediment. The chemical analyses also included Al, which is considered indicative of sediment grain size.

A detailed research of contamination with a potentially toxic element on the investigated location is important, since that systematic investigation of contamination with trace elements in Serbia is just the beginning [12]. Since then, determination of background content of trace elements and quantification of anthropogenic impact by enrichment factors is significant.

## Materials and Methods

### Sampling Location

The study area represented alluvial sediments from a canal in the industrial zone southeast of the city Pančevo, about 15 km east of Belgrade (Fig. 1). The City of Pančevo is located in Southern Vojvodina, at the confluence of the Tamiš and the Danube rivers, at the very edge of the Pannonian Plain. The most important economic branches in the Pančevo are crude oil processing, production of plastic masses (HIP Petrochemical Complex), fertilizers (nitrogen

plant), textile and fashion industries, and agriculture. Pančevo is a river port for nearby Belgrade and an industrial center.

The samples of alluvial sediments were taken in August and September 2001, along the canal which begins at the Oil Refinery Pančevo and passes different industrial formations. In this canal is placed the pipeline for wastewater and atmospheric water, which is beginning from the Pančevo Oil Refinery, and water from the pipeline is poured in a canal for wastewater that flows into the Danube. The samples were taken from 14 drill-holes (marked as S1-S14) at different depths, up to 5 m. The drill-hole (DH) denoted S1 is nearest the Refinery and S14 is nearest the entrance of the canal into the Danube (Fig. 1). The sediment samples were frozen after sampling and preserved in a freezer until analysis. The drill-holes are getting under the top level of underground water, because the level of underground water is reaching values up to 3 m under grounds surface [13]. Samples from the drill-hole for chemical analyses were collected from the whole depth interval.

### Determination of Metal Content

The sediment samples were analyzed by a modified version of the Tessier [14] sequential extraction procedure (SE). This method has since been adopted and changed by different authors [13, 15-21]. The procedure applied in the present investigation is described elsewhere [13, 15-18]. The extractants and operationally defined chemical fractions applied in this research were as follows:

- The first step (exchangeable fraction, F1): 10 g sediment sample was extracted with 1M  $\text{CH}_3\text{COO}(\text{NH}_4)$ .
- The second step (represents metals bound to carbonates and easily reducible phases, F2): extractant 0.6M HCl and 0.1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ .
- The third step (metals bound to moderately reducible phases, F3): mixture of 0.2M  $\text{H}_2\text{C}_2\text{O}_4/(\text{NH}_4)_2\text{C}_2\text{O}_4$  is used.
- The fourth step (metals bound to organic matter and sulfides, F4): extractant 30%  $\text{H}_2\text{O}_2$  adjusted to pH 2.0 with  $\text{HNO}_3$ .
- The fifth step (residual fraction, F5): extractant 6M HCl.

All the chemicals used in this work were of analytical reagent grade. All glassware and plastic material used were previously treated for 1 week in 2M nitric acid and rinsed with distilled water and then with ultrapure water [13].

For each sequential extraction series, 10.00 g of defrosted sediment was taken without drying in order to avoid chemical transformation due to chelating, oxidation processes, etc. Control samples were processed for each extraction step. The solid/liquid ratios were kept as close to 1:45 as possible during extraction of the first, second, and third fractions.

Flame atomic absorption spectrometry (FAAS) was used to determine the levels of the metals (SpectraAA55 Varian spectrophotometer, equipped with a hydride vapour system). The wavelengths used in this analysis were: 232.0 nm for Ni, 213.9 nm for Zn, 324.7 nm for Cu, 217.0 nm for Pb, 357.9 nm for Cr, 309.3 nm for Al, 228.8 nm for Cd, and

318.5 nm for V. External standard solutions were prepared from 1,000 mg·L<sup>-1</sup> stock metal solutions. For minimized interferences, multi-element standard stock solution was prepared in which the ratios of the metals in the multiple element calibration standards were analogous of their ratios in the samples. These multi-element standards and blanks were prepared in the same matrix as employed for the extraction to minimize matrix effects and for background correction [17]. In order to simulate the composition of the investigated samples, the multi-element standards also contained elements that were not determined. Possible interference effects were minimized in this manner. The calibration was checked every 10-12 samples. As a quality control, duplicate analyses were performed on all samples and precision was controlled. The relative standard deviations of the means of duplicate measurement were less than 10% [13]. The values of limit of detection (DL) for each determined element, expressed in µg·ml<sup>-1</sup>, were: Cr (0.03), Zn (0.005), Pb (0.05), Cd (0.01), Al (0.15), Ni (0.05), Cu (0.02), and V (0.5). All contents values below the detection limit were replaced by half of the DL, as suggested by Reimann and Filzmoser [22], and Relić et al. [17].

The moisture content of each sample was determined by drying a separate 1 g sample in an oven (105±2°C) to constant weight. From this, a correction to dry mass was obtained, which was applied to all reported metal contents.

The total amount of elements in sediments in this paper are defined as total extractable content and represented the sum of elements released in all five binding fractions [17, 23].

Enrichment Factor (EF)

The EF was calculated using the following equation:

$$EF = (M/Y)_{\text{sample}} / (M/Y)_{\text{background}}$$

...where *M* is the content of the potentially enriched element and *Y* is the content of the proxy element [16]. Proxy element is the element for normalizing the geochemical data to compensate for grain-size and mineralogy effects on trace element concentrations and to assess if anomalous metal contributions are present. The normalizing element, for which the literature often uses the term “grain-size proxy”

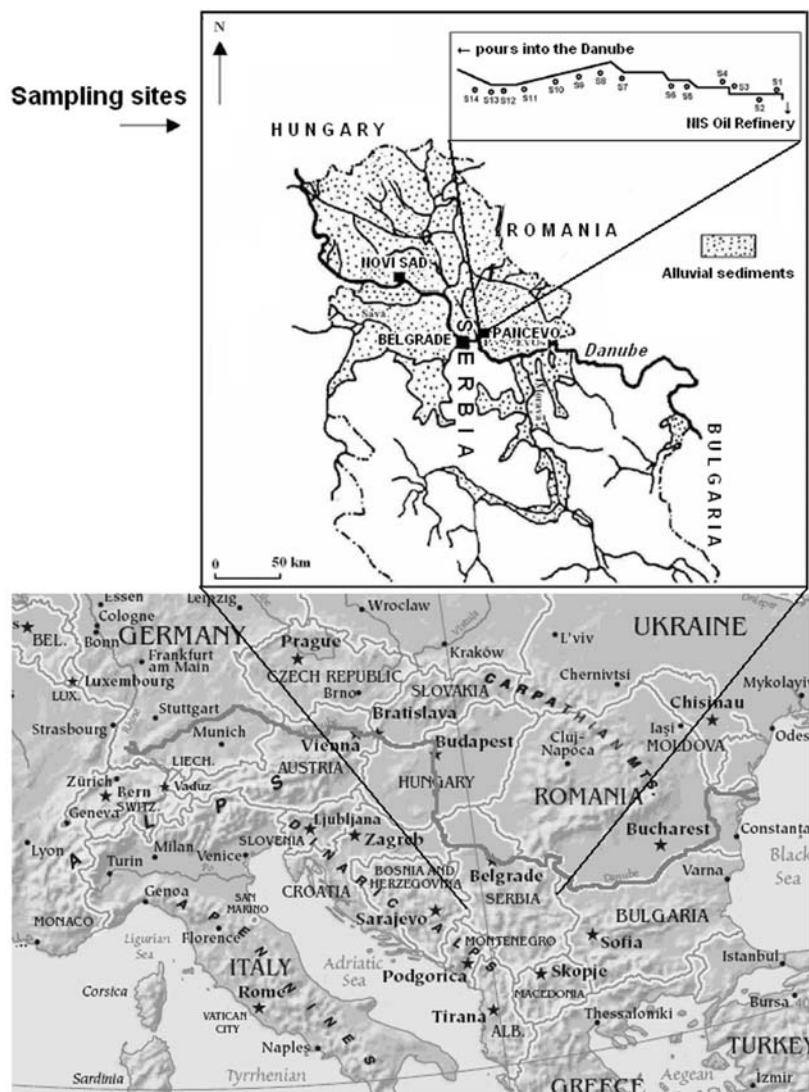


Fig. 1. Study area and sampling sites.

must be an important constituent of one or more of the major trace metal carriers and reflects their granular variability in the sediments. The choice of grain-size proxy is not universal but depends, among other things, on the study area and the anthropogenic wastes involved. Al, which is one of the most important constituents of the aluminosilicate mineral fraction, is often used as a grain-size proxy [24]. The content of the potentially enriched element and content of proxy element (in this paper proxy element is Al) are defined as the sum of the five binding fractions [18, 23]. This method results in contents normally referred to as "pseudo-total," as it does not completely destroy silicates [23]. As long as residual silicates do not normally display high metal contents [18, 23], the values obtained were considered to be representative of total heavy metal contents. Content of extractable Al in investigated sediment is determined also by the use of sequential extraction method, and total extractable content represented the sum of metal content released in all five fractions. Extractable Al represents clay minerals: therefore, it is considered to be a measure of grain size [25]. In this paper, as well as in research of Woitke et al. [26], due to the partial extraction procedure, the Al "background" is lower than published data based on total sample digestion. However, Kersten and Smedes [27] demonstrated that Al determined by partial digestion may be a better choice for normalizing heavy metal contents. The EF values were interpreted as suggested by Acevedo-Figueroa et al. [28], where  $EF < 1$  indicates no enrichment,  $< 3$  is minor, 3-5 is moderate, 5-10 is moderately severe, 10-25 is severe, 25-50 is very severe, and  $> 50$  is extremely severe. The described method for calculating EF was described and applied in by Sakan et al. [16].

### Elemental Analysis

The determination of C, H, N, and S content in the investigated sediments was performed by elemental analysis, using the Vario EL III C, H, N, S/O elemental analyzer (Elementar). Determined C content represented total carbon content, i.e. the sum of inorganic and organic carbon.

### Statistical Analysis

Factor analysis (FA) was conducted in order to group elements, based on their common geochemical behaviour (R mode) and for determination of interrelation among the studied samples (Q mode). Contents of trace elements were normalized in respect to Al content (geochemical normalization). Since distribution of environmental data sets is usually skewed [17], log-transformation data were analyzed in this paper. Kolmogorov-Smirnov test was employed to evaluate normality of the log-transformed data. After normalization, the p-values in Kolmogorov-Smirnov test were  $\geq 0.05$  for all variables. The computer package SPSS 11.5 was employed to perform the Kolmogorov-Smirnov test and Factor analysis.

## Results and Discussion

### Composition of Soil in Vojvodina

Since the sampled sediment is from the Vojvodina location (Serbia), there were given the composition of soil in this region. In accordance with results presented in [29], the salts in Vojvodina soils originate from decomposition minerals of igneous rocks and crystalline schist of the Karpate Mountains, that enclose the Pannonian plain to the east, northeastern, and north, or younger sediment rock. During the process of degradation of this rock, the salts that arrived on the plain with surface or underground water were released [29]. The results of mineralogical analysis [30] show that soils in Vojvodina are composed from: quartz, mica, and feldspar that dominate the composition, and followed in the decreasing array, with lower contents of chlorite, dolomite, calcite, clay mineral, goethite, amphiboles, and talc. Kostić [30] has shown that, due to low rainfall, the biogeochemical decomposition processes of primary minerals produce illite, smectite, and a low content of vermiculite.

Investigations of the most common types of soil in Vojvodina indicate that in 68.3% of the analyzed soil samples the reaction is alkaline, and 23.1% neutral, and only 8.6% acidic [31]. By analyzing the amount of rainfall in July and August, compared to the needs of plants for water in the same period, it was found that 83% of the year in Vojvodina is dry weather. In arid areas, alkaline soils dominate [31].

### Characteristics of the Alluvial Sediments (Pančevo)

Results of analysis of the contents of C, H, S, and N in the investigated sediments show that:

1. detection limit  $< N < 0.30\%$  (mean value is 0.13%),
2.  $0.99 < C < 8.96\%$  (mean value is 2.37%),
3.  $0.11 < H < 0.90\%$  (mean value is 0.43%), and
4. detection limit  $< S < 0.30\%$  (mean value is 0.13%).

Correlation analysis between the total content of C, H, S, and N indicates the existence of a positive correlation only between H and N contents in sediments ( $r=0.473$ ). This positive correlation could indicate the existence of an association between organic matter and clay minerals in sediments of the Pančevo. Non-existence of positive correlation between N and S may indicate that organic substances containing compounds with S are not significant element substrates in the examined sediments. Sulfur in the investigated alluvial sediments is primarily an indicator of sulfide content, and carbon dominantly represents carbonates [13].

Using granulometric analysis, we determined sediment granulometric classes with different particle size: Silt (0.002-0.02 mm), clay ( $< 0.002$  mm) and sand ( $> 0.02$  mm), results of granulometric analysis of sediment show:

1.  $0.10 < \text{Silt} < 44.9\%$  (mean value is 20.4%),
2.  $0.00 < \text{Clay} < 39.0\%$  (mean value is 15.1%), and
3.  $21.6 < \text{Sand} < 99.9\%$  (mean value is 64.5%).



Table 1. Distribution of element by fractions (%).

	F1	F2	F3	F4	F5
Cu	1.72	2.95	52.53	2.89	39.89
Cr	2.05	2.50	23.01	5.92	66.57
Zn	2.72	8.71	28.09	3.16	56.31
Pb	3.70	24.89	27.90	6.82	36.69
Cd	4.77	5.70	57.29	6.45	24.70
Ni	1.47	12.48	35.01	12.56	38.47
V	7.10	10.58	37.80	4.48	40.05

We observed increased content of the sand fraction in the Pančevo alluvial sediments, in some samples up to 99.9%. The investigated area is part of the Pannonian Plain, which is rich in sand. In the investigated alluvial sediment was noted the large differences between the maximum and minimum content of silt, sand, and clay fractions, since those sediment samples were taken from different depths.

#### Distribution of Elements by Fractions

Table 1 shows distribution of elements by fractions, represented in %. Most elements are mainly bounded in the F5 and F3 fractions. This means that silicates and oxides (Fe and Mn) are important for binding investigated elements (Cr, Zn, Cd, Ni, V Pb, and Cu). The detailed description and interpretation of element distribution by fractions is shown in Sakan et al. [13].

#### Distribution of Metal Content by Locations

In this paper, pseudototal metal content is the represented sum of metal extracted in the five binding fractions. The distribution of metal content by locations (i.e. by different drill-holes) is represented in Fig. 2.

**Chromium and Nickel:** There are no large differences between the maximum and minimum Cr and Ni contents. In some sediment we observed slightly higher Cr and Ni contents (23-S11/1.5, 24-S12/0.3, 26-S12/2.3, 29-S13/2.7, 31-S14/2.2 sampling sites), whereby it was evident that an increase of contents in one element is followed by increasing contents of the other element. This fact may point out that increased content of these elements on some locations are consequences of geochemical enrichment and it can also be assumed that there is a correlation between Cr and Ni at the studied location. The depth and denotation of sediment samples are given in Table 2.

**Zinc:** There are no large differences between the maximum and minimum content. The maximum values of Zn contents were obtained in sediment sample 10-S4/1.0 (164 mg·kg<sup>-1</sup>) and 24-S12/0.3 (111 mg·kg<sup>-1</sup>). These anomalous concentrations may indicate an anthropogenic origin of this element, considering its higher content in respect to the rest of the sediment samples.

**Lead:** The highest content of lead occurs in drill-hole sediment located nearest the refinery (samples marked as 1-S1/1.0 and 2-S1/2.4) that point out the influence of the refinery on higher Pb content. Lead concentrations decrease away from the refinery, whereby a significant drop is observed from drill-hole S13.

**Cadmium:** The highest contents of cadmium occur in sediment samples, 14-S6/0.9, 20-S10/0.8, 22-S11/0.0, and 24-S12/0.3. These sediments were taken from depths lower than 1m. The stated results point to an anthropogenic origin of Cd in these localities.

**Copper:** The content of Cu in sediment sample marked as 3-S1/3.2 is some higher respect to the other samples. This fact indicates an existence of some local anthropogenic source of this element.

**Vanadium:** The content of V in 2-S1/2.4, 29-S13/2.7, and 30-S14/0.7 sediment samples is significantly higher than in the remaining samples. Generally, V content has a high value that may be a consequence of their origin from crude oil, since that investigated area is close to the refinery. Vanadium is often used as a tracer of oil contamination, since that V is an abundant element in crude oils [32].

#### Depth Profile of Metal and N, C, H, and S Content

The graphic representation of the depth profile of metal content is shown in Fig. 3. In Fig. 4 is shown N, C, H, and S distribution by depth.

**Copper:** Copper content first grows with depth, then decreases (S3, S4, and S10 DH), while in S1 DH it is permanently growing with depth. In S12 and S13 drill-holes, Cu content first decreases, then grows with depth, as in S2, it permanently decreases with depth. Distribution by depth of Cu content is similar to H distribution, which indicates the relevant control of Cu content with clay mineral content. This result is in accordance with the result of Helios Rybicka [33]. Clay minerals are the most important mineral reservoirs of hydrogen in sedimentary rocks [34], and play an important role in the accumulation, sorption/desorption as well as exchange processes of metals in soil and sediment [33]. In the paper Helios Rybicka [33], the adsorption/desorption behaviour of Cd, Cu, Pb, Zn, and Ni on illite, beidellite and montmorillonite was investigated using a multichamber device, and the obtained results showed that the adsorbed amounts of Pb and Cu ions were high: 80% and 70% of the total concentration of the metal ions, whereas the Zn, Ni, and Cd ions were adsorbed in smaller (40-50%) amounts.

**Chromium:** Content of chromium firstly grows with depth and then declines (S1, S3, and S4 drill-holes), while in the S10 drill-hole, content permanently grows with depth. In S12 and S13 DH, content first decreases, then grows with depth, as in S2 drill-hole content permanently decreases. Distribution by depth is similar as in Ni distribution, whereas in S2, S12, S13, S3, and S4 DH, distribution is similar to Cu depth-profile. Similarity in Cr and Ni distribution by depth is probably a consequence of their geochemical similarity. Cr and Cu distribution similarity is

probably a consequence of their mutual bonding with organic compound and compound with S, which is in accordance with the result of Pruyers et al. [35].

**Nickel:** In S1, S3, S4 drill-holes, content grows with depth, then declines, while in the S10 drill-hole content permanently grows with depth. In S12 and S13 DH, content decreases and then grows with depth, whereas in S2, content permanently decreases. Distribution is similar to Cr distribution, whereas in S2, S12, S13, S3, and S4 drill-holes, distribution is similar to Cu distribution. Similarity in Cr and Ni depth profile is a consequence of their geochemical similarity and origin. Ni and Cu are often bound to organic matter and they form a compound with S [35].

**Zinc:** Content of zinc grows with depth, and then declines (S1 and S10 drill-holes). In S2, S12, and S13 DH, content decreases with depth, and then grows, while in S3 and S4, content permanently decreases. For some samples, distribution of Zn is similar to V, H, and S distribution by depth. This indicated that Zn content is significantly controlled by clay mineral content (Zn-H similarity); Zn and V similarity indicate a possible binding with organic matter as well as the existence of compound formation with S. Zinc is well-known to be fixed as a sulfide [36].

**Lead:** Content of lead decreases with depth, then it grows (S2, S12 and S13 drill-holes); it decrease regularly with depth in S1 and S10 DH, and permanently grows in S4 DH.

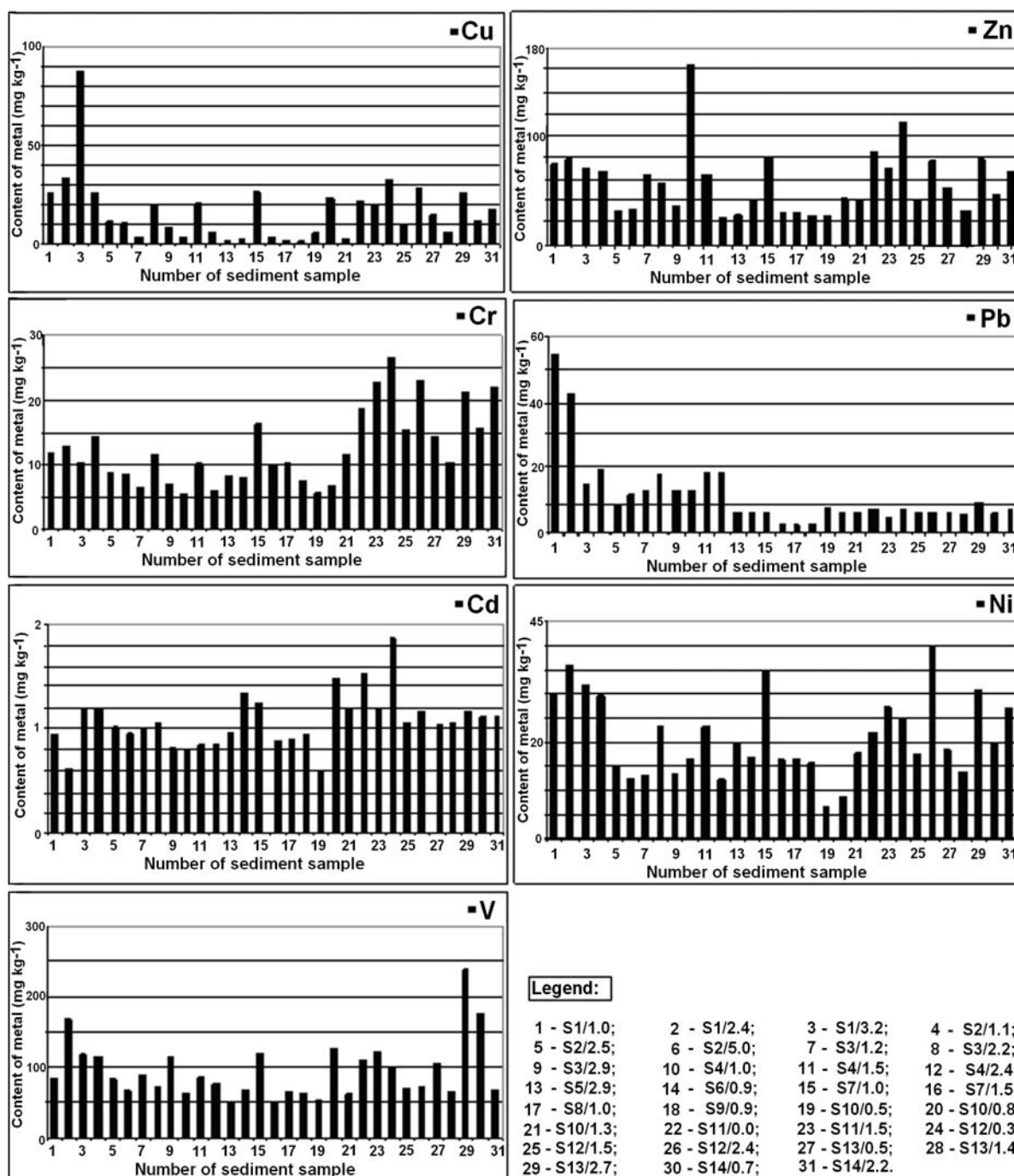


Fig. 2. Distribution of metal content by locations in investigated sediment.

Table 2. Values of EF.

Sample/depth (m)	Cu	Cr	Zn	Pb	Cd	Ni	V
1 /S1-1.00/	0.91	0.53	0.86	1.75	0.42	0.89	0.47
2 /S1-2.40/	0.85	0.42	0.67	1.00	0.20	0.78	0.70
3 /S1-3.20/	3.71	0.58	1.01	0.62	0.66	1.17	0.83
4 /S2-1.10/	0.92	0.67	0.79	0.61	0.56	0.90	0.66
5 /S2-2.50/	0.93	0.92	0.80	0.74	1.04	1.02	1.07
6 /S2-5.00/	1.00	1.04	1.00	1.03	1.15	1.01	1.00
7 /S3-1.20/	0.37	0.82	2.11	1.20	1.26	1.13	1.43
8 /S3-2.20/	0.99	0.76	0.97	0.82	0.70	1.01	0.60
9 /S3-2.90/	0.41	0.43	0.54	0.59	0.51	0.55	0.89
10 /S4-1.00/	0.87	1.68	13.12	2.86	2.47	3.29	2.37
11 /S4-1.50/	0.83	0.53	0.86	0.67	0.45	0.80	0.56
12 /S4-2.40/	1.23	1.49	1.55	3.20	2.16	2.07	2.38
13 /S5-0.90/	0.54	2.79	2.28	1.31	3.21	4.40	2.01
14 /S6-0.90/	0.45	1.60	2.12	0.89	2.73	2.28	1.73
15 /S7-1.00/	0.65	0.52	0.66	0.15	0.40	0.75	0.48
16 /S7-1.50/	0.48	1.75	1.27	0.41	1.58	1.92	1.10
17 /S8-1.00/	0.15	1.20	0.85	0.25	1.05	1.26	0.93
18 /S9-0.90/	0.13	0.74	0.66	0.22	0.92	1.03	0.77
19 /S10-0.50/	1.52	1.86	2.17	2.09	1.99	1.47	2.18
20 /S10-0.80/	1.36	0.51	0.83	0.34	1.11	0.42	1.20
21 /S10-1.30/	0.44	2.15	1.90	0.76	2.23	2.19	1.45
22 /S11-0.00/	0.67	0.76	0.90	0.24	0.61	0.59	0.56
23 /S11-1.50/	0.67	0.98	0.78	0.13	0.51	0.79	0.66
24 /S12-0.30/	0.69	0.73	0.80	0.17	0.52	0.46	0.34
25 /S12-1.50/	0.79	1.55	1.04	0.40	1.06	1.16	0.89
26 /S12-2.30/	0.86	0.92	0.80	0.17	0.47	1.04	0.36
27 /S13-0.50/	0.68	0.86	0.82	0.24	0.61	0.74	0.79
28 /S13-1.40/	0.63	1.39	1.05	0.48	1.41	1.24	1.09
29 /S13-2.70/	0.88	0.93	0.90	0.32	0.51	0.90	1.33
30 /S14-0.70/	0.79	1.32	1.01	0.32	0.95	1.11	1.90
31 /S14-2.20/	0.93	1.47	1.16	0.41	0.75	1.20	0.57

Distribution is quite similar to H distribution with depth, except in S1 drill-hole. Because of that, it can be said that Pb natural content is dominantly controlled by clay mineral content. Since the S1 drill-hole is nearest the refinery, it can be supposed that Pb is of anthropogenic origin in this location, and distribution by depth is different with respect to all other drill-holes.

**Cadmium:** Content of cadmium first decreases and then grows with depth (S1 and S12 DH). First it grows and then decreases with depth in S3, S4, and S10 DH, while it decreases with depth in S2 DH and permanently grows with

depth in S13 DH. In some drill-holes, distribution is similar to C distribution by depth, which is probably a consequence of the presence of Cd in the form of carbonates. Sakan et al. [13] demonstrates that C dominantly presents carbonates in the investigated location. It can be concluded that different processes, natural and anthropogenic, respond to various depth profiles of cadmium content.

**Vanadium:** Content of V initially grows then declines with depth (S1 and S4 DH), declines and then grows with depth (S3 and S13 DH), and permanently declines with depth (S2, S10 and S12 DH). Distribution is similar with

Zn distribution in some drill-holes, which is a consequence of the fact that V is considerably bound to organic matter and compound with S, as for Zn. Also, this similarity in V and Zn distribution may be related with their mutual origin from crude oils, since those locations of sediment sampling sites are in the vicinity of a refinery.

Soil and sediment organic matter is acknowledged as a major source of N. Considering that there was not observed similarity in distribution of metals and N distribution by depth (Figs. 3 and 4), it can be concluded that organic matter with N is not a significant scavenger for metal on investigated locations.

Evidently, element profiles in the drill-hole have been affected by various processes such as changes in geological

source material and diagenesis, including chemical alterations and postdepositional sediment mixing. Also, for some elements (Cd and Pb) it is evident that distribution is significantly influenced by anthropogenic sources, especially in surface layer. This is a consequence of the fact that top soils and sediments are main "receptors" of elements emitted to urban environments from various sources.

### Geochemical Normalization

In this paper, Al is used as an element for normalization. This estimation is based on the positive correlation found between the grain size of the material and the content of

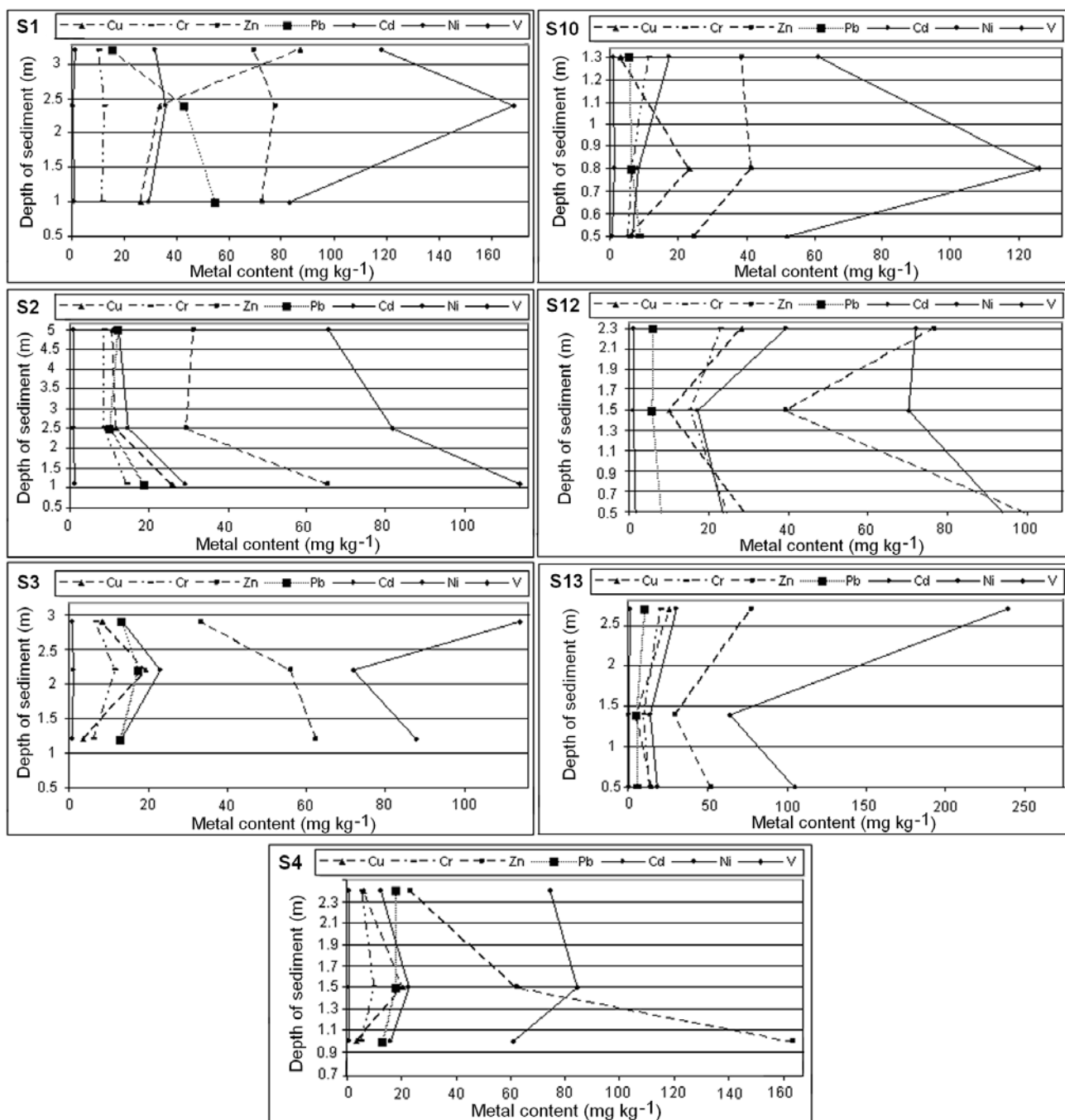


Fig. 3. Depth profiles of metal content.



extractable Al. Also, a positive correlation exists between Al and elements, for which EF is calculated. The values of Pearson's correlation coefficients that confirmed this normalization procedure is: Cu-Al ( $r=0.61, p=0.00$ ), Cr-Al ( $r=0.73, p=0.00$ ), Zn-Al ( $r=0.51, p=0.00$ ), Cd-Al ( $r=0.46, p=0.01$ ), Ni-Al ( $r=0.77, p=0.00$ ), V-Al ( $r=0.55, p=0.00$ ), Al-Silt content ( $r=0.77, p=0.00$ ), and Al-Clay content ( $r=0.87, p=0.00$ ). These values show that aluminium is suited to explain the natural variations of the contents of Cu, Cr, Zn, Cd, Ni, and V, as well as that Al can normalize the contents of these elements. The value of the correlation coefficients

( $r$ ) that are not at a significant level for Pb [ $(Pb-Al) (r=0.32; p=0.08)$ ] indicate that only a low percentage of Pb natural variability can be attributed to the textural and mineralogical variability of the sediments.

### Trace Elements Contamination Assessment Using the Enrichment Factor

For the quantification of anthropogenic impact, enrichment factor EF was calculated. EFs were calculated using the formula:

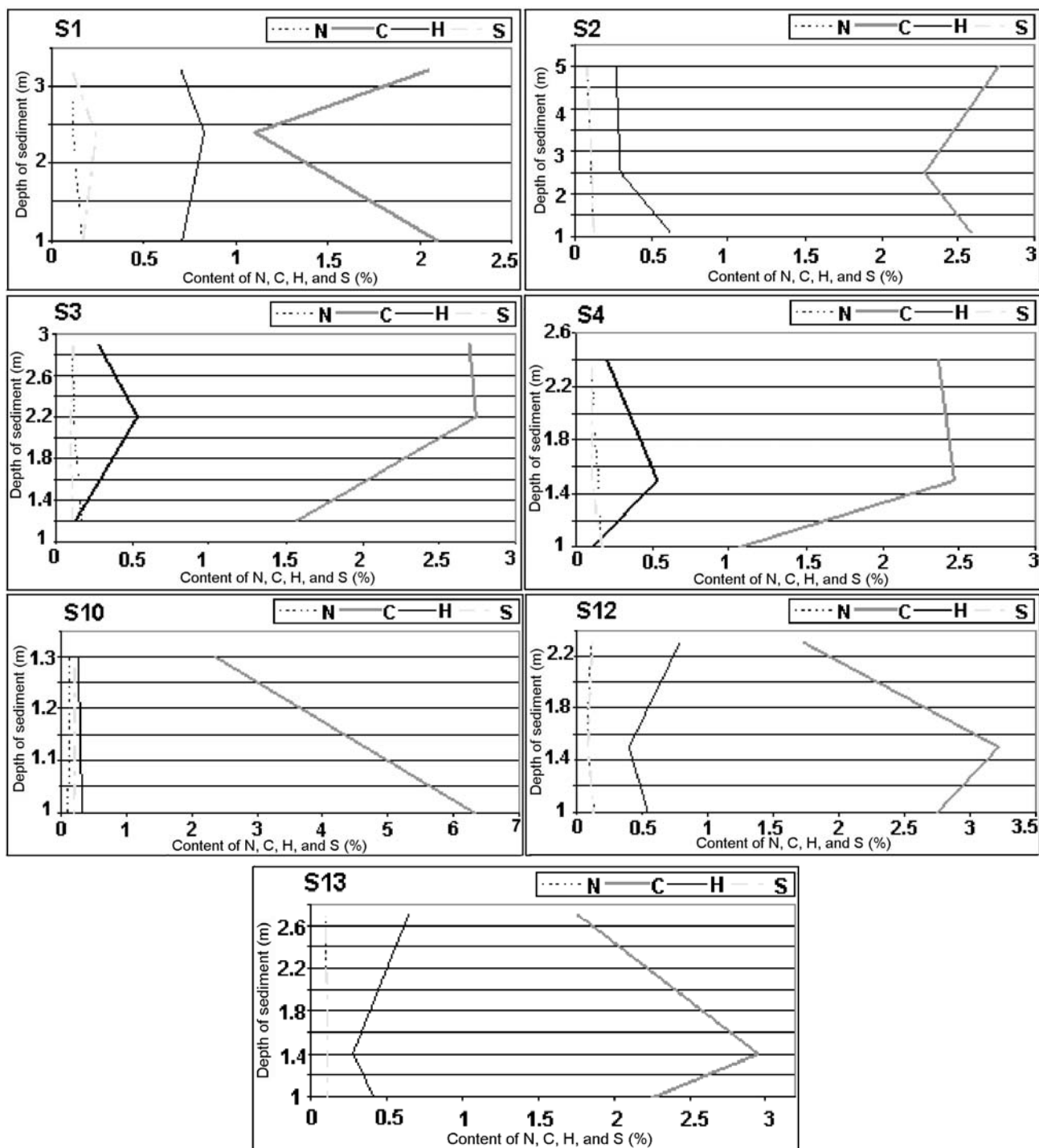


Fig. 4. Distribution by depth of N, C, H, and S.

Table 3. Principal component analysis of normalized metal contents.

Principal component loadings	Varimax normalized*	
	PC1	PC2
Cu		0.890
Cr	0.872	
Zn	0.838	
Pb	0.593	0.632
Cd	0.934	
Ni	0.914	
V	0.841	
Eigenvalue	4.246	1.329
% Total variance	60.660	18.992
Cumulative %	60.660	79.651

\*Matrix of PCA loadings of elements and communality of the PCA components; loadings below 0.5 are not shown.

$$EF = (M/Al)_{\text{sample}} / (M/Al)_{\text{background}}$$

...where (M and Al)<sub>sample</sub> represent element contents in sediment sample, and (M and Al)<sub>background</sub> represent background contents of elements. As background contents for investigated sediment we used element contents for sediment taken from the bottom of the S2 drill-hole, at 5 m depth. This sediment sample has a notation S2/5.0. The depth of 5 m represents the lowermost depth from which is taken sediment samples. This choice of background values is in accordance with results of other researches who concluded that a better approach is to use local uncontaminated sediment as a normalizing reference representing preindustrial conditions best collected from a sediment core [10]. Background values are distinctly different among different soil types, especially with respect to Na, Mg, Al, K, Ca, Ba, Sc, Ti, Fe, and Br [37]. We supposed that choosing background contents is valid, since elements content for S2/5.0 sampling site are the minimum contents found in this study for most elements. The values of determined background contents for elements in investigated alluvial sediment were (in mg·kg<sup>-1</sup>): Cu=10.77, Cr=8.62, Zn=31.45, Pb=11.97, Cd=0.95, Ni=12.48, Al=8268.0, and V=65.40.

The values of EF for sediment samples are illustrated in Table 2. The values of EF are: Cu from 0.13 to 3.71, Cr from 0.42 to 2.79, Zn from 0.54 to 13.12, Pb from 0.13 to 3.20, Cd from 0.20 to 3.21, Ni from 0.42 to 4.40, and V from 0.34 to 2.38. The highest EFs are observed for Zn at the S4/1.0 location. Based on derived results, the analyzed sediment is:

1. minorly enriched with Cr and V (EF from 1 to 3),
2. moderately enriched with Cu, Pb, Cd, and Ni (EF from 3 to 5), and
3. severely enriched with Zn on S4/1.0 location (denoted with number 10), for which the EF value is 13.12.

In case of exclusion of extreme values for Zn EF (13.1), other values for EF are from 0.54 to 2.28, which indicate minor enrichment with Zn.

It can be said that minor to moderate enrichment of sediment with Cr, V, Cu, Pb, Cd, Ni, and Zn existed except for one location, where EF for Zn is 13.12 (sample with denotation 10, S4/1.0). This fact indicated the existence of some local anthropogenic origin of Zn.

### Factor Analysis

This paper presents results of R mode and Q mode Factor Analysis. The analysis was carried out with normalized data, because of evaluation of anthropogenic origin of elements. Table 3 shows the factor loadings of principal components after Varimax orthogonal rotation obtained by PCA statistical analysis. Graphical representations of these results are shown in Fig. 5.

#### Factor Analysis in R Mode

According to the Kaiser criterion, the number of significant principal components with eigenvalue higher than 1 were selected. The first component (Fig. 5a) comprises Cr, Zn, Pb, Cd, Ni, and V, and explains 60.66% of the total variance (Table 3). The second component explains 18.99% of the total variance and exhibits positive loadings for Cu and Pb (Table 3).

It can be said that Cu has a different anthropogenic source in relation to other elements (Cr, Zn, Cd, Ni, and V), whereas Pb origin is dual, namely origin and behaviour of this element is related to PC1 and PC2 components. The presence of Pb in both components is indicative of different sources, including potential anthropogenic inputs. PC1 component is indicative of an element origin from refinery, Petrochemical Complex, as a consequence of the bombing of the Pančevo Oil Refinery, i.e. input of metal originates from the industrial complex at this location, and PC2 is related to other local contamination sources combined with traffic sources. Most probably the source of Pb is auto emissions [38, 39] and high copper loadings could be attributed to vehicle brake pad wear. Yeung et al. [40] commented that Cu can be released to an urban environment as a result of wear of the automobile's oil pump or of those metal parts that come into contact with oil caused by corrosive action.

#### Factor Analysis in Q Mode

From Fig. 5b we can distinguish five groups of sediment:

Group 1: there is assumption that in these locations the natural origin of elements prevail, since their EF values are not higher (samples with denotations 1-S1/1.00/, 2-S1/2.40, 4-S2/1.10, 5-S2/2.50, 6-S2/5.00, 7-S3/1.20, 8-S3/2.20, 9-S3/2.90, 11-S4/1.50, 15-S7/1.00, 20-S10/0.80, 22-S11/0.00, 23-S11/1.50, 24-S12/0.30, 25-S12/1.50, 26-S12/2.30, 27-S13/0.50, 28-S13/1.40, 29-S13/2.70, 30-S14/0.70, and 31-S14/2.20).

Group 2: low and comparable values of EF indicate a similar geochemical origin of elements for 17-S8/1.00 and 18-S9/0.90 samples, which is a consequence of geochemical similarity of investigated sediments.

Group 3: in general, high values of EF indicate a significant anthropogenic origin of elements for sediment samples 13-S5/0.90, 14-S6/0.90, 16-S7/1.50, and 21-S10/1.30. EFs values for Cr, Zn, Cd, and Ni are from 1.27 to 4.40, whereas in 13-S5/0.90 and 14-S6/0.90 sediment samples have a high V content–to 2.01. It is evident that the refinery influences the sediment metal content.

Group 4: for Zn, Pb, Cd, Ni, and V, EF values for all elements were from 1.55 to 3.20, except for sample 10-S4/1.00, for which EF for Zn was 13.12. In the sample 10-S4/1.00, some high value of EF for Cr and in sample 19-S10/0.50, EFs were higher than 1.5 (for Cu and Cr). The high values of EF for different elements indicate their various sources, including potential anthropogenic inputs for

these sediment samples (10-S4/1.00, 12-S4/2.40, and 19-S10/0.50): vicinity of refinery, auto emissions, consequence of NATO bombing and war in 1999, existence of local contamination source of Zn, etc. In April 1999 Pančevo oil refinery was bombed and there occurred effluence of crude oil and their derivatives, which is contaminated soil and underground water. The high content of Pb was observed in sediment investigations after the bombing [17, 41, 42]. In investigations of metal content in surface and underground Vojvodina waters it was concluded that the higher content of Zn in underground water originates from agricultural production [43].

Group 5: high value of EF (3.71) for Cu in sediment sample with denotation 3-S1/3.20 indicates the existence of a local contamination source.

It can be observed that, in general, with increasing distance from the Refinery, the anthropogenic influence on metal content is lower and dominates geochemical control of element content. This indicates the existence of refinery influence on metal content in investigated alluvial sediment. We also found influence of other anthropogenic sources on metal content in the studied locations.

### Conclusions

This study highlights the importance of evaluating environmental quality and contamination by means of trace elements in sediment, determination of element content, analyzing the distribution of metal by depth and location, geochemical normalization method, determination of metal background values, calculation of enrichment factors (EF), and multivariate statistics. Evidently, element profiles in the drill-hole have been affected by various processes such as changes in geological source material and diagenesis, including chemical alterations and postdepositional sediment mixing. Also, for some elements (Cd and Pb) it is observed that distribution is significantly influenced by anthropogenic sources, especially in surface layer.

As background contents for investigated sediment we used element contents for sediment that were taken from the bottom of the drill-holes, at 5m depth. On the base of calculated enrichment factors, it can be said that analyzed sediment is:

1. minorly enriched with Cr and V (EF from 1 to 3),
2. moderately enriched with Cu, Pb, Cd, and Ni (EF from 3 to 5), and
3. severely enriched with Zn on S4/1.0, for which the EF value is 13.12. In the case of exclusion of extreme values of EF for Zn, other values are from 0.54 to 2.28, which indicates minor enrichment with Zn.

Results of PCA point out that Cu has a different anthropogenic source in relation to other elements, whereas Pb origin is dual, namely origin and behaviour of this element is related to PC1 and PC2 components. PC1 component is indicated on dominate element origin (Cr, Zn, Cd, Ni, and V) from industry complex on this location (Pančevo Oil Refinery, Petrochemical Complex, as well as contamination as a consequence of bombing of Pančevo Oil Refinery).

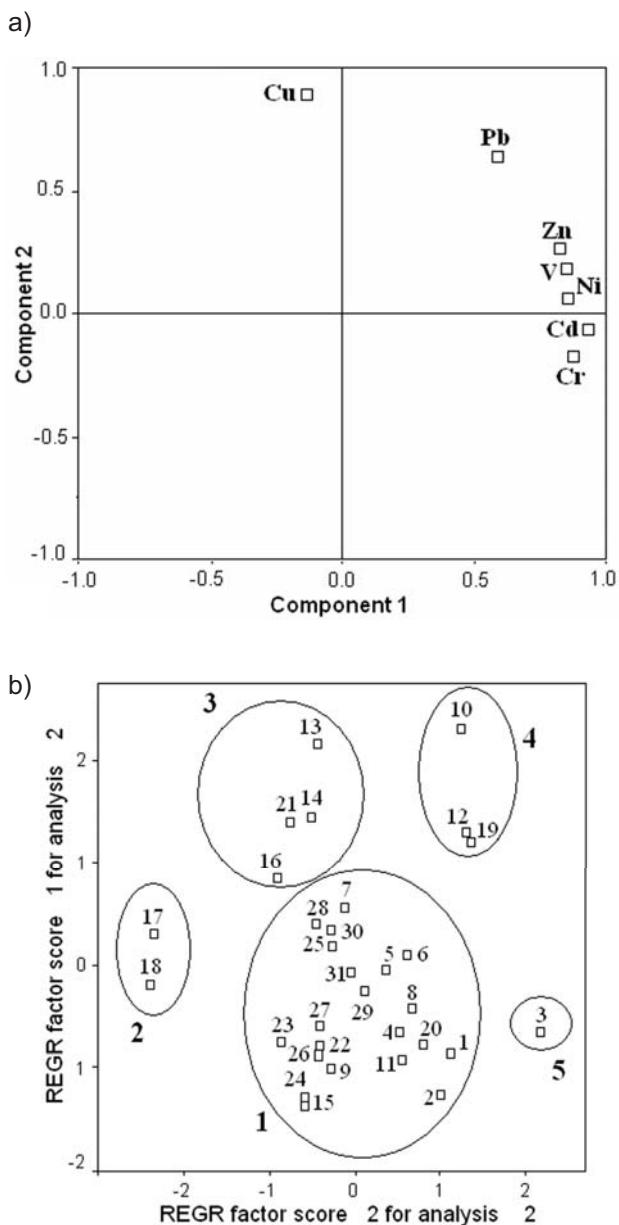


Fig. 5 (a) Results of the PCA (R mode). (b) Results of the PCA (Q mode).

The PC2 component is related to other local contamination sources combined with traffic sources. It can be observed that, in general, with increasing distance from the refinery, the anthropogenic influence on metal content is lower and dominates geochemical control of element content. This indicates the existence of refinery influence on metal contamination in sediments. The investigated alluvial sediment is, in general, affected by combined trace elements contamination, but this contamination is not significant. Therefore, the study was meaningful to establish baseline data for future use in contamination control strategies and management.

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