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# Geochemistry of Metals and Organic Matter in Water and Sediments of the Karst River Cetina, Croatia

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**Abstract:** The Cetina River Basin (CRB) belongs to a Dinaric karst area (Croatia). According to the obtained results on water and sediment quality, the Cetina River reaches the sixth goal of Sustainable Development (source of drinking water). Together with the CRB water quality assessment, it was confirmed that sediments undoubtedly contribute to the purification of watercourses from trace metals as well as organic matter. In 5 years, water samples were collected at 20 sampling sites and sediment samples were collected at 18 sampling sites. The fresh water of the Cetina River belongs to the hydrocarbonate type due to its lithology. The concentrations of the measured elements in the sediments, normalized to Al, are an indicator of possible pressures affecting the ecosystem of the river. According to the Principal Component Analysis (PCA) for elements in sediments, Principal Component 1 (PC1) describes the geogenic origin of the elements, while Principal Component 2 (PC2) describes positive values reflecting anthropogenic pressures (Total Nitrogen, TN; and Total Phosphorus, TP). Depending on element composition, the factor scores related to PC1 and PC2 resulted in four different groups of sites. The first three groups of sediments showed geological impact, while the fourth group was partially anthropogenic in origin. The hierarchical cluster analysis showed four clusters in relation to the content of the elements. Cluster analysis of all elements and the Total Organic Carbon (TOC) in the sediments showed grouping in only two clusters, the first cluster consisting of Ca, and the second of TOC with other elements.

**Keywords:** trace metals; sediment quality; karst river; multivariate statistical analysis; cluster analysis

## 1. Introduction

An important step for good water management and protection is to understand the geochemical processes in the studied sources and the environment. The most important substances in the aquatic environment that are widely considered to be persistent are trace elements. They can enter the aquatic environment naturally—from the atmosphere, from fires or floods [1,2], and from leaching of the surrounding rocks—but also from various anthropogenic activities (discharge of effluents from agricultural areas, roads, industry, etc.). Naturally occurring elements are usually found in less accessible forms, while elements from anthropogenic sources occur in bioavailable forms [3]. Depending on the nature and chemical properties of an individual element, its mobility in the environment varies. Depending on mobility, elements are classified into four groups: Cd, B, Se, As, Sb, Mo, and Sr as high mobility elements; U, Si, Li, Mn, Ba, Cu, Co, Ni, and Rb as medium mobility elements; Zn, Cr, V, Pb, Be, Fe, and Cs as low mobility elements; and Ti, Al, and Zr as very low mobility elements [4]. They are also divided into essential, biologically important elements necessary for metabolic and biogeochemical processes, and those that are not

biologically important and are usually toxic at very low concentrations (Hg, Cd, Ni, Cr, Tl, and Pb) [5,6]. The elements in the water represent the current state, but they are also deposited in the sediment, which plays an important role in their circulation in the water environment [7]. Sediment cores thus give us an overview of the pollution history of the river basin. The ecotoxic elements in sediments with high solubility under reductive and acidic conditions could be mobilized back into the water column by dissolution and by binding to the particles and colloids [8]. Particle size is the fundamental physical property of sediments, as the smallest fractions with a large active surface area contain the highest concentrations of elements as well as organic carbon [9–13]. Elements can be bound to the sediment in five fractions: as an exchangeable fraction, as a fraction bound to carbonates, as a fraction bound to iron and manganese oxides, as a fraction bound to organic material, and as residual. The elements are the most abundant in the exchangeable fraction, but as a small part of the total content of elements in the sediment, which is about 2% [14]. In this fraction, elements are retained at the sediment surface by weak electrostatic interactions and released into the water column as environmental conditions change [15,16]. Elements bound to carbonates have a higher total element content than the exchangeable fraction. This fraction is valuable, which is especially true for the elements Zn, Cd, Ni, and Mn [14].

This study helps identify the types of measures that could be implemented in the future to reduce the adverse effects of human activities on tributary freshwater quality, and then their effects on freshwater and sediment quality in the main river and power plant reservoirs. Some of the measures include long-term monitoring and installation of treatment plants. Since it is a transboundary river, monitoring of trace elements in freshwater and sediments is of particular importance. The effects of tributaries on the freshwater and sediments of the main river are discussed, with emphasis on transboundary management and the effects of different management by two independent states—the Republic of Croatia and Bosnia and Herzegovina.

The Dinaric karst area in the Central Dalmatia region of Croatia, which includes the Cetina River, is richer in surface and groundwater compared to most other karst areas in Europe. There are sporadic local impacts on the environment of the Cetina River as well as on transboundary strategic water resources. For the quality of life in karst areas, water has a significant strategic value [17], but some anthropogenic activities and climate changes are the main causes of pressures on all river ecosystem compartments [18]. At the same time, it is known that the waters of the karst area are extremely sensitive to pollution [17].

The main objective of this work was to study and highlight the water quality of the Cetina River and the role of sediments in its self-purification, especially in the reservoirs of the power plants, since the river is an aquifer for a large part of the Adriatic coastal mainland, as well as for the islands connected to the CRB.

## 2. Materials and Methods

### 2.1. Study Area Overview

The Transboundary Cetina River Basin (CRB) is located in the Dinaric Karst region in the center of the coastal hinterland of SW Croatia (the Eastern Adriatic Basin), receiving freshwater from the west of the Bosnia and Herzegovina (BiH) karst areas through underground channels (Figure 1). The Cetina River belongs to the Adriatic Basin and is the longest central Dalmatian river, and flows from springs (Glavaš vrelo, Vuković vrelo, Batića vrelo) through valleys and gorges in Croatia to an estuary in the Adriatic Sea. The Cetina River basin covers an area of about 4145 km$^2$ [19], divided into two parts by the Dinara Mountains. The eastern part of the catchment (about 2614 km$^2$), the so-called "indirect" catchment, is located mainly in Bosnia and Herzegovina (BiH), while the western part, the "direct" one, has an area of about 1531 km$^2$ (one third of the catchment). The mean annual discharge is about 100 m$^3$ s$^{-1}$, with a minimum discharge of 8 m$^3$ s$^{-1}$ [20]. The main tributaries are: Vojskova, Rumin, Ruda, Zvizda, etc. The shallow karst aquifers of carbonate are characterized by heterogeneity and anisotropy in contact with surface water through the epikarst zone [21–23], as in the Dinaric karst [24–28]. Between horizontally and

vertically distant aquifers, between which there is no isolating factor, water flows under the influence of gravity through karst channels, microfractures, and macrofractures, resulting in opposing groundwater flows [24]. Surface water in the study area flows through fractured and encrusted karst rocks, which are hydrogeologically permeable.
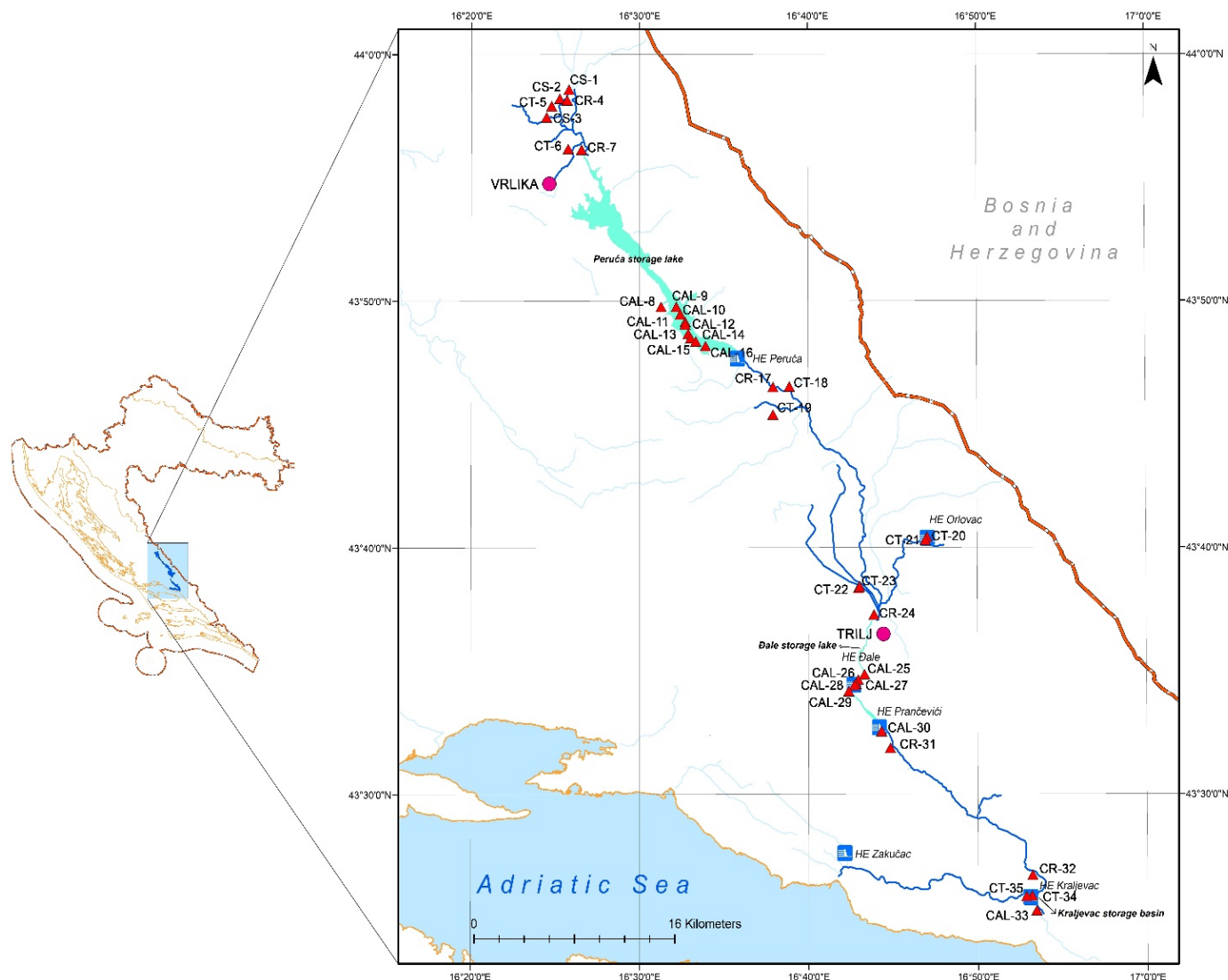


**Figure 1.** Cetina River Basin (CRB) with sampling sites through the course towards the estuary.

The CRB requires a transboundary approach to water resources management that includes protection, controlled use, and long-term sustainable management in terms of water availability and quality [26]. The two countries rely on a common groundwater resource, and have rights and obligations under the Water Convention and the Water Framework Directive. According to the methodology proposed by Shahbazbegian and Noori [29], the groundwater body/aquifer of the Cetina River belongs to the archetype "Hidden measures and open effects". Such a lithology contributes to a cleaner environment within a sustainable and blue-green approach. It relates to the protection of groundwater and surface water quality (SDG 6), and is consistent with other SDGs (2, 3, 7, 12, 13 and 15) [30–37].

Figure 1 shows the entire study area and all sampling sites (Table S1 for description and codes). Water and sediment sampling was conducted at 35 representative sampling sites where it is possible to observe long-term changes. The study period was from June 2016 to June 2021, during which water samples were taken approximately once a month, partly as

a part of the multi-annual national monitoring system of Croatian Waters, while sediment samples were taken only once in 2018. Recommendations were used for the selection of sampling sites, e.g., the Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Guidance Documents No. 15 and No. 19. The study area is divided into four parts. The sources of the Cetina River (CS-1, CS-2, CS-3) and the sampling point CR-4 are located in the area of scattered, sparsely populated rural areas surrounded by agricultural fields and roads. The same is true for the tributaries of the Cetina River, CT-5 and CT-6, with treated wastewater from the town of Vrlika also flowing into CT-6. All of the above sites, including CR-7, are located upstream of the Peruća reservoir and belong to the first group of samples. Sampling sites CAL-8 to CAL-16 are located at the Peruća reservoir and belong to the second group of sampling sites with downstream sampling sites CR-17, CT-18, and CT-19.

Sampling sites CT-20, CT-21, CT-22, and CT-23 are predominantly surrounded by agricultural land. The sampling site CR-24 is located downstream of the inlet of the tributaries CT-22 and CT-23 and the inlet of the treated wastewater of the city of Trilj, but upstream of the city center. Downstream of the town of Trilj, at the Đale reservoir, are the sampling points CAL-25 to CAL-29. Immediately downstream of the Đale reservoir is the Prančevići reservoir, to which the sampling point CAL-30 belongs. Downstream from the Prančevići reservoir is the sampling site CR-31, the last of the third group of sampling sites. Site CR-32 is the fourth group of sampling sites located near sparsely populated rural areas without agricultural land. Additionally, the sampling point CAL-33 represents a reservoir and is located within the Kraljevac hydropower plant. Sampling site CT-34 is located in a forested area upstream of the Kraljevac hydropower plant, while sampling site CT-35 is located downstream from the Kraljevac hydropower plant. The criteria for selecting the sampling sites were based on the loads detected upstream.

*2.2. Sampling*

Sediment and water sampling was conducted in accordance with Guidance No. 25 [38] for surface sediments. Water samples were collected at 20 sampling sites in the period from June 2016 to June 2021, while sediment samples were collected at 18 sampling sites once during 2018. Sediment cores (CAL-25 to CAL-28) were collected to a depth of 80 cm and cut into subsamples every 5 cm.

2.2.1. Methods for Water Analyses

Electrical conductivity, pH, and dissolved oxygen (DO) were measured on site using a SevenMulti instrument (Mettler Toledo, Greifensee, Switzerland). Quality control of the measurements was performed by measuring certified reference material (CRM) KEFO 7018.0500 (Kefo, Sisak, Croatia) for pH, and natural lake water LON-07 Major Ions and Nutrients (Environment Canada, Burlington, ON, Canada) for electrical conductivity. Total hardness and alkalinity were measured by the titrimetric method. Total dissolved solids and $HCO_3^-$ were calculated according to Gupta [39] and Boyd [40]. Total suspended solids and turbidity were measured using a HACH 2100 N turbidimeter (Hach, Loveland, CO, USA). Ammonium, nitrates, nitrites, orthophosphates, and sulphates were measured using a Perkin Elmer Lambda 25 (Perkin Elmer, Shelton, CT, USA). Chlorides were measured by the titrimetric method. Fluorides and cations (Ca, K, Mg and Na) were determined by ion chromatography using a Dionex ICS 3000 instrument (Dionex, Sunnyvale, CA, USA). Quality control of measurements was performed by measuring CRM LON-07 Natural lake water Major ions and nutrients (Environment Canada, Burlington, ON, Canada) for ions and Fluka QC3198 Nutrients, WP (Fluka, Buchs, Switzerland) for orthophosphates. Total organic carbon (TOC), dissolved organic carbon, and total nitrogen were measured using a Shimadzu TOC-V$_{CPH}$ analyzer (Shimadzu, Kyoto, Japan). Quality control of the TOC measurement was performed using CRM Fluka QC1308, TOC-WS (Fluka, Buchs, Switzerland). The concentrations of twenty-eight (28) dissolved elements (Al, As, B, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb, Sb, Si, Sn, Sr, Ti, Tl, U, V, Zn and Zr) were

measured by inductively coupled plasma mass spectrometry on Elan 9000 ICP-MS (Perkin Elmer, Shelton, CT, USA, with a solution of 20 $\mu gL^{-1}$ Rh, Ge, and Re as internal standard, and Agilent 8900 ICP-MS Triple Quad (Agilent, Tokyo, Japan) with a solution of 30 $\mu gL^{-1}$ Y, In, and Tb. Quality control of the method ICP-MS was performed by analyzing the certified reference material ANAS-38 (Inorganic Ventures, Christiansburg, VA, USA). Chemical oxygen demand (COD) was measured by the titrimetric method, while dissolved oxygen (DO) and biological oxygen demand (BOD) were measured using a Hach HQ430d digital oximeter (Hach, Loveland, CO, USA). Dissolved mercury was measured by the method EPA 245.7 using a QuickTrace M-8000 mercury analyzer (CETAC, Omaha, NE, USA) and an Agilent 8900 ICP-MS Triple Quad. The accuracy of the analytical procedure and the quality control of the method were performed by analyzing the CRM at the beginning and after the analysis of each sample series. Good agreement within 15% was found between our data and the certified values.

The hydrochemical relationships of the main ions $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $HCO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$, and $Cl^-$ in the water samples are shown in the trilinear diagram of Piper's.

### 2.2.2. Methods for Sediment Analyses

Sediment samples were dried in a thermostat at a temperature of 40 °C and digested with 7.5 mL of suprapure nitric acid and 2.5 mL of pure hydrochloric acid in a Berghof speedwave XPERT, Microwave Digestion System DAK-100X (Berghof, Eningen, Germany). Elements in the sediment, including total phosphorus, were detected by inductively coupled plasma mass spectrometry on an ICP-MS Perkin Elmer Elan 9000, with a solution of 20 $\mu gL^{-1}$ Rh, Ge, and Re as the internal standard, and on an Agilent 8900 ICP-MS Triple Quad with a solution of 30 $\mu gL^{-1}$ Y, In, and Tb.

Quality control of the method ICP-MS was performed by analyzing the elements of interest in a standard reference material CNS392-0.50 (RTC, trace elements on freshwater sediment). Total nitrogen (TN) was determined by the spectrophotometric method using a PerkinElmer Lambda 25 spectrophotometer, with samples previously digested with concentrated reagents ($H_2SO_4$, $K_2SO_4$, and $SeO_2$) and treated with hydrogen peroxide, releasing organic N as ammonium. Mercury was analyzed according to the method EPA 245.7, the QuickTrace M-8000 mercury analyzer, and the Agilent 8900 Triple Quad instruments. Total organic carbon (TOC) was determined using a TOC analyzer, TOC-V$_{CPH}$ (Shimadzu, Kyoto, Japan), with solid sample module SSM-5000A (Shimadzu, Kyoto, Japan). Mass is converted to percent carbon based on dry weight. The accuracy of the analytical procedure and the quality control of the method were performed by analyzing the CRM at the beginning and after the analysis of each series of samples. Good agreement within 20% was found between our data and the certified values.

### 2.2.3. Data Treatment

The Piper diagram was used to define hydrochemical facies using the free USGS software GW Chart [41]. Factor analyses, Principal Component analyses (PCA), and Cluster analyses were determined using the STATISTICA 10.0 program. Normalization of geochemical data was used as a type of standardization, with the presence of a standardization component that is a result of natural processes. With normalization of geochemical data, it is possible to distinguish natural from anthropogenic enrichment of sediments with heavy metals and to identify areas affected by anthropogenic influences. The conservative elements, such as Al, Fe, Li, and Cs, are used as normalization agents. These elements were selected because they represent the average crustal abundance data as a reference base [42]. One of the major constituents of the aluminosilicate mineral fraction is Al, and it is commonly used as a grain size proxy [43]. However, geochemical normalization is usually based on a specific principle that the ratio of metal concentrations to the reference element in the Earth's crust is mainly stable [44,45].

## 3. Results and Discussion

### 3.1. Water Analyses

From the obtained data, it is evident that dissolved anions and cations in water show that groundwater and surface water belong to the calcium type (Ca–HCO$_3$). Only two sampling points in tributary watercourses (CT-6 and CT-18) are closer to the Ca-SO$_4$/HCO$_3$ type of water, according to the major ions (Figure 2).



**Figure 2.** Piper tri-linear diagram showing the hydrochemical facies of the CRB study area.

However, the samples show the type dominated by calcium carbonate (Ca-HCO$_3$), which represents an alkaline environment, and the alkali components of the carbonate exceed more than 50%. Among the cations, it is obvious that calcium dominates in most water samples. The calcium carbonate type of water indicates the presence of limestone in the CRB bedrock. The author groups [27,28] reported that the neighboring areas of Dinarides have the same hydrogeochemical water type, which is due to the carbonate lithology of the CRB area. The measurement results of physico-chemical parameters, nutrients, ions, DOC, TOC, BOD, and COD, at the sampling points of the Cetina River and its tributaries are presented in Table S2. The mean value of the pH was 7.94 in the Cetina River main course, and 7.7 in the tributaries, which was slightly higher than the mean annual pH values of springs in the Biokovo Mountain [27,46]. The mean concentration of TN in the water column of the Peruća Reservoir (CAL-11) was 0.401 mgNL$^{-1}$, and TP was 0.009 mgPL$^{-1}$, which was far lower than the mean concentration in the Sabalan Lake and most reservoirs around the world, as reported by Noori et al. [47]. During the spring/summer period of 2021, water temperatures in the water column were also measured, and varied from the lake surface to a depth of 30 m between 12.1 and 8.9 °C in April, 16 and 12.5 °C in May, 24.8 and 14.9 °C in June, 23.9 and 15.4 °C in July, 25.3 and 11.8 °C in August, and 20.7 and 15.4 °C in September. If we use a conservative approach to define stratified conditions, as suggested by Noori et al. [48], where it is stated that the temperature difference between surface and bottom waters should exceed 3 °C, Lake Peruća is a stratified reservoir like Lake Inari in their study.

The mean measured ammonium concentration in the tributaries was 0.479 mgNL$^{-1}$, which is more than nine times the level allowed under the Water Quality Standards Regula-

tion. The highest ammonium concentrations were measured at CT-22 (28.3 mgNL$^{-1}$) and CT-23 (5.84 mgNL$^{-1}$). The mean value of orthophosphate concentration in the tributaries was 0.060 mgPL$^{-1}$, twice the permissible value. The highest values were found at CT-22 (3.01 mgPL$^{-1}$) and CT-23 (1.07 mgPL$^{-1}$). In the tributaries, the mean concentration of total nitrogen (TN) was also 2.13 mgNL$^{-1}$, and the highest values were recorded at CT-22 (41.0 mgNL$^{-1}$) and CT-23 (47.4 mgNL$^{-1}$). The mean concentration of total phosphorus (TP) at the tributaries was 0.094 mgPL$^{-1}$, with the highest values also at CT-22 (4.19 mgPL$^{-1}$) and CT-23 (1.67 mgPL$^{-1}$), which belong to the third group of sampling sites (Figure 1). Elevated concentrations of ammonium, nitrates, TN, and TP at the tributaries, especially CT-22 and CT-23, are most likely related to anthropogenic impacts from agricultural activities and local rural runoff. The highest measured concentration of DOC in the Cetina River was 1.50 mg L$^{-1}$ in CR-31, which is consistent with the values of springs in the Gacka River and karst springs in the Biokovo Mountains [46,49], which are examples of two extremely pristine springs. Namely, the concentration of DOC is usually below 2 mgL$^{-1}$ but can occur in concentrations up to 10 mgL$^{-1}$.

The concentrations of twenty-nine dissolved major, minor, and trace elements are presented in Table S3a,b using descriptive statistics, and do not exceed the allowable limits. Although the concentrations of all elements are below the permissible limits, according to Table S3a, the average concentration of Al is four times higher, and that of Mn is eight times higher than the concentrations measured in the Zrmanja River [50] and in the karst springs of the Biokovo Mountain [27].

In addition, the concentration of Cu was 13 times higher than in the Zrmanja River [50], the average concentrations of Pb and Zn were 8 and 2 times higher, respectively, than in the karst springs of the Biokovo Mountain, while the Ni concentration was 6 times higher than in the Zrmanja River (Table S3b), most likely due to the lithology of the rock. On the other hand, the average measured concentrations of Al, As, Cu, Fe, and Mn at the sampling sites upstream and downstream of the Peruća reservoir (CR-7 and CR-17) were 5 to 10 times lower than the concentrations measured in the Sabalan reservoir [51].

The results of the factor analyses (factor loadings) for the indicators in the water at the sampling sites of the Cetina River and its tributaries are shown in Table 1.

**Table 1.** Factor analyses (factor loadings) for indicators in the Cetina River (a) and in their tributaries (b) *.

| | a | | | | b | | |
|---|---|---|---|---|---|---|---|
| | Factor—1 | Factor—2 | Factor—3 | | Factor—1 | Factor—2 | Factor—3 |
| Cl$^-$ | 0.758 | 0.137 | 0.079 | TDS | 0.897 | 0.340 | 0.204 |
| SO$_4{}^{2-}$ | 0.617 | 0.092 | 0.589 | NO$_3{}^-$ | 0.047 | 0.900 | 0.169 |
| TOC | 0.871 | 0.029 | −0.321 | Cl$^-$ | 0.939 | −0.159 | −0.071 |
| COD | 0.876 | 0.070 | −0.183 | SO$_4{}^{2-}$ | 0.939 | −0.089 | 0.114 |
| Fe | −0.001 | −0.912 | 0.155 | TOC | −0.344 | 0.329 | −0.057 |
| TN | −0.014 | −0.260 | 0.710 | Ca$^+$ | 0.209 | 0.630 | 0.575 |
| TP | 0.274 | 0.002 | −0.576 | Mg$^+$ | 0.851 | 0.201 | 0.253 |
| Zn | −0.202 | −0.905 | 0.045 | TN | 0.024 | 0.907 | −0.067 |
| Expl.Var | 2.598 | 1.752 | 1.352 | TP | −0.015 | 0.080 | −0.913 |
| Prp.Totl | 0.325 | 0.219 | 0.169 | Na$^+$ | −0.430 | −0.231 | −0.524 |
| | | | | Expl.Var | 3.642 | 2.388 | 1.600 |
| | | | | Prp.Totl | 0.364 | 0.239 | 0.160 |

Note: * Factor loadings (varimax normalized [52]); marked loadings are >0.70).

Three factors (varimax-normalized) were extracted, and the obtained results are in agreement with Hair et al. [53], according to which the principal components should explain at least 60% of the total variance. In our study (factor model with 8 and 10 indicators), 71.3% and 76.3% of the total variance could be explained by three factors. In Table 1 for the Cetina River sampling site, factor 1 had a very good positive correlation with Cl$^-$, TOC,

and COD. Therefore, it could be concluded that this factor is not a natural factor, but is caused by anthropogenic influences (both wastewater and agriculture).

CAL-29 and CAL-30 (Figure 3) are downstream of the town of Trilj. Factor 2 shows excellent negative correlations with Fe and Zn, from which it can be concluded that this factor is also caused by local anthropogenic influences (wastewater and agriculture). The relatively high values of this factor (Table 2) are found in the upper reaches at CR-4 and CAL-11, in Trilj (CR-24), and downstream (Figure 3). Factor 3 has a very good positive correlation with total nitrogen, showing the anthropogenic influence with high values at CR-32 (downstream of Trilj).
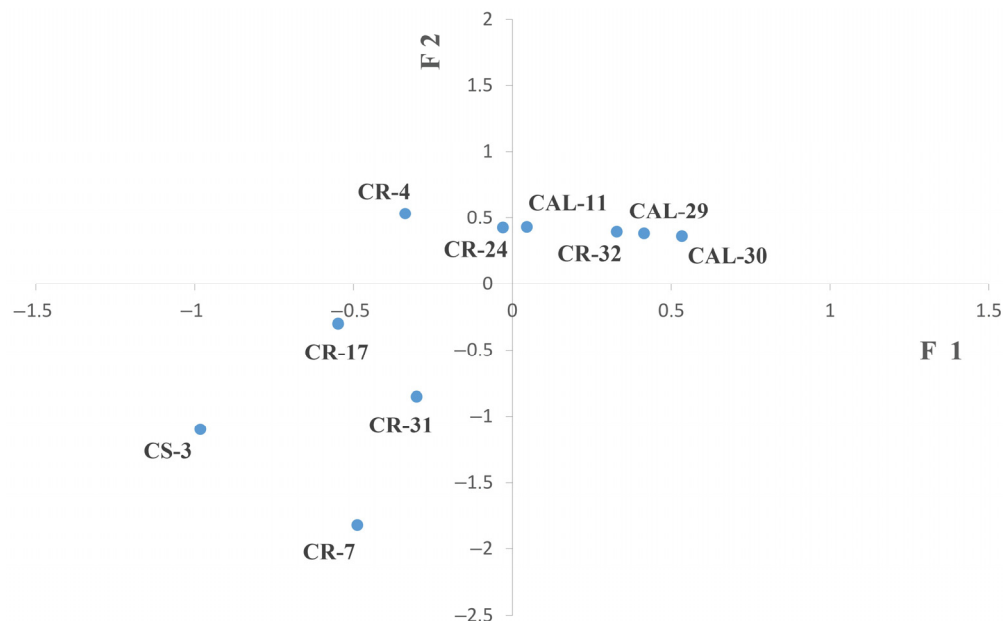


**Figure 3.** Factor scores analyzed for sampling sites in the Cetina River.

**Table 2.** Factor scores for analyzed samples in the Cetina River (a) and in its tributaries (b).

| | **a** | | | | **b** | | |
| | **Factor—1** | **Factor—2** | **Factor—3** | | **Factor—1** | **Factor—2** | **Factor—3** |
|---|---|---|---|---|---|---|---|
| CS-3 | −0.983 | −1.098 | 0.096 | CT-5 | 0.077 | −0.523 | −0.160 |
| CR-4 | −0.337 | 0.533 | −0.802 | CT-6 | 1.371 | 0.030 | −0.571 |
| CR-7 | −0.488 | −1.825 | −0.549 | CT-18 | −0.612 | −0.273 | −0.100 |
| CAL-11 | 0.046 | 0.430 | 0.014 | CT-19 | −0.313 | −0.277 | 1.110 |
| CR-17 | −0.549 | −0.299 | −0.260 | CT-20 | −0.530 | −0.440 | −0.381 |
| CR-24 | −0.030 | 0.427 | −0.491 | CT-21 | −0.364 | −0.329 | −0.221 |
| CR-29 | 0.414 | 0.383 | 0.109 | CT-22 | −0.363 | 0.758 | −0.368 |
| CAL-30 | 0.534 | 0.361 | 0.072 | CT-23 | −0.170 | 0.771 | 0.061 |
| CR-31 | −0.302 | −0.851 | 0.482 | CT-34 | 0.380 | −0.300 | 0.453 |
| CR-32 | 0.329 | 0.395 | 0.849 | CT-35 | 0.007 | −0.462 | 0.530 |

In Table 1, factor analyses for indicators in tributaries and the Cetina River show that Factor 1 has an excellent correlation with TDS, $Cl^-$, $SO_4^{2-}$, and $Mg^+$. Although this factor could be considered of natural origin, it is under anthropogenic influence, as the results of the factor scores (Table 2) perfectly match the sampling point CT-6 (Vrlika city) (Figure 4). On the other hand, factor 2 shows excellent correlation with TN and $NO_3^-$ and can be associated with agricultural activities. The highest factor values (Table 2) are found in the most polluted samples at the sites CT-22 and CT-23 (Figure 4, red circle). Factor 3 shows a negative correlation with TP at the sampling site CT-9, which can be attributed to anthropogenic influences.
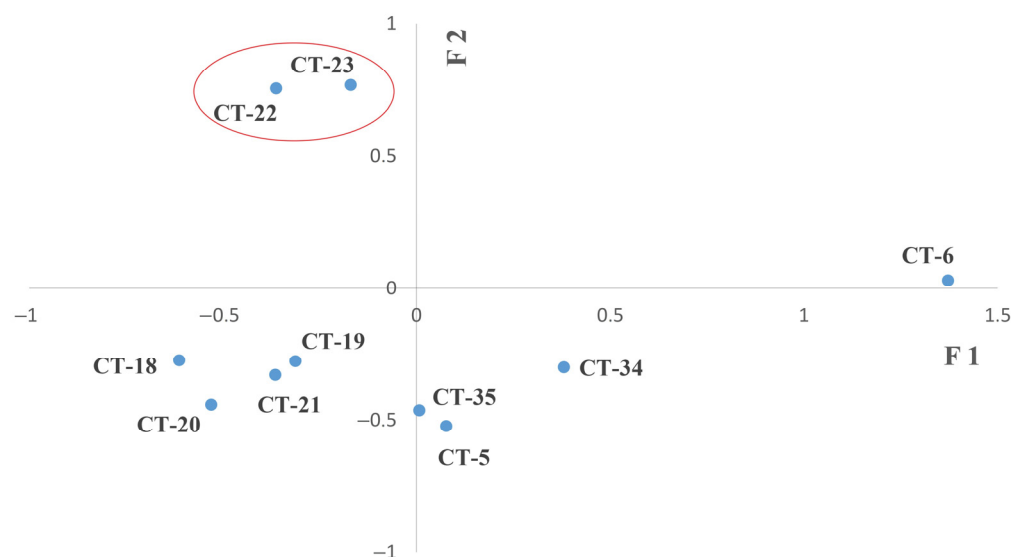
**Figure 4.** Factor scores analyzed for sampling points on the Cetina River tributaries.

*3.2. Sediment Analyses*

Since there are no limits for the concentration of elements in sediment in the legislation of the Republic of Croatia, they were taken from the existing sediment quality criteria (SMSP and FALCONBRIDGE NC SAS 2005) of British Columbia (Canada), Ontario (Canada), St. Lawrence River (Canada), and the federal criteria of the USA, Great Lakes, and compared with those causing minimum and maximum toxic effects (Table S4). The concentrations of all elements in the Peruća and Đale reservoirs are slightly higher than the minimum values that have a toxic effect: CAL-8 (Hg 1.59 mg kg$^{-1}$), CAL-9 (Fe 3.8%, Mn 1100 mg kg$^{-1}$), CAL-12 (Cu 46.6 mg kg$^{-1}$, Pb 94.2 mg kg$^{-1}$, Zn 118 mg kg$^{-1}$), CAL-15 (Ni 66.1 mg kg$^{-1}$, Cr 77.0 mg kg$^{-1}$), CAL-16 (As 31.2 mg kg$^{-1}$, Cd 2.42 mg kg$^{-1}$), CAL-26 (Ba 174 mg kg$^{-1}$), and CAL-27 (N 2768 mg kg$^{-1}$, P 1230 mg kg$^{-1}$). The toxic effects threshold shows up only for Mo at the sampling sites CR-7 (5.28 mg kg$^{-1}$), CAL-12 (4.79 mg kg$^{-1}$), and with a maximum at CAL-16 (14.3 mg kg$^{-1}$) in Lake Peruća, most likely due to lithogenic influence.

The measured element concentrations were compared with the median concentration values in the main fraction of the pristine sediments of the Zrmanja River [50], the sediments of the nearby springs on the Biokovo Mountain [46], and with the median values in the sediments of rivers from all over Europe (Table S4, [54]). The measured element concentrations from the CRB are comparable to both studies, but are slightly higher for most elements when comparing values from the Cetina River and the Zrmanja River. Moreover, the concentrations of the measured elements in the sediments of the karst springs of the Biokovo Mountains are higher than in the Cetina River—especially Cr, Ni, Pb, Sb, and V—indicating different lithological features [27,46]. The concentrations in the sediments of the Cetina River are even comparable to the median values in river sediments from all over Europe [54]. However, Ca values are significantly higher and Si values are significantly lower, which is probably due to the natural lithology of the carbonate rocks. Comparing the measured concentrations of Al, As, Co, Ni, and Pb in the sediment of the Peruća reservoir with the values from the study of Aradpour et al. [55], these concentrations in the sediment of the Peruća reservoir were higher than the concentrations in the sediments of the Sabalan reservoir and reservoirs around the world. On the other hand, according to this study, the concentrations of Al, As, and Co were the lowest in the sediments of the Đale reservoir. The mean Hg concentration in the sediments of the Đale reservoir was similar to the mean Hg concentration in the sediments of La Sabana tropical karst lake reported by Cohuo et al. [56], while the mean concentration of the Peruća reservoir was slightly higher. The Peruća Reservoir belongs to the oligotrophic lakes with a low organic matter content and a high oxygen content (Figure 5), while the elevated concentrations of almost

all elements in the sediment of Peruća Lake are most likely due to Neogene clay-marl deposits with bauxite alternations [57].
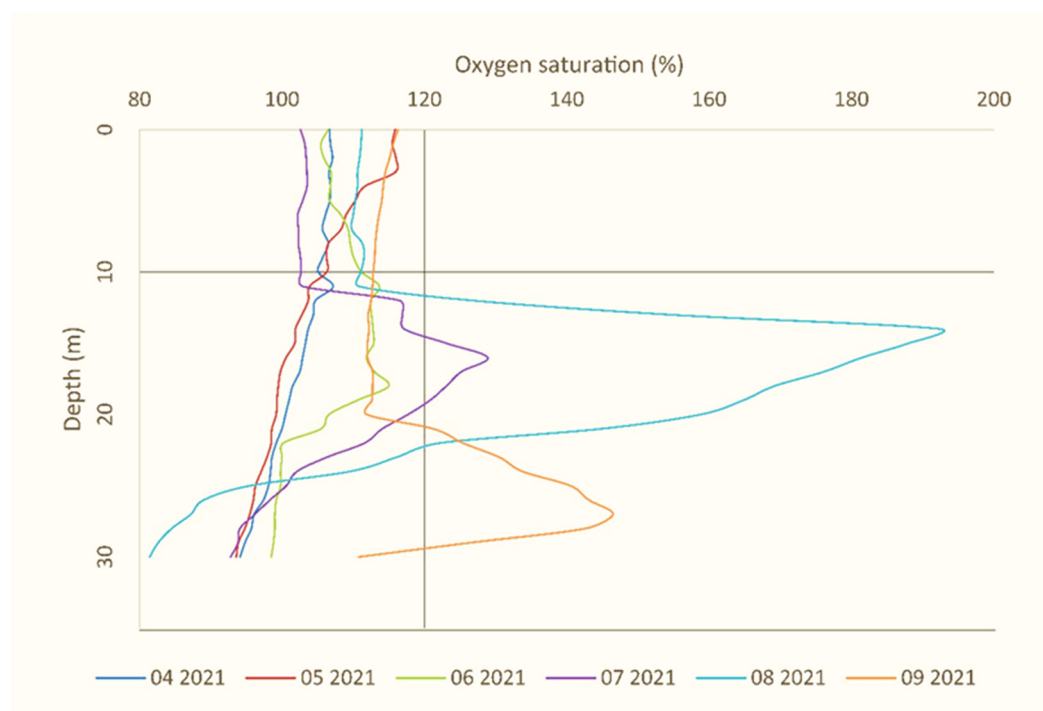


**Figure 5.** Display of oxygen saturation in relation to depth in the Peruća accumulation lake for the period April 2021–September 2021.

After normalization of selected elements to Al (Figure 6a,b), it can be said that the sediments of the Peruća reservoir are naturally enriched in elements, especially Fe, Mn, and Al, and their oxides [14,15], and represent a reservoir of geogenic origin. On the other hand, the elevated normalized concentrations of N and P, as well as the normalized concentration of TOC (Figure 6c,d) in the sediments of the Đale reservoir indicate anthropogenic influences by the city of Trilj. Elevated metal and TOC concentrations, after normalization to Al, at karst springs CS-3 and CS-1 are slightly elevated, which is due to anthropogenic influence (roads and tourist activities).

Table S5 shows the correlation analysis of the log-transformed data of 35 elements and TOC in the sediment bulk fraction, and most of them were strongly correlated with each other, with positive relationships dominating over negative ones (497 cases: 133 cases). The calculated correlation coefficient is a measure of the strength and direction of a linear relationship between two random variables. The coefficient represents the ratio between the covariance of two variables and the product of their standard deviations [58]. The following points are the accepted guidelines for interpreting the correlation coefficient r (absolute values): values between 0.00–0.20 indicate no correlation or a low correlation, 0.20–0.40 a weak correlation, 0.40–0.70 a significant correlation, and 0.70–1.00 a high or very high correlation [59]. Overall, there were 264 cases with a high or very high correlation (41.9%), 213 cases with a truly significant correlation (33.8%), 78 cases with a weak correlation (12.4%), and 75 cases with no or a low correlation (11.9%).

TOC showed a weak positive correlation with N, P, Se, and Sr, and a really significant positive correlation with Ca and Si, while it showed negative correlations with all other elements. Ca also showed a negative correlation with all elements except Si with a weak positive correlation, and Sr with a significant positive correlation. A very strong positive relationship (r = 0.99) was found between Ni-Cr, Pb-Cs, and V-Fe. The PCA analysis, shown in Figure 7, shows the dependence diagram of components PC1 and PC2. The first component describes 52.6% and the second 18.8% of the data variance of the total variability

of the 25 variables. The first component shows high negative values for Ba, Zn, Cu, Cd, Ti, Cr, Ni, Pb, Fe, Al, V, and Sb, while on the other hand, a high positive value is recorded for TOC. Therefore, it could be assumed that the first component describes elements of lithological origin and TOC is related to Paleogene clay deposits enriched in organic carbon. TN and TP have the greatest influence on the second component with the highest positive values suggesting an anthropogenic or non-lithological influence. The relative remoteness of Se, Mo, and U, or their higher PC1 and PC2 values, can be explained by their mobility and sensitivity to environmental redox conditions that affect their distribution in the sediment.
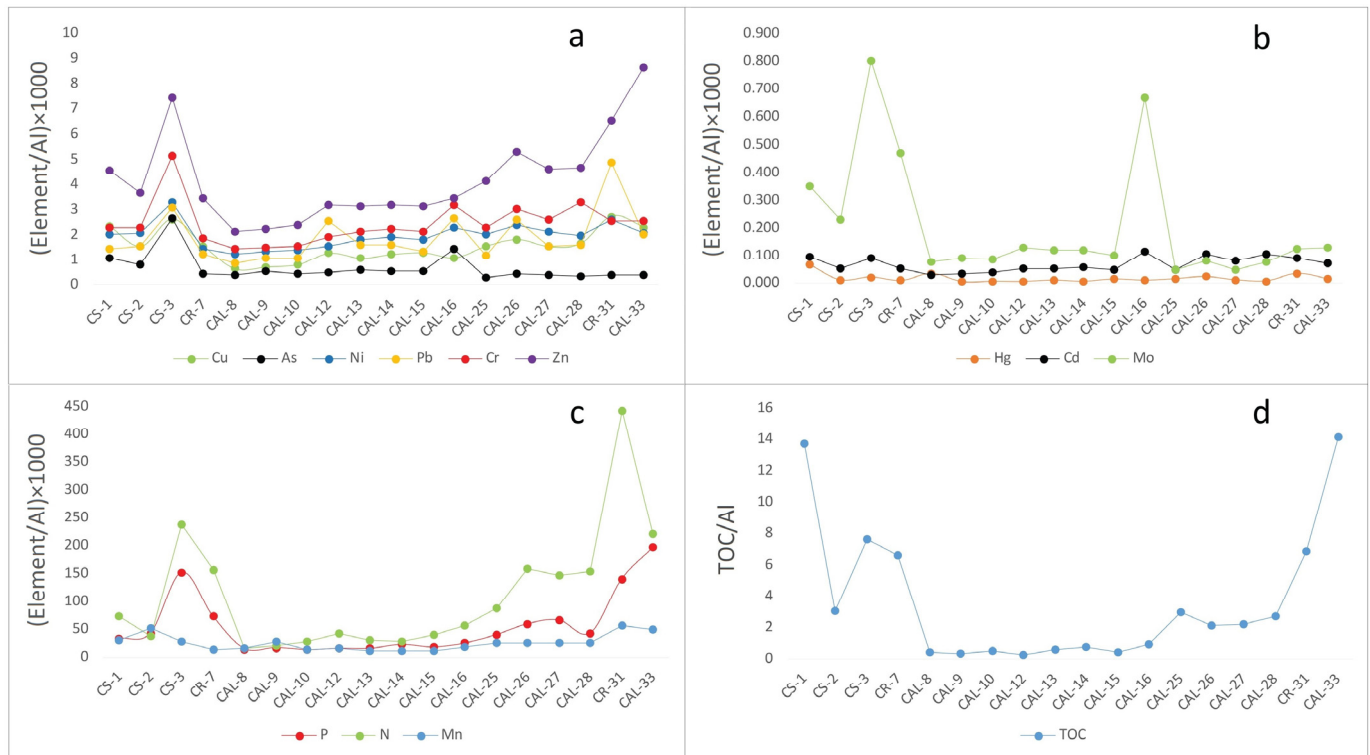


**Figure 6.** Dependence of selected elements concentrations normalized to Al in surface sediment—bulk fraction in the Cetina River: (**a**) Cu, As, Ni, Pb, Cr, and Zn; (**b**) Hg, Cd, and Mo; (**c**) P, N, and Mn; (**d**) TOC.

The dependence of factor scores on PC1 and PC2 is shown in Figure 8. The distribution based on factor scores shows four different groups of sites in terms of elemental composition (red circles): the first group consisting of spring sediments (CS-1 to CS-3), the second of sediments from the Peruća reservoir (CAL-8 to CAL-16), the third group from the Cetina River (CR-7 and CR-31), including sediments from the Kraljevac hydroelectric power plant reservoir, and the fourth group of sediments from the Đale reservoir (CAL-26 to CAL-28), with the exception of sample CAL-25, which settled near the third group. Based on the location of CAL-25, the sediment should be attributed to the fourth group. However, due to the fast water flow of the Cetina River at this site, the results of the factor analysis show that the sediment CAL-25 is excluded from this group. In the other three places (CAL-26 to CAL-28), the flow slows down and the elements on the particles are deposited along the edges of the Đale reservoir due to the hydrodynamic characteristics [51].

The sediments of the Đale reservoir are under anthropogenic pressure, as the accumulation of TN and TP was detected after the mouth of the highly polluted tributaries CT-22 and CT-23.
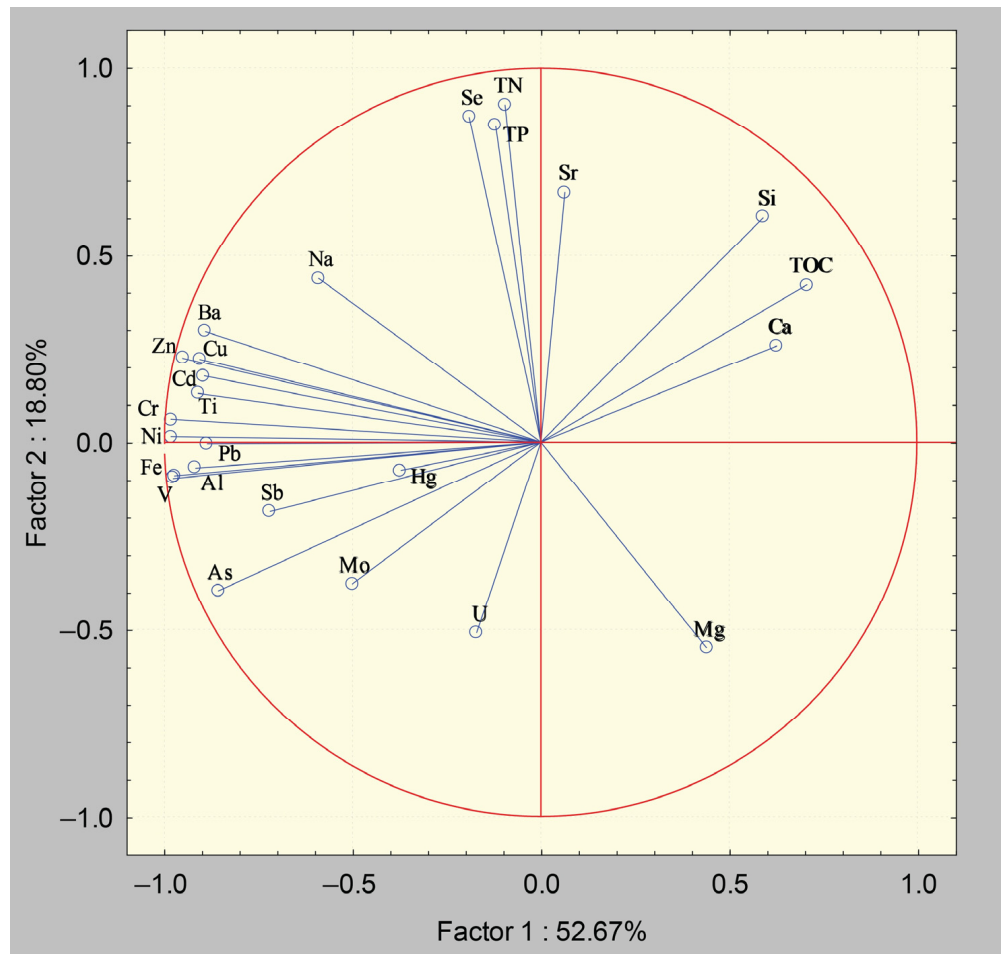
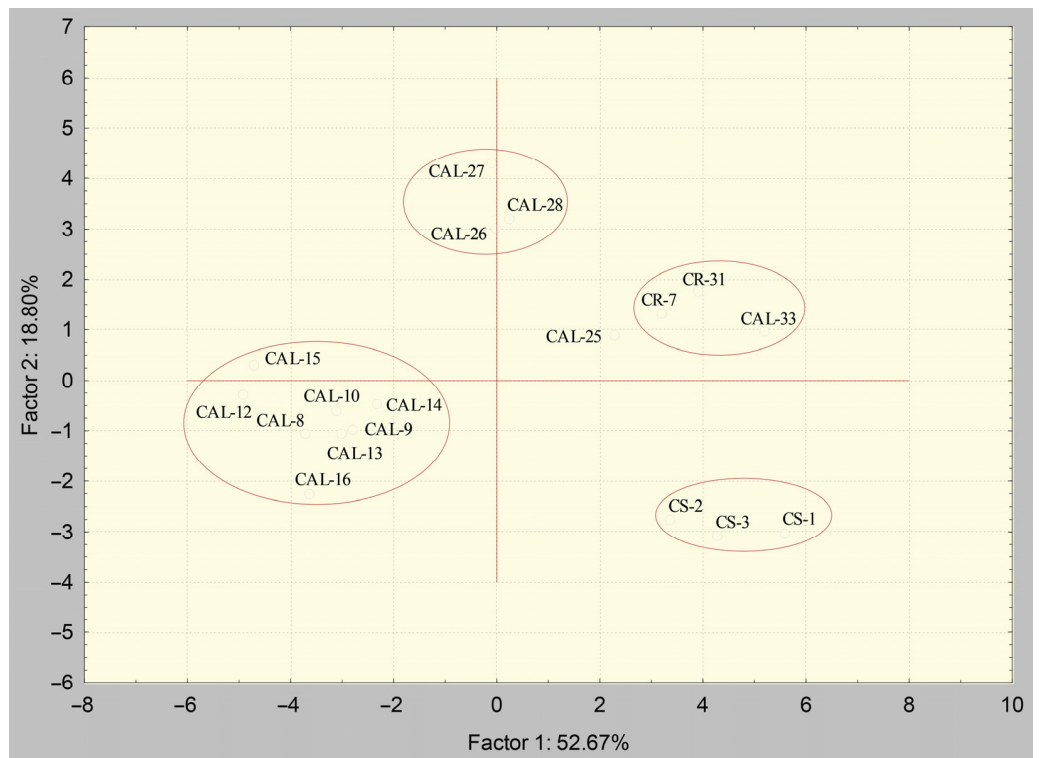**Figure 7.** Diagram of the dependence of elements, with respect to PC1 and PC2.



**Figure 8.** Dependence diagram of factor scores, with respect to PC1 and PC2.

The dendrogram of the hierarchical cluster analysis shows four clusters (Figure 9). The sediments of sources CS-3 and CS-2 are closely related and together with the sediments of the Peruća reservoir (CAL-8 to CAL-16) form the first cluster (C1—cluster 1). The river sediments CR-31, together with the sediments from the Đale reservoir (CAL-25 to CAL-28) and the sediments from the Kraljevac hydroelectric power plant reservoir (CAL-33), form the second cluster (C2—Cluster 2). The river sediment CR-7 has the most similarities with the first cluster, but still forms a separate, third cluster (C3—cluster 3), as well as the spring sediment CS-1, which has the greatest distance from all other sediments and forms the fourth cluster (C4—cluster 4). The Glavaš spring (CS-1) is an upwelling spring with deeper karst water originating from a cave and draining a vast karst area, which is not anthropogenically influenced, with a dominant lithogenic influence of the limestone in the geological basement of the watershed. The Vuković spring (CS-3) is also an upwelling spring with deeper karst water, while the Batića spring (CS-2) is a shallow karst aquifer dominated by a dolomite component. Therefore, the sediments of these three springs are found in different clusters, with the CS-1 sediment strongly separated from all others. The entire C1 (cluster 1) can be described as being under combined lithogenic and anthropogenic influence. Upstream of the sampling point CR-7 (cluster 2, C2), tributaries CT-5 and CT-6 inflow agricultural wastewater and treated wastewater from the city of Vrlika, so C2 is under anthropogenic and subordinate lithogenic influence, as is C4 (cluster 4) due to the upstream inflow of the heavily polluted tributaries CT-22, CT-23.
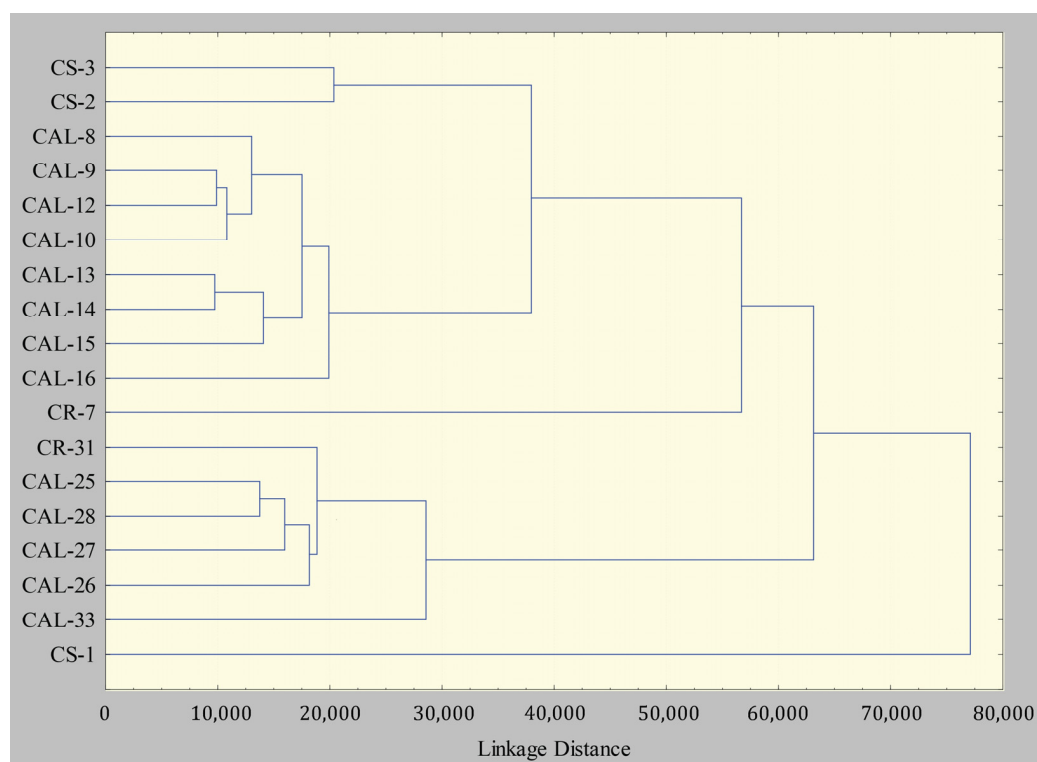


**Figure 9.** Cluster analysis of examined sampling sites according to the contents of elements.

The cluster analysis, in terms of the content of elements and TOC, is shown in Figure 10. According to the results, only two clusters can be identified: The first cluster consists of Ca (C1) and the second of TOC with all other elements. Calcium is a lithogenic element that produces carbonate deposits in the catchment area of the Cetina River and its tributaries (Dinaric karst). Cluster 2 clearly separates TOC from other elements, which could be further divided into two subclusters, the first consisting of Al and Fe, and the second of Mg, Si, and K with all other elements. The separation of TOC indicates its dual origin, which is geogenic to a greater extent, while its weak association with other elements indicates that the organic matter content has less influence on the concentration of other elements. As in

the case of Lake Namak in Iran reported by Nodefarahani et al. [60], the separation of Al and Fe indicates their lithogenic origin, which in our case is an important component of "terra rossa" present as a fill component of eroded carbonate rocks [61]. The elements Mg, Si, and K have a common origin from clayey clastic deposits, indicating a geogenic origin.
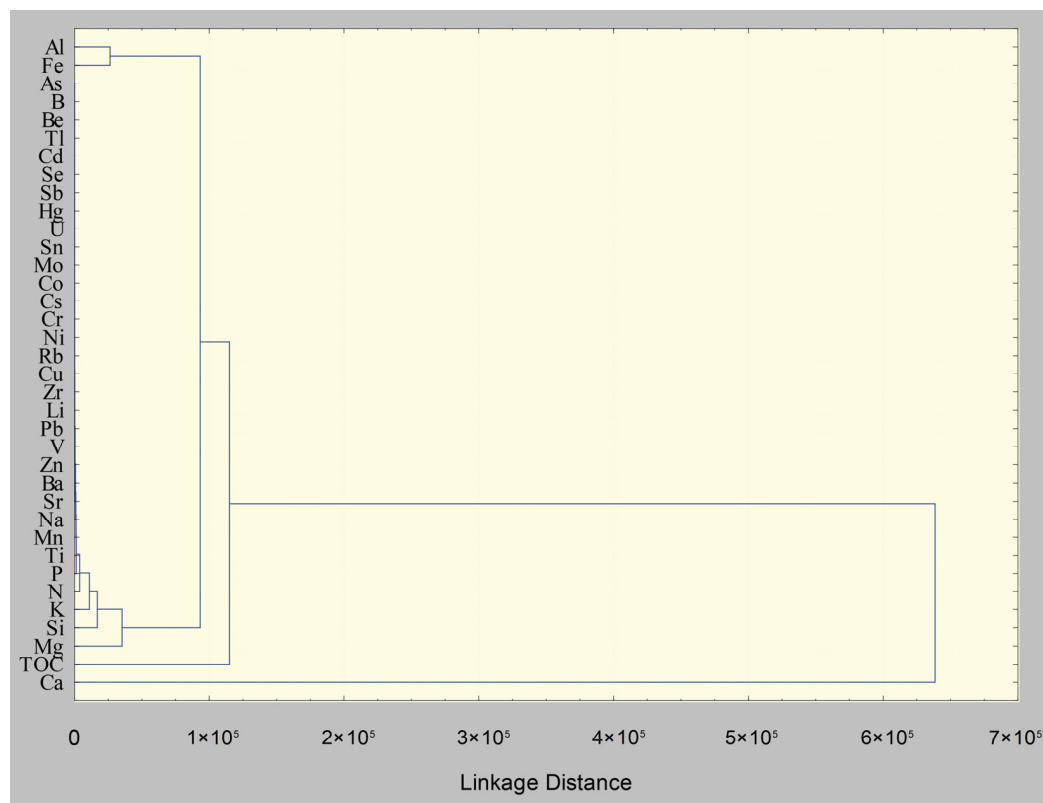


**Figure 10.** Cluster analysis of examined sediments samples according to observed elements and TOC in the surface sediments bulk fraction.

Figure 11 shows the concentrations of Cr, Ni, Pb, and TOC normalized to Al from four sediment cores (CAL-25 to CAL-28). The normalized values of Cr show a more uniform distribution in the sediment core CAL-25, while they are more sinusoidal in the other cores, with a maximum in core CAL-28 at 50 and 60 cm, respectively. Nickel has a more sinusoidal distribution in all sediment cores with a maximum in the sediment core of the sampling site CAL-26. For Pb, the sediment core CAL-26 has a sinusoidal distribution with two maxima at 5 and 25 cm, while the other cores have a more uniform distribution. The highest TOC concentration, normalized to Al, is found in the sediment core of sampling site CAL-26, with two maxima at 25 and 55 cm, where the distribution of TOC in this core shows the greatest variation. The other sediment cores show smaller fluctuations but a more uniform vertical distribution. The normalized concentrations of anthropogenic elements Ni, Pb, and TOC show larger fluctuations in the sediment core CAL-26, which is most likely due to the decrease in flow energy causing greater deposition of particles.
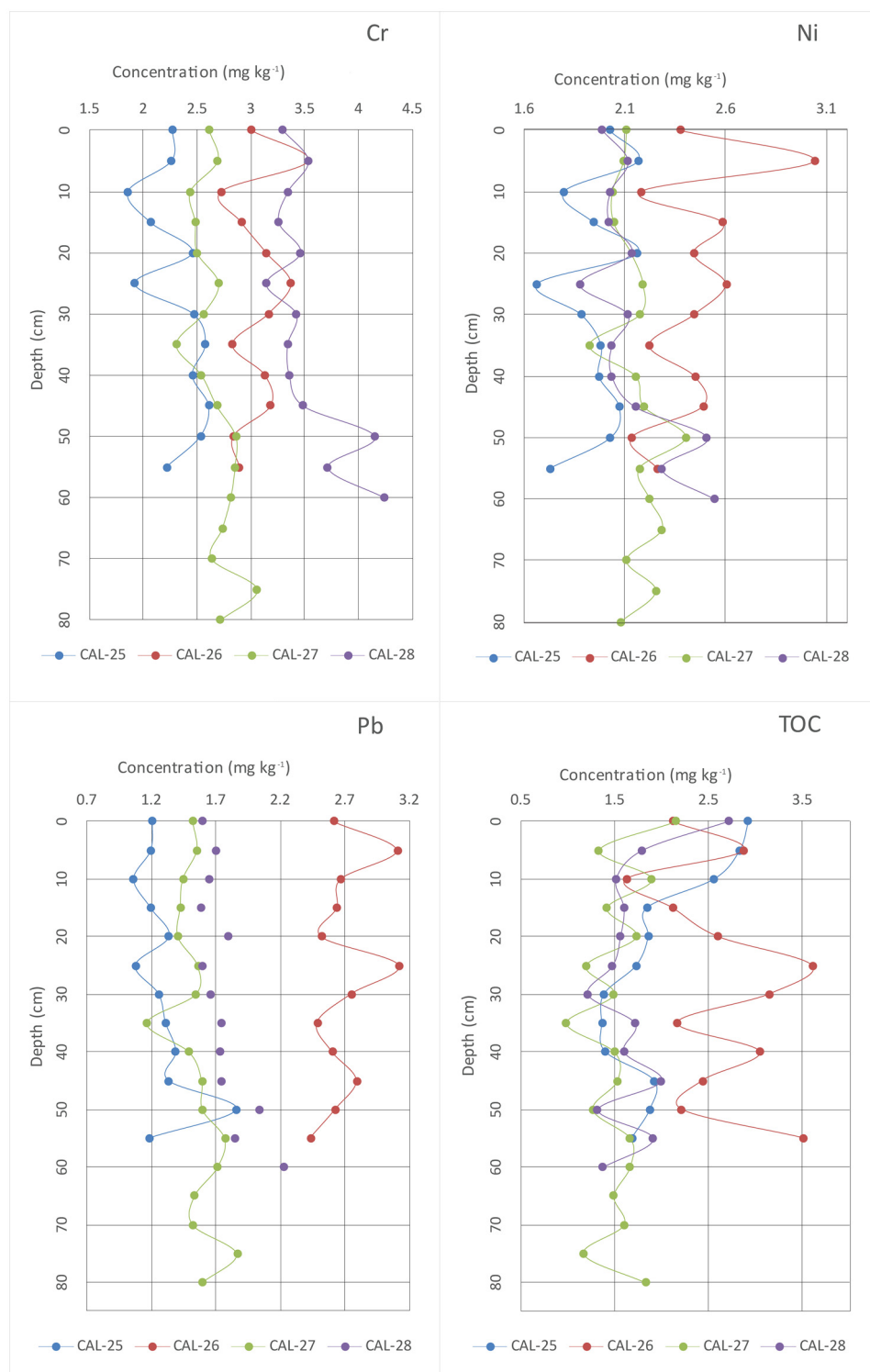
**Figure 11.** Concentration of Cr, Ni, Pb, and TOC normalized to Al in the bulk fraction in the sediment core in the Đale storage lake (CAL-25–CAL-28).

## 4. Conclusions

Karst freshwater and sediment quality (physicochemical parameters, nutrients, ions and elements, COD, BOD, DOC, and TOC) of the transboundary CRB was investigated. It was found that the mean values of all measured parameters of the Cetina River in the period from 2016 to 2021 are within the allowable limit values prescribed in the EU Water Framework Directive. In particular, the low concentrations of all measured elements in

the water show that the Cetina River is clean and suitable as a drinking water resource. According to the SDG 6 indicator 6.3.2, the freshwater of the Cetina River has good water quality. In some of its tributaries, elevated values of ammonium, nitrates, orthophosphates, TN, TP, COD, and BOD were occasionally observed. The freshwater of all karst springs in the Cetina River basin is naturally enriched with Ca, Mg, and Si due to the predominant carbonate lithology. In accordance with the sediment legislation in force in the USA and Canada, all measured parameters were found to comply with the permissible values, with the exception of Mo. After normalization to Al, which neutralized the geogenic background, the sediment from the Vukovic source was found to be enriched in elements (Zn, Cr, Ni, Pb, As, Cu, Mo, N, and P), mainly due to the anthropogenic influence (agricultural activities). In addition, slightly higher concentrations of the measured elements in the other sources were due to a predominant lithogenic influence. Finally, the values of the measured elements in the Peruća reservoir sediments also reflect the prevailing lithogenic influence.

Concentrations of measured elements in water and sediment (normalized to Al), together with the measured values of the relevant physico-chemical parameters, are indicators of potential pressures affecting river ecosystems. The dissolution of carbonate rock and naturally enriched Al and Fe clay deposits play the main role as "pollution catalysts" in reservoirs of hydroelectric power plants, which undoubtedly affects the purity of the Cetina River. The Peruća and Đale reservoirs play the most important role as retention factors for the measured elements, including heavy metals, from the water. They play a crucial role in maintaining the purity of the water and preventing the pollution of sediments with critical elements (N, P) and heavy metals—considering the combined influence of both, natural and anthropogenic influences. Limited and controlling influence of anthropogenic activities in the area of the CRB, both in water and sediments, enabled a sustainable water supply for this area of Croatia, including some of the Adriatic islands. It is important to emphasize that the river Cetina flows through the karst area, which is very sensitive, so strict protection measures are required. A holistic and integrated scientific approach, based on several geochemical factors, provides qualitative data for an attractive "United Nations goal (UN) for sustainable development—SDG 6". This study contributes to the achievement of SDG 6, in particular indicator 6.3.2 ("Proportion of water bodies with good water quality"), and to building knowledge on the current status of water and sediments, which will add to the database on long-term pollution and impacts and environmental degradation. In addition, this study supports water resource management of the CRB and provides data on the intensity of various anthropogenic and geogenic pressures. Furthermore, it provides a reference for the study of water and sediment in the other river basins.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15071429/s1. Table S1: Sampling points of sediment and water in the Cetina River (2016 to 2021); Table S2: Descriptive statistics of measured parameters in surface water samples at sites CS-1, CS-2, CS-3, CR-4, CR-7, CAL-11, CR-17, CR-24, CAL-29, CAL-30, CR-31, CR-32 in the Cetina River and CT-5, CT-6, CT-18, CT-19, CT-20, CT-21, CT-22, CT-23, CT-34, CT-35 in tributaries in the period 2016–2021; Table S3a: Descriptive statistics of elements in surface water samples at sites CS-3, CR-7, CR-17, CR-31 in the Cetina River in the period 2016–2021; Table S3b: Descriptive statistics of elements in surface water at sites CS-3, CR-7, CR-17, CR-31 in the Cetina River between in the period 2016–2021; Table S4: Measured concentrations of observed elements in bulk fraction of the surface sediments; Table S5: Correlation coefficients of log-transformed data for 35 elements and TOC in bulk fraction of sediment.

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**Data Availability Statement:** Data will be made available on request.

**Conflicts of Interest:** The authors declare no conflict of interest.

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