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Determination of Heavy Metal Sources in an Agricultural Catchment (Poland) Using the Fingerprinting Method

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Abstract: This study investigates the heavy metal contamination of soils and suspended sediments in the Nurzec River catchment (Eastern Poland), focusing in particular on the effects of catchment land use. The fingerprinting technique has been combined with the classic, I_{geo}, and EF index-supported contamination analysis to identify heavy metals sources. A wide range of elements (31 chemical elements including heavy metals) allowed the author to analyse the pathways and to identify the pressures of heavy metal contamination. The developed statistical models of heavy metal source distribution displayed results at a statistically significant level. The results have revealed the significant impact of land use connected with urban areas (URBAN) and pastures (PAST), which together constitute less than 20% of the river catchment area. These results are relevant to the local authorities and stakeholders, as they highlight the significant impact of low-density urban areas that are not locally considered as the major sources of heavy metal pollution. These results will contribute to sustainable decisions in the field of contaminated catchment area remediation.

Keywords: heavy metal contamination; fingerprinting; suspended sediment; land development; water quality

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Citation: Bojanowski, D. Determination of Heavy Metal Sources in an Agricultural Catchment (Poland) Using the Fingerprinting Method. *Water* **2024**, *16*, 1209. https://doi.org/10.3390/w16091209

Academic Editor: Laura Bulgariu

Received: 19 March 2024
Revised: 5 April 2024
Accepted: 20 April 2024
Published: 24 April 2024

1. Introduction

Agriculture is the branch of the economy that is responsible for most (over 60%) of the nutrients that flow into the Baltic Sea from Poland [1]. However, agricultural areas can also be the source of other pollutants that are traditionally associated with heavy industry and highly transformed areas (e.g., development of mineral resources, metal processing and metallurgy, chemical production, etc.). It is generally agreed that broadly defined agronomic activities contribute to the emission of heavy metals, while some of them, such as Cd, are even considered as indicators of agricultural activities such as fertilization [2], while others, like Hg or Pb, are present in the agricultural lands and cause background losses to the environment [3,4]. Moreover, the accumulation of heavy metals in soil causes serious pollution that affects the safety of food production [5]. Since the actual forms of land use affect the level of pollution of soil and can vary significantly within individual agricultural catchments, studies on a local scale can elucidate the sources of heavy metals related to this type of anthropogenic pressure.

In this study, a suspended sediment flux, commonly recognized as a particle-bound contaminant carrier in surface waters [6], has been used to investigate the sources of heavy metals within an agricultural catchment. Suspended sediment contamination has been tracked using the fingerprinting method [7–9]. This method relies on the assumption that sediments in rivers represent an integral sign of particles, and thus provide information on particle-related contaminants within a corresponding part of the basin. The discrimination between source contributions is typically based on land-use/land-cover typology and their fingerprint properties selected during a statistical analysis.

The research was carried out in the agricultural catchment of the Nurzec River (Eastern Poland), where the occurrence of pollutants mainly associated with industrialized/urbanized areas was hard to expect in the past. The main aim of the study was to determine the sources of heavy metals transported by suspended sediment and to assess their content in soil. To fully address this aim, the author of this study utilised a "hybrid approach" [10], combining information from classic field monitoring with a statistical model. This approach allowed them to estimate the importance of sources of heavy metals by predicting the impact of land use of the analysed catchment on the quality of suspended sediment. The analysis was carried out for the three most common forms of land use present in the analysed area (arable lands, pastures, and urban areas).

Field soil monitoring within the State Environmental Monitoring (SEM) in Poland is entirely focused on arable lands and relatively scant in terms of localisation and frequency. Therefore a study that is based on the assessment of soil quality (containing a wide range of elements, including heavy metals) will be extremely useful for the purposes of further soil studies in this area and in similar catchments. It would also serve as a recommendation for other catchments with insufficient soil information and provide conclusions on similar subjects. This approach also enabled the assessment of the current state of heavy metal contamination in the analysed catchment area. The statistical model in turn facilitated the identification of their transport routes through suspended sediment from known land-use categories. Results obtained using this hybrid approach are of direct significance to local stakeholders in terms of the adaptation of activities aimed at the assessment of sources of heavy metal pollutants in the catchment area and the limitation of their transport.

2. Materials and Methods

2.1. Study Area

The Nurzec River is a 108.5 km water course with a catchment area of 2081 km^2 [11]. It is located in the eastern part of Poland and as a right-bank tributary of the Bug River (Figure 1d) and constitutes a part of the Vistula River basin. Its average flow rate is 4.59 m^3·s^{-1} (period: 1980–2020), as measured at a gauge station located in the middle section of the water course, which covers approximately 58% of the Nurzec River catchment [12]. The river source is located near the Polish–Belarusian border (Lat: 52.49, Lon: 23.38) and its mouth is located approximately 15 km downstream of a large reservoir (Ciechanowiec) that disturbs the natural river flow (Lat: 52.61, Lon: 22.41). Moreover, hydrotechnical structures that regulate the river flow for agricultural irrigation purposes are present along the entire length of the river. Slopes present within the studied area are low and do not exceed 1‰ [11]. The climate in this area is mainly continental-transitional, with a mean annual temperature of 7.5 °C and with the precipitation of 600 mm [12] recorded during the 1980–2020 period. The Nurzec River catchment is dominated by rather extensive agriculture (67% of the total area). Forestry covers 29.3% of its area, while less than 4% is occupied by scattered-type dwellings (Figure 1a). The catchment area accommodates one of the largest livestock breeding centres, which mainly caters for cattle, but also horses and sheep [13]. The total population of this area is approximately 56,000, with an average density of about 26 people/km^{-2} [13].

The Nurzec River catchment area mainly consists of soils of podzolic origin (37% of catchment area) and cambisoils (26%) that are present in the upper and lower section of the catchment (Figure 1b). Chernozems constitute 16% of the total study area. Unclassified soils (mainly of forest origin) constitute 8% of the catchment area. The remaining soil types include: fluvisols, peat soils, gleysols, and histosols. The riverbed consists mainly of histosol and fluvisols. Soil types present in the river catchment area are shown in Figure 1b. The granulometric composition of the topsoil layer is mainly made up of loamy sands (70% of the area). Sandy clays constitute approximately 12% of the surface. Peat soils constitute 5% and sands constitute 4.5%. The remaining soils constitute unclassified forest soils.

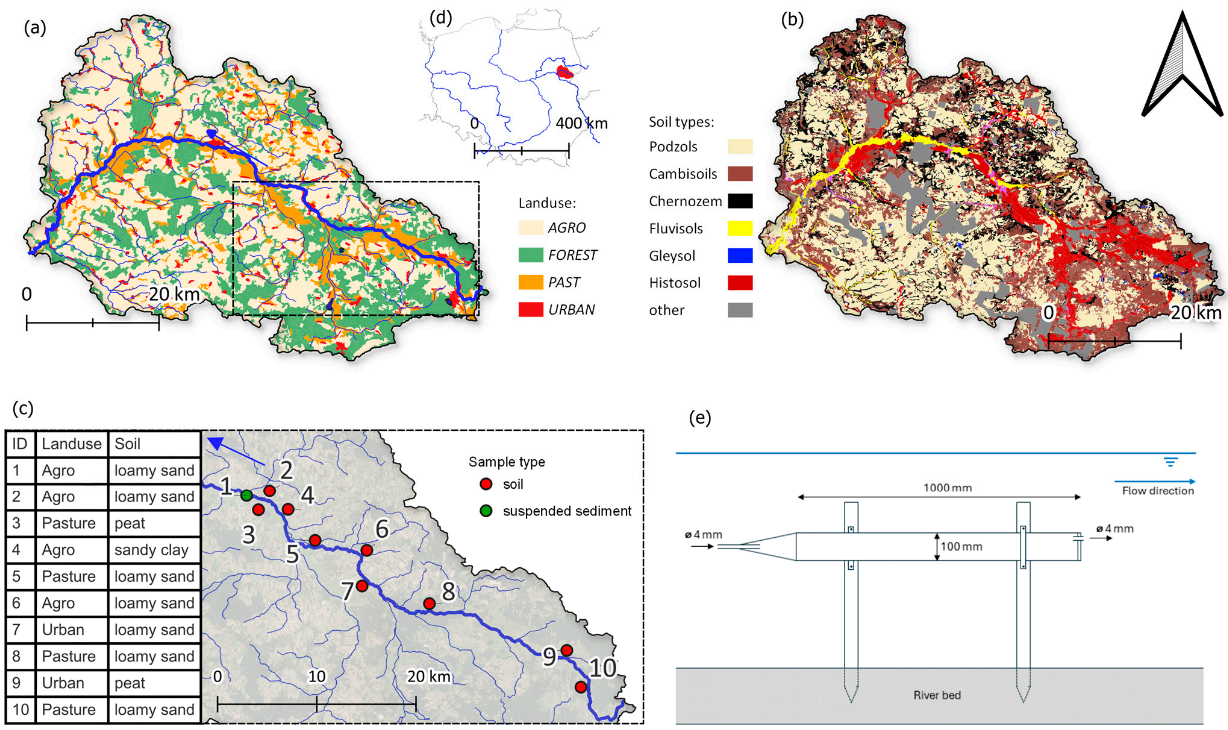


Figure 1. Nurzec River catchment with land use (**a**), soil structure (**b**), sampling points locations (**c**), location on the map of Poland (**d**), and suspended sediment sampler [14] (**e**). Sources of background layers: Landuse—Corine Land Cover EEA, 2018; Soils—Institute of Cultivation, Fertilization and Soil Science, 2019; Orthophoto—Head Office of Geodesy and Cartography, 2023; Country borders—Head Office of Geodesy and Cartography, 2023.

2.2. Sample Collection

Samples of suspended sediment and soil were collected during four surveys: in August 2021, February, April, and August 2022, during both warm and cold seasons of the year. The locations of sampling sites have been shown in Figure 1c. The study involved 10 sampling sites, including one site for suspended sediment and nine for soil samples. The studied section of the river was 53 km long (49% of the total length of the river). Sites were selected to obtain a set of measurements that was then used to verify which form of land use has the strongest influence on the quality of suspended sediment (the fingerprinting method). Selected sites represented all relevant forms of land use present along the river catchment (AGRO, PAST, URBAN). Land-use classification and analysis was based on Corine Land Cover 2018—CLC18 [15]. In the analysed area, the CLC18 categories of permanent crops, and heterogeneous agricultural areas jointly constitute less than 5% of the total area. Therefore, they were classified along with arable lands as AGRO. The PAST category represents agricultural land used for cattle grazing (category pastures of CLC18), while the URBAN category represents low- and medium-density urban areas (discontinuous urban fabric of CLC18). Samples of soils present in the catchment were collected manually from points located no further than 15 m from the riverbank, at the depth of 0–15 cm and in the amount of approximately 1 kg. The locations of soil sampling sites have been selected after the consideration of the soil structure and land-use distribution. Each soil sample was compiled from 5 subsamples collected within a 10 m^2 plot. The samples were transported and stored at a temperature of 4 °C before further analysis. Suspended sediments were collected using a time-integrated sampler, embedded permanently in the riverbed [14]. The location of the sampler (Site 1, Figure 1c) was selected due to logistic limitations (accessibility of the installation site). The design of the sampler promotes the deposition of particles < 0.063 mm, which were subsequently used as suspended sediments in the current study (Figure 1e). Sites 2 and 3 were located within a short distance from the location of the suspended sediment sampler, to represent the specific land-use forms present on both side of the riverbed (AGRO on the north side and PAST on the south). Sites 4–10 were located further downstream the river catchment.

2.3. Laboratory Analyses

The solid phase of suspended sediments collected in the samples was separated in the laboratory by way of centrifugation (4000 rpm). Soil samples were wet-sieved using a FRITSCH ANALYSETT shaker (Fritsch GmbH, Idar-Oberstein, Germany) to obtain a fraction of <0.063 mm. Wet-sieved and centrifugated samples were dried in the temperature of 60 °C. After homogenisation, the samples were analysed in terms of aqua-regia extractable elements present in the tested sediments and soils. Approximately 0.5 mg of each soil sample was digested in an UltraWAVE microwave mineraliser (Milestone Srl, Sorisole BG, Italy). Aqua regia (3:1, *v*/*v*, HCl to HNO_3) was used in the extraction procedure (ISO 11466 [16]). The process was carried out at a temperature of 230 °C and a maximum pressure of 80 bar for 25 min. After the analysis, the digests were diluted with deionised water to the final volume of 50 mL.

The concentrations of Al, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sr, V, and Zn were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). An Optima 7300DV spectrometer (Perkin Elmer, Waltham, MA, USA) was used for this purpose. The analyses of Ag, As, Be, Bi, Cd, Cs, Mi, Sb, Se, Tl, W, and Hg were performed using inductively coupled plasma mass spectrometry with an iCAP RQ (C2) spectrometer (Thermo Scientific Waltham, MA, USA). All measurements were performed according to international standards (ISO 11885 [17], ISO 17294-2 [18]). Quantification limits for all elements ranged from 0.0001 mg/L to 0.1 mg/L, and for some elements equalled 1, depending on the analytical technique and on the element. Quality control was implemented during the whole analytical procedure. Certified reference materials—LGC6187 (LGC, Teddington, UK), HAMIL-20.2 and TMDA-64.3 (Environment and Climate Change Canada, Gatineau, QC, Canada) were used to determine precision and accuracy. Precision, expressed as relative standard deviation, did not exceed 20%, while recovery was in most cases between 75 and 125%.

The resulting database containing 1240 chemical determinations of 31 elements and compounds, including LOQ RSD [%] and R [%], has been stored in the project database (Bojanowski, 2023) [19].

2.4. Data Analysis

The statistical data analysis for this study was carried out using Statgraphics 19.4.04 in order to compute descriptive statistical measures (the mean value, standard deviation, coefficient of variation, skewness, kurtosis are shown in Table S1) and the correlation between elements (Table S2) and tests for the normal distribution of data (Shapiro–Wilk and Kolmogorov–Smirnov tests). Since most of the data did not meet the criteria of normal distribution, the values were log-transformed (base 10) and further statistical analyses and results were performed and presented as log-transformed values. In the case of values that were below the limit of quantification (LOQ) or were rejected, the value of the LOQ was used as a measurement value. Since these values constitute only 8% of all measurements, methods based on estimation or regression were not applied. These substitutions concerned mainly B, Bi, Ag, and Se (58%, 42%, 39%, are 33% measured below LOQ, respectively). The LOQ for each measurement is demonstrated in the project database.

2.5. The Assessment of Soil Pollution within the Catchment

The geochemical index (I_{geo}) and Enrichment Factor (EF) were applied to determine the degree of soil contamination used for the fingerprinting analysis. Both methods are commonly used in the field of soil analysis [20]. The I_{geo} index [21] is an indicator that classifies the geochemical pollution of heavy metals in analysed samples on the basis of its measured value and the value of geochemical background, in accordance with the following formula:

$$I_{geo} = \frac{C_n}{B_n \times 1.5}, \quad (1)$$

where I_{geo} is the geochemical index, C_n is the analysed heavy metal concentration, B_n is the concentration of the geochemical environment of the metal (geochemical background) and 1.5 is the background value of lithological variability. I_{geo} is classified between 0 (uncontaminated) and 6 (extremely contaminated). The Enrichment Factor (EF) quantifies the enrichment of a soil sample with a specific chemical element relative to a reference value [22]). Its value is normalized by the value of an element that remains unchanged in the natural environment. EF is calculated in accordance with the following formula:

$$EF = \frac{\left[C_x / C_{ref}\right]_{sample}}{\left[C_x / C_{ref}\right]_{soil\ background}} \quad (2)$$

where C_x is the concentration of the analysed element and C_{ref} is the concentration of the reference element. Al was used as the reference element. EF values range from 1 (minimal enrichment) to 5 (extremely high enrichment). The geochemical background values for both methods, for 11 elements (As, B, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn), were adopted from Kabata-Pendias and Mukherjee [23]. In the case of aluminium, the value of 20,000 mg·kg^{-1} from Turekian and Wedepohl [24] (1961) was applied. All values are shown in Table S3 and in the project database [19].

2.6. Fingerprinting

The sources of heavy metals (and also of some other elements outside this category) in suspended sediments were categorised using the fingerprinting technique. This technique involves the analysis of suspended sediment in a selected sampling point and the analysis of soil within the catchment, in order to track the sources of contamination of suspended sediments [7,9]. It enables the identification of particular areas as the most influential to the quality of suspended sediment. Soil data from 9 sampling sites was classified in accordance with the land use category (AGRO, PAST, URBAN). Two statistical tests were carried out to verify significant differences among the groups. On the basis of that assumption, the fingerprinting procedure consisted of three steps [7,9,25]. In the first step, the non-parametric Kruskal–Wallis H test ($p > 0.05$) was used to exclude any elements that did not exhibit any significant variation among the different land-use categories (AGRO, PAST, URBAN). In the second step, the non-parametric Wilcoxon test ($p > 0.05$) was applied to verify the elements that showed significant differences among the different land use types in the previous test. In the third and final step, only the elements that passed both tests were selected for the proper fingerprinting analysis. The third stage of the analysis was based on Linear Discriminant Analysis—LDA. Discriminant Analysis is a procedure that enables the differentiation between two or more groups of data on the basis of the analysed quantitative variables. The variables selected for this procedure included: the concentration of nth heavy metal in suspended sediment (sampler), agricultural samples (AGRO), pasture samples (PAST), and urban samples (URBAN). The LDA provided a set of coefficients that was sufficient to describe one variable by the other parameters using a linear function. As a result of this step, an equation was developed that reflected the concentration of a given element in the suspended sediment matter on the basis of concentration levels known from soils present across the catchment area. The coefficients of different land use categories in this equation demonstrate the influence of landscape on heavy metal content in suspended sediment measured at the selected sampler location point.

3. Results

3.1. Soil

The analysis of the correlation between individual elements (Spearman rank correlation coefficient) revealed a statistically significant (p = 0.05) correlation (>0.8) between 14 pairs of elements. Following an analysis of the concentrations of the tested elements in terms of outliers, 1 measurement was rejected. The main components of soil in the analysed samples included Fe (mean value: 34,067 mg·kg^{-1}), Al (24,577 mg·kg^{-1}), and Ca (18,999 mg·kg^{-1}). Out of all 1116 chemical determinations, 1025 (91.8%) were above the limit of quantification value (LOQ). Among the values below LOQ, 21 concerned B, 15: Bi, 14: Ag, 12: Se, 9: Hg, 8: W, 6: Cd, 4: Ni, and 1: Sr. The testing of values for the normal distribution of data (Shapiro–Wilk and Kolmogorov–Smirnov tests) revealed that 17 of the elements failed to demonstrate normal distribution at a statistically significant level (p = 0.05). Following the application of a logarithm (base 10) function, the hypothesis on the normal distribution of 14 variables was rejected.

Seasonal variability of the data series was tested to verify the consistency of data and to ensure that the obtained data series mainly depended on land-use characteristics. The verification was based on a non-parametric Kruskal–Wallis H test (p > 0.05). The data turned out to be seasonally unaffected, which enables the performance of further fingerprinting analysis on the compiled data.

3.2. Soil Pollution Assessment

The implemented methods enabled the calculation of I_{geo} and EF for 440 samples (11 elements, 4 surveys, 10 sampling points). The values for suspended sediment were calculated for provisional assessment, as the applied geochemical background refers to the soil samples. The results for both indices were consistent and their Spearman rank correlation was 0.81. Among the calculated results, 78.8% of samples had the lowest I_{geo} (0) and EF (1) class, which corresponded with uncontaminated or minimally enriched samples. In total, 10.4% of samples had an I_{geo} class in the range of 2–6, while 8.1% of samples had an EF class in the range of 2–5. Only two samples of Hg taken from sampling points 2 and 3 were assigned to the maximum classes of I_{geo} and EF of 6 and 5, respectively. Figure 2 shows the results of classification of both indices for the samples of soils within the Nurzec River catchment.

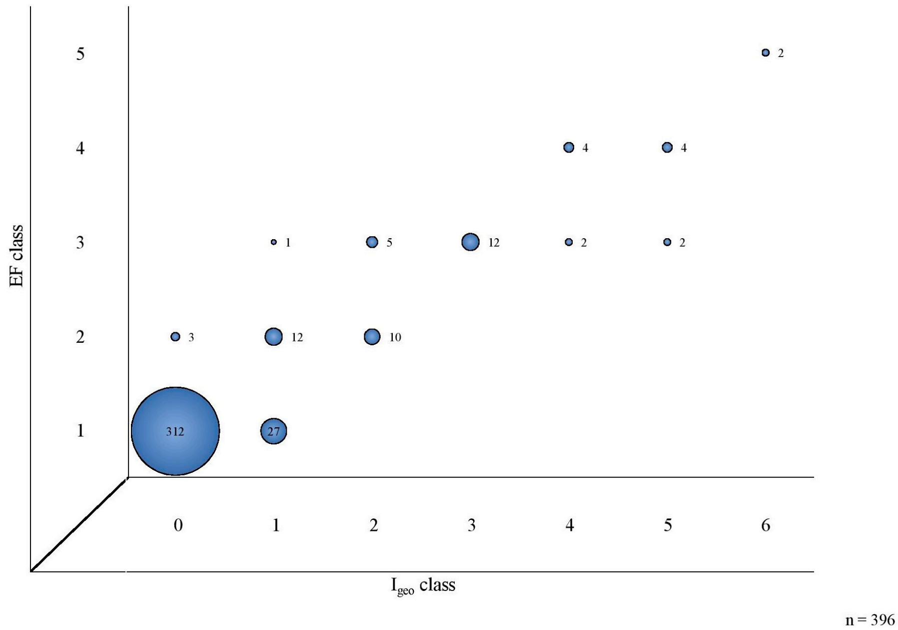


Figure 2. Classification of I_{geo} and EF indices of soils samples within the Nurzec River catchment. The values in the chart represent the number of samples classified into each class of both indices.

The overall results of I_{geo} and EF demonstrate that most of the soil samples from the Nurzec River catchment were uncontaminated by the studied elements. Heavy contamination by heavy metals was observed locally and involved only Hg (14 samples classified as heavily contaminated). Moderate contamination (2nd or 3rd class of I_{geo} or EF) was observed broadly among Zn samples (12 soil samples) and As (9 soil samples). The maximum values of I_{geo} and EF categorized according to elements and land-use types are shown in Figure 3.

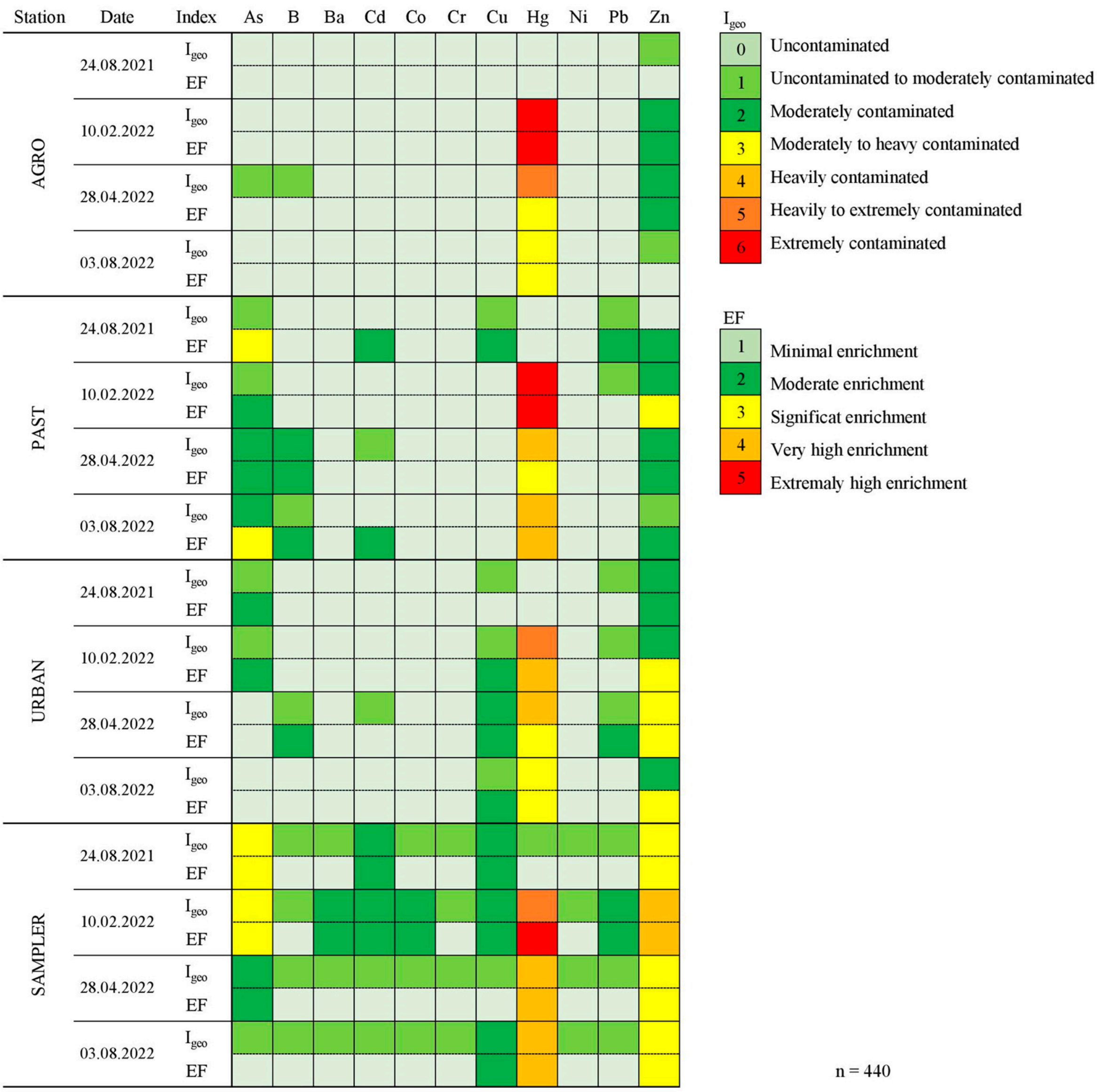


Figure 3. Maximum I_{geo} and EF classes observed for each analysed land-use category, in comparison with suspended sediment (SAMPLER).

Samples with values higher than the I_{geo} = 0 or EF = 1 classes were more common among samples from PAST (23 samples) and URBAN (20 samples) land-use categories. Nevertheless, the maximum I_{geo} or EF values (6 and 5, respectively) were observed in the AGRO and PAST areas (Hg). Moreover, AGRO samples were not contaminated by As and B, while in the case of PAST and URBAN samples, the highest I_{geo} or EF class was the second (B) and third (As) class for these elements. The highest contamination (I_{geo} and EF above 5) was observed only in Hg samples. This situation was present in most of the sampling points. The absolute values of mercury in these samples ranged between 2.4

and 8.9 mg·kg^{-1}. High concentrations of Zn (up to 367.4 mg·kg^{-1}) were found across all land-use categories, with the highest values found in URBAN areas. This was reflected in the classification of both I_{geo} and EF indices (class 2 or 3).

Suspended sediment samples demonstrated higher values of I_{geo} and EF in comparison with the results of soil analysis. Classes of I_{geo} in the range of 4–6 and EF of 4–5 were observed among Hg samples. This indicates heavy/extremely high contamination and the content of Hg in suspended sediment from the Nurzec River. High values of I_{geo} and EF were observed among Zn (3–4) and As (I_{geo} and EF class 3) samples. Moderate contamination (I_{geo} and EF class 2) was also attributable to Cd and Cu samples, as well as Ba, Co, and Pb samples. The values of indices were higher in suspended sediment than in soils. Other samples demonstrated I_{geo} and EF classes lower than 2, which corresponds with minimal contamination/enrichment.

3.3. Fingerprinting

The first step of the fingerprinting procedure (Kruskal–Wallis H test) resulted in the elimination of 13 out of 31 of the chosen parameters. The elements that passed the test were: Al, As, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, P, Pb, S, Sb, Sr, V, and Zn. The results of the test are shown in Table 1. The selected elements were subsequently examined during the second testing stage (Wilcoxon test) to additionally eliminate all non-significant parameters. The final set of parameters selected for the fingerprinting procedure included 14 elements: Al, Ca, Cr, Cu, K, Li, Mg, Mn, Ni, Pb, S, Sb, Sr, and V. The results of the Wilcoxon test are shown in Table 2. Fisher's linear discrimination analysis was then performed in order to develop a set of discriminating functions that can help to predict sampler values on the basis of the values of other quantitative variables. The analysis resulted in the achievement of a set of discriminant function coefficients for each of the analysed variables. Table 3 presents the discriminant function coefficients.

Table 1. H Kruskal–Wallis test results. Statistically significant results ($p < 0.05$) are in bold.

Element	Statistic	*p*-Value	Element	Statistic	*p*-Value
Ag	0.237	0.888	**Li**	**11.315**	**0.003**
Al	**11.445**	**0.003**	**Mg**	**10.545**	**0.005**
As	**7.241**	**0.027**	**Mn**	**10.64**	**0.005**
B	0.515	0.773	Mo	5.615	0.06
Ba	2.445	0.294	Na	0.815	0.665
Be	2.142	0.343	**Ni**	**11.12**	**0.004**
Bi	0.377	0.828	**P**	**12.255**	**0.002**
Ca	**10.635**	**0.005**	**Pb**	**10.64**	**0.005**
Cd	5.263	0.072	**S**	**15.5**	**0**
Co	4.22	0.121	**Sb**	**8.915**	**0.012**
Cr	**12.515**	**0.002**	Se	0.195	0.907
Cs	3.605	0.165	**Sr**	**10.64**	**0.005**
Cu	**8.295**	**0.016**	**V**	**10.305**	**0.006**
Fe	**6.045**	**0.049**	W	2.973	0.226
Hg	0.387	0.824	**Zn**	**7.715**	**0.021**
K	**13.095**	**0.001**			

Table 2. Wilcoxon test results. Statistically significant results ($p < 0.05$) are in bold.

	Ag			K	
	Agro	Past		Agro	Past
Past	**0.0054**	-	Past	**0.0019**	-
Urban	**0.0039**	0.6365	Urban	**0.0054**	0.2271
	As			Li	
	Agro	Past		Agro	Past
Past	**0.0136**	-	Past	**0.0039**	-
Urban	0.1278	0.1278	Urban	**0.0101**	0.2701
	Ca			Mg	
	Agro	Past		Agro	Past
Past	**0.9581**	-	Past	**0.0101**	-
Urban	**0.0239**	0.0014	Urban	0.4309	**0.0054**
	Cr			Mn	
	Agro	Past		Agro	Past
Past	**0.0028**	**-**	Past	**0.0074**	-
Urban	**0.0019**	**0.0406**	Urban	**0.0074**	0.3184
	Cu			Ni	
	Agro	Past		Agro	Past
Past	0.8748	-	Past	**0.0028**	-
Urban	**0.0054**	**0.0406**	Urban	0.2701	**0.0181**
	Fe			*p*	
	Agro	Past		Agro	Past
Past	0.1278	-	Past	**0.0014**	-
Urban	**0.0406**	0.0831	Urban	0.0520	0.0661

Table 3. Discriminant Function Coefficients for suspended sediments.

	1	**2**	**3**
URBAN	0.641923	1.11086	−0.69085
PAST	0.605001	0.408692	0.944951
AGRO	−0.0202849	−1.61618	−0.246216

On the basis of the obtained coefficients, the first standardised discriminating function is:

$$\text{suspended sediment} = 0.641923 \times \text{URBAN} + 0.605001 \times \text{PAST} - 0.0202849 \times \text{AGRO}, \quad (3)$$

The implementation of the above equation as a model of predicting the contamination of suspended sediments by heavy metals resulted in the achievement of the following measures: $r^2 = 0.67$, RMSE = 1.151, KGE = 0.774. The obtained linear function coefficients show a major influence of urban areas and pastures on the levels of contamination with heavy metals observed in suspended sediments and a minor contribution of the agricultural areas. Figure 4 presents the fit between the model results and the modelling results obtained following the application of the fingerprinting procedure.

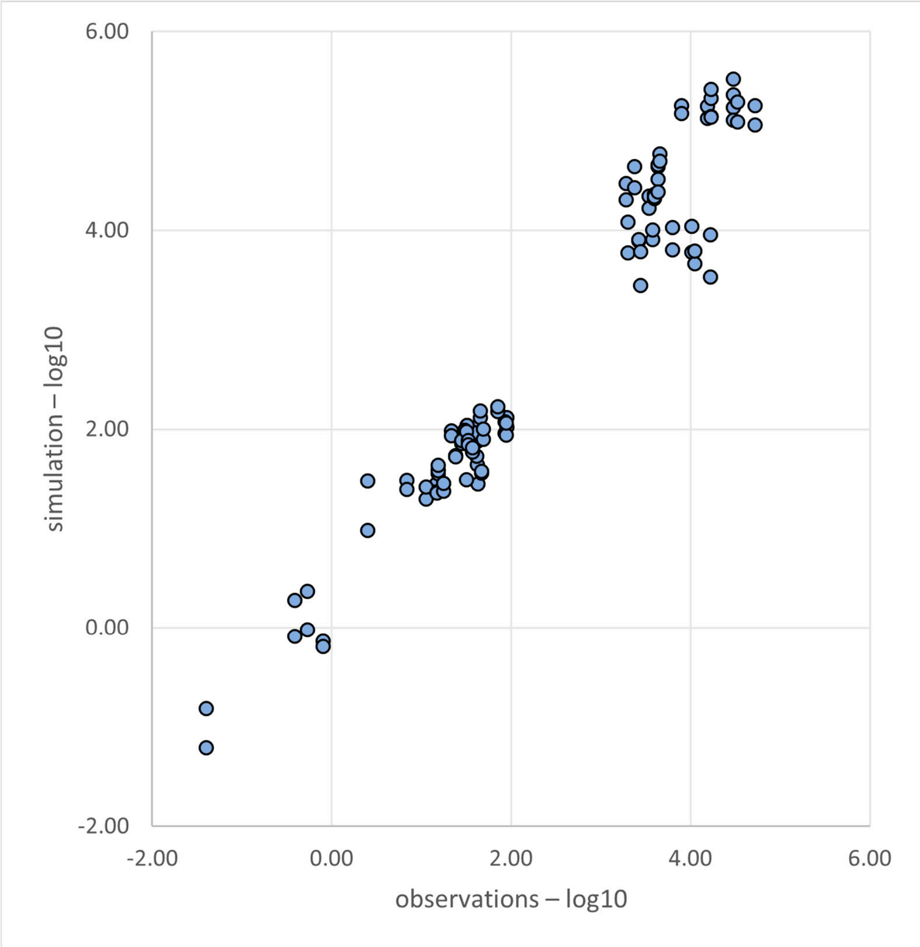


Figure 4. Comparison between a simulation based on the fingerprinting model and an analysis of the suspended sediment (log_{10} transformed).

4. Discussion

The results demonstrated varied contamination of soils in the studied catchment, with 78.8% samples classified in the lowest classes of I_{geo} or EF. Geochemical background values were exceeded in 42.4%, 32.4%, and 50.0% of all samples for AGRO, PAST, and URBAN categories, respectively. High I_{geo} or EF (above 4) categories were observed in similar numbers across all land-use categories (below 2.5% of all samples). Samples with index values representing heavily to extreme contaminated soil were observed in two samples and concerned high Hg concentrations.

High contamination level (above geochemical background values) was recorded for Hg in 27 samples (75% of all Hg determinations). I_{geo} and EF classes for this element reached maximum values. The concentration levels of this element in some samples were significantly higher than the geochemical background levels and were up to 80 times higher than the reference values. These values were recurrent at the same measurement points during different surveys and were confirmed using blank samples that excluded measurement errors. The maximum absolute value of this element was observed in the AGRO land-type category and reached 8.88 mg·kg^{-1}. The Nurzec River catchment area is used mainly as an agricultural area, with minor industrial emission sites.

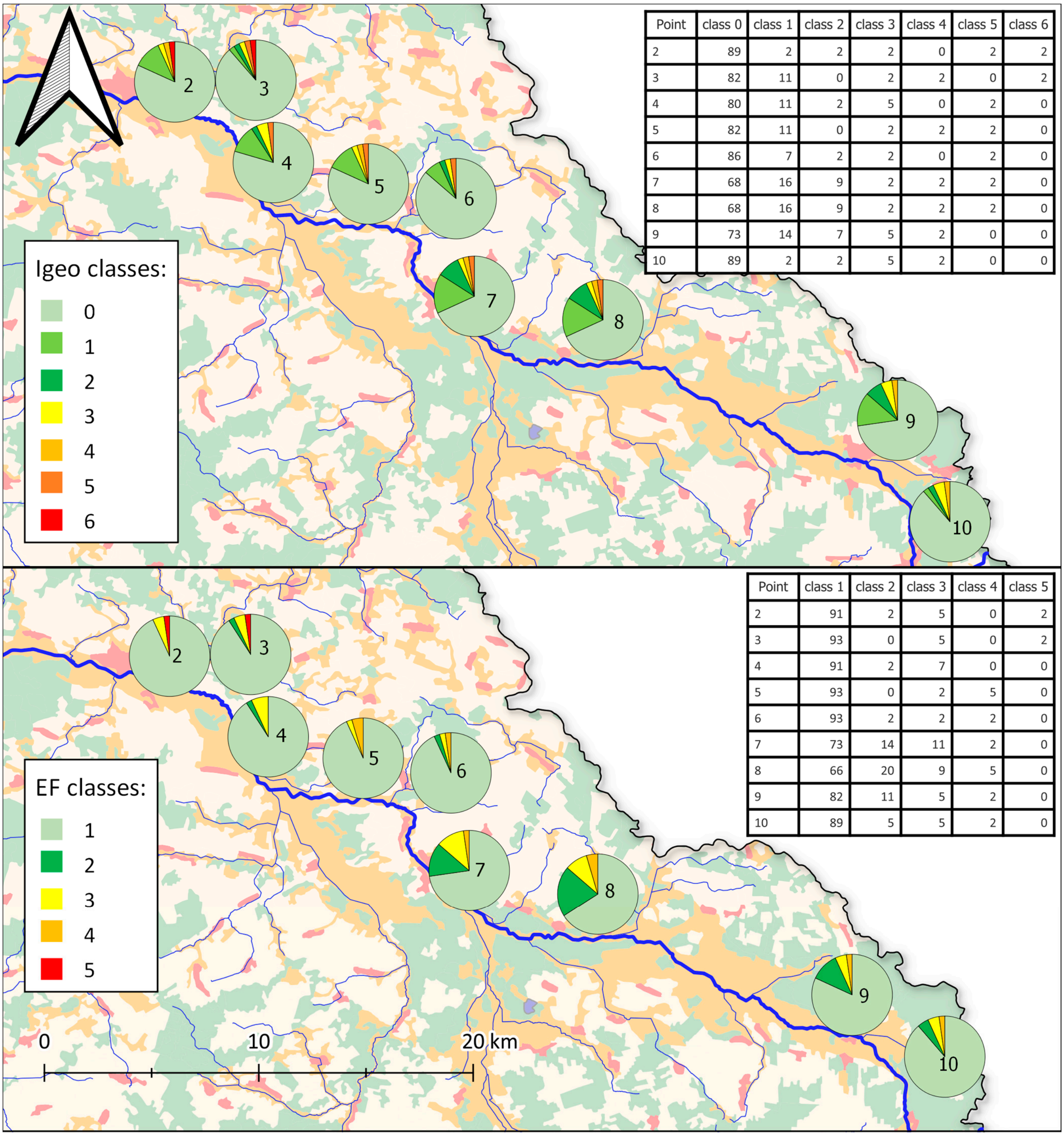
Industrial activity represents the main source of Hg in soil, but recent studies indicate that Hg losses on agricultural lands are relatively high due to higher erosion and historical Hg pollution, including plant protection products (pesticides) [4]. High values of Hg in this area can also be found in biota, with a mean value of 25 µg·kg^{-1} (above the environmental quality standard, EQS). Nevertheless, water monitoring tests did not reveal any excessive values for Hg [26]. But since the performed statistical test did not confirm any statistically significant differences between the individual land-type use categories, Hg was not used in the fingerprinting procedure.

Another element that was found in higher concentrations in almost all samples along the studied river catchment was Zn. Concentrations above the geochemical background value were found in almost all samples (95%). In total, 55% of samples of Zn had I_{geo} or EF higher than minimum. The moderate enrichment of Zn was observed more frequently in samples from the URBAN category, where I_{geo} or EF reached the third class of enrichment. Its range varied between 44.5–367 mg·kg^{-1}, which represented up to 612% of the geochemical background value. However, these values are not considered to be environmentally hazardous [23].

The fingerprinting procedure, used as a tool to discriminate sources of heavy metal pollution within the Nurzec River catchment, enabled the development of a model equation that reflects the concentration values observed at the measurement point of the suspended sediments at a satisfactorily level (r^2 = 0.67, RMSE = 1.151, KGE = 0.774). The coefficients obtained using the equation indicated the high influence of URBAN and PAST land categories on the level of heavy metal contamination in suspended sediments in the Otapy section. Agricultural type of land with a calculated discriminant function coefficient = −0.0202849 indicates the minor influence of this land-type category on the level of contamination of suspended sediments. Among the elements that remained after the final selection and were considered for the fingerprinting procedure, the highest concentration levels were observed among the samples from PAST areas. The soil structure of areas along the river is of peaty origin. These areas are not suitable for the growing of permanent crops, but they could act as a natural riparian zone between AGRO lands and the riverbed, to reduce the transport of some pollutants. Additionally, high concentration levels in soils from PAST areas could enhance the statistical correlation between the soil and suspended sediment concentrations. Some studies have confirmed that heavy metals may be of agricultural origin and their source may be fertilization [27,28], which represents the second possible cause of the presence of heavy metals in the Nurzec River catchment area.

A fingerprinting procedure based on the combination of statistical tests [9,29] successfully eliminated any elements that did not demonstrate any statistical differences among the individual land-use categories and between selected measuring points. The final set of 14 elements allowed the author to develop a model equation with satisfactory goodness-of-fit measure values. However, since the initial set consisted of 31 chemical elements, only 45% of the analysed heavy metals were suitable to perform further analysis. Smaller sets of elements may not be sufficient for this method, especially in heavily polluted areas. The application of fewer markers may produce a dataset without any significant differences between all markers, which is necessary for the fingerprinting procedure. Hg pollution was common and significant in the Nurzec River catchment. In comparison with the results of the geochemical index of enrichment values, the set of fingerprinting markers included four heavy metals: Cr, Cu, Ni, and Pb. The levels of contamination with each element within the analysed catchment were highly variable (from uncontaminated to extremely contaminated), but high heavy metal concentration levels were observed in individual samples. The general results of the study are shown in Figure 5.

Data obtained in this analysis can be effectively used for the tracking of pollutants transported with the suspended sediment. The knowledge of the structure of geochemical pollutants within the catchment allows us to combine these results with information on sediment load obtained not only from monitoring, but also via mathematical modelling. Sediment is one of the basic water quality parameters calculated as part of mathematical modelling [30,31]. The calibration of the model for the amount of suspended sediment is performed right after the hydrological calibration of the model. However, modelling provides information only on sediment load transported via a watercourse, while information on adsorbed compounds is not available [32]. Thus, by combining information obtained from field studies with information from mathematical modelling, new quality could be added to the results of the analysis. A similar approach has been successfully used to carry out similar analyses of mountain river catchments, where erosion is much stronger [9]. Nevertheless, the application of a similar analysis to lowland areas, in an extremely homogeneous catchment in terms of land use, will make such an analysis even more valuable. It confirms the proper adjustment of the model for tracking the transport of suspended sediment in such conditions.



Point	class 0	class 1	class 2	class 3	class 4	class 5	class 6
2	89	2	2	2	0	2	2
3	82	11	0	2	2	0	2
4	80	11	2	5	0	2	0
5	82	11	0	2	2	2	0
6	86	7	2	2	0	2	0
7	68	16	9	2	2	2	0
8	68	16	9	2	2	2	0
9	73	14	7	5	2	0	0
10	89	2	2	5	2	0	0

Point	class 1	class 2	class 3	class 4	class 5
2	91	2	5	0	2
3	93	0	5	0	2
4	91	2	7	0	0
5	93	0	2	5	0
6	93	2	2	2	0
7	73	14	11	2	0
8	66	20	9	5	0
9	82	11	5	2	0
10	89	5	5	2	0

Figure 5. Visualisation of the I_{geo} and EF classes across the analysed sampling points. Pie charts represent the number of samples in each point and classes of I_{geo}/EF. The tables show the percentage of samples in each class of each index. n = 396.

The study also confirmed the validity of using the so-called hybrid approach introduced by the author in previous publications. In this case, the hybrid approach combines the aspect of field research with the use of a statistical model. The approach originally proposed for the analysis of sources of nutrients is also effective in wider applications, e.g., with heavy metal contamination. It facilitated the classification of the current state of heavy metal contamination of soils and sediments in the Nurzec River catchment, as well as the identification of its sources. The implemented measurement method is simple and does not require any complicated equipment or time-consuming maintenance, while the applied statistical model is easy to reproduce. The advantages are significant on the catchment scale. However, it must be said that the implemented sampling method has limitations, mainly logistic ones—in the case of larger watercourses, the selection of a representative measuring point could be challenging. It should be noted that other studies on the impact of land use categories on heavy metal contamination provide insight on the discussed topic. Agricultural areas remain polluted with heavy metals across Europe. Sources of this pollution are associated with areas of metal ore mining. Poland is relatively unpolluted and has a low content of heavy metals in soils, in comparison with other European countries [2,4,5].

The limitation of this study is that even though it predicts the pathways and spatial sources of heavy metal pollution, it does not enable the tracking of source-specific markers. Identification is based on the sensitivity analysis, where Discriminant Function Coefficients enable the identification of a set of the most sensitive parameters. Those parameters are classified using the land-use criterion, which allows the identification of a particular area (Hot Spot). In this study, for example, fingerprinting identified pasture and urban areas as the main source of heavy metal transport. However, the question of whether this pollution originates directly from, for example, cattle grazing, or atmospheric deposition remains unresolved. This necessitates further analysis and does not eliminate the need for a proper input/output inventory in a given catchment area. The device's design itself is an additional limitation: using it to examine larger streams may require additional equipment, which complicates its application.

The general outcome of the study will provide additional knowledge on the transport of heavy metal pollutants within the Nurzec River catchment to the local authorities, residents and NGOs. Varied level of contamination of soils with heavy metals within the river catchment was confirmed and the transport of these pollutants has been proven. The observed contamination of suspended sediments is higher than the observed contamination of all types of land use in the catchment and indicates geo-accumulation of heavy metals. In addition, it demonstrates the significant impact of urban areas on water quality, even in an area with a low population density. It is therefore important to take appropriate actions at the local level and to consider the possibility of remediation in these areas, since anthropogenic heavy metal contamination can affect even the most pristine environments, such as national parks [33]. This analysis may serve as a basis for the future implementation of projects aimed at the restoration of contaminated areas and the maintenance of a sustainable environmental economy in the catchment area.

5. Conclusions

This study enables the identification of the sources of heavy metals transported via suspended sediments in the Nurzec River catchment. It also allows the author to conclude the level of heavy metal contamination in the suspended sediment and soil environment. Additionally, it provides a framework for future investigations. The main source of heavy metal content in suspended sediments in the Nurzec River proves to be of urban and pastural origin. Agricultural land that is predominant in the vicinity of the river has a minor influence on heavy metal concentration levels measured at the suspended sediment sampling point. Elevated heavy metal concentrations in soil observed within the direct river catchment mainly originate from Hg and Zn. The concentration of Hg in the analysed samples can be up to 80 times higher than the geochemical background. This study investigates the influence of land-use categories on suspended sediment composition.

Therefore, it does not provide any information on the direct factors of the observed pollution (e.g., the use of fertilizers, industrial emissions, and municipal management). Thus, further investigation of the contamination of the Nurzec River catchment with heavy metals is required to fully understand the sources of pollution and to plan sufficient and sustainable remediation activities. The proposed model exhibits a satisfactory level of performance in predicting the sources of metal contamination in the analysed catchment. These results will be included in subsequent research, which will involve the hydrological modelling of this catchment. Moreover, the fingerprinting technique has proved to be useful in the identification of factors and the analysis of pressure in this catchment. It has the potential to be used in further studies involving pharmaceuticals or substances included in a new priority list adopted by the European Commission.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16091209/s1, Table S1: Summary statistics of the analysis. Table S2: Correlation between individual elements (Spearman rank correlation coefficient). Values in bold represent statistically significant (p = 0.05) correlation. Table S3: Geochemical background values (Kabata-Pendias and Mukherjee, 2007) [23].

Funding: This research was supported by the "Excellence initiative–research university" program for the AGH University of Krakow and IMGW–PIB (sub. FBW–16).

Data Availability Statement: The data presented in this study are generally accessible in Mendeley Data at https://doi.org/10.17632/p7vdjx79jy.2.

Acknowledgments: The author would like to kindly thank the Hydrogeology and Engineering Geology Department (AGH University of Krakow) for the laboratory support.

Conflicts of Interest: The author declares no conflicts of interest.

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