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The distribution of Trace Elements in the Stream Sediments from the Jijia River Basin

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Abstract

The aim of the present study is to assess the environmental quality in the Jijia Basin by use of stream sediment samples.

The study of the distribution of trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Pb, Th and As) in the stream sediments from the Jijia Basin generally indicated that the environment is either unaffected or slightly affected. Local anomalies determined after defining the background and the threshold values are due to both anthropogenic factors and geogenic factors. A particular case is that of Ni, where over 75% of the data exceed the target value. However, the normal distribution of this element, as well as the high levels of Ni found in some soils from the studied area, suggest that we are dealing with a geogenically-enriched environment. The median values for most of the elements contents are close to those determined for European stream sediments.

Keywords: stream sediment, trace elements, background, threshold value, Jijia Basin, environment quality.

Introduction

In recent years, environmental quality has received special attention in Europe. In most European countries, environmental authorities have established action limits for certain chemicals that are found in surface environments and can have potential toxic effects on living organisms.

Geochemists have emphasized the fact that the action limits established must be consistent with the geochemical background, considering that, in certain situations, the natural levels of certain elements can be as high or even higher than those caused by man-made sources of

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pollution (Salminen et al., 2005). Furthermore, it has been indicated that the geochemical background depends on location and spatial scale and it changes from area to area of investigation (Reinmann and Garett, 2005). In this respect, the Forum of European Geological Surveys (FOREGS) has launched a Geochemical Baseline Mapping Program with the aim of providing multipurpose environmental geochemical baseline data for 26 European countries. This program can also be useful to the environmental authorities in defining action limits. It should be noted, however, that Romania did not take part in the program, and that at least some of the action limits provided by the Romanian environmental legislation have been adopted (with or without minor changes) from the legislation of other countries. For instance, Romanian standards for stream sediment quality are, for most of the chemicals, the same as those provided by Dutch environmental regulations (after Bird et al., 2003), even if the geological conditions in the two countries are quite different.

Stream sediments represent a valuable tool in assessing environmental quality, given that they generally reflect the average geogenic composition (rocks and soil) of a catchment basin for most elements, and that they are also sensitive to pollution.

Nevertheless, few studies regarding the geochemistry of stream sediments have been carried out in Romania, most of them focused on highly affected environments, such as those found in mining areas (Bird et al., 2003).

The aim of the present study is to assess the environmental quality in a slightly affected or unaffected area using the lowest number of stream sediment samples that is still statistically representative.

Materials and Methods

Study Area

The Jijia river has a length of 275km and is the main tributary of the Prut river, which, in turn, constitutes the eastern border of Romania. Jijia has three major tributaries (Sitna, Miletin and Bahlui), all located on its right. The catchment basin, with an area of about 5760km^2, is entirely located in the Moldavian Plain.

Geologically, the study area belongs to the Moldavian Platform, which consists of a crystalline basement (studied only in core samples) and a sedimentary cover ranging from the Vendian to the Neogene (Ionesi, 1994). Nevertheless, at the surface, only Sarmatian (Volhynian, Bessarabian and Khersonian) and Quaternary (Pleistocene and Holocene) deposits are found (Fig. 1).

The lithology consists of clays, silts and sands with intercalations of sandstones and limestones (especially in the western part). Along the rivers, Quaternary terrace deposits have developed.

The soils are represented mainly by chernozems, luvisoils and fluvisoils (Pantazică, 1974).

Several cities are located in the study area and, with the exception of Iași, they generally rely on light industry. The main industrial branches are textiles, chemicals, steel, pharmaceutics, food, energy and furniture. In the rural areas, small farms with annual crops, permanent crops (vineyards and orchards) and grassland are predominant.

Sampling and analysis

A number of 30 samples of about 3 to 4kg each (wet weight) were collected from the study area. After drying and quartering, approximately 300 g out of each sample were wet-sieved using a small quantity of deionized water. The fraction less than 0.15mm was retained for further analysis. After having been pulverizing by an electric agate mortar to a size <0.063mm, 20g of sample were mixed with 5g of C2H2 binder and homogenized using a Fritsch Planetary

Mill Pulverisette 5, for 15 minutes, at a constant speed of 180rpm. For each sample, 2 pressed pellets weighing 9g (powder weight) were prepared using a Fluxana PR-25A Press (30 seconds at 20t/cm^2). The chemical analysis for 16 elements (Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Pb, Th, and As) was carried out using an ED-XRF Epsylon 5 spectrometer equipped with 15 secondary targets. Several Certified Reference Materials (SO1-4, LKSD1-4, STSD1-4) were used for calibration.

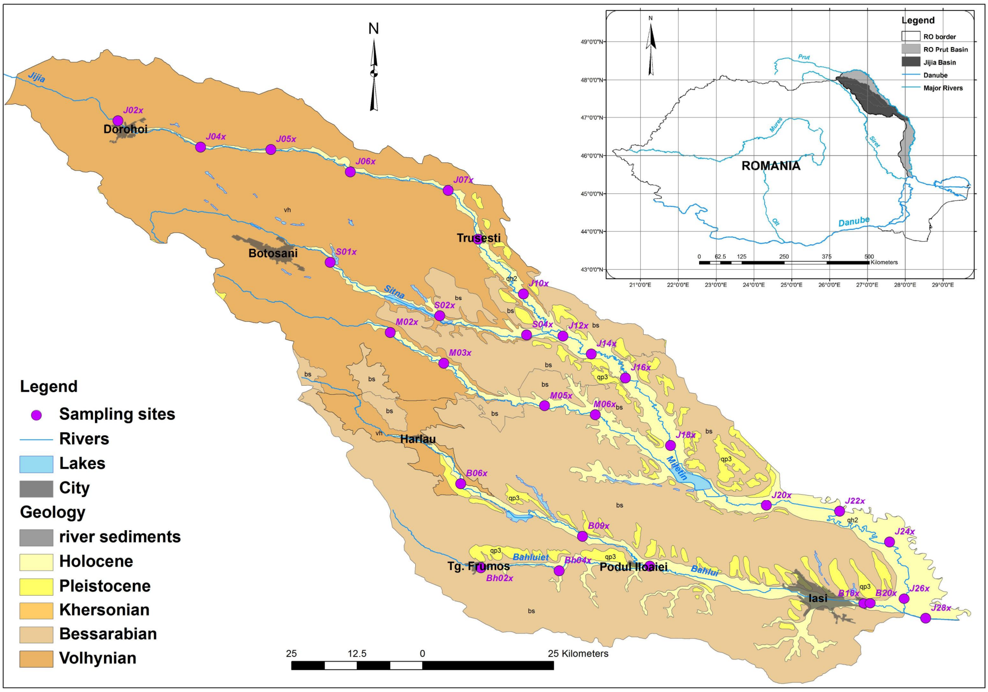

Fig. 1 Geological map of the Jijia Basin, including sampling sites.

Statistical analysis and graphic representation

The set of results obtained from the chemical analysis was later analyzed statistically using DAS+R, GCDKit for R and the XLStat add-on for Microsoft Excel in order to determine the main statistical parameters, the background limits and the threshold values.

The graphical representation was devised using ESRI ArcGis Desktop, the topographic information being obtained from 1:100 000 scale topographic map sheets. Taking into account the irregular sampling network, the spline method was used for interpolating data.

Results and discussion

Statistical analysis of trace elements content

The main statistical parameters of the trace elements contents in the stream sediments investigated are presented in Table 1.

Most of the trace elements follow a normal distribution, with skewness and kurtosis generally between –1 and +1. Only four elements, namely Cu, Pb, Zn and As, have leptokurticpositive skewed distributions. The Kolmogorov-Smirnov univariate normality test, with a significance level of 5%, rejects the null hypothesis (namely, the samples follow a normal distribution) only for Zn (p=0.006) and Pb (p=0.008), but the probabilities for Cu (p=0.099) and As (p=0.063) are also small, compared with those of all the other elements investigated. The situation improves if the same test is carried out on log-transformed data regarding these four elements, the null hypothesis (namely, the samples follow a log-normal distribution) being accepted.

Tab. 1 Statistical parameters of trace elements content (mg/kg) in the stream sediment samples (n=30) of the Jijia Basin

Element		Sc	V	Cr	Co	Ni	Cu	Zn	Rb
Minimum		12.42	49.17	63.91	6.76	22.86	20.76	42.08	52.61
Maximum		21.70	114.5	96.66	29.00	64.69	76.98	349.33	113.1
Range		9.28	65.35	32.75	22.25	41.84	56.23	307.26	60.56
1st Quartile		15.61	66.27	72.29	11.78	36.78	25.91	61.91	68.91
Median		17.14	76.67	76.67	14.88	42.98	27.97	70.89	79.30
3rd Quartile		18.44	86.61	85.37	18.67	50.74	34.64	82.32	88.40
Mean		17.02	77.93	78.77	15.57	43.16	31.76	84.54	78.90
Standard deviation		2.09	16.34	9.55	5.19	10.34	11.76	57.76	14.49
Coef. of variation (%)		12.27	20.96	12.13	33.35	23.95	37.03	68.32	18.37
Skewness		-0.28	0.27	0.37	0.47	0.12	2.40	3.56	0.21
Kurtosis		0.13	-0.61	-0.88	-0.10	-0.50	6.16	13.24	-0.19
p-value of K-S test	N distrib.	0.955	0.993	0.622	0.988	1.000	0.099	0.006	1.000
	Log-N	0.786	0.993	0.788	0.976	0.999	0.539	0.198	0.987

Element		Sr	Y	Zr	Nb	Ba	Pb	Th	As
Minimum		112.1	19.33	182.6	11.05	300.9	12.66	5.30	7.12
Maximum		184.1	30.72	553.0	15.11	504.0	49.24	10.68	22.21
Range		72.02	11.39	370.3	4.06	203.1	36.59	5.38	15.10
1st Quartile		128.5	22.07	232.8	12.75	353.4	16.58	6.94	9.62
Median		148.7	24.78	282.6	13.63	383.7	19.10	8.16	10.58
3rd Quartile		158.6	25.87	351.1	14.25	403.9	20.13	9.02	11.05
Mean		147.6	24.14	296.4	13.44	380.4	20.18	8.10	10.73
Standard deviation		19.32	2.66	86.08	1.11	45.02	7.05	1.35	2.52
Coef. of variation (%)		13.09	11.02	29.04	8.27	11.84	34.95	16.63	23.51
Skewness		0.11	-0.03	1.02	-0.56	0.56	2.72	-0.01	3.15
Kurtosis		-0.88	-0.21	1.00	-0.48	0.80	8.24	-0.71	12.62
p-value of K-S test	N distrib.	0.655	0.511	0.406	0.626	0.938	0.008	0.915	0.063
	Log-N	0.621	0.347	0.598	0.800	0.881	0.066	0.695	0.304

Assessment of the background, threshold value and outliers

In Environmental Geochemistry, defining the background (as the main range of normal variation of an element) and the outliers (as the extreme values derived from a different, affected, distribution) are of special interest. In this respect, the upper limit of the background is considered the threshold value (Reinmann et al., 2008).

The main methods of determining the geochemical background, threshold values and outliers have been reviewed by Reinmann et al. (2005), the authors considering that the most suitable in this respect is the use of the boxplot and [median ± 2MAD] methods. They also offer a heuristic method for data inspection and selection of background variation, and suggest the use of boxplot if the number of outliers is below 10%, and [median ± 2MAD] if the proportion of the outliers exceeds 15%.

In the present study, the background limits and outliers were determined using both methods in order to choose the best one. The results of this assessment (Tab. 2) generally indicate a higher proportion of outliers (most of them situated in the inferior part of the distribution) when the [median ± 2MAD] method is used. In this case, the boxplot method seems to be the most suitable for defining the background, considering the fact that the proportion of outliers is never higher than 10%, and it is also more expressive in graphical representation.

Tab. 2 Background limits (mg/kg) and outlier proportion (%) of analyzed trace elements

Element	Sc	V	Cr	Co	Ni	Cu	Zn	Rb
Inter-quartile range (IQR)	2.82	20.34	13.08	6.89	13.96	8.74	20.41	19.50
Median absolute deviation	1.38	10.41	6.77	3.58	7.58	4.21	10.53	10.10
Boxplot Background								
Lower background limit	11.37	35.77	52.66	1.44	15.85	12.8	31.29	39.66
Upper background limit	22.67	117.1	104.9	29.0	71.67	47.7	112.9	117.6
Outliers (%)	0	0	0	0	0	6.7	10	0
[median±2MAD] Background								
Lower background limit	14.39	55.85	63.13	7.72	27.82	19.5	49.83	59.11
Upper background limit	19.90	97.48	90.21	22.0	58.14	36.3	91.96	99.49
Outliers (%)	10	3.3	16.6	3.3	0	10	10	3.3

Element	Sr	Y	Zr	Nb	Ba	Pb	Th	As
Inter-quartile range (IQR)	30.16	3.81	118.3	1.51	50.56	3.56	2.08	1.43
Median absolute deviation	13.66	1.63	55.63	0.79	26.55	2.14	1.17	0.89
Boxplot Background								
Lower background limit	83.29	16.36	55.30	10.4	277.5	11.2	3.82	7.48
Upper background limit	203.9	31.58	528.7	16.5	479.8	25.4	12.13	13.20
Outliers (%)	0	0	3.3	0	3.3	10	0	10
[median±2MAD] Background								
Lower background limit	121.4	21.52	171.3	12.0	330.6	14.8	5.83	8.80
Upper background limit	176.0	28.04	393.8	15.2	436.8	23.3	10.49	12.36
Outliers (%)	0	13.3	6.7	6.7	10	13.3	0	13.3

Total content of trace elements

The complete set of data can be provided by the authors, and the matrix of correlation coefficients is not presented in the present paper.

The trace element content from the stream sediments of the Jijia Basin was compared with the results of previous studies, one of the best suited for this approach being the Geochemical Atlas of Europe (Salminen et al., 2005), which provides values determined on fractions of the same size (<0.150mm) and using the same analytical method (XRF) as in the case of the present study.

The average content of Sc in the continental crust is quoted as 21.9mg/kg by Rudnick and Gao (2004). In sedimentary rocks, the Sc content is between 1mg/kg in sandstones and carbonate rocks, and 10–30mg/kg in argillaceous rocks (Salminen et al., 2005). In soils, the average Sc content is 9.5mg/kg (Kabata-Pendias and Mukherjee, 2007).

The median value of the Sc content in 3024 stream sediment samples from Japan is 13mg/kg (Ohta and Imai, 2011).

In the investigated area, the Sc content in stream sediments ranges from 12.4mg/kg to 21.7mg/kg, with a median value of 17.1mg/kg.

The average V content in the continental crust is 138mg/kg (Rudnick and Gao, 2004), this value being generally higher in mafic rocks and lower in acidic rock. Regarding sedimentary rocks, low contents of V are present in sandstones and limestone (20mg/kg), and high contents are present in shale (90–260mg/kg) and clays (200mg/kg) (Adriano, 2001). The average content of V in soils is 60mg/kg (Kabata-Pendias and Mukherjee, 2007). In stream sediments, V is adsorbed or coprecipitated by Fe-oxides/hydroxides.

The median value of the V contents is 62mg/kg in European stream sediments, and 120mg/kg in Japanese stream sediments (Salminen et al., 2005; Ohta and Imai, 2011).

The Vanadium content in the stream sediments from the Jijia Basin is between 49mg/kg and 114.5mg/kg, with a median value of 76.7mg/kg. Vanadium has strong correlations with Ni (0.85), Co (0.90), Rb (0.94) and Th (0.80).

The average abundance of Cr in the continental crust is 135mg/kg (Rudnick and Gao, 2004). The content of Cr tends to be higher in areas where ophiolites are present. In sedimentary rocks, the Cr content varies from 10mg/kg in limestone and 35mg/kg in sandstones, to 120mg/kg in shale and clays (Adriano, 2001), while the average content of Cr in soils is 54mg/kg (Kabata-Pendias and Mukherjee, 2007). In stream sediments, Cr may be present as primary detrital minerals, such as chromite, magnetite and ilmenite, or as adsorbed cation in secondary oxides and clays, resembling the behavior of Fe and Al.

In the European stream sediments, the median value of Cr contents is 63mg/kg, while this value is 53mg/kg in Japanese stream sediments, and 59.1mg/kg in 208 stream sediment samples from India.

The Chromium content in the stream sediments from the Jijia Basin displays a narrow range (63.9–93.7mg/kg) and a median value of 76.7mg/kg.

In the continental crust, Cobalt has an average content of 26.6mg/kg ((Rudnick and Gao, 2004). In sedimentary rocks, the content of Co decreases from 19mg/kg in shale to 0.3mg/kg in sandstones, while the average content of Co in soils is quoted as 8mg/kg by Kabata-Pendias and Mukherjee (2007). The distribution of Co in stream sediments is mainly controlled by adsorption and coprecipitation with Mn and Fe oxides. Higher values of Co are generally reported in areas where ultrabasic rocks are abundant.

The median value of the Co content is 8mg/kg for European stream sediments (Salminen et al, 2005), 14mg/kg for Japanese stream sediments (Ohta and Imai, 2011), and 11.4mg/kg for 208 samples of stream sediments from India (Krishna et al, 2011).

In stream sediments from the studied area, the Co content is between 6.76mg/kg and 29mg/kg, with a median value of 14.9mg/kg.

The average content of Ni in the continental crust is quoted as 59mg/kg by Rudnick and Gao (2004). In sedimentary rocks, Ni is mostly held in detrital ferromanganese silicate minerals, detrital Fe oxides and clay minerals, its abundance decreasing from 90mg/kg in shale to less than 5mg/kg in limestone (Salminen et al., 2005). The estimated value of the Ni content in clays is 68mg/kg, while the average value for soil is 20mg/kg (Adriano, 2001). In stream sediments, a large proportion of Ni is present in silicate and oxide minerals resistant to weathering and the rest is sorbed by clay minerals or by Fe and Mn oxyhydroxides.

The same value of 21mg/kg is provided as the median for Ni abundance in stream sediments from Europe and Japan (Salminen et al., 2005; Ohta and Imai, 2011). In 208 samples of stream sediments from India, however, this value is slightly higher (23.3mg/kg) (Krishna et al., 2011).

The Ni content in the studied area ranges from 22.9mg/kg to 64.7mg/kg, with a median value of 43mg/kg. The target level of the Ni content in stream sediments provided by the Romanian environmental legislation is 35mg/kg, which leads to 76% of the samples exceeding this value. The statistical treatment of the data proved that Ni follows a normal distribution, while the background estimation did not reveal the presence of any extreme value. This could mean that the Ni content represents a geogenically-enriched background unaffected by anthropogenic activities. This hypothesis may also be supported by the median value of the Ni content in 1030 soil samples from the Iași area – 34.86mg/kg (Iancu and Buzgar, 2008), this value being sensibly higher than the median value of the Ni content in European topsoil (18mg/kg) or subsoil (21.8mg/kg) provided by Salminen et al. (2005).

In the studied area, Ni displays strong correlations with Co (0.95) and V (0.85).

Rudnick and Gao (2004) estimated a value of 59mg/kg for the Cu content in the continental crust. The average contents of Cu in clays, sandstones an limestone are 35mg/kg, 20mg/kg and 6mg/kg, while the average content of Cu in soils is 30mg/kg (Adriano, 2001). In stream sediments, the distribution of Cu is controlled by mafic detritus, secondary Fe and Mn oxides, clay minerals and organic matter.

The median value for Cu contents is 17mg/kg in European stream sediments, 27mg/kg in Japanese stream sediments and 15.9mg/kg in 208 samples of stream sediments from India. In affected areas, such as the Baia Mare mining district, the Cu content may reach 24500mg/kg (Bird et al., 2003).

In the stream sediments from the Jijia Basin, the Cu content ranges between 20.8mg/kg and 77mg/kg, with a median value of 28mg/kg. The threshold value of Cu determined by means of the boxplot method is 47.75mg/kg, which leads to 2 samples being considered as outliers. At the same time, the target value for Cu provided by the Romanian environmental legislation – 40mg/kg – is exceeded by 10% of the samples.

The average content of Zn in the continental crust is 72mg/kg (Rudnick and Gao, 2004). For sedimentary rocks, the average Zn content is 97mg/kg in shale, 30mg/kg in sandstones and 20mg/kg in limestone (Adriano, 2001). The average Zn content in soils is quoted as 63mg/kg by Kabata-Pendias and Mukherjee (2007). In stream sediments, the distribution of Zn is controlled by detrital oxides, such as magnetite, Fe and Mn oxyhydroxides and organic matter.

The median value of Zn contents in European stream sediments is 71mg/kg, while the median value in Japanese stream sediments is 107mg/kg.

The content of Zn in stream sediments from the studied area is between 42mg/kg and 349mg/kg, and the median value is 71mg/kg. The threshold value for Zn determined in the present study is 113mg/kg, while the target value for Zn provided by the Romanian environmental legislation is 150mg/kg. In the stream sediments from the Jijia Basin, only 3 samples exceed the threshold value and only 6.6% of the samples exceed the target limit. Zn has a strong correlation with Pb (0.92).

Rubidium has an average content in the continental crust of 49mg/kg (Rudnick and Gao, 2004). The levels of Rb in sedimentary rocks are of 140mg/kg in shale, 60mg/kg in sandstones and 3mg/kg in limestone (Salminen et al., 2005). The average content of Rb in soils depends on the type of soil, ranging from 10mg/kg to140mg/kg (Kabata-Pendias and Mukherjee, 2007). The distribution of Rb in stream sediments is controlled by sorption processes in clay minerals.

The median value of Rb contents is 70mg/kg in European stream sediments, and 66mg/kg in Japanese stream sediments (Salminen et al., 2005; Ohta and Imai, 2011). Higher levels of Rb are usually reported in areas where acidic rocks are abundant.

In the stream sediments of the Jijia Basin, the Rb content is between 52.6mg/kg and 113mg/kg, with a median value of 79.3mg/kg.

The continental crust has an average Sr content of 320mg/kg (Rudnick and Gao, 2004). Sr is abundant in carbonaceous rocks (460–600mg/kg) due to the substitution for Ca. Argillaceous rocks contain 300–450mg/kg Sr, while sandstones contain 20–140mg/kg Sr (Kabata-Pendias and

Mukherjee, 2007). In stream sediments, Sr is incorporated in detrital feldspars and clay minerals, and is strongly fixed by the organic matter.

The median value of Sr contents in the stream sediments investigated (148.7mg/kg) is between the median value for European stream sediments (126mg/kg) and that of Japanese stream sediments (150mg/kg).

The average content of Y in the continental crust is 19mg/kg (Rudnick and Gao, 2004). In sedimentary rocks, the Y content is largely determined by the abundance of weathering-resistant minerals, such as zircon, xenotime and garnet. Shale (40mg/kg) and greywacke (30mg/kg) are typically rich in Y, compared to carbonate rocks (4mg/kg) and sandstones (15mg/kg). A value of 12mg/kg is quoted by Kabata-Pendias and Mukherjee (2007) as average content of Y in soils. In stream sediments, the Y content is controlled by the abundance of heavy minerals, such as garnet, apatite, titanite, monazite and zircon, and by sorption processes on hydrous Fe oxides and clay minerals.

The median value of the Y contents in the stream sediments from the Jijia Basin (24.8mg/kg) is close to that determined by Salminen et al. (2005) for European stream sediments (25.7mg/kg).

The average content of Zr in the continental crust is 132mg/kg (Rudnick and Gao, 2004). As in the case of Y, the abundance of Zr in sedimentary rocks is determined by the presence of detrital heavy minerals. Typically, greywacke (140–800mg/kg) contains more Zr than shale (100–300mg/kg), sandstones (160–220mg/kg) and limestone (20–130mg/kg). The average Zr content in soils is 300mg/kg (Kabata-Pendias and Mukherjee, 2007).

The median value of Zr contents in the stream sediments investigated (282mg/kg) is between the median value determined by Salminen et al. (2005) for European stream sediments (391mg/kg) and the median value determined by Ohta and Imai (2011) for Japanese stream sediments (54mg/kg).

Rudnick and Gao (2004) estimated a value of 8mg/kg for the average content of Nb in the continental crust. As Kabata-Pendias and Mukherjee (2007) report, argillaceous rocks typically contain more Nb (15–20mg/kg) than sandstones (0.5–10mg/kg) and calcareous rocks (0.05–0.1mg/kg). In stream sediments, the Nb content is largely controlled by the presence of heavy minerals.

The median value of Nb contents in stream sediments from Europe is 13mg/kg (Salminen et al., 2005), while in Japanese stream sediments the median value is 7.2mg/kg (Ohta and Imai, 2011).

In the stream sediments from the studied area, the Nb content varies within a narrow interval (11.05–15.11mg/kg) and has a median value of 12.75mg/kg.

The average content of Ba in the continental crust was quoted as 456mg/kg by Rudnick an Gao (2004), while the average level in soils is 362mg/kg (Kabata-Pendias and Mukherjee, 2007). In sedimentary rocks, the concentration of Ba is related to the abundance of potassium-feldspar and clay minerals, due to the substitution of Ba for K. The Ba content is higher in argillaceous rocks (500–800mg/kg) than in sandstones (20–40mg/kg) and carbonaceous rocks. The distribution of Ba in stream sediments is controlled by the adsorption processes of clay minerals and Fe oxyhydroxides.

The median value of the Ba contents in the stream sediment investigated (353mg/kg) is close to those determined for European stream sediments (386mg/kg) and Japanese stream sediments (410mg/kg). Barium displays good correlations with As (0.62), Sr (0.60) and Y (0.60).

The continental crust has an average Pb content of 11mg/kg (Rudnick and Gao, 2004), while the average content in soils ranges from 15mg/kg to 28mg/kg (Kabata-Pendias and Mukherjee, 2007). Limestone and sandstone (ca. 10mg/kg) are typically depleted in Pb, compared to shale and greywacke (ca. 23mg/kg). In stream sediments, most of the Pb is associated with clay minerals, micas, Fe and Mn oxide precipitates and organic matter (Salminen et al., 2005).

The median value of Pb contents from the stream sediments of the Jijia Basin (19.1mg/kg) is very close to those determined by Salminen et al. (2005) for European stream sediments (20.5mg/kg), and by Ohta and Imai (2011) for Japanese stream sediments (21mg/kg). In the stream sediments investigated, the Pb content is strongly correlated (0.92) with the Zn content.

Usually, compared to the average determined for the continental crust (5.6mg/kg) by Rudnick and Gao (2004), Thorium has a higher content in shale (10–13mg/kg). Sandstones may contain up to 10mg/kg Th (Salminen et al., 2005), while the abundances of Th in soils are between 3.4mg/kg and 10.5mg/kg (Kabata-Pendias and Mukherjee, 2007). The distribution of Th in stream sediments is largely controlled by the presence of heavy minerals and by the sorption processes on clay minerals.

The median value for the Th contents (8.2mg/kg) in the stream sediments from the Jijia Basin is between the median value for European stream sediments (10mg/kg), determined by Salminen et al. (2005), and the median value for Japanese stream sediments (5.4mg/kg), determined by Ohta and Imai (2011). In the investigated area, Th displays strong correlations with Rb (0.83), Y (0.82) and V (0.80).

The average content of As in the continental crust is quoted as 2.5mg/kg by Rudnick and Gao (2004). Regarding sedimentary rocks, higher contents of As are found in shale (13mg/kg), while sandstones and carbonate rocks may contain up to 5mg/kg As (Salminen et al., 2005). In soils, As may reach 67mg/kg, depending on the type of soil (Kabata-Pendias and Mukherjee, 2007). The abundance of Arsenic in stream sediments is mainly determined by sorbing processes related to hydrous oxides of Fe and Mn, clay minerals and organic matter.

The As content in the stream sediments from the Jijia Basin ranges from 7mg/kg to 22mg/kg. The median value of the As content in the investigated area (10.6mg/kg) is higher than both that determined by Salminen et al. (2005) for European stream sediments (6mg/kg) and that determined by Ohta and Imai (2011) for Japanese stream sediments (8mg/kg).

The background limits for As contents in the stream sediments of the studied area reveal the presence of 3 outliers (2 outliers over the threshold value and one outlier under the lower limit of the background). Nevertheless, all the values are below the target limit of 29mg/kg adopted by the Romanian environmental legislation.

Spatial distribution of trace elements

As Reinmann et al. (2008) state, defining the background and threshold value is not complete until the spatial component of the geochemical data is considered. High values of an element may be determined both by geogenic and anthropogenic sources and the contribution of each component has to be evaluated.

The spatial distribution maps for the elements investigated are presented in figures 2 to 17.

The maps have been devised using the Esri ArcGis Desktop platform. The break values considered for defining the content classes are those provided by the boxplot method, namely lower inner fence (1st quartile – 1.5*IQR), 1st quartile, median value, 3rd quartile, upper inner fence (3rd quartile+1.5*IQR), outliers/extreme outliers limit (3rd quartile+3*IQR). Where available, the action limits provided by the Romanian environmental legislation were marked on the map. The color code used includes shades of green for background values, yellow for outliers and orange to red hues for extreme outliers (except where the action limit is exceeded). Shades of gray were used for interpolated areas.

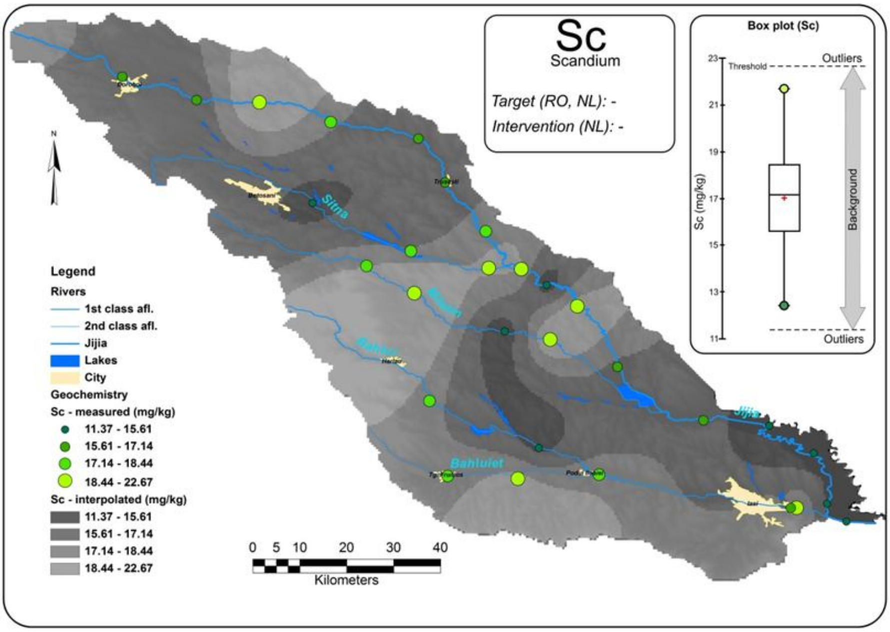

Fig. 2 The distribution of Sc in the stream sediments from the Jijia Basin

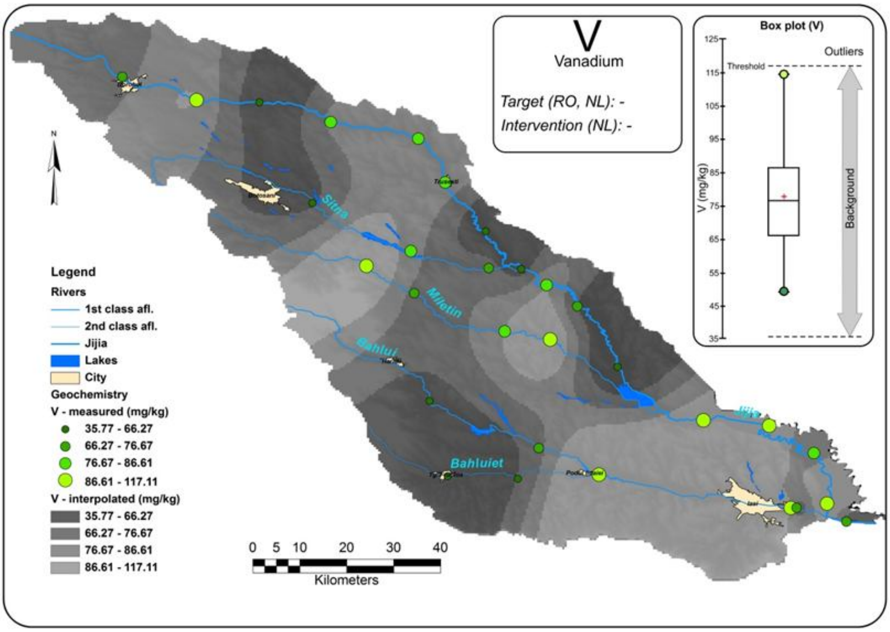

Fig. 3 The distribution of V in the stream sediments from the Jijia Basin.

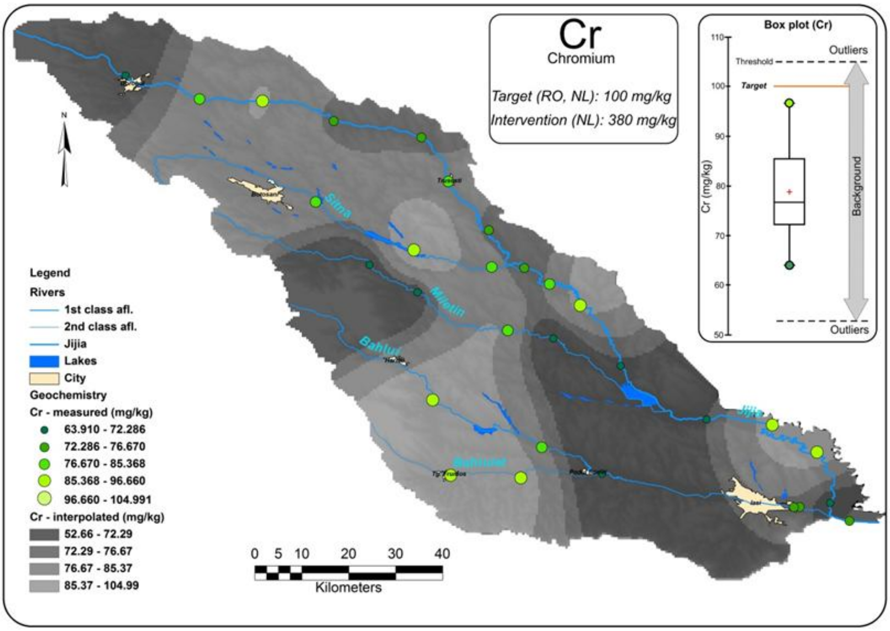

Fig. 4 The distribution of Cr in the stream sediments from the Jijia Basin.

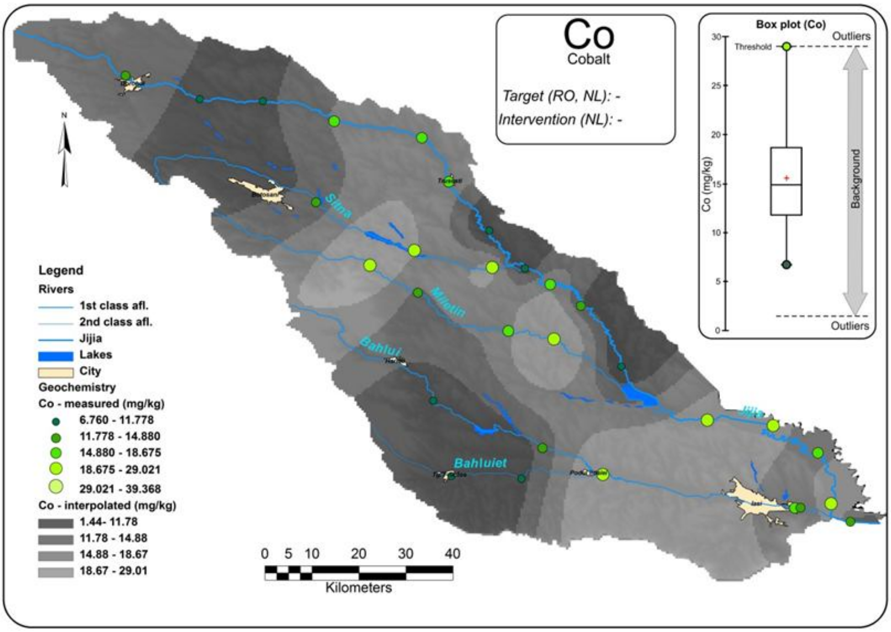

Fig. 5 The distribution of Co in the stream sediments from the Jijia Basin.

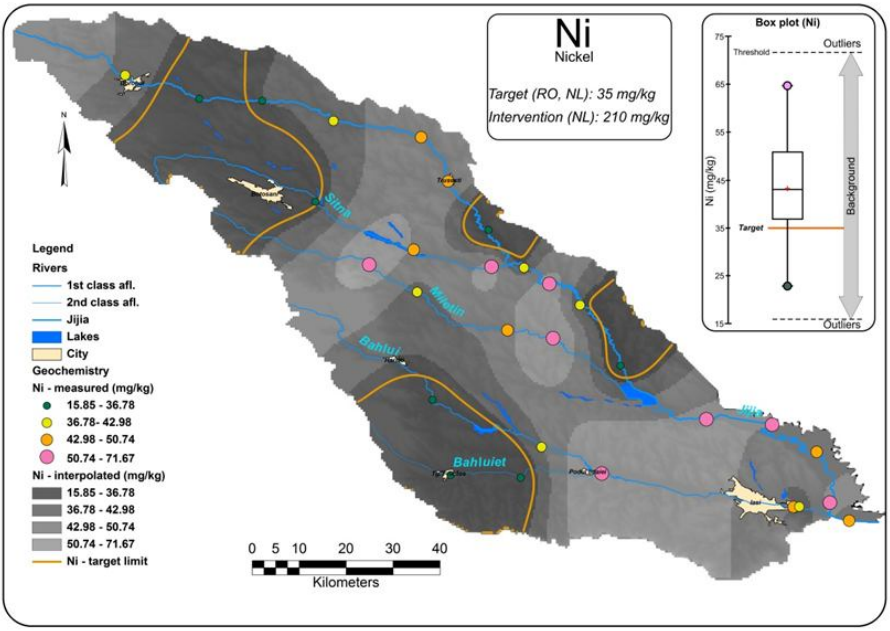

Fig. 6 The distribution of Ni in the stream sediments from the Jijia Basin.

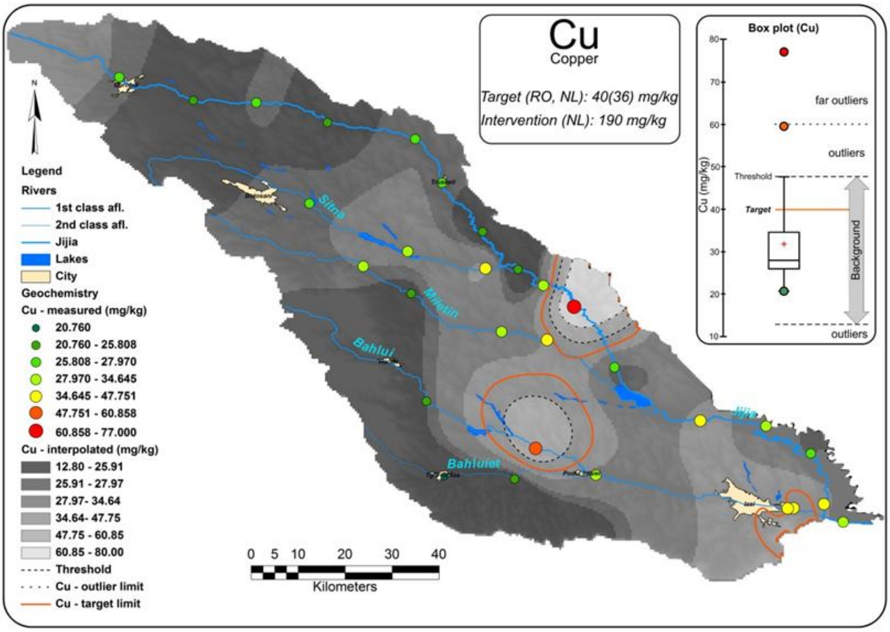

Fig. 7 The distribution of Cu in the stream sediments from the Jijia Basin.

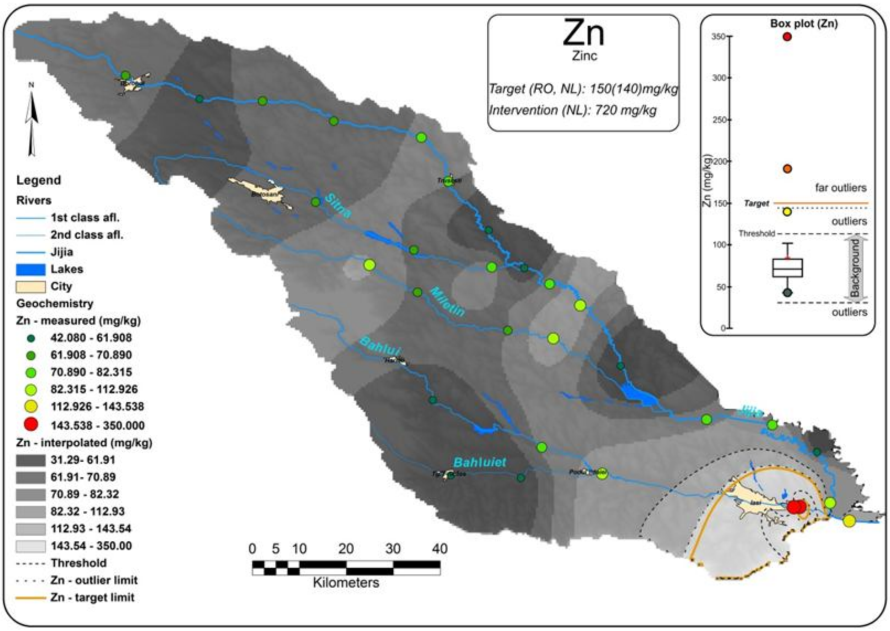

Fig. 8 The distribution of Zn in the stream sediments from the Jijia Basin.

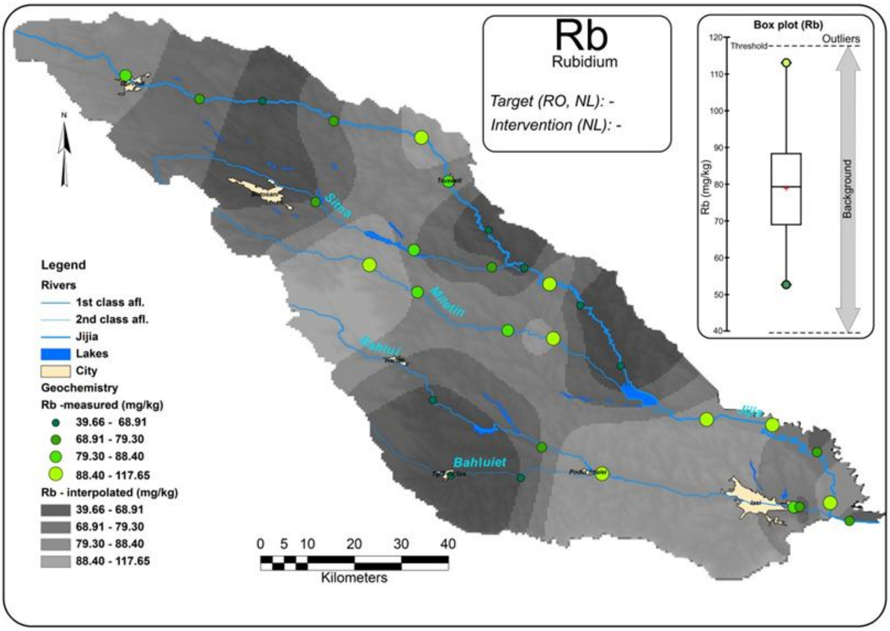

Fig. 9 The distribution of Rb in the stream sediments from the Jijia Basin.

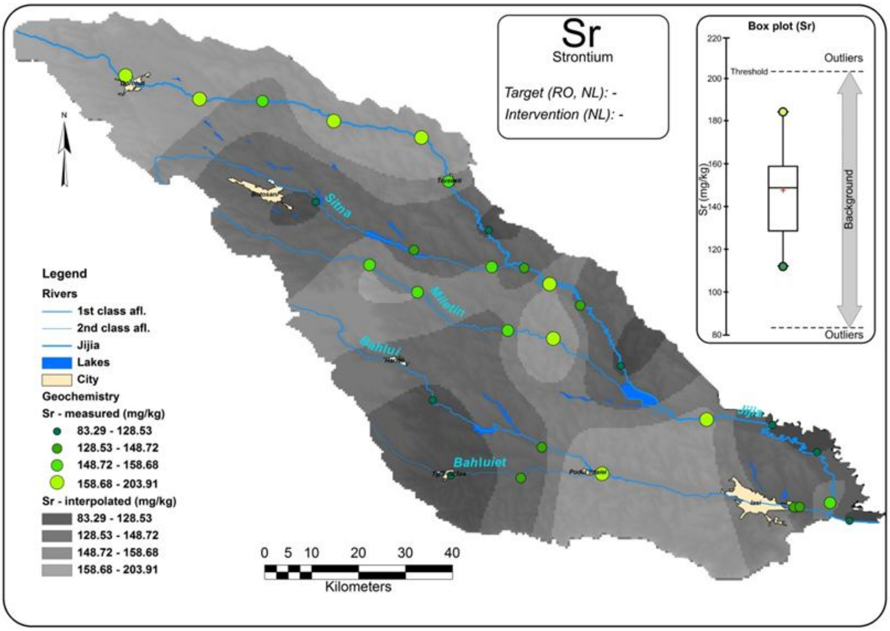

Fig. 10 The distribution of Sr in the stream sediments from the Jijia Basin.

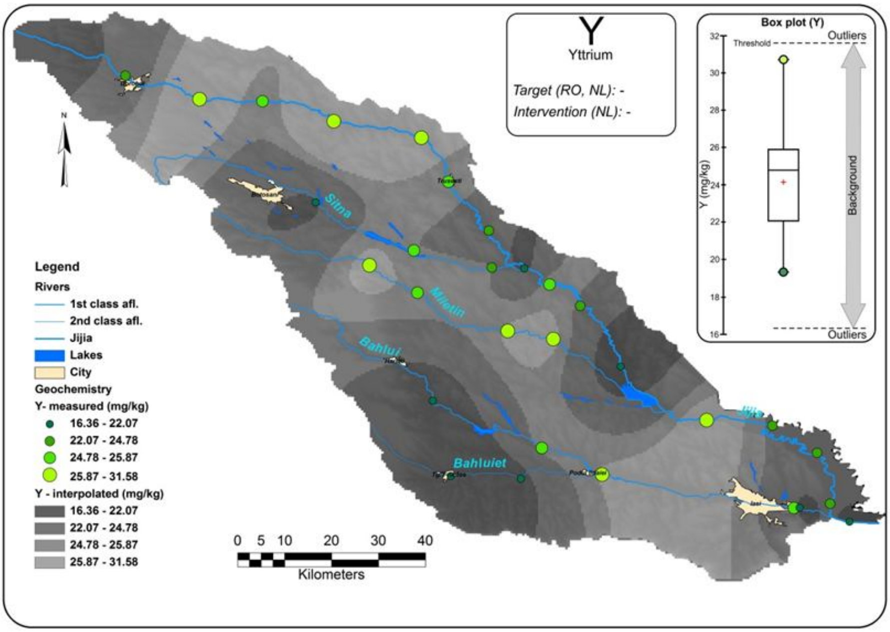

Fig. 11 The distribution of Y in the stream sediments from the Jijia Basin.

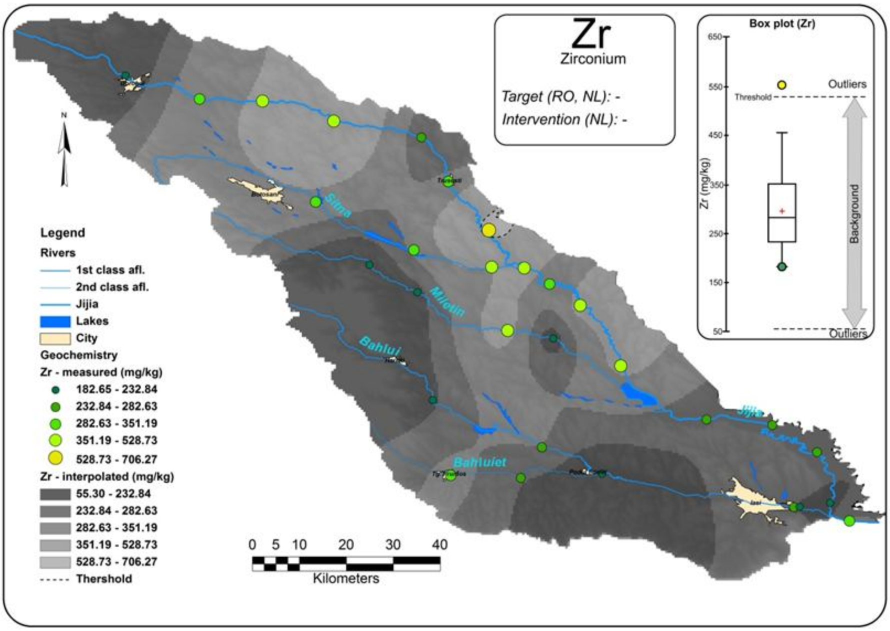

Fig. 12 The distribution of Zr in the stream sediments from the Jijia Basin.

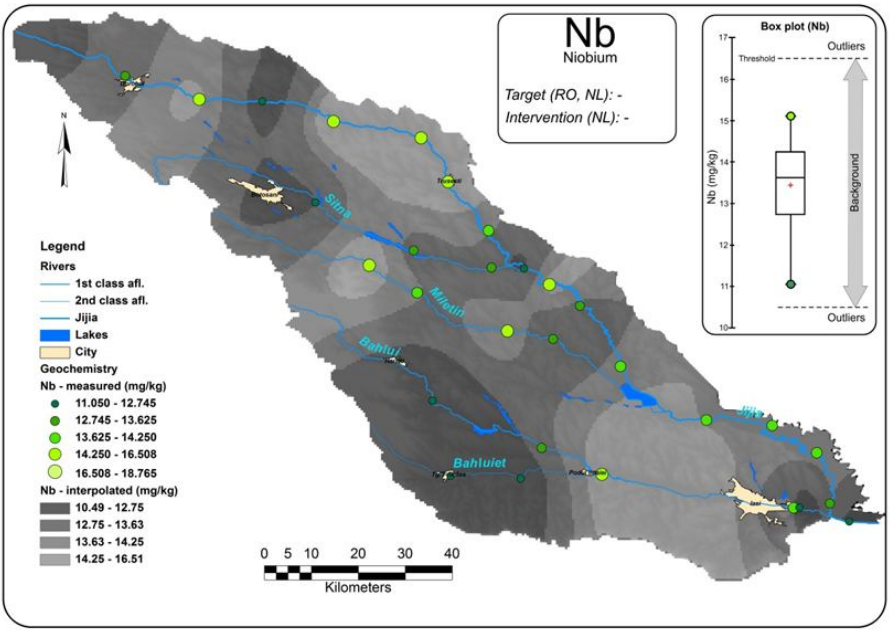

Fig. 13 The distribution of Nb in the stream sediments from the Jijia Basin.

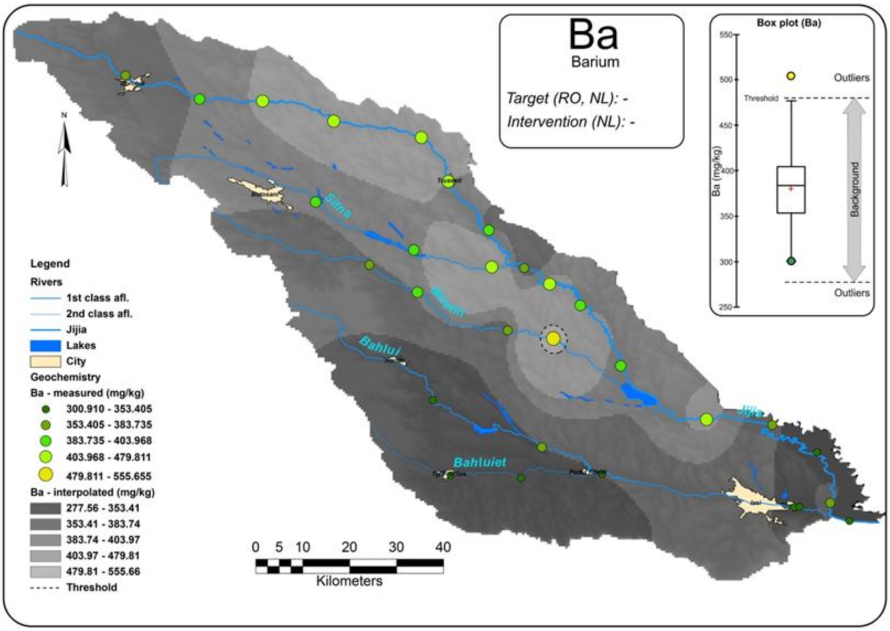

Fig. 14 The distribution of Ba in the stream sediments from the Jijia Basin.

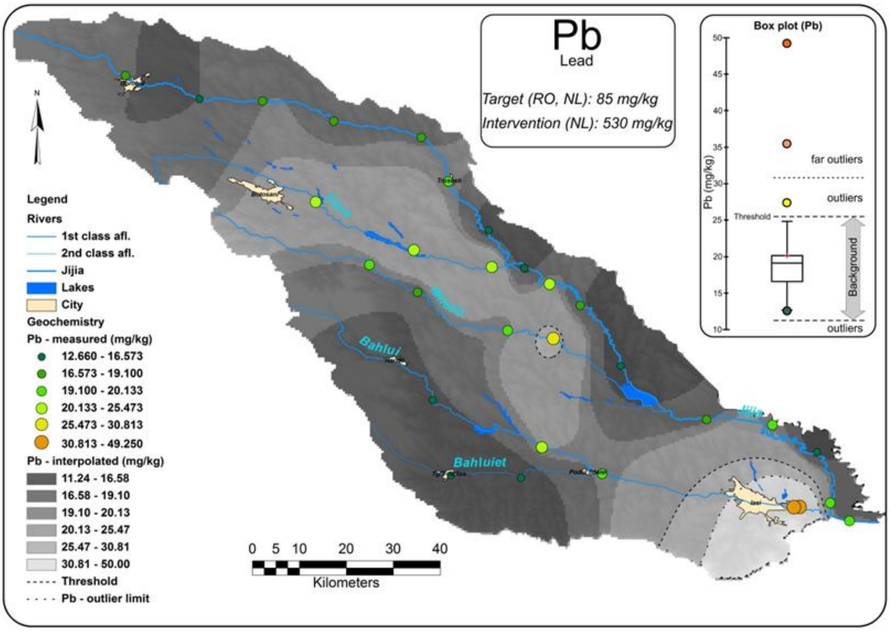

Fig. 15 The distribution of Pb in the stream sediments from the Jijia Basin.

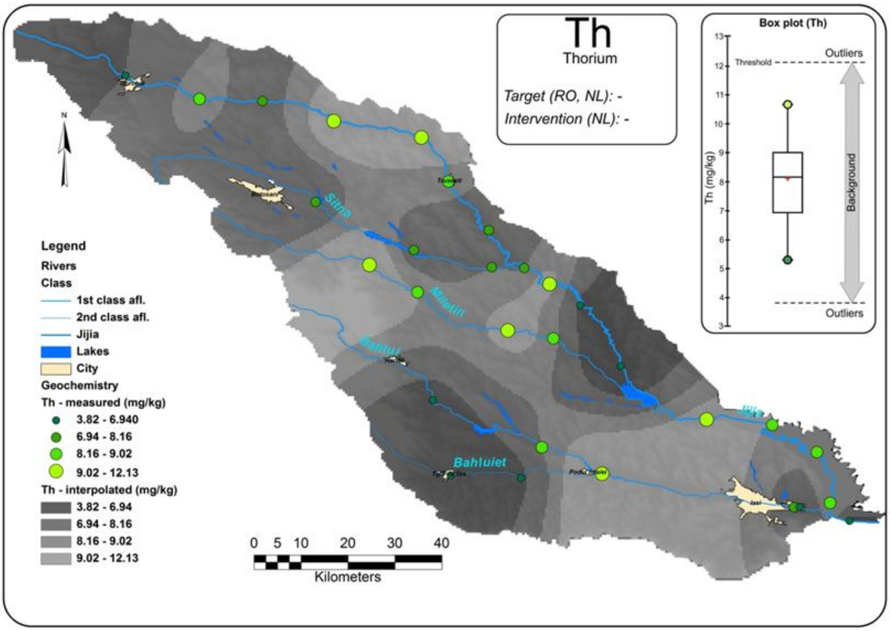

Fig. 16 The distribution of Th in the stream sediments from the Jijia Basin.

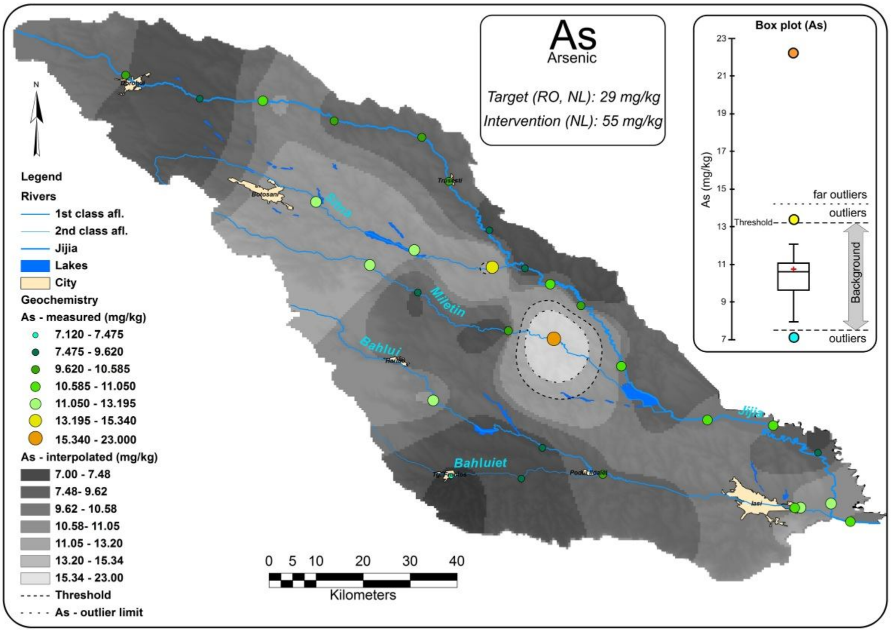

Fig. 17 The distribution of As in the stream sediments from the Jijia Basin.

A number of 10 elements from the 16 investigated, namely Sc (Fig. 2), V (Fig. 3), Cr (Fig. 4), Co (Fig. 5), Ni (Fig. 6), Rb (Fig. 9), Sr (Fig. 10), Y (Fig. 11), Nb (Fig. 13), and Th, follow a normal distributions, with all the values included in the background limits (Fig. 16). For most of these elements, no action limit is defined and we may state that they represent the real background values. The action limits were defined for Cr (Fig. 4), but, even if the threshold value determined in the present study is slightly higher than the target value defined by regulations, no sample exceeds this limit. A particular case is that of Ni (Fig. 6), where over 75% of the samples exceed the target value. Given how large and diverse the area is, there is no reason to believe that the high values are due to the anthropogenic input.

Barium (Fig. 14) and Zr (Fig. 12) also follow normal distributions, but each of them presents one outlier. Although these 2 elements are used in the industry, there is no anthropogenic source in the investigated area and, as a result, we may consider that the outliers are determined by geogenic sources.

The distribution map of Cu (Fig. 7) reveals the presence of two outliers in the central-southern part of the investigated area. Moreover, 10% of the samples exceed the target value. Considering the extensive use of Cu in various compounds, both in agriculture and industry, all these anomalies may have an anthropogenic source.

The distribution maps of Zn (Fig. 8) and Pb (Fig. 15) reveal the presence of an anomaly in the southern part of area, near the city of Iași, but only the Zn target limit is exceeded. The cause of this anomaly is entirely anthropogenic, given the fact that the samples are located at a short distance from the Wastewater treatment plant, the thermal power station and the waste dump, which all act as sources of pollution.

Arsenic (Fig. 17) is the only element investigated which presents an outlier below the background, as well as two outliers above the threshold value. However, there is no situation where the target value is exceeded. The presence of an anthropogenic source for the higher values is not excluded, given the use of As in agriculture (fertilizers, herbicides, insecticides and fungicides) or the contamination of the environment with pig and poultry sewage, but, at least for the minimum and maximum values, other processes seems to be involved. As mentioned above, As is rapidly absorbed by Fe and Mn oxyhydroxides in stream sediments. After checking the contents of Fe and Mn (Pintilei, unpublished work) in all the samples, we noticed that the sample with the lowest As content also displays the lowest contents of Fe and Mn, while the sample with the higher As content also has the highest contents of Fe and Mn. In conclusion, independent of the sources of As, its distribution in stream sediments is largely controlled by the abundance of Fe and Mn oxyhydroxides.

Conclusions

The aim of the present study was to assess, for the first time, the environmental quality in the Jijia Basin, and to determine the background and threshold values for 16 trace elements, some with known toxic effects. The statistical interpretation revealed that all the elements investigated follow normal or log-normal distribution laws, and the median values for the contents of these elements are close to those determined by previous studies. After determining the background, a small number of outliers and extreme values were identified, indicating that the environment in the studied area is unaffected or only slightly affected by the anthropogenic factor. Moreover, the presence of certain anomalies (especially in or near the big cities) suggests that human activities have affected the environment locally. However, in other instances, it was shown that the geogenic factor is also important. Even if in certain cases the target levels were exceeded slightly, the values measured are far below the intervention levels.

For a better assessment of the environmental features of sediments, a more complex study, involving all the components of the environment, is needed. The present study could act like a starting point for such an approach.

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