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The distribution of the major elements in the stream sediments from the Jijia River basin

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Abstract

The aims of the present study are to assess the normal variation limits of nine major chemical elements from the stream sediments of the Jijia river basin, as well as to explain the presence of any anomalous values. Statistical interpretation revealed that Al_2O_3, MgO, Na_2O and K_2O are normally distributed in the investigated sediments, while the Fe_2O_3 contents follow a log-normal distribution. The rest of the components (SiO_2, TiO_2, MnO and CaO) do not follow either normal or log-normal distributions, exhibiting anomalous values. The median values for the contents of most of the major components in the stream sediments from the Jijia river basin are close to both European and Romanian standards for stream sediments. The anomalous values recorded for certain components are determined either by lithological variations (in the case of SiO_2), or by the specific fauna of the Sarmatian deposits (in the case of CaO). The geochemical background, calculated through several methods, has indicated the following values for the geochemical threshold: 71.06% SiO_2, 0.94% TiO_2, 19.15% Al_2O_3, 7.29% Fe_2O_3, 0.165% MnO, 2.87% MgO, 10.77% CaO, 2.39% Na_2O, and 3.54% K_2O.

Keywords: stream sediment, major elements, geochemical background, threshold value, Jijia basin, Moldavian Plain.

Introduction

Stream sediments represent a complex environment, which bears the marks of both the geological formations traversed by rivers, and those of anthropogenic activities.

Starting with the middle of the 20th century, when the fact that the presence of some geochemical anomalies of the elements in stream sediments can lead to the discovery of ore deposits was recognized, great significance has been attributed to geochemical studies carried out on this

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environment. The presence of high amounts of these chemical elements even in the areas where ore deposits are improbable has led to the idea that they can be a useful tool in the assessment of environmental quality.

Normally, the major chemical components of stream sediments are not considered toxic to aquatic life forms, but they could provide important information regarding the distribution of potentially toxic components.

To date, the data on the geochemistry of the major elements from the stream sediments of the Jijia river basin are scarce.

The aims of the present study are to assess the normal variation limits of the major chemical elements from the stream sediments of the Jijia river basin, and to explain the presence of any anomalous values.

Materials and Methods

1. Study area

Jijia is the main tributary of the Prut river. It has, in turn, three major tributaries (Sitna, Miletin and Bahlui), all located on its right, and a catchment basin with an area of about 5760 km^2 (Pintilei and Pintilei, 2011). The entire Jijia river basin is located in the Moldavian Plain (north-western Romania).

In terms of stratigraphy, only Sarmatian (Volhynian and Bessarabian) and Quaternary (Pliocene and Holocene) outcrops are found at the surface of the studied area (Fig. 1) (Ionesi, 1994).

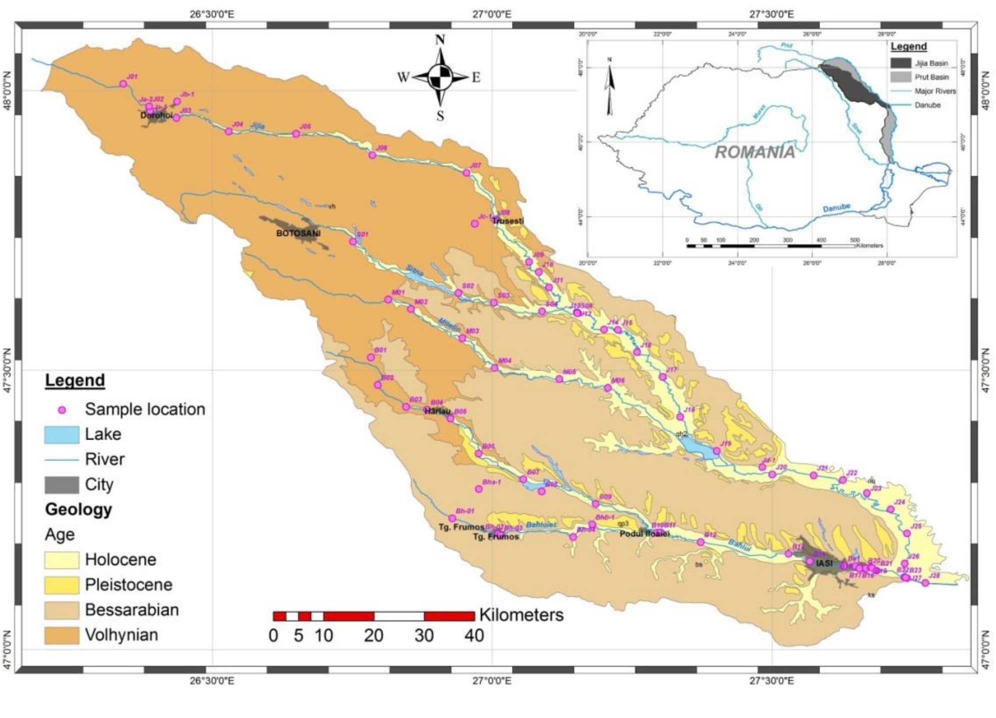

Fig. 1 Geological map of the Jijia River Basin, including samples' locations

The lithology is dominated by clays and silts with intercalations of sand lenses, sandstones, limestone and marlstones (Ionesi, 1994).

From a mineralogical point of view, quartz predominates, followed by alkaline and plagioclase feldspars, carbonate minerals (calcite and dolomite), clay minerals and micas (muscovite and biotite). Locally, iron and manganese oxi-hidroxides become important mineral phases, while biogenic calcite, represented by submilimetric foraminifera tests, is abundant in all the stream sediments investigated (Pintilei, unpublished work).

2. Sampling and analysis

A number of 74 samples of about 3 to 4 kg each (wet weight) were collected from the study area (Fig. 1). After drying and quartering, approximately 100g out of each sample were wet-sieved through the 10 mesh-size (2mm) sieve and retained for further analysis. The resulting material was pulverised by an electric agate mortar to a size less than 0.004 mm. A quantity of 30g from each sample was mixed with 6g of wax and homogenized by means of a planetary mill for 20 min. The mixed material was pressed into aluminium cups at 20t/cm2 in order to prepare two pressed pellets for each sample. The chemical analyses for 9 major components (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O and K_2O) were carried out using a Panalytical Epsylon 5 ED-XRF spectrometer equipped with 15 secondary targets.

Several certified reference materials (LKSD 1-4, STSD 1-4, SO 1-4) were used for calibration, while FP (fundamental parameters) served for error correction.

3. Statistical analysis of the geochemical data

The set of results obtained from the chemical analyses was statistically analyzed using NCSS (NCSS Statistical Software) and the XLStat (Addinsoft) add-in for Microsoft Excel. The graphical representation was achieved using the ArcGIS Desktop (ESRI) platform.

Table 1 Statistical parameters of the contents of major elements (wt%) in the stream sediments of the Jijia River basin

Component	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
No. of obs.	74	74	74	74	74	74	74	74	74
Minimum	40.38	0.25	3.00	2.22	0.07	0.67	4.19	1.03	1.04
Maximum	83.46	0.79	16.78	11.18	0.60	2.50	21.22	2.08	3.20
Range	43.08	0.54	13.78	8.96	0.53	1.83	17.03	1.05	2.16
1st Quartile	59.43	0.52	6.93	3.64	0.09	1.40	6.21	1.42	1.90
Median	61.35	0.62	10.01	4.45	0.11	1.64	6.78	1.62	2.27
3rd Quartile	64.08	0.69	11.82	5.10	0.14	1.99	8.03	1.81	2.56
Mean	61.65	0.59	9.67	4.56	0.13	1.68	7.53	1.60	2.24
Variance	40.49	0.02	10.49	2.28	0.01	0.19	6.69	0.06	0.22
St. dev.	6.36	0.13	3.24	1.51	0.08	0.43	2.59	0.25	0.47
Coef. of var. (%)	10.25	21.20	33.27	32.91	61.72	25.50	34.12	15.45	20.76
Skewness	0.33	-0.69	-0.07	1.38	4.08	-0.01	2.68	-0.10	-0.23
Kurtosis	3.34	-0.41	-0.60	3.97	19.03	-0.63	10.09	-0.78	-0.31
MAD	2.46	0.08	2.34	0.79	0.02	0.31	1.04	0.20	0.33
S-W p (N)	*	0.001	0.528	*	*	0.380	*	0.352	0.719
S-W p (log-N)	*	*		0.429	*		*		

* p<0.0001

Results and discussion

1. Statistical analysis of the contents of major elements

The statistical parameters of the contents of major elements in the stream sediments of the Jijia river basin are presented in Table 1.

By analyzing these data, we can observe that most of the major elements have almost symmetrical distributions, with skewness values close to 0. Only MnO and CaO have a significant positive skewness and kurtosis. Reimann et al. (2008) suggest the use of the Shapiro-Wilk (S-W) normality test in order to verify the normal or log-normal distribution of the data. The p-value calculated for a significance level of 5% indicates that Al_2O_3, MgO, Na_2O and K_2O have a normal distribution, Fe_2O_3 has a log-normal distribution, while SiO_2, TiO_2, MnO and CaO have neither normal, nor log-normal distributions.

2. Assessment of the geochemical background

The phrase "geochemical background" was defined by Rose et al. (1979) as the "normal abundance of an element in unmineralized earth materials." They also stated that the background must be regarded as a range, rather than a unique value, due to the lack of homogeneity of geochemical environments. The upper limit of the background is considered the threshold which separates background values from anomalous values (Rose et al., 1979). Even if the phrase was originally used in the field of geochemical exploration, it was quickly adopted in studies focusing on environment quality. In recent years, several methods have been proposed so as to determine the geochemical background (e.g. Matschullat et al., 2000; Reimann et al., 2005; Galuszka, 2007, Reimann et al., 2008) but there is none that is generally accepted.

In the present study, a combination of histogram, box-plot, normal probability plot and Q-Q plot was used in order to asses the geochemical background, the threshold values and the anomalous values. Additional information was obtained by using interelement correlation diagrams and by investigating distribution maps. A summary of all the operations is presented in Table 2.

As expected, no anomalous value was recorded in the case of the components which follow a normal distribution (Al_2O_3, MgO, Na_2O and K_2O). The highest proportion of anomalous values (outliers) was found in the case of SiO_2 (12.2%), MnO (8.2%) and CaO (8.2%).

Table 2 The limits of the geochemical background (wt%), threshold values (wt%) and proportion of outliers (%)

Component	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
Background									
Lower limit	52.46	0.27	3.00	1.44	0.02	0.52	3.47	0.84	0.92
Upper limit (threshold)	71.06	0.94	19.15	7.29	0.165	2.87	10.77	2.39	3.54
Outliers									
Outliers %	8.1	1.4	0.0	2.7	4.1	0.0	4.1	0.0	0.0
Far outliers %	4.1	0.0	0.0	1.4	4.1	0.0	4.1	0.0	0.0

3. Total content of trace elements

The contents of the major elements in the stream sediments of the Jijia river basin were compared with the results provided by other recent studies.

The average content of SiO_2 in the continental crust is 60.6% (Rudnick and Gao, 2003). In sedimentary rocks, the content of silica is usually high in sandstones (65 to 95%) and conglomerates, and low in limestone and evaporites.

Silicon is the most abundant chemical element in the stream sediments investigated in the present study, its median value of 61.35% being nearly identical to the median value determined by Salminen et al. (2005) for the stream sediments of Europe (61.3% SiO_2), and very close to the median value of SiO_2 contents in Romanian stream sediments (64.4% SiO_2) provided by Andăr et al. (2006). The highest silica contents are recorded in the western part of the studied area (the area with the highest altitudes), and they are linked to the presence of quartz sandstones. Higher contents of SiO_2 are found locally in the eastern part (in the stream sediments of the Jijia river) due the intersection of the river with some sand lenses.

In the continental crust, titanium oxide has an average content of 0.72% (Rudnick and Gao, 2003). The abundance of TiO_2 in stream sediments is generated by the presence of insoluble minerals such as rutile, ilmenite and titanite. Small amounts of TiO_2 are present in Fe and Mg silicates (amphiboles and micas) due to the substitution of Fe^{2+} and Mg^{2+} by Ti^{4+} (Salminen et al., 2005).

The median value of the TiO_2 contents in the stream sediments of the Jijia river basin (0.62% TiO_2) is nearly identical to the median value of 0.625% TiO_2 determined by Salminen et al. (2005) for the stream sediments of Europe, and close to the median value of TiO2 contents (0.72% TiO_2) provided by Ohta and Imai (2011) for 3024 samples of Japanese stream sediments. The median value of TiO_2 contents in Romanian stream sediments (1.15% TiO_2) is sensibly higher.

In the stream sediments investigated, TiO_2 has strong correlations with Al_2O_3 (r=0.92) and K_2O (r=0.94) and with some trace elements (V, Nb, Rb, Cs) which are not, however, presented in the present paper.

Aluminium is the most abundant metal in the continental crust, its average content being evaluated by Rudnick and Gao (2003) at 15.9% Al_2O_3. Aluminium forms numerous minerals (corundum, sillimanite, and kaolinite) and is an important constituent of silicates (feldspars, micas, amphiboles and garnets) (Salminen et al., 2005).

The median value of the Al_2O_3 contents (10.01%) in the stream sediments of the Jijia river basin is close to the median values provided by other studies: 10.3% Al_2O_3 in European stream sediments (Salminen et al., 2005), 10.9% Al_2O_3 in Romanian stream sediments (Andăr et al., 2006), and 10.87% Al_2O_3 in Japanese stream sediments (Ohta and Imai, 2011).

The average content of Fe_2O_3 in the continental crust is quoted as 7.45% by Rudnick and Gao (2003). Iron forms numerous minerals (hematite, magnetite, limonite, siderite, and pyrite) and is an important component of several subclasses of silicates (micas, amphiboles, pyroxenes, garnets). In stream sediments, iron is present in both primary and secondary minerals (oxi-hidroxides).

The median value of the Fe_2O_3 contents in the stream sediments of the Jijia river basin, namely 4.45%, is slightly higher than the median value for Romanian stream sediments (4.33% Fe_2O_3) provided by Andăr et al. (2006). The median value for European stream sediment is 3.57% Fe_2O_3 (Salminen et al., 2005). In the stream sediments studied, Fe_2O_3 has moderate-to-good correlation with Al_2O_3 (r=0.57) and MnO (r=0.70). The iron distribution displays three anomalous values. The microscopic investigation of the samples with anomalous values revealed high quantities of coatings of Fe oxi-hidroxides on the primary minerals.

The average content of MnO in the continental crust is of 0.10% (Rudnick and Gao, 2003). Manganese forms some minerals on its own (piroluzite, manganite, and rodocrozite), but is present more often in iron minerals, due to the substitution. In stream sediments, manganese may by present in the form of oxi-hidroxide coatings on other minerals.

The median value of the MnO contents in the stream sediments of the Jijia river basin (0.11% MnO) is identical to that provided by Andăr et al. (2006) for Romanian stream sediments, but higher than the median value for European stream sediments (0.079% MnO) provided by Salminen et al. (2005). Due to the many similarities and the good correlation, the distribution of MnO generally resembles that of iron.

In the continental crust, magnesium has an average content of 4.66% MgO (Rudnick and Gao, 2003). The median value of the MgO content in the stream sediments investigated (1.64% MgO) is higher than median value of this component in both Romanian stream sediments (1.45% MgO, Andăr et al., 2006) and European stream sediments (1.20% MgO, Salminen et al., 2005). This fact could reflect a higher abundance of magnesium carbonate and phyllosilicatic minerals in the investigated sediments.

The average content of CaO in the continental crust is quoted as 6.41% by Rudnick and Gao (2003). The median value of the CaO contents in the stream sediments investigated (6.78% CaO) is much higher than the median value for Romanian stream sediments (3.33% CaO) provided by Andăr et al. (2006) and the median value for European stream sediments (2.33% CaO) established by Salminen et al. (2005). This high median value is determined not only by the presence of marlstone intercalations, but also by the high abundance of submilimetric foraminifera tests in the Sarmatian sediments which represent the main lithological background of the studied area.

In the continental crust, K_2O has an average content of 1.81% (Rudnick and Gao, 2003). The median value of the K_2O contents (2.27%) in the stream sediments of the Jijia river basin is slightly higher than the median value for European stream sediments (2.01% K_2O, Salminen et al., 2005) and that for Romanian stream sediments (1,72% K_2O, Andăr et al., 2006). The areal distribution of this component generally reflects the abundance of alkaline feldspars and certain phyllosilicates (mainly muscovite) in the studied area.

The average content of Na_2O in the continental crust is quoted by Rudnick and Gao (2003) as 3.07%. The median value of the Na_2O contents (1.62%) in the stream sediments investigated is close to that provided by Andăr et al. (2006) for Romanian stream sediments (1.55% Na_2O), but higher than the median value of Na_2O contents in European stream sediments (0.90%, Salminen et al., 2005). The areal distribution of this component is a complex one, the higher contents reflecting, in part, de abundance of feldspar. However, there are areas that suggest that other mineral phases could also be involved in the distribution of Na_2O.

Conclusions

The aim of the present study were to assess, for the first time, the normal variation limits of the major chemical elements from the stream sediments of the Jijia river basin, and to explain the presence of any anomalous values.

Statistical interpretation revealed that Al_2O_3, MgO, Na_2O and K_2O are normally distributed in the investigated sediments, while the Fe_2O_3 contents follow a log-normal distribution. The rest of the components (SiO_2, TiO_2, MnO and CaO) do not follow normal or log-normal distributions, exhibiting anomalous values. The median values of the contents for most of the major components in the stream sediments from the Jijia river basin are close to those of both European and Romanian stream sediments.

The anomalous values recorded for certain components are determined either by lithological variations (in the case of SiO_2), or by the specific fauna of the Sarmatian deposits (in the case of CaO).

The threshold values determined for the contents of the major components in the stream sediments investigated are the following: 71.06% SiO_2, 0.94% TiO_2, 19.15% Al_2O_3, 7.29% Fe_2O_3, 0.165% MnO, 2.87% MgO, 10.77% CaO, 2.39% Na_2O, and 3.54% K_2O.

It is a well-known fact in geochemistry that trace elements may form their own minerals, but more often they substitute the major elements in minerals. The data obtained as a result of the present study could be used to explain the abundance of certain trace elements in the stream sediments of the Jijia river basin.

References

Andăr, P., Robu, I.N., Nicolescu, R., Siewers, U., Lorenz, H., 2006. Geochemical Atlas of Romania 1:3.000.000. Inst. Geol. Rom., Bucharest, 98p.

Galuszka, A., 2007. A review of the geochemical background concepts and an example using data from Poland. Environ. Geol., **52**, 861–870.

Ionesi, L., 1994. The Geology of the platform units and the North Dobrogean Orogen. Publisher Ed. Tehnică, Bucharest, 280p. (In Romanian).

Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background – can we calculate it?. Environ. Geol., **39**, 990–1000.

Ohta, A., Imai, N., 2011. Comprehensive Survey of Multi-Elements in Coastal Sea and Stream Sediments in the Island Arc Region of Japan: Mass Transfer from Terrestrial to Marine Environments. Advanced topics in Mass Transfer InTech, **17**, 373–398. Online at www.intechopen.com/books/show/title/advanced-topics-in-mass-transfer.

Pintilei, M., Pintilei, C., 2011. The distribution of trace elements in the stream sediments from the Jijia River Basin. An. Şt. Univ. „Al. I. Cuza" Iaşi, Geologie, **57**, 1, 49–67.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Science of the Total Environment, **346**, 1–16.

Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. Statistical Data Analysis Explained. Applied Environmental Statistics with R. John, Wiley & Sons Ltd., England, 343p.

Rose, A.W., Hawkes, H.E, Webb, J.S., 1979. Geochemistry in mineral exploration, 2nd edition. Academic Press, 657p.

Salminem, R., Batista, M.J., Bidovec, M., Demetrias, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.A., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. Geochemical Atlas of Europe. Part I – Background Information, Methodology and Maps, EuroGeoSurveys, 525p.

Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. In Rudnick R. (Ed.), Treatise on Geochemistry (Vol. 3): The Crust, Elsevier, Amsterdam, 1–64.

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