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ASSESSMENT OF POLLUTANTS INPUT OF ACID MINE DRAINAGE AND DOMESTIC ACTIVITIES IN ARIES RIVER WATER, ROMANIA –A CHEMOMETRIC APPROACH

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Abstract

To assess the pollutants input of acid mine drainage (AMD) and domestic activities in Aries River, the water was monitored monthly, during one year, in 15 sampling points along the River. Beside the dissolved metals (Ca, Mg, Na, K, Fe, Cu, Zn, Mn), anions (SO_4^{2-}, NO_3^- and Cl^-), pH and electrical conductivity were analyzed. The obtained data were assessed against the water quality standards and using Principal Component Analysis (PCA) and Hierarchical Cluster Analysis. The results revealed the water contamination mainly with Fe, Mn and Cu. The PCA showed a high variability of the system and revealed the anthropogenic origin of Zn, Mn, Fe and SO_4^{2-} associated with AMD, of NO_3^- and Cl^- associated with domestic activities but also the autochthonous origin of alkaline, alkaline-earth elements, Mn and SO_4^{2-} associated with dissolution of minerals in the river bed. The cluster analysis highlighted the grouping of pollutants according to their sources and the grouping of samples according to locations of ore processing centers. Although most of the mining and ores processing activities in the area have been closed, the Aries River continues to be subjected to pollution with metals coming mostly from waste dumps.

Key words: Aries River, Acid mine drainage, domestic activities, multivariate statistics

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1. Introduction

Surface waters are highly vulnerable to pollution especially in industrial or highly urbanized areas (Giri and Singh, 2014). The European Commission has set quality standards for priority hazardous elements (Cd, Pb, Ni, Hg) in freshwaters, while other potential toxic elements such as Cr, Cu, Fe and Zn are under attention (Crane et al., 2007; EC, 2000). The outcome was an increasing interest for the quality of waters mainly in mining areas (Bird et al., 2010; Canovas et al., 2007; Celebi et al., 2014; Macklin et al., 2006; Modoi et al., 2014; Moldovan et al. 2011; Moldovan et al., 2013; Pulford et al., 2009).

Mining is an important branch of the economy, nevertheless has the potential to affect the nearby environment (Dold, 2008; Frentiu et al., 2008; Senila et al., 2012; Zobrist et al., 2009).

Situated in northwestern Romania, the Apuseni region has both an important economic potential for precious and non-ferrous metals resources and a substantial touristic potential, given the numerous natural reserves and caves there (Constantin et al., 2015; Florea et al., 2005; Levei et al., 2011; Levei et al., 2013; Marin et al., 2010; Ştefănescu et al., 2013).

Underground or opencast mining covered the extraction of auriferous pyrite in Baia de Aries, Cu and Au ores in Rosia Montana, Cu-porphyry ores in Rosia Poieni and Fe ores in Masca Baisoara. Ores were processed by flotation and gold was extracted by cyanide leaching in Baia de Aries.

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Currently, all the mines and ore processing facilities are decommissioned or in conservation except the opencast Cu mining at Rosia Poieni. A renewal of opencast mining of Au-Ag at Rosia Montana is expected (Ioan and Carcea, 2014).

The intensive exploitation of ores in the past and poor management of the resulted mining waste deposited in tailing ponds and waste dumps, some of them very close to the Aries River, led to severe historical pollution and destruction of the catchment ecosystem (Bird et al., 2005; Buza et al., 2001; Friedel et al., 2008; Levei et al., 2013).

Previous studies on Aries River revealed the water enrichment in a large number of elements mainly in the section that cut across the mining area (Friedel et al., 2008; Milu et al., 2002; Ozunu et al., 2009). The existence of two river sections were defined: a low polluted section upstream and a more polluted section downstream of Baia de Aries that decline downstream with the distance (Bird et al., 2005; Marin et al., 2010).

The metals bioavailability in waters was studied by Senila et al. (2015). However, the comparison of chemical parameters of the water with quality standards does not allow the identification of the complex relationships among different parameters nor reflect the multivariate dimension of natural systems like river waters, especially those impacted by multiple pollution sources.

The multivariate statistical methods allow the understanding of complex water quality data, contaminants grouping according to their sources and the sampling sites grouping according to their characteristics (Spanos et al., 2015). The release of toxic elements by studying the tailings mineralogical and chemical composition and the enrichment of Cd, Cu, As, Zn, Pb and Ni in the river sediments was observed using contamination indices while multivariate statistics enabled the identification of metals origin in sediments (Levei et al., 2013; Levei et al., 2014; Milu et al., 2002).

The aim of this paper was to develop a strategy for determining the anthropogenic and natural sources of pollution in the Aries River using quality standards and multivariate statistics. For this purpose the dissolved metals (Ca, Mg, Na, K, Fe, Cu, Zn, Mn), anions (SO_4^{2-}, NO_3^- and Cl^-), pH and electrical conductivity (EC) were analyzed monthly during one year. Some of these parameters as Fe, Cu, Zn, SO_4^{2-} are related to mining and could be an indicator of acid mine drainage (AMD), others as NO_3^- and Cl^- are related to domestic activities, while the alkaline and alkaline-earth elements appears naturally in the surface waters and could be an indicator of the geological background.

These tracers were chosen as they have high and constant levels and are relatively free from anthropogenic influences (Stanimirova, 1999).

2. Experimental

2.1. Site Description and Sampling

The Aries River (164 km length, 24 m^3 s^{-1} average flow rate) collects its tributaries on an area of around 3000 km^2 (Forray and Hallbauer, 2000). The catchment is characterized by a diverse lithology, including igneous (porphyritic andesite) rocks, metamorphic rocks (mica, chlorite, hornblende, and pyrite) with small veins of $CaCO_3$ and sedimentary rocks (Florea et al., 2005; Forray and Hallbauer, 2000). The river crosses a mining area where precious (Au, Ag) and non-ferrous metals (Cd, Cu, Pb, Zn) have been mined since Roman times and reached the peak of production during the 19th century (Borcos and Udubasa, 2012) and two towns (Campeni and Baia de Aries) and several villages with a total population of 40000.

Water samples were collected monthly, between March 2011 and February 2012 from 15 sampling points along the Aries River over a distance of 92 km (Fig. 1).

The sampling scheme covered the following sectors: (i) upstream of Campeni, outside of the anthropogenic pollution sources (S1-S3); (ii) upstream of Baia de Aries, impacted by tributaries containing acidic waters (S4-S6); (iii) downstream of Baia de Aries, where several tailing dumps are located near the river (S7-S11) and (iv) downstream of the mining area (S12-S15).

Samples were also collected from three of the most polluted tributaries (Abrud- T1, Muscani- T2, Sesei- T3), since the previous data (Bird et al., 2005) identified them as the key pollution sources of the Aries River with AMD caused by tailing ponds exposure to rainfall.

2.2. Analytical methods and instrumentation

The dissolved metals in the river water were determined after removing the particulates with a 0.45 μm filter followed by mineralization with 5 mL ultrapure grade 65 % HNO_3 (Merck, Darmstadt, Germany) to 100 mL water. Ca, Mg, Na, K and Fe were determined by inductively-coupled plasma optical emission spectrometry (ICP-OES) using the OPTIMA 5300DV multichannel spectrometer (Perkin-Elmer, Norwalk, USA), Cu, Zn, Mn by ICP mass spectrometry (ICP-MS) using the ELAN DRC II Spectrometer (Perkin-Elmer Sciex, Toronto, Canada). Anions were quantified directly in the filtered water by ion chromatography using the 761 Compact IC (Metrohm, Herisau, Switzerland).

The accuracy of metals determination was tested by analyzing NIST 1643e freshwater (National Institute of Standards and Technology – NIST, Canada), while that of anions using the BCR 616 artificial groundwater certified reference sample (Institute for Reference Materials and Measurements, IRMM, Belgium). Recovery degrees ranged between 95-103 % for metals and 98-100 % for anions.

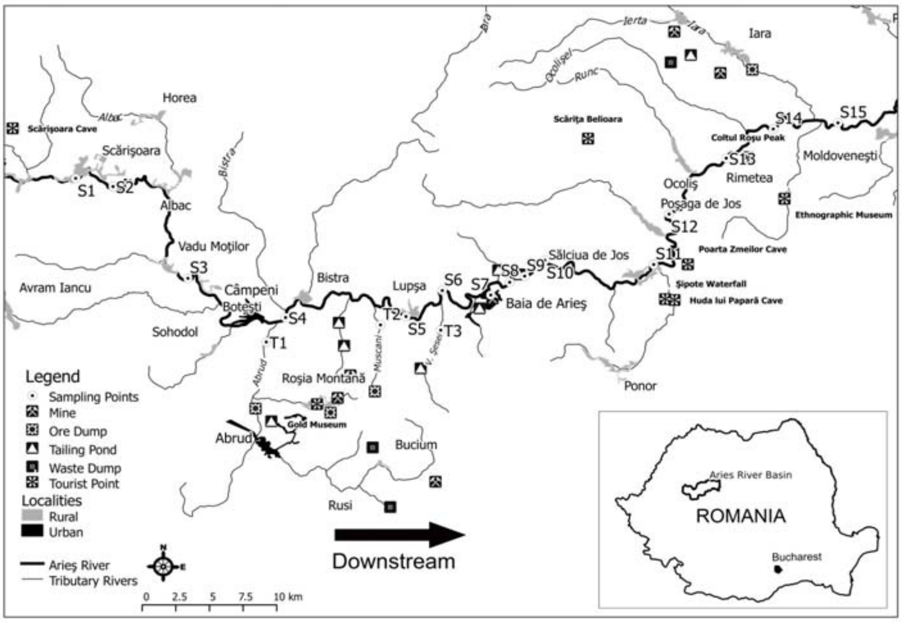


Fig. 1. Map of mining facilities, sights and sampling points of Aries River. S1- Aries in Scarisoara, S2- Aries in Albac, S3- Aries in Vadu Motilor, S4- Aries after confluence with Abrud River, S5- Aries after confluence with Muscani River, S6- Aries after confluence with Sesei River, S7- Aries in Baia de Aries, S8- Aries after confluence with Sartas, S9- Aries in Brazesti, S10- Aries in Brazesti, S11- Aries in Salciua, S12- Aries in Posaga, S13- Aries in Vidolm, S14- Aries in Rimetea, S15- Aries in Moldovenesti, T1-Abrud River, T2-Muscani River, T3-Sesei River

2.3. Statistical analysis

The Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) are important classification and modelling tools for water chemistry data, since they are very efficient in identifying sources of pollutants and detecting similarities or dissimilarities between sites (Frentiu et al., 2009; Levei et al., 2009; Levei et al., 2014; Papazova and Simeonova, 2013; Pejman et al., 2009; Shrestha and Kazama, 2007; Spanos et al., 2015; Zhang et al., 2008). PCA allows data reduction by introducing new variables named principal components (PC's) that are weighted linear combinations of the original variables and describes the original data set with minimum loss of information. Generally, PC's with eigenvalue higher than 1 are retained and subjected to varimax rotation (Giri and Singh, 2014; Oketola et al., 2013; Spanos et al., 2015). HCA allows objects classification based on their properties by detecting similarities or dissimilarities within the objects and grouping successively the most similar objects to construct a dendrogram. The objects within a group are related to one another and unrelated to the objects in other groups. The clustering is effective when the similarity within a group and the difference between groups are high (Oketola et al., 2013; Spanos et al., 2015). For the HCA the Ward linkage method using squared Euclidian distance as a measure of similarity was used.

For the PCA and HCA analysis data was *z*-scale standardized (mean = 0; variance = 1) in order to avoid misclassifications arising from the different orders of magnitude. The statistical treatment of data was performed using Microsoft Office Excel 2007 with XLSTAT plug-in (Addinsoft).

3. Results and discussion

3.1. Monitoring data

Descriptive statistics of the annual average (March 2011 - February 2012) chemical parameters of water in the Aries River compared to the annual average quality standards (AA-QS) for dissolved metals (Crane et al., 2007) are presented in Table 1. Concentrations of Fe, Zn and Cu in the Aries River were 9 - 65, 6 - 17 and 1.2-10 times higher than the AA-QS values. The large standard deviations associated to EC, Cu, Zn, Fe, Mn, SO_4^{2-} revealed a high variability of these parameters during the monitored period. Results in Table 2 show higher levels for Cu, Zn, Mn, Fe and SO_4^{2-} in the studied tributaries than in the Aries River water. Diagrams in Fig. 2 show large variations in the water quality parameters among sampling points along the Aries River relative to the distance from the pollution sources. This fact can be explained on the one hand by the variable flow rate of polluted tributaries and on the other hand by the dilution effect of some tributaries that deliver uncontaminated waters in the Aries catchment. Moreover the high pH of the water (7.34-8.00) favors the adsorption of dissolved metals.

In accordance with the Romanian environmental law 161/2006 (MEWM, 2006), the surface waters are classified in five quality classes in terms of ecological status. At the time of the study the Zn concentration in the water of the Aries River corresponded to class II – good quality (100-200 μg L^{-1} Zn), those of Mn and Fe to class III-fair quality (100-300 μg L^{-1} Mn and 500-1 000 μg L^{-1} Fe), while that of Cu to class IV-poor quality (50-100 μg L^{-1} Cu). Pollution with these elements was found upstream of Baia de Aries and no improvement of the ecological status was observed downstream. The content of anions corresponded to class I- very good (Cl^- < 25 mg L^{-1}; NO_3^- < 4.4 mg L^{-1}; SO_4^{2-} < 60 mg L^{-1}). Cl^- and NO_3^- showed generally a uniform spatial distribution over the whole river length, while SO_4^{2-} presented a pattern similar to that of heavy metals. Overall, the Aries River water was found to belong to class IV-poor quality as established by the worst quality parameter (Cu). The three tributaries of the Aries River considered in the study were much more polluted, which classified waters in class V- very poor quality.

The concentrations of metals found in the present study were comparable with those reported by Senila et al. (2015) but higher than those reported by Marin et al. (2010) and Bird et al. (2005) for the same area. Compared to other mining areas, our results were, one order of magnitude lower than those found in Certej River (Zobrist et al., 2009), comparable in case of Fe and much higher for Cu, Zn and Mn than in the Upper Isle River, France (Grosbois et al., 2009), and in the same order of magnitude as those from Tinto River (Nieto et al., 2007), except for Mn that was higher in our study.

3.2. Multivariate statistics

Correlation analysis is commonly used to assess the natural or anthropogenic origin of elements in sediments and surface water. Several physico-chemical characteristics of surface water such as pH, EC and the salt content (Na, Mg, Ca, K) can be used as tracers to identify the natural origin of elements (Kucuksezgin et al., 2008). The Pearson's correlation matrix is presented in Table 3. The correlation matrix do not allow the source apportionment of Cu and Zn, as weak to moderate correlations was found both with tracers (Mg, K, Ca) and pollutants (Mn, Fe). The very weak to weak correlation of Cl^- and NO_3^- with pH and EC and the weak positive correlation with Cu, Zn and Fe could suggest the anthropogenic origin of these anions. The strong to moderate correlations of SO_4^{2-} with all metals under study make impossible to distinguish its origin using this approach.

Table 1. Descriptive statistics of annual average chemical parameters in Aries River water

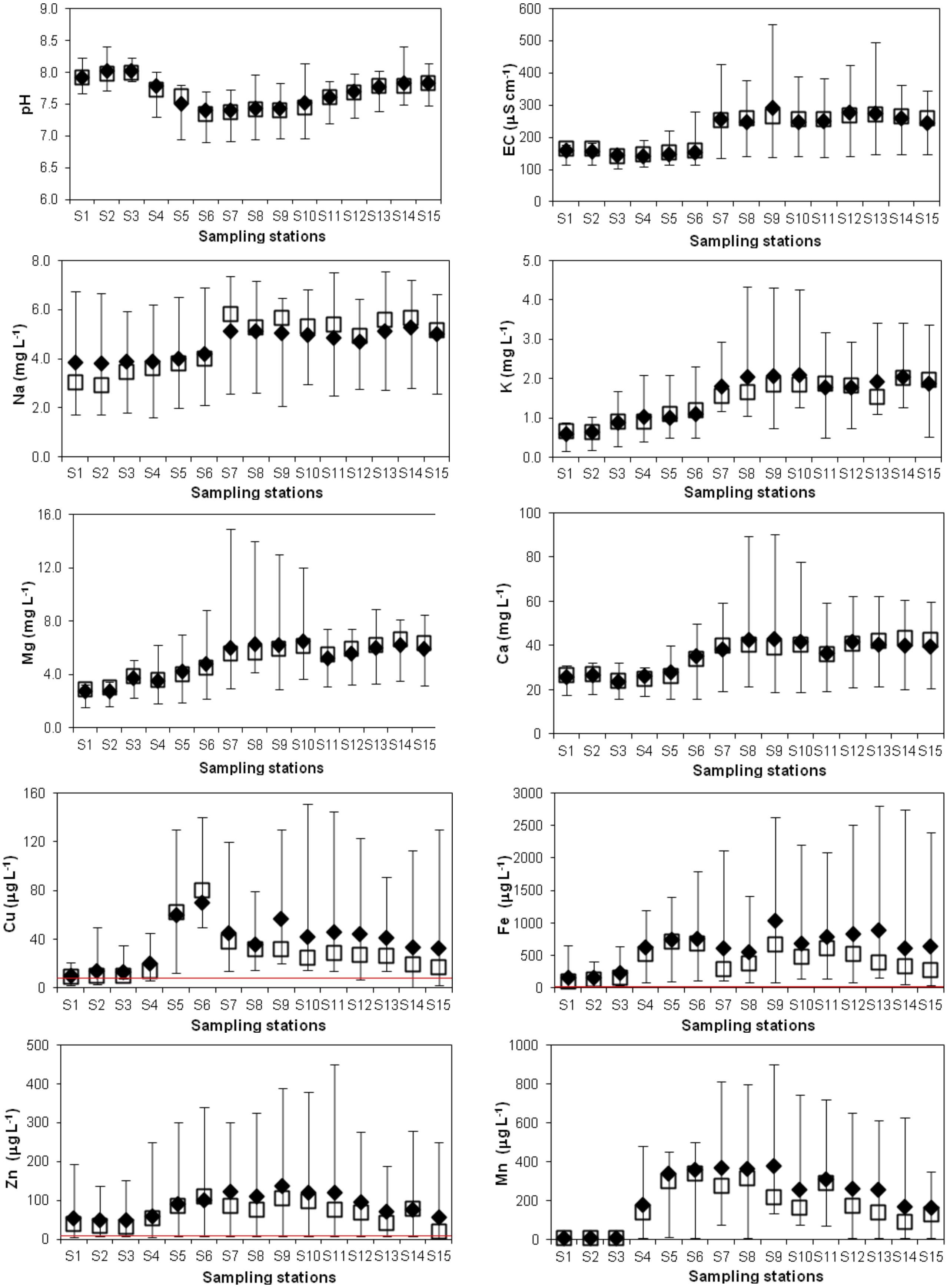
Parameter	***Unit***	***Min.***	***Max.***	***Average***	***Median***	***Std. Dev***	***AA-QS[a]***
pH		7.34	8.00	7.67	7.68	0.23	-
EC	μS cm^{-1}	143	291	219	246	55	-
Cu	μg L^{-1}	10	85	39	41	20	8.2
Zn		50	134	95	95	32	7.8
Mn		10	380	220	260	130	-
Fe		150	1 050	625	650	265	16
Na	mg L^{-1}	3.8	5.3	4.6	4.8	0.6	-
Mg		2.7	6.5	5.1	5.6	1.3	-
K		0.6	2.1	1.5	1.8	0,5	-
Ca		24	43	35	38	7	-
Cl^-		4.7	7.1	5.2	5.1	0.6	-
NO_3^-		1.8	3.1	2.2	2.2	0.3	-
SO_4^{2-}		6	47	36	44	16	-

[a]*annual average quality standard (Crane et al., 2007)*

Table 2. Descriptive statistics of annual average chemical parameters in Aries River tributaries

Parameter	***Unit***	***Abrud***		***Muscani***		***Sesei***		***AA-QS[a]***
		Range	***Average***	***Range***	***Average***	***Range***	***Average***	-
pH		7.02-8.20	7.48	7.12-8.63	7.69	2.79-3.20	3.00	-
EC	μS cm^{-1}	160-275	205	350-670	450	1200-2890	1580	-
Cu	μg L^{-1}	21-155	70	225-2400	1100	5800-12200	8100	8.2
Zn		13-570	160	16-670	170	240-9700	3250	7.8
Mn		55-2640	990	15-550	414	60-2900	2100	-
Fe		370-5600	2950	400-5500	2920	5200-85000	35500	16
Na	mg L^{-1}	1.6-6.2	3.9	5.1-16.0	10.1	3.4-11.0	6.8	-
Mg		2.2-7.3	4.1	4.1-15.0	9.0	9.1-36	20	-
K		0.7-3.5	1.8	1.0-4.2	2.0	2.2-10	4.78	-
Ca		16-28	24	31-77	54	44-148	96	-
Cl^-		2.6-13.0	5.2	8.4-38	17	2.8-11.5	5.3	-
NO_3^-		0.9-3.4	3.2	1.0-4.0	2.9	2-6	3	-
SO_4^{2-}		13-72	44	13-65	50	420-2400	1526	-

[a]*annual average quality standard (Crane et al., 2007)*


pH
EC (µS cm-1)
Na (mg L-1)
K (mg L-1)
Mg (mg L-1)
Ca (mg L-1)
Cu (µg L-1)
Fe (µg L-1)
Zn (µg L-1)
Mn (µg L-1)
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10 S11 S12 S13 S14 S15
Sampling stations

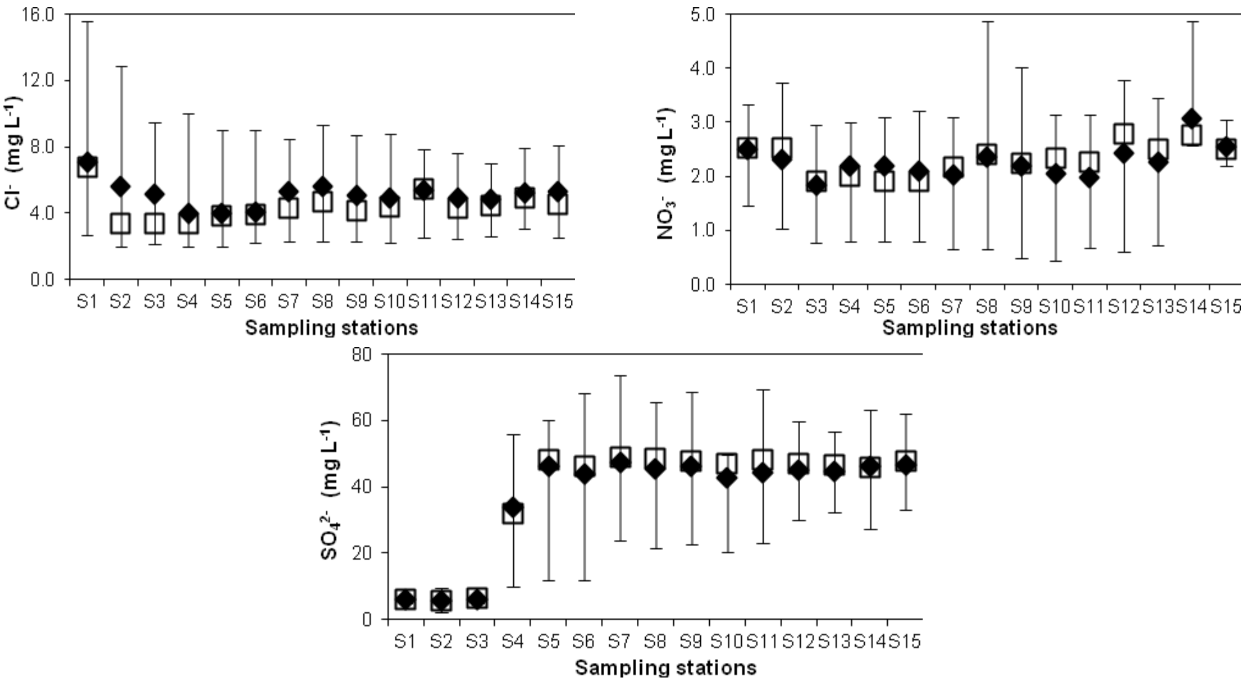


Fig. 2. Spatial distribution of pH, EC, Na, K, Mg, Ca, Cu, Fe, Zn, Mn, Cl^-, NO_3^-, SO_4^{2-} in the Aries River water from upstream to downstream (minimum (-), average (♦), median (□), maximum (-))

Table 3. Pearson's correlation matrix between pH, EC, metals and anions in Aries River (n=141)

	pH	*EC*	*Cu*	*Zn*	*Na*	*Mg*	*K*	*Ca*	*Mn*	*Fe*	*Cl⁻*	*NO_3^-*	*SO_4^{2-}*
pH	1	-0.04	-0.31[b]	-0.38[b]	0.01	-0.23[c]	-0.09	-0.13[c]	-0.29[c]	-0.20[c]	0.03	-0.19[c]	-0.44[b]
EC		1	0.16[c]	-0.05	0.54[a]	0.61[a]	0.63[a]	0.69[a]	0.33[b]	0.16[c]	0.11[c]	-0.13[c]	0.48[b]
Cu			1	0.44[b]	0.41[b]	0.28[c]	0.11[c]	0.19[c]	0.36[b]	0.50[a]	0.30[c]	0.23[c]	0.49[b]
Zn				1	0.12[c]	0.27[c]	0.19[c]	0.17[c]	0.36[b]	0.43[b]	0.09	0.31[b]	0.27[c]
Na					1	0.64[a]	0.52[a]	0.62[a]	0.28[c]	0.38[b]	0.67[a]	0.15[c]	0.44[b]
Mg						1	0.83[a]	0.87[a]	0.45[b]	0.32[b]	0.19[c]	0.06	0.56[a]
K							1	0.85[a]	0.48[b]	0.24[c]	-0.03	-0.12[c]	0.52[a]
Ca								1	0.51[a]	0.25[c]	0.19[c]	-0.01	0.44[b]
Mn									1	0.52[a]	0.09	0.01	0.57[a]
Fe										1	0.25[c]	0.20[c]	0.47[b]
Cl^-											1	0.46[b]	0.13[c]
NO_3^-												1	0.24[c]
SO_4^{2-}													1

Strength of relationship: a–strong (>0.5), b–moderate (0.3-0.5), c–weak (0.1-0.3)

The varimax rotated factor loadings of PC's for pH, EC, metals and anions contents in the water of the Aries River are presented in Table 4. Three PC's with eigenvalues higher than 1 explains 69 % of the system's total variance. The low variance explained by the 3 PC's indicates a high variability of the system and the week correlation between most of the parameters. PC1 is responsible for 40 % of the total variance could be associated with *minerals in the river bed* and reflects the autochthonous origin of alkaline, alkaline-earth elements and partially Mn and SO_4^{2-}.

These elements come from the river bed but may result also from mine tailings impoundments in the Muscani, Sesei, Sartas Valleys or dumps situated very close to the river and exposed to floods (Marin et al., 2010). The presence of SO_4^{2-} within PC1 can be attributed to the jarosite as well as to gypsum, resulted from the oxidation of sulfide minerals. These findings are in good correlation with the distributions of Mg, Ca, K and SO_4^{2-} in water along the river. A detailed discussion about the lithology of the Aries area can be found elsewhere (Forray and Hallbauer, 2000; Friedel, 2008, Levei et al., 2014). PC2 with 17 % of the variance includes the variables negatively correlated with pH and is associated with *AMD* as it explains the anthropogenic origin of Cu, Zn, Mn, Fe and SO_4^{2-}. The lack of the alkaline and alkaline-earth elements of autochthonous origin in this PC ascertains that heavy metals and partially Mn and SO_4^{2-} in the water of the Aries River are of allochthonous origin having as source the left side tributaries. The existence of Fe and SO_4^{2-} together with Cu, Mn and Zn in this factor is the consequence of sulfides oxidation from mine tailings impoundments, which results in AMD with high metal loads (Abbassi et al., 2009; Dold and Fontbote, 2002; Milu et al., 2002). These findings are consistent with pH, SO_4^{2-} and metals contents in the tributaries and with the spatial distribution of these parameters in the Aries River. The analysis of annual data showed higher concentrations of Cu, Fe, Mn and Zn in the Aries and its tributaries during the wet seasons (autumn and winter). PC3 explaining 13 % of the system variability reflects the influence of *forest litter and domestic activities* and attributed to biogenic elements and explains both natural and anthropogenic source of NO_3^- and Cl^-. The absence of heavy metals in this PC suggests that anions are of allochthonous origin, totally different from metals. This origin of NO_3^- and Cl^- in the river water was also observed by other authors (Meybeck, 2003; Valdes et al., 2007). In the Aries River area there is no mineral source of NO_3^- and Cl^- so that these anions come from natural source or human activities other than mining. The natural origin is consistent with forest litter biodegradation, which generates NO_3^- and Cl^- (Haggblom and Bossert, 2003). The monthly distribution showed higher concentrations of NO_3^- and Cl^- in water along the river during winter and spring when the meteoric water leached them from forest litter. The presence of Na in PC3 suggests another possible source of Cl^-, namely NaCl used as antiskid material during winter on the roads in the proximity of the river. The higher Na concentration in water found between November and March supports this statement. The concentration of NO_3^- could be also altered by soil amendment with agricultural fertilizers and sewages, since the area is sparsely urbanized with villages settled along the river.

The dendrogram considering the chemical parameters as objects is shown in Fig. 3. The variables are grouped in 3 clusters similarly to PCA results. The C1 cluster contains EC and the alkali and alkaline-earth elements (K, Ca, Mg) derived from the river bed minerals. C2 includes Mn, Fe, Cu, Zn and SO_4^{2-} coming from the anthropogenic pollution as previously shown, while C3 includes pH, Na and NO_3^-, Cl^-, the last two of biogenic origin or resulting from domestic activities other than mining. Generally, in AMD the Fe, Pb, Cu and Zn are closely associated with SO_4^{2-} as a consequence of sulfides oxidation. The high similarity between Mn and SO_4^{2-} in C2 is probably determined by their both autochthonous and allochthonous/anthropogenic origin. The Mn solubility increase in the presence of high SO_4^{2-} contents, as Mn is released from minerals and reduced to its most soluble form, Mn(II) (Nadaska et al., 2010).

Cluster analysis considering the sampling points as variables is illustrated in Fig. 4. This approach reveals 3 clusters according to spatial distribution of parameters along the river. Cluster (C1) includes samples collected upstream of Campeni, where pollution is not a matter of concern. Sampling points next to the confluence of the Aries River with the tributaries draining acidic waters with high levels of heavy metals are grouped in cluster (C2). The third cluster (C3) contains two subclusters grouping the sampling points immediately downstream of Baia de Aries area, where several waste dumps are located, and points situated far away from dumps, respectively.

Table 4. Varimax rotated loadings of significant PCs

	PC1	***PC2***	***PC3***
Eigenvalue	5.1	2.2	1.6
Variability (%)	40	17	12
Cumulative (%)	40	57	69
pH	-0.047	-0.704*	0.159
EC	0.824**	-0.059	0.073
Cu	0.130	0.638*	0.383
Zn	0.031	0.747*	0.086
Na	0.637*	0.041	0.683*
Mg	0.862**	0.233	0.152
K	0.915**	0.116	-0.082
Ca	0.914**	0.095	0.119
Mn	0.505*	0.579*	-0.055
Fe	0.227	0.623*	0.292
Cl^-	0.072	0.016	0.927**
NO_3^-	-0.220	0.360	0.603*
SO_4^{2-}	0.532*	0.588*	0.123

***strong influence on the latent factor (>0.75); *moderate influence on the latent factor (0.50-0.75)*

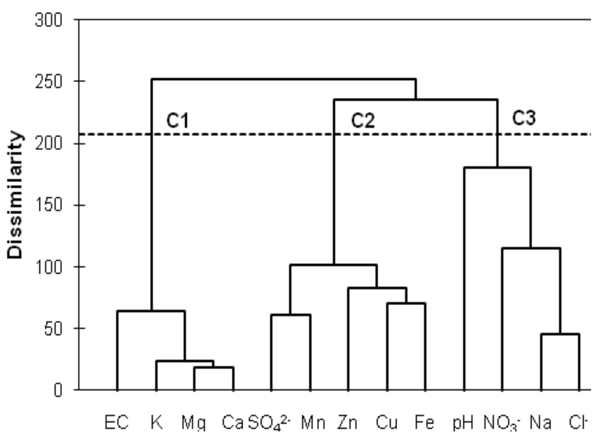


Fig. 3. Dendrogram of chemical variables of the Aries River water

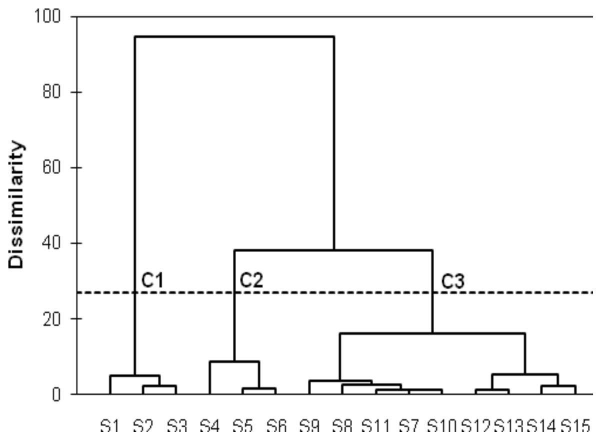


Fig. 4. Dendrogram of sampling locations on the Aries River

4. Conclusions

The Aries River water was found to be polluted mostly with Cu, Mn and Fe, but large variations in the water quality parameters were found relative to the distance from the pollution sources. A number of 3 possible pollution sources of the Aries River water were identified: dissolution of river bed minerals, acid mine drainage and domestic activities. The minerals in the river bed or domestic activities did not result in significant amounts of heavy metals, while the AMD carried by the Aries River tributaries explained the relatively high contents of Cu, Mn, Fe, Zn. The SO_4^{2-} and Mn have both autochthonous and allochthonous/anthropogenic origin. The Cl^- and NO_3^- were found to result from forest litter, fertilizers and sewage effluents. Another source of Cl^- could be the use of NaCl as antiskid material during winter. The PCA revealed that the influence of AMD on the elements input is lower than that of river bed minerals, but the most toxic elements come from the AMD.

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