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HYDROCHEMICAL STUDY OF THE SOURCE REGION OF IER (ER) STREAM IN SATU MARE (SZATMAR) COUNTY, ROMANIA

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ABSTRACT. A one-time environmental analytical study was carried out concerning small watercourses in the source region of Ier (Ér) Stream, a tributary to Barcău (Berettyó) River, in order to explore the extent of contamination and to identify main pollution sources. More than 70% of this land belonged to the marsh of Ier (Ér) before the 1960's when water control of the area resulted in a vast network of well-defined small watercourses. Water and bottom sediment samples were collected from 22 sampling sites on streams. The samples of both types were analyzed in accordance with the current Hungarian Standards. The chemical data were evaluated by principal component analysis and Ward's hierarchical cluster analysis and found to be in good correlation with the geological and hydrological characteristics of the study area. Evidence for anthropogenic contamination was found in 3 water samples out of the 22 collected.

Keywords: Ier (Ér) Stream, environmental status, chemical analysis, principal component analysis, cluster analysis

INTRODUCTION

In the present survey, we interpret data obtained during the chemical analysis of water and bottom sediment samples collected in April 2008 from sampling sites located on small tributary watercourses of Ier (Ér) stream near its source in Satu Mare (Szatmár) County, Romania. The aim of this study was to characterize the environmental status of this region, identify the possible contaminants and find the sources of pollution. The survey has immediate importance, as the residents in the study area live in low-population villages where they are directly and indirectly in contact with the sampled small watercourses every day. In some cases, communal sewage water is led into streams, which cause serious environmental pollution even in small concentrations because of the low water output (Jordao et al., 2007). On the other hand the pollution poses an immediate threat to human health because many watercourses remain the natural source of irrigation and drinking water for domestic animals in this region. In spite of the fact that chemical analyses of natural water samples provide detailed information on their environmental status, certain types of contaminants, characteristically heavy metals tend to accumulate in bottom sediments and preserve environmental history (Nguyen et al., 2009) due to chemical precipitation, coagulation and other sedimentation processes (Salomons et al., 1984). Thus, in order to extensively survey the current extent of pollution in the study area, both water and bottom sediment samples were collected and analyzed (Forstner et al., 1983). Measured contaminant concentrations provide sufficient data for an environmental survey (Temnerud et al., 2005), however, the deviation of some chemical parameters from the well established correlations with geological properties (Skoulikidis et al., 2006) could also carry beneficial information. Statistical methods (Massart et al., 1983) have been proved indispensible in finding correlations between chemical parameters (Singh et al., 2005), which also facilitates the projection of chemical data to geographical characteristics (Lambrakis et al., 2004). For this reason, the chemical data in the present study are first analyzed by principle component analysis and cluster analysis and then the results are compared with hydrogeographical and geographical characteristics of the study area.

Study Area

The ca. 900 km^2 study area, the map of which is shown in Figure 1, lies in the source region of Ier (Ér) Stream that is situated in Satu Mare (Szatmár) County, Western-Transylvania, Romania. The town of Tăşnad (Tasnád) is in the center of the surveyed region, concerned settlements among others are: Andrid (Érendréd), Pir (Szilágypér), Santău (Tasnádszántó), Tiream (Mezőterem), Căuaş (Érkávás), Ady Endre (Érmindszent) and Săcăşeni (Érszakácsi). For an extensive survey, a total of 22 sampling sites were appointed in Ier (Ér) and in its tributary streams (Simeonov et al., 2003). The study area is the easternmost part of the ca. 1600 km^2 Érmellék Region (Benedek, 1996) that includes the catchment area of Ier (Ér) and is bordered by Crasna (Kraszna) River from the north, Nyírség Region from the west, Barcău (Berettyó) River from the south and Munţii Apuseni (Erdélyi-középhegység) Mountains from the south-west. The geography and the geomorphology of this region are characterized by diversity (Benedek, 1960, 1996). Ier (Ér) Stream flows in a ca. 80 km long and ca. 10 km wide valley which is surrounded by several low hills. The bed of Ier (Ér) lies in a rupture that was formed during the Variscan orogeny in the Late Palezoic Era. During the Mesozoic Era massive marly-sand, sandy-clay and clay layers formed from the deposits of the Pannonian Sea. However, these rock

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types can hardly be found near the surface any longer since in the Upper Pleistocene red clay and loes deposited in the region. The rivers Tisa (Tisza), Someşul (Szamos) and Crasna (Kraszna) shaped the region before the Ice age and built large alluviums there. The different classes of soils found in the region are characteristic of the latter mentioned rock types, on which the soils formed, except in the swampy valley of Ier (Ér) where organic-soils evolved.

In its natural form, more than 75% of Érmellék Region was covered by swamps and marshes that evolved ca. 7000 years ago as residues of the floods of Someşul (Szamos) and Crasna (Kraszna). The marshes were finally drained in the 1960s which resulted in the formation of well defined small watercourses throughout the region. The remains of the marshes belong to protected natural areas (Petrişor, 2009). Part of Érmellék is the drainage basin of Ier (Ér) a ca. 80 km long 16 cm/km downfall stream that is the most significant right tributary to Barcău (Berettyó) River.

In Érmellék, many watercourses run through small settlements characteristically of 500-4000 residents. In some cases, natural stream water is used for household purposes; artificial ponds were created in multiple locations and serve as centers for holiday areas. Drainage is rarely established in the region, which increases the risk of contamination of watercourses and groundwater (Jordao et al., 2007). Large industrial plants that could pose a risk of regional environmental pollution are not present in the area but small workshops were found to let sewage water into streams. Animal husbandry is significant in the region (mainly neat, sheep and goat) animals often dip in the watercourses and are watered from there.

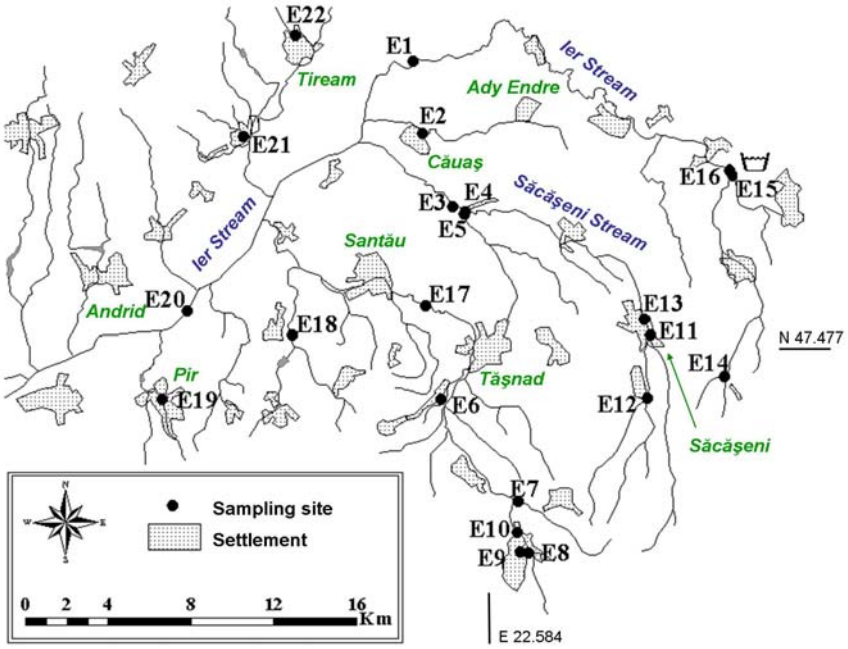

Fig. 1 The study area (Edited by Tünde Fórián)

MATERIALS AND METHODS

Experimental

Sample collection, sample storage and sample analysis both for water and bottom sediment samples were carried out in accordance with the current Hungarian Standards listed in the pertinent laws (Order No. 10/2000, 201/2001).

Water samples were collected in 1 L plastic bottles. The bottles were carefully filled to full capacity and sealed without leaving any air bubbles inside. The samples were refrigerated and stored in the dark. Each analysis was carried out before the elapse of the time limit given in the related standard. Conductivity, pH, Cl^- concentration, chemical oxygen demand with $KMnO_4$ and total alkalinity were determined from the clear samples after settling. Concentrations of HCO_3^- and CO_3^- were calculated from total alkalinity. For elemental analysis, the samples were microfiltered (Millipore 0.45 µM) and the acidified filtrates (1 M HNO_3) were analyzed with a Thermo INTERPID II ICP-OES instrument calibrated with standard solutions. The mass increases of the filter membranes were determined after drying at 90ºC. Concentrations of PO_4^{3-}, NH_4^+, NO_2^- and NO_3^- were determined spectrophotometrically (Avantes AVASPEC 2048) from the filtrates after derivatization.

Bottom sediment samples were collected from 0-5 cm depth and stored in sealable plastic cups in a refrigerator. After removing the coarse debris, 0.1 g samples were digested under normal pressure first with cc. HNO_3 then with 30% H_2O_2. The boiled-down

samples were taken up with 1 M HNO_3 and analyzed with ICP-OES after settling (Somogyi et al., 1997).

Data treatment

Both for water and for bottom sediment samples, the most relevant chemical properties were chosen for mathematical analysis i.e. principal component analysis and Ward's hierarchical cluster analysis (Massart et al., 1983). The correlation between certain chemical properties and the cluster structure of the samples are discussed in the view of the geological characteristics of the study area (Skoulikidis et al., 2006). MS Excel 2003, SPSS 11.5 and instrument controlling software were used for data treatment.

Table 1

Chemical properties of water samples
First line: limit values from Order No. 10/2000, grey background: values above limit, bold: unusual values

	floating mg/100ml	COD_{Mn} O_2mg/l	conduct. mS/cm	pH	CO_3^{2-} mg/l	HCO_3^- mg/l	Cl^- mg/l	PO_4^{3-} mg/l	NH_4^+ mg/l	NO_2^- mg/l	NO_3^- mg/l
		5	*2.5*	*6.5-9.5*			*250*		*0.5*	*0.5*	*50*
E/1	0.244	0.346	0.91	7.73	0.00	477.0	20.79	0.199	0.022	0.000	0.005
E/2	0.384	0.066	0.78	7.53	0.00	275.8	58.03	0.024	0.039	0.011	0.074
E/3	0.505	0.617	**2.13**	7.60	0.00	415.5	472.7	**1.133**	0.179	**0.183**	**0.110**
E/4	0.640	0.444	0.71	7.49	0.00	373.0	29.31	0.034	0.045	0.000	0.007
E/5	0.473	0.798	**2.38**	7.62	0.00	426.4	569.7	**1.333**	0.152	**0.159**	**0.110**
E/6	**5.160**	**1.037**	0.69	7.38	0.00	189.6	86.08	0.516	**0.691**	0.003	0.010
E/7	2.230	0.354	0.69	7.66	0.00	402.3	13.91	0.084	0.195	0.023	0.016
E/8	0.750	0.173	0.65	7.91	0.00	393.1	23.40	0.147	0.131	0.000	0.006
E/9	0.805	0.091	0.78	7.78	0.00	399.4	23.51	0.101	0.265	0.070	0.072
E/10	4.485	0.198	0.75	7.72	0.00	412.6	26.63	0.086	0.214	0.033	0.036
E/11	0.710	0.346	0.63	7.84	0.00	298.8	32.85	0.076	0.163	0.020	0.008
E/12	0.975	0.379	0.59	7.79	0.00	327.6	16.20	0.049	0.089	0.000	0.005
E/13	1.453	0.370	0.59	7.92	0.00	270.1	32.93	0.100	0.179	0.009	0.017
E/14	**7.850**	0.881	0.25	7.36	0.00	114.9	5.11	0.074	0.049	0.000	0.004
E/15	**6.613**	**1.868**	0.42	7.17	0.00	173.0	29.43	0.085	0.308	0.005	0.011
E/16	**7.020**	**4.815**	**11.29**	8.03	**16.39**	**949.4**	**3731**	0.131	0.291	0.000	0.008
E/17	0.650	0.856	**2.66**	7.77	0.00	527.6	619.0	**1.854**	**0.534**	0.020	0.024
E/18	0.375	0.091	0.70	**8.34**	**11.31**	304.6	29.72	0.214	0.076	0.026	**0.190**
E/19	**23.733**	0.181	0.93	8.05	0.00	451.7	38.58	0.618	0.228	**0.191**	**0.201**
E/20	0.750	0.255	0.93	8.11	0.00	333.3	105.2	0.176	0.120	0.004	0.018
E/21	0.400	0.066	0.66	8.27	0.00	381.0	12.49	0.204	0.064	0.000	0.015
E/22	0.850	0.247	0.74	8.02	0.00	408.6	16.73	0.192	0.077	0.019	0.115

RESULTS AND DISCUSSIONS

Water

It can be clearly seen from the obtained analytical data (Table 1 and 2) that several of the samples are contaminated (Adam et al., 2001) mainly with floating material, organic material, heavy metals, PO_4^{3-}, NH_4^+, NO_2^-, NO_3^- or show high salinity. The most contaminated samples were from sampling sites E/14, E/16 and E/19. Site E/14 is in a holiday area, a small artificial pond was sampled through which a stream flows. Floating material contents and concentrations of the elements B, Na, Mg and S were unusually high, although conductivity and organic material content were normal. Building construction took place near the site at the time of sampling, construction debris is supposed to cause the contamination. The sample from site E/16 resembled thermal water more than surface water as conductivity, overall salinity and even Ba concentration were extremely high. We found that the source of contamination was sewage water from a nearby thermal bath that was led to the sampled stream via a small channel. After the inlet, the smell of the stream became characteristic of thermal water and all forms of natural life disappeared from it suggesting that the contamination was permanent. Sample E/19 was collected in Pir (Szilágypér) with higher concentrations of NO_2^-, NO_3^-, PO_4^{3-} and extremely high floating material content. The most probable reason could be chemical fertilizer and/or household washing agent contamination (Jordao et al., 2007).

Anamalous values for chemical properties (Adam et al., 2001) were also found in water samples from sites E/3, E/5, E/6, E/15 and E/17. High salinity and higher concentrations of PO_4^{3-}, NO_2^-, NO_3^- and B were characteristic of samples E/3 and E/5 which anomaly could originate from Tăşnad (Tasnád). Site E/6 is near a heavily used pasture, animal excrement could have caused the higher organic material content, also higher concentrations of Fe and Pb were measured. The composition of sample E/17 is similar to samples E/3 and E/5, differs only in higher NH4+ concentration instead of NO_2^-, NO_3^-, and site E/17 is in another stream that also flows through Tăşnad (Tasnád), which proves that the source of contamination is in the town (Temnerud et al., 2005). The measured chemical characteristics of sample E/15 are not really representative as the water output of this stream was very low.

Table 2

Concentrations of elements in water samples
First line: limit values from Order No. 10/2000, grey background: values above limit, bold: unusual values

	As mg/l	Ba mg/l	B mg/l	Ca mg/l	Cd mg/l	Co mg/l	Cr mg/l	Cu mg/l	Fe mg/l	K mg/l	Mg mg/l	Mn mg/l	Mo mg/l	Na mg/l	Ni mg/l	Pb mg/l	S mg/l	Zn mg/l
	0.01		*1*		*0.005*		*0.05*	*2*	*0.2*			*0.05*		*200*	*0.02*	*0.01*	*85*	
E/1	<0.01	<0.01	0.48	19.47	<0.01	<0.01	<0.01	0.02	0.01	5.30	25.80	<0.01	<0.01	41.2	<0.01	<0.01	28.03	<0.01
E/2	<0.01	<0.01	1.09	24.86	<0.01	<0.01	<0.01	<0.01	0.02	5.76	23.00	0.01	<0.01	56.7	<0.01	<0.01	**32.33**	<0.01
E/3	<0.01	0.1	2.95	**94.23**	<0.01	<0.01	<0.01	0.01	<0,01	17.50	27.85	0.02	<0.01	364.7	<0.01	<0.01	24.65	<0.01
E/4	<0.01	<0.01	0.56	17.00	<0.01	<0.01	<0.01	<0.01	0.07	5.29	23.67	<0.01	<0.01	37.3	<0.01	<0.01	8.51	<0.01
E/5	<0.01	0.1	2.48	**102.33**	<0.01	<0.01	<0.01	<0.01	<0.01	15.20	25.87	0.02	<0.01	345.7	<0.01	<0.01	**32.89**	<0.01
E/6	<0.01	<0.01	0.78	26.32	<0.01	<0.01	<0.01	0.01	**0.58**	18.20	26.48	<0.01	<0.01	39.0	<0.01	**0.01**	6.36	<0.01
E/7	<0.01	<0.01	0.26	20.31	<0.01	<0.01	<0.01	<0.01	0.06	1.99	19.08	<0.01	<0.01	16.0	<0.01	<0.01	4.01	<0.01
E/8	<0.01	<0.01	0.91	14.63	<0.01	<0.01	<0.01	<0.01	<0.01	1.50	26.18	<0.01	<0.01	16.1	<0.01	<0.01	5.67	<0.01
E/9	<0.01	<0.01	0.48	18.34	<0.01	<0.01	<0.01	<0.01	<0.01	4.21	24.81	<0.01	<0.01	21.3	<0.01	<0.01	9.00	<0.01
E/10	<0.01	<0.01	0.47	15.82	<0.01	<0.01	<0.01	<0.01	<0.01	3.32	25.83	<0.01	<0.01	20.3	<0.01	<0.01	7.09	<0.01
E/11	<0.01	<0.01	0.43	31.83	<0.01	<0.01	<0.01	<0.01	0.03	6.07	25.58	0.02	<0.01	28.3	<0.01	<0.01	12.13	<0.01
E/12	<0.01	<0.01	0.30	18.91	<0.01	<0.01	<0.01	0.01	<0.01	5.13	18.78	0.01	<0.01	18.6	<0.01	<0.01	4.39	<0.01
E/13	<0.01	<0.01	0.51	25.02	<0.01	<0.01	<0.01	<0.01	0.02	5.34	19.46	0.01	<0.01	25.0	<0.01	<0.01	9.50	<0.01
E/14	<0.01	<0.01	4.48	9.32	<0.01	<0.01	0.01	<0.01	<0.01	13.48	**61.00**	0.01	<0.01	**455.9**	<0.01	<0.01	11.90	<0.01
E/15	<0.01	<0.01	0.35	52.41	<0.01	<0.01	0.02	<0.01	0.13	10.01	12.49	0.02	<0.01	18.2	<0.01	<0.01	21.65	<0.01
E/16	<0.01	**1.1**	**34.24**	11.95	<0.01	<0.01	<0.01	<0.01	0.09	**71.96**	25.42	<0.01	<0.01	**1926.0**	<0.01	<0.01	5.58	<0.01
E/17	<0.01	0.1	4.04	42.77	<0.01	<0.01	<0.01	<0.01	<0.01	12.81	26.67	0.05	<0.01	386.5	<0.01	<0.01	11.56	<0.01
E/18	<0.01	<0.01	0.42	50.65	<0.01	<0.01	<0.01	<0.01	0.10	3.59	22.13	0.01	<0.01	23.8	<0.01	<0.01	10.97	<0.01
E/19	<0.01	<0.01	0.47	18.65	<0.01	<0.01	<0.01	<0.01	<0.01	9.87	29.32	<0.01	0.01	47.2	<0.01	<0.01	11.09	<0.01
E/20	<0.01	<0.01	1.70	16.49	<0.01	<0.01	<0.01	<0.01	<0.01	6.00	25.12	<0.01	<0.01	97.8	<0.01	<0.01	21.32	<0.01
E/21	<0.01	<0.01	0.36	17.17	<0.01	<0.01	<0.01	<0.01	0.06	0.56	23.03	<0.01	<0.01	16.3	<0.01	<0.01	9.15	<0.01
E/22	<0.01	<0.01	1.44	19.18	<0.01	<0.01	0.03	0.02	0.08	3.07	25.90	0.01	<0.01	18.6	<0.01	<0.01	10.20	<0.01

Table 3

Principal components for the water data matrix

	Principal Component		
	1	2	3
PO_4^{3-}	**0.930**	*0.169*	*0.239*
Conductivity	**0.916**	*0.024*	*0.362*
Cl^-	**0.888**	*0.154*	*0.387*
Na	**0.874**	*0.109*	*0.429*
Mg	**0.647**	*-0.427*	*-0.059*
HCO_3^-	**0.641**	**-0.566**	*-0.058*
COD_{Mn}	*0.136*	**0.920**	*0.133*
Floating	*-0.256*	**0.833**	*-0.215*
pH	*-0.042*	**-0.799**	*-0.092*
NH_4^+	*0.460*	**0.685**	*-0.376*
K	**0.593**	**0.634**	*0.341*
Ca	*0.459*	*0.276*	**0.799**
S	*0.130*	*0.089*	**0.759**
NO_2^-	*0.511*	*0.015*	**0.707**
NO_3^-	*0.093*	*-0.297*	**0.687**
Variance	60.43%	13.72%	10.01%

The following 15 relevant chemical properties were chosen to be the basis of principal component and cluster analyses: floating material content, chemical oxygen demand with KMnO4, conductivity, pH, and concentrations of HCO_3^-, Cl^-, PO_4^{3-}, NH_4^+, NO_2^-, NO_3^-, Na, K, Mg, Ca, S. Samples E/14, E/16 and E/19 were left out from the mathematical analyses because the extreme values from these samples would highly distort the results of the applied mathematical methods (Aruga et al., 1993). More than 84% of the variance of the chemical data matrix of 19 samples is covered by the first 3 principal components. Factors of different chemical properties are listed in Table 3. The conductivity and concentrations of major components of natural waters as HCO_3^-, Cl^-, alkaline metals and alkaline earth metals were categorized into the first principal components. The second principal component includes characteristics that give information on the organic matter content of water samples: floating material content, chemical oxygen demand, pH and NH_4^+ concentration. Chemical fertilizers and washing agents can increase the concentrations of NO_2^-, NO_3^-, Ca and S, characteristics categorized together as third principal component (Singh et al., 2005).

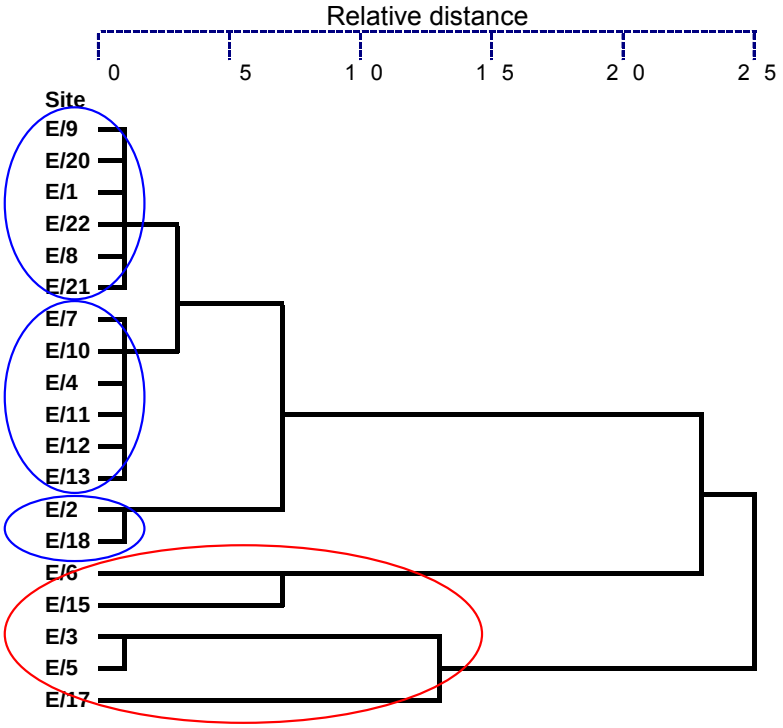

Fig. 2 Water sample clusters in the obtained dendogram

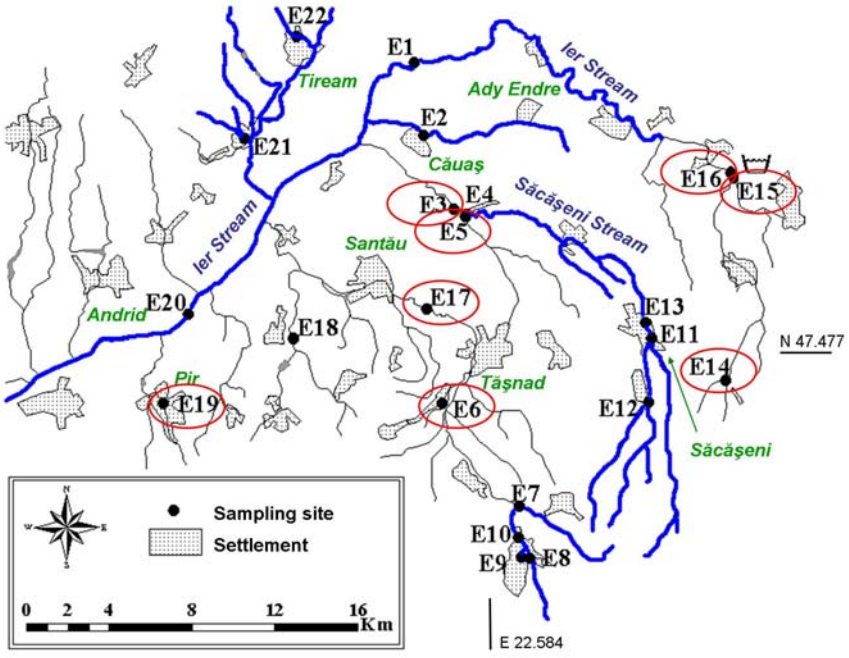

Fig. 3 Spatial distribution of the water cluster structure
Blue line: clear streams, Red ovals: traces of contamination

Ward's cluster analysis classified the 19 samples into 4 clusters. Then dendogram of the cluster structure can be seen in Figure 2. The first 2 clusters represent the hydrographical structure of the study area (Skoulikidis et al., 2006) the fourth contains sites where traces of contamination were detected: E/3, E/5, E/6, E/15, E/17. Samples E/2 and E/18, which form the third cluster, are unique in a way that no other samples

were collected from these two small streams, only the NO_3^- concentration is higher in E/18. The second cluster is the most representative as it includes samples from streams of a common local source area and contaminated samples, in spite of being on the same stream (Al-Khashman, 2008), were excluded from this cluster. For instance it can be clearly seen when Săcăşeni (Szakácsi) Stream is followed from its source through sites E/12, E/11, E/13, E/4 until E/3 that contaminated water from Tăşnad (Tasnád) through site E/5 reaches the stream at site E/3. After Săcăşeni (Szakácsi) Stream flows into Ier (Ér) Stream even traces of pollution disappear because of dilution as the composition of sample E/20 resembles that of E/1 and E/2: all of these three are in the first cluster. The spatial distribution of the sample clusters are visualized in Figure 3.

Table 4

Concentrations of elements in bottom sediment samples

	Al g/kg	As mg/kg	Ba mg/kg	Ca g/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Fe g/kg	K g/kg	Mg g/kg	Mn g/kg	Na g/kg	Ni mg/kg	Pb mg/kg	S g/kg	Sr mg/kg	Zn mg/kg
E/1	20.28	0.36	222.4	12.49	0.44	5.3	17.2	14.61	13.72	3.73	5.49	1.12	0.81	22.0	22.7	3.06	52.93	62.99
E/2	22.34	<0.01	267.1	18.57	0.47	4.7	16.1	15.18	14.76	3.11	5.09	0.66	0.83	18.9	37.3	2.09	67.00	62.78
E/3	23.20	<0.01	347.6	10.37	0.47	8.2	20.5	23.69	15.53	3.39	4.82	0.98	1.88	22.0	33.5	1.07	81.80	117.1
E/4	23.83	<0.01	201.7	7.09	0.56	8.5	24.3	18.94	19.47	3.01	4.82	0.55	0.31	24.2	34.9	0.95	39.78	93.21
E/5	15.57	0.31	213.4	8.11	0.50	8.0	22.1	21.14	15.05	2.21	3.71	0.74	0.46	18.5	34.4	0.68	59.83	91.80
E/6	18.01	2.68	178.6	19.25	0.69	10.9	21.4	34.12	20.52	3.68	5.35	0.85	0.71	22.3	42.7	2.08	71.99	89.25
E/7	9.32	0.20	116.7	4.26	0.14	5.8	5.0	7.93	6.25	1.33	2.46	0.56	0.24	11.0	12.7	0.11	21.91	24.96
E/8	16.88	0.17	138.3	20.66	0.45	10.0	16.1	27.03	16.56	3.26	4.68	0.45	0.27	21.2	29.3	2.08	53.77	62.70
E/9	13.70	0.47	106.6	10.31	0.30	10.0	13.8	13.55	12.94	2.03	3.55	0.34	0.36	19.3	24.8	0.41	32.60	42.62
E/10	19.49	<0.01	128.8	8.45	0.38	9.2	16.8	15.47	16.01	2.62	4.61	0.55	0.12	21.2	27.0	0.28	35.42	57.70
E/11	7.80	1.24	88.2	5.53	0.19	9.9	10.1	6.78	10.92	1.02	1.94	0.50	0.10	12.7	20.4	0.27	21.25	31.43
E/12	15.53	1.59	143.8	4.20	0.04	10.5	9.4	8.92	11.54	2.55	2.89	0.63	0.78	14.4	19.8	0.40	23.58	38.05
E/13	6.59	0.69	99.2	4.07	0.45	15.2	11.0	7.03	10.43	0.92	1.76	0.71	0.12	15.0	20.0	0.16	20.77	193.4
E/14	13.65	0.68	89.1	1.79	0.08	4.9	12.4	9.43	8.67	1.56	1.96	0.18	0.26	10.1	18.7	0.18	13.52	22.47
E/15	17.73	0.13	133.1	3.15	0.30	5.9	16.4	10.37	13.36	2.35	3.11	0.15	0.17	16.5	24.5	0.37	22.63	42.23
E/16	16.80	<0.01	323.4	5.13	0.24	6.7	14.5	11.74	12.58	2.49	3.04	0.13	7.20	16.7	23.4	0.55	128.3	42.40
E/17	9.74	0.32	161.4	4.15	0.09	3.7	5.1	7.66	6.27	1.60	2.58	0.26	1.54	9.7	10.4	0.30	36.30	52.73
E/18	16.84	<0.01	184.2	16.49	0.30	5.6	14.7	14.16	15.41	2.61	3.84	0.77	0.24	18.7	19.6	0.82	51.83	51.19
E/19	11.03	0.69	117.0	7.43	0.29	5.5	9.8	17.12	9.90	2.33	2.97	0.21	0.29	14.9	23.7	0.44	34.04	71.38
E/20	20.34	<0.01	199.3	35.79	0.42	6.0	18.5	12.83	18.45	2.93	5.68	0.63	0.80	22.0	25.1	0.79	104.8	60.65
E/21	16.46	29.59	539.4	23.80	0.66	8.7	9.9	21.86	23.48	4.67	5.57	1.59	0.65	20.0	39.7	1.21	91.34	143.8
E/22	13.96	1.94	206.8	24.63	0.46	5.9	18.1	25.29	13.51	3.06	4.13	2.25	0.38	15.1	17.6	1.09	62.23	117.3

Table 5

Principal components for the sediment data matrix

	Principal Component		
	1	2	3
Ni	**0.936**	*0.079*	*0.182*
Cr	**0.919**	*-0.032*	*-0.065*
Fe	**0.876**	*0.074*	*0.355*
Pb	**0.843**	*-0.006*	*0.257*
Al	**0.799**	**0.467**	*-0.185*
Mg	**0.782**	**0.477**	*0.235*
Cd	**0.754**	*0.020*	**0.548**
Cu	**0.746**	*0.250*	*0.355*
S	**0.707**	**0.476**	*0.271*
K	**0.692**	**0.582**	*0.224*
Ca	**0.578**	*0.347*	**0.495**
Na	*0.049*	**0.842**	*-0.028*
Ba	*0.370*	**0.733**	*0.417*
Sr	**0.517**	**0.681**	*0.311*
Co	*0.277*	**-0.651**	*0.405*
As	*-0.135*	*0.061*	**0.803**
Mn	*0.274*	*0.062*	**0.751**
Zn	*0.393*	*-0.019*	**0.716**
Variance	55.64%	18.52%	9.93%

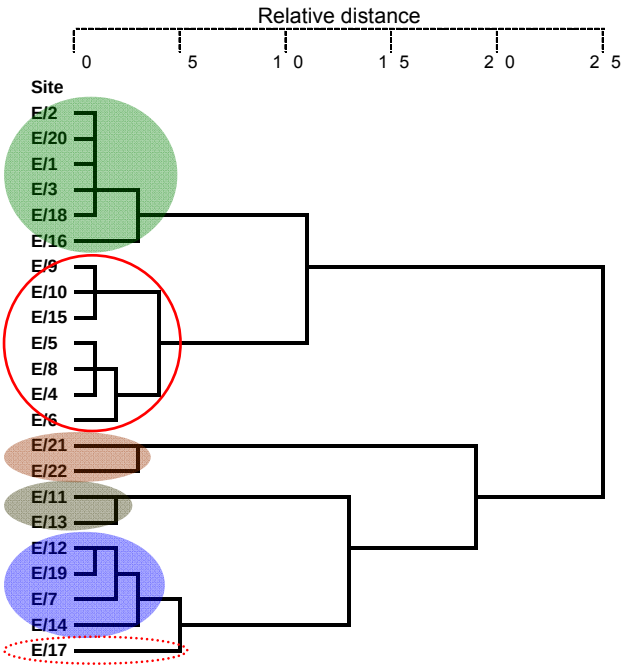

Fig. 4 Bottom sediment sample clusters in the obtained dendogram

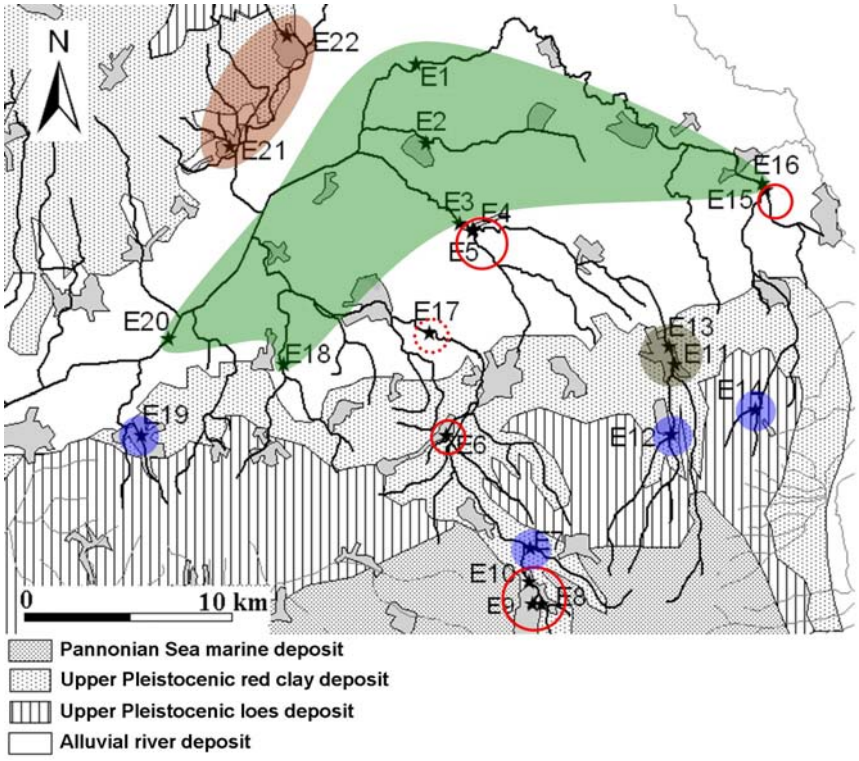

Fig. 5 Spatial distribution of the bottom sediment cluster structure on the geological map of the study area (edited by Tünde Fórián)

Bottom sediment

There are no extreme or unusual values among the measured elemental concentrations of bottom sediment samples and no heavy metal pollution were detected (Table 4). This observation was expected as no accumulated heavy metal contamination was measured in the water samples (Enguix Gonzalez et al., 2000). For principal component analysis and cluster analysis, concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sr, Zn were used. The first 3 principal components characterize more than 84% of the variance of the chemical data matrix. The calculated factors for the concentrations are listed in Table 5. Concentrations of 12 elements contribute significantly to the first principal component making it rather heterogeneous. The second principal component includes the concentrations of Al, alkaline metals and alkaline earth metals that are the main components of Earth's crust. Metals from mainly anthropogenic sources are classified into the third principal component: As, Cd, Zn and Mn (Zhou et al., 2008). The cluster system of the bottom sediment samples is more structured than that of the water samples and correlates well with the bedrock distribution in the study area (Dinelly et al., 2005). The obtained dendrogam is shown in Figure 4 while the spatial distribution is visualized on the geological map of the region in Figure 5. Sampling sites E/1, E/2, E/3, E/4, E/5, E/15, E/16, E/17, E/18, E/20 are situated on alluvial river deposit. These samples, with the exceptions of E/4, E/5, E/15 and E/17, form a closely related cluster. In spite of being spatially far from each other, sites E/12, E/19 and E/7 are also closely related as these are all situated on the border of red clay and loes deposit areas. The only site lying on loes deposit, E/14, is in loose relation with the former 3. Distinct pairs are sites E/21 and E/22 on alluvial river deposit near loes deposit and E/11 and E/13 on loes deposit near alluvial river deposit. Sites E/4, E/5, E/6, E/8, E/9, E/10, E/15 are classified into one loose cluster in spite of being situated on geologically rather different areas that indicates different sediment forming processes in action than in the previous cases (Enguix Gonzalez et al., 2000). Site E/17 is classified relatively distant from every other site in the cluster structure for no clearly understandable reason.

CONCLUSIONS

It can be directly concluded from the present work that a one-time environmental chemical analysis is sufficient for providing basic information on the status of the study area. Samples with chemical properties deviating from the study average were selected both manually and by mathematical methods with the same results by the two approaches: 3 water samples were polluted and traces of contamination were found in 5 more. The quality of the remaining 14 samples was excellent. In spite of the fact that possible sources of environmental pollution were pointed out, we concluded that the residents' attitude towards natural water treatment and usage is environmentally conscious in the source region of Ier (Ér) Stream. Principal component analysis and Ward's cluster analysis proved to be powerful tools to classify environmental samples systematically into closely related groups based on multiple chemical properties. It was found that the mathematically obtained cluster structure of water samples represented the hydrological structure of the study area and the bottom sediment clusters correlated well with the bedrock distribution in the region.

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