We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter 12

Aspects on the Accumulation of Trace Metals in Various Environmental Matrices (Water, Soil, Plant and Sediments): Case Study on Catchment Area of the Somes River, Romania

Cezara Voica, Andreea Maria Iordache,
Roxana Elena Ionete and Ioan Ștefănescu

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/65700

Abstract

A study was carried out to determine the accumulation of trace metals in water, sediments, and soil from several locations in the Transylvania region (Romania), using the inductively coupled plasma mass spectrometry (ICP-MS) technique. A significant number of metals (range of several μg L^{-1}) were identified, the toxic metal concentrations in mostly of the investigated waters being within the permissible limits. A seasonal variation in the metal content was also observed. Comparison of the metal concentrations to samples of sediment, soil, and vegetation coming from the surrounding areas of the same water reservoir revealed a higher accumulation of rare and toxic metals in sediments than in soil and vegetation.

Keywords: surface water, pollution, environmental quality

1. Introduction

The main strategic objective of Romania in the field of water is linked to European integration, which involves harmonization and implementation of the *acquis communautaire* in the field of water quality protection. National Water Law No. 107/1996 [1], updated in July 2015, legally enshrines a novel conception on the status of water (Article 1, paragraph 1):

INTECH
open science | open minds

© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. CC BY

renewable natural resource, vulnerable, and confined; indispensable for life and society (its physical dimension); raw material for productive activities, source of energy, and transport route (its economic dimension); critical element in maintaining the ecological balance (its environmental dimension). The European Union (EU) Water Framework Directive (WFD) [2] establishes a framework for the protection of waters and consists of a new vision for the management of water resources in Europe. Mainly sustained on ecological elements, the ultimate objective of the WFD is the achievement of at least "*a good ecological quality status*" for all surface waters.

According to the estimation of the World Health Organization, about two-thirds of diseases are caused by the polluted water. Through its accession to the EU, Romania has undertaken to comply with the European regulations on water quality [3]. Within the United Nations Environment Programme, which supports the surveillance of water quality in freshwater ecosystems worldwide, by its global system of environmental monitoring (GEMS)/Water Global Network [4], the determination of heavy metals concentration is mandatory when the water quality is assessed.

The proposed subject represents a highly current field; the concentration of heavy metals in water being an intensive subject researched worldwide [5–7]. Some researchers have determined metal concentrations in water, sediment, plant; others have studied the metals effect on live organisms [8–10]. Heavy metals are seen as potential hazard for human health and ecosystem as they cannot be degraded, being continuously deposited and incorporated in water, sediments, soil, and vegetation. Anthropogenic activities may lead to important accumulations of toxic metals into the environment; therefore, the assessment of contamination degree in the aquatic and terrestrial environments by means of elemental analysis became a common monitoring activity of our days.

2. Sample preparation and analytical methods selection for analyzing contaminant elements in environmental samples

2.1. Study area

Somes is a transboundary catchment located in the north-western Romania. Its main sources of water are the surface waters, reservoirs, and ground waters. The overall water resources in the basin are theoretical about 4.348 billion m^3 (of which 4.012 billion m^3 coming from surface waters and 336 million m^3 of groundwater), but only 21.7% are technically usable. In this region, there are 23 reservoirs with areas over 0.5 km^2 such as the Gilau Lake (0.67 km^2), Tarnita (2.2 km^2), Somes Cald (0.8 km^2), and Fantanele-Belis (8.15 km^2).

The main objective of this study was to characterize the surrounding areas of raw water accumulations from the catchment, in terms of its content in heavy metals and rare earth, correlated with the supply mechanism of these surface waters. Thus, an assessment of the quality of surface flowing waters, during 2009–2011, was performed. Waters from eight surveillance sections were sampled: the Gilau dam (Area 1); the Somes Cald River (Area 2); the end of Gilau Lake intersection with the Somes Cald River (Area 3); the Somes Cald Lake (Area 4);

the confluence of Somes Cald Lake with Somes Rece Lake (Area 5); the Somes Rece Lake (Area 6); Tarnita (Area 7); and the end of Tarnita Lake bottom (exit from hydro plant—Area 8). The measurements were made with a variable frequency. Once with establishing the sampling data, we envisaged the possibility to set any correlations between the values of the monitored parameters and the climatic factors. Samples of sediment, soil, and vegetation corresponding to the surface water sampling points were also taken.

2.2. Samples preparation

Water samples were collected in high-density polyethylene containers previously washed in a solution of 10% nitric acid in an ultrasonic bath for 15 min followed by repeated rinsing with bi-distilled water and finally rinsed with ultrapure water (resistivity 18.2 MΩ cm^{-1}). Until sampling, the containers were kept in sealed polyethylene bags. Water samples were stabilized with ultrapure nitric acid (0.5% HNO_3).

Samples of *sediment, soil, and vegetation* require a digestion process to bring them into solution. For inductively coupled plasma mass spectrometry (ICP-MS) analysis, the digestion process should satisfy some conditions: the entire quantity of sample has to be dissolved, only ultrapure reagents must be used, any loss of analyte has to be avoided, the vessels in which the sample is kept must not react with the sample or the reagents used for the digestion, and the entire process should be fast and reliable. The samples were lyophilized, and then, 0.1 g aliquot of each sample was weighed. These aliquots were then digested in an acid mixture (3 ml HNO_3 60% + 2 ml HF 40%) at high pressure and temperature. After cooling, the liquid was transferred through a semi-automatic pipette in a 50 cm^3 volumetric flask of high-density polyethylene and was brought to the required volume with ultrapure water.

2.3. Analytical procedure

The analytical methods used in environmental monitoring have greatly evolved. Inductively coupled plasma mass spectrometer offers fast multielement capabilities, a high dynamic range, and excellent detection limits in a large number of matrices. It can be used for a variety of aqueous samples like natural waters or environmental samples that can be dissolved [11, 12]. The mass spectrometry with inductively coupled plasma (ICP-MS) is among the most successful existing methods applied when concentrations of trace and ultra-trace elements (under ppb) are envisaged [13].

For this work, measurements were performed with a mass spectrometer ICP-MS model Elan DRC-e, Perkin Elmer, with the following characteristics: detection limit 0.001–0.01 μg L^{-1}; resolution <0.5 at 10% peak height; abundance sensitivity 1–5 × 10^{-7}; and precision: <2% at 20 min. The performance of an ICP-MS instrument strongly depends on the operating conditions. Working parameters for plasma were chosen so as to obtain a good compromise between high sensitivity and low oxide levels. The following instrumental parameters of Elan DRC-e spectrometer were set: 0.92 L min^{-1} nebulizer gas flow (NEB); 1.2 L min^{-1} auxiliary gas flow (AGF); 15 L min^{-1} plasma gas flow (PGF); 1100 W. ICP RF Power; 0.0 quadrupole rod offset; and 70.00 discriminator threshold.

2.4. Reagents and standards

Ultrapure deionized water (18.2 MΩ cm^{-1}) from a Milli-Q analytical reagent-grade water purification system (Millipore) and ultrapure HNO_3 60% were used. All the plastic lab ware employed for sampling was either new or cleaned by soaking 24 h first in 10% HNO_3 then in ultrapure water. A 10 mg L^{-1} solution of Mg, Cd, Cu, In, Ba, Ce, Pb, and U (in 1% HNO_3, PerkinElmer Atomic Spectroscopy Standard–Setup/Stab/Masscal Solution) was used as external standard. The calibration solutions for quantitative measurements were prepared from a multi-element standard purchased from PerkinElmer (standard ICP-MS containing 29 elements, matrix: 5% HNO_3, PerkinElmer Life and Analytical Sciences), of 10 mg L^{-1}. To determine the rare metals in the water samples, a multi-element standard (multi-element calibration standard 2: 10 mg L^{-1}: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Y, Yb), PerkinElmer (atomic spectroscopy standard), was used.

2.5. Parameters of performance

A method for determining the concentrations of heavy metals in water by ICP-MS was developed and validated. The performance parameters were within specifications of SR EN ISO 17294-2: water quality—application of inductively coupled plasma mass spectrometry (ICP-MS). Limit of detection recorded by the validated method for the elements under study provides the minimum limit of quantification required for quantitative determinations of the concentrations of these elements in the investigated waters, very good linearity (with correlation factors $R > 0.999$) for most elements.

The minimum detection limit is the lowest concentration or quantity of analyte which can be measured with reasonable statistical certainty. To determine the limit of detection 3SD, a method developed by PerkinElmer (Estimating Instrument Detection Limits, Elan version 3.4., and Software Guide) was used. Ultrapure water of 18.2 MΩ cm^{-1} was aspired, and signal intensities for blank were recorded. The limit of detection was calculated by Eq. (1) where SD_{blank} is the standard deviation for the signal recorded on the blank for the element studied, $conc._{sample}$ is the concentration (μg L^{-1}) of the analyte in the sample, and I_{sample} and I_{blank} are the signal intensities recorded for the sample and blank, respectively:

$$LOD = 3 \cdot SD_{blank} \cdot conc_{sample}/(I_{sample} - I_{blank}). \quad (1)$$

The limit of quantitation (LOQ) is the lowest concentration that can be quantitatively determined with an acceptable level of repeatability and accuracy. It is generally considered to be approximately ten times the minimum detection limit (LOD). The analytical quality control included daily analysis of standards and triplicate analysis of samples and blanks. The accuracy and precision of the analytical technique were evaluated by analyzing a certified standard reference material. Precision of the instrument was determined by introducing the same quantity of one sample ten times, and then, the relative standard deviation (RSD) was calculated. RSD values ranged from 0.4 to 6.4% confirming the high precision of the method. Accuracy expresses the correlation between the arithmetic mean of the measured values and

http://dx.doi.org/10.5772/65700

the accepted reference value. RE ranged from −0.3 to 13% confirming the accuracy of the implemented method (**Table 1**).

Elements	**Parameters**											
				Intra-day studies				*Inter-day studies*				
	R[1]	**LOD (ng L^{-1})**	**LOQ (ng L^{-1})**	**Added (μg L^{-1})**	**Found (average) (μg L^{-1})**	**SD[2] (%)**	**RSD[3] (%)**	**Added (μg L^{-1})**	**Found (average) (μg L^{-1})**	**SD[2] (%)**	**RSD[3] (%)**	**RE[4] (%)**
Al	0.9994	1.7	16.7	25	25.59	0.23	0.9	25	25.69	0.18	0.72	2.76
Cr	0.9999	1.3	13.2	2.5	2.53	0.01	0.6	2.5	2.56	0.05	2.22	2.6
Mn	0.9995	2.6	26.5	2.5	2.51	0.04	1.5	2.5	2.60	0.07	2.93	4.0
Ni	0.9999	1.2	12.4	2.5	2.40	0.03	1.2	2.5	2.58	0.14	5.36	3.4
Cu	0.9997	1.3	12.7	2.5	2.57	0.03	1.2	2.5	2.64	0.07	2.61	5.5
As	0.9999	3.5	34.5	2.5	2.73	0.03	1.0	2.5	2.71	0.02	0.66	8.5
Sr	0.9989	0.5	5.3	25	25.32	0.11	0.4	25	25.24	0.26	1.02	0.95
Cd	0.9999	1.1	10.9	2.5	2.58	0.05	1.9	2.5	2.67	0.06	2.22	7.0
Ba	0.9998	0.9	8.7	2.5	2.67	0.04	1.7	2.5	2.83	0.18	6.48	13.3
Pb	0.9993	0.5	4.9	2.5	2.31	0.07	1.7	2.5	2.49	0.14	5.59	−0.3
Fe	0.9989	6.5	64.7	25	25.43	0.14	0.6	25	25.53	0.48	1.88	2.76
Ti	0.9998	15.8	157.8	25	25.82	0.08	0.3	25	26.19	0.54	2.06	2.76
Zn	0.9968	4.6	45.7	25	24.87	0.13	0.5	25	24.74	0.23	0.94	-1.06
La	0.9993	5.1	50.9	2	2.03	0.02	0.9	2	1.87	0.16	8.79	−6.4
Ce	0.9995	5.3	52.7	2	2.16	0.02	1.1	2	2.06	0.20	9.88	3.2

[1]R—correlation coefficient; [2]SD—standard deviation; [3]RSD—relative standard deviation, RSD (%) = SD/[metal] $_{mean}$ × 100; [4]RE—relative error, RE (%) = ([metal] $_{found}$ − [metal] $_{added}$/[metal] $_{added}$) × 100.

Table 1. Performance parameters obtained for heavy metals studied.

3. Experimental

3.1. Element concentrations in surface waters

Quantitative determination of the elements content in studied surface waters showed an increase, from 2009 to 2011, of Al and Mn concentrations in three sampling areas (Area 2, Area 4, and Area 5); an increase of Zn and Pb to Area 7; of Fe, Ti, Zn, and Pb concentrations to Area 2; of Cu and Pb to the Area 5; and of Fe and Cu to Area 6 (**Table 2**). High values were also registered for Zn and As in all sampling areas, during 2011 campaign, but below the permissible minimum level [14]. Increased concentrations of Cu, Zn, As, and Pb were observed in samples of

surface water collected in 2010 compared with those collected in 2009 and 2011. These concentrations can be correlated with the registered rainfalls that were much higher in 2010. Seasonal changes in the concentrations of the analytes of interest observed in surface waters result from the dilution effect that occurred during rainfall. The content of heavy metals from the sampled river waters reduces due to the mixing with large volumes of uncontaminated water draining from the slopes. When the river flow decreases, the reverse phenomenon occurs. The contaminant concentrations increase both due to the evaporation and of the bacterial activity of sulfides oxidation once with the increase of temperatures.

	Sampling area/concentration (μg L^{-1})											
Elements	***Area 7***			***Area 2***			***Area 5***			***Area 6***		
	2009	**2010**	**2011**	**2009**	**2010**	**2011**	**2009**	**2010**	**2011**	**2009**	**2010**	**2011**
Al	2.74	4.47	18.16	4.84	5.86	15.58	9.81	9.88	17.86	3.98	8.16	12.89
Mn	0.24	8.39	5.68	0.72	1.58	12.41	1.31	2.036	4.41	1.23	4.29	6.81
Fe	6.36	28.15	24.20	7.48	24.43	62.86	51.22	45.99	31.12	29.70	35.75	39.28
Ni	0.38	0.33	0.49	0.38	0.76	0.70	0.50	0.29	0.58	0.56	0.29	0.61
Ti	13.24	12.54	15.63	14.56	17.29	28.94	15.61	11.89	11.09	30.02	16.97	10.15
V	0.12	0.12	0.07	0.05	0.01	0.24	0.072	0.10	0.096	0.17	0.06	0.09
Co	0.03	0.63	0.43	0.03	1.37	0.613	0.032	0.56	0.398	0.07	0.53	0.52
Cu	0.69	0.59	0.71	1.42	0.71	1.348	0.588	0.50	0.727	0.59	0.54	0.68
Zn	0.23	0.16	13.08	0.19	0.14	1.26	0.202	0.13	0.532	0.87	0.14	1.57
As	0.61	0.43	1.24	0.54	0.44	2.186	0.500	0.47	1.167	0.85	0.49	1.11
Pb	0.08	0.02	0.061	0.08	0.01	0.071	0.018	0.02	0.163	0.04	0.02	0.04

Table 2. Comparative situation of metal concentrations in water sampled during the monitoring campaign.

3.1.1. Metals in water: seasonal influence

Water quality is affected by the weather conditions. This was revealed by studying the seasonal influence on the content of metals in water samples taken from the same areas in different calendar periods. A variation of heavy metal concentrations was observed in samples of water, sediment, and soil, depending on the season and certain times of year.

Characterization in terms of Cr, Pb, and Cu concentrations in water samples taken from the accumulation of fresh water of Tarnita (Area 8), Somes Cald (Area 2), and Somes Rece (Area 6) in early 2010 showed that the highest concentrations of these elements (Area 7) were registered in June and the lowest in January. This could be explained by the fact that the pollution originates in the driving effect of heavy metals by precipitation water that "wash" the adjacent area before reaching the lake. In the summer months, it is normal that the effect is more pronounced than in the cold winter months when the ground is frozen and therefore less exposed to erosion. The occurrence in July of higher concentration levels for some metals (e.g., Co, Cu, As) could be explained by the elevated temperatures recorded in this month that

led to partial oxidation and solubilization of the sulfides, including biotransformation processes. Moreover, the intense evaporation enabled the crystallization of minerals containing large amounts of constituents of the elements Co, Cu and As. These minerals may contain soluble salts, which dissolve when rainfall is recorded in higher amounts. **Table 3** shows the minimum and maximum values of the concentrations of elements in waters depending on the areas and sampling periods.

		Area of sampling					
Elements/concentration range	**Sampling period**	***Area 1***	***Area 2***	***Area 4***	***Area 5***	***Area 6***	***Area 7***
Al/2.6–31.78 μg L^{-1}	March						
	May						
	July	min.	min.	min.	min.	min.	min.
	September	max.	max.	max.	max.	max.	max.
Ti/0.18–50.37 μg L^{-1}	March	max.					max.
	May				max.	max.	
	July		min.	min.	min.		
	September	min.	max.	max.		min.	min.
Mn/0.16–25.5 μg L^{-1}	March	min.	min.			min.	
	May		max.		max.	max.	
	July			min.	min.		min.
	September	max.		max.			max.
Fe/5.6–86.8 μg L^{-1}	March	min.		max.			max.
	May						
	July		min.	min.	min.	min.	min.
	September	max.	max.		max.	max.	
Ba/7.8–40.1 μg L^{-1}	March						max.
	May	max.	max.	max.	max.	max.	
	July				min.	min.	min.
	September	min.	min.	min.			
Sr/15.6–101.2 μg L^{-1}	March	min.		min.	min.	min.	min.
	May		min.				
	July	max.		max.	max.	max.	
	September		max.				max.

Table 3. The registered minimum and maximum values of the metal concentrations in waters by sampling area.

Determination of rare earths from various types of environmental samples is particularly important because it can serve to establish a sample fingerprint, and thus, the results could be used in determining the origin of the concerned sample and to identify sources of pollution

[15, 16]. Mass spectrometry with inductively coupled plasma offers the possibility to measure the rare earths with an excellent accuracy, which cannot be achieved by any another method [17, 18]. In this context, systematic observations correlated with the climatic conditions were performed in this work for a prolonged period. Thus, by comparing the data on a sampling site, in different periods, higher concentrations of La, Ce, and Pr were observed in September.

Analyzing data obtained in the 3 years of monitoring (2009, 2010, and 2011) for the same sampling month, a constancy of the rare metal concentrations was revealed, except for Sc, which recorded a significant decrease in 2009 (**Table 4**). Determination of trace amounts of rare earth elements dissolved in water was correlated with their concentration in the soil; concentrations of rare metals can originate from the soils adjacent to waters that once washed by rainfalls reach these waters. Quality of surface water and sediments, in terms of chemical species concentrations of the metals, was discussed based on the results obtained for the surface water and sediment analyzed samples taken from locations.

	Sampling area/concentration (μg L^{-1})											
Elements	***Area 8***			***Area 7***			***Area 5***			***Area 6***		
	2009	**2010**	**2011**	**2009**	**2010**	**2011**	**2009**	**2010**	**2011**	**2009**	**2010**	**2011**
Sc	2.686	0.693	0.428	1.493	0.862	0.403	1.680	0.817	0.423	2.515	0.842	0.429
Y	0.033	0.056	0.035	0.028	0.058	0.031	0.017	0.065	0.030	0.065	0.064	0.034
La	0.037	0.036	0.057	0.025	0.047	0.02	0.019	0.037	0.052	0.082	0.038	0.036
Ce	0.073	0.103	0.047	0.029	0.053	0.012	0.038	0.069	0.07	0.142	0.041	0.093
Pr	0.017	0.009	0.018	0.005	0.008	0.005	0.004	0.011	0.014	0.023	0.010	0.01
Nd	0.039	0.056	0.03	0.016	0.032	0.011	0.013	0.039	0.047	0.090	0.045	0.046
Sm	0.013	<0.001	0.005	0.004	0.003	<0.001	0.003	0.007	<0.001	0.020	0.001	<0.001
Eu	0.002	0.001	0.002	0.003	0.002	<0.001	0.004	0.003	<0.001	0.009	0.004	<0.001
Gd	0.009	0.012	0.007	0.005	0.007	0.002	0.003	0.014	0.007	0.018	0.009	0.014
Tb	0.002	0.001	0.002	0.001	0.002	0.003	0.001	0.002	0.002	0.004	0.003	0.002
Dy	0.005	0.010	0.005	0.006	0.010	<0.001	0.002	0.004	0.005	0.018	0.012	0.003
Ho	0.001	0.002	0.001	0.001	0.003	<0.001	0.001	0.003	0.003	0.003	0.002	0.002
Er	0.003	0.004	<0.001	0.002	0.005	<0.001	0.001	0.008	<0.001	0.010	0.007	<0.001
Tm	0.001	0.001	0.001	<0.001	0.002	<0.001	0.001	0.001	0.001	0.002	0.001	0.003
Yb	0.001	0.005	<0.001	0.002	0.003	<0.001	<0.001	0.004	<0.001	0.008	0.004	<0.001
Lu	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001
Th	0.022	0.013	0.057	0.028	0.010	0.02	0.020	0.010	0.052	0.027	0.033	0.036

Table 4. Comparative situation of the rare metal concentrations during the monitoring campaign.

http://dx.doi.org/10.5772/65700

3.2. Element concentrations in sediments samples

Valuable data regarding the distribution of pollutants in sediment [19–22] were published in recent years. However, there is a limited analysis of the sedimentological characteristics on the pollutant distribution, which can play a key role in distinguishing the different sources, transport processes, and conservation status of specific contaminants in the environment. All the physicochemical and biochemical processes in aquatic systems take place at interfaces water-atmosphere-lithosphere, and a particularly important role is assigned to chemical and biochemical reactions at the water-sediment interface, which adjust the composition of natural waters. Studying the influence of physicochemical factors on the distribution of metals in sediments and water is important when the retention of metals by various types of sediments is assessed, developing thus predictions that may assure data comparison, interpretation, and their extrapolation, as an important contribution to the sustainable management of the investigated area.

Trace elements are one of the main sources of pollution of the aquatic chain. Since they tend to be adsorbed in sediment, the study of the adsorption/desorption of heavy metals in sediment and the effect of sediment transport are of particular importance. Sediments from lakes are an excellent witness of the water quality since they preserve important information on the environment and are recognized as a source of contaminants in aquatic systems due to the local physicochemical conditions. It is worth mentioning that the sediments are the best environment for toxic metals due to their high absorption capacity; therefore, sediment plays an important role in storing and releasing metals.

Correlations of climatic factors with the sampling locations were performed in relation to pollution sources. The most important factor in determining the concentration values of chemical species of the pollutant metal proved to be the location of the sampling point relative to the anthropogenic sources of pollution. A correlation was also found between the concentrations values of chemical species of the metal and the climatic factors registered during the monitoring period. As shown in **Table 5**, the concentration values for the most elements (Cd, Cu, Pb, Hg, and Zn) in sediment samples collected from the study area are within the permissible limits.

Based on the analysis of experimental data, it can be concluded that there is a match between the total concentrations of chemical species of the metals studied in samples of surface water and sediments collected from the same locations. Possible transfers of metal compounds in both directions may occur, from the sediment into the surface water and vice versa.

The levels for most metals in sediment samples collected from the study area generally were within the limits of admissibility, except for As present in quantities that exceeded the mean admitted values (sediments sampled in 2010 from the Areas 2 and 5). The average concentrations of some metals such as As, Pb, Co, U, and Cd were higher in the dry season than in the wet season. This is possible due to the dilution by rainwater influencing the concentration and mobility of heavy metal. In contrast, the mean concentration of Fe in sediment samples taken from the driest month was lower than concentrations in samples collected within the wet

period, probably due to the rainfall. Higher values of metal concentrations were found in sediments taken from lakes versus those sampled from rivers.

		Sampling area/concentration (mg kg^{-1})							
Elements/permissible limits [23]	**Month**	***Area 1***	***Area 2***	***Area 3***	***Area 4***	***Area 5***	***Area 6***	***Area 7***	***Area 8***
As/17 mg kg^{-1}	March	17.33	16.53	14.66	11.23	111.39	12.91	21.75	20.17
	May	35.43	34.69	55.95	19.41	133.79	51.06	76.34	48.22
	July	20.15	22.37	55.93	28.28	26.78	26.30	87.48	80.34
	September	19.07	25.43	35.78	36.12	172.32	159.34	169.63	34.49
Cd/3.5 mg kg^{-1}	March	0.16	0.11	0.07	0.10	0.12	0.15	1.12	0.96
	May	0.35	0.32	0.41	0.22	0.16	0.56	1.65	0.13
	July	0.10	0.14	0.25	0.15	0.12	0.15	2.97	1.54
	September	0.08	0.12	0.15	0.20	0.38	0.36	0.31	0.26
Cr/90 mg kg^{-1}	March	11.95	20.55	19.38	21.13	39.02	18.59	20.75	19.12
	May	31.23	36.74	42.56	82.38	44.24	88.55	72.90	32.28
	July	16.40	16.57	16.39	71.97	60.19	21.84	61.04	60.34
	September	11.19	32.92	49.64	53.23	102.47	91.17	89.18	35.83
Cu/200 mg kg^{-1}	March	11.03	10.62	9.91	10.59	20.08	11.21	11.65	10.15
	May	25.41	24.16	27.71	47.66	27.81	60.78	66.97	17.93
	July	10.29	11.62	14.30	41.52	30.23	17.76	85.25	80.56
	September	10.26	17.53	25.38	40.54	54.80	52.78	49.90	16.50
Pb/90 mg kg^{-1}	March	40.24	33.56	39.81	25.78	26.15	20.96	21.17	21.76
	May	39.27	39.77	39.87	13.14	13.78	20.12	22.24	22.60
	July	19.56	18.43	17.03	8.41	8.23	19.29	24.28	24.18
	September	17.54	17.13	27.44	25.43	23.53	22.93	22.92	26.80
Hg/0.5 mg kg^{-1}	March	<0.001	0.07	0.12	<0.001	0.09	<0.001	<0.001	<0.001
	May	<0.001	0.28	0.18	0.03	<0.001	<0.001	0.15	0.12
	July	0.01	0.01	<0.001	<0.001	<0.001	0.08	0.09	<0.001
	September	0.07	0.04	0.17	0.19	0.24	0.20	0.11	0.07
Zn/300 mg kg^{-1}	March	51.41	44.35	53.09	50.17	42.63	31.59	50.19	30.20
	May	81.56	79.43	86.77	80.40	51.30	85.03	167.01	66.27
	July	42.71	46.64	57.63	64.72	63.12	54.76	193.75	190.82
	September	62.76	64.44	81.60	90.53	103.85	98.82	96.48	134.67

Table 5. Metal concentrations in the analyzed sediment samples.

The predominance of metals in the free ionic form and as soluble compounds in water, in an acidic environment, favors both the exchange processes at the water-sediment interface and the bioabsorbtion processes with direct consequence on the toxicity of these metals. Hence,

appears obvious the need to study the distribution of the metals contained in the sludge fractions where the metals are attached in combination with different abilities of participating to the heterogeneous equilibrium sediment-aqueous phase.

Thus, to study the heterogeneous equilibrium occurring at the water-sediment interface, the metal concentrations of sediment pore water were determined. The literature presents the calculation mode (Eqs. (1) and (2)) of trace metals distribution in the interstitial sediment-water interface following the formula:

$$P_{sed.} = (M_s/M_t)\ \ 100 \quad (2)$$

$$P_{int.water} = 100 - P_{sed}, \quad (3)$$

where $P_{sed.}$ (%) is the proportion of metal in the sediment, $P_{int.water}$ (%) is the proportion of the metal in interstitial water, M_s (mg) is the amount of metal in the sediment, M_t (mg) is the total amount of the metal (sediment + interstitial water) in the sample.

Experimental data showed that for the studied metals, the concentrations in pore water samples exceed those in surface water, which suggests that sediment through interstitial water may become a potential source to chemical species mobilization of the metals in water (**Table 6**). Characterization in terms of rare metal concentrations, comparing water samples with water resulting after settling sediment, revealed that the sediments accumulate rare metals (the concentrations both in water and in sediment are very low, but there is a slight increase in sediment). It was also highlighted that sediment accumulates a larger amount of rare earth metals than soils.

		Metal concentrations (μg L^{-1})					
Sampling area	**Sample**	**As**	**Zn**	**Pb**	**Co**	**Cu**	**Ni**
Area 1	Water	1.396	0.583	0.137	0.529	1.422	0.586
	Water sediment	1.582	0.699	0.294	0.585	1.595	0.773
Area 4	Water	0.951	0.106	0.03	0.417	0.434	0.411
	Water sediment	1.100	0.131	0.044	0.532	0.512	0.587
Area 6	Water	1.131	0.084	0.031	0.535	0.462	0.521
	Water sediment	1.372	0.103	0.098	0.619	0.510	0.588
Area 7	Water	0.869	0.081	0.016	0.594	0.415	0.398
	Water sediment	1.187	0.102	0.044	0.827	0.546	0.448

Table 6. Trace element concentration in water/water from sediment, year 2011.

3.3. Metal concentrations in soil samples

The catchment of Somes River fits in the temperate continental area, the bioclimatic conditions in the area causing a moderately active or slow biological circuit, and a strong acidification of soils. Soil research and its quality assessment closely related to the dynamic use of land offer

many possibilities in terms of approach. Chemical characteristics of the soil and organic carbon content, pH, the oxides forms, carbonates, and some physical properties such as clay content may influence the concentration of chemical elements.

This work has also proposed an assessment of heavy metals distribution in soils in the studied areas and an investigation of the extent to which heavy metal content in soil from the areas of waters accumulation may influence their concentration in water. **Table 7** highlights the concentrations of toxic elements in soils versus the limit values according to the Romanian laws [24].

	Metal concentrations (mg kg^{-1})						
Area	**Cu**	**Pb**	**Zn**	**Cd**	**Ni**	**Cr**	**Mn**
Area 1	37.46	33.59	99.23	0.45	43.91	37.05	249.73
Area 2	16.70	31.76	62.43	0.19	24.23	28.55	264.95
Area 3	11.14	22.81	44.37	0.12	14.95	23.81	151.71
Area 4	52.92	75.30	382.66	1.95	38.75	52.93	1027.20
Area 5	37.85	23.52	65.18	0.25	45.94	55.39	534.97
Area 6	58.72	26.50	85.57	0.97	53.84	63.55	807.63
Area 7	42.77	17.31	102.40	0.89	57.18	33.87	513.54
Area 8	71.07	22.59	77.05	0.22	19.57	30.26	207.05
NV	20	20	100	1	20	30	900
TA	100	50	300	3	75	100	1500
IT	200	100	600	5	150	300	2500

NV, normal values; TA, threshold alert; IT, intervention threshold [24].

Table 7. Heavy metal concentrations in soil samples collected in May 2011, in different areas.

Cd in soil ranged from relatively narrow limits (0.19–1.95 mg kg^{-1}), with an overwhelming dominance (>99%) of the contents lower than the alarm threshold. It can be considered as representative for the natural geochemical background of the investigated area. These abundances are consistent with the geological structure, relatively uniform, which is determined by sedimentary rocks, which are known for their low content in Cd. An exceeding of the normal values was observed to Area 4 (Somes Cald Lake), but below the alert threshold.

Mn content is between relatively wide limits (120–1100 mg kg^{-1}), with a similar distribution to that described by the normal distribution law. Therefore, 99.90% of the samples were below the maximum content of normal, and only 0.10% of the samples exceed the normal range, but not the alert threshold. The monitoring carried out on soil during year 2011 revealed an exceeding of normal values in almost all areas, but below the alert threshold.

Chromium is considered as one of the most harmful metals for human health. In aquatic environment, it is presented as Cr^{3+} ion as well as anionic species and CrO_4^{4-} si $Cr_2O_7^{2}$, these

two forms being produced by human activities. The values determined for Cr and Ni in the soils of the studied areas fluctuate in the range between 12.1 and 86.0 mg kg^{-1} (for Cr) and 17.0–70.0 mg kg^{-1} (for Ni), with exceedings of normal values without reaching the alert threshold.

Pb ranges from relatively low limits of 20–80.4 mg kg^{-1}. Most samples showed an exceeding of lead concentrations than normal, except for samples collected from Somes Cald Lake where values above the alert threshold were reported. This clearly reflects the effects of human intervention in this area.

Zn content determined in 2011 on the analyzed soils varies widely (26–146 mg kg^{-1}) with a significant dominance (>95%) of the contents, not exceeding normal values for soils. In the Area 4 (Somes Cald Lake), Zn anomalies are spatially overlapping, largely over the Pb, suggesting the same originating polluting sources.

Comparing the content of heavy metals in soil and water samples to each sampling point, it can assert that there is a correlation only in certain areas (e.g., Al, Zn, Ti, and Pb for Area 1), where the concentrations of metals in water samples may result from soil washing during rainfall. Here are the results obtained for soil samples collected in different months (**Table 8**): in March, the highest concentrations recorded for Pb (Areas 1, 2, 3, 5), Cu, Co, Cr (Area 2), Zn (Areas 2, 7, 8), and Mn (Areas 1, 5); in May, for Zn (Area 4), Ni (Area 7); in July, for As (Areas 2, 3, 4, 5, 7), Cu (Areas 4, 7, 8), Pb, Cr, Mn, and Co (Area 7), Zn (Area 4); and in September, for As (Areas 1, 6, 8), Cu, Ni, Cr, Zn (Areas 1, 3, 5, 6), Co (Areas 6, 7), and Mn (Areas 2, 3, 4).

Following the values obtained for samples of soil taken from the same area, in different years, a growing trend 2009–2011 in the concentrations of Pb, As, Ni, Zn, Co, and Cu, was observed (**Table 9**).

3.4. Determination of metal concentrations in vegetation samples

The toxic effect of the metals in the tissues and plant cells varies according to the concentration, leading that at high concentrations the whole process of plant growth and development is inhibited. Plants heavily suffer due to the harmful action of impurities from polluted air, their behavior representing a good indicator of pollution.

The ability of removing metals is a general characteristic of the organisms tolerant to metals. Many organisms/plants instead to eliminate metals accumulate them in high concentrations, especially in roots and leaves. The manner in which plant metabolism responds to the exposure at different concentrations of heavy metals is an important step in determining the fate of plants, tissues, or cells and their ability to survive. Metal tolerance issues related to development are increasingly the focus of researchers [25].

The ability of plants to takeover chemical elements varies within a wide range. Elements such as Br, As, B, Cs, and Rb are easily taken, while others such as Ba, Ti, Zr, Sc, Bi, Ga, and Fe are less available; these aspects are being adjusted depending on the particularities of the soil plant. Specific to the fungi, these show an affinity for taking over metals like Hg, Cd, Se, Cu, and Zn. The problem of heavy metal pollution of soil and plants in the general context of

ensuring the health of living beings (humans, animals, plants), avoiding disturbance on the balance of the ecosystem and the need to address and to elucidate issues related to quality greenhouse products in order to improve culture techniques without soil, requires intense monitoring differences in the content of pollutants in the plant.

		Area sampling/metal concentrations (mg kg^{-1})							
Elements	**Period sampling**	***Area 1***	***Area 2***	***Area 3***	***Area 4***	***Area 5***	***Area 6***	***Area 7***	***Area 8***
As	March	12.36	14.67	10.72	13.06	16.74	39.64	40.05	27.87
	July	16.95	26.27	28.62	93.30	169.74	53.41	90.18	33.73
	September	82.67	25.22	21.36	13.18	25.88	67.62	19.51	49.58
Cu	March	16.63	21.03	5.15	20.34	28.64	55.6	73.23	80.54
	July	37.21	15.37	13.4	60.53	39.01	52.86	74.87	121.06
	September	58.54	13.7	14.88	45.31	45.9	67.71	10.68	21.09
Pb	March	48.6	54.4	29.44	49.06	32.26	15.68	10.86	12.42
	July	32.56	23.56	21.27	73.06	18.82	20.13	19.84	21.06
	September	19.63	17.32	17.73	77.55	19.5	43.70	14.78	24.12
Zn	March	102.25	65.12	26.96	108.71	49.2	66.79	106.89	102.85
	July	53.85	61.03	55.7	432.00	59.87	77.18	146.37	55.27
	September	141.59	61.14	58.46	333.33	86.49	112.76	50.44	98.84
Cd	March	0.32	0.27	0.06	1.96	0.21	0.43	0.58	0.16
	July	0.27	0.23	0.20	1.95	0.27	1.70	1.64	0.14
	September	0.77	0.18	0.12	1.95	0.27	0.8	0.08	0.30
Ni	March	17.07	22.74	11.93	25.21	28.65	48.08	52.04	21.32
	July	21.09	15.13	15.03	32.81	33.18	40.31	100.92	17.39
	September	93.59	34.84	17.1	44.69	76	73.13	13.44	21.76
Cr	March	24.26	36.39	12.11	45.31	37.46	56.6	34.16	24.05
	July	20.95	23.03	27.28	50.73	59.72	47.51	59.76	24.04
	September	65.94	26.23	32.06	55.13	68.99	86.54	7.98	36.48
Mn	March	304.55	265.56	127.98	324.06	679.78	387.65	250.13	205.02
	July	220.33	207.68	235.08	376.52	289.36	1434.76	655.86	228.02
	September	224.33	321.63	220.06	1077.88	635.78	600.5	371.23	186.09
Co	March	8.75	11.00	3.57	4.25	12.4	24.55	20.71	17.12
	July	8.96	7.12	7.81	19.13	13.35	33.34	23.07	15.82
	September	11.93	7.25	8.96	18.55	16.45	29.68	6.69	9.01

Table 8. Comparative situation for metal concentration in soils.

We also considered in our work the characterization of vegetation samples from surrounding areas of raw water reservoirs. We noticed that higher concentrations were found in moss than

in leaves, so they accumulate more quickly the toxic metals. Also, there was observed a concentration of heavy metals in aquatic plant tissues; in the same area of sampling, analyzing samples of terrestrial and aquatic vegetation, we observed higher concentrations values of Fe, Co, Ni, Zn, As, and Pb in the lacustrine vegetation. So there is the possibility of using certain plant species for "extracting" the potential toxic heavy metals from water. **Table 10** contains the metal concentrations of vegetation collected in May 2011, while **Table 11** presents the comparative data for soil-vegetation.

		Area sampling			**PA**		**PI**	
Elements	**Sampling year**	***Area 4***	***Area 6***	**VN**	**Sensitive**	**Less sensitive**	**Sensitive**	**Less sensitive**
Pb	2009	24.89	27.04	20	50	250	100	1000
	2010	39.89	36.72					
	2011	73.06	43.70					
As	2009	10.54	8.38	5	15	25	25	50
	2010	18.82	18.43					
	2011	13.18	67.62					
Ni	2009	14.28	8.61	20	75	200	150	500
	2010	28.77	26.55					
	2011	44.69	73.13					
Cd	2009	0.18	0.23	1	3	5	5	10
	2010	1.14	2.33					
	2011	1.95	0.80					
Zn	2009	46.47	48.24	100	300	700	600	1500
	2010	137.35	106.96					
	2011	333.32	112.76					
Cu	2009	17.00	28.65	20	100	250	200	500
	2010	58.12	34.12					
	2011	45.31	67.71					
Co	2009	11.63	11.26	15	30	100	50	250
	2010	12.85	25.50					
	2011	18.55	29.68					
Hg	2009	0.11	0.10	0.1	1	4	2	10
	2010	0.24	0.62					
	2011	0.05	0.16					

VN, normal values; PA, threshold alert; PI, intervention threshold [24].

Table 9. Element concentrations for 3 years of sampling (mg kg^{-1}).

Elements	Sampling area/metal concentrations (mg kg^{-1})								
	Area 1		*Area 2*	*Area 3*	*Area 4*	*Area 5*	*Area 6*	*Area 7*	
	Leaves	*Moss*	*Leaves*	*Leaves*	*Leaves*	*Leaves*	*Leaves*	*Leaves*	*Moss*
Ti	44.78	283.50	47.64	121.20	223.20	23.16	41.64	55.34	236.95
V	0.90	31.83	0.47	11.65	21.09	0.34	0.21	2.71	69.19
Cr	3.38	17.44	1.28	9.09	17.28	2.07	1.37	2.62	45.07
Mn	47.74	257.27	41.98	196.11	399.35	93.22	76.17	79.23	252.88
Fe	357.01	9104.51	161.19	3147.62	5580.78	109.56	98.10	631.14	11290.76
Co	0.24	5.62	0.33	2.10	4.47	0.24	0.67	0.86	7.87
Ni	2.05	11.04	2.89	4.72	10.09	3.13	2.15	5.88	24.75
Cu	8.52	20.02	19.34	10.50	19.11	14.51	8.32	20.73	18.75
Zn	44.78	79.84	33.91	32.75	44.88	27.43	27.38	51.31	54.50
As	0.66	11.47	0.36	7.40	13.30	0.66	0.14	2.01	45.97
Cd	0.04	0.72	0.11	0.36	0.35	0.22	0.45	0.95	1.05
Ba	34.23	132.58	64.13	117.8	121.47	26.64	21.40	130.86	703.31
Pb	1.12	35.90	1.88	4.02	8.20	1.84	1.11	1.80	12.25

Table 10. Metal concentrations in vegetation collected in May 2011, from the studied areas.

Elements	Sampling area/metal concentrations (mg kg^{-1})			
	Area 1		*Area 3*	
	Soil	*Vegetation*	*Soil*	*Vegetation*
Co	8.96	0.13	7.81	1.13
V	48.67	0.17	58.72	0.22
Ni	21.09	1.72	15.82	2.69
Cu	37.21	2.54	13.40	6.10
Zn	53.85	48.26	55.70	36.32
As	16.95	0.15	28.62	0.34
Pb	32.56	0.12	21.27	0.10

Table 11. Metal concentrations in soil and vegetation samples from July 2011.

3.5. Drinking water

The surface water pollution's main impact in the studied area is on the water processing plant in terms of providing potable water. The drinking water released from the water treatment plant at good quality parameters and distributed through the public network could reach the end users

http://dx.doi.org/10.5772/65700

at a less quality level, in which the distribution network of water may represent a potential source of chemical contaminants in the processed water. All the investments undertaken for the rehabilitation and modernization of water supply chain have as final aim the improvement in water quality. Even if the public distribution of water from sources and treatment facilities to the networks and connections are upgraded, there is a gap in the rehabilitation of some buildings internal networks, and thus, water with appropriate quality to the branch may get degraded to the end user tap due to the poor state of the interior outdated pipes.

Due to the increasing influence of the anthropogenic factors on water sources, the ensuring of water quality is of primary importance. At global level, the environmental monitoring is assured by the IGBM (integrated global background monitoring of environmental pollution) and GEMS (global system of environmental monitoring) networks. IGBM deals with background monitoring (before the intervention of pollution), and GEMS follows the impact monitoring (after the intervention of pollution). Over 20 EEC Directives regarding the protection of aquatic environment and many guidelines laying down the quality standards regarding the use of water and the checking of wastewater discharge are in force to support these activities (e.g., Council Directive 76-464-EEC—pollution caused by the discharge of dangerous substances into the aquatic environment; Council Directive 88/20/EEC—limit values for discharges of certain dangerous substances). Metals with potentially harmful effect on groundwater are Zn, Cu, Ni, Cr, Pb, Se, As, Sb, Mo, Ti, Sn, Ba, Be, Bi, U, V, Co, Tl, Te, and Ag. The maximum permissible limits for metal concentrations in drinking water given by some international directives are shown in **Table 12**.

Elements	NS30	EU	USA	Romania
Ag	10	–	100	–
Al	200	200	200	200
As	50	10	10	–
Ba	1000	–	2000	–
Cd	5	5	5	5
Cr	50	50	100	50
Cu	3000	1000	1000	100
Fe	200	200	300	–
Hg	1	1	2	–
Ni	50	20	–	20
Pb	50	10	15	10
Sb	10	5	6	–
Se	10	10	50	10
U	–	–	30	–
V	–	50	–	–
Zn	5000	–	5000	5000
Mn	–	–	–	50

Table 12. Permissible limits, in μg L^{-1}, for drinking water in England (NS300), European Union (EU), United States of America (USA) and Romania.

In Germany, the maximum permissible limits for drinking water are the same as those for the member states in the EU, exception As (40 μg L^{-1}) and Pb (40 μg L^{-1}). In Spain, the quality criteria for wastewater that may affect quality of surface water has recently been amended, setting values of 50 μg L^{-1} for As_{total}, 5 μg L^{-1} for Cr (VI), and 1 μg L^{-1} for $Se_{dissolved}$. In Romania, certification of potable water is performed in accordance with the Laws 458/2002 and 311/2004, which are aligned with the European Framework water Directive 2000/60/EC (**Table 13**). They concern the organoleptic (sensory), physical, chemical (general and toxic), radioactive, bacteriological, and biological characteristics of water.

			Metal concentrations (μg L^{-1})				
Area/sampling period			**As**	**Cd**	**Pb**	**Co**	**U**
2011	Water treatment plant	Raw water	0.302	<0.001	0.002	0.338	0.102
		Decant water	0.250	<0.001	0.016	0.147	0.010
		Filtered water	0.165	0.007	0.033	0.284	0.041
		Chlorinated water	0.221	<0.001	0.005	0.255	0.026
	City water entry point		0.229	<0.001	0.003	0.230	0.076
2010	Gilău treatment plant	Raw water	0.220	<0.001	0.003	0.244	0.101
		Decant water	0.125	<0.001	0.002	0.159	0.058
		Filtered water	0.247	0.003	0.078	0.245	0.105
		Chlorinated water	0.234	<0.001	0.010	0.228	0.114
	City water entry point		0.184	<0.001	0.002	0.201	0.101
2009	Water treatment plant	Raw water	0.345	<0.001	0.007	0.453	0.078
		Decant water	0.236	<0.001	0.012	0.245	0.056
		Filtered water	0.188	0.101	0.051	0.387	0.074
		Chlorinated water	0.268	<0.001	0.003	0.368	0.066
	City water entry point		0.298	<0.001	0.005	0.392	0.069

Table 13. Characterization of waters from water treatment plant (entrance to city).

The waters investigated in this study ensure the drinking water sources of the cities from Cluj county, but also provide industrial water for energy purposes and water for a trout farm in the area downstream the dam. The trace elements present in the water supplied as drinking water to population but also in the wastewaters and water of sewage plants before discharging into the rivers were determined for this work. Quality of water at the inlet in the distribution networks versus the one at the household consumer was characterized to highlight potential sources of contamination due to the technical condition of pipe networks. The water quality monitoring consisted of three phases:

i. Monitoring the water quality of Gilau Lake in order to establish a realistic image in terms of physicochemical parameters value of the water before entering the treatment plant—samples collected directly from the lake. In terms of toxic metals, the studied surface

water fall in first quality class, with few minor exceptions. Overall, the overruns, in the absence of an organized source of pollution, would lead to the conclusion that it is a natural pollution, which could be confirmed geochemical.

ii. Water quality monitoring inside the treatment plant; water samples collected after each stage of the raw water treatment (coagulation, filtration, sedimentation, chlorination). Referring to their content in metal with toxic effect was characterized the water treatment plant from the point of entry in the city (located 10 km away from the water treatment plant) taken in 2009, 2010, 2011. The obtained concentration values for As were in the range of 0.1–0.6 μg L^{-1}, Cd <0.001 μg L^{-1}, Pb in the range 0.03–0.7 μg L^{-1}, and U between 0.007 and 0.2 μg L^{-1}. **Table 13** presents a quantitative characterization of metals from period 2009, 2010, 2011.

iii. Water quality monitoring in the drinking water distribution network.

The water samples were collected from many urban districts. Comparing the obtained data with the permissible values in Romania, we can state that in terms of toxic metals content the drinking water is adequate and is well below the admissible limits (**Table 14**).

			Metals concentrations (μg L^{-1})								
City distribution area/sampling period			***As***	***Cd***	***Pb***	***Ni***	***Co***	***Fe***	***Zn***	***U***	***Cu***
2011	Area 1 city		1.271	0.007	0.909	2.944	0.288	42.890	143.930	0.133	43.94
	Area 2 city		1.422	0.015	0.070	0.590	0.239	39.671	4.000	0.137	1.600
	Area 3 city	Cold	1.330	0.017	0.074	0.661	0.238	43.880	16.201	0.124	1.991
		Warm	1.710	0.073	0.774	3.222	0.330	42.670	168.77	0.160	5.740
	Area 4 city		1.290	0.017	1.270	0.744	0.151	45.226	8.925	0.131	14.070
	Area 5 city		1.500	0.007	0.106	2.275	0.172	41.987	13.47	0.122	8.866
	Area 6 city	Cold	1.180	0.026	0.052	0.760	0.166	35.770	36.35	0.124	1.921
		Warm	1.103	0.027	0.126	0.369	0.204	46.905	20.544	0.093	4.659
	Area 7 city		1.435	0.005	0.034	0.594	0.288	45.223	5.226	0.132	1.696
	Area 8 city center		1.023	0.022	0.268	1.059	0.209	43.990	142.88	0.113	2.785
	Area 9		1.545	0.022	0.268	2.257	0.142	42.991	43.053	0.113	6.028
2010	Area city 1		0.247	<0.001	0.142	0.443	0.201	45.772	1.445	0.132	1.331
	Area city 2		0.195	<0.001	0.011	0.521	0.206	35.984	1.994	0.106	1.207
	Area city 3		0.167	<0.001	0.005	0.61	0.185	52.806	1.553	0.092	1.094
2009	Area city 1		1.060	0.006	0.143	0.592	0.032	36.536	4.162	0.062	1.408
	Area city 2		1.063	<0.001	0.043	0.528	0.047	46.900	0.831	0.069	1.209
	Area city 4		1.003	0.016	3.433	0.682	0.027	58.758	9.481	0.064	2.175
	Area city 3		1.013	0.002	0.047	0.528	0.030	54.270	21.290	0.074	0.931

Table 14. Characterization of metal concentrations in waters from urban distribution areas.

4. Conclusions

The metals are considered to be one of the main sources of environmental pollution, having a significant effect on the ecological quality. Potentially toxic metals derived from the anthropogenic activities may lead to severe disturbances in the ecosystems, and therefore, the identification of pollution sources along with the assessment of the long-term pollution potential is a must in order to take actions for reducing or stopping the pollution. The anthropogenic sources lead to an increase in the metals levels in the environment due to the industrial and atmospheric pollution and their accumulation in soil, affecting thus the ecosystems. Therefore, measurements of metals in soil, plants, and sediment are very important in monitoring environmental pollution.

The primary objective of this study investigation was to characterize the surrounding areas of raw water reservoirs in terms of the content in heavy metals and rare earth, linked to establishing the supply mechanism of these surface waters. High accuracy measurements for quality assessment were performed on water samples, in terms of toxic metals, over a period of 3 years: 2009, 2010, and 2011. An increase (2009–2011) in the levels of Al and Mn was registered in three sampling sites (Somes Cald River, the confluence Somes Cald/Somes Rece, and Somes Cald Lake); of Zn and Pb to Tarnita site; of Fe, Ti, Zn, and Pb to the Somes Cald River; of Cu and Pb to the confluence Somes Cald/Somes Rece; and of Fe and Cu to the Somes Rece Lake. A large increase in the content of Zn and As was reported in 2011 for all the areas, but below the admissibility limits.

Water quality is influenced by weather conditions, and this was revealed by studying their influence on the content of metals in water samples from the same area, but different calendar period. There is a variation in the concentrations of heavy metals observed in the studied matrices (water, sediment, soil) depending on season, for certain periods of the year.

Determination of rare earths in various types of environmental samples is particularly important because it can serve to establish a fingerprint sample, and so the results could be used in determining the origin of the sample in question and to identify sources of pollution. Comparing the data of the 3 years, 2009, 2010, 2011, from the same month of sampling, there is a constant concentration of rare metals, except for Sc, where there is a significant decrease from 2009. Heavy metals are one of the main sources of pollution of the aquatic environment, they tend to adsorb in sediment, and the study of the adsorption/desorption effect of heavy metals in sediment and sediment transport has a particular importance. The concentration levels for most metals in sediment samples collected from the study area were within the general admissibility limits, with exception of As which was present in sediment samples taken in 2010 in quantities that exceeded the mean admitted (in the sediment samples collected from Areas 4—Warm Somes, 5—confluence Somes Cald/Somes Rece); also in the Area 4—Somes Cald was registered a significant increase in the Cr content (150 mg kg^{-1}, the limit was estimated to 90 mg kg^{-1}).

We found higher values of metal concentrations in sediments taken from lake versus concentration values in sediment samples taken from the river water. In soil samples taken from the same areas, in the same calendar period (2009 and 2010), an increase in the concentrations of Pb and As was observed and a decrease in the content of Co (for soil sampled in 2010).

http://dx.doi.org/10.5772/65700

Correlations with the climatic factors and the location of the sampling points were performed in relation to the pollution sources. The most important factor in determining the concentration values of the pollutant metal chemical species has proved to be the location of sampling points relative to the anthropogenic sources of pollution. A correlation between the results obtained for the concentrations of metals chemical species and the climatic factors registered during the monitoring period was also noted. Comparisons were made between the water quality at the inlet into the distribution networks and the water quality to the end user, to highlight potential sources of contamination related to the technical condition of these networks.

There is our responsibility, now and certainly in the future, to balance and control the environmental quality for each component and as overall. Thereby improving environmental quality will become the action against disorder and the reaction against the inertia and of the compromises when considering human life environment. Maybe someday each item and parameter of the environment will be integrated "in a world of balance and harmony". This calls for an efficient management of the environmental resources and for mandatory preserving of a right balance between the nature and society. It means implementation of a scientifically based management, both for the exploitation of natural resources and for the recovery and recycling of waste so that the failures and discontinuities in the evolution of ecosystems can be eliminated. The results of our research can be used by the companies that manage water resources in improving the drinking water treatment technologies. The results may be also useful for the territorial environmental agencies and authorities that have as direct responsibility the water quality.

Author details

Cezara Voica[1], Andreea Maria Iordache[2]*, Roxana Elena Ionete[2] and Ioan Ștefănescu[2]

*Address all correspondence to: andreea.iordache@icsi.ro

1 National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

2 National Research and Development Institute for Cryogenics and Isotopic Technologies, Ramnicu Valcea, Romania

References

[1] National Water Law No. 107/1996, published in The Official Gazette of Romania.

[2] EU Water Framework Directive-Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy.

[3] Council Directive 98/83/EC on the quality of water intended for human consumption, or Council Directive 91/271/EEC concerning urban waste-water treatment amended by the Commission Directive *98/15/EC*, www.apmbm.ro/MM/PPPRPC/Codificare_Directive.doc.

[4] UNEP GEMS/Water Programme Water Quality Outlook ISBN 95039-11-4 UN GEMS/Water Programme Office.

[5] Islama S, Ahmed K, Raknuzzamanb M, Mamunb H-Al, Islame MK: Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country. Ecological Indicators. 2015;**48**:282–291. doi:10.1016/j.ecolind.2014.08.016

[6] Maher A, Sadeghi M, Moheb A: Heavy metal elimination from drinking water using nanofiltration membrane technology and process optimization using response surface methodology. Desalination. 2014;**352**:166–173. doi:10.1016/j.desal.2014.08.023

[7] Wu Q, Leung JYS, Geng X, Chen S, Huang X, Li H, Huang Z, Zhu L, Chen J, Lu Y: Heavy metal contamination of soil and water in the vicinity of an abandoned e-waste recycling site: Implications for dissemination of heavy metals. The Science of the Total Environment. 2015;**506–507**:217–225. doi:10.1016/j.scitotenv.2014.10.121

[8] Roychowdhury T, Tokunaga H, Ando M: Survey of arsenic and other heavy metals in food composites and drinking water and estimation of dietary intake by the villagers from an arsenic-affected area of West Bengal, India. The Science of the Total Environment. 2003;**308**(1):15–35. doi:10.1016/s0048-9697(02)00612-5

[9] Glasby GP, Szefer P, Geldon J, Warzocha J: Heavy-metal pollution of sediments from Szczecin Lagoon and the Gdansk Basin, Poland. The Science of the Total Environment. 2004;**330**:249–269. doi:10.1016/j.scitotenv.2004.04.004

[10] Özden Ö, Erkan N, Cengiz Deval M: Trace mineral profiles of the bivalve species *Chamelea gallina* and *Donax trunculus*. Food Chemistry. 2009;**113**(1):222–226. doi:10.1016/j.foodchem.2008.06.069

[11] Salomon S, Jenne V, Hoenig M: Practical aspects of routine trace element environmental analysis by inductively coupled plasma–mass spectrometry. Talanta. 2002;**57**:157–168. doi:10.1016/s0039-9140(01)00678-6

[12] Thomas R. Practical Guide to ICP-MS. 2004. NY, USA: Marcel Dekker.

[13] Ammann A: Inductively coupled plasma mass spectrometry (ICP MS): A versatile tool. Journal of Mass Spectrometry. 2007;**42**(4):419–427. doi:10.1002/jms.1206

[14] Law no. 311/2004, Drinking Water Quality, published in The Official Gazette of Romania.

[15] Weltje L, Heidenreich H, Zhu W, Wolterbeek HT, Korhammer S, de Goeij JJM, Markert B: Lanthanide concentrations in freshwater plants and molluscs, related to those in surface water, pore water and sediment. A case study in The Netherlands. The Science of the Total Environment. 2002;**286**:191–214. doi:10.1016/S0048-9697(01)00978-0

[16] Zhang Q, He M, Chen B, Hu B: Preparation, characterization and application of *Saussurea tridactyla* Sch-Bip as green adsorbents for preconcentration of rare earth elements in environmental water samples. Spectrochimica Acta Part B. 2016;**121**:1–10. doi:10.1016/j.sab.2016.04.005

[17] Dressler VL, Pozebon D, Matusch A, Becker JS: Micronebulization for trace analysis of lanthanides in small biological specimens by ICP-MS. International Journal of Mass Spectrometry. 2007;**266**:25–33. doi:10.1016/j.ijms.2007.06.018

[18] Kumar SA, Pandey SP, Shenoy NS, Kumar SD: Matrix separation and preconcentration of rare earth elements from seawater by poly hydroxamic acid cartridge followed by determination using ICP-MS. Desalination. 2011;**281**:49–54. doi:10.1016/j.desal.2011.07.039

[19] Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Hicks MB, Mayr SM, Redmond MS: Toxicity of cadmium in sediments: The role of acid volatile sulfide. Environmental Toxicology and Chemistry. 1990;**9**:1487–1502. doi:10.1002/etc.5620091208

[20] Simpson SL, Rosner J, Ellis J: Competitive displacement reactions of cadmium, copper, and zinc added to a polluted, sulfidic estuarine sediment. Environmental Toxicology and Chemistry. 2000;**19**(8):1992–1999. doi:10.1002/etc.5620190806

[21] Fan W, Wang WX: Sediment geochemical control on Cd, Cr, and Zn assimilation by the clam *Ruditapes philippinarum*. Environmental Toxicology and Chemistry. 2001;**20**:2309–2317. doi:10.1002/etc.5620201025

[22] Papaefthymiou H, Papatheodorou G, Christodoulou D, Geraga M, Moustakli A, Kapolos J: Elemental concentrations in sediments of the Patras Harbour, Greece, using INAA, ICP-MS and AAS. Microchemical Journal. 2010;**96**(2):269–276. doi:10.1016/j.microc.2010.04.001

[23] Romanian Ministerial Order No. 1888/2007 approving the list of organohalogenated substances and heavy metals, as well as the maximum allowable limits for the organohalogenated substances and heavy metals in water and sediment substrate.

[24] Order 756/1997-modificated in 592/2001. Regulations for environmental pollution evaluation.

[25] Baytak S, Kocyigit A, Turker AR: Determination of lead, iron and nickel in water and vegetable samples after preconcentration with *Aspergillus niger* loaded on silica gel. Clean. 2007;**35**(6):607–611. doi:10.1002/clen.200700124

IntechOpen

IntechOpen