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Spatio-Temporal Evolution of Sediments Pollution with Mobile Heavy Metals in an Abandoned Mining Area from Romania

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Additional information is available at the end of the chapter

Abstract

The present chapter focuses on spatio-temporal evolution of sediments pollution with mobile heavy metals in five sampling campaigns, in an abandoned gold-bearing mining area from Certeju de Jos, Hunedoara County. The investigated zone is situated in a region where for a long period intense activities of mining exploitation was conducted. For determination of total metals content, sediment samples were dissolved with ultra-pure nitric acid to microwave digestion. For the determination of mobile metals concentrations, it used the first step of BCR 701 sequential extraction scheme in a modified form, by reducing the extraction time from 16 hours to 20 minutes by sonication. The total and mobile concentrations of metals were determined by using ICP-MS. The concentrations of the mobile fractions of Cd, As and Cu are between 60 and 98% for Cd, 10 and 38% for As and up to 44% for Cu, indicating their presence in a bioavailable form. Due to the high mobility, these metals can pass from sediment to surface water and, implicitly, to the aquatic ecosystems. The pollution indices, calculated for the total content of As, Cd, Cu, Ni and Pb, indicate the presence of a strong environmental risk of sediment degradation in most investigated site.

Keywords: sediments, heavy metals, mining area, index pollution, spatio-temporal evolution

1. Introduction

Nowadays, aquatic sediments contamination with heavy metals is a major environmental problem at both national and global level [1–3]. One of the main sources leading to heavy-metal pollution of the aquatic environment is represented by a series of industrial activities associated with mining exploitations processes [4–7].

Due to certain conditions imposed by the legislation in force, mining companies are trying to reduce the emission of effluents resulting from operating activities, but despite all the efforts and safety procedures, accidental pollution is still common within this industry.

Also, near abandoned metal mines, high levels of heavy metals can be found as a result of the discharge and dispersion of waste tailings both the aquatic environment and the soils surrounding the mining areas [8–12].

Depending on the geochemical characteristics and the mineral waste tailing loading, the degree of heavy metals contamination recorded in mining areas varies within a large range [13]. Heavy metals concentrations exceeding the permitted limits regulated by the legislation in force are the main source of aquatic toxicity [14, 15]. The sediments coming from metallic mining areas as main feature of the acid pH value that strongly influences the transport of contaminants from sediment to surface water [16–19]. Drainage of both acid mines and also discharged sediments from abandoned metal mines represents a serious threat to the biota and human health [20].

Heavy metals accumulation in sediments occurs through five major processes: precipitation of certain compounds; binding of fine solid particles having active surface points (encountered in discharges or resuspended during turbulence); coprecipitation together with Fe or Mn oxides or in form of carbonates; association with organic molecules and incorporation into mineral crystals [20]. Therefore, these processes are represented by precipitation and adsorption processes. The balance between these two process categories depends on the metal concentrations, the size of the available surfaces and also the concentrations of the complexing agents found in the water [21]. Inorganic precipitates are formed by oxides, hydroxides, carbonates, sulfates and sulfides [22]. Within aquatic systems having high mineral loading, carbonates and hydroxides are reactive species [20]. The heavy metals as Zn, Ag, Hg, Cu, Cd, or Pb have a strong affinity for sulfide ions thus forming precipitates with very low solubility, so association as sulfide is predominant in reducing conditions as well as when sulfide is released as a result of organic matter decomposition [23].

It is important to underline that heavy metals are not biologically degradable and thus can be accumulated by plants or animals by entering in biochemical where they are transformed into various organometallic compounds [14, 24]. In recent years, more and more attention has been paid for the determination of species in which metals are found, taking in account that toxicity, bioavailability, mobility and other properties depend on the chemical forms of the metals within sample [25–27]. Due to this fact, in addition to determining the total metal

concentrations, it was proposed to determine the chemical species associated with the metal using sequential extraction schemes in order to ensure the characterization of the metals' chemical forms found in sediments, soils and muds [28–31].

In Romania, there are several areas affected by heavy metals contamination such as Baia Mare, Rosia Montana, Certej and Tara Oasului, where gold-mining activities have been carried out for a long time [32–35].

The present chapter focuses on spatio-temporal evolution of sediments pollution with mobile heavy metals as Cd, As, Cu, Ni and Pb in five sampling campaigns, in an abandoned gold-bearing mining area from Certeju de Jos, Hunedoara County. For estimation level pollution of sediments with heavy metals, pollution indexes were calculated. The investigated zone is situated in an region where for a long period intense activities of mining exploitation was conducted.

2. The study area

The analyzed sector (Bajaga River) is located on the territory of Certeju de Jos village, Hunedoara County, about 20 km north of Deva City (**Figure 1**).

In the central area of the studied perimeter, the main collector is represented by the Certej Valley. Its main tributaries are Faerag and Mures streams on the right side, and Bocsa Mica (Ciongani) and Nojag Valley streams on the left side.

After crossing the mountain area, it has a large reception basin powered by a well-developed torrential network, known as the Baiaga Valley and completed downstream by the Hondol
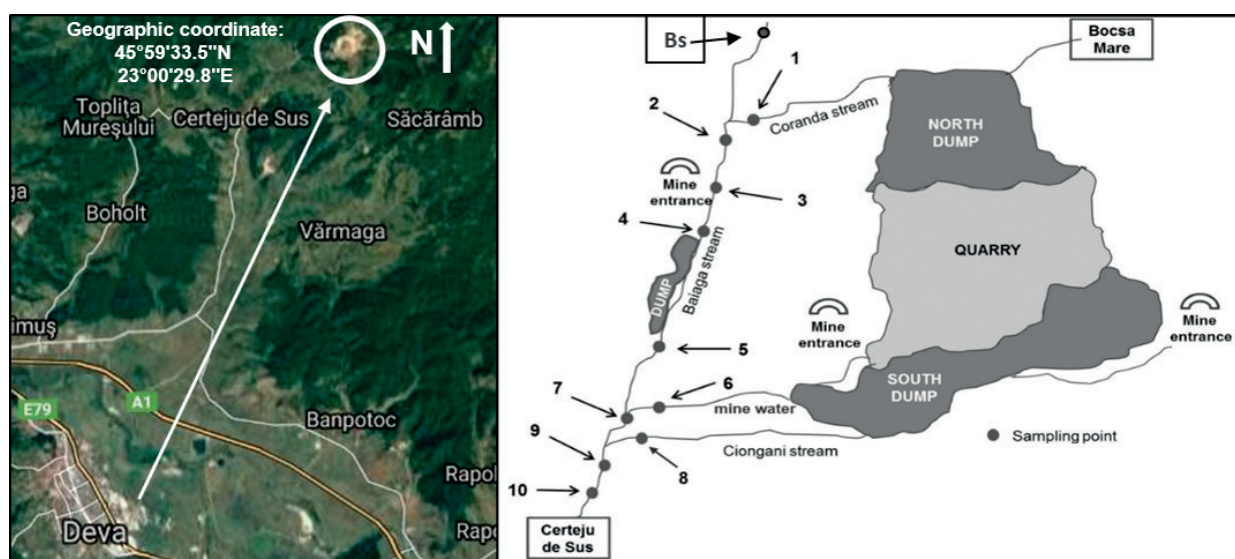

Figure 1. Sampling points location – Certej, Hunedoara County.

Valley, the Certej Valley forms a narrow meadow that gradually spreads until it flows into the Mures River.

From a topographic point of view, the studied area is part of the small mountains group, which has rounded or flat ridges with heights which do not exceed 1300 m. These kinds of mountains groups surround andesite lava beds or quaternary depressions.

Within these types of areas, the water courses are usually short, with steep slopes and insignificant average annual flows. During torrential rains, drift on the slopes occurs rapidly and facilitates the occurrence of impetuous floods, often with catastrophic effects. In these areas, the water courses are short having quick slopes and average annual flows are insignificant as values (**Figure 2**). The river flows undergo major changes during torrential rains when the slopes leakage occurs with high speeds thus facilitating the occurrence of impetuous floods, often with catastrophic effects.

In order to study the spatio-temporal evolution of heavy metal sediment pollution, five sampling campaigns were carried out over 3 years in different periods of the year. In each sampling campaign 10 samples of sediment and surface water associated with sediment within the Certej catchment were taken. In order to compare the results obtained from the polluted sediments, a blank sample was also collected. The location of the sampling points is shown in **Figure 1**, and the GPS coordinates and sample indices are shown in the **Table 1**.

Figure 2. Acid mine water – Baiaga stream.

No.	GPS coordinates	Sample type/indicative	Observations
1	45°59′84.3″ N 23°00′25.9″ E	S1	Sampling point situated on Coranda Stream – upstream
2	45°59′81.9″ N 23°00′13.1″ E	S2	Sampling point situated on Baiaga Stream, downstream of the confluence with Coranda stream
3	45°59′80.1″ N 23°00′06.3″ E	S3	Sampling point situated at the exit Nicodim gallery
4	45°59′67.7″ N 22°59′96.6″ E	S4	Sampling point situated on Baiaga Stream, downstream of the confluence with career water from Nicodim gallery
5	45°59′41.8″ N 22°59′74.0″ E	S5	Sampling point situated on Baiaga Stream, upstream of the confluence with career water
6	45°59′41.7″ N 22°59′73.9″ E	S6	Sampling point from career water, before of the confluence with Baiaga Stream
7	45°59′39.8″ N 22°59′74.1″ E	S7	Sampling point situated on Baiaga Stream, downstream of the confluence with career water and upstream of the confluence with Baiaga Stream
8	45°59′41.0″ N 22°59′72.2″ E	S8	Sampling point situated on Ciongani Stream before of the confluence with Baiaga Stream
9	45°59′39.8″ N 22°59′68.3″ E	S9	Sampling point situated on Baiaga Stream, downstream of the confluence with Ciongani Stream
10	45°59′20.7″ N 22°59′06.5″ E	S10	Sampling point situated on Baiaga Stream, in the Hondol Village
11	46°00′29.6″ N 23°00′51.3″ E	sediment blank sample (Bs)	Sampling point situated on Baiaga Stream – 2 kilometers away from the quarry area.

Table 1. GPS coordinates and description of sampling points.

3. Materials and methods

3.1. Sampling

The sampling techniques were used in accordance with SR ISO 5667-12/2000 – Guidance on the Sampling of Bottom Sediments the standard in force. The sediment harvested samples were taken from 0 to 5 cm depths using a Van Veen (Wagtech) scrubber. The samples were placed into polypropylene containers which were pre-washed with dilute hydrochloric acid solution.

Samples were transported to the test laboratory in refrigerated boxes and stored at 4°C until the analysis was done.

3.2. Sediment pretreatment

Total content – A part of each sediment sample collected from these sampling points was first prepared before the actual analysis by air-drying and homogenization. For evaluation of the

total content of heavy metals from each soil probe, after this pre-treatment was subjected to the final analysis, only the fraction having smaller dimensions than 63 µm. Through sieving process and using a Fritsch Analysette 3 Spartan Vibratory Sieve Shaker, the sediment samples were separated and finally 2 g of probe were digested in a microwave oven (Berghof, Germany) at 175°C in a 1:3 (v/v) ratio mixture formed by nitric acid (65%):hydrochloric acid (37%) mixture.

Mobile fraction – In order to perform mobile fraction determinations, the remaining part of each sediment sample was first sieved in wet condition using surface water from same sampling point in order to maintain the same structure existing in its natural condition. In this case, similar to total content analysis, the fraction having smaller dimensions than 63 µm was also collected.

3.3. Dry matter content

A separate portion of 1 g was taken from each sample at the same time with the experiments and was dried in an oven at 105 ± 2°C for 3–4 h until constant mass in order to measure dry matter. The results of metals were corrected according to dry matter (d.m.) content.

3.4. Mobile fraction determining methods

3.4.1. The BCR method

In order to correlate the existing analysis methods connected to metals deposition within sediments, an European researcher group conducted a collaboration with the Community Reference Materials Office (CRM). As a result of their common work and a viable alternative to the Tessier method [36], a sequential extraction scheme in three stages (BCR scheme) was proposed [37, 38]. Acetic acid (0.11 M, pH = 2.8), hydroxylamine hydrochloride (0.5 M, pH = 2) and ammonium acetate (1 M, pH = 2) were used as extraction agents. Thus three fractions were separated:

1. The changeable (mobile) fraction for metals having low adsorption rate that are released by ion exchange processes and carbonate-linked metals.

2. The fraction linked to Fe and Mn oxide, also called the "reducible fraction" due to the fact that these kinds of metals are released when this fraction is reduced.

3. The organic matter fraction, also called the "oxidizable fraction" due to the fact that these kinds of metals are released by oxidation.

Currently, this extraction procedure is being used on a large scale performing sediment, soil, muddy soil and also waste analysis [39–41].

The exchangeable (mobile) fraction for cadmium, copper, nickel and lead was determined through a modified BCR method that allowed the extraction time reduction from 16 hours to 20 minutes by using ultrasonic shaking [42] for 20 minutes at 50 KHz and 25°C (**Figure 3**).
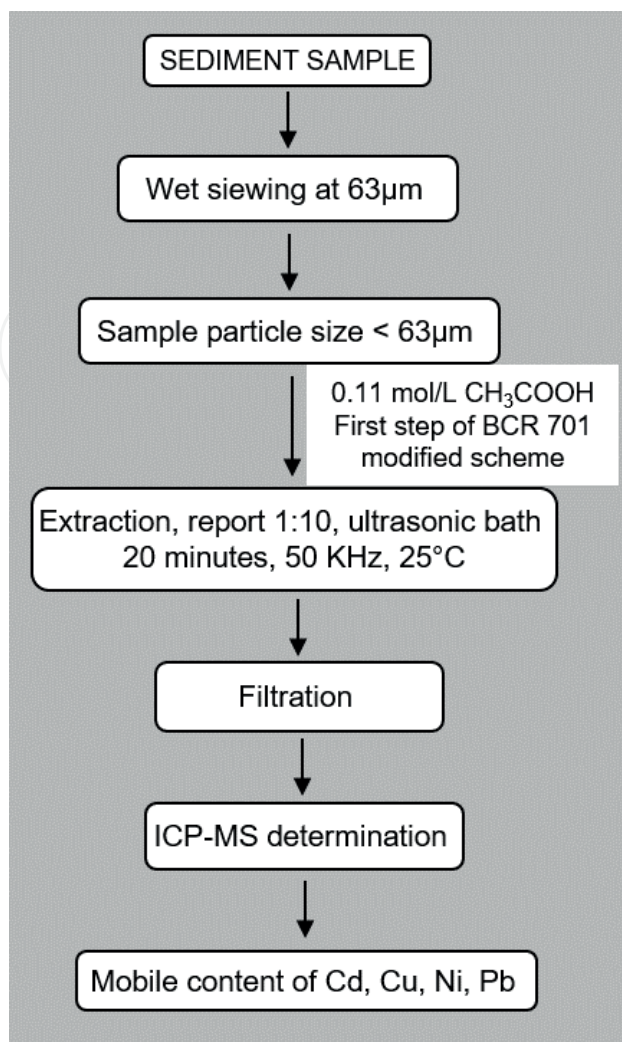
Figure 3. Scheme BCR modified.

The metals concentrations obtained by applying BCR sequential extraction scheme were verified using a certified reference material (BCR-701 – lake sediment produced by the Standards, Measurements and Testing Program – European Commission) with a recovery rate between 99.65 and 99.90%.

3.4.2. Cold extraction procedure

The mobile fraction of arsenic was determined using a cold extraction treatment (**Figure 4**). In order to verify the single chemical extraction of these two metals, this procedure was also applied on a certified reference material WQB-1: lake sediment (with a recovery rate between 99.70 and 99.88%) [43].

The BCR method and cold extraction procedures were performed three times per each sediment sample. The final results were reported as an average. To ensure the quality control of the extraction (decreasing contamination during procedure), a blank extraction (without sediment) was also used for each set of analysis.
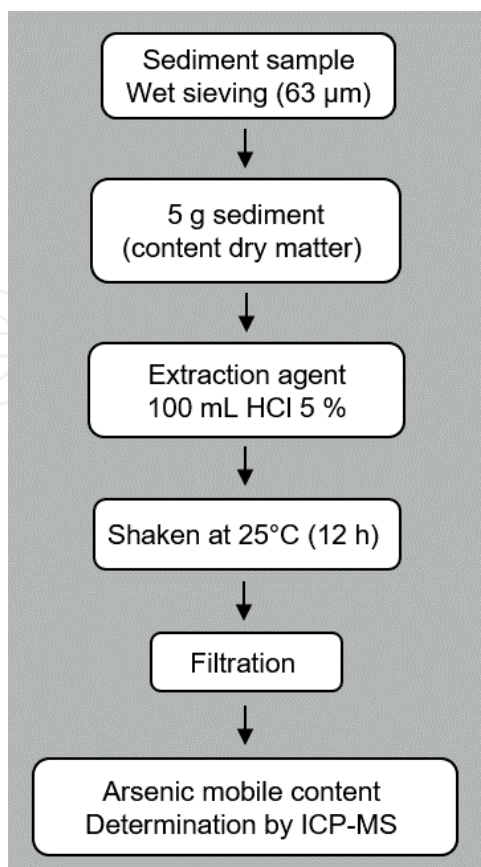
Figure 4. Cold extraction procedure scheme for arsenic mobile content.

The total and mobile content of arsenic in sediment samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Bruker: Aurora M90). All the chemicals and extraction agents were analytical reagents grade provided by Merck. Calibration curve was performed using a Certified Reference Material ICP multi-element standard solution XXI for MS (Merck quality).

3.4.3. Results and discussion

For all five sampling campaigns, the entire study area indicates an acid pH, both in sediment and in surface water ranging between 3 and 4 pH units.

The results obtained in our study were correlated to the existing limits imposed by the Romanian Order no. 161/2006 on surface water quality and sediments. In **Table 2**, the results for the total and mobile concentrations of cadmium in sediments are shown. Maximum admissible value for total cadmium in sediment according to Romanian Legislation [44] is set to 0.8 mg/kg.

After analyzing the collected data, it was found that in all sampling campaigns total cadmium content exceeded the maximum admissible concentration.

The lowest points of both total and mobile cadmium concentrations were recorded in S1 sampling point located upstream of the quarry and tailings dumps. In the same line, the highest total and mobile cadmium concentrations were recorded in S3 sampling point corresponding to the Nicodim gallery.

Sampling		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
March 2013	Cd total	1.96	2.85	4.09	3.05	3.31	4.38	4.88	6.45	6.22	6.33
	Cd mobile	1.93	2.11	3.64	2.79	2.54	3.09	4.20	5.57	5.37	4.22
January 2014	Cd total	1.82	2.76	4.82	1.35	3.88	3.06	4.98	1.35	3.21	5.46
	Cd mobile	1.08	1.25	3.76	1.26	1.08	1.43	4.35	1.09	3.00	5.15
July 2014	Cd total	3.15	3.82	8.19	3.09	2.85	5.08	2.85	3.23	3.71	2.16
	Cd mobile	2.32	3.35	7.72	2.76	1.99	2.89	2.32	3.01	3.50	1.99
October 2014	Cd total	0.98	3.98	1.76	1.1	5.23	1.51	1.39	1.52	2.24	1.82
	Cd mobile	0.38	2.82	1.07	0.58	3.10	0.8	0.84	0.72	1.49	1.09
March 2015	Cd total	2.01	1.03	3.98	2.93	1.12	3.43	1.74	2.52	1.62	2.21
	Cd mobile	1.73	0.54	2.65	2.58	0.74	2.61	1.29	2.02	1.35	1.43

Table 2. Total and mobile content of CADMIUM in sediments samples (mg/kg d.m.).

The spatio-temporal evolution of the cadmium mobile content in all five sampling campaigns is given in **Figure 5**.

In all five sampling campaigns, mobile cadmium concentrations represent at least 35% of the total cadmium content recorded in the analyzed sediments. In most samples, it was observed that the mobile cadmium content ranges between 60 and 98% of total content. Also, due to the
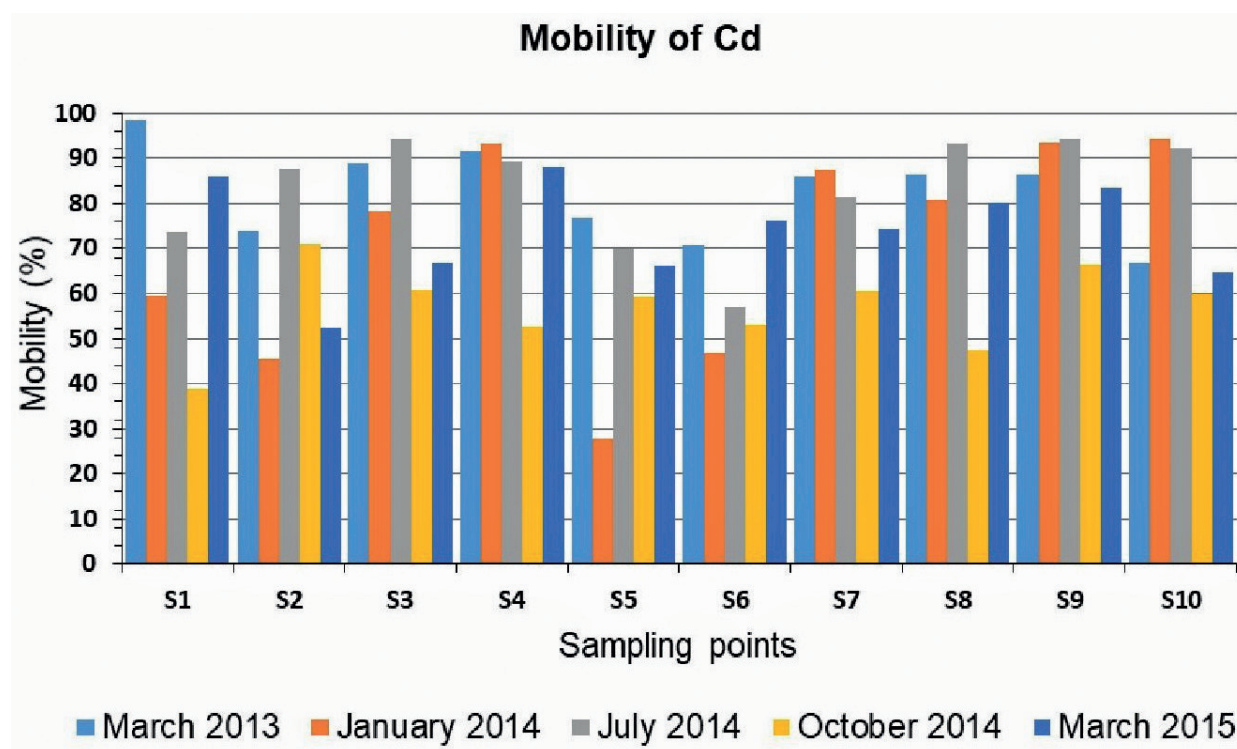

Figure 5. Spatio-temporal evolution of cadmium mobile content.

high mobility percentage, cadmium could induce strong pollution upon aquatic environment by passing from sediment within surface water.

The results obtained for total and mobile arsenic concentrations in sediments are presented in **Table 3**.

Maximum admissible value for As in sediment samples is set to 29 mg/kg, limit imposed by the Romanian legislation in force. In all sampling campaigns, total and mobile arsenic content exceeded the maximum admissible concentration. Sampling points S3 and S4 were the ones in which in all sampling campaigns, the total arsenic concentration was 10 times higher than the maximum admissible concentration.

The elevated arsenic concentrations in these points are due to the water intake from the Nicodim gallery and the water coming from the Coranda River that transports contaminants from the North Dump. It was also noted that in the spring campaigns (March 2013 and March 2015) the values obtained are comparative. This behavior confirms that metals are not biodegradable and were accumulated in aquatic systems over extended periods of time.

The spatio-temporal evolution of the mobile arsenic content in all five sampling campaigns is given in **Figure 6**.

The mobile arsenic concentrations reported to the total arsenic content varied between 10 and 38%. March 2015 sampling campaign corresponded to the highest mobile arsenic concentrations.

The average arsenic concentration obtained from all five sampling campaigns was 23%, value which represents almost a quarter of the total arsenic content. The high content of mobile arsenic induces significant sediment and aquatic ecosystem pollution.

In **Table 4** the results obtained for total and mobile copper concentrations in sediments for all five sampling campaigns are presented.

Sampling		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
March 2013	As total	282	176	658	485	386	184	312	356	331	215
	As mobil	65.4	42.1	168	89.5	74.9	57.8	56.1	98.5	88.2	55.8
January 2014	As total	202	144	588	405	289	218	222	316	209	217
	As mobil	60.9	55.1	129	105	36.1	32.6	42.8	52.4	41.6	35.6
July 2014	As total	378	285	710	512	406	173	296	411	399	381
	As mobil	71.9	51.6	145	140	93.8	59.6	43.3	91.5	94.5	92.7
October 2014	As total	198	129	775	386	276	197	189	345	277	289
	As mobil	35.6	25.8	186	81.1	52.4	49.3	29.8	75.9	49.9	46.2
March 2015	As total	274	159	614	449	298	175	294	326	246	191
	As mobil	29.7	35.4	152	110	81.1	60.3	49.2	88.6	104	56.9

Table 3. Total and mobile content of ARSENIC in sediments samples (mg/kg d.m.).
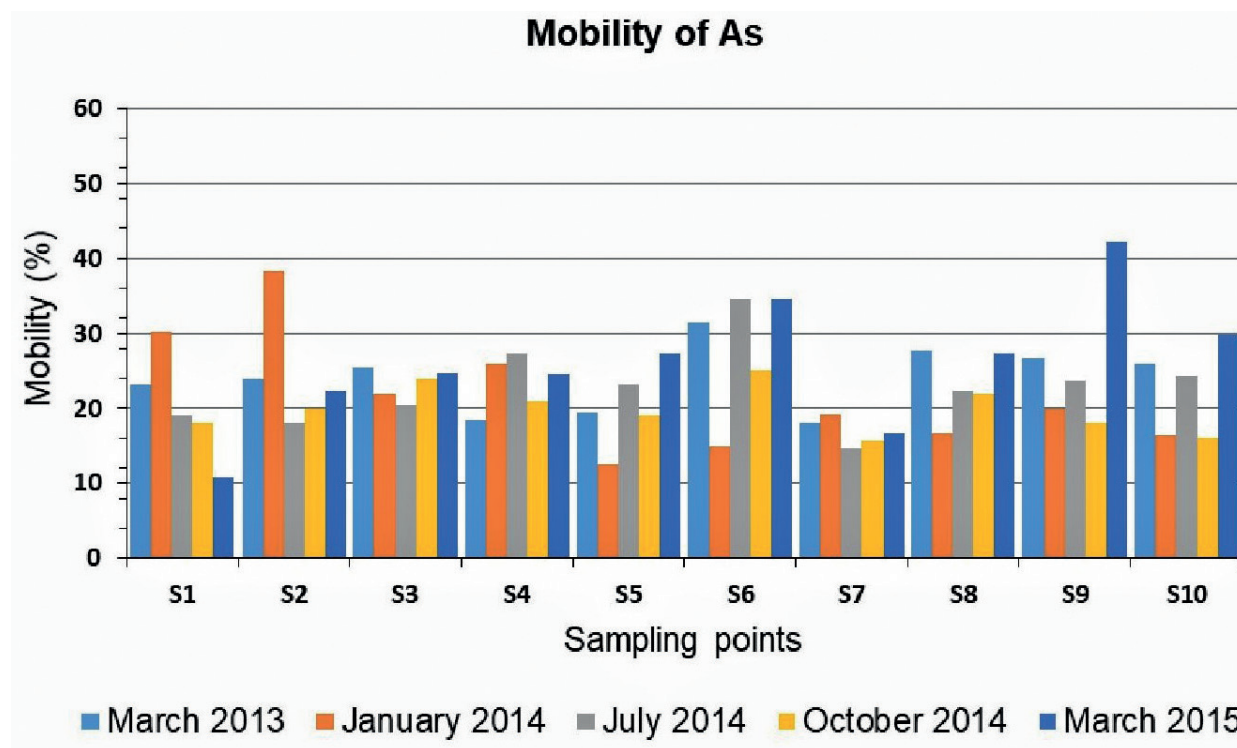
Figure 6. Spatio-temporal evolution of arsenic mobile content.

Sampling		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
March 2013	Cu total	75.2	38.9	48.2	57.6	35.4	18.8	47.1	52.6	37.5	42.1
	Cu mobil	16.9	12.8	8.27	15.6	8.91	3.56	10.44	12.35	11.9	10.8
January 2014	Cu total	28.4	32.2	43.5	70.2	29.1	48.3	35.8	36.8	26.1	25.1
	Cu mobil	6.85	14.2	9.43	18.7	4.88	19.5	6.61	5.88	7.22	5.47
July 2014	Cu total	54.2	105	57	36.4	54.9	139	29.7	54.5	35.5	32.7
	Cu mobil	11.5	25.7	13.1	8.88	12.5	30.1	5.86	12.9	8.39	8.64
October 2014	Cu total	40.4	29.6	51.4	42.8	102	64.1	44.6	109	62.2	40.3
	Cu mobil	9.6	10.8	7.8	11.4	14.7	7.37	10.5	19.2	8.6	9.6
March 2015	Cu total	66.3	15.5	40.4	25.1	48.3	20.6	37.2	33.2	20.8	50.5
	Cu mobil	6.52	4.92	7.08	2.4	4.08	7.32	1.39	1.76	1.12	1.2

Table 4. Total and mobile content of COPPER in sediments samples (mg/kg d.m.).

Regarding copper concentrations, 56% from the sediment samples has the total content above the maximum admissible concentration limit with is set to 40 mg/kg d.m. No mobile content over the limit has been recorded.

The highest concentrations exceeding twice the maximum admissible concentration are recorded at S5 and S8 (October 2014) and S2 (July 2014).

The spatio-temporal evolution of the mobile copper content in all sampling campaigns is given in **Figure 7**.

Analyzing the data presented in **Figure 7**, a decrease regarding copper content throughout the investigated route was noticed as follows: January 2014 > March 2013 > Oct 2014 > March 2015. The bioavailable content was ranged between 2 and 44%. In the same time, it was also recorded a peak in mobile copper concentration, the highest values were found in S2 (44%) and S6 (41%), corresponding to samples collected in January 2014.

All these concentrations exceeded the maximum admissible concentration according to Order 61/2006. In all the other campaigns, the mobile copper concentrations found in the investigated samples were below the maximum admissible value.

In **Table 5**, the results obtained for total and mobile nickel concentrations in sediments collected in all five sampling campaigns are presented. The data were compared with maximum admissible value, which is 35 mg/kg.
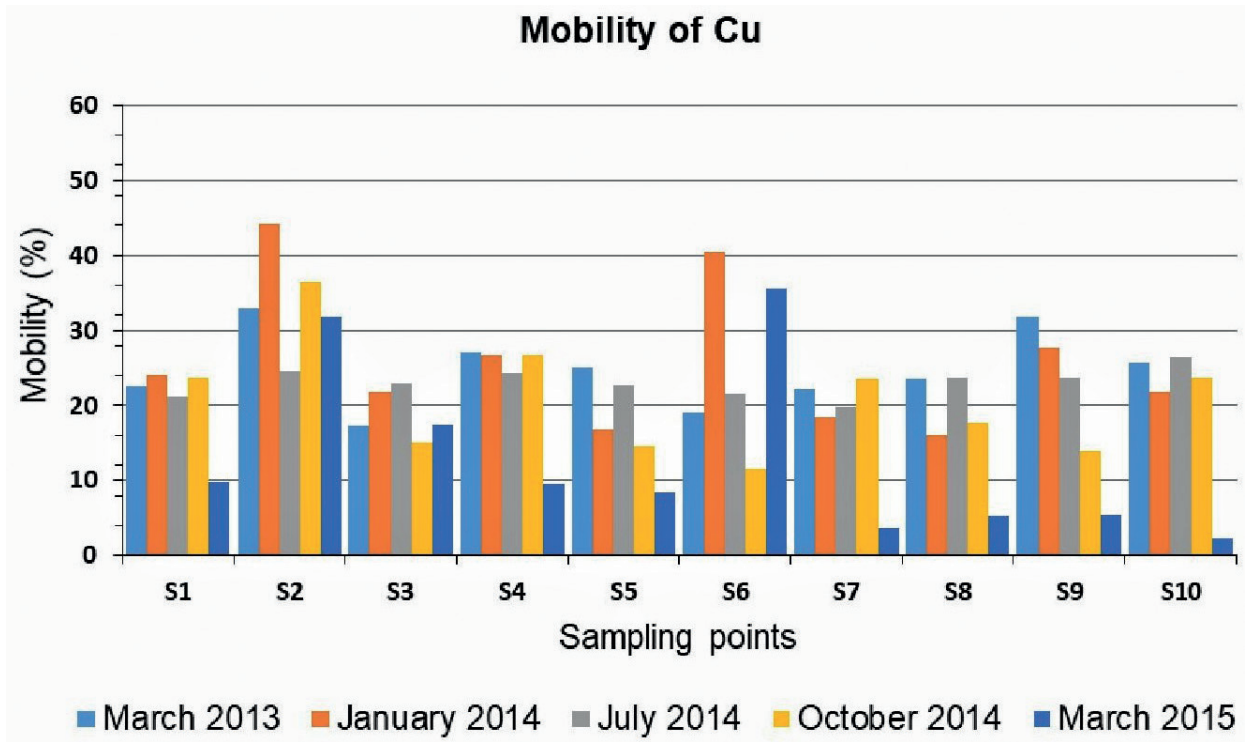

Figure 7. Spatio-temporal evolution of copper mobile content.

Sampling		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
March 2013	Ni total	32.3	16.7	62.3	18.2	33.9	16.5	8.44	43.9	30.5	30.9
	Ni mobil	8.05	6.55	14.8	8.04	19.2	8.63	2.60	8.40	9.32	10.6
January 2014	Ni total	24.3	20.5	38.6	23.1	30.8	14.2	26.2	25.2	17.6	18.6
	Ni mobil	7.35	6.28	10.7	9.84	16.5	6.82	5.86	4.79	5.88	11.7
July 2014	Ni total	34.7	25.8	75.9	29.1	40.6	24.2	19.7	38.5	32.8	27.4
	Ni mobil	7.25	8.64	17.9	5.33	11.9	9.26	3.81	4.56	7.62	6.25
October 2014	Ni total	19.1	15.2	45.1	23.4	26.9	8.03	43.9	6.58	30.1	22.9
	Ni mobil	2.83	2.60	7.94	6.83	11.9	2.17	4.56	1.79	8.28	9.71
March 2015	Ni total	27.6	22.8	65.4	25.2	30.9	12.7	15.4	25.8	22.7	31.9
	Ni mobil	5.41	6.33	20.8	7.82	6.49	4.21	8.52	10.4	13.1	16.9

Table 5. Total and mobile content of NICKEL in sediments samples (mg/kg d.m.).

The highest total nickel concentration was recorded in S3 sampling point associated with Nicodim gallery (two times higher than limit). Also nickel exceedings in S5 and S8 (July 2014), S8 (March 2013) and S7 (October 2014) were found.

At all the other sampling points, both total and mobile nickel concentrations were below the maximum admissible value.

The spatio-temporal evolution of nickel mobile content in the all sampling campaigns is given in **Figure 8**.

After the results were collected, we could conclude that in all sampling campaigns the mobile nickel concentrations varied between 10 and 63%. The highest mobile Ni concentrations were determined in the samples coming from S5, S6, S7, S9 and S10 points. In these cases, the values determined exceeded the maximum admitted concentration and represent more than 50% of the total nickel content.

The intake of contaminants accumulating in the upstream from Nicodim gallery, mine water and career water could be the main sources of these overtakings. In March 2015, the sampling campaign recorded a decrease of the Ni mobile concentrations for the majority of the investigated sediments. Sediments can change their composition, so they could be more diluted or loaded, depending on the volume of precipitation and weather conditions [43].
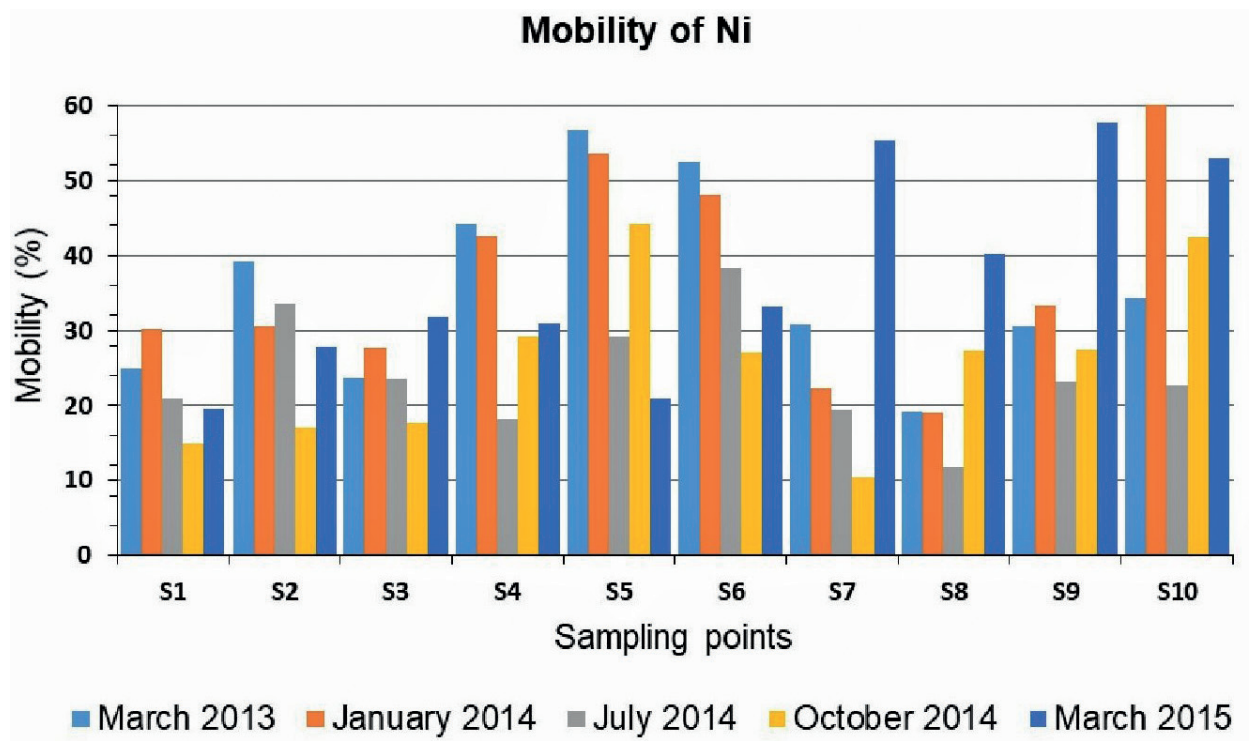
Figure 8. Spatio-temporal evolution of nickel mobile content.

In **Table 6**, the results obtained for the total and mobile lead concentrations within sediments are presented for the five sampling campaigns:

Regarding Pb content, the results obtained from the most sampling points indicate that the maximum admissible concentration, which is 85 mg/kg, was exceeded.

The highest lead concentrations were recorded at sampling point S3 where the total lead concentration ranges between 235 mg/kg d.m. (March 2013) and 539 mg/kg d.m. (October 2014).

The spatio-temporal evolution of mobile lead content in all five sampling campaigns is shown in **Figure 9**.

Although within the majority of the analyzed sediments the total lead content exceeds the maximum admissible concentration, the mobile content of Pb is below the maximum admissible value and thus in almost all investigated samples does not exceed 15 mg/kg d.m.

This behavior confirms that lead is link in a lower share within oxides, carbonates and organic matter and a greater share within residual fraction.

3.5. Estimation the pollution degree by pollution indexes

In order to assess the pollution degree of the aquatic environment with these toxic metals, we proposed the determination of two pollution indices: the contamination factor (CF) and the geoaccumulation index (I_{geo}).

Sampling		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
March 2013	Pb total	129	111	235	109	254	120	266	28.8	64.9	103
	Pb mobil	10.3	10.1	8.50	3.72	9.98	3.36	11.8	4.77	3.72	4.51
January 2014	Pb total	152	144	354	127	103	66.5	185	113	48.4	36.6
	Pb mobil	10.8	6.42	15.9	9.53	6.87	5.45	10.4	8.70	4.02	6.21
July 2014	Pb total	205	157	426	135	79.2	87.8	223	151	88.4	75.9
	Pb mobil	6.82	4.16	24.5	8.68	3.21	6.17	12.9	18.7	15.9	10.8
October 2014	Pb total	213	127	539	115	174	284	165	244	364	131
	Pb mobil	14.5	2.35	16.3	5.15	2.18	9.89	5.48	8.52	6.92	3.56
March 2015	Pb total	145	74.3	382	151	183	219	148	76.9	297	154
	Pb mobil	12.8	3.85	23.9	8.82	6.14	12.4	8.22	5.44	16.9	8.24

Table 6. Total and mobile content of LEAD in sediments samples (mg/kg d.m.).
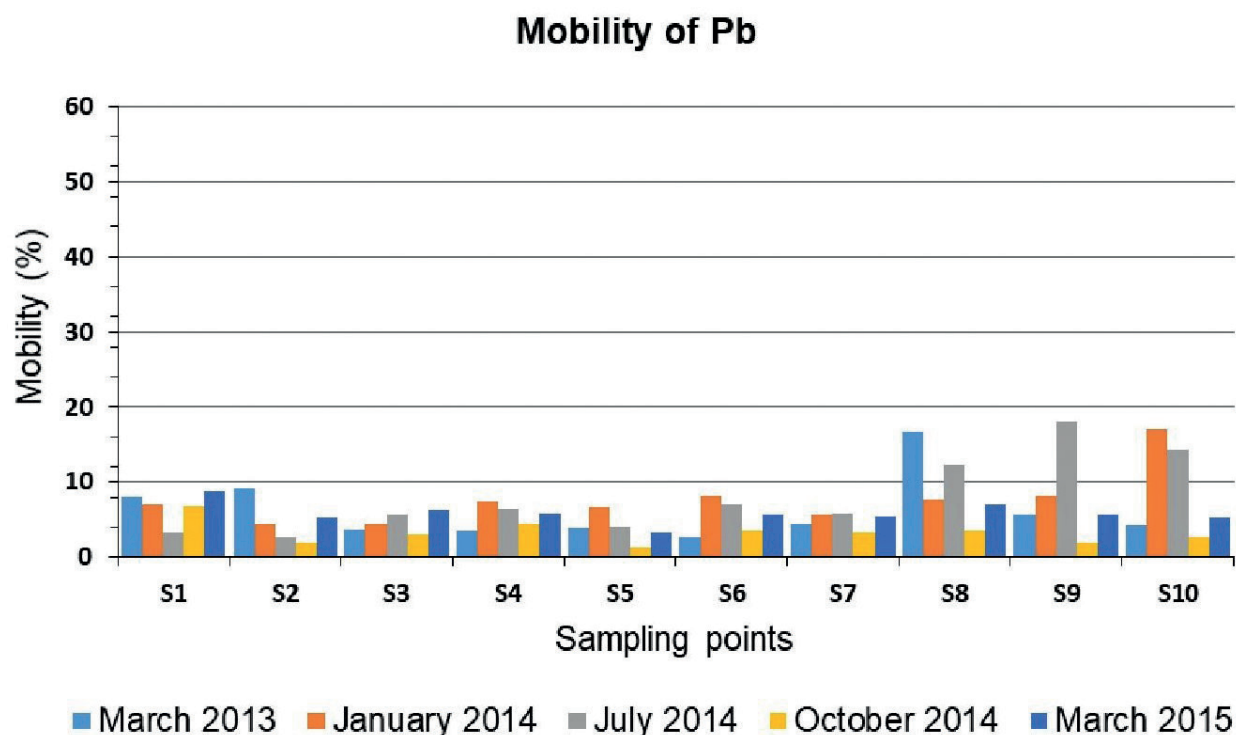

Figure 9. Spatio-temporal evolution of lead mobile content.

The contamination factor (CF) (**Table 7**)—is given by the ratio between the metal concentration within the sediment and the metal concentration in the natural background. CF is calculated according to Hakanson's formula (Eq. (1)) [45]:

$$CF = \frac{Cs}{Bs} \tag{1}$$

where *Cs* is the metal concentration within the sample and *Bs* is the metal concentration within the natural background (**Figure 1**).

The geoaccumulation index (I_{geo}) (**Table 8**) was introduced by Müller [46] and is widely used [15, 47, 48] to determine the pollution degree with heavy metal in surface sediments:

$$Igeo = \log_2\left[\left(\frac{Cs}{K \times Bs}\right)\right] \tag{2}$$

where *Cs* is the metal concentration within the sample, *Bs* is the metal concentration within the natural background and *K* is the correction factor that takes into account the variation of metal traces in the natural background as a result of the lithogenic effects (*K* = 1.5).

The geoaccumulation index provides a classification system for the pollution degree in relation to the sediment quality [46].

In **Table 9**, the concentrations of metals within the natural background are given.

The determination of contamination factor (CF) and geoaccumulation index (I_{geo}) involved assuming that each metal concentration introduced in the formulas was the average value obtained after the five sampling campaigns.

Contamination factor (CF) and geoaccumulation index (I_{geo}) values are shown in **Tables 10** and **11**.

Contamination factor (CF)	Contamination level
CF < 1	Low contamination
1 ≤ CF < 3	Medium contamination
3 ≤ CF < 6	Significant contamination
CF > 6	Very high contamination

Table 7. Contamination factor (CF) and contamination level.

I_{geo} value	Class of pollution in relation to I_{geo}	Sediment quality
≤0	0	Unpolluted level
0–1	1	Unpolluted level to moderate pollution
1–2	2	Moderate pollution level
2–3	3	Moderate pollution level to high pollution
3–4	4	High pollution level
4–5	5	High pollution level to very high pollution level
>5	6	Very high pollution level

Table 8. The relationship between I_{geo} and the pollution level.

No.	Metal	UM	Concentration within the natural background
1	Cadmium	mg/kg dm	0.43
2	Arsenic	mg/kg dm	9.34
3	Copper	mg/kg dm	23.4
4	Nickel	mg/kg dm	38.3
5	Lead	mg/kg dm	16.7

Table 9. Metal concentration within the natural background (Bs).

Concentration factor CF											
No.	Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	Cd	4.61	6.72	10.6	5.36	7.62	8.12	7.37	7.01	7.91	8.36
2	As	28.6	19.1	71.6	47.9	35.4	20.3	28.1	37.6	31.3	27.7
3	Cu	2.26	1.89	2.06	1.98	2.31	2.49	1.66	2.45	1.56	1.63
4	Ni	0.72	0.53	1.50	0.62	0.85	0.39	0.59	0.73	0.70	0.69
5	Pb	10.1	7.34	23.2	7.63	9.50	9.31	11.8	7.35	10.3	6.00
Geoaccumulation index (I_{geo})											
No.	Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	Cd	1.62	2.16	2.82	1.84	2.35	2.44	2.30	2.22	2.40	2.48
2	As	4.25	3.67	5.58	5.00	4.56	3.76	4.23	4.65	4.38	4.21
3	Cu	0.59	0.33	0.45	0.40	0.62	0.73	0.15	0.71	0.05	0.12
4	Ni	−1.10	−1.50	0.00	−1.30	−0.80	−1.90	−1.30	−1.00	−1.10	−1.10
5	Pb	2.75	2.29	3.95	2.35	2.66	2.63	2.98	2.29	2.78	2.00
Concentration factor CF											
No.	Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	Cd	4.61	6.72	10.6	5.36	7.62	8.12	7.37	7.01	7.91	8.36
2	As	28.6	19.1	71.6	47.9	35.4	20.3	28.1	37.6	31.3	27.7
3	Cu	2.26	1.89	2.06	1.98	2.31	2.49	1.66	2.45	1.56	1.63
4	Ni	0.72	0.53	1.50	0.62	0.85	0.39	0.59	0.73	0.70	0.69
5	Pb	10.1	7.34	23.2	7.63	9.50	9.31	11.8	7.35	10.3	6.00
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3	Cu	0.59	0.33	0.45	0.40	0.62	0.73	0.15	0.71	0.05	0.12
4	Ni	−1.10	−1.50	0.00	−1.30	−0.80	−1.90	−1.30	−1.00	−1.10	−1.10
5	Pb	2.75	2.29	3.95	2.35	2.66	2.63	2.98	2.29	2.78	2.00

Table 10. Contamination factor (CF) and geoaccumulation index (I_{geo}) values within sediments.

Sediment	I_{geo}	Sediment	I_{geo}
S1	4	S6	4
S2	4	S7	4
S3	6	S8	5
S4	5	S9	5
S5	5	S10	5

Table 11. The quality class for each sediment according to geoaccumulation indexes.

Both arsenic and lead induce a very high contamination (CF > 6). The same behavior was also observed for cadmium, which induces very high contamination with the exception of samples S1 and S4 where the sediments exhibit only considerable contamination. In case of nickel, we could conclude that it induces low contamination in sediments, except for the S3 sediment that also enters into moderate contamination category. In all sediments that were analyzed, copper induced moderate contamination.

Taking in consideration that each of the analyzed sediments had very high concentrations of As, Cd and Pb and without taking into account the contribution that other metals could imply on the samples, the samples were introduce in very high contamination category.

According to the classification given in **Table 8**, the geoaccumulation indexes calculated for Cd in sediments classified sediments S1 and S4 into class 2 (moderate pollution level) and all the other sediments into class 3 (moderately to high polluted).

In the same time, geoaccumulation indexes calculated for As, classified sediments S2 and S6 into class 4 (highly polluted), sediments S1, S2 and S7 into class 4 (highly polluted), sediments S1, S5, S7, S8, S9, S10 into class 5 (from highly polluted to very highly polluted) and sediment S3 and S4 into class 6 (very highly polluted).

In Cu case, the geoaccumulation index values obtained classified all sediments into class 1 (from unpolluted to moderately polluted). Regarding Ni, the geoaccumulation index values obtained classified all sediments into class 0 (unpolluted level). Geoaccumulation index values obtained for Pb, classified sediment S3 into class 4 (heavily polluted) and all other sediments into class 3 (moderately to highly polluted).

Based on the results given in **Table 11**, we could conclude that the most contaminated area is at sampling point S3, the point near Nicodim gallery exit.

4. Conclusion

In all sampling campaigns, the area investigated indicates an acid pH, both in sediment and in surface water. Concerning the total of heavy metal content, from all five metals investigated, Cd, Pb and As induce high sediment contamination with concentrations exceeding the limits imposed by the legislation in force.

From the point of view of metal mobile fraction, Cd and As are predominantly present in a bioavailable form within the analyzed sediments, thus inducing a high degree of pollution upon the aquatic environment by passing from sediments within surface water.

The pollution degree of the water depends on the amount of precipitation in the area, a heavy rain implies a less dilution and also the opposite case. Therefore, all the values recorded at most sampling points may be momentary, associated with the place and time of sampling.

The pollution indexes, calculated for the total content of As, Cd, Cu, Ni and Pb, indicate the presence of a strong environmental risk of sediment degradation.

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