„Babes-Bolyai University
Faculty of Environmental Science and Engineering
Doctoral School of Environmental Science

-PhD Thesis-

CONTRIBUTIONS TO THE ASSESMENT OF THE ENVIRONMENTAL IMPACT OF MINING ACTIVITIES FROM BAIA MARE AREA BY CALCULATING THE SPECIFIC QUALITY INDEXES

- summary -

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<u>Key words</u>: Baia Mare, mining area, environmental assessment, water, soil, sediment, quality indexes.

NOTE: The summary has the same notations for the table of contents, chapters, sub-chapters, figures and tables as the thesis.

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CHAPTER 1

Introduction. Concept and objectives

1.1. Introduction

The progress of the human civilization has largely depended on the exploitation of mineral resources. The discovery of copper, iron and the development of the smelting technologies have led to the development of agriculture, the intensive exploitation of coal, oil and non-ferrous metals led to the development of the industry. Mineral resources are very important to human progress, so mining is one of the oldest and most important activities worldwide, representing an important pillar regarding the world economy (Tiess 2007, Karadag 2012, Zhang et al 2012).

Consumption of materials made from mineral compounds (stones or metals) showed a significant growth with the development of the human civilization (Costin and Vlad 2008, Zhang et al 2012). If we want to benefit from natural resources of the subsoil we have to pay a price, the negative impact on the environment because the mining industry is one of the most important sources of environmental pollution with heavy metals (Filip 2008, Zhuang et al 2009; Ji et al 2013, Espinosa-Reyes et al 2014).

A study conducted in 2013 (Das et al 2013) argues that the environmental pollution caused by toxic heavy metal ions is one of the most important issues regarding the mining areas around the world. Heavy metals are persistent environmental contaminants since they cannot be degraded or destroyed. Heavy metals cause side effects on human health and on other living organisms from the terrestrial or aquatic environment disrupting the food chain

There are various studies that highlight the negative effects of the acid mine waters on human health (Ongen et al 2008, Ting et al 2009; Pilarezyk 2013, Zhuang et al 2009; Ji et al 2013; Butiuc-Keul 2012; Bejan et al 2007) thus, the removal of heavy metals from contaminated mining areas has become a serious problem.

The recovery of metals from contaminated areas is useful from economic point of view , recovering the heavy metals which are more expensive. Recovery of these metals may reduce the cost of the treatment operations (Bejan et al 2007).

1.2. Concept and objectives

The present thesis presents a topic of great interest at national and international level. The general concept of the thesis is to contribute to a better understanding of the environmental issues associated with mining industry in the northern part of Romania, respectively Baia Mare area. Even if mining industry was stopped in 2007, the acid mine drainage generated by the former mining exploitation and the mining waste resulting from mining activities (dumps, tailings ponds) negatively influences the quality of the environment (water, sediment and soil) in the study area.

The main objective is to contribute to the assessment of mining activities on the environment from Baia Mare area, by calculating the specific quality indexes.

In order to achieve the main objective, a number of specific objectives were outlined:

O1. The exposure of theoretical aspects regarding the mining activities and their impact on the environment.

O2. Determination of dissolved ions concentration (F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+) in collected water samples (groundwater, surface water, mine water) taken during six sampling campaigns:

- ✓ November 2013
- ✓ December 2013
- ✓ March 2014
- ✓ June 2014
- ✓ September 2014
- ✓ December 2014

O3. Determination of eight heavy metal and one metalloid concentration (Fe, Pb, Ni, Zn, Cu, Cd, Mn şi Cr, As) from collected water, sediments and soil samples.

O4. The evaluation of seasonal variation physico-chemical parameters, dissolved ions and heavy metals concentration analyzed in water, sediments and soils samples.

O5. The calculation of the specific quality indexes. The impact assessment on the environment in the study area.

The thesis is structured in 7 chapters as follows:

Chapter 1 is the introduction of the thesis, highlighting the importance of mineral resources to human progress and impact on environment components, because at the same time mining industry is one of the most important sources of environmental pollution with heavy metals. Also in this section there are presented the concept and major objectives of the thesis.

Chapter 2 presents the national and international situation of mining activities, their socio-economic importance and the mining activities associated risks such as negative impact on air, soil and water.

In Chapter 3, a detailed description of the study area was done : a short history regarding mining activities, a description of the possible sources of pollution and environmental problems associated with mining.

In Chapter 4 there are represented the monitoring network,the sampling methodology, the water samples preservation and handling, the equipment used to determine the physical-chemical parameters, dissolved ions and heavy metal concentration. In this Chapter the obtained results are also present: the physico-chemical parameter values, the dissolved ions and heavy metals concentrations and their seasonal variations.

Chapter 5 presents the methodology of sampling, processing and conservation of soil and sediment samples. The physico-chemical parameters values, heavy metal concentrations and their seasonal variations are also presented.

In Chapter 6 there has been carried out an assessment of environmental quality by calculating specific quality indexes. There were calculated 11 quality indexes to assess groundwater quality (AP), surface water (AS) and mine wastewater (AU). Three quality indexes were also calculated to determine the degree of contamination of soils and sediments monitored.

In Chapter 7, the conclusions of the thesis, the personal contributions (articles, presentations at conferences, summer schools) as well as prospects are presented.

Regarding the dissemination of results the author published 4 ISI articles and 10 BDI articles. She also participated in several national and international conferences with presentations as posters or oral presentation. She took part at two summer schools in Slovakia, focusing on environmental issues related to mining activities.

CHAPTER 2

State of knowledge in the field at national and international level

2.1. The situation at national level

Romania has a mining history of more than 2000 years and is one of the oldest activities, because our country contains significant quantities of mineral resources.

In total there are 14 mining regions in our country, and in the past (before the revolution in 1989) more than 150 localities were related to this activity. The restructuring of the mining industry started in 1997 and once Romania joined the European Union on 1 January 2007 led to the cessation or abrupt decline in mining mineral processing of copper, lead, zinc and the iron ores (Perez 2013).

Today Romania is faced with the consequences of intensive mining for decades when production was more important than protecting the environment. Environmental pollution is a great national importance problem in Romania. Heavy metals are one of the most important groups of pollutants affecting environmental factors around the mining areas.

A number of previous studies have highlighted the problem of environmental pollution with heavy metals and associated risks (Donis et al 2000, Macklin et al 2003, Mara et al 2007, Albert et al 2008, Stefanescu et al 2008, Bird et al 2009) .

2.2. The situation at international level

Europe holds important mineral resources, such as mining industry has a long tradition (www.euromines.org), being among the most important mining regions in the world (Aswathanarayana 2003). The problem of environmental pollution caused by mining activity is of great interest, with wide international connotations, being found in a number of studies in the literature (Davies 1987, Edinger et al 2007, Dold 2008, Luis 2009, Zhang et al 2012, Zheng et al 2013, Li et al 2014, Yang et al 2015).

CHAPTER 3

Mining activities from Baia Mare area

3.1. Study area

Baia Mare Depression, is one of the most important areas for mining activities, because of the soil and subsoil riches, in the area there are resources of ferrous and non-ferrous ores (Bud et al 2007, www. anpm.ro).

During 1990 several mining areas were in operation around the Baia Mare town, two processing plants of minerals, two metallurgical plants of Cu, Pb, Zn, Au, Ag operated in the Baia Mare and all of this led to a significant increase of economy (Oros et al 2011).

In recent years the economy in Maramures County suffered a dramatic drop because all the mining exploitation were closed (last in 2007), as a direct consequence of the drastic reduction of the subsidy after the 90s (Vasilescu et al 2012; Nouret al 2015,Piştea et al 2015[a]).

The impact of mining activities on the environment in Maramures County are known and have been extensively studied by many researchers (Coman et al, 2006, Bud et al 2007 Frentiu et al 2007, Levei et al 2007, Damian et al 2008, Bird et al 2009 Albert and Jordan 2011, Vasilescu et al 2012, Damian et al in 2013, Roba et al 2015[a,b]). Baia Mare is a very polluted town and now studies and efforts are taking place to establish the exact state of the environment, remediation of polluted historic areas and minimize the impact of heavy metals on human health (Oros et al 2011).Environmental degradation in Baia Mare Depression is due to human activities.

The main sources of heavy metal pollution are the mining, or processing, nonferrous metallurgy and transport.

The largest historically pollution sources of the environment in Maramures County are:

- SC Cuprom SA
- SC Romaltyn Mining SRL
- C.N.M.P.N. Remin
- SC Romplumb SA
- Waste dumps, tailings damps and acid mine water

CHAPTER 4

The water quality in the study area

4.1. Sampling points

The sampling points were chosen based on areas that represent a potential risk in terms of environmental impact, trying to cover a wide perimeter of study area.

39 water samples were taken during six campaigns (*Figure 14*), a total of 240 water samples were collected (*Figure 15*).

The samples were collected near mining areas, from waste dumps and close to them, from tailing ponds or close to them, and a control point was collected as well (*Figure 16*).

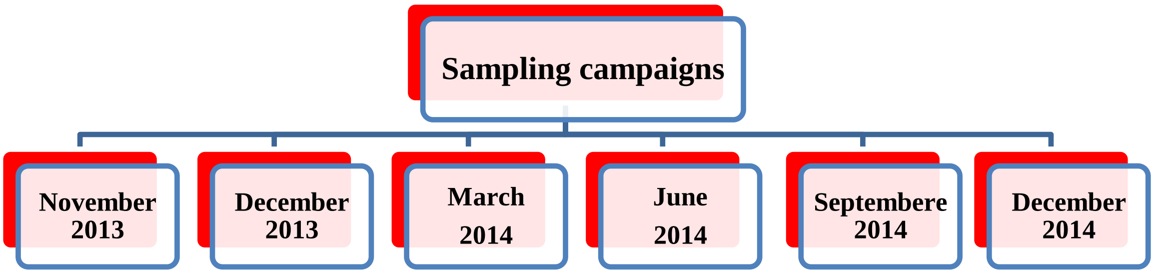

Figure 14. The sampling campaigns

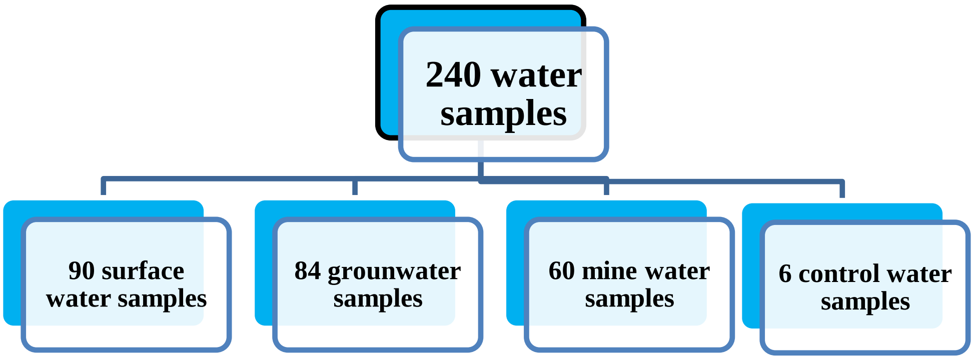

Figura 15. Description of water samples

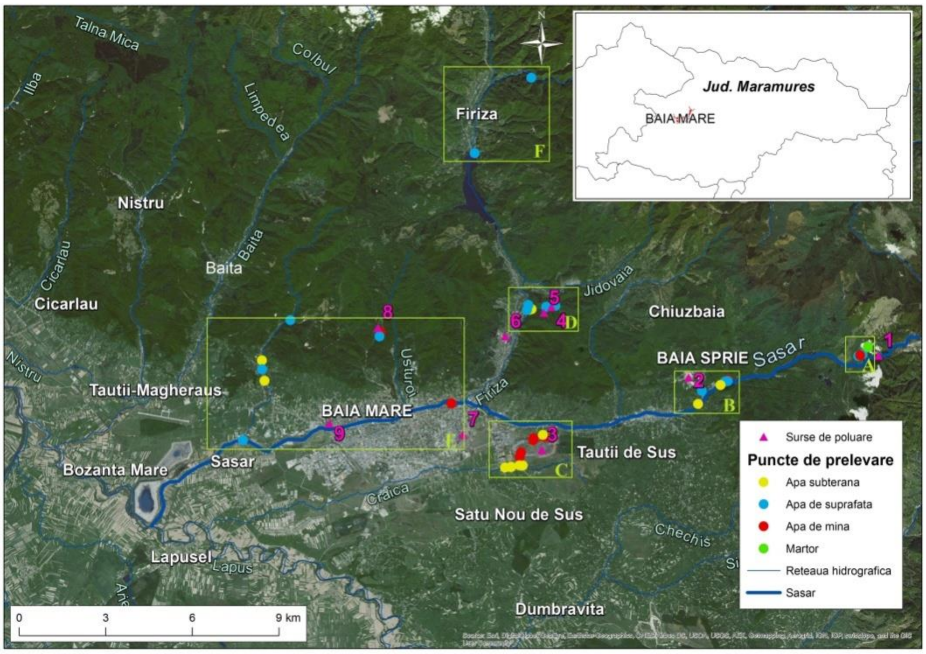

Figure 16. The investigated area and sampling points

4.2. The determinations in situ of the physico-chemical parameters

Because the physico-chemical parameters value depends on climate conditions, these determinations were done *in situ (Figure 18).*

Using a portable multiparameter WTW INOLAB 320i the following physico-chemical parameters were determinated:

- temperature (t)
- pH
- oxido-reduction potential (ORP)
- electrical conductivity (EC)
- total dissolved solids (TDS)
- salinity (Sal)
- dissolved oxygen (OD)

The turbidity was measured using a turbidimeter WTW pHotoFLEX.

Figure18. In situ deteremination of the physico-chemical parameters (31 sampling point) (Ioana Cristina Piştea, 14.09.2014)

4.3. Sampling, processing and preservation of water samples

Collecting, processing and preservation of water samples were done taking into account national and international standards.

4.3.1. Processing and preservation of water samples in order to determine the content of dissolved major ions

Processing and preservation of water samples in order to determine the content of dissolved ions was done taking into account the national and international standards [ISO 5667-2, ISO 5667-3, US-EPA 1993 US-EPA 1997 ASTM 1999 Jackson 2000 US- EPA, 2007].

4.3.2. Processing and preservation of water samples in order to determine the total concentration of heavy metals

Water samples were processed and stored in accordance with current standards [ISO 5667-2, ISO 5667-3].

4.4. The equipment used for chemical parameters determination

The concentration of dissolved ions were determined using ion chromatograph IC DIONEX 1500 and in order to determine the concentration of heavy metals (Pb, Fe, Zn, Ni, Mn, Cd, Cu, Cr) an atomic absorption spectrometer ZEENIT 700 was used.

4.5. Groundwater quality assessment in the study area and risk factors identification

4.5.1. The physico-chemical parameters

In *Table 8* it is presented a summary of statistical exposure of physico-chemical parameters values of groundwater samples.

Tabel 8. Statistical results of the physico-chemical parameters values of groundwater samples (84 samples)

Parameter	**Samples where it has been identified (%)**	**Min. val.**	**Max. value**	**Mean**	**Median**	**Stand. dev.**	**Variance**	**Coeff. var.**	**Std. error**
pH	100	5,40	7,90	6,66	6,66	0,49	0,24	7,43	0,05
ORP (mV)	100	-55,80	89,80	3,98	3,5	27,36	748,70	686,02	2,98
EC (µS/cm)	100	101,40	2110,0	404	321,5	350,52	123727,8	86,98	38,37
TDS (mg/L)	100	65,00	1348,00	256,32	204	230,99	53359,22	90,12	25,20
Salinity (‰)	100	0,00	0,90	0,1	0	0,16	0,028	200,57	0,01
OD (mg/L)	100	2,30	7,90	5,06	5,12	1,01	1,033	20,06	0,11
Turbidity (NTU)	92	0,04	33,20	4,8		6,57	43,23	136,96	0,74

Collected groundwater samples had a slightly acidic to alkaline pH. Water with a low pH may have a higher metal content since, especially when it is pumped, the pipe can leache metals, such copper, zinc or lead. An acidic pH can give water a metallic taste.

Regarding redox potential, 52% of water samples have a positive ORP value.

In terms of turbidity value 29% of water samples exceeded the maximum permitted limit imposed by drinking water law (Law 458/2002), with a value greater than 5 NTU. The high values of the turbidity can be due to high concentrations of iron that gives the water a red color.

The electrical conductivity value of groundwater samples did not exceed the maximum imposed limit (2500 µS /cm) by Law 458/2002.

The content of total dissolved solids is not legislated into national law, but referring to the United States law, the 1% of the samples exceeded the maximum permissible level of 500 mg/L (US-EPA).

4.5.2. Major dissolved ion concentrations

In *Table 9* it is presented a summary of statistical exposure of dissolved ions concentration of groundwater samples.

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Table 9. Statistical results of dissolved ions concentration of groundwater samples (84 samples)

Parameter	**Samples where it has been identified (%)**	**Min. val.**	**Max. val.**	**Mean**	**Median**	**Stand. dev.**	**Variance**	**Coeff. var.**	**Std. error**
F^- (mg/L)	100	0,02	6,88	1,03	0,6	1,35	1,83	130,59	0,14
Cl^- (mg/L)	100	0,08	184,56	24,73	12,16	34,73	1261,5	143,58	3,87
Br^- (mg/L)	8	0,20	5,26	2,12	0,32	2,35	5,55	110,78	0,89
NO_2^- (mg/L)	8	0,05	4,43	2,36	2,15	1,4	2,49	66,81	1,58
NO_3^- (mg/L)	100	1,02	97,94	18,32	12,34	18,35	344,46	101,4	2,02
PO_4^{3-} (mg/L)	4	9,00	9,63	9,42	9,63	0,36	0,13	3,86	0,21
SO_4^{2-} (mg/L)	100	5,44	488,38	87,83	54,37	87,59	7672,25	99,72	9,55
Li^+ (mg/L)	67	0,001	0,67	0,06	0,02	0,11	0,012	163,21	0,015
Na^+ (mg/L)	100	4,51	1154,72	51,80	21,8	138,27	19571,09	269,97	15,26
NH_4^+ (mg/L)		SLD							
K^+ (mg/L)	100	0,39	47,56	9,22	5,83	10,92	124,17	120,85	1,21
Mg^{2+} (mg/L)	100	2,76	115,38	15,27	11,13	17,63	321,86	117,48	1,95
Ca^{2+} (mg/L)	100	7,50	484,71	55,56	36,59	60,03	3601,64	107,82	6,54

CMA* - maximum concentration level (Law 458/2002, Order 621/2014; US-EPA, WHO)

In the water samples investigated in all six sampling campaigns, it can be seen (Table 8) that in the case of anions the fluoride, chloride, nitrate and sulphate were determined in all collected ground water samples, and in the case of cations sodium, magnesium, calcium and potassium were present in all collected samples.

4.5.3. Heavy metal concentrations

In *Table 11* it is presented a summary of statistical exposure of heavy metal concentration of groundwater samples.

Table 11. Statistical results regarding the heavy metal concentration of groundwater samples (84 samples)

Parameter	**Samples where has been identified (%)**	**Min. val.**	**Max. val.**	**Mean**	**Median**	**Stand. dev.**	**Variance**	**Coeff. var.**	**Std. error**
Mn (µg/L)	94	3,00	47.047,00	1606	124,1	6356	4,04	395,74	715,12
Zn (µg/L)	100	9,40	43.761,00	1688	302,6	6247,87	4,17	382,47	704,62
Fe (µg/L)	100	28,11	5677,00	892	610,6	966,98	935058,9	108,39	105,5
Cu (µg/L)	100	1,20	112,70	13,74	8,18	18,81	354,18	136,88	2,05
Pb (µg/L)	50	0,01	19,81	3,9	1,66	4,67	21,89	119,79	0,72
Ni (µg/L)	100	1,20	115,11	30,02	18,96	30,15	954,67	102,32	3,37
Cd (µg/L)	45	1,22	55,00	10,9	6,5	12,90	166,48	118,36	2,09
Cr (µg/L)		SLD							
As (µg/L)		SLD							

As it can be seen in *Table 11* concentrations of copper, zinc, nickel and iron have been identified in all collected groundwater samples, followed by manganese, lead and cadmium. Concentrations of chromium and arsenic were not detected. Regarding manganese most of the samples (68%) exceeded the maximum concentration level of the maximum followed by iron (81%), nickel (39%), cadmium (40%) and zinc (7%).

4.6. Assessment of surface and mine water quality in the study area and risk factors identification

During the six sampling campaigns a total of 90 samples of surface water have been collected from Săsar River and its tributaries and 60 samples of mine water at the bottom dumps, the tailings ponds and canals and pipelines where mine waters are discharged.

4.6.1. Physico-chemical parameters

In *Table 13* it is presented a summary of statistical exposure of physico-chemical paramaters values of surface water samples.

Tabelul 13. Statistical results regarding physico-chemical parameters values of surface water samples (90 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
pH	100	3,00	8,40	6,68	6,77	0,86	0,74	12,93	0,09
ORP (mV)	100	-98,40	200,00	-0,59	-11,7	47,55	2339,56	-8111,069	5,09
EC (µS/cm)	100	37,80	3110,00	307,27	175,25	435,6	189753,3	141,76	45,91
TDS (mg/L)	100	24,00	1991,00	201,44	111,5	283,05	80121,6	140,51	29,83
Salinity (‰)	100	0,00	1,50	0,065	0	0,21	0,04	329,12	0,02
OD (mg/L)	100	3,50	8,00	5,47	5,4	0,94	0,89	17,28	0,099
Turbidity (NTU)	99	0,20	530,00	36,78	8,94	74,71	5582,6	203,1	7,91

The pH of surface water samples was acid to basic, the lowest pH value was 3.02 (AS32) and the highest was 8.44 (AS28). The lowest pH value in AS32 sampling point was because the sample was collected from downstream of Valea Lungă tailing dump.

The redox potential values were between -98.4 and 200 mV, 67% of surface water samples having a negative ORP value, the highest value of 200 mV being determined in AS32 sampling point, where was the lower pH value, these two parameters being negatively correlated.

The electrical conductivity values, total dissolved solids and salinity varied significantly depending on the sampling point, the highest values were recorded at the point AS7, taken from Săsar River downstream of the discharged acid mine water from (AU4 and AU5) upstream of Baia Sprie mining area.

In *Table 14* there is a summary of the physical-chemical parameters value of mine water samples. Water samples resulting from mining activities recorded a very acidic pH to slightly basic, its value ranging between 1.63 (AU15) and 7.67 (AU5). Point AU15 being taken from Tăuţii de Sus tailing ponds. The acidity water leads to increased mobility of metals, as the pH is more acidic the mobility is higher (Salomons 1995).

Electrical conductivity values, total dissolved solids and salinity varied depending on the sampling point.

Regarding the turbidity, the highest analyzed value was 799 NTU (AU12). High turbidity value in sampling point AU12 can be due to the high concentrations of iron in the water that gives water a reddish color.

Table 14. Statistical results regarding the physico-chemical value of the collected mine waters (60 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
pH	100	1,60	7,60	4,9	5	1,76	3,12	36,1	0,22
ORP (mV)	100	-39,00	298,80	98,96	86,2	98,13	9630,60	99,15	12,66
EC (µS/cm)	100	131,00	8360,00	2259	2365	1622,28	2632765	71,81	209,74
TDS (mg/L)	100	84,00	5350,00	1456,64	2365	1038,31	2632765	71,81	209,47
Salinity (‰)	100	0,00	4,60	1,06	1,05	0,97	0,95	91,55	0,12
OD (mg/L)	100	2,00	7,80	5,19	5,22	0,12	0,97	18,98	0,12
Turbidity (NTU)	100	0,10	799,00	164	73,95	210,06	44125,96	128,08	27,11

4.6.2. Major dissolved ion concentrations

As it can be seen in *Table 15* the chloride, sulphate, sodium, potassium, magnesium and calcium were identified in all surface water samples, followed by fluoride, lithium and nitrate. The sulfate concentrations varied greatly depending on the sampling point, the lowest detected value was 5.44 mg / L (AS39) and the highest detected value was 1.432 mg / L (AS7) this sample was collected from Sasar River.

Table 15. Statistical results regarding the dissolved ions concentrations of the collected surface water samples (90 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
F^- (mg/L)	98	0,01	31,85	1,21	0,28	4,42	19,55	362,94	0,47
Cl^- (mg/L)	100	0,03	98,95	11,08	4,69	17,82	317,78	160,87	1,87
NO_3^- (mg/L)	95	0,56	52,03	5,79	3,23	7,79	60,72	134,56	0,84
SO_4^{2-} (mg/L)	100	5,44	1432,95	171,05	78,89	257,62	66372,33	150,61	27,15
Li^+ (mg/L)	71	0,0003	1,17	0,123	0,03	0,242	0,05	196,57	0,03
Na^+ (mg/L)	100	2,45	122,15	16,85	6,95	24,96	623,11	148,10	2,63
K^+ (mg/L)	90	0,55	116,60	7,45	3,2	14,6	213,27	195,9	1,53
Mg^{2+} (mg/L)	100	0,89	227,88	21,03	5,74	42,46	1803,4	201,85	4,47
Ca^{2+} (mg/L)	100	3,82	526,97	64,32	31,7	104,69	10961,01	162,75	11,03
Br^- (mg/L)		SLD							
NO_2^- (mg/L)		SLD							
PO_4^{3-} (mg/L)		SLD							
NH_4^+ (mg/L)		SLD							

The order of dissolved ions concentrations in collected mine water samples SO_4^{2-}> Ca^{2+}> Mg^{2+}> K^+>> Na^+> Cl^-> NO_3^-> F^-> Li^+ (*Table 16*).

High sulfur concentration can be due to oxidation of sulphide minerals (pyrite FeS2 in particular, which is the most common and most frequently sulfide minerals) (Akcid and Koldas 2006).

Table 16. Statistical results regarding the dissolved ions concentrations of the collected mine water samples (60 samples)

Parameter	**Samples where it has been identified (%)**	**Min. val.**	**Max. val.**	**Mean**	**Median**	**Stand. dev.**	**Variance**	**Coeff. var.**	**Std. error**
F^- (mg/L)	57	0,006	27,34	6,4	4,54	6,85	47,04	107,16	1,17
Cl^- (mg/L)	98	0,35	154,49	42,31	35,35	35,79	1280,97	84,58	4,65
NO_3^- (mg/L)	57	0,44	70,37	19,84	13,43	19,73	389,54	99,47	13,43
SO_4^{2-} (mg/L)	100	20,55	6647,72	2129,45	2064,525	1624,42	2638769	76,28	209,71
Li^+ (mg/L)	77	0,004	1,59	0,51	0,33	0,47	0,22	92,33	0,07
Na^+ (mg/L)	97	3,38	171,18	56,01	45,47	47,58	2264,14	84,94	47,58
NH_4^+ (mg/L)		SLD							
K^+ (mg/L)	100	1,00	246,5	57	29,92	63,29	4006,48	111,03	8,17
Mg^{2+} (mg/L)	100	2,97	965,28	183,16	87,41	207,38	43009,46	113,22	26,77
Ca^{2+} (mg/L)	100	21,41	1068,41	296,211	263,89	221,34	48991,49	74,72	28,57
Br^- (mg/L)		SLD							
NO_2^- (mg/L)		SLD							
PO_4^{3-} (mg/L)		SLD							

4.6.3. Heavy metal concentrations

From 8 heavy metals and metalloid investigated, 8 metals have been identified in surface water samples in the following order: Mn > Zn > Fe > Cu > Ni > Pb > Cd> Cr (*Table 17*). The highest variations between points over the entire monitoring period were recorded in case of zinc, the lowest detected value was 9.27 mg / L (AS2) taken from Săsar River downstream of the discharge pipe of mine water from Şuior Mine and the highest value was 19.105 mg / L (AS23), these sampling point was taken from Herja creek downstream of Herja Herja Mine which is a deposit of lead and zinc.

The high concentration of heavy metals is the result of several factors: mining activities in the past upstream of Baia Mare (Şuior Mine, Baia Sprie Mine), waste mining resulting from these, and industrial activities carried out the study area (Modoi 2010)

Table 17. Statistical results regardind heavy metals concentration of the collected surface water samples (90 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
Mn (mg/L)	100	0,002	28,09	3,04	1,01	4,89	25,06	164,21	0,52
Fe (mg/L)	100	0,004	13,10	2,04	0,92	2,77	7,77	136,47	0,29
Zn (µg/L)	100	9,27	19105,00	1631,48	372,2	2949,09	8697182	180,76	310,86
Cu (µg/L)	98	0,48	273,40	28,91	16,22	38,05	1448,37	131,62	4,05
Pb (µg/L)	65	0,10	140,20	9,99	3,53	20,34	413,72	203,6	2,67
Ni (µg/L)	89	1,10	198,50	37,23	22,5	46,03	2119	123,64	5,14
Cd (µg/L)	61	0,60	43,19	10,88	9,3	10,32	106,51	94,85	1,39
Cr (µg/L)	6	4,12	13,57	7,63	6,52	3,99	15,97	52,33	1,78
As (µg/L)		SLD							

The order of heavy metals concentration in mine water samples was as follows: Fe > Mn > Zn > As > Cu > Pb > Ni > Cd > Cr (*Table 18*).

High concentrations were registered in case of manganese, its variations ranging from 1.61 mg / L (AU30) and 89.54 mg / L (AU11), all the mine water samples exceeded the maximum allowable concentration of 1 mg / L (Governmental Decision 352/2005).

Iron was dominant, its concentrations ranged between 0.22 mg / L (AU4) and 856.6 mg / L (AU15), its average (103.97 mg / L) concentration exceeding 20 times the maximum permissible limit (5 mg / L) (Governmental Decision 352/2005).

From all the 240 water samples taken arsenic was identified only in mine water samples, its values ranging from 0.009 mg / L (AU13) to 9.02 mg / L (AU15), averaged almost exceeding CMA 16 times.

High concentrations were determined in case of copper, the copper concentrations ranged between 2.32 mg / L (AU5) and 21 104 mg / L (AU30), its average concentration exceeding 25 times the maximum permissible concentration (100 mg / L) .

Lead concentrations ranged between 0.1 mg / L (AU16) and 1,188 mg / L (AU12), the mean concentration exceeding the maximum permissible limit (200 mg / L).

Laboratory analysis showed that the zinc concentration values ranging between 350 mg as / L (AU31) to 57800 mg / L (AU4), the average being 17 times more than the maximum allowable concentration (500 mg / L).

Nickel, cadmium and chromium had the lowest concentrations in mine waters, their value being between 0.031 mg / L - 601.5 mg / L for nickel, 1.32 mg / L - 194 mg / L cadmium and 1 mg / L - 61 mg / L for chromium.

As it can be seen the dominant metals are iron, manganese and zinc, as well as their high concentration in mine waters as a consequence of mining, processing of ores and non-ferrous metallurgy.

Tabel 18. The statistical results regarding the heavy metal concentration in mine water samples (60 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
Mn (mg/L)	100	1,61	89,54	36	16,23	30,13	907,99	83,68	3,89
Fe (mg/L)	100	0,22	856,60	103,97	62,60	181,03	32772,67	174,11	23,37
As (mg/L)	25	0,009	9,02	1,56	0,049	3,07	9,44	196,89	0,79
Cu (μg/L)	100	2,32	21104,00	2468	240,2	5700	3,24	230,89	735,91
Pb (μg/L)	75	0,10	1188,00	156,81	18,5	304,68	92835,94	194,3	45,42
Ni (μg/L)	100	0,031	601,50	160,5	113,55	151,81	23048,27	94,58	19,59
Cd (μg/L)	100	1,32	194,00	37,14	18,75	78,51	2354,08	130,61	6,26
Cr (μg/L)	40	1,00	61,00	23	15,5	19,31	373,06	82,66	3,94
Zn (μg/L)	100	350,00	57800,00	8529	5120	11971,82	1,43	140,35	1545,55

The variation of physico-chemical parameters values, dissolved ions concentration, and heavy metals concentrations over the monitoring period in groundwater samples, surface water samples and mine water samples, may be due to meteorological factors. In March, June and December 2014 increased rainfall before sampling campaign.

CHAPTER 5

The soils and sediments quality in the study area

5.1. Soil and sediment sampling

Soil and sediment samples were collected from the same locations as water samples, taking into account the pollution sources identified in the study area (Figure 39, Figure 40).

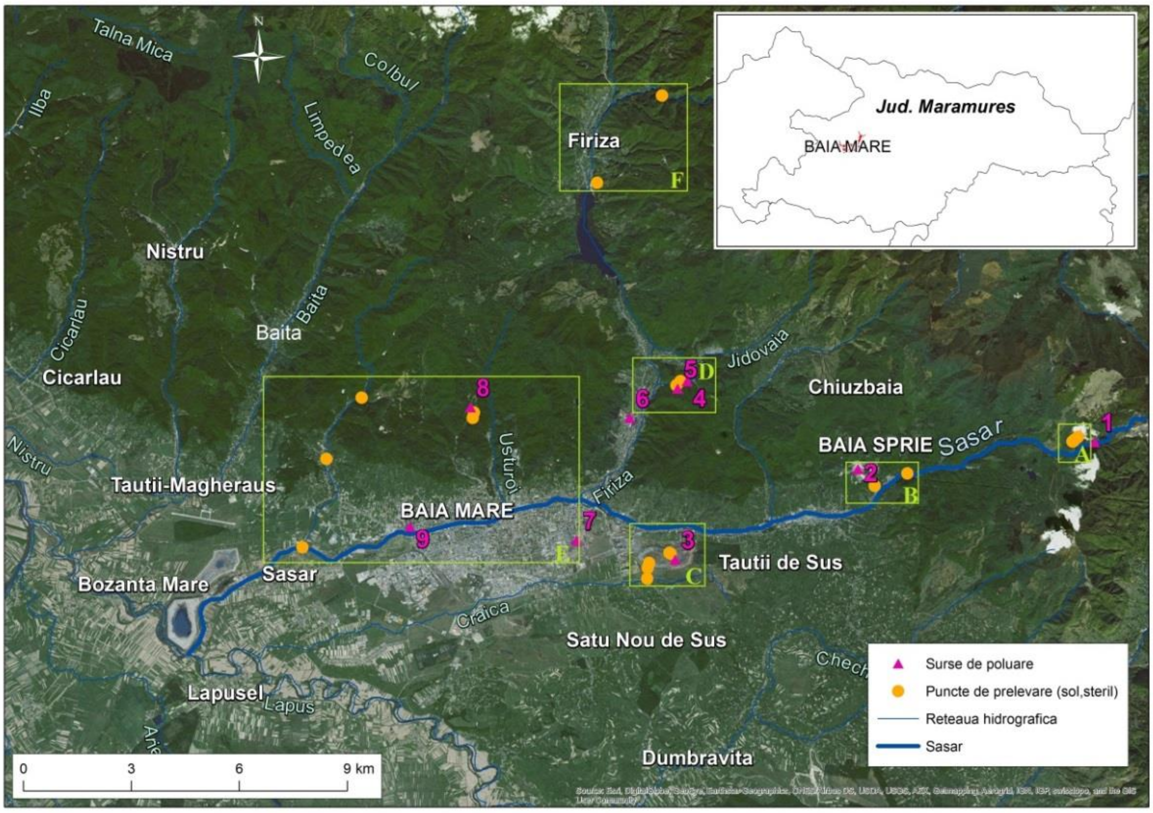

Figure 39. The study area with soil sampling point

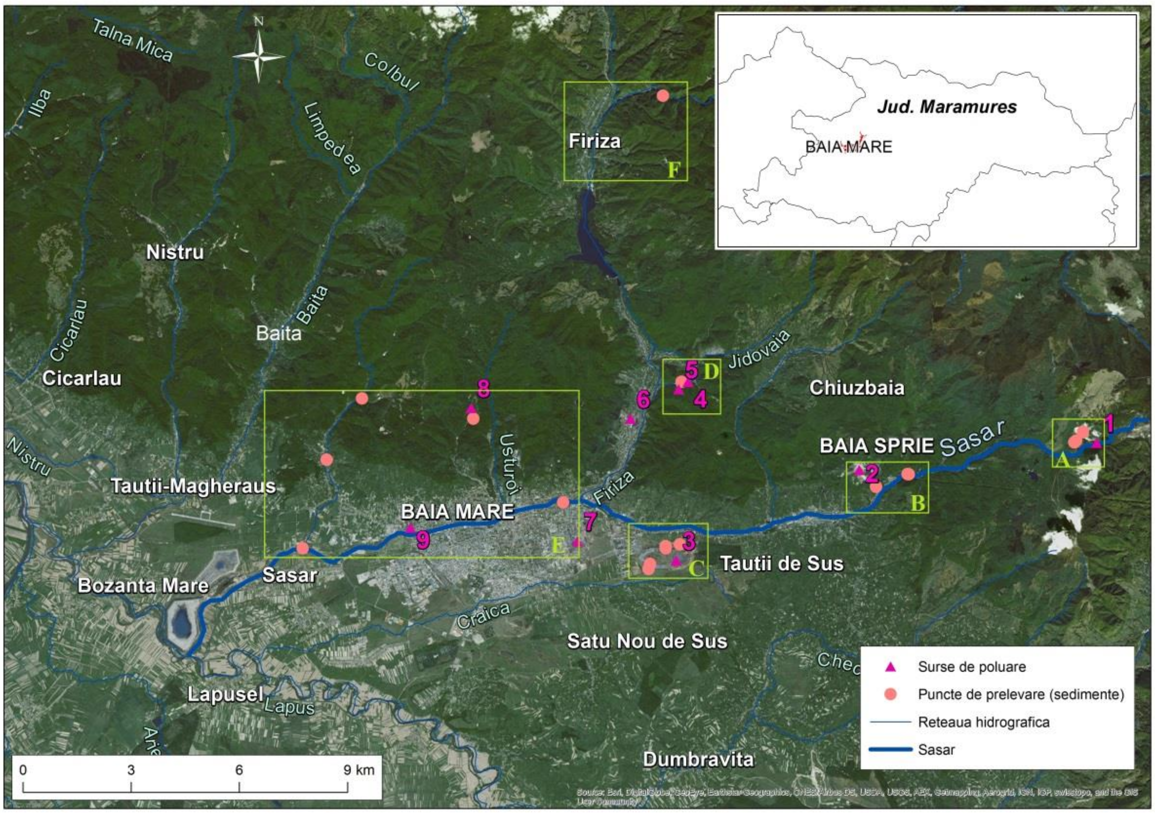

Figure 40. The study area with sediment sampling point

5.2. Processing and conservation of soil and sediment samples

5.2.1. Processing and conservation of soil and sediment samples in order to determine the physico-chemical parameters value and the heavy metals concentrations

In order to determine the physico-chemical parameters value and the heavy metal concentration have been followed the international standards [US-EPA 3050B, ISO 11464, ISO 10390, ISO 11466].

5.3. Assessment of soil and sediments quality collected from study area and identify the risk factors

5.3.1. The physico-chemical parameters

A summary of the results in terms of value physico-chemical parameters of analyzed soil and sediment samples is shown in *Table 19* and *Table 20*.

Table 19. Statistical results of the physico-chemical parameters values in monitored soil samples (95 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
pH	100	1,05	7,33	5,2	5,78	1,74	3,03	33,5	0,17
ORP (mV)	100	-19,10	316,00	82,52	40,3	97,74	9554,12	118,44	10,02
EC (µS/cm)	100	25,30	18560,00	1281	129,5	3212,78	1,03	250,79	329,62
Salinity (‰)	100	0,00	11,00	0,59	0	1,81	3,29	290,1	0,18

Tabel 20. Statistical results of the physico-chemical parameters values in monitored sediment samples (108 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
pH	100	1,37	7,19	5,35	5,93	1,46	2,13	27,25	0,14
ORP (mV)	100	-43,80	294,00	67,4	35,4	83,65	6998,77	124,11	8,05
EC (µS/cm)	100	59,70	5880,00	904,23	485,5	1140,31	1300323	126,1	109,27
Salinity (‰)	100	0,00	3,20	0,40	0,1	0,65	0,42	160,99	0,06

As it is shown in *Table 19* and *Table 20* the pH value of collected soils and tailings samples ranged from 1.05 (ST12A) to 7.33 (SL20) almost all the samples can be classified as highly acidic. The pH values of collected sediments samples were very similar to pH values of tailings and soil samples, ranging from 1.37 (SD15) to 7.19 (SD8). The high acidity of soil samples, tailings and sediment increases the mobility of heavy metals.

Extreme pH values lead to toxic concentrations of metals such as Al and Mn and can precipitate certain nutrients in soil, making that these nutrients can not be assimilated by plants (Prieto-Méndez et al 2011).

ORP of soil and sterile samples ranged between -19.1 mV (ST23) and 316 mV (ST12A) with an average of 85.52 mV, values being generally positive.

Oxido-reduction potential values of the sediment samples were slightly lower, ranging between -43.8 mV (SD8) to 294 mV (SD15), with an average of 67.4 mV.

pH and ORP are two important parameters of biological life quality and strongly influences the mobility of nutrients (Gambrelli and Patrick 1978; Laanbroek 1990).

Electrical conductivity values for collected tailings and soil samples ranged from 25.3 µS / cm (SL1) and 18560 µS / cm (ST12A), while salinity reached values of up to 11 ‰ (ST12A).

In case of sediments samples the values of these parameters were lower, electrical conductivity varying between 59.7 µS / cm (SD1) and 5880 µS / cm (SD15), and the highest detected value for salinity was 3.2 ‰ (SD15), indicating a low content of organic and inorganic salts dissolved.

5.3.1. Heavy metals concentration

In *Table 21* and *Table 22* it is presented a summary of the heavy metals concentration in soil, sterile and sediments samples

Tabel 21. Statistical results regarding the heavy metal concentration in soil and sterile samples (95 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
Cu(mg/kg)	100	11,30	26841.5,00	2465,51	195,94	6815,89	4,64	276,44	699,29
Cd (mg/kg)	92	0,01	7,71	2	1,28	1,91	3,65	95,2	0,2
Pb (mg/kg)	100	29,99	12671,00	2163,79	1008,7	3059,65	9361475	141,4	313,91
Cr (mg/kg)	100	1,10	89,66	12,01	9,33	14,28	204,03	118,84	1,46
Ni (mg/kg)	100	1,99	35,53	15,52	15,44	6,99	48,98	45,07	0,71
Zn (mg/kg)	100	133,50	83229,00	5087,13	1476,5	14282,16	2,03	280,75	1465,31
Fe (mg/kg)	100	30976,13	62616,00	37395,04	35846,1	36349,89	3,69	16,25	623,49
Mn (mg/kg)	100	10,66	2520,76	997,99	584,7	773,44	598219,9	77,5	79,35

Analytical data regarding the heavy metals concentration in collected soil and sterile samples (Table 20) reveals large ranges of values, depending on soil type and sampling point. Analyzed sterile and soil samples were found to be heavily contaminated with heavy metals, except chromium and nickel, other heavy metals exceeding normal levels imposed by legislation (Law 758/1997).

The heavy metals concentration order in analyzed soil and sterile samples were: Fe> Zn > Cu > Pb > Mn > Ni > Cr > Cd.

The highest levels were registered in case of iron, its concentration ranged between 30976.13 mg / kg (SL8) and 62616.00 mg / kg (ST12B), with an average of 35846.10 mg / kg

Zinc was the second dominant metal, its concentrations ranged between 133.50 mg / kg (SL32) and 83229.00 mg / kg (SL2), with an average value of 5087.13 mg / kg that exceeding 50 times the normal level for zinc in soil (100 mg / kg).

The copper concentration in analyzed sterile and soil samples ranged from 11.30 mg / kg (SL20) to 26841.50 mg / kg (SL2), the average value of 2465.51 mg / kg exceeding 123 times the normal concentration of copper in soil (20 mg / kg), 20% exceeding the alert threshold (250 mg / kg) and 23% exceeding the intervention threshold (500 mg / kg).

Soil and sterile samples collected from Baia Mare and adjacent areas were found to be highly contaminated with lead, its concentration ranged from 29.99 mg / kg (ST31) and 12671.00 mg / kg (ST15). The average concentration 2163.79 mg / kg was 108 times higher than normal levels of lead in soil (20 mg / kg). A total of 15% exceeded the alert threshold (250 mg / kg) and a total of 65% exceeded the intervention threshold (1.000 mg / kg).

Manganese was identified in all soils and sterile samples, the concentration ranged between 10.66 mg / kg (ST15) and 2520.76 mg / kg (SL32), the mean concentration (997.99 mg / kg) exceeding the normal value for manganese in soil (900 mg / kg).

In case of chromium and nickel, the average concentration 12.01 mg / kg for chromium and 15.52 mg / kg nickel did not exceed normal levels.

The concentration of cadmium in soils and sterile sampled ranged from 0.01 mg / kg (SL16) to 7.70 mg / kg (SL8), with a mean concentration of 2 mg / kg which is twice higher than normal level of cadmium in soil.

The highest heavy metals concentrations in soil and steriles have been identified in samples collected downstream of Şuior Mine, Herja Mine, near Cuprom, Romplumb and near Tautii de Sus tailing pond.

Table 22. Statistical results regarding the heavy metal concentration in sediment samples (108 samples)

Parameter	Samples where it has been identified (%)	Min. val.	Max. val.	Mean	Median	Stand. dev.	Variance	Coeff. var.	Std. error
Mn (mg/kg)	100	22,00	2.575,00	1033,57	510,50	885,92	784.856,10	85,71	85,24
Fe (mg/kg)	100	25.267,77	57.733,33	35202,89	33.926,14	5.804,72	3,36	16,48	558,56
Cu (mg/kg)	100	9,47	26.824,27	1745,60	235,46	5.979,65	3,57	342,55	575,39
Pb (mg/kg)	100	11,46	12.891,00	1738,01	762,99	2.609,17	6807.803	150,12	251,06
Ni (mg/kg)	100	5,30	318,00	23,38	15,55	37,23	1.386,34	259,23	3,58
Cd (mg/kg)	91	0,10	63,66	5,30	2,28	10,57	111,83	199,21	1,06
Cr (mg/kg)	100	0,23	226,66	16,10	7,37	32,31	1.044,41	200,65	3,10
Zn (mg/kg)	100	29,52	8.453,00	2.450,26	1.775,96	2.057,69	4234.121	83,97	198,00

As in the case of soil and sterile samples, the concentration of heavy metals in collected sediment samples (*Table 22*) highlights large intervals, depending on the metal and sampling point.

The order of heavy metal concentration in collected sediment samples was: Fe> Zn>Cu > Pb> Mn> Ni> Cr> Cd. The sediments sampled were found to have a high content of heavy metals, 93% of sediment samples collected exceeded the maximum permissible limit for copper, zinc and lead, 69% for cadmium, 3% exceeding the maximum admissible limit for chromium and 6% exceeding the maximum permissible imposed limit for nickel (Order 161/2006).

The iron concentration ranged between 25267.77 mg / kg (SD16) to 57733.33 mg / kg (SD15), with an average of 35202.89 mg / kg.

Zinc values ranged between 29.52 mg / kg (SD3) to 8453.00 mg / kg (SD23), the mean concentration (2450.26 mg / kg) exceeded 16 times the maximum allowable concentration required for zinc concentration in sediment (150 mg / kg) (Order 161/2006).

Cooper has been identified in all sediment samples, the concentration ranged from 9.47 mg / kg (SD3) to 26824.27 mg / kg (SD30), the mean concentration (1745.6 mg / kg) exceeded almost 44 times the maximum permissible concentration (40 mg / kg).

Lead was fourth dominant metal in sediment samples. Lead concentrations ranged between 11.46 mg / kg (SD3) to 12891.00 mg / kg (SD15), the mean concentration (1738.01 mg / kg) is 20 times higher than the maximum allowable limit (85 mg / kg).

Manganese varied significantly depending on the sampling point, the concentration ranged between 22 mg / kg (SD15) to 2575.00 mg / kg (SD4).

Cadmium has been found in 91% of sediment samples, its values ranged from 0.1 mg / kg (SD15) to 63.66 mg / kg (SD30), the average concentration (5.3 mg / kg) exceeded amlost 7 times the maximum permissible concentration (0.80 mg / kg). The concentrations of heavy metals such as nickel and chromium are relatively low. Nickel concentrations ranged between 5.30 mg / kg (SD32) to 318.00 mg / kg (SD30) and chromium concentrations ranged from 0.23 mg / kg (SD23) to 226.66 mg / kg (SD30) average values did not exceed the maximum permissible concentration for nickel and chromium.

The high concentration of heavy metals in sediments samples is a good indicator of pollution caused by humans, high concentrations of heavy metals is often attributed to anthropogenic influences.

As in the case of water samples, sediment, soil and sterile samples were collected collected seasonally. Seasonal variations and differences in concentrations of sampling points is mainly due to geographical factors (many of sampling points are located very close to pollution sources such as mining exploitation, processing plants, tailing dumps or tailings ponds) and the climate (especially in the case of sediments ex .: rainwater can wash the surrounding soils or slopes, affecting water and sediment quality).

CHAPTER 6

Assessment of environmental quality by calculating specific quality indexes

In the last decades have developed a series of indexes to assess the environmental quality and not only. Using indexes for environmental assess has both advantages and disadvantages. During the data conversion may lose some information, but at the same time they are very useful, providing a very simple and clear data overview which can be understood by people outside the scientific field (Caeiro et al 2005).

The main objective of this study was to select different types of indexes to assess the environmental quality (water, sediment, soil) of the study area.

6.1. Evaluation of water quality by calculating specific quality indexes

In *Table 31* is a summary of the calculated indexes in order to assess the water quality.

Tabel 31. Assessment of water quality by calculating specific quality indexes

Nr. crt.	**Water Quality Indexes**		**Clasification**	**Water quality**	**Number of samples**	**The percentage from total sampling point (%)**
1	**WQI** **W**ater **Q**uality **I**ndex		50 < WQI < 100	Good	6 / 39	**15 %**
			100 < WQI < 200	Poor	7 / 39	**18 %**
			200 < WQI < 300	Very poor	4 / 39	**11 %**
			WQI > 300	Unsuitable	22 /39	**56 %**
2	**MI** **M**etal **I**ndex		MI > 1	Threshold of warning	39 / 39	**100 %**
3	**HPI** **H**eavy **M**etal **P**ollution **I**ndex		HPI < 100	Suitable	6 / 39	**15 %**
			HPI > 100	Unsuitable	33 / 39	**85 %**
4	**PI** **P**ollution **I**ndex	**PIMn**	<1	No effect	3 / 39	**8 %**
			1 - 2	Slightly affected	5 / 39	**13 %**
			2 - 3	Moderately affected	2 / 39	**5 %**
			3 - 5	Strongly affected	8 / 39	**21 %**
			> 5	Seriously affected	21 / 39	**54 %**
		PIFe	<1	No effect	4 / 39	**10 %**
			1 - 2	Slightly affected	2 / 39	**5 %**
			2 - 3	Moderately affected	3 / 39	**8 %**
			3 - 5	Strongly affected	13 / 39	**33 %**
			> 5	Seriously affected	17 / 39	**44 %**
		PIZn	<1	No effect	21 / 39	**54 %**
			1 - 2	Slightly affected	4 / 39	**10 %**
			3 - 5	Strongly affected	3 / 39	**8 %**
			> 5	Seriously affected	11 / 39	**28 %**
		PICu	<1	No effect	29 / 39	**74 %**
			1 - 2	Slightly affected	2 / 39	**5 %**
			2 - 3	Moderately affected	2 / 39	**5 %**
			3 - 5	Strongly affected	1 / 39	**3 %**
			> 5	Seriously affected	5 / 39	**13 %**
		PIPb	<1	No effect	33 / 39	**85 %**
			1 - 2	Slightly affected	3 / 39	**8 %**
			2 - 3	Moderately affected	2 / 39	**5 %**
			3 - 5	Strongly affected	1 / 39	**3 %**
		PINi	<1	No effect	25 / 39	**64 %**
			1 - 2	Slightly affected	8 / 39	**21 %**
		PICd	<1	No effect	20 / 39	**51 %**
			1 - 2	Slightly affected	4 / 39	**10 %**
			2 - 3	Moderately affected	7 / 39	**18 %**
			3 - 5	Strongly affected	5 / 39	**13 %**
			> 5	Seriously affected	3 / 39	**8 %**
		PICr	< 1	No effect	39 / 39	**100 %**
		PIAs	< 1	No effect	36 / 39	**92 %**
			> 5	Seriously affected	3 / 39	**8 %**
5	**SAR** **S**odium **A**dsorption **R**atio		< 10	Excellent	39 / 39	**100 %**
6	**%Na** Sodium Percentage		< 20	Excellent	19 / 39	**48 %**
			20 - 40	Good	17 / 39	**44 %**
			40 - 60	Permissible	2 / 39	**5 %**
			60 - 80	Doubtful	1 / 39	**3 %** **AP33**
7	**SSP**		0 - 20	Excellent	18 / 39	**46 %**

	Soluble **S**odium **P**ercentage	20 - 40	Good	8 / 39	**21 %**
		40 - 60	Permissible	7 / 39	**18 %**
		60 – 80	Doubtful	6 / 39	**15 %**
8	**PS** **P**otential **S**alinity	< 3	Suitable for agriculture	28 / 39	**72 %**
		> 3	Unsuitable for agriculture	11 / 39	**28 %**
9	**MH** **M**agnesium **H**azard	> 50	Unsuitable for agriculture	4 / 39	**10 %**
10	**MR** ***M**agnesium **R**atio*	< 1,5	Excellent	39 / 39	**100 %**
11	**KR** **K**elley **R**atio	< 1	Suitable for agriculture	38 / 39	**97 %**
		> 1	Unsuitable for agriculture	1 / 39	**3 %** **AP33**

By calculating Water Quality Index WQI, 56% of water samples are very polluted, MI indicates that the threshold of warning has been exceeded for all water samples and HPI indicates a percentage of 85% of the sampling points like of pollution as highly polluted and unsuitable for consumption in case of groundwater (AP) and surface water (AS) and in case of mine waters (AU) they can not be discharged into natural emissaries.

In order to use those monitored waters as irrigation sources in the present study were calculated seven specific indexes SAR, % Na, SSP, PS, MH, MR and KR which proving that the majority of monitored water sources can be used as irrigation water because of the fact that the respective indicators relying only on major dissolved ion concentrations.

Calculating the specific quality indexes it can be noticed observed that the problems with monitored water sources are represented mainly due to the concentrations of heavy metal, highlighting the impact of mining activities on the water.

6.2. Evaluation of soil and sediment quality by calculating specific quality indexes

In *Table 37* is presented a summary of calculated quality indexes for soil samples, sterile and sediment.

Table 37. Assessment of soil and sediments quality in study area based on specific quality indexes

Nr. crt.	**Quality Index**		**Clasification**	**Contamination Degree**	**Number of samples**	**Procent din totalul punctelor de prelevare (%)**
1	**$I_{geo-sol}$**	**I_{geo}Mn**	$I_{geo}Mn < 0$	Unpolluted	11 / 19	**58 %**
			$0 < I_{geo}Mn < 1$	From unpolluted to moderately polluted	3 / 19	**16 %**

		$I_{geo}Zn$	$1 < I_{geo}Zn < 2$	Moderately polluted	5 / 19	**26 %**
			$0 < I_{geo}Zn < 1$	From unpolluted to moderately polluted	3 / 19	**16 %**
			$1< I_{geo}Zn < 2$	Moderately polluted	2 / 19	**10 %**
			$3 < I_{geo}Zn < 4$	Strongly polluted	6 / 19	**32 %**
			$4 < I_{geo}Zn < 5$	From strongly polluted to extremely polluted	4 / 19	**21 %**
			$I_{geo}Zn > 5$	Extremely polluted	4 / 19	**21 %**
		$I_{geo}Cu$	$0 < I_{geo}Cu < 1$	From unpolluted to moderately polluted	4 / 19	**21 %**
			$1 < I_{geo}Cu < 2$	Moderately polluted	4 / 19	**21 %**
			$2 < I_{geo}Cu < 3$	From moderately polluted to strongly polluted	4 / 19	**21 %**
			$3 < I_{geo}Cu < 4$	Strongly polluted	3 / 19	**17 %**
			$4 < I_{geo}Cu < 5$	From strongly polluted to extremely polluted	2 / 19	**10 %**
			$I_{geo}Cu > 5$	Extremely polluted	2 / 19	**10 %**
		$I_{geo}Pb$	$0 < I_{geo}Pb < 1$	From unpolluted to moderately polluted	1 / 19	**5 %**
			$1 < I_{geo}Pb < 2$	Moderately polluted	1 / 19	**5 %**
			$2 < I_{geo}Pb < 3$	From moderately polluted to strongly polluted	4 / 19	**21 %**
			$3 < I_{geo}Pb < 4$	Strongly polluted	2 / 19	**10 %**
			$4 < I_{geo}Pb < 5$	From strongly polluted to extremely polluted	1 / 19	**5 %**
			$I_{geo}Pb > 5$	Extremely polluted	10 / 19	**54 %**
		$I_{geo}Ni$	$I_{geo}Ni < 0$	Unpolluted	19 / 19	**100 %**
		$I_{geo}Cd$	$I_{geo}Cd < 0$	Unpolluted	2 / 19	**10 %**
			$0 < I_{geo}Cd < 1$	From unpolluted to moderately polluted	1 / 19	**5 %**
			$1 < I_{geo}Cd < 2$	Moderately polluted	3 / 19	**17 %**
			$2 < I_{geo}Cd < 3$	From moderately to strongly polluted	4 / 19	**21 %**
			$3 < I_{geo}Cd < 4$	Strongly polluted	1 / 19	**5 %**
			$4 < I_{geo}Cd < 5$	From strongly polluted to extremely polluted	6 / 19	**32 %**
			$I_{geo}Cd > 5$	Extremely polluted	2 / 19	**10 %**
		$I_{geo}Cr$	$I_{geo}Cr < 0$	Unpolluted	18 / 19	**95 %**
			$0< I_{geo}Cr >1$	From unpolluted to moderately polluted	1 / 18	**5 %**
	$I_{geo-sed}$	**$I_{geo}Mn$**	$I_{geo}Mn < 0$	Unpolluted	12 / 18	**67 %**
			$0 < I_{geo}Mn < 1$	From unpolluted to moderately polluted	6 / 18	**33 %**
		$I_{geo}Zn$	$0 < I_{geo}Zn < 1$	From unpolluted to moderately polluted	1 / 18	**6 %**
			$1 < I_{geo}Zn < 2$	Moderately polluted	1 / 18	**6 %**
			$2< I_{geo}Zn < 3$	From moderately to strongly polluted	2 / 18	**11 %**
			$3 < I_{geo}Zn < 4$	Strongly polluted	6 / 18	**33 %**
			$4 < I_{geo}Zn < 5$	From strongly polluted to extremely polluted	6 / 18	**33 %**
			$I_{geo}Zn > 5$	Extremely polluted	2 / 18	**11 %**
		$I_{geo}Cu$	$I_{geo}Cu < 0$	Unpolluted	2 / 18	**11 %**
			$0 < I_{geo}Cu < 1$	From unpolluted to moderately polluted	3 / 18	**17 %**
			$1 < I_{geo}Cu < 2$	Moderately polluted	6 / 18	**33 %**
			$2 < I_{geo}Cu < 3$	From moderately to strongly polluted	2 / 18	**11 %**
			$3 < I_{geo}Cu < 4$	Strongly polluted	4 / 18	**22 %**
			$I_{geo}Cu > 5$	Extremely polluted	1 / 18	**6 %**
		$I_{geo}Pb$	$0 < I_{geo}Pb < 1$	From unpolluted to moderately polluted	1 / 18	**6 %**
			$1 < I_{geo}Pb < 2$	Moderately polluted	2 / 18	**11 %**
			$3 < I_{geo}Pb < 4$	Strongly polluted	3 / 18	**17 %**
			$4 < I_{geo}Pb < 5$	From strongly polluted to extremely polluted	2 / 18	**11 %**
			$I_{geo}Pb > 5$	Extremely polluted	10 / 18	**55 %**
		$I_{geo}Ni$	$I_{geo}Ni < 0$	Unpolluted	17 / 18	**94 %**
			$0 < I_{geo}Ni < 1$	From unpolluted to moderately polluted	1 / 18	**6 %**
		$I_{geo}Cd$	$I_{geo}Cd < 0$	Unpolluted	3 / 18	**17 %**
			$0 < I_{geo}Cd < 1$	From unpolluted to moderately polluted	3 / 18	**17 %**
			$1 < I_{geo}Cd < 2$	Moderately polluted	3 / 18	**17 %**
			$2 < I_{geo}Cd < 3$	From moderately to strongly polluted	3 / 18	**17 %**
			$3 < I_{geo}Cd < 4$	Strongly polluted	4 / 18	**20 %**
			$4 < I_{geo}Cd < 5$	From strongly polluted to extremely polluted	1 / 18	**6 %**
			$I_{geo}Cd > 5$	Extremely polluted	1 / 18	**6 %**

		I_{geo}Cr	$I_{geo}Cr < 0$	Unpolluted	17 / 18	**94 %**
			$0< I_{geo}Cr < 1$	From unpolluted to moderately polluted	1 / 18	**6 %**
2	**PLI SOL** **P**ollution **L**oad **I**ndex		PLI SOL >1	Progressive contamination	19 / 19	**100 %**
	PLI SED **P**ollution **L**oad **I**ndex		PLI SED < 1	Unpolluted	1 / 18	**6 %**
			PLI SED > 1	Progressive contamination	17 / 18	**94 %**
3	**SPI** **S**ediment **P**ollution **I**ndex		0 < SPI < 2	Natural sediment	3 / 18	**17 %**
			2 < SPI < 5	Low polluted sediment	3 / 18	**17 %**
			5 < SPI <10	Moderately polluted sediment	3 / 18	**17 %**
			10 < SPI < 20	Highly polluted sediment	5 / 18	**27 %**
			SPI > 20	Dangerous polluted sediment	4 / 18	**22 %**

After selecting and calculating specific quality indexes it can be concluded that the biggest problems, according to the $I_{geo-sol}$ and Igeo-sed were recorded for lead, zinc, copper and cadmium due to mining activities and processing minerals. Calculation indexes like PLI SOL, PLI SED and SPI highlights that soil and sediment in the Baia Mare mining area is highly contaminated, even if the mining and processing activities are stopped, heavy metals continues to be a risk factor for both environment and for human health.

Chapter 7

Final conclusions. Personal contributions. Perspectives

The present thesis aim was to assess the impact of mining activities on the Baia Mare environment by calculating specific quality indexes.
In order to achieve the main objective, mentioned above, a number of specific objectives were outlined:

►O1. The exposure of theoretical aspects regarding the mining activities and their impact on the environment – this was done in Chapter 3, which contains a detailed description about investigated area regarding the geographical, geological, hydrogeological, and climate characteristics as well as some aspects regarding flora and fauna from the study area. In Chapter 3 was presented a short history about mining activities in the area which area which area known from the Roman Empire and in this Chapter were also presented the possible sources of pollution and environmental problems associated with mining activities in the study area.

►O2. Determination of dissolved ions concentration (F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+) in surface water, mine water and groundwater samples taken during the six sampling campaigns (November 2013, December 2013, March 2014, June 2014, September 2014 and December 2014) – It was fulfilled in Chapter 4, were are presented aspects regarding the used equipment, the methodology of processing and preserving collected samples in accordance with national and international standards. Also in this chapter are presented the results highlighting the seasonal variations.

In collected groundwater samples was detected a high concentration of fluoride, it was detected in 100% of water samples, 20% exceeded the maximum allowed level.

Chloride was identified in all analyzed groundwater samples but none of them exceeded the maximum allowable concentration, all concentrations were below 250 mg / L.

Chloride was determined in all surface water and mine water samples but its concentrations were relatively low, in mine water the highest concentration was about 3 times lower than the maximum permissible concentration and in surface waters 90% of the samples were belonged to quality class I, 4% were belonged to quality c class II and 6% were belonged to quality class III.

Regarding the sulfate, 5% of groundwater samples exceeded maximum allowable concentration required by law 458/2002. Large concentrations of sulfates were detected in samples AP14, AP17 and AP18, these water sources are located near the Tăuţii de Sus tailing ponds.

Following the laboratory analyzes were determined high concentrations of sulfate in surface and mine waters, 77% of mine water samples exceeded the maximum permissible limit, and 39% of surface water samples belong to quality class I, 27% to quality class II, 18% to quality class III, and 3% respectively 13% belong to quality class IV and V. Those values are mainly due to pyrite oxidation.

Nitrate concentrations were detected in 13% of analyzed groundwater samples, all of them exceeded the maximum allowable concentration. High levels of nitrite indicate oldest pollution of water sources.

The high concentration of nitrite and nitrate in investigated groundwater sources are due to intensive practiced agriculture in the gardens around monitored water sources.

The nitrate was identified in 57% from mine water samples, 11% of them exceeding the maximum allowable concentration. With respect to collected surface water samples the nitrate has been identified in 94% of samples: 7% belong to quality class I, 33% belong to quality class II, 31% belong to quality class III, 13% belong to quality class IV and 10%

belong to quality class V. The highest concentration of nitrite ion was determined in sampling point AS37, which was taken from Săsar River at its confluence Borcut Valley. Nitrite concentration may be a consequence of the use of fertilizers or sewage disposal.

Phosphate was identified only in two groundwater investigated sources (AP25 and AP26).

Bromide was detected in 8% of collected groundwater samples, the highest concentration was recorded in the sampling point AP25, possibly through the use of fertilizers containing bromides (ww.epa.gov).

In all investigated groundwater samples potassium concentrations were detected, its value ranged between 0.3 mg / L (AP21) and 47.56 mg / L (AP14).

Sodium content was relatively low regarding the groundwater samples, only sampling point AP33 exceeded the maximum concentration level.

Regarding the sodium concentration in collected surface and mine waters, the highest concentrations were detected in sampling points collected from Săsar River (AS6, AS7, AS37) in surface waters and in AU4 in case of mine water.

Lithium has been identified in 67% of groundwater samples. The highest lithium concentrations were detected in AP24, AP25 and AP33. The lithium concentration in AP24 and AP25 may be due to infiltrations from Herja Valley (AS23), where were found high concentrations of lithium.

Calcium and magnesium concentrations were detected in all water but their concentration was low.

►O3.Determination of eight heavy metals and one metalloid (Fe, Pb, Ni, Zn, Cu, Cd, Mn and Cr, As) in collected surface water, mine water, groundwater, sediment and soil collected - was fulfilled in Chapters 4 and 5, of treating these details regarding processing and preservation of samples, the used analytical method and the obtained results.

Regarding collected groundwater samples over the monitoring period copper, zinc, nickel and iron concentrations were found in all investigated water samples, followed by manganese, lead and cadmium.

There were no identified concentrations of chromium and arsenic.

Regarding the manganese concentrations were most overruns (68%) of the maximum concentration followed by iron (81%), nickel (39%), cadmium (40%) and zinc (7%).

From the nine investigated heavy metals eight metals were identified in surface water samples, the concentration increase as follow: Mn > Zn > Fe > Cu > Ni > Pb > Cd > Cr.

In collected mine waters the heavy metal concentration increase as follow: Fe > Mn > Zn > As > Cu > Pb > Ni > Cd > Cr.

Regarding the heavy metal concentration in collected soil and sediment samples it increase as follow: Fe > Zn > Cu > Pb > Mn > Ni > Cr > Cd.

In case of sediment samples the heavy metal concentration increase as follow: Fe > Zn > Cu > Pb > Mn > Ni > Cr > Cd.

Zinc was detected in 100% of collected groundwater samples, the concentrations ranged between 9.4 mg / L (AP17) and 43731 mg / L (AP24), 7% exceeding the maximum allowed by legislation.

As regards the surface and mine waters zinc is the third dominant metal, 32% belongs to V quality class and 97% of mine water samples exceeded the maximum permissible limit.

All sterile and soils samples showed high concentrations level in terms of zinc, 27% exceeded the alert threshold for less sensitive soils, and 44% exceeded the intervention threshold.

Zinc has exceeded the maximum allowable concentration in 94% of sediment samples in some cases the maximum allowable concentration was exceeding 16 times.

Manganese was detected in 94% of collected groundwater samples, 68% have exceeded the maximum allowed.

Manganese exceeded the maximum concentration level both in collected surface and mine waters, 47% from surface water samples belong to V quality class and all mine water samples exceeded maximum allowable concentration.

From collected soil samples 58% do not exceed the normal concertation of manganese in soil (900 mg / kg), while 12% exceeded the intervention threshold (2.000 mg / kg).

Regarding the iron concentration, it was detected in all investigated water sources. In case of groundwater, 81% exceeded the limit, 26% of surface water samples belongs to V quality class and 93% from mine water samples exceeded the maximum permissible value, these high values may be due to oxidation of the sulfide minerals in the dissolved iron.

Iron presented the highest concentrations being dominant heavy metal in collected soil sterile and sediment samples.

Copper was detected in all collected water samples, 1% of groundwater samples had exceeded the maximum permissible limit, 4% from surface water samples belong to V quality class and 77% from mine water samples exceeded the maximum permissible limit.

In case of collected soil and sterile samples, 56% exceeded the normal value for copper in soil (20 mg / kg) l, 20% exceeded the alert threshold (250 mg / kg), and 23% exceeded the intervention threshold.

Regarding the sediment samples copper concentration was exceeded in 94% of samples.

Concentrations of lead were detected in 47% of collected water samples, 2% from surface water samples belongs to quality class V while 13% from mine water samples exceeded the maximum allowable concentration.

In soil and sterile samples the lead concentrations were relatively high, 35% of the samples exceeded the normal value for lead in soil (20 mg / kg), 15% exceeded the alert threshold (250 mg / kg) and 51% exceeded the intervention threshold (1.000 mg / kg).

The sediments sampled were found to be heavily polluted with lead, 94% of 108 sediment samples exceeded the maximum permissible limit.

In all collected water samples were found nickel concentrations, 39% exceeded the maximum permissible level in the case of groundwater samples, 6% of surface water samples belongs to V quality class and 8% of mine water samples exceeded the maximum allowable limit.

Cadmium exceeded the maximum permissible in case of 40% collected groundwater samples and in case of surface water samples 42% belong to V quality class.

Concentrations of cadmium were detected in 92% of sterile and soil samples, 47% exceeded the normal level for cadmium in soil (1 mg / kg), while 8% have exceeded the alert threshold (5 mg / kg).

Cadmium concentration was identified in 91% from collected sediment samples,69% exceeding the maximum permissible concentration.

Arsenic was identified in 91% of collected mine water samples, the highest concentrations were detected in samples collected from Tauţii de Sus tailing ponds area. On Tăuţii de Sus tailings ponds were stored arsenious pyrites and the meteoric water that washes the ponds get into the channel which surrounds the tailing pond, representing a potential source of pollution for surface water where this channel is discharged or for groundwater (wells) sources located near tailing ponds which are used by the owners as a consumer secure sources.

In case of ground water samples the sampling point AP24, which is a private well, proved to be the most contaminated possible monitored groundwater sources due to position of this close to Herja Valley (20 m), where all untreated mine waters from Herja Mine are discharged.

In case of surface waters the highest concentrations of heavy metals were identified in samples AS6, AS7 (taken from Săsar River downstream of Şuior Mine) and AS8 (taken from downstream of Baia Sprie Mine).

Elevated concentrations of zinc, copper and lead in the surface water samples AS6, AS7, AS8 taken from Săsar River from Baia Sprie are due to the geological background of the area.

Sampling point SL2 located downstream of the pipe where are discharged the mine waters from Suior Mine, presented the highest values of the heavy metals concentration regarding the soil samples and in terms of collected sediment samples the sampling point SD30, taken from a pipe proved to be the most heavily contaminated.

That high concentration of heavy metals is the result of several factors: past mining activities upstream of Baia Mare (Şuior Mine, Baia Sprie Mine), mining wastes resulting from these, and industrial activities found in the study area.

►**O4. Assessment of seasonal variation of physico-chemical parameters, dissolved ion concentrations and heavy metals concentrations analyzed in collected samples –** was fulfilled in Chapter 4 and 5, which were exposed in graphic form seasonal variation of the investigated quality parameter**.**

The variation of physico-chemical parameters, dissolved ion concentrations and heavy metal concentrations over the monitoring period may be due to meteorological factors, due to rainfalls in the sampling period because rainwater dissolved additional quantities of heavy metals in soil. In March, June and December 2014 increased the amount of precipitation before sampling campaign.

In case of soil, sterile and sediment samples the seasonal variations and differences in concentrations between sampling points is mainly due to geographical factors (many of sampling points are located very close to pollution sources such as mining exploitation, plants ore processing, waste dumps or tailings ponds) and the climate (especially in the case of sediments ex .: rainwater can wash the surrounding soils or slopes, affecting water quality and sediment quality as well).

►**O5. The calculation of specific quality indexes. The environmental impact assessment in the study area –** it was fulfilled in Chapter 6 where have been calculated specific quality indexes for each studied environmental factor: Water Quality Index of (WQI), Metal Index (MI), Heavy Metal Pollution Index (HPI), Pollution Index (PI), Sodium Absorbtion Ratio (SAR), Sodium Percentage (% Na), Soluble Sodium Percentage (SSP), Magnesium Hazard (MH), Magnesium Ratio (MR) and Kelley Index (KR) for all collected water samples and geoacumulare index I_{geo}, Pollution Load Index (PLI), Sediment Pollution Index (SPI) for soil, sterile and sediment samples.

By calculating the water quality index (WQI) were obtained values between 55.24 (AP19) and 3280.76 (AS23), 56% of groundwater samples (AP) surface water (AS) and mine waters (AU) highly polluted, having a value of WQI > 300, they are not recommended for consumption, while 11% of the analyzed water samples had a very poor quality (200 < WQI < 300), 18 % had a poor quality (100 < WQI < 200) and only 15% have a good quality (50 < WQI < 100).

For metal contamination index (MI) were obtained values ranging from 3.68 (AP9) and 426.22 (AS23), all the sampling points in of water value of the heavy metal contamination exceeded the warning threshold, which results that the groundwater and surface waters samples can not be used as reliable sources of consumer and mine water samples can not be discharged directly into the natural emissaries without being treated before.

Heavy metal pollution index HPI values ranged between 17.97 (AP21) and 6849.8 (AU30), the highest value recorded was nearly 69 times higher than the critical value (100), 85% of water sources investigated exceeded the critical value.

By calculating pollution index PI the biggest problems is highlighted in case of PI_{Mn} and PI_{Zn}. 54% of the sampling belongs to quality class 5 in case of PI_{Mn}, with a value > 5 that means that these water sources are excessively contaminated with high concentrations of manganese; 29% belongs to quality class V in case of zinc as having a PI_{Zn} value > 5 that means is excessively polluted with zinc, 7% of the sampling points is excessively polluted with cadmium and 8% is excessive polluted with arsenic. The highest PIAs values have been determined in water samples taken from and around the tailings pond Tăuţii de Sus. The high content of arsenic in two sampling points is a consequence of the fact that on these ponds have been deposited arsenious pyrites.

Sodium adsorption ratio SAR had values between 0.14 (AU15) and 7.41 (AP33), the ratio is excellent, generally with higher SAR values the more inadequate is the water supply to be used for irrigation. A total of 97% of the sampling points have a value of SAR's below 3, which means there is no risk to vegetation.

Based on the sodium percentage % Na, 48% of water samples have excellent quality, 43% have a good quality, 5% have a quality permitted, and 3% have doubtful quality and can be used with moderation as irrigation sources.

Soluble sodium percentage SSP values ranged between 0.32 (AU12) and 72.37 (AS39), 46% of water samples with excellent quality of the SSP, 21% having a good quality while 18% have a permissible quality.

Potential salinity index PS values ranged between 0.09 mEq / L (AS39) and 19.08 mEq / L (AU3), 28% had a value of PS > 3 which means that are not good to be used in agriculture.

Regarding the magnesium hazard index MH, 10% from collected water sources had a value of MH greater than 50%, which means the using of these waters like of irrigation waters can affect the crop and soil alkalinity increases. The highest values of MH have been identified in water samples collected from Tăuţii de Sus tailing point and from the chennel where acid mine water are discharged .

Magnesium Ratio certifies that all water samples have excellent quality and can be used as safe sources of irrigation.

According to Kelley index KR most of the of water samples are recommended to be used in agriculture

The calculation of quality indexes as SAR, % Na, SSP, MH, MR, KR it has been shown that approximately 80% from water samples can be used in agriculture.

By calculating $I_{geo\text{-}sol}$ and $I_{geo\text{-}sed}$ the highest contaminations were determined for zinc, copper, lead and cadmium, they were identified even in the control sample which indicates whether the geochemical background of Baia Mare is higher than the earth's crust or historical mining activities had left their mark so intensely that pollution has reached even in those places considered unpolluted.

The highest pollution index PLI values were recorded in SL2, and SL8 SL23, sampling point which were collected from downstream of Şuior Mine (SL2), Baia Sprie Mine (SL8) and Herja Mine (SL23). For sediment samples the highest PLI value was recorded at the SD30 sampling point due to the water which is discharged in this channel from where the sediment samples was collected.

Regarding the sediment pollution index SPI, 22% of the sediments samples where extremely contaminated (dangerous polluted sediment), 27% are hightly contaminated, 17% are moderately contaminated, 17% are low polluted sediments and 17% are natural sediments.

By calculating Igeo-sol and $I_{geo\text{-}sed}$, PLI and SPI can conclude that points SL2 (sampled downstream of Şuior Mine) and SD30 (taken from a pipe where are discharged mine waters) should be given special attention being points that pose the greatest problems.

Perspectives:

► investigating certain aspects concerning the provenance of manganese and nickel in water investigated sources and geochemical processes which involve those chemical elements with a negative impact on human health and the environment;

► extending the study area including other mining areas in the country, which have been exploited and recovered ores with similar chemical composition but also specific mining areas differently than Baia Mare area;

► investigation of the aluminum content in Baia Mare, in order to determine specific environmental indexes that require in calculation formula the concentration of aluminum;

► investigation of air quality from Baia Mare area by determination the heavy metal concentrations from suspended particulate matter;

► correlations between physico-chemical and chemical parameters for sediments and surface water samples to identify the processes between water / sediment.

► identification of other specific indexes for assessing the environmental quality and the using the specialized software to calculate these indices (AquaChem, etc.);

► using information acquired during phD studies, the phD student intends to identify a more complex calculation formula for creating a quality index.

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