



Use of geochemical characteristics and isotopes for assessing migration of harmful substances at three mine sites: Kittilä mine in Finland and Roșia Montană and Zlatna mines in Romania

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Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

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Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites: Kittilä mine in Finland and Roşia Montană and Zlatna mines in Romania

Authors D. C. Papp, I. Cociuba, C. Larkins, I. Măntăre, K. Turunen, Y. Lahaye, N. Hendriksson, P. Forsman, S. Nieminen, C. Băciu, A. Cozma, L. Lazar, I.C. Pop, C. Roba		Type of report GTK Open File Work Report	
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Abstract Mining tends to increase, especially airborne and water related emissions of possibly harmful elements and transforming them into more mobile and toxic forms. Therefore, it is important to estimate the effects of mining activity and compare it with the natural background to understand the contaminant sources and the processes controlling the water quality in the recipient water systems. The purpose of this research was to evaluate and test usability of different geochemical characteristics and isotopes for assessing migration of harmful substances at three mine sites: the Kittilä mine in Finland, and two old mining areas in Romania, Roşia Montană and Zlatna. Romania has the largest gold resources in Europe but no currently operating gold mines, whereas Kittilä mine in Finland is the Europe's largest operating gold mine. The abandoned Roşia Montană and Zlatna sites have been mined since Roman time. As they lacked environmental regulations and resulted in significant environmental consequences, the sites still require monitoring for designing appropriate measures to diminish the contaminant release. In contrast Kittilä, as rather recently opened and still operating mine, has always had stricter environmental regulations and thus lesser environmental issues, but nevertheless needs also monitoring. A combination of isotopic analysis of $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{34}\text{S}/^{32}\text{S}$ of SO_4 , $^7\text{Li}/^6\text{Li}$, and $^{26}\text{Mg}/^{24}\text{Mg}$, major and trace element analysis was tested to evaluate the usability of these isotopes to study the longterm contamination around mine sites as well as the transport, mixing and dilution of contaminants in nearby lakes and rivers.			
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Synopsis

1. Purpose of research

The purpose of this research was to evaluate and test usability of different geochemical characteristics and isotopes for assessing migration of harmful substances at three mine sites: the Kittilä mine in Finland, and two old mining areas in Romania, Roşia Montană and Zlatna. Whereas Romania has the largest gold resources in Europe but no currently operating gold mines, Kittilä mine in Finland is the Europe's largest operating gold mine.

The study was carried out in the SUSMIN project (Tools for sustainable gold mining in EU) in close cooperation between Geological Survey of Romania, Babes Bolyai University and Geological Survey of Finland. This study was part of the environmental work package in which also novel monitoring and environmental risk assessment tools and method were tested (Lahtinen *et al.* 2018 and Baciú *et al.* 2018).

2. Material and analysis

The abandoned Roşia Montană and Zlatna sites have been mined since Roman time. As they lacked environmental regulations and resulted in significant environmental consequences, the sites still require monitoring for designing appropriate measures to diminish the contaminant release. In contrast Kittilä, as rather recently opened and still operating mine, has always had stricter environmental regulations and thus lesser environmental issues, but nevertheless needs also monitoring. Therefore, due to distinct history as well as geological background, the case study sites had slightly different research aims, and different study methods were applied at each site.

At the Kittilä mine in Finland a combination of isotopic analysis of $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{34}\text{S}/^{32}\text{S}$ of SO_4 , $^7\text{Li}/^6\text{Li}$, and $^{26}\text{Mg}/^{24}\text{Mg}$, major and trace element analysis was tested to evaluate the usability of these isotopes to study the transport, mixing and dilution of contaminants in nearby lakes and rivers.

At the Roşia Montană site in Romania a combination of isotopic analysis of $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, and major and trace element analysis was tested to evaluate the long-term contamination around old mine site. In addition, one-time isotopic analyses of strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and SO_4 sulphur ($^{34}\text{S}/^{32}\text{S}$ - SO_4) isotopes were conducted to evaluate the usability of these isotopes to study the contaminant transport and mixing in receiving water bodies.

At the Zlatna site a combination of isotopic analysis of $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, and major and trace element analysis was tested to evaluate the long-term contamination around old mine site.

3. Methods applicability

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ (δD) were particularly useful for assessing hydrological connectivity and mixing, as they are the only truly conservative tracers of water. These isotopes provided important evidence of groundwater relation to meteoric water, and provided unique indication of water subject to industrial processes.

$^{87}\text{Sr}/^{86}\text{Sr}$ provided insight to water source and mixing. The conservative behaviour of $^{87}\text{Sr}/^{86}\text{Sr}$ in solution allowed delineation of water pathways and estimates of water mixing. However, the accuracy of these estimates is dependent on accurate end-member characterization and sampling.

$\delta^{34}\text{S}$ - SO_4 showed variability across site waters that suggests it may provide a valuable tracer of SO_4 origin and transport between different waters as well as biological reduction processes due to microbial activity.

$\delta^7\text{Li}$ was consistently distinct within different mine water types, though evidence of its non-conservative behaviour in solution suggests it may provide a more practical tracer of solute attenuation processes than of solute source and mixing at the mine site and river reach scale.

$^{26}\text{Mg}/^{24}\text{Mg}$ was not found to provide additional insight into water mixing due to lack of isotopic variability between different samples. Further, the controls on isotopic variation in Mg are not well constrained, complicating interpretation of these results in a field setting.

Geochemical and isotopic data were successfully used to assess mining effects on groundwater and surface water.

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites: Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

4. General evaluation and awareness

The geochemical and isotope methods are, if carefully planned and conducted, accurate and useful tool to study the environmental impact of mining, contaminant transport and mixing in receiving water bodies as well as the hydrological connectivity and interactivity of different water sources. However, sampling and analysing are laborious, span over a long period of time and require a large volume of samples to be collected and analysed. Furthermore, the sampling represents only the prevailing conditions during sampling, lacking the time between individual sampling events. The decision over the number of sampling sites is also challenging: too many sites results in high costs and time input; not enough sites results in detrimental data gaps. Therefore, the selection of monitoring sites for accurate water sampling is crucial and should be commutable, if needed due to mine expansion and relocation of operations. With the help of an online monitoring system, the sampling intervals and locations can be defined adequately for representative samples. It also works as early warning system for detecting any sudden changes in physicochemical characteristics that an immediate sampling and analysis can be undertaken and possible intervention procedures started to prevent adverse effects.

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1 Introduction

Elevated concentrations of heavy metals and other harmful substances in soils and natural waters are met in specific areas with natural abundance of metallic minerals in bedrock and in these sites nature has developed to tolerate these elevated concentrations. However, mining tends to increase, especially airborne and water related emissions of these possibly harmful elements and transforming them into more mobile and toxic forms. Therefore, it is important to estimate the effects of mining activity and compare it with the natural background to understand contaminant sources and seasonal variation in mixing and dilution processes controlling the water quality in the recipient water systems.

1.1 Aims of the study

The purpose of this study was to enhance the environmentally sustainable mining by characterizing and evaluating anthropogenic emissions relative to geogenic background. This report describes the application of geochemical and isotopic methods at three case study sites in Romania and Finland to monitor the migration of harmful substances from mine sites to surface and ground waters. This study is related to ecological risks and monitoring studies by Baciú *et al.* 2018 and Lahtinen *et al.* 2018. Geochemical characterization of background ground and surface waters, those affected by mining as well as mine waters was conducted to assess interactions of mine site emissions with the surrounding environment. Isotopic analysis was used to provide supplemental insight to geochemical characterization. The stable isotope composition of water (O and H) at these sites was used as a natural tracer for assessing groundwater sources, flow paths and interaction with surface waters. A multi isotope approach including isotopes of Sr, S, Li, and Mg, was also applied to provide insight on contaminant sources and transport mechanisms. Further, the benefits and limitations of the studied multi-isotope application for the specific case study sites and to general mine-site environmental monitoring applications are discussed.

1.2 Site Background

This study provides perspectives from contrasting European gold mine sites: the Kittilä mine in Finland, and two mining areas in Romania, Roşia Montană and Zlatna. Whereas Romania has the largest gold resources in Europe, Kittilä mine is Europe's largest operating gold mine. Characteristics from each of the three sites are summarized in Table 1.2.1.

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Table 1.2.1 Summary of environmental and historical mine site conditions

	Kittilä mine, Finland	Roşia Montană mine, Romania	Zlatna mining area, Romania
Average annual temperature	-1.3 °C	7.4°C	10.5 °C
Average annual precipitation/evaporation	Precipitation: 55 cm/yr Evaporation: 25 cm/yr	Precipitation: 74.5 cm/yr (SRK 2012)	60 cm/yr 45 cm/yr
Vegetation	Northern boreal vegetation	Nemoral formations (temperate forest – deciduous and coniferous)	Nemoral formations (temperate forest – deciduous and coniferous)
Proximity to residential areas	50 km northeast of Kittilä, Finland (population 6 421)	5 km northeast from Abrud, Romania (population 5000)	4-5 km NW of Zlatna 2-3 km N of Almaşul Mare 1-2 km N of Techereu
Economic mineralisation	Refractory gold (Au) within arsenopyrite and pyrite	Native gold, electrum gold (gold-silver) associated with sulphides (predominantly pyrite)	Au-Ag and Au-Ag-Pb-Zn-Cu mineralisations
Host rock	hydrothermally altered meta-oceanic sediments with 10% sulphides within tholeiitic basalt (Proterozoic Kittilä group)	Neogene maar-diatreme volcanic complex intruding Cretaceous detrital sediments	ophiolite, conglomerate, sandstones and clays, andesites
Underground workings	exist beneath open pits and are being actively expanded	140 km of underground workings	underground workings 2 mines: Haneş and Stănişia
Open pits	2 open pits totalling 35 ha	2 open pits totalling 24.95 ha	no open pits
Mining operation dates	production began in 2009 and projected to continue to 2037	>2,000 years bp to 2006	>2,000 years bp to 2007
Current mining activity	Underground mining ongoing with planned expansion	No current mining, but mining permit being sought by Roşia Montană Gold Corporation	mining activities were abandoned in 2007 without planned reopening

2 Kittilä Mine

2.1 Geographic and geologic setting

The Kittilä mine is located in Finnish Lapland approximately 50 km northeast of the town of Kittilä. The mine site is within the lower reaches of the 307 km² Seurujoki River catchment, which drains to the Loukinen River south of the site. The soil surrounding the mine site is mainly low permeability glacial till and there are not significant alluvial groundwater deposits in the mine vicinity. The wetlands surrounding the mine area consist of 1 to 2 m of peat over top of 3 to 6 m of moraine deposit. (AVI 2013). The mine is situated in the subarctic zone with mean annual temperature of -1°C and about 550 mm of mean annual precipitation (Ramboll 2015).

The Kittilä mine is currently the largest operating gold mine in Europe, with more than 2 million ounces of known gold resources. The average grade of proven and probable reserves is 4.9 g/t, and 3.5 g/t for additional resources (Wyche et al. 2015). The mineralisation is classified as a Proterozoic orogenic gold deposit. Gold mineralisation occurs along a 5 km stretch of the Kiistala shear zone within the Kittilä group of the Central Lapland Greenstone Belt (CLGB), and is associated with carbon (amorphous carbon and graphite), silica, albite alteration and carbonate alteration of meta- sedimentary and volcanoclastic host rocks within the Kittilä group (Wyche et al. 2015, Lehtonen et al. 1998). These host rocks are in a transitional zone between Fe rich to Mg rich tholeiitic basalts, from east to west, respectively, and consist of mafic tuff, black chert and banded iron formation (BIF) (Figure 2.2.1). The gold is predominantly refractory, and exists within the lattice structures of arsenopyrite and pyrite. Sulphide content within the host rock ranges from 2 to 30%, and is on average 10% (Doucet et al. 2010).

2.2 Mining and water management

Mining at Kittilä began in 2008 by Agnico Eagle Finland Oy, with the first commercial production of Au in early 2009. The mining area encompasses 857 ha and includes the two open pits, underground workings, ore processing and water treatment facilities, two settling ponds, waste rock dumps, and other mine facilities (Figure 2.2.1). Initially ore was extracted from open pits. The Suurikuusikko open pit to the south and the smaller, Rouravaara open pit to the north were mined until 2012. Underground mining began in 2010 with about 8 km of underground tunnels mined per year. Underground stopes are backfilled with a tailings-cement paste and water from the NP3 pond (Agnico Eagle Finland 2015). Approximately 1.4 million tons of ore are mined annually to produce approximately 6,000 kg Au (Agnico Eagle Finland 2015).

Due to the refractory nature of the gold, cyanide leaching is required for gold extraction from the ore. Ore beneficiation entails crushing, grinding, froth flotation, pressure oxidation, dissolution and electrowinning (Agnico Eagle Finland 2015). Approximately 3 Mm³ of water is used annually during mineral beneficiation, 65% of which is recycled between tailings ponds and the beneficiation plant. The remaining 1.1 Mm³ of beneficiation water is diverted from the river Seurujoki (AVI 2013) (Figure 2.2.2).

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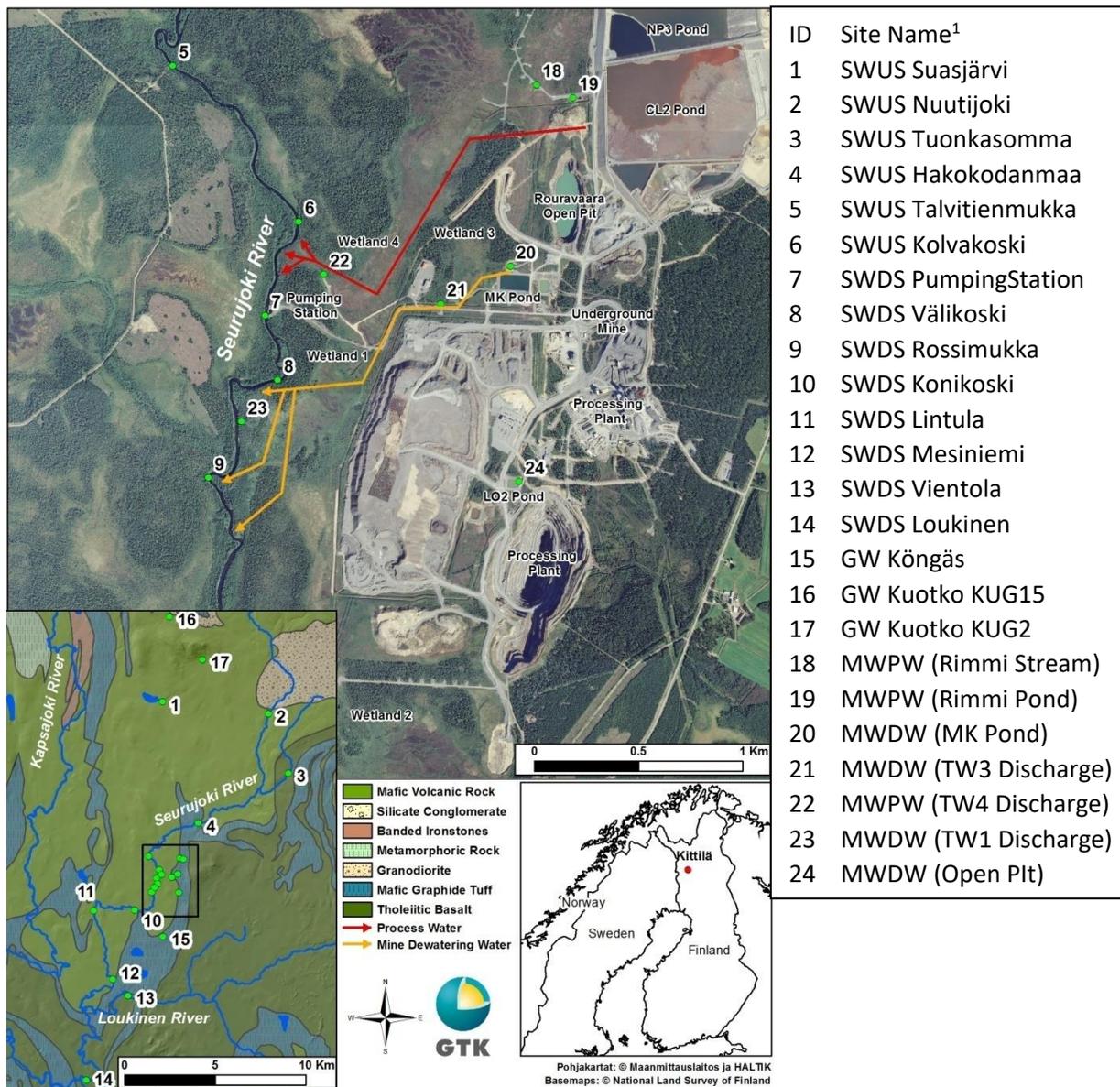
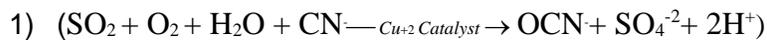


Figure 2.2.1 Location of Kittilä mine operations major regional lithologies, water sampling sites and mine water discharge flow paths. ¹ Water sampling sites labeled based on sample origin, where SWUS = river surface water upstream of mine discharge, SWDS = river surface water downstream of mine discharge, GW = groundwater up gradient of mine, MWPW = mine process water, and MWDW = mine dewatering water

Ore is transported from the mine to the semi-autogenous grinding mill by truck. Sulphide minerals are separated by froth flotation. The slurry extracted during flotation is neutralized and discharged to the NP3 tailings impoundment. The sulphide concentrate extracted during flotation is moved to a pressure oxidation autoclave for gold extraction. The gold concentrate is pumped to the carbon-in-leach (CIL) circuit in which gold is extracted from the slurry by cyanide leaching and adsorbed to carbon granules. The gold concentrate is further treated for gold recovery, and the cyanide

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leach tailings are moved to a reactor for cyanide destruction using the INCO method, following equation 1 (Agnico Eagle Finland 2015).



The INCO treated tailings and effluent from the cyanide leaching process are directed to the CIL2 and CIL3 (directly to the east of CIL2, not pictured in Figure 2.2.1) tailings ponds, which are in a closed circuit with the mill. (Agnico Eagle Finland 2015).

Mine dewatering and waste rock drainage waters are managed separately from process waters. Effluent from NP3 is discharged to an open fen-type peatland infiltration field, treatment wetland 4 (TW4), which drains to the Seurujoki River (Doucet et al. 2010). TW4 has been measured to currently be approximately 60 ha, with approximately 50% actively flowing area (Pöyry 2012). Discharge of process water from NP3 to TW4 and subsequently into the Seurujoki River began in 2010. In 2015 1.1 Mm³ of process effluent was discharged to Seurujoki River. (Pöyry 2012). Underground mine dewatering water is pumped to the MK pond, treated with PIX (ferrisulphate) coagulant, and discharged to the 5.5 ha peatland infiltration field, treatment wetland 3 (TW3). From TW3 effluent is routed to a second 17 ha peatland infiltration field, treatment wetland 1 (TW1), from which it subsequently drains to the Seurujoki River. Discharge of underground mine dewatering water to TW3 began in 2006 and in 2015 altogether 3.4 million m³ was discharged to Seurujoki River. (Palmer et al. 2015). The Suurikuusikko open pit is dewatered to the LO2 storage pond to be used in the mill for processing, for underground drilling, or pumped to the Rouravara open pit for storage. Seepage water from the waste rock facility is directed to the SISU pond and any excess water will be directed further to the CIL2 pond (Ramboll 2015).

Water discharged from the Kittilä mine to treatment peatlands has an electrical conductivity of over ten-fold natural surface water in the area (Pöyry 2012). Mine water includes elevated concentrations of trace metals/metalloids (As, Sb, Ni, Zn, Al, Cu, Mn, and Fe), sulphate (SO₄) and other elements (Cl, P and N) (AVI 2010, Pöyry 2012). Process water discharged to TW4 contains relatively high loads of SO₄, P, and N, while mine dewatering water discharged to TW3 contains relatively high metal loads (As, Sb, and Ni) (Palmer et al. 2015). Further, the quality of the mine dewatering water is variable, and depends largely on the lithology of the area being dewatered at a given time (Pöyry 2012). Mine water-surface water relationships are illustrated in figure 1.2.2. This figure also indicates the locations of different surface water sampling points.

Additives are used throughout the beneficiation process, as well as for water treatment of both process and dewatering waters. Table 1.2.2 provides a list of industrial additives applied at the Kittilä site. The mine waters are treated with PIX coagulant to remove suspended solids prior to discharge to treatment wetlands (Table 2.2.1). The effectiveness of treatment wetlands to attenuate contaminants is seasonally dependant in Finland, and is greatest during summer months during maximum biological activity. The treatment capacity of the wetlands is lowest during spring flooding, and it has been predicted that nutrients and contaminants could potentially be flushed from the wetlands to the River Seurujoki during these periods of high flow (Pöyry 2012,

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Palmer et al. 2015). Further, continual contaminant loading to treatment wetlands poses the potential to alter redox and pH conditions within the wetlands, and could result in mobilization of metals to the surrounding environment. These conditions highlight how an understanding of contaminant sources, pathways, and fluxes at the Kittilä site are crucial for guiding environmentally sustainable mining and water management practices.

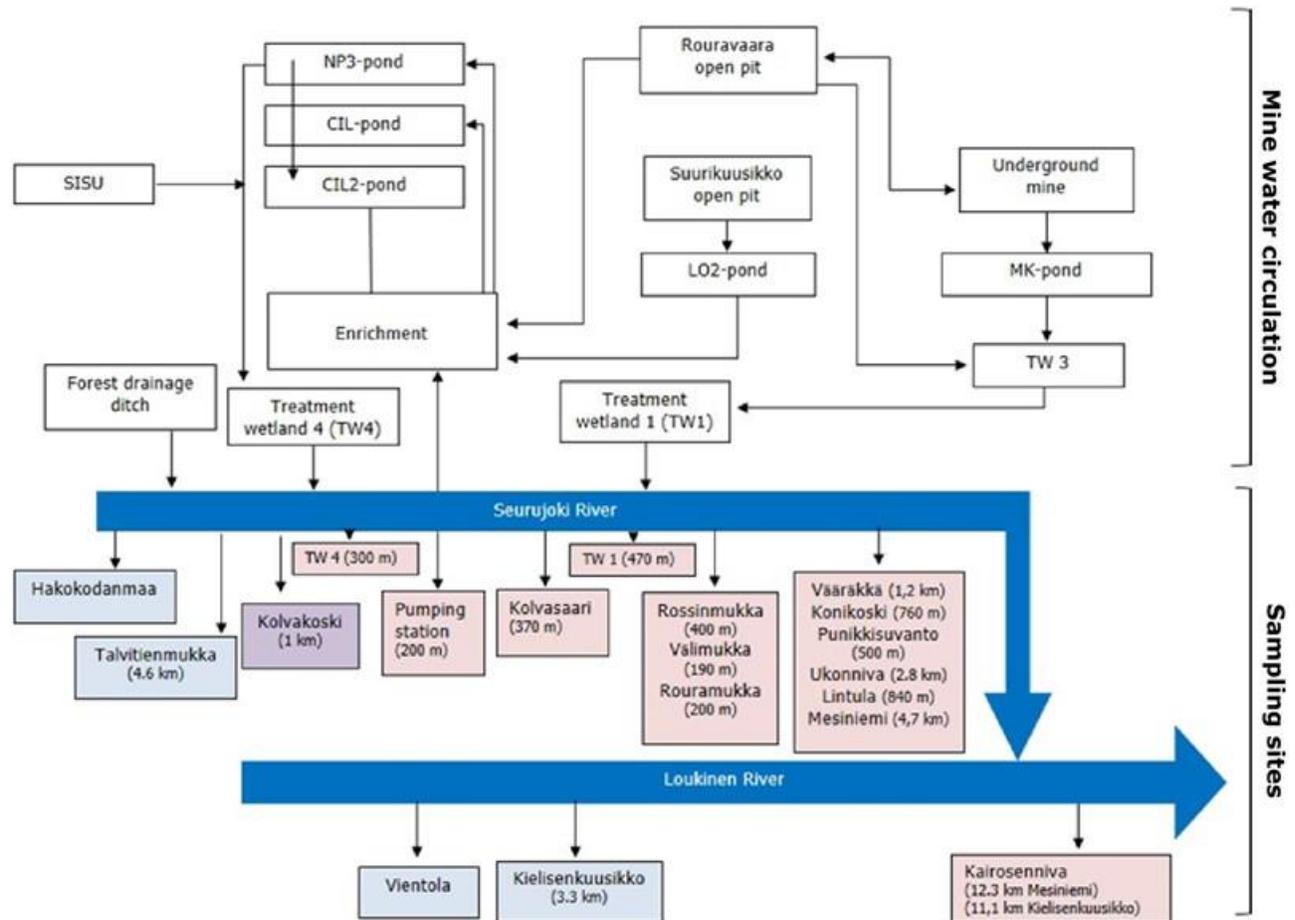


Figure 2.2.2 Chart of mine water circulation in Kittilä mine and sampling points in recipient Seurujoki and Loukinen Rivers. The distance to previous sampling point in Seurujoki and Loukinen Rivers is presented in brackets. The total distance from Hakokodanmaa to Ka Kairosenniva is approx. 31km. (Modified from Hämäläinen E. 2015 and Malinen 2016).

Table 2.2.1 Chemicals used during mineral beneficiation and water treatment at the Kittilä mine site (Pöyry 2009).

Chemical	Chemical formula	Use
foaming chemical MIBC	C ₆ H ₁₄ O	foaming
Xantate PAX	C ₅ H ₁₁ OCS ₂ K	foaming chemical
Sodium isobutyl xantate	C ₅ H ₁₀ OS ₂ Na	foaming chemical
Flocculent		thickening
Oxygen	O ₂	autoclave
Hydrated lime	Ca(OH) ₂	neutralization/pH increase
Burnt lime	CaO	pH adjust
Nitric acid	HNO ₃	acid wash
Lye	NaOH	pH adjust
Cyanide	CN	Gold extraction
Activated carbon		CIL-circle gold extraction
Copper sulphate	CuSO ₄	foaming, cyanide elimination
Metabisulphite SMBS	Na ₂ S ₂ O ₅	cyanide elimination
FerriSO4 PIX	Fe ₂ (SO ₄) ₃	water treatment

2.3 Study methods

2.3.1 Sampling

Water sampling for isotopic and geochemical analyses was conducted at and around the Kittilä mine site in June 2013, March 2015, and June 2015. Water sample sources included surface water from upstream of mine site discharge (background surface water), surface water downstream of mine water discharge points (downstream surface water), groundwater wells upgradient of mine impacted waters (background groundwater), mine water entering treatment wetlands and discharging from wetlands to the Seurujoki river, mine water from holding ponds, and deep groundwater from boreholes and seeps within the underground mine (mine water groundwater). Figure 2.2.1. shows sample locations in relation to mine site features from an aerial perspective. Field blanks and duplicate samples were collected during each sampling campaign. Water samples were collected for isotopic analysis of ¹⁸O/¹⁶O, ²H/¹H, ⁸⁷Sr/⁸⁶Sr, ³⁴S/³²S of SO₄, ⁷Li/⁶Li, and ²⁶Mg/²⁴Mg, major and trace element analysis. The analyses conducted varied by sample date, as described in Table 2.1.1. Additionally, results from water samples collected from underground mine boreholes as part of a separate study in September, 2013 and February, 2014 were also considered in this report assessment. These samples were analysed for water isotopes and a limited set of major ions (Table 2.3.1). A description of each sample site and the dates of sampling are provided in table 2.1.2.

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Table 2.3.1 Analyses conducted by sample date

Sample date	$^{18}\text{O}/^{16}\text{O}$ & $^2\text{H}/^1\text{H}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{34}\text{S}/^{32}\text{S}$	$^7\text{Li}/^6\text{Li}$	$^{26}\text{Mg}/^{25}\text{Mg}$ & $^{25}\text{Mg}/^{24}\text{Mg}$	Trace metals	Dissolved anions
06.2013	x	x	x	x		x	x
09.2013	x					x	
02.2014	x					x	
03.2015	x	x	x	x	x	x	x
06.2015	x	x	x	x	x	x	x

During each sampling event GPS coordinates were recorded at each sample site and water quality parameters (pH, T, EC, Do and ORP) were collected using a YSI Professional Plus multi-parameter probe. The alkalinity of water samples was also measured on-site by sulphuric acid titration using a HACH® titrator. Table 2.3.2 summarizes all water samples collected. The number of sample bottles collected from each site was dependant on the desired analytes per site. From each site unfiltered, unpreserved water was collected in 50 ml bottles for oxygen ($\delta^{18}\text{O}$) and hydrogen isotope ($\delta^2\text{H}$) analysis and in 500 ml bottles for analysis of major anions. Prior to $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis the samples were filtered (<0.45 μm) in the laboratory. Two 250 to 500 ml bottles of water were filtered using 0.2 μm ultrafiltration and preserved with ultrapure HNO_3 for analysis of all other isotope analytes. In addition, a 100 ml bottle of 0.2 μm ultrafiltered water and 100 ml bottle of unfiltered water were collected and preserved with suprapure HNO_3 for soluble and total trace element analysis. The sample pretreatment was conducted in the laboratory facilities of Kittilä mine on the same day as sample collection to avoid contamination in field conditions. Samples were kept cold and dark and transported immediately to the Labtium and GTK laboratories for analysis.

2.3.2 Analytical methods

Here is given only a short description of the solute separation and isotope analysis. The more detailed information of the techniques can be found in Larkins *et al* (2018).

Chemical analysis of water samples was conducted by Labtium. Dissolved metals and metalloids were analysed by ICP-MS or ICP-OES following ISO standard methods SFS-EN ISO 17294-2 and SFS-EN ISO 11885, respectively. Anions were measured by IC techniques following standard method SFS-EN-ISO 10304. All isotopic analyses were conducted at the GTK Research Laboratory in Espoo, Finland. The methods for isotope analysis for each sampling campaign are presented in Table 2.3.3.

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Table 2.3.2 Summary of unique sample points and analytes

Sample name	description	coordinates		Sample date				
		Northing	Easting	06.13	09.13	02.14	03.15	06.15
Köngäs well	GW	7531406	431574	x			x	x
KUG2	GW	7546685	433746				x	x
KUG15	GW	7549035	431909				x	
MK_Pond	MWDW	7534860	432385	x			x	x
TW3	MWDW	7534680	432051	x			x	x
TW1	MWDW	7534115	431096					x
R150_pond	MWGW				x	x		
R210	MWGW				x	x		
RÄ350	MWGW				x	x		
S225	MWGW				x	x		
250TP2	MWGW				x			
R150	MWGW				x			
S200TP2	MWGW				x			
VT1_115	MWGW				x			
KUP663	MWGW					x	x	
200TP2	MWGW					x		
425Lip	MWGW					x		
PV_Suuri	MWGW					x		
S440	MWGW					x		
VT1_680	MWGW					x		
VT1675	MWGW					x		
TUT 1088	MWGW							x ¹
TUT 863	MWGW							x ¹
RUG15015	MWGW							x
SUG15047	MWGW							x
SUG15049	MWGW							x
LO_Pond	MWOP	7533828	432426	x	x	x		
Rouravaara quarry water	MWOP				x			
TW4 discharge ditch	MWPW	7534821	431490	x			x	x
Process water (Rimmi)	MWPW	7535669	432686	x				x
Process water (Rimmi pond)	MWPW	7535732	432510				x	
Seurujoki pumping station	SWDS	7534624	431209	x	x			x
Lintula	SWDS	7532836	427740	x			x	x
Mesiniemi	SWDS	7529047	428791					x
Rossinmukka	SWDS	7533845	430938					x
Konikoski	SWDS	7532856	430010					x ²
Loukinen DS	SWDS	7523484	427330					x ²
Välikoski	SWDS	7534314	431269					x ²
Talvitiemukka	SWUS	7535925	430678	x				x
Hakokodanmaa	SWUS	7537659	433498				x	x
Nuutiojoki	SWUS	7543687	437364				x	
Seurujoki upstream (3)	SWUS	7540405	438467				x	
Suasjärvi	SWUS	7544340	431538				x	
Kolvakoski	SWUS	7535074	431370					x ²
Vientola	SWUS	7528155	429636					x ²

GW = groundwater, MWDW = mine dewatering water, MWGW = borehole water, MWPW = mine process water, SWDS = Seurujoki surface water downstream of mine discharge, SWUS = Seurujoki surface water upstream of mine discharge, and MWOP = Rouravaara open pit dewatering water

¹ Samples analysed for ¹⁸O/¹⁶O, ²H/¹H, dissolved anions and trace metals only

² Samples analysed for dissolved anions and trace metals only

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Table 2.3.3 Solute separation method/analytical method for isotopic analyses shown for each sample event per analyte.

	⁸⁷ Sr/ ⁸⁶ Sr	⁷ Li/ ⁶ Li	²⁵ Mg/ ²⁴ Mg and ²⁶ Mg/ ²⁴ Mg	³⁴ S/ ³² S -SO ₄ ²⁻	¹⁸ O/ ¹⁶ O and ² H/ ¹ H
Standards	NBS987	LSVEC	DSM-3	VCDT	VSMOW
Error (2σ)	<0.00003 MC-ICPMS 0.002% TIMS	<1.1‰	<1.06	<1‰	<0.1‰ δ ¹⁸ O; <0.5‰ δ ² H
Reproducibility	0.710231 ± 0.0003	±1.2‰	<0.50‰ (δ ²⁶ Mg) <0.25‰ (δ ²⁵ Mg)	±0.68‰	<0.1‰ (δ ¹⁸ O) <0.5‰ (δ ² H)
Ref.	Meynadier et al. 2006	Jeffcoate et al. 2004 and Millot et al. 2004	Meynadier et al. 2006	Krouse and Coplen, 1997	
Sampling					
06.2013	IC/MC-ICPMS	CC/MC-ICPMS	na	CC/MC-ICPMS	CRDS
03.2015	IC/TIMS	CC/MC-ICPMS	IC/MC-ICPMS	CC/MC-ICPMS	CRDS
03.2015	IC/MC-ICPMS	CC/MC-ICPMS	IC/MC-ICPMS	CC/MC-ICPMS	CRDS

CC is conventional column, IC is ion chromatograph, CRDS is cavity ring down spectroscopy, and na is not analysed. Methods described in text.

Deionised Milli-Q water (resistivity of ≥18.2 MΩ•cm) was used for all sample preparation. The Teflon vials used during digestions and column separation were washed with either single or double-distilled (sub-boiling) acids depending on the initial acid purity class. For analyses conducted by MC-ICPMS, samples were dissolved in single-use acid cleaned HDPE (high-density polyethylene) tubes with a known amount of 2% HNO₃ to achieve the desired element concentration for analysis (Larkins *et al* 2018).

Magnesium (Mg) and strontium (Sr) were sequentially separated following the protocol from Meynadier *et al.* (2006) and using an automated Dionex ICS-3000 High Performance Ion Chromatography (HPIC). The isotope fractionation resulting from the collection process was monitored by adding international isotope standards DSM-3 for Mg and SRM987 for Sr in the sample sets. (Larkins *et al* 2018).

Sulphur in sulphate and Lithium (Li) were eluted using classic liquid column chromatography. Column separation of Li was conducted following Seitz *et al.* (2004), which is a modified protocol from Tomasack *et al.* (1999) and Bouman (2004). SO₄ was separated using 100-200 µl of AG50X8 Bio-Rad cationic resin in pipette columns following a modified protocol from Paris *et al.* (2013), omitting the addition of NaCl to increase the signal intensity (Larkins *et al* 2018).

The water isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were analysed using Cavity Ring Down Spectroscopy (CRDS) in which the absolute abundances of isotopologues, i.e. water molecules with different combinations of ^1H , ^2H , ^{16}O and ^{18}O , are measured from a vaporized sample in an optic chamber (Larkins *et al* 2018). Light stable isotopes are reported using delta (δ) notation as per mil (‰) values relative to Vienna Standard Mean Ocean Water (VSMOW) international standard, according to following equation 2.

$$2) \delta_{(\text{‰})} = \left(\frac{R_x - R_{std}}{R_{std}} \right) * 1000$$

Where R is the ratio of heavy to light isotope in the sample (x), and known standard (std).

Isotopic analyses of $\delta^7\text{Li}$, $\delta^{26}\text{Mg}$, $\delta^{25}\text{Mg}$, $\delta^{34}\text{SSO}_4$, and $^{87}\text{Sr}/^{86}\text{Sr}$ were conducted using a 50 μl PFA MicroFlowTM nebulizer to Nu InstrumentsTM Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) and analysed at low mass resolution ($\Delta m/m = 400$) for Mg, Sr and Li, and at high mass resolution ($\Delta m/m = 3000$) for S. The analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ from the March 2015 sample set were conducted using thermal ion mass spectrometry (TIMS). For isotopic analysis of Mg, Sr, S and Li by MC-ICPMS the purified solutes were diluted depending on the concentrations down to 500ppb, 50 to 500ppb, 10-20ppm, and 10-20ppb, respectively. (Larkins *et al* 2018). For TIMS analyses, purified Sr fractions were loaded onto a Ta filament with one drop of 0.75 N H_3PO_4 in the centre position and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured dynamically (masses 84, 85, 86, 87, 88). Samples were normalized using the $^{86}\text{Sr}/^{88}\text{Sr}$ (0.1194) ratio of SRM 987, which was run as a continuous quality control. The total procedural blank was $\leq 1\text{ng}$ of Sr. For S analysis an acid blank was measured between every sample to correct for possible changes in the background due to cross contamination from the previous sample. The total procedural blank (chemistry plus instrumental) is typically below 10 ppb S. All isotope analytes, with the exception of Sr, were reported using δ notation relative to their respective standards, described in table 2.3.3

2.4 Results and discussion

In the following section geochemical and isotopic data from the Kittilä site are used to characterize different site waters. Interactions between the different water types are evaluated through a qualitative analysis of the combined data set, and where possible, quantitative mixing models are applied to strengthen interpretations.

2.4.1 Geochemical characterization

Sampled waters at the site exhibit different chemical characteristics, depending on their source as well as season. Ion compositions from each water source are listed in appendices in tables A1 to A7. A systematic positive charge balance error ranging from 10 to 24% was identified in all river water samples collected in June 2015, and 1 of 5 river water samples from March of 2015. This error is attributed to a time delay between sample collection and alkalinity titration in the field which allowed carbonate precipitation in un-acidified sample aliquots that did not occur in the acidified samples used for metals analysis (e.g. Fritz 1994). However, when comparing the

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samples with charge imbalance to balanced river water samples they still generally resemble the major ion composition of balanced waters and are distinct from mine waters (Figure 2.4.1). Because trace metals and major cations were measured from acidified sample aliquots, carbonate precipitation is not anticipated to have otherwise impacted analytical results.

A tri-linear diagram comparison of major ion compositions shows distinct compositional differences between water sources (Figure 2.4.1). The process water is a Mg- SO₄ type water. Although dewatering water is a Ca- SO₄ water, the majority of underground mine waters from boreholes are enriched with sodium (Na) and chloride (Cl). Upgradient groundwater and river water is dominated by Ca and bicarbonate (HCO₃), but as expected, river water down stream of mine discharge exhibits a major ion composition between that of mine water and upstream river water.

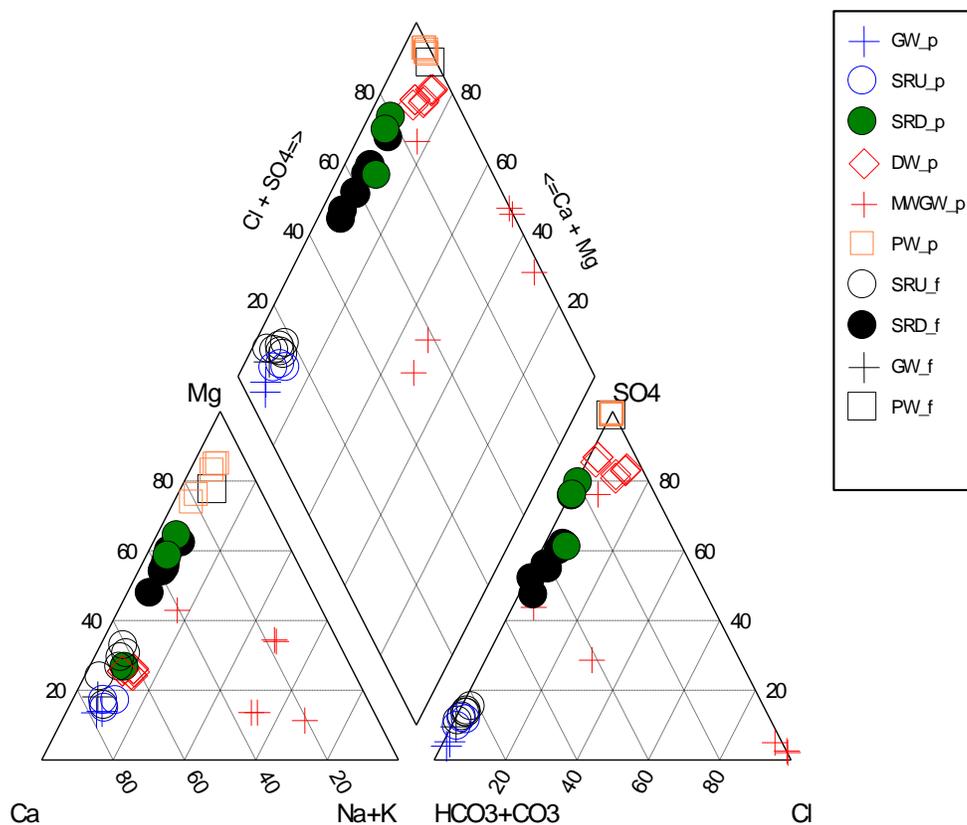


Figure 2.4.1 Piper diagram showing major ion composition from different site water sources. Symbols in black (ending in _f, for fail) show samples with charge imbalance > 10%, while samples in color (ending in _p, for pass) exhibited charge balance within 10%. GW- background groundwater, SRU- Seurujoki upstream, SRD- Seurujoki downstream, DW- dewatering water, PW- process water. (Larkins et al. 2018).

Surface waters upstream of mine discharge have low metal and ion concentrations, with an average electrical conductivity of 87 $\mu\text{S}/\text{cm}$ (Figures 2.4.2 and 2.4.3). Groundwater samples

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collected from outside the mining area are compositionally similar to surface waters, but exhibit relatively elevated specific conductivity values, on average 140 $\mu\text{S}/\text{cm}$, due to natural emissions from local soil and bedrock. These groundwater sources, together with upstream surface water sources, will be referred to as background water, as they are believed to reflect natural weathering of the surrounding lithologies.

Mine dewatering and process waters have elevated solute concentrations, with average electrical conductivity values of 1871 and 9791 $\mu\text{S}/\text{cm}$, respectively. As illustrated for the June 2015 sample event, in addition to elevated SO_4 and Ca, these waters exhibit notable concentrations of Sr, Mn, Sb, and Ni. High proportions of Sr, Sb and Ni in trace element composition are characteristic of mine dewatering water, high proportions of Mn and As are characteristic of mine process water. Process water has the highest SO_4 concentrations of all water sources. The elevated solute concentrations in mine dewatering waters likely reflect mining induced mineral weathering (e.g. pyrite, arsenopyrite, stibnite), explosives residue, and deep saline groundwaters. The unique composition of process water likely reflects process chemical residues (K- and Na-xanthates, cupric sulphate and sodium sulphide) in addition to accelerated mineral weathering.

Process water discharge through wetland TW4 increases the anion, metal and metalloid concentrations in the River Seurujoki, as evident at the Pumping station in Figures 2.4.2 and 2.4.3. Contaminant concentrations decrease within 300 m of the TW4 discharge point, which was interpreted in previous studies to indicate rapid mixing of process water with river water (Hämäläinen 2015a and 2015b). At the Välikoski sampling point, about 600 m downstream from the TW4 discharge ditch, ion concentrations of SO_4 , Mg, Ca, Na, K and NO_3 remain elevated relative to background levels, while the other measured ions were near background levels. A gradual rise in EC and solute concentration after the TW1 discharge point suggest slower homogenization of mine process water with river water. This was attributed to more diffuse discharge of dewatering water, as well as more laminar river flow in the river reach where dewatering effluent enters (Hämäläinen 2015a and 2015b). The concentrations of most elements remain elevated in the Seurujoki River from 7 to 12 km downstream of mine water discharge, as evident in a comparison of samples collected from Lintula and Mesiniemi to background levels. The largest relative increases in solute concentration were observed in SO_4 , Mg, Na, Mn, Sr, Se, B, As, and Sb. Small increases were also evident in Ca, Co, NO_3 , and Li.

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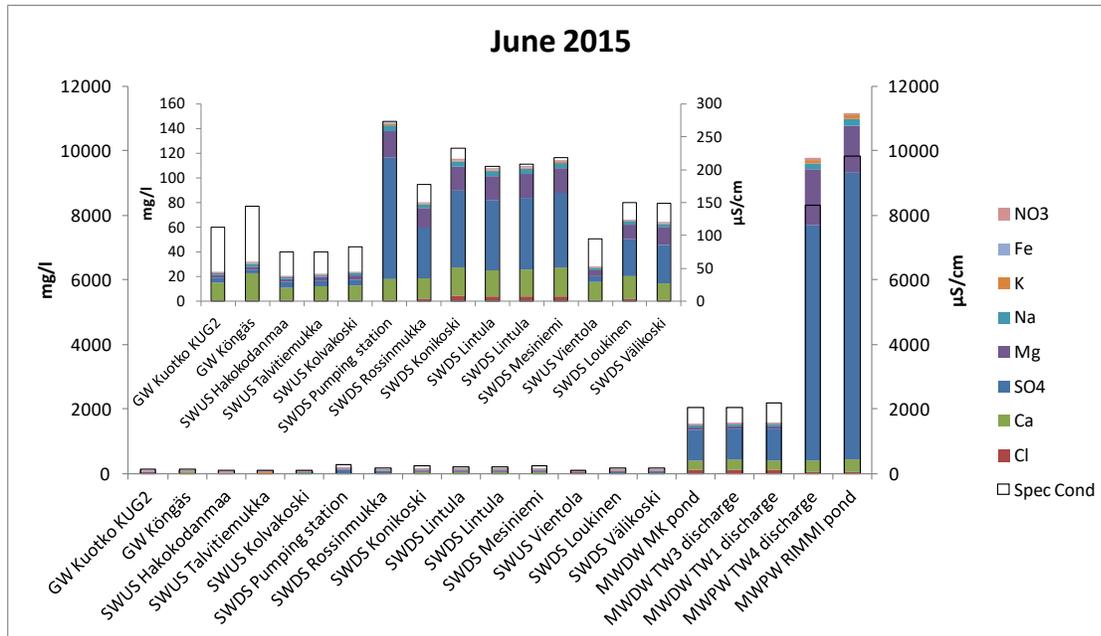


Figure 2.4.2 Major element concentrations (mg/L) and conductivity in Kittilä waters. *MWDW = mine dewatering water, MWPW = mine process water, SWDS = Seurujoki surface water downstream of mine discharge, SWUS = Seurujoki surface water upstream of mine discharge.

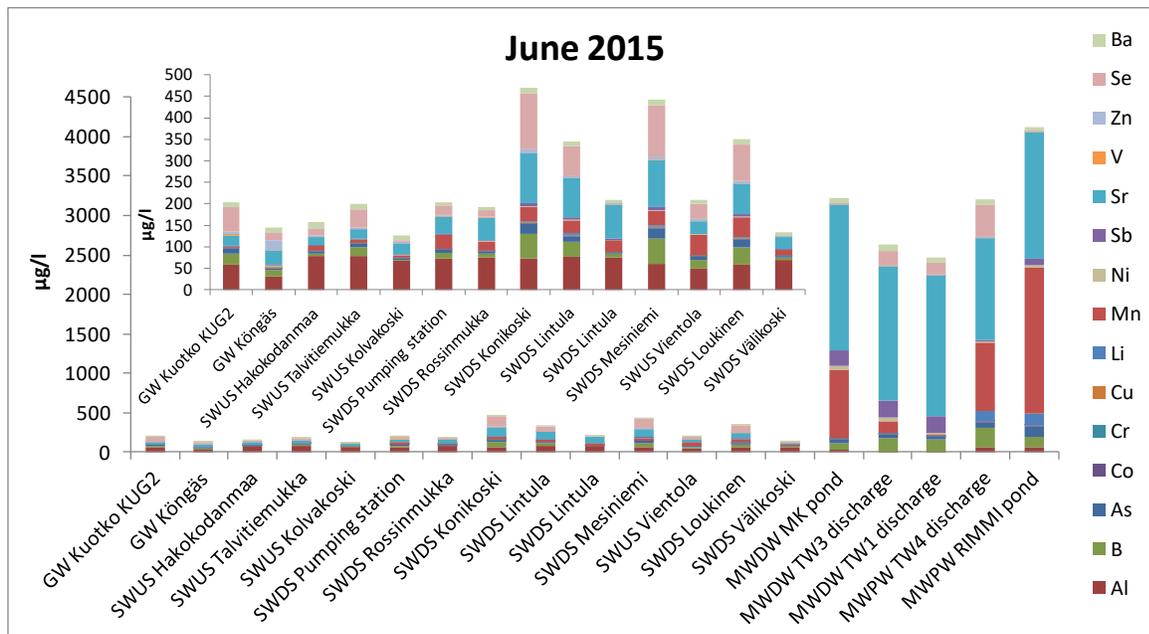


Figure 2.4.3 Trace metal and metalloid concentrations ($\mu\text{g/L}$) Kittilä waters. *MWDW = mine dewatering water, MWPW = mine process water, SWDS = Seurujoki surface water downstream of mine discharge, SWUS = Seurujoki surface water upstream of mine discharge

Mine borehole waters collected from fracture systems connected to the underground mine exhibit relatively elevated Na, Cl, earth alkali and alkali metals, while other major ion concentrations were

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intermediate between mine dewatering and background waters (Figure 2.4.4 and Tables A1 to A3 in Appendices). The chemistry of underground mine borehole samples taken from 863 m and 1088 m below ground surface differs considerably from samples from upper levels in the underground mine, with characteristically high concentrations of Na and Cl. The shallower mine borehole waters contained higher proportions of SO₄, NO₃, As and Sb. The sample from 663 m bgs is compositionally in between the deepest and shallowest borehole samples, suggesting mixing of different water sources.

Electrical conductivity of the waters correlated well with SO₄ concentration as well as with earth alkali and alkali metals associated with process chemicals (Figure 2.4.5) and mineral weathering (either naturally occurring or due to mining processes such as extraction, quarrying, and mineral processing). In addition, two distinct trends can be seen in Cl concentration and EC in river water downstream of mine effluent. Downstream river waters from 2013, and those 2015 samples that were downstream of process water, but upstream of dewatering water (Välikoski and the pumping station), exhibit a Cl composition that reflects mixing between process water and upstream river water. River water samples from downstream of dewatering discharge collected in 2015 reflect mixing between the elevated Cl dewatering water and upstream surface waters, illustrating the influence increased Cl concentration in mine dewatering water has had on downstream river water.

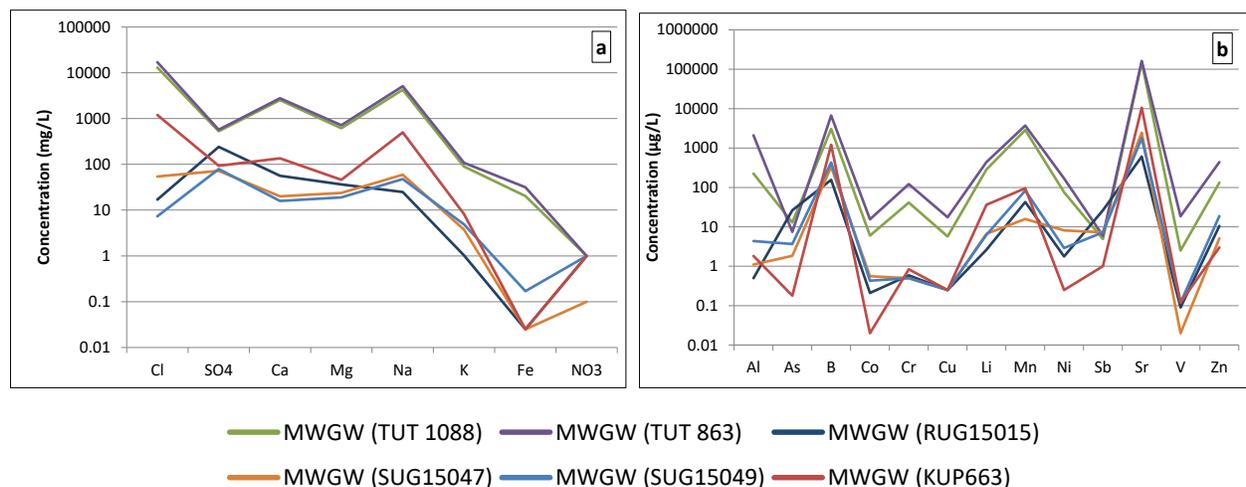


Figure 2.4.4 Major ion and trace element composition of mine borehole samples

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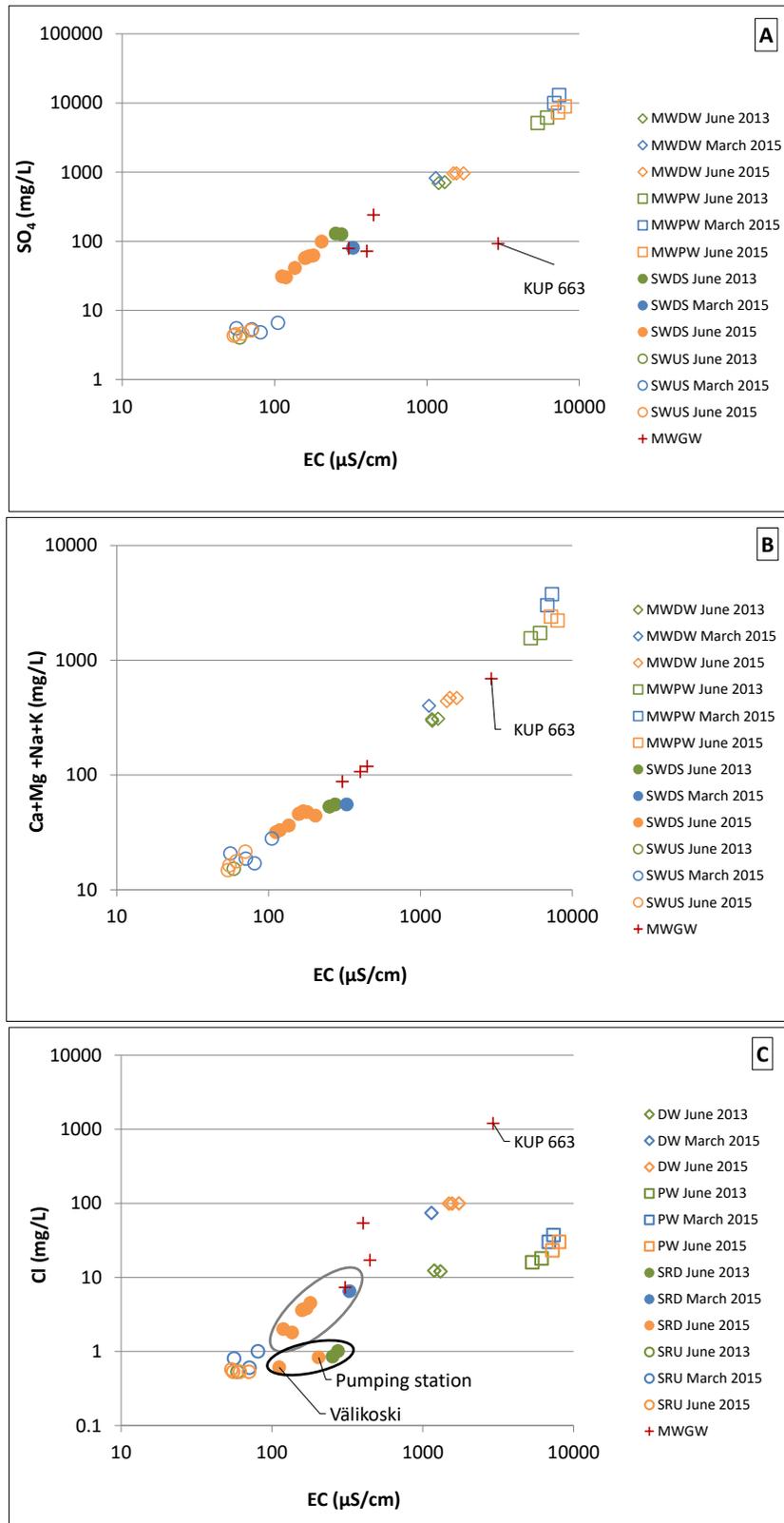


Figure 2.4.5 Correlation between solute concentration and electrical conductivity (EC). a) sulphate (SO₄) concentration, b) concentration sum of calcium, magnesium, sodium and potassium, and c) chloride (Cl) concentration.

2.4.2 Oxygen and hydrogen isotopes

The results for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for Kittilä waters are plotted relative to the local meteoric water line (LMWL, Kortelainen 2002) in Figure 2.4.6. It illustrates three distinct groups of water. The first group includes all surface water samples, mine water dewatering samples, groundwater samples, and as well as most mine borehole (MWGW) samples. These plot on, or slightly to the right of the local meteoric water line. The second group is composed of Kittilä mine process water plus the borehole sample TUT 1088. These samples are significantly enriched relative to the local meteoric water line and exhibit negative d-excess values. A third distinct isotopic composition was observed in the sample collected from mine borehole water, TUT 863, which exhibits a large d-excess value, and plots well above the meteoric water line.

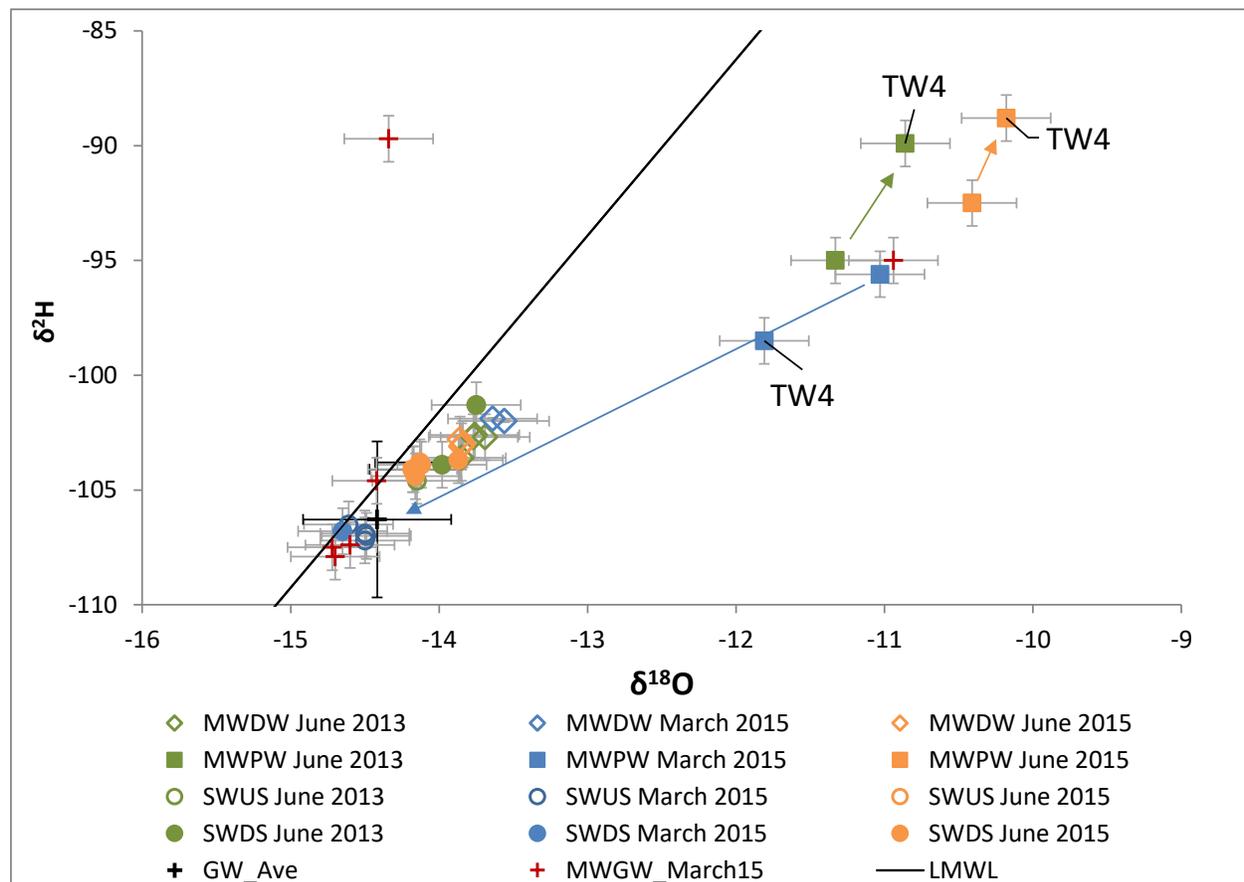


Figure 2.4.6 Correlation in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ across Kittilä sample sites. *LMWL = Local (Finland's) meteoric water line (Kortelainen & Karhu 2004).

The distinct $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature of process water likely reflects fractionation that occurs during the mineral beneficiation process, related to, for example, froth flotation or accelerated water-rock interactions. Mine dewatering water is also enriched, though to a lesser degree, in ^{18}O and ^2H relative to surface waters collected in March, mine borehole waters, and average groundwater. The distinctly enriched ^{18}O and ^2H of mine water suggests water isotopes may provide a tracer of mixing between mine waters and isotopically lighter surface waters. Surface waters, both

upstream and downstream of mine discharge, however, generally exhibit similar water isotope compositions during a given sample event, indicating that mine water mixing with surface water cannot be resolved from water isotopes.

Seasonal variation in surface and mine waters, however, provide clues to water source and physical processes affecting different water types. Surface water is depleted in ^{18}O and ^2H in March relative to June. Surface water is typically depleted by isotopically light snow or snow-melt run-off in the late winter and early spring, and enriched by evaporation in the summer. Similar seasonal variation is also evident in process water from settling pond discharge to TW4 discharge, indicating that treatment wetland 4 water undergoes notable summer evaporation, and is diluted by an isotopically light water source in March (fig 2.4.7). If the source of light water, assumably snowmelt or precipitation, is similar to contemporaneous surface water, two-part mixing between surface water at Talvitiemukka and process water from settling pond discharge can be applied to estimate water source contributions (Equation 3). Oxygen and hydrogen isotope based mixing calculations suggest from 22.5 to 25% contribution of precipitation-like water to treatment wetland 4 in March 2015, respectively.

$$3) f_{\text{SWUS}} = (\delta_{\text{TW4}} - \delta_{\text{MWPW pond}}) / (\delta_{\text{SWUS}} - \delta_{\text{MWPW pond}})$$

,where δ is the isotopic composition ($\delta^{18}\text{O}$ or $\delta^2\text{H}$) of the sample source and f is the fraction of water contributed by the sample source, indicated in the subscript.

In contrast to surface and process waters, no seasonal variation in water isotopic composition is evident across TW3 or TW1, suggesting these waters are not substantially influenced by evaporation or precipitation inputs. Further, dewatering waters were consistently enriched relative to background groundwaters, indicating influence from a temporally consistent source enriched relative to modern meteoric waters at the site.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of mine borehole samples was highly heterogeneous, with the deepest borehole waters being highly enriched in ^2H . The sample from TUT863 has a uniquely high deuterium excess value, in addition to high Cl concentration, similar to formation waters observed elsewhere in Finnish crystalline bedrock (Kietäväinen et al 2013). The deepest borehole sample, TUT1088, shares a similarly enriched ^2H , but exhibits a negative d-excess similar to process water (Figure 2.4.6). Based on this sample's high Cl and Na content, it is also likely formation water that is not in direct hydrologic connection with modern meteoric waters. Influence from such ^2H enriched waters may explain the enrichment of dewatering water relative to local groundwater. Shallower borehole samples (RUG 15015 from 390 m below Rouravaara open pit, SUG15047 and SUG15049 from 625m below the Suurikuusiko open pit), resemble the relatively depleted ^{18}O and ^2H of contemporaneously collected surface water. This similarity may be coincidental, and simply reflect large heterogeneity in the water isotope composition of borehole waters, or alternatively, may indicate rapid hydrologic connection between surface water and bedrock fracture systems that persists during winter months. Such hydrologic connection may result from intersection of a fracture system with the river bed, and has implications for the potential impacts of ongoing mine dewatering on river discharge. KUP663, collected from 663 m bgs in the vicinity of wetland 4, plots on the LMWL, and is enriched in ^{18}O and ^2H relative to March surface water.

The chemical composition of this sample is similar to TUT863, though at much diluted solute concentrations (Figure 2.4.5). The water isotope composition of KUP663 is between surface water, meteoric groundwater, and high d-excess water similar to TUT863, supporting the interpretation that the KUP663 sample reflects mixing between formation water and shallower mine waters diluted by captured river water.

With further end member characterization, water isotopes show promise as a means of quantifying water source and mixing within the underground mine, including potentially elucidating capture of river water to the subsurface, and subsequently mine dewatering water. Water isotopes also generally support geochemical interpretations suggesting that the exhumation of high saline formation water contributes to mine dewatering water.

2.4.3 Strontium isotopes

The $^{87}\text{Sr}/^{86}\text{Sr}$ composition of site waters appears to relate to variation in bedrock lithology across the study site. The highest $^{87}\text{Sr}/^{86}\text{Sr}$ was in surface water up gradient of mine water discharge and generally decreases in the downstream direction from Tuonkasomma to Talvitiemukka. The Seurujoki River drainage area upstream from Tuonkasomma is comprised of granodiorite bedrock, while the downstream and mine area bedrock is dominated by mafic lithologies (Figure 2.1.1). The granodiorite bedrock likely contributes higher $^{87}\text{Sr}/^{86}\text{Sr}$ to solution due to a greater proportion of K (and subsequently Rb) bearing minerals than the surrounding mafic lithologies. Accordingly, the decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ in the downstream direction reflects increasing river water contribution from mafic tuff and basalt lithologies.

The $^{87}\text{Sr}/^{86}\text{Sr}$ from the Lake Suasjärvi sample is much lower in contrast to other SWUS samples. Lake Suasjärvi is surrounded by mafic volcanic rocks and removed from granodiorite influenced drainage (Table A2 in Appendices). The background groundwater wells KUG2 and KUG15 are located in similar mafic volcanic rocks north of the mine, and exhibited $^{87}\text{Sr}/^{86}\text{Sr}$ compositions similar to those observed in Lake Suasjärvi (Table A1 in Appendices).

The underground mine dewatering water, open pit dewatering water, and background groundwater from Köngäs well exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ compositions between those of Surface water and Suasjärvi. These samples provide insight to $^{87}\text{Sr}/^{86}\text{Sr}$ compositions characteristic of mine area lithologies across a range of solute concentrations. While Sr concentrations in underground mine dewatering water were much higher than those in Köngäs well background groundwater, the $^{87}\text{Sr}/^{86}\text{Sr}$ of dewatering water was consistently within the range observed in Köngäs samples, suggesting a $^{87}\text{Sr}/^{86}\text{Sr}$ composition characteristic of the mine lithology, despite differences in solute concentration (Table A1 and A4 in Appendices). Mine process waters exhibited slightly lower $^{87}\text{Sr}/^{86}\text{Sr}$ than in Köngäs well and Sr concentrations similar to those in underground dewatering water. The slightly lower $^{87}\text{Sr}/^{86}\text{Sr}$ of mine process water likely reflects influence from Ca bearing water treatment chemicals (Table 2.2.2). Samples collected from mine boreholes (MWGW samples) exhibited some of the highest Sr concentrations, and have $^{87}\text{Sr}/^{86}\text{Sr}$ compositions similar to or slightly higher than Köngäs background groundwater. The $^{87}\text{Sr}/^{86}\text{Sr}$ higher than Köngäs waters (SUG15047 and SUG15049) likely reflect mineralogical heterogeneity

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across discrete water sources influent to the mine. Alternatively, the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions in these samples could result from the mixing of surface water with water that has a high Sr concentration and an $^{87}\text{Sr}/^{86}\text{Sr}$ similar to that of underground mine dewatering waters.

Surface water samples downstream of mine discharge exhibited Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ in between those of mine waters and Seurujoki River water up stream of mine discharge, suggesting that Sr provides a conservative tracer of mine water discharge to surface water (Figure 2.4.7).

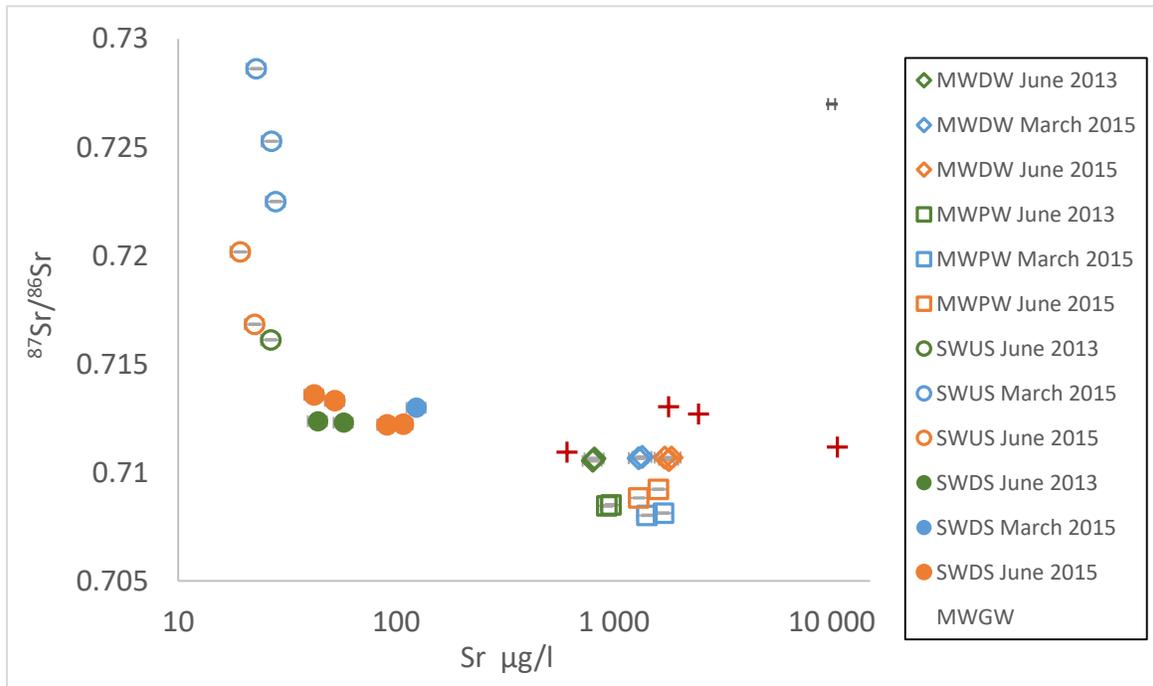


Figure 2.4.7 $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentrations for Kittilä mine area samples. Gray Y error bars show 2σ internal analytical repeatability, and X error bars show largest observed % error between laboratory duplicates per sample run. Black Y error bars positioned in the corner of figure show the average 2σ of external standard run repeatability, and X error bars show average % error observed between laboratory duplicates across all sample runs.

Sr concentration and isotope composition was applied as a solute tracer for mine water discharge to surface water. However, because the $^{87}\text{Sr}/^{86}\text{Sr}$ of both process water and dewatering water was lower than that of river water, relative mine water contribution to surface water cannot be resolved from a single downstream sample location. Subsequently, a sequential mixing approach was utilized to resolve process water from dewatering water contributions to the river. Because process water is discharged to the river from a point source upstream of dewatering discharge, and because samples were collected from reaches of the Seurujoki subject to only process water discharge (i.e. the pumping station site), as well as reaches subject to both process water and dewatering water discharge (i.e. Rossimukka, Lintula, and Mesiniemi sites), influent mine water could be calculated sequentially, according to equation 4. However, pumping station samples

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were only collected in June 2013 and June 2015, such that mine waters could not be allocated from sequential mixing calculations for the March 2015 sample event. Additionally, the sequential mixing approach also allowed for mixing estimates to be made independently based on Cl concentrations, following equation 5, to provide a point of comparison for Sr based estimates.

$$4) f_a = [\delta_c - \delta_b(B/C)] / [\delta_a(A/C) - \delta_c(B/C)]$$

Where f_a is the fraction of end member a present in water c resultant of conservative mixing between a and b, and where δ_n is the $^{87}\text{Sr}/^{86}\text{Sr}$ and where A, B, and C are the Sr concentrations in the respective samples.

$$5) f_1 = (C_3 - C_2) \div (C_1 - C_2)$$

Where C is concentration, f is the fraction contributed by a given end member, 1 and 2 are end member waters (e.g. mine water and upstream river water), and 3 is the mixed water (e.g. downstream river water).

For the mixing calculations and the process water contributions it was anticipated that river water collected from the Pumping Station site is a two-part mixture of process water from treatment wetland 4 discharge and upstream river water collected from the Talvitiemukka site. Secondly for the dewatering contribution it was anticipated that river water from the Lintula site is a two-part mixture of water from the pumping station and dewatering water treatment wetland discharge. A sample from treatment wetland 3 discharge was used as the dewatering water end member in June 2013, and from treatment wetland 1 in June 2015. Additionally, in June 2015 the second step of mixing was also calculated independently using sample results from Rossimukka and Mesiniemi sample sites to evaluate what influence the distance between end members has on subsequent estimates of mine water inputs. The contribution of mine water estimated from each analyte and for both mixing steps is compared to monthly monitoring data in Table 2.4.1. The estimated mine water contribution to total Seurujoki River discharge based on sequential mixing of Sr and Cl were slightly greater than monthly average monitoring results in 2013 and slightly lower than monthly monitoring results in 2015. However, the source estimates of these two tracers were derived independently and the estimations aligned well with each other at each stage of mixing and during both sample events. The consistency of the results suggest they exhibit similar reactivity in site waters at the scale of this study and the Cl concentration and Sr isotope composition are interpreted to provide the most accurate available approximation of mine water contributions to river water specific to the time of sampling. (Larkins et al 2018).

Process water is discharged to the river via a single culvert and based on electro conductivity studies conducted by Hämäläinen (2015b), process and river water homogenize within 0.3 km of the point source discharge. Mine dewatering water, on the other hand, drains to the river from multiple points, entering the river where river flow is naturally lower and resulting in a slower homogenization rate, with homogenization being reached up at lengths up to 9 km downstream of the discharge area (Hamalainen 2015b). Therefore the low mine water contribution estimated from tracers at Rossinmukka likely reflects a lack of homogenization between dewatering and river water. Further, as illustrated in Figure 1.2.1, additional dewatering effluent may enter the

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river downstream of the Rossinmukka sample point. The increasing estimate of dewatering contribution to river water in the downstream direction is interpreted to be due in part to homogenization, but may also be a relic of weathering and naturally increasing solute concentrations in the downstream direction. This highlights the importance of sample sight selection in tracer studies, where the ideal downstream sample location will reflect well homogenized end members, while minimizing the potential for dilution of additional solute influx. Based on the results of the electro conductivity studies by Hamalainen (2015b), samples from the Lintula site are expected to provide the most representative downstream end member.

Table 2.4.1 Mine water contribution to total Seurujoki River discharge based on sequential mixing of Sr and Cl

	June 2013			June 2015				
analyte	PW at Pumping station	DW at Lintula	Total mine water input	PW at Pumping station	DW at Rossimukka	DW at Lintula	DW at Mesiniemi	Total mine water input ²
Cl conc. ¹	2.1 %	1.4 %	3.5 %	1.3 %	0.98 %	2.8 %	3.4 %	4.1 %
⁸⁷ Sr/ ⁸⁶ Sr	1.9 %	1.8 %	3.7 %	1.5 %	0.59 %	2.8 %	3.8 %	4.1 %
^{δ7} Li	2.6 %	-32%	<0%	1.6 %	-8.3 %	NA	15 %	NA
mean monthly discharge	0.58 %	1.53 %	2.1%	1.49 % ¹		3.35% ¹		4.84 % ¹
	June 2013			June 2015				
analyte	PW at Pumping station	DW at Lintula	Total mine water input	PW at Pumping station	DW at Rossimukka	DW at Lintula	DW at Mesiniemi	Total mine water input ²
Cl conc. ¹	2.1 %	1.4 %	3.5 %	1.3 %	0.98 %	2.8 %	3.4 %	4.1 %
⁸⁷ Sr/ ⁸⁶ Sr	1.9 %	1.8 %	3.7 %	1.5 %	0.59 %	2.8 %	3.8 %	4.1 %
mean monthly discharge	0.58 %	1.53 %	2.1%	1.49 % ¹		3.35% ¹		4.84 % ¹

¹Monthly mean discharge values based on June 2014 monitoring results, as June 2015 results were not available at the time of writing.

²June 2015 total mine input calculated using DW at Lintula.

The unique Sr composition of Seurujoki river water may also provide insight to surface water infiltration to groundwater, as reflected in mine dewatering. Hämäläinen (2015b) observed a decrease in Seurujoki discharge in the reach adjacent to mine workings, indicating that mine dewatering may impact local and regional hydrology. The ⁸⁷Sr/⁸⁶Sr composition of mine borehole water samples collected in March 2015 was in between those of surface water and mine dewatering water, as may be expected to result from the mixing of surface water with groundwater in discrete fracture systems surrounding the mine. However, if the water observed in mine boreholes results from groundwater mixing with river water, an undiluted groundwater end member with solute concentrations higher than those observed in the borehole samples must

contribute to mixing. While such an end member has yet to be characterized, this kind of end member may be available on site for characterization. For example, water from TUT_864, which appeared to not be in hydrologic connection with meteoric water, exhibited a Sr concentration of 16,200 µg/l, but was not analysed for $^{87}\text{Sr}/^{86}\text{Sr}$. Targeted sampling of borehole sites such as TUT_864, believed to be representative of a high solute groundwater end member will provide insight to lithology induced $^{87}\text{Sr}/^{86}\text{Sr}$ in deep groundwater. If $^{87}\text{Sr}/^{86}\text{Sr}$ in deep groundwater is distinct from meteoric water sources, Sr can be applied as a tracer to determine surface water-groundwater mixing pathway, and supplement water isotope data for estimating rate and volume of surface water capture into the underground mine.

2.4.4 Lithium isotopes

The $\delta^7\text{Li}$ observed across Kittilä site water types varied by approximately 30‰, and showed distinct variation dependant on the sample water type (Table A1 to A7 in Appendices and Figure 2.4.8). Mine waters generally exhibited elevated Li concentrations, process waters being the most concentrated. Mine borehole water exhibited $\delta^7\text{Li}$ compositions and Li concentration similar to dewatering water. The $\delta^7\text{Li}$ of surface water in upstream was distinct from both mine water sources during both June sampling events, but was similar to dewatering water in March 2015. In June 2013 surface water downstream had $\delta^7\text{Li}$ similar to process water, while in March 2015 it was similar to dewatering water. The distinct isotopic composition of downstream surface water in June 2015 allowed for evaluation of Li as a source tracer following the sequential method applied for Sr.

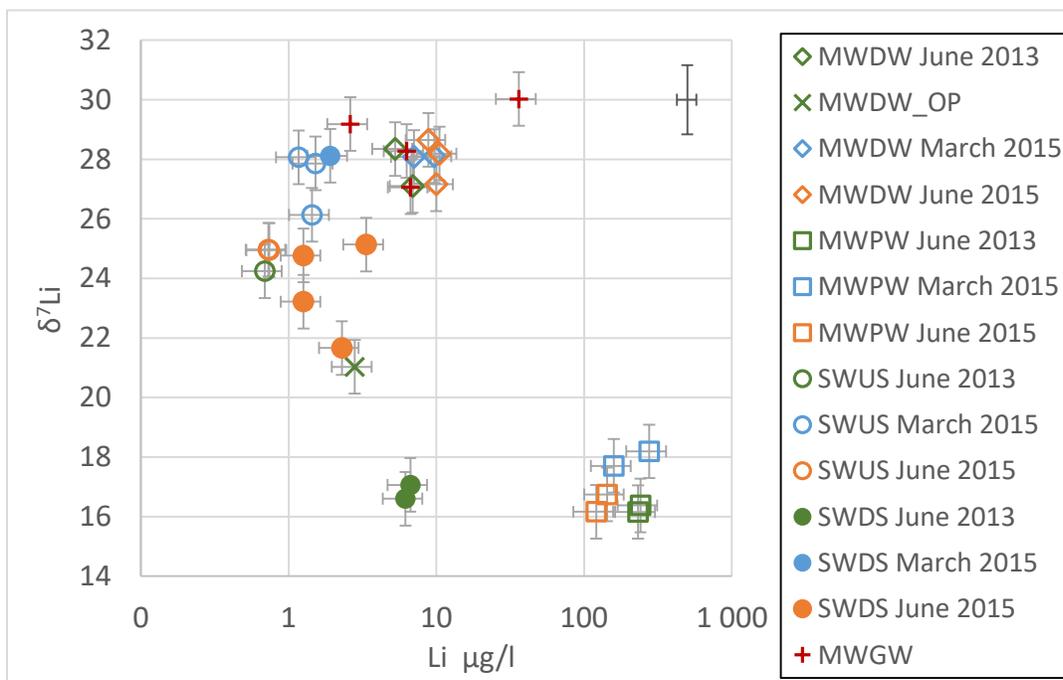


Figure 2.4.8 $\delta^7\text{Li}$ and Li concentration for Kittilä site waters. Gray Y error bars show 2 σ internal analytical repeatability, and X error bars show largest observed % error between laboratory duplicates per sample run. Black

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Y error bars positioned in the corner of figure show the average 2σ of external standard run repeatability, and X error bars show average % error observed between laboratory duplicates across all sample runs.

Table 2.4.2 Mine water contribution to total Seurujoki River discharge based on sequential mixing of Li

	June 2015				
	PW at Pumping station	DW at Rossimukka	DW at Lintula	DW at Mesiniemi	Total mine water input ²
$\delta^7\text{Li}$	1.6 %	-8.3 %	NA	15 %	NA
mean monthly discharge	1.49 % ¹		3.35% ¹		4.84 % ¹

The apparent negative contribution of dewatering water estimated from $\delta^7\text{Li}$ at Lintula in June 2013 reflects the non-conservative behavior of Li in solution downstream of mine water inputs. Non-conservative behavior of Li in solution at the scale of this study is also supported by the general deviation in Li based estimates from those of the Sr and Cl tracers, as well as mean monthly monitoring data. The apparent non-conservative fractionation of Li can, however, be further characterized with the help of dilution factors determined from Cl and Sr based mixing results, with the goal of providing insight to processes influencing solute source and attenuation.

Influences on $\delta^7\text{Li}$ in solution include silicate weathering processes, mineralisation, and cation exchange reactions (e.g. Hogan & Blum 2003, Millot et al. 2010, Dellinger et al. 2014, Wang et al. 2015). The process related fractionation of Li isotopes results, in general, from the preferential loss of ^6Li from solution (namely to cation exchange reactions and incorporation into secondary minerals) (e.g. Zhang et al. 1998, Anghel et al. 2002, Pistener & Henderson 2003, Kisakurek et al. 2004). Characterization of process related fractionation in field studies has provided insight into watershed scale weathering mechanisms (e.g. Millot et al. 2010, Pogge von Strandmann et al. 2006, Lemarchand et al. 2010). Additionally, where Li source plays a major role in the $\delta^7\text{Li}$ of the dissolved load, Li isotopes may serve as a solute source tracer (Hogan & Blum 2003, Negrel et al. 2010, Wang et al. 2015).

$\delta^7\text{Li}$ in downstream river water appears to reflect a combination of solute source (e.g. mine waters) and processes that have influenced fractionation. The apparent non-conservative fractionation of Li can be further characterized with the help of dilution factors determined from Cl and Sr based mixing results. The average of Cl and Sr based estimates for process water and dewatering water contributions to the river in June 2013 were 2.0% and 1.6%, and in June 2015 1.4 and 2.8%, respectively. The projected estimates of Li concentration and isotopic composition expected from conservative mixing were calculated according to equations 5 and 4. Projected Li compositions are plotted with respect to end member waters and the observed Li compositions of mixed waters (Figure 2.4.9).

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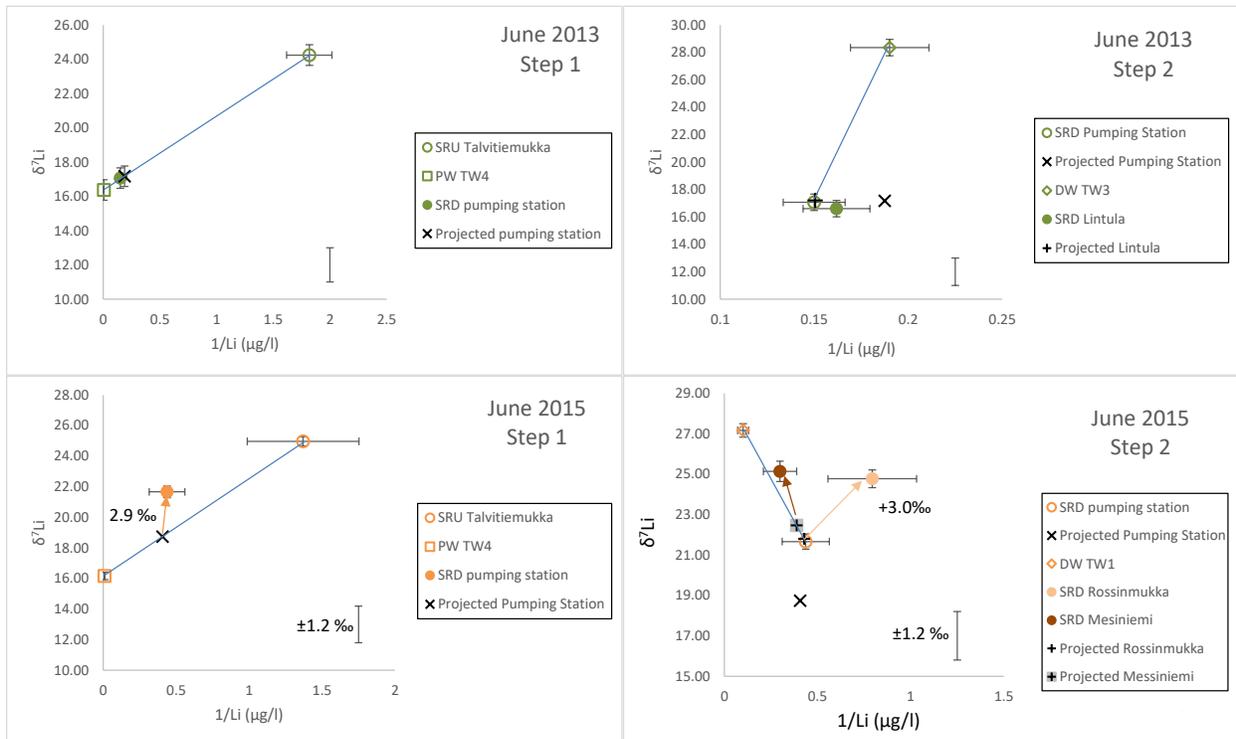


Figure 2.4.9 Isotopic compositions of Li are plotted against the inverse of concentration for each sample step and sample event. Blue lines depict conservative mixing between proposed end members. Projected compositions shown in black. X error bars on sample points are percent analytical error based on duplicate analyses, while Y error bars are 2 σ internal repeatability. Because the error of external standard repeatability are larger than sample repeatability, Y error bars illustrating 2 σ of standard repeatability are shown with no symbol.

In June of 2013 Li reflected conservative projected values at both stages of mixing, when consideration is given to analytical precision, whereas in June of 2015, there were resolvable differences in observed and projected $\delta^7\text{Li}$. In 2015 pumping station water and downstream river water were enriched in $\delta^7\text{Li}$ by 2.9‰ and 3‰ relative to that projected based on conservative mixing (Figure 2.4.9). During 2015 sample analysis, Li concentration varied by 28% between laboratory duplicates, which was used to define the x axis error bars in Figure 2.4.9. Therefore, no difference in Li concentration could be resolved between projected to observed values in either step of mixing. Despite no evidence for changes in Li concentration, the occurrence of ^7Li enrichment in downstream river water relative to conservative projections suggests either an unconstrained source of Li to solution, or process induced Li fractionation. Further, enrichment in 2015 samples not observed in 2013 samples suggests a temporal change in Li sources and/or mobility in river water not otherwise evident from concentration alone.

The lack of discernable deviation between projected and observed Li concentrations in downstream waters suggest the isotopic disparity does not result from contribution from an unidentified Li source. Li fractionation may, however, be related to solute mobility. The ^7Li enrichment in river water could occur through an increasing proportion of Li in downstream river water being derived from preferential leaching of ^7Li during surficial chemical weathering, or re-dissolution of secondary Li bearing precipitates within the river. Therefore the non-conservative

behavior of Li within river water provides evidence for the accumulation of unstable precipitates or secondary minerals within the river, which in turn, have implications for estimates of contaminant loading and transport in solution.

2.4.5 Sulphur isotopes

While SO_4 concentrations were characteristic of different water sources, the $\delta^{34}\text{S}_{\text{SO}_4}$ was less distinct between different sources. Mine process water was slightly enriched in ^{34}S relative to dewatering water. However, there was much overlap in the $\delta^{34}\text{S}_{\text{SO}_4}$ of process water with river water, both upstream and downstream of mine discharge (Figure 2.4.10). Therefore, $\delta^{34}\text{S}_{\text{SO}_4}$ could not be used as a source tracer of mine waters to the river.

Mine borehole waters showed spatially dependent $\delta^{34}\text{S}_{\text{SO}_4}$ values suggesting SO_4 isotopes may provide a useful tracer of mineral SO_4 source in the underground mine. At 625 m bgs, SUG15047 and SUG15049, exhibited the most negative $\delta^{34}\text{S}_{\text{SO}_4}$ values. At RUG15015 (390 m bgs) and KUP663 (663 m bgs), $\delta^{34}\text{S}_{\text{SO}_4}$ was similar to contemporaneously collected surface waters. With further isotopic characterization of potential mineral SO_4 sources at the site, S isotopes show potential to provide a unique fingerprint of SO_4 source in underground mine waters. For example, the small temporal enrichment of ^{34}S that occurs in mine process water from June 2013 to June 2015 may indicate an increasing SO_4 contribution from the mineral source reflected RUG15015 and KUP663 relative to that of KUP663.

The $\delta^{34}\text{S}_{\text{SO}_4}$ of solution is influenced by process related fractionation in addition to SO_4 source plus (Field 1966, Seal 2006, Hoefs 2009). Therefore an approach similar to that applied to Li using the average of Cl and Sr derived dilution factors, was utilized to characterize the behavior of SO_4 in river water downstream of mine inputs. The lack of isotopic variability between process water and river water upstream limit the potential for quantifying either mixing or fractionation between these two end members, obviating observations in step one of mixing. Additionally, in June 2013 SO_4 concentrations and $\delta^{34}\text{S}_{\text{SO}_4}$ reflected conservative mixing downstream of dewatering inputs (i.e. in step two of mixing). June 2015, however, SO_4 concentrations in river water downstream of dewatering inputs were lower than projected by conservative mixing, suggesting SO_4 attenuation within the river (Figure 2.4.11). The difference in $\delta^{34}\text{S}_{\text{SO}_4}$ between projected and observed values was within 2σ of standard run repeatability, and therefore could not be resolved. In this case, the lack of significant isotopic change concurrent with SO_4 attenuation provides some insight to the attenuation mechanism.

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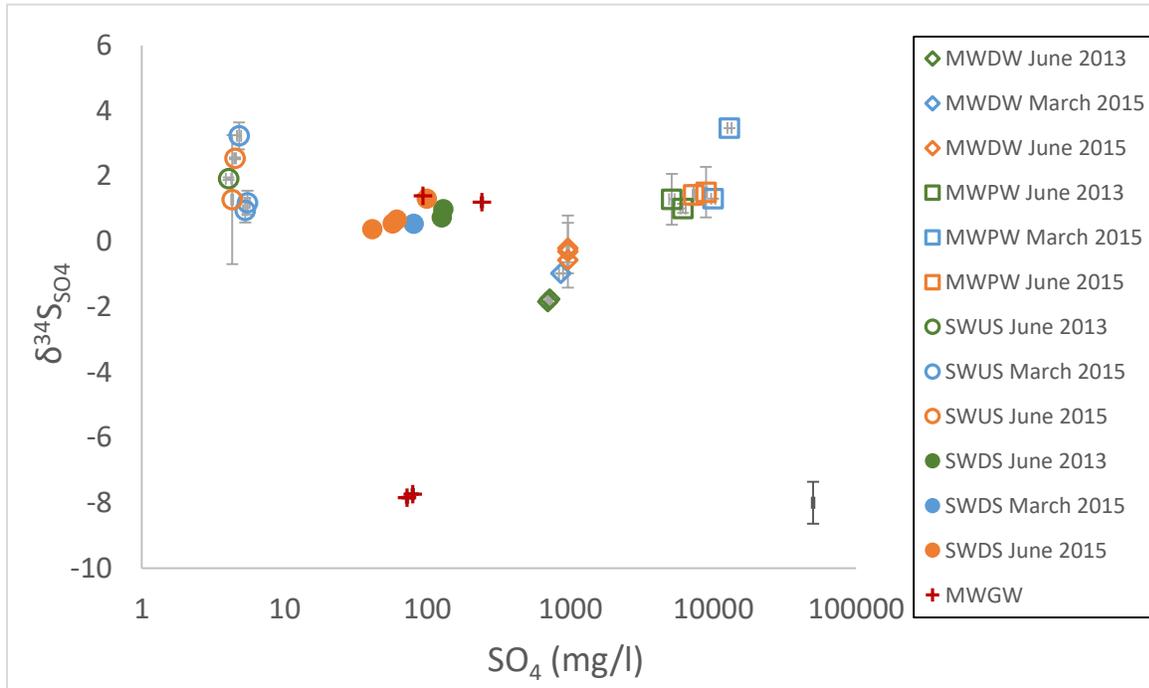


Figure 2.4.10 Relationship between $\delta^{34}\text{S}(\text{SO}_4)$ and $1/(\text{SO}_4)$ for Kittilä mine area samples. Gray Y error bars show 2σ internal analytical repeatability, and X error bars show largest observed % error between laboratory duplicates per sample run. Black Y error bars positioned in the corner of figure show the average 2σ of external standard run repeatability, and X error bars show average % error observed between laboratory duplicates across all sample runs.

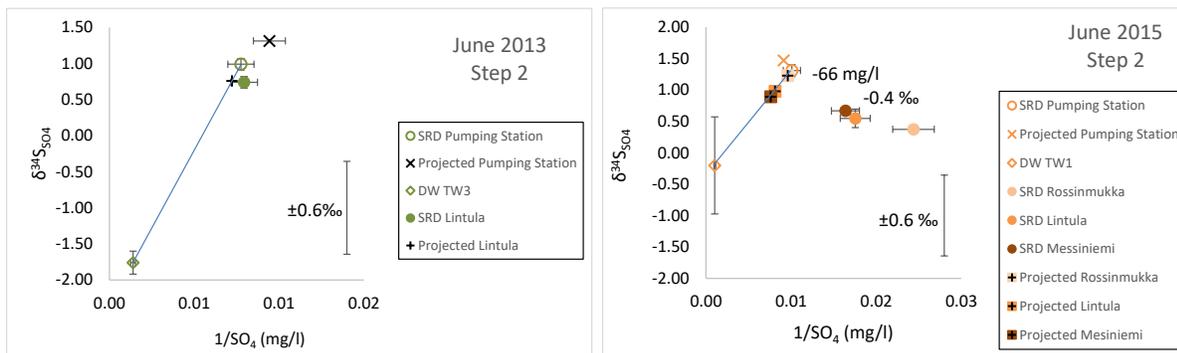


Figure 2.4.11 Isotopic compositions of S_{SO_4} plotted against the inverse of concentration for mixing step 2 for June 2013 and June 2015. Blue lines depict conservative mixing between proposed end members. Projected compositions shown in black. X error bars on sample points are percent analytical error based on duplicate analyses, while Y error bars are 2σ internal repeatability. Because the error of external standard repeatability are larger than sample repeatability, Y error bars illustrating 2σ of standard repeatability are shown with no symbol.

While many factors influence the isotopic composition of SO_4 in solution, the greatest driver of S fractionation is the preferential removal of ^{32}S from solution through anaerobic microbial reduction (Faure & Mensing 2005). The observed SO_4 attenuation from the projected 123 mg/l to the measured 57 mg/l ($f = 0.46$) at the Lintula site in 2015, was applied in [equation 6](#) to estimate the

anticipated $\delta^{34}\text{S}_{\text{SO}_4}$ associated with bacterial reduction as an attenuation mechanism. While the fractionation factor (α) associated with microbial sulphate reduction is dependent on environmental and physiological variables, field and laboratory based studies suggest H_2S may be enriched in ^{32}S from 22 to 75‰ relative to the SO_4 source (Harrison & Thode 1958, Kaplan & Rittenberg 1964, Habicht & Canfield 1997, Fraure & Mensing 2005). To provide a conservative estimate of $\delta^{34}\text{S}_{\text{SO}_4}$ resultant of anaerobic bacterial reduction, an enrichment of ^{32}S in H_2S by 22‰ ($\alpha=1.022$) was applied in equation 6. Due to the preferential reduction of ^{32}S , SO_4 attenuation by bacterial SO_4 reduction is expected to result in a positive shift in $\delta^{34}\text{S}_{\text{SO}_4}$ relative to conservative mixing, from 0.98 to 0.99 ‰, in contrast to the observed shift to 0.55‰.

$$6) R = R_0 * f^{1/(\alpha-1)}$$

Rayleigh equation that describes the isotopic evolution of SO_4 undergoing reduction to H_2S , where R is the $^{34}\text{S}/^{32}\text{S}$ of SO_4 at a given f , R_0 is the $^{34}\text{S}/^{32}\text{S}$ of SO_4 before the start of fractionation, f is the fraction of SO_4 remaining, and α is the $R^{\text{SO}_4}/R^{\text{H}_2\text{S}}$ (from Faure & Mensing 2005)

While such differences in $\delta^{34}\text{S}_{\text{SO}_4}$ are small relative to external error at 2σ (0.6‰), the relatively low internal error and consistency between the three downstream river samples suggests a lack of $^{34}\text{S}_{\text{SO}_4}$ enrichment associated with SO_4 attenuation. This suggests that the mechanism(s) of SO_4 attenuation in river water was not anaerobic microbial reduction. While other mechanisms such as the precipitation of sulphate salts and oxy-hydroxide minerals also act to co-precipitate toxic metals and metalloids, they are typically more susceptible to remobilization than sulphide minerals. Therefore the inference on S attenuation facilitated by characterizing process induced fractionation in ^{34}S provides information relevant to contaminant stability within the river.

In a similar fashion, SO_4 source and mobility can be evaluated from isotopic shifts across the treatment wetlands. Process water discharging TW4 was enriched in ^{34}S by 2‰ relative to water entering the wetland from the settling pond in March 2015 (Figure 2.4.11). The isotopic enrichment was concurrent with an increase in SO_4 concentration from 10000 to 13000 mg/l. The mechanisms proposed for SO_4 attenuation within the treatment wetland include surficial precipitation of hydroxides and sulphide precipitation in deeper anoxic layers of the wetland (Palmer et al. 2015). As described above, sulphide precipitated from solution through microbial reduction will be depleted in ^{34}S relative to SO_4 in solution. Additionally, the re-dissolution of sulphide has been observed to occur quantitatively, such that the ^{34}S depleted signature of the sulphide would be retained in SO_4 produced through re-dissolution. Because the increase in SO_4 across the treatment wetland resulted in ^{34}S enrichment, the SO_4 leached from the wetland in spring time can be inferred to not result from the redissolution of secondary sulphides, but rather one, or some combination of primary sulphides, sulphate salts or hydroxides.

2.4.6 Magnesium isotopes in water at the Kittilä site

Despite the distinct Mg concentrations observed among water types, relatively little isotopic variation was observed in either $\delta^{26}\text{Mg}$ or $\delta^{25}\text{Mg}$. The maximum $\delta^{26}\text{Mg}$ was -0.21‰, the minimum was -1.10‰, and 2σ of analytical reproducibility ranged from 0.04 to 1.06‰ (Figure 2.4.12).

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Subsequently there was insufficient isotopic variation in Mg across sample sources to utilize Mg isotopes as tracers at the scale of this study.

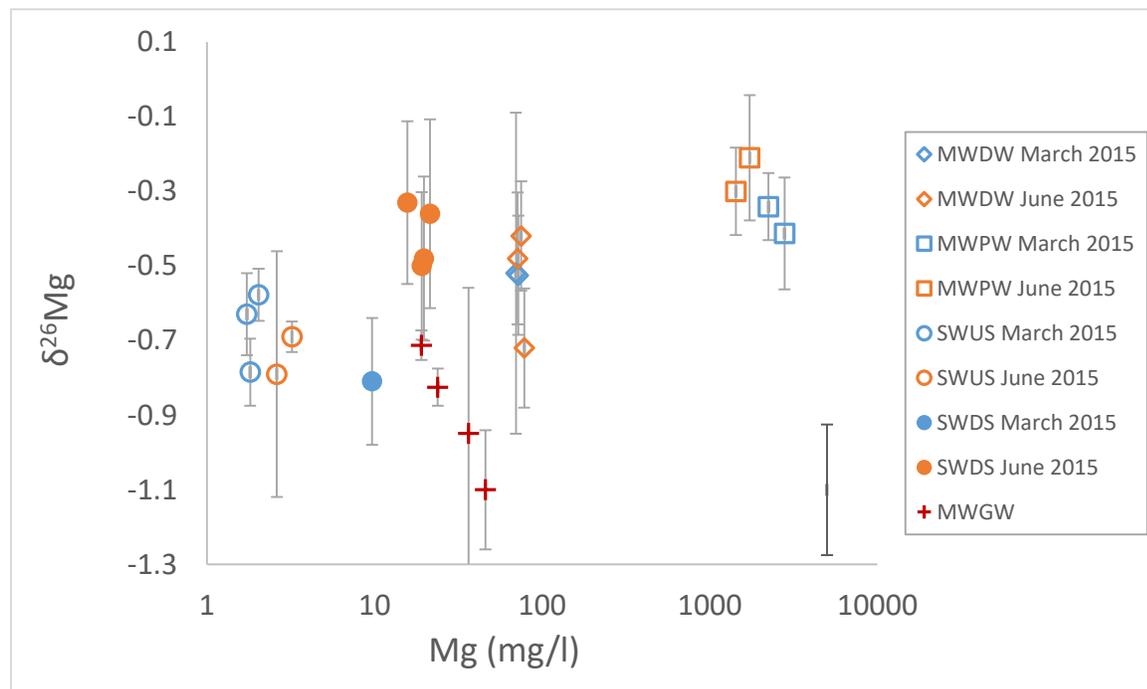


Figure 2.4.12 Relationship between $\delta^{26}\text{Mg}$ and Mg (mg/l) for Kittilä mine area samples. Gray Y error bars show 2σ internal analytical repeatability, and X error bars show largest observed % error between laboratory duplicates per sample run. Black Y error bars positioned in the corner of figure show the average 2σ of external standard run repeatability, and X error bars show average % error observed between laboratory duplicates across all sample runs.

3 Roşia Montană

3.1 Geographic and geologic setting

Roşia Montană is located in the Southern Apuseni Mountains (western Romania) and belongs to the *Golden Quadrilateral*, one of the most important gold areas and probably the biggest gold deposit in Europe, with proved reserves of about 10 Moz Au. Regarding the water resources, the area (elevation range of 556 – 1196 m) is a medium-rain area (~75 cm/y), with a snow cap that lasts for 3 - 4 months in winter. The average annual temperature is 7.38°C, with a maximum monthly average of 18.6°C during the summer period, and minimum monthly average of -2.4°C during the winter. The Arieş River is the most important watercourse in the Apuseni Mountains and flows about 10 km north of Roşia Montană, collecting water from various tributaries, including Abrud River. Roşia Montană is crossed by Roşia stream which flows to Abrud River. All the adjacent streams from Roşia Montană are flowing to Roşia valley. Two other tributaries of Abrud River, Sălişte and Corna streams are flowing approximately parallel to Roşia Valley. Several artificial lakes have been built in the area, mainly during the 19th century, with the aim to store

water for the processing of ore. The biggest lakes are: Tau Mare, situated upstream from Roşia Montană, with an area of approximately 32,120 m², Tau Brazi has an area of about 7,800 m², and Tau Corna, located upstream Corna valley, with an area of about 8,830 m² (RMGC, 2006). The region includes gold-, silver-, and copper-bearing deposits, which are related to three approximately parallel belts of Neogene volcanism. Roşia Montană is part of the northernmost belt.

The mining region has a Paleozoic and Precambrian basement which is covered by marine and non-marine Mesozoic sedimentary rocks. Most of the area is covered by Cretaceous deposits (flysch facies). The sedimentary rocks have been intruded by Tertiary magmatites, occurring as volcanic and sub-volcanic bodies. During the Neogene, three different magmatic episodes have been recognised (Tamas, 2007). The gold and silver mineralisation from Roşia Montană is hosted by rocks belonging to the second magmatic cycle. This episode was formed in the late Badenian to early Pannonian (13.5–9 or even 7 Ma) and is represented by different types of andesites and dacites, with the largest spatial extension.

The Roşia Montană volcanogenic complex is a maar-diatreme structure, which intersects Cretaceous fine grained sediments (black shales) with intercalations of sandstones and conglomerates. This structure includes distinct types of breccias (e.g. phreatomagmatic breccias) and volcanoclastics. Two dacitic bodies, named Cetate Dacite and Carnic Dacite, have played an essential role in the mineralisation process, generating the gold and silver bearing deposit. The gold occurs as electrum (gold-silver), associated with sulphides (pyrite – most of the time), but occurs also in native form (RMGC, 2006).

3.2 Mining history in Roşia Montană area

The region is well known for a long mining tradition, which spans over the last 2000 years. During the Roman times, in the first stage of exploitation, Roşia Montană was called Alburnus Maior. The Romans introduced the first systematic extraction and ore processing techniques in the Apuseni Mountains. They dug trapezoidal-shaped galleries which followed the gold-rich veins. The tools they used were hammers and chisels and for simplifying their work, they heated the rock with fire and sprayed it with water, causing a rapid contraction and making the detachment of the fragments much easier. About 7 km of Roman mining galleries have been identified out of the 140 km of underground works, most of them dating from modern times. Some of the ancient workings are conveniently preserved and still can be visited.

After the fall of the Roman Empire, the mining activity suffered some fluctuations, in accordance with the major historical events that took place. At the end of the 17th century, the Austro-Hungarian Empire expanded the underground mining operations, and focused on Cetate, Carnic, Jig, and Orlea, along the high grade veins. During the interwar period (between 1918 and 1939), people were attracted to mining and they received concession contracts for a defined period of operation. At that time, most of the operations were manually performed.

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During the communist period, the underground work continued until 1985. The industrial mining operations used room and pillar bulk mining methods. In 1970, the mining activity was continued using open pit methods, gold being extracted in a flotation plant (Gura Roşiei processing plant). At the end of the flotation process, gold and silver were recovered using conventional cyanide leaching techniques.

In the last two decades, due to the economical context and to insufficiently adapted technology, mining operations were significantly reduced. The mine was closed in 2006, and currently the mining area is inactive.

3.3 Environmental issues

Roşia Montană has a long history of mining with significant environmental consequences related to the former ore extraction and processing. Acid mine drainage (AMD) and the related transfer of heavy metals represents the main pollutant factor that affects the environment in this mining area. Acid drainage forms as a consequence of the chemical reactions between water and rocks containing sulphur-bearing minerals, especially pyrite. Once exposed, pyrite reacts with air and water and forms sulphuric acid (H_2SO_4) and dissolved iron. The iron hydroxide ($Fe(OH)_3$) forms a red, yellow or orange precipitate, deposited on the bottom of the streams containing mine drainage. Further on, the acid runoff dissolves heavy metals such as Cu, Pb, Zn, etc., contaminating the ground- and surface water.

The acid water comes from the Cetate open pit (19.75 ha) and the Carnic open pit (5.2 ha), from the tailings management facilities (Sălişte and Gura Roşiei), from the several open galleries, and numerous waste dumps which are placed very close to the extraction sites.

There are some open galleries that release important amounts of acid water with a very low pH, very often lower than 3 (e.g. Adit RO88, Cetate Adit, 714 Adit). These acid waters are collected by the main watercourses in the region (Roşia and Corna steams, and Abrud River) and high concentrations of elements such as Cu, Zn, Pb, Cd, Ni are present also in stream sediments, disturbing the aquatic environment (Florea et al. 2005; Bird et al. 2005).

Monitoring of surface water, groundwater, and mine water quality is still necessary for designing appropriate measures to diminish the contaminant release that could harm human health or the environment. Further on, stable isotope analysis can be used to distinguish contaminant source, evaluate transport pathways and geochemical controls on contaminant mobility.

3.4 Study methods

3.4.1 Sampling

Water sampling at Roşia Montană site was performed on a monthly basis between January 2014 and August 2015. Table 3.4.1 summarizes all water samples collected and the sampling points distribution is shown in Figure 3.4.1. Samples were analysed for pH, electrical conductivity, temperature, salinity, total dissolved solids, turbidity, dissolved oxygen, redox potential, metals, ion contents and ^{18}O , ^2H (D) isotopes. The main goal of the study was to understand the source, flow and mixing dynamics of water resource systems. Additionally, one-time isotopic analyses of strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and SO_4 sulphur ($^{34}\text{S}-\text{SO}_4$) isotopes were conducted in May 2015 to further evaluate mine water interactions with surrounding surface waters. The objective of these additional isotopic analyses was to provide supplemental insight to water source, pathways, mixing, and contaminant attenuation across the site. In addition, precipitation samples were collected for the isotopic study using the IAEA standardized methodology, in order to draw the local meteoric water line. Two locations were selected for the collection of samples, one was located at the Roşia Montană weather station, at an altitude of about 1196 m, and the second collector on the roof top of a building in Cluj-Napoca, at an altitude of about 360 m (Figure 3.4.2 and Figure 3.4.3).

The water samples were collected at and around the former Roşia Montană mining site, on the same period of each month, in order to ensure the representativeness of the samples. Water sources included surface water from a stream which is away of the mine site discharge (background surface water), surface water from upstream and downstream of mine water discharge points, groundwater (from wells and springs). The last category is represented by acid mine waters coming from the tailings ponds, waste rock dumps or gallery outlets. In addition, artificial ponds were also included in the surface water category, but they were analysed separately. These ponds accumulate rainwater mainly. The sampling network consists of 28 sampling points (Table 3.4.1 and Figure 3.4.1). The main types of analysed waters consist of 12 surface waters, four lakes, four groundwaters, and eight mine waters. After obtaining the preliminary results, the network was reconfigured at 24 sampling points, by choosing the most representative sampling sites. A total number of 1428 water samples were acquired during the entire sampling period. GPS coordinates were recorded at each sampling site.

Multiple sample bottles were collected at each site, dependant on the desired components to be analysed. For heavy metal analysis, water samples were collected in polyethylene bottles with a volume of 100 ml, and each individual sample was filtered through a $0.45\ \mu\text{m}$ pore filter. After filtration, the samples were acidified to $\text{pH} = 2-3$ using 65% HNO_3 , according to SRISO8288, 2001. Other water samples for a complete set of major ions were collected in polyethylene bottles with a volume of 50 ml, each individual sample being filtered through a $0.45\ \mu\text{m}$ porosity filter. Sample dilution was calculated according to the electrical conductivity, samples being diluted to an electrical conductivity lower than $100\ \mu\text{S}/\text{cm}$. Ultrapure water was used for all sample preparation (dilution). For isotopic analysis a specific methodology proposed by the IAEA (International Atomic Energy Agency Vienna; Water Resources Program), was followed. The

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procedure was designed to avoid evaporation of precipitation samples. The first step consists in filtering the sample through a 0.45 µm pore filter in the field. Sampling vessels with a volume of 4 ml are made out of glass in order to avoid diffusion and have a special closure system. At the end of the sampling method the vessels are sealed to avoid fractionation. Water samples were labelled and stored in a cool box at 4°C, for a better preservation during transport to the laboratory.

Table 3.4.1 GPS coordinates of the water sampling points

Sample no.	Name	Water types	Long E	Lat N	Elevation (m)	Status
S1	Vârtop	Surface water	23 03 37	46 19 01	581	
S2	Downstream confluence Roşia river with Abrud river	Surface water	23 03 27	46 18 43	576	
S3	RO11 spring	Groundwater	23 04 50	46 18 27	766	
S4	Downstream Roşia river	Surface water	23 05 00	46 18 23	692	
S5	Adit 714	Acid mine water	23 06 09	46 18 16	734	
S6	Downstream adit 714	Surface water	23 05 56	46 18 18	708	removed
S7	Cetate Dump 2	Acid mine water	23 06 36	46 17 59	756	
S8	Adit RO88	Acid mine water	23 07 06	46 18 04	811	
S9	Cetate Adit	Acid mine water	23 07 19	46 18 02	838	
S10	Cetate Dump 1	Acid mine water	23 07 21	46 18 01	849	
S11	RO78 dug well	Groundwater	23 07 20	46 18 41	891	
S12	Upstream Roşia river	Surface water	23 08 01	46 18 25	879	
S13	Tău Brazi	Artificial lake	23 08 16	46 18 08	959	
S14	RO43 spring	Groundwater	23 08 25	46 18 36	960	
S15	Tău Mare	Artificial lake	23 08 40	46 18 37	1077	
S16	Downstream confluence Sălişte river with Abrud river	Surface water	23 03 37	46 17 21	612	removed
S17	Upstream confluence Sălişte river with Abrud river	Surface water	23 03 38	46 17 18	579	removed
S18	Downstream Sălişte T.M.F	Surface water	23 03 44	46 17 22	593	
S19	Sălişte Gallery	Surface water	23 03 55	46 17 25	604	
S20	AMD exfiltration (Sălişte tailings)	Acid mine water	23 03 57	46 17 25	600	
S21	Lake pond Sălişte	Acid mine water	23 04 29	46 17 30	635	removed
S22	Upstream Sălişte tailings	Surface water	23 05 29	46 17 24	771	
S23	Corna Valley	Surface water	23 07 20	46 17 13	761	
S24	C120 dug well	Groundwater	23 07 19	46 17 23	781	
S25	C122 Adit	Acid mine water	23 07 22	46 17 31	795	
S26	Tău Cartuş	Artificial lake	23 07 24	46 17 28	798	
S27	Tău Corna	Artificial lake	23 08 13	46 17 46	971	
S28	Abruzel Valley	Surface water	23 08 16	46 15 53	676	

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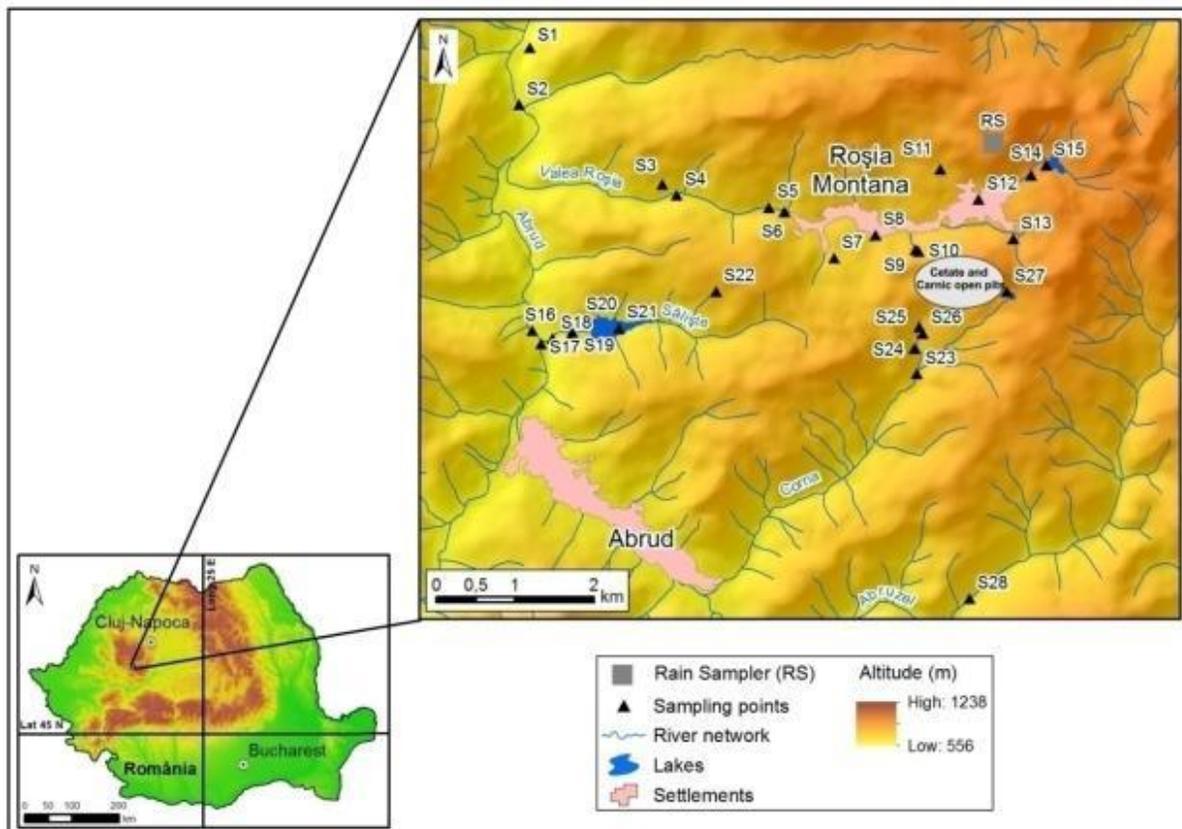


Figure 3.4.1 Location of water sampling points

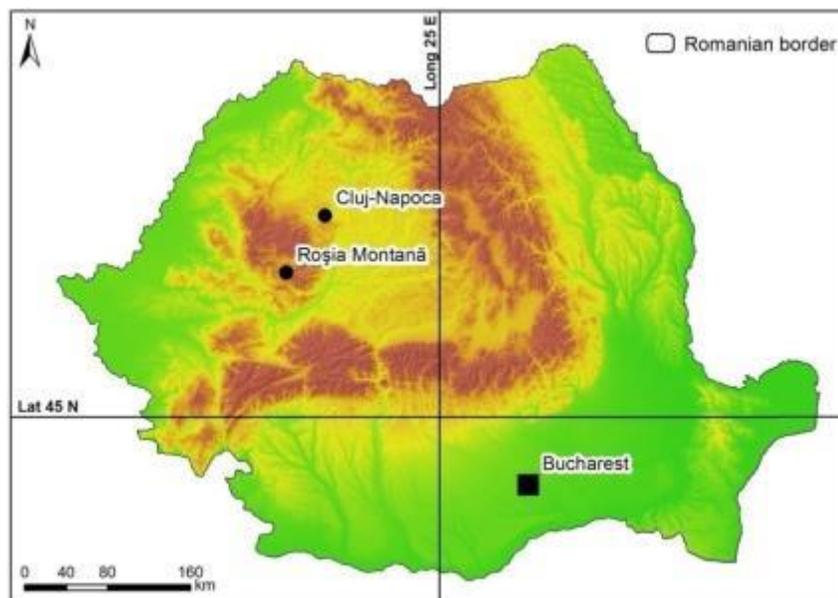


Figure 3.4.2 Location of the two rain samplers (Cluj-Napoca and Roşia Montană)



Figure 3.4.3 (a) Roşia Montană, (b) Cluj-Napoca collector for precipitation sampling

3.4.2 Analytical methods

3.4.2.1 Physico-Chemical analysis

Chemical analysis of water samples were conducted in Babeş-Bolyai University's laboratories at. Heavy metals were analysed by atomic absorption spectrometer (AAS) ZEE nit 700. The atomic absorption spectrometer ZEE nit 700 is a compact spectrometer with transversely heated graphite tube atomizer with Zeeman background correction at the furnace, as well as flame atomizer with deuterium background correction. For the flame technique (type of flame: acetylene/air) in the single or dual-beam operation with deuterium background correction, the PC controls 6-lamp turret for fully automated operation which uses hollow cathode lamps HCL for elements with line radiation in the UV/VIS range (Fe, Ni, Cd, Pb, Cr, Zn, Cu). For the graphite tube technique, the ZEE nit 700 works as a single-beam device without D₂HCL, but with a movable crystal polarizer in the sample radiation beam. For the calibration curve, standards for each metal (Merck, Germany) were used. The detection limits for flame atomizer and graphite tube, are presented in Table 3.4.3.

The ions were analysed with a Dionex Ion Chromatograph ICS1500. For the separation of the major anions (F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻), an analytical column IonPac AS23 for ion exchange was used. An ASRS 300 ULTRA II (4 mm) Anions Self Regenerating Suppressor and an anion mixture standard Seven Anion Standard II (Dionex, USA), were used. The volume

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injection is 25 μL , and the flow rate, 1.0 mL/min. The eluent was an aqueous solution consisting of 4.5 mM Na_2CO_3 and 0.8 mM NaHCO_3 . For the separation of the major cations (Na, K, Ca, Mg, NH_4 , and Li), an Analytical column IonPac CS12A for ion exchange and a CSRS 300 ULTRA II (4 mm) Cations Self Regenerating Suppressor, were used. The cation standard mixture used is Six Cation II Standard (Fluka, Germany) and the eluent was an aqueous solution consisting of 20 mM of methanesulfonic acid. The detection limits are presented in Table 3.4.2.

For physicochemical measurements on water samples a WTW Multi 350i portable multimeter and a portable turbidity meter WTW Turb 430IR were used. Before the measurements, the devices were calibrated.. Physicochemical measurements were taken directly in the field.

Table 3.4.2 Detection limits for ions

Ion	Detection limit ($\mu\text{g/l}$)
Fluoride	10
Chloride	20
Nitrite	20
Bromide	20
Nitrate	20
Phosphate	20
Sulphate	20
Ammonia	5
Lithium	1
Sodium	5
Potassium	8
Magnesium	7
Calcium	7

Table 3.4.3 Detection limits for metals

Metal	Cr	Cd	Ni	Zn	Pb	Cu
Flame atomizer (AAS) ($\mu\text{g/l}$)	35	12	38	13	83	36
Graphite tube (AAS) ($\mu\text{g/l}$)	0.24	0.077	0.26	0.09	0.61	0.35

3.4.2.2 Oxygen and hydrogen isotopes

Oxygen (^{18}O) and hydrogen (^2H) isotopes in water were analysed by laser (IR) based cavity ring-down spectroscopy (CRDS) using a Picarro isotopic water analyser (Picarro CRDS analyser L2130-I) (Figure 2.2.8.a, b). Light stable isotopes are reported using delta (δ) notation as per mil (‰) values relative to known standards, according to equation 2.

In the CRDS method the absolute abundances of isotopologues, i.e. water molecules with different combinations of ^1H , ^2H , ^{16}O and ^{18}O , are measured from a vaporized sample in an optic chamber. The isotope ratios are reported using the δ notation relative to the Vienna Standard Mean Ocean Water (VSMOW) international standard. Two internal standards calibrated using standards provided by IAEA Vienna, were used. One standard has a low isotopic composition while the other one, a high isotopic composition.

For laboratory analysis, 2 ml of re-filtered sample (0.20 µm porosity) are required (Figure 2.2.9). Filters and syringes are individual for each sample (5 ml syringes). At every 5 samples, the analyser injected two different standards in terms of isotopic composition. These two standard solutions are consistent with the international VSMOW standard.

The analyser is set to perform 9 injections/sample or standard solution, each injection lasting 15 minutes. The first 5 injections are only for washing the previous sample, only the last 4 readings for oxygen and the last 3 readings for hydrogen are taken into account. The latter readings are averaged, and this is the value attributed to the sample. The precision of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements are $\pm 0.12\text{‰}$ and $\pm 0.8\text{‰}$, respectively.

3.4.2.3 Sulphate and strontium isotope analysis

Water samples collected from the Roşia Montană site in June 2015 were analysed for isotopes of sulphur in sulphate and Sr in addition to the more regularly conducted water isotope and geochemical analyses. Both $^{34}\text{S}/^{32}\text{S}\text{-SO}_4^{2-}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ were analysed at the GTK Research Laboratory in Espoo, Finland using a Nu Instruments™ MC-ICPMS. Deionised Milli-Q water (resistivity of $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$) was used for sample preparation. Acid washed Teflon vials were used during digestions and column separation. All acids were either single or double-distilled (sub-boiling), depending on the initial acid purity class. Prior to MC-ICPMS analyses, samples were dissolved in single-use acid cleaned HDPE tubes with a known amount of 2% HNO_3 to achieve the desired element concentration for analysis.

Strontium separation was conducted using Sr specific resin by evaporating sufficient sample volume to produce 1 ml of 80 or 500 ppb Sr-solution. The evaporated sample was digested into 0.2 ml of 1N ultra clean HNO_3 and run through pipette columns containing approximately 200 µl of Sr-specific resin (TrisKem Sr Resin, 50–100 µm). Sr was eluted with 0.05 N HNO_3 . Isotopic analysis of Sr and S were conducted by MC-ICPMS, following the methods described in section 2.2.2.

3.5 Results and discussion

3.5.1 Geochemical characterization

A summary of the distribution of the temperature, pH, total dissolved solids (TDS), EC, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, as well as of the main ions (Cl, NO_3 , SO_4 , Li, Na, K, Mg, Ca) and metals (Cd, Cr, Pb, Cu, Ni, Zn) for the ground- and surface water sources is shown in Table 3.5.1. For all the parameters, the displayed values represent the mean values for 19 months of observation with an exception in the case of the major ions, where the displayed values represent the mean values of 13 months of observation.

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Mean temperature values are similar for all water sources, varying between 8.6 °C and 11.8 °C. The lakes recorded the highest temperature values compared to the other types of waters because of water stagnation and water exposure to external factors. Surface waters, lakes, springs, dug wells and mine water show seasonal variation of the pH, TDS, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, as well as major ion concentrations as of the main ions content, but the sequence of minimum and maximum is different from one source to another.

3.5.1.1 EC

Lakes display the lowest EC values. Groundwaters (springs and domestic wells) are rather neutral with low EC values; point S24 is an exception in the groundwater category, because it is located very close to the dumps, on Corna Valley. In this case, the pH and EC values are slightly different compared to the other groundwaters. Also, this dug well is located under a country road, which is intensively used. Mine waters are characterized by lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, acidic pH, and high EC values. Mine water displays high variability in EC and pH compared to other types of waters (Figure 3.5.2.).

In the case of EC, 2 groups of mine waters could be distinguished: mine water showing EC values similar to some groundwaters and other surface water sources (S7, S20, S25), and mine waters with much higher dissolved solids content (S5, S8, S9, S10). The majority of the mine water sources display pH values between 2 and 4. The mine water discharged from S7 and S20 displays slightly higher pH values (~ 5-6). In the case of S7, the water coming from the waste dump is mixed with water from a small stream, relatively clean.

For most mine waters, springs and domestic wells, the EC seasonal variation is relatively low (Figure 3.5.2). The underground flow regime inhibits to some extent the EC variation of the infiltration water. Great seasonal variation was found in the AMD exfiltration from Sălişte TMF (S20). The springs show relatively constant EC values, with more pronounced variations during the summer 2015.

For the running surface waters, the EC values display an increasing trend during summer and autumn months, for both years. The trend is more pronounced in the downstream area (Figure 3.5.2), because of intersecting points with the mine waters. Lakes show a constant seasonal trend for EC values, while the recorded values are different from one lake to another. The lowest TDS concentrations were recorded in the winter period and in the early spring period, in relation with the dilution generated by precipitations and snow melt.

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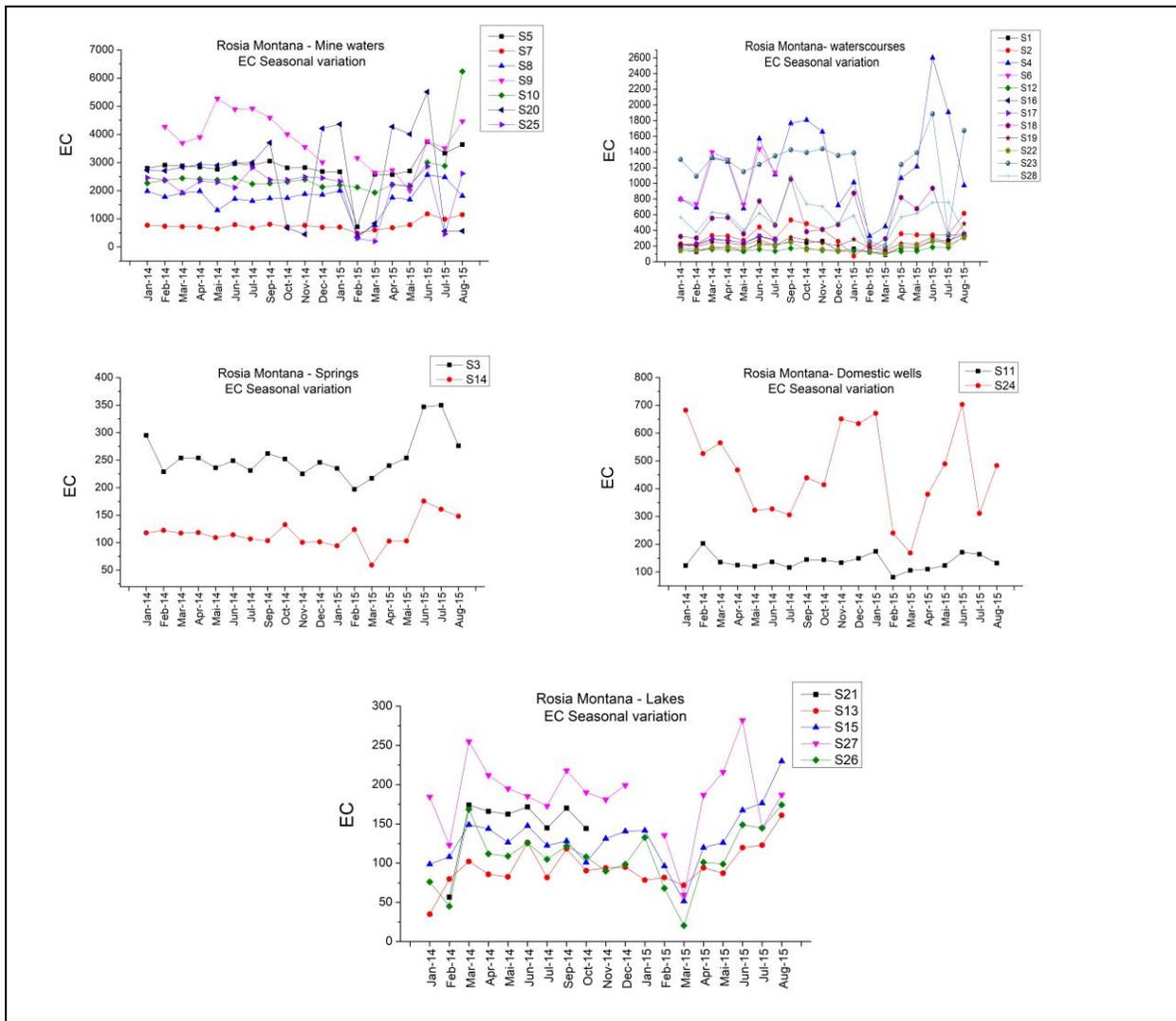


Figure 3.5.1 EC seasonal variation in different water sources: mine water; streams; springs; domestic wells and lakes

3.5.1.2 pH

The mine waters are less affected by seasonal variations, which suggest good underground mixing systems (Figure 3.5.3). Most of the mine waters (S5, S8, S9, S10), which have a common source of contamination, show pH values almost constant, with a slight decrease of the pH during the warm period. Cetate Dump 2 (S7) from Roşia Valley is a combination between mine water and stream water and the sampling point is at certain distance from the source of contamination. This shows a slight increase in the pH values, compared with the other mine waters. S20 (AMD exfiltration Sălişte), shows important variability, suggesting the shallow circulation of water within the tailings.

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The pH of the running surface waters is relatively constant during the entire monitoring period (Figure 3.5.3). Most of them have pH values between 6 and 8, with four exceptions (S2, S4, S6, S28) because these sampling points are confluence points between mine waters and surface waters. S2 is the most affected by the seasonal variation, since it collects all the acid waters coming from Roşia Montană and Sălişte Valley.

For both the domestic wells and springs, the pH seasonal variation patterns are different from one source to another (Figure 3.5.3). In general, springs have strong seasonal variation while domestic wells have a constant trend. The pH values record increases and decreases from one month to another and the amplitudes of variation are greater than one unit for both springs and dug wells. A somehow similar variation can be observed in the case of lakes.

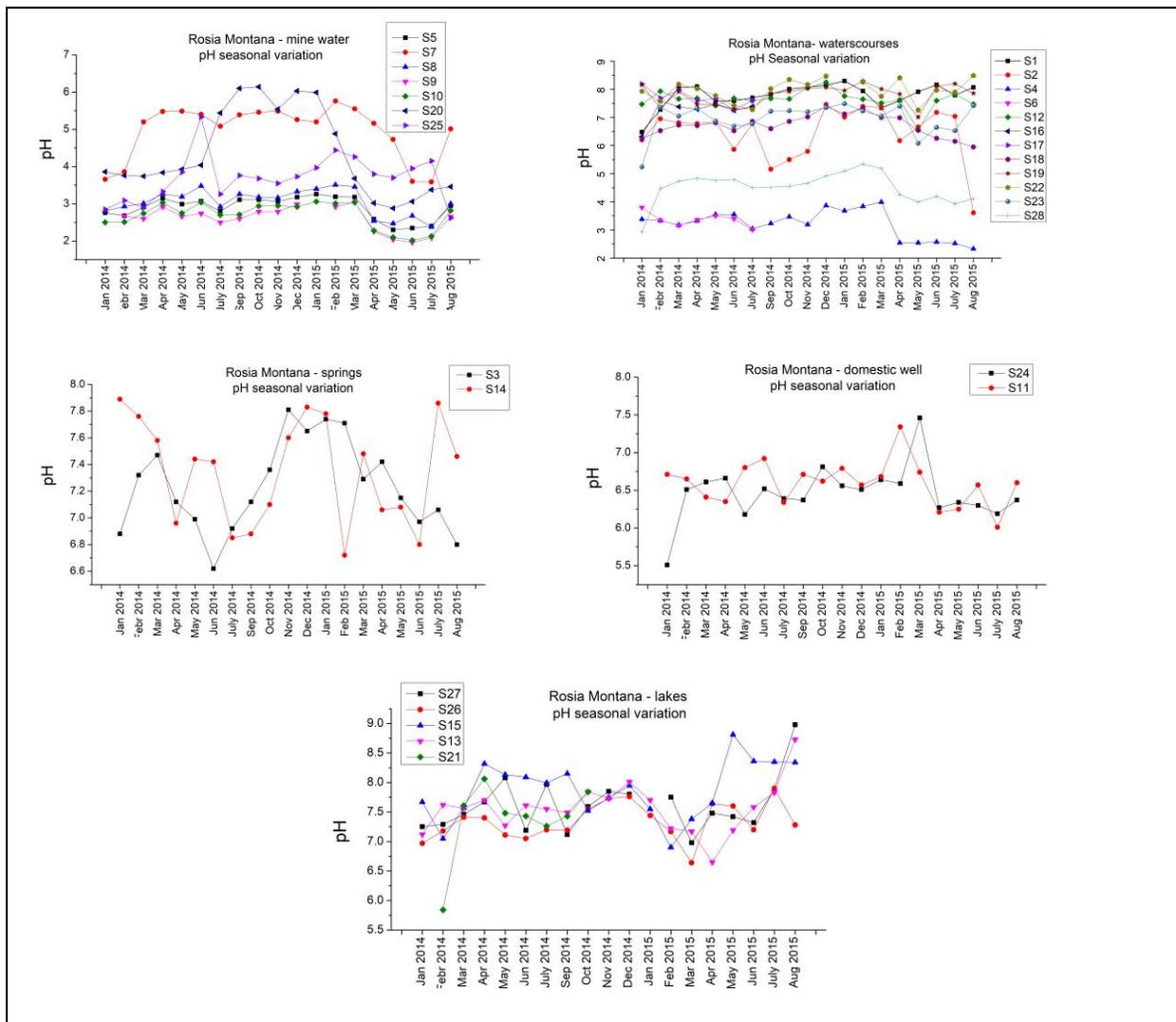


Figure 3.5.2 pH seasonal variation in different water sources: mine water; streams; springs; domestic wells and lakes

3.5.1.3 Major ions

Mine water is characterized by higher calcium (Ca) content relative to other water types whereas domestic wells are characterized by higher Ca content relative to springs. Mg is also found in high amounts in mine water. The contents of Na and K are low in all water types, though they are a little higher in mine waters. Li content is below the detection limits in all water samples.

In terms of anion concentrations, the mine waters also display the highest nitrate (NO₃) and SO₄ values. Secondary, higher NO₃ and SO₄ concentrations were obtained in the case of surface waters. The domestic wells, the springs and lakes have similar concentration in the case of NO₃, while in terms of SO₄, only lakes and springs still have similar values, and in the case of the domestic wells the values are slightly higher. The SO₄ content is highly variable from one month to another in all water types. High values of NO₃ were recorded in June 2015 relative to the values recorded in the winter period. The potential sources of NO₃ include the explosives that were used during the active period of the mine, but also the household septic systems and fertilizers which are easily transported in streams and groundwater.

The chloride (Cl) content is much higher in mine waters and secondary in surface waters compared to lakes, domestic wells and springs, where the concentrations are much lower. The bromide (Br) content is below the detection limits in all water samples. Distribution of major ions for all types of water sources is shown in Figure 3.5.3. On the Piper diagram, the mine water has a SO₄ dominant water type (e.g. S5, S7, S8, S9, S20, S25). The surface water is characterized by a SO₄ and Mg-Ca dominant water type. Some of the points (S3, S11, S12, S13, S14, S15) show no dominant cation, while S24, S26, and S27 show Mg-Ca dominant water type.

3.5.1.4 Heavy metals

Distribution and concentration of heavy metals (Cr, Pb, Cu, Ni, Zn, Cd) differs from one water source type to another (Figure 3.5.4). In mine waters and also in surface waters, the metal concentration distribution pattern follows the decreasing order: Zn>Cu>Ni>Cd>Pb>Cr. The highest concentration was found in mine water from the Cetate Adit (S9). Very low Zn concentrations were recorded at Cetate Dump 2 (S7) with a 19 month average of 391.54 µg/l. The highest Zn concentration, in the case of surface waters was found in S4 (Downstream Roşia River), and the lowest average Zn concentrations was found in S12 (Upstream Roşia River).

The highest concentrations of copper (Cu) were found in mine waters. High concentrations were also found in surface waters in the case of Rosia stream, which collects mine water discharge from Cetate and Carnic open pits. Also, elevated concentrations of nickel (Ni) and cadmium (Cd) were recorded in mine and surface waters. It was noticed that the S5 and S9 recorded the highest Ni concentrations during the entire sampling period, while in the same points, plus S8, Cd concentrations were also higher and mostly constant during the same period of sampling. In surface waters, the highest Ni and Cd concentrations were recorded in S4 sampling point. In

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domestic well water and springs, the maximum permissible concentrations for drinking water in the Romanian legislation (Cd 10 µg/l and Pb 5 µg/l) were occasionally exceeded. Relatively high concentrations of Cd were found also in lakes.

Seasonal variation was observed in heavy metal concentrations in running water, lakes, springs, domestic wells and mine water. Also heavy metal concentrations in each water category were compared with the maximal values imposed by the Romanian legislation for drinking water quality, surface water and wastewater (Table 3.5.1).

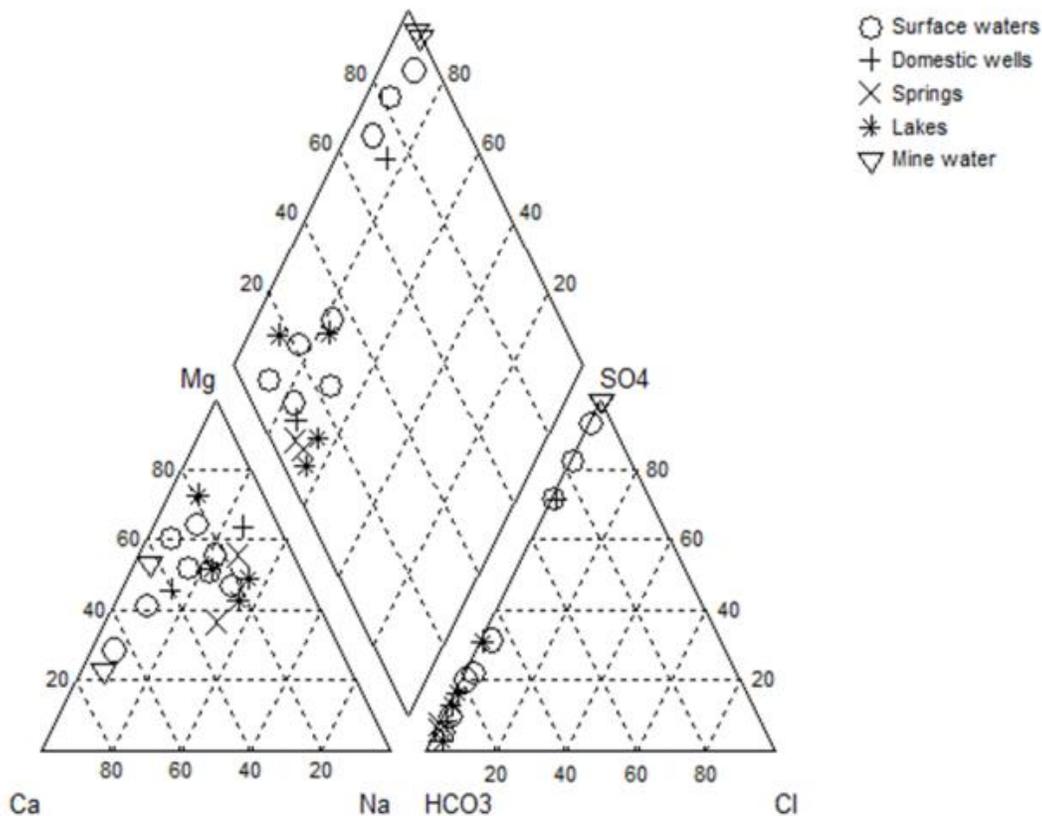


Figure 3.5.3 Piper diagram for water sources from Roşia Montană mining area. All displayed values are representative for June 2015

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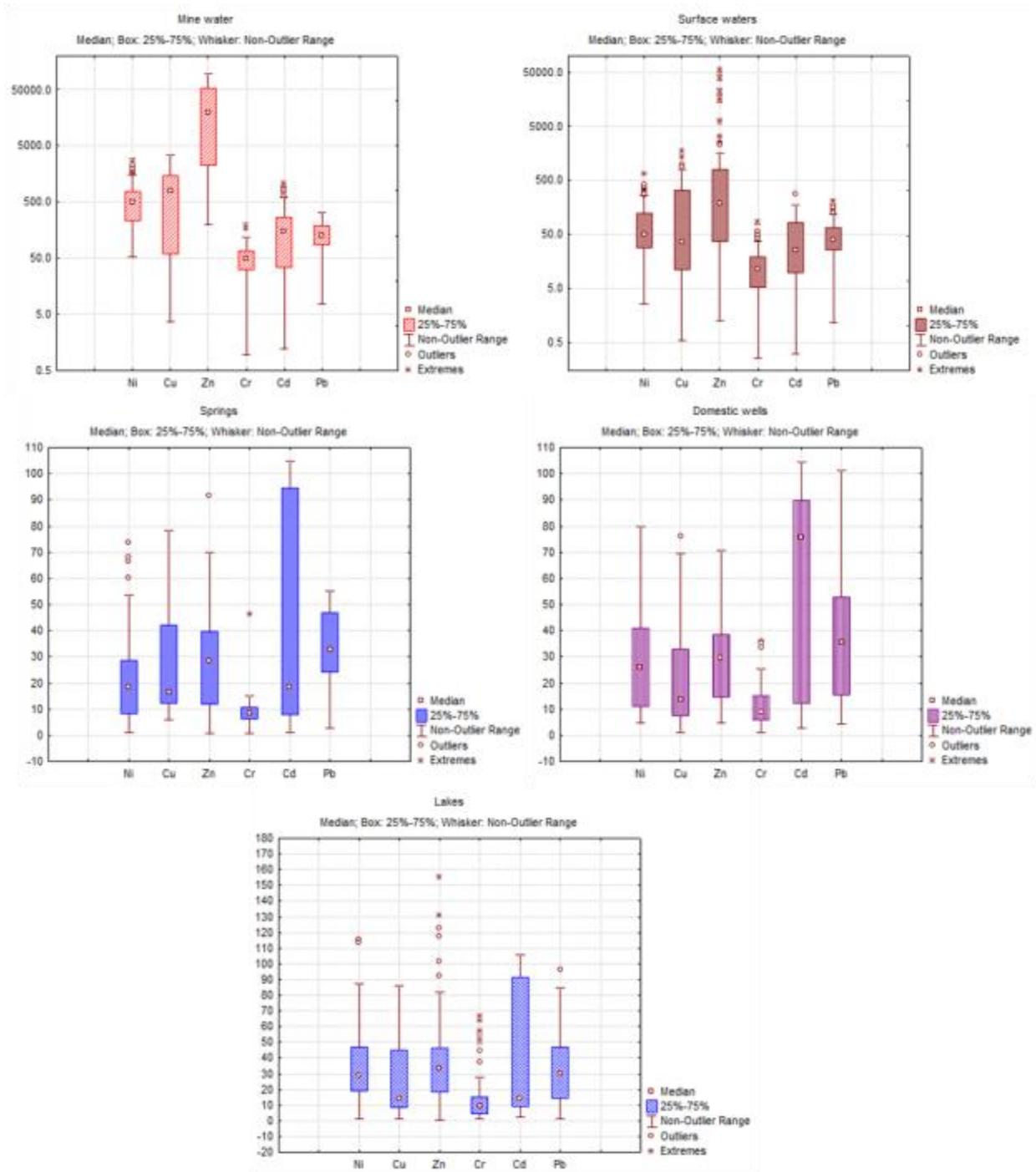


Figure 3.5.4. Distribution of heavy metals among different water sources at Roşia Montană mining area

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Table 3.5.1 Maximum permitted heavy metals concentrations after Romanian Legislation (for drinking water, surface water and wastewater)

Physicochemical elements for water quality	Quality classes for surface waters after Romanian Standard (no.161/2006)					Drinking water quality after Romanian Standard (no.458/2002)	Quality indicators for wastewater after Romanian Standard (188/2002 – updated 352/2005)
	I Very good	II Good	III Moderate	IV Weak	V Bad	Maximum permissible concentrations	Limit values
pH	6,5 – 8,5		< 6,5; > 8,5			≥ 6,5; ≤ 9,5	6,5-8,5
EC (µS/cm) over 20° C	Not mentioned					2500	Not mentioned
Total dissolved solids(mg/L)	Not mentioned					Not mentioned	Not mentioned
Turbidity (NTU)	Not mentioned					1	Not mentioned
Salinity (%)	Not mentioned					Not mentioned	Not mentioned
Temperature (°C)	Not mentioned					Not mentioned	35° C
Pb(µg/l)	5	10	25	50	>50	10	200 (µg/l)
Ni(µg/l)	10	25	50	100	>100	20	500 (µg/l)
Cu(µg/l)	20	30	50	100	>100	100	100 (µg/l)
Zn(µg/l)	100	200	500	1000	>1000	5000	500 (µg/l)
Cd(µg/l)	0.5	1	2	5	>5	5	200 (µg/l)
Cr(µg/l)	25	50	100	250	>250	50	1000 (µg/l)
F(mg/l)	Not mentioned					1.2	5
Cl(mg/l)	25	50	250	300	>300	Not mentioned	500
NO ₂ (mg/l)	0.01	0.03	0.06	0.3	>0.3	0.50	1 (2)
Br(mg/l)	Not mentioned					Not mentioned	Not mentioned
NO ₃ (mg/l)	1	3	5.6	11.2	>11.2	50	25 (37)
PO ₄ ³⁻ (mg/l)	0.1	0.2	0.4	0.9	>0.9	Not mentioned	Not mentioned
SO ₄ ²⁻ (mg/l)	60	120	250	300	>300	250	600
Li ⁺ (mg/l)	Not mentioned					Not mentioned	Not mentioned
Na ⁺ (mg/l)	25	50	100	200	>200	200	Not mentioned
K ⁺ (mg/l)	Not mentioned					Not mentioned	Not mentioned
Mg ²⁺ (mg/l)	12	50	100	200	>200	Not mentioned	100.6
Ca ²⁺ (mg/l)	50	100	200	300	>300	Not mentioned	300
NH ₄ ⁺ (mg/l)	0.4	0.8	1.2	3.2	>3.2	Not mentioned	2 (3)

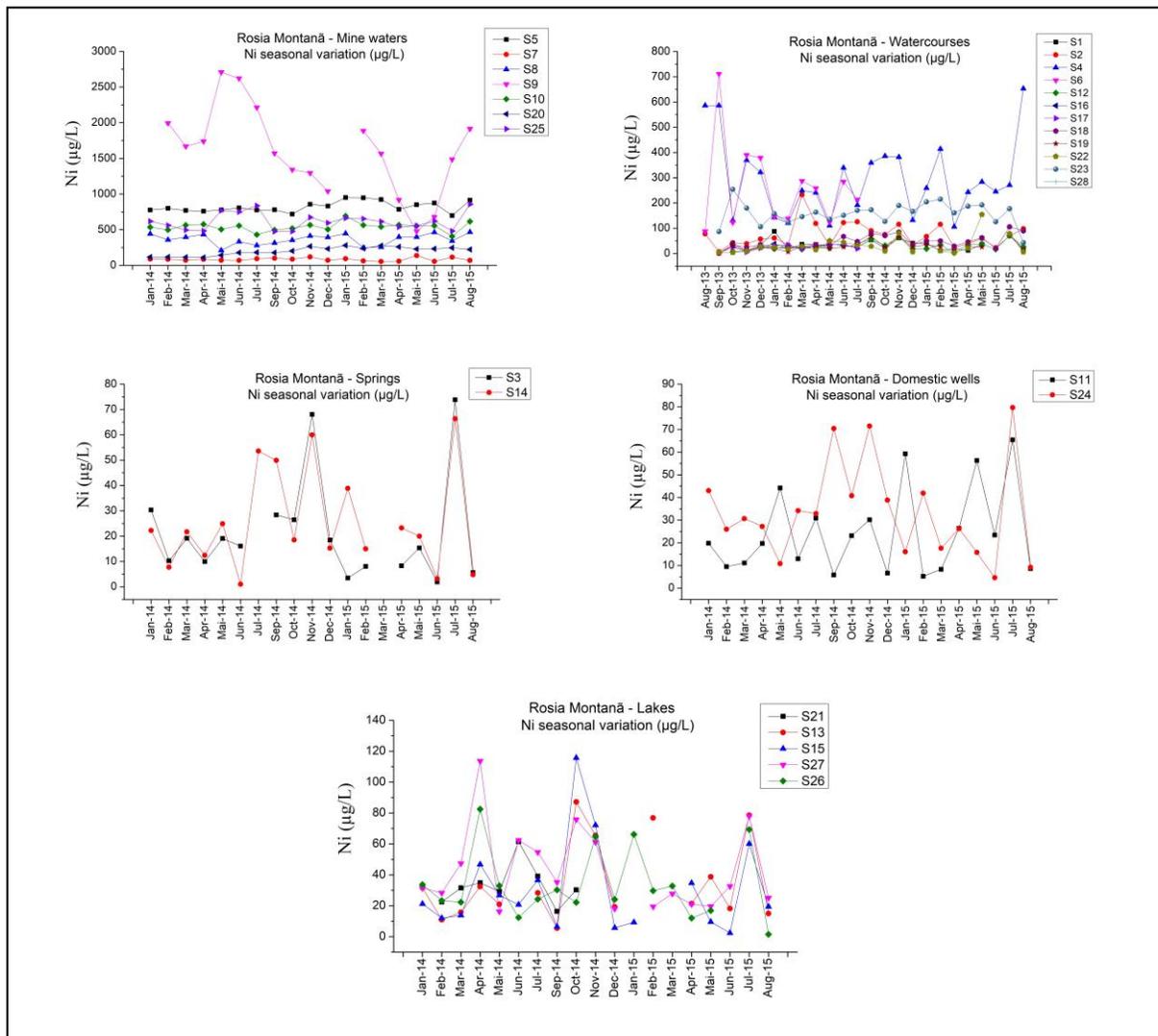
Regarding the mine water, Ni concentration varies from one source to another and has a constant trend. There is one exception, in the case of the Cetate Adit, which shows a greater seasonal variation (Figure 3.5.5). In this case, higher Ni concentrations were recorded during the warm period. After Romanian Standard (RMO 188/2002, updated 352/2005), the maximum allowed Ni concentration in wastewater is 500 µg/l. Half of the sampled mine water exhibited Ni concentrations below the maximum value imposed by the Romanian Legislation and the other half (S5, S7, S9, S25), above the maximum value. In surface waters, Ni concentration shows little seasonal variation for most of the samples and most of the points follow the same trend (Figure 3.5.5). The variation is stronger especially in S2, S4, S16, S28, with water intake from several sources. RMO 161/2006 is setting up five classes of surface water quality based on their properties. Based on the permissible limits regarding Ni concentration, most of the surface waters were included in the third category (most of them, upstream points) and some were included in the 4th and 5th categories (downstream points). Lakes are classified as surface waters but with stagnant water and the obtained values for this subcategory are compared also with the maximal values imposed by RMO 161/2006. Nickel concentration shows irregular succession of minimum and maximum values, differing from one source to the other (Figure 3.5.5). Higher values were recorded in April 2014 and October 2014 (up to 115.7 µg/l) in S15 and S27. In terms of Ni

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concentration, the lakes have been included in the 3rd, 4th and 5th category of water quality. The Ni seasonal variation in springs and domestic wells is clearly strong from month to month (Figure 3.5.5). According to RMO 458/2002 for drinking water quality standards for Ni, the springs are more appropriate for human consumption than dug wells.

Figure 3.5.5 Seasonal variation of Ni concentrations in streams, lakes, springs, domestic wells and mine water

The highest concentrations of copper (Cu) were recorded in mine water (S5, S8, S9, S10). In mine water, Cu concentration varies from one source to the other and has a constant trend, with one exception being the Cetate Adit (S9), which shows a greater seasonal variation as in the case



of Ni seasonal variation for the same point (Figure 3.5.6). After Romanian Standard (RMO 188/2002, updated 352/2005), the maximum allowed Cu concentration in wastewater is 100 µg/l. The minimum value for Cu concentration in sampled mine water was in S20 (AMD exfiltration Sălişte tailings), February 2014. In surface waters, Cu was found in rather low concentrations. The majority of the sampled surface waters show a constant seasonal variation in Cu

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concentration and most of the points follow the same trend (Figure 3.5.6). Similar to Ni variation, the downstream points (S4, S6, S28) show the greatest seasonal variation and the highest Cu concentration. Cu concentration increases in the autumn period, when the temperatures are still quite high. Based on the permissible limits regarding Cu concentration, most of the surface waters were included in the third category (the upstream points) and three of them were included in the 4th and 5th category (polluted waters). In lakes, Cu concentration has the same pattern, showing a maximum during the autumn period, as in the case of surface waters. Based on the permissible limits of Cu concentration the lakes are classified in the 1st, 2nd and 3rd category for water quality. Copper was found in very low concentration in springs and dug wells, and according to RMO 458/2002 for drinking water quality standards, all these source of drinking water are potable, by respect to Cu. The variation of Cu concentration in springs and domestic wells follows more or less the same pattern during the entire sampling period (Figure 3.5.6).

Very high zinc (Zn) concentrations were found in all mine waters. The highest Zn concentration is constant throughout the year in S9 (Cetate Adit). In general, Zn concentrations show little seasonal variation but vary from one source to the other (Figure 3.5.7). A slow decrease in concentration was recorded in July, September and October 2014. After Romanian Standard (RMO 188/2002, updated 352/2005), the maximum allowed Zn concentration in wastewater is 500 µg/l. The lowest Zn concentrations, bellow the maximal imposed value, were recorded on Cetate Dump 2 (S7), during almost the entire sampling period, and in S20, only at the beginning of 2014. Surface waters show the largest variation of Zn concentration, but the variation pattern differs from one source to the other (Figure 3.5.7). Vârtop (S1) is supposed to be the cleanest river while it is localized far away from the mining site and S4 collects all the waste water coming from the mining site. As in the case of Ni and Cu, Zn has the highest concentration in downstream points. The permissible limits regarding Zn concentration classify the surface waters in all categories. In lakes, the seasonal variation of Zn concentrations is more or less constant, and most of the lakes follow the same pattern. According to the RMO 161/2006 for Zn concentration, lakes can be classified as almost clean waters (1st and 2nd class). Zn concentration in springs and domestic wells is very low when compared with the maximal value imposed by the Romanian Legislation (5000 µg/l) and from this point of view, these water sources are clean and potable. The variation of Zn concentration in springs and domestic wells follows the same pattern during the entire sampling period (Figure 3.5.7).

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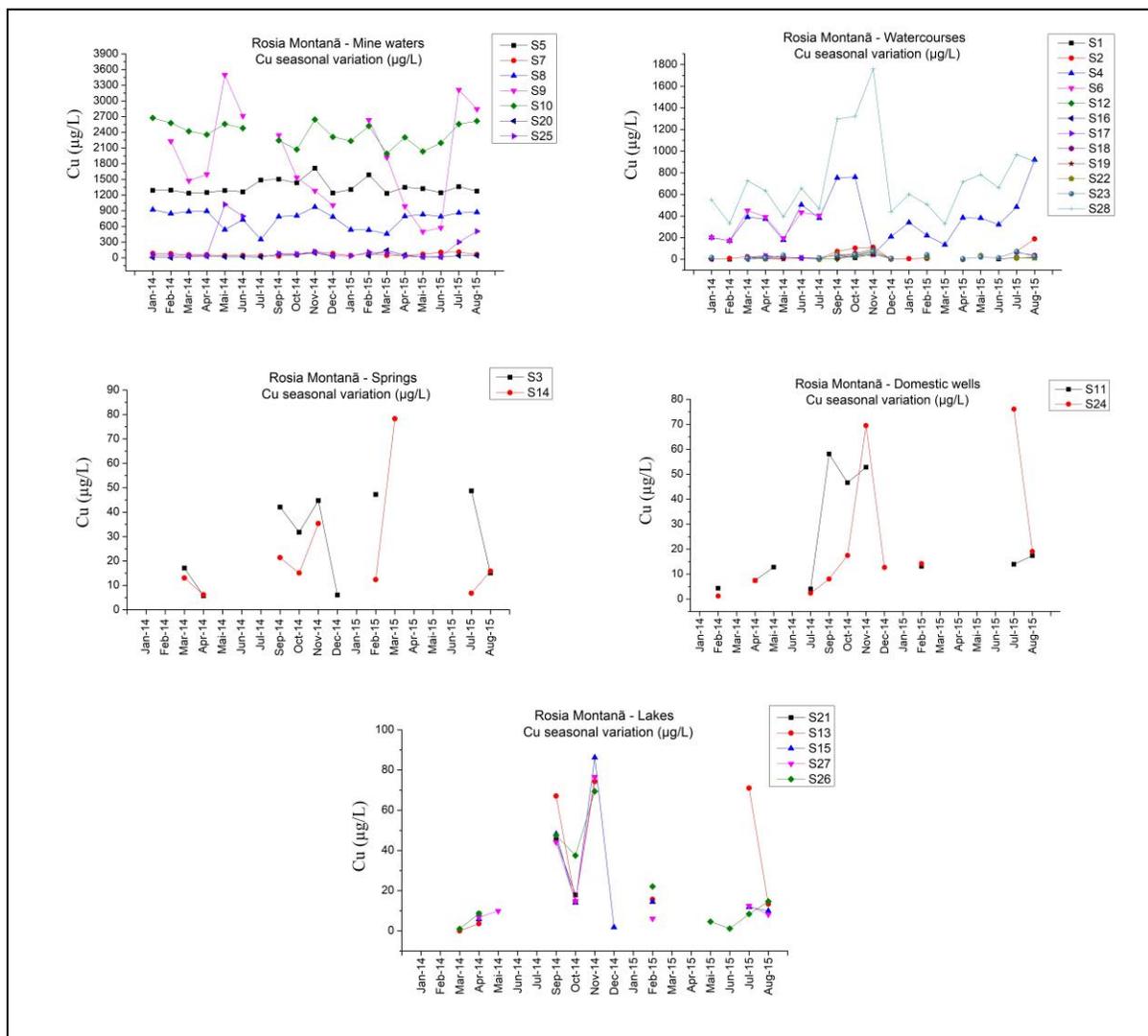


Figure 3.5.6 Seasonal variation of Cu concentrations in streams, lakes, springs, domestic wells and mine waters

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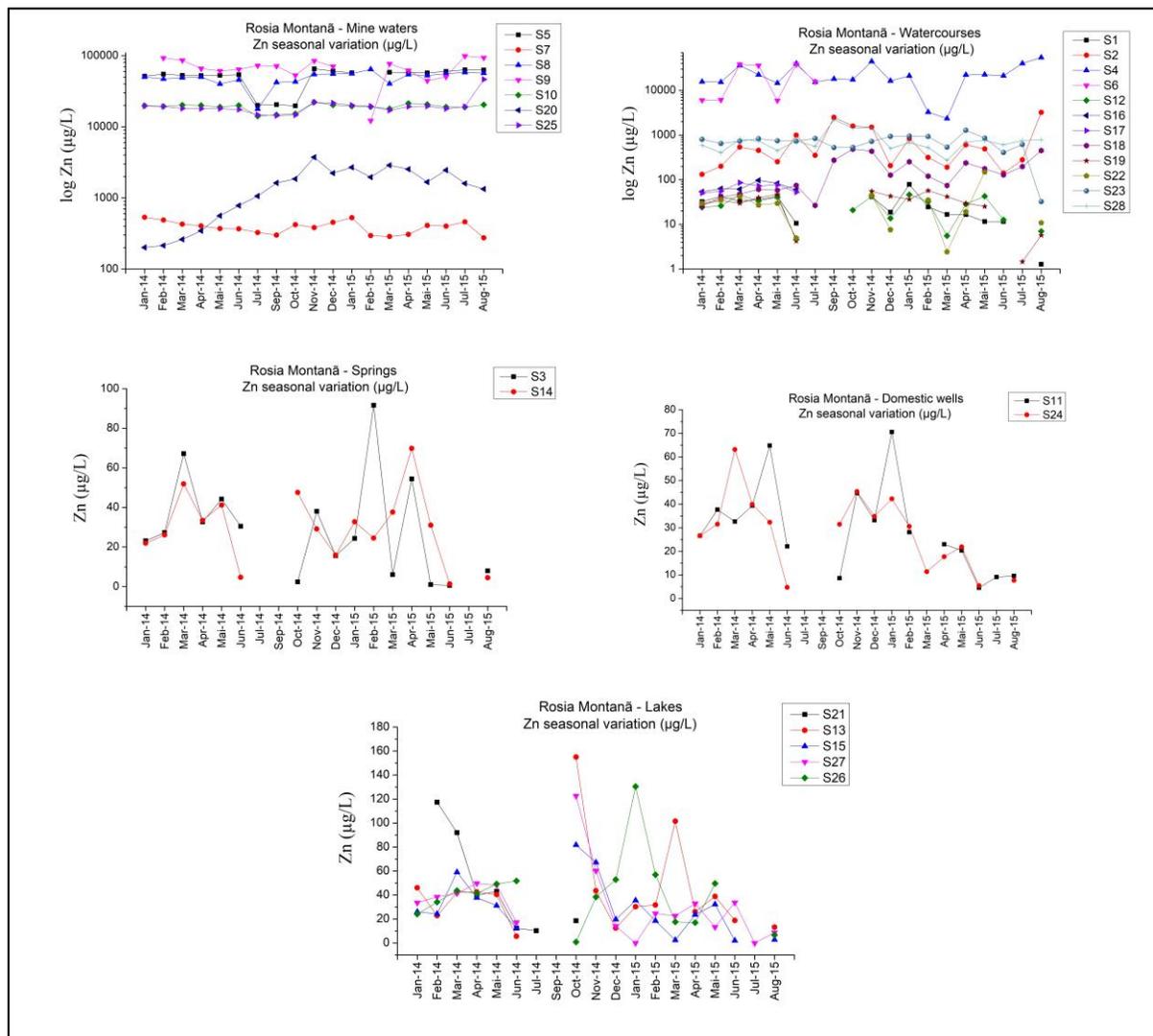


Figure 3.5.7 Seasonal variation of Zn concentrations in springs, lakes, springs, domestic wells and mine waters

Low concentrations of chromium (Cr) were found in all water types. In mine water, Cr concentration has a very constant trend of variation and most of the points follow the same pattern. It seems that S9 (Cetate Adit) is the sampling point with the greatest seasonal variation and with Cr concentration greater than the values recorded in other sampled mine waters (Figure 3.5.8). In surface waters Cr concentration follows, in most of the cases, the same pattern but the seasonal variation is greater (Figure 3.5.8). Moreover, the greater seasonal variation appears in downstream points again. Based on the permissible limits of Cr concentration, most of the surface waters were included in the third category (primarily upstream points) and some were included in the 1st and 2nd category. Lakes also have a constant variation for Cr concentration. Most of the lakes follow the same pattern, with one exception being Brazi Lake, which shows a maximum

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from January to June 2014 (up to 66.42µg/l). In the other months, from July 2014 to August 2015, the trend of variation is similar to the other lakes. According to the RMO 161/2006, in terms of Cr concentration, lakes can be classified in the 1st, 2nd and 3rd quality classes. The seasonal variation of Cr concentration in springs and domestic wells is more or less the same (Figure 3.5.9). Cr was found in low concentration in springs and dug wells and according to RMO 458/2002 for drinking water quality standards for Cr, all these sources of drinking water are potable.

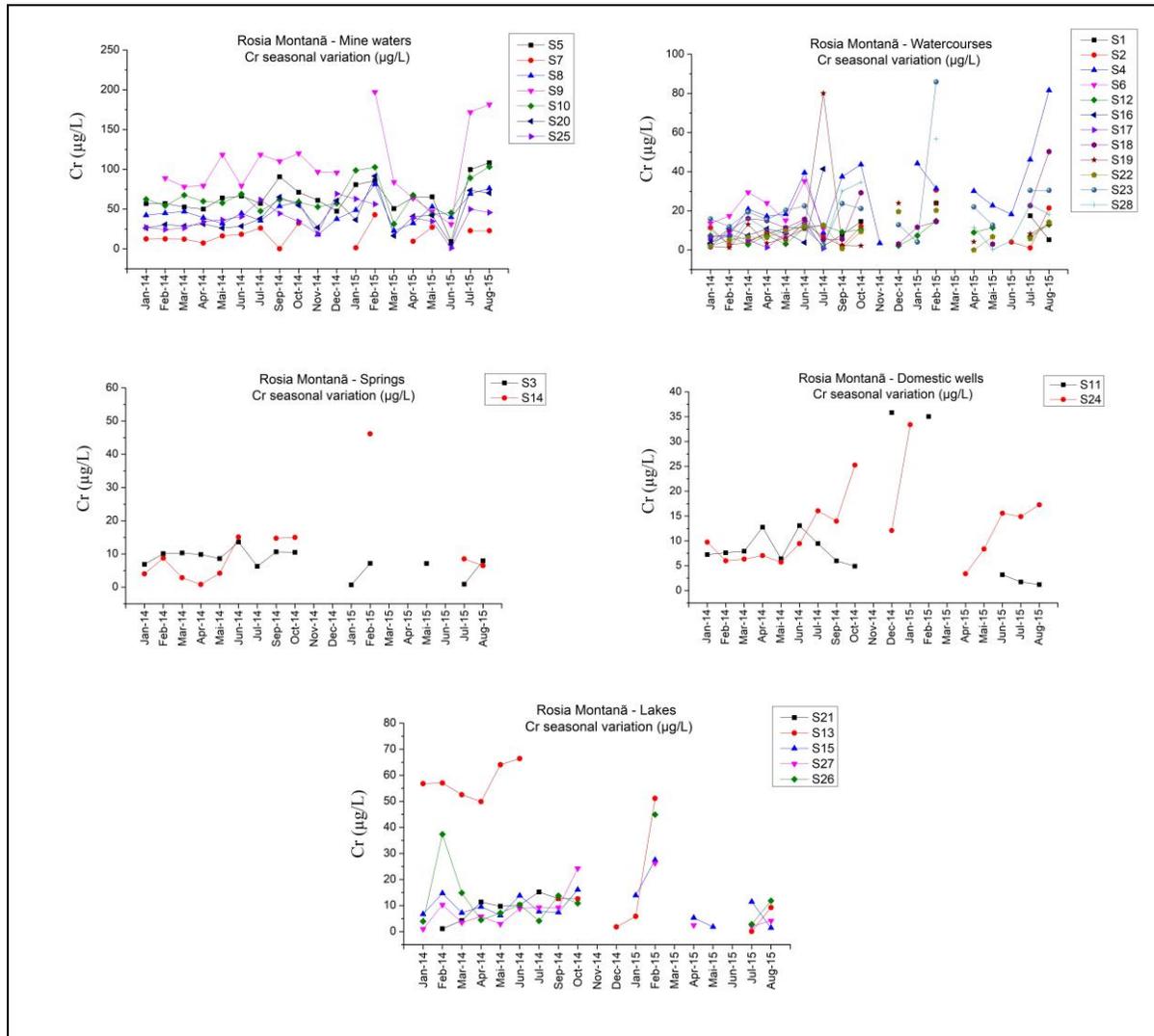


Figure 3.5.8 Seasonal variation of Cr concentrations in surface waters, lakes, springs, domestic wells and mine water

In all water sources the variation of Cd concentration has the same pattern, showing a maximum in November 2014, January 2015, March 2015, July 2015 and August 2015. The highest concentrations were recorded in mine water (S5, S8, S9), up to 1093 µg/l. In mine water, Cd

concentration varies from one source to the other and follows the same pattern, with the exception of S9 (Cetate Adit), which shows the greatest seasonal variation as in the case of all the other studied metals for this point. After Romanian Standard (RMO 188/2002, updated 352/2005), the maximum allowed Cd concentration in wastewater is 200 µg/l. Cetate Adit clearly exceeds this maximum value (Figure 3.5.9), while S5 and S8 are approximately on the maximal line. Surface water shows larger variation of Cd concentration, but the variation pattern is constant (Figure 3.5.9). The recorded Cd concentrations range from 0.3 µg/l (S23, April 2014) to 284.2 µg/l (S4, August 2015). Again, the highest values were recorded in downstream points. Based on the permissible limits regarding Cd concentration, most of the surface waters and the lakes were included in the 2nd, 3rd, 4th and 5th category. In springs and dug wells Cd concentration follows, in most of the cases, the same pattern, but the seasonal variation is greater (Figure 3.5.9). According to RMO 458/2002 for drinking water quality standards, most of the wells and springs exhibited high relatively high Cd concentration.

In general, Pb concentration varies from one source to another and has a clearly strong seasonal variation, although it follows the same pattern (Figure 3.5.10). Higher Pb concentrations were recorded during the warm period for all water types. In mine water, greater seasonal variation was observed for S5, S9, and S20. After RMO 188/2002, updated 352/2005, the maximum allowed Pb concentration in wastewater is 200 µg/l. During the warm period, S5, S9, S20,, and S25 exceeded the maximum imposed value. In surface waters, Pb concentration has a high seasonal variation (Figure 3.5.10). Moreover, the greater seasonal variation and higher values appear in downstream points again (Roşia and Corna streams). Based on the permissible limits regarding Pb concentration, most of the surface waters and the lakes were included in the 2nd, 3rd, 4th and 5th category. In springs and dug wells, Pb concentration follows, in most of the cases, the same pattern, but the seasonal variation is greater (Figure 3.5.10). According to RMO 458/2002 for drinking water quality standards, all these sources of drinking water exhibited high Pb concentration (most of the concentrations above the maximum limit of 10 µg/l). Springs and dug wells exhibited maximal concentrations during the year of 2014, while during 2015, the concentration decreased.

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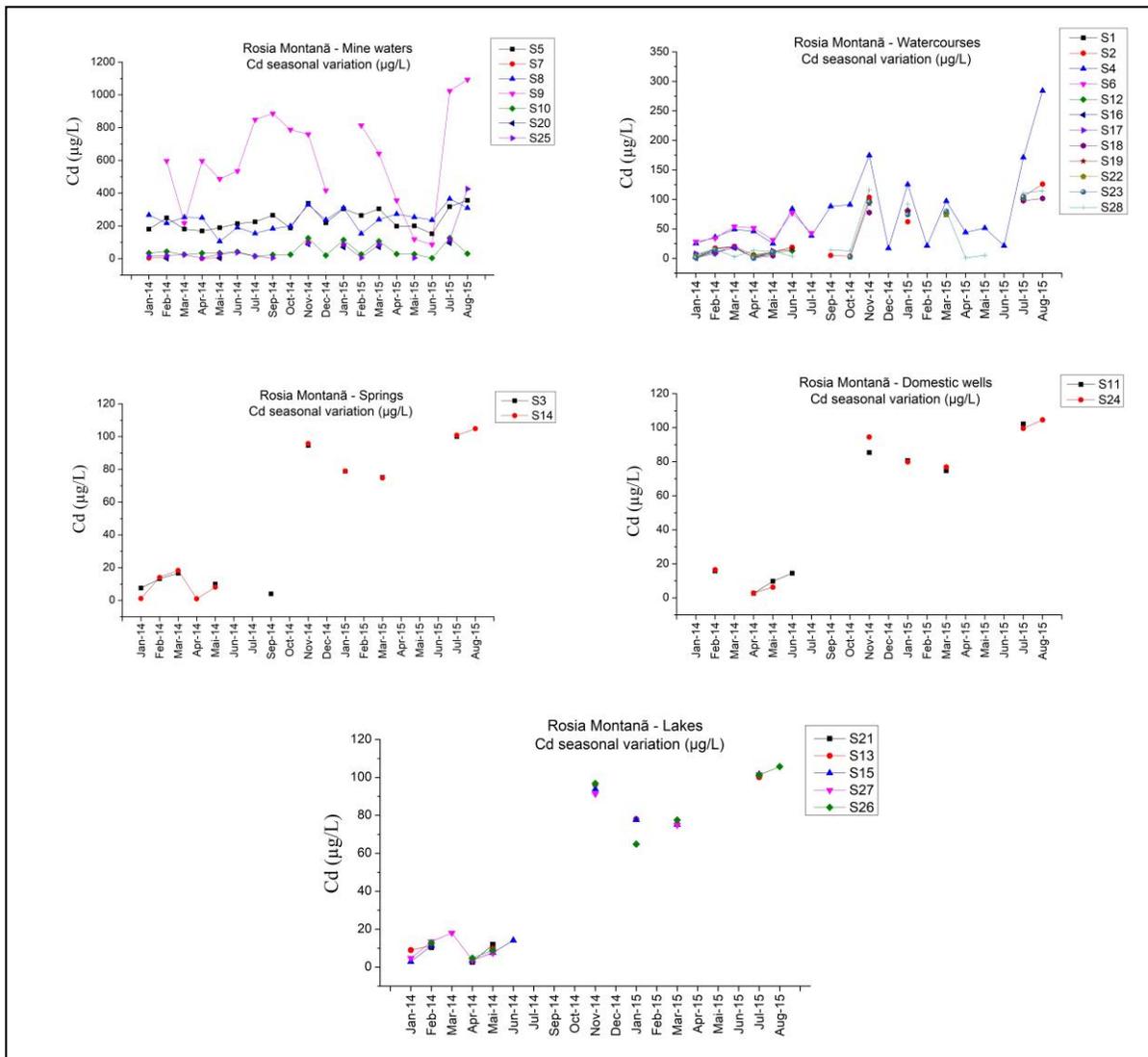


Figure 3.5.9 Seasonal variation of Cd concentrations in surface waters, lakes, springs, domestic wells and mine water

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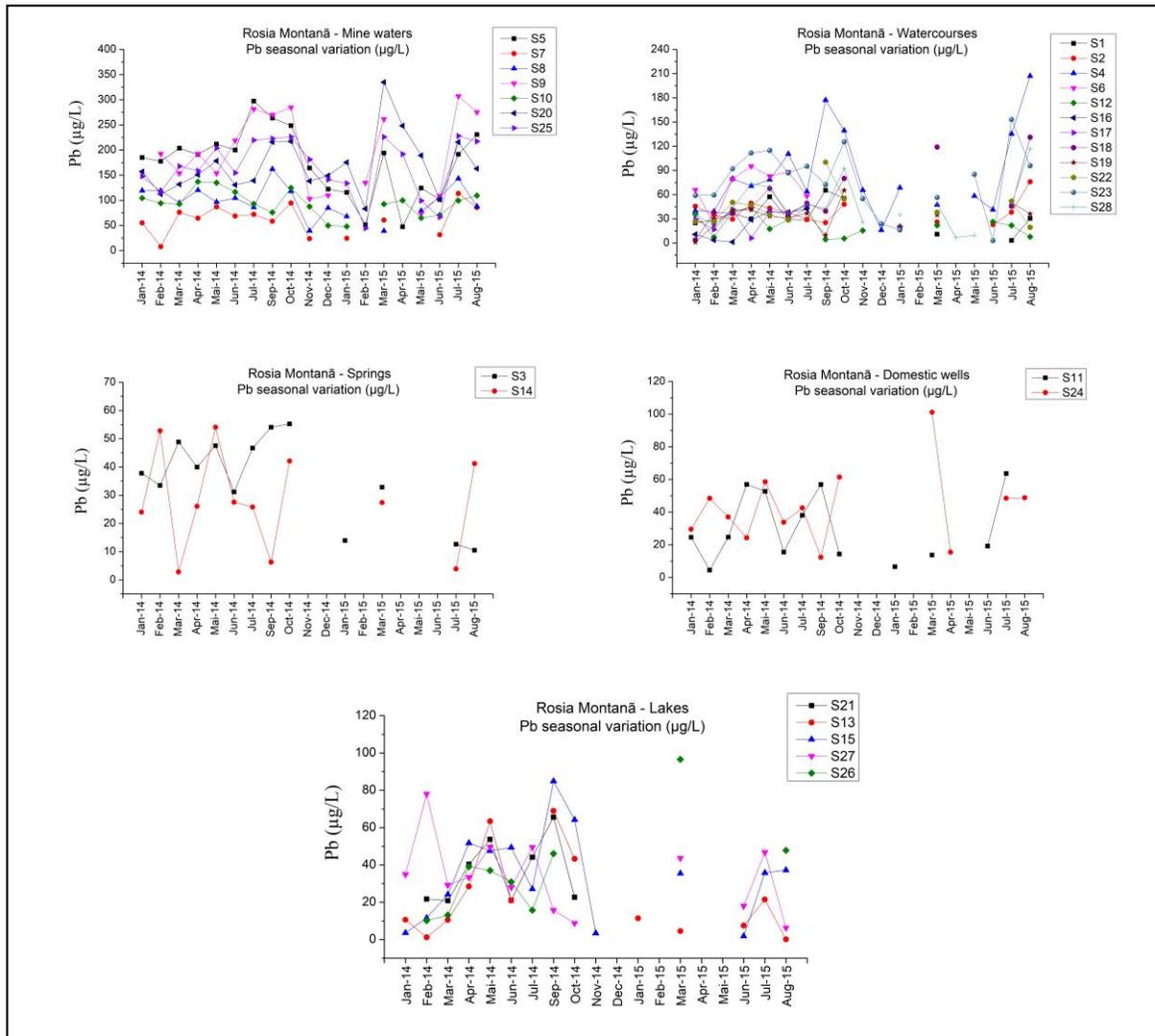


Figure 3.5.10 Seasonal variation of Pb concentrations in surface waters, lakes, springs, domestic wells and mine water

Table 3.5.2 Summary of the distribution of t, pH, TDS, EC, Ni, Cu, Zn, Cr, Cd, Pb, $\delta^{18}\text{O}$, $\delta^2\text{H}$ and major ions content of waters from the Roşia Montană mining area

	T°C	pH	EC ($\mu\text{s}/\text{cm}$)	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Cl (mg/L)	NO3 (mg/L)	SO4 (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Ni ($\mu\text{g}/\text{L}$)	Cu ($\mu\text{g}/\text{L}$)	Zn ($\mu\text{g}/\text{L}$)	Cr ($\mu\text{g}/\text{L}$)	Cd ($\mu\text{g}/\text{L}$)	Pb ($\mu\text{g}/\text{L}$)
Watercourses (n=12)																		
Mean value	9	6.5	518.74	-9.90	-67.90	10.3	7.8	649.7	9.3	15.8	25.2	106.40	89.60	197.35	3707	14.84	47.77	49.1
Min. value	0.1	2.33	73.90	-11.40	-73.90	1.2	0.2	10.1	0.6	2.6	3.6	3.60	2.57	0.55	1.28	0.26	0.3	1.17
Max. value	22.5	8.49	2600	-8.00	-56.60	102.3	67.8	4959	85.4	78.6	1076	1076	653.4	1758	54713	85.89	284.2	207
Std. dev.	5.5	1.69	470.31	0.50	3.20	13.2	10.5	1005	10.6	12.7	135	135.00	94.54	310.40	9682	14.63	48.11	35.55
Domestic wells (n=2)																		
Mean value	9.7	6.53	299.26	-9.80	-68.00	4.2	5.6	259	11.7	14.3	78.5	78.50	29.07	22.93	28.82	11.90	54.16	36.67
Min. value	4.7	5.51	81.40	-10.80	-73.40	1.2	0.3	12.6	6.6	6	2.6	2.60	4.58	1.21	4.57	1.2	2.65	4.49
Max. value	14.6	7.46	703.00	-8.90	-63.00	8.3	17.2	613.2	71.3	90.5	220.7	220.70	79.65	76.07	70.57	35.82	104.6	101.1
Std. dev.	2.8	0.33	200.16	0.40	2.20	2	5.6	274	12.7	16.9	73	73.00	20.41	23.524	17.32	9.312	41.50	22.6
Springs (n=2)																		
Mean value	9.5	7.29	185.52	-10.50	-71.70	1.9	2.3	17.2	6.7	5.1	34.5	34.50	23.47	25.71	29.39	9.487	47.23	31.95
Min. value	0.0	6.62	59.20	-11.50	-75.20	0.4	0.1	6.1	4.4	2.7	2.6	2.60	1.01	5.77	0.61	0.72	0.97	2.84
Max. value	18.1	7.89	350.00	-10.10	-69.50	4.9	15.1	35.8	11.5	11.4	66.3	66.30	73.81	78.26	91.61	46.15	104.8	55.27
Std. dev.	3.4	0.37	77.53	0.30	1.70	1.3	3.8	9.4	2.2	2.5	19.3	19.30	20.02	19.98	21.89	8.716	42.00	16.61
Mine waters (n=7)																		
Mean value	8.6	3.48	2308	-10.10	-68.90	73	40.1	9011	16.4	49.9	533.2	533.20	588	932.63	29178	54.98	212.46	139.13
Min. value	0.7	1.96	198.50	-11.40	-73.20	0.4	1.9	420.7	0.3	1.9	24.5	24.50	53.35	3.69	201.2	0.95	1.21	7.81
Max. value	21.9	6.14	6236	-9.20	-62.10	2274	85	79618	94.9	188	2314	2314	2708	3499	98929	197.2	1093	334.7
Std. dev.	4.6	1.04	122.09	0.40	2.30	348.8	32.2	13423	19.4	32.7	470.4	470.40	508	938.07	26396	33.67	234.8	69.50
Lakes (n=4)																		
Mean value	11.8	7.57	131.06	-8.40	-61.50	4.4	2.2	32.6	4.1	6.4	23.2	23.20	35.26	25.49	38.5	15.8	45.15	32.85
Min. value	0.0	5.84	20.40	-11.60	-80.50	0.4	0.2	3.6	0.5	1.9	1.9	1.90	1.5	1.02	0.82	0.99	2.65	1.25
Max. value	29.1	8.98	282.00	-2.60	-32.10	17.4	15.4	78.8	8.5	20.1	48.7	48.70	115.7	86.25	155	66.42	105.7	96.57
Std. dev.	8	0.48	50.04	1.80	9.90	3.5	3.3	18.9	2.2	3.7	11.6	11.60	25.11	25.65	30.91	17.35	41.17	22.16

3.5.2 The Isotopic composition of waters

3.5.2.1 $\delta^2\text{H}$ and $\delta^{18}\text{O}$

In order to draw the local meteoric water lines, two precipitation collectors were installed at Rosia Montana and at Cluj-Napoca. The sampling has followed the procedure recommended by IAEA. The Rosia Montana LMWL has been used for the further interpretations of the isotopic data obtained for the four types of water investigated in the study: streams, lakes (artificial ponds), groundwater (wells/springs) and mine waters from the mining area.

The obtained local meteoric water lines for Cluj-Napoca and Rosia Montana are falling close to Craig's GMWL (1961). The local CJ line is located closer to the global line, while the local RM line is located to the left side of the global line (Fig. 3.5.11). The Roşia Montană and Cluj-Napoca precipitation were found to have intercepts of 11.722, and 11.287 respectively, which are slightly higher than that of the GMWL. The correlation between oxygen and deuterium is 0.995 at Roşia Montană and 0.997 at Cluj-Napoca.

Linear correlation between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicates that all water sources belong to the meteoric cycle. In the case of lakes, the trend of evaporation is visible. The regression equation of all waters in Roşia Montană is:

$$\delta^2\text{H} = 4.86 \delta^{18}\text{O} - 20.12.$$

The slope of the regression line for the surface water from the study area has a value of 6.03.

The seasonal variation of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values differ from one source to another, but for each source the variation patterns of the two isotopes are analogous (Figure 3.5.12). All water categories are strongly affected by seasonal variation suggesting not very well mixed systems (they are open systems) and fast flow recharge pathways. Less seasonal variation occurs in the mine water from S5 (714 Adit) which is more or less a homogeneous system and which collects infiltration from the outside system. A similar process takes place in one spring, S3 (RO 11). During the cold season, for both years of sampling, the surface waters have a low and more or less constant isotopic composition (due to contribution also from snow melt), while during the warm season, enrichment in heavy isotopes takes place due to the heavy rain falls (July 2014). In the lakes an intensive and delayed evaporation process occurs during the warm season. For the S24 (C120 domestic well), the isotopic ratios are more constant, grouped in a narrow range, and have a slight tendency of increase during the sampling months. On the other hand, S11 (RO 78 domestic well) shows a strong seasonal variation.

The artificial lakes show a different behaviour due to the intense evaporation during summer.. Cartus Lake is the smallest one from the mining area and with the lowest volume of water. This lake has a fairly pronounced trend of evaporation, caused by several factors: area and volume of the pond, the depth, but also the presence of vegetation. Corna Lake has a slight trend of

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evaporation which is not as pronounced as in the case of Cartus Lake. In Tau Mare and Tau Brazi, evaporation is less influential due to the surrounding vegetation and morphology (Brazi Lake is surrounded by dense vegetation that blocks most of the solar radiation, limiting evaporation, and Tau Mare is the biggest and deepest lake).

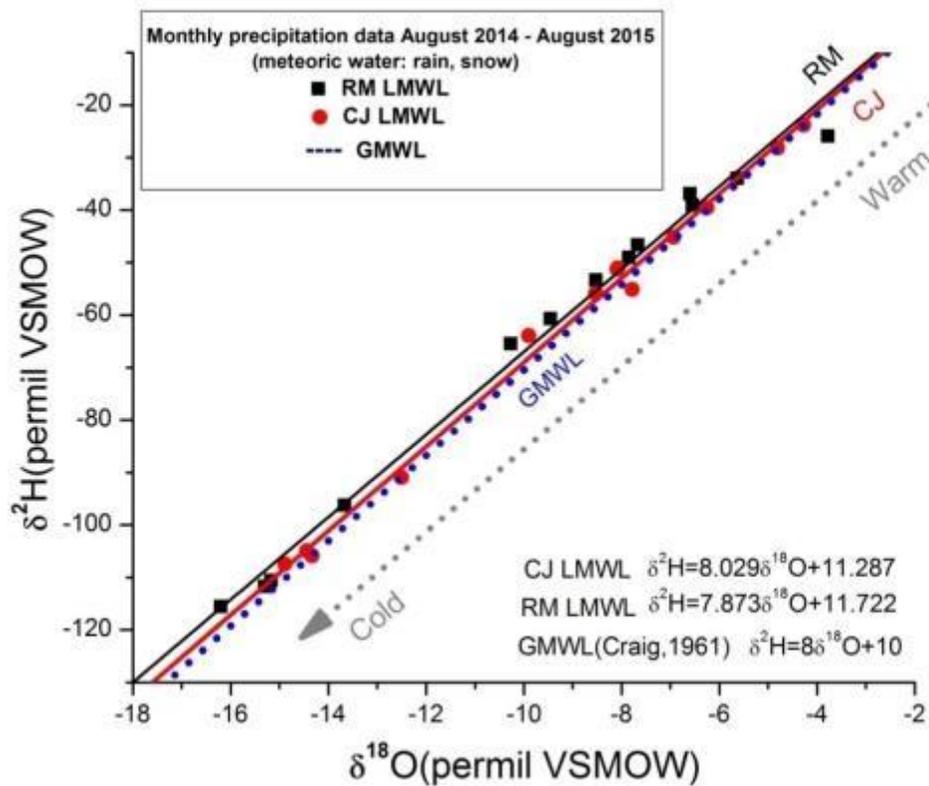


Figure 3.5.11 Plot of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ for precipitation samples. Local meteoric lines position (Cluj-Napoca and Roşia Montană) against the global meteoric line (Craig, 1961)

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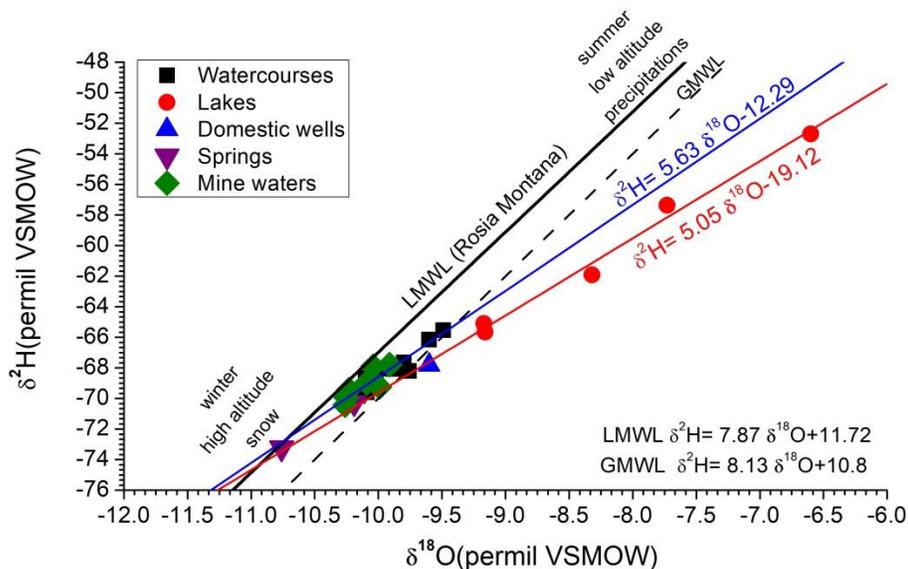


Figure 3.5.12 The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$. All displayed values are the mean values for one year of observation.

The mine water has the characteristics of winter precipitation and of higher altitude precipitation, showing the lowest concentrations of deuterium and ^{18}O . This finding reflects the major influences of snow-melt and run-off in the late winter on the recharge of mine water.

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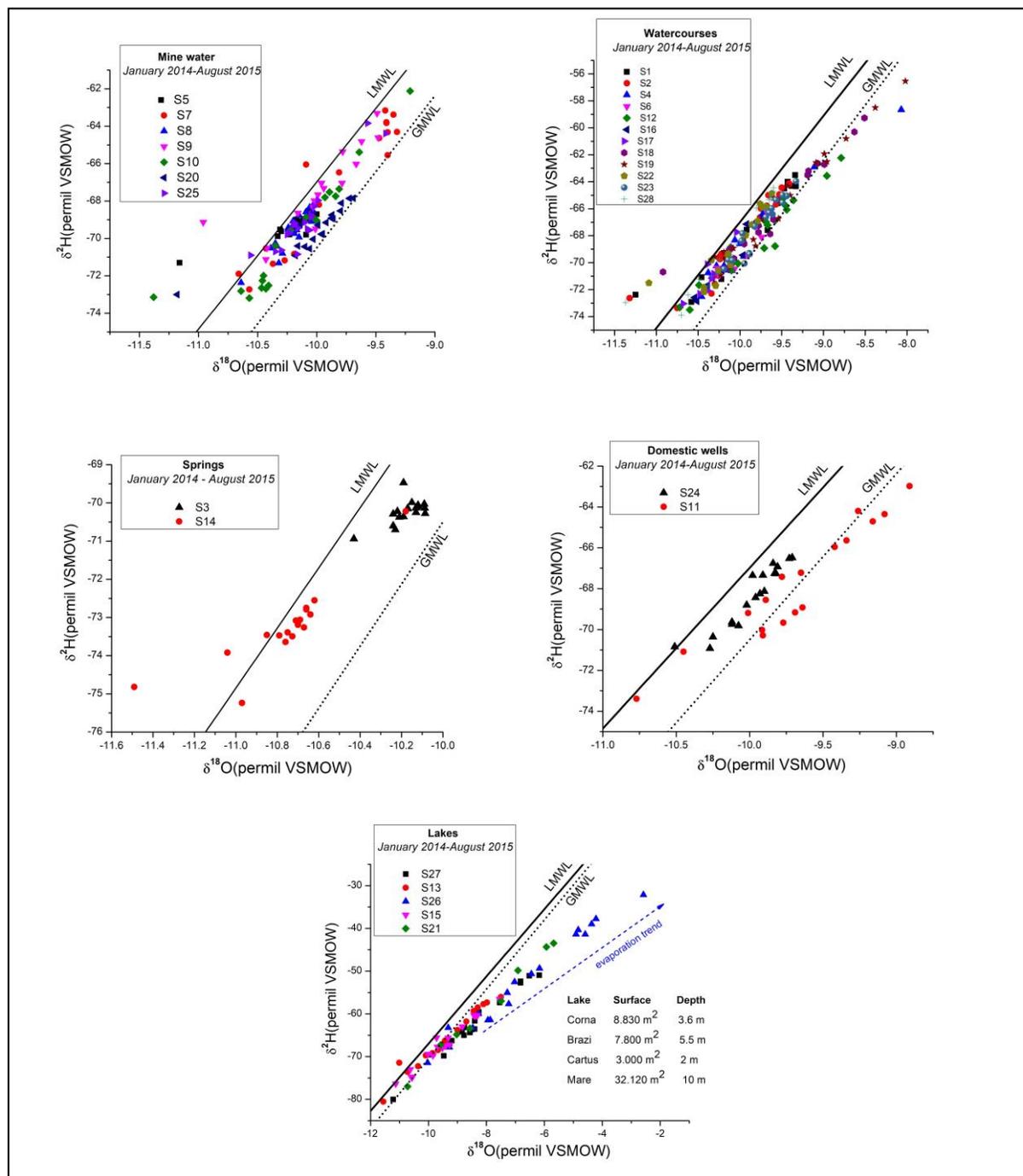


Figure 3.5.13 Plot of $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ in all types of waters for all campaigns of observation. LMWL – local meteoric line for Roşia Montană, GMWL – global meteoric water line

3.5.2.2 Sulphur isotope characterization

Sulphur isotopes of SO_4 may be used to help further distinguish mine impacts from natural background conditions. A plot of $\delta^{34}\text{S}\text{-SO}_4$ against SO_4 concentration shows two distinct groups of samples (Figure 3.5.15a). The first group includes three samples uniquely depleted in $^{34}\text{S}\text{-SO}_4$, ($\delta^{34}\text{S}$ compositions ranging from -10.2 to -6.1‰), and some of the lowest observed SO_4 concentrations. Based on their low SO_4 to major cation concentrations, low metals, and near neutral pH values, these sites have not been impacted by mining. The relatively ^{34}S depleted signatures of these samples may directly reflect influence from a local, non-mine related SO_4 source, or oxidation-reduction cycling of mobile sulphur. The second group includes all other sampled sites (both samples identified as mine impacted and natural waters), and is more enriched in $^{34}\text{S}\text{-SO}_4$, with $\delta^{34}\text{S}$ compositions ranging from 6.0 to -2.1‰. Within this group sites identified as mine impacted based on geochemical parameters described above exhibit a weak logarithmic correlation ($R^2 = 0.57$) between $\delta^{34}\text{S}\text{-SO}_4$ and SO_4 concentration which potentially reflects a two-part mixing relationship (Fraure & Mensing 2005). In contrast, the samples defined as natural waters show no correlation between $^{34}\text{S}\text{-SO}_4$ and SO_4 concentration.

Evidence for two-part mixing in mine impacted water not present in natural waters may indicate that mining-related SO_4 exhibits an isotopically discrete signature. In this case, the negative slope of $^{34}\text{S}\text{-SO}_4$ and (SO_4) correlation indicates that the mining-related SO_4 source is relatively depleted in ^{34}S .

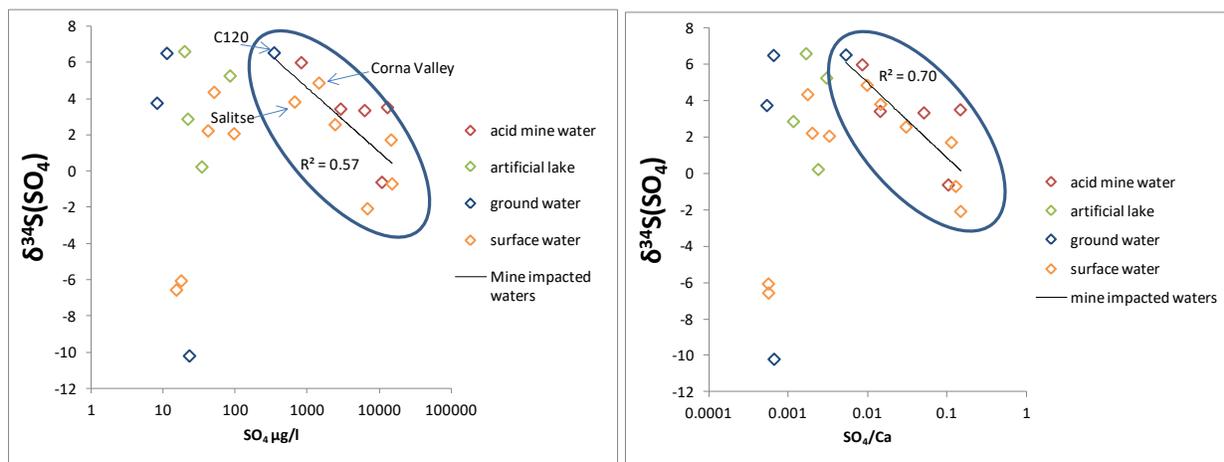


Figure 3.5.14 $\delta^{34}\text{S}\text{-SO}_4$ as a tracer of mine derived SO_4 . A) $\delta^{34}\text{S}\text{-SO}_4$ vs SO_4 concentration. B) Comparison of $\delta^{34}\text{S}\text{-SO}_4$ to $(\text{SO}_4)/(\text{Ca})$ concentration. The circled samples are those implicated as mine impacted sites by geochemical characterization. The trend lines include only the circled samples

By normalizing SO_4 to Ca concentration, the correlation with $\delta^{34}\text{S}\text{-SO}_4$ among the mine impacted waters improves ($R^2 = 0.70$) (Figure 3.5.15b). The improved correlation suggests that a calcium-containing sulphur source (e.g. gypsum or anhydrite) contributes sulphur to solution with a $\delta^{34}\text{S}$ -

SO₄ different than the negative $\delta^{34}\text{S-SO}_4$ end member driving the two-part mixing relationship depicted by the best fit line in Figure 3.2.35a. Normalizing SO₄ concentration by Ca reduces the spread along the x-axis resulting from calcium sulphate derived SO₄. Therefore, while SO₄ input from a discrete sulphur source appears to result in a systematic depletion in ³⁴S with increasing SO₄ concentration, dissolution of Ca sulphate minerals also appears to contribute SO₄ of more isotopic variability to solution.

3.5.2.3 *Isotopic variation of strontium in waters across the Roşia Montană site*

Sr isotopes at the Roşia Montană site provide insight to water origins, mixing, and dilution. In order to utilize the Sr isotope composition it is first necessary to understand the source of isotopic variation. Observed Sr isotope compositions span a range from 0.70549 to 0.71467. The samples with the lowest ⁸⁷Sr/⁸⁶Sr ratios were collected from sites within volcanic breccias which drain andesite outcrops to the north of the mine's open pits. The samples with the highest ⁸⁷Sr/⁸⁶Sr ratios were observed in close proximity to the open pits, and may reflect the mineralized dacite host rock. Groundwater and artificial lake waters collected from within volcanic breccias and undifferentiated marine sediment lithologies exhibited intermediate ⁸⁷Sr/⁸⁶Sr compositions (Figure 3.5.17). Therefore, while the lowest and highest observed ⁸⁷Sr/⁸⁶Sr compositions can be attributed to source lithology, intermediate compositions likely reflect either a) influence from isotopically intermediate lithologies, b) mixing of waters sourced from isotopically distinct end member lithologies, or c) some combination of both a and b.

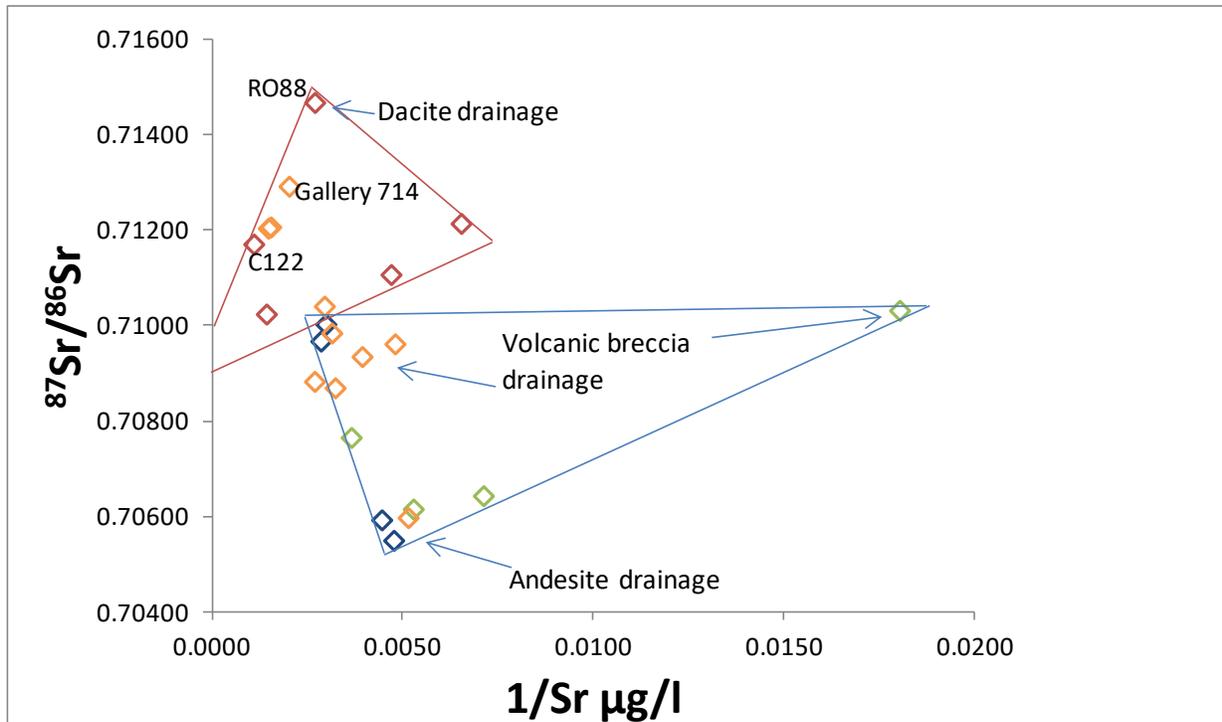


Figure 3.5.15 Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ to $1/(\text{Sr})$. Blue lines illustrate possible range of $^{87}\text{Sr}/^{86}\text{Sr}$ and (Sr) water types influencing unimpacted waters originating from andesitic and volcanic breccias lithologies. Red lines indicate observed range of $^{87}\text{Sr}/^{86}\text{Sr}$ and (Sr) water types influencing mine impacted waters.

The $^{87}\text{Sr}/^{86}\text{Sr}$ composition observed in the sample from Gallery 714 is elevated and similar to those observed at sample locations in and around the mineralized dacite host rock. Gallery 714, however, is located approximately 1 km west of the dacite intrusions, within the volcanic breccias, from which most water samples exhibit a low to intermediate $^{87}\text{Sr}/^{86}\text{Sr}$. Therefore, the notably high $^{87}\text{Sr}/^{86}\text{Sr}$ observed at Gallery 714 suggests the water originates as drainage from the mine site and suggests the rapid channelling of mine water to this point via adits.

The isotopic composition of Sr observed at Gallery 714 can also be used to estimate the mixing of waters contributing to the discharge from this adit. However, the accuracy of such mixing estimates are dependent on how well the source water end members are defined. The mine water contribution to discharge from Gallery 714 could reasonably be explained by the mixing of waters similar to those observed at the C122 adit and sample site RO88, representative of mine water drainage at different locations across the mine. The Sr composition of water from Gallery 714 is, however, slightly offset from the mixing line between these two points, which could be presumed to result from dilution of mine impacted water by unimpacted waters (Figure 3.5.17). The Sr composition of the diluting, uncontaminated end member may be approximated as the average of Saliste upstream and well C120, which represent surface water and groundwater, respectively, believed to be unimpacted and draining volcanic breccias similar to that surrounding Gallery 714. If the mine water end members are assumed to mix prior to dilution, mixing can be calculated following a sequential, two-part mixing equation, as described in section 2.4.3 (Faure & Mensing 2005). Applying the assumptions described above into equation 3 (Section 2.4.6), 84% of the water discharged from Gallery 714 is derived from the mine (a mixture of 36% water similar to

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that at RO88, and 64% water similar to C122), while the remaining 16% drains from the local, unimpacted breccia.

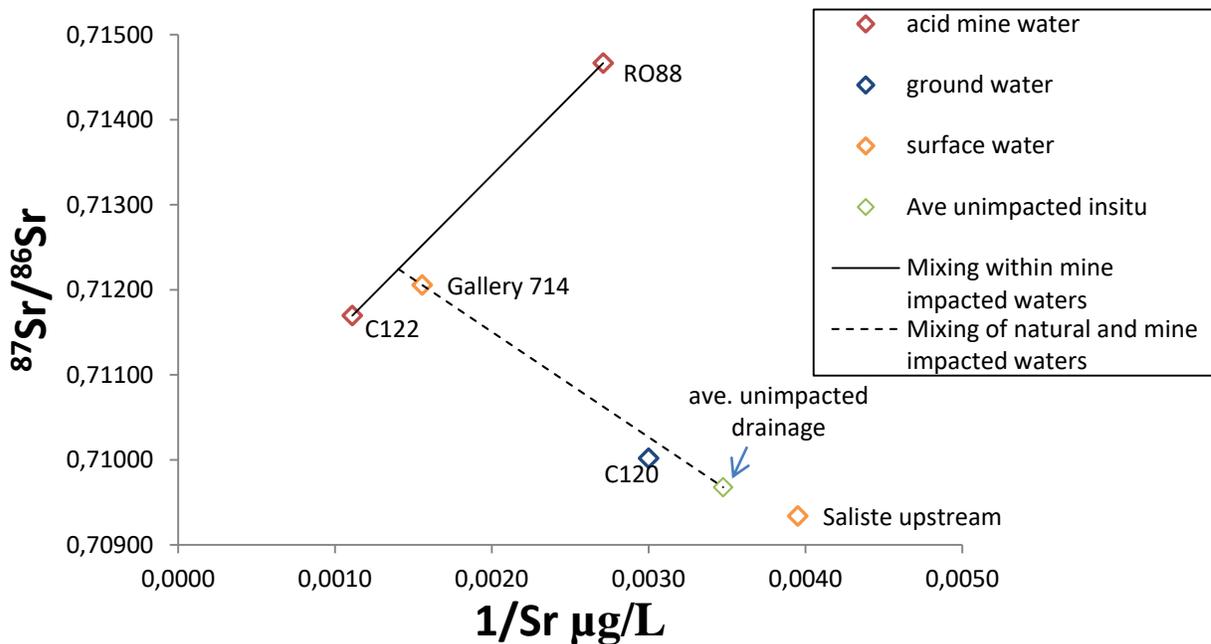


Figure 3.5.16 Mixing estimate for source waters observed at Gallery 714 using ⁸⁷Sr/⁸⁶Sr and (Sr) from hypothetical end members

Sr isotopes can also be applied to estimate dilution of mine impacted waters by comparing Sr composition at Gallery 714 to that observed approximately 1.3 km downstream, from Roşia Valley surface water. Again, a multi-end member mixing calculation can be made. However, in this calculation the unimpacted water end member must provide consideration for the influence of lithologies drained upstream of the mine. To estimate the isotopic signature of the unimpacted water end member, Sr compositions from Roşia upstream, RO43 (spring water), Sălişte upstream, and C120 were averaged (Figure 3.5.18). Mixing between this average unimpacted end member and the mine site end members considered previously (RO88 and C122) indicates approximately 31% of the water at the Roşia Valley surface water site has originated from mining impacted sources, suggesting 63% dilution (from 84% mine impacted water at Gallery 714 to 31% at Roşia Valley) of impacted waters discharged at Gallery 714.

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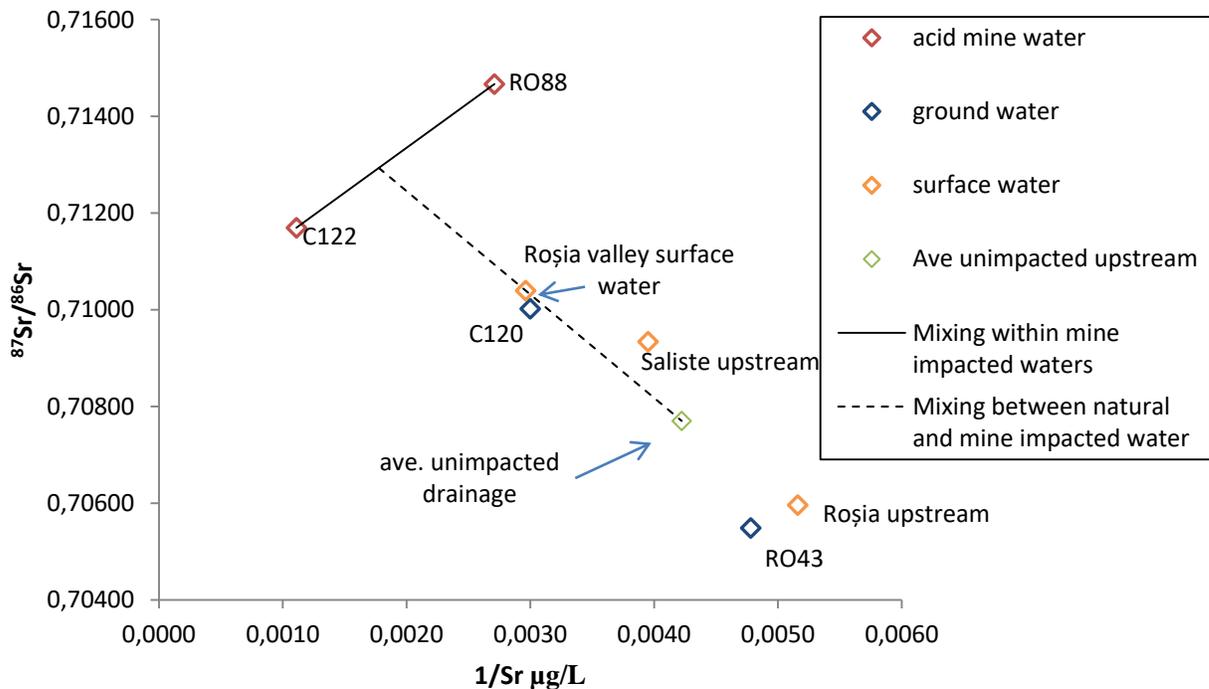


Figure 3.5.17 Estimating attenuation/dilution of mine impacted water based on ⁸⁷Sr/⁸⁶Sr and (Sr) using average isotope-concentration of the different unimpacted water sources

For each of the isotope-based interpretations made above it is important to recognize sources of uncertainty and the potential error associated with given uncertainty in order to both draw conclusions from the data and to inform ongoing sampling strategies. A large source of uncertainty in mixing and dilution estimates is associated with the selection of isotopic end members. For calculations based on Sr, simple end member scenarios were defined following site specific geologic, topographic, and hydrologic conditions. However, the Sr isotope variation within both mine impacted and unimpacted waters suggests the influence of at least three potential isotopic end members influencing both types of waters, as illustrated by the triangles in Figure 3.5.16. Potential end members are defined where the sides of a triangle meet. Accordingly, while the mixing estimate above assumes some influx of unimpacted waters to the water discharging from Gallery 714 (i.e. the selection of an unimpacted end member), the water composition observed at this site could alternatively be explained entirely by mixing of mine impacted waters. Further, the dilution calculated from Gallery 714 to the Roşia Valley surface water is dependent on the estimated unimpacted water end member. The average Sr composition chosen for this end member provides only a rough estimate for the possible composition of mixed waters draining the relevant lithologies, but does not provide consideration for the relative inputs of Sr from these different sources. For example, if mixed unimpacted waters originated primarily from the low ⁸⁷Sr/⁸⁶Sr sources north of the site, the end member used in the calculation above would result in an overestimation of dilution. These examples illustrate how additional site information could inform and improve the application of isotopes in the determination of water source, mixing, and solute attenuation.

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Detailed statistical analysis has been performed for each of the 28 water sources. Seasonal variation of the pH, TDS, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, and heavy metal concentrations were considered. Due to evaporation during warm seasons, which determines the enrichment both in heavy isotopes (D and ^{18}O) and salts, positive correlations between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values vs. TDS values was expected for the surface water and lakes. As an example, for the Roşia River (S4) the correlation coefficient between $\delta^2\text{H}$ and TDS is $r=0.52$ and between $\delta^{18}\text{O}$ and TDS is $r=0.64$ ($n=19$). Similar values for the correlation coefficient were obtained for the points S1, S2, S6, S16, S17, S22, and S28.

In other cases (S12, S18, S19, S23), low correlation coefficients were obtained between the TDS values and the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, indicating relations with the phreatic waters (table 3.5.3). Compared to streams, the lakes (which are stagnant water and more isolated systems) display stronger positive correlation coefficients between these parameters.

For most mine water sources, the correlation coefficient between the TDS values and the $\delta^2\text{H}$ and the $\delta^{18}\text{O}$ values are negative or slightly positive, but without statistical significance. The only exception is the mine water from S7 (Cetate Dump 2) which displays a positive correlation coefficient between the TDS values and the $\delta^2\text{H}$ values (Table 3.5.3) and the $\delta^{18}\text{O}$ values, respectively.

The other underground water sources (springs and domestic wells) display negative or slightly positive correlation coefficients between these parameters, but without statistical significance. There is one exception in the case of S11 (domestic well) which displays weak positive correlations ($p = 0.13$) between TDS and the $\delta^2\text{H}$ ($r=0.36$) (Table 3.5.3) and $\delta^{18}\text{O}$ values ($r=0.42$). Direct recharge from surface waters can explain these correlations. For all types of waters from Roşia Montană mining area, if considered individually, the pH values do not correlate with the TDS values (Table 3.5.4). However, the majority of waters display a weak negative correlation between pH and TDS, excepting the lakes, where the correlation between pH and TDS is a positive one.

Table 3.5.3 Correlation coefficient between ^{18}O , ^2H , pH and TDS for all types of water, individually taken

Correlation coefficient	TDS/ $\delta^{18}\text{O}$	TDS/ $\delta^2\text{H}$	TDS/pH
Surface waters			
Vârtoş	0.6	0.66	0.37
Downstream confluence Roşia river with Abrud river	0.34	0.42	-0.83
Downstream Roşia river	0.64	0.52	-0.41
Downstream 714 Adit	0.51	0.54	-0.49

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Upstream Roşia river	0.1	0.14	-0.02
Downstream confluence Abrud river with Sălişte river	0.86	0.72	0.31
Upstream confluence Abrud river with Sălişte river	0.55	0.67	-0.62
Downstream Sălişte T.M.F.	0.05	0.16	-0.06
Sălişte Gallery	0.09	0.14	0.04
Upstream Sălişte Valley	0.39	0.53	0.14
Corna Valley	0.39	0.25	0
Abruzel Valley	0.36	0.38	-0.25
Domestic wells			
RO 78 dug well	0.42	0.36	-0.25
C 120 dug well	-0.02	-0.1	-0.39
Springs			
RO 11 spring	-0.01	-0.14	-0.45
RO 43 spring	0.18	0.2	-0.09
Artificial Lakes			
Pond Sălişte	0.46	0.48	0.88
Tau Brazi	0.66	0.68	0.49
Tau Mare	0.79	0.75	0.59
Tau Corna	0.42	0.44	-0.01
Tau Cartus	0.57	0.52	0.39
Acid Mine Waters			
Adit 714	0.04	-0.02	-0.43
Cetate Dump 2	0.47	0.45	-0.63
Adit RO 88	-0.14	-0.12	-0.55
Cetate Adit	-0.01	-0.38	0.15
Cetate Dump 1	0	-0.01	-0.07
AMD exfiltration Sălişte tailings	-0.08	-0.05	-0.09
C 122 Adit	0.15	0.1	-0.44

For each of the 28 water sources, statistical correlation analysis was performed on the Cd, Cr, Pb, Cu, Ni, and Zn concentrations, and pH, TDS and EC values. Statistical correlation analysis was performed on the mean values of each parameter computed for each water source from one year of observation. The correlation coefficients are shown in Table 3.2.5.

If all water types are considered together, significant statistical correlations were obtained between Cd, Cr, Pb, Ni, Zn, pH, EC, TDS. In surface waters, almost all metals correlate with each other, except Cu which shows no correlation with other metals. A strong positive correlation was obtained between Ni and Cr ($r=0.913$). This suggests these metals may come from natural input. Ni occurs often in combination with Cr and the two elements have similar transport mechanism, so the positive correlation is normal. Strong significant negative correlations were obtained between pH and all the metals, except for Cd, in the case of which the correlation was still negative but not statistically significant. An inverse correlation between pH and the other parameters such as metals and EC is normal, since a decreasing pH leads to an increase in EC and in metal

concentration. In lakes there is a strong significant correlation between Cu – Cr ($r = 0.953$) and also there is a strong negative correlation between Pb and Cu – Cr.

In mine water, strong correlations were obtained between almost all the metals, excepting Pb (which displays no significant correlations) and Cu that correlates very well with Cr. Cr has a good correlation with Ni, Cu and Zn.

3.5.3 Water quality and issues of concern

The impacts of mining at Roşia Montană mine site are evident in streams intercepting the mining area, and revealed by low pH, elevated SO_4 and metal concentrations (Bird et al. 2005, RMGC 2006). However, where waters are highly buffered, mining impacts may not be immediately evident through decreased pH and metals dissolution, but can be inferred from other parameters. For example, in S18 and S23 pH was near neutral and the metals Zn, Cu, Cd, Pb, Co and Ni, indicators of mine impacts at other sites, were relatively low in concentration. However, SO_4 and Mn at these sites were elevated relative to other waters that have not been impacted by mining (Figure 3.5.19). Elevated Mn concentration in solution may indicate Mn desorption or dissolution from buffering minerals during neutralization of incoming acid (Larsen & Mann 2005). Therefore, where mine impacts to waters with high buffering capacity are not evident based on pH or concentrations of previously defined indicator metals, elevated SO_4 concentrations in combination with geochemical evidence of ongoing acid buffering should also be considered when evaluating potential mine impacts. The standard maximal values were applied on the mean values of the specified parameters for all water sources under study. In the Table 3.5.4., marked values are above the standard limits.

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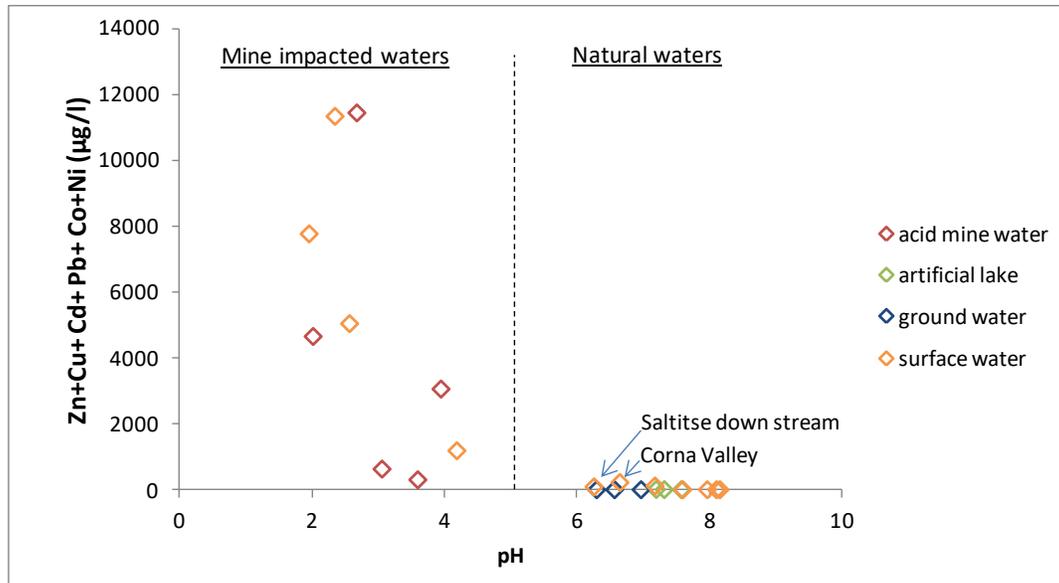


Figure 3.5.18 Defining mine impacts across sample sites from different parameters based on May 2015 sample results. A) Indicator metals vs pH. B) Mn vs SO₄.

Seasonal variation of the $\delta^2\text{H}$ and TDS values of meteoric groundwater, as compared to surface water, provide an important tool to assess underground dynamics. For all the valleys, the seasonal variation patterns of TDS, pH, $\delta^{18}\text{O}$, $\delta^2\text{H}$ and heavy metals reflect a difference between upstream and downstream, due to increasing load from tributaries along the valleys. Naturally the TDS values increase in the downstream direction in all the rivers, with a strongly seasonal variation compared to the upstream point. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ show a similar trend between upstream and downstream sites within the same valley.

For most mine water, the highest TDS values were recorded during the warm season and high levels of precipitation, which enhanced the weathering of the exposed rocks.

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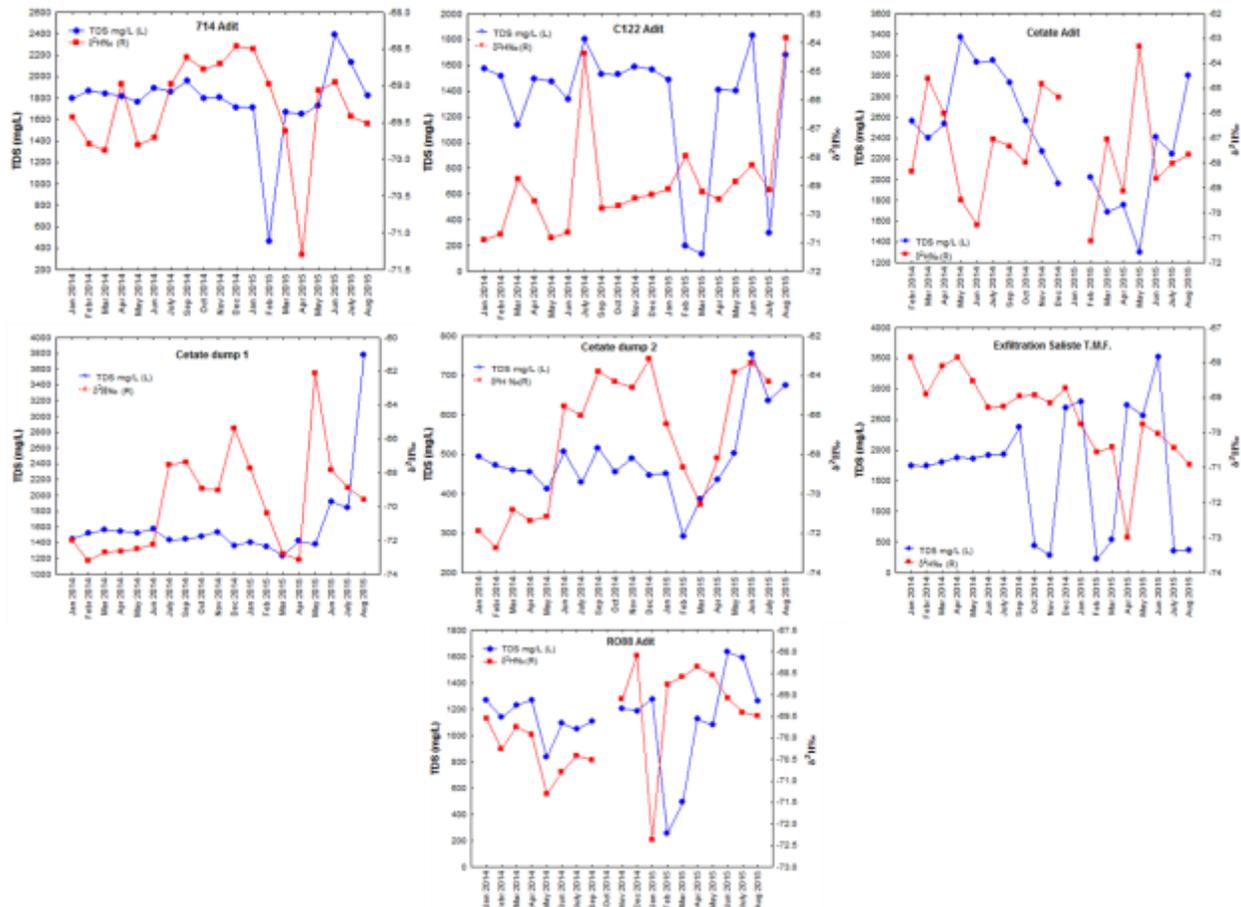


Figure 3.5.19. The seasonal variation of TDS and $\delta^2\text{H}$ in mine waters

Roşia stream is the most representative watercourse within Roşia Montană mining area, as it collects most of the surface water, and mine waters coming from adits, open pits and waste dumps. Roşia stream is the most affected and a five pH units difference between upstream and downstream for pH was observed, which suggests the extent of AMD over the mining area. Hence, downstream of the mining workings, the water is included in the 5th quality class of surface waters according to RMO 161/2006, whereas the upstream is one of the cleanest surface waters at the site. The drop in pH values was the most obvious in August 2015 (pH=2.33) and correlates with the increase in the total dissolved solids, SO_4 content, as well as the heavy metal concentrations (Figure 2.5.21). This is due to extreme evaporation and desorption of the acid iron hydroxide precipitate from the bottom of the stream during very low flow conditions. High concentration of NO_3 , SO_4 , Ni, Cu, Zn Cd, Pb were found in four samples collected in the vicinity of Roşia River and Abruzel Valley (S2, S4, S6 and S28). These values exceeded the standard limits for the 3rd class of water quality and are included in the 4th class. The high metal concentration in Roşia River is also a consequence of numerous points of mine water discharge from Cetate and Carnic open pits and also from the underground works.

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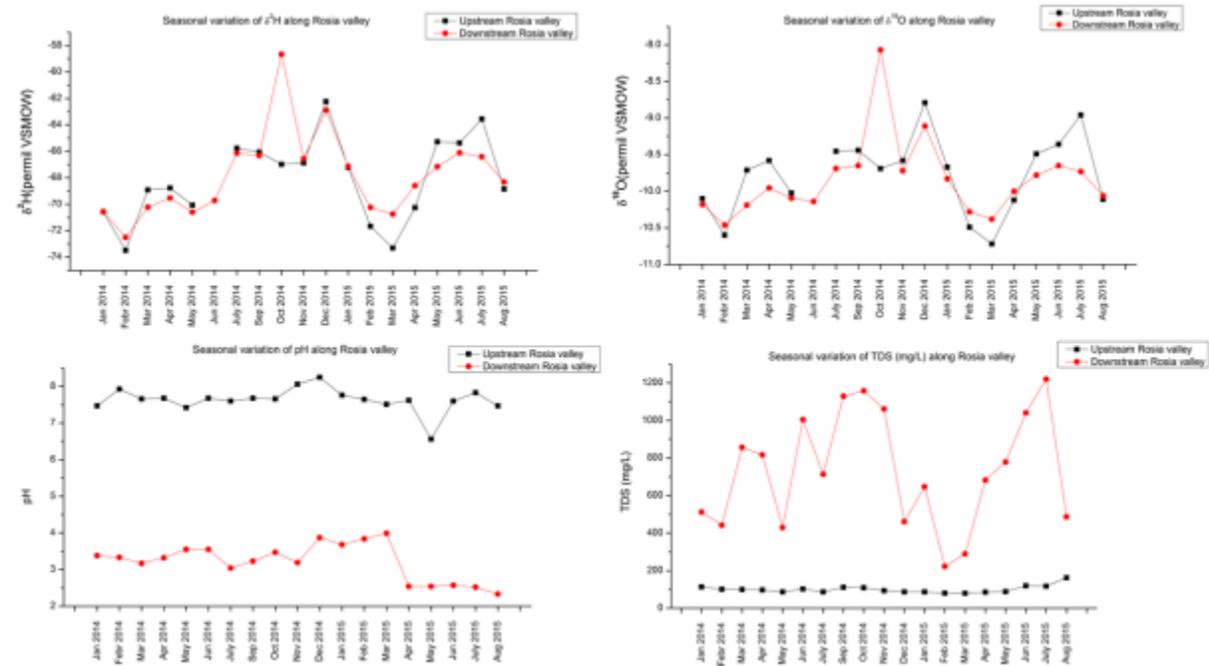


Figure 3.5.20 Seasonal variation of pH, TDS, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values along Roşia Valley

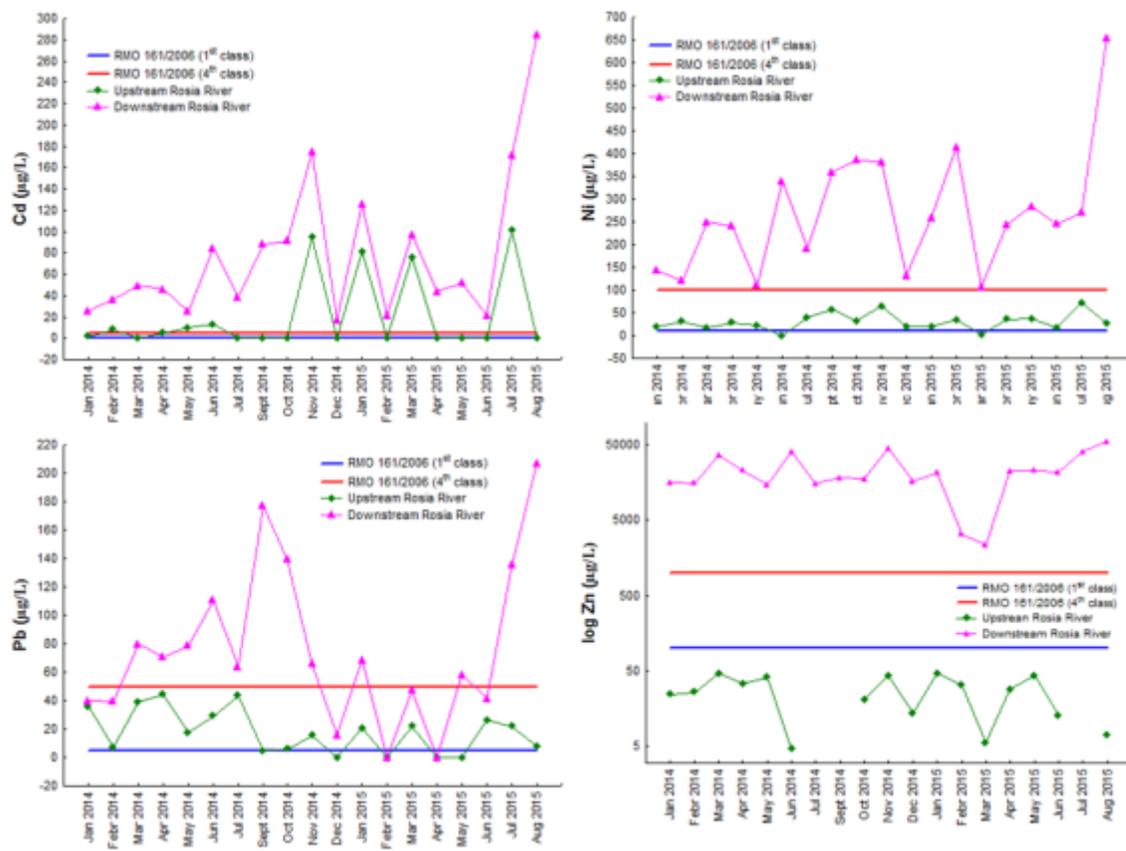


Figure 3.5.21 Seasonal variation of metal concentrations along Roşia River

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Sălişte stream is a tributary of Abrud River, and it collects mine waters from the Sălişte tailings impoundment, and also the small streams that cross the valley. In contrast to Roşia Valley, the changes in pH were not as drastic and only a small decrease of pH occurs in the summer months. On Sălişte stream the mine water coming from the tailings has a small contribution and Sălişte gallery, which has a higher flow rate, dilutes the contaminants released by the tailings. The TDS values have distinctive trends for the selected sites as a consequence of the water input from the Sălişte tailings pond (Figure 3.5.23). However, high concentration of NO_3 , SO_4 , Ni, Zn, Cd, and Pb were recorded in S18 and S23 (Figure 3.5.24). For these two points the pH values are normal, as the main source of pollution is not very close to the sampling points and a more pronounced mixing process between the surface waters and mine water occurs.

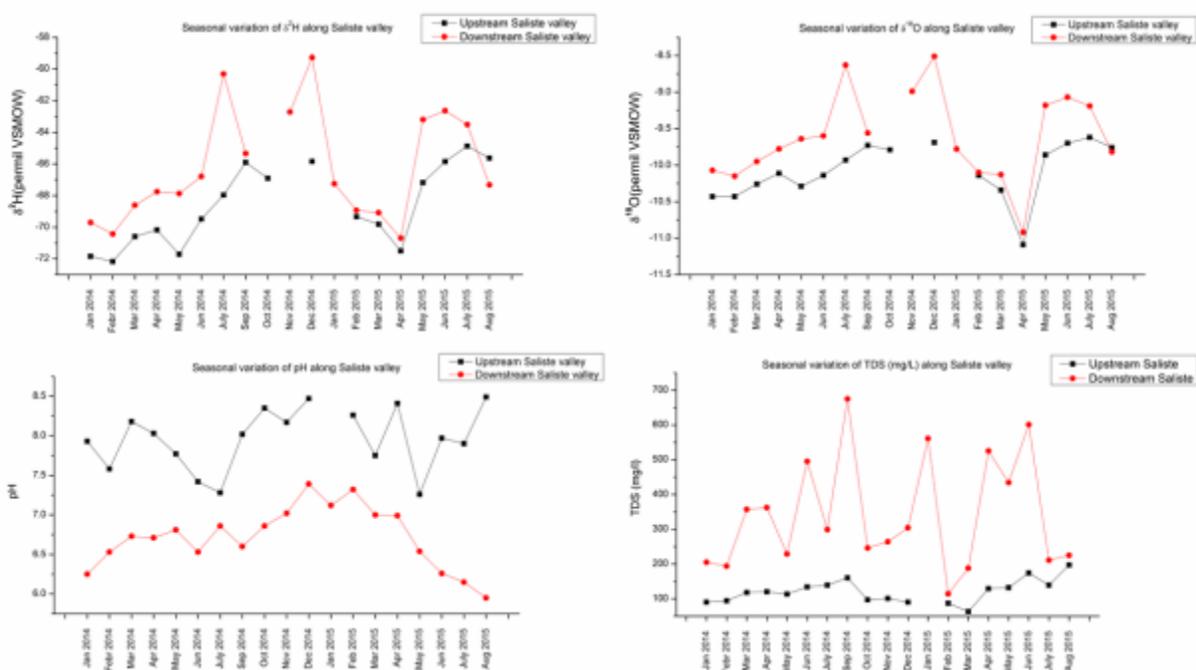


Figure 3.5.22. Seasonal variation of TDS and $\delta^2\text{H}$ along Saliste valley

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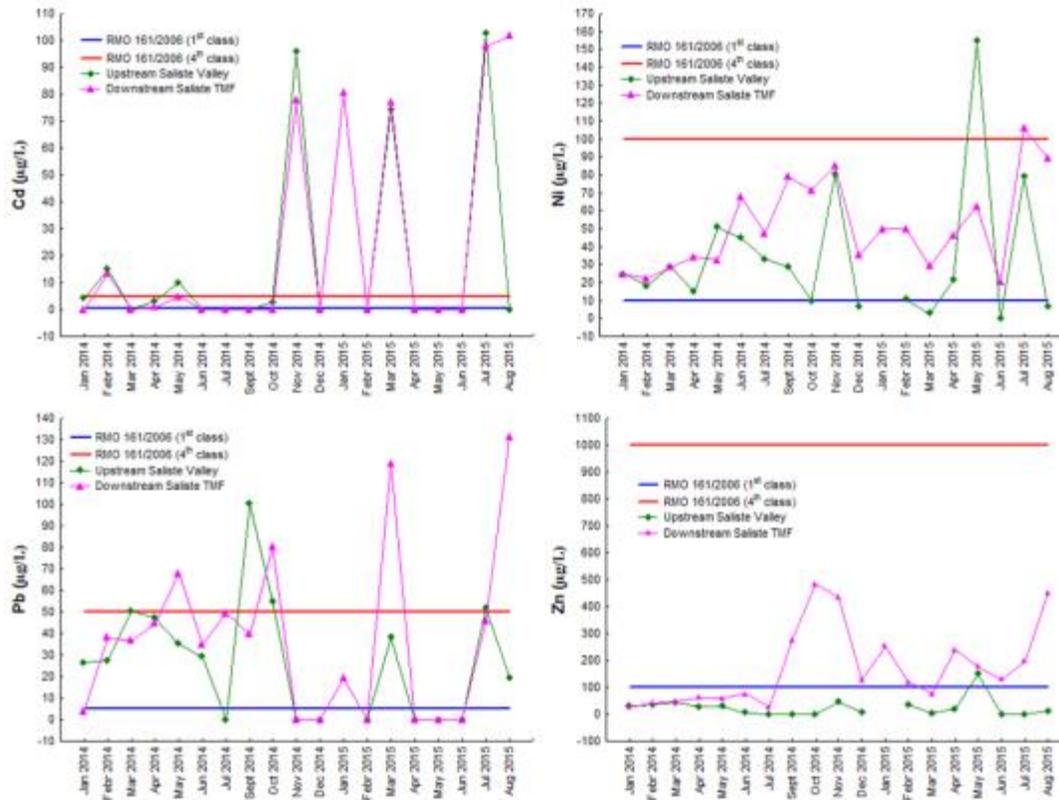


Figure 3.5.23 Seasonal variation of heavy metals along Saliste Valley

Corna stream is the second most polluted after Rosia stream, due to the several waste deposits located upstream of the valley (Figure 3.5.25). Furthermore the flow rate of the stream is very low. Along Corna Valley, large variation of heavy metal concentrations has been observed (Figure 3.5.26). Only the Zn concentrations ranged in the normal limits, while other metals were above the limits imposed by the regulations.

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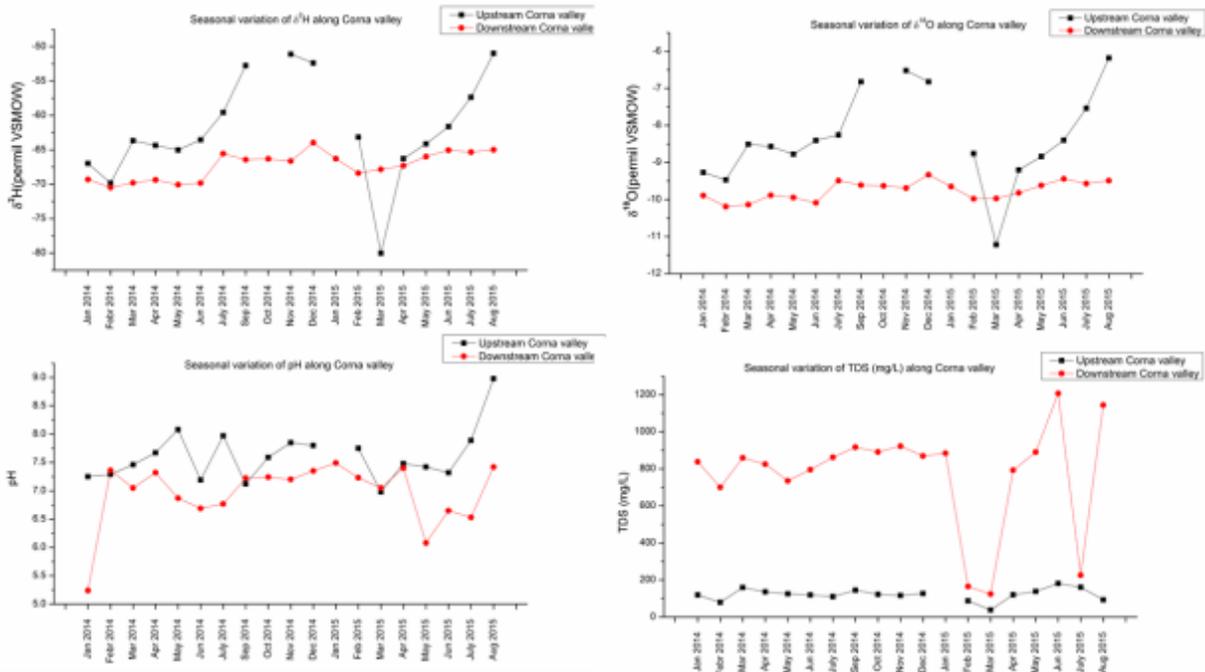


Figure 3.5.24 Seasonal variation of TDS and $\delta^2\text{H}$ along Corna Valley



Figure 3.5.25 Seasonal variation of heavy metals along Corna Valley

Abrud River, although receiving all the adjacent streams, has the lowest SO₄ content, total dissolved solids, and heavy metal concentrations due to the highest flow rate and water volume. All springs and domestic wells exhibited low values of NO₃, far below than the standard for drinking water allows and only in one well SO₄ exceeded the standard. However, they occasionally exhibited high concentrations of Pb, Cd and Ni, exceeding the drinking water standards. The domestic wells and springs show also a strong seasonal variation during the monitoring period.

4 Zlatna

4.1 Geographic and geologic setting

Zlatna gold mining area (approx. 40 km²) is located in the Metaliferi Mountains of the South Apuseni mountain range (Romania) approximately 24 km south of Roşia Montană (Figure 1.2.4). It belongs to the “Golden Quadrilateral” mining district (900 km²). From a hydrogeological point of view, the area (elevation range of 420 – 1100 m) is a medium-rain area (~ 480 – 700 mm/year), with a snow cap that lasts for 2 - 3 months in winter. The average annual temperature is 10.5°C, with a maximum monthly average of 28°C during the summer period, and minimum monthly average of –5°C during the winter. The density of the hydrographical network is about 1 km/km².

The Zlatna mining group includes three mines: Haneş, Almaş and Stănişia. The Almaş mine was closed during the World War II. At present the amount of drainage water from the Almaş mine is insignificant. The mining operations at the Haneş and Stănişia mines ceased in 2007. Currently, the mine openings are secured, but significant flow of acid mine water continues to discharge into the river system.

The Haneş mine was developed starting from the Haneş – Larga adit which has a length of 2.5 km. A branch was opened toward the Valea Babei adit. The Haneş mine opens dozens of gold veins at a height of 170 m, of which 80 m below the level of the main adit. Among the mined veins, the most important is vein no. 11 which contains gold in quartz and calcite gangue associated with sulphides (pyrite, sphalerite, galena, and marcasite).

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Figure 4.1.1 Location of the Zlatna study area

The Podul Ionului adit (Techereu Valley) also drains mine water from the Muncăceasca-East adit located at higher elevation. The Podul Ionului adit opens lenticular Au veins hosted by basic rocks belonging to the Măgura Ferice andesitic body. At depth the veins of Stănița mine are linked to porphyry-copper mineralisations containing Au and Mo, which were not sufficiently explored.

In the area, the basement is made up of Jurassic ophiolites (Figure 4.1.1.). The ophiolites outcrop in the western and south-western part of the study area. At their upper part, sporadic intercalations of jasper and radiolarite or Middle Jurassic limestones with intercalations of basic rocks can be found. The sedimentary cover, with a thickness of few hundred meters, consists of Late Jurassic – Hauterivian reef limestones which are found on restricted areas, followed by a suite of detrital formations, Cenomanian - Early Turonian in age. The detrital formations have a dominant pelitic character, and outcrop in the north-eastern part of the study area (Trâmboiele Valley and Izvorul Ampoiului). The Cretaceous detrital formations are (Borcoș et al., 1981; Ianovici et al., 1976): (1) the Curechiu strata (jasper, clays and marly clay shales with intercalations of basic pyroclastites); (2) the grey limestone complex (calcarenite alternating with purple clay marls); (3) the striped series (marl with purple and green strips); (4) the Pârâul Izvorului strata (silts alternating with micaceous pelites); (5) the Negruleasa conglomerates, Cenomanian in age.

The Turonian tectonic events, which led to the formation of Tisia block and to the development of the Codru and Biharia nappes in the North Apuseni, fundamentally changed the conditions of sedimentation in the South Apuseni. In the south-eastern part of the Metaliferi Mountains, the Late Cretaceous sediments are deposited mainly in sedimentary basins and have a molasse character. The overlying Badenian molasse formations are unconformable and include: (1) the Fața Băii Formation (Early Badenian) made up of conglomerates, sandstones, clays and marls; (2) the Almaşul Mare Formation (Middle Badenian) made up of gravels, reddish clay sandstones, gypsum lenses, limestones, and red marls, and (3) the volcanogenic sedimentary formation (Late Badenian) made up mainly of blackish grey marls with gypsum and salt lenses. At its upper part, tuffs, andesite breccia, and sandstone with plant fragments also occur.

During the Laramic movements (Late Cretaceous – Paleogene) the “banatitic” magmatism developed along a N–S alignment, crossing through both the Apuseni Mountains and the western part of the South Carpathians (e. g. Berza et al. 1998), and was partly coeval with the molasse deposition. The banatitic rocks have a large extent in the Apuseni Mountains, but in the Zlatna area their occurrence is restricted. However, it is supposed that the metallic content of the banatitic magmas from depth was remobilized during the subsequent Neogene calc-alkaline magmatism (Roşu 2001) to which the gold mineralisation from Zlatna is related. The mechanism of formation of the Neogene magmas is due to the rotational and transtensional movements of the Tisia block which resulted in uplifting and decompression of the asthenosphere and in melting of its upper part, and of the lower crust (Seghedi et al. 2004).

The volcanic activity had two peaks at 14.6 - 10.8 Ma and 9.3 - 7.4 Ma, ending 1.6 Ma ago with the last eruption of Magura Uroi (Roşu et al. 2004). Quartz andesite with amphibole and pyroxene, and quartz andesite with amphibole and biotite are the main petrographic types. Basalt andesites occurred at the end of the magmatic activity, showing an obvious evolution trend towards adackite (Seghedi et al. 2007).

The mineralisation is not directly related to a specific magmatic body. The magmatic bodies which underwent early differentiation by crystallization within the magma chamber produced an enrichment in volatiles that were subsequently released as hydrothermal solution. Such hydrothermal solutions retrieved the bulk of the metal content and deposited it as veins or as dissemination, throughout the magmatic bodies. Three types of polymetallic mineralisation occur: (1) porphyry type (with or without veins at the upper part); (2) vein type, and (3) breccia pipe type with transitional forms generated by remobilization. All mineralisations contain Au +/- Ag, Cu, Pb, and Zn in various proportions.

4.2 Mining history within the Zlatna area

Several well preserved mining works and many archaeological findings confirm very early gold extraction within the Apuseni Mountains, first by the Dacians and later by the Romans. During Roman administration, there was mining in Baia de Arieş, Roşia Montană, Bucium, Zlatna, Stănişia, Ruda, Musariu and Măgura. Production in the Apuseni Mountains was estimated at

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around 500 tons of gold and 960 tons of silver throughout the Roman period. Of these amounts, 255 tons were extracted only at Zlatna - Stănişia (Papa 2000). After the Roman withdrawal, gold mining was almost completely abandoned. The Slavs who arrived in the former Dacia in the sixth century, renamed places that previously had Roman names (ex. Ampelum = Zlatna), as a proof of their interest in areas of gold mining.

Gold mining in the Apuseni Mountains witnessed a new period of development after 1699 (Peace of Karlowitz) when Transylvania came under Austrian (Habsburg) jurisdiction. A number of regulations and investments were made in gold mining. It was estimated that during the 18th and 19th century a quantity of about 250 tons of gold and 1300 tons of silver was extracted (Helka 1934, *in* Şerban & Orlandea 2004).

In the early 20th century, the Apuseni Mountains were the largest supplier of gold in Europe. The mineral resources became state property in 1924, after the unification of Transylvania with Romania. Gold production increased rapidly and the geological and technological research intensified. Publications appeared and mining schools and universities were established. After World War II mining was based on socialist-Soviet planned development. In the Zlatna gold mining area, new processing plants were built after 1960. Increasing polymetallic sulphide ore extraction demanded the construction of a copper plant in 1988, which resulted in polluting the area.

After the collapse of the communist regime in 1989, there was a disturbance of mining industry, and the lack of investment made business unprofitable. In 2004, activity at the copper plant ceased. In 2007, Romania joined the EU and because EU legislation does not allow state aid in unprofitable mining industry, the mining operations were completely ceased. There were a number of ecological programs following the mine closure, but their effects are barely visible. In addition to such programs, pollution was reduced by natural mechanisms, such as: (1) the gradual depletion of sulphides exposed to alteration; (2) biological activity of (micro)organisms in water and soil; (3) water buffering due to the presence of ophiolites, marl and limestones.

4.3 Environmental issues

The Zlatna mining area shares the same environmental concerns as the majority of gold and complex sulphides mining areas. The opening of mineralized magmatic bodies by mining works, the extraction of ores and then the cessation of operation results in the formation of AMD by allowing infiltrating water to come into contact with reactive minerals. The mineral responsible for the vast majority of AMD formation is pyrite. Pyrite reacts when it comes in contact with water and oxygen. Sulphuric acid (H_2SO_4), a product of this reaction, may have major environmental consequences. Iron hydroxide $Fe(OH)_3$, also known as yellow boy, forms an orange or yellow precipitate that is deposited on the bottoms of streams, affecting aquatic life. In addition, the acid water can further dissolve other rocks and minerals with high metal content. The contaminated water may thus carry a large variety of pollutants and may migrate downgradient into local aquifers.

The quantity and the composition of mine water is controlled by: (1) location of recharge zones; (2) amount of infiltration; (3) flow pathways and their contact with mineralisation; (4) ore mineralogy; and (4) mineralogical and petrographic composition of dissolved rocks. After the discharge into the surface water system, the environmental impact of mine water depends on: (1) quantity and composition of surface water; (2) mineralogical and petrographic composition of rocks in the streambeds, (6) biotic activity; and (7) anthropogenic activity.

In most cases, mine water infiltrates into the waste rock pile located in front of the mine adits, before it discharges into the river system. Waste rock piles may contain large amounts of trace metals and metalloids (e. g. Pb, Zn, Ni, Al, Cu, Mn, Fe and As) which add to the initial load of mine water, as well as SO₄ which causes a drop in water pH. As an example, on October 2015, the mine water we collected at the opening of the IPEG adit (Trâmpoiele Valley) showed a neutral pH of 6.9. At the base of the waste rock pile (toe seepage) the water was acidic with a pH as low as 5.0. At the two edges of the pile (face seepage), the change in the pH of water was less significant.

4.4 Study methods

4.4.1 Sampling

In the present study we have sampled mine water drained from the Haneş mine (adits: Larga, Haneş, Haneş 2, and Toţi Sfinţii) and the Stănişia mine (adits: Podul Ionului and 23 August), as well as from a mining exploration adit (IPEG). In January 2015 we started to collect water samples on a monthly basis according to the sampling scheme established in the preparatory phase (October 2014). The sampling scheme includes 25 sources, of which samples are collected from: 8 sources of mine water (collected at mine openings), 10 sources of running water (i.e. rivers and streams), 4 underground springs and 3 domestic wells. A summary of the sampling scheme is displayed in Table 4.4.1. The location of the 25 sampling sites is shown on the geological map in Figure 4.4.1.

There are three sampling zones: (1) Trâmpoiele – Zlatna; (2) Haneş – Ardeu; and (3) Techereu. They correspond to the drainage basins of the main valleys in the area. The Ampoi River and its tributary, the Trâmpoiele stream, are the main water courses in the Trâmpoiele – Zlatna zone. In the Haneş – Ardeu zone the main collector is the Ardeu stream. In the Techereu zone the main collector is the Techereu stream. In each zone we selected for sampling: mine water from all adits that drain water, the main water courses and a few representative springs and domestic wells. The main water courses were sampled upstream of the discharge point of mine water, as well as downstream of the discharge point at a distance of approximately 4 km for the Ampoi stream, 2 km for the Trâmpoiele stream, 5 km for the Ardeu stream, and 3 km for the Techereu stream. The Larga adit communicates with the Haneş adit, and the Valea Babei adit communicates with the Haneş 2 adit. The flow rate of the springs is relatively constant over the year, but low. The water level in the wells decreases drastically during the summer months. Thus, the Trâmpoiele domestic

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well was totally dry during August, and the Ardeu domestic well was dry in September. Photos of all sampling sites at different moments of the year are shown in Figure 2.3.2.

Table 4.4.1 Sample scheme for water sources from the Zlatna mining area

Crt. no.	Source name	Source location	Water type	GPS coordinates	Altitude (m)	Sampling zones
1	A1	Ampoi river upstream	running water	N46 08 01.5 E23 11 14.0	497	Trâmpoiele - Zlatna
2	A2	Trâmpoiele stream downstream	running water	N46 08 01.8 E23 11 08.0	455	
3	A3	IPEG adit	mine water	N46 08 02.7 E23 10 15.8	537	
4	A5	Larga spring	spring	N46 08 09.0 E23 10 11.3	518	
5	A7	Larga adit	mine water	N46 07 53.9 E23 09 09.9	726	
6	A8	Larga creek	running water	N46 07 56.5 E23 09 07.2	734	
7	A10	Trâmpoiele stream upstream	running water	N46 08 52.3 E23 08 51.2	585	
8	A11	Trâmpoiele domestic well	phreatic water	N46 08 54.7 E23 08 43.0	581	
9	A12	Zlatna spring	spring	N46 06 59.2 E23 12 26.9	435	
10	A13	Ampoi river downstream	running water	N46 06 39.5 E23 12 59.0	421	
11	A16	Ardeu stream downstream	running water	N46 06 31.4 E23 07 15.7	635	Haneş - Ardeu
12	A17	Haneş spring	spring	N46 06 45.6 E23 07 11.7	654	
13	A18	Toţi Sfinţii adit	mine water	N46 06 55.1 E23 07 14.6	668	
14	A19	Haneş Mine	mine water	N46 07 16.8 E23 07 27.6	705	
15	A20	Haneş stream	running water	N46 07 20.7 E23 07 26.4	717	
16	A21	Haneş 2 adit	mine water	N46 07 11.6 E23 07 16.3	727	
17	A22	Valea Babei adit	mine water	N46 07 03.2 E23 06 34.6	652	
18	A23	23 August adit	mine water	N46 08 06.8 E23 04 52.5	880	
19	A24	Ardeu stream upstream	running water	N46 08 09.7 E23 05 05.9	824	
20	A25	Ardeu domestic well	phreatic water	N46 07 09.3 E23 05 38.0	702	
21	A26	Techereu stream downstream	running water	N46 05 29.8 E23 04 13.2	426	Techereu
22	A27	Techereu domestic well	phreatic water	N46 05 29.8 E23 04 13.2	427	
23	A28	Techereu spring	spring	N46 06 27.5 E23 03 45.0	503	
24	A29	Podul Ionului adit	mine water	N46 06 59.4 E23 03 51.3	609	
25	A30	Techereu stream upstream	running water	N46 06 59.3 E23 03 51.6	626	

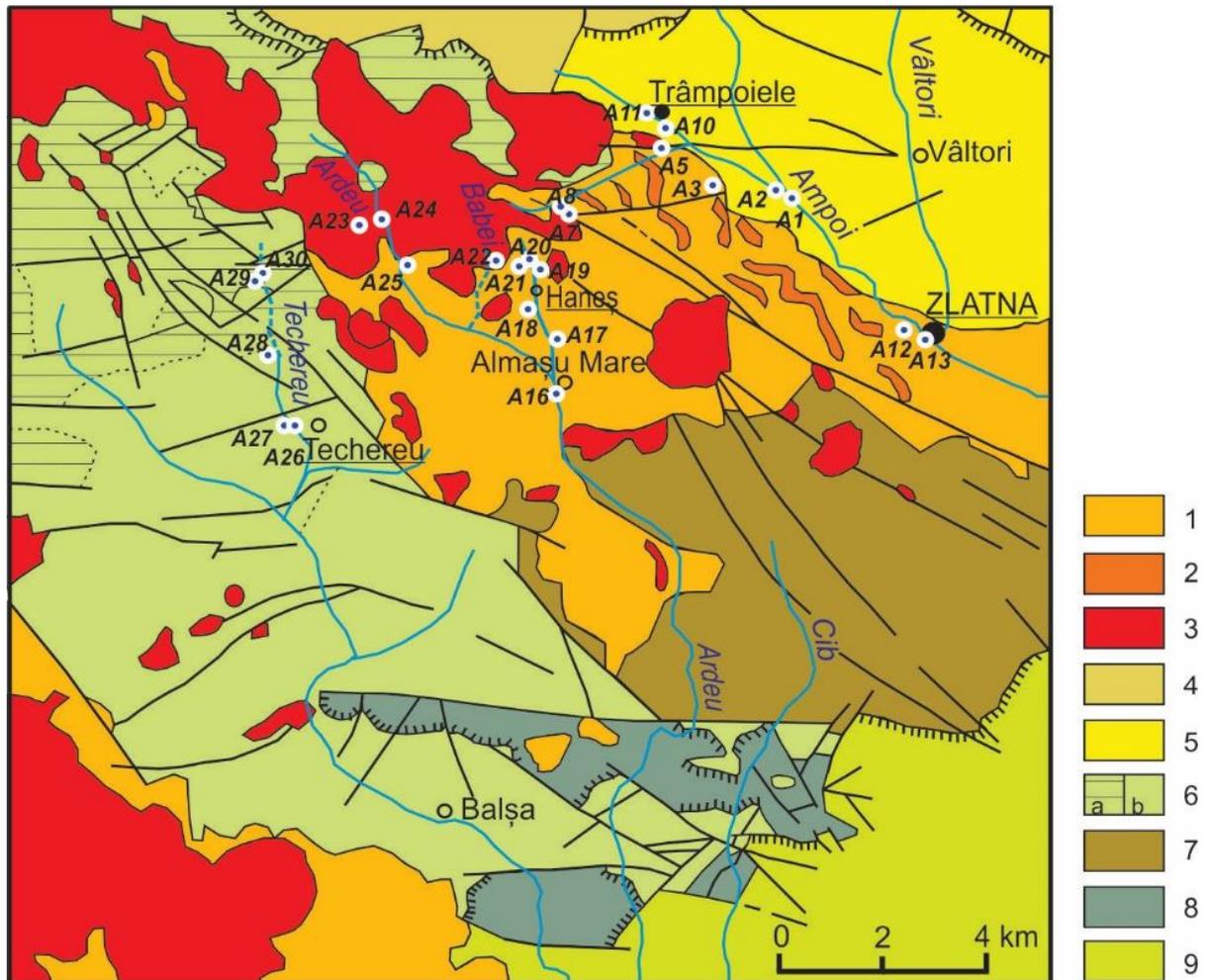


Figure 4.4.1 Geological sketch map of the Zlatna mining area showing the location of the 25 sampling sites (redrawn after the Geological map of Romania scale 1:50000, sheet 74C-Zlatna);

Legend: 1 – Neogene molasse; 2 – Neogene magmatites stage II (rhyolites and quartz andesites with Miocene sedimentary intercalations); 3 – Neogene magmatites stage I (biotite, amphibole andesites +/-pyroxene); 4 – Early Cretaceous – Middle Jurassic flysch, Bucium Unit (sandstones and conglomerates); 5 - Early Cretaceous – Late Cretaceous flysch, Feneş Unit (sandstones, conglomerates and limestones; 6a – Early Cretaceous – Turonian flysch, Techereu Unit; 6b – Late Jurassic ophiolites (basalts, pyroxene andesites and rhyolites); 7 – Late Cretaceous wild flysch, Galda Unit; 8 – Jurassic – Early Cretaceous reef limestones, Ardeu Unit; 9 – Senonian – Maastrichtian flysch, Bozeş Unit (marls, sandstones)).

4.4.2 Analytical methods

4.4.2.1 Chemistry and isotopes

For each water source the following parameters were determined in the field: pH, temperature, TDS, and conductivity using a Hanna HI9828 portable multiparameter meter. Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water. Total dissolved solids (TDS) combine the sum of all ion particles

that are smaller than 2 microns (0.0002 cm). TDS measurements are derived from conductivity. As the two parameters are equivalent, further in Zlatna case studies we will use only TDS, expressed in mg/l.

Water samples were collected for laboratory analyses in order to determine the hydrogen and oxygen isotopic composition, as well as the major ions and the heavy metals concentration (Cd, Cr, Pb, Cu, Ni, Zn, Fe). For each source, 4 ml of water were collected in glass vials for isotopic analysis. Parafilm was attached to the vials in order to avoid isotope fractionation through evaporation. Hydrochemical constituents and heavy metals were sampled using new 2x200ml plastic sampling bottles. Sample bottles were sealed and labelled appropriately. During sample collection the water samples were filtered using a CME 0.45µm filter. After sampling was completed, the samples were stored in a cool (<10 °C) and dry storage place until delivered to the laboratory. The water was not treated in any way before or after sampling.

The analyses were performed at “Babeş-Bolyai” University, Cluj-Napoca. The isotopic composition of hydrogen and oxygen was determined using a Picarro CRDS L 2130-I with autosampler. Two internal standards calibrated using standards provided by IAEA Vienna were used. The precision of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (δD) measurements is $\pm 0.12\text{‰}$ and $\pm 0.8\text{‰}$, respectively. All isotopic data are expressed in conventional δ notation as the permil deviation of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios with respect to the V-SMOW standard (equation 2). Major ions were analysed using ion-exchange chromatography. The cations analysed were: Li, Na, K, Mg, Ca, NH_4 , and the anions were: F, Cl, NO_2 , Br, NO_3 , PO_4 , SO_4 . Metals concentration (Ni, Cu, Zn, Cr, Cd, Pb, Fe) was determined using atomic absorption spectroscopy.

4.5 Results and discussion

4.5.1 Distribution of the studied parameters in different water sources

A summary of the distribution of the temperature, pH, total dissolved solids (TDS), $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, as well as of the main ions (Cl, NO_3 , SO_4 , Li, Na, K, Mg, Ca) and metals (Cd, Cr, Pb, Cu, Ni, Zn, Fe) is shown in Table 4.5.1. The displayed values for the main ions represent the mean values for four months of observation (from January to March). The displayed values for all the other parameters represent the mean values for one year of observation.

Mean temperature values are similar for all water sources, and the range is similar to the average annual temperature in the area (10.5 °C). Running water and groundwaters display similar $\delta^2\text{H}$, $\delta^{18}\text{O}$ and total dissolved solids (TDS) values and neutral pH.

Mine water is characterized by lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, neutral to acidic pH and high TDS values). Mine water displays high variability in TDS and pH as compared to other types of waters (Figure 4.5.1.). On the variability plot of TDS, two distinct groups of mine water could be distinguished: mine water showing TDS values similar to other underground water and surface water sources (IPEG, Toţi Sfinţii, 23 August, Larga, Podul Ionului) and mine waters with much higher salts content (Haneş, Haneş 2, and Valea Babei). The majority of mine water sources

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display pH values between 4 and 5. The mine water discharged from the Podul Ionului adit, displays slightly higher pH values (~ 6). This could be due to the interaction with the ophiolitic rocks through which the adit crosses and which have high pH buffering capacity. The mine water with neutral pH does not come into direct contact with mineralisation, either because it is discharged from an exploration adit (IPEG) or because of the depletion of pyrite and other sulphides exposed to alteration in old abandoned mining works (Toţi Sfinţii, 23 August).

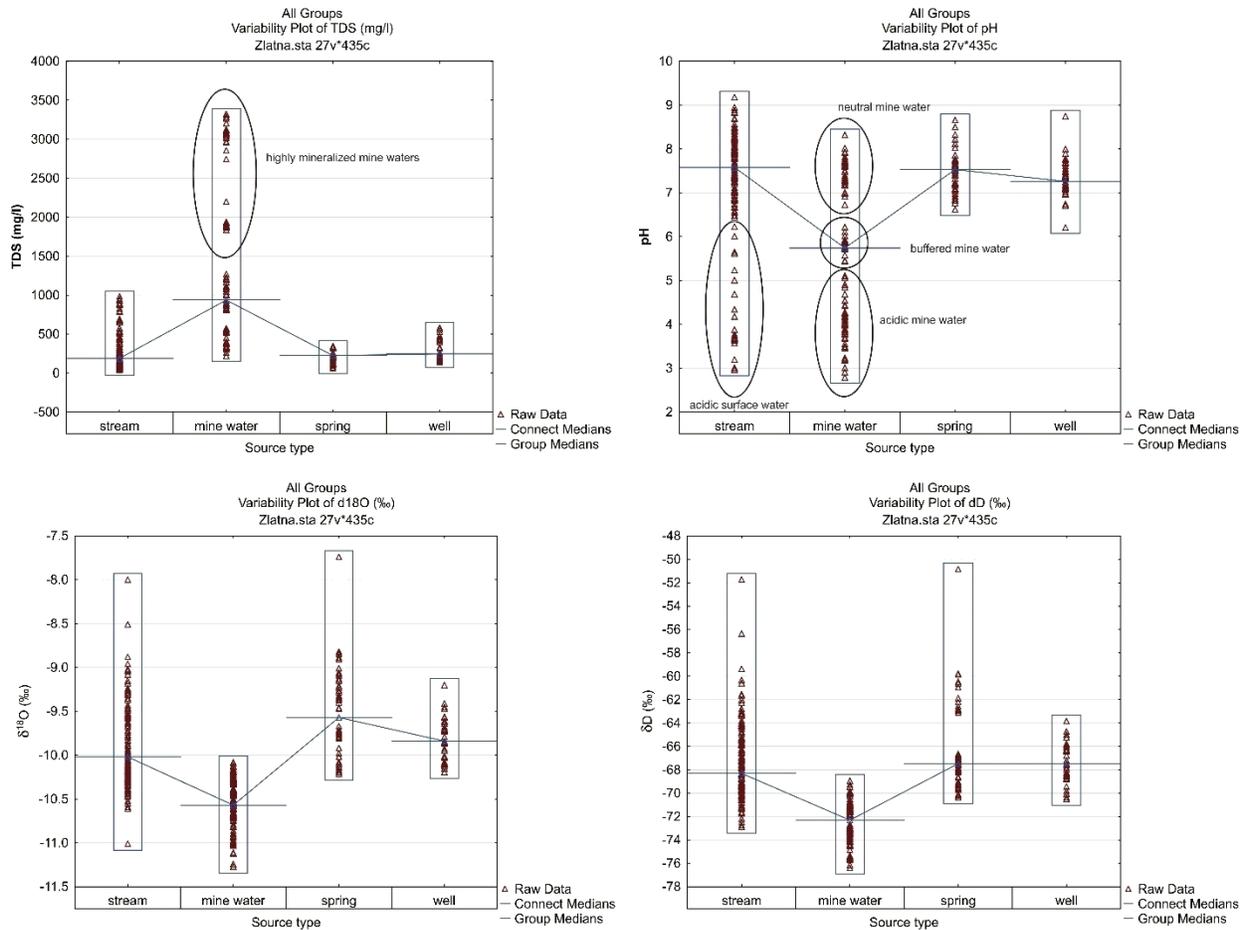


Figure 4.5.1 Variability plot of TDS, pH, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in different water types

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Mine water is characterized by higher Ca content relative to other water types. Phreatic water captured in domestic wells is characterized by higher Ca content relative to springs. Mg is also found in major amounts in mine water. The content of Na and K is less significant in all water types. The Li content is below the detection limits in all water samples.

Spring water displays the lowest NO_3 and SO_4 mean values, while mine water displays the highest values. The NO_3 content is highly variable from one month to another in all water types (Dev. standard = 1095.4). Very high values were recorded in March and April relative to the values recorded in January and February. NO_3 is highly soluble in water and is stable over a wide range of environmental conditions. Common sources of NO_3 in water include plant and animal matter, human and animal waste, household septic systems, and fertilizers. It is easily transported in streams and groundwater. Snow melt and soil thaws, along with intensification of biotic activity, resulted in transportation of a greater amount of NO_3 from soil in streams and groundwater, thus explaining the high NO_3 content in water during spring months.

The content of Cl is relatively high in domestic wells compared to springs and streams. Much higher Cl content was found in mine water in March and April. A slight increase of the Cl content during spring months was also recorded in Ardeu domestic well and in Trâmboiele well. Mine water discharge is likely responsible for some of the chloride load into the phreatic water. The Br content is below the detection limits in all water samples.

Distribution of major ions for all types of water sources is shown in Figure 4.5.2. On the Piper diagram, mine water occupies the same field as surface water and groundwater, all being Ca dominant type water, indicating the same mechanisms of mineralisation. The mine water from Podul Ionului adit (A28) contains more Mg relative to other mine waters. This is due to weathering of ferromagnesian minerals contained in the basic ophiolites through which the adit crosses. The Larga spring (A5) and the Techereu spring (A28) have a distinct position, showing no dominant cation. All mine waters have very high SO_4 concentrations and plot on the Piper diagram in the field of SO_4 -type water. Lower SO_4 concentration was found in the mine water from the 23 August adit. The majority of surface and groundwater sources are also classified as SO_4 type water. The Techereu spring (A28) and the Ampoi river show no dominant anion.

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Table 4.5.1 Summary of the distribution of t, pH, TDS, $\delta^{18}\text{O}$, $\delta^2\text{H}$ and major ions content of waters from the Zlatna mining area

	T °C	pH	TDS mg/l	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Cl ⁻ mg/l	NO ₃ ⁻ mg/l	SO ₄ ²⁻ mg/l	Na ⁺ mg/l	K ⁺ mg/l	Mg ⁺ mg/l	Ca ⁺ mg/l	Cd mg/l	Cr mg/l	Pb mg/l	Cu mg/l	Ni mg/l	Zn mg/l	Fe mg/l
Running water (no. of obs. 9)																			
Mean value	10.9	7	296	-9.9	-67.2	3.9	371.3	301.3	7.1	6.4	12	63.5	0.035	0.034	0.046	0.042	0.045	5.658	219.054
Min. value	9.4	3.9	68	-10.2	-69.4	1.4	14.1	16.5	2.5	2.5	2.3	29.5	0.027	0.02	0.024	0	0.014	0.011	0.049
Max. value	11.8	8.1	792	-9.6	-64.9	9.5	1082.9	1314.4	10.7	14.3	22.3	108.6	0.069	0.055	0.074	0.338	0.13	38.59	1174.923
Std. Dev.	0.8	1.4	243	0.2	1.4	2.8	407.5	410.4	2.7	3.5	6.3	33.1	0.013	0.012	0.015	0.106	0.04	12.153	396.633
Domestic well (no. of obs. 3)																			
Mean value	10.2	7.3	283	-9.9	-68	12.3	181.2	309.1	20.2	15.9	21.2	103.82	0.026	0.031	0.05	0	0.023	0.074	0.073
Min. value	9	7	174	-10.2	-69.4	3	158.3	47.5	6.2	8.7	8.5	58.8	0.022	0.029	0.038	0	0.017	0.008	0.039
Max. value	10.8	7.6	429	-9.6	-65.9	23.4	220.5	820.5	34.2	29.5	41.2	181.8	0.032	0.034	0.059	0.001	0.035	0.18	0.123
Std. Dev.	1	0.3	132	0.3	1.9	10.3	34.2	442.8	14	11.6	17.5	67.8	0.006	0.003	0.011	0.001	0.01	0.093	0.044
Spring (no. of obs. 4)																			
Mean value	10.2	7.5	219	-9.5	-66.3	3.5	102.1	72.2	23.6	4.4	22.1	46.1	0.028	0.028	0.044	0.001	0.022	0.013	0.054
Min. value	9.2	7.2	104	-10.1	-69.3	2.1	20.7	14.3	4.2	1.3	3.4	25.1	0.027	0.027	0.034	0	0.019	0.009	0.028
Max. value	11.1	7.8	336	-8.9	-60.6	5.1	269.8	183.2	56.9	9.6	50.1	58.3	0.029	0.029	0.057	0.001	0.024	0.017	0.096
Std. Dev.	0.8	0.2	97	0.5	3.9	1.3	113.3	77.1	23.7	3.7	19.9	14.8	0.001	0.001	0.012	0.001	0.002	0.004	0.032
Mine water (no. of obs. 8)																			
Mean value	11	5.6	1404	-10.6	-72.6	25.3	1903.9	15877	47.7	45.8	163.5	718.8	0.066	0.061	0.146	0.067	0.24	43.169	1649.064
Min. value	8.3	4	316	-11	-75.7	1.7	67.8	286	11.7	14.8	31	128.4	0.028	0.028	0.057	0	0.019	0.039	0.07
Max. value	14.6	8	3122	-10.3	-70	82.1	3962.1	67541	122.3	91.6	398.6	1871.9	0.143	0.109	0.266	0.248	0.481	108.176	3098.361
Std. Dev.	2.2	1.6	1132	0.3	1.9	3.7	1340.5	23266.5	43	29.1	147.2	642.9	0.049	0.029	0.085	0.108	0.191	46.093	1411.423

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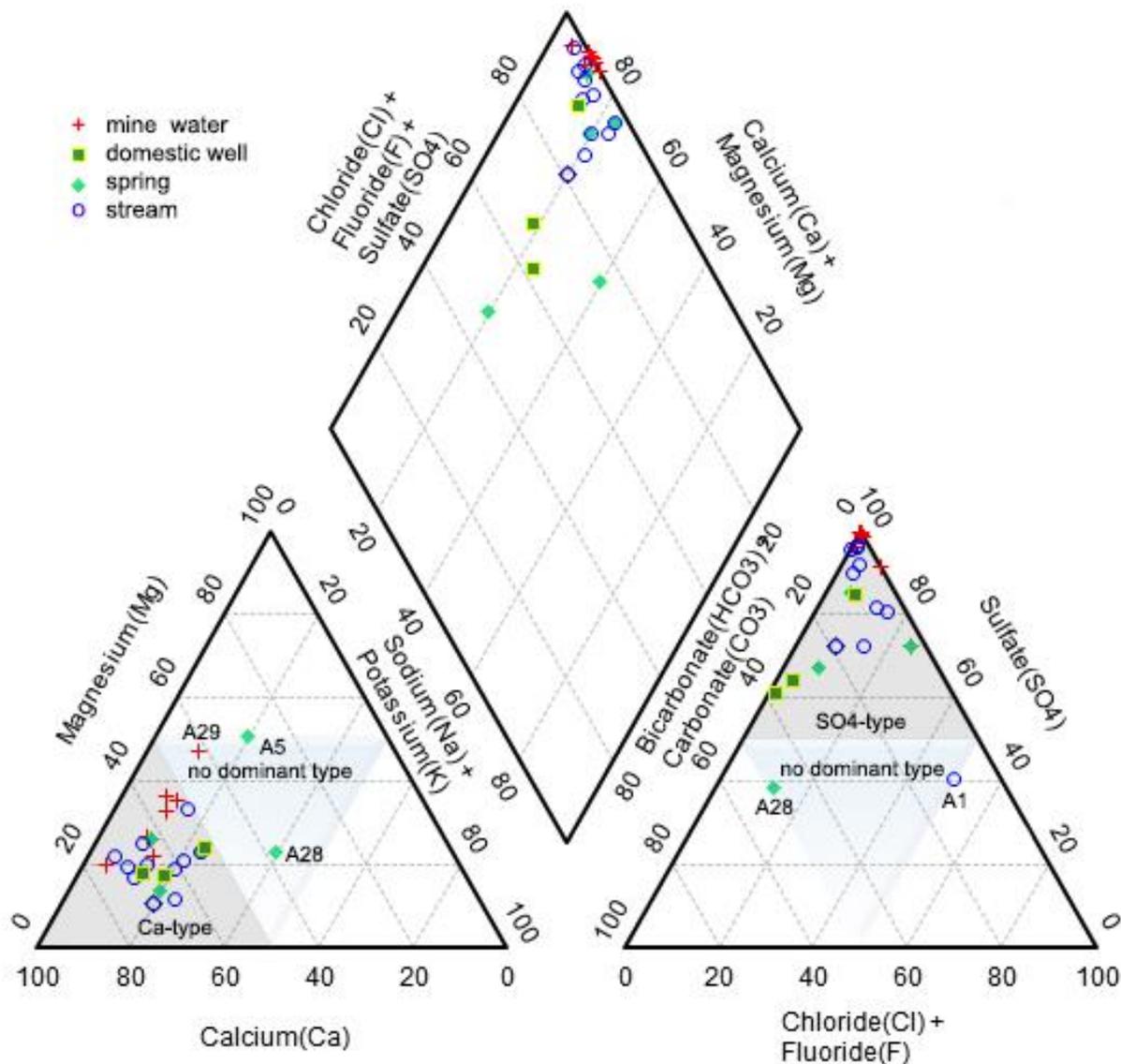


Figure 4.5.2 Piper diagram for water sources from Zlatna mining area. All displayed values are mean values for four months of observation (January to April).

Distribution of heavy metals concentration (Cr, Pb, Cu, Ni, Zn, Fe, Cd) differs from one water source type to another. In running water, mine water and spring water Fe is the dominant metal. As expected, the highest concentration was found in mine water (up to 3100 mg/l), except the mine water drained from the Toţi Sfinţii adit which shows very low Fe concentration. Mine water also shows the highest concentrations of Zn, Pb, Ni and Cd. The highest concentration of Cu was found in running water in the Larga creek. High concentrations were also found in mine water discharged from the Haneş and Larga adit. Running water also displays elevated concentrations

of Ni and Pb. In domestic well water, the dominating metals are Zn and Fe. As an issue of concern, elevated concentrations of Pb were also found in well water in Techereu well. The Pb concentration in spring water is also high in Larga spring. The lowest concentration of Pb was found in Ardeu stream upstream and the highest concentration in Haneş 2 mine water.

4.5.2 Seasonal variation of the studied parameters in different water sources

Both surface water and groundwater (springs, domestic wells, mine water) show seasonal variation of the pH, TDS, $\delta^{2}\text{H}$ and $\delta^{18}\text{O}$ values, as well as of the main ions and metals concentration, but the sequence of minimum and maximum is different from one source to another.

4.5.2.1 pH seasonal variation

There is a slight decreasing trend of the pH values of surface waters during the entire monitoring period, probably due to evaporation and low rainfall (Figure 4.5.3a). For the Ardeu stream, downstream of the mine water discharge, the seasonal variation is V-shaped with the lowest value occurred in July. A pH value as low as 3.7 was recorded. The severe decrease in water flow during the summer months may explain this low value. An obvious increase of pH values during autumn - winter period occurred in the case of the Larga creek, which collects mine water from the Larga adjacent adits. Similar pH values and similar variation shape was recorded for the mine water discharged directly from the Larga adit.

For both domestic wells and springs, the pH seasonal variation patterns are different from one source to another. They record increases and decreases from one month to another, but the amplitudes of variation are not greater than one unit (Figure 4.5.3b and d). Extreme values were recorded in August and September when the wells dried. In such cases, the drastic increase (Ardeu well) or decrease (Trâmpoiele well) of the pH values depends on the nature of the soil.

The mine waters are less affected by seasonal variation which suggest well-mixed underground systems (Figure 4.5.3c). A slightly increasing trend of pH occurred in the case of mine waters belonging to the Haneş mine (Haneş, Haneş 2, Valea Babei, and Larga). The mine water discharged from the Podul Ionului adit shows pH values almost constant. The group of mine waters (IPEG, Toţi Sînţii, 23 August) that are not acidic waters (pH > 6.7), show a minor decrease in pH values, similar to the surface waters.

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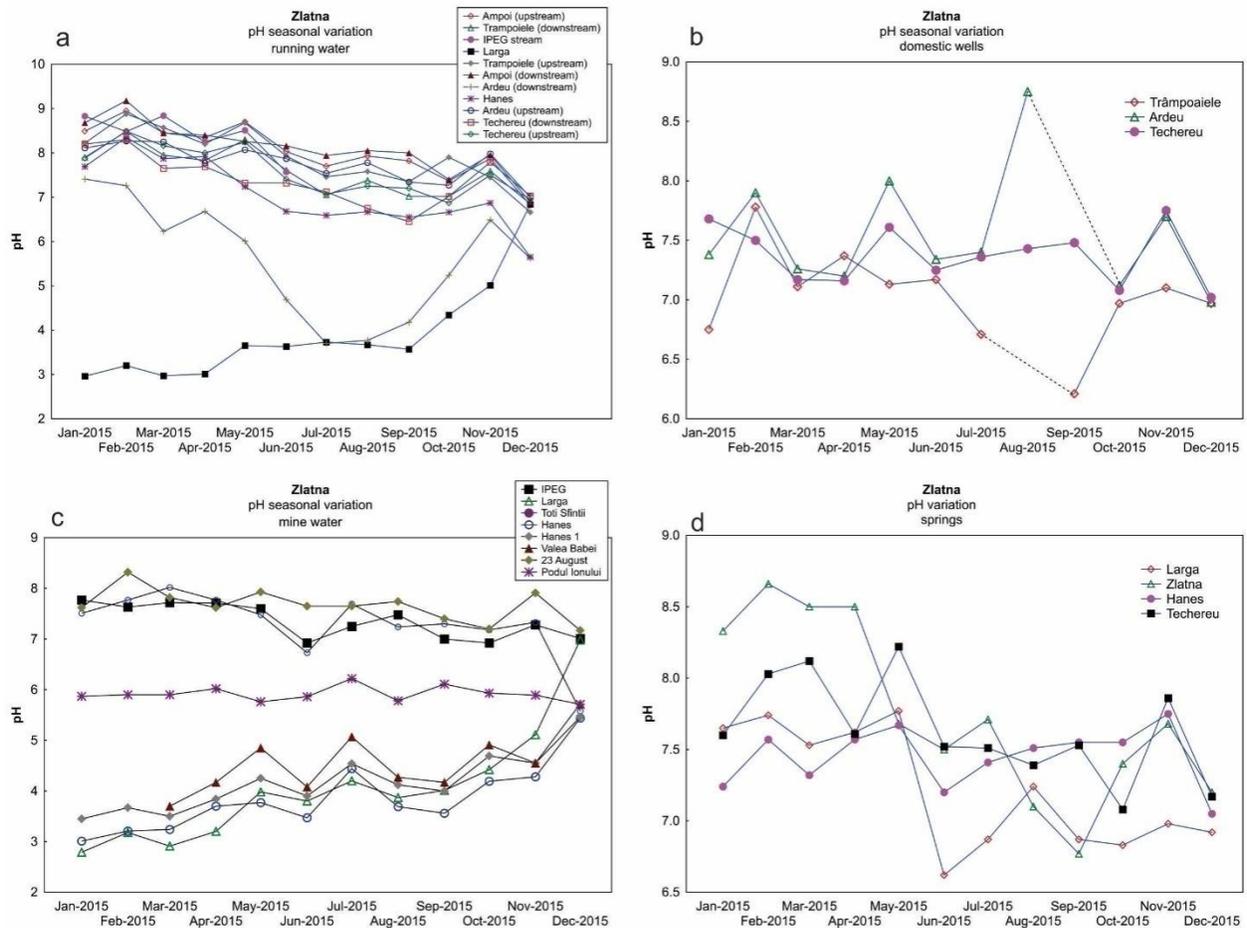


Figure 4.5.3 pH seasonal variation in different water sources: (a) running water; (b) domestic wells; (c) mine water; (c) springs

4.5.2.2 TDS seasonal variation

For the surface waters, the TDS values display an increasing trend during summer months. The trend is more pronounced downstream (Figure 4.5.4a). For the Ardeu stream, downstream of the mine water discharge, the increase of the TDS values in July is the most noticeable and it correlates with the drop of pH values. This is due to the extreme evaporation and desorption of the acid iron hydroxide precipitate from the bottom of stream, in very low flow conditions. Some water courses, of which the Larga creek is the best example, show the lowest TDS value in June when the amount of precipitation was high.

For the domestic wells, the highest TDS values were recorded during autumn months, probably as a consequence of evaporation during summer months (Figure 4.5.4b). For the Techereu well the minimum value was recorded in June, similar to the running waters.

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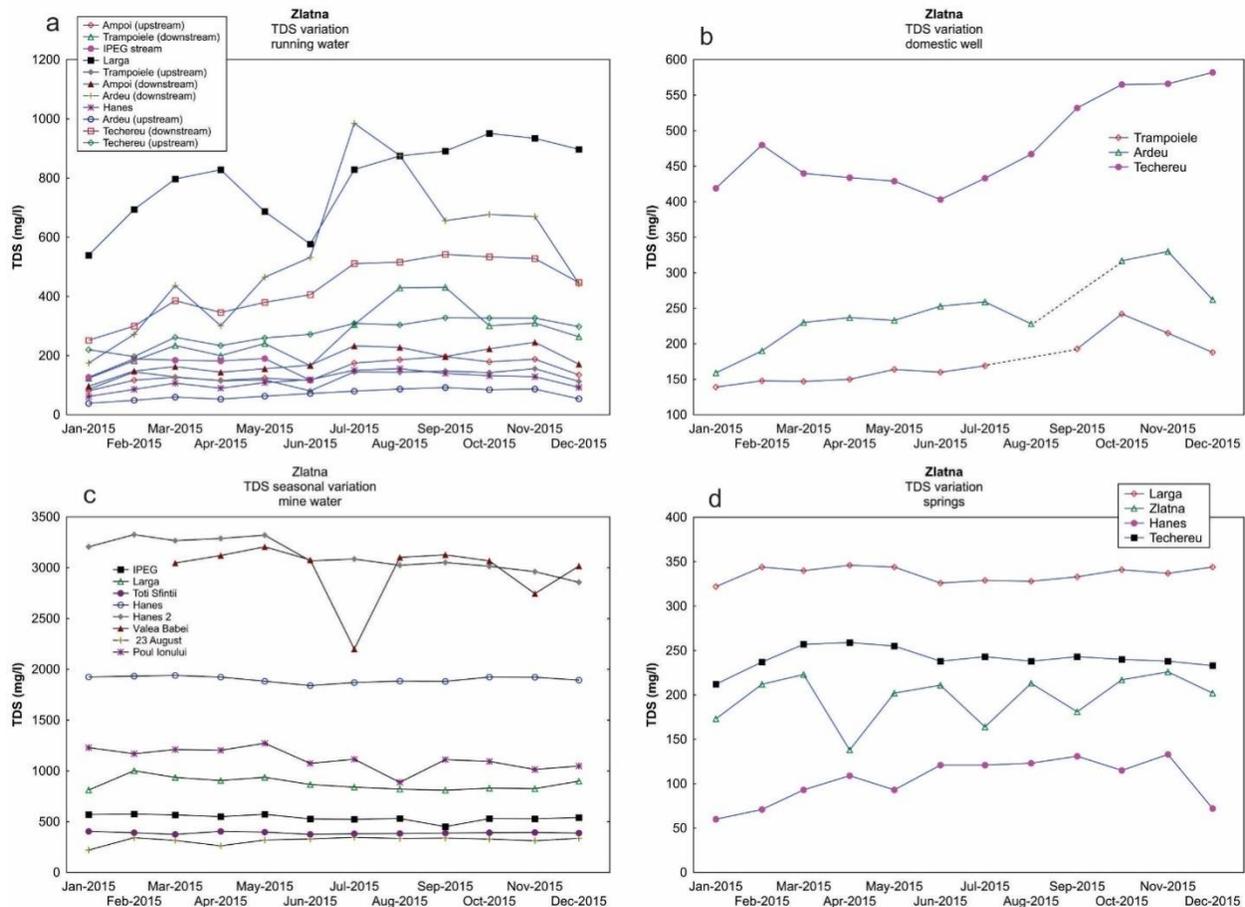


Figure 4.5.4 TDS seasonal variation if different water sources: (a) running water; (b) domestic wells; (c) mine water; (c) springs

For the other groundwater sources (springs and mine water), the TDS seasonal variation is relatively restricted (Figure 4.5.5c and d). The underground flow regime inhibits to some extent the TDS variation of the infiltration water. At high flow rates the seasonal variation is easily detected at the discharge point, while at low flow rates and/or long underground pathways the seasonal variation is attenuated. The Zlatna spring shows the largest variation, with dense succession of minimum and maximum.

4.5.2.3 Seasonal variation of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values

The seasonal variation of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values differ from one source to another, but for each source the variation patterns of the two isotopes are analogue (Figure 4.5.5 and Figure 4.5.6). For most running water courses, an enrichment in heavy isotopes occurred due to intense evaporation, with the highest $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values being recorded in September. For the Techereu stream, both upstream and downstream, the variation is small. A slight decrease occurs in spring months, as a contribution of snow melt (Figure 4.5.5a and b).

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Due to the evaporation produced during warm seasons, which determines the enrichment both in heavy isotopes (D and ^{18}O) and salts, positive correlations between both $\delta^2\text{H}$ and TDS, and $\delta^{18}\text{O}$ and TDS values were expected for running water. As an example, for the Trâmpoiele stream (downstream) the correlation coefficient between $\delta^2\text{H}$ and TDS is $r=0.86$, and between $\delta^{18}\text{O}$ and TDS is $r=0.89$ ($n=12$). Similar values for the correlation coefficient were obtained for the Ampoi river upstream, the Larga creek, the Ardeu stream (upstream and downstream), and the Haneş stream.

In other cases (Ampoi river - downstream, Trâmpoiele stream - downstream) a low correlation coefficient, or even a negative correlation (Techereu stream) was obtained between the TDS values vs. the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, indicating relationships with phreatic waters.

For the domestic wells (Figure 4.5.5c and d), the enrichment in heavy isotopes is delayed in time due to infiltration, being observed in October and November. The lowest $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are recorded in spring when the infiltration of the snow melt occurs.

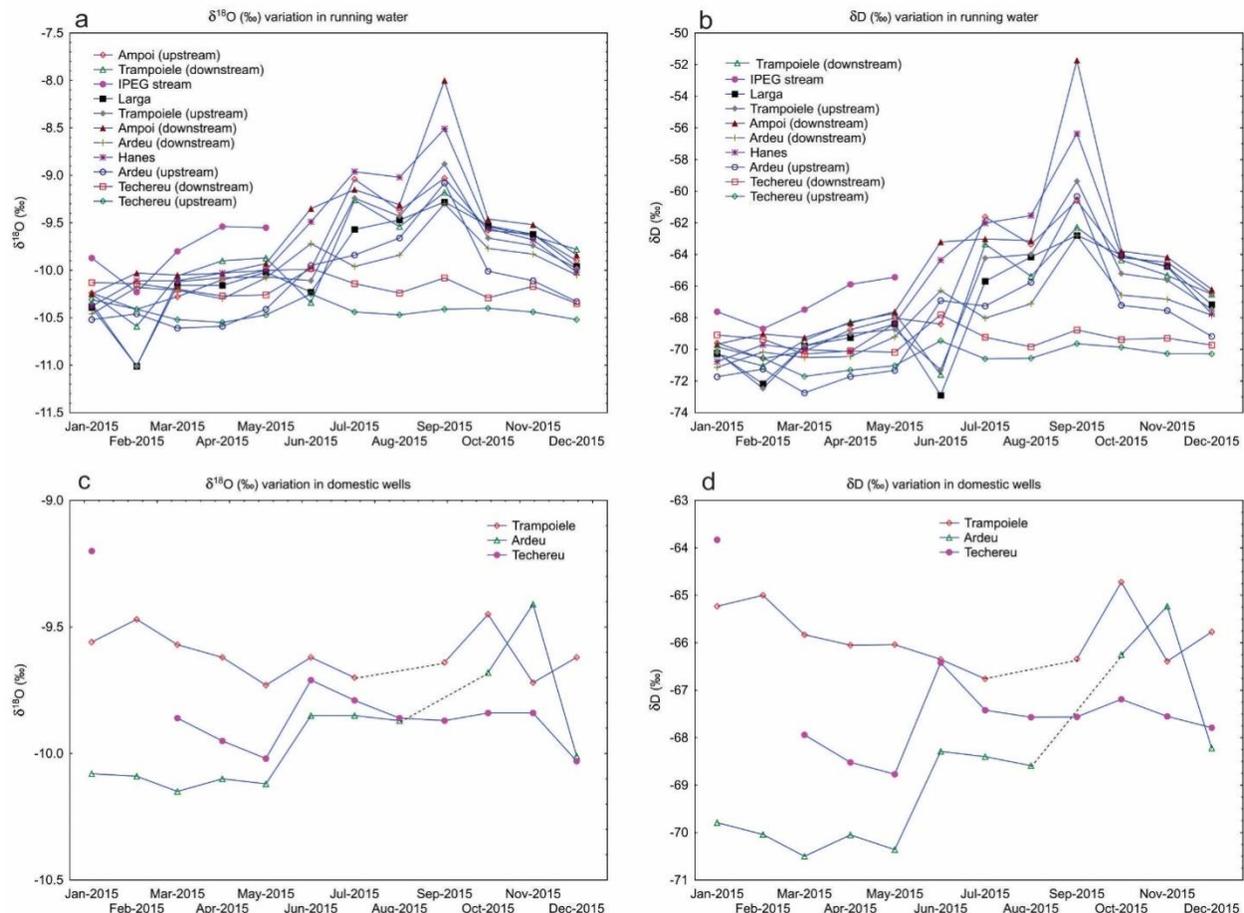


Figure 4.5.5 $\delta^2\text{H}$ (δD) and $\delta^{18}\text{O}$ seasonal variation in different water sources: (a, b) running water; (c, d) domestic wells.

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The mine waters and springs are less affected by seasonal variation, suggesting well-mixed systems and/or slow flow recharge pathways. Larger seasonal variation occurs in the case of mine water from the Larga adit (Figure 4.5.6a and b). In the lack of mining works below the adit's level, the adit acts like a rapid drainage pathway for infiltration water, not allowing underground mixing. The Zlatna spring displays the largest variation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ as compared to other springs (Figure 4.5.6c and d). It shows analogous variation patterns to the Ampoi river near which it is found, both displaying strong enrichment in heavy isotopes in September (Figure 4.5.5a and b.). This finding suggests genetic relationships.

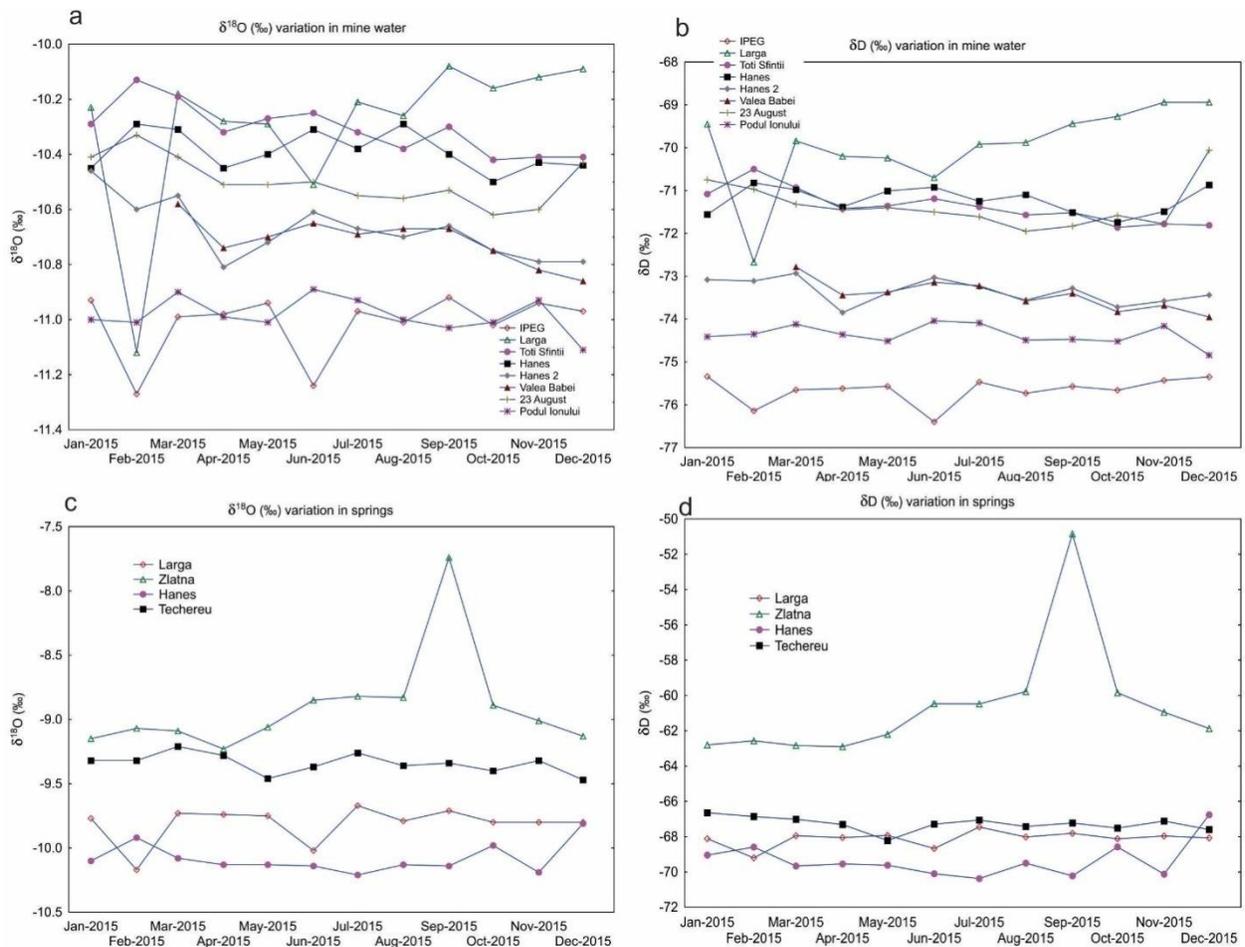


Figure 4.5.6 $\delta^2\text{H}$ (δD) and $\delta^{18}\text{O}$ seasonal variation in different water sources: (a,b) mine water; (c, d) springs

4.5.2.4 Seasonal variation of heavy metals concentration

Seasonal variation of heavy metal concentrations was observed in running water, springs, domestic wells and mine water (Figure 4.5.7.).

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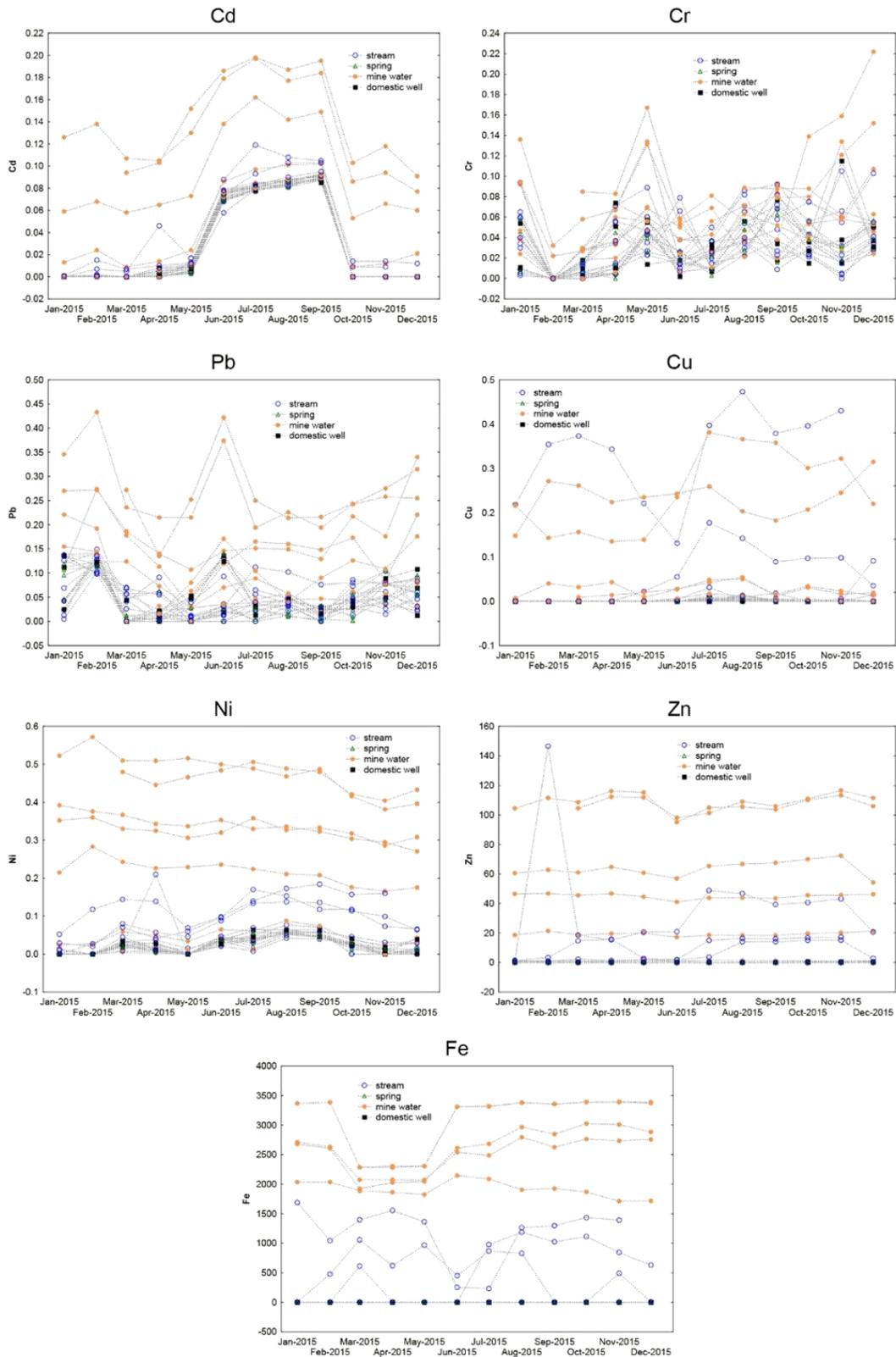


Figure 4.5.7 Seasonal variation of heavy metals concentration in running water, springs, domestic wells and mine water

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In all water sources the variation of Cd concentration has the same pattern, showing a maximum during the warm season from May to October. The unity of the variation pattern makes it clear that Cd originates from a single source. The increase of Cd concentration during the warm season might be related to bioaccumulation. Cd is known to have significant mobility and bioavailability, acting like a nutrient-like element (Lottermose 2007; Li et al. 2010, Rehkämper et al. 2010). However, Cd is a toxic heavy metal and in polluted area, its isotopes can be used to trace pollution source (Gao et al., 2013). Its geochemical behaviour is similar to that of Zn because of the similar electron structure and ionization potential of the two elements. Both are found in ferromagnesian minerals. In weathering processes, Cd separates from Zn and combines with S forming greenockite (CdS), the only Cd mineral of importance, which is nearly always associated with sphalerite (ZnS). Therefore a good correlation between the two elements in water samples from Zlatna was expected. However, none of the water sources shows significant positive correlation between the two elements. In most cases a negative correlation coefficient was obtained (e. g. Larga adit, Trâmpoiele stream, Podul Ionului adit, Techereu stream) or a low positive correlation coefficient in a few other cases (e. g. IPEG adit, Haneş spring, Haneş adit, Techere spring).

Zn concentration shows little seasonal variation. Zn concentration varies from one source to another. The highest concentration of Zn was found in the Haneş 2 and Valea Babei mine waters and is quasi-constant throughout the year. The lowest concentration of Zn, which also remains almost constant, was recorded in springs and domestic wells, as well as in the Toţi Sfinţii and 23 August mine water. Running water shows the largest variation of Zn concentration but the variation pattern differs from one source to another.

In groundwater and running water, Ni concentration increases in March, then decreases sharply in May, and then rises again, showing the highest concentration in July to August. Conversely, mine water shows restricted variation of Ni concentration. Nickel occurs most often in combination with Fe, therefore similar variation is expected for the two metals.

Iron (Fe) shows restricted variation in mine water, except for the spring period (March to May) when it drops in concentration, most likely related to dilution of mine water by snow melt infiltration. In running water, variation in Fe concentration shows irregular succession of minimum and maximum, different from one source to another. In underground water (springs) the variation of Fe has a similar pattern in all sources: the highest values were recorded in March and December and constant low values were recorded from April to October. The phreatic water sampled in domestic wells follows in good approximation the variation of Fe concentration in the local running water. Thus, the Trâmpoiele and Techereu wells show two variation heights in March and August-September, similar to the variation patterns recorded in the Ampoi river and the Trâmpoiele stream, and the Techereu stream respectively. The Ardeu well shows large variation throughout the year that matches the variation pattern recorded in the Ardeu stream (downstream).

Cu was found in low concentration in all water sources. In general, higher concentration of Cu occurs in summer months. Because of the high solubility of copper sulphates, Cu can be transported in solution far away from the primary source.

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The variation curves of Cr are erratic, however in all water sources a minimum was recorded in February, followed by an obvious increasing trend in May. Cr found in basic and ultrabasic rocks and is associated with Mg and Fe. In exogenous processes, Cr from mafic minerals is mobilized in water and is partially concentrated in hydroxides. In the oxidation zone of sulphide ores, it may combine with Pb, forming lead chromates ($Pb_3O(CrO_4)$ and/or $PbCrO_4$).

In magmatic processes, Pb is associated with Zn, but in weathering processes Pb forms compounds that are less soluble in water than the compounds of Zn. Therefore Pb concentrates closer to the primary source. The variation pattern of Pb concentration is similar in all water types and suggests a unique source of Pb; most likely the local geochemical background. In all water sources, the highest values were recorded in February and June.

In order to test the differences in metals concentration variation in the 4 groups of water type (surface water, mine water, springs and domestic wells), the One Way Analysis Of Variance (ANOVA) statistical test that compares the variability between the groups to the variability within the groups was assessed. ANOVA is based on two assumptions:

- 1) The observations are random samples from normal distributions.
- 2) The populations have the same variance, σ^2 .

We have checked if the largest standard deviation is less than twice the smallest standard deviation, which means the assumptions hold.

The mean square for each source of variation is defined as being the sum of squares divided by its degrees of freedom. Thus:

$$MSB = SSB/(k - 1) \text{ and } MSW = SSW/(N - k),$$

where

SSB = Between groups sum of squares;

SSW = Within groups sum of squares;

N = the total number of observations;

k = the number of groups.

If the null hypothesis is true and there are no differences between the population means, MSB and MSW will be very similar. On the other hand, if the means are different, MSB will be greater than MSW. The ratio MSB/MSW is a ratio of variances, and follows the F distribution with $k - 1$ and $N - k$ degrees of freedom. In order to reject the null hypothesis the significance level for the ANOVA test's statistic p is 0.05 ($p < 0.05$). This means that the concentration of metal in at least one group is different from at least another group and the difference is statistically significant.

For the 4 groups of water (running water, mine water, springs and domestic wells) we obtained $p=0$ for all metals, showing that the differences in metal concentration between the groups are statistically significant. This can be assessed from the graphical representation (Figure 4.5.8.). Mine water stands apart from the other water types displaying much higher metal concentrations. If mine water is excluded, we obtained $p > 0.05$ for Cd, Cr and Pb. This means that as far as the concentration of these elements is concerned there is no statistically significant difference

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between running water and underground water. For Cu, Ni, Zn and Fe we obtained $p < 0.05$. The concentration of these elements in running water is higher than in underground water and the difference is statistically significant.

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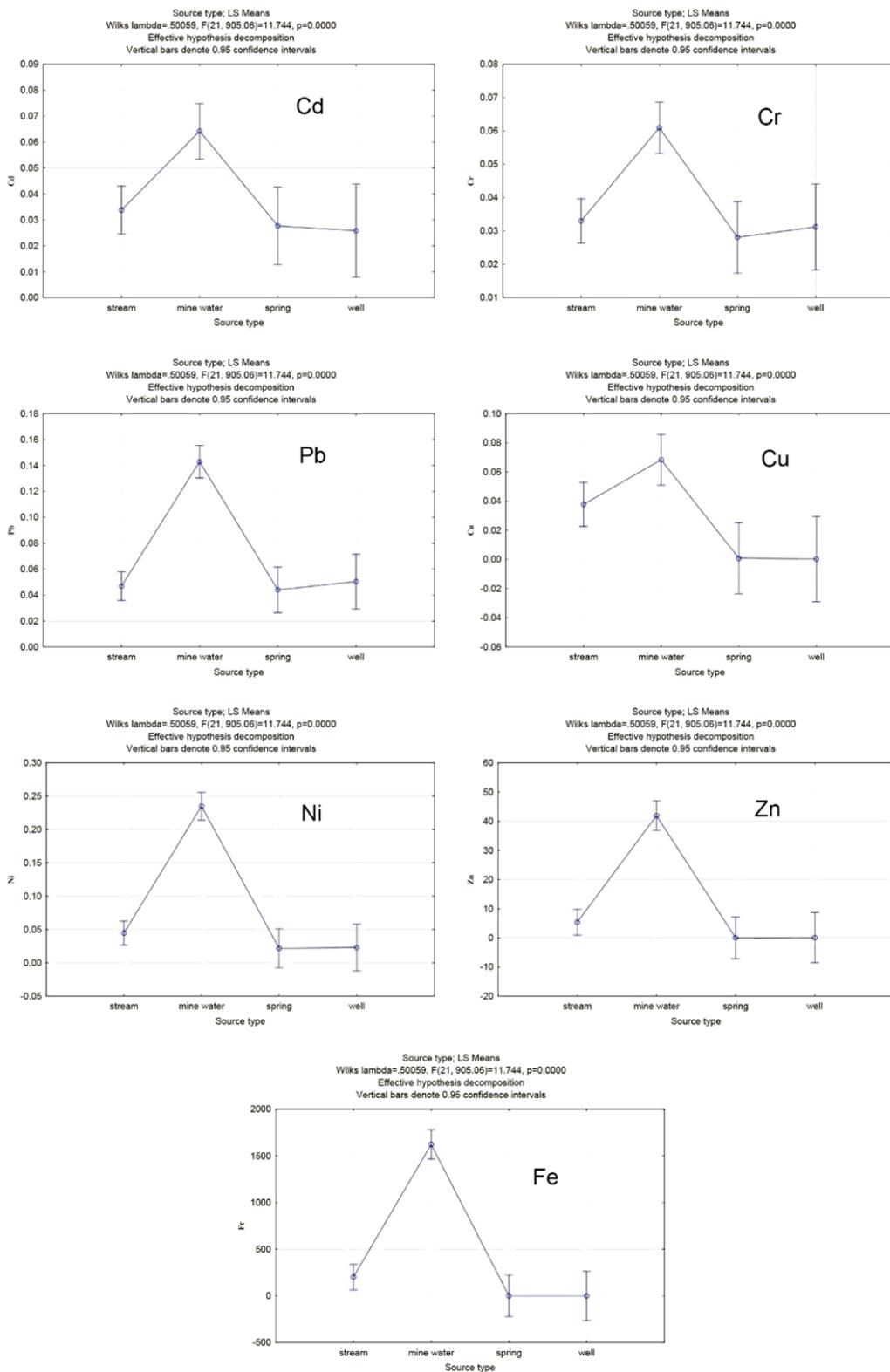


Figure 4.5.83 ANOVA test for the variability of metals concentration in running water, mine water, springs and domestic wells

4.5.3 Genetic relationships, underground dynamics, and evaluation of recharge areas

Linear correlation between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicates that all water sources belong to the meteoric cycle (Figure 4.5.9.) and consequently there is a continuous interaction between them. The regression equation in this case is:

$$\delta^2\text{H} = 6.48 \delta^{18}\text{O} - 3.69.$$

The local meteoric water line (LMWL) at Roșia Montană, determined between December 2014 and August 2015 by monthly measurements performed by the Faculty of Environmental Sciences and Engineering, "Babes - Bolyai" University, Cluj-Napoca, is defined by:

$$\delta^2\text{H} = 7.87\delta^{18}\text{O} + 11.72 \text{‰}.$$

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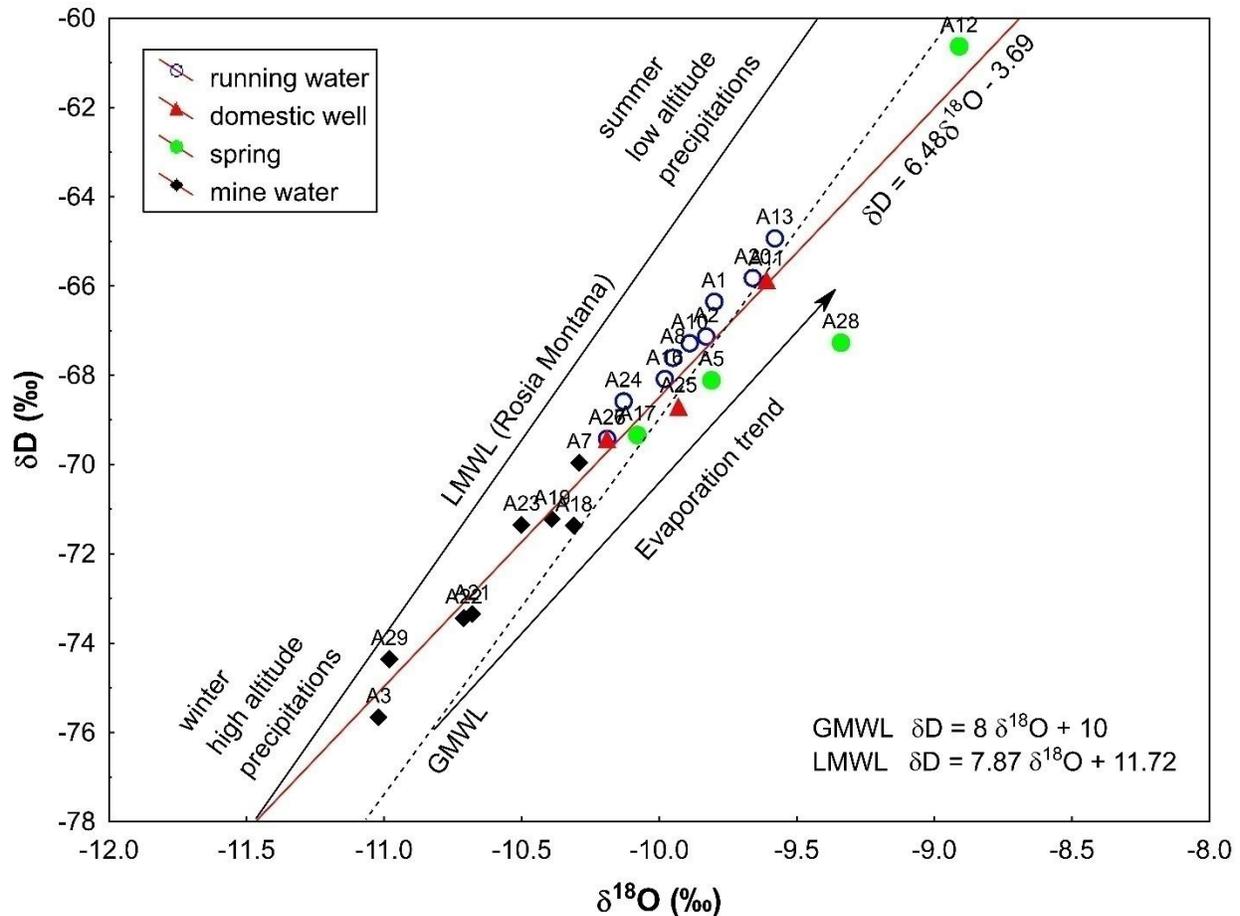


Figure 4.5.9 The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (δD). All displayed values are the mean values for one year of observation. Points are identified by the water source name.

The slope of the regression line for the surface water from the study area (i. e. 6.5) has a normal value for areas with moderate to high relative humidity. The Zlatna spring displays the highest $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, approaching those of summer precipitation. The Techereu spring plots somewhat out of the regression line, suggesting either water - rock interaction or underground mixing with water having different isotopic composition. Low correlation coefficient between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ($r = 0.70$, $n=12$) was obtained for this spring. The other springs and wells plot in the same position on the regression line as the surface water, indicating continuous recharge from the surface water.

The surface waters from the Ampoi hydrographic basin are characterized by higher $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values as compared to the surface waters from the Ardeu and the Techereu hydrographic basins. A higher rate of evaporation is assumed for these waters. The underground water sources from the Ampoi basin (Trâmpoiele domestic well, Larga spring) are also enriched in deuterium and ^{18}O , indicating genetic relationship with the surface water in the area.

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The mine water has the characteristics of winter precipitation and of higher altitude precipitation, showing the lowest concentrations of deuterium and ^{18}O . This finding reflects the major influences of snow-melt and run-off in the late winter on the recharge of mine water.

For the watercourses, the seasonal variation patterns of all studied parameters are comparable downstream and upstream, but in most cases, the variation range is larger downstream than upstream. The pH values are lower downstream because of the AMD. The difference is more pronounced in the summer months when the water flow decreases. The TDS values increase toward downstream. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values also increase along the watercourses as effect of evaporation.

The possibility to define mixing lines on $\delta^2\text{H}$ or $\delta^{18}\text{O}$ vs. TDS (or its equivalent EC) correlation plots represents a tool to establish genetic relationships and to estimate the recharge areas for the underground water (e. g. Gat 1971; Blaga et. 1975; Payne 1981; Papp 2000; Papp & Cociuba 2011; Vermeulen et al. 2014). For water belonging to the meteoric cycle, equivalent mixing lines are obtained for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ because of a linear relationship links $\delta^2\text{H}$ and $\delta^{18}\text{O}$. For the underground waters it is preferred to use the $\delta^2\text{H}$ values because hydrogen isotope composition of water is much less affected by water-rock interactions, as in general, rocks contain less hydrogen than oxygen.

The mine water from the Haneş 2, Valea Babei, Haneş, and Larga adits and the surface water from the Haneş - Ardeu zone (i. e. Ardeu Stream upstream and downstream and Haneş stream) define such a mixing line (Figure 4.5.10). Statistically significant correlation is obtained in this case. Another mixing line can be defined between the mine waters from the Toţi Sfinţii, 23 August, Haneş 2 and Valea Babei adits. The correlation is again significant. The mine water from the Haneş 2 adit (A21) is the intersection point of the two lines and can be considered as mine water end-member. As expected, the mine water from the Valea Babei adit (A22) plots very close to the Haneş 2 mine water, as the two adits are directly connected. The Haneş spring and the Ardeu domestic well lies between the two lines. The Haneş – Ardeu zone can be considered the recharge zone for these sources of mine water and groundwater. In the underground, mine water end-member can mix in different proportions with inflows of local surface water or/and groundwater. For example, if hydrogen isotopes are used in a mass balance calculation and if the Ardeu stream upstream (A24) is taken as the end-member for surface water (surface water background), then the mine water type from Haneş adit (A19) is obtain by mixing the two end-members in a 1:1 ratio.

The mine waters from the IPEG and the Podul Ionului adits plot apart from the two mixing lines (Figure 4.5.10). The low $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of these waters suggest a more important contribution of winter precipitation to the genesis of these mine waters. The TDS values are also significantly lower than the Haneş 2 (and Valea Babei) mine waters.

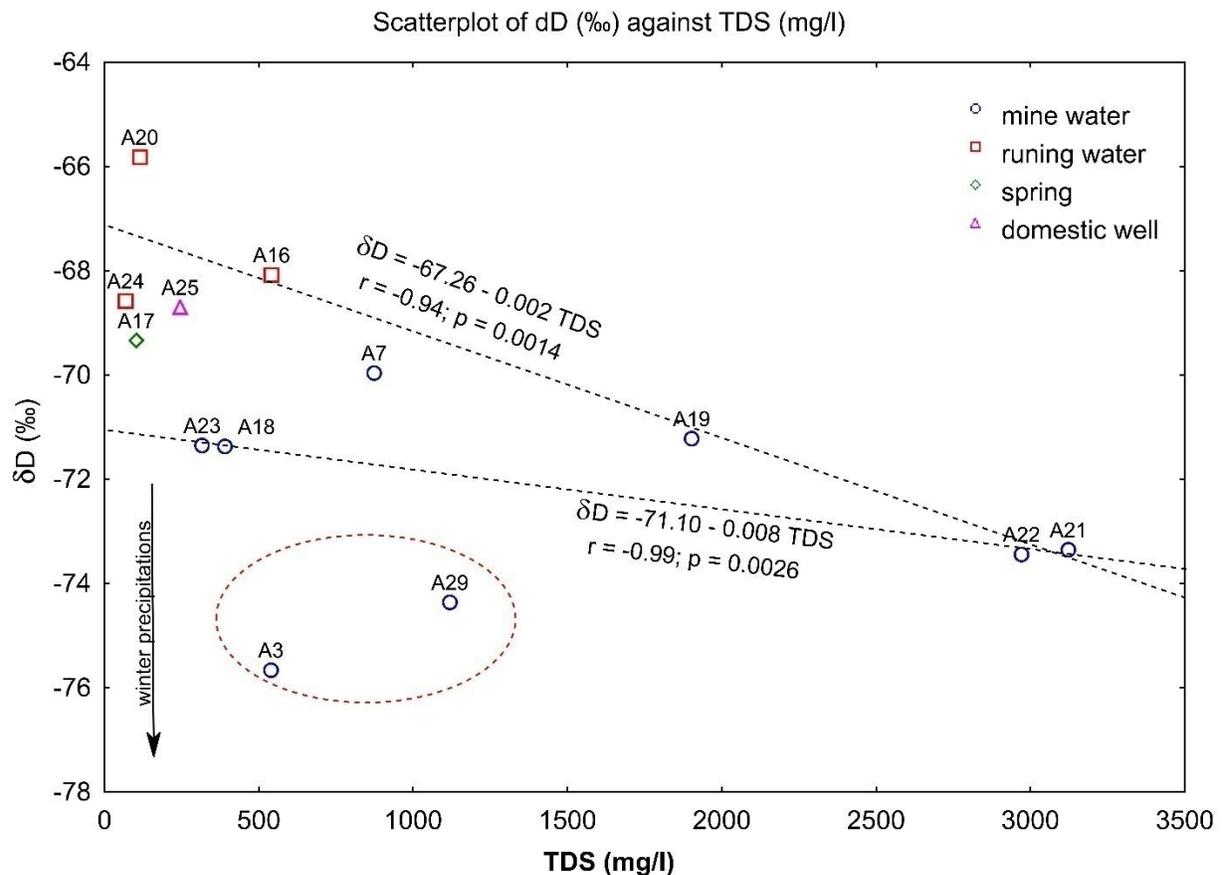


Figure 4.5.4 Mixing lines between different water sources. All display values are mean values for one year of observation. Points are identified by the water source name.

Seasonal variation of the δ^2H and TDS values of meteoric underground water, as compared to surface water, provides an important tool to assess their underground dynamics. For the study area, no relevant contamination of springs and phreatic water by mine water could be revealed. This suggests different underground pathways for the two types of water. Conversely, running water is contaminated by mine water and the negative effects of AMD occur mainly in the summer months when the flow of running water decreases.

For most mine water, the highest TDS values are recorded during winter months when the contribution of precipitation and infiltration water is diminished. During springtime (March – April) the infiltration of surface waters intensifies due to snow melting, and as a result, the dilution of mine water increases. A shift of 1 to 4 months could be observed in the variation sequences of TDS and δ^2H for these mine waters which reflects the flow recharge (Figure 4.5.11.). An exception is the Larga adit, for which the seasonal variation of the isotopic composition is. An increasing trend of the δ^2H values along with a decreasing trend of the TDS values were recorded from March to September, suggesting continuous dilution of the mine water with surface water (Figure 4.5.11b.). In this case fast underground circulation is to be taken into account.

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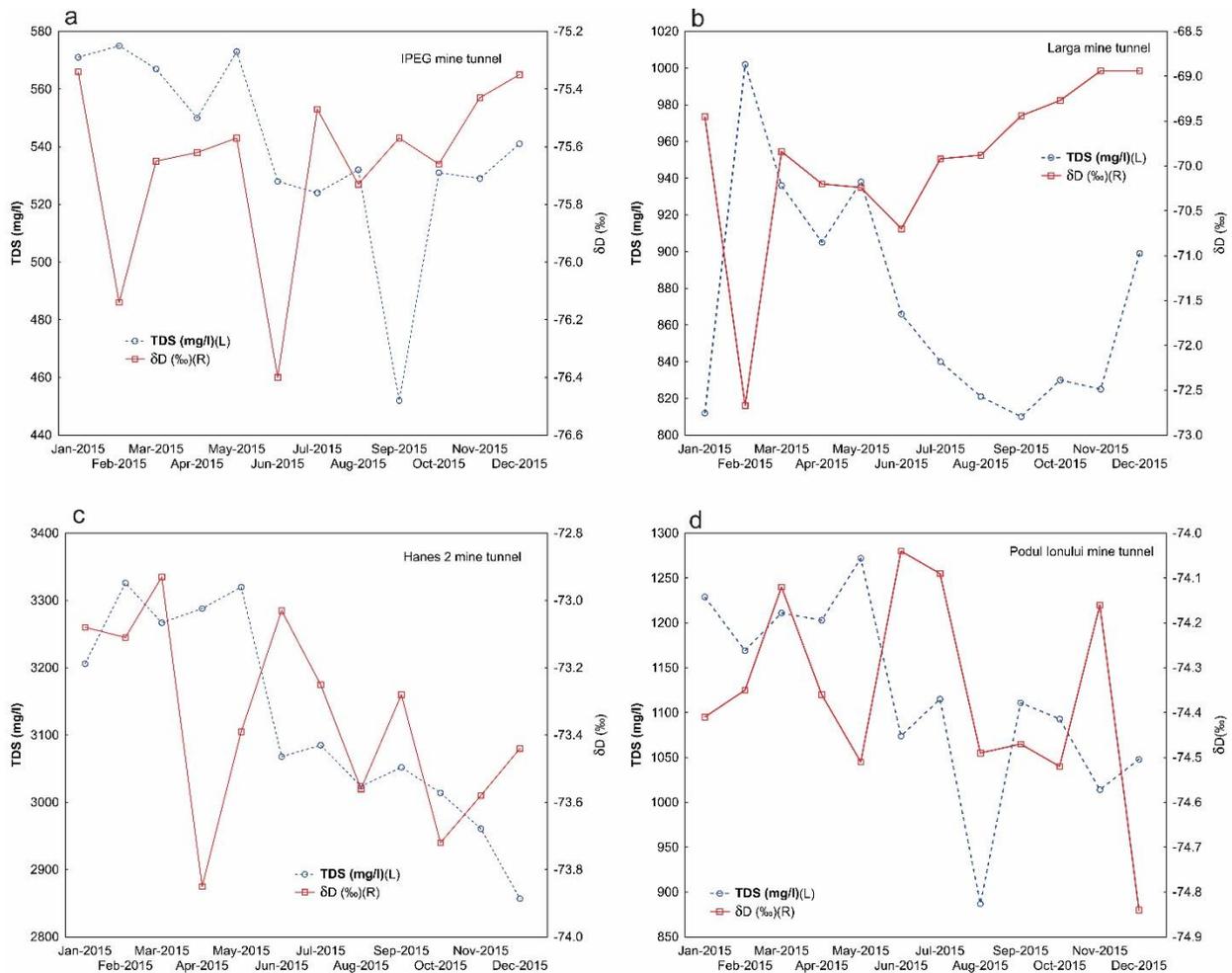


Figure 4.5.11 Seasonal variation of the $\delta^2\text{H}$ and TDS values in several mine waters from Zlatna mining area

The variation patterns of the $\delta^2\text{H}$ and TDS values differ from one spring to another. For the Larga spring, the sequences of minimum and maximum are similar for both $\delta^2\text{H}$ and TDS, pleading for fast underground circulation. Both $\delta^2\text{H}$ and TDS show a minimum in June. During springtime, the infiltration of surface water intensifies due to snow melting, and as a result, the dilution of spring water increases. As compared to the surface waters in the area (Trâmpoiele stream, Larga creek, Ampoi river upstream), analogous variation patterns for the $\delta^2\text{H}$ and TDS values are observed, suggesting genetic relationships (Figure 4.5.12a). These water sources show maximum $\delta^2\text{H}$ and TDS values in April-May, minimum values in June, and then increasing values during the summer months, followed by a decrease in late autumn months (Figure 4.5.12b).

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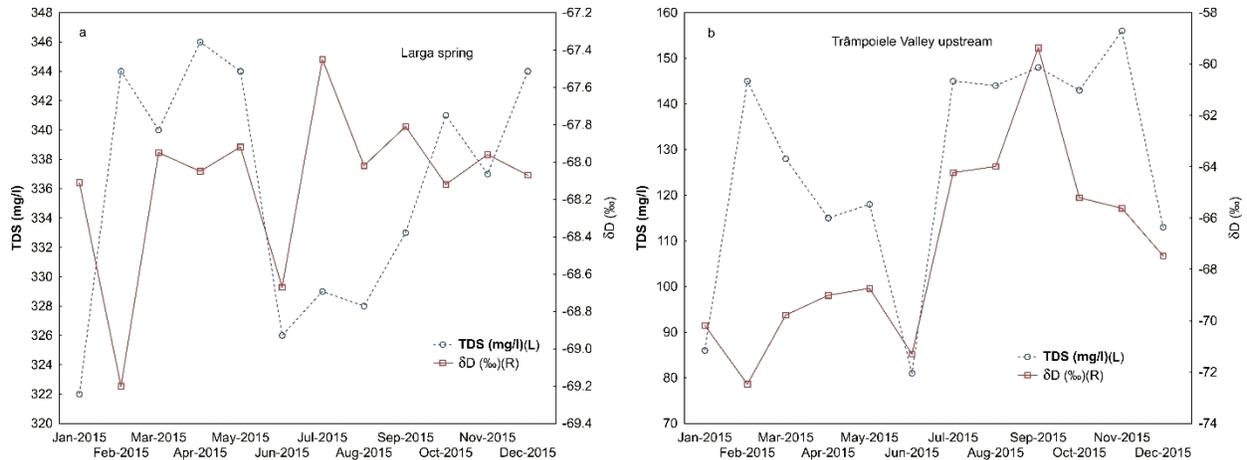


Figure 4.5.12 Analogous seasonal variation of the δ^2H and TDS values between groundwater (a) and surface water (b) from Trâmpoie area

The Ampoi river is the most important collector within the area, with permanent high water flow, and it has the capacity to intake the polluted mine waters without substantial modification of pH and TDS values (Figure 4.5.13.). This can be seen also in metals concentration which doesn't show significant increase downstream of the discharge points of the mine waters. Even more, there is a decrease in Fe concentration downstream, because the river intakes unaffected water from its downstream tributaries. In March, Zn concentration significantly increases upstream.

For the Zlatna spring the seasonal variation pattern of δ^2H is similar to the δ^2H variation pattern of Ampoi river downstream, showing continuous increase from January to September, followed by constant decrease until December (Figure 4.5.13). The highest δ^2H value in both cases is approximately -51 ‰. The variation of TDS for both sources are within the same range, between 138 mg/l and 226 mg/l for the Zlatna spring and between 97 mg/l and 245 mg/l for the Ampoi river downstream. On the Piper diagram they plot very closely (Figure 4.5.2) and the variation of metal concentration is very similar (Figure 4.5.14). These findings allow us to consider phreatic water in the vicinity of Ampoi River downstream as the source of recharge for the Zlatna spring. The similarities between the two sources are not surprising, considering the fact that they are located very close to each other.

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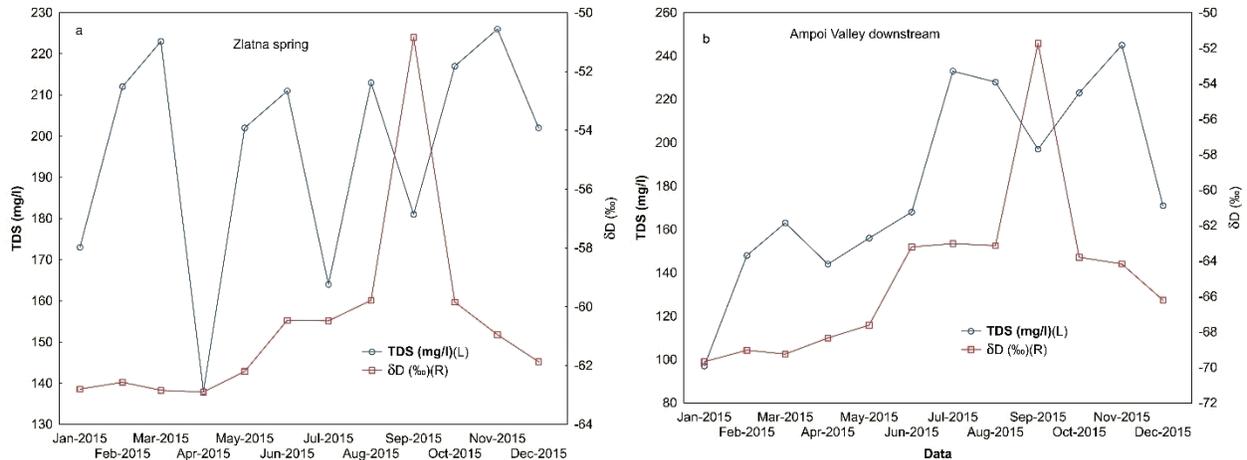


Figure 4.5.13 Analogous seasonal variation of the $\delta^2\text{H}$ (δD) and TDS values between the Zlatna spring and the Ampoi river downstream

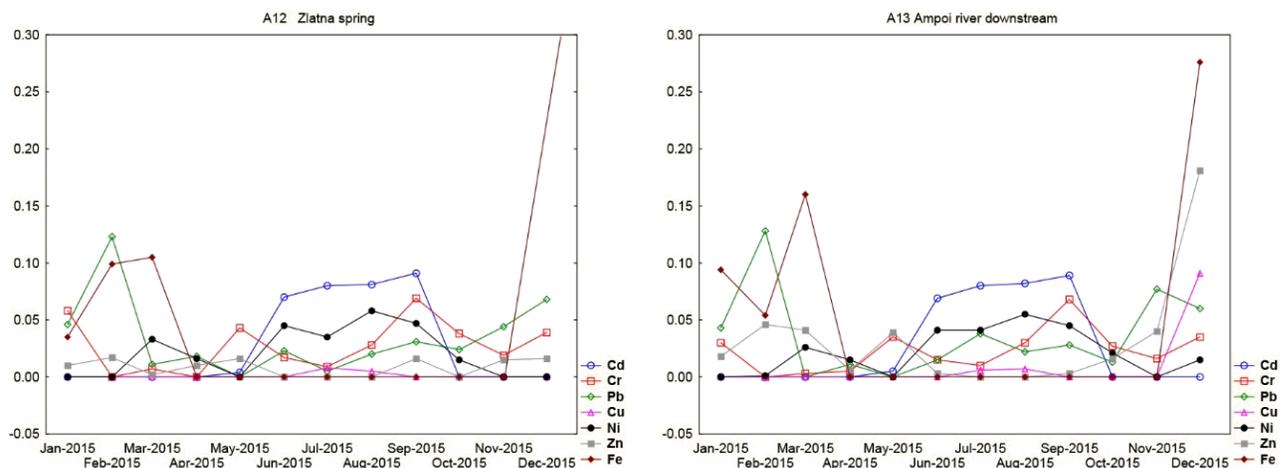


Figure 4.5.14 Analogous seasonal variation of metals concentration between the Zlatna spring and the Ampoi river downstream

The Trâmpoiele stream is a tributary of the Ampoi river and it collects the mine waters from the Larga and IPEG adits. The TDS values increase significantly during July – October downstream of the mine water discharge (Figure 4.5.15.). Contribution of mine water to stream pollution can be clearly seen in the increase of metals concentration downstream. The largest difference occurs in the case of Zn. Cr shows two peaks of variation in March and September both upstream and downstream. There is a decreasing trend of Pb concentration during spring followed by an increasing trend during autumn and winter. Low concentration of Cu occurred both upstream and downstream from January to May. During summer months Cu concentration increased. The increase is more significant upstream than downstream. Ni concentration is at its highest level in August, probably due to the intense evaporation during the warm season. Upstream, Fe concentration is at its highest level in February. Downstream, Fe concentration is at its lowest level from May to August and increases sharply in September.

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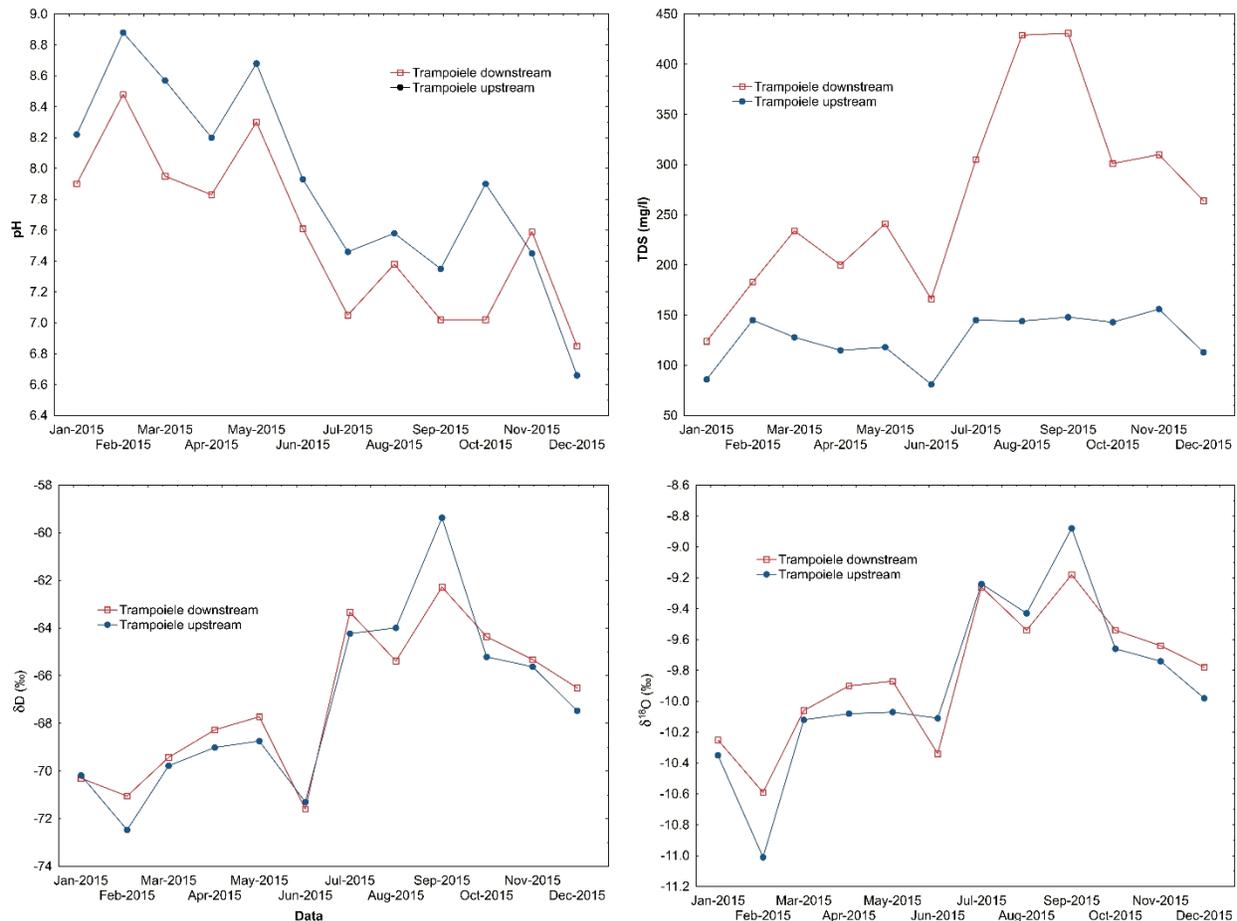


Figure 4.5.5 Seasonal variation of pH, TDS, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values along the Trâmpoiele stream

The Haneş spring shows an increasing trend of the TDS values from March to November that corresponds to a decreasing trend of $\delta^2\text{H}$ values. At the beginning and the end of this period the trends are reversed. The two variation curves are phase shifted from each other with a period of 8 months. A longer period of monitoring of at least two years would be required to better constrain the variation patterns of $\delta^2\text{H}$ and TDS in this case. Slow flow recharge pathways can be taken into consideration for this underground water source. (Figure 4.5.6a). Similar variation patterns of $\delta^2\text{H}$ and TDS occur in the case of mine water from 23 August adit (Figure 4.5.6b.), suggesting possible inflows of groundwater similar to that at the Haneş spring. In the case of the 23 August adit mine water, both $\delta^2\text{H}$ and TDS vary in more restricted ranges because of mixing inside the mine. The TDS shows a minimum in April, most likely as a response to snow melt infiltration.

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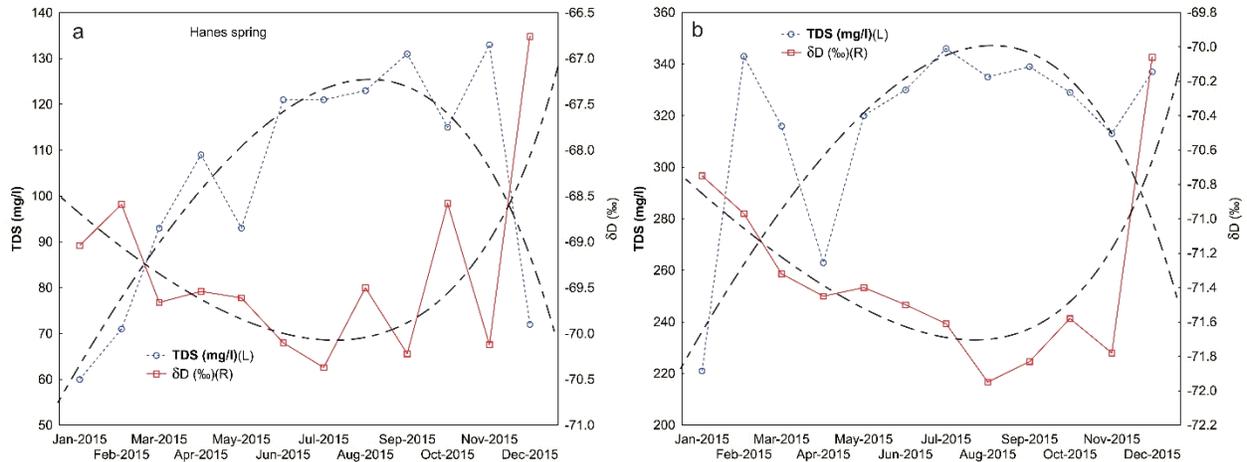


Figure 4.5.16 Seasonal variation of the $\delta^2\text{H}$ (δD) and TDS values in the Hanes spring (a) and mine water from the 23 August adit (b)

For the Techereu spring the seasonal variation of the $\delta^2\text{H}$ is V-shaped with the lowest value recorded in May, which reflects influences of snow-melt (Figure 4.5.17). An increasing trend of the TDS value was recorded from January to April, when the contribution of precipitation and infiltration is diminished. Starting from June, the variation patterns of both $\delta^2\text{H}$ and TDS are analogous, suggesting relatively fast underground circulation. The recharge zones for the Techereu springs cannot be inferred from the available data.

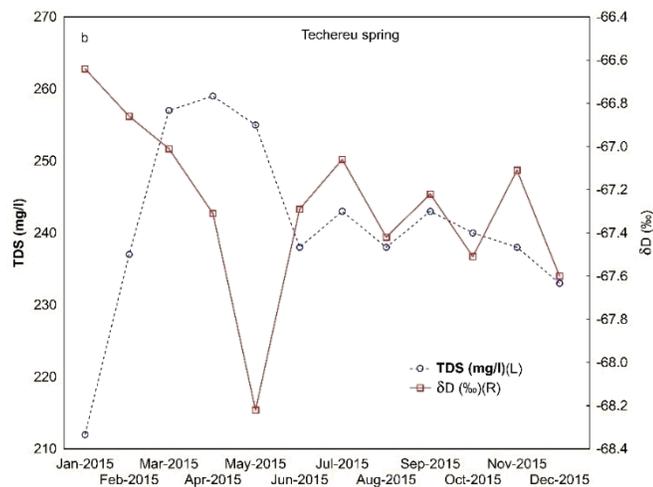


Figure 4.5.17 Seasonal variation of the $\delta^2\text{H}$ (δD) and TDS values in the Techereu spring

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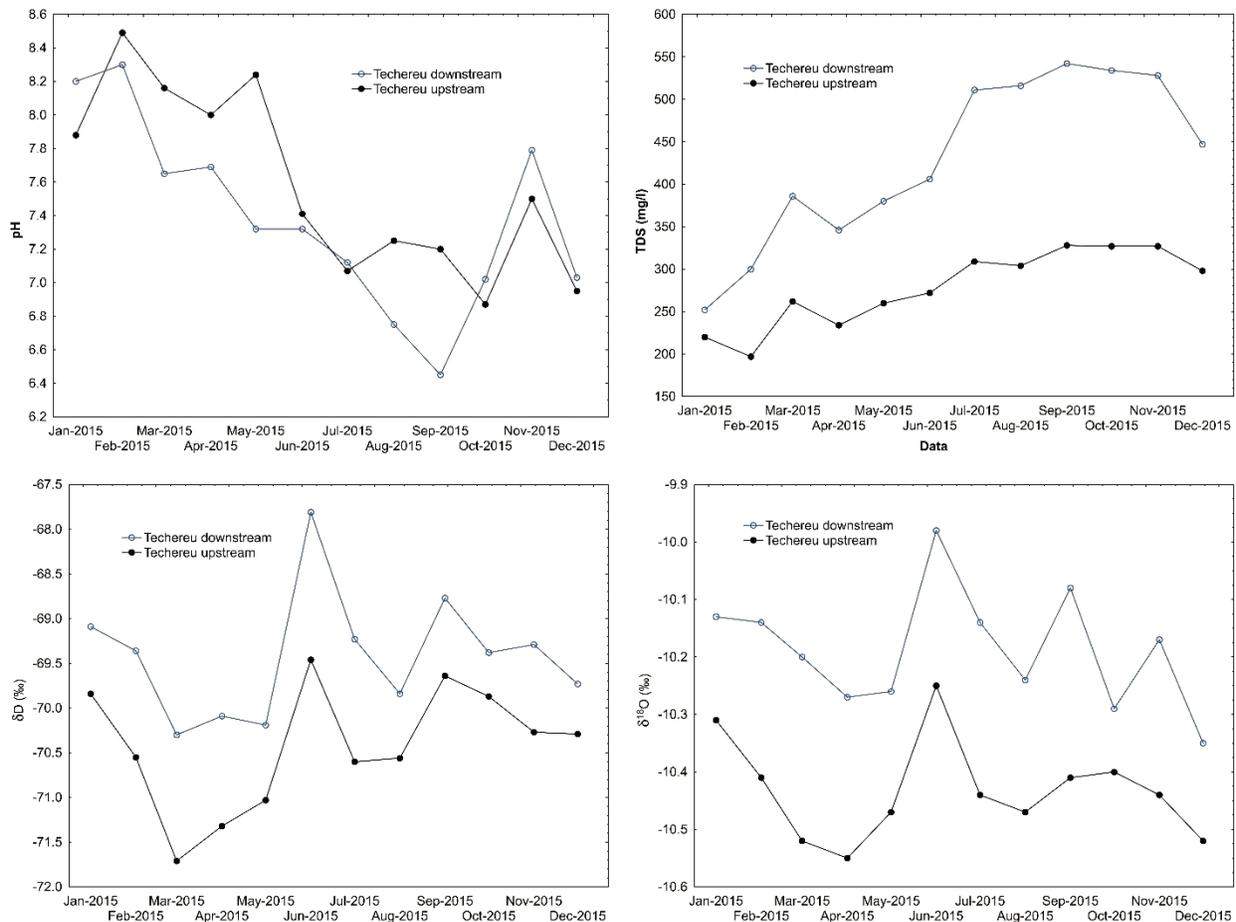


Figure 4.5.18 Seasonal variation of pH, TDS, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values along the Techereu stream

The Techereu stream receives mine waters discharged from the Podul Ionului adit. The largest differences in the pH and TDS values between upstream and downstream were recorded in September when the water flow is at its lowest rate and the contribution of mine water increases (Figure 4.5.18). In the case of the Techereu stream, the isotopic composition of water downstream is significantly enriched in heavy isotopes relative to upstream. For all other watercourses the enrichment in heavy isotopes along the course is less significant. This characteristic of the Techereu stream could be explained by the fact that upstream it passes dominantly through wooded areas which prevents evaporation, while downstream is more exposed to sun. All other water courses are equally exposed to sun, both upstream and downstream. Both upstream and downstream, have relatively high SO_4 content, but because of its high buffering capacity, no drop in pH was recorded during summer months, as would have been expected due to important increase in TDS. Cd concentration shows no variation along the stream. Chrome concentration is more elevated upstream. The concentration of Pb downstream exceeds the concentration found upstream. Much more elevated concentrations of Fe, Zn, and Ni were recorded downstream. Copper concentration increases during summer months. The increase is more significant upstream than downstream. The seasonal variation pattern of $\delta^2\text{H}$ in the Techereu well is similar to the seasonal variation pattern of $\delta^2\text{H}$ in the Techereu stream (upstream and

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downstream),, all sources show a peak in June (Figure 4.5.19.). The negative correlation coefficients between $\delta^2\text{H}$ and TDS, confirm the relationship with phreatic water. For the Techereu stream upstream, the correlation coefficient between $\delta^2\text{H}$ and TDS is $r=-0.08$ ($n=12$), and for Techereu stream downstream, $r=-0.10$ ($n=12$).

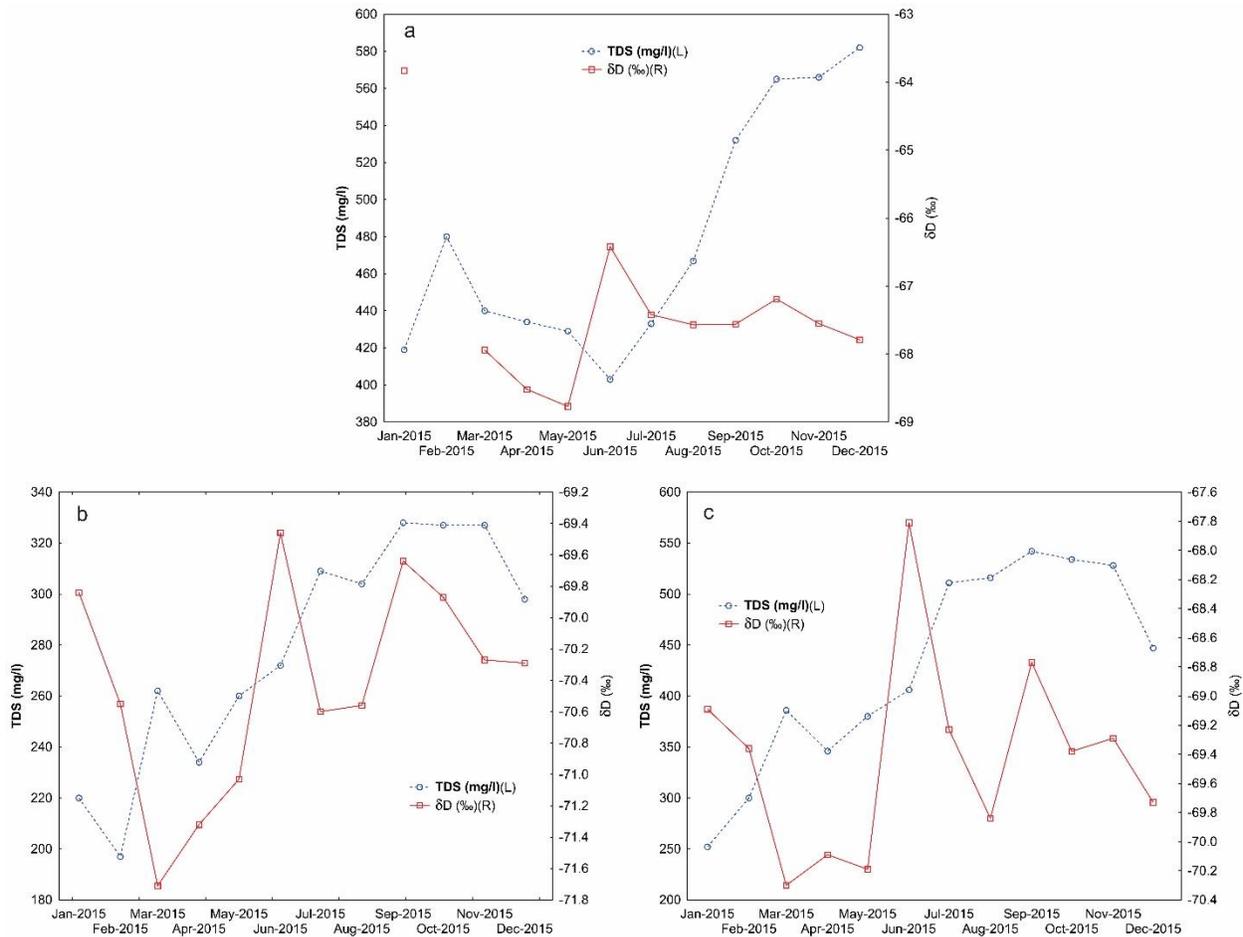


Figure 4.5.19 Seasonal variation of the $\delta^2\text{H}$ (δD) and TDS values in the Techereu domestic well (a), Techereu stream upstream (b) and Techereu stream downstream (c)

The Ardeu stream shows large variation in pH and TDS along its course. During summer months there is a significant drop in pH downstream, after the stream collects the acid mine waters discharged from the Haneş, Haneş 2 and Valea Babei adits. The drop of the pH is accompanied by a large increase of the TDS and SO_4 content (Figure 4.5.20.). The Ardeu stream also shows large variation of metals concentration along its course). This is due to extreme evaporation and desorption of the acid iron hydroxide precipitate from the bottom of stream, in very low flow conditions. The Ardeu stream is by far the most effected water course in the area. Cu is completely absent upstream. Fe and Zn concentrations are also very low. Much more elevated concentration of Fe, Zn, Ni and Cu was recorded downstream. The concentration of Pb, Cr and Cd also exceed the concentration found upstream, but at a lower extend. The concentration of these metals is

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relatively elevated upstream which is the unaffected part of the stream, suggesting that the geochemical background of these elements is high in the area.

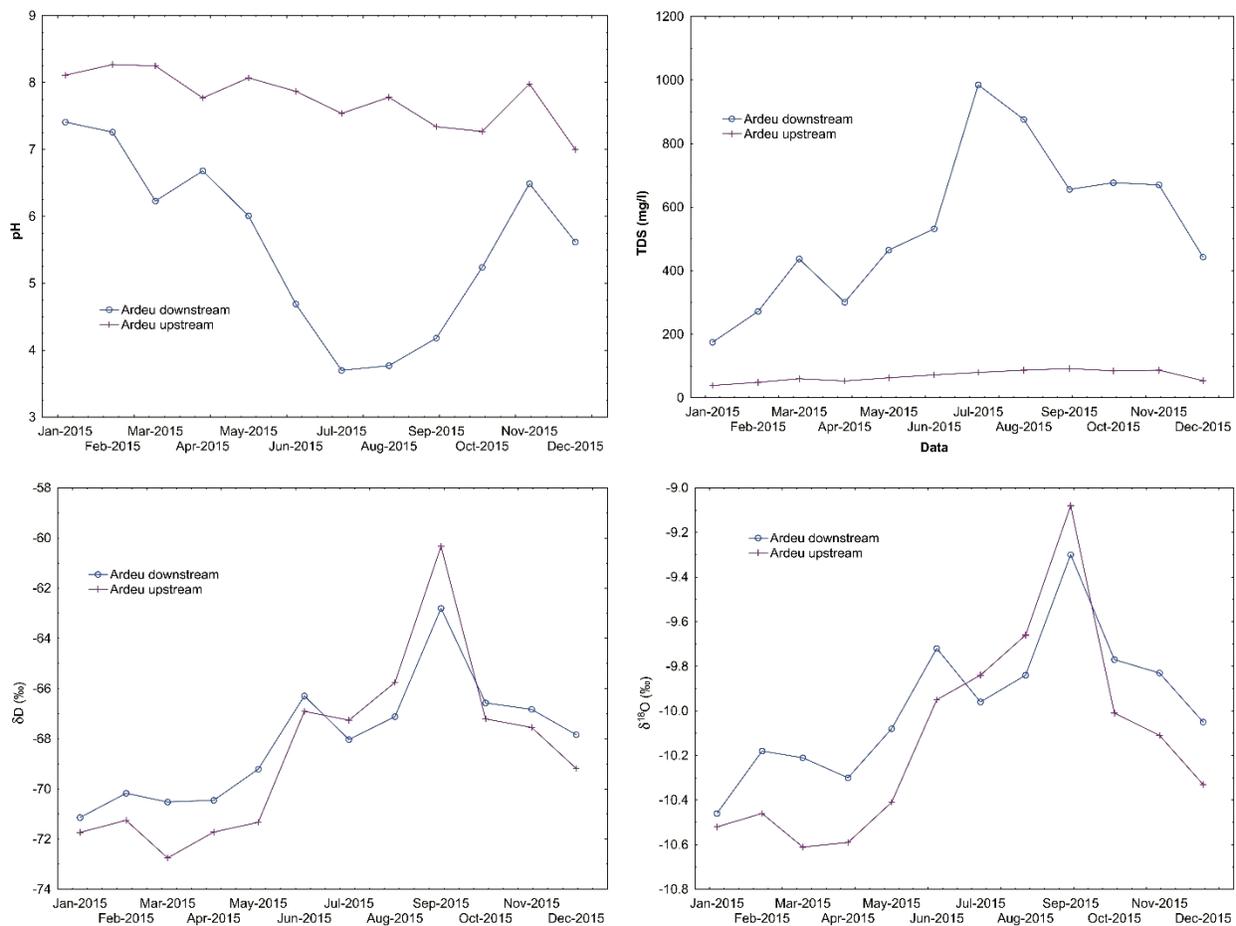


Figure 4.5.6 Seasonal variation of pH, TDS, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values along the Ardeu stream

The domestic wells under study reflect the characteristics of the phreatic water in the area. They show the highest $\delta^2\text{H}$ and TDS values in September-November as a delayed consequence of evaporation during summer month. The lowest $\delta^2\text{H}$ values which reflects the influences of snow melt occurred between March and May in the Ardeu well and the Techereu well. For the Trâmpoiele well, the lowest $\delta^2\text{H}$ value was recorded in July (Figure 4.5.21).

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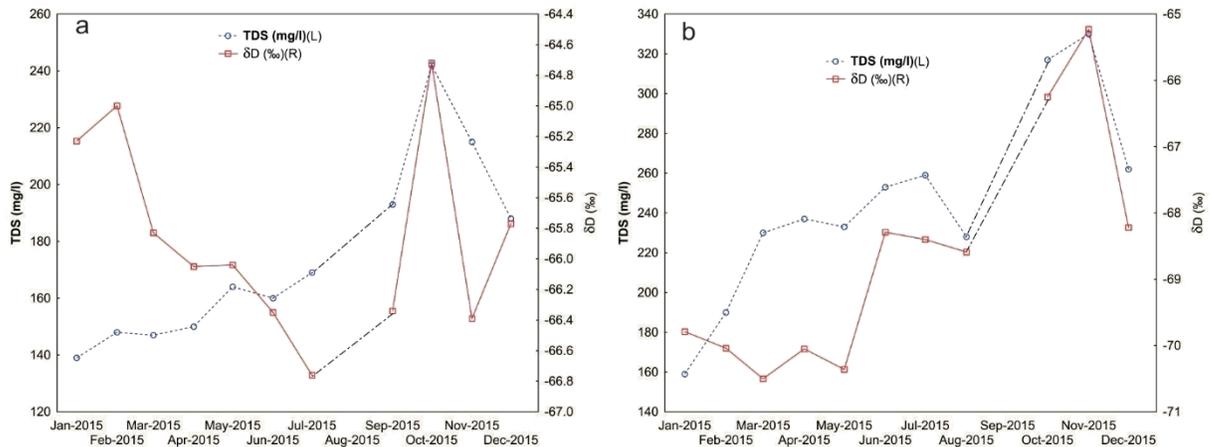


Figure 4.5.21 Seasonal variation of the $\delta^2\text{H}$ (δD) and TDS values in a) the Trâmpoiele and b) Ardeu domestic wells

4.5.4 Water quality and issues of concern

In order to assess the rock source for water mineralisation a few geochemical indexes based on the cation and anion content of water were used (Hounslow, 1995). The attention values of the used indexes and their significance are given in Table 4.5.2. For the Zlatna mining area, the values of these indexes were calculated for each water source using the mean values of ion contents for one year of observation and are given in table 4.5.3.

For all water sources the $(\text{Na}+\text{K}-\text{Cl})/(\text{Na}+\text{K}-\text{Cl}+\text{Ca})$ index is between 0.2 and 0.8 and the $\text{Na}/(\text{Na}+\text{Ca})$ index ≥ 0.5 , suggesting that plagioclase weathering is the main source of Na. This is in accordance with the wide presence of magmatic rocks in the area. The $\text{Mg}/(\text{Ca}+\text{Mg})$ index is ≤ 0.5 indicating that limestones/dolomites and ferromagnesian minerals are possible sources for Ca and Mg. The lack of Si determinations makes discrimination between the two sources impossible. For most mine waters, and also for the Larga creek and the Ardeu stream downstream, the $\text{Ca}/(\text{Ca}+\text{SO}_4)$ index is < 0.5 and the pH is < 5.5 , which is an indication for pyrite oxidation. Conversely, for the mine water drained from the 23 August adits the $\text{Ca}/(\text{Ca}+\text{SO}_4)$ index is > 0.5 , suggesting that this water was not in contact with pyrite. The waters showing $\text{Ca}/(\text{Ca}+\text{SO}_4)$ index < 0.5 , but pH values > 5.5 have buffering capacity that may protect the water body from fluctuations in pH (e.g. IPEG adit, Toţi Sfinţii adit, Techereu stream).

Table 4.5.2 Summary of the criterion for the rock source deduction

Parameter	Attention Value	Significance
Na/(Na+Cl)	> 0.5	Sodium Source other than halite - albite, ion exchange
	$= 0.5$	Halite Solution
	< 0.5 and TDS > 500	Reverse Softening, seawater
	< 0.5 and TDS < 500 and > 50	Analysis Error
	< 0.5 and TDS < 50	Rainwater
Mg/(Ca+Mg)	$= 0.5$ and $(\text{HCO}_3/\text{Si}) > 10$	Dolomite Weathering
	< 0.5	Limestone-Dolomite Weathering

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	>0.5 <0.5 and (HCO ₃ /Si)<5 >0.5	Dolomite Dissolution, calcite precipitation, or seawater Ferromagnesian Minerals Granitic weathering
Ca/(Ca+SO ₄)	=0.5 <0.5 and pH<5.5 <0.5 and pH neutral >0.5	Gypsum dissolution Pyrite oxidation Calcium removal - ion exchange or calcite precipitation Calcium source other than gypsum - carbonate or silicates
(Na+K-Cl)/ (Na+K-Cl+Ca)	0.2 - 0.8 <0.2 or >0.8	Plagioclase weathering possible Plagioclase weathering unlikely

Table 4.5.3 Geochemical indexes for water sources from the Zlatna mining area

Crt. no.	Source name	Source location	Water type	Plz Wth ¹	Na source ²	Mg source ³	Ca/(Ca+SO ₄)	pH
1	A1	Ampoi river upstream	running water	0.1	0.6	0.2	0.9	>5.5
2	A2	Trâmpoiele stream downstream	running water	0.2	0.5	0.2	0.4	>5.5
3	A3	IPEG adit	mine water	0.1	0.8	0.1	0.2	>5.5
4	A5	Larga spring	spring	0.2	0.8	0.3	0.4	>5.5
5	A7	Larga adit	mine water	0.4	0.9	0.5	0.2	<5.5
6	A8	Larga creek	running water	0.2	0.9	0.2	0.1	<5.5
7	A10	Trâmpoiele stream upstream	running water	0.2	0.7	0.2	0.5	>5.5
8	A11	Trâmpoiele domestic well	phreatic water	0.2	0.7	0.1	0.6	>5.5
9	A12	Zlatna spring	spring	0.2	0.8	0.2	0.5	>5.5
10	A13	Ampoi river downstream	running water	0.1	0.5	0.2	0.4	>5.5
11	A16	Ardeu stream downstream	running water	0.1	0.6	0.1	0.2	<5.5
12	A17	Haneş spring	spring	0.2	0.6	0.1	0.6	>5.5
13	A18	Toţi Sfinţii adit	mine water	0.2	0.9	0.3	0.3	>5.5
14	A19	Haneş Mine	mine water	-	-	0.3	0.2	<5.5
15	A20	Haneş stream	running water	0.2	0.9	0.1	0.4	>5.5
16	A21	Haneş 2 adit	mine water	0.2	0.9	0.2	0.1	<5.5
17	A22	Valea Babei adit	mine water	-	-	-	-	<5.5
18	A23	23 August adit	mine water	0.1	1.0	0.1	0.8	>5.5
19	A24	Ardeu stream upstream	running water	0.1	0.8	0.1	0.8	>5.5
20	A25	Ardeu domestic well	phreatic water	0.2	0.7	0.1	0.5	>5.5
21	A26	Techereu stream downstream	running water	0.2	0.9	0.2	0.2	>5.5
22	A27	Techereu domestic well	phreatic water	0.3	0.7	0.2	0.4	>5.5
23	A28	Techereu spring	spring	0.6	1.0	0.3	0.6	>5.5
24	A29	Podul Ionului adit	mine water	0.2	0.9	0.2	0.1	<5.5
25	A30	Techereu stream upstream	running water	0.1	0.8	0.1	0.3	>5.5

¹ plz wth – plagioclase weathering (Na+K-Cl)/(Na+K-Cl+Ca)

² Na source – Na/(Na+Ca)

³ Mg source – Mg/(Ca+Mg)

Missing data are out of range

Different water quality parameters are set by several international and national regulations. In order to assess the quality of water at the Zlatna mining area we applied the following standards:

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- the European 98/83/EC standard for drinking water → for springs and wells that are currently used for drinking water;
- the national NTPA-013/2002 standard for water that is suitable for treatment to produce drinking water → for running water;
- the national standard for waste water HG 188/2002 → for mine water.

The following table (Table 4.5.4) presents a summary of some of the more common water quality parameters which are regulated under the 3 standards.

Table 4.5.4 Water quality parameters regulated under different standards

Parameter	98/83/EC standard (drinking water)	NTPA-013/2002 standard (surface water)	HG 188/2002 standard (waste water)
pH	>6.5	>6.5	>6.5
F (mg/l)	1.5	1.7	5
Cl (mg/l)	250		500
NO ₃ (mg/l)	50	50	25
SO ₄ (mg/l)	250	250	600
Cd (mg/l)	0.005	0.005	0.2
Cr (mg/l)	0.05	0.05	1
Pb (mg/l)	0.01	0.05	0.2
Cu (mg/l)	2.0	5	0.1
Ni (mg/l)	0.02	0.1	0.5
Zn (mg/l)	3	5	0.5
Fe (mg/l)	0.2	1	5

These standards were applied on the mean values of the specified parameters for all water sources under study. The marked values in the Table 4.5.65 are above the standard limits.

Table 4.5.5 Values of water quality parameters in different water sources from Zlatna mining area

Source	Source type	pH	Anions mg/L				Heavy metals mg/L						
			F	Cl	NO ₃ ⁻	SO ₄ ⁻	Cd	Cr	Pb	Cu	Ni	Zn	Fe
A1	rw	8.04	0.00	7.52	1082.89	16.51	0.069	0.020	0.044	0.001	0.019	0.050	0.088
A2	rw	7.58	0.09	5.54	146.38	149.58	0.027	0.023	0.054	0.004	0.028	0.357	0.081
A3	mw	7.36	0.51	5.69	2759.00	1323.12	0.03	0.030	0.07	0.00	0.05	1.124	0.07
A5	sp	7.22	0.11	4.20	269.76	183.24	0.027	0.028	0.057	0.000	0.023	0.009	0.028
A7	mw	4.04	2.82	4.42	3962.15	3614.88	0.043	0.084	0.190	0.233	0.216	19.363	1917.566
A8	rw	3.88	0.85	1.77	1076.76	1314.37	0.040	0.055	0.053	0.338	0.130	11.054	1174.923
A10	rw	7.91	0.06	4.27	116.04	51.28	0.027	0.032	0.024	0.001	0.019	0.011	0.072

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A11	we	7.02	0.04	10.55	158.29	59.44	0.022	0.029	0.038	0.001	0.017	0.008	0.039
A12	sp	7.75	0.15	2.69	56.15	64.69	0.027	0.027	0.034	0.001	0.021	0.009	0.062
A13	rw	8.11	0.14	9.44	65.30	57.64	0.027	0.023	0.036	0.009	0.022	0.033	0.049
A16	rw	5.61	0.00	4.07	546.72	534.28	0.045	0.033	0.074	0.060	0.083	38.590	480.697
A17	sp	7.45	0.05	2.13	20.72	14.26	0.028	0.029	0.034	0.001	0.019	0.017	0.030
A18	mw	7.30	1.74	2.84	189.31	1288.71	0.028	0.028	0.057	0.001	0.028	0.039	0.282
A19	mw	3.83	0.00	41.11	2297.90	27678.80	0.091	0.064	0.148	0.248	0.327	63.590	2610.100
A20	rw	7.06	0.09	1.40	57.32	40.61	0.029	0.047	0.027	0.001	0.020	0.099	0.727
A21	mw	4.16	14.78	56.40	2519.20	21063.31	0.133	0.083	0.266	0.028	0.481	107.862	3098.361
A22	mw	4.55	24.35	82.10	2308.20	67541.04	0.143	0.109	0.260	0.024	0.461	108.176	3040.921
A23	mw	7.67	0.04	1.72	67.85	286.04	0.030	0.050	0.063	0.000	0.019	0.203	2.641
A24	rw	7.77	0.07	1.48	14.08	17.47	0.029	0.038	0.045	0.000	0.014	0.023	0.404
A25	we	7.55	0.06	3.01	220.52	47.58	0.023	0.034	0.054	0.000	0.017	0.035	0.123
A26	rw	7.39	0.17	1.91	216.97	547.34	0.029	0.023	0.063	0.004	0.084	6.148	533.094
A27	we	7.37	0.10	23.39	164.77	820.46	0.032	0.030	0.059	0.000	0.035	0.180	0.056
A28	sp	7.64	0.32	5.13	61.63	26.47	0.029	0.028	0.051	0.001	0.024	0.016	0.096
A29	mw	5.91	3.13	8.47	1127.38	4220.12	0.029	0.043	0.111	0.004	0.336	44.996	2522.570
A30	rw	7.59	0.19	1.69	390.49	283.91	0.031	0.042	0.043	0.001	0.032	0.214	0.405

rw – running water; mw – mine water; sp – spring; we – domestic well; marked values exceed the quality standards: green – 98/83/CE for drinking water; orange – NTPA-013/2002 for surface water; purple – HG 882/2013 for waste water

In the Larga creek (A8), the Ardeu stream (A16) and the Techereu stream downstream (A26), the NTPA-013/2002 standard values for pH, NO₃, SO₄, Fe and Zn are exceeded. High concentration of NO₃ was found in the Ampoi stream (A1 and A13) and the Trâmpoiele stream (A2 and A10). The NO₃ and SO₄ concentration in the Techereu stream upstream (A30) exceed the standard values. To a lesser extent the concentration of Pb is exceeded in the Trâmpoiele stream (A2), the Ardeu stream downstream (A16), the Larga creek (A8) and the Techereu stream downstream (A26). In all surface waters the standard value for Cd concentration is exceeded by up to 6 times. The least affected running water in the area is the Ardeu stream upstream (A24). In this source only the Cd concentration standard is exceeded.

All springs and wells show much higher values of NO₃ concentration than the standard for drinking water (98/83/EC) allows. The high values of NO₃ were recorded in March and April. In the Techereu well (A27) the concentration of SO₄ is also above the standard value for drinking water. The Larga spring (A5), the Zlatna spring (A17) as well as the Techereu well (A27) and the Techereu spring (A28) have Ni and Pb concentration slightly higher than the standard values. All springs and wells show more elevated Cd concentration than the standard permits.

The mine waters from the Haneş 2 and the Valea Babei (A21 and A22) adits discharge the largest amount of pollutants. They are acid waters and in their composition F, NO₃, SO₄, Pb, Zn and Fe far exceed the standard values for waste water (HG 188/2002). The mine water from the 23 August adit (A23), with the exception of NO₃ concentration, is within all standard limits for wastewater.

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Elevated concentration of SO_4 , Zn and Fe in mine waters are the main issues of concern. They directly affect surface water. The most affected watercourses are the Ardeu stream and the Techereu stream, downstream of mine water discharge. Another concern is related to the high concentrations of NO_3 that was recorded in all water sources in March and April. However, this could be due to organic matter or could be a consequence of using fertilizers in agriculture and is not directly related to mining pollution. The analytical results for the entire year will allow the source of NO_3 to be better constrained.

In groundwater, Zn and Fe concentration do not exceed the standard values for drinking water. The Pb and Ni concentration exceed these standards by less than 1 % and can be considered borderline values. On the other hand, Cd concentration is higher than the standard value for drinking water and could be a consequence of groundwater contamination by mine water. However, if we take in consideration the fact that Cd concentrations and their seasonal variation are very similar in all sources of groundwater and in unaffected surface water, then the elevated Cd concentration could be due to geochemical background which, due to the presence of sulphide ores in the area, is high. Supplementary isotopic analysis of Cd and Pb are necessary for accurate determination of the source of these elements in groundwater, as well as in surface water.

5 Conclusions

5.1 Summary of mine – environment interactions at each site

5.1.1 Kittilä

Chemical characterization of different waters based on dissolved anions, trace element and total metal concentrations suggest numerous water types interact at the Kittilä mine. Groundwater and upstream surface waters reflect natural weathering of local lithologies and exhibit relatively low electrical conductivities and low concentrations of mine water indicator species. Mine waters can be distinguished as process water, mine dewatering water, and formation water. Mine process water has the highest SO_4 concentrations of all water sources, which is attributed to process chemical residues and enhanced sulphide mineral weathering during ore processing. In contrast, formation water exhibits elevated Na and Cl concentrations, and has relatively low metals concentrations. Downstream of where underground mine dewatering and process waters discharge to the Seurujoki River, river solute concentrations remain elevated relative to background concentrations in SO_4 , Mg, Na, Mn, Sr, Se, B, As, and Sb. Small increases were also evident in Ca, Co, NO_3 , and Li.

Select isotope systems provided additional insight to distinguish end member water sources, identify flow pathways and quantify mixing. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions were distinct between process waters (with uniquely negative d-excess values), formation water (with a uniquely high d-excess value), and meteoric waters. Slight enrichment and lack of seasonal variability in dewatering ^{18}O and ^2H suggests influence from non-meteoric water. Similarity in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water from borehole (SUG15047, SUG15049 and RUG 15015) and surface water samples in March suggests the possibility of rapid recharge to deep bedrock fracture systems surrounding the underground mine workings. Rapid hydraulic conductivity from surface water to deep fracture systems has implications for the impacts of mine dewatering on surface water bodies. This relationship can be further evaluated and recharge rates could be estimated through increased monitoring frequency of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in borehole and surface waters at the site. Increased monitoring frequency can also help improve the application of water isotopes to assess mixing by constraining temporal isotopic variability in different water source.

Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) and Cl concentrations were applied as tracers to calculate relative contributions of mine process water and mine dewatering water to the Seurujoki River for June 2013 and June 2015. The results approximately aligned with hydrologic flow measurements from June 2014 (Ramboll 2015). Further characterization of end member water sources may also facilitate the application of Sr as a tracer of surface water capture to the underground mine. Distinct variation in the $\delta^{34}\text{S}-\text{SO}_4$ and the $\delta^7\text{Li}$ compositions of different water types at the mine site show promise as a tracer for SO_4 source, as well as mechanisms of solute attenuation. However, further isotopic characterization of end member sources contributing to SO_4 and Li in solution, for example in ore minerals, process chemicals, and secondary mineral precipitates from wetland and river bed surfaces, will facilitate further characterization of solute source and attenuation mechanisms at the Kittilä site.

5.1.2 Roşia Montană

The mine water from all sources discharges large amounts of pollutants. The sources are acid waters and in their composition, F, NO₃, SO₄, Ni, Cu, Zn and Cd exceed the standard values for wastewater. According to the standard maximal values, the mine water from Cetate Adit (S9) and C122 Adit (S25) seem to be the most polluted, while Cetate Dump 2 (S7) is within all standard values for wastewater, with the exception of SO₄.

High values of SO₄, NO₃, Zn, Cu in mine waters represent the main issues of concern in Roşia Montană mining area. These sources flow directly into the streams/ surface waters and affect the quality of the water bodies, e.g. Roşia valley, Corna valley and Sălişte valley. The most affected one is Roşia valley, with the downstream point having a pH value very low and greater Zn and Cu concentrations during the entire sampling period. Another concern is related to the high concentration of NO₃. This could be a consequence of using nitrate fertilizers in agriculture are not directly related to mining pollution. The analytical results for the entire year will allow better constraints on the source of NO₃. In lakes the concentrations of heavy metals are within normal limits, with a few exceptions in the case of Cd and Pb for some months of sampling in the year 2015. The Cd concentration exceeds the limits for drinking waters (up to 8 times higher). Cd concentration is much higher than the standard value for drinking water and could be a consequence of groundwater contamination by mine water. However, if we take into consideration the fact that Cd concentration and its seasonal variation is very similar in all sources of groundwater, then the elevated Cd concentration could be due to geochemical background in the area (sulphides ores).

The mine water was characterized by high TDS values and a very low pH, around 2 (especially those waters coming directly from the open galleries). Some exceptions include Cetate Dump 2 and Sălişte tailings AMD, which displayed higher pH values (~ 5 - 6). An explanation could be the interaction with another small stream which probably has an intake of clean water that can dilute the mine water at these points. Also in terms of anion concentrations, the mine waters display the highest NO₃, SO₄ and Cl⁻ values (as was expected). These concentrations are variable from month to month. The metal concentration distribution pattern follows the decreasing order: Zn>Cu>Ni>Cd>Pb>Cr. In the case of pH and TDS, the mine waters are less affected by seasonal variation, while δ²H and δ¹⁸O values are strongly affected (by individual mine water source) suggesting fast flow recharge pathways. Compared with the other water types, mine water has the characteristics of winter precipitation and of higher altitude precipitation, showing the lowest concentrations of ²H and ¹⁸O.

The other underground water (springs and domestic wells) display low TDS values and a neutral pH (~ 6 - 7). C120 dug well is an exception, because of its location very close to the dumps (on Corna Valley) and under a country road, which is highly traveled. The domestic wells and the springs have similar NO₃⁻ concentration, while SO₄ in the domestic wells was slightly higher than in the springs. Elevated concentrations of Pb and Cd in wells (up to 101.1 and 104.6 µg/L) and springs (up to 55.27 and 104.8 µg/L) represent an issue of concern, since they exceed the maximum permissible concentrations of Cd for drinking water, imposed by the Romanian

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legislation. The domestic wells and springs belong to the meteoric cycle, the groundwater recharge being provided by precipitation and by stream water from the surrounding area.

In case of surface waters, variation patterns are a characteristic of each hydrologic basin. The TDS values are high and pH values varying from 2.3 to 8.49. After mine water, also higher NO_3^- and SO_4 concentrations were obtained in case of surface waters. In surface waters, as in the case of mine water, the metal concentration distribution pattern follows the decreasing order: $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cd} > \text{Pb} > \text{Cr}$. Roşia and Corna are the most affected of all of the analyzed valleys. The high metal concentration in Roşia River is a consequence of numerous mine water discharges from Cetate and Carnic open pits and also from the undergrounds works. pH and TDS are less affected by seasonal variation, similar to the process occurring in mine water. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values have strong seasonal variation and most of the points follow the same trend.

Lakes registered the lowest TDS values and neutral pH (~7.5). The artificial lakes are special in structure and have a different stratification and homogeneity. It was noted that, similar to the other types of water, the source of the water is coming from rainfall and runoff.

The majority of the water sources within the study area represent either SO_4 dominated (the mine water and also most of downstream points) or Mg-Ca dominated water types (upstream from mining site and lakes). RO 11 spring, RO 43 spring, RO 78 dug well, Mare Lake and Brazi Lake, and Upstream Roşia Valley show no dominant cation.

$\delta^{34}\text{S}$ signatures of mine impacted waters loosely correlate with SO_4 concentration, while no correlation was observed in non-impacted waters, suggesting that SO_4 from mined lithologies has a discrete $\delta^{34}\text{S}$ signature. Further, this correlation improves when normalized to Ca concentration, which indicates that dissolution of Ca SO_4 minerals may also contribute to SO_4 concentration in mine impacted waters, but do not resemble the discrete $\delta^{34}\text{S}$ of primary sulphides suspected to drive the observed correlation.

Isotopic variation in $^{87}\text{Sr}/^{86}\text{Sr}$ across site waters is likely related to variation in site lithology. Therefore Sr is a valuable tracer of water origins and provides insight to hydrogeologic dynamics across the site. For example, $^{87}\text{Sr}/^{86}\text{Sr}$ results suggest that water discharged from Gallery 714 originates from the mineralized dacite host rock located in open pit mines approximately one km to the east, and provides insight into contaminant source and pathway to the Roşia Valley stream. In the mining works, the water-rock interactions that occur may alter the initial isotope ratios of the infiltration water to an extent that should be further assessed. A deeper understanding and quantitative assessment of the water flow and processes in the mining area, resulting from a complete study, will allow us to propose measures to reduce the AMD generation and contribute to more efficient environmental remediation in the area.

While it appears $\delta^{34}\text{S}$ - SO_4 may provide a useful tracer of SO_4 derived from the mine site lithology, this method does not necessarily facilitate distinction between accelerated SO_4 generation related to mining and naturally occurring SO_4 generation. For example, water collected from the dug well

at site C120 (S24) exhibits elevated SO_4 concentration relative to other sampled natural waters, with a $\delta^{34}\text{S}\text{-SO}_4$ composition indicative of a mineralized host rock sulphide source. However, because C120 is located within the host lithology, $\delta^{34}\text{S}\text{-SO}_4$ does not elucidate whether the elevated SO_4 reflects mine impacts, or the unimpacted state of groundwater within this lithology. While the annual average water quality from this well currently exceeds Romanian drinking water standards for SO_4 , Ni and Cd concentrations (Table 3.2.6), when compared to surrounding water sources impacted by mine runoff (e.g. S23), it seems likely metal and SO_4 concentrations have the potential to increase in the future, resulting in additional standard exceedances.

Additional data that could be used to refine interpretations based on isotope analyses include assessment in temporal variability of isotope compositions. Specific to the application of sulphur isotopes, sulphur isotope analysis of the major sulphur bearing minerals observed across the site would provide end member source information, while isotopic analysis of oxygen within SO_4 would also allow for a more robust assessment of both mixing and process related fractionation (e.g. Holt & Kumar 1991, Wright & Nordstrom 1999).

5.1.3 Zlatna

All sources of groundwater (domestic wells, springs, mine water) belong to the meteoric cycle. Surface running water and infiltration of local precipitation are the sources of recharge to the groundwater system. The influence of snow melt manifests both in surface water and underground water. The surface waters from the Trâmboiele – Ampoi hydrologic basin show a minimum salt content, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ in June as the result of snow melt. For other surface waters (Ardeu stream and Techereu stream) the influence of snow melt is less obvious. At these sites evaporation during summer months substantially changes both the salt content and isotopic composition of waters. Such variation patterns are distinct within each hydrologic basin. Underground water shows seasonal variation similar, but off-set in time, to the surface water. Seasonal variation of TDS and isotopic composition of underground water, as compared to surface water, provided information on recharge zone and underground dynamics. For the Larga spring, local surface water is the main source of recharge. The Zlatna spring has genetic relationships with the phreatic water in the vicinity of the Ampoi Stream. Relatively fast underground circulation was estimated for these springs. The seasonal variation of TDS and isotopic composition of the Haneş spring suggest a slow flow recharge pathway. For the Techereu spring the recharge source could not be assessed. For the Techereu spring the seasonal variation of the $\delta^2\text{H}$ is V-shaped with the lowest value recorded in May, which reflects influences of snow-melt, suggesting relatively fast underground circulation.

For the study area no relevant contamination of springs or phreatic water by mine water was revealed, suggesting different underground pathways for the two types of water. In groundwater, Zn and Fe concentration do not exceed the standard values for drinking water. The Pb and Ni concentration exceed these standards by less than 1 %. Elevated concentration of Cd was recorded in all water sources. In groundwater, Cd concentration is up to 6 times higher than the

quality standard for drinking water. However, such elevated concentration could be due to elevated geochemical background in the area.

The infiltration of local precipitation is considered the main source of recharge for mine water. Mine water from the Haneş 2 adit can be considered a mine water end-member. The mine water is less affected by the seasonal variation of temperature. A slight increase of the pH values occurs during warm seasons when the infiltration of surface water increases. In most cases the variation in isotopic composition are within narrow limits (less than 1 ‰ for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$). The highest TDS values are recorded during winter months when the contribution of precipitation and infiltration water is diminished. During springtime (March – April) the infiltration of surface waters intensifies due to snow melting, and as a result, the dilution of mine water increases. A shift of 2 - 3 months could be observed in the variation sequences of and TDS and $\delta^2\text{H}$ for these mine waters. An exception is the Larga mine adit, for which the seasonal variation in isotopic composition is larger. An increasing trend in the $\delta^2\text{H}$ values, along with a decreasing trend in the TDS values was recorded from March to September, suggesting a continuous dilution of the mine water with surface water directly derived from precipitation. Due to flooding of mine workings after mine closure, favourable conditions for mixing are created and therefore seasonal variation in the chemical and isotopic composition of mine waters are flattened. Where there is a lack of mining works below, adits may act like rapid drainage pathways for infiltration water, not allowing underground mixing. In such cases, larger seasonal variation occur. The Larga adit is an example.

The majority of water sources within the study area are Ca- dominant water type, which contributes to their buffering capacity. Due to pyrite oxidation, the mine water coming into direct contact with mineralisation is more acidic (e. g. Haneş mine, pH~4) than the mine water which only interacts with host rock in old abandoned mining works (e.g. Toţi Sfinţii mine adit, pH~7). All mine waters have very high SO_4 concentrations (up to 67541 mg/l) and are SO_4 -type water. Elevated concentration of SO_4 , Zn and Fe in mine waters are the main issues of concern.

Running water is contaminated by mine water and the negative effects of AMD occur mainly in the summer months when the flow of running water decreases. The most affected watercourses are the Ardeu stream, the Techereu stream and the Larga creek, downstream of water mine discharge. The SO_4 , NO_3 , Fe and Zn concentrations far exceed the national quality standard for surface water. The highest concentration of contaminants was found in the Larga creek. However, its negative impact on the environment is less important due to low flow throughout the year. Both the Ardeu stream downstream (pH = 5.6) and the Larga creek (pH = 3.9) are more acidic than the allowable limit (pH > 6.5). The Ampoi river and the Trâmpoiele stream, which have high flow rates throughout the year, have the ability to collect contaminated water from the mine adits without recording radical changes of composition and acidity.

5.2 Summary of method applicability

In applications at the Kittilä and Roşia Montană sites, environmental isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^7\text{Li}$ were found to be useful tracers of both water source and mixing as well as processes influencing solute mobility. For tracer applications end member waters must

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exhibit discrete isotopic compositions and ion concentrations, and controls on isotopic variability must be well constrained. $^{26}\text{Mg}/^{24}\text{Mg}$ was not found to provide additional insight into water mixing due to lack of isotopic variability between different samples. Further, the controls on isotopic variation in Mg are not well constrained, complicating interpretation of these results in a field setting.

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ are particularly useful for assessing hydrologic connectivity and mixing, as they are the only truly conservative tracers of water. These isotopes provided important evidence of surface water capture to the underground mine and provided unique indication of water subject to industrial processes. At the Kittilä site, isotopic variability between end members was not great enough to quantify mine water contributions to river water. $^{87}\text{Sr}/^{86}\text{Sr}$ provided insight to water source and mixing at both sites based on lithologically driven isotopic variability across the sites. The conservative behaviour of $^{87}\text{Sr}/^{86}\text{Sr}$ in solution allowed delineation of water pathways and estimates of water mixing. However, the accuracy of these estimates is dependent on accurate end member characterization. $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^7\text{Li}$ showed variability between water sources at the mine site scale suggesting these systems provide potential solute source tracers. However, consideration must be given to non-conservative solute behaviour, which was characterized at the Kittilä site to provide insight to solute mobility mechanisms. For each of these isotope systems, thorough identification of isotopically distinct fluxes, as well as temporal variation within each flux will improve isotope based characterization.

In application at the Zlatna site correlation of geochemical and isotope data were successfully used to assess:

- genetic relationships between surface water – underground water – mine water;
- groundwater flow models and sources of recharge;
- tracking of mine water inflows and outflows;
- water-rock interactions;
- mining effects on groundwater and surface water;
- contaminants and water sanitation.

Once the meteoric origin of water was assessed, the use of hydrogen isotope composition of water for the purpose of identifying the origin of underground water was preferred to the use of oxygen, because the hydrogen content of rocks is too low to significantly affect the isotopic composition of underground water. The correlation between the seasonal variation of TDS and $\delta^2\text{H}$ was of a particular importance in assessing the genetic relationships between different underground sources and surface water sources. To better constrain the source of contaminants the use of isotopes of other elements is desirable (i. e. Sr, Mg, Cd, Pb). In the case of mass balance calculations, the identification of end members is essential in determining a mixing ratio between different water sources.

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7 Appendices

7.1 Kittilä data tables

Table A1. Background groundwater sample results

event	June 2013	March 2015			June 2015	
site	GW Köngäs	GW Kuotko KUG15	GW Kuotko KUG2	GW Köngäs	GW Kuotko KUG2 GW Köngäs	
T (C°)	13.8	-	-	3.1	10.74	7.7
pH	7.156	-	-	7.694	7.592	7.28
ORP (mV)	170.54	-	-	211.52	161.1	174.78
DO (mg/L)	8.136	-	-	7.674	11.8	11.738
SC (uS/cm)	59.46	-	-	246.34	112.38	143.86
Ca (mg/l)	16.8	26.3	19.9	37.6	14.5	21.9
Fe (mg/l)	0.0	0.2	6.3	-	0.0	0.0
K (mg/l)	1.3	-	-	-	0.3	1.1
Mg (mg/l)	1.9	7.3	3.5	5.6	1.9	2.4
Na (mg/l)	1.6	1.4	1.6	3.4	1.4	2.0
Si (mg/l)	4.4	2.7	7.1	6.0	3.4	4.4
Br (mg/l)	0.1	0.1	-	-	0.1	0.1
Cl (mg/l)	0.4	0.5	0.5	1.0	0.4	0.6
F (mg/l)	0.1	0.1	-	0.1	0.1	0.1
SO4 (mg/l)	2.5	8.0	3.7	15.0	4.4	3.2
NO3 (mg/l)	0.1	0.4	1.8	1.7	0.9	0.1
DOC (mg/l)	2.7	-	-	-	-	-
Fe ⁺⁺ (µg/l)	0.00	-	-	-	-	-
NO2 (µg/l)	-	-	-	-	-	-
NO2-N (µg/l)	-	-	-	-	-	-
Ag (µg/l)	0.01	0.12	1.12	0.01	0.08	0.02
Al (µg/l)	11.80	53.00	1900.00	2.26	57.80	31.40
As (µg/l)	0.26	6.20	4.30	3.23	11.60	3.72
B (µg/l)	6.72	5.11	8.86	14.00	26.30	13.10
Ba (µg/l)	2.68	3.22	7.17	7.46	9.98	11.40
Be (µg/l)	0.05	-	-	-	0.09	0.03
Cd (µg/l)	0.09	-	0.00	0.04	0.17	0.10
Co (µg/l)	0.07	-	2.74	0.08	0.10	0.07
Cr (µg/l)	0.64	-	4.35	1.13	1.72	0.94
Cu (µg/l)	2.56	-	10.04	1.82	1.21	3.47
I (µg/l)	1.00	-	-	7.09	2.62	2.92
Li (µg/l)	0.38	-	0.78	0.47	0.18	0.34
Mn (µg/l)	0.37	4.93	130.50	2.62	1.90	0.37
Mo (µg/l)	0.13	0.47	0.31	0.48	0.35	0.13
Ni (µg/l)	3.89	1.50	3.77	4.51	0.25	3.09
P (µg/l)	21.40	-	330.00	40.50	10.00	10.00
Pb (µg/l)	0.06	-	-	-	0.37	0.16
Rb (µg/l)	1.33	0.15	0.38	0.49	0.08	1.23
Sb (µg/l)	0.12	-	-	-	1.00	1.00

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

event	June 2013	March 2015			June 2015	
site	GW Köngäs	GW Kuotko KUG15	GW Kuotko KUG2	GW Köngäs	GW Kuotko KUG2	GW Köngäs
Se (µg/l)	0.25	-	-	0.60	58.75	18.40
Sr (µg/l)	30.10	61.00	27.30	27.60	24.80	33.80
Th (µg/l)	0.01	-	-	-	1.00	1.00
Tl (µg/l)	0.01	-	0.03	-	0.11	0.02
U (µg/l)	0.03	0.06	0.05	0.07	0.03	0.05
V (µg/l)	0.74	1.60	19.50	1.68	2.87	0.78
Zn (µg/l)	21.10	13.80	20.65	52.65	4.77	22.80
$\delta^{18}\text{O}$ ‰	-15.69	-14.2	-14.17	-13.5	-14.76	-14.56
$\delta^2\text{H}$ ‰	-115.7	-105.9	-104.6	-100.9	-106.9	-107.6
$\delta^{34}\text{S}$ ‰	5.3	1.4	5.9	-2.7	4.9	4.9
$\delta^{26}\text{Mg}$ ‰	-	-1.0	-0.8	-0.7	-0.4	-0.5
$\delta^7\text{Li}$ ‰	11	23	26	2	24	1
$^{87}\text{Sr}/^{86}\text{Sr}$	0.71070	0.70427	0.70651	0.71023	0.70630	0.71138

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
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Table A2. Surface water collected upstream (background) of mine discharge samples results

event	June 2013	March 2015				June 2015		
	SWUS Talvitie mukka	SWUS Suasjärvi	SWUS Tuonkas omma	SWUS Nuutioj oki	SWUS Hakodan maa	SWUS Hakokodanmaa	SWUS Talvitie mukka	SWUS Kolvako ski
T (C°)	12.4	0.5	2.8	1.96	0	10.4	11.3	11.4
pH	6.756	7.694	7.39	7.706	7.41	7.56	7.65	7.658
ORP (mV)	170.06	164.04	202.04	201.78	178.66	117.82	137.7	216.38
DO (mg/L)	9.784	5.49	9.82	12.138	11.266	10.548	9.572	11.706
SC (uS/cm)	77.88	197.6	140.68	126.82	107.74	74.82	75.12	82.98
Ca (mg/l)	11.8	21.8	12.4	14.4	16	10.5	11.4	12
Fe (mg/l)	0.22	0.1	0.15	0.025	0.06	0.23	0.24	0.25
K (mg/l)	0.395	0.25	0.71	0.62	0.63	0.25	0.25	0.25
Mg (mg/l)	1.65	4.39	1.81	1.73	2.03	2.61	3.21	3.64
Na (mg/l)	1.385	1.41	2.04	1.91	2.02	1.45	1.42	1.79
Si (mg/l)	4.285	3.95	6.57	6.03	6.36	4.01	3.88	4.27
Br (mg/l)	0.05	0.05	0.05	0.05	-	0.05	0.05	0.05
Cl (mg/l)	0.5305	0.5	1	0.6	0.8	0.57	0.53	0.53
F (mg/l)	0.05	0.05	0.2	0.05	0.2	0.05	0.05	0.05
SO4 (mg/l)	4.05	6.6	4.8	5.3	5.5	4.3	4.5	4.6
NO3 (mg/l)	0.1	0.4	0.5	0.5	0.5	0.1	0.1	0.1
DOC (mg/l)	4.9	-	-	-	1.08	5.7	6	5.3
Fe++ (µg/l)	0.1365	-	-	-	-	-	-	-
NO2 (µg/l)	-	-	-	-	-	0.02	0.02	0.02
NO2-N (µg/l)	-	-	-	-	-	0.005	0.005	0.005
Ag (µg/l)	0.005	0.005	0.005	0.005	-	0.0225	0.06	0.005
Al (µg/l)	18.65	0.5	3.17	0.5	-	78.1	78.2	66.9
As (µg/l)	2.975	15	0.92	2.03	1.06	4.645	9.24	3.32
B (µg/l)	3.015	2.5	2.5	2.5	-	5.825	20	2.5
Ba (µg/l)	3.35	6.76	15.1	11.1	11.6	13.9	12.7	9.89
Be (µg/l)	0.05	0.025	0.05	0.025	-	0.0375	0.025	0.025
Cd (µg/l)	0.01	0.01	0.01	0.01	-	0.045	0.12	0.01
Co (µg/l)	0.065	0.02	0.02	0.02	0.02	0.055	0.09	0.02
Cr (µg/l)	0.1	0.77	0.55	0.29	0.24	0.49	0.83	0.37
Cu (µg/l)	0.165	0.25	0.25	0.25	-	0.43	0.61	0.25
I (µg/l)	3.36	3.66	3.25	2.12	4.07	1.505	1	1
Li (µg/l)	0.69	0.17	1.52	1.44	1.17	0.74	0.73	0.58
Mn (µg/l)	15.3	8.8	4.25	2.2	5.7	11.75	7.87	7.02
Mo (µg/l)	0.665	0.63	0.67	1.12	0.85	0.545	0.57	0.54
Ni (µg/l)	0.22	0.25	0.25	0.25	-	0.25	0.25	0.25
P (µg/l)	18.4	33.5	25.8	34.8	257	10	10	10
Pb (µg/l)	0.025	0.05	0.05	0.05	-	0.14	0.27	0.05
Rb (µg/l)	0.335	0.13	0.19	0.08	0.12	0.155	0.16	0.21
Sb (µg/l)	0.03	1	1	1	-	1	1	1
Se (µg/l)	0.25	0.15	0.15	0.15	0.16	17.4125	41.7	4.8
Sr (µg/l)	26.6	48.3	22.8	26.8	28	19.25	22.4	24.8
Th (µg/l)	0.01	1	1	1	-	1	1	1

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

event	June 2013	March 2015				June 2015		
	SWUS Talvitie mukka	SWUS Suasjärvi	SWUS Tuonkas omma	SWUS Nuutioj oki	SWUS Hakodan maa	SWUS Hakokoda nmaa	SWUS Talvitie mukka	SWUS Kolvako ski
site								
Tl (µg/l)	0.005	0.01	0.01	0.01	-	0.035	0.07	0.01
U (µg/l)	0.105	0.04	0.11	0.29	0.18	0.135	0.11	0.12
V (µg/l)	0.45	0.72	0.15	0.4	0.23	0.41	0.42	0.36
Zn (µg/l)	0.18	3.27	4.57	2.16	1.45	2.765	2.95	3.54
$\delta^{18}\text{O}$ ‰	-14.15	-14.5	-14.49	-14.61	-14.5	-14.17	-14.13	-
$\delta^2\text{H}$ ‰	-104.6	-106.9	-107	-106.5	-107.2	-104.1	-103.8	-
$\delta^{34}\text{S}$ ‰	1.9	0.2	3.2	1.0	1.2	1.3	2.5	-
$\delta^{26}\text{Mg}$ ‰	-	-0.23	-0.78	-0.63	-0.58	-0.79	-0.69	-
$\delta^7\text{Li}$ ‰	24.2	27.1	27.9	26.1	28.1	25	25	-
$^{87}\text{Sr}/^{86}\text{Sr}$	0.71612	0.70595	0.72863	0.72528	0.7225	0.72018	0.71684	-

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites: Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

Table A3. Underground mine borehole water sample results

event	March 2015					
site	MWGW KUP663	MWGW RUG15015	MWGW SUG15047	MWGW SUG15049	MWGW TUT 1088	MWGW TUT 863
T (C°)	9.6	8.3	10.38	8.5	-	-
pH	8.17	8.2	8.178	8.1	-	-
ORP (mV)	-111.42	145.26	126.34	77.18	-	-
DO (mg/L)	2.314	9.246	5.848	6.848	-	-
SC (uS/cm)	4148.8	655	559	446.56	-	-
Ca (mg/l)	135.0	56.4	20.0	15.9	2530.0	2780.0
Fe (mg/l)	0.0	0.0	0.0	0.2	20.3	31.7
K (mg/l)	8.2	1.0	3.8	4.9	89.4	108.0
Mg (mg/l)	45.8	36.3	23.8	19.0	617.0	714.0
Na (mg/l)	500.0	24.9	59.4	47.7	4260.0	5090.0
Si (mg/l)	5.9	4.8	3.9	3.9	3.4	6.3
Br (mg/l)	16.0	0.5	0.7	0.5	200.0	230.0
Cl (mg/l)	1200.0	17.0	54.0	7.3	13000.0	17000.0
F (mg/l)	0.5	1.3	0.2	1.3	0.5	0.5
SO4 (mg/l)	93.0	240.0	72.0	79.0	530.0	570.0
NO3 (mg/l)	1.0	1.0	0.1	1.0	1.0	1.0
DOC (mg/l)	-	-	-	-	-	-
Fe++ (µg/l)	-	-	-	-	-	-
NO2 (µg/l)	-	-	-	-	-	-
NO2-N (µg/l)	-	-	-	-	-	-
Ag (µg/l)	0.01	0.01	0.01	0.01	0.66	1.08
Al (µg/l)	1.82	0.50	1.10	4.37	225.00	2100.00
As (µg/l)	0.18	26.30	1.84	3.66	13.00	7.45
B (µg/l)	1210.00	156.00	336.00	430.00	3040.00	6690.00
Ba (µg/l)	1420.00	131.00	348.00	235.00	2930.00	10800.00
Be (µg/l)	0.03	0.03	0.03	0.03	-	-
Cd (µg/l)	0.01	0.02	0.01	0.03	-	0.28
Co (µg/l)	0.02	0.21	0.56	0.43	6.01	15.60
Cr (µg/l)	0.84	0.59	0.50	0.50	41.10	122.00
Cu (µg/l)	0.25	0.25	0.25	0.25	5.71	17.50
I (µg/l)	227.00	6.78	16.50	11.90	-	-
Li (µg/l)	36.20	2.61	6.69	6.28	285.00	439.00
Mn (µg/l)	95.10	42.70	15.80	83.40	2880.00	3720.00
Mo (µg/l)	0.65	4.09	0.45	0.82	66.40	50.00
Ni (µg/l)	0.25	1.77	8.14	2.91	75.50	169.00
P (µg/l)	21.70	10.00	10.00	95.20	490.00	590.00
Pb (µg/l)	0.05	0.05	0.05	0.12	1.66	5.75
Rb (µg/l)	12.90	1.79	3.17	11.50	128.00	163.00
Sb (µg/l)	1.00	26.40	7.27	7.27	4.94	5.95
Se (µg/l)	0.05	0.63	0.03	0.08	2.50	2.50
Sr (µg/l)	10600	609.00	2450.00	1780.00	150000	162000.00
Th (µg/l)	1.00	1.00	1.00	1.00	0.10	0.10

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

event	March 2015					
site	MWGW KUP663	MWGW RUG15015	MWGW SUG15047	MWGW SUG15049	MWGW TUT 1088	MWGW TUT 863
Tl (µg/l)	0.01	0.02	0.01	0.02	0.03	0.06
U (µg/l)	0.00	0.05	0.01	0.01	0.10	0.27
V (µg/l)	0.12	0.09	0.02	0.12	2.52	18.60
Zn (µg/l)	3.00	10.50	5.09	18.80	132.00	441.00
$\delta^{18}\text{O}$ ‰	-14.42	-14.6	-14.7	-14.72	-10.94	-14.34
$\delta^2\text{H}$ ‰	-104.6	-107.4	-107.9	-107.5	-95	-89.7
$\delta^{34}\text{S}$ ‰	1.4	1.2	-7.8	-7.7	-	-
$\delta^{26}\text{Mg}$ ‰	-1.1	-0.9	-0.8	-0.7	-	-
$\delta^7\text{Li}$ ‰	30	29	27	28	-	-
$^{87}\text{Sr}/^{86}\text{Sr}$	0.71118	0.71094	0.71270	0.71304	-	-

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

Table A4. Mine dewatering water sample results

event	June 2013			March 2015		June 2015		
	MWDW LO pond	MWDW MK pond	MWDW TW3	MWDW MK pond	MWDW TW3	MWDW MK pond	MWDW TW3	MWDW TW1
T (C°)	10.8	13.968	17.96	3.2	-	11.1	13	14.1
pH	7.524	8.02	6.592	7.832	-	8.078	7.258	7.22
ORP (mV)	138.26	168.98	231.06	229.48	-	232.72	235.86	225.38
DO (mg/L)	10.076	9.852	8.536	13.536	-	10.608	6.96	7.42
SC (uS/cm)	1224	1510.6	1512	1954	-	2032.6	2026	2193
Ca (mg/l)	201.0	206.0	216.0	266.0	276.0	297.0	315.0	310.5
Fe (mg/l)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K (mg/l)	2.9	10.7	11.6	9.9	10.1	12.7	13.8	12.6
Mg (mg/l)	37.8	51.7	52.1	69.7	71.9	71.3	74.8	78.1
Na (mg/l)	6.8	28.7	29.2	54.8	56.7	59.4	66.3	67.1
Si (mg/l)	6.7	6.7	5.7	7.7	7.8	7.4	6.9	5.8
Br (mg/l)	0.5	-	0.5	0.5	0.5	1.0	1.0	5.0
Cl (mg/l)	5.4	-	12.0	74.0	73.0	99.0	99.0	99.5
F (mg/l)	0.5	-	0.5	0.5	0.5	0.5	0.5	0.5
SO4 (mg/l)	540.0	-	716.0	820.0	860.0	960.0	960.0	960.0
NO3 (mg/l)	21.8	-	58.8	43.0	51.0	38.0	48.0	49.0
DOC (mg/l)	2.2	-	1.6	2.9	1.9	2.8	2.0	2.5
Fe++ (µg/l)	0.00	0.00	0.00	-	-	-	-	-
NO2 (µg/l)	-	-	-	1.18	0.39	0.45	0.22	0.02
NO2-N (µg/l)	-	-	-	0.36	0.12	1.48	0.72	0.01
Ag (µg/l)	0.01	0.02	0.01	0.01	0.01	0.24	0.25	0.23
Al (µg/l)	12.40	34.00	1.97	6.05	0.50	26.40	2.01	0.50
As (µg/l)	326.00	33.20	60.40	19.30	23.30	42.90	52.70	31.75
B (µg/l)	23.10	43.20	49.20	102.00	101.00	92.00	170.00	163.50
Ba (µg/l)	23.60	28.30	31.30	60.10	46.10	63.30	78.80	69.25
Be (µg/l)	0.05	0.05	0.05	0.03	0.03	0.03	0.72	0.29
Cd (µg/l)	0.15	0.04	0.03	0.03	0.03	0.04	0.73	0.54
Co (µg/l)	29.30	3.04	0.16	5.57	0.47	2.87	0.64	0.48
Cr (µg/l)	0.10	0.10	0.10	0.76	0.53	1.33	3.55	2.54
Cu (µg/l)	1.20	0.71	0.22	0.70	0.25	1.33	2.41	2.01
I (µg/l)	1.00	2.72	2.53	18.90	20.90	17.90	17.40	1.00
Li (µg/l)	2.80	4.70	5.26	9.71	7.05	8.84	10.50	9.98
Mn (µg/l)	847.00	966.00	18.30	1590.00	324.00	874.00	147.00	11.25
Mo (µg/l)	7.36	11.20	8.66	16.30	11.40	22.40	14.50	9.62
Ni (µg/l)	341.00	61.00	46.30	62.30	54.60	53.20	58.30	22.30
P (µg/l)	31.30	80.10	23.80	10.00	10.00	10.00	10.00	10.00
Pb (µg/l)	0.47	0.22	0.03	0.05	0.05	0.05	1.68	1.06
Rb (µg/l)	3.96	26.90	29.10	24.40	23.30	39.30	37.60	32.90
Sb (µg/l)	527.00	316.00	348.00	181.00	166.00	196.00	202.00	206.50
Se (µg/l)	0.83	0.25	0.50	0.28	0.56	12.00	188.00	152.50
Sr (µg/l)	428.00	789.00	799.00	1300.00	1350.00	1840.00	1710.00	1790.00
Th (µg/l)	0.01	0.01	0.01	1.00	1.00	1.00	1.00	1.00
Tl (µg/l)	0.04	0.01	0.03	0.03	0.02	0.39	0.87	0.50

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
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event	June 2013			March 2015		June 2015		
site	MWDW LO pond	MWDW MK pond	MWDW TW3	MWDW MK pond	MWDW TW3	MWDW MK pond	MWDW TW3	MWDW TW1
U (µg/l)	1.41	0.98	0.84	0.75	0.74	0.65	0.42	0.27
V (µg/l)	0.41	0.87	0.29	0.68	0.35	2.27	0.87	0.43
Zn (µg/l)	16.30	6.21	5.79	2.93	2.33	3.08	7.08	6.22
$\delta^{18}\text{O}$ ‰	-13.77	-13.76	-13.69	-13.64	-13.56	-13.85	-13.84	-13.86
$\delta^2\text{H}$ ‰	-102.7	-102.6	-102.7	-101.9	-102	-103.1	-103	-102.8
$\delta^{34}\text{S}$ ‰	-6.7	-1.8	-1.8	0.0	-1.0	-0.6	-0.3	-0.2
$\delta^{26}\text{Mg}$ ‰	-	-	-	-0.5	-0.5	-0.5	-0.4	-0.7
$\delta^7\text{Li}$ ‰	21	27	28	28	28	29	28	27
$^{87}\text{Sr}/^{86}\text{Sr}$	0.71001	0.71065	0.71054	0.71066	0.71072	0.71069	0.71069	0.71058

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

Table A5.Mine process water sample results

event	June 2013		March 2015		June 2015	
	MWPW RIMMI pond	MWPW TW4 discharge	MWPW RIMMI pond	MWPW TW4 discharge	MWPW RIMMI pond	MWPW TW4 discharge
site						
T (C°)	15.48	13.5	2.6	-0.4	15.4	18.4
pH	8.52	6.802	8.648	6.44	7.83	6.65
ORP (mV)	159.18	170.1	188.54	157.1	228.08	176.9
DO (mg/L)	7.93	11.618	9.218	4.16	8.422	4.22
SC (uS/cm)	7512	6833.8	11983	14294.6	9821.8	8298.6
Ca (mg/l)	492.0	395.0	387.0	440.0	404.0	366.0
Fe (mg/l)	0.0	0.0	0.0	1.3	0.0	0.3
K (mg/l)	97.2	88.0	147.0	189.0	138.0	108.0
Mg (mg/l)	1050.0	983.0	2240.0	2790.0	1430.0	1730.0
Na (mg/l)	83.6	82.0	235.0	327.0	241.0	188.0
Si (mg/l)	1.7	0.7	1.4	3.2	1.8	0.3
Br (mg/l)	0.5	0.5	0.5	0.5	1.5	1.5
Cl (mg/l)	17.9	15.9	30.0	37.0	30.0	23.0
F (mg/l)	0.5	0.5	1.3	1.1	0.5	0.5
SO4 (mg/l)	6140.0	5130.0	10000.0	13000.0	8900.0	7300.0
NO3 (mg/l)	22.5	18.8	21.0	6.2	35.0	52.0
DOC (mg/l)	1.3	3.8	4.4	6.9	3.1	4.2
Fe++ (µg/l)	0.00	0.02	-	-	-	-
NO2 (µg/l)	-	-	5.58	0.10	1.15	0.02
NO2-N (µg/l)	-	-	1.70	0.03	3.78	0.01
Ag (µg/l)	0.01	0.04	0.02	0.05	0.01	0.69
Al (µg/l)	31.80	42.30	0.50	7.31	69.90	57.60
As (µg/l)	62.80	0.82	196.00	2.39	128.00	67.60
B (µg/l)	39.20	46.30	97.90	63.70	131.00	256.00
Ba (µg/l)	25.80	21.50	38.40	42.50	50.20	58.10
Be (µg/l)	0.05	0.14	0.03	0.03	0.03	0.99
Cd (µg/l)	0.10	0.01	0.09	0.05	0.04	1.66
Co (µg/l)	3.46	0.28	5.53	6.02	8.01	3.19
Cr (µg/l)	0.51	0.10	0.25	0.91	0.05	6.12
Cu (µg/l)	0.05	0.05	1.12	0.25	2.75	5.12
I (µg/l)	2.43	1.00	23.10	50.80	17.70	1.00
Li (µg/l)	232.00	241.00	159.00	276.00	143.00	121.00
Mn (µg/l)	137.00	135.00	2200.00	6110.00	1850.00	870.00
Mo (µg/l)	25.00	4.20	50.00	17.10	52.40	4.71
Ni (µg/l)	16.50	11.60	21.00	3.43	37.10	17.30
P (µg/l)	42.20	160.00	10.00	10.00	10.00	32.40
Pb (µg/l)	0.03	0.34	0.10	0.05	0.05	2.58
Rb (µg/l)	112.00	101.00	192.00	262.00	225.00	168.00
Sb (µg/l)	48.50	16.80	52.70	16.20	75.70	13.40
Se (µg/l)	23.80	13.90	14.40	3.28	13.90	404.00
Sr (µg/l)	968.00	927.00	1420.00	1690.00	1600.00	1300.00
Th (µg/l)	0.01	0.01	1.00	1.00	1.00	1.00

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

event	June 2013		March 2015		June 2015	
	MWPW RIMMI pond	MWPW TW4 discharge	MWPW RIMMI pond	MWPW TW4 discharge	MWPW RIMMI pond	MWPW TW4 discharge
site						
Tl (µg/l)	0.12	0.05	0.08	0.09	0.01	1.31
U (µg/l)	0.54	0.01	1.98	0.08	1.80	0.00
V (µg/l)	0.79	0.03	0.73	0.06	0.15	1.20
Zn (µg/l)	15.80	20.20	3.09	11.70	3.40	19.10
$\delta^{18}\text{O}$ ‰	-11.33	-10.86	-11.03	-11.81	-10.41	-10.18
$\delta^2\text{H}$ ‰	-95	-89.9	-95.6	-98.5	-92.5	-88.8
$\delta^{34}\text{S}$ ‰	1.0	1.3	1.3	3.5	1.5	1.4
$\delta^{26}\text{Mg}$ ‰	-	-	-0.3	-0.4	-0.3	-0.2
$\delta^7\text{Li}$ ‰	16	16	18	18	17	16
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70851	0.70846	0.70803	0.70813	0.70923	0.70883

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites: Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

Table A6. Surface water downstream of mine discharge sample results from multiple sample events

event	June 2013		March 2015	June 2015	
	SWDS Pumping station	SWDS Lintula	SWDS Lintula	SWDS Pumping station	SWDS Lintula
Site					
T (C°)	9.7	12.5	1.6	11.7	13
pH	7.068	7.2	7.226	7.668	7.662
ORP (mV)	126.92	144.76	179.4	173.36	158.38
DO (mg/L)	10.066	9.726	9.12	8.308	5.202
SC (uS/cm)	356.62	360.48	591.2	273.3	205.42
Ca (mg/l)	20.5	24.6	38.0	16.8	21.5
Fe (mg/l)	0.2	0.3	0.1	0.3	0.3
K (mg/l)	2.4	2.4	1.4	1.6	0.9
Mg (mg/l)	26.8	24.7	9.7	21.4	19.1
Na (mg/l)	3.2	3.5	6.2	4.3	4.3
Si (mg/l)	3.9	4.2	6.5	4.2	4.1
Br (mg/l)	0.1	0.1	0.1	0.1	0.1
Cl (mg/l)	0.9	1.0	6.5	0.8	3.6
F (mg/l)	0.1	0.1	0.1	0.1	0.1
SO4 (mg/l)	129.0	126.0	80.0	99.0	57.0
NO3 (mg/l)	0.1	0.1	3.6	0.6	1.1
DOC (mg/l)	7.5	5.2	0.9	5.6	4.2
Fe++ (µg/l)	0.17	0.14	-	-	-
NO2 (µg/l)	-	-	0.02	0.02	0.02
NO2-N (µg/l)	-	-	0.01	0.01	0.01
Ag (µg/l)	0.01	0.01	0.01	0.04	0.33
Al (µg/l)	35.20	18.00	0.50	72.50	76.50
As (µg/l)	2.24	2.66	0.70	6.00	14.20
B (µg/l)	4.34	5.54	9.97	13.90	34.50
Ba (µg/l)	3.56	4.66	9.93	7.59	11.40
Be (µg/l)	0.05	0.05	0.03	0.11	0.36
Cd (µg/l)	0.01	0.01	0.01	0.10	0.64
Co (µg/l)	0.10	0.11	0.05	0.15	0.45
Cr (µg/l)	0.10	0.10	0.21	0.55	1.58
Cu (µg/l)	0.13	0.13	0.25	0.25	1.33
I (µg/l)	1.00	1.00	4.03	1.00	1.00
Li (µg/l)	6.67	6.18	1.91	2.29	2.86
Mn (µg/l)	28.20	45.40	38.40	31.90	29.40
Mo (µg/l)	0.48	0.67	1.41	0.64	1.56
Ni (µg/l)	0.45	0.70	2.83	0.50	1.40
P (µg/l)	16.90	16.90	78.50	10.00	10.00
Pb (µg/l)	0.03	0.03	0.05	0.26	0.95
Rb (µg/l)	2.67	2.89	1.99	2.17	1.88
Sb (µg/l)	0.26	3.40	11.60	1.00	6.65
Se (µg/l)	0.25	0.25	0.14	22.50	69.00
Sr (µg/l)	43.70	57.40	124.00	42.10	91.00

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

event	June 2013		March 2015	June 2015	
Site	SWDS Pumping station	SWDS Lintula	SWDS Lintula	SWDS Pumping station	SWDS Lintula
Th (µg/l)	0.01	0.01	1.00	1.00	1.00
Tl (µg/l)	0.01	0.01	0.01	0.11	0.64
U (µg/l)	0.12	0.11	0.20	0.12	0.10
V (µg/l)	0.34	0.38	0.09	0.44	0.72
Zn (µg/l)	0.75	6.95	2.01	2.40	4.20
$\delta^{18}\text{O}$ ‰	-13.75	-13.98	-14.65	-14.18	-14.12
$\delta^2\text{H}$ ‰	-101.3	-103.9	-106.8	-104.1	-103.9
$\delta^{34}\text{S}$ ‰	1.0	0.7	0.5	1.3	0.5
$\delta^{26}\text{Mg}$ ‰	-	-	-0.8	-0.4	-0.5
$\delta^7\text{Li}$ ‰	17	17	28	22	0

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

Table A7. Surface water downstream of mine discharge June 2015 sample results

event	June 2015						
	SWDS Välikoski	SWDS Rossinmu kka	SWDS Konikoski	SWDS Mesinie mi	SWUS Vientola	SWDS Loukinen	SWDS Lintula1
T (C°)	12.1	12.8	13.1	13.3	11.5	14.1	13.2
pH	7.69	7.78	7.678	7.752	7.754	7.7	7.778
ORP (mV)	202.96	186.08	164.44	157.8	152.02	143.64	156.94
DO (mg/L)	11.818	11.228	11.128	3.33	4.032	4.37	5.388
SC (uS/cm)	148.48	177.52	232.7	218.26	95.14	150.06	208.3
Ca (mg/l)	13.9	16.8	23.0	23.2	14.7	18.3	22.1
Fe (mg/l)	0.3	0.3	0.3	0.4	0.5	0.5	0.3
K (mg/l)	0.6	0.7	0.9	0.9	0.3	0.3	0.9
Mg (mg/l)	14.8	15.7	19.3	19.7	4.8	11.6	19.2
Na (mg/l)	2.4	3.1	4.3	4.4	1.7	2.9	4.2
Si (mg/l)	4.3	4.1	4.2	4.1	4.6	4.0	4.1
Br (mg/l)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cl (mg/l)	0.6	1.8	4.5	3.8	0.5	2.0	3.7
F (mg/l)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SO4 (mg/l)	31.0	41.0	62.0	61.0	5.1	30.0	58.0
NO3 (mg/l)	0.3	0.7	1.3	1.0	0.1	0.5	1.1
DOC (mg/l)	3.4	5.3	4.7	4.4	5.1	2.7	3.1
Fe++ (µg/l)	-	-	-	-	-	-	-
NO2 (µg/l)	0.02	0.02	0.02	-	-	-	0.02
NO2-N (µg/l)	0.01	0.01	0.01	-	-	-	0.01
Ag (µg/l)	0.01	0.02	0.16	0.41	0.07	0.30	0.01
Al (µg/l)	69.80	75.40	72.20	60.20	48.40	57.40	75.30
As (µg/l)	3.51	4.72	23.70	22.50	8.08	17.60	3.31
B (µg/l)	5.61	9.32	57.60	59.10	21.50	42.00	8.44
Ba (µg/l)	7.63	7.99	14.10	12.20	9.92	12.60	7.49
Be (µg/l)	0.03	0.03	0.53	0.60	0.08	0.45	0.03
Cd (µg/l)	0.01	0.05	0.43	0.98	0.19	0.77	0.01
Co (µg/l)	0.01	0.10	0.34	0.75	0.19	0.65	0.01
Cr (µg/l)	0.05	0.38	2.11	2.35	1.04	1.91	0.05
Cu (µg/l)	0.25	0.25	1.85	2.18	0.68	1.74	0.25
I (µg/l)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Li (µg/l)	0.17	1.26	2.19	3.35	0.81	1.92	0.91
Mn (µg/l)	13.30	20.50	32.10	32.40	48.10	46.00	26.70
Mo (µg/l)	0.01	0.64	1.35	1.68	0.29	0.98	0.01
Ni (µg/l)	0.25	0.51	1.71	1.95	0.56	1.55	0.25
P (µg/l)	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Pb (µg/l)	0.05	0.10	0.88	1.37	0.30	1.15	0.05
Rb (µg/l)	0.55	1.08	2.58	2.40	0.44	1.48	1.22
Sb (µg/l)	1.00	2.61	8.41	8.43	1.00	5.16	4.19
Se (µg/l)	0.03	14.80	131.00	120.00	35.10	84.80	0.03
Sr (µg/l)	28.20	52.40	115.00	108.00	29.20	69.60	78.10
Th (µg/l)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Tl (µg/l)	0.01	0.04	0.31	0.92	0.10	0.69	0.01

Geochemical and Isotope Methods for Assessing Contaminant Transport at Three Mine Sites:
Kittilä mine in Finland and Roşia Montana and Zlatna mines in Romania

event	June 2015						
site	SWDS	SWDS	SWDS	SWDS	SWUS	SWDS	SWDS
	Välikoski	Rossinmu kka	Konikoski	Mesinie mi	Vientola	Loukinen	Lintula1
U (µg/l)	0.07	0.11	0.12	0.08	0.00	0.04	0.06
V (µg/l)	0.01	0.40	0.54	0.83	0.26	0.55	0.01
Zn (µg/l)	3.73	1.86	7.90	7.53	4.78	7.00	3.94
$\delta^{18}\text{O}$ ‰	-	-13.87	-	-14.16	-	-	-
$\delta^2\text{H}$ ‰	-	-103.7	-	-104.4	-	-	-
$\delta^{34}\text{S}$ ‰	-	0.4	-	-	-	-	-
$\delta^{26}\text{Mg}$ ‰	-	-0.3	-	-0.5	-	-	-
$\delta^7\text{Li}$ ‰	-	25	-	25	-	-	-