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An integrated interdisciplinary approach to evaluate potentially toxic elements sources in a mountainous watershed

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Corresponding Author:	Gilberto Binda Università degli Studi dell'Insubria - Sede di Como Como, Lombardia ITALY
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Università degli Studi dell'Insubria - Sede di Como
Corresponding Author's Secondary Institution:	
First Author:	Gilberto Binda
First Author Secondary Information:	
Order of Authors:	Gilberto Binda
	Andrea Pozzi
	Franz Livio
Order of Authors Secondary Information:	
Funding Information:	
Abstract:	Potentially toxic elements (PTEs; i.e., Cd, Ni, Cr) and their source apportionment in waters are of major environmental concern. Different approaches can be used to evaluate PTEs sources in environment, but single-way approaches are often limited and can easily fail. PTEs sources apportionment should include the evaluation of geochemical background and spatiotemporal trends analyses. We propose an integrated approach and we apply it to a mountain catchment in the italian central Alps, where ultramafic terranes crop out. We collected water and glacial sediment samples during the melting season. Then we analyzed major ions and PTEs in waters, and we quantified the total PTEs load in sediments through acid digestion. Data were then processed through spatial and temporal trends analysis, clustering of variables and the evaluation of partition between the different compartments. We found a high geochemical background of part of the PTEs, consistently with results from other areas worldwide on mafic and ultramafic terranes (high concentrations of Ni, Cr and Fe). Thanks to this integrated approach, an additional atmospheric deposition source for Zn, Cd and Ag has been identified. Also, redundant observations on Cu, As and Pb indicated a possible mixed source. This study elucidates the need of an integrated approach to avoid un-necessary or misleading assumptions in the PTE's source appointment. A single-way approach application, in fact, can fail in understanding element source in a complicated and dynamic compartment like surface water.
Response to Reviewers:	Dear editor, We would like to thank you for considering our manuscript for publication after major revision to your journal. Thanks to the reviewer and the coordinating editor for their helpful comments. We here address their comments and briefly list the main changes made to our manuscript. We are also grateful to the reviewer for their appreciation of the scientific quality of our manuscript.

Moving to the specific response to the reviewers:

Coordinating Editor:
MAJOR COMMENTS
COMMENT: Abstract: Central Alps???Give correct location..Italian????
Some sentences are vague and the meaning of the sentences is hard to follow due to awkward sentences structures. Ex" Also, redundant observations suggest a possible mixed source on Cu, As and Pb, highlighting also the erroneous source appointment applying a single-way approach.
English should be checked and corrected in entire manuscript.
ANSWER: Abstract was revised, more precise location was inserted and some sentences were revised in order to be clearer.

COMMENT: Conclusion: Not clear. Please revise the sentense "Therefore, also in the single step of the application of the integrated approach part of the elements (i.e., Cu, Ag, Cd) showed controversial trend, which could lead to erroneous source apportionment without considering all the possible influencing factors.
ANSWER: We reviewed the whole conclusion section to make sentences clearer.

COMMENT: Appendix section is too long and need to be arranged by incorporating only most relevant details. For example, no point of including all raw data of samples analyzed. Delete table S1
ANSWER: We decided to make the Appendix section shorter, but sincerely we do not agree with the editor regarding the fact of not include the supplementary table s1. This table, in fact, gives the possibility to check the total number of samples, and to verify the QA/QC protocols used for analytical techniques (i.e., the ionic balance for major ions). Therefore, we decided to keep it as electronic supplementary material.

COMMENT: References should be checked and arranged.
ANSWER: References were checked and modified as also suggested by reviewer #1.

COMMENT: Table 1: What do you mean by "(ordered by concentrations)???Not clear
ANSWER: We decided to explain in caption that elements are ordered from the most to the less abundant in rock samples.

COMMENT: What was the reason for not analyzing those data??/ Fe, Mn and As data for Poland are not present in graph because they were not analyzed by the Authors.
ANSWER: We deleted the sentence in the manuscript because it was misleading. Actually, we inserted in graph only data reported from the authors of the cited studies. We added a sentence in the caption to make this point clearer.

MINOR COMMENTS
COMMENTS: Line 23: correct as "in water"…correct it in all places
Line 216-217: Give instrument model name ICP- MS.
Line 268: include equation numbers
Line292: equation???
Please increase the resolution of figure 1
Capitalize first letter of figure/table captions"
ANSWER: All these revisions were made following the reviewer suggestions.

Reviewer #1
MAJOR COMMENTS
COMMENT: Good description of the study area, including both the geology and mineralogy of the site. However, I would like the figure of the study area map to be updated and improved to better match with these descriptions. Overall, I think including a larger area on figure (as in Binda et al. 2018) would be useful, with things like Northern Italy, Central Alps, Milan, Lake Pirola and Ventina Valley. The Pirola fault, important to interpreting the study data, would be nice to see this fault laid out on the figure.
Line 195 - Fig.2 a descriptive table of mineral abbreviations is required
ANSWER: In order to improve the quality of the figure, we modified it and we added a descriptive table of minerals as suggested by the reviewer.

COMMENT: Line 28 - Jakub Kierczak et al. 2008 review this reference according to

line 689
Lines 118 and 119 - Trommsdorff et al. 2007 and Bedogné et al. 1993 published where?
Bedogné, F., Montrasio, A., & Sciesa, E. (1993). I minerali della provincia di Sondrio, Valmalenco.
Trommsdorff, V., Montrasio, A., Hermann, J., Muntener, O., Spillmann, P., & Giere, R. (2007). The geological map of Valmalenco. (link ??)
Line 134 - J. Kierczak et al. 2007 review this reference according to line 686
Line 291 - (Fdez-Ortiz de Vallejuelo et al., 2014) reference must be consistent with the one that figures in References section
de Vallejuelo, S. F.-O., Gredilla, A., de Diego, A., Arana, G., & Madariaga, J. M. (2014). Methodology to assess the mobility of trace elements between water and contaminated estuarine sediments as a function of the site physico-chemical characteristics. Science of the Total Environment, 473, 359-371
Line 453 - Jakub Kierczak et al. 2016 review this reference according to line 693
ANSWER: As suggested also by the editor, we revised the references through the whole manuscript.

COMMENT: Line 91 - authors refer in the text figure 2 before figure 1, so why not change the figures numbers? the first figure that appears in the manuscript should be figure 1 and not figure 2.
ANSWER: As suggested from the reviewer, we modified figures order.

COMMENT: Line 411 - lower mean values in the whole study area, but concerning concentrations in the all the sampling……
ANSWER: This sentence was rewritten in order to be clearer.

MINOR COMMENTS
COMMENTS: Line 146 - generally caption in figures is placed below the figure and in tables caption is placed above the table. If it´s not a journal requirement please review all tables of the manuscript.
Line 211 - Table 2 missing * in sample V11
Line 413; 418; 430; 449; 452; 465; 473 and 479 - When start a sentence with a chemical element, the element should be written out in full and not the chemical symbol.
Line 301 - an instead am
Line 441 - delete ss
Line 442 - concentrations for human consumption and environmental risk, (comma here) the cause would be …..”
ANSWER: All the highlighted misspellings were corrected, and the other suggested revisions were made to our manuscript.

An integrated interdisciplinary approach to evaluate potentially toxic elements sources in a mountainous watershed

Authors: Gilberto Binda[a]; Andrea Pozzi[a]; Franz Livio[a];
[a] Università degli Studi dell'Insubria, Science and High Technology Department (Di.S.A.T.), via Valleggio, 11 - 22100 Como – Italy

Corresponding author: Gilberto Binda
Email: g.binda2@uninsubria.it
Address:
Dipartimento di Scienza e Alta Tecnologia
Università degli Studi dell'Insubria
Via Valleggio, 9
22100 Como (Italy)

Other author's email:
Andrea Pozzi: andrea.pozzi@uninsubria.it
Franz Livio: franz.livio@uninsubria.it

1. Introduction

Source apportionment for trace metals and metalloids in water is an issue of high concern in environmental research, legislation and decision making. In fact, it is fundamental to understand the human impact on trace elements load, especially for potentially toxic elements (PTEs; i.e., Cd, Pb, Ni, Cu, Cr), because their increase in concentration can compromise water quality and is of major concern for human and ecosystem health (Devic et al. 2014; Dung et al. 2013; Kierczak et al. 2008).

Generally, the first step in source apportionment of PTEs is the geochemical background evaluation (i.e., the natural load), including possible anomalies (Dung et al. 2013). Then, the natural background is subtracted from the total PTEs load observed to evaluate anthropic emissions.

In this field, strategies relying on single analytical approaches or statistical analyses usually tend to overlook spatial or temporal trends or, conversely, assume the stationarity of some of the variables, potentially introducing some bias. Therefore, we here propose an integrated approach which integrates chemical analyses in water and glacial sediments samples, with the evaluation of main spatial and temporal trends and correlations of variables.

Several studies focused on sources apportionment in soils and sediments (e.g., Gong et al., 2010; Hinsby et al., 2008; Jiang et al., 2017; Liang et al., 2017; Pelica et al., 2018; Sollitto et al., 2010; Zhang et al., 2008); nevertheless only few works tried to identify metal sources from surface water analysis (Muhammad et al. 2011; Su et al. 2011). The main reason resides in the fast and variable dynamics of this environmental compartment, with seasonal changes and complex temporal trends. Therefore, despite different standard European methodologies are diffuse to evaluate geochemical background in soil and sediments (Ander et al. 2013; Reimann et al. 2018), for surface water a generally accepted and standardized methodology to assess geogenic background values for metals does not exist (Schneider et al. 2017), and some authors (i.e., Galuszka 2007) consider impossible to evaluate the geochemical background for water.

The high dynamicity of surface water limits also the applications of spatial trends analysis as tool to understand PTEs sources in this compartment: even though geostatistical methods are often used to recognize spatial trends for assessment in soils and sediments (Albanese et al. 2007; De Vallejuelo et al. 2014; Zhang et al. 2008), still applying this approach to water is generally more complicated (e. g., Dalla Libera et al. 2017 in ground water; Ou et al. 2012 in lakes).

Multivariate statistics (i.e., Principal Component Analysis, Analysis of Variance, Factor Analysis; Borůvka et al. 2005; Busico et al. 2018; Devic et al. 2014) is widely used to understand sources of metals and infer anthropic emissions. Nonetheless, this approach requires large datasets, usually requires data transformations to obtain a normal distribution (i.e., logarithmic) and needs anyway an a-priori assumption of terrigenous or anthropic-derived elements (Zhou et al. 2008).

Also, in remote settings, where point sources of pollutants emissions are not present, medium and long-range transport of metals can mark anthropic source of metals, which can be deposed through hydrometeors and dry depositions (Dossi et al. 2007; Gabrielli et al. 2008; Shah et al. 2012). This effect makes more difficult to establish possible sources of pollutant especially with high geochemical background of PTEs.

All these factors require a careful evaluation to successfully identify and measure metals and metalloids sources. Thus, even in simple-structured and apparently unpolluted basins, the understanding of the main drivers of elements concentration in water is subordinate to the characterization of natural background and to the analysis of spatial and temporal trends.

High mountain sites are excellent field laboratories to separate geochemical background from anthropic emissions: watersheds are relatively simple-structured, climatic factors directly control the hydrology, the underlying geology mainly influence the hydrochemistry (e. g., Fortner et al. 2011; Hindshaw et al. 2011; Lecomte et al. 2008), and the limited soil development, with typically low concentrations of organic matter, reduce possible disturbance in metals dissolution (Tranter 2003). These areas, typically far from direct human impact, do not present local spot emissions of trace elements; the only anthropogenic sources are usually represented by atmospheric long-range transport and deposition (Gabrielli et al. 2008; Loska and Wiechuła 2003).

In this study, an integrated approach including the quantification of different potentially toxic elements in different environmental compartment, the application of multivariate statistical analysis, and the observation of spatial and temporal trends is proposed, aiming to understand the geochemical background of PTEs and to assume possible anthropic contributions in a remote high mountain catchment in the Italian central Alps.

2. Study area

The experimental area chosen to set up this approach include a little catchment in the Italian Alps presenting a high geochemical background of PTEs, caused by the bedrock lithology (Binda et al. 2018).

2.1 Geographic setting

Our study area is located in the Ventina valley (Central Alps, Northern Italy) (Fig. 1), encompassing an area of ca. 4 km^2, and with an elevation drop from 2450 to 1960 m a.s.l. A cold and temperate climate characterizes the region, with a mean annual temperature of 2 °C and precipitations of 1123 mm (data from Lombardia Regional Environmental Protection Agency, weather forecast section, www2.arpalombardia.it/siti/arpalombardia/meteo).

The study area is located about 100 km far north from Milan and the northern fringe of the Po plain, which represents a highly urbanized area and the main source of different emissions reaching the site (Finardi et al. 2014); considering the remote setting of the study area, the precipitation in the area would be the only possible anthropogenic enrichment of metals due to urban emissions (Dossi et al. 2007). Most of the precipitation come from the south, accordingly with the mesoscale atmospheric circulation in central Alps (Ambrosetti et al. 1998), therefore emissions from the relatively close urbanized area could come from this direction.

The study area includes two hydrological basins: i) the Ventina glacier basin, where an ice tongue actively supplies the Ventina river and ii) the adjacent Pirola lake basin, collecting contributions by atmospheric precipitations and periglacial landforms (i.e., melting of rock glaciers and snowfields).

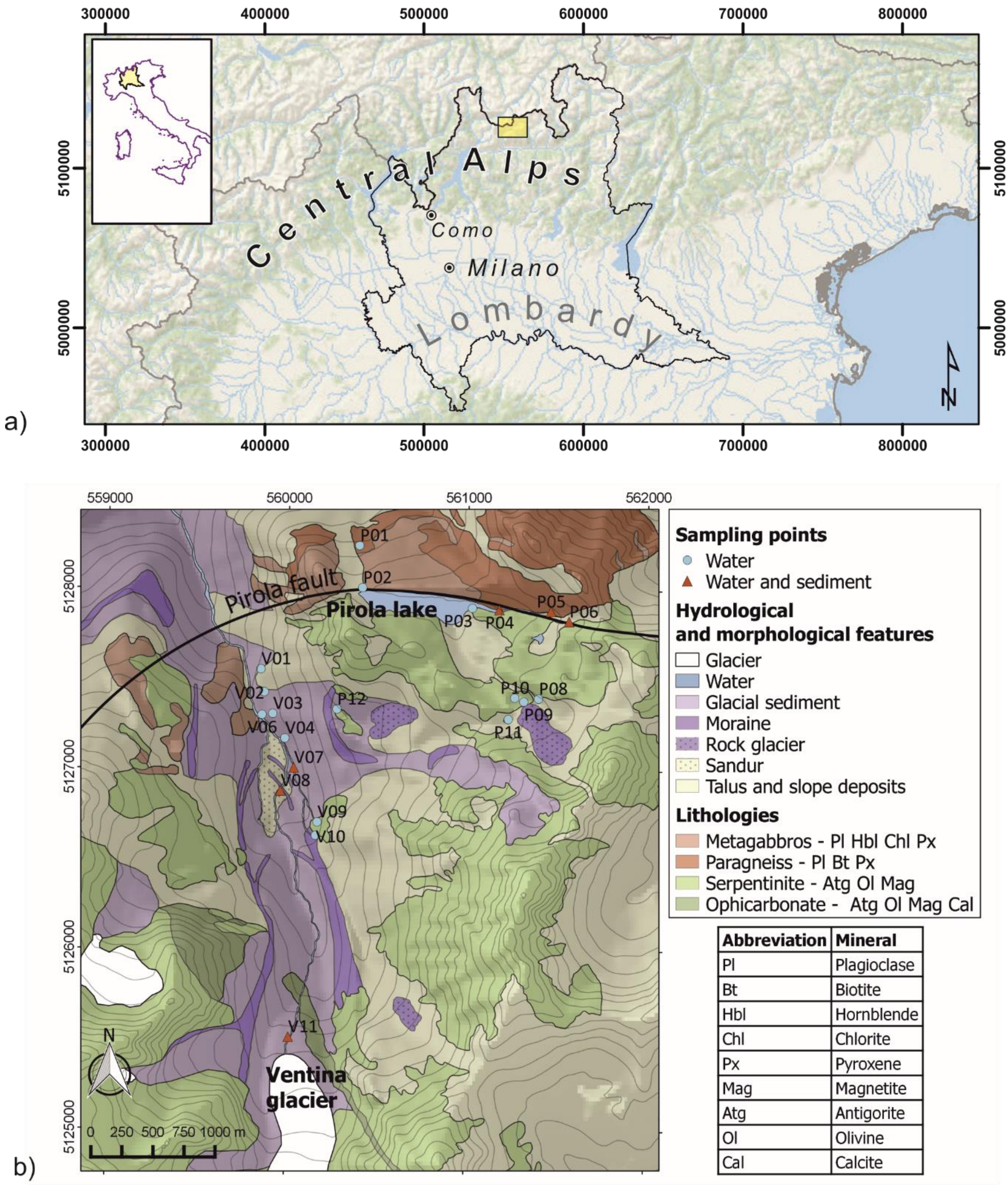

Fig. 1 *a) Geographic setting of the study area (highlighted in yellow). b) Study area detailed map, indicating: sampling points, morphological features and outcropping lithologies (main and accessories minerals are indicated in legend and minerals abbreviations are reported in table). Coordinates are indicated in UTM32N format.*

2.2 Geological and geomorphological setting

Two different metamorphic terranes, whose emplacement is the result of a complex tectonic history during alpine collision, crop out in the study area: the Margna nappe, to the north, and the Suretta nappe, to the south (Coward and Dietrich 1989; Schmid et al. 2004), separated by an E-W trending sub-vertical fault (Pirola fault, in Fig. 1).

Margna nappe lithologies are represented by metagabbros and paragneiss. The metagabbros present foliated or lenticular texture, and the most abundant minerals are plagioclase, (i.e., albite; $NaAlSi_3O_8$ and anortite; $CaAl_2Si_2O_8$) and pyroxenes (i.e., diopside; $CaMgSi_2O_6$); small lenses of hornblende ($Ca_2(Mg,Fe,Al)_5$ $(Al,Si)_8O_{22}(OH)_2$), are included (Trommsdorff et al. 2005). Accessory minerals are prehnite ($Ca_2Al_2Si_3O_{10}(OH)_2$), natrolite ($Na_2[Al_2Si_3O_{10}]\cdot 2(H_2O)$) and sfalerite (ZnS) (Bedogné et al. 1993). To the NE, albitic and chloritic paragneiss crops out, (Bonsignore et al. 1971). Main minerals included are plagioclase ($(Na,Ca)(Si,Al)_4O_8$), biotite ($K(Mg,Fe)_3[AlSi_3O_{10}(OH,F)_2$) and quartz ($SiO_2$) (Bedogné et al. 1993). Also, As bearing minerals as realgar (As_4S_4) are present especially in the fault area (Bedogné et al. 1993). Geochemical studies made on Margna nappe rocks samples report possibly concerning concentrations of: Fe, Zn, Mn, Co, As (Burkhard 1989; Muntener et al. 2000).

The Suretta nappe lithologies outcropping south of the Pirola fault, along the Ventina valley, include ultramafic rocks (i.e. serpentinites). These are hydrothermally altered metamorphic rocks derived from igneous Mg- Fe rich protolith (i.e. peridotite).

The major minerals are antigorite ($(Mg,Fe)_3Si_2O_5(OH)_4$) both as aggregate and in big sheets, chlorites, pyroxenes and olivine ($(Mg,Fe)_2SiO_4$). Magnetite (FeO x Fe_2O_3) is often present in serpentinites as lenses or grains (Bonsignore et al. 1971), this mineral can contain also Cr_2O_3 , up to ca. 10,8% in wt. Serpentinites present accessory minerals containing significant amount of heavy metals, such as Ni and Cr and Cu: Taenite (Ni, Fe), pentlandite ((Fe,Ni)9S8), calcocite (Cu_2S) digenite (Cu_9S_5) and galena (PbS) (Bedogné et al. 1993; Kierczak et al. 2007; Morrison et al. 2015). Therefore Fe, Ni, Cr, Cu Co and Mn are PTEs presenting high load in these rocks, as also was observed in other studies collecting rock samples in proximity of the study area (Bloise et al. 2016; Cavallo 2018).

In proximity of the glacier terminus, lenses of ophicarbonates are present (Bedogné et al. 1993). This zone consists of a 10 to 400 m wide tabular volume that strikes ca. NW-SE and is exposed approximately 6 km within the Malenco ultramafic body (Bonsignore et al. 1971; Trommsdorff and Evans 1977). These rocks exhibit a prevalently brecciated texture containing fragments of serpentinite, embedded in a fine- to medium-grained white matrix of predominantly calcitic ($CaCO_3$) composition (Pozzorini and FruhGreen 1996).

Following this brief description of study-area geological framework, it’s possible to estimate expected principal metals both in water and sediment samples (Table 1).

Table 1 *Expected metals in the analyzed samples from the different geological units in the study area. Metals are ordered from the most to the less abundant in concentration in rock.*

Geological unit	**Expected PTEs**

Margna nappe	Fe, As, Zn, Co, Mn
Suretta nappe	Fe, Ni, Cr, Cu, Co, Mn

Considering the typical sediment present in the glacial and periglacial forms typical on high mountain sites (i.e. glacial *diamicton* or *till*) helps to correctly interpret the source of metals and metalloids in water from water-rock interaction. These sediments present low permeability due to its dominant silty-to-clayey grain size, and are often subject to interaction with glaciofluvial activity, which can promote metals mobility (Evans 2013; Tranter 2003). Different moraines (i.e., frontal and lateral glacial deposits) are present in the study area: more recent moraines (i.e., ascribable to the Little Ice Age; XIV -mid IXX Cent. AD; Matthews and Briffa 2005) in the Ventina glacier forefield (Trommsdorff et al. 2005), and older lateral moraines (from the Last Glacial Maximum; 26.5 – 20 ka BP; Clark et al. 2009) at higher elevation (Trommsdorff et al. 2005). The Ventina river flows from south to north into a glacio-fluvial plain (i.e., *sandur*), ca. 700 m long and 200 m wide (Fig. 1); further down-valley in the NW part of the study area the water is collected into a single stream channel (Carrivick and Russell 2007).

3. Materials and methods

We present an integrated approach, particularly suitable to understand sources of metals in water catchments, including a three-steps investigation strategy, combining water and sediment samples analyses, which output should be finally combined to critically interpret the different sources of PTEs (Fig. 2):

- Sampling and Analysis: a prepared sampling design, collection, and chemical analysis of samples;
- Data Treatment: data treatment with careful observation of seasonal trends and clustering of variables;
- Output evaluation: data output interpretation and source apportionment in water.

In the following, we will describe assumptions and procedures for each step of the investigation.

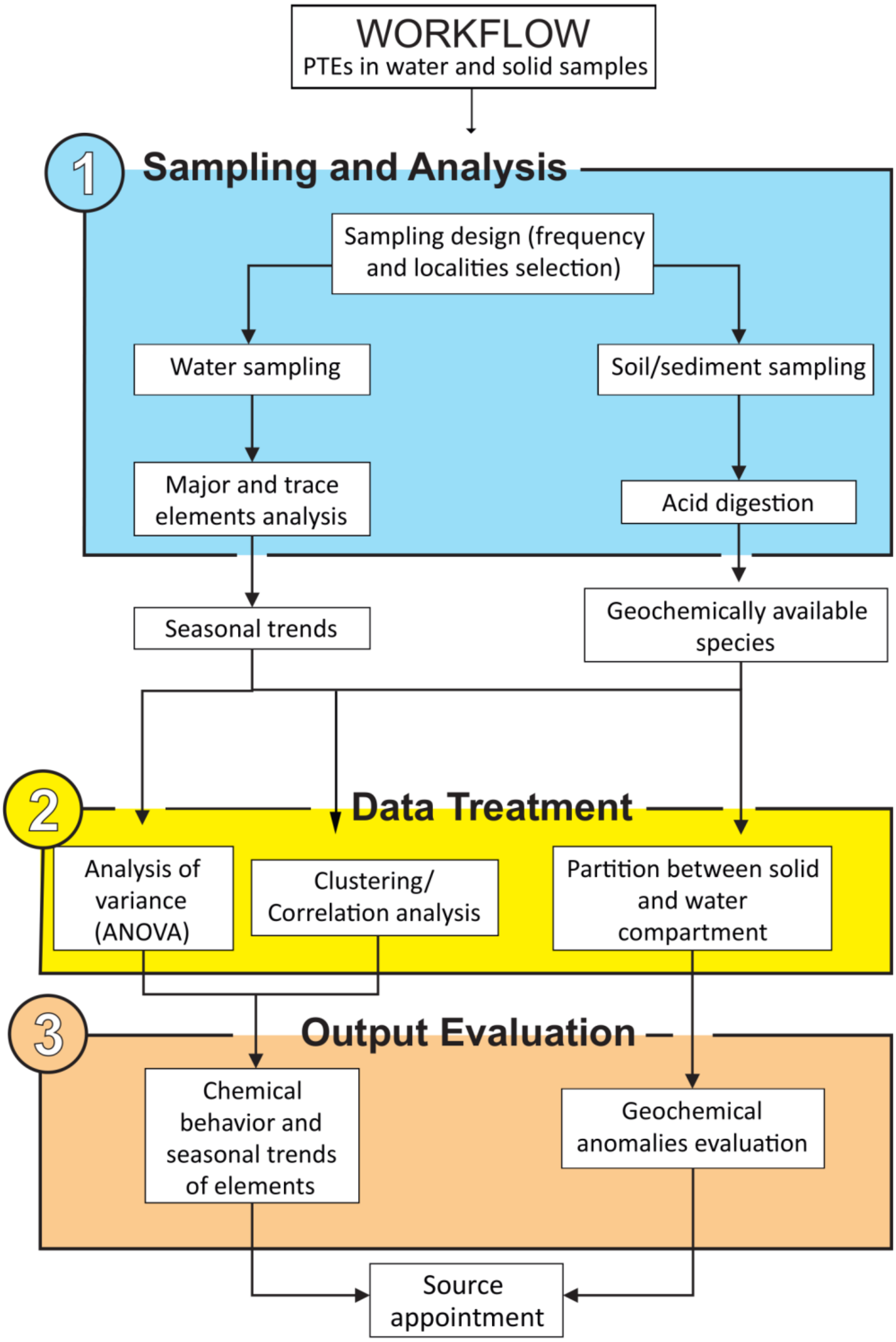

Fig. 2 Workflow of the integrated approach to understand metal sources and decouple geochemical background, with emphasis on the three main steps

3.1 Step 1: Sampling and Analysis

First step includes: sampling design, collection, and analysis for water and solid (soils and sediment) samples. We assume that the bedrock geochemistry (at least regarding main mineral components) and water flow and source are already known. Thus, the sampling of water samples should be made collecting water outflowing from different sources, covering the main spatiotemporal heterogeneities. The analysis of solid samples is fundamental to evaluate the geochemical load available for dissolution: sampling design for this kind of samples should be made mainly in function of lithologies distribution (Filgueiras et al. 2002; Pueyo et al. 2008):

3.1.1 Water samples

Water samples were obtained monthly, during four sampling campaign in 2014, three samplings in 2015 and three in 2016. A total of 150 water samples were collected in all sampling campaigns. Samples were collected only during the melting season (early summer to early fall), because of the thick snow cover during winter and spring, with scarce water from snow melting in springs and a high avalanche risk.

Water samples were collected at 21 localities (Fig. 1) and included water from different surface and underground sources (Table 2).

Five of the sampled springs outflow from fractures in bedrock, flowing through a low-permeability rock volume, possibly leading to an enrichment in metals, if passing through mineralized bodies and veins (MacQuarrie and Mayer 2005).

We also collected water from small lakes and ponds, where the presence of biota is typically scarce and with water bodies sensitive to atmospheric deposition and to temperature changes, usually freezing during winter (Santolaria et al. 2017; Sommaruga-Wögrath et al. 1997).

Two sampling points were obtained at the outlet of an ice glacier (V11) and of a rock glacier (P08). Even if both the water come from ice thawing, ice glaciers show a faster response in melting during the summer season and are more sensitive to atmospheric deposition than rock glacier sources (Brown 2002).

Other samples were obtained from stream water, resulting from a concurrent contribution from the sources described above (Table 2).

Table 2 *Typologies of water collected during the sampling campaigns*

SAMPLING POINT	SOLID SAMPLE	BEDROCK	TYPE OF WATER SOURCE
P01		Margna nappe	Stream outlet from Pirola lake
P02		Pirola fault zone	Pirola Lake at the outlet
P03			Pirola Lake at the inlet
P04	*		Stream inlet into Pirola lake
P05	*	Margna nappe	Spring from fracture
P06	*	Suretta nappe	Spring from fracture
P08			Rock glacier melting outflow
P09			Lake

P10		Lake
P11		Lake
P12		Spring from phreatic aquifer into slope deposit close to a moraine ridge
V01		Spring from fracture
V02		Spring line from phreatic aquifer in slope deposits
V03		Stream
V04		Spring line from phreatic aquifer in slope deposits
V06		Stream
V07	*	Stream
V08	*	Stream in the *sandur*
V09		Spring from fracture
V10		Spring from fracture
V11	*	Ventina glacier melting outflow

Samples collected were analyzed for:

- Physico-chemical parameters (electrical conductivity, pH and temperature) with specific field probes;
- Major ions and cations through titrations and ionic chromatography (Eco IC, Metrohm, Swiss confederation);
- 11 PTEs (Zn, Cr, Mn, Fe, Co, Ni, Cu, Cd, As, Ag and Pb) were analyzed through ICP-MS (Icap Q ICP-MS, Thermo Fisher Scientific, USA).

Physico-chemical parameters and major ions should be collected to have a preliminary idea of main dissolutions conditions, and PTEs to evaluate the final dissolved load. More details about water analysis and QA/QC protocols can be found in appendix.

3.1.2 Solid samples

Six outcropping glacial sediments and soils were sampled at the same location of some of the water samples (water and sediment samples collected in the same point have the same name) using plastic bags. Selection of sampling sites was conducted in function to cover the heterogeneities between different bedrock and different morphologies outcropping in the study area. We collected the samples both in the glacier forefield and in the nearby of the glacier front (V11). We also collected sediments in the glacifluvial plain (V08) and from a lateral moraine deposed during the Little Ice Age (V07). Moreover, we collected a sediment sample (P04) at the contact between the two terranes (i.e., along the Pirola fault) in order to observe the background values due to the different surrounding lithologies.

Table 3 *Classification and bedrock lithology of solid samples*

Sample	Source rock	Type of deposit	Grain size distribution

V08	Serpentinite	Sandur	gravelly sand
V11	Serpentinite	Subglacial lodgement till	diamicton (clay/silt and pebbles)
V07	Serpentinite	Little Ice Age moraine ridge	clayey silt
P04	Metagabbros	Poorly developed soil, with sparse vegetation cover	clayey silt
P06	Serpentinite	Poorly developed soil, without vegetation	clayey silt
P05	Metagabbros	Poorly developed soil, with sparse vegetation cover	clayey silt

A pseudo total acid digestion using *aqua regia* was applied. This digestion is defined as "pseudo-total" because this acid mixture cannot dissolve most recalcitrant silicate phase of minerals (Kanellopoulos et al. 2015). More details about methods used for solid samples analysis are included in appendix.

3.2 Step 2: Data treatment

Second step includes data statistical processing, and we propose to: analyze temporal trends in water, focusing on seasonal analysis and clustering of variables, and then to evaluate concentrations ratios between the water samples and the solid ones to clarify if the PTEs derived mainly from geochemical source in the bedrock or from other sources. We assume that the main natural source for PTEs in water would be rock weathering, that sediments generally maintain a good marker of rock geochemistry, and that temporal changes in sediments could be negligible.

Also, all the concentration data resulting under the limit of detection (which are called censored data) were substituted with LOD/10 values (Alier et al. 2009; Giussani et al. 2016).

3.2.1 Seasonal variations and trends

In more detail, temporal trends should be analyzed in water, to monitor how main climatic seasonal conditions (i.e., dry or wet season, tidal changes, snow/ice melting; de Vallejuelo et al. 2014; Hindshaw et al. 2011; Jung 2001) act on dissolution and/or transport of PTEs.

We divided water dataset in two subsets, in function of the sampling period: an early summer dataset (for samplings in June and July, including 74 samples) and a late one (for samplings in September and October, including 76 samples). This operation was made in function of the main seasonal trend observed in our dataset, showing differences in these period (as will be confirmed by ANOVA analysis, section 4.2) and presumably caused by ice and snow melting in the beginning of summer period.

Also, as observed by other authors in glaciated environment (Hindshaw et al. 2011), elements due to atmospheric deposition concentrate mostly in the first part of summer, with high snow and ice melting, while elements dissolved by water-rock and water-sediment interaction reach their baseline natural concentrations in the late summer. The snow layer thickness data for long term monitoring in the Alps with similar altitude of the study areas confirm this choice (Marty and Meister 2012). Therefore, even in a short time span, dissolution dynamics vary in mountainous catchments.

Thus, a difference between the means was measured to understand if the trend indicates an increasing or a decreasing in concentration from early to late summer, and then normalized on the total mean as in equation 1:

$$\frac{\mu_{LS}-\mu_{ES}}{\mu_{TOT}} \qquad \text{Eq.1}$$

Where μ_{LS} is the late summer period mean, where μ_{ES} is the early summer period mean, and μ_{TOT} is the total mean of the whole sampling campaign. This process was applied for alla measured chemical variables.

Then, observed trends should be confirmed: analysis of variance (ANOVA) is a useful tool to compare seasonal changes with inter-annual variability, and so to understand the significance of these changes (Ross and Willson 2017).

3.2.2 Seasonal clustering

A clustering analysis of variables (through multivariate statistics; i.e., Cluster Analysis) should be performed to observe how clustering of variables changes in the different seasons (or observed periods). Therefore, Cluster Analysis is a useful method to classify similarities between variables, showing distances among them. In this way, variables can be classified in groups, but the interpretation of the anthropic or naturally-derived elements is not preliminary assumed and is only evaluated afterward through the entire approach

Therefore, we applied hierarchical cluster analysis to the 2 seasonal datasets for major ions and trace elements variables, using Ward's method (Ward 1963).

3.2.3 Partition between water and sediment

Water data should be then compared with the bedrock-derived samples ones (sediments, soils), to quantify if the geochemically available species could be dissolved after water/rock interactions. Then, observing the ratio between dissolved and geochemically available elements will have clearer idea about the geochemical background of the elements.

In order to compare water with sediment samples data, a partition coefficient between dissolved and liquid phase of metals was calculated through a K_r coefficient (De Vallejuelo et al., 2014) expressed as in equation 2:

$$K_r = \frac{C_{metal\,sed}}{C_{metal\,wat}} \quad \text{Eq. 2}$$

Were $C_{metal\,sed}$ indicates the total metal concentration in the sediment sample in mg/kg and $C_{metal\,wat}$ indicates the metal concentration in the water in µg/L. We obtained K_r coefficient of the analyzed PTEs using the mean concentration in water along the entire time series, and concentration in solid samples from pseudo total acid digestion. The data obtained were then expressed after a logarithmic transformation. This approach permits to quantify how likely the concentration of a trace element in water reflects the bedrock concentration

3.3 Step 3: Output evaluation

Third step aims to finally understand the sources of trace elements in water through an integrated interpretation of the output from the previous steps. We clearly assume that PTEs grouping in the same way in the different approaches highlight similar sources, and that a high presence in water compare to the solid sample highlight an anthropic enrichment. Therefore, observing specific seasonal trends and clustering of variables, we could group PTEs presenting the same source, and then combining the geochemically available metals we could quantify if the available chemical species could dissolve from bedrock, or if we have an enrichment coming from anthropic emissions.

4. Results

4.1 Major and trace elements in water

Regarding physico-chemical parameters, water analyzed in this study presents low mineralization (max EC values is 98 µS/cm), and changes in EC mainly remark seasonal trend increasing in the end of summer. Also, analyzing major ions, water present principally dissolved Ca^{2+} ang Mg^{2+}, which correlate with HCO_3^-. All samples present ionic balance beneath 10%.

Data for trace elements are synthetized in table 4: observing the threshold limits for drinking water defined by WHO, most of the samples show concentration which are not concerning for human risk, but the maximum values for Ni slightly goes over, and As show an high maximum value, which is double of the threshold value. Therefore, these elements result the more concerning among the analyzed in the study area watershed.

More details about physico-chemical parameters, major ions and trace elements are listed in supplementary material, table S1, including all variables measurements for all sampling sites.

Table 4 *Descriptive statistics of PTEs concentrations in water samples, and comparison with WHO limits for human consumption of water*

Element	Measure unit	25th percentile	Mean	Median	75th percentile	Maximum	WHO limit
Ag	µg/L	<LOD	0.052	0.010	0.061	0.838	-
As	µg/L	0.019	1.228	0.107	0.327	28.596	10
Cd	µg/L	<LOD	0.020	0.003	0.020	0.109	3
Co	µg/L	<LOD	0.056	0.035	0.084	0.670	50
Cr	µg/L	0.478	1.027	0.911	1.400	2.861	50
Cu	µg/L	0.0001	0.231	0.117	0.314	1.982	2000
Fe	µg/L	1.695	8.874	5.884	12.107	41.174	-
Mn	µg/L	0.071	0.481	0.193	0.494	6.242	500
Ni	µg/L	3.885	6.544	6.568	8.439	20.438	20
Pb	µg/L	0.015	0.091	0.061	0.106	1.106	10
Zn	µg/L	1.470	6.839	4.326	9.494	39.604	3000

4.2 Seasonal trends analysis (ANOVA)

Significant ($p<0.05$) F value outcoming from ANOVA is plotted against the normalized Δ mean in Fig. 3. Sodium, NO_3^-, K^+, Pb, Mn, As, Fe were not plotted because these variables show a seasonal difference between early summer and late summer which is not significantly higher than the variance among the different years of sampling.

Elements decreasing from early summer to late summer are: Cu, Zn and Cl^-; the latter presenting a high F value, as an index of its high significance according to the ANOVA test. Conversely, variables showing an increment in the late summer are: Ca^{2+}, Cr, Ni, HCO_3^-, Mg^{2+} and SO_4^{2-} concentrations.

Also, Ag, Cd, NH_4^+ and Co show a high increment from early to late summer if normalized to the mean, but for these elements a major warning comes from the fact that several measured concentrations are close to the instrumental LODs, resulting in possible inaccuracies.

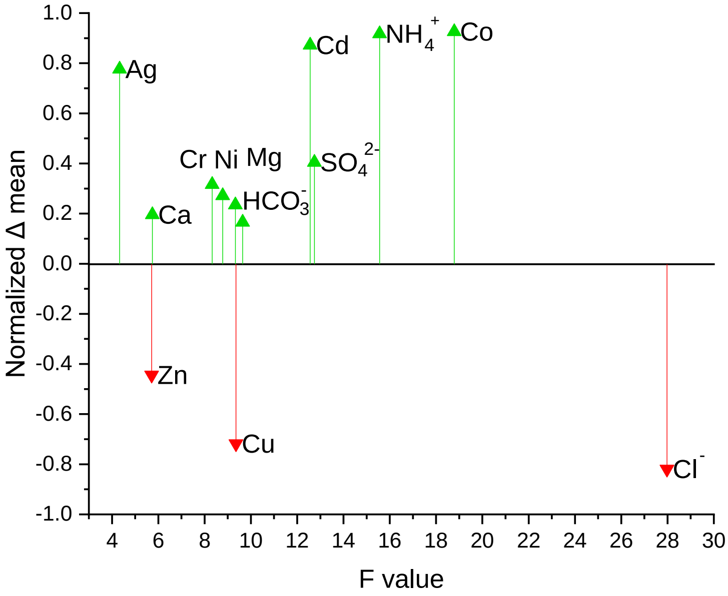

Fig. 3 *Plot of F value (x axis) and different of the early and late summer mean normalized for total mean (y axis) for all variables showing a significant difference (p<0.05)*

4.3 Seasonal clustering

Fig. 4 shows the hierarchic clusters for early and late summer including major ions and trace elements. The clustering of elements in the beginning and the end of the melting season can highlight similarity in sources, or same chemical behavior in dissolution from bedrock. In early summer four main clusters are present: one containing Cl^-, NO_3^-, Ni and Cr; one containing Mg^{2+}, HCO_3^- and As; one containing Na, K^+, NH_4^+ and SO_4^{2-}; and one containing the other analyzed trace elements.

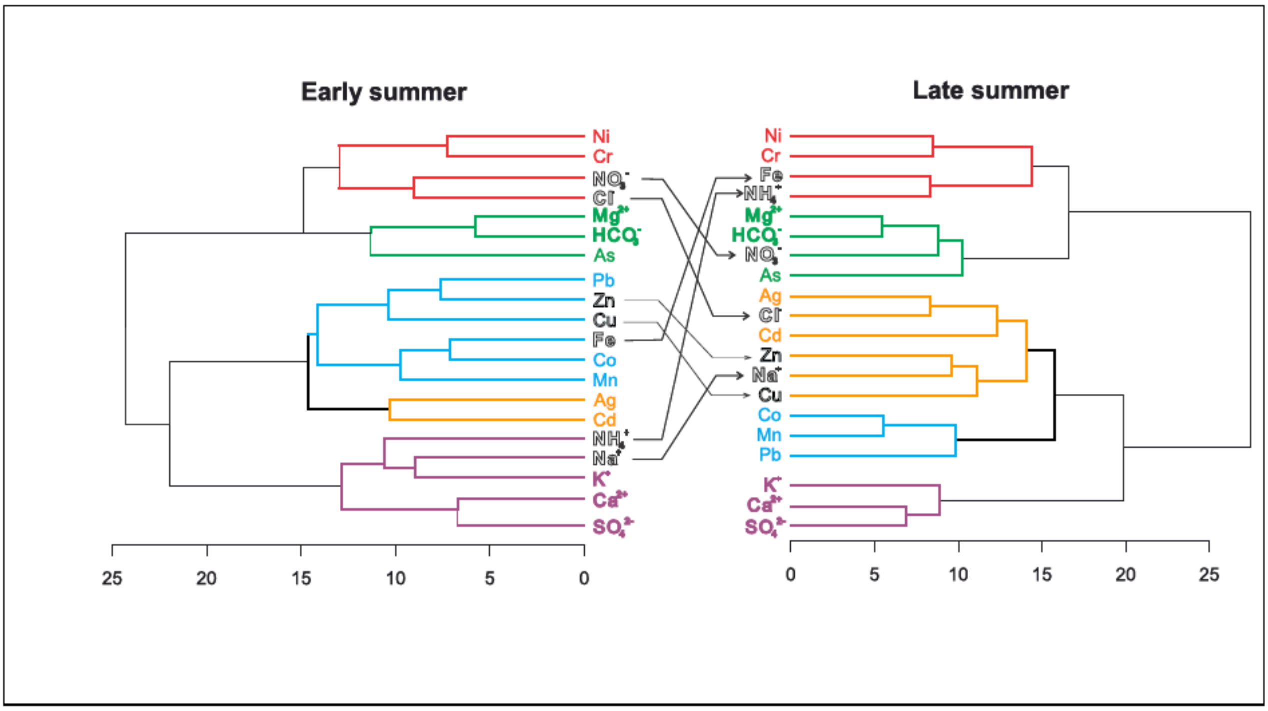

Fig. 4 *Cluster diagrams for early and late summer and their clustering changes in the different periods*

Late summer clustering partly remarks the early summer one, but the setting for trace elements partly changes. Zinc and Cu, for example, plot with Co, Mn and Pb in the early summer, while plot together with Ag, Cd, Na^+ and Cl^- in late summer.

4.4 Acid digestion for solid samples

In Fig. 5, acid digestion results in our samples are normalized on the mean upper crust values (Wedepohl 1995), and are compared with other studies presenting similar bedrock type (i.e., serpentine-derived soils in Greece; (Kanellopoulos et al. 2015) and two soil profiles in Poland; (Kierczak et al. 2008)). In this way, possible geochemical anomalies could be highlighted.

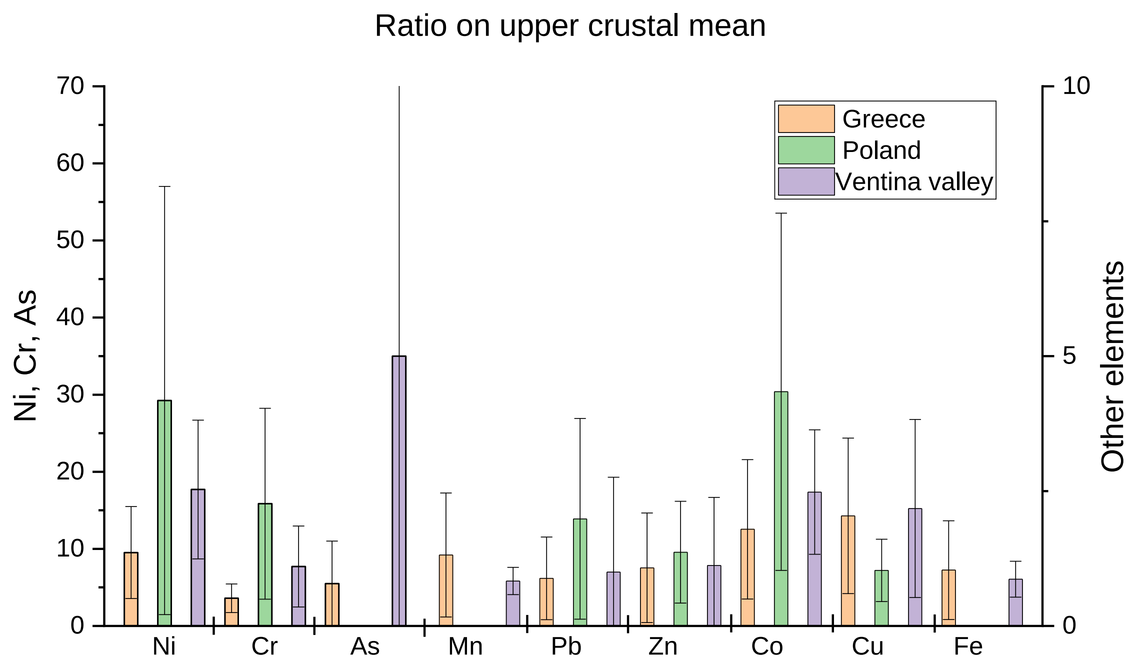

Fig. 5 *Ratio of some PTEs on the upper earth crust average abundance (from Wedepohl 1995) for some case studies in Poland (Kierczak et al. 2008), Greece (Kanellopoulos et al. 2015) and this study. Values are shown when reported by the authors*

Metals as Co, Ni and Cr already present higher load than the mean crustal one, but this is correlated to the lithology of the site, presenting a high geochemical background (Binda et al. 2018). Thus, sediment samples show mainly a natural load of analyzed metals, and present similar concentration with other areas presenting same bedrock lithology. The only element showing a higher load compared to other studies is As. This element presents a relatively high concentration in sediment of the study area, but with big variance in the different sites (high value was observed in sampling site P06, proximal to the Pirola fault; all data for acid digestion are reported in supplementary material, table S2).

Cd and Ag present concentration lower than the detection limits of acid digestions in all our samples, and they are not shown in Fig. 5.

4.5 Partition between solid and water compartments

Log K_r for all analyzed PTEs is shown in Fig. 6. Lower values of K_r indicate a greater presence in dissolved phase compared to the concentration in the solid phase. We can distinguish 3 main groups of PTEs according to the graph: a first group (including Fe, Cr, Mn, Co, Cu) with high values, indicating the typical elements included in serpentinites, which present low dissolution rates; another group indicating Ni and As (with mean log K_r values between 2 and 3) presenting medium values; a third group with values less than 1.5 (including Zn, Cd, and Ag) presenting a possible enrichment due to other sources, different from water/rock interaction (i.e., from atmospheric deposition).

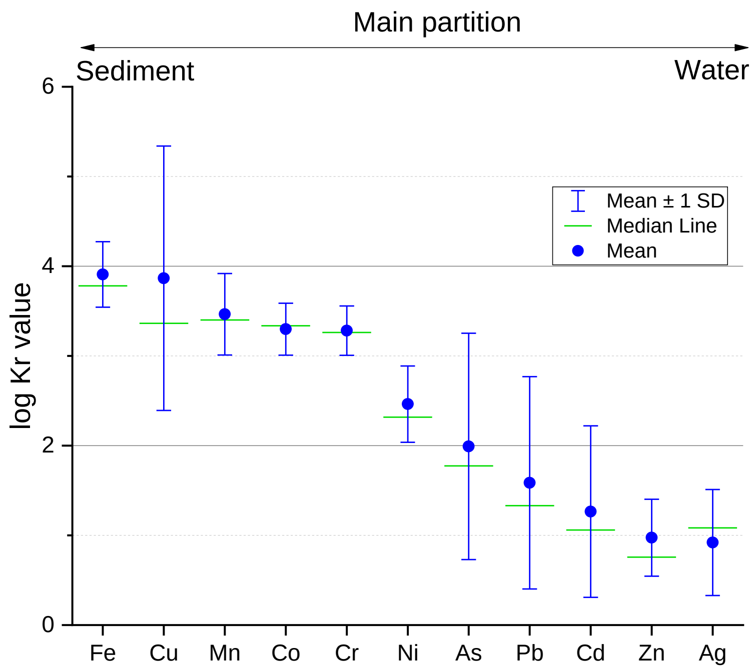

Fig. 6 *Values of Kr index exposed in logarithmic scale for the five water and glacial sediment sampling points, bars indicate the mean values, whiskers indicate the standard deviation*

5. Discussion

Results obtained in this study elucidate specific trends during the summer season for trace elements and relevant differences of concentrations between solid and water samples. Combining the outputs of the proposed integrated approach and analyzing the bedrock main minerals and geochemistry, we can finally infer PTEs sources in the analyzed watershed. Following the seasonal clustering of variables and their temporal trend, we recognized groups of PTEs which can possibly have similar sources. Then, analyzing the partition of elements between water and sediment samples, we evaluated if the geochemically available species justify a presence of PTE in water, or whether an enrichment due to atmospheric depositions is present. Table 5 summarizes the different approaches outputs (whose results are discussed below) and the evaluated PTE source. The discussion will firstly focus on the PTEs showing possibly concerning concentrations in water samples, and then will move to other analyzed PTEs.

5.1 Source apportionment for concerning PTEs: Ni and As

Among the analyzed elements, the only ones showing possible concerning concentrations are Ni and As. Nickel presents a relatively high concentration in water from all the sampling sites, with higher concentrations close to WHO limits for drinking water. Arsenic, instead, presents generally a low concentration considering the whole study area average, but a single spring presents concerning concentrations in the all the sampling campaigns, reaching values which are double than the WHO drinking water standard (Fig. 7).

Nickel is an element which could be present in high concentration on mafic and ultramafic terrains and show clustering with other elements defined as natural (i.e., Cr). Also, observing the results in the other approaches this element shows an increase from the melting season through the end of summer (typical of elements outcoming from water-rock interaction, Hindshaw et al., 2011), and a partition of solid/water concentration of an intermediate value. Nickel shows a relatively high mobility and high concentration in water samples, but this behavior comes from a high dissolution of sulphides in the study area, which was deeply analyzed in another study (Binda et al. 2018).

Moving to As, this PTE does not show a significant seasonal trend, and present a medium-low K_r value, with a high variance in the study area (Fig. 6), suggesting an anthropic enrichment. Nevertheless, its correlation with Mg and HCO_3, species typically dissolving from rocks, is an indicator for rock dissolution sourcing.

The high As concentration in part of the analyzed sediment samples can support a dissolution from water of this elements (Fig. 5). The breccias in the fault area present in fact As bearing minerals (Bedogné et al. 1993; Burkhard 1989) and other authors highlighted the high concentration background of As in freshwater in other areas of the central Alps (Peña Reyes et al. 2015).

Arsenic, also, presents a high concentration along all the sampling sequence in only one spring (P06, with a mean value above WHO limits, supplementary material, Table 1), while the concentration results lower in all the other springs of the study area. At least for this spring, were high As concentration were observed in sediment sample too, a geochemical anomaly can be the cause of this PTE presence. In fact, as observable in Fig. 7, the only one spring present values at least closer to P06 is P04, which was collected in the same stream just few meters downstream and presenting dilution of P06 initial concentration caused by mixing with other water.

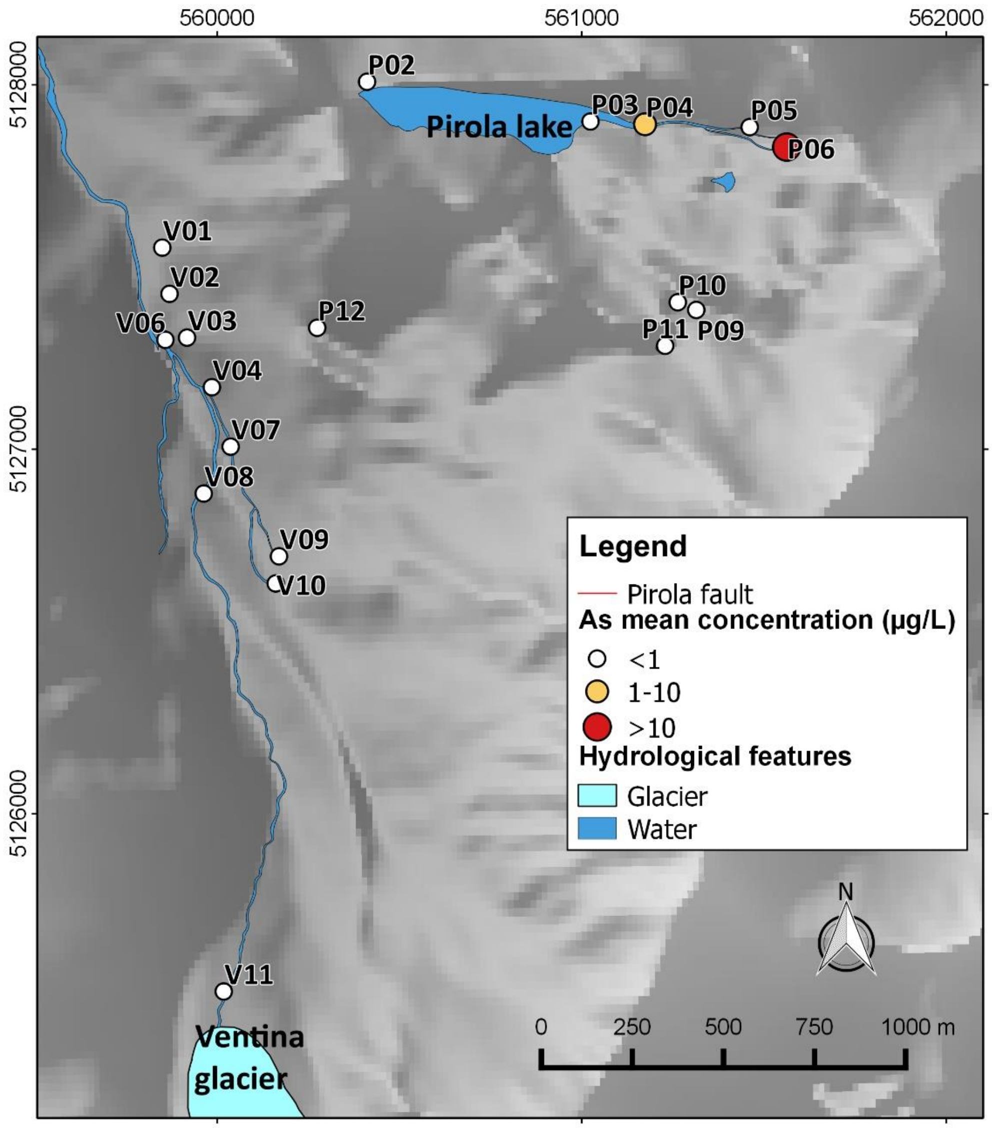

Fig. 7 *Distribution map of mean As values (in µg/L) in water for all sampling campaigns*

Consequently, while considering the whole study area As concentrations could be inferred as coming from a mixed source, surely in the single spring presenting alarming concentrations for human consumption and environmental risk, the cause would be a geochemical anomaly.

5.2 Source apportionment for other PTEs

5.2.1 Other PTEs from natural sources: Cr, Co and Mn.

Elements such as Ni and Cr maintain a clustering throughout the sampling season and plot together to major ions in the ANOVA test, with a slight increase from early to late summer. Cobalt and Mn plot together in Fig. 4, maintaining their clustering, and present similar Kr value. But differently from Co, Mn does not show a statistically significant increase during the melting season.

Manganese and Co are elements which can easily dissolve from mafic rocks, and their presence in water can be justified as mainly from water/rock interaction (Kierczak et al. 2016). Also, these elements present quite low concentrations in water of the study area, especially if compared with solid samples (they present in fact a K_r value which is more than 3, Fig. 6). Iron does not show a significant change from early summer to late summer (Fig. 3), and plot with Co and Mn in early summer, and then group with NH_4, Ni and Cr in late summer (Fig. 4). Also, it presents high K_r value similar to the other elements discussed so far.

These elements show relatively high concentrations in water samples too, consistently with their high concentrations in the bedrock and, in turn, in glacial sediments. Other case studies with serpentinite bedrock reported similar values (Bonifacio et al. 2010; Kierczak et al. 2016; Morrison et al. 2015; Voutsis et al. 2015).

Consequently, these PTEs can be considered as sourced by natural water-rock interaction.

5.2.2 PTEs with anthropic enrichment: Ag, Cd, and Zn.

Silver, Cd and Zn present a low value in K_r values and separate from the others PTEs in the late summer cluster plot, as indexes of effects of atmospheric depositions (Fig. 4). Zn shows a decreasing trend from early to late summer too as an index of higher load at the beginning of summer due to snow and ice melting (Hindshaw et al. 2011).

Differently, the trend of Ag and Cd shows an increment along summer period (Fig. 3): this effect could be due to the high number of samples which presents values below detection limits. Ag and Cd, anyway, show too low concentrations in the sediment samples to be considered naturally sourced in the study area.

Cadmium, Ag, Zn were also reported as anthropic elements in other studies in the Alps (Gabrielli et al. 2008), supporting the possible anthropic enrichment of these elements in our study area too.

5.2.3 Other problematic PTEs: Cu and Pb.

Not all the analyzed elements can be easily attributed to a single source by the approaches applied in this study. Some problems arise, in fact, to interpret result from Cu and Pb.

Lead shows a lower K_r value than metals derived from a natural source (even if this element shows high spatial variability, with large range in the different points values) the difference between early summer and late summer are not statistically significant compared to the inter-annual ones, and the cluster analysis shows that Pb groups with Zn and Cu (considered anthropic) in early summer, but groups with Mn and Co (considered natural) in late summer.

Finally, Cu shows a significant decrease in the mean concentration from the beginning to the end of the melting season as Zn (Fig. 3), presents a clustering with other PTEs considered anthropically enriched. Nonetheless, it shows a high value of K_r ratio which indicates a high availability for dissolution.

Considering the differences in behavior functionally to the applied approach, these metals can be sourced naturally and then anthropically enriched. Therefore, the application of a single-way approach would probably give misleading source apportionment of these elements, and the different trends observed highlight the need of an integrated approach, with a careful evaluation of statistical outputs.

Table 5 *Interpretation of the integrated approach output and source evaluation, PTEs are indicated in bold in the clustering columns.*

Element	**Presence in minerals of the bedrock**	**Clustering with (early summer)**	**Clustering with (late summer)**	**Trend from early to late summer**	**Kr**	**Anthropic influence?**
Fe	Major element in serpentinites and metagabbros	**Co**, **Mn**	NH_4, **Ni**, **Cr**	Not significant	High	No
Cr	Minor element in serpentinite rocks	**Ni**, Cl^-, NO_3^-	**Ni**, **Fe**, NH_4^+	Increasing	High	No
Mn	Minor element in serpentinite rocks	**Co**, **Fe**	**Co**, **Pb**	Not significant	High	No
Co	Minor element in serpentinite rocks	**Mn**, **Fe**	**Mn**, **Pb**	Increasing	High	No
Ni	Minor element in serpentinite rocks	**Cr**, Cl^-, NO_3^-	**Cr**	Increasing	Medium-high	No
Ag	Not present	**Cd**	**Cd**, Cl^-, **Zn**, Na^+, **Cu**	Increasing	Low	Yes
Cd	Not present	**Ag**	**Ag**, Cl^-, **Zn**, Na^+, **Cu**	Increasing	Low	Yes
Zn	Minor element in metagabbros	**Cu**, **Pb**	**Cu**, Na^+, Cl^-, **Ag**, **Cd**	Decreasing	Low	Yes
Pb	Trace element in serpentinites	**Cu**, **Zn**	**Co**, **Mn**	Not significant	Medium-low	Unclear
Cu	Minor element in serpentinite rocks	**Pb**, **Zn**	**Zn**, Na^+, **Cd**, Cl^-, **Ag**	Decreasing	Medium-high	Unclear
As	Trace element in some breccias of the Margna nappe	Mg^{2+}, HCO_3^-	Mg^{2+}, HCO_3^-, NO_3^-	Not significant	Medium low	Unclear

5.3 Geochemical anomalies as source of harmful PTEs concentrations

It is important to highlight, that among all elements analyzed to understand their source in the study area, the ones showing higher and possibly dangerous concentration for human and ecosystem health are characterized as probably from natural source or of a mixed one, and are Ni (with different values close to the WHO limit for concentration in water), and As, which present a concentration higher of WHO limit value in one spring along all the sampling sequence (Table 4).

This maximum value outcome from only one spring in the study area (point P06, in every sampling campaign) indicating a geochemical anomaly in the fault zone, possibly related to the presence of veins of As-bearing minerals (e.g., realgar). Similar results are also obtained for solid samples collected in this point, presenting an enrichment in As too (Fig. 5 and supplementary material, Table S2). Similar mineral anomalies are observed in a location about 10 km far from the study area (Burkhard 1989).

5.4 Integrated approach applicability

The proposed approach helps to understand trace element sources in water, especially in areas with a high geochemical load of PTEs where is hard to separate the natural and the anthropic ones. Nonetheless, such an approach requires a big amount of analyses and a good knowledge of the bedrock geochemistry of the study area to have guidance in data interpretation for the search of the natural background. We here applied the approach to a relatively simple-structured catchment, but it could be considered as a preliminary case study for future investigations on a more regional scale. This approach could also work better in areas with remote settings, where direct sources of pollution are not immediate to observe.

Through these observations, we remark the need to applicate of an integrated approach to understand possible sources of elements in catchments, because the application of only one of the methods used would probably fail to clearly understand sources of elements (i.e., seasonal trends and clustering of Cd and Ag).

Through this study, we also remark the importance of high mountain catchments monitoring: these settings, in fact, need high attention in water quality checks for ecological and human risk assessment, because they present an important water source for human populations (Viviroli et al. 2007), and usually these catchments have ecological communities that are highly sensitive to slightly changes in water chemistry, and potentially toxic elements could increase through the food web (Ilyashuk et al. 2014).

6. Conclusions

We here propose a method to evaluate the source of natural and anthropic PTEs in freshwater through a multidisciplinary integrated approach including:

- the analyses of water and sediments in relation to spatiotemporal trends;
- a multiple statistical data treatment aiming to understand seasonal clustering of variables and the partition of elements between solid and water phases;
- a combined output evaluation to obtain metals sources in water.

We applied this approach in a mountainous watershed to evaluate the sources of 11 PTEs (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd and Pb).

We observed a high natural background in water for Ni (with maximum concentrations observed closer to the WHO drinking water limits) and the natural sources of Fe, Co, Mn, Cr without severe risk for human beings and the biota. Metals observed as coming from anthropic sources are Ag, Cd and Zn. Elements showing controversial trends are instead Cu, As, and Pb, which possibly present a mixed source. Arsenic also presents a geochemical anomaly in a spring, which show a concentration which is twice as much of the WHO limit for water consuming.

This study highlights the need of a multidisciplinary integrated approach for the source apportionment of PTEs. The proposed approach, in fact, helped in the understanding of PTEs sources and, while still requiring high number of samples and analyses, elucidate the failure of single way approaches when dealing with geochemical anomalies.

The observation of controversial trends for part of the analyzed elements (i.e., Cu, Ag, Cd) through the integrated approach highlights that a single-way procedure could potentially lead to erroneous source apportionment, without considering all the possible influencing factors. This study elucidates also that the only alarming concentrations observed in water are outcoming from a natural source, suggesting that geochemical anomalies can be harmful in some cases also for water human consumption.

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Electronic supplementary material

Electronic supplementary material includes two tables, indexed as follow: Table s1, including the chemical data for all collected water samples, and Table s2, indicating the chemical results for acid digestion of glacial sediment samples.

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A1. Appendix: detailed methods

A1.1. Detailed water analyses

Physico-chemical parameters (pH, temperature and EC) were evaluated *in situ* using specific field probes: a HANNA instruments HI 9025 pH-meter equipped with a thermometer for pH and temperature and a HANNA Instruments HI 9033 conductivity meter for electrical conductivity. Nitrile gloves were used in all the field practices. Water samples for laboratory analysis were collected in LPDE bottles, preventively washed.

Carbonates, as HCO_3^-, were estimated by colorimetric titration using 0,01 M HCl and Bromocresol Green as indicator. Major anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, NH_4^+, K^+) were estimated using an ionic chromatography Metrohm Eco IC (Swiss Confederation).

Samples for trace element analysis were collected in LPDE bottles, washed in NALGENE (USA) solution, and then washed twice in a 2% HNO_3 solution. Afterward, water samples were filtered through 0.45 µm filters and acidified adding 2% volume ultrapure HNO_3, and analyzed using an iCAP-Q ICP-MS instrument from Thermo Fisher Scientific (USA). These elements were selected functionally to the geochemistry of the site, and for their environmental interest as PTEs. All samples were spiked with In as internal standard and instrumental drift was beneath the 10% for all samples.

LOD for major ions, as referenced from the instrument, is 0.05 ppm. We calculated LOD for trace elements as 3 times standard deviation of blank samples (Long and Winefordner 1983).

A1.2. Detailed solid samples analysis

Once in laboratory, the samples were air dried in oven at 105 °C for 2-3 hours (Quevauviller 1998) and then < 2 mm fraction was sieved and selected for analysis (Chabukdhara and Nema 2012). Then, 500 mg of sample were inserted in Teflon vessels, and 3 ml of solution (pure hydrochloric and nitric acid solution in proportion 1: 2) were added. The digestion was made in a MLS-1200 Mega, Milestone (USA) microwave. After cooling, the solution was diluted with ultrapure water. The solutions obtained from acid digestion were analyzed using a Thermo Fisher Scientific (USA) Icap Q ICP-MS instrument. Samples were run in triplicate and present less than 5% of relative standard deviation.

A1.3. Analysis solutions

All the solutions used in laboratory for this study were made using ultrapure water from a Millipore MilliQ system (18.8 MΩcm resistivity).

Acid solutions for digestions were obtained from a Carlo Erba® reagents (Italy) 65% volume solution. Ultrapure acids were obtained through sub-boiling distillation using a Milestone (USA) DuoPUR system.

Standard solutions for major ions and trace-element analysis was obtained from dilution of MERCK (Germany) multi-elemental standard.

A1.4. Detailed statistical methods

A1.4.1. ANOVA

This statistical test compares the mean and the variances of two different dataset in function of a categorical variable (in this case the sampling period). The null hypothesis is that these datasets are the same, and the variance among samples is basically the same as the difference between the datasets, and an F value is calculated as the ratio of variance inside groups and among the groups, and also a p value is calculated as well (Ross and Willson 2017).

A1.4.2. Cluster analysis

Ward's method starts from a singleton (single-point clusters) and aims to create clusters with the lowest possible increment of sum of squares. We decided to use this method because it creates small clusters (Ward 1963).

To avoid interferences due to different measure units in the application of cluster analysis, all the measured variables in the data matrix were scaled and centered on mean, using the following equation A1:

$$x_i' = \frac{x_i - \mu}{s} \quad \text{Eq. A1}$$

Where μ is the mean, s is the standard deviation, x_i is the original value and x_i', is the standardize value (Sahariah et al. 2015).

Statistical analysis was performed using R version 3 (R Core Team 2014), and the package "dendextend" to perform cluster analyses (Galili 2015).

A1.5. Appendix References

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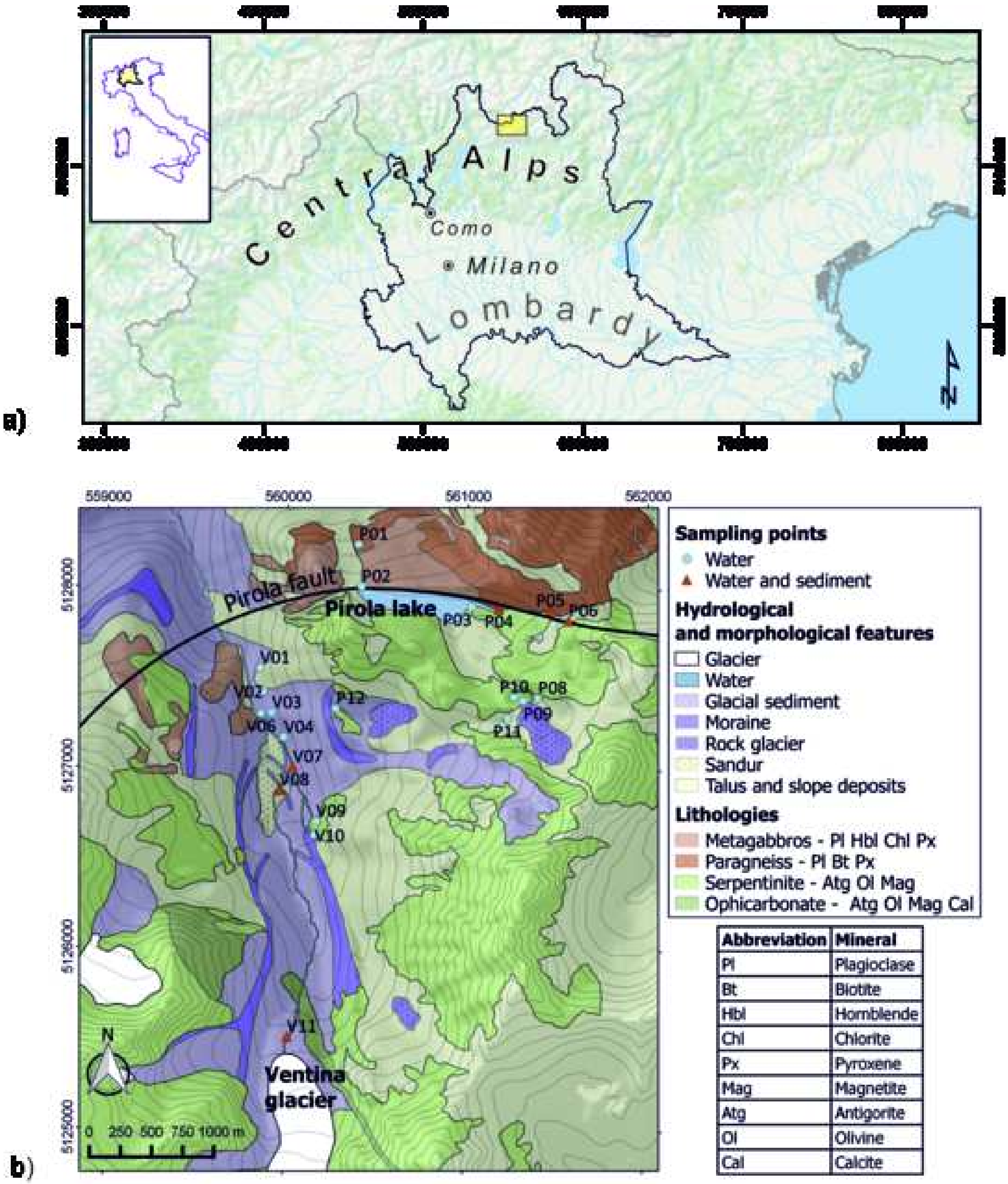
Fig 1 Study area map



Abbreviation	Mineral
Pl	Plagioclase
Bt	Biotite
Hbl	Hornblende
Chl	Chlorite
Px	Pyroxene
Mag	Magnetite
Atg	Antigorite
Ol	Olivine
Cal	Calcite

Fig 2 Integrated approach workflow

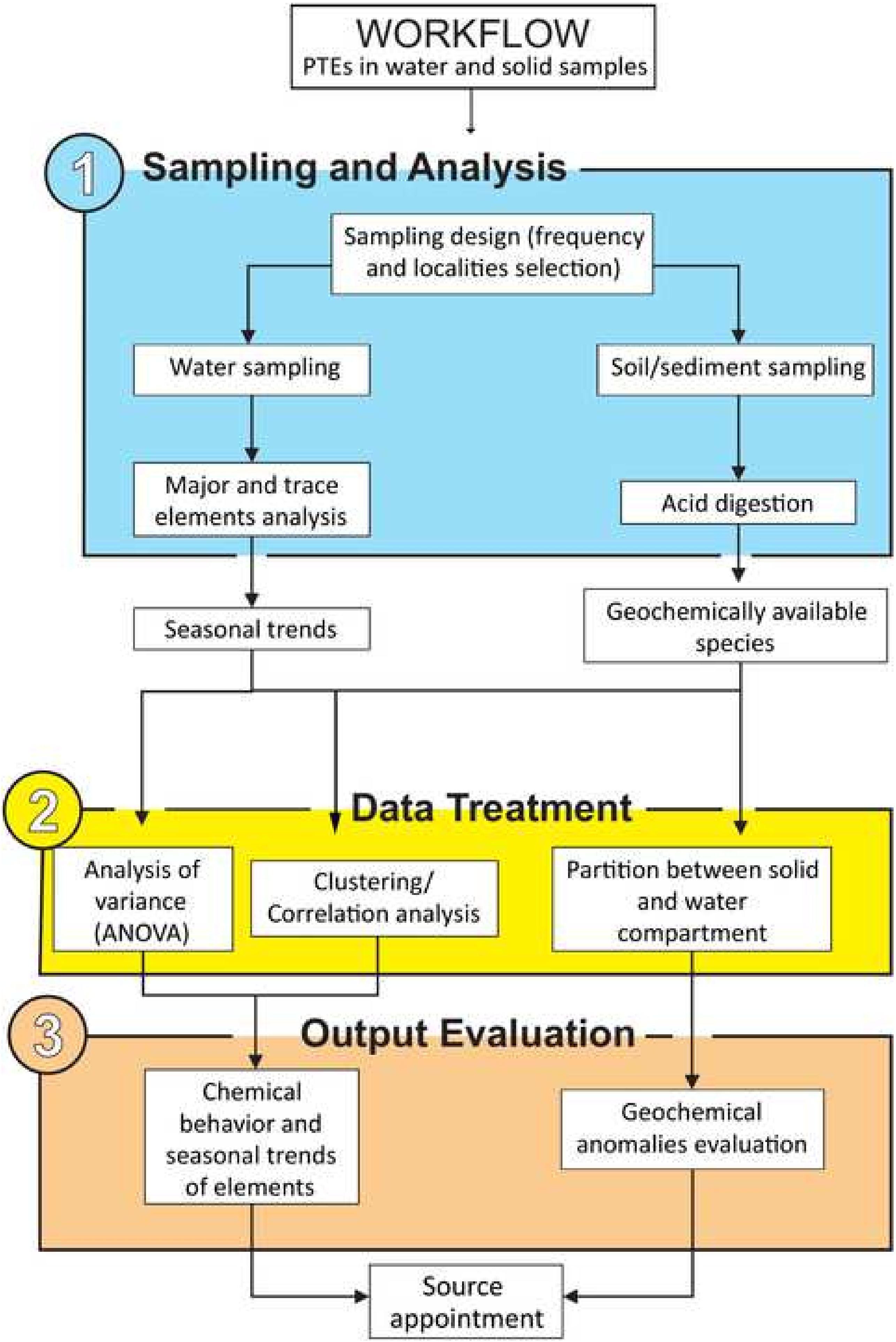
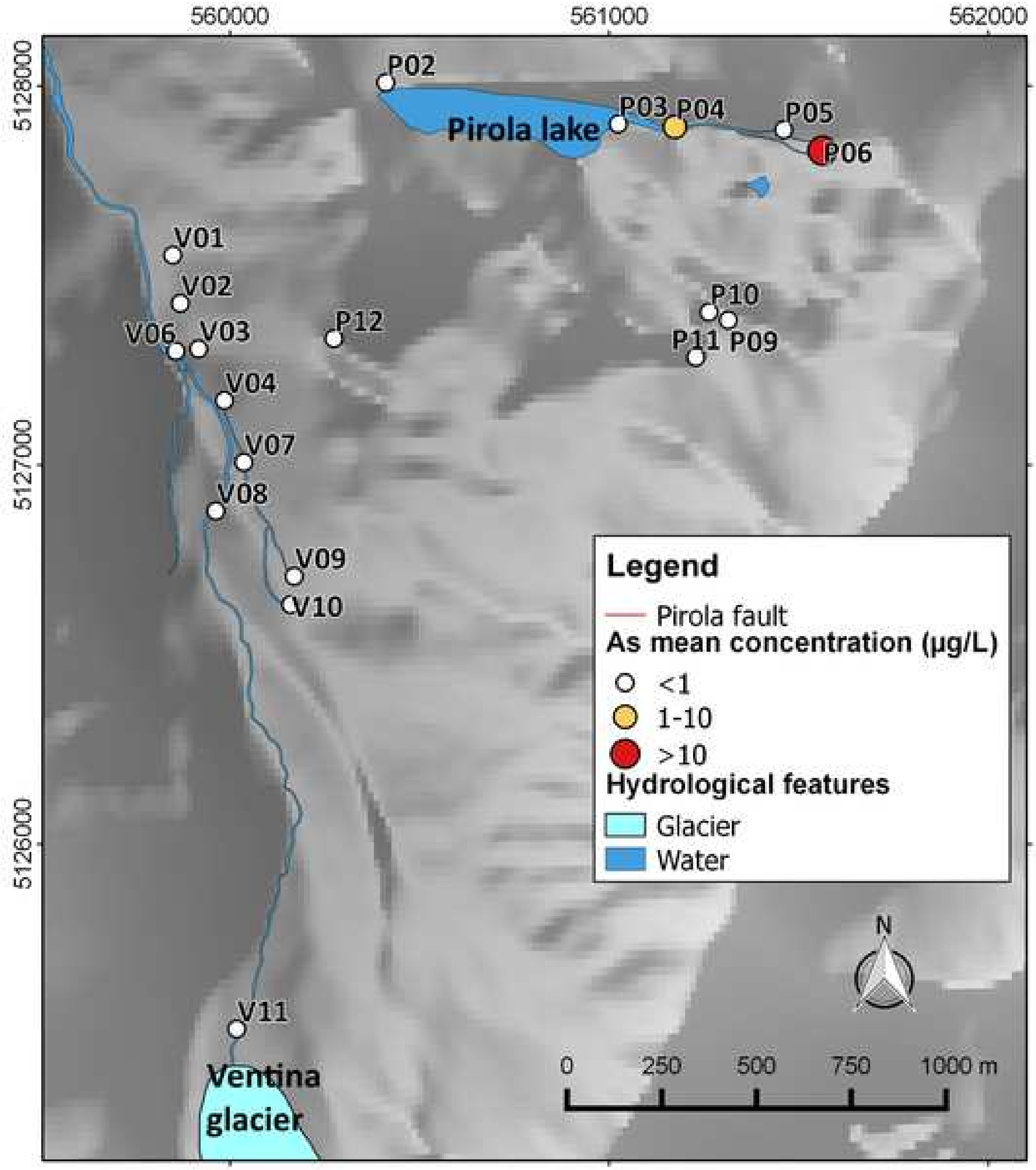


Fig 7 map of As distribution

Click here to access/download;Figure;Fig07_map As.tiff



Supplementary tables S1 and S2

Table S1: All water samples values and limits of detection for physicochemical parameters, major ion

		physico-chemical parameters				
	Measure unit	°C	-	µS/cm	mg/L	mg/L
Sample	**Date**	**Temperature**	**pH**	**Electrical conductivity**	**HCO_3^-**	**Cl^-**
P01	7/30/2014	6.6	7.1	26	18.04	0.27
P02	7/30/2014	12.5	7.35	27	17.31	0.29
V10	7/30/2014	3.1	7.68	45.3	28.04	0.05
V09	7/30/2014	3.1	7.64	46.5	31.52	0.06
V08	7/30/2014	5.5	7.31	21.4	11.08	0.24
V06	7/30/2014	6.1	7.33	31.6	14.79	0.04
P09	7/30/2014	6.3	7.5	30	25.27	0.57
P10	7/30/2014	10.5	7.55	26	18.17	0.28
P03	7/30/2014	14.9	7.35	28	17.12	0.30
P12	7/31/2014	6.5	8.8	39	24.19	0.47
P08	7/31/2014	0.7	7.1	29	22.12	0.24
V11	7/31/2014	1.8	7.38	14.7	9.88	0.23
P04	7/31/2014	0.8	7.23	40	28.68	0.20
P05	7/31/2014	5.6	7.53	52	25.07	0.24
P06	7/31/2014	2.3	8.1	49	26.03	0.28
V01	7/31/2014	4.3	7.4	43.7	30.84	0.01
V02	7/31/2014	5.6	7.62	34.5	22.72	0.05
V03	7/31/2014	6.4	7.32	34	23.86	0.03
V04	7/31/2014	3.3	7.36	39.5	31.71	0.01
V07	6/25/2014	3.66	7.73	48.3	24.77	0.25
V08	6/25/2014	4.31	8.01	30.9	14.60	0.26
V06	6/25/2014	3.66	7.73	42.5	21.67	0.22
P09	6/25/2014	1	8.25	17.1	16.91	0.86
P10	6/25/2014	4.45	7.79	5.2	3.14	0.25
P03	6/25/2014	4.36	7.97	26.9	19.13	0.43
P08	6/25/2014	0.12	8.44	27.7	16.35	0.30
V11	6/26/2014	0.76	8.27	20.8	12.69	0.34
P04	6/26/2014	0.8	8.01	35.8	20.84	0.27
V01	6/26/2014	3.28	7.61	41	24.28	0.14
V02	6/26/2014	4.73	7.54	32.4	20.40	0.11
V03	6/26/2014	4.59	7.91	30.7	21.03	0.13
V04	6/26/2014	2.29	7.61	41.8	31.72	0.18
P01	10/1/2014	9.1	7.37	27.6	17.08	0.32
P02	10/1/2014	11.7	7.79	27.3	17.73	0.27
P03	10/1/2014	12	7.75	26.8	16.75	0.28
P04	10/1/2014	8.3	7.23	54.4	29.93	0.16
P05	10/1/2014	5.2	7.8	57.2	25.07	0.25
P06	10/1/2014	9.8	7.99	85	52.05	0.04
P08	10/1/2014	2.3	7.6	41.4	27.32	0.28
P09	10/1/2014	7.8	7.94	39.2	25.21	0.59
P10	10/1/2014	11.4	8.42	37.9	21.21	0.26
P12	10/1/2014	8.4	7.73	40	25.37	1.29
V01	10/2/2014	4.9	7.43	49.1	32.12	0.07
V02	10/2/2014	7	7.42	41.9	24.02	0.04
V03	10/2/2014	6.7	6.58	35	27.16	0.02
V04	10/2/2014	3.4	6.6	53.9	35.54	0.01

V06	10/2/2014	5	6.62	43.3	25.21	0.06
V07	10/2/2014	4.1	7.48	38.4	20.45	0.25
V08	10/2/2014	8.3	7.36	26.1	14.48	0.23
V10	10/2/2014	4	6.95	38.1	22.26	0.06
V11	10/2/2014	2	6.6	19.3	12.04	0.25
P01	9/2/2014	9.5	7.74	26.6	15.26	0.27
P02	9/2/2014	11.6	7.61	26.1	14.30	0.26
P03	9/2/2014	12.1	7.13	47.3	14.66	0.25
P04	9/2/2014	8.1	7.05	45.6	27.07	<LOD
P05	9/2/2014	5.9	7.24	49.1	24.14	0.24
P06	9/2/2014	5	8.25	76.6	36.85	0.02
P08	9/2/2014	1.9	7.79	39.2	25.87	0.25
P09	9/2/2014	9.3	8.39	30.5	26.94	0.23
P10	9/2/2014	10.6	8.41	28.4	16.95	0.21
P12	9/2/2014	7.1	7.4	39.7	24.20	0.26
V01	9/3/2014	5.1	7.54	44.6	28.49	0.04
V02	9/3/2014	7.5	7.66	38.5	22.30	0.02
V03	9/3/2014	7.4	7.8	36.6	21.10	0.01
V04	9/3/2014	3.8	7.63	50	30.00	0.04
V06	9/3/2014	6.4	7.54	37.9	18.75	0.06
V07	9/3/2014	4	6.82	37.2	22.17	0.28
V08	9/3/2014	6.7	6.85	27.8	15.36	0.23
V09	9/3/2014	3.7	7.9	38.5	20.36	0.06
V10	9/3/2014	5.2	7.2	39.8	22.06	0.08
V11	9/3/2014	2.4	7.72	18.8	10.85	0.23
P01	6/23/2015	4.87	7.6	27	16.47	0.35
P02	6/23/2015	6.72	7.95	30	15.86	0.39
P03	6/23/2015	8.41	8.6	29	16.35	0.34
P04	6/23/2015	6.93	7.56	41	23.18	0.33
P05	6/23/2015	3.8	7.76	40	25.01	0.32
P06	6/23/2015	0.59	9.11	31	20.01	0.33
P08	6/23/2015	0.35	8.41	19	12.20	0.33
P09	6/23/2015	9.52	8.02	23	12.20	0.36
P10	6/23/2015	11.51	8.02	17	4.25	0.35
P11	6/23/2015	6.94	8.16	44	26.11	0.40
P12	6/23/2015	6.26	7.96	33	20.01	0.32
V01	6/24/2015	3.38	7.95	42.5	26.84	0.38
V02	6/24/2015	5.55	7.86	34.1	22.20	0.39
V03	6/24/2015	4.51	8.32	33.1	20.74	0.36
V04	6/24/2015	2.49	8.07	45.9	29.28	0.37
V06	6/24/2015	5.71	8.23	39.7	21.96	0.35
V07	6/24/2015	2.5	8.08	47.1	26.27	0.37
V08	6/24/2015	4.18	8.39	32	16.59	0.36
V09	6/24/2015	2.09	8.17	46.2	28.30	0.35
V10	6/24/2015	2.12	7.95	47.5	27.98	0.36
V11	6/24/2015	0.75	7.8	25	11.96	0.39
P05	10/12/2015	6.7	8.12	63.5	32.04	<LOD
P06	10/12/2015	3.4	8.67	84.3	42.70	<LOD
P08	10/12/2015	2.7	8.1	98	42.78	<LOD
P09	10/12/2015	4.6	8.22	63	35.48	<LOD
P11	10/12/2015	2.6	8.2	75.1	35.99	<LOD
V01	10/13/2015	5.1	7.38	46.9	28.30	<LOD
V02	10/13/2015	6.2	7.71	35.7	23.98	<LOD

V03	10/13/2015	7.64	5.9	35.4	22.29	<LOD
V04	10/13/2015	3.5	7.53	54.2	34.65	<LOD
V07	10/13/2015	4	7.87	55.7	32.05	<LOD
V11	10/13/2015	2.5	7.29	35.3	18.71	<LOD
P03	9/28/2015	10.7	8.37	33.7	21.32	<LOD
P05	9/28/2015	5.3	7.98	60	30.26	<LOD
P06	9/28/2015	2.1	8.51	75.1	43.43	<LOD
P08	9/28/2015	1.6	7.7	83.8	42.70	<LOD
P09	9/28/2015	5	8.34	56.8	33.72	<LOD
P10	9/28/2015	6.2	8.64	40.1	28.23	<LOD
P11	9/28/2015	5.4	8.21	66.5	39.65	<LOD
P12	9/28/2015	6.1	6.78	28.5	26.30	<LOD
V01	9/29/2015	6.6	6.7	60.4	29.70	<LOD
V02	9/29/2015	7.6	6.75	40.1	22.31	<LOD
V03	9/29/2015	7.6	6.72	40.1	22.50	<LOD
V04	9/29/2015	3.6	7.54	43.1	31.07	<LOD
V06	9/29/2015	5.4	7.67	59.7	32.47	<LOD
V07	9/29/2015	3.3	8.04	60	29.03	<LOD
V08	9/29/2015	7.2	7.9	58.8	28.47	<LOD
V10	9/29/2015	3.1	7.74	58	28.95	<LOD
V11	9/29/2015	1.6	7.2	37.3	18.43	<LOD
P05	7/25/2016	5	6.95	57.9	27.15	0.64
P06	7/25/2016	3.4	7	79.3	45.14	0.68
P08	7/25/2016	1.3	6.93	52.9	26.54	0.68
P11	7/25/2016	1.6	7.09	61.1	30.81	0.87
P12	7/25/2016	7.9	7.14	39.5	24.71	0.64
V01	7/26/2016	4.8	6.76	49.7	27.76	0.66
V02	7/26/2016	5.81	5.81	36.9	22.88	0.74
V03	7/26/2016	6.5	6.71	34.1	22.88	0.66
V04	7/26/2016	4	6.85	52.5	28.37	0.65
V07	7/26/2016	3.2	6.4	46.6	24.40	0.65
V10	7/26/2016	3.1	6.4	45.5	23.49	0.73
V11	7/26/2016	1.8	6.15	15	9.15	0.65
P05	6/23/2016	4.3	5.93	49.2	28.49	0.01
P06	6/23/2016	0.8	6.07	27	17.17	<LOD
P08	6/23/2016	0.6	6.28	25.6	16.17	<LOD
P11	6/23/2016	1.1	6.1	38.5	23.49	<LOD
P12	6/23/2016	5.7	7.12	31.1	20.96	<LOD
V07	6/24/2016	3.11	7.1	48.7	29.59	<LOD
V09	6/24/2016	2.8	6.73	51.9	29.59	<LOD
V10	6/24/2016	2.9	6.47	48.4	28.37	<LOD
V11	6/24/2016	0.75	7.8	22	10.98	<LOD
P03	10/10/2016	2.6	8.28	37	10.60	0.44
P08	10/10/2016	2.6	8.28	95.2	31.65	0.24
P11	10/10/2016	1.6	8.9	87	26.57	0.19
V01	10/11/2016	3.7	6.89	57.8	20.47	0.43
V02	10/11/2016	4.1	6.09	46.2	20.40	0.18
V03	10/11/2016	5.3	6.19	48.2	20.42	0.26
V04	10/11/2016	3.6	5.23	57.3	30.50	0.32
V07	10/11/2016	3.5	5.98	57.1	24.52	0.16
V11	10/11/2016	1.5	6.55	36.1	8.50	0.16
LOD	-	-	-	-	0.05	0.05

s and trace elements

major ions (milligrams per liter)								
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	meq/L	meq/L
NO_3^-	**SO_4^{2-}**	**NH_4^+**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**HCO_3^-**	**Cl^-**
1.13	3.36	0.11	3.15	1.71	0.69	0.13	0.296	0.008
1.07	2.76	0.12	2.50	2.10	0.66	0.05	0.284	0.008
1.18	5.74	0.12	3.66	3.80	0.12	<LOD	0.460	0.002
1.21	5.94	<LOD	4.19	4.69	0.10	<LOD	0.517	0.002
0.97	4.44	<LOD	4.02	0.59	0.05	<LOD	0.182	0.007
0.89	3.92	0.28	2.45	2.13	0.04	<LOD	0.243	0.001
1.08	1.71	0.01	3.46	4.72	0.28	<LOD	0.414	0.016
0.85	1.45	0.12	2.01	3.60	0.03	<LOD	0.298	0.008
0.90	2.79	0.09	2.31	1.80	0.66	0.06	0.281	0.008
0.73	1.88	<LOD	2.69	3.19	0.04	<LOD	0.397	0.013
1.08	3.08	0.06	2.58	3.25	0.14	<LOD	0.363	0.007
0.89	2.38	0.04	2.25	1.05	<LOD	<LOD	0.162	0.007
0.38	6.95	1.11	8.29	1.62	0.72	0.23	0.470	0.006
0.52	10.44	<LOD	8.49	0.91	0.78	0.55	0.411	0.007
1.06	4.63	<LOD	2.26	4.64	0.07	<LOD	0.427	0.008
1.40	3.19	0.02	3.33	4.00	0.10	<LOD	0.506	0.000
0.75	1.76	0.04	2.02	2.99	0.12	<LOD	0.373	0.001
0.84	1.23	0.46	2.02	2.92	0.09	<LOD	0.391	0.001
1.13	3.13	0.06	3.55	4.47	0.17	0.01	0.520	0.000
1.21	5.66	0.04	3.29	4.02	0.12	0.01	0.406	0.007
1.47	5.25	0.02	4.05	1.77	0.03	<LOD	0.239	0.007
1.38	4.83	0.16	3.14	2.92	0.09	0.11	0.355	0.006
0.89	1.42	0.24	2.01	2.80	0.55	0.13	0.277	0.025
0.46	0.73	0.04	0.63	0.50	0.03	<LOD	0.051	0.007
1.30	3.06	0.26	2.57	2.06	0.71	0.13	0.314	0.012
1.27	2.88	0.06	1.94	2.43	0.18	<LOD	0.268	0.009
1.61	5.05	0.01	3.19	1.69	0.02	<LOD	0.208	0.010
0.70	5.31	0.21	7.53	1.48	0.73	0.21	0.342	0.008
1.41	3.15	0.12	2.69	3.19	0.20	<LOD	0.398	0.004
0.86	1.86	0.03	1.93	2.68	0.15	0.03	0.334	0.003
0.97	1.62	0.24	1.82	2.65	0.21	<LOD	0.345	0.004
1.39	2.15	0.50	3.30	3.78	0.40	0.10	0.520	0.005
0.92	3.34	0.12	3.29	1.62	0.75	0.18	0.280	0.009
0.80	2.82	0.11	2.55	2.07	0.66	0.06	0.291	0.008
0.79	2.90	0.10	2.57	2.06	0.69	0.08	0.275	0.008
0.40	9.96	0.11	9.80	1.92	0.80	0.32	0.491	0.004
0.63	13.74	0.10	9.62	0.83	0.85	0.64	0.411	0.007
1.64	10.18	0.03	4.07	8.36	0.17	<LOD	0.853	0.001
1.95	6.90	<LOD	3.16	4.11	0.55	<LOD	0.448	0.008
1.18	3.23	<LOD	2.61	4.44	0.11	<LOD	0.413	0.017
1.06	2.88	<LOD	2.08	3.55	0.06	<LOD	0.348	0.007
1.02	2.48	0.01	2.62	3.23	0.59	0.54	0.416	0.037
1.64	3.70	<LOD	4.18	4.69	0.16	<LOD	0.527	0.002
1.22	2.94	<LOD	2.43	3.34	0.19	<LOD	0.394	0.001
1.13	3.03	0.06	2.69	3.70	0.18	0.03	0.445	0.001
1.67	5.22	0.00	4.34	4.60	0.43	0.12	0.583	0.000

1.01	5.99	<LOD	4.58	3.85	0.05	<LOD	0.413	0.002
1.11	6.52	<LOD	3.96	2.86	0.07	<LOD	0.335	0.007
0.87	4.44	0.03	3.17	1.70	0.03	<LOD	0.237	0.007
1.08	5.74	0.01	3.30	3.18	0.09	0.00	0.365	0.002
1.04	4.19	<LOD	3.40	1.56	0.05	<LOD	0.197	0.007
0.83	3.23	<LOD	3.26	1.65	0.69	0.17	0.250	0.008
0.82	2.80	<LOD	2.52	2.09	0.66	0.04	0.235	0.007
0.84	2.75	0.10	2.48	1.98	0.67	0.09	0.240	0.007
0.20	8.09	<LOD	8.16	1.70	0.74	0.28	0.444	<LOD
0.41	12.12	<LOD	8.60	0.84	0.82	0.55	0.396	0.007
1.41	8.72	<LOD	3.12	6.53	0.12	<LOD	0.604	0.001
1.50	5.22	<LOD	3.23	4.06	0.35	<LOD	0.424	0.007
0.73	1.91	<LOD	3.52	4.69	0.11	<LOD	0.442	0.007
0.47	1.65	<LOD	1.43	3.26	0.06	<LOD	0.278	0.006
1.06	2.26	0.02	2.59	3.24	0.17	<LOD	0.397	0.007
1.44	3.11	<LOD	3.48	3.91	0.14	<LOD	0.467	0.001
0.76	1.66	<LOD	2.12	3.05	0.16	0.11	0.366	0.001
1.02	2.34	<LOD	2.48	3.35	0.17	0.08	0.346	0.000
1.40	4.50	<LOD	3.37	3.98	0.31	0.07	0.492	0.001
0.99	4.07	<LOD	2.69	2.59	0.01	0.07	0.307	0.002
1.40	6.33	1.77	4.29	3.43	0.10	<LOD	0.364	0.008
1.04	4.95	0.05	4.75	1.21	0.05	<LOD	0.252	0.007
1.07	5.73	<LOD	3.25	2.85	0.08	0.01	0.334	0.002
1.12	5.47	0.04	3.59	3.12	0.17	0.01	0.362	0.002
0.91	3.63	<LOD	2.80	1.32	<LOD	<LOD	0.178	0.007
1.80	1.88	<LOD	3.00	1.43	0.30	0.40	0.270	0.010
1.32	1.39	0.53	2.55	2.06	0.17	0.22	0.260	0.011
1.33	1.38	0.54	2.59	2.06	0.16	0.23	0.268	0.010
0.51	2.53	0.42	4.97	1.84	0.29	0.46	0.380	0.009
0.72	4.18	0.48	8.72	0.79	0.46	0.82	0.410	0.009
1.10	1.19	0.66	1.71	3.41	0.42	<LOD	0.328	0.009
0.95	0.70	0.31	1.30	1.68	<LOD	<LOD	0.200	0.009
0.83	0.60	0.37	1.10	2.00	<LOD	<LOD	0.200	0.010
0.80	0.53	0.30	0.34	0.66	<LOD	<LOD	0.070	0.010
1.57	2.08	0.47	3.31	3.87	0.23	<LOD	0.428	0.011
1.12	0.80	0.28	2.35	2.90	<LOD	<LOD	0.328	0.009
1.39	1.35	0.37	3.32	4.00	0.12	0.19	0.440	0.011
1.08	0.91	0.51	2.23	3.27	0.17	<LOD	0.364	0.011
1.07	0.88	0.35	2.19	3.10	0.11	<LOD	0.340	0.010
1.42	1.64	0.61	3.96	4.09	0.25	0.25	0.480	0.011
1.44	2.17	0.80	3.41	3.00	<LOD	<LOD	0.360	0.010
1.41	2.52	0.35	3.88	4.03	0.15	<LOD	0.431	0.011
1.86	1.95	0.14	3.14	1.91	<LOD	<LOD	0.272	0.010
1.70	2.54	0.33	3.91	4.12	0.14	<LOD	0.464	0.010
2.02	2.39	0.64	3.72	4.59	0.15	0.26	0.459	0.010
1.63	1.66	0.28	2.44	1.35	<LOD	<LOD	0.196	0.011
0.59	4.76	3.96	8.61	0.87	0.39	0.70	0.525	<LOD
2.30	3.83	1.95	3.78	7.39	0.00	0.03	0.700	<LOD
2.69	9.93	1.62	5.42	6.77	1.89	0.11	0.701	<LOD
1.69	2.17	3.64	3.06	5.17	0.12	<LOD	0.582	<LOD
1.95	4.84	2.07	5.12	5.33	0.18	0.09	0.590	<LOD
1.63	0.91	2.06	3.40	3.87	0.05	<LOD	0.464	<LOD
0.79	0.43	2.62	2.15	3.03	0.03	<LOD	0.393	<LOD

0.93	0.37	1.71	2.14	3.13	0.00	<LOD	0.365	<LOD
1.69	1.72	1.94	3.97	4.44	0.23	0.11	0.568	<LOD
1.44	3.64	2.91	4.97	3.95	0.06	<LOD	0.525	<LOD
1.97	3.08	1.91	3.90	2.03	<LOD	<LOD	0.307	<LOD
1.35	1.16	2.35	2.46	2.10	0.13	0.05	0.350	<LOD
0.56	4.63	1.87	9.52	0.88	0.40	0.71	0.496	<LOD
2.00	3.97	1.64	3.74	7.42	<LOD	0.03	0.712	<LOD
2.24	7.68	2.59	5.30	6.63	1.55	0.08	0.700	<LOD
1.70	2.29	3.10	3.04	4.93	0.40	0.21	0.553	<LOD
1.28	1.65	2.37	2.55	4.08	0.09	0.01	0.463	<LOD
1.88	3.81	4.30	4.66	5.24	0.18	0.10	0.650	<LOD
1.09	0.78	2.52	2.45	3.17	0.41	0.23	0.431	<LOD
2.00	0.80	2.99	3.28	3.82	0.05	<LOD	0.487	<LOD
1.34	0.27	1.77	2.14	3.11	0.02	<LOD	0.366	<LOD
1.37	0.15	1.80	2.13	3.08	0.05	<LOD	0.369	<LOD
1.93	1.56	1.33	3.81	4.33	0.22	0.08	0.509	<LOD
2.12	2.44	3.52	4.28	4.04	0.13	0.06	0.532	<LOD
1.61	3.04	2.63	4.57	3.73	0.06	0.01	0.476	<LOD
1.69	2.69	2.42	4.97	2.56	0.34	<LOD	0.467	<LOD
1.53	3.00	2.56	4.42	3.54	0.04	<LOD	0.475	<LOD
2.18	2.28	2.52	3.43	1.79	<LOD	<LOD	0.302	<LOD
0.87	4.13	0.83	7.76	0.88	0.70	0.87	0.445	0.018
2.40	2.77	0.72	3.31	6.38	<LOD	0.31	0.740	0.019
2.24	2.80	0.32	2.90	3.48	0.85	<LOD	0.435	0.019
2.13	2.75	0.29	3.63	4.10	0.50	0.32	0.505	0.025
1.24	1.20	0.28	2.40	2.95	0.46	0.32	0.405	0.018
1.84	1.55	0.30	3.08	3.47	<LOD	0.25	0.455	0.019
1.59	1.19	0.98	2.07	2.95	<LOD	<LOD	0.375	0.021
1.23	1.14	0.66	2.06	2.86	<LOD	0.32	0.375	0.019
1.55	2.33	0.89	3.45	3.44	<LOD	0.30	0.465	0.019
1.92	2.53	0.65	3.50	3.05	<LOD	0.31	0.400	0.019
1.56	2.56	0.28	4.29	3.91	<LOD	<LOD	0.385	0.021
1.83	1.27	0.79	1.61	0.92	<LOD	<LOD	0.150	0.018
0.57	0.73	0.26	5.08	2.16	<LOD	<LOD	0.467	0.000
1.11	4.41	0.64	6.71	0.53	0.66	0.91	0.281	<LOD
1.60	1.45	0.52	1.33	1.88	0.54	<LOD	0.265	<LOD
0.89	1.66	0.71	2.32	3.00	0.45	0.56	0.385	<LOD
0.29	0.57	0.42	1.62	2.22	0.47	<LOD	0.344	<LOD
1.07	2.46	0.78	3.14	3.80	0.48	0.52	0.485	<LOD
1.15	2.55	0.67	2.97	3.69	0.44	<LOD	0.485	<LOD
1.91	2.70	0.78	3.05	3.74	0.49	0.52	0.465	<LOD
1.08	1.32	0.71	1.73	0.88	0.44	<LOD	0.180	<LOD
1.66	2.27	<LOD	2.49	2.12	<LOD	<LOD	0.174	0.013
2.40	6.17	<LOD	5.65	6.37	0.47	<LOD	0.519	0.007
2.33	5.41	<LOD	5.09	5.62	<LOD	<LOD	0.436	0.005
1.56	1.89	<LOD	3.19	3.71	<LOD	0.12	0.336	0.012
1.76	1.45	<LOD	2.10	3.42	<LOD	<LOD	0.334	0.005
1.60	1.65	<LOD	1.68	3.05	<LOD	<LOD	0.335	0.008
1.53	4.06	<LOD	6.32	4.32	<LOD	<LOD	0.500	0.009
1.55	4.36	<LOD	4.79	3.09	<LOD	<LOD	0.402	0.004
1.58	3.31	<LOD	3.65	0.79	<LOD	<LOD	0.139	0.005
0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.0008	0.0014

major ions (milliequivalent per liter)								
meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L		µg/L
NO_3^-	**SO_4^{2-}**	**NH_4^+**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**Ionic Balance**	**Cr**
0.018	0.070	0.006	0.157	0.141	0.030	0.003	-7.42%	0.193
0.017	0.058	0.007	0.125	0.173	0.029	0.001	-4.60%	0.216
0.019	0.120	0.007	0.183	0.313	0.005	<LOD	-8.32%	0.704
0.019	0.124	<LOD	0.209	0.386	0.004	<LOD	-4.92%	0.740
0.016	0.092	<LOD	0.201	0.048	0.002	<LOD	-8.19%	0.170
0.014	0.082	0.016	0.122	0.175	0.002	<LOD	-3.74%	0.468
0.017	0.036	0.000	0.173	0.389	0.012	<LOD	8.61%	0.623
0.014	0.030	0.007	0.100	0.296	0.001	<LOD	7.24%	0.483
0.015	0.058	0.005	0.116	0.148	0.029	0.002	-9.39%	0.197
0.012	0.039	<LOD	0.134	0.262	0.002	<LOD	-7.26%	0.918
0.017	0.064	0.003	0.129	0.268	0.006	<LOD	-5.28%	0.165
0.014	0.050	0.002	0.113	0.086	<LOD	<LOD	-7.19%	0.186
0.006	0.145	0.062	0.415	0.134	0.031	0.006	1.59%	0.134
0.008	0.218	<LOD	0.424	0.075	0.034	0.014	-8.10%	0.013
0.017	0.097	<LOD	0.113	0.382	0.003	<LOD	-4.82%	0.510
0.023	0.066	0.001	0.166	0.329	0.004	<LOD	-8.52%	1.228
0.012	0.037	0.002	0.101	0.246	0.005	<LOD	-8.80%	0.933
0.013	0.026	0.026	0.101	0.240	0.004	<LOD	-7.46%	0.980
0.018	0.065	0.003	0.178	0.368	0.007	0.000	-4.09%	0.864
0.019	0.118	0.002	0.165	0.331	0.005	0.000	-4.49%	1.115
0.024	0.109	0.001	0.202	0.146	0.001	<LOD	-3.99%	0.661
0.022	0.101	0.009	0.157	0.240	0.004	0.003	-8.03%	0.801
0.014	0.029	0.013	0.100	0.230	0.024	0.003	3.52%	0.488
0.007	0.015	0.002	0.031	0.041	0.001	<LOD	-3.14%	0.354
0.021	0.064	0.014	0.129	0.169	0.031	0.003	-8.49%	0.302
0.021	0.060	0.003	0.097	0.200	0.008	<LOD	-7.30%	0.226
0.026	0.105	0.000	0.159	0.139	0.001	<LOD	-7.65%	0.952
0.011	0.111	0.012	0.377	0.122	0.032	0.005	7.48%	0.656
0.023	0.066	0.006	0.135	0.262	0.008	<LOD	-8.73%	1.216
0.014	0.039	0.002	0.096	0.221	0.006	0.001	-8.95%	1.134
0.016	0.034	0.014	0.091	0.218	0.009	<LOD	-9.03%	0.886
0.022	0.045	0.028	0.165	0.311	0.017	0.003	-6.17%	0.771
0.015	0.070	0.007	0.165	0.134	0.033	0.005	-4.37%	0.824
0.013	0.059	0.006	0.127	0.171	0.029	0.002	-5.13%	0.684
0.013	0.060	0.005	0.128	0.169	0.030	0.002	-2.98%	0.648
0.007	0.207	0.006	0.490	0.158	0.035	0.008	-0.85%	0.390
0.010	0.286	0.006	0.481	0.068	0.037	0.016	-8.04%	0.065
0.026	0.212	0.002	0.203	0.688	0.007	<LOD	-9.64%	1.288
0.031	0.144	<LOD	0.158	0.338	0.024	<LOD	-9.68%	2.465
0.019	0.067	<LOD	0.130	0.365	0.005	<LOD	-1.58%	1.360
0.017	0.060	<LOD	0.104	0.292	0.003	<LOD	-3.99%	1.303
0.016	0.052	0.001	0.131	0.266	0.026	0.014	-8.77%	2.861
0.027	0.077	<LOD	0.209	0.386	0.007	<LOD	-2.42%	2.823
0.020	0.061	<LOD	0.121	0.275	0.008	<LOD	-8.08%	2.514
0.018	0.063	0.003	0.134	0.305	0.008	0.001	-7.85%	2.234
0.027	0.109	0.000	0.217	0.378	0.019	0.003	-7.58%	2.415

0.016	0.125	<LOD	0.229	0.317	0.002	<LOD	-0.71%	1.186
0.018	0.136	<LOD	0.198	0.236	0.003	<LOD	-6.39%	0.972
0.014	0.092	0.001	0.159	0.140	0.001	<LOD	-7.58%	0.510
0.017	0.120	0.001	0.165	0.262	0.004	0.000	-7.68%	1.134
0.017	0.087	<LOD	0.170	0.129	0.002	<LOD	-1.29%	0.427
0.013	0.067	<LOD	0.163	0.135	0.030	0.004	-0.84%	0.392
0.013	0.058	<LOD	0.126	0.172	0.029	0.001	2.23%	0.397
0.014	0.057	0.006	0.124	0.163	0.029	0.002	0.80%	0.588
0.003	0.169	<LOD	0.408	0.140	0.032	0.007	-2.32%	0.587
0.007	0.252	<LOD	0.430	0.069	0.036	0.014	-9.30%	0.170
0.023	0.182	<LOD	0.156	0.537	0.005	<LOD	-7.32%	1.237
0.024	0.109	<LOD	0.162	0.334	0.015	<LOD	-4.92%	0.781
0.012	0.040	<LOD	0.176	0.386	0.005	<LOD	6.29%	0.940
0.008	0.034	<LOD	0.072	0.268	0.003	<LOD	2.51%	1.236
0.017	0.047	0.001	0.130	0.267	0.007	<LOD	-7.22%	2.184
0.023	0.065	<LOD	0.174	0.322	0.006	<LOD	-5.14%	1.441
0.012	0.035	<LOD	0.106	0.251	0.007	0.003	-5.95%	1.255
0.016	0.049	<LOD	0.124	0.275	0.007	0.002	-0.35%	1.237
0.023	0.094	<LOD	0.169	0.327	0.013	0.002	-8.76%	1.059
0.016	0.085	<LOD	0.134	0.213	0.001	0.002	-7.89%	0.673
0.023	0.132	0.098	0.215	0.282	0.004	<LOD	6.51%	0.760
0.017	0.103	0.003	0.238	0.100	0.002	<LOD	-5.00%	0.390
0.017	0.119	<LOD	0.163	0.234	0.003	0.000	-8.17%	0.799
0.018	0.114	0.002	0.180	0.257	0.008	0.000	-5.20%	0.760
0.015	0.076	<LOD	0.140	0.109	<LOD	<LOD	-4.99%	0.347
0.029	0.039	<LOD	0.150	0.117	0.013	0.010	-9.00%	0.319
0.021	0.029	0.030	0.127	0.169	0.007	0.006	2.71%	0.919
0.021	0.029	0.030	0.130	0.169	0.007	0.006	2.12%	0.860
0.008	0.053	0.024	0.249	0.151	0.012	0.012	-0.32%	0.376
0.012	0.087	0.027	0.436	0.065	0.020	0.021	4.69%	0.152
0.018	0.025	0.037	0.085	0.281	0.018	<LOD	5.10%	0.487
0.015	0.015	0.017	0.065	0.139	<LOD	<LOD	-4.02%	0.360
0.013	0.012	0.020	0.055	0.164	<LOD	<LOD	0.74%	0.835
0.013	0.011	0.017	0.017	0.054	<LOD	<LOD	-8.09%	0.925
0.025	0.043	0.026	0.165	0.319	0.010	<LOD	1.16%	1.283
0.018	0.017	0.015	0.117	0.238	<LOD	<LOD	-0.12%	1.801
0.022	0.028	0.021	0.166	0.329	0.005	0.005	2.36%	1.899
0.017	0.019	0.029	0.111	0.269	0.007	<LOD	0.57%	1.741
0.017	0.018	0.020	0.110	0.255	0.005	<LOD	0.35%	1.627
0.023	0.034	0.034	0.198	0.337	0.011	0.006	3.36%	1.367
0.023	0.045	0.045	0.171	0.247	<LOD	<LOD	2.59%	0.782
0.023	0.053	0.020	0.194	0.332	0.006	<LOD	3.32%	1.301
0.030	0.041	0.008	0.157	0.157	<LOD	<LOD	-4.68%	0.568
0.027	0.053	0.018	0.196	0.339	0.006	<LOD	0.40%	1.387
0.033	0.050	0.036	0.186	0.378	0.006	0.007	5.26%	1.501
0.026	0.034	0.016	0.122	0.111	<LOD	<LOD	-3.73%	0.660
0.009	0.099	0.220	0.431	0.071	0.017	0.018	8.83%	0.013
0.037	0.080	0.108	0.189	0.608	0.000	0.001	5.19%	1.264
0.043	0.207	0.090	0.271	0.557	0.082	0.003	2.61%	0.903
0.027	0.045	0.202	0.153	0.426	0.005	<LOD	9.19%	1.320
0.031	0.101	0.115	0.256	0.439	0.008	0.002	6.34%	1.979
0.026	0.019	0.115	0.170	0.319	0.002	<LOD	8.61%	2.572
0.013	0.009	0.146	0.108	0.249	0.001	<LOD	9.63%	2.213

0.015	0.008	0.095	0.107	0.257	0.000	<LOD	8.40%	2.278
0.027	0.036	0.108	0.199	0.365	0.010	0.003	4.02%	2.187
0.023	0.076	0.161	0.248	0.325	0.002	<LOD	8.28%	1.891
0.032	0.064	0.106	0.195	0.167	<LOD	<LOD	7.50%	0.837
0.022	0.024	0.130	0.123	0.173	0.006	0.001	4.55%	0.920
0.009	0.096	0.104	0.476	0.072	0.018	0.018	6.72%	0.048
0.032	0.083	0.091	0.187	0.611	<LOD	0.001	3.63%	0.944
0.036	0.160	0.144	0.265	0.545	0.067	0.002	6.62%	0.702
0.027	0.048	0.172	0.152	0.406	0.017	0.005	9.06%	1.311
0.021	0.034	0.131	0.128	0.336	0.004	0.000	7.31%	1.216
0.030	0.079	0.239	0.233	0.431	0.008	0.003	9.22%	2.432
0.018	0.016	0.140	0.122	0.261	0.018	0.006	8.07%	1.947
0.032	0.017	0.166	0.164	0.314	0.002	<LOD	9.35%	2.357
0.022	0.006	0.098	0.107	0.256	0.001	<LOD	8.08%	1.911
0.022	0.003	0.100	0.106	0.253	0.002	<LOD	7.93%	1.994
0.031	0.033	0.074	0.190	0.357	0.009	0.002	4.95%	1.753
0.034	0.051	0.196	0.214	0.332	0.005	0.001	9.64%	1.458
0.026	0.063	0.146	0.229	0.307	0.002	0.000	9.55%	1.564
0.027	0.056	0.134	0.249	0.211	0.015	<LOD	5.06%	0.863
0.025	0.062	0.142	0.221	0.291	0.002	<LOD	7.73%	1.837
0.035	0.047	0.140	0.171	0.147	<LOD	<LOD	8.80%	0.544
0.014	0.086	0.046	0.388	0.072	0.030	0.022	-0.40%	0.871
0.039	0.058	0.040	0.166	0.525	<LOD	0.008	-7.36%	1.240
0.036	0.058	0.018	0.145	0.286	0.037	<LOD	-6.05%	0.478
0.034	0.057	0.016	0.182	0.337	0.022	0.008	-4.78%	1.381
0.020	0.025	0.015	0.120	0.243	0.020	0.008	-7.07%	2.129
0.030	0.032	0.017	0.154	0.286	<LOD	0.006	-7.30%	2.202
0.026	0.025	0.055	0.104	0.243	<LOD	<LOD	-5.33%	1.439
0.020	0.024	0.037	0.103	0.236	<LOD	0.008	-6.60%	2.152
0.025	0.049	0.050	0.172	0.283	<LOD	0.008	-4.16%	1.272
0.031	0.053	0.036	0.175	0.251	<LOD	0.008	-3.37%	<LOD
0.025	0.053	0.015	0.215	0.322	<LOD	<LOD	6.49%	0.655
0.030	0.026	0.044	0.080	0.076	<LOD	<LOD	-5.69%	<LOD
0.009	0.015	0.015	0.254	0.177	<LOD	<LOD	-4.87%	<LOD
0.018	0.092	0.036	0.336	0.044	0.029	0.023	8.83%	0.111
0.026	0.030	0.029	0.066	0.155	0.023	<LOD	-8.02%	0.217
0.014	0.035	0.039	0.116	0.247	0.020	0.014	0.27%	0.932
0.005	0.012	0.023	0.081	0.183	0.021	<LOD	-7.91%	2.050
0.017	0.051	0.043	0.157	0.313	0.021	0.013	-0.59%	1.813
0.019	0.053	0.037	0.149	0.304	0.019	<LOD	-4.48%	2.096
0.031	0.056	0.043	0.153	0.308	0.021	0.013	-1.24%	2.053
0.017	0.027	0.039	0.087	0.072	0.019	<LOD	-1.73%	0.295
0.027	0.047	<LOD	0.125	0.174	<LOD	<LOD	6.90%	<LOD
0.039	0.129	<LOD	0.282	0.525	0.021	<LOD	8.84%	0.182
0.038	0.113	<LOD	0.254	0.463	<LOD	<LOD	9.61%	0.424
0.025	0.039	<LOD	0.160	0.305	<LOD	0.003	6.30%	1.746
0.028	0.030	<LOD	0.105	0.282	<LOD	<LOD	-1.46%	1.115
0.026	0.034	<LOD	0.084	0.251	<LOD	<LOD	-9.20%	1.193
0.025	0.085	<LOD	0.316	0.356	<LOD	<LOD	4.14%	0.540
0.025	0.091	<LOD	0.240	0.255	<LOD	<LOD	-2.77%	0.394
0.025	0.069	<LOD	0.183	0.065	<LOD	<LOD	1.89%	0.049
0.001	0.0005	0.0028	0.0013	0.0021	0.0022	0.0013	-	0.0031

Trace elements (micrograms per liter)							
µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Mn	**Co**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**	**Fe**
0.039	0.025	2.268	<LOD	1.338	0.012	0.067	<LOD
0.212	0.023	3.010	<LOD	0.837	0.012	0.069	<LOD
0.021	<LOD	2.190	0.018	1.294	<LOD	0.051	2.084
0.037	<LOD	1.418	0.016	<LOD	<LOD	0.051	2.406
1.893	<LOD	1.104	0.027	1.639	<LOD	0.053	1.698
0.176	0.038	4.595	<LOD	6.750	0.012	0.077	3.021
0.316	0.054	3.838	0.199	3.713	0.012	0.094	24.218
0.423	0.048	3.373	0.138	5.832	0.013	0.088	21.125
0.240	0.019	2.798	<LOD	0.420	0.012	0.067	<LOD
0.047	0.030	7.007	<LOD	0.650	0.012	0.069	0.048
0.083	0.027	3.103	<LOD	0.150	0.012	0.069	2.373
0.260	0.041	4.388	<LOD	0.566	0.011	0.070	<LOD
0.027	0.020	1.177	<LOD	1.293	0.012	0.068	<LOD
0.035	0.022	0.120	<LOD	1.218	0.012	0.067	<LOD
0.151	0.120	2.116	<LOD	3.682	0.103	0.152	7.016
0.055	0.028	4.302	<LOD	<LOD	0.011	0.068	1.810
0.046	0.029	5.198	0.042	2.732	0.012	0.070	1.696
0.071	0.033	5.763	0.074	1.403	0.012	0.073	4.695
0.064	0.026	2.824	0.006	1.715	0.011	0.068	4.293
2.189	0.031	3.048	0.293	7.542	<LOD	0.106	8.715
0.644	0.084	5.486	0.164	10.135	<LOD	0.082	15.930
0.274	0.035	4.358	0.528	10.448	<LOD	0.193	7.930
0.609	0.043	3.353	0.287	3.221	<LOD	0.118	19.381
0.541	0.011	2.277	0.642	8.141	<LOD	0.190	8.919
0.272	0.007	3.438	0.177	12.774	<LOD	0.112	8.598
0.203	0.011	3.371	0.193	4.431	<LOD	0.093	7.479
1.492	0.264	8.467	0.474	9.065	<LOD	0.177	41.174
0.158	<LOD	2.429	1.846	10.320	<LOD	0.211	3.490
1.060	<LOD	3.885	0.716	8.859	<LOD	0.120	3.769
0.184	0.005	4.833	0.477	4.393	<LOD	0.105	9.819
0.181	0.035	5.219	0.226	37.140	0.012	1.106	4.194
1.247	<LOD	2.348	0.141	5.554	<LOD	0.104	9.148
0.241	0.114	6.878	0.483	39.604	0.054	0.146	<LOD
0.544	0.084	8.582	<LOD	7.481	0.051	0.043	2.177
0.760	0.083	7.566	0.004	2.173	0.051	0.048	<LOD
0.253	0.087	3.112	<LOD	5.109	0.051	0.044	<LOD
0.094	0.077	0.064	0.132	12.051	0.051	0.036	8.629
0.173	0.087	6.604	<LOD	23.071	0.051	0.059	<LOD
6.242	0.670	15.836	0.775	37.206	<LOD	0.645	5.598
0.635	0.160	9.284	0.165	0.247	0.050	0.080	<LOD
0.671	0.132	7.058	0.161	<LOD	0.052	0.051	<LOD
1.568	0.212	20.438	0.102	23.307	0.051	0.111	<LOD
0.053	0.044	7.658	<LOD	1.167	0.018	0.003	19.817
0.169	0.062	10.811	<LOD	5.629	0.018	0.025	<LOD
0.374	0.069	13.874	0.121	1.606	0.020	0.056	<LOD
2.001	0.247	7.641	0.150	<LOD	0.018	0.036	<LOD

0.120	0.065	8.435	<LOD	<LOD	0.018	0.004	8.415
0.093	0.053	6.439	<LOD	4.881	0.018	0.010	28.562
0.231	0.097	11.660	<LOD	<LOD	0.019	0.025	<LOD
0.109	0.055	4.893	<LOD	5.334	0.018	0.015	12.440
0.152	0.060	7.197	<LOD	<LOD	0.018	0.004	13.320
0.153	0.126	3.115	1.147	14.511	0.104	0.199	<LOD
0.409	0.126	3.675	0.074	9.579	0.104	0.162	1.999
0.585	0.049	6.732	0.028	9.914	0.023	0.026	<LOD
0.076	0.038	3.530	<LOD	12.770	0.021	0.019	25.534
0.103	0.037	0.327	<LOD	19.216	0.020	0.063	<LOD
0.189	0.060	5.097	<LOD	12.843	0.020	0.061	<LOD
0.249	0.069	7.538	0.110	10.183	0.019	0.051	<LOD
0.725	0.180	4.435	0.222	2.389	0.104	0.176	29.356
1.236	0.101	7.283	0.284	11.682	0.023	0.051	<LOD
0.107	0.052	16.167	0.268	20.189	0.019	0.039	<LOD
0.146	0.122	4.551	<LOD	1.862	0.103	0.152	0.167
0.171	0.129	6.082	0.120	1.261	0.104	0.169	7.172
0.216	0.132	7.201	0.097	1.941	0.104	0.158	9.557
0.156	0.120	2.439	<LOD	<LOD	0.103	0.145	1.770
0.219	0.136	5.177	<LOD	2.340	0.103	0.149	5.603
0.440	0.162	3.661	<LOD	3.632	0.103	0.158	14.464
3.953	0.137	5.571	<LOD	0.224	0.109	0.147	1.252
0.306	0.145	2.838	<LOD	1.802	0.105	0.152	9.773
0.192	0.128	2.773	<LOD	2.584	0.104	0.155	2.094
0.381	0.149	5.995	<LOD	0.368	0.103	0.160	2.977
0.189	0.017	4.737	0.911	14.629	<LOD	0.233	4.232
0.822	0.139	7.871	0.545	19.876	0.033	0.100	34.833
0.618	0.072	8.451	1.015	15.324	<LOD	0.083	34.883
0.173	<LOD	2.127	0.518	26.806	<LOD	0.137	3.960
0.061	<LOD	0.254	0.398	15.154	<LOD	0.039	2.184
0.129	0.004	3.954	0.156	8.250	<LOD	0.042	8.452
0.415	0.035	5.987	0.340	11.561	<LOD	0.027	11.089
1.401	0.097	7.203	1.982	13.663	<LOD	0.180	34.601
1.228	0.082	6.619	1.435	31.463	<LOD	0.345	29.374
2.185	0.200	6.890	0.827	22.627	<LOD	0.098	33.850
0.390	0.064	13.937	0.848	32.804	0.035	0.308	12.274
0.055	<LOD	6.760	0.060	11.154	<LOD	0.001	5.209
0.102	0.001	9.071	0.319	17.541	<LOD	0.104	7.566
0.322	0.009	9.609	0.291	8.454	<LOD	0.041	13.903
0.120	<LOD	4.235	0.098	8.115	<LOD	<LOD	6.556
0.206	0.018	6.943	0.027	9.761	<LOD	0.096	5.726
0.305	0.036	6.572	0.104	9.466	<LOD	<LOD	9.649
0.305	0.035	8.224	0.040	7.952	<LOD	0.000	5.620
0.421	0.067	6.888	0.061	5.501	<LOD	<LOD	11.987
0.128	0.007	4.595	0.087	10.162	<LOD	0.004	6.471
1.568	0.206	9.506	0.161	25.647	<LOD	0.085	22.622
<LOD	<LOD	0.781	0.034	2.467	<LOD	<LOD	0.964
0.098	<LOD	5.214	<LOD	4.895	<LOD	0.036	7.230
0.383	0.010	10.613	0.205	8.809	<LOD	0.021	7.727
1.806	0.079	9.712	0.371	3.867	<LOD	<LOD	32.839
1.163	0.096	9.901	0.341	2.594	<LOD	0.234	20.607
0.004	<LOD	8.366	0.059	0.861	<LOD	0.168	4.040
0.244	0.007	10.679	0.402	2.245	<LOD	0.019	13.000

0.080	<LOD	11.371	0.213	1.470	<LOD	0.020	9.660
0.078	<LOD	4.933	0.060	1.214	<LOD	0.591	5.188
1.220	0.212	12.691	0.194	3.247	<LOD	0.844	21.636
0.231	0.010	6.564	0.012	1.776	<LOD	0.381	4.380
0.478	0.064	6.988	0.337	3.197	0.005	0.058	22.100
0.023	0.021	0.114	0.089	0.975	0.007	0.016	3.281
0.195	0.042	4.299	0.117	2.110	0.006	0.036	7.816
0.284	0.045	8.131	0.169	0.919	0.006	0.020	9.621
1.355	0.115	8.806	0.684	4.825	0.008	0.069	31.958
2.192	0.108	7.473	0.401	4.953	0.009	0.060	29.519
0.917	0.130	5.916	0.357	4.072	0.006	0.055	28.887
0.156	0.039	12.787	0.236	5.773	0.007	0.105	7.042
0.137	0.041	6.647	0.158	1.101	0.002	0.015	7.395
0.318	0.043	9.106	0.258	0.880	0.002	0.015	15.262
0.236	0.040	9.708	0.294	11.929	0.004	0.034	12.604
0.097	0.020	3.560	0.112	0.558	0.002	0.010	7.576
0.424	0.075	8.454	0.124	1.181	0.003	0.020	14.180
0.407	0.110	6.833	0.116	0.622	0.002	0.026	17.579
0.138	0.050	12.680	0.068	2.188	0.003	0.013	4.503
0.782	0.161	7.391	0.201	3.374	0.003	0.037	30.743
0.359	0.039	6.856	0.051	0.862	0.003	0.022	5.966
0.416	<LOD	6.984	1.398	6.791	<LOD	<LOD	5.844
<LOD	<LOD	9.349	<LOD	3.688	<LOD	<LOD	10.977
<LOD	<LOD	10.064	<LOD	4.955	<LOD	<LOD	19.770
<LOD	<LOD	5.223	0.431	4.258	<LOD	<LOD	11.662
5.742	<LOD	16.669	0.359	13.196	<LOD	<LOD	32.840
<LOD	<LOD	8.717	<LOD	3.345	<LOD	<LOD	5.019
<LOD	<LOD	8.416	0.681	2.620	<LOD	<LOD	4.551
<LOD	<LOD	14.199	0.709	5.724	<LOD	<LOD	7.799
<LOD	<LOD	8.930	<LOD	5.060	<LOD	<LOD	6.207
<LOD	<LOD	0.028	<LOD	6.908	<LOD	<LOD	4.882
<LOD	<LOD	4.476	<LOD	5.423	<LOD	<LOD	4.005
1.064	<LOD	10.846	<LOD	4.539	<LOD	<LOD	3.913
<LOD	<LOD	0.073	0.189	6.637	0.054	0.067	0.489
<LOD	<LOD	4.935	0.166	2.851	0.052	0.092	3.019
0.908	<LOD	7.979	0.340	5.874	0.052	0.088	20.119
0.088	<LOD	4.980	0.408	5.244	0.053	0.097	11.572
<LOD	<LOD	13.024	0.312	7.041	0.052	0.064	6.321
<LOD	<LOD	8.215	0.269	16.971	0.052	0.079	9.447
0.134	<LOD	6.321	0.407	4.950	0.052	0.106	13.900
0.567	<LOD	6.972	0.303	8.103	0.052	0.089	12.051
0.562	<LOD	7.732	0.456	2.621	0.056	0.130	5.923
<LOD	<LOD	5.423	<LOD	1.158	<LOD	<LOD	0.137
<LOD	<LOD	5.334	<LOD	2.795	<LOD	<LOD	<LOD
<LOD	<LOD	16.402	1.003	2.033	<LOD	<LOD	0.121
<LOD	<LOD	5.686	0.235	1.687	<LOD	<LOD	0.341
<LOD	<LOD	7.957	<LOD	1.430	<LOD	<LOD	0.197
<LOD	<LOD	15.807	<LOD	2.572	<LOD	<LOD	4.611
<LOD	<LOD	8.377	<LOD	1.622	<LOD	<LOD	1.192
<LOD	<LOD	8.708	<LOD	0.886	<LOD	<LOD	<LOD
<LOD	<LOD	5.387	<LOD	0.595	<LOD	<LOD	0.040
0.0021	0.0002	0.0047	0.0010	0.0096	0.0004	0.0002	0.0188

µg/L	µg/L
Ag	**As**
0.013	0.225
0.006	0.286
<LOD	0.287
<LOD	0.270
<LOD	0.058
0.010	0.152
0.035	0.020
0.014	0.025
0.004	0.271
0.004	0.046
0.002	0.028
0.002	0.042
0.009	1.222
0.005	0.010
0.113	10.286
0.003	0.117
0.003	0.046
0.008	0.049
0.006	0.196
0.012	0.241
0.007	0.120
0.069	0.209
0.019	0.016
0.012	0.016
0.103	0.315
0.008	0.037
0.004	0.145
0.003	1.612
0.010	0.106
<LOD	0.052
0.037	0.048
<LOD	0.170
0.041	0.398
0.039	0.539
0.023	0.512
0.043	2.039
0.028	0.013
0.093	22.418
0.060	0.030
0.039	0.059
0.027	0.056
2.786	0.094
<LOD	0.176
<LOD	0.047
<LOD	0.036
<LOD	0.346

<LOD	0.394
0.006	0.730
<LOD	0.071
<LOD	0.382
<LOD	0.121
0.118	0.241
0.114	0.291
2.239	0.426
0.002	2.520
0.095	<LOD
0.599	21.523
0.284	0.004
0.176	0.035
0.105	<LOD
0.081	0.023
0.100	0.144
0.144	0.062
0.117	0.054
0.257	0.262
0.091	0.196
0.095	0.340
0.099	0.045
0.103	0.245
0.156	0.228
0.097	0.057
<LOD	0.512
0.053	0.775
<LOD	0.716
0.007	2.472
<LOD	<LOD
<LOD	11.218
<LOD	<LOD
<LOD	<LOD
<LOD	0.002
0.762	0.215
0.044	0.105
<LOD	0.131
<LOD	0.037
<LOD	0.031
<LOD	0.323
<LOD	0.204
<LOD	0.420
<LOD	0.100
<LOD	0.300
0.061	0.420
<LOD	0.100
0.052	<LOD
0.018	28.596
0.024	0.021
<LOD	<LOD
0.046	0.234
<LOD	0.168
0.018	0.019

<LOD	0.020
0.021	0.591
<LOD	0.844
0.030	0.381
0.022	0.563
0.189	0.015
0.015	20.997
0.518	0.076
0.024	0.042
0.013	0.045
0.035	0.257
0.009	0.154
0.010	0.216
0.838	0.084
0.035	0.086
0.015	0.460
0.017	0.512
0.014	0.662
0.004	0.159
0.051	0.444
0.018	0.239
<LOD	0.171
<LOD	28.250
<LOD	<LOD
<LOD	<LOD
<LOD	<LOD
<LOD	0.020
<LOD	<LOD
<LOD	<LOD
<LOD	0.160
<LOD	<LOD
<LOD	<LOD
<LOD	<LOD
0.089	<LOD
0.097	8.522
0.108	<LOD
0.092	<LOD
0.095	<LOD
0.086	0.391
0.115	0.681
0.089	0.109
0.131	<LOD
<LOD	<LOD
<LOD	<LOD
<LOD	<LOD
<LOD	<LOD
<LOD	<LOD
<LOD	<LOD
<LOD	0.015
<LOD	<LOD
<LOD	<LOD
0.0003	0.0018

Table S2: Mean values ± standard deviation for 3 replicates of all single extraction:

Samples	Measure unit	Co	Cr	Cu
P04	**mg/kg**	44.1 ±0.8	454±3	40.6±1.6
V07	**mg/kg**	75.6±1.8	2160±10.3	13±0.3
V08	**mg/kg**	44.9±2.2	667±	14.1±0.63
V11	**mg/kg**	52±1.6	1080±25.5	79.2±2
P05	**mg/kg**	32.63±1.2	345.97±11	120.18±4.3
P06	**mg/kg**	107.95±4.5	1119.21±21	59.2±2
LOD	**mg/kg**	0.3	0.22	0.18

s for every site, and calculated recovery values

Mn	Ni	Fe	Zn	As	Ag
419.5±3	526±6.6	19800±15	43.75±2	154.65±6.7	<LOD
728±15.5	1310±10	40400±25.5	26.09±1.1	5.91±0.3	<LOD
389±10	941±16.7	19000±24	6.47±0.4	3.68±0.2	<LOD
494±19	1090±22.2	27200±25.5	11.72±0.4	10.73±0.5	<LOD
781.29±23.5	359.28±12.8	48730±21.4	143.58±4.3	123.74±2.3	<LOD
762.09±31.1	1726.62±11.4	45743±34	205.14±6.6	121.4±4.7	<LOD
0.12	0.03	0.08	0.41	0.95	0.75

Pb	Cd
1.02±0.1	<LOD
0.04±0.01	<LOD
0.4±0.01	<LOD
1.19±0.05	<LOD
24.17±0.9	<LOD
74.89±1	<LOD
0.03	0.39