INTERREG ITALY - SWITZERLAND PROJECT
RESERVAQUA

WP3 - Assesment of the available water resources in the transboundary area

CHEMICAL CHARACTERIZATION OF ROCK GLACIER OUTFLOWS

TECHNICAL REPORT

WP3 – ASSESSMENT OF THE AVAILABLE WATER RESOURCES IN THE TRANSBOUNDARY AREA

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Highlights

- The impact of the climate crisis on mountain water resources is increasing the attention on the hydro-chemical role of rock glaciers and permafrost related water bodies.

- The outflows of the rock glaciers considered in the RESERVAQUA project are characterised by low-moderate solute content, low concentrations of nutrients (e.g., organic C), quite high concentration of nitrate and by a very limited presence of trace metals, in contrast with what detected in other study sites in the Eastern Alps.

- The inter-comparison exercises and the sharing of sampling and analytical protocols improved the quality of the data obtained by the different laboratories.

- The variables that should be prioritised are pH, conductivity, major cations (Ca, Mg, Na, K), SO_4, $N-NO_3$ and TOC, Total N. Among trace metals, priority should be given to Al, Fe, Mn, Ni, Zn.

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Summary

The amount of water stored in the Alpine glaciers is the widest water reserve in Europe and represents an invaluable asset for millions of people. The INTERREG project RESERVAQUA aims to improve the present knowledge about the availability and use of water resources in the Alpine hydrographic basins, included the amount of water stored in permafrost and rock glaciers, and to develop proper tools for the cross-border management of the water resource itself. In this context, besides quantity, also water quality assessment plays a fundamental role. Cryosphere thawing may indeed affect water quality and freshwater ecosystems.

As part of the project, research activities aimed to evaluate water quality in selected Alpine basins have been developed, with a focus on runoff water (rock glaciers outflow). Field campaigns were performed between 2019 and 2022 at different sites in Italy and Switzerland and data gathered to perform some assessment of water chemistry and a comparison among the sites. Considering the relevance of data quality in performing such assessment, we performed an inter-comparison among the Italian laboratories to put in evidence the most critical issues and develop guidelines about the analyses of freshwater samples collected at pristine high-altitude environments.

Suggested protocols for water sampling and chemical analyses are provided as annexes to this report. These factsheets may serve as a basis for the development of further protocols for the sampling and analysis of permafrost-related water bodies, with a focus on the establishment of feasible long-term monitoring programs to tackle the evolution of these water resources under climate change.

Introduction

Most freshwaters in high-altitude environments, including glacial and periglacial lakes and running waters originating from glaciers and permafrost, are not included in the water bodies to be monitored under the Water Framework Directive (WFD 2000/60/CE, transposed in Italy with the DL 99/152) due to their limited spatial extent. More generally, they are not subject to any institutional monitoring programs under national or international legislation. Water quality and environmental data on these ecosystems, when available, are collected within national and international research projects or monitoring programs. Examples of the latter, are the LTER network (Long-Term Ecological Research; https://elter-ri.eu/) and the ICP WATERS (International Cooperative Program for assessment and monitoring of the effects of air pollution on rivers and lakes; https://www.icp-waters.no/). These programs aim at studying the long-term ecological development of high-altitude ecosystems under stressors, such atmospheric deposition of pollutants and climate change (Garmo *et al.* 2014; Rogora *et al.* 2018). These programs, being strongly based on the comparison among different sites, pay great attention to the analytical quality of the data, also through inter-comparison exercises among the laboratories and research groups contributing data to the programs (e.g., Escudero-Oñate 2018).

Recently, the issue of climate change and its effects on mountain regions have fostered the attention towards high-altitude ecosystems and their response to climate related drivers (i.e., increasing air temperature, changing precipitation regime, decrease of snow and ice covers, glacier retreat, etc.) (Huss and Hock 2018; Moser *et al.* 2019; Sadro *et al.* 2019). Permafrost-related water bodies, such as rock glacier outflow and receiving lakes and ponds, have obtained attention in recent times due to the increasing importance of these systems as water resources and to the possible impact on them by climate change (Colombo *et al.* 2018 and references therein). Several studies focused on the chemical features of these water bodies and on their seasonal and inter-annual changes in relation to meteorology and hydrology, considering major solutes, nitrogen, DOC, and trace metals (Williams *et al.* 2007; Thies *et al.* 2013; Ilyashuk *et al.* 2014; Colombo *et al.* 2019; Steingruber *et al.* 2021; Rogora *et al.* 2020).

A relevant contribution to the knowledge of permafrost-related water bodies, both from the chemical and the biological point of view, came from the PERMAQUA project (https://www.permaqua.eu/it/). PERMAQUA focused on the effects of permafrost on the hydrological balance in high altitude areas of the Eastern Alps (South Tyrol, Italy, and North Tyrol, Austria), but it also investigated several aspects of water quality and mountain ecology that could be affected by permafrost melt (Thies *et al.* 2013; Tolotti *et al.* 2020). The project also aimed to transfer the state-of-the-art knowledge about potential ecological impacts of permafrost melt and its consequence for man and the decision makers, managers, residents, and the general public (Tolotti *et al.* 2013).

A proper characterization of freshwater chemistry is fundamental, both to assess water quality for the different use, and for an environmental and ecological evaluation, considering the importance of bio-geochemical cycles in ecosystems. To this aim, laboratories involved in these evaluations should develop quality assurance/quality control (QA/QC) programs, based on both internal and external controls, to assure the reliability of the data and their comparability through time.

The recent attention towards waters originating from melting glaciers and permafrost, in the general context of the climate crisis and related water scarcity, requires an affordable evaluation

of chemical features, including trace metals. However, high-altitude waters, both as permanent water bodies as lakes and streams, and as runoff waters and temporary ponds, solute concentrations are typically low, sometimes close to the limit of detection (LOD) of the analytical methods used. The issue of data quality is particularly relevant when dealing with these waters, due to their peculiar characteristics. The same holds when seasonal and inter-annual variation of chemical parameters must be assessed properly and when different systems must be compared: research groups sharing data within projects or joint elaboration should also share sampling and analytical procedures and, if possible, develop common standardised protocols, and perform inter-comparison exercises.

Within RESERVAQUA, the Italian partners have started developing these practices, firstly through meetings of the laboratory staff (ARPA Piemonte, ARPA Valle d'Aosta, CNR IRSA), during which internal protocols for analyses and data quality assurance and control (QA/QC) have been discussed, with a focus on priority variables for the project (major ions, trace metals). As a second step, an inter-comparison exercise was designed and performed, based on the joint analysis of samples collected at different project sites.

Chemistry of rock glacier outflows

WHAT ARE "ROCK GLACIERS"?

Rock glaciers as well as ice-cored moraines are considered as morphological indicators for the occurrence of permafrost in high mountain environments. In accordance with the IPA Action Group "Rock glacier inventories and kinematics" (RGIK 2020), rock glaciers as landforms are defined here by their characteristic morphology related to long-term cohesive creep of ice-rich material. In detail, active rock glaciers display convex and elongated shape with over-steepened fronts and lateral talus as well as a typical micro-topography of furrows and ridges that reflect the internal process of deformation (Figure 1a). It is generally accepted that the morphological characteristics of rock glaciers are the product of high (excess) ice contents, as well as a complex flow behaviour controlled by negative (or near-zero) subsurface temperatures, water circulation and highly anisotropic material properties (Kellerer-Pirklbauer et al. 2022).

Rock glaciers occur in different types of lithology, which break down to particles of at least gravel size and if other conditions are favourable. However, coarse-grained sediments favour cooler near-surface temperatures and hence rock glacier existence. Three layers typically describe the stratigraphy of active rock glaciers (Figure 1b). The uppermost metres are often characterised by large boulders allowing a high porosity and voids filled with air, snow, or water. However, fine-grained rock glaciers are also found, bearing a large proportion of fine material and few coarse blocks, and show a similar but smoothed morphology and thinner overall thickness. This shallow layer is covering an ice-rich permafrost layer with 50-70% of ice and about 30-50% of debris. The lowermost layer is often characterised by large boulders that were deposited at the front and overridden by the advance of the landform (Barsch 1996; Arenson et al. 2002).
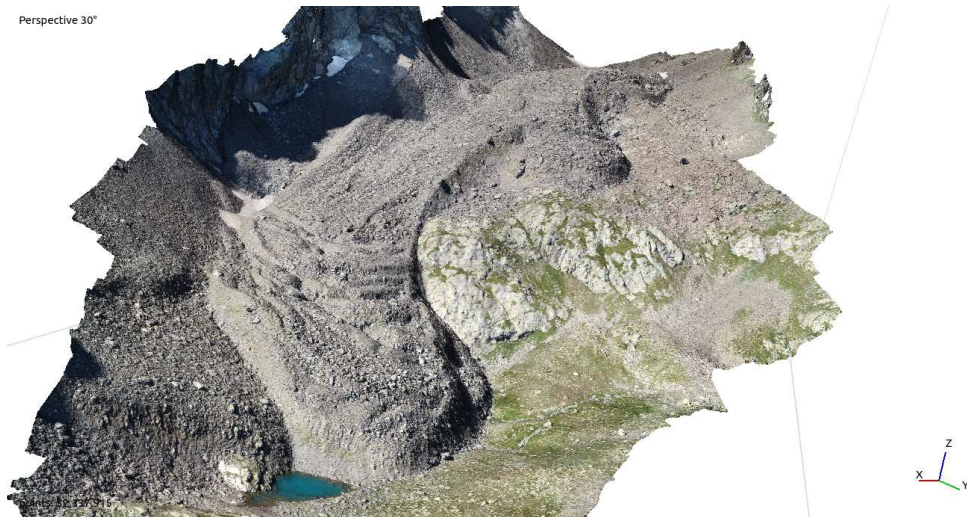
Fig. 1a - Example of an intact rock glacier (Schiantalà rock glacier, Maritime Alps, NW Italy, digital model from UAV survey by Arpa Valle d'Aosta)
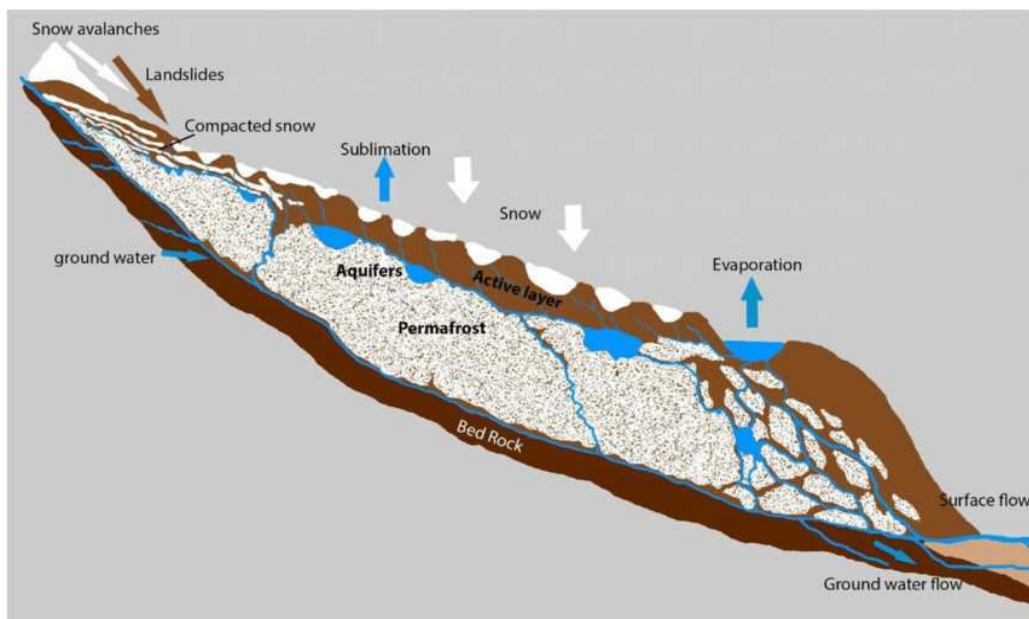

Fig. 1b – Schematic longitudinal cross-section of an active rock glacier with the indication of different components, including the active layer, permafrost core, and hydrological system, including inputs and outputs (from Shaffer et al. 2019)

SITE DESCRIPTION, SAMPLING AND ANALYSES

Table 1 shows the main characteristics of the sites considered in WP3 of the RESERVAQUA project, Figures 2 and 3 show the location of the sites and the sampling activities, respectively. Sites were sampled with different frequency, according to the research needs and to logistic constraints: for instance, sites in Piedmont are quite remote and not easily accessible, so that only one or two samples per year were collected. Sites in the Aosta Valley and in Canton Valais have been monitored from the chemical point of view also in previous years, while monitoring of the Piedmont sites started in 2020-2022. For the aim of the comparison, only one representative sample for each site has been selected.
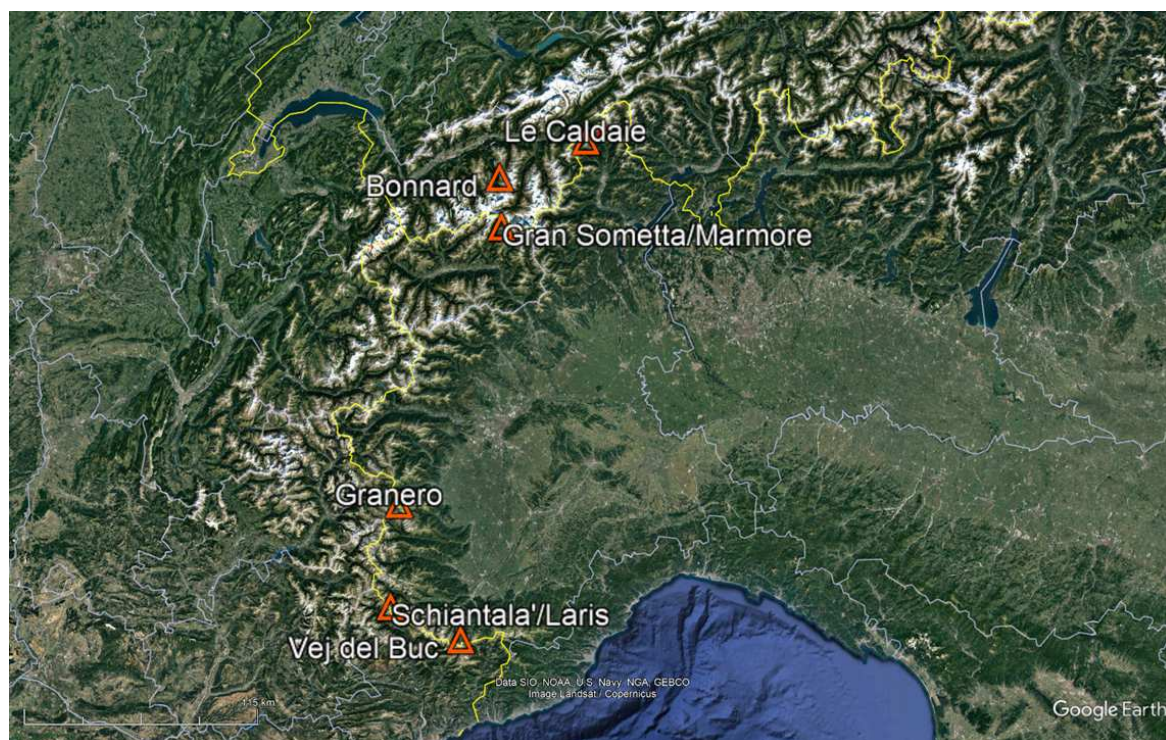
Fig. 2 – Location of the study sites

Tab. 1 - Main characteristics of the study sites

Site/catchment	Working group	Province/Federal State	Valley	Lat.	Long.	Elevation (m a.s.l.)
Le Caldaie	ARPA Piemonte/ CNR IRSA	Piedmont Region (VB), Italy	Ossola/ Cairasca	46°17'32"N	8°11'55"E	2645-2540
Vej del Bouc	ARPA Piemonte/ CNR IRSA	Piedmont Region (CN), Italy	Gesso	44°8'2"N	7°26'35"E	2500-2350
Schiantala'	ARPA Piemonte/ CNR IRSA	Piedmont Region (CN), Italy	Stura di Demonte	44°17'6"N	6°59'54"E	2640-2475
Granero	ARPA Piemonte/ CNR IRSA	Piedmont Region (TO), Italy	Pellice	44°43'31"N	7°3'1"E	2770-2560
Bonnard	CREALP/UNINE/ SFCEP	Valais, Switzerland	Val d'Anniviers	46°8'4"N	7°39'21"E	3100-2800
Gran Sometta/ Marmore	ARPA VDA	Aosta Valley (AO), Italy	Valtournanche	45°55'22"N	7°40'6.6"E	2633

Site/catchment	Status rock glacier	Geological unit	General lithology
Le Caldaie	Intact	Monte Leone Unit (Lepontine Units - Nappe)	Metamorphic (tabular, fine- to medium-grained biotite-K-feldspar-oligoclase gneiss, derived from Permian granitoids)
Vej del Bouc	Intact	Argentera "Massif" - Gesso-Stura-Vésubie Unit	Metamorphic (mainly: migmatite, ortho- and para-gneiss, micaschist, anatectic granite; secondary Bousset-Valmasque Complex Amphibolite: migmatitic amphibolite with relics of HP eclogites/granulites)
Schiantala'	Intact	Argentera "Massif" - Tinée Unit	Metamorphic (migmatitic paraderivate)
Granero	Intact	Piemonte-Ligurian oceanic domain (Monviso Unit)	Metamorphic (metabasites, prasinites, amphybolites, chloriteshists)
Bonnard	Intact	Tasté Nappe and Dent Blanche Nappe	Metamorphic (Orthogneiss, Metagabbro)
Gran Sometta/ Marmore	Intact	Combin Zone	Metamorphic (calcschists, dolomitic marbles, metabasites)

At all sites the lithology is characterised by metamorphic rocks; gneisses, granitoids and migmatites dominate at sites in Piedmont and Valais, while basic and more soluble rocks (calcschists, marbles) are present at the Aosta Valley site.

Fig. 3 – Examples of sampling and survey activities at the study sites: a) Glacier Bonnard; b) Gran Sometta; c) Le Caldaie; d) Granero

Piedmont sites

The sampling of the sites in the Piedmont Italian region (Figure 4) was performed from 2020 to 2022, with one of the sites (Le Caldaie) sampled each year and 2-3 times per year (in total, 6 samples were collected). This site is in the Cairasca Valley, a lateral valley of the main Ossola Valley, in the Province of Verbania. The site is also within the protected area "Aree Protette dell'Ossola", close to the locality "Alpe Veglia". There are three rock glaciers on the site, characterized on the surface by large blocks of gneiss, mostly tabular in shape. The rock glacier located at a higher altitude has a rather steep front at the base of which emerges a spring with a constant flow, where sampling have been carried out. The samplings considered the rock glacier outflow but also other points that could be affected by the chemistry of the outflow, in particular lakes Le Caldaie and Bianco. In the summer 2021, precipitation and snow samples were also collected and successively analysed by the University of Bolzano for the isotopic content.

The other Piedmont sites were sampled once (Granero in Province of Turin, in 2022) and twice (Vej del Bouc and Laris/Schiantalà in Province of Cuneo, in 2021 and 2022). Beside the rock glacier outflow, at Granero and Vej del Bouc also the lakes receiving the rock glacier outflow were sampled (Lake Lungo and Lake Vej del Bouc, respectively). The Granero rock glacier is characterised by basic to ultrabasic rocks and its front is quite far from the sampled spring. Vej del Bouc and Schiantalà rock glaciers consist mainly of migmatitic rocks belonging to the external Argentera massif (Maritime Alps) and are probably the southernmost intact and active rock glaciers of the Alps. Vej del Bouc rock glacier outflow is visible in the stream on the left side of the front, while the front of the Schiantalà rock glacier is bordered by a small lake Laris and the outflow from the debris body is not clearly visible.
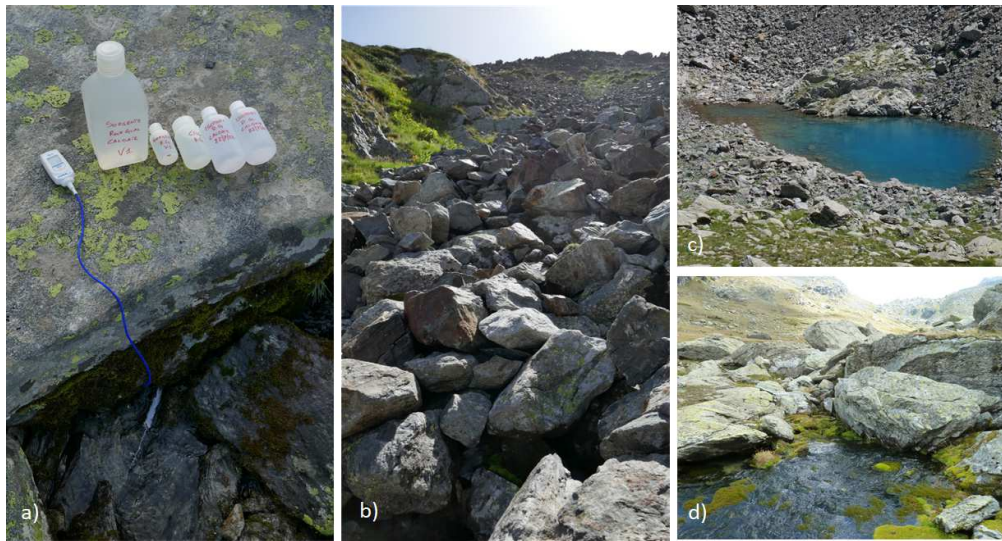
Fig. 4 - Sampling sites in Piedmont region: a) Le Caldaie; b) Vej del Bouc; c) Laris/Schiantalà; d) Granero

Gran Sometta site

The Gran Sometta rock glacier is located on the south-western side of the central Alps at the head of the Valtournenche Valley (Aosta Valley, Italy, Figure 5a). Two lobes, at an elevation ranging from 2630 to 2770 m a.s.l., compose the main body of the rock glacier. It is approximately 400 m long, between 150 and 300 m wide with a thickness of 20–30 m. The debris originates from the rock walls of the Gran Sometta peak, mainly composed of green schists with prasinites, with bands of dolomite and marbles (Bearzot *et al.* 2022). Two springs are located at the fronts of the rock glacier lobes, discharging into the mainstream (Figure 5b). Water samples were collected during three consecutive seasons, 2019-2020-2021 (Jun-Oct), along the mainstream at the sites Up and Down, and at the rock glacier springs, the "White spring" (RG bianco), and the "Black spring" (RG nero, Bearzot *et al.* 2023).
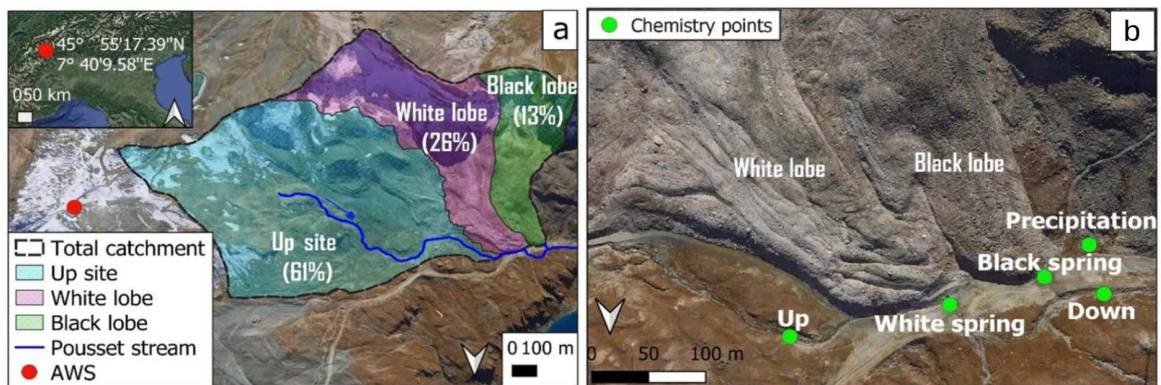

Fig. 5 - Gran Sometta rock glacier lobes and location (a) and water chemistry sampling points (b) (modified from Bearzot et al. 2023)

Bonnard rock glacier

The Bonnard rock glacier is located in the Swiss Alps, above the village of Zinal in Valais (Figure 6). It includes glacial and paraglacial features ranging from 2700 m a.s.l. to 3100 m a.s.l. at the foot of the Diablons summit (3609 m a.s.l.). The rock glacier is contained between two lateral moraines and sits on a large moraine bastion that hangs on rock cliffs above the valley. It is mainly composed of rock debris of granitic gneisses and crystalline schists coming from the cliffs of the Diablons (Dent Blanche geological formation). Water sampling has been performed for major ions and isotopic composition of water during the years 2019 and 2020. Samples were collected on the rock glacier with a peristaltic pump where water was flowing and at the outlet during field campaigns and with an automatic sampler (for isotopic composition of water). The samples presented in this report are the ones collected in summer at the outlet for major ion composition (in total 4 samples). During the years 2019-2021, precipitation and snow samples were also collected on the rock glacier and analysed for the isotopic composition of water. All the analyses have been conducted at the University of Neuchatel.
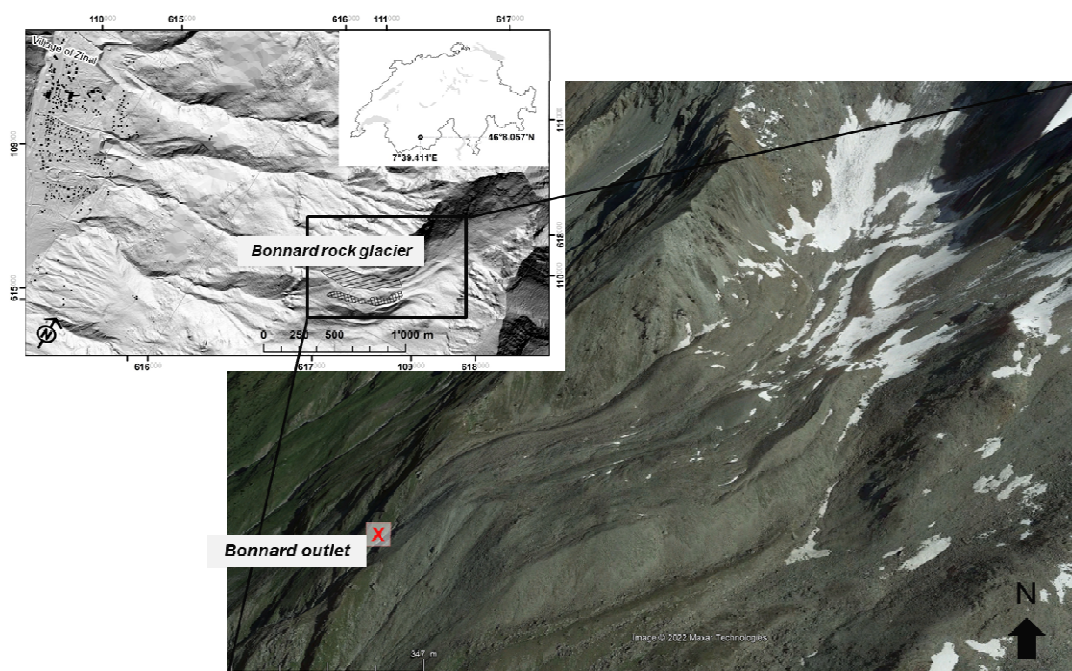
Fig. 6 – The Bonnard rock glacier, with the location of the outflow

RESULTS

A comparison of the chemical composition (major ions) of rock glacier outflowing water at the study sites is shown in Figure 7, both considering absolute concentrations and relative contribution to the total ionic content.
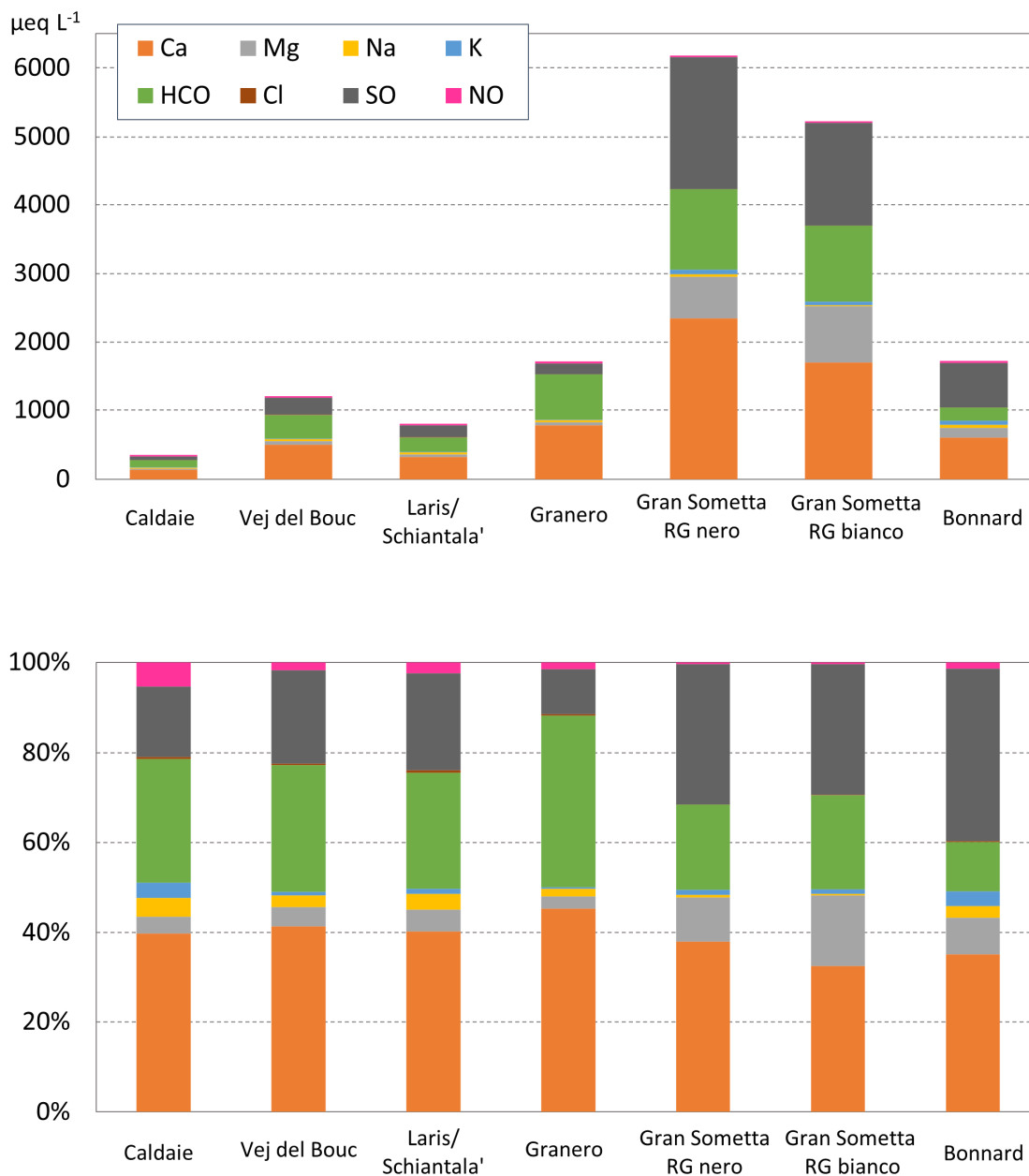
Fig. 7 – Concentrations (above) and relative contribution (below) of major ions in the RG outflows at the study sites

The four sites in Piedmont and the site in Valais showed comparable concentrations of the main solutes, with a total ionic content between 350 and 1700 µeq L[-1] and conductivity values between 20 and 90 µS cm^{-1} at 20 °C. These values can be considered typical of dilute low-mineralized water and are a direct consequence of the dominance of low-weatherable rocks in the catchment. The two sub-sites at Gran Sometta, namely the outflows of Rock Glacier Bianco (RGB) and Rock Glacier

Nero (RGN) are characterised by a much higher solute content (5200-6200 µeq L^{-1} and conductivity between 250 and 290 µS cm^{-1}), especially the former. When considering the ionic composition, calcium is the dominant cation at all the sites, representing between 35 and 45% of the total ionic content; among anions, bicarbonates are dominating at the Piedmont sites while sulphate is prevalent at the Aosta Valley and Valais sites. Magnesium is also quite important at the Gran Sometta rock glacier outflows, representing 10-15% of the total ionic content. Sodium and potassium contribute no more than 4%. The same holds for nitrate, which is however quite important at Le Caldaie (5%). Moreover, the ionic composition of the sites was compared using "tern plot" (Figure 8), where the sites are placed according to the relative importance of Ca+Mg, HCO$_3$ and SO$_4$. The sites demonstrated to be similar in terms of the Ca+Mg contribution (mostly close to 50%), while higher differences are found in the contribution of SO$_4$ (from 13 to 31%).

Total nitrogen, including the organic form, was between 0.30 and 0.40 mg N L^{-1}; nitrate was the dominant form of nitrogen, with organic N contributing between 2 and 20% according to the site. Nitrate concentrations were lower at Bonnard (about 100 µg N L^{-1}) with respect to sites in Piedmont and Aosta Valley, where concentrations ranged between 270 µg N L^{-1} (Le Caldaie) and 370 µg N L^{-1} (Granero). The latter concentrations are quite high with respect to those usually found in streams and lakes at high altitude, supporting the hypothesis that active rock glaciers could be a source of nitrate (Williams *et al.* 2007). Reactive and total phosphorus were analysed at sites in Piedmont and Aosta Valley and were always low (2-5 and 5-7 µg P L^{-1}, respectively). Total organic carbon (TOC) was mainly present in very low amounts (0.10-0.15 mg C L^{-1}), with exception of the sub-site Rock Glacier Bianco at Gran Sometta (1.1 mg C L^{-1}). Trace metals, analysed at the Italian sites, proved to be low, with several metals close or below the LOD.
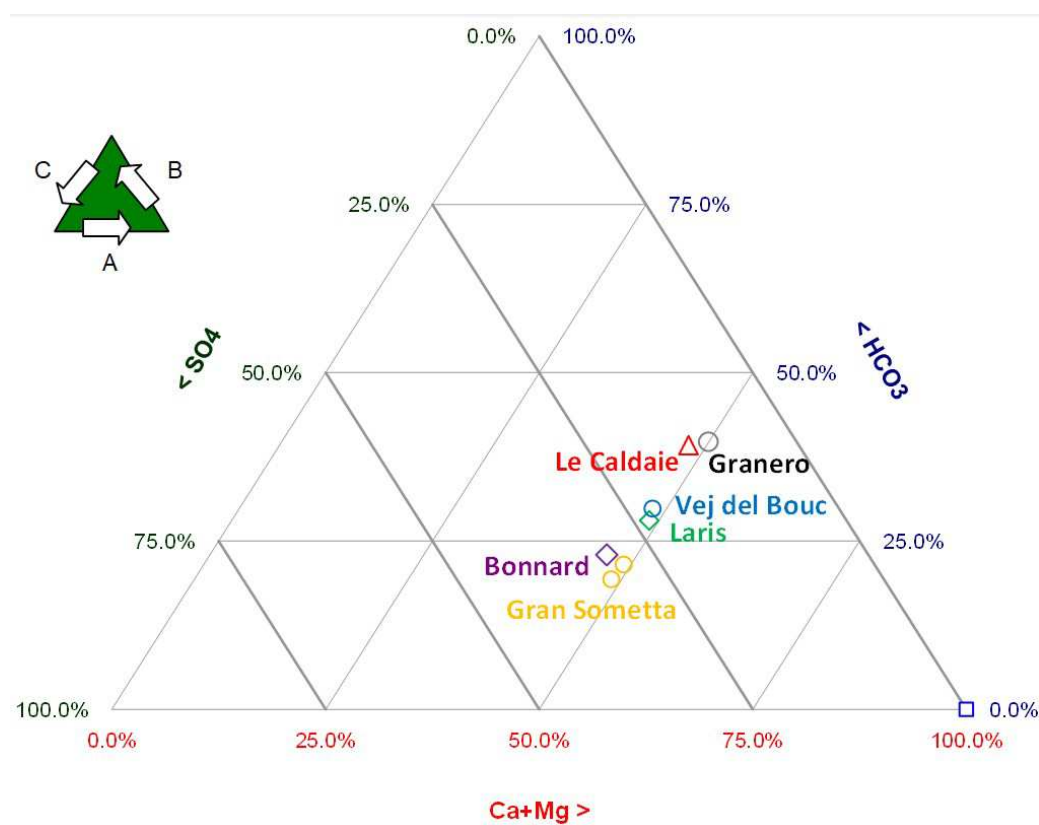

Fig. 8 – Tern plot showing the chemical composition of the rock glacier outflows at the study site

As an example of the seasonal and inter-annual variability of water chemistry at rock glacier outflow, the data collected at the Piedmont site Le Caldaie in 2020-2022 (6 samplings in total) and at the site Gran Sometta in Aosta Valley are shown in Figures 9 and 10, respectively.
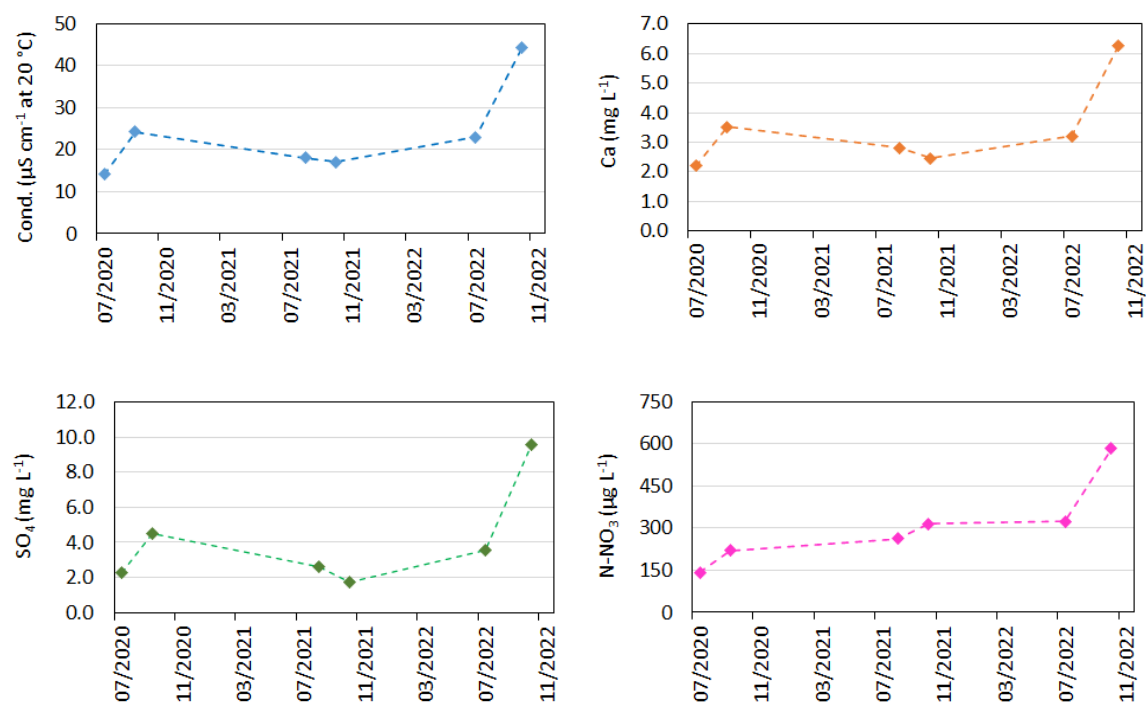
Fig. 9 – Temporal pattern of selected chemical variables in the rock glacier outflow Le Caldaie, Piedmont, in 2020-2022

In 2020, and more clearly in 2022, at Le Caldaie conductivity and the major ions increased from July to October, a pattern that has been described for other rock glacier outflows and attributed to the export of geochemically enriched ice melt (Williams *et al.* 2007; Colombo *et al.* 2018). This pattern did not emerge from the 2021 data, but it must be considered that in this year the first sampling was done in late August with respect to late July as in 2020 and 2022. In the latter year the increase of concentrations at the end of the summer season was particularly evident, also as regards nitrate which reached 580 µg N L^{-1} (Figure 9). The unusual dry condition of the summer 2022, with an almost total lack of precipitation, could explain these high values as an effect of solute concentrations, but further data and an in-depth analysis of the relationship with meteorological data are needed.

At Gran Sometta, the two sub-sites (RG bianco and RG nero) showed a similar seasonal pattern, with conductivity and the main solutes increasing from the snowmelt until autumn (Figure 10). With respect to Le Caldaie, this pattern emerged also in 2021, with the highest values reached at the end of September (e.g., Ca 46-48 mg L^{-1}, SO_4 95-110 mg L^{-1}). NO_3 concentrations were more stable, varying between 200 and 400 µg N L^{-1} (Figure 10).

The inter-annual variability of concentrations, in particular the seasonal pattern, put in evidence the importance of collecting data in the same period each year, to improve both the comparability within sites and the evaluation of long-term trends.
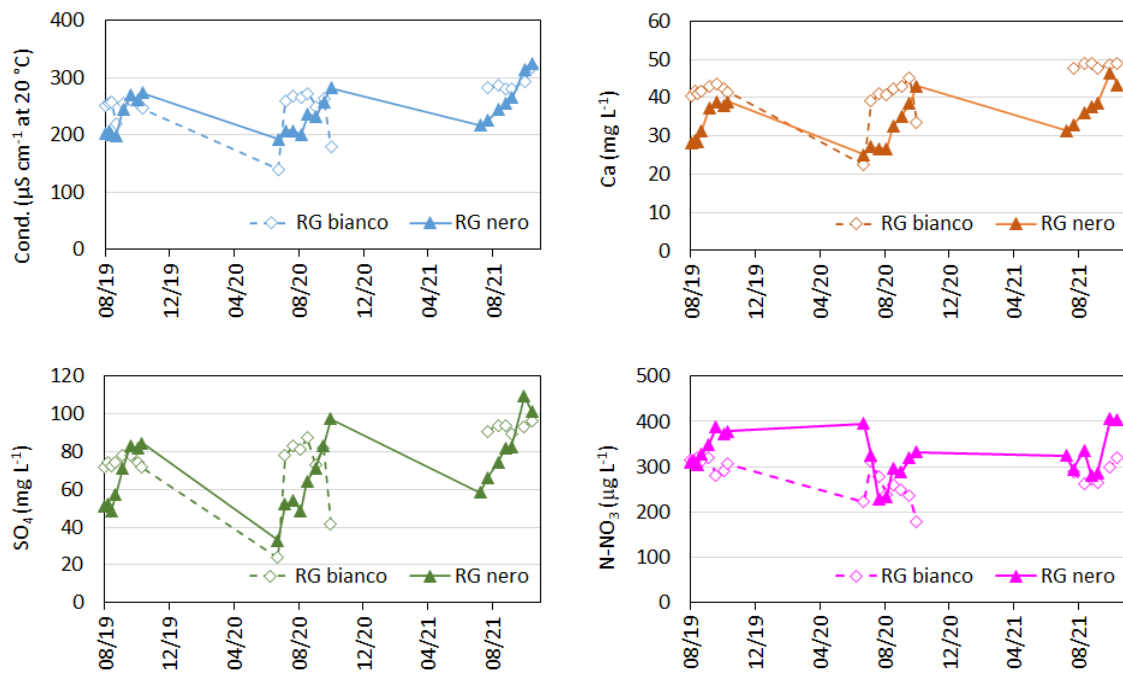
Fig. 10 – Temporal pattern of selected chemical variables in the rock glacier (RG) outflows (sub-sites RG bianco and RG nero) at the Gran Sometta site in Cervinia, Aosta Valley

The chemistry of rock glacier outflows at the RESERVAQUA sites is rather variable, mainly depending on the dominant lithology at each site. However, it can be concluded that the sites are characterised by a low to moderate solute content, quite high concentration of nitrate and a low content of nutrients, including organic carbon.

A common feature of the RESERVAQUA sites is also the very limited presence of trace metals in rock glacier outflows. This is in contrast with the very high concentrations of some trace elements (Ni, Al, Co, Cu, Fe, Mn and Zn) for some sites in the Central-Eastern Alps and attributed to the influence of ice melting within rock glaciers (Thies *et al.* 2007, 2013; Ilyashuk *et al.* 2014; Krainer 2014).

Chemical Inter-comparison

Inter-laboratory quality assurance tests are a valuable tool to evaluate and promote harmonisation of monitoring practices in the field of water quality assessment. Within monitoring programs with joint sampling and analysis, inter-comparisons may contribute to identify and control biases between analyses carried out by the participants (Gundersen and Bryntesen 2021). The inter-comparison exercise performed within WP3 of the RESERVAQUA project aimed to improve the comparability of the data gathered during the project, as well as to strengthen the collaboration and the information exchange among the laboratories involved.

The samplings for the inter-comparison exercise were done in two occasions, the first one (A) on the 12th of August 2021, within a field joint survey at the site Gran Sometta (Cervinia, AO, Italy), managed by ARPA Valle d'Aosta (Figure 11) and the second one (B) on the 22nd of August 2022, during the sampling performed at the site Granero, in the Monviso area (Piedmont, TO, Italy) by the staff of ARPA Piemonte and CNR IRSA. Five and one samples were collected respectively, representative of the different water types within each site (Table 2).

Fig. 11 – Sampling for: a) inter-comparison A, in Cervinia (AO) (RG Gran Sometta - ARPA Valle d'Aosta site); b) inter-comparison B, at the Granero site, Piedmont (ARPA Piemonte site); c) laboratory for chemical analyses at CNR IRSA, Verbania

In both cases, samples were transported or delivered to the lab and analyses performed as soon as possible (for trace metals, the analysis was performed a few weeks after the sampling, after treatment of the samples for preservation). In 2022, to focus on trace metal analysis, a synthetic sample was prepared at CNR IRSA laboratory and delivered to the other labs, to be included in the inter-calibration. The samples were analysed for all the chemical variables routinely considered by each lab; however, in the inter-comparison, we focused on those variables which have been identified as priority for the project: pH, conductivity, alkalinity, major anions (SO_4, NO_3, Cl) and cations (Ca, Mg, Na, K), trace metals (Table 3).

Meetings were organised among the project partners and their collaborators involved in the inter-comparison exercises, to discuss some technical issues (delivery of the samples to the laboratories, sample treatment and conservation, analytical methods to be employed) as well as the results. These meetings attested to be useful to all the laboratories staff, who also interacted by phone and email during the project to focus on the main analytical aspects when dealing with this type of water samples.

Tab. 2 – Water samples collected in 2021 (A) and 2022 (B) for the inter-comparison exercise

Inter-comparison A - 2021

N°	Site	Sampling date	Coordinates (Lat. Long.)	Water temperature (°C)
1	Torrente a monte	12/08/2021	45°55'23"N 7°40'13"E	7.9
2	Rock Glacier Bianco	12/08/2021	45°55'22"N 7°40'6"E	1.1
3	Torrente	12/08/2021	45°55'23"N 7°40'5"E	7.4
4	Torrente a valle uscita	12/08/2021	45°55'22"N 7°39'59"E	6.2
5	Rock Glacier Nero	12/08/2021	45°55'21"N 7°40'2"E	1.1

Inter-comparison B - 2022

N°	Site	Sampling date	Coordinates (Lat. Long.)	Water temperature (°C)
1	Granero	22/08/2022	44°43'31"N 7°3'1"E	3.5
2	Synthetic sample	-	-	-

Tab. 3 - Variables considered in the inter-calibration exercise and analytical methods used by the laboratories

Variable	Method	Units	References
pH	Potentiometry		APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Conductivity	Conductometry	$\mu S\ cm^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Alkalinity	Potentiometry	$\mu eq\ L^{-1}$	Gran 1952; Neal 2001; APHA AWWA WEF 2017
Nitrate	Ion chromatography	$\mu g\ N\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Ammonium	Spectrophotometry	$\mu g\ N\ L^{-1}$	Fresenius *et al.* 1988; APAT IRSA-CNR 2003
Total N	Spectrophotometry	$mg\ N\ L^{-1}$	Valderrama 1981
Total P	Spectrophotometry	$\mu g\ P\ L^{-1}$	Valderrama 1981
Reactive P	Spectrophotometry	$\mu g\ P\ L^{-1}$	Valderrama 1981
Reactive silica	Spectrophotometry	$mg\ Si\ L^{-1}$	Golterman *et al.* 1978
Total Organic Carbon (TOC)	High-temperature catalytic oxidation	$mg\ C\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Sulphate	Ion chromatography	$mg\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Chloride	Ion chromatography	$mg\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Calcium	Ion chromatography	$mg\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Magnesium	Ion chromatography	$mg\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Sodium	Ion chromatography	$mg\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Potassium	Ion chromatography	$mg\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003
Trace metals	ICP-OES/ICP MS	$\mu g\ L^{-1}$	APHA AWWA WEF 2005; APAT IRSA-CNR 2003; EPA 1994

INTER-COMPARISON A

Data sent by the laboratories were gathered using a template (excel spreadsheet) containing the formulas to calculate the ionic balance and compare measured and calculated conductivity, according to the provision of ICP WATERS (ICP Waters Programme Manual 2010). The results obtained by the three laboratories (CNR IRSA, ARPA Valle d'Aosta and ARPA Piemonte) in analysing the 5 samples of inter-comparison A are shown in Figure 12 for selected chemical variables.

The data obtained by the laboratories agreed fairly well as regards conductivity and major ions. Comparable results were found for those variables, which are considered relevant in the assessment of rock glacier outflows chemistry (Ca, Mg, SO_4, NO_3). When discrepancies emerged, as in the case of alkalinity, the laboratories shared experience and practices to fix the possible issues leading to these results.
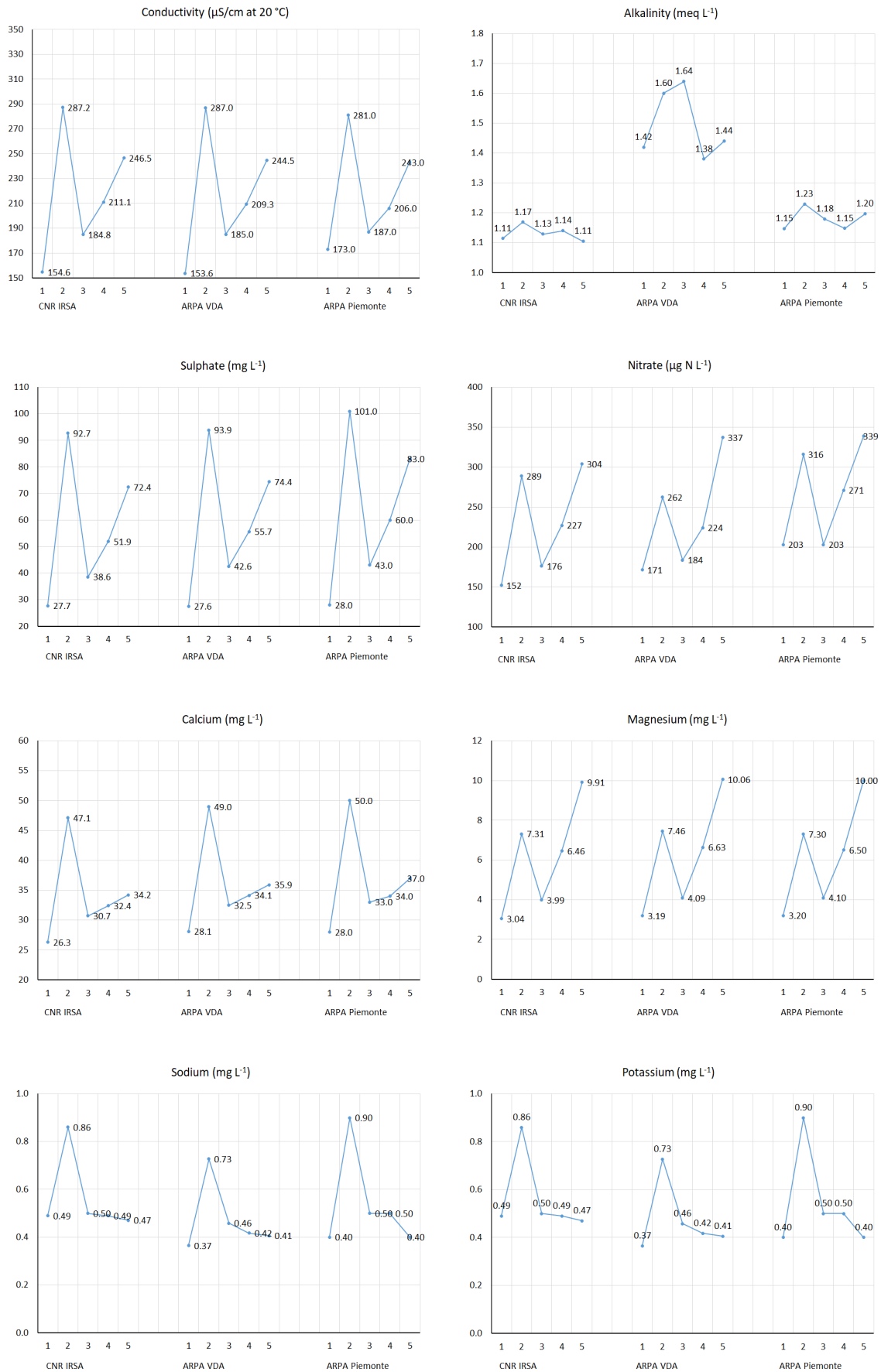
Fig. 12 – Inter-comparison A: results obtained by the laboratories for selected variables

INTER-COMPARISON B

Results obtained by the laboratories in the analysis of the rock glacier outflow sample and in the analysis of the synthetic sample for trace metals are compared in Table 4. As in the first inter-comparison, the results were fully comparable for the main variables. Good results were also obtained for trace metals, especially the most relevant ones (e.g., Al, Fe, Mn, Ni, Zn) (Figure 13).

Tab. 4 – Inter-comparison B: results obtained by the three laboratories concerning the analysis of the sample Granero rock glacier outflow and trace metal analyses of the synthetic sample

|	Unit	CNR IRSA	ARPA Valle d'Aosta	ARPA Piemonte
pH	-	7.74	7.95	7.80
Conductivity	$\mu S\ cm^{-1}\ 20°C$	81.2	81.4	78.0
Alkalinity	$meq\ L^{-1}$	0.66	0.57	0.62
$SO_4^=$	$mg\ L^{-1}$	8.18	8.42	8.00
$N-NO_3^-$	$\mu g\ L^{-1}$	370	419	452
Ca^{++}	$mg\ L^{-1}$	15.60	16.00	14.80
Mg^{++}	$mg\ L^{-1}$	0.56	0.57	0.80
Na^+	$mg\ L^{-1}$	0.66	0.48	0.60
K^+	$mg\ L^{-1}$	0.30	0.28	0.30
TN	$mg\ N\ L^{-1}$	0.41	0.44	-
TOC	$mg\ C\ L^{-1}$	0.19	0.24	<0.5
Al	$\mu g\ L^{-1}$	44	42	41
As	$\mu g\ L^{-1}$	36	41	37
B	$\mu g\ L^{-1}$	102	-	95.3
Ba	$\mu g\ L^{-1}$	40	42.1	37.6
Cd	$\mu g\ L^{-1}$	9.9	10.6	9.7
Co	$\mu g\ L^{-1}$	10	<0.3	10.3
Cr	$\mu g\ L^{-1}$	19.8	21.3	21.8
Cu	$\mu g\ L^{-1}$	18.5	22	19.9
Fe	$\mu g\ L^{-1}$	110	114	107
Mn	$\mu g\ L^{-1}$	11.8	10.8	11.9
Ni	$\mu g\ L^{-1}$	20	21.7	20.4
Pb	$\mu g\ L^{-1}$	40.4	42.5	38.6
Se	$\mu g\ L^{-1}$	100.4	96.1	84.2
Tl	$\mu g\ L^{-1}$	103.5	-	93.5
V	$\mu g\ L^{-1}$	39.8	43.4	43.5
Zn	$\mu g\ L^{-1}$	98	102	89
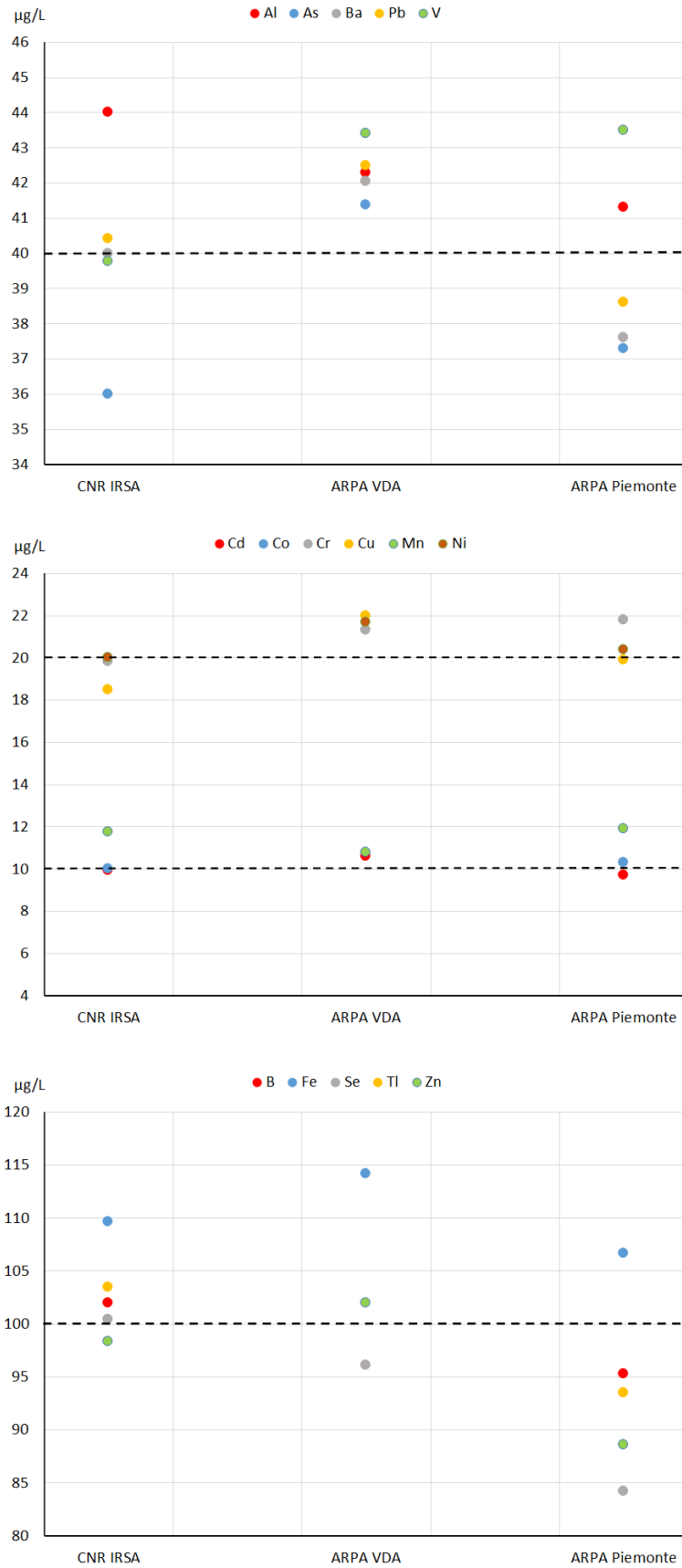
Fig. 13 – Inter-comparison B: results obtained by the laboratories in the analysis of trace metals on the synthetic sample

Conclusion / Recommendations

The activities performed within the WP3 of the RESERVAQUA project proved to be useful not only to gather new data and improve knowledge on rock glacier outflow hydrochemistry, but also to focus on a fundamental aspect in the monitoring of freshwater in high altitude environments i.e., the evaluation of analytical quality. The inter-comparison exercises and the sharing of practices and protocols about sampling and analyses contributed to improve the quality of the data obtained by the different laboratories and will be helpful in the future activities. In our opinion, the adoption and regular use of simple data quality checks, such as the calculation of the ionic balance and the comparison between measured and calculated conductivity may improve the reliability of the data collected in monitoring programs especially when dealing with dilute, low-conductivity waters. We also suggest the adoption of common protocols for sample collection, storage, and delivery, as in the factsheets provided as annexes to this technical report, especially when different people are in charge for the sampling and field measurements.

On our experience, variables that should be prioritised in the assessment of rock glacier outflows and of the water bodies potentially affected (lakes, ponds, etc.) are pH, conductivity, major cations (Ca, Mg, Na, K), SO_4, $N-NO_3$ and TOC. Total N and $N-NH_4$ could be possibly added to evaluate the relative contribution of inorganic and organic N forms. Among trace metals, priority should be given to Al, Fe, Mn, Ni, Zn.

A monthly or seasonal sampling frequency could be useful to assess the variability of water chemistry in relation to weather and hydrological drivers; however, several constraints may limit the possibility to collect monthly samples, such as weather conditions and limited accessibility of the site. In the establishment of a long-term monitoring program at selected sites, the maintenance of sampling over several years, even of a very few samples (e.g., 1 at snowmelt and 1 at the end of the summer season), must be prioritised with respect to collecting many samples per year.

The PERMAQUA project in the Eastern Alps represented a pilot experience, combining studies on geology, hydrology, water chemistry, biology, and paleolimnology to get an in-depth knowledge of the possible impact of permafrost melt on high mountain freshwaters. Based on the outcomes of PERMAQUA and similar projects, key sites should be established where monitoring the evolution of permafrost related water quality in the long-term.

We think it would be advisable to strengthen the cooperation among institutions and laboratories dealing with permafrost-related freshwater, possibly collecting data with shared protocols, and following the provision of international programs and networks like ICP WATERS and LTER, with the final aim to establish a long-term monitoring network in different parts of the Alps.

Annexes to the report

Annex 1 - Sampling protocol for high altitude runoff water, including RG outflow

Annex 2 - Suggested protocol for chemical analyses and data quality check

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RESERVAQUA

WP3 – ASSESSMENT OF THE AVAILABLE WATER RESOURCES IN THE TRANSBOUNDARY AREA

CHEMICAL CHARACTERIZATION OF ROCK GLACIER OUTFLOWS

ANNEX 1 - SAMPLING PROTOCOL

SAMPLING PROTOCOL FOR HIGH ALTITUDE RUNOFF WATER, INCLUDING ROCK GLACIER (RG) OUTFLOW

Materials needed for each sample

- 500 mL bottles for the analysis of ions and nutrients;

- For trace metals: 50 mL bottles, 60 mL syringes, disposable filters 0.45 µm with luer outlet. Bottles and syringes have to be rinsed with 2% nitric acid;

- Disposable gloves, polyethylene bags, labels and pencil;

- Thermometer;

- "GPS" or any other GNSS system (check the reference system used; it should be UTM WGS84)

Sampling procedure

- Select the site in order to have free running water; if possible, sample in an area with at least 20-30 cm of water depth (e.g., a small pool).

- Once selected the site, be careful! Avoid to:
  - contaminate the sampled water with your hands (use single-use gloves if necessary);
  - enter into the water with your feet.

- Rinse at least three times the sampling bottle and the cap.

- Completely fill the bottle as much as possible; after closing it no air bubbles should be left inside. Be careful not to touch the sample or the cap with your bare hands.

- Tighten the cap and dry the outside of the bottle.

- Label each bottle with a progressive number (ID number) and date of sampling and put the bottles in a tightly closed plastic bag.

- Collect a separate sample if trace metals analyses have to be performed. The water sample can be collected directly form the water surface with a syringe. The syringe (without the filter) has to be rinsed at least three times with the water to be samples. Syringe has then to be filled completely, the disposable filter attached to the syringe and rinsed with a volume of approximately 30-40 mL, and the filtered sample thrown away. Then remove the filter, fill in the syringe completely, attach the filter and filter about 20-30 mL of water into the 50 mL bottle. Use this water to rinse the bottle and then throw it away. Then repeat the procedure and filter slowly 50 mL of sample into the bottle. Take care to avoid bubbles when filling the syringe. Close the bottle tightly, label it and store it with the other samples.

- Measure water temperature leaving the thermometers in the water until the measure is stable.

- Fill in the form (one for each sampling site) and add the ID number of bottles used.

- Take a few pictures from which one can see the conditions of the site, the sampling points, the surrounding area.

- Samples should be stored in the dark or away from light or place them in the shipping container.

Storage and shipment of samples

Dealing with waters of very low total ionic strength, prevention of sample contamination or sample changes while in storage may be critical in obtaining accurate measurements. All containers used for either sample collection or storage must be free of any important quantity of the determinants in relation to the lowest concentration to be measured, and the containers must be of polypropylene or any other material that will neither absorb nor release measurable quantities of the determinant. Extreme care must be exercised to avoid contamination and sample containers must be entirely full and tightly capped to minimize any interchange with entrapped air (ICP WATERS Manual 2010).

The samples collected should be kept in the dark and stored cool (ideally a refrigerator at about 2-8° C, **do not freeze**) and sent to the laboratory using a thermal container (polystyrene box) as soon as possible.

References

ICP Waters Programme Manual (2010) - ICP Waters Report 105/2010. Report No. 6074-2010: 91 pp.

Site Name: . . . .

Altitudes (m): . . . .

Sampling date (day, month, year, time):

D	D		M	M		Y	Y	**Hour**	HH : mm

Operators: . . . .

Weather: . . . .

Photographic documentation on the site and the sampling points   YES   NO

Sampling of <u>out flow area site</u>

      ID number of the sample bottle: . . . .

      ID number of metals sample bottle: . . . .

      Water temperature at the sampling (° C): . . . .

GPS/GNSS Coordinates (UTM WGS84 format): . . . .

Accuracy. . . . . . **m**

Comments:

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RESERVAQUA

WP3 – ASSESSMENT OF THE AVAILABLE WATER RESOURCES IN THE TRANSBOUNDARY AREA

CHEMICAL CHARACTERIZATION OF ROCK GLACIER OUTFLOWS

ANNEX 2 – CHEMICAL ANALYSES

Suggested protocol for chemical analyses and data quality check

All chemical analyses should be completed as soon as possible, ideally in 3-4 days. Samples should be analysed for the main chemical variables according to standard methods for freshwater samples (APHA AWWA WEF 2012; APAT IRSA-CNR 2003). It is also possible to refer to ISO/CEN methods (see http://www.iso.org; https://www.cencenelec.eu/).

Samples should be possibly analysed for the following variables: pH, specific conductivity at 20 or 25 °C, alkalinity, sulphate ($SO_4^=$), nitrogen as nitrate, (NO_3^-), chloride (Cl^-), dissolved organic carbon or total organic carbon (DOC/TOC), calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^+), potassium (K^+), total phosphorus (P), total nitrogen (N), trace metals on dissolved forms (filtered sample on 0.45 μm). Additional variables may include turbidity, nitrogen as ammonium (NH_4), reactive silica (Si), orthophosphate ($P-PO_4^=$) and fluoride (F^-). Alkalinity may be omitted at pH< 5.2.

As an example, the table 1 below provides analytical methods, limit of detection (LOD) and repeatability (mean and relative standard deviation) in use at the water chemistry lab of the CNR IRSA in Verbania, Italy (https://www.idrolab.irsa.cnr.it).

Table 1

Variable	Method	Units	LOD	Repeatability		References
				Mean	RSD	
pH	Potentiometry			7.8	1	APHA AWWA WEF 2012
Conductivity	Conductometry	$\mu S\ cm^{-1}$	0.5	70	1	APHA AWWA WEF 2012
Alkalinity	Potentiometry (Gran or 2EP method)	$meq\ L^{-1}$	0.001	0.200	4	Gran 1952; Neal 2001
Nitrate	Ion chromatography	$mg\ N\ L^{-1}$	0.011	1.00	4	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Ammonium	Spectrophotometry	$\mu g\ N\ L^{-1}$	5	30	9	Fresenius *et al.* 1988
Total N	Spectrophotometry	$mg\ N\ L^{-1}$	0.06	0.50	8	Valderrama 1981; APAT IRSA-CNR 2003
Total P	Spectrophotometry	$\mu g\ P\ L^{-1}$	4	10	15	Valderrama 1981; APAT IRSA-CNR 2003
Reactive P	Spectrophotometry	$\mu g\ P\ L^{-1}$	2	10	12	Valderrama 1981
Reactive silica	Spectrophotometry	$mg\ Si\ L^{-1}$	0.02	1.00	4	Golterman *et al.* 1978; APAT IRSA-CNR 2003
Total Organic Carbon	High-temperature catalytic oxidation	$mg\ C\ L^{-1}$	0.05	0.50	15	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Sulphate	Ion chromatography	$mg\ L^{-1}$	0.05	6.0	4	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Chloride	Ion chromatography	$mg\ L^{-1}$	0.02	0.10	10	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Calcium	Ion chromatography	$mg\ L^{-1}$	0.02	10	2	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Magnesium	Ion chromatography	$mg\ L^{-1}$	0.01	0.6	7	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Sodium	Ion chromatography	$mg\ L^{-1}$	0.01	0.5	5	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Potassium	Ion chromatography	$mg\ L^{-1}$	0.02	0.8	8	APHA AWWA WEF 2012; APAT IRSA-CNR 2003
Trace metals (Al, Fe, Mn, Cd, Pb, Cu, Ni,Zn)	ICP-MS or OES	$\mu g\ L^{-1}$				ISO 11885 1996; APAT IRSA-CNR 2003

Data quality

The laboratory should adopt a rigorous quality control of all the analytical methods based on both internal and external quality control procedures. Among the internal quality controls, the check of the ion balance and the comparison of measured and calculated conductivity are recommended for each analysis. The attached file provides a form for the collection of the data and the calculation of the quality checks according to the provision of the ICP WATERS Manual (2010).

To check the ion balance, all of the necessary variables for calculating the sums of cations and anions must be analysed. Another check is to compare the measured conductivity to the conductivity calculated from the measured ions.

VALIDATION OF THE RESULTS FOR MAJOR IONS

When the concentrations of all the major ions and the electrical conductivity of the solution are measured in a water sample, data quality can be checked by means of the ion balance, i.e. by comparing the equivalent sum of anions and cations, and by estimating the electrical conductivity calculated from the concentrations of each ion multiplied by the equivalent ionic conductance.

These very simple checks of the internal consistency of the analyses are strongly recommended to verify the correctness of the analyses, as well as to detect other possible sources of error, such as incorrect transcription.

The ion balance

The basic assumption in the ion balance check is that the determination of pH, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- accounts, almost completely, for all the ions present in a solution. At pH values higher than 6.5, however, the hydrogen ion concentration can be ignored.

The ion balance check is based on the electro-neutrality of water. The total number of negative and positive charges in a solution must be equal. This can be checked by converting the concentration values for the individual ions into the unit milli- (or micro-) equivalent per litre (meq L^{-1} or µeq L^{-1}). The constants required to convert the units used in the ring test into µeq L^{-1} are given in Table 2.

Table 2. Conversion of concentrations from mg L^{-1} to µeq L^{-1}, and the equivalent conductance at infinite dilution of the individual ions.

	Unit	Factor to µeq L^{-1}	Equivalent conductance at 20°C	Equivalent conductance at 25°C
			S cm^2 eq^{-1}	S cm^2 eq^{-1}
pH		$10^{(6-pH)}$	315.1	350.0
Calcium	mg L^{-1}	49.9	54.3	59.5
Magnesium	mg L^{-1}	82.24	48.6	53.1
Sodium	mg L^{-1}	43.48	45.9	50.1
Potassium	mg L^{-1}	25.28	67.0	73.5
Ammonium	mg N L^{-1}	71.39	67.0	73.5
Sulphate	mg S L^{-1}	62.37	71.2	80.0
Nitrate	mg N L^{-1}	71.39	63.6	71.4
Chloride	mg L^{-1}	28.2	68.0	76.4
Alkalinity	meq L^{-1}	1000	39.4	44.5

The limit of acceptable errors varies according to the total ionic concentration and the nature of the solution. With ΣCat and ΣAn indicating the concentrations (meq L^{-1} or µeq L^{-1}) of cations and anions, respectively, and Alk the Gran alkalinity:

$$\Sigma \, An = Alk + [SO^{--}_4] + [NO_3^-] + [Cl^-]$$

$$\Sigma \, Cat = [Ca^{++}] + [Mg^{++}] + [Na^+] + [K^+] + [NH_4^+] + [H^+]$$

we can define the per cent difference (PD) as:

$$PD = 100 \, (\Sigma \, Cat - \Sigma An) / (0.5 \, (\Sigma \, Cat + \Sigma \, An))$$

Proposed PD thresholds for accepting analytical results are given in Table 3. Alkalinity was assumed to be wholly due to bicarbonate, which is a correct assumption over the pH range 6.0-8.5. In samples with a low DOC concentration, however, PD values higher than those given in Table 3 will indicate a lack of precision in one or more analytical techniques or the omission of important ions.

Comparison between measured and calculated conductivity

Electrical conductivity is a measure of the ability of an aqueous solution to carry an electric current. It depends on the type and concentration of the ions, and on the temperature of the measurement. It is defined as:

$$K = G * (L/A)$$

where $G = 1/R$ is the conductance (unit: ohm^{-1}, or Siemens; ohm^{-1} is sometimes written as mho), defined as the reciprocal of the resistance (R, unit ohm), A (m^2) is the electrode surface area, and L (m) is the distance between the electrodes.

In the International System of Units (SI) conductivity is expressed as Siemens per meter (S m^{-1}). In practice the unit µS cm^{-1}, where 1 mS m^{-1} = 10 µS cm^{-1}= 10 µmho cm^{-1}, is also commonly used.

Conductivity depends on the type and concentration (activity) of the ions in solution; the capacity of a single ion to transport an electric current is given in standard conditions and in ideal conditions of infinite dilution by the equivalent ionic conductance (u_i, unit: S cm^2 eq^{-1}). Values of equivalent conductance of the main ions at 20 and 25 °C are presented in Table 3.

The conductivity is calculated (CE$_\infty$) from individual ion concentrations, multiplied by the respective equivalent ionic conductance (u_i):

$$CE_\infty = \Sigma\, u_i\, C_i$$

It is assumed that the bicarbonate ions account for almost all of the alkalinity; this assumption is correct for solutions with a pH in the range from 6.0 to 8.5.

The dependence of conductivity on temperature makes it necessary to use a "reference" temperature, which in the ISO standard 7888-1985. The variation of equivalent conductance with temperature is not the same for all the ions, so that the function of conductivity on temperature will depend on the chemical composition of the solution.

The temperature correction values for conductivity are therefore a simplification, performed assuming a "standard composition" for surface water; this can introduce a systematic error in the case of a different chemical composition, such as is the case for deposition chemistry. Of course, this is also true if the correction is made automatically by the conductivity meter. For this reason, it is suggested that the measurement be made as close as possible to 25 °C.

To compare calculated conductivity (CE) to the measured value (CM), the percentage difference, CD, is be defined as the ratio:

$$CD_\infty = 100 * |(CE - CM)|/CM$$

At the low ionic strength (below 0.1 meq L^{-1}) of bulk deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles and Yost 1982). At higher ionic concentrations, such as in most of the throughfall, stemflow and soil solution

samples, the calculated conductivity can be corrected, as proposed e.g., by APHA AWWA WEF (2012), based on the ionic strength.

Ionic strength (IS), in meq L^{-1}, is calculated from the individual ion concentrations as follows:

$$IS = 0.5 \ \Sigma C_i \ z_i^2 / w_i$$

where:

C_i = concentration of ion i in mg L^{-1}

z_i = absolute value of the charge for ion i

w_i = gram molecular weight of ion i

The correction becomes relevant at ionic strengths higher than 0.1 meq L^{-1}, and uses the Davies equation for ionic strengths lower than 0.5 meq L^{-1} and for temperatures from 20 and 30 °C, in order to calculate the monovalent ion activity y:

$$Log_{10} \ y = 0.5 \ (IS^{0.5}/(1+IS^{0.5})-0.3 \ IS)$$

The calculated conductivity, used for calculating PD, is then obtained as:

$$CE = y^2 \ CE_\infty$$

The ion balance and conductivity check should be performed immediately after all the analyses have been completed, so that the analyses can be repeated if the desired quality threshold is not reached. These threshold values should be defined in relation to the aims of the laboratory and the type of sample. The threshold values proposed are given in the table.

Table 3. Threshold values for checking the analyses based on the ion balance and conductivity.

Sample conductivity	BELOW 10 μS cm^{-1}		BETWEEN 10 and 20 μS cm^{-1}		ABOVE 20 μS cm^{-1}	
Ion balance PD	± 20%	-	± 20%	-	± 10%	-
Conductivity CD	± 30%	± 30%	± 20%	± 20%	± 10%	± 10%

Focus on alkalinity

Alkalinity determination was still one of the most critical analyses as regards both missing results and the problem of dispersion and errors.

The alkalinity of a water sample is its acid-neutralising capacity, defined as the amount of acid needed to neutralise the bases present in a solution. It is a measure of the aggregate property of a solution and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is the sum of all the titrable bases in the sample and is determined by means of an acidimetric titration. In freshwater or precipitation, these bases are primarily bicarbonate, as well as hydroxyl ions at pH values above 8.0, sulphide and non-ionic compounds such as calcite or certain organic compounds.

The critical feature is the definition and determination of the equivalent point, i.e., the point at which it is assumed that all the bases have been neutralised. If we assume that the main base in solution is bicarbonate, then the equivalent point is the inflection point of the titration curve between bicarbonate and carbonic acid + carbon dioxide. This value depends on the CO_2 concentration in solution at this point, which is a function of the total concentration of the carbonate system. Consequently, the equivalence point of the alkalinity titration depends on the alkalinity to be determined. However, it ranges between pH values of 5.0-5.6. For low alkalinities the inflection point can be obtained by these methods:

1) a titration performed well beyond the end point (e.g., to pH 4.5 or less), by recording a number of pH values and the corresponding added volume of acid. Subsequent extrapolation by the least-squares regression method allows calculation of the equivalent point (Gran 1952);

2) a simplified version of the Gran titration requires only two end-points, at pH 4.5 and 4.2, thus making it simpler to calculate the equivalence point. This is the simplest method to correctly measure alkalinity.

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