



Levels and ecological risk of selected organic pollutants in the high-altitude alpine cryosphere - The Adamello-Brenta Natural Park (Italy) as a case study

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ABSTRACT

It is known that pesticides and other organic pollutants are transported from lowlands and alpine valleys to high alpine summits, where they are stored in glaciers until melting occurs between July and September. In this study, we aimed to map glacial contamination by measuring the concentrations of currently used pesticides, synthetic fragrances, and polycyclic aromatic hydrocarbons (PAHs) in glacial and non-glacial meltwater from six sites in the Italian Alps located within the protected Adamello-Brenta Natural Park. We subsequently characterised the ecological risk of these contaminants to aquatic fauna. Chlorpyrifos, chlorpyrifos-methyl, terbuthylazine, galaxolide, tonalide, and PAHs were detected in July and September 2019 and 2020 across all sites. Risk characterisation indicated that PAHs posed a low risk to the alpine ecosystem at most of the sites, and medium risk was associated only with fluoranthene and pyrene at Mandrone in 2020. Regarding fragrances, herbicides, and chlorpyrifos-methyl, the calculated risk to aquatic biocenosis was acceptable under current European guidelines. Only chlorpyrifos posed an unacceptable risk to aquatic invertebrates at two sites: Amola (in July 2019) and Mandrone (in July and September 2019 and 2020). A risk refinement of chlorpyrifos, calculated using the species sensitivity distribution, indicated an acceptable level of risk, as concentrations were consistently below the effect level. Chlorpyrifos is not the only potential threat to Alpine aquatic ecosystems; therefore, it is advised to continue monitoring other equally potentially dangerous compounds that could reach high-altitude environments through medium-range atmospheric transport. To preserve the ecological and social value of the Adamello-Brenta Natural Park, natural capital is a priority. In this context, the results of this study assume strategic importance in supporting the development of future environmental conservation initiatives and water management policies.

1. Introduction

Natural parks represent a valuable natural heritage that provides ecological, social, and economic benefits for local people and visitors (Huber et al., 2013). They comprise a range of natural elements that support a wealth of biodiversity, including endemic species (Fischer et al., 2008; Dirnböck et al., 2011; Rogora et al., 2018). Parks in mountainous areas also represent a major reserve of freshwater, including springs, lakes, and streams fed by rain, ice, and snowmelt (Wyder, 2001; Acreman et al., 2020). However, these water reserves are seriously threatened by climate change.

Climate change is causing a rapid loss of glaciers and snow cover in

mountainous regions worldwide (Slemmons et al., 2013; Zemp et al., 2015; Beniston et al., 2018; Bourbonnais et al., 2021; Haeberli et al., 2021). The retreat of glaciers involves the reduction of glacial runoff, alteration of biogeochemical cycles, and loss of cryophilous biodiversity (Brown et al., 2007; Ernakovich et al., 2014; Milner et al., 2017; Gobbi and Lencioni, 2020; Michel et al., 2020; Lencioni et al., 2021a). Additionally, glacier shrinkage deteriorates meltwater quality by releasing substances of synthetic origin transported to high altitudes by the atmosphere and temporarily trapped in glaciers (Miner et al., 2021a, Miner et al., 2021b).

Glaciers are known to accumulate pollutants by acting as cold traps for organic compounds (Miner et al., 2017). Because of their

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physicochemical characteristics, contaminants can travel long distances from emission sources and condense and accumulate in snow and ice when they reach high-altitude environments (Daly and Wania; 2005, Villa et al., 2006; Finizio et al., 2006). Rain and snowfall are particularly efficient in transferring contaminants from the atmosphere to the ground, where they can be stored for a long time (Finizio et al., 2006; Herbert et al., 2006). Consequently, glaciers have become temporal sinks for various contaminants, and both high-altitude mountainous regions and the poles have received increasing attention as receivers of airborne contaminants transported over long distances (Villa et al., 2001; Bogdal et al., 2009; Guzzella et al., 2016; Villa et al., 2017; Ferrero et al., 2019). During spring, when temperatures increase and melting begins, these substances are emitted back into the atmosphere or released into streams through meltwater. Typically, these pollutants are transferred to freshwater systems in short, concentrated pulses, posing a risk to high-altitude biotic communities because the melting of snow and ice often coincides with periods of intense biological activity and vulnerable stages of development (Meyer et al., 2011; Morselli et al., 2014). Global warming is accelerating this process because the more rapid melting of alpine glaciers generates the release of contaminants stored in deep ice (Bradley et al., 2020, Bradley et al., 2021).

Typically, studies on European glaciers have focused only on monitoring persistent organic pollutants (POPs) (Bizzotto et al., 2009; Grannas et al., 2013; Miner et al., 2018), considering the relatively negligible atmospheric transport of polar and water-soluble substances, such as current-use pesticides (CUPs) and synthetic fragrances. However, because of their solubility, CUPs and musk fragrances easily dissolve in precipitation, accumulating in glaciers after wet deposition. Temperate-zone mountainous regions characterised by high levels of precipitation, such as the European Alps, are particularly vulnerable to the accumulation of pollutants. Furthermore, Alpine regions are often surrounded by agricultural areas with high pesticide use. In Europe, recent monitoring studies have highlighted the presence of CUPs in glacial meltwater of the Italian Alps (Ferrario et al., 2017a; Rizzi et al., 2019) and glacial lakes of the Pyrenees (Santolaria et al., 2015). Similarly, the volatility of synthetic musk fragrances predisposes them to medium-range atmospheric transport, such that they have been found in snow and glacial meltwater samples from the Italian Alps (Villa et al., 2014; Ferrario et al., 2017a), an ice core from the Caucasus (Vecchiato et al., 2020), and a sediment core from a glacier-fed lake in Switzerland (Bogdal et al., 2009).

In addition to pesticides and synthetic fragrances, many other substances have been found to contaminate pristine Alpine environments. Alpine regions often lie in close proximity to densely urbanised areas, where many pollutants, such as polycyclic aromatic hydrocarbons (PAHs), are emitted. PAHs are ubiquitous compounds; their extensive presence in the environment is mainly due to the large-scale emissions from incomplete combustion processes of organic materials. PAHs are also bio-accumulative and are known to have carcinogenic properties; therefore, they are potentially harmful to aquatic ecosystems. They can undergo long-range atmospheric transport, reaching remote regions, such as the Arctic (Drotikova et al., 2020) and Antarctic (Xie et al., 2020), and high mountain chains, such as the Himalayas (Guzzella et al., 2016).

Anthropogenic contaminants temporarily stored in ice and released through melting come in direct contact with aquatic organisms living in glacier-fed streams, making them the first organisms to be affected by these substances (Bizzotto et al., 2009a; Villa et al., 2011; Miner et al., 2019). It has recently been highlighted that pesticides in ice melt affect the swimming behaviour and basal metabolism of cryophilous insect species living in these habitats (e.g. *Diamesa zernyi*, Diptera Chironomidae) (Villa et al., 2018; Di Nica et al., 2019; Muñoz-González et al., 2021). However, the hazard of pesticide contamination in these remote ecosystems is still little investigated. Indeed, to date, only Rizzi et al. (2019) have assessed the ecological risk of chlorpyrifos to high-altitude ecosystems.

In this context, the aim of this study was to assess the quality of high-altitude meltwater of some representative glaciers in the Adamello-Brenta Nature Park. Pesticides, synthetic fragrances, and PAHs were detected in early and late summer, representing periods of different ice- and snowmelt intensities. Finally, we determined the ecological risk of these pollutants to aquatic fauna following the European approach, using at least one of the standard test algae (the Green algae *Pseudokirchneriella subcapitata*, (formerly known as *Selenastrum capricornutum*), and *Desmodesmus subspicatus* (formerly known as *Scenedesmus subspicatus*) and the Diatoms *Navicula pelliculosa*), *Daphnia magna*, *Chironomus riparius*, and fish (*Oncorhynchus mykiss* or other standard test species reported in the OECD (2019) as representative aquatic organisms).

2. Materials and methods

2.1. Study area

Ice melt was collected from six sites: one spring (Grostè in the Brenta Dolomites) partially fed by permafrost and five glacier-fed streams, of which four (Amola, Nardis, Mandrone, and Carè Alto) are located in the Adamello-Presanella Mountains and one (Agola) is located in the Brenta Dolomites (Figure 1). Glaciers were chosen to be representative of the different types of glaciers present in the park's three mountain groups (e.g. with different surface area and retreating rate, at different distance from hiking trails, etc.). The highest number of sites were chosen in the Adamello-Presanella massif, located in the western region of the park, that has the largest glacial surface area of the Trentino Province and comprise 41 glaciers. The lowest number of sites were chosen in the Brenta Dolomite Group, poor in glaciers, but recognised as a UNESCO World Heritage Site because of their exceptional beauty and unique landscape, together with their scientific importance from the geological and geomorphological point of view. Samples were collected from all sites in 2019 and only from Mandrone in 2020. Two sampling expeditions were conducted each year, the first in July (the beginning of summer and the snow/ice-melting season) and the second in September (the end of the summer). Samples were collected between 2,435 and 3,032 m above sea level. The sampled glaciers have an area ranging from 0.14 km² (Carè Alto) to 10.14 km² (Mandrone) (Smiraglia and Diolaiuti, 2015).

2.2. Chemical analysis

Analytical standards were purchased from Merck Life Science (Milan, Italy), and solvents were obtained from VWR International (Milan, Italy).

The analytes selected for this study belong to three different categories:

- CUPs: terbutylazine (TBZ) and its metabolite desethyl-terbutylazine (d-TBZ), chlorpyrifos (CPY), chlorpyrifos-methyl (CPY-m), S-metolachlor (S-MTL), and pendimethalin (PEN);
- Musk fragrances: galaxolide (HHCb) and tonalide (AHTN); and
- Polycyclic aromatic hydrocarbons (PAHs): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBahA), indeno[1,2,3-cd]pyrene (IP), and benzo[ghi]perylene (BghiP).

All samples were collected using polypropylene bottles with screw caps and pre-rinsed with organic solvents (milliQ water, acetone and n-hexane). Approximately 10 L of water was collected from each sample site. To minimise any alteration during the transfer and storage of the water samples, they were refrigerated during transport and stored at

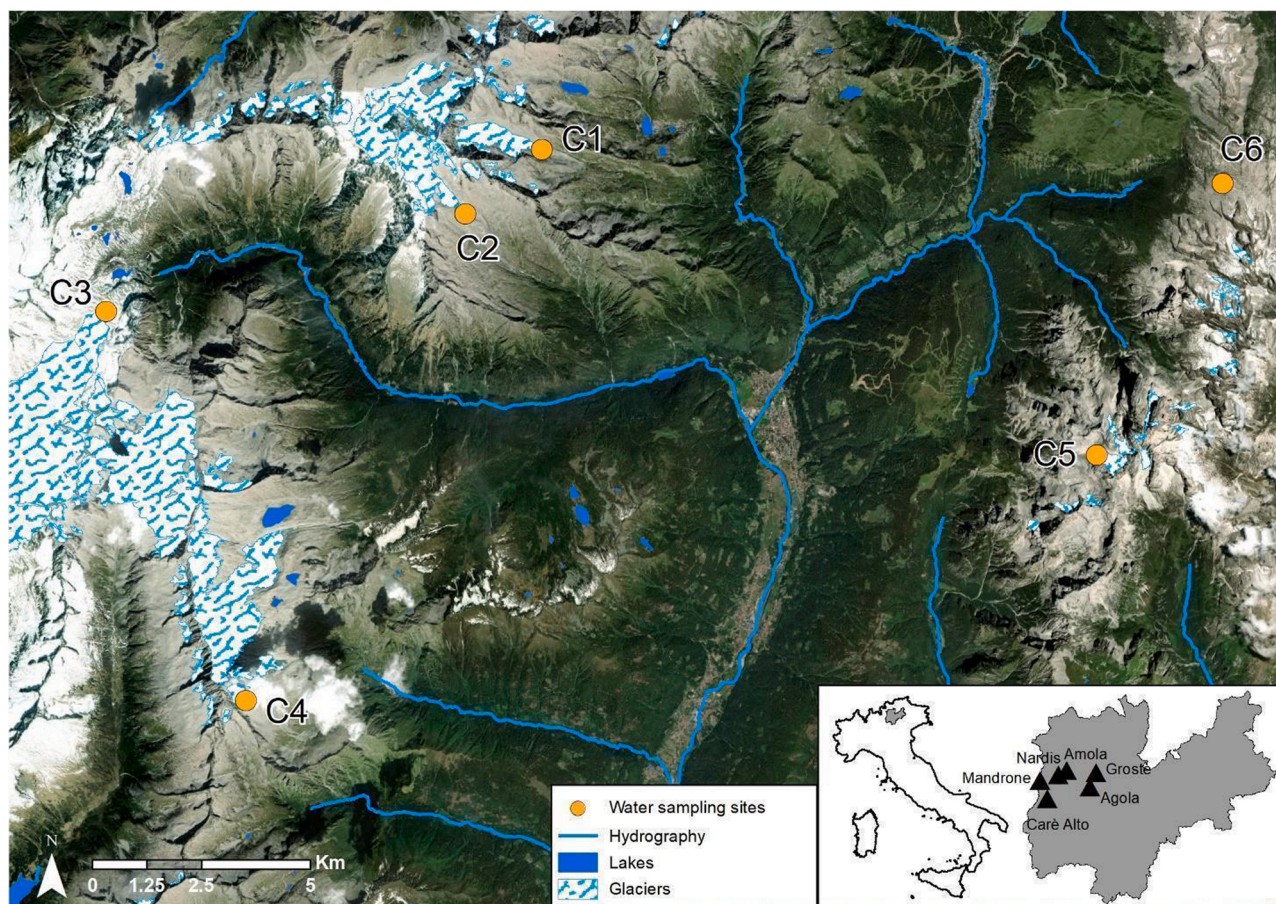


Fig. 1. Study area and sampling sites. Further details are provided in Table S1.

–20°C until analysis

Water samples were filtered through glass-fibre filters (GFFs, 0.45 mm, Whatman, England) to separate particulate matter. Before sampling, the filters were baked at 450°C for 4 h to remove impurities and stored by wrapping in pre-cleaned aluminium foil. The filtered material was stored by wrapping in decontaminated aluminium foil and refrigerated at –20°C until analysis. Filtered water samples were eluted in 1-L aliquots on solid-phase extraction (SPE) cartridges (Oasis HLB, 500 mg, 6 cc, Waters, Italy). The cartridges were pre-cleaned with 5 mL each of n-hexane ($\geq 95\%$, PESTINORM, VWR Chemicals, Milan, Italy), methylene chloride ($\geq 99.8\%$, CHROMASOLV for HPLC, Honeywell-Riedel-de Haën from VWR Chemicals, Milan, Italy), and ethyl acetate ($\geq 99.7\%$, PESTINORM®, VWR Chemicals, Milan, Italy) and conditioned with 3 mL each of methanol ($\geq 99.9\%$, CHROMASOLV for HPLC, Honeywell-Riedel-de Haën) and deionised water (Milli-Q, CHROMASOLV Plus, Honeywell-Riedel-de Haën). After extraction, the cartridges were dried under vacuum pressure. The extracts were eluted (under gravity) with 15 mL of n-hexane, 10 mL of n-hexane–methylene chloride (30:70 ratio), and 6 mL of ethyl acetate.

GFFs were extracted in an ultrasonic bath at 40°C using hexane, dichloromethane, and ethyl acetate as the extraction solvents. Recovery standards (a mixture of seven ¹³C-labelled Polychlorinated Biphenyls-PCB) were added to each sample. Water samples and GFFs were evaporated to 0.01 mL under a gentle stream of nitrogen and reconstituted to 0.04 mL with cyclohexane. Finally, the Agilent 7693A Automatic Liquid Sampler was used to add 0.2 μ L of internal standard (PCB141) to each sample. Thanks to the sandwich injection technique, two aliquots are drawn into the autosampler syringe and simultaneously vaporized and mixed in the liner. This eliminates the need to spike each vial reducing manual error from internal standard. The samples were analysed by gas

chromatography (GC)–mass spectrometry (MS) in single-ion monitoring (SIM) mode.

Compounds of interest were identified and quantified using an Agilent Technologies (Santa Clara, California, United States) 5977 B Mass Selective Detector (MSD) with 8860 GC equipped with a 30-m HP5-MS capillary column. Details on the oven program, MS setting, and limit of detection are provided in Supporting Information (Table S2).

2.3. Quality control

A set of three water blanks and three blank filters were analysed using the methods described in Section 2.2 to evaluate the potential contamination of samples due to handling during laboratory operations. Cartridges and filters were pre-cleaned before the extraction procedure as reported in Par 2.2. Traces of some compounds (HHCB, AHTN, S-MTL, Nap, Phe, Act, and Flu) were found in the blanks and used to correct the chemical concentrations in the samples. The correction percentages are 2.7% for HHCB, 2.2% for AHTN, 12.5% for S-MTL, 15% for Nap, 15.2% for Phe, 14.2% for Act, and 10.4% for Flu. The recovery efficiency of each selected compound was tested in triplicate at a fortification level of 10 ng/L. Mean recovery efficiency ranged between 70% and 130%, with a relative standard deviation (RSD) below 20% ($n = 3$; Table S3).

2.4. Risk characterisation

In current environmental risk assessment procedures, risk is usually expressed as a simple number—measured environmental concentration (MEC) or predicted no-effect concentration (PNEC)—or toxicity exposure ratio (TER), which represents a threshold that must not be exceeded to avoid adverse effects on ecosystems. For synthetic musk fragrances

and PAHs, risk characterisation is based on the risk quotient (RQ) method, which compares the MEC with the respective PNEC of each substance i as follows:

$$RQi = MECi / PNECi \quad (1)$$

where $PNECi$, derived from the potential effects on non-target organisms representative of aquatic environments (algae, invertebrates, and fish), was obtained from EU Risk Assessment Reports (ECHA 2008a,b,c) and MEC from Table S4. Under the European Existing Substance Regulation (European Commission Tech, 2003), RQ values are classified as follows: no risk ($RQ < 0.01$), low risk ($RQ = 0.01-0.1$), medium risk ($RQ = 0.1-1$), and high risk ($RQ > 1$).

The risk posed by CUPs in meltwater to cryophilic communities was calculated using TER. This approach compares the median effective concentration (EC50) and MEC as follows:

$$TERi = EC50i / MECi \quad (2)$$

where $EC50i$ is the toxicity of each pesticide i , obtained from the Pesticide Properties Database (PPDB; Lewis et al., 2016), and $MECi$ values are listed in Table S4. Following Regulation 1107/2009 (European Commission, 2009), when TER exceeds the value of 10 for algae and 100 for *D. magna* and fish, risk can be considered negligible.

In order to calculate the risk for the mixture of synthetic fragrances, PAHs, and CUPs we have applied the Concentration Addition (CA) model, which is commonly used when compounds are judged to have the same mode of action (Loewe and Muischnek, 1926).

The CA model is considered the most precautionary approach as often overestimates the risks for those compounds showing a different mode of action (McGrath et al., 2019).

The mixture toxicity (HI = hazard Index) can be mathematically expressed as follows:

$$HI = \sum_i^n \frac{Ci}{PNECi} = 1 \quad (3)$$

where n is the number of substances in the mixture that provoke $x\%$ of the total effect, Ci is the concentration of the i th component in the mixture and $PNECi$ refers to the concentration of the respective component that causes predicted no effect when applied singularly. Further details on PNEC derivation are in Rico and co-workers (Rico et al., 2021a).

When the HI is lower than 1, the ecological risks can be classified as low or insignificant, while HI higher than 1 indicates possible negative effects on the aquatic community.

The methods described to date make simple and very conservative assumptions based on the precautionary principle; in case of unacceptable risk, a more sophisticated and less conservative approach can be used. Ecological risk assessment procedures can further facilitate a probabilistic approach, based on species sensitivity distribution (SSD), which enables the determination of a safe concentration of a substance in terrestrial and aquatic ecosystems (Vighi and Villa, 2013). SSDs are cumulative functions of toxicity data for a given compound and are used to calculate the concentration of chemicals that are potentially dangerous to 5% of species of a given community (Posthuma et al., 2019; Rico et al., 2017, 2021b).

In this study, to assess the risk to the community (TER), the $HC5i$ (hazardous concentration to 5% of the tested species, predicted with 50% certainty for a compound i) was compared with the MEC as follows:

$$TERi = (HC5i / AF) / MECi \quad (4)$$

$HC5i$ was subsequently divided by an appropriate assessment factor (AF) to extrapolate the PNEC, which is frequently used to summarise the overall hazard assessment in ERA (Posthuma et al., 2019; Finizio and Vighi, 2014). As per the European Existing Substances Regulation (European Commission Tech, 2003), an AF of 5 was applied to the $HC5$

values.

3. Results and discussion

The bulk concentrations of the compounds detected in the meltwater samples (reported as the sum of the dissolved and absorbed phases) are reported in Table 1a,b. Owing to the unavailability of replicates, the results refer to individual samples.

3.1. CUPs

The insecticides, CPY and CPY-m, and the herbicide, TBZ, were frequently detected in all samples. By contrast, the herbicide S-MTL was only sporadically observed, and PEN levels were always below the detection limit. Similar results for PEN were observed by Ferrario and coworkers (2017a). Regarding the other CUPs, TBZ concentrations up to 2.96 ng/L were detected in the same area, (Ferrario et al., 2017a; Rizzi et al., 2019) while values in the range of 0.32-2.27 ng/L were observed in a glacial lake of Spain (Santolaria et al., 2015). CPY was found in the range of 0.21-70.3 ng/L in meltwater from different glaciers in the Italian Alps (Ferrario et al., 2017a; Rizzi et al., 2019) and from 0.12 to 0.62 in the Spanish Pyrenees (Santolaria et al., 2015). Finally, CPY-m was only reported by Rizzi et al. (2019) in concentrations up to 2.56 ng/L.

TBZ was found at five of six sampling sites in July 2019, with concentrations ranging from a minimum of 0.11 ng/L at Grostè to a maximum of 1.50 ng/L in meltwater from the Mandrone Glacier. No trace of this herbicide was found in samples collected from Carè Alto. In September 2019, TBZ was found only in meltwater from the Carè Alto Glacier at a concentration of 0.2 ng/L.

The lack of its trace in July at Carè Alto is in contrast with previous evidence (Ferrario et al., 2017a; Rizzi et al., 2019) and with the present data regarding the other investigated glaciers. A hypothesis that needs to be better investigated is the role of the altitude of the monitored area and the elevation of the planetary boundary layer (PBL). Carè Alto is the highest sampling site (3032 m above sea level) among those monitored in this sampling campaign and in the previous ones (Ferrario et al., 2017a; Rizzi et al., 2019) which were always below 2760 m above sea level. The atmospheric stratification plays a crucial role in determining the transport of contaminants to high elevation sites. Indeed, previous knowledge has suggested that POPs concentrations in the Italian Alps were lower above the PBL where the emission of contaminants occurs (Maggi et al., 2006; Hageman et al., 2015). Nowadays, the PBL dynamics are still not well understood in mountainous systems due to the complexity of meteorological phenomena (De Wekker and Kossmann, 2015). PBL height may vary depending on different drivers such as seasons, sites, terrain morphology, and cloud cover (Ketterer et al., 2014). Rain events are important for the scavenging of soluble molecules such as TBZ (Ferrario et al., 2017a), but, at the same time, precipitation acts to suppress the solar radiation and the development of PBL (Pan et al., 2019). Therefore, all these phenomena, that can favour the transfer of TBZ from air to the land, could not take place at the Carè Alto glacier, which could often be above the PBL during the spring season when TBZ is usually applied on crops. On the contrary, during the warmest season, the PBL is often above 3000 m above sea level, allowing the transport upwards of TBZ. This hypothesis needs to be confirmed by further studies on the relationships between the development of PBL in the Alpine area and the fate of organic contaminants.

The metabolite dTBZ showed a fluctuating trend across sampling sites: in July 2019 it was found in only three glaciers (Amola, Mandrone, and Carè Alto) at very similar concentrations (1.33–1.58 ng/L). Conversely, in September 2019, dTBZ was detected in almost all glacial meltwater samples (with the exception of Vedretta d'Amola) at a considerably large concentration range of 0.08–0.71 ng/L. Interestingly, the highest concentration (1.33 ng/L) was recorded in non-glacial meltwater from the Grostè Spring. In samples collected from the

Table 1

Concentrations of the compounds detected in the meltwater samples in July (1a) and September (1b) reported as the sum of the dissolved and the sorbed phases and expressed in ng/L.

Table 1a	Vedretta d'Amola	Vedretta di Nardis	Mandrone	Mandrone	Care Alto	Vedretta d'Agola	Groste
Sampling date	July 2019	July 2019	July 2019	July 2020	July 2019	July 2019	July 2019
dTBZ	1.33	nd	1.34	1.68	1.58	nd	nd
TBZ	0.58	0.26	1.50	0.93	nd	0.13	0.11
S-MTL	nd	nd	nd	1.00	0.40	nd	nd
PEN	nd	nd	nd	nd	nd	nd	nd
CPY-m	0.02	nd	0.08	0.06	nd	nd	nd
CPY	1.06	nd	1.27	0.28	nd	nd	0.25
HHCB	2.29	8.47	10.9	11.7	5.91	5.70	10.7
AHTN	0.48	2.38	2.94	2.42	1.56	1.43	2.10
Nap	0.73	7.10	1.55	0.33	3.44	5.07	4.14
Acy	0.13	0.18	0.27	0.04	0.06	0.14	0.24
Ace	0.31	0.44	0.05	nd	0.03	0.39	0.42
Flu	0.45	0.94	0.37	0.10	0.41	0.60	0.56
Phen	2.39	1.98	1.70	1.36	1.01	1.93	1.69
Ant	0.13	0.14	0.15	0.22	0.06	0.12	0.11
Fl	0.26	0.27	0.44	2.57	0.23	0.86	0.32
Pyr	0.42	0.02	0.60	3.74	nd	0.15	0.04
BaA	0.02	0.06	0.09	0.13	0.04	0.20	0.05
Chr	0.05	0.30	0.27	0.23	0.21	0.61	0.25
BbF	0.03	0.02	0.02	0.08	nd	0.02	0.03
BkF	nd	0.06	0.05	0.06	0.05	0.17	0.05
BaP	0.08	0.02	0.02	0.02	0.04	0.09	0.06
DBaH	0.02	nd	nd	0.02	nd	nd	nd
IP	nd	nd	nd	nd	nd	nd	nd
BghiP	0.02	0.02	0.02	0.02	0.02	0.02	0.03
Table 1b	Vedretta d'Amola	Vedretta di Nardis	Mandrone	Mandrone	Care Alto	Vedretta d'Agola	Groste
Sampling date	Sept 2019	Sept 2019	Sept 2019	Sept 2020	Sept 2019	Sept 2019	Sept 2019
dTBZ	nd	0.10	0.35	0.32	0.71	0.08	1.33
TBZ	nd	nd	nd	0.12	0.20	nd	nd
S-MTL	nd	nd	nd	28.6	nd	nd	nd
PEN	nd	nd	nd	nd	nd	nd	nd
CPY-m	1.33	0.43	0.19	0.07	0.07	0.03	nd
CPY	0.40	0.24	0.36	0.47	0.90	0.58	0.24
HHCB	7.56	4.33	1.87	16.2	7.80	4.33	2.64
AHTN	1.03	0.91	0.66	2.60	1.18	0.62	0.33
Nap	nd	0.74	nd	4.84	2.17	2.61	0.17
Acy	0.03	0.15	0.10	0.25	0.24	0.22	0.10
Ace	0.28	0.02	0.26	0.16	0.47	0.19	0.18
Flu	0.31	0.24	0.09	0.66	0.41	0.30	0.29
Phen	0.79	0.35	0.87	3.41	2.38	1.34	1.27
Ant	0.09	0.04	0.04	0.45	0.30	0.21	0.07
Fl	0.14	0.44	0.38	3.39	0.63	0.37	0.37
Pyr	0.13	0.28	0.16	2.85	0.57	0.18	0.29
BaA	0.42	0.06	0.01	0.58	0.28	0.12	0.08
Chr	0.06	0.13	0.02	1.83	0.15	0.40	0.22
BbF	nd	0.08	0.03	0.54	0.06	0.01	0.04
BkF	nd	0.03	nd	0.17	0.11	0.08	0.08
BaP	0.12	0.06	0.06	nd	0.08	0.05	0.06

Mandrone Glacier in July and September 2020, the concentrations of TBZ and its metabolite dTBZ were markedly similar to those of the same month of the previous year. TBZ concentrations of 0.93 and 0.12 ng/L were recorded in July and September 2020, respectively, comparable to the values of 1.50 and <0.01 ng/L observed in 2019. Similarly, dTBZ concentrations recorded in July and September 2020 were 1.68 and 0.32 ng/L, respectively, comparable to the values of 1.34 and 0.35 ng/L measured in 2019.

The seasonal differences observed in this study are consistent with previous findings in the Alpine region (Ferrario et al., 2017a; Rizzi et al., 2019) and could be explained by the high solubility of TBZ, which can be transported at the beginning of the melting season, when precipitation is more frequent. Conversely, the considerably lower TBZ concentrations in late summer could be due to bacterial degradation, resulting in the formation of its metabolite dTBZ (Ferrario et al., 2017a; Pittino et al., 2018).

The herbicide S-MTL was detected in only one sample from July 2019 (Carè Alto), at a concentration of 0.40 ng/L, and was found in no samples from September 2019. A small amount of S-MTL was recorded in samples collected from Mandrone in July 2020 (1 ng/L), but an

unexpectedly high peak was measured in September 2020 (28.6 ng/L). The sporadic presence and unusual peak concentrations of S-MTL in Alpine meltwater was previously observed by Rizzi et al. (2019) in meltwater collected in 2016 from the Gigo Alto and Forni Glaciers (6.81 and 4.62 ng/L respectively).

Organophosphorus insecticides like CPY and CPY-m were used for pest control on fruit trees cultivated extensively in the alpine valleys in North-Eastern Italy since the ban of the European Commission occurred in 2020. Different studies (Muir et al., 2004; Hoferkamp et al., 2010; Ferrario et al., 2017a, Rizzi et al., 2019) have modelled or observed in monitoring campaigns that CPY can travel through the atmospheric compartment for a distance up to 400 km and can be transported from the cultivated areas to the Alps. Low temperatures of high altitude areas enhance the condensation of this compound and the storage in the permanent or semi-permanent glacial masses (Gabrieli et al., 2011; Villa et al., 2014; Kirchgeorg et al., 2016). As a consequence of the melting process, insecticides stored are released with the melting water during the summer season.

In July 2019, CPY-m was found only in two glaciers (Amola and Mandrone) and CPY in three glaciers (Amola, Mandrone, and Grostè),

while both the substances were measured in almost all the samples collected in September 2019 (with the exception of Grostè). Notably, meltwater samples collected from Nardis, Carè Alto, and Agola did not present suspended material, which could explain the absence of active substances with high octanol/water partition coefficient ($\log K_{ow}$) values. Indeed, because of their high lipophilicity, organophosphorus insecticides have a marked affinity for the lipophilic organic phase and therefore favour distribution as particulate material over aqueous phase (Rizzi et al., 2019).

The concentrations of CPY-m measured in July 2019 were very similar between the glaciers of Amola (0.02 ng/L) and Mandrone (0.08 ng/L). In September 2019, marked spatial variability was observed: the lowest concentration was detected at Agola (0.03 ng/L), and the highest at Amola (1.33 ng/L). Focusing on the Mandrone Glacier, CPY-m concentrations (0.08 and 0.06 ng/L) were similar in July 2019 and 2020, respectively, but the concentrations (0.19 and 0.07 ng/L) were dissimilar in September 2019 and 2020, respectively.

In July 2019, a CPY concentration of 0.25 ng/L was recorded in the non-glacial Grostè sample, while CPY concentrations of 1.06 and 1.27 ng/L were observed at Mandrone and Amola, respectively. In September 2019, CPY concentrations ranged from 0.24 ng/L (Grostè) to 0.90 ng/L (Carè Alto). Considerable inter-annual variation was observed at the Mandrone Glacier, with concentrations of 1.27 and 0.28 ng/L in July 2019 and 2020 and 0.36 and 0.47 ng/L in September 2019 and 2020, respectively. Increased CPY concentrations at the beginning of the melting season have also been reported by other studies and are related to the melting of the annual snowpack (Santolaria et al., 2015; Ferrario et al., 2017a).

3.2. Synthetic fragrances

In July 2019, the concentrations of HHCB and AHTN in glacial meltwater samples were in the range of 2.29–10.9 and 0.48–2.94 ng/L, respectively, while concentrations in the Grostè non-glacial sample were 10.7 and 2.10 ng/L, respectively. Very similar values were detected in late summer, showing the absence of a seasonal trend; in September 2019, the concentrations of galaxolide and tonalide in glacial meltwater samples ranged from 1.87 to 7.80 ng/L and 0.62 to 1.18 ng/L, respectively. Low galaxolide and tonalide concentrations of 2.64 and 0.33 ng/L, respectively, were detected in the non-glacial sample.

The investigation of fragrances is important because they are introduced to the environment in considerable amounts, as they are present in numerous personal hygiene products. However, there is limited information on the presence of synthetic musk fragrances in meltwater samples. In the Forni Glacier (Italian Alps) Villa et al. (2014) found concentrations of HHCB and AHTN in the range of 2.13–5.07 and 2.28–9.83 ng/L, respectively, while Ferrario et al. (2017a) found mean HHCB and AHTN concentrations of 1.25 and 1.27 ng/L, respectively. High values were reported by Hu et al. (2012), who recorded mean HHCB and AHTN concentrations of 11.0 and 33.3 ng/L, respectively, in snow samples from the Beijing urban area. Fragrances have also been detected in surface snow at Svalbard (Vecchiato et al., 2018), with concentrations up to 72 ng/L, and these compounds have been monitored for the first time in the Elbro ice core (Vecchiato et al., 2020), where an increase in concentration from 1930 to 2005 was reported.

The estimated mass of HHCB and AHTN used in Europe in 2000 was 1,427 and 358 tons, respectively, with a ratio of approximately 4 (OSPAR Commission, 2004). The concentrations in the samples from the Adamello-Brenta Nature Park reflect these amounts; the HHCB/AHTN ratio of glacial meltwater samples ranged from 3.6 to 4.7 (mean 3.9) in July 2019, and a ratio of 5.1 was recorded in the Grostè sample. However, larger ratios were found in September 2019, ranging from 2.8 to 7.2 (mean 5.7) in glacial meltwater samples and measuring 8.0 in the non-glacial sample. A deviation in the HHCB/AHTN ratio from the used value has also been reported by other researchers (Buerge et al., 2003; McDonough et al., 2016), and its rise is related to an increased removal

of AHTN in surface water owing to photochemical reactions. Therefore, we hypothesise that in the meltwater of the Adamello-Brenta Nature Park, AHTN is photolysed more rapidly than HHCB, resulting in the progressive accumulation of HHCB on the glacial surface. Photochemical reactions can alter snowpack composition, as illustrated by Hullar et al. (2018) and Klän et al. (2001). Their studies showed that PAHs and halobenzenes can undergo photodegradation in snow and ice; therefore, we can assume that other classes of compounds can also be subjected to the same processes. Furthermore, such reactions frequently result in either the loss (i.e., degradation into more volatile compounds that can be released back into the atmosphere from the snowpack) or transformation of the parent compound.

Other post-depositional processes, such as hydrolysis, air-snow exchange of contaminants, and redistribution of the contaminants in firn and glacier ice and snowpack accumulation and melting on top of the ice, can influence the life cycle of contaminants deposited on the surface of glaciers (Grannas et al., 2013). Finally, microbial transformation of contaminants in snow play a significant role because microorganisms can degrade complex organic compounds, even at low temperatures (Stibal et al., 2012; Ferrario et al., 2017b; Pittino et al., 2018). These mechanisms could have modified the relative concentrations of the fragrances considered in this study.

3.3. PAHs

In 2019, the bulk concentration of the sum of the 16 analysed PAHs ($\Sigma 16\text{PAHs}$) exhibited ranges of 5.59–11.6 and 2.75–9.65 ng/L in glacial samples collected in July and September, respectively. PAH concentrations of 7.98 and 3.65 ng/L were measured in non-glacial samples in July and September 2019, respectively.

The observed concentrations were similar to those previously found in high-altitude Tyrolean snow samples (0.5–8.4 ng/L; Arellano et al., 2014), a firn core from the Eastern European Alps (0.5–6.2 ng/L; Kirchgeorg et al., 2016), and snow samples from the Pyrenees (5.6 ng/L; Carrera et al., 2001). Slightly increased PAH concentrations were found in snowpack from European mountain lakes (16–17 ng/L; Carrera et al., 2001) and surface snow from Ny-Ålesund, Svalbard (2.6–299 ng/L; Vecchiato et al., 2018). Lastly, a markedly high PAH concentration was recorded in a high-altitude lake in Slovakia (81 ng/L; Carrera et al., 2001).

The contribution of light compounds to the $\Sigma 16\text{PAHs}$ prevailed in PAHs with high molecular weight, representing an average of 95% of the total PAHs in July and 88% in September 2019. The PAH distribution pattern, calculated as the ratio of a single PAH concentration to the $\Sigma 16\text{PAHs}$ concentration, was generally dominated by the two- and three-ring PAHs. Nap and Phe were the most abundant compounds in samples from July 2019, representing 50–80% of the total PAH content. These two PAHs, in addition to Flu, Fl, and Pyr, dominated the distribution pattern of samples collected in September 2019, except those collected at Amola and Mandrone, where Nap was not detected. Nap, Phe, Fl and Pyr were also the most abundant compounds in the Mandrone Glacier in July 2020, accounting for more than 70% of the total PAHs. The prevalence of light PAHs is mainly related to their volatility, which allows their transport over long distances accumulating in the deposit fall-out before reaching high altitudes (Peters et al., 1995; Carrera et al., 2001).

Similar PAH distribution patterns have been reported in other European mountains. In the Eastern Alps, Gabrieli et al. (2010) found that light compounds, such as Nap, Fl, and Phe, dominated the PAH pattern, while Kirchgeorg (2016) observed that Phe, Fl, Ant, and Pyr were the most abundant. PAH patterns were also dominated by Phe, Fl, and Pyr in other European countries (Carrera et al., 2001). Compounds with low molecular weight were also found to be dominant in snow and ice over the Tibetan Plateau (Li et al., 2011) and an ice core from Mount Everest (Wang et al., 2008).

3.3.1. Origin of PAH contamination

To estimate the prevalent types of contamination sources, we examined four PAH diagnostic ratios: Fl/(Fl + Pyr), Ant/(Ant + Phen), BaA/(BaA + Chr), and IP/(IP + BghiP). According to Yunker et al. (2002), a Fl/(Fl + Pyr) ratio > 0.50 suggests combustion of grass, coal, or wood; a ratio < 0.40 is characteristic of petrogenic sources; and a ratio of 0.40–0.50 indicates liquid fossil fuel combustion.

An Ant/(Ant + Phen) ratio > 0.10 suggests a pyrogenic origin, while a ratio < 0.10 generally indicates petrogenic origins (Yunker et al., 2002). A BaA/(BaA + Chr) ratio > 0.35 is characteristic of combustion sources, a ratio < 0.20 implies petroleum sources, and a ratio of 0.20–0.35 may indicate either a petrogenic or combustion source (Hartwell et al., 2020). As reported by Skyaty et al. (2015), an IP/(IP + BghiP) ratio > 0.50 indicates biomass or coal combustion, a ratio < 0.20 is characteristic of a petrogenic source, and a ratio of 0.20–0.50 indicates liquid fossil fuel combustion.

Some uncertainties have been associated with the use of diagnostic ratios because of the different residence times and reactivity of PAHs. The Ant/(Ant + Phe) and BaA/(BaA + Chr) ratios are particularly influenced by atmospheric processes and environmental changes, whereas the Fl/(Fl + Pyr) and IP/(IP + BghiP) ratios are less sensitive (Tobiszewski and Namiesnik, 2012). Nonetheless, this method is commonly used to identify possible sources of contamination because of its simplicity.

In the majority of samples collected both in July and September 2019, the Fl/(Fl + Pyr) ratio was > 0.50, indicating biomass and coal combustion. By contrast, the Ant/(Ant + Phe) ratio suggests a petrogenic origin, as it was < 0.10 across all six samples from July and four samples from September 2019. Similar results were obtained by Vecchiato et al. (2020), who explained this apparent contradiction in contamination origin with the different reactivities of the isomers during their atmospheric transport and aging processes.

Similar to the Ant/(Ant + Phe) ratio, the BaA/(BaA + Chr) ratio is susceptible to atmospheric processes and environmental changes. In

July 2019, this ratio was < 0.20 in two samples, indicating a petrogenic origin, and it was between 0.20 and 0.35 in the other four samples, which is characteristic of a mixed source. In September 2019, samples showed a ratio either between 0.20 and 0.35 or > 0.35, indicating a mixed origin or combustion source, respectively.

Finally, it was not possible to calculate the IP/(IP + BghiP) ratio for the majority of the samples, as one of the two congeners was not found. When applicable, the ratio was between 0.20 and 0.50 or > 0.50, suggesting liquid fossil fuel combustion or biomass/coal combustion, respectively. The analysis of PAH ratios supports the hypothesis that there is negligible variability in emission sources among the glaciers in the Adamello-Brenta Nature Park.

3.4. Ecological risk

The RQ method (Equation 1) was used to assess the ecological risk posed by fragrances and PAHs. Mixture toxicity effects for the two groups of chemicals (fragrances and PAHs) were calculated according to Equation 3. The RQs of synthetic fragrances (Table S4) were < 0.01 in all six sites, indicating that these compounds might be of negligible concern, both when considered as single compounds and as mixtures.

The risk classification for those PAHs that presented a level of concern (classified as low, medium or high risk) along with the mixture toxicity is reported in Table 2. The RQs (Table S5) of light compounds (Nap, Acy, Ace, Flu, Phen, Ant) from all six sites were < 0.01 and indicated no risk. RQs of Fl and Pyr were between 0.01 and 0.1, suggesting low risk in many of the samples collected in 2019, while RQs between 0.10 and 1, indicating medium risk, were calculated for the samples collected from the Mandrone Glacier in 2020. The RQs of heavy compounds indicated negligible risk across all sampling sites. Following the worst-case methodology of the CA model, in few cases the effects induced by PAHs are predicted to be of concern. The only situations where a medium risk was highlighted are compounds in meltwater in Vedretta d'Agola in July 2019, Carè Alto in September 2019 and

Table 2

Risk classification of synthetic fragrances and PAHs based on the risk quotient (RQ) method in July (2a) and September (2b). RQ values are reported in brackets. (Low risk: $0.01 < RQ < 0.1$; medium risk: $0.1 < RQ < 1$).

Table 2a	Vedretta d'Amola	Vedretta di Nardis	Mandrone		Care Alto	Vedretta d'Agola	Groste
Sampling date	July 2019	July 2019	July 2019	July 2020	July 2019	July 2019	July 2019
FLNT	low risk (RQ:0.026)	low risk (RQ:0.027)	low risk (RQ:0.044)	medium risk (RQ:0.257)	low risk (RQ:0.023)	low risk (RQ:0.086)	low risk (RQ:0.032)
PYR	low risk (RQ:0.018)		low risk (RQ:0.026)	medium risk (RQ:0.163)			
BaA				low risk (RQ:0.011)		low risk (RQ:0.017)	
BkF						low risk (RQ:0.010)	
DBahA	low risk (RQ:0.015)			low risk (RQ:0.012)			
E16PAHs	low risk (RQ:0.07)	low risk (RQ:0.05)	low risk (RQ:0.09)	medium risk (RQ:0.46)	low risk (RQ:0.04)	medium risk (RQ:0.14)	low risk (RQ:0.06)
Table 2b	Vedretta d'Amola	Vedretta di Nardis	Mandrone		Care Alto	Vedretta d'Agola	Groste
Sampling date	September 2019	September 2019	September 2019	September 2020	September 2019	September 2019	September 2019
FLNT	low risk (RQ:0.014)	low risk (RQ:0.044)	low risk (RQ:0.038)	medium risk (RQ:0.339)	low risk (RQ:0.063)	low risk (RQ:0.037)	low risk (RQ:0.037)
PYR		low risk (RQ:0.012)		medium risk (RQ:0.124)	low risk (RQ:0.025)		low risk (RQ:0.013)
BaA	low risk (RQ:0.035)			low risk (RQ:0.049)	low risk (RQ:0.023)		
CHR				low risk (RQ:0.026)			
BbF				low risk (RQ:0.032)			
BkF				low risk (RQ:0.010)			
DBahA		low risk (RQ:0.012)		low risk (RQ:0.069)	low risk (RQ:0.033)		
I123cdP				low risk (RQ:0.028)			
BghiP				low risk (RQ:0.013)			
E16PAHs	low risk (RQ:0.07)	low risk (RQ:0.09)	low risk (RQ:0.05)	medium risk (RQ:0.70)	medium risk (RQ:0.18)	low risk (RQ:0.08)	low risk (RQ:0.07)

Mandrone in July and September 2020.

The risk, even if assessed with a very precautionary methodology in a small number of samples, highlights a hazard for the environment and potentially for human health as they can be transferred through the trophic chain (Miner et al., 2017).

The risk posed by CUPs (Table S6) detected at the six sites was determined using the TER (Equation 2). This ratio was calculated for non-target organisms that are representative of aquatic environments and then compared with the trigger values of 10 for algae and 100 for *D. magna* and fish. The risk classification for those CUPs with an unacceptable level of risk and the mixture of herbicides or insecticides is reported in Table 3a,b.

In all samples, the calculated risk to aquatic biocenosis owing to herbicides detected in meltwater was considered acceptable under current European standards, as the TERs obtained for *D. magna*, fish, and primary producers were above the risk thresholds. The risk induced by the mixture of herbicides is acceptable for the aquatic community living in all the studied glacial streams despite the unexpected high concentration of S-MTL detected in Mandrone in September 2020. The risk ratio, in fact, is orders of magnitude higher than the risk threshold of 10.

Regarding the insecticides considered in this study, the results indicate negligible risk of CPY-m to both consumers and primary producers. By contrast, CPY was found to pose a high risk to aquatic invertebrates at the Amola and Mandrone sites in July 2019. Even when considering *C. riparius* as a target species, an unacceptable level of risk from CPY exposure was determined, as TERs were consistently above the risk threshold. The chironomid *C. riparius* can be considered more representative than *D. magna* of high-altitude benthic communities, as they are dominated by the chironomid sub-family Diamesinae (Lods-Crozet et al., 2001; Lencioni, 2018). Although *C. riparius* is known to tolerate eutrophication and chemical pollution, it is more sensitive to trace pharmaceuticals (Muniz-Gonzalez, 2021) than *Diamesa* spp. (Lencioni et al., 2018, 2020). This makes *C. riparius* an excellent organism for toxicological evaluation, even for aquatic fauna of high-altitude streams. An unacceptable level of risk posed by CPY to aquatic organisms in streams fed by alpine glaciers has been previously highlighted by Rizzi et al. (2019).

It is not surprising that the risk posed by the mixture of the two insecticides (calculated according to Equation 3) resulted to be not acceptable as CPY itself drives the total toxicity.

To the best of our knowledge, no data regarding the toxicity of CPY-m to *C. riparius* are available; therefore, the risk deriving from the

mixture of the two insecticides to the sediment dwelling organisms has not been calculated. Notwithstanding this, as the insecticides share the same mode of action (acetylcholinesterase inhibitors), their mixture is likely to induces an unacceptable ecological effect on the sediment dwelling organism community.

In light of our TER results, the risk refinement for CPY was calculated as per Equation 4, using the HC5 value of 0.07 ug/L derived by Maltby et al. (2005) from freshwater arthropod single-species acute toxicity data. This refinement indicated a negligible level of risk in all samples because environmental concentrations were consistently below the effect level. Nevertheless, the risk calculated using the SSD approach may not be sufficiently precautionary, and we suggest that an ad hoc evaluation should be performed on this peculiar ecosystem. Indeed, it should be specified that the HC5 value was derived from tropical and temperate species through toxicity tests generally conducted at warm temperatures (> 20°C) and for fixed short time periods (< 96 h). Therefore, the representativeness and ability of these data to predict the sensitivity of high-altitude freshwater organisms to CPY is questionable. As highlighted by Chapman (2016), organisms adapted to cold environments show a delayed toxicity response because of physiological adaptations, slow uptake kinetics, slow growth and development, low metabolic rates, and high lipid storage compared with organisms adapted to other environments. Moreover, organisms in glacial streams are continuously exposed to contaminants released during the melting season. Recent evidence of induced behavioural changes by CPY under different thermal conditions (Lencioni et al., 2021b) have demonstrated the harmful combined effect of chemical and physical stressors.

4. Final remarks

All surface ‘cold’ waters of the Adamello Brenta Natural Park were found contaminated by currently used pesticides, synthetic fragrances, and polycyclic aromatic hydrocarbons. In particular, chlorpyrifos is the only chemical among the investigated compounds that presents an unacceptable ecotoxicological risk to the sediment dwelling organisms living in the proglacial streams. This evidence supports the ongoing proposal for listing this substance under the Stockholm Convention. Chlorpyrifos could not be the only risk to the aquatic ecosystem. Therefore, it is advisable to continuously monitor other potentially dangerous compounds that are introduced in the environment from human activities and that can be transported through medium-range atmospheric transport to high-altitude environments. The toxicity of

Table 3

Classification of risk posed by CUPs to aquatic non-target organisms (algae for herbicides and *D. magna* for insecticides) based on TERs in July (3a) and September (3b). (/ = when the environmental concentration are not detected and the associated risk can be assessed).

Table 3 a	Vedretta d’Amola	Vedretta di Nardis	Mandrone Mandrone	Care Alto	Vedretta d’Agola	Sorgente Groste
Sampling date	July 2019	July 2019	July 2019	July 2020	July 2019	July 2019
TER <i>D.magna</i> CPF	unacceptable risk (TER: 9.40E+01)	/	unacceptable risk (TER: 7.85E+01)	/	/	/
TER <i>C. riparius</i> CPF	unacceptable risk (TER: 2.26E+01)	/	unacceptable risk (TER: 1.88E+01)	unacceptable risk (TER: 8.47E+01)	/	unacceptable risk (TER: 9.50E+01)
£ herbicides	acceptable risk (TER: 5.81E-03)	acceptable risk (HI: 2.19E-03)	acceptable risk (HI: 1.34E-02)	acceptable risk (HI: 8.92E-03)	acceptable risk (HI: 1.13E-03)	acceptable risk (HI: 8.98E-04)
£ insecticides <i>D.magna</i>	unacceptable risk (HI: 1.07E+00)	/	unacceptable risk (HI: 1.29E+00)	acceptable risk (HI: 2.94E-01)	/	acceptable risk (HI: 2.53E-01)
Table 3b	Vedretta d’Amola	Vedretta di Nardis	Mandrone Mandrone	Care Alto	Vedretta d’Agola	Sorgente Groste
Sampling date	September 2019	September 2019	September 2019	September 2020	September 2019	September 2019
TER <i>C. riparius</i> CPF	unacceptable risk (TER: 6.06E+01)	/	unacceptable risk (TER: 6.61E+01)	unacceptable risk (TER: 5.13E+01)	unacceptable risk (TER: 2.67E+01)	unacceptable risk (TER: 4.17E+01)
£ herbicides	/	acceptable risk (HI: 6.79E+05)	acceptable risk (HI: 2.52E+04)	acceptable risk (HI: 1.25E+03)	acceptable risk (HI: 2.17E+03)	acceptable risk (HI: 9.48E+04)
£ insecticides <i>D.magna</i>	acceptable risk (HI: 6.18E-01)	acceptable risk (HI: 3.11E-01)	acceptable risk (HI: 3.95E-01)	acceptable risk (HI: 4.80E-01)	acceptable risk (HI: 9.13E-01)	acceptable risk (HI: 2.40E-01)

the mixture is another aspect that should be routinely evaluated as different risk scenarios were obtained when a single compound or the mixture were considered. The presence of these substances demonstrates that the quality of the park's high-altitude waters is compromised, with ecosystem and water-soil meta-ecosystem effects to be clarified.

We are experiencing a rapid decline of freshwater biodiversity even at high altitude due to the combined effect of global warming and pollution by contaminants. This implies the reduction or the loss of ecosystem services supplied by freshwater biodiversity and in general natural landscapes that support human welfare and livelihoods globally.

Studies such as our own supply knowledge on the present emergency state, and might help policymakers and protected area managers to draw effective conservation and management plans of freshwater ecosystems. Further research is needed to deeper investigate the relationships between aquatic and terrestrial ecosystems on the proglacial plane, necessitating a holistic view of the environment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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