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## Research Article

# Glacier foreland insect uptake synthetic compounds: an emerging environmental concern

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### Abstract

Pesticides, synthetic fragrances and polycyclic aromatic hydrocarbons contaminated two glacier-fed streams (Amola, Mandrone) and one spring (Grostè) in the Italian Alps. Ten compounds (chlorpyrifos (CPY), chlorpyrifos-methyl (CPY-m), galaxolide (HHCB), tonalide (AHTN), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (BaA)) accumulated in aquatic larvae of chironomids (*Diamesa steinboeckii*, *D. latitarsis*, *D. bertrami*, *D. tonsa*, *D. zernyi*, *Pseudokiefferiella parva*, Orthocladinae) and tipulids. Their tissue concentrations (detected by gas chromatography coupled with mass spectrometry) ranged from  $1.1 \pm 0.1$  ng/g d.w. (= dry weight) (CPY-m in *D. tonsa* from Amola) to  $68.0 \pm 9.1$  ng/g d.w. (Pyr in *D. steinboeckii* from Mandrone). HHCB, AHTN, and CPY, with one exception, were accumulated by all aquatic insects. Six compounds (CPY, CPY-m, HHCB, AHTN, Fl, Pyr) also contaminated carabids (*Nebria germarii*, *N. castanea*, *N. jockischii*) predated adults of merolimnic insects. Their tissue concentrations ranged from  $1.1 \pm 0.3$  ng/g d.w. (CPY-m in *N. germarii* from Mandrone) to  $84.6 \pm 0.3$  ng/g d.w. (HHCB in *N. castanea* from Grostè). HHCB and AHTN were accumulated by all *Nebria* species. Intersite and interspecies differences were observed, which might be attributed to different environmental contamination levels. There was a stronger similarity between species from the same site than among the same species from different sites, suggesting that uptake is not species specific. At all sites, the concentration of xenobiotics was higher in larvae than in water and comparable or higher in carabids than in larvae from the same site, suggesting trophic transfer by emerging aquatic insects to their riparian predators.

### Keywords

Chironomidae (*Diamesa*)

Carabidae (*Nebria*)

Pesticides

Synthetic fragrances  
 Polycyclic aromatic hydrocarbons  
 Insect conservation  
 Melting glaciers  
 Italian Alps

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## Introduction

Synthetic compounds are increasing in their total amount, variety, and distribution in the environment (Malaj et al. 2014; Bernhardt et al. 2017). They are transported through the atmosphere at medium-long distance from emission sources and at high altitude (Villa et al. 2001, 2006, 2017; Daly and Wania 2005; Finizio et al. 2006; Bogdal et al. 2009; Guzzella et al. 2016; Ferrario et al. 2017). Here, due to cold condensation, these compounds can be trapped in snowpack and glaciers that act for them as temporary traps (Kirchgeorg et al. 2016).

During ablation, from spring to late summer, these compounds are released in streams, ponds, and lakes fed by melting snow and ice (Villa et al. 2014; Miner et al. 2017; Rizzi et al. 2019, 2022; Pawlak et al. 2021). Some of these compounds, i.e., polycyclic aromatic hydrocarbons, pesticides, and synthetic fragrances, are contaminating alpine waters globally due to this process (Grannas et al. 2013; Miner et al. 2018). Specifically, in Northern Italy, according to the analysis of the trajectories of the air masses reported by Villa et al. (2014), the main source of these compounds is the Padana Plain, an intensively cultivated and highly urbanized area including the largest industrialized Italian cities.

Among pesticides, the organophosphorus insecticides, chlorpyrifos and chlorpyrifos-methyl, found widespread also in the mountains, may no longer be a problem in the future, having been widely used to control insect pests on a range of crops but banned by the European Commission in 2020 (Rizzi et al. 2022). Among synthetic fragrances, galaxolide and tonalide are introduced to the environment in considerable amounts, as they have been used in many consumable goods, such as perfumes, make-up, other personal care products, and household cleaners (McDonough et al. 2016). Synthetic fragrances can be found in air, surface and groundwater, sediments, and organisms, based on the complexity of biogeochemical reactions occurring during dispersion (Vecchiato 2023). The analysis of sediment and ice core archives highlighted that the amount and seasonality of accumulation of fragrances in remote areas is influenced by the melting dynamic (Vecchiato 2023). Generally, galaxolide accumulates on ice and snow more than tonalide being the latter photolyzed more rapidly than the former (Villa et al. 2014). Polycyclic aromatic hydrocarbons can also undergo degradation into more volatile compounds that return into the atmosphere or can be transformed in the secondary compounds (metabolites) (Rizzi et al. 2022).

Biota colonizing alpine habitats is exposed first to this plethora of compounds (Bizzotto et al. 2009; Miner et al. 2019). Specifically, aquatic organisms inhabiting melting waters are directly exposed to these compounds and their metabolites with effects that are still largely unknown (Bizzotto et al. 2009; Morselli et al. 2014; Miner et al. 2019; Lencioni et al. 2021). According to literature (Katagi and Tanaka 2016; Gao et al. 2022), their accumulation can occur through the body cuticle from water or orally from food and sediment. Generally, dietary exposure represents the primary route of uptake of organic and inorganic contaminants through the trophic chain, starting from primary consumers (Fletcher et al. 2022). According to Timmermans and Walker (1989), contaminant amount in aquatic insects can remain the same or change during metamorphosis and emergence into flying adults, depending on the chemical properties of the contaminant, insect species, and levels of contamination (Fletcher et al. 2022). It also depends on the mass loss in the transition from stage to another (Chételat et al. 2008; Kraus et al. 2021). Overall, there is not a rule, and not all contaminants are generally transferred from aquatic larva to later life stages (Walters et al. 2008; Fletcher et al. 2022).

A recent study by Rizzi et al. (2022) detected 22 contaminants (five pesticides, two fragrances, and 15 polycyclic aromatic hydrocarbons, all with trace concentrations < 15 ng/L) in glacial and nonglacial habitats in the Italian Alps, among which six were included in the present work. Risk characterization derived from the potential effects on nontarget organisms representative of aquatic habitats (algae, invertebrates, and fish) indicated that only polycyclic aromatic hydrocarbons and chlorpyrifos posed a low-medium risk at most of the sites, while for the other compounds, the calculated risk to aquatic communities was acceptable under the current guidelines (European Commission 2009). However, the presence and behavior of this pesticide and, in general, synthetic organic compounds in these remote ecosystems on aquatic wildlife are still little investigated, and there is no evidence in the literature on their potential transfer from the aquatic to the riparian food web through merolimnic insects in ecosystems located in glacialized areas of the planet.

Insect species from glacier-fed streams are merolimnic, with aquatic larvae and terrestrial adults that fly away from the stream. Adults of merolimnic insects serve as an important food resource for riparian consumers, such as spiders, beetles, lizards, birds, and bats (Reinhold et al. 1999; Baxter et al. 2005; Walters et al. 2008), proving them 25–100% of the necessary energy (Paetzold et al. 2005; Cristol et al. 2008; Roodt et al. 2022). Chironomids (Diptera Chironomidae) with species of the genus *Diamesa* represent the main and even exclusive taxon colonizing glacier-fed streams (Lencioni 2018). Carabids (Coleoptera Carabidae) with species of the genus *Nebria*, along with spiders, are the prevalent predators of chironomids in glacier forelands (Hågvar and Pedersen 2015; Sint et al. 2019; Gobbi 2020; Gobbi and Lencioni 2020). Specifically, in glacier forelands, chironomid emergence from streams, ponds, or lakes can be high and thus serves as an important food source for carabids (Hågvar et al. 2016). Within this context, we aimed to assess the uptake of the contaminants found by Rizzi et al. (2022) in (1) the larvae (and pupae and adults at one site) of aquatic insects (mainly *Diamesa* spp.) living in glacier-fed streams and in one high-altitude spring and (2) the ground-dwelling predator insects (adults of *Nebria* spp.) visiting the riparian zone where aquatic insects emerge, crawl, and fly.

Our hypotheses were as follows:



1. In contaminated waters, aquatic insects accumulate contaminants, with most lipophilic compounds (i.e., those with a higher n-octanol-water partition coefficient ( $K_{ow}$ ) that accumulate in lipid tissues) in larger amounts than the others and in concentrations higher than those measured in the environment (Gobas and Morrison 2000). The lipophilicity of a compound affects its ability to cross biological membranes, produce toxic effects, and concentrate in organisms, giving rise to bioaccumulation and magnification through the food chain. Additionally, if incorporated into body tissues of the larvae, we expected that at least some contaminants are also present in the pupae (still aquatic) and in the adults.
2. The compounds accumulated in chironomids are also present (at least partly) in their terrestrial predators in equal or higher concentrations than in the prey (Grisoni et al. 2016; Richmond et al. 2018).

## Methods

### Study area and animal sampling

Larvae of chironomids (*Diamesa* spp.) and adults of carabids (*Nebria* spp.) were collected in the glacier foreland of the Amola and Mandrone glaciers (both in the siliceous Adamello-Presanella Mts) and in the high-altitude spring Grostè, partially fed by permafrost (in the calcareous Brenta Dolomites Mts) (Boeckli et al. 2012; Seppi et al. 2012), in the Italian Alps (Trentino Province) (Table 1, Fig. 1).

**Table 1**

Sampling sites and number of animals collected. Glacier area ( $\text{km}^2$ ) (from Smiraglia and Diolaiuti, 2015): Amola = 0.81, Adamello-Mandrone = 0.60 (Trentino sector); 10.14 (total area including the Lombardy sector)

	Amola glacier	Mandrone glacier	Grostè spring
Mountains range	Presanella	Adamello	Brenta
Altitude (m a.s.l.)	2557 (front)	2583 (front)	2435
UTM X; UTM Y	630613; 5119545	620685; 5115,838	646305; 5118809
Sampling date	27 Aug–05 Sept 2019	01–03 Sept 2019	24–26 August 2019
N. individual collected (Chironomidae <i>Diamesa</i> spp. larvae; Carabidae adults)	~ 5000 (4 <i>Diamesa</i> species); 50 ( <i>N. germarii</i> )	~ 3700 (5 <i>Diamesa</i> species; 24 ( <i>N. germarii</i> + 11 <i>N. jockischii</i> ))	~ 1700 (2 <i>Diamesa</i> species); 17 ( <i>N. castanea</i> )

**Fig. 1**

**A** Sampling of aquatic stages of Chironomidae in the Mandrone glacier-fed stream in 2020 ©V. Lencioni. **B** Amola glacier-fed stream and glacier front in 2019 ©V. Lencioni. **C** Grostè Spring (in 2021) ©V. Lencioni. **D** Carabid *Nebria jockischii*, the model species collected in the Mandrone glacier plane

© eurocarabidae.de. **E** Carabid *Nebria germarii*, the model species collected in the Amola glacier plane ©F. Pupin. **F** Chironomid *Diamesa zernyi* larva from the Mandrone glacier-fed stream ©V. Lencioni



Specifically, chironomids were collected within 250-m downstream of the glacier front and in the spring employing a pond net (30 × 30 cm, mesh size 100  $\mu\text{m}$ ) (Scubla SNC, Italy), sorted in the field, transferred to plastic bottles filled with stream water, and transported to the laboratory in a refrigerated bag. Species name was confirmed at  $\times 50$  under the stereomicroscope (MZ 7.5; Leica Microsystems, Germany) according to Rossaro and Lencioni (2015). The larvae were reared at 2 °C in 1-L glass aquaria with stream or spring water in a thermostatic chamber (ISCO, model FTD250-plus; Teledyne ISCO, Inc., Lincoln, NE, USA); oxygen values were maintained between 90 and 100% saturation with oxygenators. The incubation temperature (2 °C) approximated the environmental temperature measured in the

two streams and in the spring measured the day of sampling using a multiparametric probe (Hydrolab Quanta, Hydrolab Corporation®, TX, USA).

Carabids were sought by hand beneath stones and any other hiding places located near the front of the glacier and along the banks of the streams and spring. The sampled individuals were preserved in plastic vials in pure ethanol and identified and sorted in the laboratory using the identification keys reported in Ledoux and Roux (2005) and a stereomicroscope (MZ 7.5; Leica Microsystems, Germany).

Overall, 10,285 chironomids (all larvae with the exception of 25 pupae and 47 adults) and 91 carabids were collected (Table 1, Table S1).

Specifically, an Amola glacier-fed stream was investigated in 2019, and approximately 5000 Chironomidae larvae belonging to four species of the genus *Diamesa* were collected (Fig. 1B): 307 *D. bertrami*, 2688 *D. steinboecki*, 481 *D. tonsa*, and 1228 *D. zernyi*. Fifty carabids were collected in the Amola glacier foreland, all belonging to the species *Nebria germarii*. The Mandrone glacier-fed stream was investigated in 2020, and approximately 3700 chironomid larvae belonging to four species of the genus *Diamesa* (697 *D. tonsa*, 325 *D. latitarsis*, 583 *D. steinboecki*, 2002 *D. zernyi*) were collected (Fig. 1A). In addition, 13 individuals of *N. germarii* and 11 of *N. jockischii* were collected. Grostè spring was investigated in 2021, and approximately 1800 aquatic invertebrates were collected, of which 99% were Chironomidae: 1698 larvae, 10 pupae, and 1 adult belonging to 2 species of the genus *Diamesa* (= larvae: 464 *D. tonsa*, 1270 *D. zernyi*), 83 larvae of *Pseudokiefferiella parva* (Diamesinae), and 21 larvae of Orthoclaadiinae. The remaining 2% was represented by 3 Simuliidae larvae, 6 *Tipula* subg. *Savtshenkia* gr. I (sensu Faasch) (Tipulidae), and 16 specimens of *Crenobia alpina* (Tricladida). Of the collected material, only the larvae of the two most abundant species of *Diamesa* (*D. tonsa* and *D. zernyi*, keeping the larval stages separate) and the larvae of *P. parva*, Orthoclaadiinae, and *Tipula* were analyzed. In addition, 17 individuals of *Nebria castanea* were sampled along the spring banks.

In Amola, in 2019, thanks to the huge number of larvae collected, we successfully reared the larvae that were not used for bioaccumulation analyses and separated approximately 25 pupae and 47 adults, with a sufficient biomass (pupae = 65 mg wet weight; adults = 56 mg wet weight, for both 15 mg of dry weight) to be suitable for bioaccumulation analysis.

Animals were weighed using a microbalance (Explorer™ Analytical Ohaus E11140, readability = 0.0001 g) and frozen at -20 °C before performing chemical analyses.

## Chemical compound analysis in chironomids and carabid tissue

In the study sites, Rizzi et al. (2022) detected five pesticides in the bulk water phase (chlorpyrifos (CPY), chlorpyrifos-methyl (CPY-m), desethylterbutylazine (dTBZ), terbutylazine (TBZ), S-metolachlor (S-MTL)), two musk fragrances (galaxolide (HHCB) and tonalide (AHTN)), and 15 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), and benzo[ghi]perylene (BghiP) (Table 2). These 22 compounds were investigated in animal samples.

**Table 2**

Average concentration of the 22 compounds detected in the meltwater samples in the Amola (in 2019) and Mandrone (in 2020) streams and in the Grostè spring (in 2021) reported as the sum of the dissolved and sorbed phases and expressed in nanograms per liter (ng/L). The average was calculated between the early and late summer values

		Amola	Mandrone	Grostè
Desethylterbutylazine	dTBZ	0.67 ± 0.94	1.00 ± 0.96	0.67 ± 0.94
Terbutylazine	TBZ	0.29 ± 0.41	0.53 ± 0.57	0.06 ± 0.08
S-metolachlor	S-MTL	-	14.80 ± 19.52	-
Chlorpyrifos-methyl	CPY-m	0.68 ± 0.93	0.07 ± 0.01	-
Chlorpyrifos	CPY	0.73 ± 0.47	0.38 ± 0.13	0.25 ± 0.01
Galaxolide	HHCB	4.93 ± 3.73	13.95 ± 3.18	6.67 ± 5.70
Tonalide	AHTN	0.76 ± 0.39	2.51 ± 0.13	1.22 ± 1.25
Acenaphthylene	Acy	0.08 ± 0.07	0.15 ± 0.15	0.17 ± 0.10
Acenaphthene	Ace	0.30 ± 0.02	0.08 ± 0.11	0.30 ± 0.17
Fluorene	Flu	0.38 ± 0.10	0.38 ± 0.40	0.43 ± 0.19
Phenanthrene	Phen	1.59 ± 1.13	2.39 ± 1.45	1.48 ± 0.30
Anthracene	Ant	0.11 ± 0.03	0.34 ± 0.16	0.09 ± 0.03
Fluoranthene	Fl	0.20 ± 0.08	2.98 ± 0.58	0.35 ± 0.04
Pyrene	Pyr	0.28 ± 0.21	3.30 ± 0.63	0.17 ± 0.18
Benz(a)anthracene	BaA	0.22 ± 0.28	0.36 ± 0.32	0.07 ± 0.02
Chrysene	Chr	0.06 ± 0.01	1.03 ± 1.13	0.24 ± 0.02
Benzo(b)fluoranthene	BbF	0.02 ± 0.02	0.31 ± 0.33	0.04 ± 0.01
Benzo(k)fluoranthene	BkF	-	0.12 ± 0.08	0.07 ± 0.02
Benzo(a)pyrene	BaP	0.10 ± 0.03	0.01 ± 0.01	0.06 ± 0.00
Dibenzo(a,h)anthracene	DBahA	0.01 ± 0.01	0.06 ± 0.06	-



		Amola	Mandrone	Grostè
Indeno(1,2,3-cd)pyrene	IP	-	0.04 ± 0.06	-
Benzo(g,h,i)perylene	BghiP	0.02 ±	0.07 ± 0.06	0.03 ± 0.01

## Sample preparation

The concentration of chemical compounds was detected in one to three replicates per site and species, depending on the abundance and biomass of a single individual. For chironomids, each replicate was represented by pools of individuals to meet the minimum mass required for extraction (15 mg d.w.). This is because the individual body mass is low (e.g., *Diamesa* larva weights from approximately 1 to 3 mg wet weight) and the dry weight (d.w.) was on average 20% of the wet weight. For carabids, the analysis was carried out on single individuals separately. Samples were freeze-dried, and then water was removed by sublimation from the frozen sample.

## Extraction of analytes of interest from biological matrix

Approximately 15 mg of freeze-dried samples were extracted in an ultrasonic bath at 40 °C using n-hexane (≥ 95%, PESTINORM®, VWR Chemicals, Milan, Italy), methylene chloride (≥ 99.8%, Chromasolv™ for HPLC, Honeywell-Riedel-de Haën, VWR Chemicals, Milan, Italy), and ethyl acetate (≥ 99.7%, PESTINORM®, VWR Chemicals, Milan, Italy) as extraction solvents. Labelled PAHs (acenaphthene-d10, phenanthrene-d10, fluoranthene-d10, benzo[a]anthracene-d12, benzo[a]pyrene-d12, dibenzo[a,h]anthracene-d14) were added to each sample as recovery standards. Extracts were centrifuged, evaporated under a gentle stream of nitrogen, and reconstituted to 0.05 mL with cyclohexane.

## Chemical identification and quantification

Identification and quantification of pesticides and fragrances compounds were performed according to the methods described by Rizzi et al. (2022), while for PAHs were carried out following the methods described by Rizzi et al. (2023). The quantification analysis was performed by gas chromatography–mass spectrometry (GC/MS) using an Agilent Technologies 5977B MSD with 8860 GC equipped with a 30-m HP5-MS capillary column in single ion monitoring (SIM) mode. Instrumental calibration was carried out before sample analysis using standard mixtures consisting of the analytes in the range from 0.1 to 100 ng/mL.

Before injection, the Agilent 7693A Automatic Liquid Sampler added 0.2 µL of internal standard (PCB141) to each calibration level and each sample. The recovery percentages were calculated by the determination of labelled compounds, and a correction factor was applied when the percentages did not fall in the range of 70–120%.

Two oven programs were set. For pesticides and musk fragrances, the oven program was the following: starting temperature of 100 °C kept for 1 min; 20 °C min<sup>-1</sup> up to 150 °C; 5 °C min<sup>-1</sup> up to 200 °C; 40 °C min<sup>-1</sup> up to 280 °C; kept for 4.5 min. The transfer line was maintained at 290 °C, and the injector was set at 250 °C. For PAHs, the oven program was the following: starting temperature of 55 °C kept for 1 min; 25 °C min<sup>-1</sup> up to 320 °C kept for 4.4 min, post run temperature of 50 °C. The transfer line was maintained at 290 °C, and the injector was set at 300 °C. Samples were run in splitless mode using helium (Helium 5.0, Sapio Produzione Idrogeno Ossigeno S.R.L., Milan, Italy) as a carrier gas (Rizzi et al. 2023). Details on the MS setting, the limit of detection and quantification, and the n-octanol–water partition coefficient (K<sub>ow</sub>) of single compounds are reported in Table S2.

## Statistical analysis

The compound concentrations were tested for a normal distribution using a Shapiro–Wilk test. Five compounds met normality assumptions (CPY, HHCb, AHTN, Ant, and Pyr); the other concentrations were ln(x + 1) transformed (Zar 1984). Following transformation, all variables were tested for significant differences among species and sites using *t* tests independent of groups and one-way ANOVA using Statistica (version 12.0 computer package StatSoft®). Values with *p* < 0.05 were considered significant. A cluster analysis (paired group—UPGMA) based on the Bray–Curtis similarity coefficient was performed to highlight similarities among species from the different sites in relation to BAF values (Sneath and Sokal 1973). The cluster analysis was performed using PAST software (version 4.03) (Hammer et al. 2001).

## Results

### Compounds that accumulate the most

Ten of 22 compounds detected overall in the waters of the three sites were found in chironomid tissues (CPY-m, CPY, HHCb, AHTN, Flu, Phen, Ant, Fl, Pyr, BaA), and six of these were found in the carabids (CPY-m, CPY, HHCb, AHTN, Fl, Pyr). Of these, CPY-m was not found in the Grostè water (neither in the larvae inhabiting the spring nor the carabids moving around), while the other nine were present in waters of the three sites (Table 2). In Table 3, the compound concentration is reported as average values at the genus or higher taxonomical level for aquatic and terrestrial animals. Specifically, only larvae collected in Amola accumulated all ten compounds, nine compounds (all except BaA) were detected in the larvae of Mandrone, and six in those from the Grostè spring (CPY, HHCb, AHTN, Flu, Ant, Pyr). Only four compounds were detected in the chironomid pupae (CPY-m, CPY, HHCb, AHTN) and adults (CPY, HHCb, AHTN, Flu) from Amola. Proportionally, fewer compounds were detected in the carabids, from two (HHCb and AHTN in Amola) to three (CPY, HHCb, and AHTN in Grostè) and six (CPY-m, CPY, HHCb, AHTN, Fl, and Pyr in Mandrone).

**Table 3**

Mean **AQ2** concentrations of ten chemical compounds (ng/g dry weight ± 1 SE) in *Diamesa* larvae (L), pupae (P) and adults (A), other chironomid larvae (Other\_Chiro), *Tipula* sp. larvae, and in carabid adults (carabids)

			CPY-m	CPY	HHCB	AHTN	Flu	Phen	Ant	Fl	Pyr	BaA
Amola	<i>Diamesa L</i>	<i>n</i> = 10	2.7 ± 1.6	5.7 ± 0.5	15.6 ± 1.2	5.8 ± 2.3	15.8 ± 4.7	34.6 ± 2.1	15.4 ± 3.3	9.4 ± 9.4	5.6 ± 2.3	1.5 ± 0.0
	<i>Diamesa P</i>	<i>n</i> = 1	2.3	4.7	45.1	8.3	-	-	-	-	-	-
	<i>Diamesa A</i>	<i>n</i> = 2	-	2.8 ± 0.7	40.1 ± 2.7	14.5 ± 0.7	3.6 ± 0.1	-	-	-	-	-
	Carabids	<i>n</i> = 3	-	-	23.3 ± 7.3	5.6 ± 0.8	-	-	-	-	-	-
Mandrone	<i>Diamesa L</i>	<i>n</i> = 10	2.1 ± 0.9	5.0 ± 1.2	20.5 ± 2.2	7.0 ± 2.3	7.6 ± 0.9	3.2 ± 3.2	8.5 ± 3.3	7.9 ± 4.6	43.9 ± 9.4	-
	Carabids	<i>n</i> = 6	1.9 ± 0.4	6.9 ± 0.3	22.9 ± 11.2	8.2 ± 1.0	-	-	-	1.6 ± 1.6	38.1 ± 0.2	-
Grostè	<i>Diamesa L</i>	<i>n</i> = 14	-	3.2 ± 0.6	9.7 ± 2.3	6.1 ± 1.5	1.3 ± 1.3	-	4.9 ± 2.8	-	5.9 ± 3.5	-
	Other_Chiro L	<i>n</i> = 2	-	2.3 ± 0.6	8.8 ± 1.0	5.2 ± 0.5	0.9 ± 0.0	-	3.3 ± 0.0	-	3.9 ± 0.0	-
	<i>Tipula sp. L</i>	<i>n</i> = 1	-	1.0	6.7	2.9	-	-	-	-	-	-
	Carabids	<i>n</i> = 2	-	2.7 ± 0.4	84.6 ± 0.3	15.1 ± 0.7	-	-	-	-	-	-

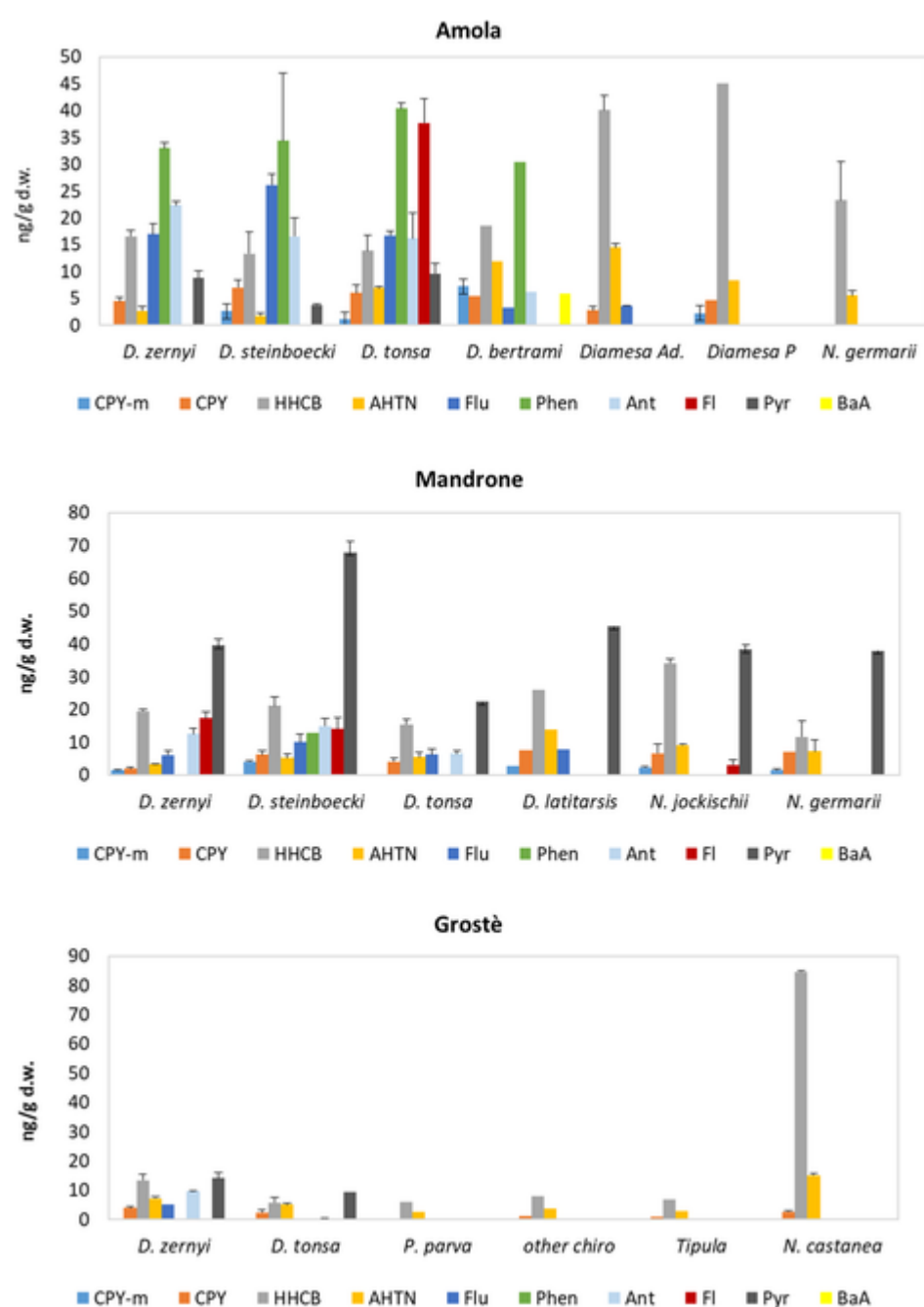
*n* = number of replicates

Only the synthetic fragrances HHCB and AHTN and the pesticide CYP (the last one with the sole exception of carabids from Amola and *P. parva* from the spring) were found in all taxa (*Diamesa* larvae, pupae, and adults; other chironomids; tipulids; carabids). Regarding the other compounds, their occurrence ranged from 1 (BaA) to 5 (Flu and Pyr) times. No compound was exclusive to carabids.

At all sites, the concentrations of all compounds were higher in the larvae than in the water (Fig. 2, Tables 2 and 3, Figure S1), with a ratio from 1.5 (from HHCB in Mandrone and Grostè) to 30–50 (Pyr in Gr, Fl in Amola, Ant in Grostè, Flu in Amola, CPY-m in Mandrone) up to 140 for Ant in Amola. Ant, Pyr, Flu, CPY, and CPY-m resulted in the highest ratios (> 10 in at least 2 of 3 sites). At all sites, the most abundant compound was HHCB in the water, but it was the most bioaccumulated by the larvae only in Grostè spring (9.7 ± 2.3 ng/g d.w.), replaced in Mandrone by Pyr (43.9 ± 9.4 ng/g d.w.) and in Amola by Phen (34.6 ± 2.1 ng/g d.w.).

**Fig. 2**

Average concentrations (ng/g dry weight ± 1 SE) of chemical concentrations in aquatic and terrestrial invertebrates. In Amola stream, Mandrone stream, and Grostè spring



Considering the average concentrations of the six common compounds found in the water and in *Diamesa* larvae (from all species) at the three sites, no significant difference was detected among the three *Diamesa* population contaminations ( $F = 3.08$ ,  $p = 0.08$ ). The same was observed for *Nebria* at the three sites ( $F = 0.81$ ,  $p = 0.464$ ).

## Interspecies differences at site level

In Amola, the transfer of contaminants from larvae to pupae and adults was detected for HHCB (significantly higher in adults and pupae than in the larvae:  $F = 40.72$ ,  $p < 0.0001$ ) and AHTN, with the addition of CPY-m in pupae and Flu in the adults. Of these, only HHCB and

AHTN were recorded in carabids collected at the same site, with no significant difference in these two compounds between carabids and chironomid adults or pupae. Significant differences were always detected between *Diamesa* larvae and *Nebria* adults for HHCB ( $t_{(12)} = 3.63, p = 0.0034$ ), which was higher in *Nebria*.

Interspecies significant differences were recorded among *Diamesa* species for AHTN ( $F = 32.04, p = 0.0004$ , higher in *D. bertrami*), Flu ( $F = 16.85, p = 0.002$ , lower in *D. bertrami*), Fl ( $F = 48.23, p = 0.0001$ , present only in *D. tonsa*), and Pyr ( $F = 6.23, p = 0.028$ , absent in *D. bertrami* and higher in *D. zernyi* and *D. tonsa*). Overall, the species more similar to each other were *D. steinboeckii* and *D. zernyi* (no significant differences were detected, apart from the absence of CPY-m in *D. zernyi*).

In Mandrone, carabids accumulated five (*N. germarii*) and six (*N. jockischii*) of ten compounds detected in the larvae, all apart from Flu ( $t_{(14)} = 2.23, p = 0.004$ , lower in *N. jockischii*), with concentrations comparable with those detected in the larvae. No significant difference was detected between the two *Nebria* species. Interspecies significant differences were recorded among *Diamesa* species for AHTN ( $F = 8.75, p = 0.013$ ), which was more abundant in *D. latitarsis*; Ant ( $F = 7.62, p = 0.018$ ), which was lower in *D. tonsa* and higher in *D. zernyi* and *D. steinboeckii*; Fl ( $F = 12.44, p = 0.006$ ), which was absent in *D. tonsa*; and Pyr ( $F = 10.10, p = 0.009$ ), which was more abundant in *D. steinboeckii*. Overall, the species more similar to each other were *D. steinboeckii* and *D. zernyi* (no significant differences were detected, apart from the absence of Phen in *D. zernyi*).

In Grostè, *Diamesa* larvae accumulated more compounds (CPY, HHCB, AHTN, Flu, Ant, Pyr) than the other chironomid larvae and tipulids, only two (HHCB, AHTN) in *P. parva* and three in Orthoclaudiinae and *Tipula* sp. (CPY, HHCB, AHTN). Of these, CYP and AHTN were significantly highly concentrated in *Diamesa* larvae (CYP:  $t_{(15)} = 2.38, p = 0.031$ ; AHTN:  $t_{(15)} = 2.30, p = 0.036$ ). Considering the two *Diamesa* species separately, they showed significant differences for HHCB ( $t_{(15)} = 2.30, p = 0.0003$ ) and Ant ( $t_{(15)} = 2.05, p = 0.04$ ), both more abundant in *D. zernyi*. Flu was detected only in *D. zernyi*. Carabids accumulated only three compounds (CPY, HHCB, AHTN), the same found in orthoclaids and tipulids but in higher amounts. Significant differences were detected between larvae of all emerging merolimnic insects and *N. castanea* for HHCB ( $t_{(14)} = -21.42, p < 0.0001$ ) and AHTN ( $t_{(14)} = -4.22, p < 0.0008$ ), which were 40 × and 3 × higher in *Nebria*, respectively.

## Comparison between aquatic and terrestrial species

Figure 3 shows the similarities between the 19 sampling units (= taxon × site) analyzed at the three sites. Two main groups were separated: all *Diamesa* larvae and carabids from Mandrone on the left and all the other taxa on the right. Specifically, carabids were always grouped with larvae of insects from the same site (e.g., *N. germarii* from Mandrone was grouped with larvae of *D. latitarsis* and *N. castanea* from Grostè with *P. parva*, orthoclaids, and *Tipula* sp.). The sole exception was *N. germarii* from Amola, which was grouped with *Diamesa* pupae and adults (i.e., no significant difference was detected between the chemical contamination in *Nebria* and *Diamesa* adults and pupae).

**Fig. 3**

Paired group (UPGMA) clustering based on Bray–Curtis similarities (ranging from 0 = total dissimilarity to 1 = complete similarity). Clustering based on square root–transformed compound concentrations. Species unit codes: D, *Diamesa*; b, *bertrami*; l, *latitarsis*; s, *steinboeckii*; t, *tonsa*; z, *zernyi*; N, *Nebria*; c, *castanea*; g, *germarii*; j, *jockischii*. Species from Mandrone (M) in blue, from Amola (A) in black, and from Grostè (G) in brown

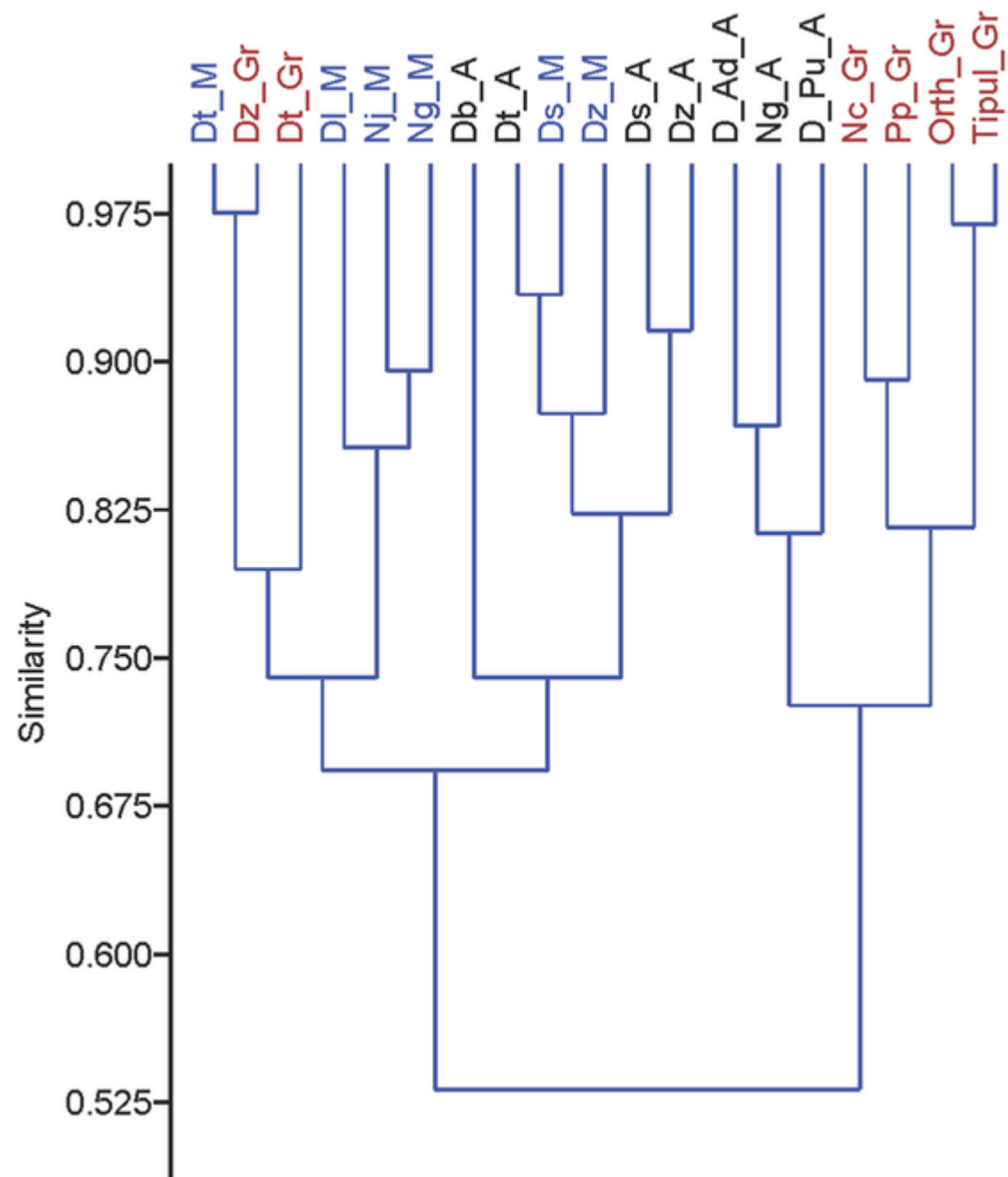
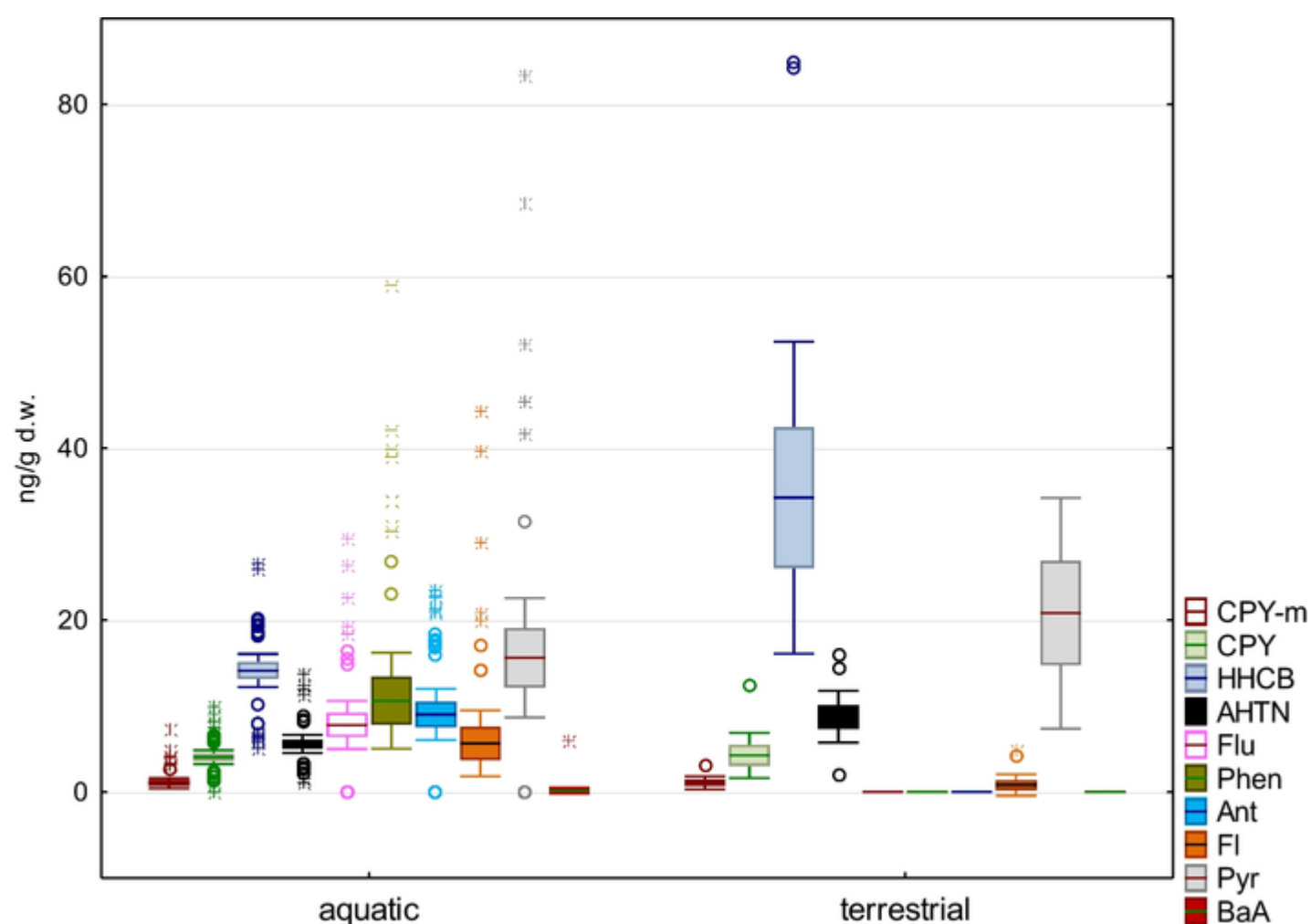


Figure 3 also highlights a stronger similarity between species from the same site (e.g., *D. steinboeckii* and *D. zernyi* from Amola) than between the same species from different sites (e.g., *D. tonsa* or *D. zernyi* from the three sites were clustered separately).

Figure 4 synthesized the comparison between aquatic (only larvae of all tested insects) and terrestrial (= carabids) taxa. Overall, considering the six compounds in common, Pyr (not significantly) and HHCB and AHTN (significantly) were more abundant in terrestrial than aquatic organisms (HHCB:  $t_{(46)} = 4.31$ ,  $p < 0.001$ ; AHTN:  $t_{(46)} = 2.66$ ,  $p = 0.011$ ); Fl was more abundant in aquatic organisms, although not significantly, while CPY and CPY-m were as the mean comparable in the two taxa (Table S3).

**Fig. 4**

Mean, 25th, 75th percentile of compound concentration (ng/g d.w.) in aquatic (larvae of aquatic insects) and terrestrial (adults of carabids) organisms. Box = mean  $\pm$  SE; Whiskers = mean  $\pm$  confidence interval. = outlier values. \*Extreme values. In the box, significant differences ( $p < 0.05$ ,  $t$  test values)





# Discussion

## Aquatic insects

Our study highlighted that among the plethora of compounds contaminating ice and snow packs and present in water, ten have been taken up by aquatic insects: chlorpyrifos-methyl (CPY-m), chlorpyrifos (CPY), galaxolide (HHCB), tonalide (AHTN), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), and benzo[a]anthracene (BaA).

According to our first hypothesis, at all sites, the concentrations of compounds found in the larvae ranged from  $1.5 \times$  to  $140 \times$  higher than in the water, as expected. In fact, it is known that depending on their physicochemical features, some xenobiotics can be stored within organisms at concentrations higher than those measured in the environment (Gobas and Morrison 2000). Additionally, our data suggest that the most abundant compounds in water are also the most bioaccumulated by the larvae. Specifically, at all sites, the most abundant compound was HHCB in the water (4.9–14.0 ng/L), but it was the most bioaccumulated by the larvae only in Grostè spring ( $9.7 \pm 2.3$  ng/g d.w.), replaced in Mandrone by Pyr ( $43.9 \pm 9.4$  ng/g d.w.) and in Amola by Phen ( $34.6 \pm 2.1$  ng/g d.w.).

Regarding PAHs, those found more concentrated in the water and in animals (Flu, Phen, Ant, Fl, and Pyr) were light PAHs and were the most accumulated PAHs in high mountains in Europe, such as in the Tibetan Plateau (Carrera et al. 2001; Gabrieli et al. 2010; Li et al. 2011). This is due to their volatility, which allows their transport over long distances, accumulating in the deposit fallout before reaching high altitudes (Peters et al. 1995). Therefore, we were not surprised to find them to be the most concentrated even in animal tissues. The analysis of PAH ratios performed by Rizzi et al. (2022) suggested that these PAHs in our study sites had a mixed origin from liquid fossil fuel and biomass/coal combustion, depending on the site and year of sampling.

It is also known that compounds with an n-octanol–water partition coefficient ( $K_{ow}$ )  $> 100,000$  (i.e.,  $\text{Log } K_{ow} > 5$  according to Kelly et al. 2007) are fat-soluble and thus more bioaccumulative than those with  $\text{Log } K_{ow} < 5$ , which are considerably poorly metabolizable, moderately hydrophobic substances that do not biomagnify. In our case, only five compounds have a  $\text{Log } K_{ow} > 5$ , HHCB, AHTN, Fl, Pyr, and BaA, among which BaA accumulated in lower concentrations and frequency (i.e., only in *D. bertrami* from Amola) than other compounds with  $\text{Log } K_{ow} < 5$ , such as CPY-m, Flu, and Ant.

Considering the mean concentration for all aquatic insects from all sites, among the compounds, PAHs and fragrances accumulated more than pesticides. Specifically, Pyr, HHCB, Phen, Ant, Flu, Fl, and AHTN were detected with concentrations ranging from 6 to 16 ng/g d.w. Risk characterization performed by Rizzi et al. (2022) derived from the potential effects on nontarget organisms representative of aquatic environments (algae, invertebrates, and fish) associated medium risk with fluoranthene and pyrene and low risk for the other PAHs. The detection of Fl (14–38 ng/g d.w.) and Pyr (4–40 ng/g d.w.) in the larvae raises concerns about these two compounds as well as the detection of CYP, for which Rizzi et al. (2022) reported an unacceptable risk to aquatic invertebrates. CYP was found in all aquatic taxa except *P. parva* but was never the most concentrated. The high relative amount of polycyclic musk fragrances is not surprising, as galaxolide (HHCB) and tonalide (AHTN) are largely used as fragrances (Vecchiato 2023) in many household and personal care products (and can be considered even-present contaminants) (Senka Terzić et al. 2008). These substances have been detected in all habitat types to date, and due to their inherent lipophilicity, they easily bioaccumulate in aquatic organisms, meaning that these types of compounds cannot be neglected from a toxicological point of view (Carlsson et al. 2000).

Apart from interspecies differences in each site and intraspecies differences from the three sites, larvae of *Diamesa* differed from the larvae of other chironomids (*P. parva* and orthoclads) and tipulids, as highlighted by the cluster analyses. This might depend on a different uptake of contaminants by the different taxa. Generally, for chironomids, exposure to contaminants can occur through two basic routes: by direct absorption through water and/or by feeding in an additive way (Katagi 2010). *Diamesa* spp., *P. parva*, and orthoclad larvae are detritivorous. This means that they ingest debris (floating or deposited), and feeding should be their primary route of exposure and accumulation of organic contaminants. However, in kryal habitats (= the first kilometer downstream of the glacier front; Lencioni 2018), organic debris is scarce, and *Diamesa* larvae ingest amounts of fine inorganic sediment suspended, filling their gut. Therefore, we can argue that they also accumulate the fraction of contaminants adsorbed on the inorganic sediment. Even sand grains may act as surfaces for microbial attachment and thus have a high nutritional value for chironomids (Pinder 1986). The *P. parva* and orthoclads we collected in the spring live in mosses, and they do not ingest suspended inorganic sediment. Tipulids are predators, so feeding is their primary route of exposure and accumulation of contaminants. Our data did not suggest a biomagnification process with increasing concentration moving across the higher trophic level, having tipulids a comparable amount of the three contaminants than *P. parva* and orthoclads and lower than those present medially in chironomid larvae.

Intersite differences were detected, partly reflecting the differences in water contamination among the three sites. For example, the highest amounts of Pyr and HHCB were detected in larvae from the Mandrone stream, which was the most contaminated by these two compounds. Conversely, Phen and Fl were more abundant in the Mandrone stream but were more accumulated by the Amola larvae. In larvae from the spring, CPY-m was not detected as expected and was absent in the water. These differences might be not ascribed to the pH of the water, which influences the bioaccumulation, depuration, and biotransformation of polycyclic aromatic hydrocarbons and other chemical compounds (Wildi et al. 1994). The water of the spring has an alkaline pH (pH = 8.0), while the pH of the glacier-fed streams is approximately 6.5. Theoretically, at higher pH, the bioconcentration rate is greater than that at lower pH. Therefore, pyrene bioconcentration rate correlated with accumulation potential. Thus, at pH 8, the larvae accumulated the most PAHs, and at pH 4, the bioconcentration of the larvae was the lowest; this was highlighted for pyrene (Pyr) in *Chironomus riparius* by Wildi et al. (1994). However, larvae from the springs did not accumulate more Pyr or other PAHs than the others.

Considered altogether, *Diamesa* larvae from glacier-fed streams accumulated more compounds (9–10) than those from the spring (6), but the six found in the spring's larvae (CPY, HHCB, AHTN, Flu, Ant, Pyr) were also detected in comparable amounts in the chironomid larvae from the glacier-fed streams. Other chironomids and tipulids accumulated only CPY, HHCB, and AHTN; these are the compounds entering the aquatic food web of all types of headwaters, independently of their origin (i.e., fed by glaciers or permafrost).

Considering sites together, uptake of contaminants did not seem species specific, i.e., the accumulation pattern of the different species reflected the water composition in which they live more than a taxonomical relationship. Therefore, *D. zernyi* from Mandrone or Amola

was more similar to *D. steinboeckii* and/or *D. tonsa* from the same site than to *D. zernyi* from another site. However, interspecies differences were detected between species at the same site. In fact, *Diamesa* species from the same site did not accumulate the same contaminants and in the same amount. These differences might be accidental, considering that the uptake of contaminants does not seem species specific.

Finally, according to our first hypothesis, in chironomid pupae and adults, we detected compounds present also in the larvae, assuming that if incorporated into body tissues of the larvae, the same contaminants should also be present in the pupae (still aquatic) and in the adults. This does not include compounds not only incorporated into body tissues but also associated with exoskeletons of larvae: in this case, contaminants could be harmless for the larva and lost with the exoskeletons during metamorphosis. Unless adults adsorb these contaminants from the air, we can assume that they inherit them from the aquatic stages. In the *Diamesa* larvae from Amola, we detected ten compounds, only four of which were detected in the pupae (CPY-m, CPY, HHCB, AHTN) and adults (CPY, HHCB, AHTN, Flu). The number of replicates was too low to provide an explanation. Pupae do not feed, so the contaminants that they do not uptake might be more available in the debris. Adults do not feed, so what they accumulate they get from the air or inherit from the de facto pupae. Due to the similarity observed between pupae and adults, we might suppose that they inherit them mainly from the pupae. This result is consistent with laboratory studies carried out by Reinhold et al. (1999) for PCBs, PAHs, and pesticides for chironomids in a freshwater tidal river in the Netherlands, i.e., a concentration ratio of adults to larvae between 0.5 and 1.4. Other authors highlighted an increase or a decrease in contaminant concentration of selected compounds during metamorphosis and emergence into flying adults, with differences among species and contaminants (Timmermans and Walker 1989; Fletcher et al. 2022).

The short- or long-term effects of these compounds on kryal fauna remain to be investigated. It is known that synthetic fragrances cause thyroid disruption and have neurobehavioral toxicity (Chae et al. 2023), PAHs interfere with reproduction by disrupting circulating steroid hormone levels in fish and by producing endocrine disruption in invertebrates (Vignet et al. 2016), and CPF is neurotoxic, enhancing accumulation of acetylcholine in synapses and disrupting nervous system function (Corbett 1974). However, no data are available on their toxicity on kryal fauna, apart from evidence of negative effects of CYP and AHTN on metabolism and behavior of *D. zernyi* larvae from the Presena Glacier (Lencioni et al. 2018). This study emphasized that *D. zernyi* larvae seem to be more sensitive to CYP than to AHTN based on lethal concentrations (CYP:  $LC_{10\_48\text{ h}} = 1.06 \mu\text{g/L}$ ;  $LC_{50\_48\text{ h}} = 5.24 \mu\text{g/L}$ ; AHTN: No Observed Effect Concentration:  $NOEC_{96\text{ h}} = 100 \text{ mg/L}$ ) but, at sublethal concentrations ( $= LC_{10}$  for CYP and  $NOEC$  for AHTN), only AHTN is genotoxic (i.e., damaging DNA as strand breaks assessed with the comet assay). Additionally, sublethal concentrations of CYP ( $= 110 \text{ ng/L}$  corresponding to  $1/10 LC_{10\_48\text{ h}}$  and approximately  $16 \times$  higher than the detected environmental concentration) at  $2^\circ\text{C}$  ( $=$  the environmental temperature) cause significant negative effects on larval swimming speed and cause oxidative stress after 72 h of exposure (Villa et al. 2018; Di Nica et al. 2020; Lencioni et al. 2021; Muñiz-González et al. 2021). We can therefore believe that at least for CYP and AHTN, the environmental concentrations detected at our sites are protective (in the short term) for kryal fauna.

Some information is available on the toxicity of synthetic fragrances, pesticides, and PAHs on other chironomids (*Chironomus* spp.) larvae exposed to contaminated sediments in microcosms or in nature. Dickman et al. (1992) reported evidence of deformities of the mouth parts of the larvae of *Chironomus anthracinus* in sediments of the Niagara River watershed by the accumulation of fluoranthene, pyrene, and benzo(a)anthracene at concentrations from  $15 \text{ ng/g}$  to  $2 \mu\text{g/g d.w.}$  This may raise some concern considering that the larvae we analyzed have accumulated amounts within this range. We did not analyze the morphology of the mouth parts of the tested larvae, so we cannot confirm such teratogenic effects of PAHs on kryal fauna.

Aikins et al. (2023) demonstrated that galaxolide at environmental concentrations  $< 2.5 \text{ mg/kg}$  in sediments, considered at low environmental risk for aquatic ecosystems, affects the emergence of *Chironomus dilutus*.

Regardless, we must consider that organisms adapted to cold environments show a delayed toxicity response to lipophilic compounds 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 (Chapman 2016). Specifically, the membrane lipid composition of *Diamesa* larvae (e.g., high unsaturation index and chain length of both phosphatidylethanolamine (PE) and phosphatidylcholine (PC) and a higher ratio PE/PC ratio) described by Trenti et al. (2022) might represent a barrier to lipophilic pollutants that cannot be adsorbed, supporting evidence of extraordinarily high toxic resistance of *Diamesa* species to pharmaceuticals and pesticides with respect to any other aquatic insect tested under the same contaminants.

## Carabids

Currently, more attention is being paid to the aquatic-to-riparian to terrestrial fluxes of contaminants (organic compounds and metals) through the emergence of aquatic insects that represents quintessentially the energetic link between aquatic and terrestrial ecosystems (Menzie 1980; Sullivan and Rodewald 2012). Therefore, contaminants can be transported from aquatic to terrestrial ecosystems, with biomagnification processes involving first riparian spiders and beetles and then vertebrates through the terrestrial food web (Fairchild and Muir 1992; Cristol et al. 2008; Walters et al. 2010; Tsui et al. 2012; Wiczorek et al. 2015; Richmond et al. 2018).

Our study highlighted that carabids accumulated fewer compounds than chironomids (from two to six in all), but those they accumulated were also present in chironomids from the same site according to our second hypothesis. Additionally, no contaminant was exclusive to carabids. All *Nebria* species accumulated HHCB and AHTN, with the addition of CPY (in Grostè) and CPY-m, Fl, and Pyr in Mandrone. Additionally, different species in the same site did not show significant differences from each other (i.e., *N. germarii* and *N. jockischii* in Mandrone), suggesting that any *Nebria* species might be used as an indicator of contamination of the terrestrial food web in a specific area. The differences we observed among species from different sites reflect different contamination in the larvae and are not species specific. For example, Pyr and Fl were found accumulated mainly in the water and by the larvae from Mandrone and were also found accumulated in carabids from this area.

We cannot exclude that carabids had taken up such compounds from prey (e.g., collembolans) other than chironomids or that they adsorbed these compounds from the air with the tracheal system or with antennae and legs from the soil if contaminated (Carlsson et al. 2000). However, the similarity in contamination of chironomids and carabids emphasized that they could intake such compounds mainly



by feeding on chironomids, considering that feeding is recognized as the major route of xenobiotics for carabids (Katayama et al. 2010) and that chironomids are one of their favorite prey in glacier forelands (Baxter et al. 2005; Paetzold et al. 2005; Walters et al. 2008; Sint et al. 2019). Our hypothesis is supported by Richmond et al. (2018), who detected in six Australian streams over 60 pharmaceutical compounds in aquatic invertebrates and in their riparian predators (spiders) in comparable concentrations. This suggested direct trophic transfer of drugs by emerging adult insects (preys) to their riparian predators. In this way, predators (carabids in our study) contribute to the metabolism of these compounds (Katayama et al. 2010). Other studies have demonstrated that terrestrial predators that feed on emerging chironomids (*Chironomus riparius*), whose larval stage lives in contaminated sediment, are exposed to polychlorinated biphenyls (PCBs) at a rate of 20 µg PCBs m<sup>-2</sup> year<sup>-1</sup> (Larsson 1984). Larsson (1984) also demonstrated that when larvae metamorphosed to adults, PCB compounds were concentrated and transferred from the aquatic to the terrestrial environment. A minor part of the compounds was retained in the exuviae. We can assume that this process regards other synthetic organic compounds, such as pesticides, fragrances, and polycyclic aromatic hydrocarbons.

The short- or long-term effects of these compounds on carabids colonizing glacial forelands remain to be investigated. Carabids are sensitive to pesticides used in farming or heavy metals contaminating soils (Koivula 2011).

Regarding the effects of pesticides and PAHs, there is consistent literature on their effects on carabid species assemblages, including bioaccumulation data but from other environmental contexts (e.g., Van Toor 2006; Gospodarek and Petryszak 2019). For example, Bednarska et al. (2009) reported 80 ng CPY/beetle d.w. as a limiting concentration associated with a nonsignificant effect on the survival of the carabid *Pterostichus oblongopunctatus*. Considering that the mean weight of *Nebria* specimens we collected ranged from 0.45 to 1.37 g, the concentration per specimen was approximately 9 ng/beetle d.w. so lower than this value. To our knowledge, no data are available on musk synthetic fragrances on carabids, and few ecotoxicological data are available on *Nebria* species. These studies referred to the main roots of contamination and effects of deltamethrin, a pyrethroid ester insecticide (Wiles and Jepson 1993a, b): mortalities occurred from direct contact with spray droplets and uptake from spray deposits but mainly from dietary intake of spray-contaminated prey.

## Conclusions

Chlorpyrifos-methyl, chlorpyrifos, galaxolide, tonalide, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and benzo[a]anthracene are organic compounds of anthropogenic origin that enter the aquatic food web, and six of them (chlorpyrifos-methyl, chlorpyrifos, galaxolide, tonalide, fluoranthene, pyrene) enter the terrestrial food web of glacial forelands and high-altitude spring areas. Of these, chlorpyrifos should not raise concerns in the future because it has recently been included in Annex A of the Stockholm Convention on Persistent Organic Pollutants (EUR-Lex—32021D0592, 2021). However, residues may remain in the environment for years.

Our results emphasize that a multispecies pool of *Diamesa* spp. larvae, and any species of *Nebria* visiting stream or spring banks, are bioindicators of contamination by synthetic fragrances, insecticides, and PAHs of high-altitude habitats with ice-snow cover or permafrost. This might be useful for monitoring and conserving mountain fauna.

Some issues remain unaddressed, such as (i) why only a few compounds of those present in chironomid larvae occur in pupae, adults, and carabids; (ii) which are the roots of uptake of such contaminants by carabids; and (iii) whether such compounds, in the concentrations we detected, are harmful for glacial fauna. Part of the solutions to these questions depends on the small number of sites and samples analyzed. Further sampling campaigns and experiments are needed to validate our hypotheses, answer these questions, and define acute and chronic limit concentrations of such compounds, which will facilitate the use of these insects as contaminant biomonitors to assess the possible toxicological impact of the Alps deglaciation on the surrounding alpine ecosystems by pesticides, fragrances, and PAHs. It should be considered that these insects are not easy to breed due to high mortality in nonnatural environments, there are serious logistic difficulties in sampling them in remote areas, such as those glacierized, and they are endangered nonmodel species in ecotoxicology. In fact, they are not ecotoxicological model species, and no guideline for toxicity tests is available for them (Lencioni et al. 2021). These factors make planning and performing ecotoxicological tests on these species even more challenging. Scientists must be cautious in sampling them because loss of individuals of these species may not be easily recovered in the short term (Lencioni and Gobbi 2021). In fact, species living in glacial habitats have small and isolated populations, their distribution is patchy or restricted (as in the case of endemism), their dispersal ability is scarce, and they can survive over a narrow range of environmental conditions (Hotaling et al. 2017; Gobbi et al. 2021). In this context, our study has an added value that is even more novel, highlighting for the first time that glacier foreland aquatic and terrestrial insect uptake organic compounds of anthropogenic origin. This represents an emerging environmental concern for glacial biodiversity, which is already at risk of extinction due to global warming. **AQ3**

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### Author contribution

VL: conceptualization, supervision, project administration, funding acquisition, chironomid sampling and identification, data analysis, writing first draft, and writing—reviewing and editing; CR: water and larval sample processing; MG: carabid sampling and identification; AM: conceptualization and funding; and SV: conceptualization, supervision, project administration, methodology, and writing—reviewing. All authors read and approved the final manuscript.

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pesticide and cosmetic contamination of glacial meltwater and risks to cryophilic entomofauna in the Adamello-Brenta Nature Park; 2019–2022; CIG code: Z4F261B768, Rep. N. 282; MTSN-0007568–18/09/2019-P).

## Declarations

**Ethics approval and consent to participate and publish** The CATENA project's studies were performed by the Science Museum of Trento (Italy), the University of Milano Bicocca (Italy), and the Natural Park Adamello-Brenta (Italy). Before examinations, all that participated in the project CATENA (Valutazione della contaminazione da pesticidi e cosmetici delle acque di fusione glaciale e rischi per l'entomofauna criofila nel Parco Naturale Adamello-Brenta/Assessment of pesticide and cosmetic contamination of glacial meltwater and risks to cryophilic entomofauna in the Adamello-Brenta Nature Park; 2019–2022; CIG code: Z4F261B768, Rep. N. 282; MTSN-0007568–18/09/2019-P) provided written informed consent to participate and publish results.

**Competing interests** The authors declare no competing interests.

## Supplementary Information

Below is the link to the electronic supplementary material.

Supplementary file1 (DOCX 33 KB)

## References AQ4

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