

# **Untargeted analysis of environmental contaminants in surface snow samples of Svalbard Islands by liquid chromatography-high resolution mass spectrometry**

Benedetta Giannelli Moneta<sup>1</sup>, Sara Elsa Aita<sup>1</sup>, Elena Barbaro<sup>2,3</sup>, Anna Laura Capriotti<sup>1</sup>, Andrea Cerrato<sup>1</sup>, Aldo Laganà<sup>1</sup>, Carmela Maria Montone<sup>1</sup>, Susy Piovesana<sup>1</sup>, Federico Scoto<sup>4</sup>, Carlo Barbante<sup>2,3</sup>, Chiara Cavaliere<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Sapienza University of Rome, p.le Aldo Moro 5, 00185 Rome, Italy

<sup>2</sup> Institute of Polar Sciences-CNR, University of Venice, via Torino, 155 - 30172 Venice-Mestre, Italy

<sup>3</sup> Department of Environmental Sciences, Informatics & Statistics, University Ca' Foscari of Venice  
Via Torino. 155 - 30172 Venice-Mestre Italy

<sup>4</sup> Institute of Atmospheric Sciences and Climate, ISAC-CNR, S.P Lecce-Monteroni km 1.2, 73100, Lecce, Italy

[benedetta.giannellimoneta@uniroma1.it](mailto:benedetta.giannellimoneta@uniroma1.it), [saraelsa.aita@uniroma1.it](mailto:saraelsa.aita@uniroma1.it), [barbaro@unive.it](mailto:barbaro@unive.it),  
[annalaura.capriotti@uniroma1.it](mailto:annalaura.capriotti@uniroma1.it), [andrea.cerrato@uniroma1.it](mailto:andrea.cerrato@uniroma1.it), [aldo.lagana@uniroma1.it](mailto:aldo.lagana@uniroma1.it),  
[carmelamaria.montone@uniroma1.it](mailto:carmelamaria.montone@uniroma1.it), [susy.piovesana@uniroma1.it](mailto:susy.piovesana@uniroma1.it), [federico.scoto@unive.it](mailto:federico.scoto@unive.it),  
[barbante@unive.it](mailto:barbante@unive.it), [chiara.cavaliere@uniroma1.it](mailto:chiara.cavaliere@uniroma1.it)

\*Corresponding author: Chiara Cavaliere, [chiara.cavaliere@uniroma1.it](mailto:chiara.cavaliere@uniroma1.it),

Department of Chemistry, Sapienza University of Rome, piazzale Aldo 5, 00185 Rome, Italy

Phone: +39 06 49913834 (off.); +39 3477834192 (cell.)

## 1    **Abstract**

2    In recent years, there is increasing attention on the contaminants of emerging concern (CECs), which  
3    include plasticizers, flame retardants, industrial chemicals, pharmaceuticals, and personal care  
4    products, since they have been detected even far away from pollution sources. The polar regions are  
5    not exempt from the presence of anthropogenic contaminants, and they are employed as a model for  
6    understanding the pollutant fate and impact.

7    During the 2021 spring campaign, sixteen surface snow samples were collected close to the research  
8    station of Ny-Ålesund located on the Spitsbergen Island of the Norwegian Svalbard Archipelago. The  
9    samples were extracted by solid-phase extraction and analyzed by liquid chromatography-high-  
10    resolution tandem mass spectrometry (LC-HRMS/MS) following an untargeted approach. Compound  
11    tentative identification was obtained with the aid of the software Compound Discoverer, using both  
12    mass spectral database search and manual validation. Among the 114 compounds identified with a  
13    high confidence level in the snow samples, more than 80 have some commercial or industrial use  
14    (drugs, plasticizers, fragrances, etc.), therefore they could be of anthropogenic origin. Nonetheless, a  
15    clear contamination trend did not appear in the snow samples collected on eight different days during  
16    one month. Even the comparison with aerosol samples collected in the same area did not provide  
17    further indications, since only a few compounds and mainly of natural origin were in common.

18    This is one of the few works performing an untargeted analysis by LC-HRMS/MS on samples  
19    collected in the Arctic; therefore, the results could provide valuable information about the sources  
20    and fate of detected CECs, which to date are widely present in environmental samples of lower  
21    latitudes. The 2021 sampling campaign was limited by the pandemic situation, therefore further  
22    campaigns are required to better elucidate the CEC environmental behavior.

23

## 24    **Keywords**

25    Arctic; polar regions; snow; aerosol; high-resolution mass spectrometry; non-target analysis

## 26    **1. Introduction**

27    To date, on the market, there are ca. 150,000 chemical substances, which could be potentially  
28    widespread in the environment; however, only a small fraction of these substances (less than 1000)  
29    are routinely monitored, therefore a correct estimate of this contamination is not feasible (AMAP,  
30    2017). In the last decade, particular attention has been focused on contaminants of emerging concern  
31    (CECs), which include plasticizers, flame retardants, industrial chemicals, pharmaceuticals and  
32    personal care products (PPCPs), etc., since they have been revealed even in remote locations.  
33    Although the polar regions are relatively isolated and far away from pollution sources, they are not  
34    exempt from the presence of anthropogenic contaminants, the increase of which is also connected  
35    with the increase in touristic and scientific activities (Balmer et al., 2019; Barbante et al., 2017; Duarte  
36    et al., 2021; Vecchiato et al., 2018; Xie et al., 2022).

37    The Arctic area, which is considered a sink of global pollutants (AMAP, 2017), comprises the Arctic  
38    Ocean and lands belonging to different continents and countries (United States, Canada, Iceland,  
39    Norway, Sweden, Finland, Denmark, and Russia), including the Norwegian Svalbard Archipelago.  
40    Pollutants, which can be in the water, air vapor phase, or adsorbed to particles (Xie et al., 2022), can  
41    be transferred to the Arctic region through long-range atmospheric transport (LRAT) phenomena and  
42    oceanic currents, local sources, and also the Arctic haze phenomenon (able to keep contaminated air  
43    in the area for months) (Kozak et al., 2013). Moreover, climate change is affecting sources, transport  
44    pathways, and the fate of contaminants, thus also increasing the human and biota exposure to  
45    persistent organic pollutants (POPs) and other chemicals of emerging Arctic concern (CEACs), e.g.  
46    PPCPs, current-use pesticides, organophosphate esters (OPEs), phthalates, etc. (AMAP, 2021a; Hung  
47    et al., 2022). The Svalbard Archipelago has been internationally adopted as a model for understanding  
48    pollutants' fate, persistence, and impact (Kozak et al., 2013) due to its peculiarities, including remote  
49    location, sparse population, the limited number of local contamination sources, and more than half  
50    (57%) of the surface covered by ice caps and glaciers; in addition, the Svalbard Archipelago  
51    represents a unique environment for the detection of new potential CEACs (Röhler et al., 2020).

52 Since 1960, an extensive literature has been published on pollution levels in the Arctic for metals,  
53 POPs (Bidleman et al., 2010; de Wit et al., 2010; Herbert et al., 2006; Szopińska et al., 2016; Vorkamp  
54 et al., 2019; Zhu et al., 2015), polycyclic aromatic hydrocarbons (Balmer et al., 2019; Vecchiato et  
55 al., 2018) and other non-halogenated compounds (Desideri et al., 1994; Herbert et al., 2006;  
56 Vecchiato et al., 2018; Vorkamp et al., 2019). The presence of POPs and CEACs is periodically  
57 reported within the Arctic Monitoring and Assessment Programme (AMAP) (AMAP, 2017), whose  
58 aim is also that of identifying new candidates for the Stockholm Convention list  
59 (<http://chm.pops.int/TheConvention/ThePOPs>).

60 The investigation of samples collected in the polar regions requires enrichment protocols followed  
61 by very sensitive detection techniques since compounds of interest are commonly present at very low  
62 concentrations. Solid-phase extraction (SPE) is the most used pre-concentration approach for non-  
63 volatile substances, and the commercially available sorbents allow covering a wide range of polarity.  
64 Nonetheless, some of these molecules could undergo degradation or be volatile enough to be lost  
65 back to the atmosphere (Giorio et al., 2018).

66 Due to the hydrophobic characteristics of POPs and other bioaccumulative compounds, gas  
67 chromatography (GC)-mass spectrometry (MS) is the coupling of choice for their analysis. However,  
68 for the study of more polar CECs (e. g. PPCPs) and their transformation/degradation products,  
69 reversed-phase (RP) liquid chromatography (LC)-MS is a more proper technique. In the literature,  
70 most of the works report targeted methods using low-resolution (LR) mass analyzers for the  
71 determination of selected contaminant classes in the polar regions, thus hindering the possibility to  
72 detect new/unexpected compounds (Röhler et al., 2020). On the other hand, new technologies and the  
73 increasing diffusion of high-resolution (HR)MS instrumentations, mainly based on Fourier-transform  
74 technology (i.e., FTICR and Orbitrap mass analyzers) and time of flight mass (TOF) analyzers, have  
75 allowed impressive advances in the analysis of chemical compounds, even unknown or unrecognized,  
76 in environmental matrices (Cortés-Francisco et al., 2011). Thus, the sensitivity and selectivity of HR  
77 mass analyzers allow the detection of thousands of  $m/z$  signals in a single analysis following the

78 suspect screening and/or the untargeted approaches. Nonetheless, only a few works employed the  
79 LC-HRMS technique for the untargeted analysis of Arctic contaminants, for example in sewage  
80 effluents and receiving seawaters (Choi et al., 2020) and sediment (Nejuma et al., 2018) using an  
81 Orbitrap and a TOF mass analyzer, respectively.

82 In this work, surface snow samples, collected in Ny-Ålesund (Spitsbergen, Svalbard) during the 2021  
83 spring sampling campaign, were subject to an untargeted analysis by LC-HRMS/MS using a  
84 quadrupole-Orbitrap hybrid mass analyzer. To evaluate the atmospheric contribution through dry  
85 deposition processes, aerosol samples collected in the same area during the snow sampling campaign  
86 were also analyzed.

87

## 88 **2. Experimental**

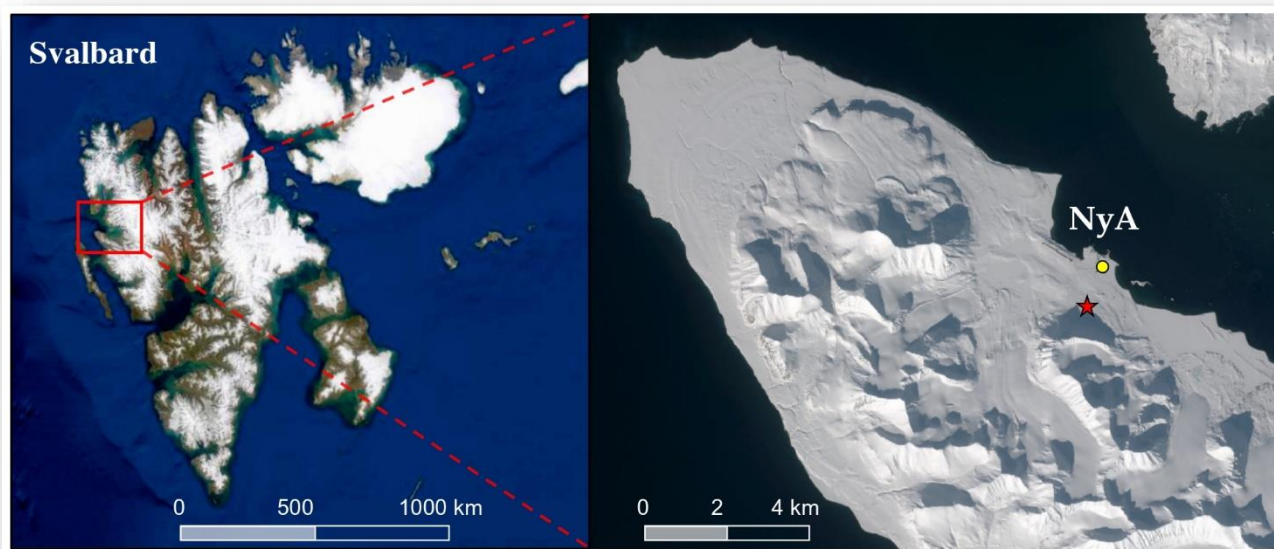
### 89 *2.1. Chemicals and Materials*

90 Oasis HLB cartridges (200 mg, 6 mL) were obtained from Waters (Milford, MA, USA). HPLC-grade  
91 methanol was purchased from VWR International (Milan, Italy), whereas LC-MS-grade methanol  
92 was provided by Romil Pure Chemistry (Pozzuoli, NA, Italy); ultra-pure water, and acetonitrile of  
93 LC-MS grade were purchased from Thermo Fisher Scientific (Waltham, MA, USA). All the other  
94 solvents, formic acid, ammonia solution, and the analytical standards were purchased from Merck  
95 Life Science (Milan, Italy).

96

### 97 *2.2. Sample collection*

98 During the spring campaign carried out between 8 April and 6 May 2021, multiple snow and aerosol  
99 samples were collected in Gruvebadet (78°55'01.8"N, 11°53'44.1"E; 50 m a.s.l., Fig. 1). The sampling  
100 site is a restricted area, located ~1 km south of Ny-Ålesund, and includes respectively a delimited  
101 snow-camp and the Gruvebadet Atmospheric Observatory. Since the area is dedicated to atmospheric  
102 and snow monitoring activities, fuel-powered motor vehicles are not allowed. Finally, the prevailing  
103 wind from the east and south-east assures a minimum impact by town emissions (Bertò et al., 2021).



**Fig. 1.** On the left, Svalbard archipelago with the indication of the sampling area on Spitsbergen island; on the right, details on Gruvebadet sampling site (red star), close to Ny-Ålesund (yellow point). Credits: TopoSvalbard.

#### 2.2.1. Snow sampling

Sixteen surface snow samples (upper 20 cm, ca. 2 L per sample) were collected on eight different days (see Table 1) using a pre-cleaned (with ultrapure water and methanol) stainless steel cutter; to avoid or minimize any contamination, sampling was carried out downwind. Each snow sample was collected in a sterile LDPE plastic bag (see Fig. S1), and then let to melt at room temperature for ca. 24 h.

#### 2.2.2. Aerosol sampling

Aerosol sampling was carried out with a multi-stage Andersen impactor (TE-6000 series, Tisch Environmental Inc.) following the methodology described in a previous study (Feltracco et al., 2021). This aerosol sampler is a high-volume collection system suitable for the chemical characterization in six different particle sizes, according to cut-off diameters of 10.0  $\mu\text{m}$ , 7.2  $\mu\text{m}$ , 3.0  $\mu\text{m}$ , 1.5  $\mu\text{m}$ , 0.95  $\mu\text{m}$ , and <0.49  $\mu\text{m}$ . The particle size distribution helps to identify the sources of each chemical

121 compound because species usually present in the coarse fraction are emitted very close to the emission  
 122 sources before of deposition processes occur. On the other hand, fine particles can undergo LRAT,  
 123 transporting several species also from the middle latitude.

124 Before the sampling, quartz fiber filters were precombusted for 4 h at 400 °C in a muffle furnace to  
 125 decontaminate from organic compounds. The sampling time was 6 days with a mean total air volume  
 126 of ca. 9500 m<sup>3</sup> per sample. Field blanks were obtained using filters installed on the sampler for 5 min  
 127 with the air pump switched off. Samples and blanks were wrapped in a double layer of aluminum foil  
 128 and stored at –20 °C until analysis. Only two samples and one field blank were used for this work  
 129 (see Table1).

130

131 **Table 1.** Surface snow samples and aerosol samples collected during the 2021 spring campaign.

| Sample type | Sampling Date<br>(2021) | Sample ID | Sample<br>volume <sup>a</sup> | Note                       |
|-------------|-------------------------|-----------|-------------------------------|----------------------------|
| Aerosol     | 08/04                   | Blank 0   |                               | Field blank                |
| Aerosol     | 08/04-14/04             | C2021_12  | 9573.75 m <sup>3</sup>        |                            |
| Snow        | 13/04                   | 1A        | 500 mL                        |                            |
| Snow        | 13/04                   | 1B        | 562 mL                        |                            |
| Snow        | 15/04                   | 2A        | 501 mL                        |                            |
| Snow        | 15/04                   | 2B        | 456 mL                        |                            |
| Snow        | 15/04                   | Blank 1   | 500 mL                        | Ultrapure H <sub>2</sub> O |
| Snow        | 19/04                   | 3A        | 491 mL                        |                            |
| Snow        | 19/04                   | 3B        | 503 mL                        |                            |
| Snow        | 22/04                   | 4A        | 516 mL                        |                            |
| Snow        | 22/04                   | 4B        | 501 mL                        |                            |
| Snow        | 26/04                   | 5A        | 499 mL                        |                            |

|         |             |          |                        |                            |
|---------|-------------|----------|------------------------|----------------------------|
| Snow    | 26/04       | 5B       | 519 mL                 |                            |
| Aerosol | 26/04-02/05 | C2021_15 | 9516.48 m <sup>3</sup> |                            |
| Snow    | 28/04       | Blank 2  | 500 mL                 | Ultrapure H <sub>2</sub> O |
| Snow    | 29/04       | 6A       | 486 mL                 |                            |
| Snow    | 29/04       | 6B       | 447 mL                 |                            |
| Snow    | 03/05       | 7A       | 500 mL                 |                            |
| Snow    | 03/05       | 7B       | 518 mL                 |                            |
| Snow    | 06/05       | 8A       | 543 mL                 |                            |
| Snow    | 06/05       | 8B       | 475 mL                 |                            |

<sup>a</sup>Sample volume refers to the amount of melted snow that, after filtration, was effectively loaded onto the SPE cartridge.

### 2.3. Sample preparation

#### 2.3.1. Snow sample preparation

In the clean laboratory facilities of the Italian Arctic Station Dirigibile Italia, once completely melted, the samples were filtered on Supor PES (hydrophilic polyethersulfone) membrane disc filters (47 mm diameter, 0.8 µm pore size, Pall Italia, Buccinasco, MI, Italy). After that, ca. 500 mL (see Table 1) were acidified with HCl to pH 4 before SPE. In preliminary experiments, performed on surface snow samples collected during the 2019 spring campaign, the sorbents Oasis HLB and Bond Elut PPL (Priority PolLutant, Agilent Technologies, Palo Alto, CA, USA) were compared according to standardized literature protocols. In the final experiments, the Oasis HLB SPE cartridges were used, previously preconditioned with 5 mL of MeOH and 10 mL of pH 4 H<sub>2</sub>O. Procedural blanks were prepared using 500 mL of ultrapure H<sub>2</sub>O as a sample and following the same procedure.

The SPE cartridges were packed in aluminum foil and stored at -20 °C until delivery at the Chemistry Department of the Sapienza University of Rome. Here the cartridges were washed with 5 mL of H<sub>2</sub>O and dried under vacuum for 15 min. Compound elution from the sorbent was obtained by sequentially

149 adding 6 mL of MeOH with 0.1% (v/v) HCOOH, 1 mL of pure MeOH and 6 mL of MeOH with 0.1%  
150 (v/v) NH<sub>3</sub>. The eluates were collected in the same glass vial, which was placed in a water bath at 40  
151 °C under a gentle nitrogen stream for solvent removal. The evaporation was stopped when the vial  
152 contained still ca. 50 µL of the eluate, and the residue was reconstituted with 250 µL of H<sub>2</sub>O/MeOH  
153 70:30 (v/v). After centrifugation (MicroCL 21R centrifuge, Thermo Scientific) at 18,000 × g for 10  
154 min to remove suspended particles, the supernatant was transferred to a clean vial for injection in the  
155 LC-MS system.

156

### 157 2.3.2 Aerosol sample preparation

158 Aerosol sample extraction was initially optimized by recovery studies using spiked blank filters  
159 (subject to precombustion at 400 °C in a muffle furnace) with 100 ng of a mixture of 9 standards (i.e.,  
160 gabapentin, acamprosate, caffeine, N-desmethylenlafaxine, acetylsalicylic acid, valpromide,  
161 lopinavir, sulfamethoxazole, and sulfadiazine) dissolved in MeOH. Filters were allowed to dry  
162 overnight at room temperature under the chemical hood in a clean environment, then they were cut  
163 and extracted with four different solvent mixtures: MeOH/H<sub>2</sub>O, 50:50 (v/v); acetonitrile/H<sub>2</sub>O, 50:50  
164 (v/v); MeOH/H<sub>2</sub>O, 90:10 (v/v); and dichloromethane/MeOH, 50:50 (v/v). MeOH/H<sub>2</sub>O, 90:10 (v/v).  
165 Recoveries and relative standard deviations (RSD, %) were calculated on three experimental  
166 replicates.

167 In the final procedure, filters were cut into quarters inside a clean room class 100 to preserve the  
168 sample and prevent contamination. Then, to improve the contact between the filter surface and the  
169 extraction solvent, the filter aliquots were cut into small pieces by a cleaned blade and subdivided  
170 into two 50 mL polypropylene centrifuge tubes (Merck Life Science), each added with 50 mL of  
171 MeOH/H<sub>2</sub>O 90:10 (v/v). The tubes were kept in an ultrasonic bath at 30 °C for 1 hour, and centrifuged  
172 at 7000 ×g for 20 min; the supernatant was collected. Filters were washed twice by adding in each  
173 polypropylene tube 15 and 10 mL of MeOH, respectively, vortexing for 2 min and putting the tubes  
174 in the ultrasonic bath for 20 min. After that, all the solvents were collected together and evaporated

175 in a speed-vac system (Speed-Vac SC250 Express, Thermo Savant, Holbrook, NY, USA) up to a  
176 small volume. The residue was finally reconstituted in 500  $\mu$ L of H<sub>2</sub>O/MeOH, 70:30 (v/v),  
177 centrifuged, and filtered through a syringe filter with 0.2  $\mu$ m GHP membrane (13 mm Acrodisc, Pall  
178 Italia).

179 A field blank filter was extracted according to the same procedure and used for blank correction in  
180 data processing by Compound Discoverer.

181

#### 182 2.4. LC-HRMS analysis

183 The LC-MS system was a Vanquish UHPLC instrument equipped with a binary pump, a thermostated  
184 column compartment, and an autosampler, coupled to a Q-Exactive hybrid quadrupole-Orbitrap mass  
185 spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA); the ion source was a heated  
186 electrospray (ESI).

187 Analytes were separated onto a Hypersil Gold (50  $\times$  2.1 mm i.d., 1.9  $\mu$ m particle size) column  
188 thermostated at 40  $^{\circ}$ C, and equipped with a Security guard Hypersil Gold (4  $\times$  2.1 mm i.d., 5  $\mu$ m  
189 particle size), both from Thermo Fisher Scientific. Mobile phase was (A) H<sub>2</sub>O with 0.1% (v/v)  
190 HCOOH, and (B) acetonitrile with 0.1% (v/v) HCOOH, operated at 200  $\mu$ L min<sup>-1</sup> flow-rate. The  
191 chromatographic gradient included an isocratic step at 10% B for 4 min, followed by a linear increase  
192 to 40% B in 8 min, an isocratic step at 40% B for 2 min, a linear increase to 70% B in 6 min, and an  
193 isocratic step to 70% B for 5 min. For column rinsing, B was brought to 99% in 3 min, and kept  
194 constant for 2 min; for column equilibration, B was brought back to 10% in 2 min and kept constant  
195 for 8 min (total run time 40 min). The injection volume was 20  $\mu$ L.

196 The LC-HRMS system was managed by Xcalibur software (v. 3.1, Thermo Fisher Scientific), and  
197 the acquisitions were carried out in both positive and negative ion modes. Tune parameters are  
198 reported in Supplementary Table S1. Spectra were acquired in the 130–1000  $m/z$  range in full-scan  
199 MS mode, with a resolution (full width at half-maximum, FWHM, @200  $m/z$ ) of 35,000. The  
200 automatic gain control (AGC) was 10<sup>6</sup> and the maximum ion injection time was 100 ms. Tandem

mass spectra of the 5 most intense ions were obtained in data-dependent acquisition (DDA) mode by higher-energy collisional dissociation (HCD) with 40% normalized collision energy, and a resolution (FWHM @200  $m/z$ ) of 17,500; the isolation window width was 2  $m/z$ , the dynamic exclusion was 3 s and AGC was  $10^5$ .

Calibration of the mass spectrometer was performed in both ion modes with Pierce positive and negative calibration solutions (Thermo Fisher Scientific) every 2 days, with a mass accuracy  $\leq 1$  ppm. Two technical replicates were acquired for each sample (including procedural blanks) and each polarity mode; a blank injection (20  $\mu$ L MeOH/H<sub>2</sub>O, 50:50, v/v) was run between samples for preventing carryover effects.

## 2.6. Compound identification

For each ion polarity mode, the raw data files obtained from the LC-HRMS acquisitions of snow or aerosol samples, with the related blanks, were submitted to Compound Discoverer v. 3.1 (Thermo Scientific) in a single batch processing. Compound Discoverer was used for data handling, elemental composition prediction, database searches, and compound tentative identification by a default workflow for untargeted environmental research with a few modifications, as previously reported (Montone et al., 2022) (detailed settings are reported in Supplementary Table S2). After processing, the list of the detected  $m/z$  features was reduced to the most significant ones by applying some filters and removing known background contaminants (e.g. polyethylene and polypropylene glycols). Compound tentative identification was achieved by matching the experimental tandem mass spectra with the mzCloud mass spectral database (HighChem LLC, Slovakia). Feature annotation and compound identification were accepted only after manual validation of the tandem mass spectra.

## 3. Results and Discussion

### 3.1. Sample collection and extraction

226 Due to adverse logistic and environmental conditions, the number of samples retrieved from the  
227 Arctic region is generally limited. Unfortunately, the ongoing global pandemic of COVID-19 has  
228 made it even more challenging with frequent delays, cancellations, postponement of expeditions, and  
229 further logistical challenges (AMAP, 2021b). In this context, after the first preliminary sampling  
230 campaign carried out in 2019, we were forced to cancel the second campaign planned for 2020, and  
231 post-pone it to spring 2021, although with a limited number of available sampling sites.

232

#### 233 3.1.1. Snow samples

234 The main challenges in analyzing organic compounds in Arctic surface snow are due to their low  
235 concentrations (typically below  $\text{ng L}^{-1}$ ), which thus require larger sample volumes than those from  
236 mid-latitude areas (Barbante et al., 2017).

237 CECs belong to several chemical classes and they possess a wide range of polarities, molecular  
238 weights, and other physicochemical characteristics, which make it difficult to determine and optimize  
239 the most suitable extraction protocol. In preliminary experiments, the SPE of snow samples was  
240 optimized by comparison of two different RP sorbents, namely Oasis HLB and Bond Elut PPL. Oasis  
241 HLB is a hydrophilic-lipophilic balanced divinylbenzene-N-vinylpyrrolidone copolymer and it is the  
242 most popular sorbent for environmental applications, whereas PPL is a proprietary functionalized,  
243 hydrophobic, styrene-divinylbenzene polymer and it is the sorbent of choice for dissolved organic  
244 matter investigations for its high efficiency in retaining nitrogen-rich molecules (Dittmar et al., 2008).  
245 The snow samples extracted by the two different SPE sorbents and analyzed by LC-HRMS/MS  
246 provided the same number of tentative identifications (ca. 90, data not shown); nonetheless, more  
247 CECs vs natural compounds were identified using Oasis HLB (56) than PPL (46) SPE material. For  
248 this reason, Oasis HLB was selected as SPE sorbent; the suitable conditions for CEC extraction  
249 (loading pH, elution solvent, etc.) were optimized in a previous work (Montone et al., 2022).

250

#### 251 3.1.2. Aerosol samples

252 Aerosol sample extraction was preliminary optimized by recovery studies using spiked blank filters  
253 with 9 representative standards and four extraction mixtures. Recovery and relative standard deviation  
254 (RSD) were calculated for each condition (Supplementary Table S3). Recoveries were in the range  
255 44-93% with RSD <17% for all analytes under the tested conditions. Better recoveries were obtained  
256 for the two MeOH/H<sub>2</sub>O mixtures (62-93%) than with acetonitrile/H<sub>2</sub>O or dichloromethane/MeOH  
257 mixtures, for which some analytes had insufficient recoveries (<60%). The best results in terms of  
258 recoveries (71-92%) and RSDs (<9%) were obtained with the MeOH/H<sub>2</sub>O, 90:10 (v/v) mixture, which  
259 was used for sample extraction.

260

### 261 3.2. LC-HRMS analysis

262 The LC-HRMS conditions were optimized in a previous work (Montone et al., 2022) and maintained  
263 because no special needs were observed for snow and aerosol samples analyzed in this study. The  
264 resolution values set for MS and MS/MS acquisitions, i.e., 35,000 and 17,500, respectively, provided  
265 mass errors <±2 ppm for most compounds. Distinct acquisitions for positive and negative ion modes  
266 allowed increasing the number of detected *m/z* features and, in turn, the number of matched  
267 compounds.

268

### 269 3.3. Compound identification

270 Compound Discoverer batch processing allowed aligning the chromatograms, automatically  
271 removing background signals (i.e., only features with a peak area in the blank < 10% than the peak  
272 area in at least one of the samples were maintained), simultaneously matching features to compounds  
273 and verifying their presence in the single samples. In a non-target analysis, Compound Discoverer  
274 assigns the molecular composition to the detected *m/z* features based on the measured accurate mass  
275 and isotopic pattern, whereas the compound name is assigned if the molecular composition matches  
276 with at least one of the submitted mass lists. However, reliable compound identification is obtained  
277 only if the MS/MS spectrum of the *m/z* feature has been acquired and it matches the mass spectral

database mzCloud (mzcloud.org). To improve the confidence of compound annotation, features matching to the mzCloud database were also manually validated and corresponded to a confidence level 2a (probable structure) in the classification proposed by Schymanski *et al.* (Schymanski et al., 2014). Some of the validated tandem mass spectra are reported in Supplementary Figs. S2-S12.

### 3.3.1 Snow samples

The untargeted analysis of snow samples provided the tentative identification of 82 and 33 compounds in the positive and negative ion modes (1 compound was detected in both polarities), respectively, for a total of 114 compounds (see Supplementary Table S4).

### 3.3.2. Aerosol samples

To evaluate the atmospheric contribution through dry deposition processes, aerosol samples collected in the same area during the snow sampling campaign were also analyzed. The compounds extracted from the two filter sets and tentatively identified were 38 in positive ion mode and 21 in negative ion mode (2 compounds were detected in both polarities), respectively, for a total of 57 compounds (see Supplementary Table S5). All species identified were found in the coarse fraction (particle size above 1  $\mu\text{m}$ ), demonstrating their local sources, since the coarse particles show an atmospheric lifetime minor than fine particles because sedimentation or wet deposition occurs (Petzold and Kärcher, 2012). For this reason, we can speculate that these species present in the coarse particles are locally emitted and then deposited on the snowpack.

## 3.4. Environmental contaminants and possible sources

More than 80 out of 114 and 35 out of 57 tentative assigned identifications in snow and aerosol samples, respectively, are potential anthropogenic compounds (industrial chemicals, drugs, plasticizers, fragrances, etc.), whereas very likely, the other remaining compounds are of natural origin. However, only general considerations are possible about the origin of detected compounds,

304 since organic compounds can derive from both natural or anthropogenic sources (Barbante et al.,  
305 2017). For example, azelaic acid, which was detected in both snow and aerosol samples, is a natural  
306 product of some grains and yeast, but also it is used in cosmetics and pharmaceuticals as an active  
307 component of some anti-acne formulations and other skin and hair care products; moreover, azelaic  
308 acid is a precursor to diverse industrial products such as polymers and plasticizers.

309 Among the 114 and 57 compounds identified in snow and aerosol samples, respectively, there were  
310 only 9 compounds in common, namely isophthalic acid, tributylamine, azelaic acid, dodecyl sulfate,  
311 caffeic acid, nootkatone, 3-methylglutaric acid, 1-carboxycyclohexaneacetic acid, and 7-  
312 hydroxycoumarine (see Supplementary Table S6). This discrepancy can be due to meteorological  
313 factors, such as wet deposition and wind drift, that can significantly alter the chemo-physical  
314 properties of the snowpack increasing snow spatial variability. We hence highlight the need for  
315 further investigation for a better understanding of the real source of the identified species in the  
316 snowpack.

317 Samples were collected near the international research station of Ny-Ålesund, one of the four  
318 permanent settlements in Spitsbergen. Its all-year permanent population is 30 to 35, while the summer  
319 population is up to ca. 120 (Choi et al., 2020). The local contamination sources of the Svalbard  
320 Archipelago are quite limited and are constituted by towns and villages, waste sites, and sewage  
321 effluents (AMAP, 2017); the total absence of outdoor agriculture on these islands implies the absence  
322 of any local pesticide source (Hermanson et al., 2020). Nonetheless, contaminants can reach this area  
323 in various ways: some industrial chemicals, pesticides, etc., are mainly released at lower latitudes  
324 (from Eurasia) and carried to the Arctic via atmospheric and oceanic currents; other substances, such  
325 as flame retardants and poly- and per-fluoralkylated substances, could be released locally from  
326 imported materials and products used within the Arctic (AMAP, 2021a). Different from other regions,  
327 Arctic deposition to surface snow is affected by the absence of interaction with plant cover, meltwater,  
328 or soil, being driven by the interaction between the atmosphere and the high scavenging of falling  
329 snow (Hermanson et al., 2020). The semi-volatile organic compounds are accumulated in the

330 snowpack by condensation (because low temperatures promote a shift of their partitioning equilibria  
331 from the vapor phase toward the condensed phase) and by precipitation (e.g. falling snow, which  
332 removes both vapor- and particulate-bound compounds from the atmosphere) (Herbert et al., 2006).  
333 Several studies have been carried out on the deposition of POPs, PAHs, and other halogenated and  
334 not halogenated persistent compounds, including OPEs (Salamova et al., 2014).

335 OPEs global consumption has increased in the last decades since they are valid substitutes for the  
336 more persistent brominated flame retardants; moreover, they are also employed as plasticizers, floor  
337 polish, and antifoaming agents. The OPE chemical properties cause their release in the environment  
338 through volatilization, abrasion, and/or dissolution (Fu et al., 2021), and their presence in the Arctic  
339 and Antarctica has been widely reported in several environmental compartments (Xie et al., 2022).

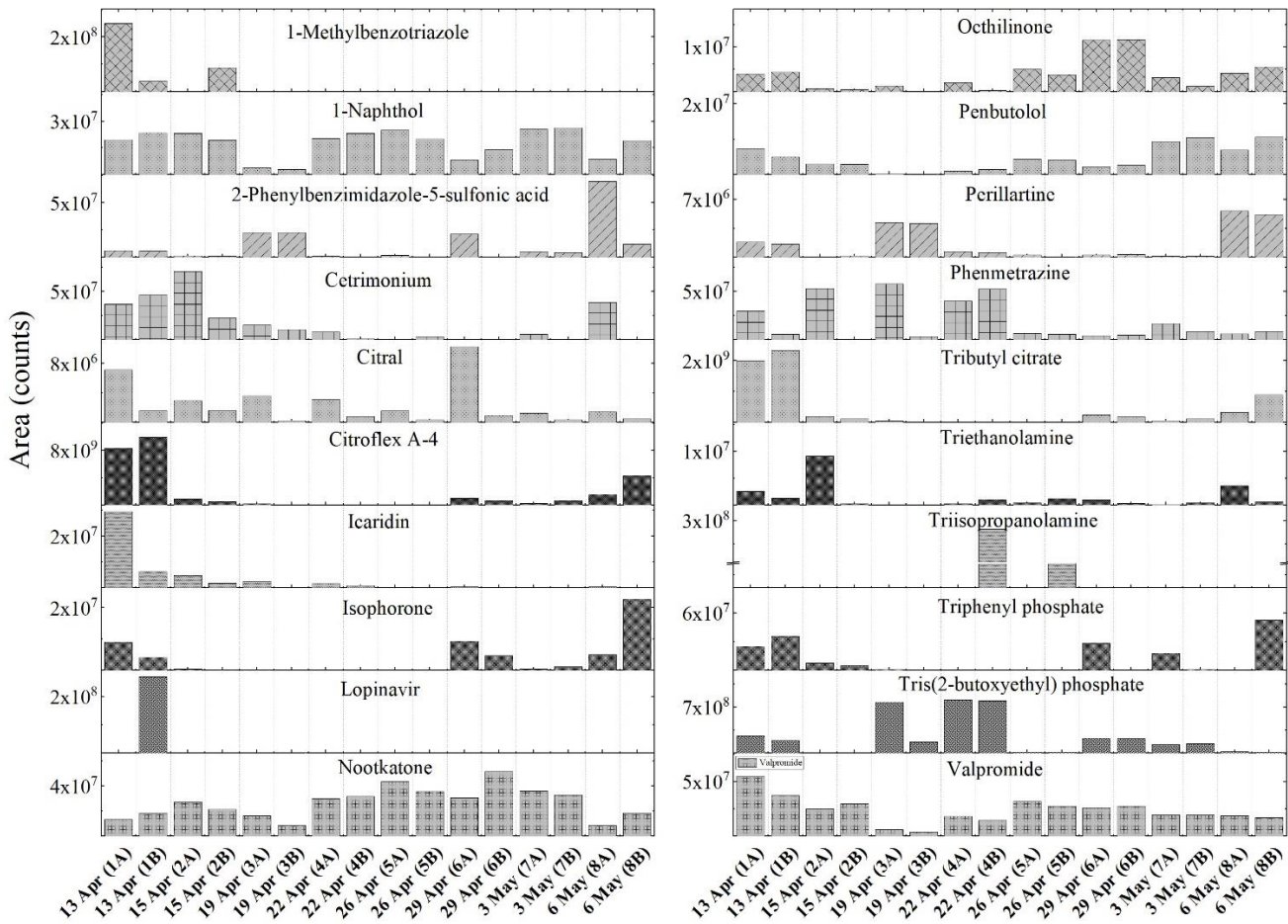
340 In this work, 3 OPEs were detected in snow samples, namely the chlorinated tris(2-chloroethyl)  
341 phosphate (TCEP, Fig. S2), and the 2 nonchlorinated triphenyl phosphate (TPP, Fig. S3) and tris(2-  
342 butoxyethyl) phosphate (TBEP, Fig. S4). Based on their predicted or experimental log  $K_{ow}$  values  
343 (Supplementary Table S4), TPP is the most bioaccumulative one (log  $K_{ow}$  4.59), followed by TBEP  
344 (log  $K_{ow}$  3.75), whereas TCEP, which has been reported as one of the two predominant chlorinated  
345 OPEs in Arctic fresh and seawater (Xie et al., 2022), is not bioaccumulative (log  $K_{ow}$  1.44), but it is  
346 toxic to aquatic organisms, carcinogenic for animals, and has adverse effects on human health (Li et  
347 al., 2017). Although OPEs short half-lives (due to the gas phase degradation by OH radicals) do not  
348 meet the minimum threshold (2 and 60 days for the gas and aqueous phase, respectively) set for  
349 LRAT in the Stockholm Convention, their widespread detection in both Arctic and Antarctic areas  
350 suggests a different environmental behavior, which some researchers ascribed to the presence of  
351 atmospheric water or OPE adsorption onto the particle phase (Fu et al., 2021). Indeed, prediction  
352 tools attributed a marked tendency of some OPEs, in particular the chlorinated TCEP, to distribute in  
353 the water compartment instead of air, and the OPE high solubility and long half-lives in water could  
354 be determinants of their oceanic current transport (AMAP, 2017; Fu et al., 2021). Arctic local sources  
355 of OPEs are constituted by indoor emissions since as flame retardants they are added to furniture,

electronics, building materials, etc. (Fu et al., 2021), and wastewater effluents, as reported by Choi *et al.* in Ny-Ålesund town (Choi et al., 2020). Regarding the Svalbard archipelago, OPE concentration levels were determined in particle phase atmospheric samples at Longyearbyen (Salamova et al., 2014), in the sewage effluents (Choi et al., 2020), water, and sediment of Ny-Ålesund (Gao et al., 2020), and the Arctic seawater (Gao et al., 2019).

Besides the LRAT of semi-volatile organic compounds in the gas phase or on aerosols/particles, some CECs, such as perfluoroalkyl sulfonates and perfluorocarboxylic acids, can undergo long-range transport to the Arctic via ocean currents due to their propensity to partition to water (de Wit et al., 2019). In this work, perfluorononanoic acid (PFNA), perfluoroundecanoic acid (PFUdA), and a PFAS degradation product were detected in snow samples, in agreement with previous reports on the presence of ionic PFASs (mainly PFOS, PFOA, and PFNA) in surface snow and ice cores from Longyearbyen and Ny-Ålesund in Svalbard (Kwok et al., 2013; Xie et al., 2022).

The scattering of the small Arctic communities in minor settlements and the harsh environmental and logistic conditions make the installation of wastewater treatment plants economically unfeasible, thus sewage is often released more or less untreated into the aquatic environment. In particular, Ny-Ålesund has a sewage treatment plant operating without any chemical or microbial treatment; the elimination mechanisms are supposed to occur by sorption onto particulate matter and/or biodegradation by soil microbes (Choi et al., 2020). Generally, PPCPs possess low environmental mobility, therefore their presence in the Arctic mainly derives from local anthropogenic sources, while their transport via ocean currents to polar regions has not been elucidated yet (Xie et al., 2022). PPCP presence in the Arctic aquatic environment is mainly attributed to the direct release from wastewater effluents, as well as the release from households and leaching from disposal sites (AMAP, 2017). Nonetheless, in the Arctic, PPCPs have been detected also in several other environmental compartments (Kallenborn et al., 2018). Among PPCPs detected in this work in snow samples, the surfactant cetrimonium, salicylic acid, and paraxanthine (Fig. S5) were previously reported in the Arctic (AMAP, 2017).

382 A few compounds tentatively identified in the snow (5) and aerosol (1) samples were previously  
 383 detected in Ny-Ålesund sewage effluents (Choi et al., 2020). These compounds are the two OPEs  
 384 TPP and TBEP, the major caffeine metabolite paraxanthine (Fig. S5), the surfactant xylenesulfonate,  
 385 and the insect repellent icaridin (Fig. S6) that were detected in snow samples, whereas another insect  
 386 repellent, DEET (Fig. S7), was detected in aerosol samples. Other spectra are reported in  
 387 Supplementary Figs. S8-S12.  
 388 In this untargeted investigation carried out on samples collected on the same site, only a comparison  
 389 between the peak areas of the identified compounds was possible. Fig. 2 reports the peak area values  
 390 (after blank subtraction) for some selected analytes detected in snow samples collected on different  
 391 days.



392  
 393 **Fig. 2.** Peak areas (after blank subtraction) for some of the identified compounds in the 16 snow  
 394 samples collected on 8 different days. The peak areas of each sample are the mean of 2 technical

395 replicates, whereas the subtracted blank area was obtained as the mean of the 2 technical replicates  
396 of the 2 procedural blanks.

397

#### 398 **4. Conclusions**

399 The untargeted analysis carried out on surface snow samples collected near the arctic research station  
400 of Ny-Ålesund, in the Svalbard archipelago, provided the tentative identification of more than one  
401 hundred compounds, most of them likely deriving from anthropogenic contamination locally sourced  
402 and/or transported from lower latitudes. Local sources such as sewage effluents and emissions from  
403 the indoor environment can be relevant especially in correlation to the increased scientific activities  
404 in this remote area, whereas long-range transport can occur via atmospheric and/or oceanic currents,  
405 depending on the compound physicochemical characteristics. Some of the tentative identifications  
406 were in agreement with previous reports, whereas other compounds were not reported previously in  
407 this location. Unfortunately, due to the pandemic situation, the snow-sampling site was the same for  
408 all 16 samples collected on 8 different days over one month. Although the analytical results of this  
409 study, one of the few applying an LC-HRMS-based untargeted analysis on samples collected in the  
410 Arctic, pointed out the presence of anthropogenic contaminants of emerging concern in the Ny-  
411 Ålesund snow layer, a clear contamination trend was not identified even after comparison with  
412 aerosol samples, thus calling the need for further campaigns to better understand the contaminants'  
413 sources and their environmental fate.

414

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429

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