1 First evidence of microplastic contamination in the supraglacial debris of

2 an Alpine glacier

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11 Abstract

Contamination by plastic debris has been documented in most regions of the world, but their 12 occurrence in high mountain areas has not been investigated to date. Here we present the first 13 14 report of the occurrence and amount of microplastic in any terrestrial glacier environment. In the supraglacial debris of the Forni Glacier (Italian Alps), we observed the occurrence of (mean ± 15 standard error) 74.4 \pm 28.3 items kg⁻¹ of sediment (dry weight). This amount is within the range of 16 17 variability of microplastic contamination observed in marine and coastal sediments in Europe. Most plastic items were made by polyesters, followed by polyamide, polyethylene and polypropylene. 18 We estimated that the whole ablation area of Forni Glacier should host 131-162 million plastic 19 20 items. Microplastic can be released directly into high elevation areas by human activities in the mountain or be transported by wind to high altitude. The amount of microplastic on Forni Glacier 21 22 may be due to the gathering of debris coming from the large accumulation area towards the 23 relatively smaller ablation area of the glacier, as a consequence of its flow and melting.

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25 Keywords: Alpine glacier; microplastics; mountain areas; supraglacial debris

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27 Capsule

28 We present the first evidence of the occurrence of microplastic contamination on an Alpine glacier.

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30 1. Introduction

31 Accumulation of plastic polymer (hereafter plastic) items is one of the most ubiquitous and long-

32 lasting changes to the earth surface that human activities have produced since mass production of

33 plastic commenced in the 1950s (Barnes et al., 2009; Thompson et al., 2004). Concerns have been raised in recent years on the potential impacts of plastic on ecosystems. Plastic is indeed persistent, 34 accumulates in the environments, can enter the trophic chain, and its impacts on ecosystems have 35 already been demonstrated (Barnes et al., 2009; Cole et al., 2011; Wright et al., 2013). In recent 36 37 years, particular attention has been focused on microplastics, plastic items smaller than 5 mm that 38 can be specifically produced to be used in diverse personal care products and in different industrial 39 applications (i.e., primary microplastics), or can be generated by the break-down of macroplastics 40 (secondary microplastics) (Eerkes-medrano et al., 2015). Surveys on marine and freshwater ecosystems have been established to monitor the temporal trends in the amount of plastic items. 41 Oceanic campaigns have estimated the amount of macro- and microplastics afloat in the sea 42 43 (Eriksen et al., 2014), and the amount transported to sea by rivers from terrestrial ecosystems. 44 Moreover, recent studies have demonstrated that microplastics can be transported to virtually any part of the globe, also in the so-called remote areas. Indeed, plastic fragments have been found in 45 deep sea, Southern Oceans, Arctic and Antarctica (Hamid et al., 2018), as well as in sub-alpine lake 46 47 sediments (Imhof et al., 2013), in pelagic water and shoreline debris from high-mountain lakes (Free 48 et al., 2014; Zhang et al., 2016), and floodplain soils in Alpine valleys (Scheurer and Bigalke, 2018). 49 In addition, recent evidence of atmospheric microplastic deposition in a remote, pristine mountain area of the French Pyrenees suggests that microplastics can reach and affect remote, sparsely 50 51 inhabited areas far from emission source through atmospheric transport (Allen et al., 2019). 52 However, to the best of our knowledge, no published study have documented the occurrence and 53 the amount of plastic items on glaciers so far.

Glaciers are accumulation sites for aerially transported debris and pollutants as glacier ice form through the transformation of accumulated snowfalls, which are particularly efficient in scavenging contaminants, including small debris, from the atmosphere (e.g., Lovett and Kinsman, 1990; Lei and

Wania, 2004). Temperate glaciers then flow down valley, and the ablation area of valley glaciers thus concentrates the debris and the contaminants collected over the much vaster accumulation area of the glacier (Nakawo et al., 1986). For this reason, supraglacial debris is particularly rich in air-transported pollutants (Cook et al., 2016; Pittino et al., 2018), including radionuclides (Baccolo et al., 2017; Łokas et al., 2016). We thus hypothesized that similar processes may act also for microplastics, and we present here the first evidence of the occurrence and the first estimate of the amount of microplastic in the supraglacial debris of a large valley glacier in the Italian Alps.

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65 2. Materials and Methods

66 2.1 Study Area

This study was carried out on the ablation tongue of Forni Glacier, one of the widest Italian glaciers, with a total surface area of 11.34 km² and an ablation area of 0.59 km² (Azzoni et al., 2018). This glacier is located in the Ortles-Cevedale group (Stelvio National Park, Central Italian Alps), not far (~90 km) from a high-urbanized area as the Po Plain and it is very popular with mountaineers and hikers due to the presence of numerous path and alpine route.

72 2.2 Sample collection

On 20 and 24 July 2018, we collected two cryoconite samples and four samples of sparse supraglacial debris from the surface of the ablation area of Forni Glacier (Table S1). Cryoconite is a thin supraglacial debris of mostly aeolian origin that, when heated by solar radiation, can melt the undelaying ice forming small ponds. These 'cryoconite holes' are considered the most biologically active environments on glaciers (Cook et al., 2016). Sparse debris is a debris similar to cryoconite, occurring in glacier surface, but not forming ponds. To avoid contamination, samples were collected in glass jars with a gardening metal shovel or a metal laboratory spoon. Jars and sampling tools were accurately cleaned with acetone before sampling. We also took care to avoid contamination by plastic fibres released by the clothes and shoes of the operator that collected samples by wearing a 100% cotton surgical gown and 100% wooden clogs (Fig. S1). Only the operator entered the area where we collected samples, while the other members of the team remained > 10 m apart for avoiding sample contamination.

85 2.2 Microplastic floating and identification

86 Extraction of microplastic items from supraglacial and cryoconite debris samples was performed according to the method first developed by Thomspon and co-authors (Thompson et al., 2004), and 87 adapted by Klein and co-authors (Klein et al., 2015) to river sediments. All the glassware and 88 89 stainless forceps used during extraction procedure was previously washed with ultrapure filtered 90 water to avoid potential laboratory contamination. The extraction was performed under a laminar-91 flow hood. The synthetic polymers were separated from glacial sediments by density separation 92 using a saturated sodium chloride solution (density = 1.2 g cm^{-3} ; 365 g L⁻¹). About 50 g of sediments (dry weight; range 50.87 - 53.52 g; see Table S1) were mixed with 300 mL of the NaCl solution, 93 previously filtered on glass fibre filters (ϕ = 0.45 µm, Whatman GF/A 47 mm, GE Healthcare Europe 94 95 GmbH), and stirred for 15 min. The sediment particles were allowed to settle overnight. Then, the solution containing the floating particles was transferred by using a 50 mL glass volumetric pipette 96 97 to a glass separation flask, where it was filtered on glass fibre filters by using a water-jet pump. The 98 saturated NaCl solution was continuously added to the separation flask. At the end of the filtration process, the flask was rinsed three times with 20 mL of ultrapure filtered water to recover potential 99 100 plastic particles adherent to the glass flask. Natural, organic debris was removed by filters through an overnight treatment with a hydrogen peroxide (H₂O₂) solution (15%). The excess of H₂O₂ solution 101 was then rinsed twice with ultrapure filtered water, vacuum-filtrated through glass fibre filters, 102

103 rinsed again, and dried under a laminar-flow hood for 48 h. During all steps of sample preparation, 104 glassware and filtration flask were covered with tinfoil to prevent contamination by plastic items. A blank sample was performed before and after the extraction from supraglacial sediment and 105 cryoconite samples to check for any laboratory contamination. Saturated salt solution (300 mL) was 106 stirred for 15 min, settled overnight and then filtered on glass fibre filters as described above. Filters 107 108 were then digested with H₂O₂ (15%) overnight and, after rinsing with ultrapure filtered water, dried 109 under a laminar-flow hood for 48 h. All the glassware used for filtration was accurately rinsed with ultrapure filtered water between samples. All the obtained filters were examined under a binocular 110 microscope (Leica DM750; 20x – 40x of magnitude) and plastic items were classified by their shape 111 into fragments or fibres. The size of plastic items observed on the filters was measured with the 112 image processing package Fiji freeware software (Schindelin et al., 2012). Visual examination of all 113 114 the particles was carefully performed to exclude natural debris (e.g. insect exuviae) and/or mineral components. These residual materials were removed with stainless steel forceps. All the plastic 115 116 items collected on filters were chemically characterized using the Fourier Transform Infrared Microscope System (µFTIR; Survey IR Microspectroscopy Accessory coupled with Nicolet iS5 FTIR 117 118 Spectrometer, Thermo Fisher Scientific; detection limit ~ 100 µm) to confirm their plastic nature and 119 to identify polymer typologies. Analysis was performed in attenuated total reflection (ATR) mode operating on single reflection mode in the range of 600 and 3,800 cm⁻¹ and with 16 scans per 120 121 analysis.

122 2.3 Estimate of the amount of fine debris

The quantification of supraglacial debris was performed using image classification technique from high-resolution airborne orthophotos (pixel size 0.5 m × 0.5 m) of the glacier surface. Classification of surface characteristics and properties of glaciers from remote-sensed data is a common activity in glaciology (e.g. Paul et al., 2004). The area covered by scattered and sparse debris was estimated

127 with a maximum likelihood classification in ESRI ArcMap software (ESRI, Redlands, California) excluding areas covered by moraines (Azzoni et al., 2018) (Fig. 1). This procedure is a supervised 128 classification method of the spectral signature of high-resolution images of the glacier (ESRI, 2011). 129 First, the user manually classifies a sample of pixels as bare ice or debris based on his or her 130 experience and *a priori* knowledge of the Forni Glacier. Then the software calculates statistics from 131 132 the spectral signature of these pixels and creates a parametric signature for bare ice and one for debris. Finally, it classifies each pixel in the image as bare ice or debris based on these spectral 133 statistics (ESRI, 2011). For increasing the reliability of the classification, both the manual 134 classification of pixels and the following automatic characterization of the whole image were 135 repeated ten times and the minimum and maximum value of the extent of the area covered by 136 debris were considered. The total volume of debris was then calculated assuming a mean debris 137 138 thickness of 0.5 cm (R.S. Azzoni, unpublished data) and its total weight was finally calculated using debris density values (from 1600 kg m⁻³ to 2000 kg m⁻³) obtained following Ponce (1989) on the basis 139 of supraglacial debris size distribution (Azzoni et al., 2016). 140

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142 **3. Results and discussion**

We found 2-7 plastic fragments per sample that correspond to 74.4 ± 28.3 SE items kg⁻¹ of sediment 143 144 (dry weight) on average, with no difference between cryoconite (70.5 ± 32.9 SE items kg⁻¹) and 145 sparse supraglacial debris (78.3 ± 30.2 items kg⁻¹) (see Supporting Information; Table S1). No plastic item was found in blank samples. Fibres represented 65.2% and fragments 34.8% of items in all 146 samples pooled. Both microplastic fragments and fibres were of diverse colour (Fig. 1). Overall, most 147 plastic items were made from polyesters, followed by polyamide, polyethylene and polypropylene 148 (Fig. 1). Unfortunately, 39% of plastic items could not be characterized because their size was below 149 the limit of detectability (\sim 100 μ m) of the FTIR we used (see Methods and Table S1). 150

By using image processing (see Methods), we estimated that the ablation area of the Forni Glacier covered by cryoconite and sparse debris was 0.21-0.23 km². Cryoconite and sparse debris weighed 1,640-2,307 tons. According to the amount of plastic items we found in our samples, the ablation area of the glacier should therefore include 131-162 million of microplastics, corresponding to 570-801 million items km⁻².

This is the first report published on a scientific journal of microplastic contamination in any 156 157 terrestrial glacier environment. The amount of microplastics we detected is within the range of variability of contamination observed in marine and coastal sediments in Europe (Hamid et al., 2018) 158 and similar to those detected in lakeshore sediments from four lakes located in a region with very 159 160 low population density and lacking of industrial and agricultural activities within the Siling Co basin in northern Tibet, where a microplastic abundance up to 563 \pm 1,219 million items km⁻² was 161 162 observed (Zhang et al., 2016). Microplastic contamination on Forni was also intermediate between 163 that measured in soils from mountain floodplains in different parts of Switzerland, where up to 593 items kg⁻¹ were found (Scheurer and Bigalke, 2018). and that observed in the pelagic water of Lake 164 165 Hovsgol, a large, remote mountain lake in Mongolia, where an average microplastic density of 20,264 items km⁻² was found (Free et al., 2014). Clearly, comparisons among levels of microplastic 166 contaminations from very different environmental matrices should be taken very cautiously. 167 168 However, these results suggest that microplastic contamination on Forni Glacier is within the range 169 of contamination observed in the few remote mountain areas investigated worldwide to date.

Plastic can reach high elevation areas from several paths. Human activities in the mountain environment produce large amount of garbage, which sometimes can hardly be transported down valley. Most alpinist equipment, for instance, is made of plastic polymers, and can be abandoned on mountains in emergency or deliberately. For instance, in 1990, the "Free K2" expedition recovered about 2 tons of garbage from the second highest mountain of the planet, most of which

175 were plastic (Ardito and Mountain Wilderness, 1995). Forni Glacier is visited each year by hundreds of tourists whose clothes and equipment may release plastic fibres and items. The presence of 176 polyesters and polyamide fibres in glacier debris seems consistent with this hypothesis. Equipment 177 used during scientific surveys conducted on Forni Glacier can also have determined plastic fibres 178 179 release (R.S. Azzoni, personal information). However, Forni Glacier is also close to densely inhabited 180 areas like the Po plain in northern Italy, which can contribute to the amount of plastic fragments 181 observed. Indeed, small plastic items can be transported by wind to high altitude, where they can be deposited by both wet and dry deposition (Allen et al., 2019; Dris et al., 2016). Indeed, a recent 182 study by Allen and co-authors (2019) performed in a pristine mountain catchment of French 183 184 Pyrenees, confirmed that fibres up to ~750 μ m long and fragments \leq 300 μ m can be transported by air and deposited in remote areas up to 95 km from potential sources (Allen et al., 2019). This 185 186 distance is similar to that between Forni Glacier and the densely inhabited Po Plain, which is ~90 km 187 from the glacier. Atmospheric transport of plastic items might therefore contribute to the amount 188 microplastic we found on Forni Glacier. Unfortunately, the relative amount of plastic items that reaches the Forni Glacier from local or remote sources could not be assessed with the data available 189 190 for the present study and should be further investigated.

191 4. Conclusion

Our findings of microplastic contamination on glaciers, albeit not unexpected, demonstrated that also this contaminant can reach remote, high mountain areas. When trapped in the sediment, microplastics can persist on glaciers for an unknown amount of time and there is therefore the potential for long-term persistence of microplastic on glaciers, which may have already accumulated an unknown amount of plastic since the 1950s, when plastic have started to be released in the environment. These particles might be potentially released by glaciers, entering melting waters and contributing to freshwater contamination and, ultimately, also to marine contamination. The

current amount of contamination and the fate of microplastics in glaciers should therefore be
carefully evaluated by further studies beside this very preliminary investigation.

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202 5. References

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Figure 1. Study area and microplastic composition. Top-left panel: the ablation area of the Forni glacier with sample collection sites (red dots) and its geographical location within Europe. The blue shaded area indicates the part of the glacier tongue covered by scattered and sparse debris. Topright panel: proportion of plastic items per colour (upper diagram) and per polymer composition (lower diagram). Bottom line: polyester fibres (a and b) and an unknown fragment (c).

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