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Characteristics and quantification of small microplastics (<100 μm) in seasonal svalbard snow on glaciers and lands

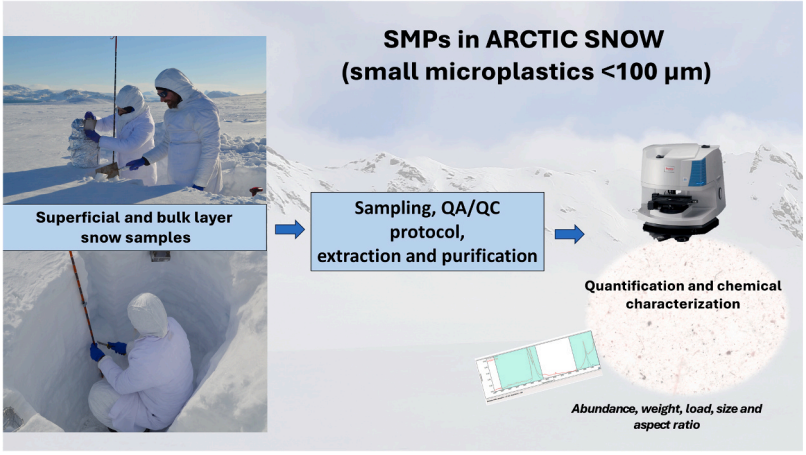
Beatrice Rosso [a,b], Federico Scoto [b,c], Ingeborg G. Hallanger [d], Catherine Larose [e], Jean Charles Gallet [d], Andrea Spolaor [a,b], Barbara Bravo [f], Carlo Barbante [a,b], Andrea Gambaro [b], Fabiana Corami [a,b,*]

[a] Institute of Polar Sciencies, CNR-ISP, Campus Scientifico Ca' Foscari University, Via Torino 155, 30172 Venezia Mestre, Italy
[b] Department of Environmental Sciences, informatics, and Statistics, Campus Scientifico - Ca' Foscari University of Venice, Via Torino 155, 30172, Venezia-Mestre, Italy
[c] Institute of Atmospheric Sciences and Climate, National Research Council, CNR-ISAC, Lecce, Italy
[d] Norwegian Polar Institute, Fram Centre, Tromsø 9296, Norway
[e] Environmental Microbial Genomics, Laboratoire Ampère, École Centrale de Lyon, Université de Lyon, Écully, France
[f] Thermo Fisher Scientific, Str. Rivoltana, Km 4, 20090 Rodano, MI, Italy

HIGHLIGHTS

- Small microplastics (SMPs <100 μm) were observed at the summit of Arctic glaciers.
- Spatial variability was observed among glaciers.
- SMPs were also observed at the glacier Holtedahlfonna above the boundary layer.
- Long-range atmospheric transport contributed to SMPs deposition in Arctic snow.
- Potential impacts of SMPs in the snow may affect Arctic ecosystems and biota.

GRAPHICAL ABSTRACT



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ABSTRACT

Small microplastics (SMPs < 100 μm) can easily be transported over long distances far from their sources through the atmospheric pathways and reach even remote regions, including the Arctic. However, these sizes of MPs are mostly overlooked due to different analytical challenges; besides, their pathways through atmospheric depositions, such as snow depositions, are mostly unknown. The spatial variability in bulk snow samples was investigated for the first time in distinct sites (e.g., glaciers) near Ny Ålesund, the world-known northernmost permanent research settlement in the Svalbard Islands, to better comprehend the presence of SMP pollution in

* Correspondence to: Institute of Polar Sciences, CNR-ISP, Campus Scientifico - Ca' Foscari University of Venice, Via Torino, 155, 30172 Venezia, Mestre, Italy.
E-mail address: fabiana.corami@cnr.it (F. Corami).

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snow. Seasonal snow deposited over the tundra and the summits of different glaciers were also sampled. A sampling procedure was designed to obtain representative samples while minimizing plastic contamination, thanks to rigorous quality assurance and quality control protocol. SMPs' weight (μg SMP L^{-1}) and deposition load (mg SMPs m^{-2}) result from being lower in the remote glaciers, where they may be subject to long-range transport. The SMPs' minimum length was 20 μm, with the majority less than 100 μm. Regarding their size distribution, there was an increase in the size length deriving from the local input of the human presence near the scientific settlement. The presence of some polymers might be site-specific in relation to the pathways that affect their distribution at the sites studied. Also, from the snow surface layer collected at the same sites to evaluate the variability of SMPs during specific atmospheric deposition events, the results confirmed their higher weight and load in surface snow near the scientific settlement compared to the glaciers. The results will enhance the limited knowledge of the SMPs in polar atmospheric compartments and deposition processes.

1. Introduction

Over the last century, versatility and durability have allowed microplastics (MPs) to become the most ubiquitous synthetic materials in the worldwide environment, with the potential to cause significant ecological damage. However, while many of the studies carried out so far have focused on their assessment of aquatic and terrestrial ecosystems, the atmospheric compartment is very limited investigated [33,60]. Airborne MPs have been identified in atmospheric aerosol from urban areas (Pandey et al., 2022); [67,73], in the fallout from atmospheric deposition in urban cities [16,28,44], and in remote regions worldwide, such as high mountains in the Alps [4], the Tibetan Plateau [85], or in Antarctic snow [6], suggesting that atmospheric transport must be a key component in the spreading of MPs in different compartments [72].

Once MPs are emitted from their source, they can be conveyed by wind and air circulation, deposited, and resuspended, crossing over confines between terrestrial and aquatic environmental compartments in a dynamic exchange [60]. This allows MPs to reach far and remote places, may be transported long distances (over thousands of km) with regional air masses, deposited through dry or wet (rain or snowfall) depositions, depending on different factors such as wind speed, erosion, turbulence, bubble bursting, movement of water masses, etc. [60,81]. Wet and dry deposition processes are considered the positive drivers of aerosol particles to the ground since they are the current scavenging mechanisms to make the MPs settle onto an Earth-bound surface, posing risks for biota and human health [4,29]. Scavenging processes depend on the particle size, weight, typology, terminal velocity of the particle, and aerodynamic properties [58,60,80]. The SMPs' weight is relevant for their ecological impacts and environmental distribution and for modeling different scenarios [54,64]. In this perspective, the smallest microplastics (SMPs $<$ 100 μm) are crucial to investigating atmospheric aerosol and depositions since they are more easily transported far from their source and subject to long-range transport pathways, rather than the larger and heavier particles (MPs $>$100 μm).

Further, their potential implication for the entire food chain has raised significant concern in all ecosystems, including the polar food web ([11,32]; Iannili et al., 2019). Only recently, the increase in plastic pollution production and usage worldwide has impacted the remote Arctic region ecosystems, which are believed to serve as temporary storage for anthropogenic litter, such as MPs [34].

The presence of MPs and SMPs may affect global radiative forcing in the climate processes, such as altering cloud formation acting as cloud condensation nuclei in the atmosphere or changing the optical properties of the snow by contributing to ice/snow melting processes; therefore, it is crucial to investigate MPs' and SMPs' occurrence in the atmosphere, including wet depositions processes such as snow depositions [2,66]. These latter can capture airborne MPs and SMPs by falling to the ground, and the gradual but continuous accumulation of snow during multiple deposition events provides different temporal distributions since snow can act as a store for emerging pollutants [1,75]. Besides, MPs may have significant negative impact on fresh and marine waters [49] and the active layer of permafrost ([86]), as a direct result of the snowmelt process in the area; this negative impact could be enhanced for SMPs since they can be ingested by invertebrates [40], posing a risk for the whole polar food web.Nevertheless, the impact of the potential release of SMPs over time from the snow compartment is still unknown and must be investigated thoroughly, with the help of robust and replicable abundance and distribution data, for which there is still a knowledge gap.

Scarce studies have investigated MPs in Arctic environments, such as Arctic snow [10], sea ice [42,43,79] or seawater [25,47]. Besides, SMPs were often overlooked due to the size limitation of sampling, pre-treatment methods for the extraction and purification, techniques for their analysis, and the lack of a standardized procedure for their quantification and chemical characterization. There is a substantial lack of knowledge of the atmosphere pathways in the most remote places, including the retention and scavenging processes on the transport of SMPs ([48]; O' Brien et al., 2022; [72,81]).

Furthermore, the discrimination between the long-range and short-range SMPs' sources is fundamental to investigate. Long-range atmospheric transport has been already studied in the Arctic; it can convey various types of pollutants from mid-latitudes toward the Arctic, mainly from Europe and Asia [24,26,56,69,82,9]. Besides, this transport is dominant in winter and spring, and is especially effectual in the latter period, giving rise to the so-called Arctic haze phenomenon; as a matter of fact, especially during spring, the meterology of the Arctic air mass is characterized by rapid transport from mid-latitudes, reduced vertical mixing, and low temperature ([7]; Bazzano et al., 2019; [52,77]).

Hence, a better comprehension of the concentration and distribution of SMPs in Arctic snow is crucial to assessing the total environmental load in these remote regions, enhancing the atmospheric long-range transport knowledge, and developing effective mitigation to prevent further deterioration of Arctic ecosystems and communities.

The first aim of this study is to investigate for the first time the spatial variability of distinct sites in the Svalbard Islands for an in-depth comprehension of the occurrence of SMPs in snow. To achieve this, bulk snow samples were collected from snow pits near a scientific settlement and at the summits of different surrounding glaciers, where local sources might be excluded because of the site's remoteness. The SMPs' quantification, chemical characterization, and size were provided for each sample. Another focus of the study is the evaluation of the variability of SMPs on the snow surface layer at the same site during specific atmospheric deposition events and their influence on the atmospheric cycle. Finally, the representativity of the variability from bulk samples of a single site will be evaluated to confirm the entire development of our procedure in SMP analysis (e.g., sampling, contamination, pre-treatment procedures, transport, and analysis).

2. Materials and methods

2.1. Area description and sample collection

The snow sampling campaign was performed in the spring of 2021 (from 12th April 2021 to 29th April 2021), when the snowpack was at its most developed, and there was the greatest likelihood of heavy and frequent snowfall [71]. Different snow samples (surface and bulk snow

samples) were collected at the Gruvebadet site (78.918 N, 11.895 E, GRV; 40 m a.s.l), which is located approximately 1 km as crow flies to the south of the dedicated scientific settlement of Ny-Ålesund. The latter is located in North-Western Spitsbergen (Svalbard archipelago, 334 km as crow flies from Longyearbyen (Fig. S1)), and it is a permanent international scientific research settlement. Samples of surface and bulk snow were also collected at the summit of surrounding glaciers: the Midtre Lovénbreen (MDL; 78.871 N, 11.984 E; as the crow flies distance 6.29 km from Ny-Ålesund), the Austre Brøggerbreen (ABRG; 78.872 N, 11.915 E; as the crow flies distance 6.13 km from Ny-Ålesund) and the Holtedahlfonna (HDF; 79.133 N, 13.393 E; as the crow flies distance 33.9 km from Ny-Ålesund. The map of the sites is shown in Fig. 1. The first two glaciers (altitude of 480 m and 450 m, respectively) are near the coast, while the third one is more inland and isolated from the research scientific settlement (altitude of 1010 m) and is above the Arctic Boundary Layer (ABL).

Specifically, the snowpack was sampled and divided into the upper layer (last surface snow deposition) and the lower layer down to the ground (bulk snow). While surface samples were collected to assess variability related to different snowfalls, bulk samples were taken to investigate spatial variability. Then, several snow pits were dug at the Gruvebadet site to test the representativeness of the samples in the same area and the validity of the developed sampling method. Details are reported in Supplementary Materials (Table S1).

The principal physical properties of the snowpack (snow depth, density, and temperature) were manually recorded during each snow pit and compared to observations collected by the automated nivometric station located next to the GRV site [74]. Snow density was measured using a 250 cm^3 triangular steel snow cutter after the sampling for the SMPs' analysis to avoid any potential contamination. While the digging activity was performed using a decontaminated aluminum snow shovel, a decontaminated stainless-steel trowel was employed to collect the snow. Then, snow was stored in decontaminated 10 L stainless steel canisters. A decontaminated glass jar was placed near the snow pits to collect field blanks during each sampling activity. All canisters and the glass jars for the field blanks were then carefully transported in an aluminum box to the Italian Arctic Station "Dirigibile Italia" laboratories, where the pre-treatment procedures were carried out.

2.2. Reagents

Milli-Q® water (Millipore, Merck KGaA, Darmstadt, Germany). Ultrapure water (UW; ELGA, Elga Lab water, High Wycombe UK). Cold pressed sunflower seed oil (SSO, Crudolio, Camisano Vicentino (VI), Italy), hexane (puriss. p.a., ACS reagent, reag. Ph. Eur., ≥99% (GC) Sigma Aldrich, Merck, Darmstadt, Germany), ethanol (absolute, for HPLC, ≥99.8%, Sigma Aldrich, Merck, Darmstadt Germany), methanol ((for HPLC ≥99.9% Sigma Aldrich, Merck, Darmstadt, Germany), aluminum oxide filters (0.2 μm, 47 mm diameter, ANODISC (Anopore Inorganic Membrane Whatman purchased from Merck (Merck, Darmstadt, Germany)). Citranox® detergent (Alcoxon Inc., purchased from Merck (Merck, Darmstadt, Germany)). Silver grey particles of polyamide 12 (PA 12, range 40 μm-250 μm, average size 90 μm; Goodfellow GmbH (Hamburg, Germany)).

2.3. QA/QC

A detailed protocol was designed to minimize potential plastic contamination of samples during sampling, sample transport, pre-treatment, and analysis. Glassware and steelware were washed with a 1% (v/v) solution of Citranox®; then, they were rinsed several times with either Milli-Q® water or UW and finally, a 50% solution (v/v) of methanol-ethanol. Before use, benches, glassware and steelware were decontaminated with a 50% solution (v/v) of methanol-ethanol and ethanol.

During sampling, the synthetic lab overalls commonly employed were entirely covered with a cotton lab coat, and nitrile gloves were employed; specific cotton boot covers were worn to protect the technical boots made of plastic rubbers and synthetic and natural textiles. All the tools, bins, and boxes employed during the sampling collection and transport were clean and decontaminated to minimize potential plastic contamination. Sampling activities were performed upwind. Field blanks were collected using a decontaminated glass jar left open during the sampling collection.

A dedicated room at the Italian Arctic Station, "Dirigibile Italia," was used for all the pre-treatment activities, and no plastic materials were employed inside. Each site's field blanks and snow samples were oleo-extracted in batches, together with procedural blanks employing the Milli-Q® water available on site. Together with Milli-Q® aliquots (about 2 L) stored in decontaminated amber glass bottles to be used as reagent

Fig. 1. Map of the snow samples collection sites: Gruvebadet site located in the proximity of the Ny-Ålesund settlement (78.918 N, 11.895 E, GRV) and at the summit of surrounding glaciers: the Midtre Lovénbreen (MDL; 78.871 N, 11.984E), the Austre Brøggerbreen (ABRG;78.872 N, 11.915E) and the Holtedahlfonna (HDF; 79.133 N, 13.392E).

blank, all the oleo-extracts (i.e., snow samples, field blanks, and procedural blanks) were stored in decontaminated 25 mL glass bottles and shipped at 4 °C at CNR-ISP in Venice, Italy, where they will be processed at the plastic-free cleanroom ISO 7. The plastic-free cleanroom ISO 7 has walls, floor and ceiling, cabinets, benches, and fume hoods made of stainless steel; the air pre-filters do not present plastic particles. At this laboratory, filtration and purification of all the oleo-extracts, reagent, and procedural blanks were processed with UW under a decontaminated fume hood.

Before the analysis, filters were mounted on the stage for analysis in the cleanroom and then carried to the instrumental laboratory, covered with half of a Petri dish wrapped in decontaminated aluminum foil. A recovery test was performed by spiking replicates of one of the snow samples under exam with PA 12 particles (range 40 μm-250 μm, average size 90 μm).

No SMPs were detected on reagent and procedural blanks. SMPs were observed in a few field blanks; these particles were identified, quantified, and then subtracted from the samples (all the details can be found in Table S2, the Supplementary Information). Considering the lack of QA/QC sections in studies on SMPs and MPs analysis in remote places [18], our quality protocol was crucial to consider when analyzing SMPs in remote areas for the accuracy of the final results. The average yield of the recovery test was > 90% (94%); hence, the pre-treatment was accurate and replicable.

2.4. Oleo-extraction, filtration, and purification procedure

The oleo-extraction procedure for snow samples was optimized based on the pre-treatment method of Corami et al. [23]. The oleo-extraction of each sample was run in triplicate. After melting, snow samples were homogenized, and identical aliquots were put in the decontaminated glass separating funnels; the snow volume ranged from 0.7 L to 0.9 L, according to the amount of snow collected per sample. Then, to extract SMPs, 10 mls of SSO were added to the separating funnel. After stirring for 10 min for the emulsion to form, the separatory funnel was left to rest for 6 h for the complete separation of phases. Then, the aqueous phase was discharged, while the oil phase was recovered with 10 mL of hexane and 15 mL of ethanol and placed in decontaminated 25 mL glass bottles. The same procedure was performed for procedural blanks using Milli-Q® water. For field blanks, the glass jars employed during sampling activities were carefully rinsed with the Milli-Q® water, which was then oleo-extracted like the snow samples. Also, spiked replicates for testing the yield were oleoextracted like the samples.

All oleo-extracts were then shipped to CNR-ISP in Italy at 4 °C. The oleo-extracts and blanks were filtrated under a decontaminated fume hood in the clean room, employing a decontaminated glass vacuum filtration system and aluminum oxide filters. The purification procedure was performed according to Corami et al. [21,23]; the oleo-extracts were poured alternating hexane, a 70% solution (v/v) of ethanol-methanol, and then ethanol alone until all the oleo-extracts were filtered.

All filters were stored in previously decontaminated glass Petri dishes, coated with aluminum foil to prevent contamination, and left to dry at room temperature for 72 h in the cleanroom until the analysis via Micro-FTIR.

2.5. Quantitative analysis and polymer identification of SMPs using Micro-FTIR

Each filter was analyzed via Micro-FTIR Nicolet™ iN10™ (Thermo Fisher Scientific), equipped with an ultra-fast motorized stage and liquid nitrogen-cooled MCT detector (mercury cadmium telluride detector). Quantification and simultaneous identification of SMPs were performed according to Corami et al. [21,23]; further details in the (Supplementary Information). Briefly, microscopic counting was performed; at least 20 known-sized areas (i.e., count fields 2000 μm x 1200 μm) were randomly chosen with no overlapping, and on each count field, an average of 250 particles was selected by employing the Particles Wizard section of the Omnic™ Picta™ software. 64 co-scans were collected (aperture 100 μm × 100 μm, spectral range 4000–1200 cm^{-1}) on transmittance mode to collect the spectrum of each particle. Each spectrum was compared with specific polymer reference libraries (see Supplementary Information); by using a similarity algorithm, the identification was expressed as a match percentage (match). Optimal identification for a spectrum corresponds to a match % ≥ 65%; only particles identified optimally were counted. Thanks to the imaging section of the software, particle sizes (length and width) were retrieved, with a limit of detection (LOD) of 5 μm. Each particle's aspect ratio (AR) was calculated (further details in the Supplementary Information). SMPs' weight (μg SMPs L^{-1}), abundance (SMPs L^{-1}), and load (mg SMPs m^{-2}) were evaluated according to Corami et al. [21,23]; the equations are in the (Supplementary Information).

2.6. Statistical analysis

SMPs' abundance data follow a Poisson distribution, and Poisson's confidence interval was calculated accordingly [22,23,31,55]. After verifying the non-homoscedasticity of the variances (F-Test $\alpha = 0.05$), non-parametrical statistical tests were employed on the collected data. Mann-Whitney U test was employed for pairwise comparison, and the Kruskall-Wallis test ($p < 0.05$) was employed for multiple comparisons to evaluate significant differences in abundances of SMPs in snow samples. Statistical analyses were performed using STATISTICA software (TIBCO, Palo Alto, CA, USA).

3. Results and discussion

3.1. Spatial distribution of SMPs in the bulk snow in the Svalbard Archipelago

Snow bulk samples were investigated to assess the spatial distribution of SMPs to have an overview of the potential cumulative accumulation of these particles during different seasons and deposition events. To our knowledge, there is no data for the occurrence and distribution of SMPs in bulk snow and Arctic glaciers.

The complete list of identified and quantified SMPs, with their acronyms, is reported in the supplementary information (Table S3 in Supplementary Information). SMPs were found in all bulk samples, and according to their AR, most were elongated and could be assimilated to an ellipsoid (AR ≥2; Fig. S2). Since the polymers observed in the samples are on a wide range of density, the data are reported as SMPs L^{-1} (Fig. S3a, in supplementary information) and as μg SMP L^{-1} (Fig. 2a). Since they followed the Poisson distribution, each site's confidence limit (error) is reported. The highest SMPs' abundance and weight were detected in GRV (3400 ±81 SMPs L^{-1} and 206.5 ± 20 μg SMP L^{-1}, respectively), while the lowest ones were observed in the HDF glacier (535 ± 32 SMPs L^{-1} and 24.7 ± 7 μg SMP L^{-1}, respectively).

The variances of the samples were not homoscedastic (F test, $\alpha = 0.05$); thus, non-parametrical statistical tests were applied. The Mann-Whitney U test ($\alpha = 0.05$) showed that the abundance of SMPs in the samples differed significantly. These differences were highly statistically significant according to the Kruskall-Wallis test ($p < 0.01$). The same trend was observed in the abundance of SMPs at each site (SMPs L^{-1}, Fig. S3a).

SMPs observed at GRV compared to the summit of the three glaciers might originate from a combination of long-range transport and short-range sources, indicating that the scientific settlement of Ny-Ålesund could be a potential source of short-range pollution. For instance, the release of fibers from clothes, plastic equipment, maintenance work, building activities, waste management, and rubber wear from boots and shoes, vehicle tires and snowmobiles may contribute to the

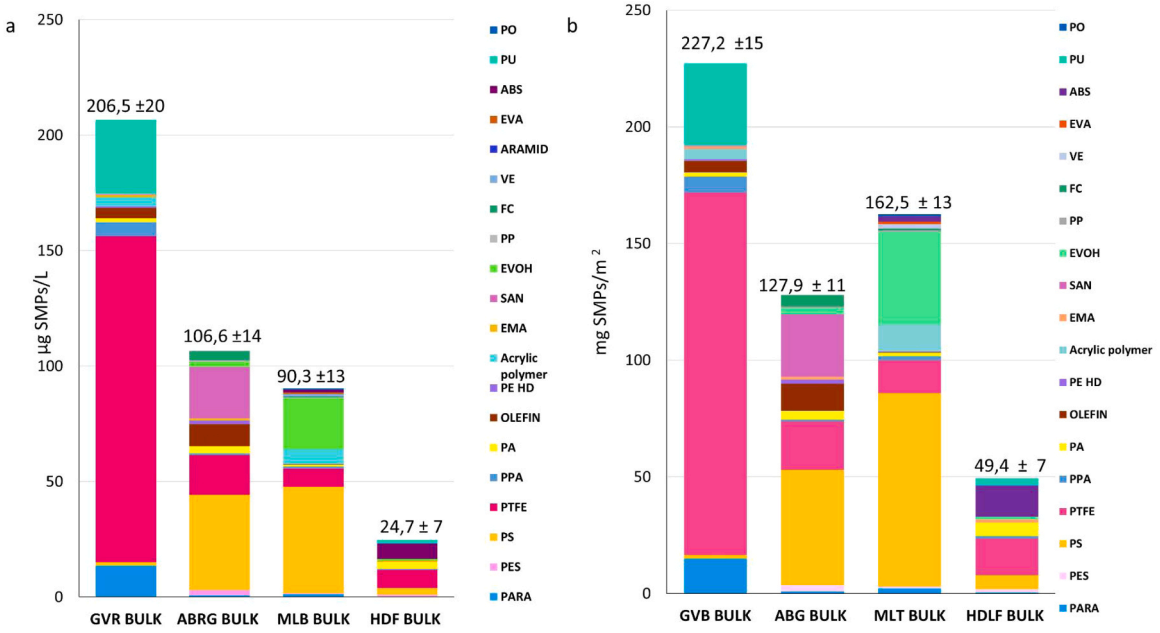

Fig. 2. Fig. 2 SMPs weight reported as μg SMP L^{-1} (Fig. 2a) and SMPs load reported as mg SMPs m^{-2} for bulk snow samples (Fig. 2b).

concentration of SMPs at GRV. The three glaciers have different characteristics, e.g., height, orientation, distance from the sea and the research scientific settlement, etc.; together with meteorological and orographical parameters, these characteristics can affect the particles' transport [46]. The SMPs' weight and abundance were lower at the three glaciers than at GRV; in particular, it was observed a decrease at glaciers with increasing remoteness to GRV. HDF, above the ABL, is characterized by the lowest weight amount and is the most remote sampling location in this study. ABRG and MLD are comparatively nearer to Ny Ålesund and GRV (Fig. 1), and they may be subjected to a mix of both short-l and long-range transport plastic contamination, as already observed for other pollutants in Svalbards [24,46,69]. The height of the ABL in Svalbard, and in particular in the Ny-Ålesund area, is challenging to be estimated due to effects induced by winds and by the orography of the Brøgger Peninsula [8,70]. However, experimental studies indicate that the ABL's height is conservatively confined below 1000 m [13,27,53]; hence, HDF is mainly above the ABL and most influenced by long-range transport. During atmospheric transport, plastic fragments > 100 μm, which may originate near urban sources at high- and mid-latitudes, could be broken into SMPs by mechanical processes and degradation [58].

The polymer distribution at the summit of the three glaciers and GRV differed, suggesting that distinctive atmospheric pathways and short and long-range sources might have influenced them. Some of the best spectra of the polymers identified are shown in the supplementary information (Fig. S3). While the greatest variety of the polymers identified was observed at GRV, where PTFE was the most abundant (141.2 μg SMPs L^{-1}; 2805 SMPs L^{-1}), followed by PU and PARA, at ABRG and MLB, the most abundant polymer was PS (41.18 and 55 SMPs L^{-1}, and 46.09 μg SMPs L^{-1} and 55 SMPs L^{-1}, respectively). PTFE (7.85 μg SMPs L^{-1}, 240 SMPs L^{-1},) was the predominant polymer, followed by ABS (6.68 μg SMPs L^{-1}, 18 SMPs L^{-1},), also at HDF. PTFE is used for cookware, automotive, chemical, medical industries, and rainwear; this polymer has a higher density (2.2 g cm^{-3}) than other plastic polymers identified and quantified. PTFE was also found in recent work in the surface water of the Arctic Central Basin, potentially derived from the fragmentation, abrasion, or weathering of cables and printed circuit boards [38].

Other polymers, i.e., PE HD, PP, PS, PO, PPA, and VE, may be derived from containers, bags, bottles, recipients, components of the snow motors, wraps, safety kits, and fabrics, and they may be more influenced by diffuse rather than point sources. It should be highlighted that some SMPs were observed only at specific sites and may have a specific origin or source; this is the case of PO and EVA observed at MLB.

PA 6, which is extremely common in other environmental matrices from urban environments to remote areas, including in Arctic seawater and sea ice [42,63] sediments [20] and biota [30,40], was found in all snow samples. The primary sources of PA 6 are synthetic textiles or maritime activities (e.g., fishing gears, nets, and ropes), but its fragments have also been identified and quantified in aerosol [67,73]. Some pre-treatment procedures for the analysis of microplastics employed aggressive or strong solutions (e.g., acid or alkaline solutions) coupled with high temperatures with consequences of denaturation/degradation or total loss of some polymers, such as PA6 and PE [19,22,3,39,65]. The temperature employed in the extraction procedures can affect polymers' physical and chemical characteristics according to their Tg (glass transition temperature), with consequences regarding identification and quantifications ([22], 2021; [57]). The oleo extraction and purification procedure employed in this study avoided denaturation and degradation of plastic polymers, allowing an optimal identification and a simultaneous quantification of SMPs, including PA 6 (with matches of similarity >95%; Fig. S4).

Besides weight and polymer identification, particle size is a significant characteristic of scavenging particles in the atmosphere [72]. Because the smaller the particle, the more easily it is carried by atmospheric currents in long-range transport, evaluating size distribution can be of considerable help in understanding the dynamics of atmospheric transport [10,12,29,5,50]. Size distribution in length (μm) was shown for all bulk samples considering SMPs abundance (SMPs L^{-1}, Fig. 3). The SMPs' maximum length retrieved in the snow samples was 750 μm, while the minimum length was 20 μm (Fig. S5 in supplementary information), with the majority less than 100 μm. The presence of SMPs at glaciers and GRV may pose a critical risk to any level of the trophic web by the time of the snowmelt, as they can be carried to the sea and other polar environmental compartments.

According to the size distribution observed, SMPs might come from both short and long-range transport; this is most noticeable for GRV. On the other hand, SMPs in HDF shifted to a smaller size, i.e., from 26 to 65 μm with a small amount in abundance > 60 μm; long-range distribution might become prevalent.

Acrylic, PARA, PP, and PS were > 100 μm in GRV, and they could

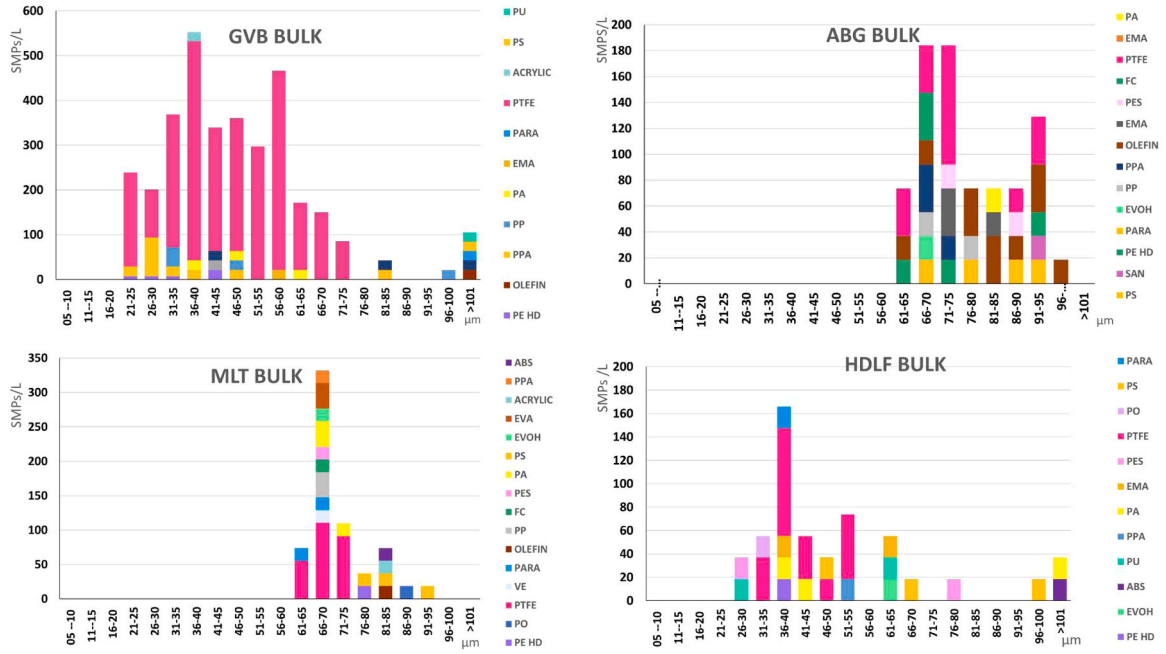

Fig. 3. Size distribution in length (µm) for all bulk snow samples considering SMPs abundance (SMPs L^{-1}).

have originated mainly from functional synthetic fabrics or plastic packaging used in Ny-Ålesund. The smallest SMPs found in both GRV and the glaciers could be more easily transported through the atmospheric compartment from far sources and reach even remote areas such as at the summit of the glaciers. For instance, PTFE was found with the minimum size in all the samples and may be fragmented from far sources. Similarly, at HDF, PU and PES were the smallest polymers observed (26–30 µm range), suggesting that these smaller particles may be derived from long-range transport.

Deposition loads were calculated for all the sites under exam to provide information on the input of SMPs in the snow; the highest one was observed at GRV (227.2 ± 15 mg SMPs m^{-2}), while the lowest was observed at the HDF glacier (49.4 ± 7 mg SMPs m^{-2}), confirming the same trend of the SMPs' weight distribution (Fig. 2b). On the other hand, the SMPs' load at MLT was higher than in ABRG ((162.15 ± 13 mg SMPs m^{-2}, 127.9 ± 11 mg SMPs m^{-2}, respectively), in contrast with the weight distribution. The snow density and total surface area of each sample could give important information on the distribution of SMPs in the snow layers since the snowpack originated from accumulating consecutive snowfall events with different characteristics. However, the snow's physical properties could change within hours after a snowfall event [37], and it is worth underlining that the bulk snow analyzed in this study represents a composite sample of different layers to investigate the presence of SMPs. More investigations on SMPs load between the different snow depositions are needed in future studies.

The representativity of the spatial variability was evaluated to confirm the entire development of our procedure in SMPs analysis (i.e., sampling, contamination, pre-treatment procedures, transport, and analysis) and possible spatial differences in the same collecting site by analyzing two different bulk samples from GRV. The weight (µg SMPs L^{-1}), load (mg SMPs m^{-2}), and abundance (SMPs L^{-1}) of SMPs in the bulk samples from GRV 1 and GRV 2 are shown in the supplementary information (Fig. S6 a and b). The variances of the samples were not homogenous (F test, $\alpha = 0.05$), and non-parametrical statistical tests were applied. The bulk samples of GRV did not show significant statistical differences (Mann Whitney U, $\alpha = 0{,}05$; Kruskall-Wallis test ($p < 0.05$). Therefore, the bulk snow samples sampled at the same site did not show significant spatial variability. However, few polymers were present in one of the two sites, e.g., PU IN GVB 1 and ABS in GVB 2; hence, they could have originated from specific pointed sources. On the other hand, PTFE was confirmed as the most abundant polymer in both samples, followed by PARA, PPA, and PS.

According to the AR, as already observed in the snow bulk samples, most SMPs were elongated (AR ≥ 2, Fig. S7a and b). The two sites showed the same trend regarding the length size distribution in µm (Fig. S8). The SMPs' maximum length retrieved in the two samples was between 700 and 750 µm, while the minimum length was 20 µm, with the majority less than 100 µm as for the other snow samples.

3.2. SMPs in the surface snow layer and variability over time

SMPs were also analyzed in the surface snow layer of GRV and the three glaciers, ABG, HDF, and MLT, to study the variability of their concentrations throughout time. Surface snow is significantly affected by atmospheric winds and currents, transport, and deposition of atmospheric particulate matter. Local wind conditions can play a relevant role in the presence and transport pathways of pollutants and MPs in surface snow; winds can be a primary transport pathway for airborne SMPs to snow, soil, sea, et cetera, and a driving force behind the conveyance of SMPs in remote regions ([17,29]; Liu et al., 2019a; [85]).

Weight (µg SMPs L^{-1}), load (mg SMPs m^{-2}), abundance (SMPs L^{-1}, Fig. S3b in supplementary information), AR, and size (µm) were calculated according to the equations in supplementary materials. The results confirmed the higher weight and load of SMPs in surface snow at the Gruvebadet site compared to the glaciers (Fig. S9; Fig. 4a and b). Also, regarding the size, the distributions of SMPs among the GRV and the glaciers had different trends (Fig. 5), confirming the potential influence of long-range transport of pollutants in the glaciers [24,46,69]; on the other hand, the increase of the size length may result from from the short-range transport of pollutants from the Svalbard archipelago (Vecchiato et al., 2018). At HDF, PS was found with a size > 100 µm. Although this particular polymer was not identified in the field blank collected at the site, it should be highlighted that the boxes for carrying the collected samples were polystyrene boxes, and the particles observed might have been possibly released during a previous sampling performed a few days earlier. Therefore, these results emphasize the importance of collecting field blanks during sampling and drawing sampling guidelines to avoid misinterpretations due to contamination

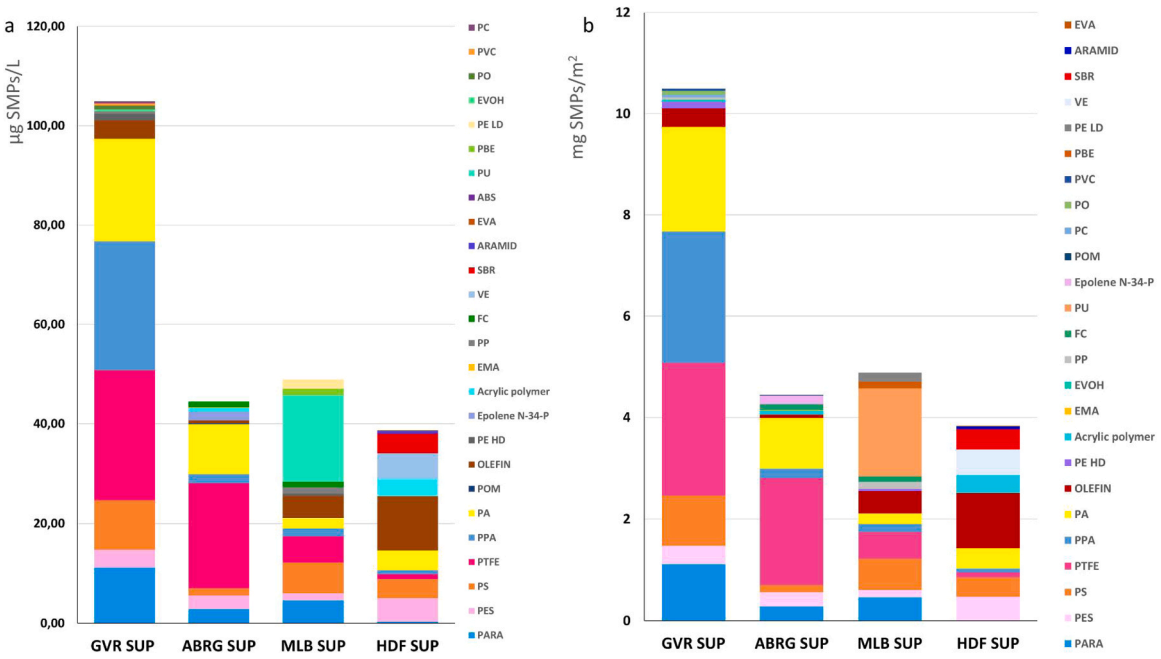

Fig. 4. SMPs weight reported as µg SMP L-1 (Fig. 4a) and SMPs load reported as mg SMPs m^{-2} for superficial snow samples (Fig. 4b).

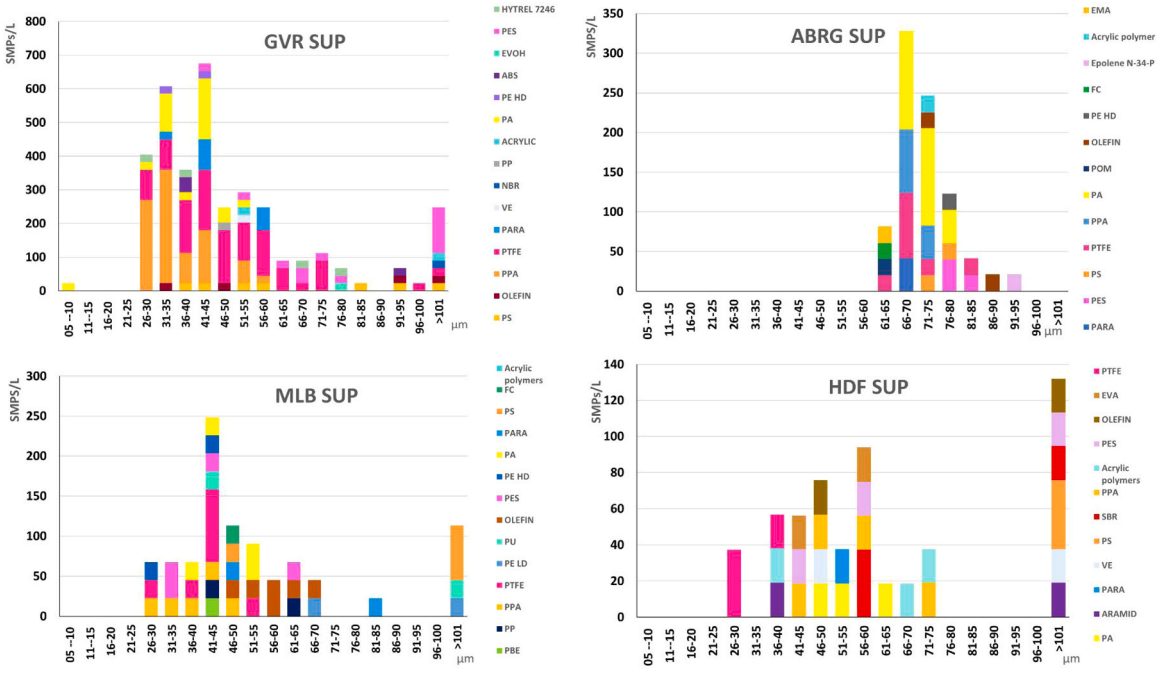

Fig. 5. Size distribution in length (µm) for all superficial snow samples considering SMPs abundance (SMPs L^{-1}).

by sampling.

The presence of SBR in surface snow samples at HDF glacier should be underlined (3.94 µg SMPs L^{-1} and 94 SMPs $L^{-1,}$ respectively). SBR was not observed at GRV or the other glaciers. Tire wear particles (TWPs) are a major contributor to microplastic emissions to the environment [36,67,73,87]. SBR is synthetic rubber for vehicle tires and snowmobile belts [76]. This significant result confirms that TWPs could be transported through long-range atmospheric pathways. However, there is a substantial lack of data regarding the abundance and distribution of TWPs, especially in remote regions [29,45,51]; therefore, further studies are needed, especially regarding markers to acknowledge and validate the presence of TWPs. High transport efficiencies of these particles to remote areas such as Arctic areas have been estimated [29] because the light-absorbing properties of TWPs and other MPs [35,41,68] may also intensify the climatic risk of plastic pollution and consequently decrease the albedo in the Arctic and accelerate warming and melting of the cryosphere. Also, the negative impact on polar biota should be stressed since SMPs and TWPs can be easily ingested by the organisms at the lower layers of the food web and may be bioaccumulated and biomagnified.

The presence of plastic particles from vehicles (e.g., snowmobiles, vans, cars, etc.) can be corroborated by the observation at ABRG of a powdered polyethylene commonly used as a plastic additive, i.e., dispersing aid for pigments in color masterbatch, widely used in vehicles

and automotive applications, but also adhesives, industrial and packaging applications. Vehicle sourcing was similarly observed at MDL due to the occurrence of PU, a durable elastomer in wheels and tires and for vehicle suspensions, also widely used in electrical, paints, and construction, and PBE, which is one of the most widely used thermoplastics for automotive, aircraft, medical and security components.

To the best of our knowledge, this is the first study to assess the SMPs concentration in the Arctic surface snow from the Svalbard Islands; therefore, comparing our results with other studies is challenging. However, the SMPs concentration (SMPs L^{-1}) observed on the surface snow collected at GRV and the three glaciers are comparable to the values of snow from ice floes of the Svalbard archipelago ([10]; particles ranging from 11 μm to 475 μm).

The SMPs' concentration observed in the three glaciers investigated was higher than that observed in a tropical Andean Glacier [14,15], where samples were taken above 5000 m, and the range of the analyzed particle was 60–2500 μm, while in our study most of the particles were < 60 μm in length. This supports the idea that the smaller MPs are, the more numerous they can be [4,63].

Furthermore, the MPs' concentrations in the mountains of several European locations and the rest of the world differed from the SMPs' concentrations in this study, e.g., Western Italian Alps [61], Carnic Alps in Italy [62], the Canary Islands in Spain [78], Northern Iran [1], Mount Everest [59], the Mongolian Plateau [83]. The observed differences are not only attributable to the size class investigated but also to the sampling procedure and analytical methodology, making data comparison very challenging. On a further note, it should be underlined that the differences may also be related to atmospheric currents that determine long-range and short-range transport [4]. Papers on atmospheric microplastic, especially those below 100 μm, are somewhat scarce; hence, comparing our results with other studies is difficult. Most of these papers studied MPs focusing on atmospheric deposition in urban areas, while they are scarce in remote areas [84]. Thus, the results of this work may contribute significantly to filling the knowledge gap on the transport of atmospheric SMPs in remote polar regions, especially at the glaciers.

4. Conclusions

The sampling procedure was designed to obtain representative samples while minimizing plastic contamination, thanks to rigorous QA/QC. The oleo-extraction procedure allowed the extraction of SMPs in a wide range of densities, and the purification procedure resulted in recognized spectra with an optimal percentage match (according to the similarity algorithm). Besides, in combination with all these and a detailed QA/QC, the optimal yield of the method provided robust, accurate, and repeatable data. The evidence of SMPs in these collecting sites highlighted the role of global long-range transport of these pollutants in the atmosphere compartment and, consequently, a potential accumulation zone from lower latitudes. Besides, the Arctic area is considered highly vulnerable to environmental perturbations and thus operates as sentinels of global changes.

Regarding the spatial distribution, our results on snow bulk samples confirmed that SMPs could be transported through the atmospheric aerosol in remote areas, and they may be influenced by spatial variability, resulting in significant differences in the abundance of SMPs falling out via snow. At GRV, the occurrence of SMPs may be affected by both long-range and local pollution. The presence of some polymers might be site-specific in relation to the pathways that affect their distribution at the sites studied. To the best of our knowledge, these are the first results of SMPs focusing on temporal variability in surface snow at polar areas; therefore, further in-depth investigations will be crucial, especially taking into account other parameters (e.g., wind speed, temperature, humidity, density). The SMPs' load was higher in GRV than in the three glaciers under study, with HDF showing the lowest value. The atmospheric transport influenced the occurrence and the load of SMPs observed at the three glaciers. SMPs distribution may be related to specific sources and pathways from local or mid-latitude areas; the results of this study contribute to enhancing the knowledge of atmospheric pollution by these emerging pollutants in remote Arctic areas. Since the Arctic is among the most vulnerable places on Earth to environmental perturbations, the impact of atmospheric microplastics on transport and deposition is an emerging global concern. Further investigations are needed to thoroughly understand the role of meteorological parameters and seasonality and the adverse effects throughout the polar food web.

Environmental implication

The issue of the SMPs' presence in polar regions has been addressed by several working g, e.g., that of the Arctic Council, since the Arctic has become a global research priority. MPs, specifically SMPS, can be considered hazardous materials because they may have toxic effects in relation to the presence of different plastic additives and pollutants adsorbed/absorbed on their surface. Their role in altering the climate process (ice/snow melting, the ocean and air circulation, enhancing ice nucleation, and altering cloud formation) may significantly affect ecosystems, such as altering biological communities with implications in the entire polar food chain.

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CRediT authorship contribution statement

Scoto Federico: Writing – review & editing, Writing – original draft, Resources. **Hallanger Ingeborg G.:** Writing – review & editing, Resources. **Larose Catherine:** Writing – review & editing, Resources, Conceptualization. **Gallet Jean Charles:** Resources. **Gambaro Andrea:** Writing – review & editing, Supervision. **Corami Fabiana:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Rosso Beatrice:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation. **Spolaor Andrea:** Writing – review & editing, Writing – original draft, Resources, Conceptualization. **Bravo Barbara:** Resources. **Barbante Carlo:** Writing – review & editing, Supervision.

Declaration of Competing Interest

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

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.133723.

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