A novel procedure for the detection of Personal Care Products (PCPs) in outdoor air: occurrence in urban, coastal, alpine, and polar areas.

Marco Vecchiato[1]*, Giorgia Trevisanato[1], Diego Costa[1], Elena Barbaro[2], Marianna D'Amico[1], Giovanna Mazzi[1], and Andrea Gambaro[1,2]

1) Department of Environmental Sciences, Informatics and Statistics (DAIS), Ca' Foscari University of Venice, Mestre - Venice, via Torino 155, 30172, Italy

2) Institute of Polar Sciences, National Research Council (CNR-ISP), Mestre - Venice, via Torino 155, 30172, Italy

*vecchiato@unive.it

Abstract

Personal care products (PCPs) are compounds largely emitted and detected in the water compartment. However, as emerged in recent literature, their presence in the atmosphere is fundamental to understanding their environmental fate. Standardized procedures for the determination of PCPs in the atmosphere are still lacking. We developed a new analytical method to determine fragrances and UV filters in outdoor samples, focusing on their distribution both in the gas (Polyurethane foam; PUF) and Total Suspended Particulate (TSP; quartz filter) phases. A low-temperature (40°C) solvent extraction procedure was adopted, followed by GC-MS/MS instrumental analyses. The method was tested on samples collected during summer 2023 in low and high anthropogenic-impacted sites: urban, coastal, and alpine areas of the Veneto Region in Italy, and a remote area in the Norwegian Arctic (Ny-Ålesund, Svalbard). Results showed the highest levels of ΣPCPs near the seashore (13-16 ng m^{-3}), reflecting the widespread use of sunscreen products in summer by touristic and recreational activities. Lower concentrations were observed in the urban area (ΣPCPs = 6.0-8.5 ng m^{-3}), followed by the alpine samples from the Dolomites (ΣPCPs = 1.6-3.0 ng m^{-3}). In the Arctic, ΣPCPs were orders of magnitude lower (0.11–1.3 ng m^{-3}) compared to the other sites. Among PCPs, Galaxolide, Tonalide and Ethylene Brassylate were generally the main musk fragrances, while Salicylates were the most abundant compounds among UV filters and

non-musk fragrances. The selected PCPs were mainly distributed in the gas phase, with the exception of Octocrylene. This agrees with previous hypotheses and findings that associate this UV filter with the atmospheric particulate. The analytical method presented in this study will contribute to further understanding the behavior of PCPs in the atmosphere and to assess their long-range transport.

1. Introduction

Personal care products (PCPs) can enter the environment through direct discharges or ineffective removal of residues of soaps and detergents in wastewater treatment plantsc [1]. Fragrances and UV filters are ingredients commonly used in PCPs and, especially during summer, recreational activities in lakes and beaches are additional direct sources of these contaminants [2]. Consequently, there is a rising concern about their potential effects on marine invertebrates [3,4]. Despite PCPs are largely emitted into the water, their emission into the atmosphere can result from direct inputs during on purpose use (e.g., perfumes and fragrances), or through re-volatilization from various environmental media acting as secondary sources [5].

The atmosphere is a key matrix for the understanding of PCPs' environmental fate. Recent research showed the presence of fragrances and UV filters in snow samples from the Arctic and Antarctica [6,7]. Their presence in polar remote regions, as observed for other organic pollutants, can potentially derive from the deposition and the cold-condensation of long-range transported aerosols [8]. Research on PCPs in air samples from polar and remote areas is limited [9], and, even in anthropized areas at lower latitudes, the knowledge on their distribution in outdoor environment is limited compared to the studies reported for indoor air [5,10,11].

Table 1: analytical methods for the determination of personal care products in the gas and particulate phases of outdoor air. Only compounds in common with this study are reported. *

Analytes	Sampling	Procedure	References
MX, MK, AHTN, HHCB, ATII	Kjeller, Oslo, Norway HV-AAS Part.: GF/F Gas: PUF 500-600 m^3/24-36 h	Extraction: Soxhlet (HEX:diethyl ether, 9:1; 300 mL/ 8h) Purification: silica (8 g HEX–ethyl acetate) Instrument: GC-MS DB-5 MS 30m	[12]
MX, MK, AHTN, HHCB, ATII, ADBI, AHMI, DPMI	Lake Michigan; Milwaukee (USA) HV-AAS Part.: QF/F Gas: XAD-2 59-601 m^3/4-14 h	Extraction: Soxhlet (HEX:ACE 1:1 350 mL/ 24 h). Purification: silica (HEX, HEX:DCM, methanol) Instrument: GC-MS HP-5 MS 30m	[13]

MX, MK, AHTN, HHCB, ATII, ADBI, AHMI	Iowa; Great Lakes (USA) HV-AAS Part.: GF/F Gas: XAD-2 av. 835 m^3/24 h	Extraction: Soxhlet (HEX:ACE 1:1 350 mL/ 24 h. Purification: 0.75 g Florisil (ethyl acetate 4 mL). Instrument: GC-MS HP-5 MS 30m	[1]
DPMI, ADBI, AHMI, HHCB, AHTN	Guang Zhou, China HV-AAS Part.: GF/F Gas: PUF 72-524 m^3/210-1530 h	Extraction: Soxhlet (DCM 72h) Purification: silica–alumina (HEX, HEX:DCM, DCM) Instrument: GC-MS HP-5 MS 30m	[14]
HHCB, AHTN	Germany, North Sea and Arctic HV-AAS Part.: GF/F Gas: PUF/XAD-2 914-2000 m^3/96-168 h	Extraction (PUF/XAD-2): Soxhlet (HEX: diethyl ether 4:1 + DCM 300 mL/16h) Extraction (GF/F): Soxhlet (DCM 150mL /16 h) Purification: 2,5 g silica 5% H_2O (HEX 15 mL + HEX: diethyl ether 3:1 25 mL + HEX: diethyl ether 1:1 25 mL + HEX:ACE 1:1 20 mL Instrument: GC-MS HP-5 MS 30m	[9]
MX, MK, AHTN, HHCB, ATII, ADBI, AHMI	Landfills, Germany HV-AAS Part.: GF/F Gas: PUF/XAD-2/PUF 350-33.600 m^3/24-96 h	Extraction (PUF/XAD-2/PUF): CE (HEX:ACE 1:1; 3 cycles tot: 450 mL/2.5 h) Extraction (GF/F): ASE (HEX:ACE 1:1, 35 mL, 100 °C) Purification: 3 g Alox + 5 g Silica (HEX + HEX:DCM). Instrument: GC-MS with PCI HP-5 MS 30m	[15]
MX, MK, AHTN, HHCB, ATII, ADBI, AHMI	Lüchow, Lüneburg, Germany HV-AAS Part.: GF/F Gas: PUF/XAD-2/PUF 8.400 -25.200 m^3/24-72 h	Extraction (PUF/XAD-2/PUF): CE (HEX:ACE 1:1; 3 cycles tot: 450 mL/2.5 h) Extraction (GF/F): ASE (HEX:ACE 1:1, 35 mL, 100 °C) Purification: 3 g Alox + 5 g Silica (HEX 35mL + HEX:DCM 3:1 30mL). Instrument: GC-MS (EI) HP-5 MS 30m	[16]
DPMI, ADBI, AHMI, MA, ATII, HHCB, MX, AHTN, MK.	Cosmetics plant. LV-AAS Part.: GF/F Gas: PUF 1.6 m^3/8 h	Extraction: microwave-assisted extraction (cyclohexane: ACE 1:1, 60 ml/1 h) Instrument: GC-MS/MS DB-5ms	[17]
ADBI, AHMI, ATII, HHCB, AHTN	Great Lakes, Toronto, Canada. PAS No particulate Gas: Polyethylene (PEs) 32-221 days	Extraction: CE (pentane/18-24 h) Purification: silica/sodium sulfate Instrument: GC-MS DB-5 30m	[18]
HHCB, AHTN	Hanoi, Vietnam HV-AAS Part.: GF/F No Gas 70-388 m^3/5-13,5 h	Extraction: sonication (DCM 20 mL/ 15') Centrifugation Solvent exchange with HEX Instrument: GC-MS HP-5 MS 30m	[19]
MK, MX, DPMI, ADBI, AHMI, HHCB, AHTN, Musk-T	Ontario, Toronto, High Artic, Canada. PAS Gas: PUF 1-3 months HV-AAS Part.: GF/F Gas: PUF and PUF/XAD/PUF 340-2.000 m^3/14 h – 12 d	Different procedures according to sample types. Extraction: ASE (DCM or HEX or Petroleum ether: ACE 83:17); Soxhlet (DCM or HEX) 18 h Purification: silica (25 mL DCM:HEX 50:50) or florisil. Instrument: GC-MS and GC-MS/MS	[20]
EHS, BP3, 4-MBC, Z-EHMC E-EHMC, OCR	WWTP in Ontario, Canada PAS Gas: PUF 250-336 m^3/2 months	Extraction: ASE (Petroleum ether:ACE 83:17 2cycles). Instrument: GC-MS/MS HP-5 MS 30m	[21]

EHS, BP3, 4-MBC, Z-EHMC	Toronto, Canada. HV-AAS Part.: GF/F Gas: PUF/XAD-2/PUF 245 – 351 m^3/24 h	Extraction (PUF): Soxhlet (Petroleum ether:ACE 85:15/6h) Extraction (GF/F): sonication (DCM 3 cycles) Instrument: GC-MS/MS HP-5 MS 15m	[22]
BP3, OCR, EHS, EHMC	Beijing, China LV-AAS Particulate $PM_{2.5}$: GF/F No Gas 530 m^3/240 h	Extraction: sonication (HEX:DCM 5:1), Purification: ProElut C18 SPE (HEX:DCM 4:1) Instrument: GC-MS/MS DB-5ms	[23]

*Acronyms:

HV-AAS: HigH Volume Active Air Sampler

LW-AAS: Low Volume Active Air Sampler

PAS: Passive Air Sampler

GF/F: Glass Fiber Filter

QF/F: Quartz Fiber Filter

PUF: Polyurethane Foam

PE: Polyethylene

ASE: Accelerated Solvent Extraction

CE: Cold Extraction

SPE: Solid Phase Extraction

HEX: *n*-Hexane

ACE: Acetone

DCM: Dichloromethane

Most of the sampling procedures reported in the literature for outdoor air (Table 1) are generally based on High Volume Active Air Sampler (HV-AAS), collecting the particulate phase on Glass or Quartz Fiber Filters (GF/F, QF/F), and the gas phase on Polyurethane Foam plugs (PUF) [1,9,12,13,15,16,19,22], while only a few studies rely on passive sampling [18,20,21]. The methods used for the extraction of PCPs from these supports are little standardized, reporting different solvent mixtures and alternative strategies adopted during the pre-analytical steps (Table 1). Most of the extraction methods found in literature (Table 1) for the analysis of fragrances and UV filters in atmospheric samples generally use Soxhlet, sonication, or cold extraction procedures. These methods require long extraction times and large quantities of solvents, potentially leading to possible losses of the most volatile analytes during the sample concentration. Some of the studies avoided purification steps [17,19,21,22], relying on the low complexity of the atmospheric matrix.

The determination of PCPs in outdoor and indoor air samples presents different analytical challenges: confined indoor environments are generally characterized by high PCP concentrations, allowing the use of low-volume sampling techniques [24] and solid-phase microextraction [25].

These methods could be applied also to outdoor samples of urbanized areas [26], however it might result difficult to adapt them to the low PCPs concentrations expected in the air of remote and polar locations, where HV-AAS or PAS are better suited. A review of the environmental levels of PCPs in the atmosphere is reported in Table SI1. Concentrations generally span between several orders of magnitude, mainly depending on the proximity to potential sources: while musk fragrances can be detected at few pg m^{-3} in remote areas [9] the same compounds can rise up to hundreds of ng m^{-3} close to WWTPs [15,20].

Preliminary tests on PCPs were performed using Accelerated Solvent Extraction (ASE) methods that were previously developed to analyze POPs and PAHs in aerosol samples [27,28]. However, these extraction procedures, requiring high temperature conditions (100°C), showed unsatisfactory performance when applied to PCPs. For example, low and irreproducible recoveries (<12%) were obtained for Salicylates. These compounds resulted to be the major fragrances detected in seawater and snow samples of different environments [6,7,29], accounting for their relevance as environmental contaminants among PCPs.

To ensure comparability with the available literature, in this work, we relied on HV-AAS sampling using PUF and Q/FF. ASE extraction procedures were adopted to minimize the solvent consumption, but to avoid the potential degradation of the analytes, a low-temperature (40°C) protocol was tested. This was counterbalanced by a limited, still acceptable increase of time for the analysis. The method was then applied to exploratory air samples collected during summer 2023 in sites impacted either by low or high consumption of PCPs.

This work aimed to develop a novel preparative procedure for the analysis of fragrances and UV filters in the particulate and gaseous phases of atmospheric samples, applicable to both high-impacted environments and remote areas.

Fragrance compounds, including ten **musks**, Celestolide (ADBI; 6-tert-butyl-1,1-dimethylindan-4-yl methyl ketone), Phantolide (AHMI; 1,1,2,3,3,6-hexamethylindan-5-yl methyl ketone), Tonalide (AHTN; 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one), Traseolide (ATII; 1-[2,3-dihydro-1,1,2,6-tetramethyl-3-(1-methylethyl)-1H-inden-5-yl]ethan-1-one), Cashmeran (DPMI; 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one), Galaxolide (HHCB; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylindeno[5,6-c]pyran), Ethylene brassylate (M NN; 1,4-Dioxacycloheptadecane-5,17-dione), Musk ambrette (MA; 4-tert-Butyl-3-methoxy-2,6-

dinitrotoluene), Musk Ketone (MK; 4'-tert-butyl-2',6'-dimethyl-3',5'-dinitroacetophenone), Musk Xilene (MX; 5-tert-butyl-2,4,6-trinitro-m-xylene)), seven **non-musks** (Amyl and Isoamyl Salicylate (AmyS and IAmyS; pentyl 2-hydroxybenzoate and 3-methylbutyl 2-hydroxybenzoate), Hexyl Salicylate (HexS; hexyl 2-hydroxybenzoate), Benzyl Salicylate (BenS; benzyl 2-hydroxybenzoate), Oranger Crystals (Ora; 1-naphthalen-2-ylethanone), Peonile® (Peo; 2-cyclohexylidene-2-phenylacetonitrile), and Ambrofix (Amb; Dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1-*b*]furan)), and five **UV filters** (2-Ethylhexyl 4-methoxycinnamate (EHMC; 2-ethylhexyl 3-(4-methoxyphenyl)prop-2-enoate), Benzophenone-3 (BP3; (2-hydroxy-4-methoxyphenyl)-phenylmethanone), Ethylhexyl Salicylate (EHS; 2-ethylhexyl 2-hydroxybenzoate), Enzacamene (4-MBC; 4-Methylbenzylidene camphor) and Octocrylene (OCR; 2-ethylhexyl 2-cyano-3,3-diphenylprop-2-enoate) were selected for this study.

Among the PCPs detected in the atmosphere, Musk fragrances, particularly HHCB and AHTN, are the most studied compounds in literature (Table 1). On the contrary, non-musk fragrances were previously reported only in indoor air samples [5,25], however, there are emerging concerns about their potential for long-range transport [30]. Most of the PCPs selected for this study tend to partition predominantly in the gas phase regardless the atmospheric temperature, especially the Salicylates. Conversely, the less volatile octocrylene is expected to be sorbed to atmospheric particles [30]. Depending on the physicochemical properties of the PCPs, temperature may play a relevant role in determining their equilibrium partitioning in the atmosphere, and consequently their dominant deposition process. In this context, improving the understanding of the environmental behavior of PCPs and the mechanisms involved in their transport is essential. The development of analytical methods allows the comparison between the theoretical atmospheric distribution of PCPs and their occurrence in real-word samples.

2. Materials and Methods

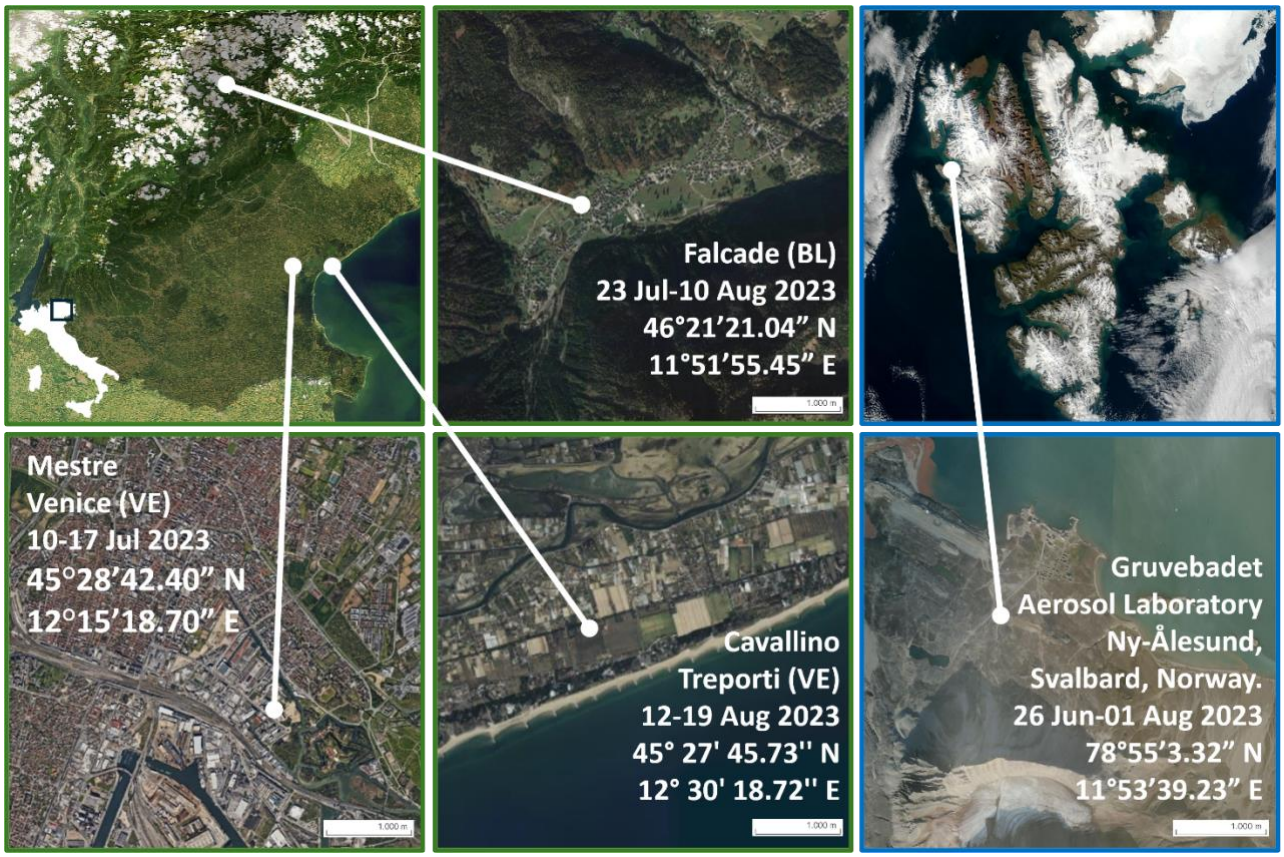


Figure 1: Sampling sites of gas and particulate collected during the summer 2023 in Mestre, Cavallino Treporti and Falcade, Veneto Region, Italy (green borders), and in the Norwegian Arctic (Ny-Ålesund, Svalbard Islands; blue borders).

During the summer of 2023 a total of 24 air samples (including both gaseous and particulate fractions) were collected in low- and high-impacted areas of the Veneto region, Italy, encompassing mountain (Falcade), coastal (Cavallino-Treporti), and urban (Mestre) environments (Fig. 1). Additional samples were collected at Ny-Ålesund, a remote area in the Norwegian Arctic, less impacted by human activities. All details about the sampling conditions are reported in Table SI7.

Four samples were collected in Mestre on the roof of the Scientific Campus of Ca' Foscari University of Venice. This site was previously recognized as representative of emissions from local urban sources [31].

Seven samples were collected 500 m from one of the beaches of Cavallino-Treporti. This is an area highly impacted by the local use of PCPs. In fact, the northern Adriatic coast, where the beach is located, is an European hotspot for seaside tourism; notably, five out of the ten most visited cities in Italy are set along the Venetian coast. Cavallino-Treporti had 6.8 M nights spent in

accommodation in 2023 and the impact of this seaside tourism, linked to a high consumption of UV filter products, is concentrated in a few weeks during summer, peaking with the Assumption week of holiday.

Falcade, in the Belluno Dolomites, (1180 m a.s.l.; eight samples) has approximately 1700 inhabitants and a lower number of touristic presences (267.000 nights spent in accommodation in 2023). Despite mountain environments could be impacted by the direct use of products containing UV filters, in particular during hiking and outdoor activities, the lower density of residential and touristic activities makes Falcade representative of a background area for PCPs contamination in the region. Finally, the occurrence of these compounds in the atmosphere of remote polar environments was investigated at the Gruvebadet Aerosol Laboratory, close to Ny-Ålesund (Svalbard Archipelago, Norway). Five samples were collected with a weekly resolution in a restricted area not directly affected by local emissions from the town of Ny-Ålesund [32]. In addition, during the method development a previous preliminary sample (PUF_{WWTP}) was collected close to a wastewater treatment plant (Treviso, Italy; N 45° 39' 50.36; E 12° 14' 51.50; 473 m^{-3}) to test on a real sample the possible fractionation of PCPs during sequential PUF extractions.

An AirCube PUF HVS Touch (AMS Analitica, Pesaro, Italy) was used in Mestre, Falcade, and Cavallino-Treporti samplings, with a flux of 150 L min^{-1} for 24 hours. Higher air volumes were collected at Gruvebadet, sampling at 600 L min^{-1} for approximately 7 days with an AirFlow HVS Touch (AMS Analitica, Pesaro, Italy). The samples were transported and stored at -18°C until analysis.

To minimize external contamination of the samples, all glassware, cells, and clamps entering in contact with the samples were previously washed with an aqueous 5 % (*v*/*v*) Contrad® solution, dried and then solvent-rinsed with two aliquots of ACE, two of DCM and two of. Pesticide-grade solvents (Romil Ltd., Cambridge, UK) were used for decontamination and for sample preparation. Polyurethane foam (PUF) plugs with dimensions of 6 cm OD x 7.6 cm length (Restek s.r.l., Cernusco S/N, Italy) were used for the gas-phase sampling, while the Total Suspended Particulate (TSP) phase was collected on quartz filters (MQF FilterLab, diameter 102 mm). Before tests and sampling, the PUFs were pre-cleaned using a Thermo Scientific™ Dionex™ ASE 350 instrument extracting them twice with toluene (100°C; 1500 psi; 5’ static) and twice with a HEX:DCM mixture (1:1, v/v; 100°C; 1500 psi; 5’ static). The same instrument was used also for sample preparation using a separate kit of ASE cells (33 ml, stainless steel) dedicated only to atmospheric samples, to avoid possible cross-contamination with the analysis of other matrices (e.g. sediment or biota). Quartz filters were

decontaminated in a muffle furnace at 400°C for 4 hours before use. Both PUFs and quartz filters were stored wrapped in a double layer of aluminum foil before and after sampling.

Following the extraction, an aliquot of anhydrous ACS Na_2SO_4 (≥ 99%) from Sigma Aldrich (Saint Louis, USA) was used to dry the extracts. The Na_2SO_4 was previously dried overnight at 150°C and then ultrasonic cleaned three times with dichloromethane and three times with *n*-hexane. Samples were reduced to 200 µL with a gentle nitrogen flow at 23 °C (Turbovap II®, Caliper Life Science, Hopkinton, MA, USA) and then transferred into glass vials equipped with spring insert.

Instrumental analyses were conducted by GC-MS/MS (Thermo Scientific™ TRACE™ 1310 coupled with Thermo Scientific™ TSQ™ 9000) on a 60-m HP-5MS column (0.25 mm I.D., 0.25 µm film thickness; Agilent Technologies, Avondale, USA): Inj.: 300 °C; Aux: 300 °C; Oven: 120 °C for 1 min, 25 °C min^{-1} to 180 °C, 10 °C min^{-1} to 250 °C, 20 °C min^{-1} to 310 °C for 11,6 min; Carrier: He at 1 mL min^{-1}; PTV splitless: 5 °C s^{-1} to 320 °C for 1 min, 14,5 °C s^{-1} to 350°C for 6 min. Retention times and SRM transitions are reported in Table SI2. Quantification was performed adding 50 µL of $^{13}C_6$-phenanthrene at 1 ng μL^{-1} as internal standard (CLM-2451, Cambridge Isotope Laboratories Inc., Andover, MA USA). Natives were purchased at Sigma Aldrich (UV filters), LGC standards (musk solution DRE-LA19020100CY; Milan, Italy) or were provided by Givaudan (non-musk fragrances; Vernier, Switzerland). Crude concentrations were corrected using instrumental response factors. Seven field blanks were collected in the different sampling sites, showing no significant differences and the method detection limits (MDL) were calculated as three times the standard deviation of the field blanks (Table SI3).

3. Results and discussion

3.1. Method Validation

The pressurization of the ASE system (1500 psi) during the statics is reached and maintained both by I) pumping the solvent in the extraction cell and II) through the increase of pressure due to the solvent heating. Using low temperatures may have significantly affected the solvent consumption due to repeated activations of the pump during long extraction times. Table SI4 reports the extraction tests of one PUF cartridge conducted at three different times (5 min, 30 min, 60 min) and temperatures (40°C, 70°C, 100°C). The volume of solvent used is not influenced by extraction time, while the lowest solvent consumption (approx. 20 mL) was achieved at 40°C, with relatively higher

221 volumes needed at higher temperatures. A mixture of HEX:DCM 1:1, as in [28], was used for these
222 tests but in the following extraction tests the solvent consumption remained consistent even using
223 different solvent mixtures.

224

225 The extraction efficiency of three different solvent mixtures (HEX:DCM - 1:1, HEX:ACE - 1:1, and
226 DCM:ACE - 1:1) was tested under the selected 40°C and 30 min static conditions (Table SI5). A
227 working solution containing all the analytes, each at a concentration of 1 ng/μL was prepared in
228 dichloromethane and 50 μL were added to precleaned PUFs before extraction. To evaluate the
229 possible fractionation during the extraction cycles, each PUF was extracted 3 times with the same
230 solvent mixture, collecting the extracts in separate vials (Figure 2 a,b,c). Following the extraction,
231 50 μL of $^{13}C_6$-phenanthrene were spiked and samples were concentrated to 200 μL before GC-
232 MS/MS analysis. As shown in Figure 2c, DCM:ACE resulted the most effective solvent mixture
233 achieving quantitative extraction of PCPs in one single cycle: average extraction recovery was 105%,
234 ranging from a minimum of 96% for Ambrofix to a maximum of 114% for Musk Xylene (Table SI5).

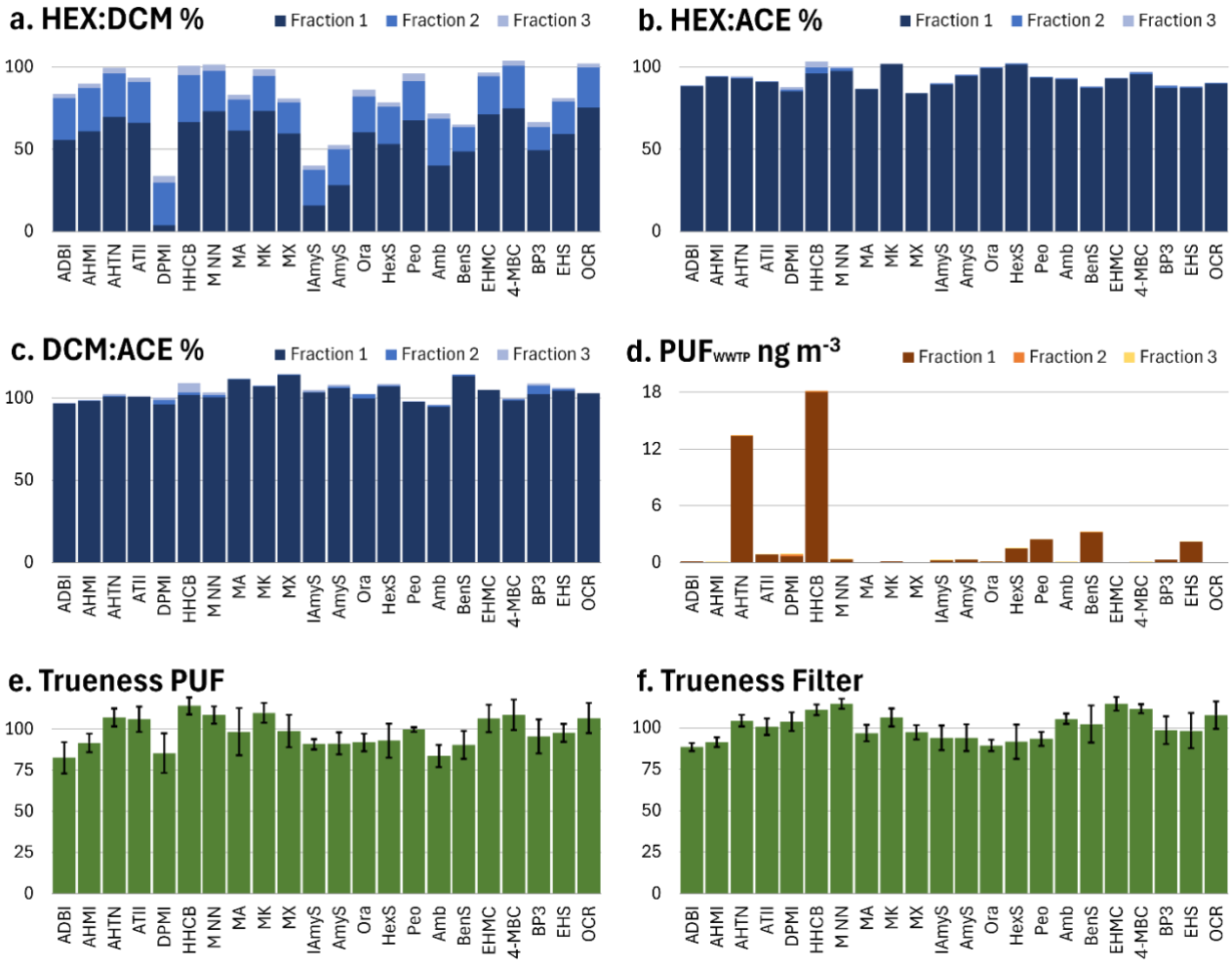


Figure 2. PUF extraction efficiencies with percentage recoveries after three ASE cycles at 30 min - 40°C (Fraction 1; Fraction 2; Fraction 3) testing three different solvent mixtures (2a. *n*-hexane : dichloromethane - 1:1, HEX:DCM; 2b. *n*-hexane : acetone - 1:1, HEX:ACE; and 2c dichloromethane : acetone - 1:1, DCM:ACE). Figure 2d. report the sequential extraction using the DCM:ACE mixture on a preliminary real PUF sample collected close to a WWTP (ng m^{-3}), while 2e and 2f report the percentages obtained in trueness tests for the DCM:ACE extraction of spiked PUF and filters, respectively.

The fractionation of PCPs after three sequential DCM:ACE extractions was tested also on a preliminary sample (PUF_{WWTP}), collected close to a wastewater treatment plant (Figure 2d). The efficiency of one cycle of extraction using the DCM:ACE mixture (Table SI5) resulted comparable to the tests conducted with spiked PUF. However, only the gas phase was available for the PUF_{WWTP} sample and therefore it was not included in the following discussion.

Trueness tests were performed adding 50 μL of the working solution at 1 ng/μL, along with the internal standard, to precleaned PUFs (n=3; Figure 2e) and quartz filters (n=3; Figure 2f), and then applying the final analytical procedure. Trueness was expressed as the percentage of the quantified value compared to the theoretical spiked quantity. Quartz filter samples were extracted with the same DCM:ACE extraction procedure developed for the PUFs, maintain consistency and to ensure that the PCPs collected on the two different sampling supports were subjected to the same conditions during the sample preparation, avoiding potential method-derived biases in the calculations of the gas/particulate phase repartitions. Pre-extracted 6 mm glass spheres were added in the cells together with the filters as inert volume fillers. Trueness tests showed average differences with the true spiked values below 10% for most of the PCPs, with comparable results for the extraction of both PUF and filters (Table SI6).

3.2. Occurrence of PCPs in atmospheric samples

Results show that concentrations and patterns of atmospheric PCPs reflect their distinct sources across the four sampling sites, generally following the same scheme: coastal > urban > alpine > polar areas. The values reported in Figure 3 refer to the sum of the gaseous and particulate phases. The highest concentrations of ΣPCPs (Figure 3; Table SI7) were observed near the seashore (13-16 ng m^{-3}), due to high levels of UV filters linked to the widespread use of sunscreen products associated with touristic activities. In the urban area of Mestre relatively lower cumulative concentrations (ΣPCPs = 6.0-8.5 ng m^{-3}) were observed, however with levels of musk and non-musk fragrances comparable to the coastal samples (Figure 3; Table SI7). PCPs were also detected in the Alps, but at lower concentrations (ΣPCPs = 1.6-3.0 ng m^{-3}) compared to high-impacted sites, consistent with the limited human presence in the area. In the Arctic samples, PCPs resulted at orders of magnitude lower (ΣPCPs = 0.11–1.3 ng m^{-3}) than samples collected in Veneto. Nevertheless, indicating that these substances can be detected in the atmosphere even in remote locations.

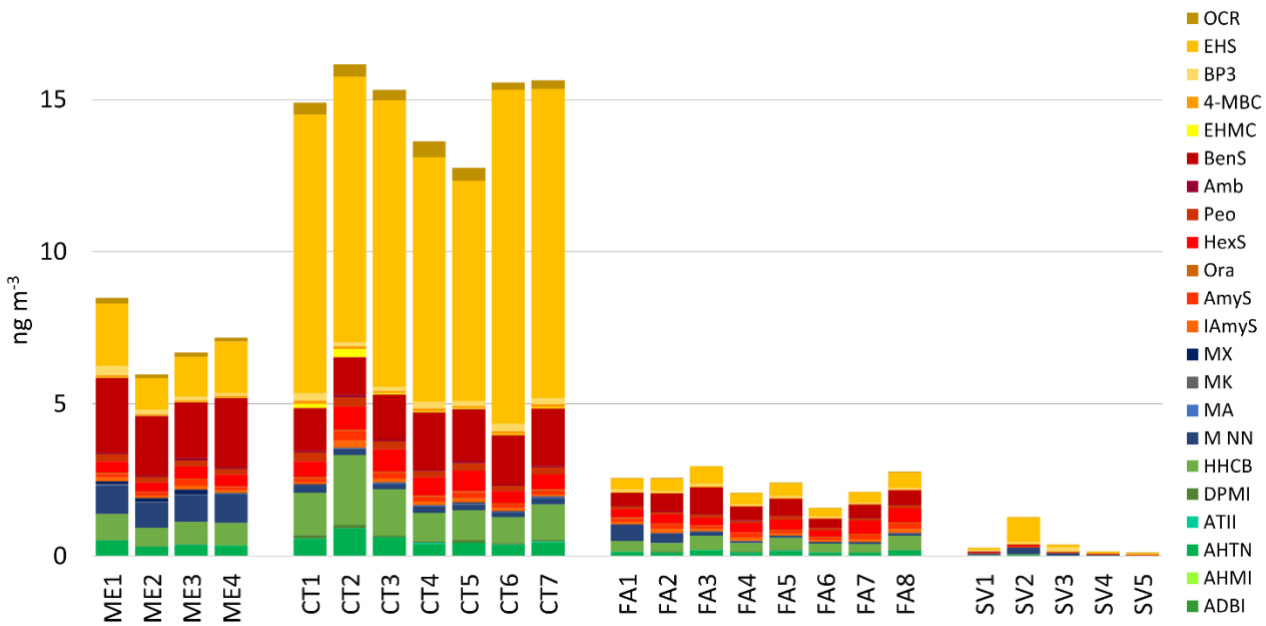


Figure 3. Concentrations of ∑PCPs (sum of the gaseous and particulate phases) in the atmosphere of urban (Mestre; ME1-4), coastal (Cavallino-Treporti; CT1-7), alpine (Falcade; FA1-8) and polar (Svalbard; SV1-5) sites.

Among the analyzed UV filters, EHS resulted in the dominant PCP in the atmosphere, being detected with the highest concentrations at all sampling sites. This is in agreement with the distribution previously reported by [21,22] , even if in these studies Homosalate, here not analyzed, was found at concentrations generally higher than EHS. In the seaside, near the beach of Cavallino-Treporti, the levels of EHS (7.2-11 ng m^{-3}) were similar to those detected during Summer at the on-site WWTPs (0.54-17 ng m^{-3}) [21]. The EHS concentrations detected in the urban area of Mestre (1.0-2.0 ng m^{-3}) were higher than those found in Toronto (0.02-0.58 ng m^{-3}) [22], which in turn were comparable to the alpine background levels in Falcade (0.27-0.56 ng m^{-3}). EHS was the most abundant PCP also in the Arctic samples, with concentrations generally lower than 0.08 ng m^{-3}, with the exception of sample SV2 (0.81 ng m^{-3}) (Table SI7). Similar abrupt variations of PCP levels were also observed in surface snow samples from Station Nord in Greenland [30]. In that case, results reflected a change in the origin of air masses reaching the Arctic, suggesting PCPs were emitted at lower latitudes. The other UV filters, EHMC, 4-MBC, BP3 and OCR, followed a distribution pattern similar to EHS, with higher levels in the coastal and urban samples, but with concentrations always remaining at fractions of ng m^{-3} (Table SI7). Similar values were previously detected close to sources and off-sites [21].

297 The distribution of the musk fragrances was dominated by the polycyclic HHCB, AHTN, and by the
298 macrocyclic M NN. Together they account for 9-40% of the ΣPCPs, and for over 90% of the analyzed
299 musks (Table SI7). In the urban samples M NN concentrations (0.84-0.95 ng m^{-3}) were higher than
300 HHCB (0.61-0.86 ng m^{-3}) and AHTN (0.30-0.51 ng m^{-3}). At the coastal site, M NN concentrations
301 were lower (0.14-0.25 ng m^{-3}), while concentrations of HHCB (2.3 ng m^{-3}) and AHTN (0.90 ng m^{-3})
302 were the highest among all sites. Despite a more variable distribution in the two other sites, HHCB
303 was generally the most abundant musk in Falcade, while M NN was in the Arctic (Table SI7). The
304 other musk fragrances (ADBI, AHMI, ATII, DPMI, MA, MK and MX) constituted less than 1% of the
305 ΣPCPs in most of the samples. Among these musk fragrances, levels above 0.1 ng m^{-3} were observed
306 for MX in urban samples, and DPMI in coastal air (Table SI7).

307 The concentrations of HHCB and AHTN in this study are comparable to those reported in the
308 literature for low-medium impacted sites, (Table SI1), while literature data show that
309 concentrations may increase orders of magnitude close to cosmetic plants [14] and WWTPs [15,20].
310 This is in accordance with the results of the preliminary PUF_{WWTP} sample (only gas phase available;
311 Table SI1), where HHCB and AHTN concentrations were 18 ng m^{-3} and 13 ng m^{-3} respectively.
312 Sample collected at Gruvebadet are characterized by lower concentrations of musks, with HHCB and
313 AHTN below 0.04 ng m^{-3} (Table SI7) and are comparable to levels previously detected in the Arctic
314 [9].

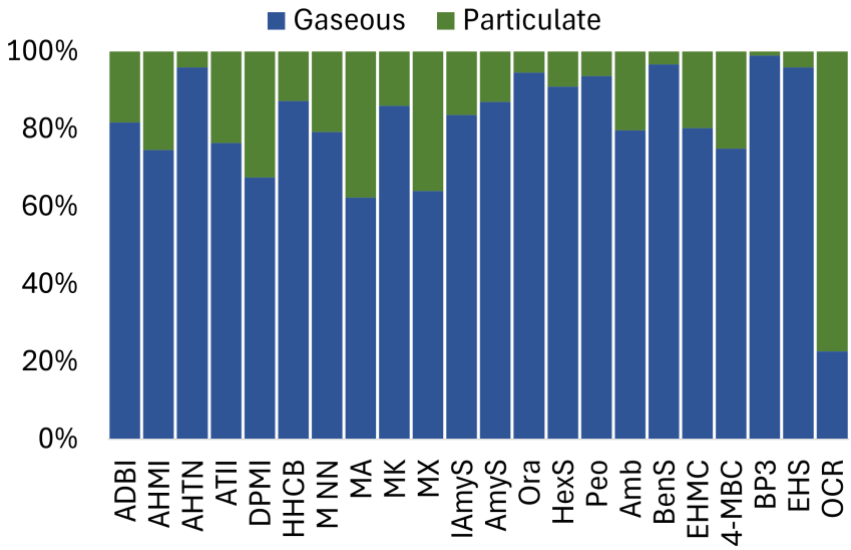
315 Among non-musk fragrances, BenS was the most abundant PCP in Mestre (1.8-2.5 ng m^{-3}) and in
316 most of the alpine samples (0.30-0.87 ng m^{-3}; Table SI7). Relatively high concentrations of BenS
317 were also found in the coastal samples (1.2-1.9 ng m^{-3}), with slightly lower levels than in urban
318 areas, probably reflecting a more intense use of this compound as a fragrance, instead as an active
319 sunscreen product. The levels of BenS detected in outdoor air resulted significantly lower than
320 indoor air samples, where this compound was previously found at concentrations up to 170 ng m^{-3}
321 [25]. The other salicylate fragrances at urban, coastal and alpine sites were lower than BenS (Table
322 SI7) and characterized by a more homogeneous distribution, with ranges of 0.07-0.24 ng m^{-3} for
323 IAmyS, 0.08-0.31 ng m^{-3} for AmyS, and 0.20-0.77 ng m^{-3} for HexS. Notably, in the seawater of the
324 urban canals of Venice, BenS was detected at concentrations comparable or lower than IAmyS,
325 AmyS and HexS [29]. This may indicate a differential distribution of the salicylates in air and water
326 matrices: at 25°C the LRET potential of BenS was higher when emitted into the water [30]. In the
327 Arctic, atmospheric concentrations of all the salicylate fragrances (BenS, IAmyS, AmyS, HexS) were
328 significantly lower than the other sites, with concentrations below 0.04 ng m^{-3}. However, in contrast

329 to the urban samples, BenS was not the prevalent salicylate fragrance in the Arctic. Previous studies
330 conducted on Arctic snow samples collected in Svalbard [6,33] and Greenland [30], show that BenS
331 was found at concentrations lower than the other salicylate fragrances. The observed
332 concentrations and trends for the different salicylates suggest how they are subject to different
333 environmental processes affecting their possible degradation during atmospheric transport that still
334 need to be fully understood [30]. The other non-musk fragrances showed a spatial distribution
335 similar to salicylates. Peo and AmyS have similar concentration up to 0.30 ng m^{-3} in the coastal area,
336 and comparable values in Mestre (Table SI7). Ora and Amb remained below 0.1 ng m^{-3} in all
337 sampling sites.

338 **3.3. Phase distribution**

339 Most of the analyzed PCPs were distributed predominantly in the gas phase (Figure 4; Table SI8), in
340 accordance with the literature (Table SI1). All samples were used to calculate phase repartition and
341 half of the detection limit was considered for those compounds with values resulting below MDL.
342 This predominance of the gaseous phase was observed in previous studies on PCPs distribution for
343 both musk fragrances [16] and UV filters [22]. Differences observed in urban, coastal and alpine
344 areas were generally associated with concentrations below MDL in at least one phase (Table SI8).
345 However, OCR differs from the other PCPs, constituting an exception, as it was generally associated
346 with the particulate phase. It is below detection limits in most of the gaseous samples, while it was
347 always detected in the particulate phase, generally representing the most abundant UV filter (Table
348 SI8), confirming previous predictions on its equilibrium partitioning in the atmosphere both in warm
349 and cold environments [30]. OCR has low volatility, promoting the sorption to atmospheric particles
350 and increasing its Longe Range Environmental Transport (LRET) potential, possibly due to reduced
351 reactions with photooxidants.

352 In Gruvebadet the repartition of the PCPs in the gaseous phase was generally lower in comparison
353 to the other sites, likely reflecting the lower temperatures characterizing the polar areas (Table SI7).



354

355 Figure 4. Average distributions of PCPs in the gaseous and particulate phases.

356

357 **4. Conclusions**

358 In this study we validated a novel procedure for the low-temperature ASE extraction of the gaseous
359 and particulate fractions of PCPs in the atmosphere. This new analytical method contributes to the
360 development of a standardized common procedure for the determination of atmospheric
361 fragrances and UV filters in the atmosphere. Touristic and recreational activities were recognized as
362 relevant sources of PCPs in coastal areas, mainly due to the large local use of sunscreens. Urban and
363 alpine sites also resulted affected by the presence of these compounds. Notably, levels of PCPs were
364 also detected in a remote polar environment, supporting previous findings in Arctic snow, and
365 highlighting the need of further investigations to better understand the long-range transport
366 hypothesis. Most PCPs are distributed in the gas phase, with OCR as an exception, being mainly
367 adsorbed onto particulates, which confirms previous model predictions.
368 Results reported in this study showed a significant spatial variability of the levels and patterns of
369 atmospheric PCPs, also reflecting the peculiar characteristics of each sampling site. The main open
370 question regards their temporal trends, as these products are characterized by a relevant
371 seasonality in their consumption. We can expect that high concentrations detected in summer in
372 the high-impacted sites, especially for UV filters, will decrease during winter. Therefore, monitoring
373 PCPs in the atmosphere on an annual basis is necessary to understand how seasonal changes in low
374 latitudes sources can affect the distribution of these contaminants in remote areas.

375

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