



# Plastic breeze: Volatile organic compounds (VOCs) emitted by degrading macro- and microplastics analyzed by selected ion flow-tube mass spectrometry

Jacopo La Nasa, Tommaso Lomonaco, Enrico Manco, Alessio Ceccarini, Roger Fuoco, Andrea Corti, Francesca Modugno\*, Valter Castelvetro, Ilaria Degano

Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 13 I-56124, Pisa, Italy

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## ABSTRACT

Pollution from microplastics (MPs) has become one of the most relevant topics in environmental chemistry. The risks related to MPs include their capability to adsorb toxic and harmful molecular species, and to release additives and degradation products into ecosystems. Their role as a primary source of a broad range of harmful volatile organic compounds (VOCs) has also been recently reported. In this work, we applied a non-destructive approach based on selected-ion flow tube mass spectrometry (SIFT-MS) for the characterization of VOCs released from a set of plastic debris collected from a sandy beach in northern Tuscany. The interpretation of the individual SIFT-MS spectra, aided by principal component data analysis, allowed us to relate the aged polymeric materials that make up the plastic debris (polyethylene, polypropylene, and polyethylene terephthalate) to their VOC emission profile, degradation level, and sampling site. The study proves the potential of SIFT-MS application in the field, as a major advance to obtain fast and reliable information on the VOCs emitted from microplastics. The possibility to obtain qualitative and quantitative data on plastic debris in less than 2 min also makes SIFT-MS a useful and innovative tool for future monitoring campaigns involving statistically significant sets of environmental samples.

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## 1. Introduction

World production of synthetic polymers in 2019 was around 360 Mton, about a half of which was used in packaging and other disposable items characterized by a short lifecycle. Plastics contribute heavily to the generation of waste, and due to improper disposal, an estimated 5 to 13 million tons end up in the oceans every year (Silva et al., 2018).

Once in the environment, and depending on their exposure conditions, synthetic polymers undergo chemical, physical and biological degradation. In some polymer types, particularly polyolefins such as polyethylene and polypropylene, and vinyl polymers such as polystyrene, fragmentation of the embrittled material occurs with gradual downsizing of the resulting plastic debris (Barnes et al., 2009; Andrady, 2011; Gewert et al., 2015). The general definition of microplastics (MPs) includes particles sized from 2 to 5 mm down to 1  $\mu\text{m}$  (Frias and Nash, 2019).

In the last few years, the pollution from MPs gathered importance among the emerging problems studied in environmental chemistry

(Betts, 2008; Horton et al., 2017). The most investigated risks for biota in terms of MPs are ingestion by living organisms (Toussaint et al., 2019), the transport of hazardous chemicals and pollutants adsorbed on them (Teuten et al., 2009), and the release of additives and degradation products into the environment (Hermabessiere et al., 2017).

The emission of harmful volatile organic compounds (VOCs) from plastic debris as a consequence of the chemical and physical degradation processes has been recently investigated (Royer et al., 2018; Lomonaco et al., 2020), with findings suggesting that the research on the consequences of environmental pollution by MPs should be extended also to the released VOCs. Studies in different fields have demonstrated that the photo-oxidative/radical processes involved in the ageing of plastics lead to the release of different types of VOCs, such as oxygenated compounds, aromatic species, and hydrocarbons that affect air quality and could also be leached in natural waters. The full characterization of the VOCs profile would allow to better understand the extent of degradation of the original materials and to assess more exhaustively their environmental impact (Gallet et al., 2002; Hakkarainen et al., 2003; Hakkarainen, 2008; Curran and Strlič, 2015; Curran et al., 2016, 2018).

Most of the studies related to identifying and quantifying MPs in environmental samples exploit analytical approaches based on mi-

\* Corresponding author.

E-mail address: [francesca.modugno@unipi.it](mailto:francesca.modugno@unipi.it) (F. Modugno)

croscopy with infrared and Raman spectroscopies, chromatography-mass spectroscopy coupled with thermoanalytical approaches, or wet-chemical isolation and purification of hydrolysis products, followed by chromatographic quantitative analysis (Qiu et al., 2016; Wang et al., 2017; Li et al., 2018; Silva et al., 2018; Schwaferts et al., 2019; Castelvetro et al., 2020; La Nasa et al., 2020a).

However, the above mentioned approaches are not (or only partially) able to detect the VOCs released upon the degradation of polymeric materials. Yet the characterization of the VOC profile can play a key role for understanding the mechanisms and extent of degradation of MPs and to better assess their role in environmental pollution.

A reliable, fast and transportable instrumentation capable of detecting the emission of VOCs from plastic debris with high sensitivity would be a step forward in revealing the presence of macro- and microplastics in specific environmental sites and in correlating the detected emissions with the increasing evidences of harmful interaction of microplastics with biota.

Moreover, environmental studies generally entail the sampling of large numbers of plastic debris that cannot be straightforwardly processed with the traditional approaches used for the analyses of microplastics. The possibility to use a fast screening approach during the sampling campaign or sub-set selection to identify the most interesting samples to be processed with other complementary analytical approaches, or the most significant sampling sites, could also be a step forward to improve the data quality and the sampling procedures in environmental studies.

Among the transportable technologies available on the market, selected ion flow tube-mass spectrometry (SIFT-MS) is one of the few capable of performing real-time qualitative and quantitative analyses of VOCs at trace levels in air or sample head-spaces. By applying precisely-controlled ultra-soft chemical ionization using different reagent ions (e.g.  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^+$ ), it allows achieving good chemical selectivity for different classes of chemical species without the use of chromatographic separation systems (Smith and Španěl, 2005; Smith et al., 2020). SIFT-MS has been successfully used for the chemical characterization of breath samples to develop clinical diagnostic methods (Španěl and Smith, 2011; Kumar et al., 2013; Walton et al., 2014; Spesyvyi et al., 2015; Ioannidis et al., 2018; Zhu et al., 2018), for food quality control (Olivares et al., 2010; Bajoub et al., 2018; Dryahina et al., 2018; Van Kerrebroeck et al., 2018), and in the field of heritage science (La Nasa et al., 2019a, 2019b, 2020b).

In this study, we used SIFT-MS to characterize the VOCs emitted from a set of macro/microplastics collected from several areas of a sandy beach in northern Tuscany (Italy). Since the amount of volatile compounds still present in the sampled specimens was not known *a priori*, our main aim was first to assess the possibility to detect them in environmental samples, and secondly to verify the selectivity of the pro-

posed approach on a pilot case study. We verified that employing SIFT-MS in combination with principal component analyses (PCA) allowed us to perform the characterization of the VOC profiles of plastic debris in less than 2 min for each sample. Moreover, SIFT-MS was also used to obtain quantitative data on the most abundant emitted volatile species. Thus, this study serves as a proof-of-concept for the future application of SIFT-MS for the investigation of the VOC profiles of plastic debris in environmental campaign.

## 2. Materials and methods

### 2.1. Environmental samples

A total of 39 macro- and microplastic (up to 1 cm) debris samples were collected as sieve fractions (2 mm) from sand samples collected in a marine beach in northern Tuscany (Fig. 1, Marina di Vecchiano, Pisa, Italy) (Ceccarini et al., 2018): 3 from the foreshore (swash area), 15 from the summer berm, and 21 from the winter berm. 54% of the samples were identified by infrared spectroscopy and analytical pyrolysis-gas chromatography-mass spectrometry as low density polyethylene (LDPE), 38% as polypropylene (PP), and 8% as polyethylene terephthalate (PET). The instrumental conditions used for the identification are reported in (Ceccarini et al., 2018; Corti et al., 2020).

### 2.2. Selected ion flow tube-mass spectrometry

The samples (50–500  $\mu\text{g}$ ) were sealed in 22 mL gas-tight glass vials and kept at 60 °C for 20 min equilibration time before the analysis. Procedural blanks were run using empty sealed vials pre-treated as those with the samples. The study was performed using a Voice 200ultra instrument (SYFT Technologies, New Zealand). The transfer line of the system directly sampled the headspace inside the vials using a heated needle. Nitrogen was used as a carrier gas (flow 25 mL/min, 99.999% purity). The reagent ions used for ionizing the analytes were  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^+$ . The ions produced by reaction of the analytes with the reagent ions were scanned by the second quadrupole in the  $m/z$  15–400 range. The acquisition time for each mass was set at 100 ms with steps of 1.0  $m/z$  for an average total run time of c.a. 2.0 min, for the total of the three reagent ions. LabSyft 1.6.2 software (SYFT Technologies) was used for data acquisition and analysis. The SIFT-MS instrument was calibrated using a multiple component certified gas standard (Syft Calibration Standard, SYFT Technologies).

### 2.3. Data elaboration

The attribution of the species was performed by comparison with literature data (Smith and Španěl, 2005; La Nasa et al., 2019b, 2020b) and using the LabSyft Compound Library (SYFT Technologies). The identification of the chemical species was independently confirmed

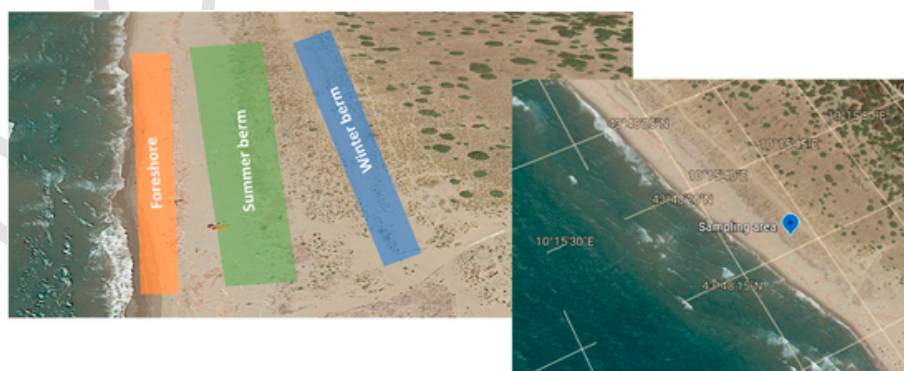


Fig. 1. Geographical coordinates and sampling area.

with headspace analyses performed on a selection of samples with needle trap microextraction and gas chromatography/mass spectrometry analyses (Lomonaco et al., 2020) and by SIFT-MS performed on reference materials. The use of three reagent ions allowed us to identify the different compounds exploiting the different reactivity of the functional groups with each reagent ion thus overcoming the absence of a chromatographic separation (Španěl and Smith, 2011). Table 1 summarizes the species identified by SIFT-MS in the plastic debris samples.

Principal component analysis (PCA) was performed on the normalized mass spectral data. The range of the mass spectra selected for the data analysis were in the  $m/z$  15–250 range, as the intensity of the signals at higher mass-to-charge ratio was negligible. In detail: subtraction of the blank and of the excess of reagent ions were applied. The mass spectra for each sample were normalized by expressing the relative intensity (counts/sec) for each ion as a percentage of the total intensity obtained by summing the intensities of all the considered ions. The PCA on the covariance matrix of the normalized SIFT-MS data was performed with Xlstat 10.0 (Addinsoft, France).

SIFT-MS allows to perform a real time quantitative evaluation of the concentration of specific VOCs without the use of calibration curves (and avoiding any bias related to selective sampling on SPME). Quantitative analyses were performed on the reprocessed full scan raw mass spectra obtained for each plastic debris using the LabSyft 1.6.2 software (SYFT Technologies) which exploits an integrated compound library to calculate analyte's absolute concentration (Langford et al., 2019). The ions selected for each species to build the method for the quantitative analyses are reported in Table 1.

### 3. Results and discussion

#### 3.1. Qualitative analyses

All the acquired spectra featured a broad range of oxidation products indicative of the complex mechanisms involved in the photo-oxidation of hydrocarbon polymers, such as short chain carboxylic acids, alcohols, aldehydes, and ketones, including aromatic ones from PET and PS. The oxidation products identified in the VOC profiles of the environmental plastic debris matched well those detected from artificially aged reference micro powders of LDPE, PP, and PET (Lomonaco et al., 2020). After normalization, the mass spectral data acquired by SIFT-MS with the three different reagent ions were subjected to PCA in order to assess whether the sampling spot, and in particular the zone of the beach, could be related to differences in the VOC profile. The aim was also to understand if and which species could be considered as markers of a given polymer species and/or of the extent of its degradation. The first two components (PC1 + PC2) accounted for 89% of the total variance of the data set. Fig. 2a and b shows the score plot with a color classification associated with the sample collection zone and with the polymer type as identified by ATR-FTIR, respectively.

Fifteen plastic samples from the foreshore and three samples from the summer berm (that is, the zones where swashing is more intense and most plastic debris is likely to be cyclically accumulated and removed) are clustered together in the score plot, at negative values of PC1 and PC2 (Fig. 2a). All the mass spectra obtained for the samples in this cluster featured ions related to unspecific oxidation products: formaldehyde, acetaldehyde, and acetic acid were the most abundant. The mass spectra of the 15 samples from the winter berm all scored higher PC1 values than those of the other zones. A group of them are relatively similar to each other, clustered together at values slightly below zero in PC1, and averaging zero in PC2. On the other hand, twelve of them were found at positive values in PC1, and highly dispersed in PC2.

From the collected data, it seems that PCA does not readily discriminate the type of polymer (Fig. 2b). In particular, the PET samples clus-

**Table 1**

–Compounds identified by SIFT-MS analyses for the three classes of polymers investigated in this study. The ions used for quantitative analyses are underlined and *Italic*.

Polymer	VOC classes	Identified species (SIFT-MS characteristic ions)				
		Compound	H <sub>3</sub> O <sup>+</sup>	NO <sup>+</sup>	O <sub>2</sub> <sup>+</sup>	
PP	carboxylic acids	<i>formic acid</i>	47	46	45, 46	
		<i>acetic acid</i>	<u>61</u> , <u>79</u>	<u>90</u>	<u>60</u> , <u>61</u> , <u>79</u>	
		<i>propionic acid</i>	57, 75	104	56, 74	
		<i>butyric acid</i>	71, <u>82</u> , <u>107</u> , <u>125</u>	<u>118</u>	<u>60</u> , 88	
		<i>pentanoic acid</i>	85, 103	132	102	
		<i>hexanoic acid</i>	99, 117	146	116	
		<i>heptanoic acid</i>	113, 131	160	130	
		<i>octanoic acid</i>	127, 145	174	144	
		aldehydes	<i>formaldehyde</i>	31	30	30
			<i>acetaldehyde</i>	<u>45</u> , <u>63</u> , 89	<u>43</u> , <u>61</u>	43, <u>44</u>
			<i>propionaldehyde</i>	41, 59	57	58
			<i>butanal</i>	55, 73	71	<u>44</u> , 72
	<i>pentanal</i>		69, 87	85	44, 58, 86	
	<i>hexanal</i>		83, 101	130	44, 56, 100	
	<i>heptanal</i>		97, 115	144	96, 114	
	<i>octanal</i>		111, 129	158	84, 110, 128	
	ketones		<i>acetone</i>	<u>59</u> , <u>77</u>	<u>88</u>	58
		<i>butanone</i>	73, 91	102	43, 72, 57	
	alcohols	<i>ethanol</i>	<u>47</u> , <u>65</u>	<u>45</u> , <u>63</u>	45	
		<i>butanol</i>	57, <u>75</u> , <u>93</u>	<u>73</u>	45	
		<i>propanol</i>	43, 61, 79	59	45	
<i>pentanol</i>		71, 107	87	44, 45, 71		
<i>hexanol</i>		<u>85</u> , 101	82, <u>100</u>	43, 56, <u>84</u>		
LDPE		carboxylic acids	<i>formic acid</i>	47	46	45, 46
	<i>acetic acid</i>		<u>61</u> , <u>79</u>	<u>90</u>	<u>60</u> , <u>61</u> , <u>79</u>	
	<i>propionic acid</i>		57, 75	104	56, 74	



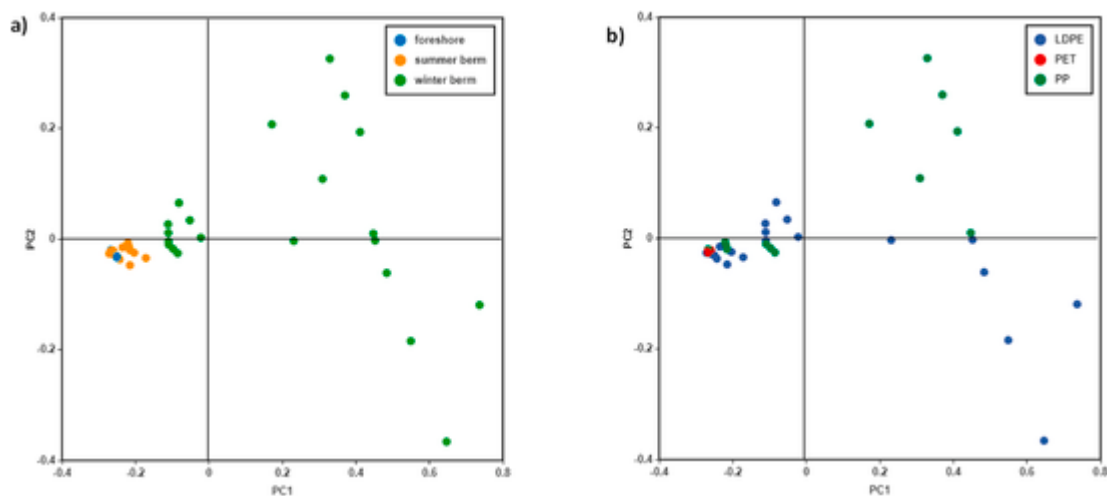


Fig. 2. Score plot from the PCA analysis of the SIFT-MS data; a) color classification according to the sampling zone; b) color classification according to the polymer type. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

score at negative values of PC2, suggesting PC2 as a discriminant between the two polymers when they are oxidized due to environmental ageing.

The loadings of PC2 are best interpreted by comparing them with the mass spectra of the individual samples. Fig. 4a reports the mass spectra acquired with the three different reagent ions for a PP sample, representative of the six PP samples from the winter berm which score at positive PC1 and PC2 (the complete list of all the VOCs identified in the headspace of the samples is reported in Table 1). The mass spectra are characterized by the presence of the ions typical of aldehydes and carboxylic acids with chain lengths up to eight carbon atoms, with acetic acid being the most abundant. The mass spectra also featured, with low abundance, the ions characteristic of alcohols with chain lengths of up to six carbon atoms. Finally, the ions characteristic of ketones with chain lengths of up to four carbon atoms were also identified.

Fig. 4b shows the mass spectra acquired with the three different reagent ions for the VOCs emitted by the LDPE sample characterized by the lowest PC2 values (the complete list of all the VOCs identified in the headspace of the samples is reported in Table 1). The mass spectra featured ions characteristic of aldehydes, ketones, carboxylic acids, and alcohols with chain lengths of up to 12 carbon atoms.

The profiles of the species identified by SIFT-MS in the emissions of these PP and LDPE polymers were thus significantly different both in terms of molecular weights and relative abundances. More specifically, the VOCs released from the LDPE sample collected from the winter berm were characterized by carbonyl species with higher molecular weights (up to 200 Da) compared to those released by the PP samples collected from the same area (up to 144 Da), which were centered mainly on acetic acid. The volatile species released by the LDPE samples clearly included alcohols, which were only minimally present in the PP samples. As expected, all the ions related to the low molecular weight carbonyl compounds, most abundant in the PP samples collected from the winter berm, have a positive loading for PC2, while those typical of LDPE have a negative loading for PC2 (see Fig. 1c). In particular, the ion  $m/z$  45 for the reagent ion  $[O_2]^+$ , due to the fragmentation of alcohols in the flow tube, has a negative loading value for PC2.

In summary, the different profiles of the VOCs emitted by PP and LDPE are mainly ascribable to the changes in the molecular weight of the alcohols generated during polymer oxidation. On the one hand, as highlighted in the score plot, PP and LDPE showed two different behavior: the PP moved from negative to positive values of both PC1 and PC2

for increasing oxidation, while LDPE starts from negative values of both the principal components to positive values of PC1 only. In other words, the discrimination of the two polymers was not possible at low degrees of oxidation due to the similarities in molecular weights of the VOCs emitted at the beginning of the degradation processes; however, differentiation became possible when the polymers reached more advanced stages of degradation.

The chemical structure of PET differs from those of the two polyolefins, resulting in quite a distinctive degradation mechanism, entailing the generation of low molecular weight degradation by-products that do not fit with the model highlighted for the polyolefins. This aspect requires further studies (Lomonaco et al., 2020).

### 3.2. Quantitative analyses

The different oxidation degree of the VOCs emitted by LDPE and PP debris was also evaluated by quantifying the alcohols, carboxylic acids, aldehydes, and ketones with 2, 4, 6, and 8 carbon atoms chain lengths. The oxidation degree of the VOCs can be considered a proxy of that of the plastics, or at least of their surface. Considering the radical oxidation process of hydrocarbon polymers, the different classes of compounds can be associated to different oxidation stages of the material (Guillet, 1980; Hakkarainen and Albertsson, 2004). To highlight the trend in the oxidation of the plastic debris in the different beach areas, and to overcome the variability related to different porosity, size and surface area, we normalized the sum of the concentrations of the compounds of the same class for the total concentration of the ketones in each sample. Ketones can be considered an intermediate oxidation product, only slowly and gradually depleted during time (Guillet, 1980; Hakkarainen and Albertsson, 2004). Fig. 5 reports the acids/ketones, aldehydes/ketones, and alcohols/ketones concentration ratios obtained for eight selected samples of LDPE and PP, versus the corresponding PC1 values.

For both LDPE (Fig. 5a) and PP samples (Fig. 5b) we observed a gradual decrease in the alcohols/ketones concentration ratio and an increase of the aldehydes/ketones and acids/ketones concentration ratios when moving from negative to positive values of PC1, roughly corresponding to an increasing distance from the seashore. This behavior, highlighted for both LDPE and PP samples, was consistent with an increasing polymer oxidation when moving from the summer berm to the winter berm, mostly associated with the oxidation of alcoholic into carbonyl groups. This interpretation is in agreement with the PCA results. From a quantitative point of view, the absolute concentration of the



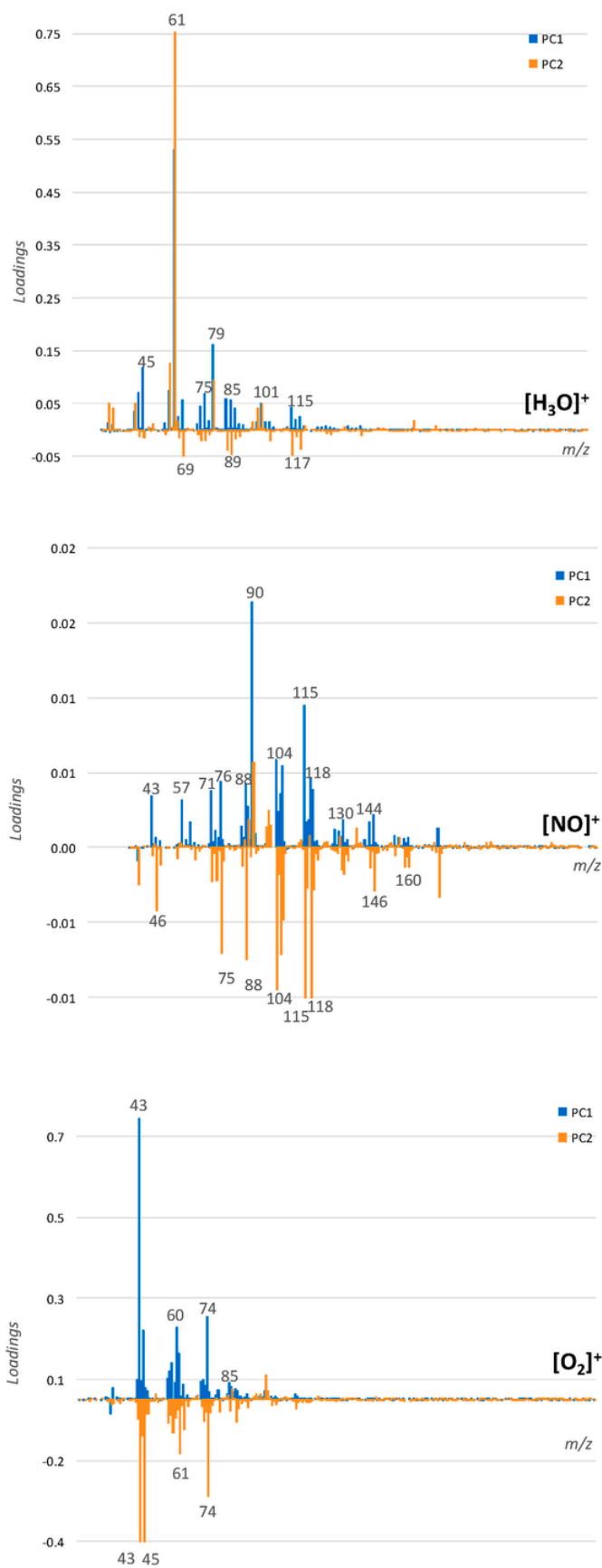


Fig. 3. PC1 and PC2 loading values corresponding to the ions in the mass spectra obtained with the three different reagent ions.

more oxidized VOCs fraction in the summer berm was in the 0–1.9 ppmv range for LDPE and in the 0.08–2.1 ppmv range for PP, while in the winter berm were in the 0.06–18 ppmv range for LDPE and in the 0.6–13.4 ppmv range for PP. Thus, the winter berm samples were characterized by VOC concentrations up to ten times higher than those emitted from the foreshores and summer berm, confirming that the emission of VOCs is strictly correlated with the oxidation degree of the polymers (Lomonaco et al., 2020). Finally, the concentration of the species emitted from PET (acetone, acetic acid, acetophenone, and benzaldehyde) were in the 0.02–0.96 ppmv range.

#### 4. Conclusions

The results of this pilot study on the characterization of VOCs emitted by weathered plastic debris using SIFT-MS enables, in combination with multivariate data analysis (PCA), to classify the samples in relation to the sampling zone, highlighting a general trend towards increasing levels of oxidation from the foreshore to the winter berm for both PP and LDPE. Even if the number and variety of samples is limited, the variation of the oxidation degree of the plastic debris (or at least, of its surface) was further confirmed by the quantification of the total amount each of alcohols, carboxylic acids, aldehydes, and ketones with 2, 4, 6, and 8 carbon atoms chain lengths, respectively. We believe that the possibility to perform VOCs analyses in real time, along with the implementation of the database with other polymer types (especially those that are more likely to be found as pollutant MPs) such as e.g. polystyrene, polyvinylchloride, and polycarbonate, will improve in future studies the accuracy and exhaustiveness of the information provided by this new approach. Moreover, the fast analysis time (less than 2 min) makes SIFT-MS a good option to preliminary screen the samples collected during environmental monitoring campaigns, and to identify the best ones to be subjected to more complex and time-consuming analytical protocols. Finally, the data obtained on the volatile compounds emitted from the surfaces of microplastics can be integrated with those gathered by complementary analytical approaches, such as thermal analyses or infrared spectroscopy, and thus provide us with a deeper understanding and a clearer assessment of the degradation and the impact of microplastics on the environment. This information will contribute to improve the decision-making process related to pollution containment measures.

#### Author contribution

JLN: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, writing (original draft), Writing - review & editing; TL: Conceptualization, Data curation, Methodology, Writing - review & editing; EM: Data curation, Investigation, Writing - review & editing; AC: sampling, Conceptualization, Formal analysis, Methodology, Validation, Supervision, Writing - review & editing; RF: Formal analysis, Methodology, Supervision, Validation, Writing - review & editing; AC: sampling, Investigation, Methodology, Validation, Writing - review & editing; FM: Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Supervision, Writing - review & editing; VC: Investigation, Formal analysis, Validation, Supervision, Writing - review & editing; ID: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing - original draft, Writing - review & editing.

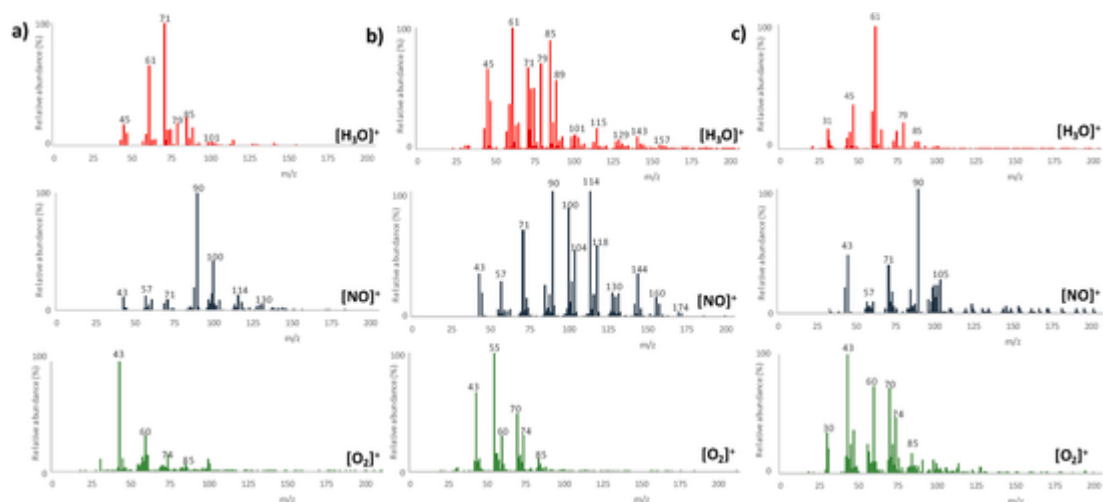


Fig. 4. SIFT-MS mass spectra obtained for a selection of samples originally constituted by PP (a) LDPE (b), and PET (c) with  $[H_3O]^+$ ,  $[NO]^+$ , and  $[O_2]^+$  as reagent ions (range  $m/z$  15–200).

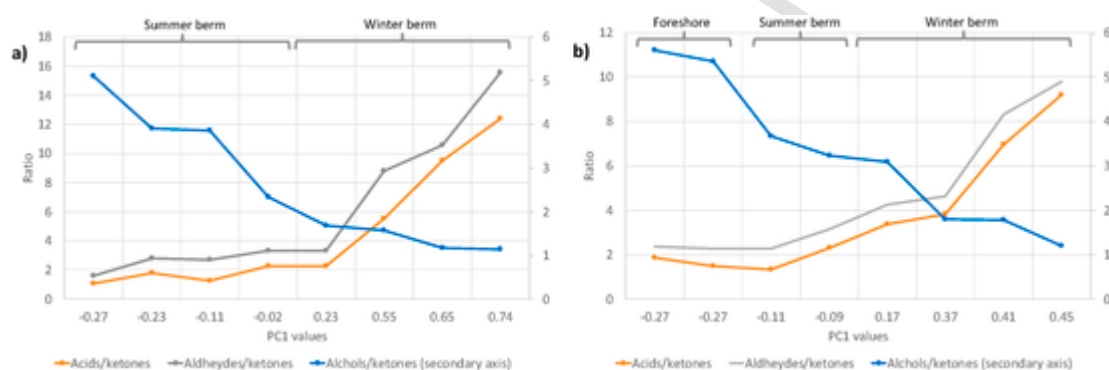


Fig. 5. Acids/ketones, aldehydes/ketones, and alcohols/ketones concentration ratios obtained for: a) eight samples of LDPE (four collected from the summer berm and four from the winter berm); b) PP (2 from the foreshore, 2 from the summer berm and 4 from the winter berm) versus PC1 values.

### 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.

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