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Project title	Photoreactivity of nanoplastics in the aquatic environment
Name of the accessed chamber	ISAC
Number of users in the project	1
Project objectives (max 100 words)	Micro- and nanoplastic are present in surface waters and their degradation can release small compounds in gas and aqueous phase. In this project, we evaluated the emission of volatile organic compounds from the degradation of nanoplastics dispersed in water. Moreover, we investigated the possible reactivity of emitted VOCs under atmospheric relevant conditions. This project can provide useful information to understand the environmental and in particular the atmospheric impact of nanoplastic pollution in surface waters.
Description of work (max 100 words):	In this work, we degraded polystyrene derivate nanoparticles dispersed in water under environmental like conditions. In particular, we exposed nanoplastics to ozone (gas phase), light and hydroxyl radicals (liquid phase). The VOCs emitted during the degradation of nanoplastics were injected and concentrated in the simulation chamber. These VOCs were then exposed to ozone, ozone/UV and ozone/UV-vis light in order to evaluate their reactivity under atmospheric relevant conditions. Some of the compounds detected in the chamber were degraded under these conditions and the formation of small oxygenated compounds was observed.

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[1] Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

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[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

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- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Monica Passananti
Chamber name and location: ISAC – Lyon, France
Campaign name and period: Photoreactivity of nanoplastics in the aquatic environment (25/3/19-5/4/19)
Text:

Introduction and motivation

Nowadays we are surrounded by plastic materials, more than 340 million tonnes of plastics were produced in 2017 and this amount is expected to grow every year.[1] The malleability, the light weight and the durability have made plastics used worldwide in many fields. These characteristics, mainly the resistance to the degradation, has led to environmental problems with a significant accumulation of plastic debris in the environment.[2] The size of plastic debris can cover different orders of magnitude (from nm to cm), small plastic particles have been observed worldwide: at the surface of oceans, water columns, in deep sea sediments and also in Artic sea ice.[3, 4] In the last decades, the scientific community and authorities have been focusing the attention on the impact and environmental fate of microplastics (MPs).[5] Only recently, lower scale plastics (nanoplastics) have begun to be considered and the term "nanoplastics" (NPs) is still under discussion.[5, 6] In this project, we considered a nanoplastic a plastic particle with a size lower than 1 µm, this definition has been used by several authors.[5-8]

NPs, as well as MPs, can be directly released into the environment (primary particles) or they can derive from breakdown of larger plastic pieces (secondary particles)[6, 9]. The amount of NPs in the aquatic environment is unknown, due to the limitation of analytical techniques, and only recently the occurrence of nanoplastic in oceans has been demonstrated.[10] Although there is a lack of data, it is likely to expect a high concentration of NPs in natural waters, considering that every year up to 12.7 million of tonnes of plastic are entering the marine environment.[11] NPs are expected to float at the surface of the oceans and interact with both atmosphere and the body water. These interactions, the surface processes and the heterogeneous reactions cannot be neglected in order to understand the impact of NPs on the environment. Moreover, as reported by Mattsson and co-authors the surface effects of a nanoplastic particle can be significantly enhanced compared to larger size particles, indeed if a plastic bag is degraded in particles of 40 nm of diameter, they will expose a surface of 2600 m^2.[12] Therefore, considering the huge surface area of a nanoplastic particle and the possible high concentration in surface waters, the impact of NPs on the environment could be significant and it has been only poorly investigated until now.

Scientific objectives

Primary and secondary nanoplastic particles in the aquatic environment can undergo degradation processes. Although these transformations are very slow, they can have a significant impact on the ecosystem because the degradation of plastics material can release chemical compounds in bulk, as well as in gas phase. Study of the degradation of plastic material (e.g. plastic bags) and polymers (mainly films) under environmental conditions have shown that polymers are degraded by atmospheric agents (light, temperature, oxygen, etc.) and they can produce smaller size plastic particles as well as small polymer fragments and volatile compounds[13-15] . We expect that nanoplastics will react faster than MPs due to the higher surface to volume ratio, therefore also the formation of degradation products could be relevant. Indeed, the degradation reactions take place first at the surface of the polymers, which is the most exposed to atmospheric agents. In this project, the emission of chemicals from the abiotic degradation of nanoplastics in the aquatic environment was investigated. Floating plastic debris in surface waters are mainly degraded by sunlight and oxidation processes,[16] therefore we investigated the reactivity of NPs versus light and oxidants present in surface waters and in the atmosphere. In particular, we studied the transformation of plastics mediated by ozone in gas phase, hydroxyl radicals in aqueous phase and by light. We investigated the emission from polystyrene (PS) and polystyrene co-polymer with a particle size ranging from 200 up to 400 nm. We decided to study PS because it is photoreactive and the photo-initiated oxidative degradation is predominant compared to the biodegradation. Although we focused this study only on PS and PS co-polymers, other plastic materials, such as polyethylene and polypropylene are mainly degraded in the environment through UV-initiated processes and for them the biodegradation is a secondary process, as well as for all the carbon backbone polymers.[13]

The identification of the degradation products of nanoplastics, in particular the volatile compounds can be used to evaluate the possible impact of NPs pollution on the atmospheric processes. Overall, this objective had the objective of providing useful information on emission from NPs degradation in the environment. These kind of data are still scarce; however they are crucial to assess the impact of nanoplastics in the environment.[17]

Reason for choosing the simulation chamber/ calibration facility

The indoor simulation chamber ISAC has been the perfect setup to carry out this project. It was built to investigate interfaces processes, indeed a tank on the floor of the chamber can be filled with liquids to study interface air-liquid reactions. However, the chamber can also be used without the tank to study processes that take place in gas phase. In this project, we used the chamber to concentrate the volatile organic compounds (VOCs) emitted by nanoplastic degradation to better characterize the emissions. Plastics are slowly degraded by atmospheric agents (oxidants and light), therefore in order to study, in lab scale experiments, the environmental degradation of NPs there are two possibilities:

1) to expose NPs to extreme conditions (high concentration of oxidants, high temperature and energetic light irradiation)
2) to use facilities, such us simulation chambers and high sensitive instruments, to highlight processes that otherwise will be difficult to observe.

The first option is the most common, however the degradation of plastics under extreme conditions could be different from the one observed in mild environmental conditions. Instead, the second option is challenging but it is more environmental relevant. In this project, we chose the use of a simulation chamber (ISAC) in order to accumulate VOCs emitted by nanoplastic degradation. Moreover, we carried out experiments in the chamber on the emitted VOCs to evaluate their reactivity. Indeed the chamber is equipped with an irradiation system (UV and visible), a system to inject and control the concentration of ozone and relative humidity. Together with the advanced analytical equipment connected to the chamber these systems can allow the study of gas phase processes that could take place in the atmosphere.

Method and experimental set-up

We studied the degradation of two polymers: polystyrene (PS) and poly(styrene-co-methyl methacrylate) (PSMMA); the structures of these polymers are reported in Figure 1. Both were synthetized in the laboratory (University of Turin) and have been characterized to define the particle size.[18, 19] We investigated PS and PSMMA spheres of 200nm and 400nm of diameter, respectively.

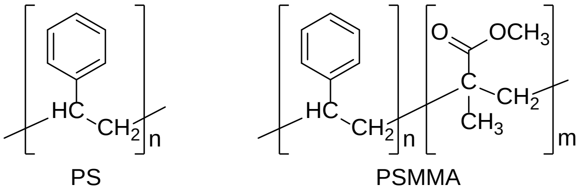

Figure 1. Chemical structure of polystyrene (PS) and poly(styrene-co-methyl methacrylate) (PSMMA) polymers.

We had access to the ISAC facilities for 10 days, therefore we decided to study the degradation of these polymers in a small reactor to understand their behavior to degradation and then we chose the best conditions to carry out the experiments in the simulation chamber.

Nanoplastics (PS and PSMMA) were dispersed in 10 mL of milli-Q water (particle concentration = 5x10^9 #/mL) and exposed to:

1) light
2) 100 ppb of ozone (in gas phase)
3) hydroxyl radicals (in liquid phase), generated by H_2O_2 (1mM) photolysis

These experiments were performed using a 82 cm^3 quartz reactor with a gas inlet near to the top. The reactor was irradiated by a xenon lamp (150 W Xe, LOT-QuantumDesign, France) from the top to maximize the irradiation surface. A gas flow at a flow rate of 100 sccm (standard cubic centimeter per minute) was continuously introduced into the reactor, with 80 sccm of the outgoing gas flow sampled for analysis by a proton transfer reaction ion-time of flight-mass spectrometer (8000 PTR-ToF-MS, Ionicon Analytik GmbH, Innsbruck, Austria). The experiments were performed under purified compressed dry air and the residence time in the cell was 48 s.

In order to accumulate the VOCs emitted by NPs degradation in the simulation chamber, we generated VOCs from PSMMA dispersed in water under irradiation in two cylindrical quartz cells in parallel and we injected in continuous the output flow (total flow = 1600 sccm) inside the simulation chamber. After 16h, we connected the PTR-ToF-MS to the simulation chamber to measure the VOC's concentration and we injected ozone to study the reactivity of the emitted VOCs. The experiments in the chamber were carried out at RH = 55±10 % and 25±3 ˚C. An ozone monitor, a CPC (condensation particle counter), an RH and T sensor and the PTR-ToF-MS were connected to the chamber. During the chamber experiments, the irradiation system was switched on (both UV and visible light) to evaluate the effect of light on VOCs reactivity.

Data description

To measure the VOCs produced by the degradation of NPs, plastic particles were dispersed in water, introduced in a quartz reactor and exposed to the oxidants or light under a flow of dry air. A PTR-ToF-MS was connected to the output of the reactor and was used to identify the emitted products.

For PS particles dispersed in water and exposed to O_3, we observed the formation of small organic compounds deriving from the oxidative cleavage of alkyl chain of the PS, such as butanal. We also observed, in these conditions, the degradation of benzaldehyde, benzene and styrene emitted by the NPs. The degradation of PS by hydroxyl radical, generated by H_2O_2 photolysis, led to formation of small carboxylic acids, in particular to acetic acid. The emission of aromatic compounds was not observed probably because the oxidation process took place in bulk and the oxidized compounds remains in aqueous phase due to their low volatility. However, only traces of acetophenone were observed under UV-vis irradiation of PS dispersed in water, probably due to the slow kinetic of photodegradation and the low residence time in the cell.

Many compounds observed during PS degradation were also emitted by oxidation of PSMMA particles. For PSMMA under ozone exposure, the formation of butanal, propionic acid and acetic acid (or methyl formate) was observed. Only the emission of formic acid was detected in presence of hydroxyl radical, instead the formation of benzaldehyde and butanal was observed under irradiation of PSMMA in pure water. The benzaldehyde is photoreactive, therefore we decided to concentrate the emission products formed by PSMMA irradiation in the simulation chamber and carry out experiments on the produces VOCs.

The chamber experiment showed the emission of benzaldehyde and butanal (compounds also detected in the small reactor) by PSMMA photodegradation, but once emitted, these compounds can be degraded by O_3 and light with a different degradation rate in the two conditions. In addition to the compounds observed in the reactor, acetic acid, formaldehyde were emitted in small amount under irradiation in the chamber. Besides these emissions, some compounds like propanoic acid, methanol, styrene detected in the chamber showed a faster decrease under UV irradiation due to their oxidation.

Preliminary results and conclusions

The use of the chamber allowed us to detect VOCs that were not observed in the small reactor. As we expected we detected the compounds at m/z 107 and m/z 73, tentatively identified as benzaldehyde and butanal, respectively. These compounds, observed also in the reactor, react with ozone and light; indeed, Figure 2 shows a decrease due to the oxidation of the compounds while the ozone was in the chamber.

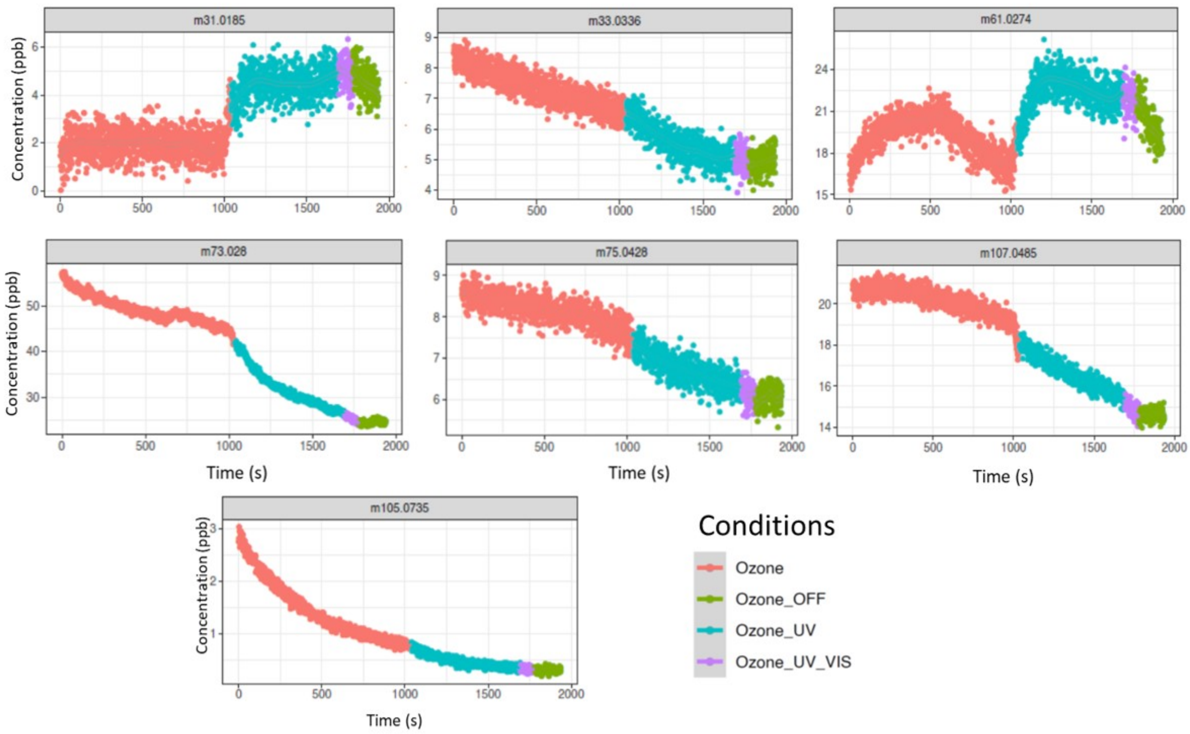

Figure 2. Time traces of main VOCs emitted by PSMMA photodegradation measured in the chamber under different conditions.

Furthermore, results reported a faster concentration decrease in the ozone/UV condition. We also observed the presence of other compounds, tentatively identified as: formaldehyde (31 m/z) methanol 33(m/z), acetic acid (61 m/z) and styrene (105 m/z). For the 75 m/z any identification was possible but we suggest that it could be a product of the PSMMA exposure to the ozone. Figure 2 shows an increase of formaldehyde and acetic acid under irradiation, instead the other compounds are degraded under ozone and ozone/UV conditions.

In order to differentiate the VOC profiles between each condition we performed the Principal Component Analysis (PCA, package FactormineR, Ade4 Version 1.0.153–©2009-2017 R Studio). The PCA performed described the 40% of the total dataset variability (30,6% for the first dimension and 9 % for the second one). The PCA was specifically used to identify the VOCs that differentiate between each condition. Results from Figure 3 shows that every condition has a very differentiated VOC profile. In fact, the ellipses grouping the different conditions are clearly separated except for a negligible overlap between the Ozone/UV and the Ozone/UV/VIS conditions. It is noticeable also that 23 of the 25 compounds explaining the variance between the different conditions are driven by the Ozone condition. This means that the Ozone condition has the most different VOC profile. Finally, PCA allowed to draw the conclusion that VOC emission profiles depend on the condition into the chamber and that, as expected, Ozone/UV and Ozone/UV/VIS affects the VOC emissions in a different way than Ozone condition does. These data show that the emitted VOCs from nanoplastic degradation in surface waters are reactive under atmospheric conditions. The observed different VOC emission profiles highlight that some of these VOCs can reacts with ozone and/or light leading to a the formation of d compounds in the atmosphere.

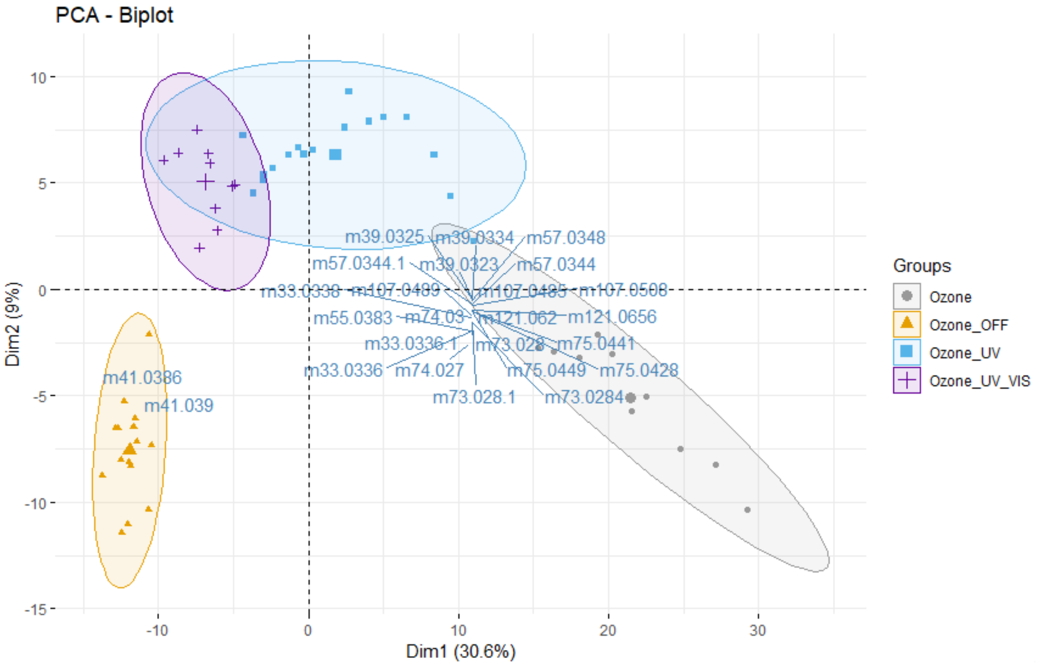

Figure 3. Effect of the different condition in the chamber on the VOCs emissions. The m/z of the 25 compounds that are most explaining the variance in the two first components are shown on the graph. The percentage of the eigenvalues of the two first components are shown on each axes.

Outcome and future studies

Micro- and nanoplastic are present in surface waters and their degradation can release small compounds in gas and aqueous phase. In this project, we evaluated the emission of volatile organic compounds from the degradation of polystyrene and polystyrene co-polymer nanoplastics in water. We studied the degradation of these nanoplastics under exposure to ozone, light and hydroxyl radicals and observed the formation of some small oxidized organic compounds. We filled the simulation chamber with the emitted VOCs to highlight the formation of degradation products from nanoplastics and to evaluate their reactivity under atmospheric conditions. The use of the simulation chamber, allowed us to detect a larger number of VOCs, not observed from nanoplastic degradation in the small reactor. Moreover, we observed that some of the emitted products can further react with ozone and light leading to the formation of small oxygenated organic compounds such as formaldehyde and acetic acid. This is the first time that the emission of nanoplastics dispersed in water have been evaluated and the reactivity of the emitted VOCs tested under atmospheric conditions. These data could be used to evaluate the potential impact of nanoplastics degradation in surface water. In order to quantitatively estimate the possible contribution of VOCs, emitted from plastics above the surface waters, further studied are needed to measure, under different conditions, the emission rate of VOCs identified in this work. Moreover, other experiments could be carried out in presence of salts and humic substances that are naturally present in surface waters, to evaluate their interaction with nanoplastic under irradiation.

References

1. PlasticsEurope, *Plastics – the Facts*, **2018**.
2. A. Cozar et al., *Proc. Natl. Acad. Sci. U. S. A.*, **2014**, 111, 10239-10244.
3. H. S. Auta et al., *Environ. Int.*, **2017**, 102, 165-176.
4. R. W. Obbard et al., *Earths Future*, **2014**, 2, 315-320.
5. J. Gigault et al., *Environ. Pollut.*, **2018**, 235, 1030-1034.
6. J. P. da Costa et al., *Sci. Total Environ.*, **2016**, 566, 15-26.
7. M. A. Browne et al., *Integr. Environ. Assess. Manag.*, **2007**, 3, 559-561.
8. A. L. Dawson et al., *Nat. Commun.*, **2018**, 9.
9. O. S. Alimi et al., *Environ. Sci. Technol.*, **2017**, DOI: 10.1021/acs.est.7b05559.
10. A. Ter Halle et al., *Environ. Sci. Technol.*, **2017**, 51, 13689-13697.
11. J. R. Jambeck et al., *Science*, **2015**, 347, 768-771.
12. K. Mattsson et al., *Environ. Sci. Process. Impacts*, **2015**, 17, 1712-1721.
13. B. Gewert et al., *Environ. Sci. Process. Impacts*, **2015**, 17, 1513-1521.
14. S. Lambert et al., *Sci. Total Environ.*, **2013**, 447, 225-234.
15. T. O'Brine et al., *Mar. Pollut. Bull.*, **2010**, 60, 2279-2283.
16. S. Lambert et al., in *Reviews of Environmental Contamination and Toxicology*, ed. D. M. Whitacre, Springer International Publishing, Cham, **2014**, vol. 227, pp. 1-53.
17. K. L. Law et al., *Science*, **2014**, 345, 144-145.
18. F. Sordello et al., *Chem. Comm.*, **2011**, 47, 6147-6149.
19. F. Sordello et al., *J. Mater. Chem.*, **2011**, 21, 19144-19152.