



Degradation of nanoplastics in aquatic environments: reactivity and impact on dissolved organic carbon

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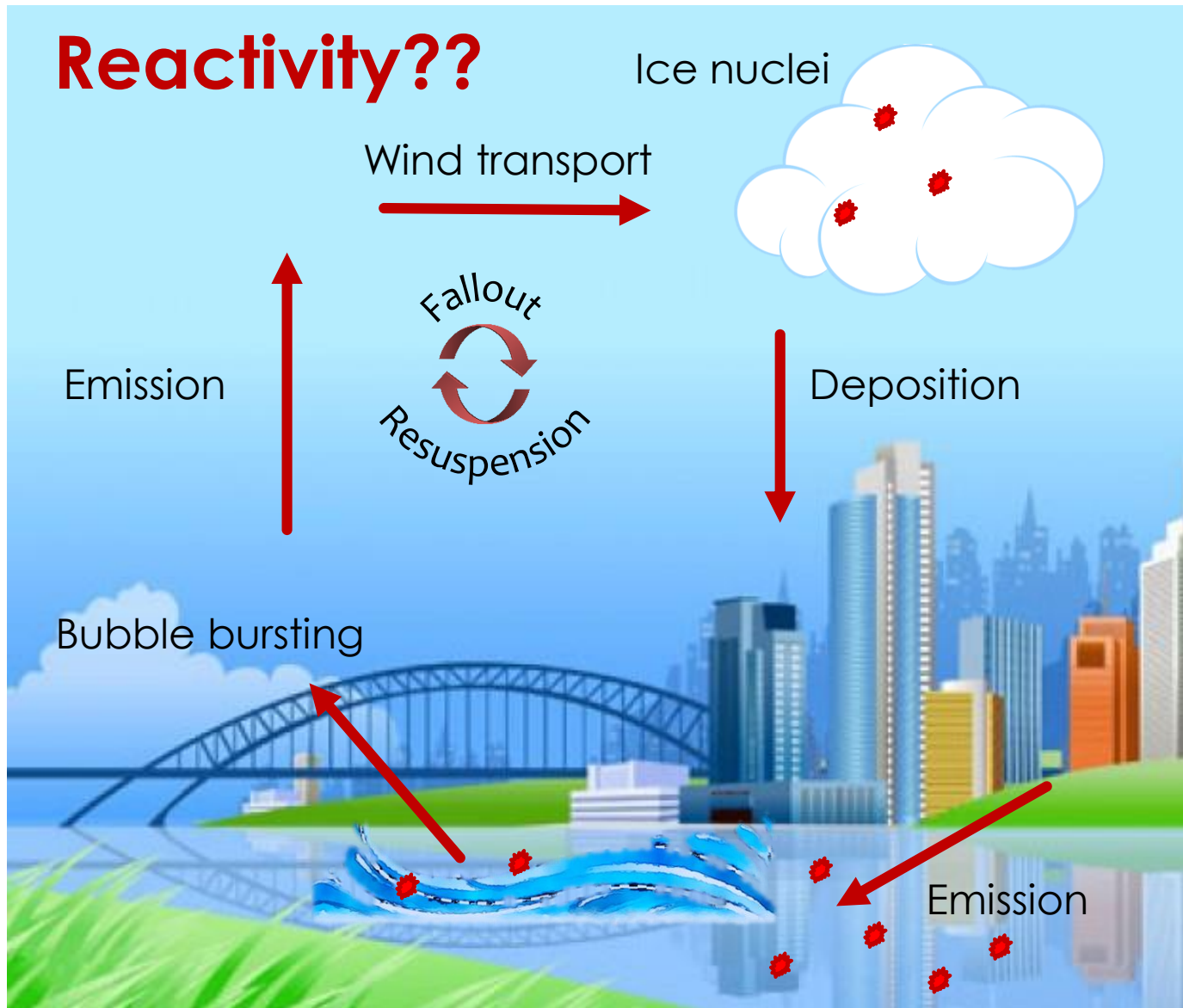


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Sources of micro- and nanoplastics

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Microplastics (MPs) and nanoplastics (NPs) are ubiquitous and contaminate soil, surface waters, atmospheric aerosol, precipitations, indoor and outdoor environments. However, **the occurrence, transformation and fate of NPs in the environment are still unclear**. In this work, polystyrene nanoparticles (PS-NPs) are used as a proxy of NPs to study their **reactivity and potential impact on atmospheric and surface waters**. In particular, the reactivity with **hydroxyl radicals ($\cdot\text{OH}$)** in aqueous phase is investigated.

Small plastic particles have been observed worldwide



Surface of oceans



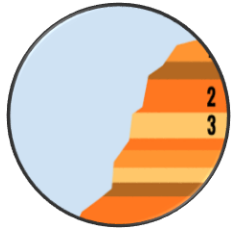
Arctic sea ice



Water columns



Deep sea



Sediments

Indoor & outdoor air
in polluted cities like Paris,
Dongguan...



... and more recently (2019)



RESEARCH ARTICLE | ATMOSPHERIC SCIENCE

White and wonderful? Microplastics prevail in snow from the Alps to the Arctic

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ARTICLES

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Atmospheric transport and deposition of microplastics in a remote mountain catchment

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Pristine mountain catchment
(French Pyrenees)

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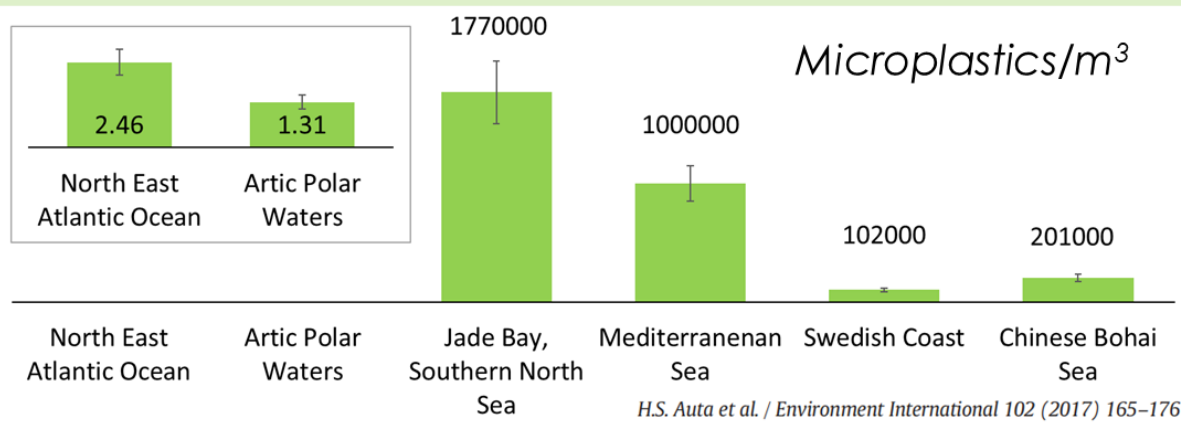


How many microplastics?

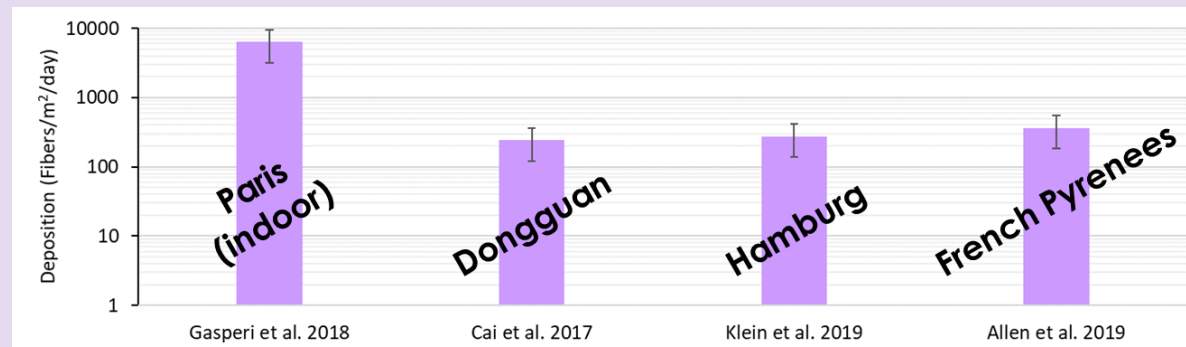
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Surface of oceans



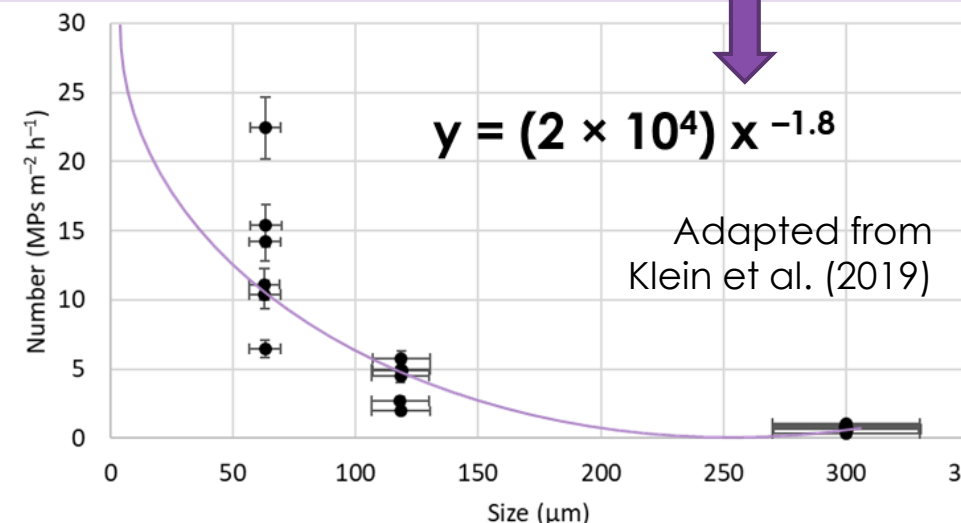
Indoor & outdoor air



How many nanoplastics?

The occurrence of NPs in the environment is almost unknown, mainly due to sampling and instrumental limitations.

The concentration (in number) of NPs may be higher than MPs for both surface waters and atmosphere, as suggested by the extrapolation from the data of Klein et al. (2019).



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What do we know about degradation?

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When a plastic piece degrades down to parts with sizes in the nanometre scale, **the exposed area increases drastically and so does the surface reactivity**. However, the dependence of plastics degradation kinetics upon their particle size is almost unknown.



**Impact on
REACTIVITY**

The main abiotic degradation process of plastics is **photo-initiated oxidation**, which leads to polymer chain scission, branching and formation of polymer fragments as well as of volatile compounds. **Photochemistry plays a key role in these transformation processes, directly (direct photodegradation) or indirectly (indirect photolysis, through the photogeneration of reactive transient species such as the hydroxyl radical, $\cdot\text{OH}$)**. MPs and NPs in the atmosphere and in surface waters are exposed to sunlight and $\cdot\text{OH}$. Bubble bursting and wind action can suspend MPs and NPs in air, where they could be present as dry or deliquescent (in-droplet) particles. In atmospheric waters, like cloud and fog droplets, MPs and NPs are even more exposed to gas and aqueous phase oxidants.

Reactivity with hydroxyl radicals

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Most plastics degrade first at the polymer surface, which is exposed and available for chemical or enzymatic attack.

Smaller the size - faster the degradation (due to the surface to volume ratio).

Degradation rate:

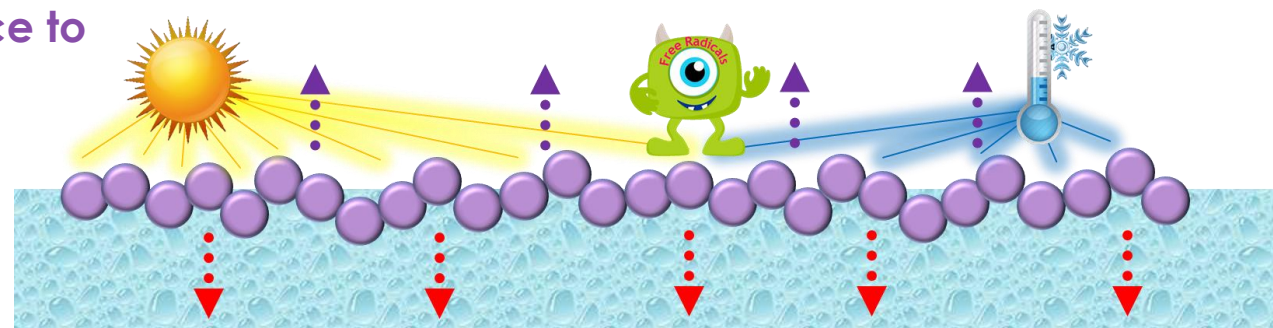
Nano > Micro > Meso > Macro

Surface cracking makes the inside of the plastic material available for further degradation.

Hydroxyl radical ($\cdot\text{OH}$) is the main oxidant in the aqueous phase

PS-NPs (polystyrene nanoplastics) react with $\cdot\text{OH}$, but **no information on the reactivity rate constants is reported** in previous works. Reactivity constants are essential for modelling studies, with the aim of assessing PS-NPs degradation in different environmental scenarios as well as their ability to scavenge $\cdot\text{OH}$ and to affect the photo-oxidation cycles in natural waters.

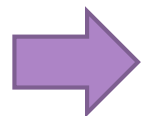
For the first time, the rate constant of PS-NPs with $\cdot\text{OH}$ is determined with the competition method.



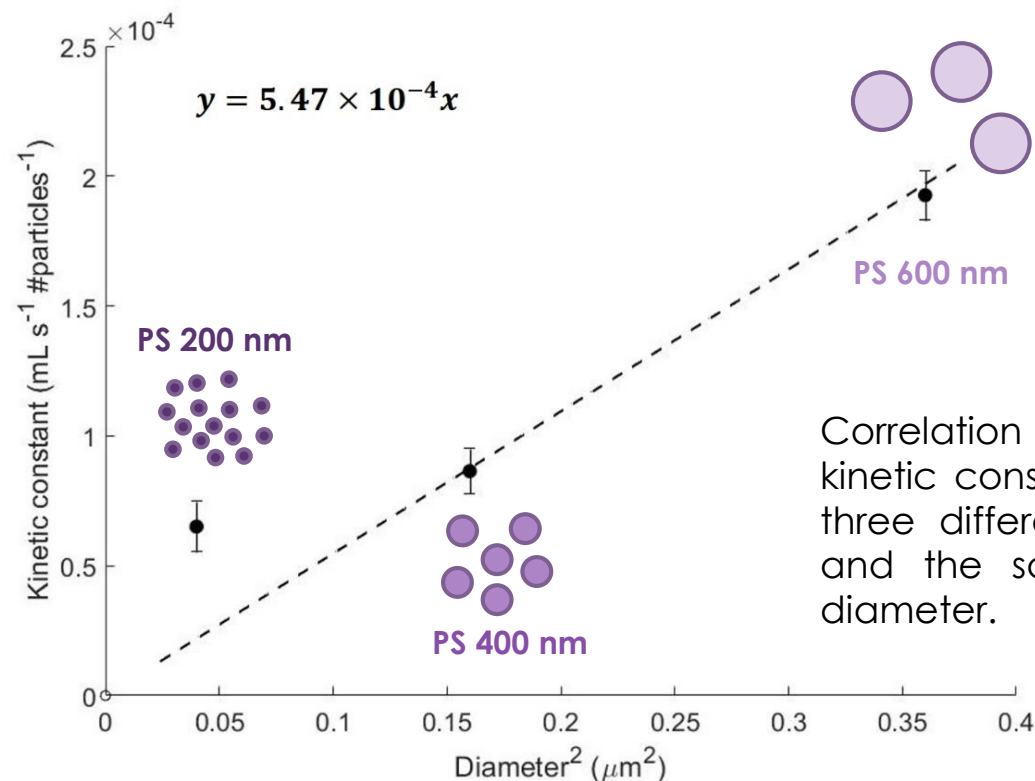
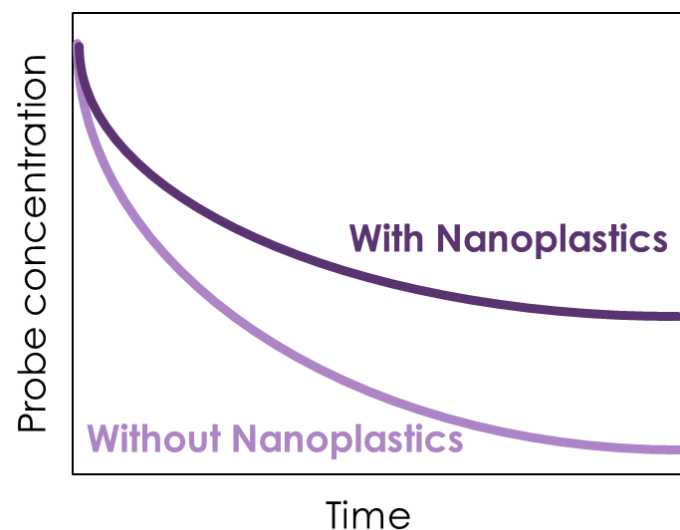
Reactivity with hydroxyl radicals

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Probe: Benzoic acid



Nanoplastics consume (scavenge) hydroxyl radicals



To get insight into the environmental significance of the present findings **we have compared the potential effect of PS-NPs and Dissolved Organic Matter (DOM) as $\cdot\text{OH}$ scavengers**. The DOM is, indeed, the main scavenger of $\cdot\text{OH}$ radicals occurring in freshwater and cloud-water.

Reactivity with hydroxyl radicals

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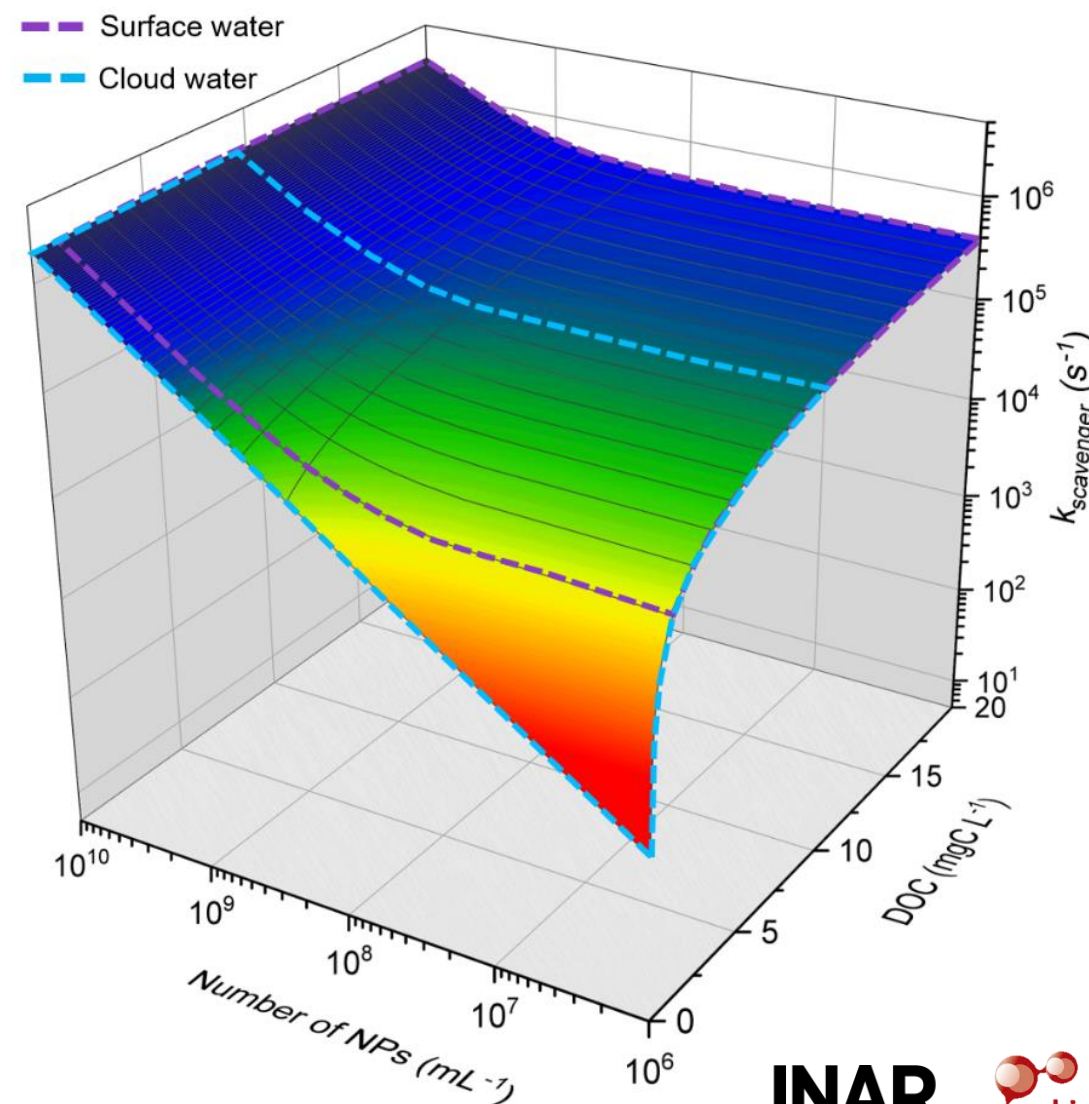
There is potential for NPs to **significantly scavenge** $\cdot\text{OH}$, if the content of natural organic matter is not too high.

Estimated rate constants ($k_{\text{scavenger}}$) for the scavenging of $\cdot\text{OH}$ by PS-NPs and DOM expressed in DOC (dissolved organic carbon).

Representative concentrations of DOC for **surface waters** (higher than 1 mgC/L) and **cloud water** (0-10 mgC/L) are marked in purple and light blue, respectively.

Additional data are needed on:

- the $\cdot\text{OH}$ reactivity of other plastic types (e.g., polyethylene and polypropylene)
- the correlation between size of particles and reactivity
- on the concentration of NPs in a wide variety of aquatic environments.



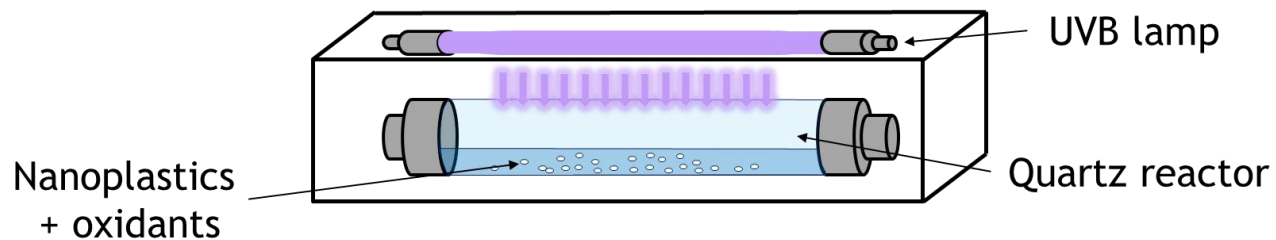
Identification of degradation products

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Little is known about the impact of degraded plastics on the environment, in particular concerning the **release of organic compounds**. We investigated how plastic degradation by $\cdot\text{OH}$ affects dissolved organic matter (DOM) chemical composition.

Suspensions of PS-NPs were exposed to **4 experimental conditions**. This set-up allowed for estimating the impact of:

- (1) direct photodegradation + photogenerated $\cdot\text{OH}$ (indirect photolysis)
- (2) direct photodegradation alone
- (3) reactivity with H_2O_2 in dark conditions
- (4) possible hydrolysis/degradation in dark conditions.



4 Experimental conditions

Light + H_2O_2

H_2O_2

Light

No Light + No H_2O_2

t0

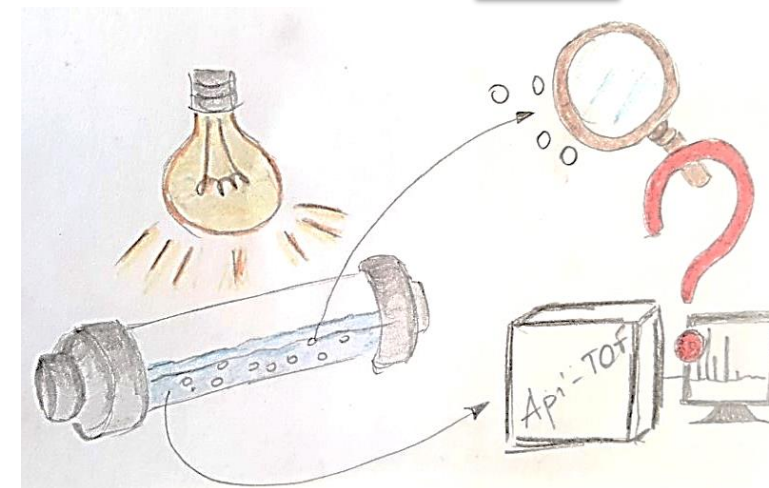
t1 Day

t2 Days

t3 Days

t4 Days

ESI – DMA –
API-TOF (6)
Negative ionization



Identification of degradation products

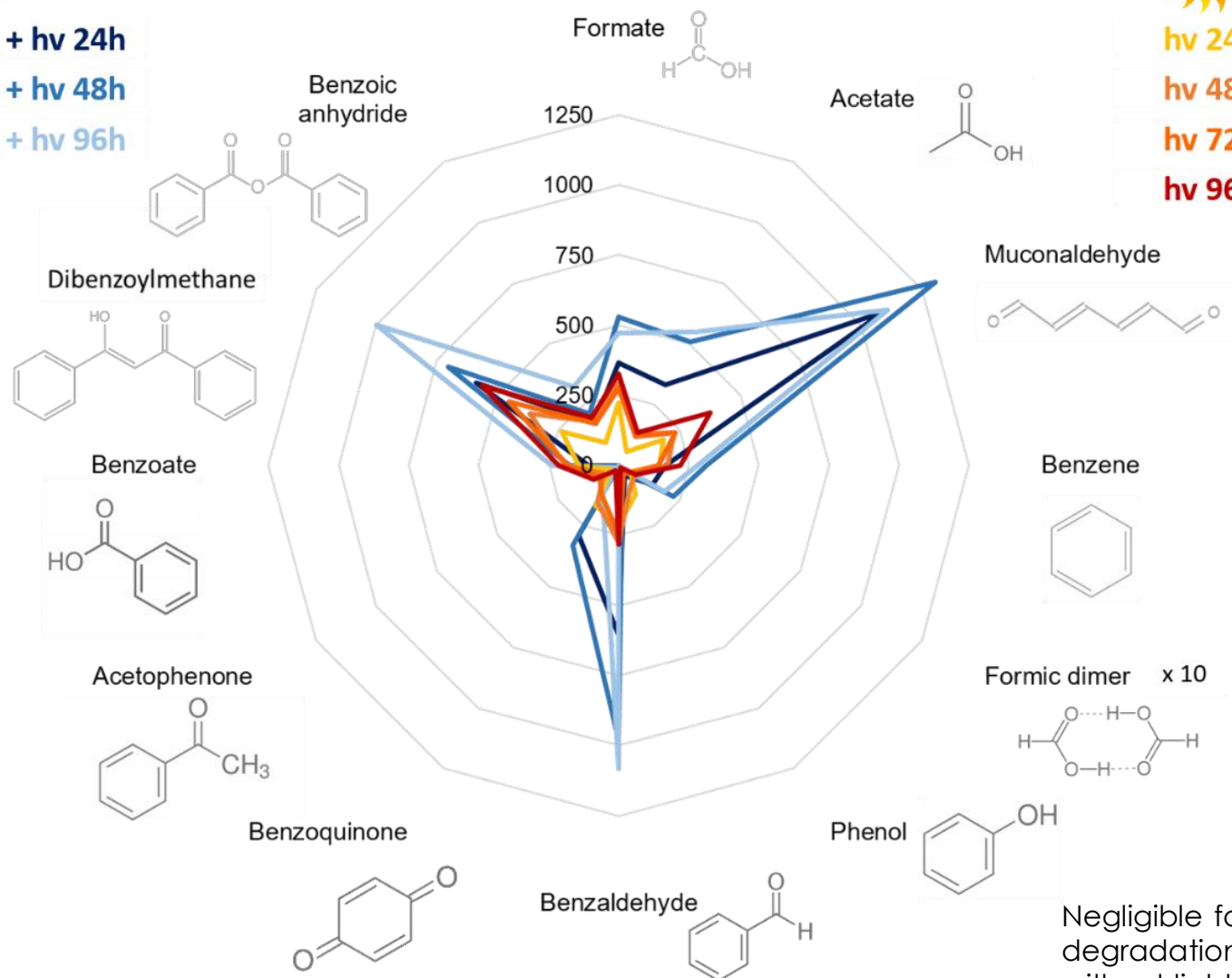
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$\text{H}_2\text{O}_2 + \text{h}\nu$ 24h

$\text{H}_2\text{O}_2 + \text{h}\nu$ 48h

$\text{H}_2\text{O}_2 + \text{h}\nu$ 96h



$\text{h}\nu$ 24h

$\text{h}\nu$ 48h

$\text{h}\nu$ 72h

$\text{h}\nu$ 96h

Signal increase (%) of degradation products over time under: **direct photolysis + hydroxyl radical mediated oxidation ($\text{H}_2\text{O}_2 + \text{h}\nu$)** and **direct photolysis ($\text{h}\nu$)**

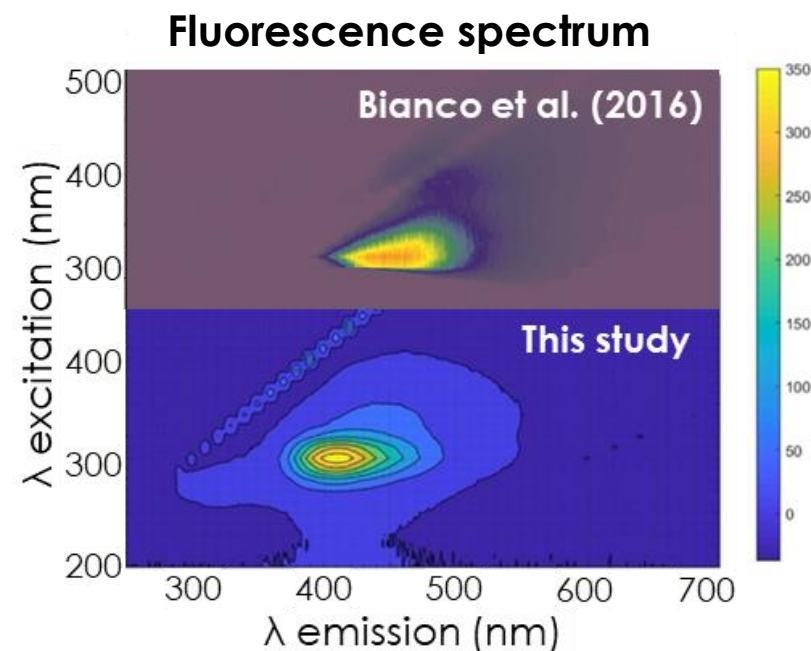
During the first 24h of irradiation, **the concentration of acetic and formic acids increases rapidly**, up to 9.1 and 3.0 mgC/L, respectively. The formation of these degradation products contributes to the dissolved organic carbon (DOC). **PS-NPs degradation could potentially impact the composition of the aqueous phase in both atmospheric and surface waters.**

Negligible formation of degradation products without light exposure

Degradation in real environmental conditions





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Laboratory irradiations give a first rapid estimate of the degradation of PS-NPs in the aqueous phase. However, **long irradiations in closer environmental conditions are more suitable to investigate the release of organic compounds during PS-NPs degradation**. A suspension of PS-NPs was exposed to sunlight for 14 months.



Mass spectra reveals the presence of **many unidentified compounds**, with a spectrum shape similar to those obtained for riverine and cloud dissolved organic matter. This similarity is probably due to the presence of a **large variety of organic compounds, with hydroxyl, carboxylic and carbonyl functions**, which might be similar to the composition of natural dissolved organic matter. This hypothesis is supported by the **Fluorescence spectrum** of the liquid phase. The presence of an emission signal around 410 nm induced by excitation around 300 nm recalls one of the **characteristic peaks of humic substances**, which is routinely observed in surface waters. A similar peak was also observed for HULIS in the atmosphere and it could be due to highly oxygenated small compounds that could derive from several oxidation steps during many months of sunlight exposure. **The production of light-absorbing species could interfere with the natural photochemical equilibrium in environmental waters.**

Micro and Nanoplastics

-  Nanoplastics reactivity with $\bullet\text{OH}$ is size-dependent: smaller particles show higher reactivity.
-  Reactivity constants of polystyrene nanoparticles degradation with $\bullet\text{OH}$ are calculated.
-  Degradation of nanoplastics release in the aqueous phase organic compounds.
-  There is potential for NPs to significantly scavenge $\bullet\text{OH}$ in the environment.

Thank you!