

# Synergistic effects of marine pollutants and microplastics on the destabilization of lipid bilayers

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## Abstract

The increasing production of plastic worldwide results in increasing amounts of plastic waste dumped into the oceans. Plastic waste is fragmenting into smaller pieces up to micro and nanoplastics, which may cross physiological barriers and affect the functions of living organisms. Microplastics can travel with rain and clouds; they are present in soil, snow-capped mountains, and even in the organs and blood of human beings. The potential health implications of microplastics in living organisms raise concerns and are intensively investigated. Recently, we reported the effect of mechanical stretching of microplastics on a lipid bilayer. By combining experimental and theoretical approaches, we have shown that microplastic particles adsorbed on lipid membranes increase membrane stress even at low particle concentrations. In this manuscript, we demonstrate the synergetic effect of marine pollutants on the mechanical interaction

induced by microplastics. For this purpose, bare microplastics are incubated in seawater containing marine pollutants. We show that pollutants, such as chemical solvents, significantly increase the mechanical stretching induced by microplastics. In turn, microplastics can be viewed as vectors for solvent molecules, facilitating their penetration into the core of lipid membranes and thus strongly affecting their biophysical properties.

## Introduction

Marine pollution is a threat to human health and marine life. Every year, enormous quantities of plastic accumulate in the oceans.<sup>1-3</sup> and plastic became one of the first sources of ocean pollution from human industrial production.<sup>4,5</sup> As soon as they reach the ocean, plastic decomposes in smaller pieces when exposed to ultraviolet light and finally become microplastics.<sup>6</sup> Microplastics are tiny plastic particles, with an average size distribution between  $\approx 0.1\mu\text{m}$  and 5 mm.<sup>7,8</sup> Microplastics may be carried into the atmosphere through evaporation due to their small size and physical characteristics,<sup>9,10</sup> where they are spread out evenly everywhere when it rains or snows.<sup>11,12</sup> As a consequence, microplastics have been detected in human blood and organs. Therefore, these pollutants present a significant risk to human health that is not yet fully understood.<sup>13-17</sup> Microplastic particles are rarely directly responsible for the death of living organisms.<sup>18</sup> However, they may have an impact on cellular and subcellular levels.<sup>19,20</sup> For instance, they trigger oxidative stress, membrane damage, an immunological response, or tissue inflammation that results in cellular toxicity.<sup>21,22</sup> Such effects are, in general, mediated by biological or chemical pathways.<sup>21,22</sup> However, the presence of microplastics may also cause significant cell membrane instability through purely physical means.<sup>23</sup> For example, mechanical stretching applied by the microplastics on the cell membrane can destabilize the membranes.<sup>23-25</sup>

Apart from microplastics, there are a myriad of chemical components that can interact with microplastics in the environment and sea water.<sup>26</sup> In the following, we briefly present

four important pollutant families that can be found in the oceans. These four families of contaminants are: endocrine disrupting chemicals (EDCs), heavy metals, persistent organic pollutants, and commercial sunscreen (POPs). Mercury and other heavy metals can reach the ocean, mainly as a result of industrial activity, air deposition, and rock erosion.<sup>27-29</sup> Complex chemical mixtures in the ocean include many endocrine disrupting chemicals (EDCs).<sup>30-32</sup> A common type of EDC is a pesticide, and one of the most historically used was dichlorodiphenyltrichloroethane (DDT).<sup>33-36</sup> For this reason, DDT is one of the pesticides most present in the oceans.<sup>33-36</sup> A third family of common marine pollutants are persistent organic pollutants (POPs), which are toxic carbon-based compounds that have contaminated the oceans and marine ecosystems.<sup>37,38</sup> Examples of POPs are perfluoroalkyles, perfluorosurfactant, aliphatic hydrocarbon, aromatic hydrocarbon.<sup>37</sup> We are considering plain commercial sunscreen as the last category of common chemical pollutant.<sup>39-41</sup>

In the following, we look into how chemical pollution affects the physical interactions between lipid membranes and microplastics. We concentrate our discussion on the forms of microplastics that are primarily found in the oceans because unique interactions between microplastics and cells depend on their size and chemical composition.<sup>42</sup> The average microplastic size distribution is estimated at  $\approx 0.1\mu\text{m}$  to  $\approx 5\text{ mm}$ .<sup>7,8</sup> As a result, we only used spherical microplastics with a diameter of  $\approx 1\mu\text{m}$ . Since real microplastics can have extremely complicated geometrical shapes, we restrict our investigation to the situation of spherical objects for simplicity.<sup>7,8</sup> The most widely used microplastics are made of acrylics, polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyamide (PA).<sup>8,43</sup> In this study, we focus on microplastics made of PE, PS, or PA as a material.

## Results and Discussion

The microplastics were first washed with ethanol to eliminate any surfactant residue that might have been utilized to stabilize microplastics in solution (see Methods section). Then,

we incubate 0.1 mg/mL microplastics in 2 mL of sea water containing one type of pollutant in a glass falcon and place it on a shelf to incubate for a month without light. After this step, microplastics were extracted by centrifuging. They were washed several times with pure water and, finally, dispersed in a phosphate-buffered saline (PBS) solution to achieve a final concentration of 0.5 mg/mL. This model process of microplastics treatment mimics the microplastics destiny in the environment: they are floating in the ocean and fragmenting until they evaporate into the atmosphere and are inhaled or absorbed by living beings and make contact with cell membranes. The following pollutants were utilized during incubation: 0.639 ppm/L for mercury, 0.526 mg/L for toluene, 25  $\mu\text{g/L}$  for DDT, 1.3 g/mL for perfluorooctanol and 1-octanol, 0.014% of volume for hexane, 1.1 g/mL of Zonyl, and 1 mg/mL of a mixture from numerous commercial sunscreens. Except for sunscreen and perfluorooctanol, these values correspond to their maximum solubility in pure water, although we can assume their solubility is probably slightly less in sea water. In summary, we studied one heavy metal (mercury), four POPs (hexane, toluene, 1-octanol, perfluorooctanol, zonyl), one EDC (DDT), and several sunscreens. Using the water pendant droplet method, these microplastics were used to measure the surface tension  $\gamma$  of the phospholipid monolayer at the water/squalene oil interface (see Methods section).<sup>44</sup> We kept the concentration of microplastics  $c \approx 50 \mu\text{g/ml}$  constant throughout these measurements (see Fig.1). The PBS values correspond to the control surface tension  $\gamma$  values ( $\gamma \approx 2 \text{ mN/m}$ ). At this condition, the microplastics were incubated in filtrated sea water from the Mediterranean Sea without any pollutants before being washed out and dispersed in PBS. These values do not appear to be impacted by the presence of mercury. DDT and sunscreen induced a slight increase in the measured surface tension values ( $\gamma \approx 2 - 2.3 \text{ mN/m}$ ). However, a significant increase is measured for zonyl, hexane, toluene, 1-octanol, and perfluorooctanol ( $\gamma \approx 3 \text{ mN/m}$ ). These measurements indicate that POPs may modify the surface properties of microplastics and that pollutants are absorbed on the microplastic surface.

Based on these surface tension data, we can now calculate the bilayer tension in the

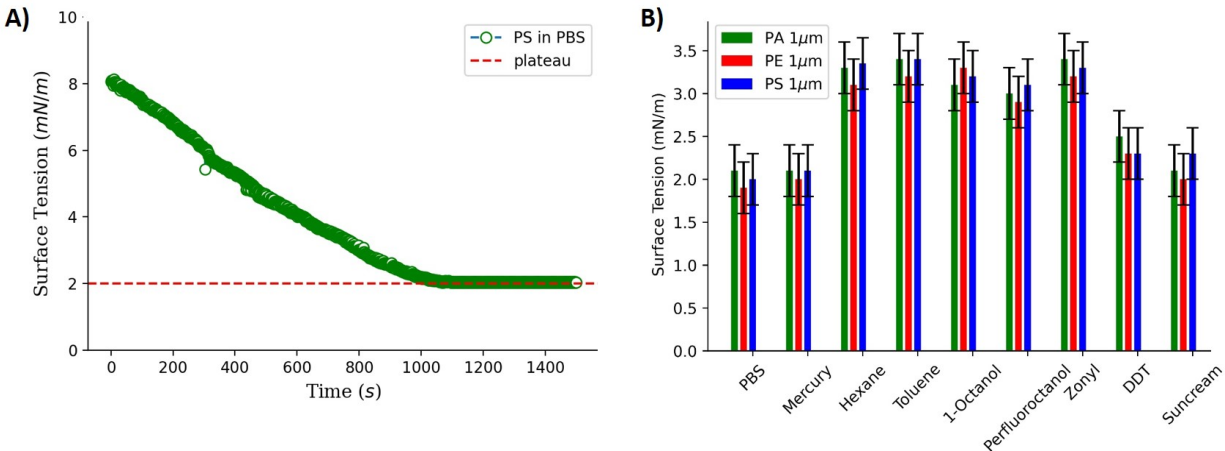


Figure 1: A) One example of surface tension measurement from the water pendant method. The dashed line indicates the surface tension plateau, which is the measured value. The pendant droplet consists of a PBS buffer and its shape is analyzed as a function of time (s). The buffer droplet was produced in an oily phase (squalene), which contains phospholipids. For this measurement, PE beads were dispersed in the buffer droplet at a concentration of 50  $\mu$ g/mL. B) Surface tension measurements using the water pendant droplet method (see method section) and a fixed microplastics concentration of approximately  $c \approx 50 \mu\text{g/ml}$  are plotted after incubation in sea water with different marine pollutants.

presence of microplastics incubated with various marine pollutants. For this purpose, we employ the Droplet Interface Bilayer (DiB) technique to produce free-standing lipid bilayers.<sup>46</sup> In this technique, two water droplets of comparable size are formed in an oily phase that contains phospholipid (see Methods section). Each water-oil interface is decorated by a lipid monolayer, and a bilayer is formed when these two droplets come into contact. Under a microscope, a visual optical confirmation of the bilayer formation may be seen, and the Young-Dupr e law can be utilized to determine the associated bilayer tension  $\Gamma$ :<sup>44</sup>

$$\Gamma = 2\gamma.\cos(2\theta), \tag{1}$$

where  $2\theta$  is the contact angle measured from the DiB method (see Fig. 2 and Ref 46). One benefit of the DiB approach is that it enables the high-throughput creation of bilayers and avoids issues with sedimentation or buoyancy (the bilayer is vertical).<sup>23</sup> Table 1 and Table-3 list the measured tensions for various types of microplastics and concentrations.

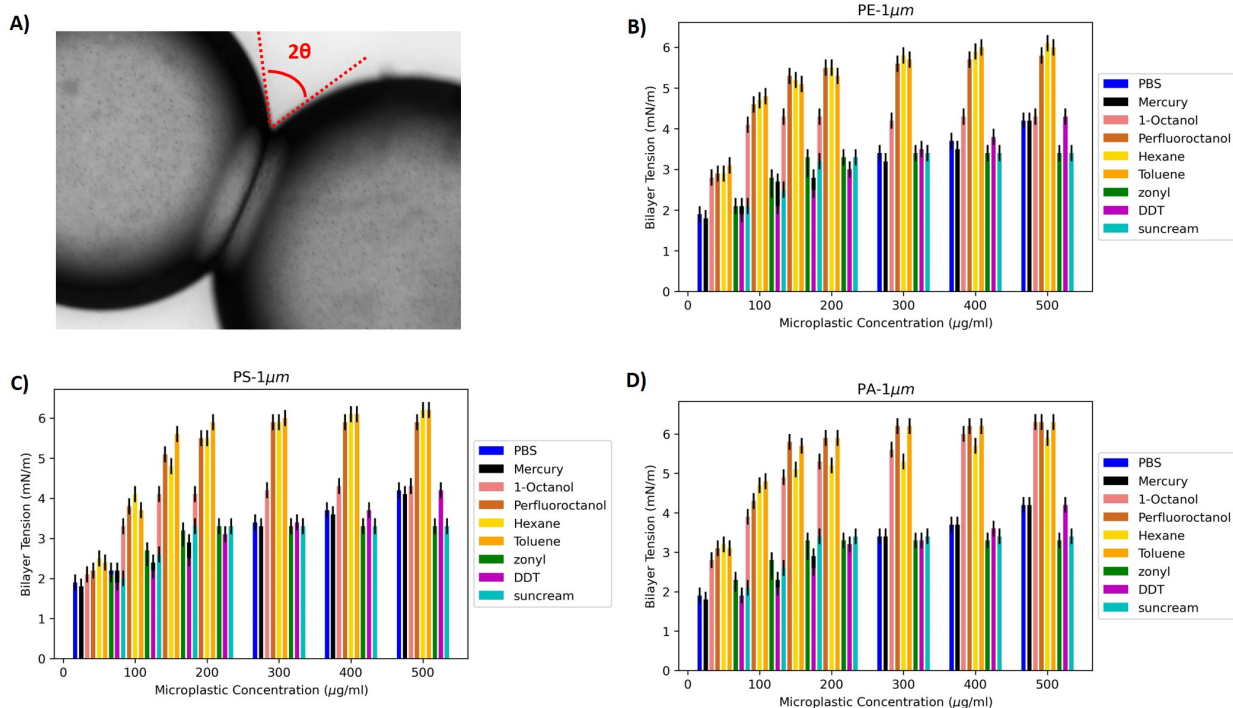


Figure 2: A) A microscopic picture of a bilayer formed by the DiB method. The two buffer droplets are made of PBS and contain  $100 \mu\text{m}/\text{mL}$  PE beads. B) present bilayer tension measurements obtained from the Young-Dupr e equation , as a function of different  $1 \mu\text{m}$  PE microplastics concentration after incubation in seawater with different marine pollutants. The reported bilayer tension values are obtained from an average of  $\approx 20$ -30 measurements. B) and C) are the same measurements as reported for A), except that they correspond to PS and PA microplastics, respectively.

The bilayer tension increased with the concentration of microplastics. PS microplastics incubated in pure sea water and re-dispersed in PBS show an increase in bilayer tension  $\Gamma$  from  $\approx 2 \text{ mN}/\text{m}$  for  $c \approx 50 \mu \text{ g}/\text{ml}$  to  $\Gamma \approx 4 \text{ mN}/\text{m}$  for  $c \approx 500 \mu \text{ g}/\text{ml}$ . This behavior is similar for PS, PA, and PE microplastics that were incubated with mercury and DDT. PS microplastics incubated with sunscreen or Zonyl are showing a slightly increasing bilayer tension from  $\Gamma \approx 2 \text{ mN}/\text{m}$  for  $c \approx 50 \mu \text{ g}/\text{ml}$  to  $\Gamma \approx 3 - 4 \text{ mN}/\text{m}$  for  $c \approx 500 \mu \text{ g}/\text{ml}$  (see Fig. 2). This slight increase is also notable in the case of PE and PA microplastics. The most striking bilayer tension increase was measured for all the microplastics incubated with POPs (Hexane, Toluene, 1-Octanol and perfluorooctanol), where the bilayer tensions are increasing from  $\Gamma \approx 2 \text{ mN}/\text{m}$  for  $c \approx 50 \mu\text{g}/\text{ml}$  to  $\Gamma \approx 4 - 6 \text{ mN}/\text{m}$  for  $c \approx 500 \mu\text{g}/\text{ml}$ .

Similar behavior for PA and PS microplastics with the POPs pollutants is again showing the most striking increase in bilayer tension. Where PA and PE microplastics present values from  $\Gamma \approx 2$  mN/m for  $c \approx 50 \mu\text{ g/ml}$  to  $\Gamma \approx 4 - 6$  mN/m for  $c \approx 500 \mu\text{ g/ml}$  (see Fig. 2).

In order to investigate the nature of physical interaction between microplastics and a lipid bilayer, we produced a horizontal bilayer and dispersed fluorescent PS microplastics around it (see Fig. 3A). It appears that these microplastics diffuse continuously on the bilayer surface and do not become immobile after touching it. We track and analyze these microplastics' motions in order to determine their mean square displacement (MSD)  $\langle r^2 \rangle$  and the corresponding diffusion constant  $D = \frac{\langle r^2 \rangle}{4Dt}$ . The measured diffusion constant  $D \approx 0.6 \mu\text{m}^2 \cdot \text{s}^{-1}$  is close to the bulk diffusion value for a  $1 \mu\text{m}$  microplastic (see Fig. 3.B-C).<sup>23,47</sup> This characteristic motility and diffusion stay unchanged for all the considered microplastics in this article.

Fig. 3C shows the effect of microplastics incubated with hexane on the bilayer tension for different concentrations of microplastics. The curve is gradually increasing with the same law as in the absence of pollutants. This result suggests that the diffusion properties of the incubated microplastics are not quantitatively changed by the presence of hexane.<sup>23</sup> However, the incubation with hexane increases the bilayer tension, thus suggesting a stronger destabilization of the lipid bilayer in the presence of a pollutant and stronger mechanical deformation of the lipid bilayer.

To understand the effects of pollutants on the stretching of the lipid bilayer, we use the same elastic layer model of a lipid bilayer interacting with bare spherical microplastics described in Ref. 23. This model describes the mechanical stretching of the lipid bilayer due to the adsorption of microplastics and the resulting local deformation of the lipid bilayer around microplastics. A similar model was used to stretch cell membranes<sup>48</sup> with nanopillars and to mechanically deform bacteria cell membranes with gold nanoparticles.<sup>25</sup> Within this model, the area available per microplastic particle is split into two parts: the free-standing or "suspended" part A and the "adsorbed" part B. The balance of the stretching/compression of

the layers A and B and the attraction to the microplastics in the contact region A determines the equilibrium position of the layer. In the case of the adsorption of the particles onto the membrane, the free-standing region A is stretched to increase the contact of the membrane with the particle in the region B. Thus, the free energy of the membrane is the sum of two terms: the energy gain due to adsorption in the region B and the membrane stretching in the region A,<sup>48</sup>

$$F = \int_{A+B} \frac{k}{2} \alpha^2(r) \frac{n(r)}{n_0} d\sigma + \int_A \varepsilon n(r) d\sigma \quad (2)$$

where  $\varepsilon$  is the dimensionless interaction parameter between the surface of the particle and the membrane,  $k$  is the compressibility constant,  $\alpha = (S - S_0)/S_0$  is the dimensionless parameter describing local stretching,  $S$  is the actual area and  $S_0$  is the equilibrium unperturbed area before the contact with the particle.  $n(r) = n_0/(1 + \alpha(r))$  and  $n_0$  are the local density of adsorption points at the position  $r$  and in the unperturbed membrane, correspondingly. This free energy is then minimized with the constraint of the conservation of the total area.

As a result, the set of nonlinear equations for the areas in the regions A and B provides the stretching in both regions as a function of adsorption strength. Within this model, the mechanical stretching is controlled by the ratio

$$\zeta = \frac{\varepsilon n_0}{k} \quad (3)$$

where  $\varepsilon n_0$  is the attractive interaction energy per area. The estimates from experimental measurements of the adhesion energies of polystyrene microparticles are of the order  $1 \text{ mJ/m}^2$ ,<sup>49,50</sup> while the compressibility constant of a lipid bilayer is  $k \sim 100 - 300 \text{ mN/m}$ . This gives the range of the control interaction parameter  $\zeta = -0.003$  to  $-0.01$  for bare plastics.

The experimental tension of bare microplastics in PBS, Fig. 3D) can be compared directly with predicted value from the model, assuming the value of the control parameter  $\zeta = -0.01$ .

The theoretical curve with only one parameter fits well with the experimental data, Fig. 3D). If the attraction to the bilayer is 10 times stronger,  $\zeta = -0.1$ . The bilayer tension of PS microplastic incubated with hexane can be approximated with the theoretical curve with no additional parameters. Thus, if qualitatively the physical interaction seems not to have changed, quantitatively we observed a notable increase (10 times for hexane) in the attraction to the bilayer with respect to bare microplastics. The most significant tension increases are measured for microplastics incubated with POPs. As the polluted sea water is washed out and replaced with PBS, we can assume that the quantity of pollutants in the buffer is negligible. Thus, we believe that some pollutant molecules adsorb onto the surface of the microplastics and alter the surface properties, resulting in a significant change in the adsorption strength of the bilayer. These findings go in line with recent studies indicating that POPs may alter the surface properties of microplastics, which may change their adherence to a bilayer.<sup>51-55</sup>

In addition, POPs are used as solvents to dissolve phospholipids.<sup>56-59</sup> Due to its amphiphilic nature, these chemicals can even infiltrate the bilayer core and alter its potent biophysical characteristics.<sup>56-59</sup> To examine the ability of microplastics to serve as a vehicle for transport into the lipid bilayers of contaminants such as POPs, a free-standing vertical bilayer was produced in a microfluidic chip.<sup>45</sup> Hexane-incubated microplastics ( $c \approx 500 \mu\text{g}/\text{mL}$ ) were dispersed near a bilayer for two hours before washing them away from the bilayer. Then we inject small unilamellar vesicles (SUVs) (see Materials and methods, Fig. 4) around the bilayer.<sup>60,61</sup> While there are no fluorescent molecules in the lipid bilayer, these SUVs do contain some fluorescent lipids (DOPE-Atto647N, 2% in molar ratio). We performed tests to ensure that these SUVs are stable and do not fuse or hemifuse with the lipid bilayer in the absence of microplastics. However, following exposure to microplastics incubated in hexane, we see that after scattering SUVs close to the bilayer, the lipid bilayer starts fluorescing after 10-20 minutes. This observation indicates the presence of SUV fusion or hemifusion with the bilayer. This can occur in the presence of fusogenic molecules like hexane, so we

assume that microplastics have delivered hexane into the bilayer core.<sup>62</sup> This demonstrates that microplastics can serve as a vector into a lipid bilayer for chemical molecules.

Finally, it may be a surprise that we also report some minimal or nonexistent mechanical impacts for the other categories of contaminants. For example, we do not measure an increase in tension for mercury and DDT. It may be explained by the low quantities of mercury and the high hydrophobicity of DDT, such that they may not bind to microplastics, at least in our experiments. Zonyl is a perfluorated surfactant, so it can have an antagonistic interaction with the oil-water interface. As a surfactant, it may decrease the surface tension of a pure oil-water interface, but it may also increase bilayer tension once inside a lipid bilayer, which may explain the weak measured tension with zonyl-contaminated microplastics. Notably, our study investigates only physical interactions between microplastics and lipid bilayers; it does not take into account biological or other toxicological pathways associated with marine pollutants.

## Conclusion

In this manuscript, we investigate the physical interaction between microplastics and a lipid bilayer in the presence of typical marine pollutants. The sea water with added typical marine pollutants is incubated with typical microplastics found in the environment to simulate the contamination of microplastics in sea water closer to real environmental conditions. We let them for one month and dispersed the contaminated microplastics in the PBS. This step models the microplastics' evaporation from the ocean and their ingestion by a living organism. Using a microfluidic setup, we produce a free-standing lipid bilayer and measure the microplastics' effect on the bilayer tension. We measure that microplastics contaminated by persistent organic pollutants (POPs) increase the bilayer tension significantly. Using a theoretical model, we could estimate the effective increase of the microplastic adhesion properties in the presence of chemical pollutants. We hypothesize that this higher tension may be the

result of a change in the surface characteristics of microplastics subsequent to POP incubation. Moreover, hexane molecules have been measured to be able to enter the bilayer core. Using a home-made microfluidic fusion assay, we demonstrate that chemical molecules can be vectored by microplastics into the core of lipid bilayers. Our study highlights potential consequences of environmental contamination by chemicals (such as oil spills or industrial accidents) that may increase microplastics’ toxicities to living organisms.

## Tables

Table 1: Bilayer tension of PS microplastics measured in the presence of marine pollutants as a function of microplastic concentration  $c$ . The reported values are obtained by averaging of approximately 20–30 measurements. For the PBS, it means that the microplastics were incubated in filtrated sea water without any pollutants before being washed out and dispersed in the PBS.

Chemicals	PS - Bilayer Tension $\Gamma$ (mN/m)					
	0 $\mu\text{g/mL}$	50 $\mu\text{g/mL}$	100 $\mu\text{g/mL}$	150 $\mu\text{g/mL}$	300 $\mu\text{g/mL}$	500 $\mu\text{g/mL}$
PBS	1.7±0.2	1.9±0.2	2.2±0.2	2.5±0.3	3.4±0.3	4.2±0.4
Mercury	1.7±0.2	1.8±0.2	2.2±0.2	2.4±0.3	3.3±0.3	4.1±0.4
Hexane	1.7±0.2	2.5±0.5	4.1±0.5	4.8±0.5	5.9±0.5	6.2±0.5
Toluene	1.7±0.2	2.4±0.5	3.7±0.5	5.6±0.5	5.9±0.5	6.2±0.5
1-Octanol	1.7±0.2	2.18±0.5	3.3±0.5	4.3±0.5	4.3±0.5	4.3±0.5
Perfluorooctanol	1.7±0.2	2.2±0.4	3.8±0.4	5.1±0.5	5.9±0.5	5.9±0.5
Zonyl	1.7±0.2	2.1±0.3	2.7±0.3	3.2±0.4	3.3±0.4	3.3±0.5
DDT	1.7±0.2	1.9±0.2	2.2±0.2	2.5±0.3	3.4±0.3	4.2±0.4
sunscreen	1.7±0.2	2±0.3	2.6±0.3	3.3±0.4	3.3±0.4	3.3±0.5

## Materials and methods

### Molecules and Microplastics

In this paper, the formed bilayers have a DOPC:DOPE lipid composition (60:40 in molar ratio).<sup>63,64</sup> DOPC is the abbreviation of 1,2-dioleoyl-sn-glycero-3-phosphocholine, DOPE

Table 2: The table summarizes the bilayer tension for PE microplastics measured in the presence of marine pollutants and as a function of microplastic concentration  $c$ . The reported bilayer tension values are obtained from an average of approximately 20–30 measurements. For the PBS, it means that the microplastics were incubated in filtrated sea water without any pollutants before being washed out and dispersed in the PBS.

Chemicals	PE - Bilayer Tension $\Gamma$ (mN/m)					
	0 $\mu\text{g/mL}$	50 $\mu\text{g/mL}$	100 $\mu\text{g/mL}$	150 $\mu\text{g/mL}$	300 $\mu\text{g/mL}$	500 $\mu\text{g/mL}$
PBS	1.7 $\pm$ 0.2	1.9 $\pm$ 0.2	2.1 $\pm$ 0.2	2.5 $\pm$ 0.3	3.4 $\pm$ 0.3	4.2 $\pm$ 0.4
Mercury	1.7 $\pm$ 0.2	1.8 $\pm$ 0.2	2.1 $\pm$ 0.2	2.7 $\pm$ 0.3	3.2 $\pm$ 0.3	4.2 $\pm$ 0.4
Hexane	1.7 $\pm$ 0.2	2.9 $\pm$ 0.5	4.7 $\pm$ 0.5	5.2 $\pm$ 0.5	5.8 $\pm$ 0.5	6.1 $\pm$ 0.5
Toluene	1.7 $\pm$ 0.2	3.1 $\pm$ 0.5	4.8 $\pm$ 0.5	5.1 $\pm$ 0.5	5.7 $\pm$ 0.5	6 $\pm$ 0.5
1-Octanol	1.7 $\pm$ 0.2	2.8 $\pm$ 0.5	4.1 $\pm$ 0.5	4.3 $\pm$ 0.5	4.2 $\pm$ 0.5	4.3 $\pm$ 0.5
Perfluorooctanol	1.7 $\pm$ 0.2	2.9 $\pm$ 0.4	4.6 $\pm$ 0.4	5.3 $\pm$ 0.5	5.6 $\pm$ 0.5	5.8 $\pm$ 0.5
Zonyl	1.7 $\pm$ 0.2	2.1 $\pm$ 0.3	2.8 $\pm$ 0.3	3.3 $\pm$ 0.4	3.4 $\pm$ 0.4	3.4 $\pm$ 0.5
DDT	1.7 $\pm$ 0.2	1.9 $\pm$ 0.2	2.1 $\pm$ 0.2	2.5 $\pm$ 0.3	3.5 $\pm$ 0.3	4.3 $\pm$ 0.4
sunscreen	1.7 $\pm$ 0.2	2.1 $\pm$ 0.3	2.5 $\pm$ 0.3	3.2 $\pm$ 0.4	3.4 $\pm$ 0.4	3.4 $\pm$ 0.5

Table 3: The table summarizes the bilayer tension for PA microplastics measured in the presence of marine pollutants and as a function of microplastic concentration  $c$ . The reported bilayer tension values are obtained from an average of approximately 20–30 measurements. For the PBS, it means that the microplastics were incubated in filtrated sea water without any pollutants before being washed out and dispersed in the PBS.

Chemicals	PA - Bilayer Tension $\Gamma$ (mN/m)					
	0 $\mu\text{g/mL}$	50 $\mu\text{g/mL}$	100 $\mu\text{g/mL}$	150 $\mu\text{g/mL}$	300 $\mu\text{g/mL}$	500 $\mu\text{g/mL}$
PBS	1.7 $\pm$ 0.2	1.9 $\pm$ 0.2	2.2 $\pm$ 0.2	2.5 $\pm$ 0.3	3.4 $\pm$ 0.3	4.2 $\pm$ 0.4
Mercury	1.7 $\pm$ 0.2	1.8 $\pm$ 0.2	1.9 $\pm$ 0.2	2.3 $\pm$ 0.3	3.4 $\pm$ 0.3	4.2 $\pm$ 0.4
Hexane	1.7 $\pm$ 0.2	3.2 $\pm$ 0.5	4.7 $\pm$ 0.5	5.1 $\pm$ 0.5	5.3 $\pm$ 0.5	5.9 $\pm$ 0.5
Toluene	1.7 $\pm$ 0.2	3.1 $\pm$ 0.5	4.8 $\pm$ 0.5	5.7 $\pm$ 0.5	6.2 $\pm$ 0.5	6.3 $\pm$ 0.5
1-Octanol	1.7 $\pm$ 0.2	2.8 $\pm$ 0.5	3.9 $\pm$ 0.5	4.9 $\pm$ 0.5	5.6 $\pm$ 0.5	6.3 $\pm$ 0.5
Perfluorooctanol	1.7 $\pm$ 0.2	3.1 $\pm$ 0.4	4.3 $\pm$ 0.4	5.8 $\pm$ 0.5	6.2 $\pm$ 0.5	6.3 $\pm$ 0.5
Zonyl	1.7 $\pm$ 0.2	2.3 $\pm$ 0.3	2.8 $\pm$ 0.3	3.3 $\pm$ 0.4	3.2 $\pm$ 0.4	3.3 $\pm$ 0.5
DDT	1.7 $\pm$ 0.2	2.6 $\pm$ 0.2	3.2 $\pm$ 0.2	3.3 $\pm$ 0.3	3.5 $\pm$ 0.3	4.2 $\pm$ 0.4
sunscreen	1.7 $\pm$ 0.2	2.1 $\pm$ 0.3	2.6 $\pm$ 0.3	3.4 $\pm$ 0.4	3.4 $\pm$ 0.4	3.4 $\pm$ 0.5

is 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine. This lipidic composition is different than the one used in Ref. 23. This is because the bilayer present a lower tension for this lipidic composition. This is mandatory as the presence of pollutants increases the bilayer tension. Thus, we employed a composition with a lower bilayer tension to allow measurement in presence of microplastics contaminated with pollutants. We also used purchased DOPE-Atto647N is 1,2-Dioleoyl-sn-glycero-3- phosphoethanolamine labeled with Atto 647N. All the lipids were purchased from Avanti Polar Lipids (USA). As heavy metal we used Mercury, as POPs we used hexane (CAS 110-54-3), toluene (CAS 108-88-3), 1-Octanol (CAS 111-87-5), perfluorooctanol (CAS 647-42-7), zonyl (CAS 65545-80-4), as EDC we employed dichlorodiphenyltrichloroethane (DDT, CAS 50-29-3) and all these products were purchased from Sigma Aldrich. sunscreen were purchased from several commercial sunscreen products available in supermarket. Filtrated sea water was purchased from Holoslife. Due to the quantity and pollutants chemical nature, we can ignore plastic dissolution.<sup>54</sup>

Three different types of microplastic beads were used: PS (0.8  $\mu\text{m}$ ), PE ( 1  $\mu\text{m}$ ) and PMMA (1  $\mu\text{m}$ ). Polystyrene (PS) microbeads (Bangs Lab, USA, 0.798  $\mu\text{m}$ , Shamrock Green uniformly dyed, Catalog number: DSSG005). Polyethylene (PE) microbeads (Cospheric, Catalog number CPMS-0.96) from diameter 1  $\mu\text{m}$  to 10  $\mu\text{m}$  (sorted to  $\approx$  1  $\mu\text{m}$  by a standard microfluidic filter). Polymethacrylate (PMMA) microbeads, as an alternate to (PA), (Sigma-Aldrich, catalog number 90875) with diameter of 1  $\mu\text{m}$ . Red fluorescent microplastic (PS) beads were purchased from Thermo-Fisher (R0100), with a diameter of 1  $\mu\text{m}$ . Each of them, are dry from their solution, disperse in ethanol to remove the surfactant, and extract via centrifuging (3000 rpm during 10 min). The microplastics are re-disperse in pure water. The process of surfactant removal is repeat three times.

## Surface Tension Measurements

Surface tension of various lipid monolayers at the oil-water interface was obtained by the pendant drop method using a commercial measurement device (OCA 20, DataPhysics In-

struments GmbH, Filderstadt, Germany). An oil solution containing 5 mg/ml lipids was produced by introducing a droplet from a steel needle into the surrounding oil phase. The interfacial tension was obtained from fitting of the shapes of the droplets by the Young-Laplace equation.<sup>44</sup>

## **Droplet Interface Bilayers Fabrication**

Lipids were dissolved in squalene oil at concentration of 5 mg/mL. The lipids were left for 24 h at 50 °C under magnetic stirring. The OTS-coated glass container, which has a cylinder shape that is 1 cm in height and a diameter of 7 cm, is filled with the oil-lipid mixture. This device is placed on a hot plate and disposed at desired temperature. A large area of the cylinder can be observe by reflection using a Leica Z16 Microscope connected to a PCO1600 camera. The optical quality is reduced using this technique. However, it is enough to distinguish DiB (Droplet interface Bilayer) that have merge from others. For formation and manipulation of an aqueous microdroplet, a micropipette with a desired tip, having a typical diameter in the range 1 mm was formed using a micropipette puller (Eppendorf). By this method, two water droplets of nearly equal size are produce manually in this container, and left at rest for 30 min. They are brought, gently, into contact via a needle. After a few minutes, a bilayer appears spontaneously at the contact area between the droplets.<sup>23,46,65</sup> The buffer composition of each droplet could be determined before droplet production. Thus, a controlled amount of microplastics could be dissolved into buffer prior to droplet production.

## **Microfluidic Free-standing Bilayer Fabrication**

A 3D microfluidic chip is used to produce an horizontal bilayer. To produce an horizontal bilayer, we produce two molds from 3D printing technique and used it to mold a polydimethylsiloxane (PDMS - Sylgard 184 - Dow Corning) block. The PDMS block is, then, plasma bound to a glass coverslip after plasma treatment (Diener). This technique is describe in more detail in the following references.<sup>23,64,66,67</sup> Then an oil-lipid mixture is injected into this

chip until filling this chip. Lipids were dissolved in squalene oil at concentration of 5 mg/mL. The lipids were left for 24 h at 50 °C under magnetic stirring prior to injection into the chip. Then, two buffer phases are injected face-to-face until they meet at a desired location. Each water-oil interface is covered by a lipid monolayer and after the two monolayers are brought into contact to produce a bilayer.<sup>23,64,66,67</sup>

## **Small Unilamellar Vesicles**

We disperse 2.6 mM of total phospholipids in a glass test tube, using the desired molar ratio of phospholipids (e.g., 78 mol% DOPC, 20 mol% DOPS, 2% Atto647N-DOPE) in 1 mL of chloroform (Sigma). The mixture is then dried with nitrogen and dispersed in 2 mL of PBS (using several falcons). Then, using a Vibracel titanium-tip sonicator (Bandeli, sonopuls, Germany) with a maximum power of 600 W and frequency of 20 kHz, ultrasonic radiation is applied to this mixture. Each sample underwent repetitive 3 Hz cycles that consisted of 1 s pulses at a power of 150 W to control thermal effects. Finally, these samples are placed in the fridge for one day.

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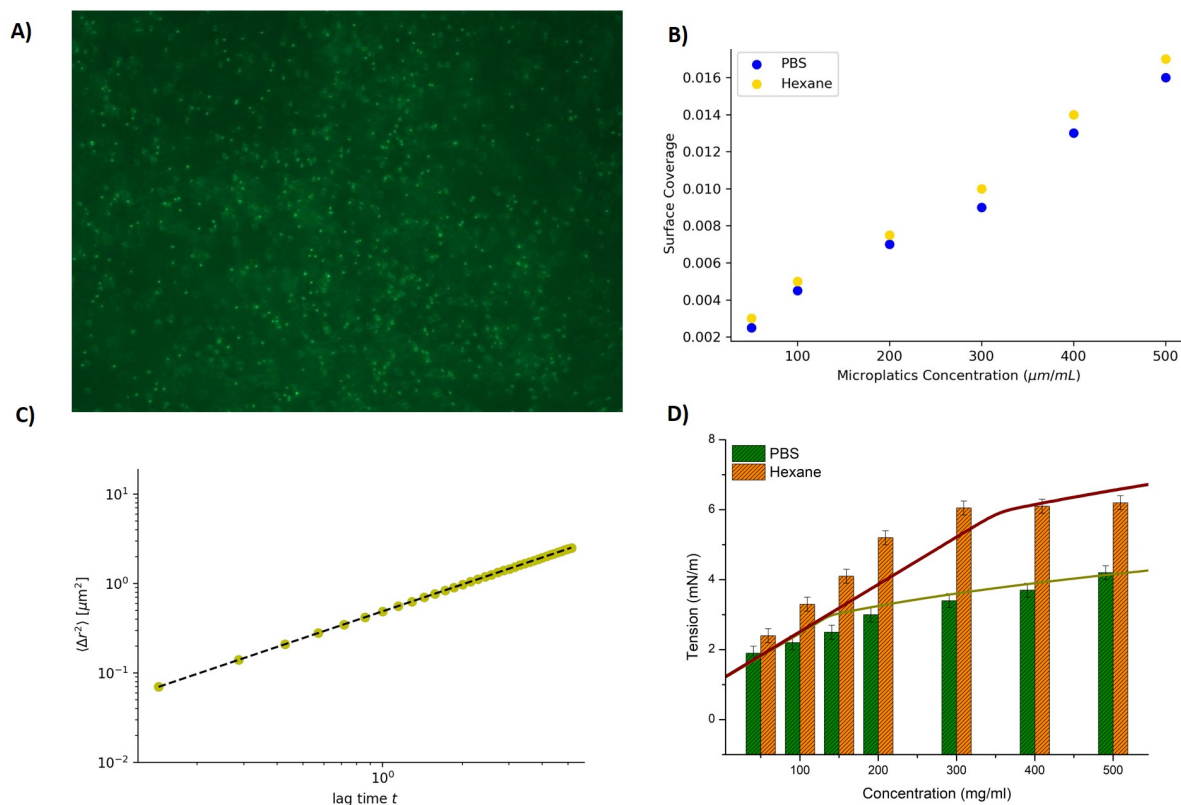


Figure 3: A) A micrograph of red fluorescent 1  $\mu\text{m}$  PS microplastics adsorbed on a free-standing lipid bilayer. B) The adsorption isotherm of 1  $\mu\text{m}$  PS (yellow circles) microplastics, incubated in sea water with 0.014% volume of hexane, adsorbed on a free-standing lipid bilayer. Blue circles are plots for 1  $\mu\text{m}$  PS microplastics incubated in sea water plus hexane, which are adsorbed on a free-standing lipid bilayer. C) The extracted mean square displacement as a function of time on a log-log scale, for a 1  $\mu\text{m}$  PS incubated in hexane. The measured average microplastic diffusion coefficient  $D \approx 0.6 \mu\text{m}^2 \cdot \text{s}^{-1}$ . D) Bilayer tensions measured similar to Fig. 2C), except that PS microplastics were incubated in sea water in presence of hexane. The experimental data are represented as bar plot, while the continuous line represents the theoretical plot. It was obtained using the surface coverage data plotted in B).

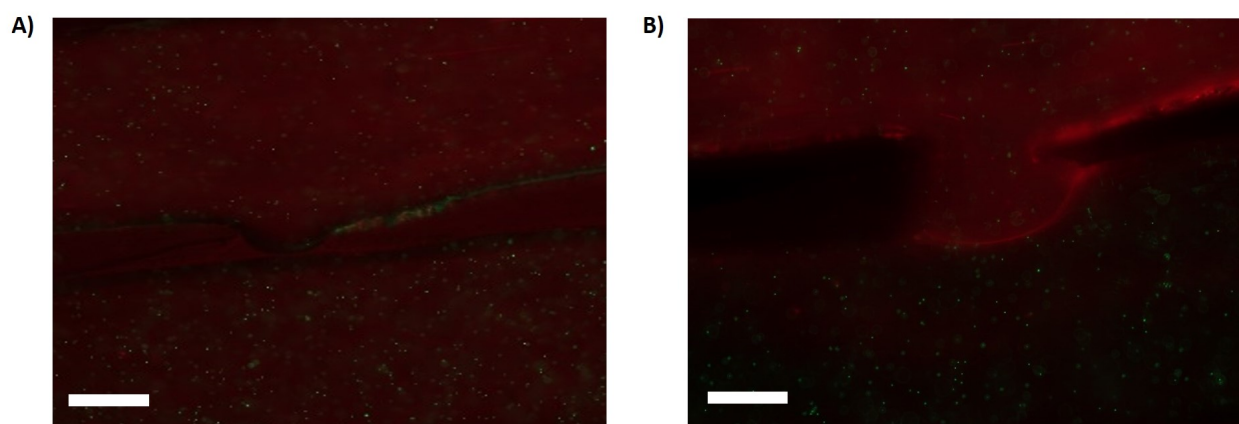


Figure 4: A) Microfluidic channels to from a vertical free-standing lipid bilayer.<sup>45</sup> The bilayer was exposed to SUVs ( $c \approx 1$  mM), visible as red dots. The green dots correspond to PS microplastics ( $1 \mu\text{m}$ ). A), the bilayer is in contact with bare PS microplastics, and B) the bilayer is in contact with PS microplastics contaminated with hexane. The bilayer does not present a fluorescent signal in A), while the bilayer is fluorescent in B), which means that the SUVs can fuse in the presence of PS microparticles contaminated with hexane. Bar lengths in panels A and B correspond to 200 microns.