

# Floating Microplastics in the Northwestern Mediterranean Sea: Temporal and Spatial Heterogeneities

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## 1 Introduction

Attention on marine litter, and their economic, social, and environmental issues, has been increasingly paid over the last few decades [1]. Litter has been found everywhere, from rivers to central open oceans, in coral reefs and polar oceans, floating at the sea surface, deposited on the seafloor, stranded on beaches or ingested by marine fauna (e.g., [2–7]).

Plastics can represent more than 70% of items described within floating marine litter [8]. Among plastic litter, an important part has a size below 5 mm (e.g., >98% [9]). These small size particles, called microplastics (MPs), can be ingested by small organisms, extending the problem to a large part of the marine trophic network.

Mediterranean ecosystems are exposed to high anthropogenic pressures such as densely populated coastlines, busy shipping routes, and strong tourism activities. In addition, the semi-enclosed morphology of the Mediterranean Sea leads to an accumulation and a density of marine litter as important as within the great accumulation zones in the oceanic gyres [10].

The Mediterranean Sea is one of the most sampled areas for floating MPs. However, only a few investigations have been conducted at small spatial and temporal scales in coastal areas. To overcome this gap, MPs (<5 mm) were

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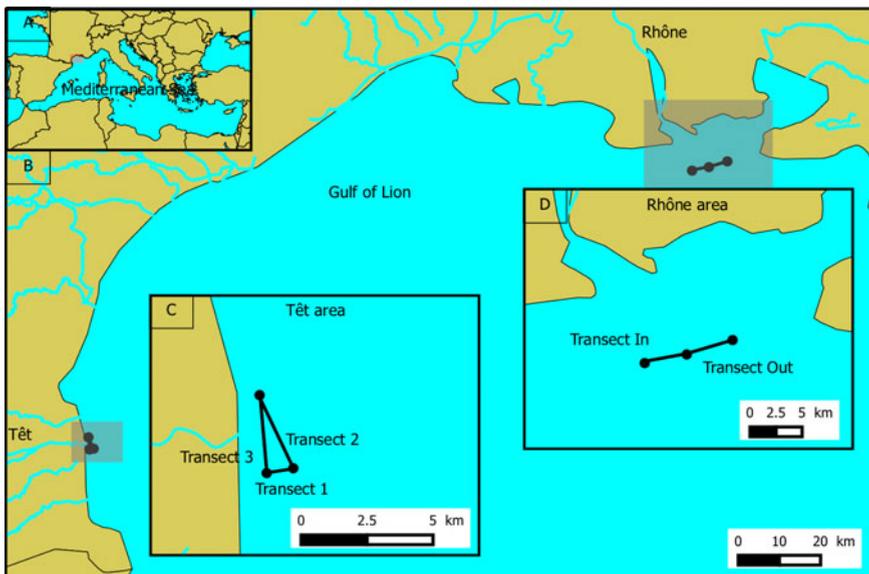
collected off the mouths of two contrasted rivers discharging into the Northwestern Mediterranean Sea: the Rhône River, the largest continental inflow to the Mediterranean Sea, and the Têt River, a small typical Mediterranean river.

## 2 Materials and Method

### 2.1 Sea Surface Sampling

Between May and November 2016, 13 samples were taken at different seasons in the Rhône area. Two transects were performed at the sea surface close to the river mouth. During the same period, a total of 18 samples were obtained in the Têt area. A triangle of three transects close to the river mouth was performed every month (Fig. 1).

Transects were carried out using a manta trawl (60 × 25 cm opening; 333 µm mesh) towed at the top 20 cm of the sea surface at 2 knots for 30 min–1 h. Sampled water volumes were recorded with a mechanical flowmeter (Hydro-bios; model 438 110). Once on board, the trawl was rinsed, the content of the collector was emptied over a 200 µm metal sieve and then transferred to glass bottles.



**Fig. 1** Map of sampling sites. **A:** Mediterranean Sea; **B:** Gulf of Lion; **C:** Têt area; **D:** Rhône area. Grey rectangles represent zoom box **B**, **C** and **D**

## **2.2 *Laboratory Work***

Contamination of the samples was minimized by wearing laboratory cotton coats and using equipment made of glass or steel. Every step with an air exposure was performed under a laminar flow cabinet and beakers were covered by an aluminum foil.

### **2.2.1 Preparation of Samples**

Collected materials were transferred into beakers and biological debris was removed using hydrogen peroxide  $\text{H}_2\text{O}_2$  (modified from [11]). Two mL of  $\text{H}_2\text{O}_2$  40% were added repeatedly until most of the organic matter was digested. During the entire digestion process, beakers were heated at 50 °C on a heating plate. The resulting solutions were filtered on paper filters (Whatman). Filters were examined under a Wild Heerbrugg dissecting stereomicroscope (25 × and 50 × magnifications). MPs were separated into four categories: fibers (including filaments and fishing lines), fragments (3-D pieces of plastic, including spherules), films (2-D pieces of plastic), and foams (pieces or spherules with a spongy, soft structure).

### **2.2.2 Polymer Identification**

Forty fibers and 80 other items of each category were randomly selected and analyzed for polymer nature. Fibers were analyzed with an FTLA2000 FTIR spectrometer (ABB). Other particles were analyzed with a Frontier FTIR spectrometer (PerkinElmer). Following background scans, 100 scans per particle were performed. For each particle, scans were performed between 4000 and 700  $\text{cm}^{-1}$ . Essential FTIR trial version software was used for the output spectra and identification of polymers was performed by comparison with a self-collected spectrum database.

## **2.3 *Data Analysis***

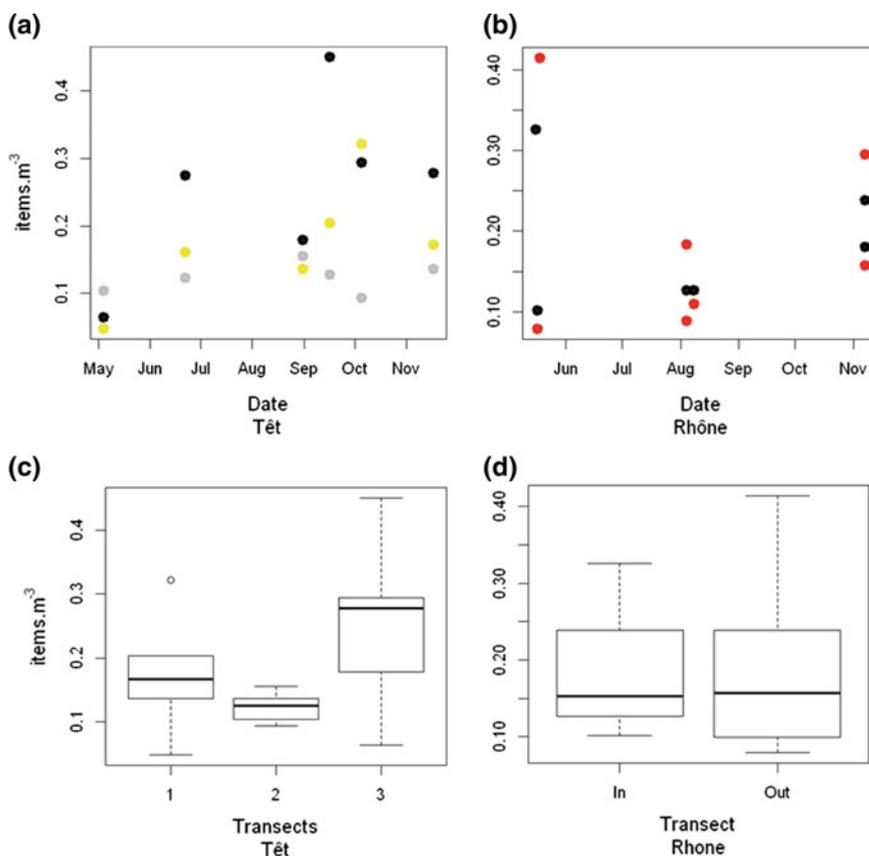
FTIR analyses allowed to estimate the number of plastic items collected. For each category, a “plastic” ratio was applied to the number of collected particles. This ratio results from the division of the number of particles which have a “plastic spectra” with the total number of particles analyzed. Finally, concentrations of MPs were estimated by dividing the adjusted numbers of plastic particles by the sampled water volumes.

### 3 Results and Discussion

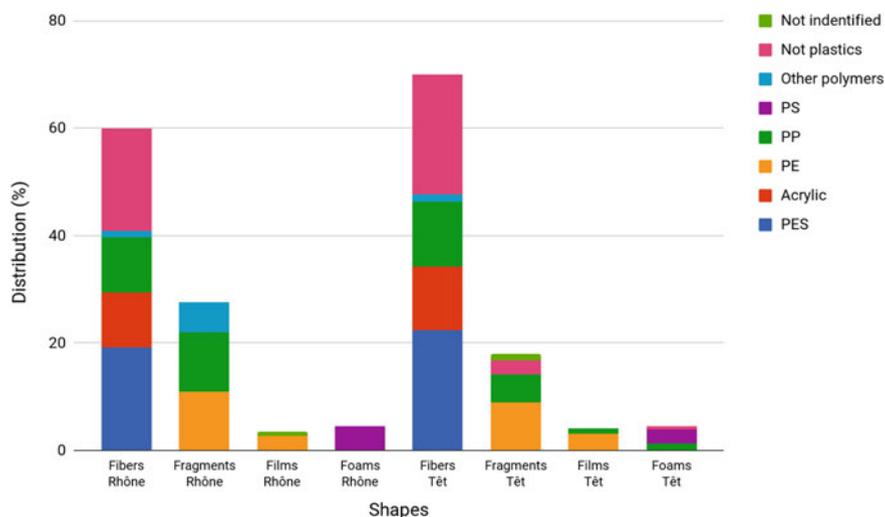
#### 3.1 Results

Adjusted concentrations ranged from 0.05 to 0.45 items.m<sup>-3</sup> for the Têt area with an average of 0.18 items.m<sup>-3</sup> (Fig. 2a) and from 0.08 to 0.41 items.m<sup>-3</sup> with an average of 0.19 items.m<sup>-3</sup> for the Rhône area (Fig. 2b), which is not significantly different (t-test; p-value = 0.96).

Concentrations inside the Têt area were most of the time higher at transect 3 (Fig. 2c), but differences between the three transects are not significant (ANOVA; p-value = 0.168). Concentrations for each transect have changed highly during the



**Fig. 2** Concentration of MPs (items.m<sup>-3</sup>) during the year 2016 **a** in the Têt area (yellow dots: transect 1; grey dots: transect 2; black dots: transect 3) and **b** in the Rhône area (black dots: transect In, red dots: transect Out); Boxplot of MPs concentration according to transects **c** in the Têt area and **d** in the Rhône area. “In”: in the Rhône plume, “out”: upstream the Rhône plume



**Fig. 3** Distribution of shape categories and corresponding polymer nature

year but combined concentrations did not significantly differ between months (ANOVA;  $p$ -value = 0.293).

Similarly, concentrations inside the Rhône area were not significantly different between the two transects (Fig. 2d;  $t$ -test;  $p$ -value = 0.91) or between the three different sampling periods (ANOVA;  $p$ -value = 0.274). Nevertheless, concentrations could occasionally change by a factor of 5 between two consecutive days at the same location (e.g., May samples), and by a factor of 3 between two consecutive trawls on the same day (e.g., August samples).

The Rhône and the Têt areas had similar categorical distributions (Fig. 3). Fibers were the most abundant shape (60–70%), followed by fragments (18–28%). Foams and films were less represented (3–5%). FTIR analysis indicates that fibers were polyester (32%), cotton (32%), PP (17%), acrylic (17%), and PA (2%). Fragments and films were mostly PE (54%) and PP (17%), while foams were essentially made of PS (67%).

### 3.2 Discussion

The Rhône River is the largest source of freshwater and sediments into the Mediterranean Sea while the Têt River is a typical small Mediterranean coastal river, with extreme low-water stages and occasional massive flood events. MPs concentrations in the downstream parts of both rivers ranged between 1 and 2 items.m<sup>-3</sup> (Constant, unpublished results), thus, about 10 times more than off

both mouths. This strong decrease in concentration has been mainly attributed to the oceanic dilution [12].

The Rhône River has an average water flow 200 times higher than the Têt River. The total amount of MPs discharged by the Rhône River, so far not precisely calculated, should be, due to the close riverine concentrations, much higher than those released by the Têt River. One could have thus expected surface concentration differences more in connection with the large differences in inputs rather than the observed similarities between both areas. These preliminary results suggest that the influence of rivers on the spatial distribution of MPs rapidly decreases with distance to the river mouths, a hypothesis supported by the fact that highest concentrations off the Têt River were observed in the transect closest to the river mouth. Alternately, the similarities in offshore MP concentrations could also indicate that the floating plastics collected within our experimental areas are not provided by straight, direct river inputs. Some mixing and dispersion processes must rapidly take place once the MPs enter the marine environment.

Concentrations estimated in this study are relatively close to previous observations from the Northwestern Mediterranean (0.1–0.3 items.m<sup>-3</sup> [13–15]) or in the costal water of the East China Sea (0.2 items.m<sup>-3</sup> [12]), but 45 times lower than concentrations observed along the Israeli coast (7 items.m<sup>-3</sup> [16]) or in the Southern California coastal waters (7.3 items.m<sup>-3</sup> [17]). Such differences may have numerous reasons ranging from hydrodynamic features to the use of different trawls and methodologies. Indeed, most of the old investigations did not check the polymeric nature of their collected particles and especially fibers, probably leading to overestimations.

No spatial or temporal trends were found but high changes at daily and kilometer scale were observed. Presence of lint composed of hundreds of fibers can partly explain the high differences observed at small scales, as well as fast-changing river inputs.

Strong spatial heterogeneities of floating MPs have been previously reported at regional scales, up to a factor of 40 [14] and 30 at subregional scales [13]. Van der Hal et al. [16] indicated a factor of 300 at subregional and seasonal scales. Collignon et al. [18] investigated fluctuations of a costal transect on a semi-monthly basis and observed differences up to a factor of 60 during the same week. Wind had been found to be a factor of heterogeneity [15]. Large hydrological structures, like central oceanic gyres, accumulate MPs [2, 10] but influence of meso and small structures, like eddies and fronts, remain unknown.

## 4 Conclusions

This study confirms that heterogeneities of floating MPs can act at small scales. These extended observations in the NW Mediterranean coastal environment underline the necessity of performing replicate sampling to get a better insight into the spatial and temporal distribution patterns of these worrying pollutants.

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