ESRF	**Experiment title:** Micro and nanoplastics as significant As vectors?	**Experiment number**: ev417
Beamline: ID16B	**Date of experiment**: from 20th Apr 2021 to 22th Apr 2021, the 28th Apr 2021 and from 28th Oct 2021 to 31st Oct 2021	**Date of report**:
Shifts:	**Local contact(s)**: Rémi Tucoulou Tachoueres	*Received at ESRF:*
Names and affiliations of applicants (*indicates experimentalists): Charlotte Catrouillet*, Mélanie Davranche*, Delphine Vantelon*, Julien Gigault		

Report: The beamtime was divided into two due to the Covid pandemic: (i) in April 2021 on-line (Rémi Tucoulou placed the samples at ESRF), during which we performed elementary maps, (ii) in October on-site, which was dedicated to the As speciation (XANES spectrum). The aim of this experiment was to determine in which form(s) As is in environmental plastic debris. Two zones inside the plastic debris were compared: the surface layer, which is altered and can adsorb external elements through complexing sites (mostly carboxylic) and the core of the plastic debris, which is unaltered and can contain metallic additives. During the two different beamtimes, we analysed 7 samples and 5 standards (As(III) and As(V) in several organic and inorganic forms).

A total of 79 debris plastic were analysed for their elementary composition (data being submitted in ACS Earth & Space Chemistry). Whatever the geographical origin and the composition of the plastic, As is present at low concentrations (0-8.8 µg g^{-1}) in plastic debris. The largest As concentrations were found for the plastic debris from the Guadeloupe Island (exposed to the gyre North-Atlantic, which is a plastic accumulation zone). Furthermore, by comparing concentrations in As determined after an acidic leaching and after an acidic total digestion, we found that As was mainly present in a bioavailable form in all samples analysed (i.e., through acidic digestion-route). Based on the acidic digestion, samples with largest As concentrations (i.e., from the Guadeloupe Island) were analysed by NanoXRF. Only results from CC25 are presented here (Figure 1).

- Titanium. It is present in nanoparticles form, with sizes comprised between 300 and 500 nm. These nanoparticles were found in both zones: the core and the altered one. This means that nanoparticles of Ti were used as additives in the debris plastic. Due to their large uses for this purpose in the plastic, it can hypothesed that Ti was used as an anti-oxidant in the environmental plastic used;
- Arsenic. Whatever the plastic debris analysed (data not shown), As was never found in the core of the plastic, meaning that As was not originally used as an additive in those plastic debris, corroborating the acidic leaching results. Arsenic is found in the microfractures and is colocalized with Cl, Ca, Sr, which are major cations of seawater (Figure 1). It can thus be concluded that As (i) is mainly present at the surface of the plastic, probably adsorbed to complexation sites such as carboxylic ones, which are present at the surface of altered plastic, and (ii) originates from external environment such as seawater;
- Cupper. It is present in two different forms: (i) as nanoparticles with sizes comprised between 300 and 400 nm. These nanoparticles were used as additives in this sample because they were found in the core and the altered zone. Due to the blue colour of the sample, nanoparticles of Cu has been probably used as a pigment (blue colour) in this sample. (ii) Cu is also present in a diffused form (absence of nanoparticles), only in altered zones, especially in micro-fractures. It is colocalised with As in such zones.

Note that correlation diagrams will be soon performed in order to determine what is the correlation of different elements in the different maps and different samples.

During the second part of the beamtime, XANES spectrum were performed at the K-edge of As (Figure 2a). Using references analysed during the beamtime and references from the literature (calibrated in energy with references re-analysed), we determined As speciation in different datapoints in CC25. We found that As speciation is similar in all the different datapoints (Figure 2b). As is present in inorganic and organic forms, mainly as methyl-As(III). The sample CC8 (from the Guadeloupe Island) present similar As speciation (Figure 2c). This speciation, especially the presence of organic and inorganic forms of As(III) and As(V) should be due

to the presence of Sargassum in large amount in the sampling area (Guadeloupe Island). In fact, Sargassum present large concentrations in As and a complex organic/inorganic and As(III)/As(V) speciation. However, no Sargassum debris was observed at the surface of the debris plastic by microscopy (data not shown). Therefore, either As comes with another vector, or the association Sargassum-plastic was removed/destroyed, but As stayed attached to plastic, maybe due to chemical interactions (e.g., organic-organic, surface complexation).

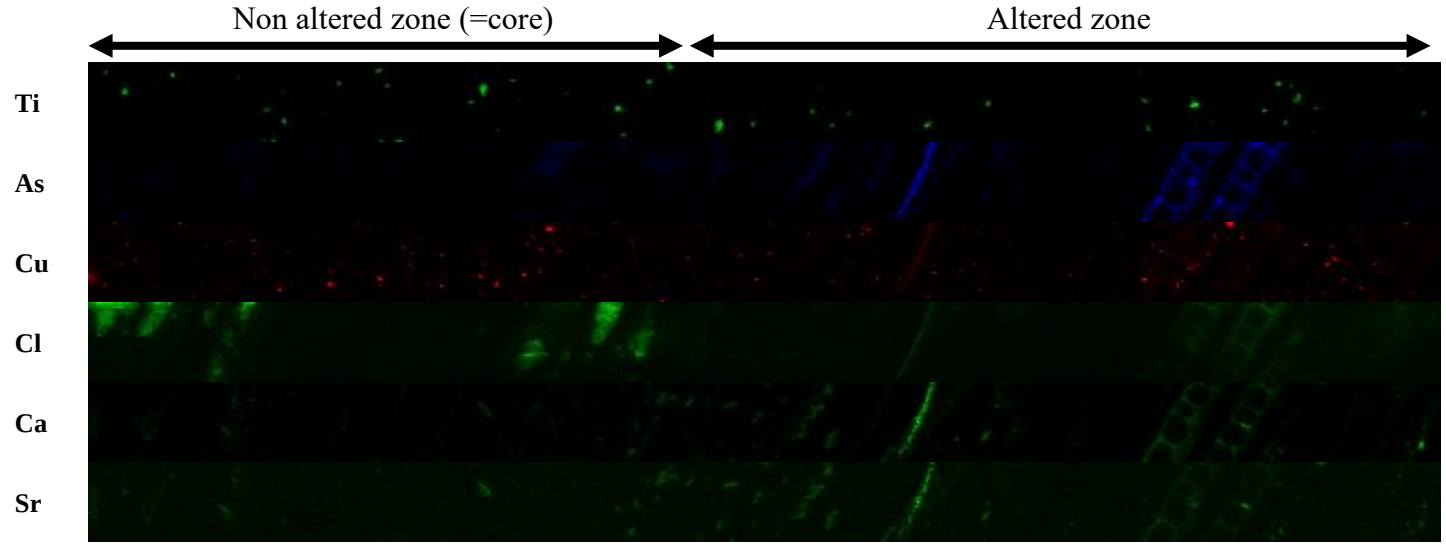

Figure 1: Example of nano-XRF map performed in CC25 sample for Ti, As, Cu, Cl, Ca and Sr.

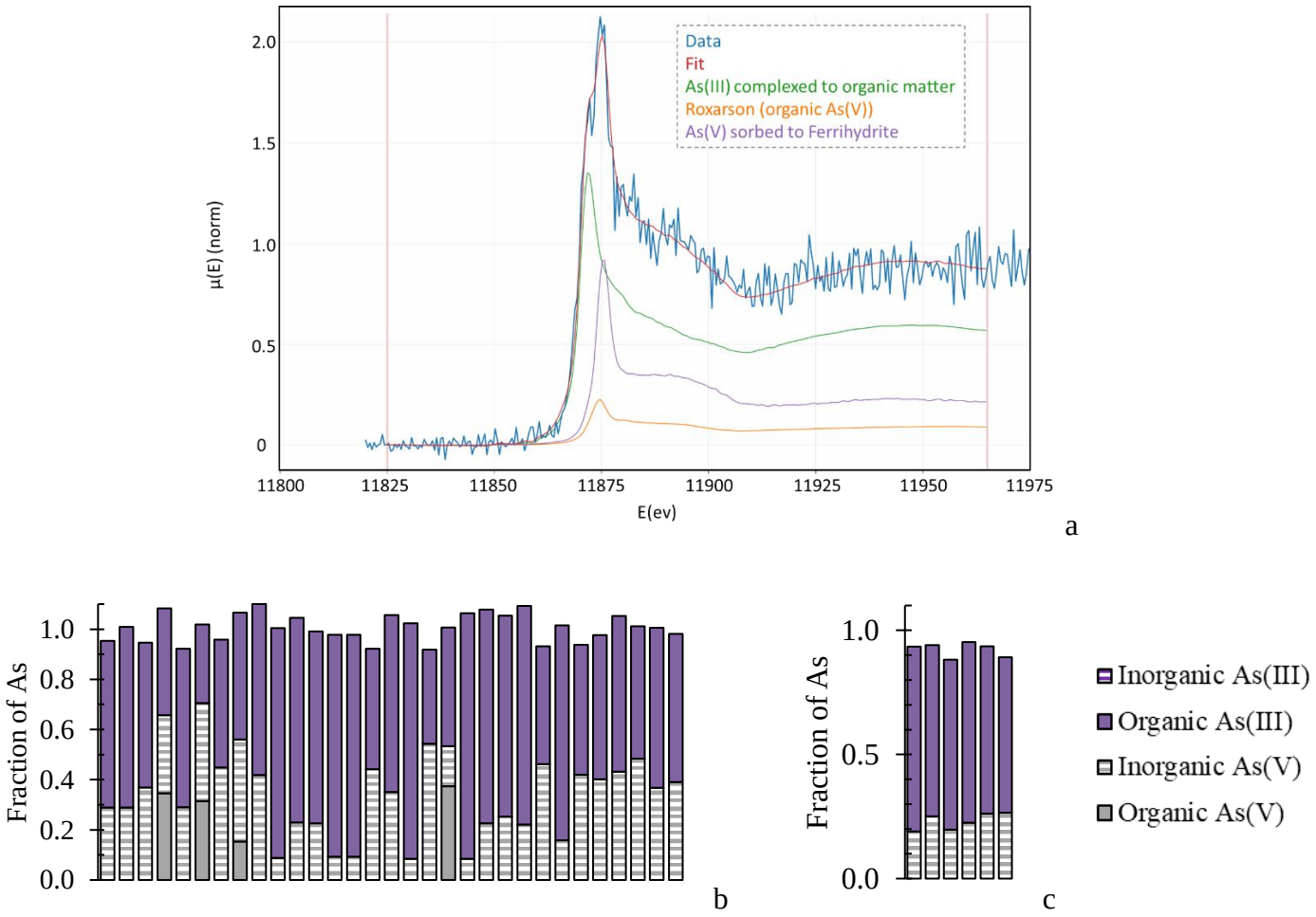

Figure 2: a) XANES spectrum and fit of one datapoint measured on CC25 in the altered zone, b-c) Speciation of As determined from the LCF performed on the different datapoints on b) CC25 and c) CC8.

The dataset obtained during this project will lead to a publication dedicated to the speciation of As in environmental plastics. The results were presented at the "Groupe de recherche Polymères et Océan" (oral presentation) in July 2022.