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Arsenic speciation and intracellular localization in Sargassum algae

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In recent years, unprecedented amounts of algae from the Sargassum genus have washed ashore on the beaches of the Caribbean1. During their life cycle, these seaweeds accumulate a high concentration of pollutants, especially arsenic (As). They are disposed of by collecting them and then spreading them along shorelines or inland. Their degradation, as well as rainfall, generate leachates that also contain several mg/L of As, causing environmental issues.
In this context, an in-depth characterization of As speciation and distribution in Sargassum algae (before and during its degradation) is essential to understand the mechanisms of As uptake and leaching, and to assess the risk for the environment.
The distribution of As in the leaves, stems and floats of sargassum algae was determined using both nano-XRF and Nano secondary ion mass spectrometry (NanoSIMS). Both techniques are able to achieve a high lateral resolution, of around 50-100 nm, which allows the mapping at the sub-cellular scale. The same samples were also studied by Transmission Electron Microscopy (TEM). A sample preparation adequate for the three techniques enabled the obtention of correlative imaging of the same cell.
Thus, it was shown that arsenic was mainly accumulated in the cell walls, in agreement with previous studies2, with a small amount of arsenic also visible in the cell internal organelles.
In the same manner, in order to determine the forms in which As is bound into the cell walls, speciation was studied by XAS and HPLC-ICP-MS. The characterization with HPLC-ICP-MS showed that inorganic species of As are the main components in the algae, but that organic species, especially DMA, but also AsB and TMAO, are also present. It also revealed that the fraction of organic As increases with the degradation of the algae.
In addition, X-Ray Absorption Spectroscopy (XAS) permits the investigation of frozen samples, removing the need for pre-treatment and extraction steps, and enables the determination of labile species such as As bound to sulfur and As bound to carbon. XAS demonstrated that fresh algae collected in the open sea contains mainly inorganic As(III) and As bound to sulfur, with some As bound to carbon present in a lower amount. However, during the decomposition of algae at the beach, As speciation evolves to more organic forms, where As is bound to carbon, and to As (V), possibly due to microbiological processes and oxidation involved in the fouling process.
The obtained arsenic distribution and speciation knowledge can contribute to understand better the toxicity and environmental impact of the sargassum and their As-rich leachates. It can enable the development of adequate remediation technologies in order to handle the stranded Sargassum.

1. Milledge, J. and Harvey, P. (2016), Golden Tides: Problem or Golden Opportunity? The Valorisation of Sargassum from Beach Inundations, J. Mar. Sci. Eng., 4, 60
2. Ender, E. et. al. (2019), Why is NanoSIMS elemental imaging of arsenic in seaweed (Laminaria digitata) important for understanding of arsenic biochemistry in addition to speciation information?, J. Anal. At. Spectrom., 34, 2295

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