## Seasonal variation of Phragmites australis response to copper(II) exposure, in terms of ALMWOAs exudation

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Rhizodeposition of aliphatic low molecular weight organic acids (ALMWOAs) into the root environment (rhizosphere) is a natural phenomenon which occurs in all living plants. Several features, such as plant species, plant age and the physicochemical nature of the medium, have been shown to influence the composition and concentration of ALMWOAs liberated by plant roots [1, 2]. However, in case of plant exposure to toxic substances, little is known about the effect of seasonality on plant response, in terms of ALMWOAs release.

Phragmites australis (Cav.) Trin. ex Steudel is a perennial macrophyte which presents, in temperate climate, a distinct seasonal cycle. The vegetative cycle initiates in spring and achieves its maximum of development in summer. On the other hand, in winter, is characterized by the dying back of the above-ground parts. However, the underground rhizomes are constantly active throughout the seasons [2].

This study aimed at investigating, in controlled conditions, the influence of *P. australis* life cycle on the exudation of ALMWOAs in response to the presence

of Cu<sup>2+</sup>. For this purpose, roots of groups of *P. australis* specimens were collected at a marsh from Lima River Estuary in spring, summer and autumn (due to methodological limitations the experiment was not performed in winter). Plants were exposed for 2 hours to river freshwater in the presence and in the absence of Cu<sup>2+</sup> (at two different added Cu<sup>2+</sup> concentrations: 100 μg/L and 10 mg/L). Before and after exposure, Cu<sup>2+</sup> was determined both in solutions and in plant tissues (by atomic absorption spectrometry after high pressure microwave digestion). Initial and final ALMWOAs concentrations in solution were determined by high pressure liquid chromatography (HPLC) after pre-concentration by solid phase extraction (SPE).

The exudation of oxalic and formic acid was enhanced in spring, as a response to the highest Cu<sup>2+</sup> concentration, but inhibition occurred in summer. In autumn, the presence of Cu<sup>2+</sup> did not influence significantly these ALMWOAs secretion, despite there being a trend for a higher exudation of formic acid when the plant roots were exposed to the highest

concentration of Cu<sup>2+</sup>. As regards to citric acid, a different behaviour was observed. In spring and autumn, Cu<sup>2+</sup> did not cause a significant influence on citric acid release, whereas in summer *P. australis* roots seemed to respond to the contaminant. In this season, at the lowest Cu<sup>2+</sup> concentration, *P. australis* roots exuded significantly more citric acid comparing to the medium without metal addition. However, the exposure to the highest Cu<sup>2+</sup> concentration inhibited the release of citric acid by *P. australis* roots as observed for oxalic and formic acids.

Therefore, the liberation of ALMWOAs by plant roots in response to Cu<sup>2+</sup> contamination may vary among seasons, depending on the plant activity. Similar results may occur for other contaminants and, thus,

when the response of a plant to a contaminant is investigated, the physiological cycle of the plant must be taken into consideration.

## References

[1] DL Jones, Plant and Soil, 1998, 205(1): 25-44

[2] D. Baldatoni et al., Journal of Geochemical Exploration, 2009, 101(2): 166-174

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