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First steps towards the assessment of PTEs availability through simple TXRF analysis of guttation drops

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In the last decades, guttation has been often used to assess insecticide, fungicide and weedicide residues present in crop plants. In fact, guttation fluids have been investigated as a potential route of entry of pesticides in bees and other pollinators feeding on such plant saps. More generally, analysis of guttation drops could also provide a non-invasive way for qualitatively and quantitatively investigating the translocation from roots to shoots not only of pesticides but also of mineral elements (including potentially toxic elements - PTEs). In this context, the elemental composition of guttation fluids could be indirectly indicative of both plant nutritional status and PTEs availability in polluted soils; however, this field has been scantly explored.

Total reflection X-ray fluorescence (TXRF) spectrometry can be considered an appealing technique for guttation water elemental analysis, because of the very low limits of detection (down to ppb for heavy elements), minimal sample preparation and extremely small quantity of sample required for the analysis. In fact, micro-volumes (1-10 µL) are sufficient for a full elemental analysis of liquid samples: this would allow, in - principle, even the determination of the elemental content of a single guttation drop.

For this purpose, we have collected guttation fluids from *Lolium rigidum* plants grown in mesocosms containing a PTEs-polluted (Pb, Cd, Zn, Sb, As) soil from Sassari (Italy), and from *Piptatherum miliaceum* and the mixed species *Dactylis glomerata* and *Festuca arundinacea* grown in another soil sampled in Acerra (Italy) and polluted by Pb, Cd, Zn and Sb. The Sassari mesocosms were subjected to three different treatments of phytostabilization: PTEs+Plant Growth Promoting Bacteria (PGPR), PTEs+Biochar, PTE+PGPR+Biochar. The Acerra ones were instead treated as follows: PTE+Compost, PTE+Biochar, PTE+mineral fertilization – all treatments either adding or not PGPR. A control mesocosm without any stabilization treatment was also prepared for each soil type. Sampling of fluids was performed twice, the first time in winter, the second in mid-spring.

Then, samples were stored at -20 °C and are being analysed by means of TXRF using an *ad hoc* analytical protocol, with the aims of investigating possible correlations between:

I. PTEs concentration in guttation fluids and their availability in soils;
II. PTEs and other elements concentration in guttation fluids comparing different plant species;
III. PTEs and other elements concentration in guttation fluids comparing different soil amendments.

Preliminary results show differences in element translocation: for instance, higher concentrations of both nutrients and PTEs are observed for guttation fluids sampled from *L. rigidum* plants grown in PGPR amended mesocosms. On the other hand, no Pb is detected in guttation drops of plants grown in the Acerra soil, suggesting no uptake of this element from the soil. This is in accordance with the very limited mobility of Pb, already investigated in this soil, due to Pb immobilization as insoluble phosphates.

These early evidences encourage us to continue this research, with the final scope of developing a non-invasive reliable and expeditious method for assessing the element uptake and translocation to shoots using TXRF for guttation fluids analysis.

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