Geophysical Research Abstracts, Vol. 8, 04993, 2006
SRef-ID: 1607-7962/gra/EGU06-A-04993

Metal accumulation on pectins and mobilization by root exudates as affected by esterification

S. Deiana, G.P. Lauro, A. Premoli, and C. Senette

Dipartimento di Scienze Ambientali Agrarie e Biotecnologie Agroalimentari, Università di Sassari, V.le Italia 39, 07100 Sassari, Italy.

e-mail: sadeiana@uniss.it

Pectic polysaccharides are constituted mainly of galacturonic acid residues that are commonly partially esterified. Methyl ester groups affect the cross-linking of pectinate molecules by Ca^{2+}, thus controlling the organization of polisaccharides in plant cell walls, apoplast and at the soil root-interface, and, consequently, affecting the transport and accumulation of micronutrients.

A network of Ca-polygalacturonate (Ca-PGA) has been employed as a model of the root mucilage to study the mechanisms which regulate the transfer of nutrients through the roots mucillages. These studies gave evidence of the ability of the polysacharidic matrix to complex ions, such as Cu(II), Al(III), and Fe(III) and allowed to define the mechanisms of complexation as well as the modification induced by such ions on the fibrillar structure which characterize the Ca-polygalacturonate network (1). With the aim to investigate whether esterification with methanol of the carboxylic groups can affect the accumulation of Cu(II), Pb(II), Cd(II), Zn(II), Fe(III) and Cr(III) and their mobilization by citric, malic and pyruvic acid, a study about the interactions which these metal ions can establish with Ca-polygalacturonate (PGA) and a Ca-polygalacturonate network with a degree of esterification of 65% (PGADE) was carried out.

The absorption kinetics at pH 3.5, 4.7 and 6.0 of Cu(II), Pb(II), Cd(II) and Zn(II), at different initial metal concentrations (from 180 to 540 μM), by a PGA network containing 162 μmoles of COOH groups, in the presence of $CaCl_2$ 3.0 mM to simulate the real conditions, indicate a higher affinity of Pb(II) and Cu(II) respect to Zn(II) and Cd(II) towards the polysacharidic matrix. In particular, the amounts of Cu(II) e Pb(II) absorbed at an initial concentration of Cu(II) and Pb (II) equal to 540 μM, at pH 3.5, 4.7 and 6.0, were 61, 65, 70 and 65, 70 and 74 μmoles, respectively. The simultaneous absorption kinetics of Pb(II) and Cu(II) at the same pH values indicate a higher affinity of Pb(II) towards the binding sites of PGA.

The absorption kinetics of Cr(III) and Fe(III) show a high capacity of PGA to accumulate these ions, in particular Fe(III) whose accumulation is about three-fold that of Cu(II), Pb(II) and Cr(II). The FT-IR spectra of the Pb(II)-, Cu(II)-, Cu(II)-Pb(II)-, and Cr(III)-PGA systems suggest that the carboxylate groups are mainly involved in the coordination of the metal ions through a sole oxygen atom (inner-sphere complexes). In contrast, the spectra of the Cd(II)-, Zn(II)-PGA, and Fe(III)-PGA, similar to those of the Na- and Ca-PGA, indicate a bidentate structure of the carboxylate groups (outer-sphere complexes) (2).

The absorption of these ions, excepted Fe(III), is strongly conditioned by the esterification and appears controlled by the carboxylate content (two carboxylate groups for each metal ion). The different behaviour observed for Fe(III) is attributable to the formation of hydroxy-polymers, as suggested by FT-IR and X-ray analyses. However, the presence of methyl ester groups lowers the amount of Fe accumulated of about 37%. This aspect can be explained by considering that carboxylate groups tend to expand the structure of pectins as a result of their charge. Methylated groups do not modify substantially the space available to accumulation but their hydrophobic character causes a different effect on the accumulation of Fe(III).

Citric, malic and, at a minor extent, pyruvic acid mobilize from both PGA and PGADE a discrete fraction of the all the ions tested. It is important to underline that mobilization of the metal ions from PGADE occurs at times longer than those of the analogous PGA systems which is attributable to the hydrophobic action of the ester groups towards the organic acid considered as well as to conformational modifications induced by the metal ion accumulated.

1. Deiana S., Manunza B., Palma A., Premoli A., Gessa C.. 2001. Interaction and mobilization of metal ions at the soil root interface. In “Trace Elements in the Rhizosphere”, G. Gobram Ed., CRC Press. pp.127-148.
2. Deiana S., Premoli A., Senette C., Gessa C. 2004. Influence of copper on the accumulation of iron by the root polyuronic components. Recent Research in Soil Sci., vol. 2, 161-180.