Geophysical Research Abstracts
Vol. 16, EGU2014-13421, 2014
EGU General Assembly 2014

Spin Labeling ESR Investigation of a Role of Humic Acids at Covalent Binding of Xenobiotics to Soil

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The environmental risk of organic xenobiotic chemicals released into soils is controlled by their sorption and binding processes. However, the molecular mechanisms of reversible and irreversible interactions of xenobiotics with soil constituents and an influence of humic substances on this interaction are only partly understood. New methods and approaches aimed at understanding of molecular mechanisms in the soil environment and a role of humic substances in the sorption and binding processes are today required to manage and keep the quality of soil used and fertilized in agricultural industry.

The paper presents a new approach of using stable ESR spin labels to investigate a role of humic substances in the interactions of organic xenobiotic chemicals with constituents of natural soil via the typical functional groups of xenobiotics, such as Amines. At the experiment, the nitroxide spin labels, such as TEMPO (2,2,6,6-Tetramethylpiperidin-1-oxyl), Amino-TEMPO (4-amino-2,2,6,6-Tetramethylpiperidin-1-oxyl) and Aniline spin labels (2,5,5-Trimethyl-2-(3-aminophenyl)pyrrolidin-1-oxyl), were added to samples of different natural soils, such luvisol, cambisol and chernozem. Amino-TEMPO and Aniline spin labels include the aliphatic amino and aromatic amino functional groups, respectively.

A significant broadening of the ESR spectrum of Aniline spin labels incubated in different soils indicated a stable effect of covalent binding of the spin labels to soil constituents via the aromatic amino, whereas the ESR spectra of the other two spin labels were not broadened that pointed at the absence of covalent binding of spin labels via the aliphatic amino. As shown, a part of bound spin labels via the aromatic amino increased with increasing of the concentration of humic acids in soil. The same broadened signals were also be detected with the humic acids extracted from the investigated soils. A strong covalent binding of spin labels to humic substances via the aromatic amines was also revealed by the incubation of spin labels with Leonatdite and Pahokee. The effect became stronger with an increase in the aromaticity of humic acids, and in the case of Leonardite, a broadened ESR signal was observed for more than a half a year. A broadened ESR spectrum of Aniline spin label incubated with Leonardite also pointed at the formation of associates of a large size (> 50 kDa).

The experimental results showed a preference for the aromatic amino functional group in irreversible simultaneous binding of xenobiotics to soil constituents in contrast to the aliphatic amino. The unchanged signals of soil organic radicals incubated with Aniline spin labels rules out radical coupling and suggests a nucleophilic addition reaction as the covalent binding mechanism. The experimental results with humic acids from investigated soils, as well as with Leonardite and Pahokee shows that humic acids substantially influence the effect of covalent binding. They stably bind xenobiotics via the aromatic amines and strongly grow in size.