



## Elucidation of meso- and microporosity in soil components with $^{129}\text{Xe}$ NMR spectroscopy of adsorbed xenon

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Soil meso- and micropores (2-50 nm and  $<2$  nm) are usually studied with the use of common adsorption methods. As a complementary technique,  $^{129}\text{Xe}$  NMR spectroscopy of adsorbed xenon was only recently suggested for the use in soil science. In this present study, we applied both conventional, i.e. thermally polarised (TP), and hyperpolarised (HP)  $^{129}\text{Xe}$  NMR for elucidating pore environments of a series of samples representing porous soil constituents. Aluminium (hydr)oxides,  $\text{Al}_2\text{O}_3$  and  $\text{AlOOH}$ , both pure and subjected to the sorption of dissolved organic matter (DOM) were chosen as model mineral systems. Charcoals were used for understanding adsorption behaviour of xenon within organic polymeric structures formed by thermally altered bio-macromolecules. Natural soil particle size fractions were obtained from a non-allophanic Andosol and from Arenosol, i.e. soils containing charred residues and also characterised by a high content of Al oxides (case of the Andosol).

DOM sorption on the studied Al oxides occurred inhomogeneously as it was inferred from the existence of the “empty” pores and the pores coated with OM. The latter were evidenced by the different Xe adsorption enthalpies estimated from the temperature dependences of the chemical shift. The increased sensitivity of the HP  $^{129}\text{Xe}$  NMR allowed us detecting micropores in the charcoals, where the  $\text{N}_2$  adsorption method underestimated porosity due to the restricted diffusion of  $\text{N}_2$  at 77 K. The observed differences between the HP and TP  $^{129}\text{Xe}$  patterns were explained by the slow diffusion of xenon within an interconnected but highly constricted pore system of the charcoals. The estimated width of those constricted pore openings was of the order of one or two diameters of the Xe atom. Similar “bottle neck” effects may also exist in the natural soil particle size fractions, as it was inferred from the increased pore access for Xe adsorption performed at elevated pressures (2-4 bar). The unusually large  $^{129}\text{Xe}$  shifts (up to 170 ppm) detected for the for the  $\text{H}_2\text{O}_2$ -treated clay fractions of the Andosol (Bw horizon) coincided with their large specific surface areas (up to 220  $\text{m}^2/\text{g}$ ) and were attributed to the pores formed by agglomerates of the nano-sized Al – humus complexes with contribution from the charred residues. Micropores found in the Arenosol fractions were attributed to the charred residues.

Briefly,  $^{129}\text{Xe}$  NMR spectroscopy shows its potential for studying soil meso- and micropores due to: i) higher sensitivity for probing micropores within polymeric organic structures, e.g. charcoals, as compared to the  $\text{N}_2$  adsorption; ii) possibility to use elevated pressures of the adsorbate for increasing the pore accessibility; iii) evaluating not only the pore size range but also adsorption enthalpies that reflect the nature of Xe - pore surface interactions. On the other hand, a combination of the HP- and TP  $^{129}\text{Xe}$  NMR was shown to be helpful for modelling the pore structures of solids, since relaxation phenomena determining appearance of the HP  $^{129}\text{Xe}$  NMR patterns also relate to the pore attainability.