Geophysical Research Abstracts
Vol. 16, EGU2014-13105-1, 2014
EGU General Assembly 2014

Exploring new Routes for Identifying Phosphorus Species in Terrestrial and Aquatic Ecosystems with ^{31}P NMR

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Phosphorus (P) is the primary growth-limiting nutrient in some of the world's biomes. Rock phosphate is a non-renewable resource and the major source of agricultural fertilizers. Predictions of P consumption indicate that rock phosphate mining may peak within 35 years, with severe impacts on worldwide food production[1]. Organic P compounds constitute a major fraction of soil P, but little is known about the dynamics and bioavailability of organic P species. Our aim is to develop new liquid and solid state ^{31}P-NMR (nuclear magnetic resonance) techniques to identify P-species in water and soils; information required for correlating P speciation with plant and soil processes[2], and eventually to improve P use. Soil organic P is frequently extracted using NaOH/EDTA, followed by characterization of the extract by solution ^{31}P-NMR. However, the obtained NMR spectra usually have poor resolution due to line broadening caused by the presence of paramagnetic ions. Therefore, we successfully developed an approach to avoid paramagnetic line broadening by precipitation of metal sulfides. Sulfide precipitation dramatically reduces NMR line widths for soil extracts, without affecting P-composition. The resulting highly improved resolution allowed us to apply for the first time 2D ^{1}H,^{31}P-NMR methods to identify different P monoesters in spectral regions which are extremely crowded in 1D NMR spectra.[3] By exploiting 2D ^{1}H-^{31}P NMR spectra of soil extracts we were able to unambiguously identify individual organic P species by combining ^{31}P and ^{1}H chemical shifts and coupling constants. This approach is even suitable for a structural characterization of unknown P-components and for tracing degradation pathways between diesters and monoesters[3,4].Currently we apply our approach on boreal[4] and tropical soils with focus on Burkina Faso. In addition we also monitor P-species in aqueos ecosystems. For this purpose stream water from the Krycklan catchment in northern Sweden[5] has been used to develop a new method to retrieve and characterize P components in water. By utilizing passive sampling with ion-exchange resin and subsequent analysis with solid state ^{31}P MAS NMR we could identify various P-species extracted from the aquatic systems. By using this approach we can also study the dynamics of the absorption process at the resin as a function of P-species and temperature. This even enabled us to extract the fraction of bound versus free P as a function of temperature for different model P-components (manuscript in preparation).

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