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Selective preservation of carbohydrates in volcanic ash soils

J Kaal (1), P Buurman (2), KGJ Nierop (3), and A Piccolo (4)

(1) IEGPS-CSIC-XuGa, Instituto de Estudios Gallegos Padre Sarmiento, Santiago de Compostela, Spain (joeri@samage.net), (2) Earth System Science, Wageningen University. P.O. Box 47, 6700 AA Wageningen, the Netherlands, (3) Earth Sciences - Organic Geochemistry, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, Netherlands, (4) Dipartimento di Scienze del Suolo, della Pianta, dell'Ambiente e delle Produzioni Animali (DISSPAPA), Università di Napoli Federico II, 80055 Portici, Italy

Volcanic soils (Andosols) are formed in volcanic ash and depending on environmental and climatic factors they develop to two main forms, either allophanic Andosols (dominated by amorphous minerals) or non-allophanic Andosols (dominated by Al/Fe organic matter complexes). Andosols contain the largest amounts of organic carbon of all mineral soil orders. In recent studies using analytical pyrolysis techniques on the soil organic matter (SOM) of allophanic soils from the Azores Islands (Portugal) there was no indication of preservation of plant-derived organic matter by allophane or Al3+, but the presence of large amounts of (microbial) polysaccharides and chitin suggested that secondary organic matter products were stabilized. In the present study we used 13C NMR to further explore the organic matter of the Andosols of the Azores, and applied a molecular mixing model (MMM; ascribing characteristic resonances to the main biocomponent classes carbohydrate, protein, lipid, lignin and char) to the quantified NMR spectra to allow for a quantitative comparison with pyrolysis-GC/MS.

The dominance of O-alkyl and di-O-alkyl C in the NMR spectra and carbohydrate contribution to the predictions made by the MMM (50 $\pm$ 8%) confirms that the majority of the SOM can still be recognised as carbohydrate. The accumulation of secondary/microbial carbohydrates (and, to a lesser extent, secondary proteinaceous matter and chitins) is thus a key characteristic of these Andosols.

NMR-MMM and pyrolysis-GC/MS were in rough agreement. However, NMR does not recognise chitin (N-containing carbohydrate-like material) and chitin-associated protein, nor can it be used to estimate the degree of degradation of the carbohydrates. Therefore, NMR (as applied here) has a very limited capacity for characterisation of the SOM particularly in the Andosols studied. On the other hand, large peaks from carboxylic and amidic functional groups detected by NMR were not observed by pyrolysis-GC/MS. It is therefore recommended that the chemistry of Andosol SOM is assessed by a combination of these complementary methods.