Analysis of carbon forms in chemically-modified peat humic acids by partial least squares regression analysis of solid-state nuclear magnetic resonance spectra

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Classical structural studies on soil organic matter often show that the natural variability in C- and N forms in soil humic acids (HAs) is in many cases not enough to distinguish significant differences amongst HAs from different origin. In the present research contrasting C-distribution patterns are obtained when the HAs are modified in the laboratory through chemical treatments (derivatization reactions or methods focused to incorporation or removal of specific structural constituents). For instance, oxygen functionality can be modified by introducing or blocking the major functional groups (methylation, acetylation, oximation, nitration, sulphonation, etc). Other treatments lead to selective hydrolysis or drastic peroxydation of the HA carbon backbone. Apart from this, N-groups can be introduced in the HA structure by e.g., nitration, oximation, amidation or ammonification.

A series of chemically-modified HA preparations were obtained from a sapric peat (Vivero peat, Northern Spain) and their 13C nuclear magnetic resonance spectra (13C NMR) were obtained, showing the success of the above treatments which lead to contrasted NMR profiles. This set of 12 HA preparations was considered suitable material to assess the extent to which 13C NMR spectroscopy reflect the induced structural modifications, as well as to help the assignation of signals in conflicting chemical shift ranges.

In order to improve the interpretation of the 13C NMR spectra, partial least squares regression (PLS) was used as a multivariate chemometric tool based on covariance. This is a convenient method in cases where the number of variables (spectral points in the 200–(-25) ppm spectral range with 1-ppm resolution) is high as regards the number of individuals (modified HAs), mainly when there is large redundancy in data sets of variables mutually correlated. The spectroscopic information in the spectral matrix is processed by successively examining independent variables from an external matrix of up to 150 HA descriptors (elementary composition, infrared-, visible- and fluorescence-spectroscopies, pyrolytic compounds, in vitro biodegradability, effects of HA on soil physical, chemical and agro-biological properties, etc).

By means of PLS regression, a factor analysis is carried out to describe the data structure aiming to the automated interpretation the spectra. After selecting the models in which the independent variables are more significantly forecasted from the spectral data, the resulting values of variable importance for projection (VIP) for each independent variable were plotted in the whole chemical shift (after moving averages smoothing) to obtain a profile illustrating spectral signals explaining most of the variability of each of the independent factors. The results suggest the possibility of identifying characteristics of the HAs with a role on its environmental properties. The structural characteristics of the HAs studied here which were reflected in the whole 13C NMR spectra corresponded mainly to oxygen containing functional groups (r= 0.751), aromaticity as indicated by optical density at 465 nm (r= 0.651) and (inversely) by H/C atomic ratio (r= 0.638) or infrared spectroscopy (band at 1540 cm-1, r= 0.424). To a lower significance level, the raw NMR data showed promising predicting potential as regards HA molecular size, concentration of N-compounds and yield of typical pyrolytic fragments mainly alkylphenols. The VIPs also showed the interest of the some 13C NMR signals in forecasting important physical properties of soils treated (4 Mg ha-1) with these HAs (mainly water holding capacity and aggregate stability). Further studies based on the combined analysis of 13C and 15N spectra of HAs are in progress in order to examine distribution of N-forms in peat and its possible correlation with soil agroecological properties.