



ADVANCES IN NATURAL ORGANIC MATTER
AND HUMIC SUBSTANCES RESEARCH
2008-2010

XV Meeting of the
International Humic Substances Society
Puerto de la Cruz, Tenerife, Canary Islands, 27 June - 2 July 2010

Proceedings
Vol 2



J.A. González-Pérez, F.J. González-Vila, G. Almendros Eds



Characterization of Peatland Soils from the High Andes by ^{13}C NMR Spectroscopy

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1. Introduction

Wetlands constitute around 1 % of the global landmass and their soils are home to many specialized organisms that are found nowhere else. Soils formed from waterlogged organic matter are known as peats, and contain a high percentage of organic matter. Peatlands are estimated to currently store 224 to 455 Pg of carbon, equal to 12-30% of the global soil carbon pool. In the high Andean mountains these ecosystems are valued for their role as regulator of the hydrological cycle, habitat for plant and animal species, carbon sink, good quality grassland, and their scenic value. These tropical and sub-tropical peatlands from the Andean highlands or cushion peat bogs are also known by local farmers as bofedales, which areas can sensitive to environmental conditions and climate change that might have direct and indirect effects on the sustainability of the agroecosystem [1].

The objectives of this study were: 1) to study whole soils samples from Andean peat lands using Solid-State ^{13}C Nuclear Magnetic Resonance (NMR); 2) to make a qualitative characterization of predominant chemical structures of these kind of soils; and, 3) to evaluate the usefulness of principal component analysis of ^{13}C NMR spectra to hypothesize distributional patterns of these soils and to characterize the changes throughout the soil profile.

2. Materials and Methods

Permanent waterlogged and wet grassland (seasonal) bofedales from Huayllapata, Peru at an average altitude of 3,881 m asl, were selected as representative wetlands of the Central Andes. Seasonal bofedales presented scarcely vegetal coverage, since this grassland type is heavily

grazed by sheep, bovines and cameloids during the rainy season that in this study ended right before the sampling. The permanent waterlogged bofedales sampled had a more dense vegetation and much higher pasture availability. Soil samples were collected in April 2008 at different depths: 0-2.5 (1), 2.5-5 (2), 5-10 (3), 10-20 (4) and 20-30 (5) cm in seasonally flooded (A) and permanently flooded bofedales (B). Dry soil samples were ground and sieved to pass 0.25 mm particle size, in order to reduce the heterogeneity of the samples. The total organic carbon concentration of the evaluated wetland soils varied from 121.7 to 215.6 g C kg⁻¹, in the top 30 cm. Variable-amplitude cross-polarization (VACP) NMR experiments were performed using a VARIAN INOVA spectrometer at ¹³C and ¹H frequencies of 100.5 and 400.0 MHz, respectively, and a Jackobsen 5-mm MAS double-resonance probe head. Magic-angle spinning (MAS) at 5 kHz, with total suppression of spinning sidebands (TOSS), was employed to suppress spinning sidebands. The TOSS sequence was implemented with composite π pulses, to achieve a better inversion of the magnetization [2]. Two-Pulse Phase-Modulation (TPPM) proton-decoupling technique with field strength of 60 kHz, cross-polarization contact time of 1ms, and recycle delay time of 500 ms were used. Principal component analysis (PCA) was carried out using the spectra, obtained after area normalization and mean-centering of the data.

3. Results and Discussion

The ¹³C NMR spectra (Fig. 1) presented typical features of soil organic matter, dominated by fresh plant debris such as cellulose and alkyl C groups, probably of plant origin, such as cutin, suberin and wax. As expected, the lignin signals were imperceptible due to the major contribution of cellulose in fresh material. However, there seems to be an ongoing oxidation (humification), since the carboxyl signal is prominent, indicating a partial oxidation of this vegetable material, probably cellulose to glucuronic acids. The contribution of fatty acids (cutin, suberin and wax) to this signal is also expected [3]. The samples from the upper layers (A1 and B1) are very similar, but this similarity decreases with depth. Additional carboxylic signal at 169 ppm can be observed in the deeper layers of both soils, but more evident in the samples from soil A. This signal can be attributed to carboxyl groups attached to aromatic rings.

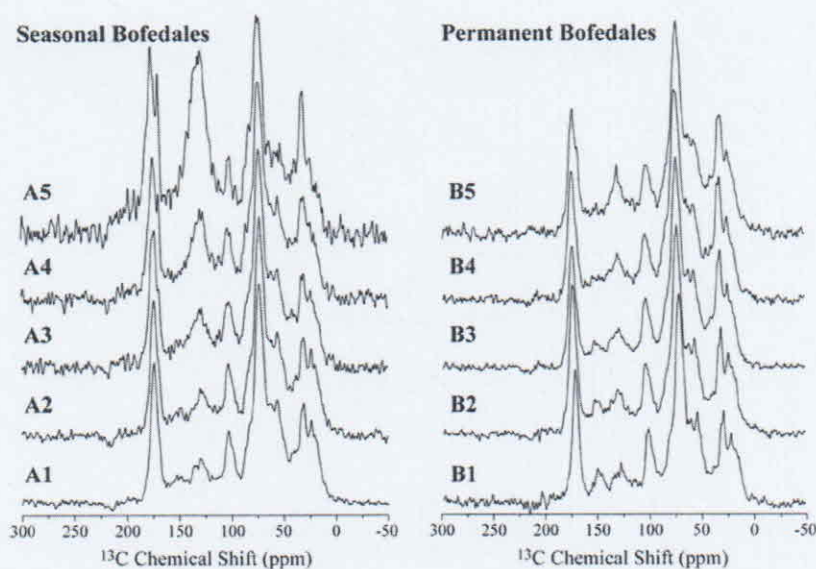


Figure 1: Spectra of peatland soils obtained by VACP/MAS ^{13}C NMR.

In general, ^{13}C NMR results can be properly summarized by the PCA analysis (Fig. 2). The first principal component (PC1), which accounted for 78% of the total variance, is characterized by positive loadings at 130 and 169 ppm, typical of aromatic structures with carboxylic moieties, and negative loadings for fresher material such as cellulose (104 and 73 ppm), methoxyl from lignin, or more probably N-alkyl from proteinaceous material (56 ppm) and fatty acids (21, 33 and 172 ppm). This last signal can also be related to oxidised cellulose. The scores of this PC showed a clear gradient along the sampling depth, in the soil A. In the soil B, this component is present in lower concentration, or even absent. This means that in soil A, samples from the bottom of the layer presented a higher concentration of carboxylated aromatic structures and lower concentration of fresh material. Soil B, in turn, was better characterized by the PC2, which explained 8 % of the total variance. The gradient shown by samples from this soil also increased with depth. This component is characterised by positive loadings for crystalline polymethylene (33 ppm) and some polyalcohol (77 ppm), probably the C-4 of the cellulose or aliphatic portion of lignin structure (unsaturated alcohol) and a sharp aryl signal (131 ppm). The negative loadings (i.e., compounds more abundant in the surface samples) can be attributed to partially oxidised cellulose to glucuronic acids (172, 103 and 72 ppm), guaiacyl and/or syringyl from lignin (56 and 152 ppm) and terminal methyl groups (16 ppm).

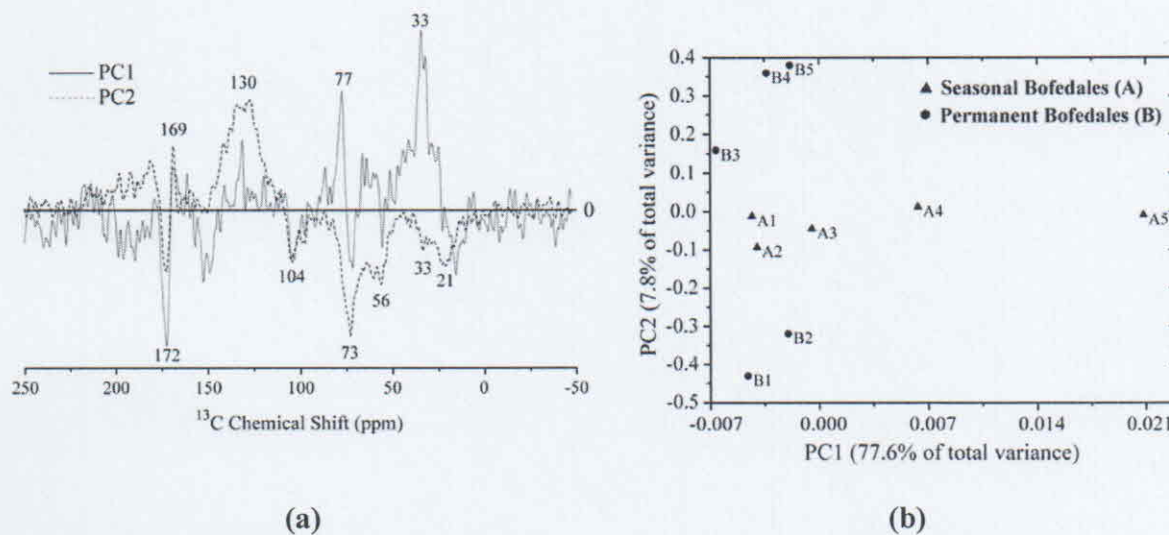


Figure 2: PCA results from ^{13}C NMR spectra: (a) loadings and (b) scores

4. Conclusions

These results indicated that the humification process occurs at the bottom of the top layer and onwards, where a larger proportion of humified materials are found. This was expected due to the constant input of fresh material in the surface. Notwithstanding this process is different in each soil. In soil A, the accumulated recalcitrant material is mainly composed of carboxylated aromatic moieties; whereas in soil B, the accumulated material is mainly crystalline polymethylene. This difference could be due to the specific edaphic conditions in each soil and/or differences in the vegetation. On the other hand, the degradable (labile) material is similar in both soils (i.e., mainly cellulose and partially oxidised cellulose). The difference in the lignin composition in the permanent bofedales soil can indicate a change in the vegetation. In the past (deeper samples) the area would have a predominance of C-4 herbaceous vegetation whose lignin has more coumaryl alcohol at the expense of guaiacyl and syringyl units, and more recently a predominance of C-3 herbaceous vegetation.

Acknowledgements

International Potato Center (CIP), through its CIDA-funded project ALTAGRO.

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