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Pyrolysis-Gas Chromatography/Mass Spectrometry Characterization of Humic Acids in Spodosols Under Tropical Rain Forest in Southeastern Brazil

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1. Introduction

The present study aims to contribute to a better understanding of the podzolization processes in intrazonal tropical podzols, specifically in the Restinga forest of São Paulo state. Podzolization is the main pedogenic process in Restinga and the most common soils are Spodosols (podzols) and Quartzipsamments (Arenosols) with incipient podzolization. This study addresses the same samples that were earlier studied by González-Pérez et al. [1] by ^{13}C Nuclear Magnetic Resonance Spectroscopy using Variable Amplitude Cross Polarization and Magic Angle Spinning Technique (^{13}C VACP/MAS NMR) and by Fourier Transform Infrared Spectroscopy (FTIR). Pyrolysis in combination with gas chromatography and mass spectrometry (Py-GC/MS) adds to previous results information about molecular fragments, individual structures such as polysaccharides, lignin moieties, and fatty acids. This latter information can be used to reconstruct the origin (microbial, plant-derived, specific species), degradation mode, degradation state of the SOM and also their role in podzolization process [2, 3]. Although HAs constitute only part of the SOM in podzols, it is expected that conclusions based on this fraction can be extrapolated to the total SOM.

2. Materials and Methods

General comments on soils and previous analysis

Three of the sandy spodosols of Cardoso Island (a Natural Park in the State of São Paulo, Southeast – Brazil) under Restinga forest, were selected for this study. Profile H13 is a Histic Alaquod, profile C14 is a Typic Alorthod, and profile H9 is an Arenic Alorthod [4]. The horizon sequences are given in Table 1. All profiles are hydromorphic and virtually iron depleted.

Table 1: Particle size fractions and some chemical properties of the three profiles

Soil/ Horizon	Depth cm	Sand	Silt	Clay	pH H_2O	C/Me[1]	C	N	C/N
		----------g kg^{-1}----------					------g kg^{-1}------		
Profile H13 - Histic Alaquod									
Ho	0–10	n. d.	n. d.	n. d.	3.8	14.9	319.0	15.3	20.9
Hd	10–20	n. d.	n. d.	n. d.	4.0	40.5	241.0	5.4	44.6
A1	20–30	n. d.	n. d.	n. d.	4.2	40.5	68.9	1.0	68.9
E	30–38	970	0	30	4.3	0.0	4.7	0.5	9.4
Bhs1	38–55	970	0	30	3.3	13.5	30.3	0.9	33.7
Bhs2	55–75	960	0	40	3.2	11.1	15.5	0.4	38.8
Bhs3	75–130	950	10	40	3.3	6.1	8.8	0.5	17.6
Profile C14 - Typic Alorthod									
A	0–15	960	0	40	4.3	12.4	35.8	1.9	18.8
AE	15–20	980	0	20	4.3	16.0	2.2	0.3	7.3
E	20–50	980	10	10	5.0	0.0	0.3	0.3	1.0
Bhs1	50–58	920	0	80	4.0	14.8	37.4	1.4	26.7
Bhs2	58–75	900	0	100	4.0	10.4	64.2	1.9	33.8
Bhs3	75–100	920	10	70	4.8	2.5	17.5	0.8	21.9
Bs1	100–120	910	30	60	4.8	1.4	9.8	0.8	12.3
Profile H9 - Arenic Alorthod									
A	0–20	970	0	30	4.7	28.8	16.4	1.0	16.4
AE	20–28	980	0	20	4.6	75.0	2.9	0.7	4.1
E1	28–41	980	0	20	4.8	80.0	0.8	0.2	4.0
E2	41–95	980	0	20	5.0	80.0	0.3	0.2	1.5
Bhs1	95–103	940	10	50	4.2	9.9	28.6	1.1	26.0
Bhs2	103–130/140	950	10	40	3.4	9.1	17.1	0.8	21.4
Bhs3	130/140–180+	960	10	30	3.4	5.4	9.0	0.5	18.0

[1]C/Me = carbon/metal ratio; Me=Al_P+Fe_P

Description of the area, morphology of profiles and chemical and mineralogical data are given by Gomes et al. [5]. Micromorphological characteristics, the procedure used for extraction and purification of humic acids, and the results of ^{13}C VACP/MAS NMR and FTIR spectroscopy are described in a previous paper [1].

Pyrolysis- Gas Chromatography/mass-spectrometry (Py-GC/MS)

Humic acids were pyrolyzed using a Horizon Instruments Curie-Point pyrolyzer (Curie temperature of 600 °C) connected to a Carlo Erba gas chromatograph. The pyrolysis products were separated on a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51b (film thickness 0.40 μm). Helium was used as carrier gas. The initial oven temperature was 40 °C with a heating rate of 7 °C min^{-1}. The final temperature of 320 °C was maintained for 20 min. The GC column was connected to a Fisons MD800 mass spectrometer (mass

range m/z 45-650, cycle time 1s). Products were identified using the internal NIST library and published sources [6, 7].

Statistical analysis

Factor analysis was carried out using Statistica Version 6 (StatSoft, Tulsa, UK). Factor analysis allows the recognition of correlations between variables and the detection of structures in the data set. It is a prime method to reduce the number of variables and to classify variables.

3. Results and Discussion

The 136 different pyrolysis products were identified in all samples and quantified using the two main fragment ions of each compound. Pyrolytic compounds were grouped according to probable origin and chemical similarity. The dominant groups in all horizons are aromatics, lignins and phenols, but there is significant variation within and between profiles. There do not appear to be consistent depth trends for any of the chemical groups.

Factor analysis was carried out using all 136 quantified pyrolysis products for the 15 samples. Two factors explained 53.2% of all variation, while four factors explained 72.9%.

Micromorphology indicates that horizons Bhs3 and Bs1 of profile C14 are fully dominated by monomorphic (DOC-derived) organic matter. The Bhs2 and Bhs3 horizons of profile 9 have a large amount of roots in various stages of decomposition. The other B-horizons have varying amounts of—largely decomposed—roots. These observations are in agreement with the plot of samples in the Factor score Diagram.

The Py-GC/MS results corroborate those obtained by ^{13}C VACP/MAS NMR and FTIR [1].This is especially true for the following features:

- The highly aliphatic character in the topsoil of profile H13.
- The high aromatic (lignin) content in the lower horizons of profile H9.
- Similarities among chemical composition of B horizons of profiles H13 and C14 and their differences with profile H9.

In addition, the pyrolysis data give reliable information concerning the relative amounts of DOC- and root-derived SOM. There appear to be degradation paths for alkanes and alkenes (shorter chain lengths), lignins (loss of methoxyls and OH-groups) and phenols (loss of OH groups). Aerobic decay in topsoils appears to lead to a relative accumulation of aliphatics.

This is not clearly illustrated by the present samples because E-horizons and EB horizons have not been sampled. Anaerobic decay in subsoils, on the other hand, appears to lead to a relative accumulation of methylbenzenes and degraded polysaccharides at the expense of lignin and phenols.

4. Conclusions

Although morphological description of the three profiles did not indicate major differences, the chemical composition of the HAs obtained from pyrolysis data in the B horizons of profiles H13 and C14 of the three profiles was dominated by dissolved organic carbon, while the profile H9 was dominated by root-derived material. A dominance of DOC is witnessed especially by high abundances of phenol, methylphenols, and acetic acid. Some B horizons show a very strong degradation of the accumulated DOC. The cause of this degradation is still unclear. In hydromorphic podzols such as the ones studied here, both vertical and lateral DOC transport play a role in SOM accumulation in the B horizon. The morphology of profiles H13 and C14 suggests a major influence of lateral transport. Except for the two deepest horizons of profile C14, all horizons show chemical (and micromorphological) evidence of root-derived OM. Therefore, also in these tropical and largely badly drained podzols, both SOM illuviation and decay of roots play a large role in the accumulation of B-horizon OM.

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