

# Study of Humification of Soil Organic Matter in a Lowland Area

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**Abstract** The drainage process of organic soils can significantly alter the dynamics of soil organic matter (SOM) because, among other things, it promotes oxygenation of speeding through microbial activity. Spectroscopic techniques such as electron paramagnetic resonance (EPR) and laser-induced fluorescence (LIF) have been used in the study of humification of organic matter without the need for fractionating samples chemically or physically. The use of these techniques allows obtaining information free of the effects caused by fractioning. In this work, the EPR and LIF techniques were used to study the degree of humification of SOM from non-fractionated soil samples, collected in a lowland area at three levels and with different historical usage.

**Keywords** Humic acid • Laser-induced fluorescence • Electron paramagnetic resonance

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## Introduction

Little oxidative environments tend to modify and reduce microbial activity (Lüdemann et al. 2000). Consequently, the process of decomposition of soil organic matter (SOM) becomes slower and may in waterlogged soils provide reduction in the degree of humification of SOM with depth. The drainage process can significantly alter the dynamics of SOM in these soils by promoting increased oxygenation of the medium. Flooded soils generally present low concentration of  $\text{Fe}^{3+}$  ion, which enables the analysis using electron paramagnetic resonance (EPR) without physical or chemical fractioning of the samples (Saab and Martin-Neto 2004). The degree of humification of SOM samples collected in a lowland area in the following three points with different backgrounds was studied: (1) drainage and fallow for 24 years, (2) then drain rice cultivation in conventional tillage fallow for 10 and 14 years, and (3) reforestation with eucalyptus for 24 years. The profiles were collected at 0–10, 10–20, and 20–30 cm. In this work, samples of the areas a, b, and c are called noncultivated area (N), cultivated area (C), and area of reforestation (R), respectively.

## Materials and Methods

The soil samples studied in this work were collected in Ponta Grossa, PR, Brazil, at coordinates  $25^{\circ}10'20.11''$  and  $50^{\circ}0'21.99''$ .

In the noncultivated area, which is in fallow for the longest, the drainage process was less efficient. The area of reforestation still retains many original features such as high moisture content, however, and has been reforested with exotic species; it has been targeted for illegal burning for several years. The cultivated area was the one that suffered most intensely because the soil was plowed intensively for the 10 years than it has been cultivated. The degree of humification of the samples was evaluated by the techniques of laser-induced fluorescence (LIF), and electron paramagnetic resonance (EPR).

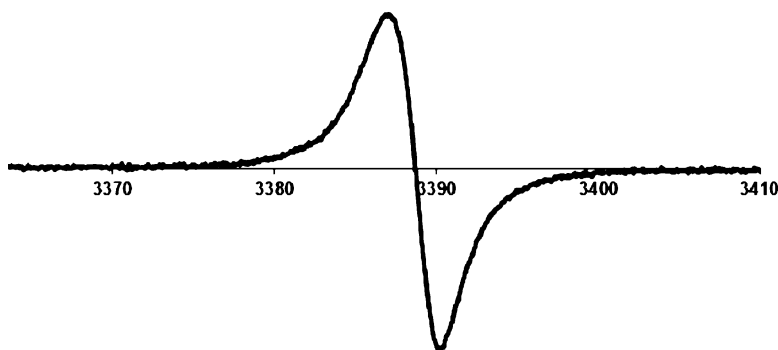
Measurements of LIF were performed in duplicate using soil samples crushed and sieved in 250 microns mesh. The equipment was operated under the following conditions: (1) lock in 100 mV, (2) photomultiplier 850 V, and (3) in an argon laser wavelength of 458 nm and 300 mW power. The degree of humification, as proposed in Milori et al. (2006), is proportional to the ratio between the area under the curve of the spectrum and the carbon content of the sample. EPR measurements were performed with a Bruker EMX X-band (9 GHz), with a modulation frequency of 100 KHz, using a rectangular cavity. The samples were placed in a 3.5-mm-diameter quartz tube, in duplicate, with 5 mm height and sample mass from 5 to 30 g. The center field was  $H_0 = 338$  mT and  $f = 9.52$  GHz, and the microwave power was 0.201 mW with an amplitude modulation of 10 mT at room temperature. The semiquinone free radicals were quantified by standard secondary using a

crystal of ruby ( $\text{Al}_2\text{O}_3$ ) containing 0.5%  $\text{Cr}^{3+}$ . Its factor is 1.9797 g and, therefore, does not interfere with the signal for semiquinone free radical, about  $g = 2.003$ . For elemental analysis, approximately 150 mg of dried soil aired and sieved to 1 mm mesh was used. The measurements were performed at elemental determinators C and N, TruSpec LECO CN, where the samples were burned at  $950^\circ\text{C}$  and the resulting combustion gas was analyzed through infrared detector.

## Results and Discussion

The use of electron paramagnetic resonance for studies of soil organic matter which is not chemically fractionated strongly depends on the mineralogy of the sample. In samples with high concentrations of paramagnetic metals as  $\text{Fe}^{3+}$ , the EPR signal of the semiquinone free radical signal can be overlaid by the metal (Bayer et al. 2000). The samples studied in this work have low concentrations of these metals, allowing the study by EPR without the need for any paramagnetic metal. Figure 1 shows the region of the free radical type of fractioning (Saab and Martin-Neto 2008). Figure 1 shows the EPR spectrum of the nine samples studied in this work. The indices of humification of the samples were evaluated by EPR and LIF. The data obtained is shown in Table 1.

The degree of humification evaluated by EPR and LIF can lead to different conclusions when analyzed separately. But when combined, we can see some points of agreement between the techniques. Under both techniques, the degree of humification of the samples from the reforestation area (R) is lower in more depth, which probably occurs due to decreased microbial activity in the profiles with higher humidity and lower oxygen content (Six et al. 2006). Another point in common between the two techniques is that the humification of the samples from the noncultivated area gradually increases with depth. The reason is probably the same as that for the opposite trend observed in the area forestry, since drainage



**Fig. 1** EPR spectrum of a sample of soil which is not discontinuous with low concentration of paramagnetic metal

**Table 1** Indicators of humification of the SOM

ERR Spins/gC ( $10^{18}$ )	LIF $H_{\text{FIL}}$ (a.u.)	C(g/kg)
$C_1$	$2.39 \pm 0.09$	$303.2 \pm 18.8$
$C_2$	$1.23 \pm 0.10$	$242.6 \pm 20.3$
$C_3$	$3.25 \pm 0.23$	$254.7 \pm 21.0$
$C_4$	$1.68 \pm 0.12$	$314.7 \pm 14.2$
$C_5$	$1.06 \pm 0.07$	$142.2 \pm 10.6$
$C_6$	$1.39 \pm 0.05$	$149.2 \pm 14.0$
$C_7$	$2.63 \pm 0.14$	$151.0 \pm 15.0$
$C_8$	$1.76 \pm 0.02$	$181.4 \pm 17.0$
$C_9$	$3.21 \pm 0.01$	$231.6 \pm 30.9$

EPR, LIF, and carbon content (C). The indexes 1, 2, and 3 represent the profiles 0–10, 10–20, and 20–30 cm, respectively

was performed in the noncultivated area, increasing oxygenation of the medium. The oxygenation of cultivated and noncultivated areas provided by the drainage favored the stabilization of the SOM and the accumulation of carbon in comparison to the reforestation area. These results highlight the need for simultaneous use of different techniques in studies of SOM, since the information provided by each one can lead to contradictory conclusions.

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