



## Partitioning of N in growing plants, microbial biomass and soil organic matter after amendment of N-ammonoxidized lignins

José M. De la Rosa<sup>a,\*</sup>, Falk Liebner<sup>b</sup>, Georg Pour<sup>b</sup>, Heike Knicker<sup>a</sup>

<sup>a</sup> Instituto de Recursos Naturales y Agrobiología, Consejo Superior de Investigaciones Científicas (IRNAS-CSIC), Reina Mercedes 10, 41012 Seville, Spain

<sup>b</sup> Department of Chemistry, University of Natural Resources and Life Sciences Vienna (BOKU), Konrad-Lorenz-Str. 24, A-3430 Tulln, Austria

### ARTICLE INFO

#### Article history:

Received 6 August 2012

Received in revised form

18 January 2013

Accepted 28 January 2013

Available online 13 February 2013

#### Keywords:

N fertilization

Plant-available N

Recalcitrance of technical lignins

Soil amendment

Soil organic N stabilization

### ABSTRACT

Nitrogen (N) availability is a crucial factor for maintaining soil productivity, but application of mineral N-fertilizer raises environmental concerns. Based on earlier humification models, ammonoxidized technical lignins were suggested as potential slow N-release fertilizers. In order to obtain first insights on their efficiency as plant fertilizer, their impact on soil organic matter composition and stability, and its role within the N cycle in soils, pot experiments were performed in which perennial ryegrass (*Lolium perenne* L.) was grown on a typical Andalusian soil (*Luvisol, chromic*) after amendment of N-lignins highly enriched in <sup>15</sup>N (Sarkanda and Indulin ammonoxidized lignins) for 75 days. For comparison, the incubation study was also carried out with soils with and without <sup>15</sup>NO<sub>3</sub> fertilization. Among these experiments, the addition of K<sup>15</sup>NO<sub>3</sub> resulted in the greatest aboveground plant production. However, most of the growth occurred during the first 28 days. Thereafter, a fast decrease of the bioavailable N pool occurred. The application of ammonoxidized lignins altered the pH and electrical conductivity of the soil. At higher concentrations a retardation of seed germination was evidenced. After 75 days, the plant shoots from the pots amended with <sup>15</sup>N-Indulin and <sup>15</sup>N-Sarkanda accumulated 8% and 20% of the initial <sup>15</sup>N present in the amended soils at the beginning of the experiment (<sup>15</sup>N<sub>0</sub>). In the <sup>15</sup>N-Indulin pots the N was efficiently sequestered from fast release or leaching and most of <sup>15</sup>N<sub>0</sub> remained in the soil (64%). In contrast, the <sup>15</sup>N-Sarkanda pots showed a lower efficiency in N retention. After 28 days of incubation only 42% of <sup>15</sup>N<sub>0</sub> was retained in the <sup>15</sup>N-Sarkanda amended soil, but more than 17% was recovered within the soil microbial biomass. Until the end of the incubation time, the <sup>15</sup>N<sub>0</sub> detected in the soil microbial biomass decreased to less than 3%, whereas the amount associated with the soil matrix maintained around 37%. The notable increase of <sup>15</sup>N in the above-ground plant production (20%) evidences an efficient use of <sup>15</sup>N released from the <sup>15</sup>N-Sarkanda for plant production. Solid-state nuclear magnetic resonance (NMR) spectroscopy revealed that the <sup>15</sup>N of the added <sup>15</sup>N-lignins was quickly transformed into peptide-type N, most tentatively of microbial origin, without major alteration of the lignin backbone. This indicates that in soils the competition for nutrients favors N immobilization into biomass with its subsequent sequestration within recalcitrant biopolymers rather than its stabilization via covalent binding to lignins.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Nitrogen (N) represents an important limiting nutrient in agricultural ecosystems. Most of the soil N is bound in organic forms, of which at least half is relatively inert and only gradually available to higher plants through microbial fixation and mineralization. Consequently, the use of N fertilizer (15 Tg yr<sup>-1</sup> in Western and Central Europe (Heffer and Prud'homme, 2011)) is necessary to maintain

constant levels of crop production. However, the intensive use of synthetic N fertilizers for agricultural crops has an unintended cost to the environment and human health due to surplus and inefficient application. Nitrogen runoff from farms threatens to contaminate surface and groundwater. Ammonia from fertilized cropland has become a major source of air pollution, whereas emissions of nitrous oxide form a potent greenhouse gas. Therefore, it is very important to find a rational fertilization strategy that can ensure a competitive production with minor impact on the environment.

As an alternative to costly conventional chemical N fertilizers the use of N-lignins produced by ammonoxidation of technical lignins was suggested (Neff et al., 2003). The latter are by-products

\* Corresponding author.

E-mail address: [jmrosa@irnase.csic.es](mailto:jmrosa@irnase.csic.es) (J.M. De la Rosa).

of the pulp and paper industry. Although generated in kilotons p.a. only about 2% of them (1 Mt yr<sup>-1</sup> lignosulphonates, 0.1 Mt yr<sup>-1</sup> Kraft lignin) are used commercially (Gosselink et al., 2004). However, since lignin represents an important precursor of soil organic material (SOM), its amendment to soils is expected to be helpful in the battle against desertification and to improve the global C balance toward C sequestration.

The ammonoxidation (also known as ammoxidation) was developed in the 1930s by Franz and Palm (Franz and Palm, 1930) as an industrial process for the production of nitriles using ammonia and oxygen. Based on the assumption that condensation of lignin with ammonia represents an important process during humification, the technology was later advanced for converting technical lignin into N-rich organic fertilizers (Flaig and Söchtig, 1967). The process was further improved in the 80s by introducing an ambient pressure technology that afforded products that contained lower amounts of N-heteroaromatic compounds in favor of higher portions of N-binding forms more easily mineralizable in soil and lower degree of structural lignin alteration (Fischer and Schiene, 2002). Here, the incorporation of N is achieved by the application of gaseous oxygen and aqueous ammonia at slightly elevated temperature which partly breaks down aromatic lignin moieties and introduces N in the form of urea, amides and amines. Although the respective products of this reaction were not yet detected in notable concentrations in natural soils (Schnitzer, 1985; Knicker, 2011), their assumed high resistance against microbial degradation may justify the application of N-lignins in agriculture. However, before they can be used, it has to be assured that their production and application is economically viable and environmentally sustainable. The latter requires that the N is bioavailable and can be used efficiently for plant growth. Further, it has to be ensured that neither the amendment nor the degradation products are harmful to the environment.

First tests of ammonoxidized lignins as slow N-release fertilizers in pot experiments with *Sorghum* confirmed that in comparison to fertilization with ammonium sulfate the application of N-lignins can lower N-leaching rates (Ramírez et al., 1997). Toxic effects on the plants were not reported. Thus, in theory, amendment of N-lignins may represent a feasible solution to reduce water pollution by nitrates from conventional fertilizers or liquid cattle manure with a concomitant increase of the recalcitrant soil organic C pool. However, further studies with *Sorghum* (Ramírez-Cano et al., 2001) indicated lower yields after application of N-lignins than after fertilization with urea during the first growing period. Only, during the second growing cycle, the N-lignin amended plants performed better than those treated with urea, supposedly because then the nitrogen from the N-lignin became readily available. Still, the mechanisms, involved in this process are not well understood. Comparably scarce is the knowledge about the impact of their degradation products on SOM composition and stability.

In order to fill this gap and to obtain a better understanding of the partitioning of N derived from N-lignins among growing plants, microorganisms and the SOM pool, pot experiments were performed using a typical soil of the Andalusian region (Southern Spain) on which *Lolium perenne* was grown for 75 days under the controlled conditions of a greenhouse. We applied ammonoxidized lignins with high <sup>15</sup>N-enrichments (<sup>15</sup>N-Sarkanda and <sup>15</sup>N-Indulin) and followed the partitioning of the released <sup>15</sup>N among the biological pools (plants and microorganisms) and SOM as a function of incubation time. In addition, soil without amendment and soil with K<sup>15</sup>NO<sub>3</sub> as fertilizer were tested for comparative purposes.

Compared to many other tracer studies, considerably high <sup>15</sup>N enrichments of up to 2.9 atm% for the <sup>15</sup>N-lignins and 98 atm% for the K<sup>15</sup>NO<sub>3</sub> were used. With this we ensured that the insensitive solid-state <sup>15</sup>N nuclear magnetic resonance (NMR) spectroscopy

can be applied as a tool for characterizing the chemistry involved in N immobilization and mobilization pathways. Analysis of the organic C fraction by solid-state <sup>13</sup>C NMR spectroscopy gave information about the impact of the lignin addition and N-availability on SOM quality.

## 2. Materials and methods

### 2.1. Soil sampling and characteristics

The soil matrix for incubation was obtained from the A horizon of a Terra rossa (*Luvisol, chromic*) (IUSS Working Group WRB, 2007) located below an olive tree plantation, close to Aljarafe in the province of Seville (SW Spain; 37° 21.32' N, 6° 4.07' W). Such soils are typical arable soils of Mediterranean regions and are described in detail by Mudarra Gómez (1988). Prior to the incubation experiments, the soil was dried and sieved (<2 mm) and small branches, fresh mosses and plant remains, as well as roots were removed manually.

### 2.2. Production of <sup>15</sup>N enriched ammonoxidized lignins

The ammonoxidation of the two technical lignins (Pine kraft lignin Indulin AT™, MeadWestvaco, Charleston, USA; Sarkanda grass soda lignin, Granite, Switzerland) was carried out in a stirred reactor using a 10% (v/v) aqueous solution of ammonia enriched with the <sup>15</sup>N isotope by a factor of ten in relation to its natural abundance. Reaction conditions were as follows: 0.5 MPa O<sub>2</sub>, 100 °C, 180 min.

During the ammonoxidation process the C content of <sup>15</sup>N-Indulin decreased from 59.9 to 53.5%, whereas nitrogen contents increased by a factor of four (from 1.0 to 4.2%). Enrichment to 2.9 atm% was achieved for <sup>15</sup>N. Similar values were obtained for <sup>15</sup>N-Sarkanda lignin changing the carbon and nitrogen content from 59.6 to 52.7% and from 1.5 to 5.9% respectively. Here, the <sup>15</sup>N enrichment comprised 2.6 atm%. The final C/N ratios (12.7 and 8.9 respectively) are appropriate for being used as a fertilizer (<20) (Meier et al., 1994).

### 2.3. Incubation experiments

A pre-experiment was carried out to determine i) the appropriate amount of lignin amendment to avoid an overload of nitrogen, and ii) the maximum running time of the incubation experiment. Therefore pots (250 cm<sup>3</sup>) were filled with 150 g of soil and the impact of adding 150, 300, 500, 1000, 1500 and 2000 mg of N-Indulin (not enriched with <sup>15</sup>N) on the growth of 0.5 g grass seeds (*Lolium perenne* L.) was tested in triplicate. After adjusting the soil humidity to 55% of the maximal water holding capacity, the pots were placed into a greenhouse under similar conditions to those reported by De la Rosa and Knicker (2011), briefly, 22 °C for 75 days (14 h light day<sup>-1</sup>) and water supply equivalent to 700 mm yr<sup>-1</sup>. The bottom of the jars was perforated to allow leaching of surplus water. The leachate was collected but its amount after freeze drying was not sufficient for further analysis. The aboveground plant biomass production (PBP<sub>above</sub>) was measured after 14, 28, 50, 60 and 75 days of incubation. Therefore, the shoots were cut, dried (24 h at 40 °C) and weighed at each of those intervals.

Based on the results of this pre-experiment and taking into account the C, N and <sup>15</sup>N contents of the soil and <sup>15</sup>N-lignins, the volume of the pots (250 cm<sup>3</sup>), as well as the detection limit of solid-state <sup>15</sup>N NMR spectroscopy, an addition of 2.0 g of <sup>15</sup>N-lignin per pot was chosen for the final incubation study. For each experiment, pots for four sampling dates were prepared in triplicate according to the conditions described above. For comparison, an additional series of pots with soil amended with K<sup>15</sup>NO<sub>3</sub> (99 atm%) was set up.

Download English Version:

<https://daneshyari.com/en/article/8365291>

Download Persian Version:

<https://daneshyari.com/article/8365291>

[Daneshyari.com](https://daneshyari.com)