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Research article

Synthesis and evaluation of a superabsorbent-fertilizer composite for maximizing the nutrient and water use efficiency in forestry plantations

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ABSTRACT

Reducing fertilizer use is a priority in the quest for sustainable forestry systems. In short rotation *Eucalyptus* plantations, NPK pellets are routinely added to the seedling's top soil layer at planting, potentially leading to increased seedling mortality, nutrient loss and environmental degradation. To address this triple challenge, the development of efficient fertilization practices is essential. In the present work, we synthesized a crosslinked acrylic-cellulosic superabsorbent composite (SAPH-BAL) containing small amounts of specific nutrients integrated in the polymer matrix. We analyzed the composite's chemical and rheological properties, and assessed the viability of *Eucalyptus* plantations supplied with it at planting. Physiological measurements confirmed the suitability of SAPH-BAL in greenhouse-grown potted seedlings subjected to different growth conditions, showing that it efficiently delivers nutrients while protecting seedlings from drought stress. Field experiments carried out at ten South American locations covering an ample range of environmental conditions confirmed the beneficial effect of SAPH-BAL on growth and survival in comparison to the conventional fertilization scheme (superabsorbent + 75 g NPK). Furthermore, it was found that plants treated with SAPH-BAL were less affected by the differences in rainfall regimes during the experiments compared to those fertilized conventionally. To the best of our knowledge this is the first report describing the successful use of superabsorbents for root targeted delivery of fertilizers in forestry operations.

1. Introduction

Due to the sustained demand for pulp and solid wood recorded worldwide, the forest industry has seen the need to develop tools for its expansion (Kröger, 2012). Silvicultural management of *Eucalyptus* plantations has allowed the extension of cultivated forests into lands that previously were not considered suitable (Booth, 2013; Montagu et al., 2003). In this regard, South America registered the highest worldwide annual increase in *Eucalyptus* plantations (ABRAF, 2013; FAO, 2008). There are still many challenges regarding the outplanting of greenhouse-grown seedlings to the field, where the availability of water and nutrients in the immediate vicinity of the rhizosphere determines the survival of individuals and affects the health and future performance of the plantation (Dell et al., 2003; Grossnickle and Folk, 1993; Tng et al., 2014).

Soil additivation at the site of final transplantation aims to improve two key aspects: the availability of water and the nutritional status (Whitehead and Beadle, 2004). In conditions where the supply of water and mineral nutrients is optimal, *Eucalyptus* has the potential of attaining fast carbon assimilation rates driven by a high stomatal conductance and net photosynthesis, which confers

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the attractiveness of the species for wood production (Albaugh et al., 2016; Hernandez et al., 2016). Specifically, to outcompete the natural flora at seedling establishment it is desired: *i)* a rapid increase in height and canopy volume to maximize irradiance use efficiency and, *ii)* a fast development of the root system, to reach ground water and soil nutrients (Davis and Jacobs, 2005; Grossnickle, 2005; Jacobs et al., 2004).

In order to obtain high initial growth rates, *Eucalyptus* plantations are mainly supplemented with granulated fertilizers containing nitrogen, phosphorous and potassium (a formulation traditionally known as NPK; Attiwil and Adams, 1996; Smethurst, 2010; Forrester, 2013). Although nitrogen (N) and potassium (K) are known to be limiting elements for *Eucalyptus* development (Christina et al., 2015; Dell et al., 2003; Herbert, 1990; Knecht and Göransson, 2004), phosphorous (P) supply at tropical and subtropical cultivated woods has shown to strongly correlate with performance in short and long term (Graciano et al., 2006; Herbert and Schonau, 1989; Tng et al., 2014). Due to its low mobility and the high initial demand of seedlings, P enriched fertilizers need to be applied in close proximity to the seedlings at planting so that the solutes are steadily available to the roots (Barros et al., 1992; Fernandez et al., 2000; Xu and Dell, 2003). Studies showed that forests that are initially properly fertilized produce a better canopy structure and are highly efficient in using nutrients, being poorly responsive to further fertilization (Stape et al., 2004). However, this initial fertilization may be inefficient if it does not adequately contemplate the nutritional deficiencies or environmental conditions of a particular location (Binkley and Fisher, 2013; Graciano et al., 2004; Sands et al., 1992). Micronutrients and some macronutrients, whose nutritional relevance is well documented, are generally missing in commercial NPK pellet formulations (Dell et al., 2003). Furthermore, if water supply is limited, salinity increases due to fertilization can overwhelm the tolerance mechanisms of the recently planted seedlings, leading to a reduction in growth or even plant mortality (Davis and Jacobs, 2005; Jacobs et al., 2004; Munns and Tester, 2008; Weggler et al., 2008).

In spite of the potential benefits granted by fertilization schemes in cultivated forests and other agricultural systems, there is growing concern about their long-term sustainability and their undesired environmental effects. From the total fertilizer mass that is applied onto the field, only a small proportion is effectively used by the crop (Good and Beatty, 2011; Zhang et al., 2015), while the unused part generally contributes to soil and ground water pollution (Sitthaphanit et al., 2009; Sharma et al., 2016) or fertilizes competing natural flora. In this context, and also from an economic perspective (FAO, 2015), there is a clear need to develop alternative fertilization practices to increase the nutrient use efficiency of agricultural and forests plantations (Abreu-Junior et al., 2017; Madejón et al., 2016; Shen et al., 2013; Zhang et al., 2015). For such task, proper management of the root/rhizosphere interface appears as an interesting possibility (Chapman et al., 2012).

Several strategies are being studied to improve delivery and mobilization of nutrients into plants rhizospheres. A group of hydrophilic polymers collectively named *hydrogels* have been shown to be very efficient at delivering molecules such a drugs and nutrients in many biological systems (Hoare and Kohane, 2008). Hydrogels have a great capacity of retaining water within the polymer matrix, which makes them suitable to use in water management tasks (Ullah et al., 2015). Compared to other materials, hydrogels are also highly biocompatible, given their high water content and physicochemical similarity to the native extracellular matrix (Calo and Khutoryanskiy, 2015).

Since the 1970's superabsorbent hydrogels (SAPs) have been used to manage moisture within the rhizosphere of many plant species (Landis and Haase, 2012). Due to the high cost of raising tree seedlings and the watering demands of their outplanting process, SAPs have been adopted widely in forestry for water management during tree seedling establishment, far compensating the expenses and technical difficulties generated by their utilization (producers have even developed tailor-made machinery to apply them; see Erazo, 1987; Hüttermann et al., 1999; Viero et al., 2000). The routine use of SAP in water management opens the possibility of an additional role for these polymers in nutrient delivery. Although previous studies have pointed to hydrophilic polymers for delivering fertilizers into the root systems of trees, food crops or other plants (Bohlenius and Overgaard, 2014; Davidson et al., 2013; Mikkelsen, 1994; Smith and Harrison, 1991) most of the published work focused on polymer preparation or polymer testing with poor evaluation of the compound's behavior in real plantations or in varying environmental conditions (Guo et al., 2004; Liang and Liu, 2006; Liu et al., 2006; Rabat et al., 2016). As the availability of acrylic acid (AA) monomer has dramatically increased due to extension of production by major chemical companies (Research and Markets, 2015), AA-based SAPs have become inexpensive enough to explore their potential use for root targeted delivery of fertilizers in large scale operations.

In the present work, we propose that applying a combination of minimum amounts of macro- and micronutrients structurally integrated within a cross-linked SAP polymer would constitute an environmentally friendly alternative to dispense nutrients into *Eucalyptus* root systems. We show that a relatively low input of specific nutrients is sufficient to produce a strong impact on growth if properly delivered to the root/rhizosphere interface. Strategies as the one we propose here could contribute to address the novel challenges of sustainability in forestry systems (Diaz-Balteiro et al., 2016).

2. Materials and methods

2.1. Reagents

All the materials used for polymer synthesis were industrial grade and obtained from commercial sources (see below for sources and specifications). The fertilizer salts utilized were also industrial grade (see sources and origins in Table 1a).

2.2. Preparation of the superabsorbent polymer composites

For polymerizing acrylic acid (AA), we utilized the dry bulk radical polymerization method (Mikita et al., 1987) because it requires less solvent (water) compared to solution polymerization, simultaneously allowing for the use of simple equipment (no agitation, atmospheric or temperature control devices are required) and for the fast drying of the polymer crystals. This allows additives (such as salts and stabilizers) to be readily included in the synthesis. For synthesis of the **SAPH** superabsorbent polymer, 500 g AA (99% purity, Dow Chemical, USA) were first dispensed into a large polyethylene flask. Then, 1.5 ml of the cross-linker agent (Trimethylolpropanol trimethacrylate, Sartomer, USA) and 2 ml of ammonium persulphate (APS-5F, United Initiators GmbH, Germany; 100 mg.l^{-1}, in distilled water) were added into the container, carefully blending in all the ingredients. Separately, 20 g of hydroxyethyl cellulose (HEC; Cellozise QP 52000H, BASF) were added to 680 g of a solution made of 50% (w/w) potassium hydroxide -KOH-(99% purity; Jinyuan, Tianjin, China) in deionized water until complete solubilization. This KOH-HEC solution was poured into the acrylic acid container. As the neutralization begun, temperature rose to 90 °C, which was enough to trigger the radical polymerization reaction. Given the working quantities of AA and KOH, 67% of the AA was neutralized and 33% remained as acid