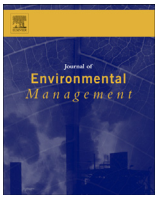
Journal of Environmental Management 210 (2018) 239–254

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman



Research article

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

E. Tubert [a, b], V.A. Vitali [a, b], M.S. Alvarez [c, d], F.A. Tubert [e], I. Baroli [a, b], G. Amodeo [a, b, *]

[a] Departamento de Biodiversidad y Biología Experimental, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2160, Ciudad Universitaria, Pabellón II, (C1428EGA), Buenos Aires, Argentina
[b] Instituto de Biodiversidad y Biología Experimental y Aplicada (IBBEA), CONICET-Universidad de Buenos Aires, Argentina
[c] Departamento de Ciencias de la Atmósfera y los Océanos, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina
[d] Centro de Investigaciones del Mar y la Atmósfera (CIMA), Instituto Franco Argentino sobre Estudios del Clima y sus Impactos (UMI IFAECI)/CNRS, CONICET-Universidad de Buenos Aires, Buenos Aires, Argentina
[e] Tetraquímica S.A., Hurlingham, Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 25 August 2017
Received in revised form
11 December 2017
Accepted 24 December 2017

Keywords:
Eucalyptus
Mineral nutrition
Superabsorbent polymer
Silviculture
Water management

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

---

[*] Corresponding author. Departamento de Biodiversidad y Biología Experimental, Facultad de Ciencias Exactas y Naturales, and Instituto de Biodiversidad y Biología Experimental y Aplicada, CONICET-Universidad de Buenos Aires, C1428EHA, Buenos Aires, Argentina.
E-mail address: amodeo@bg.fcen.uba.ar (G. Amodeo).

https://doi.org/10.1016/j.jenvman.2017.12.062
0301-4797/

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

Table 1
Composition of the BAL and NPK nutrient mixes. A. Chemical composition. B. Macro and micronutrient content along with the main nutrient ratios of the BAL and NPK mixes at the dose of use, compared also to those of a commercial loamy soil and the widely used Hoagland's nutrient solution (Hoagland and Arnon, 1950). The chemical source and origin are referenced below the table.

a. General composition (w %)

	$NH_4H_2PO_4^a$	KNO_3^b	$Ca(NO_3)_2\ 4H_2O^b$	$MgSO_4\ 7H_2O^c$	Fe (EDTA)^d	$H_3BO_3^d$	$MnSO_4\ H_2O^d$	$CuSO_4\ 5H_2O^d$	$MoO_4Na_2\ 2H_2O^d$	$ZnSO_4\ 7H_2O^d$	TOTAL (w %)
BAL	33.00	33.00	21.84	10.00	2.00	0.12	0.01	0.01	0.01	0.01	**100.00**
NPK	87.00	13.00	–	–	–	–	–	–	–	–	**100.00**

b. Nutrient content at dose of use (ppm)

	N	P	K	Ca	S	Mg	Fe	B	Mo	Mn	Cu	Zn	N:P	Ca:Mg	K:P
BAL	219.00	175.00	250.00	72.00	25.48	19.60	2.74	0.35	0.07	0.07	0.06	0.05	1.25	3.67	1.43
NPK	242.00	418.00	120.12	–	–	–	–	–	–	–	–	–	0.58	–	0.29
Hoagland	210.00	31.00	235.00	200.00	64.00	48.00	5.00	0.50	0.01	0.05	0.02	0.05	6.77	4.17	7.58
Loam	341.00	6.50	938.00	22.00	N/A	37.00	N/A	N/A	N/A	N/A	N/A	N/A	52.46	0.59	144.3

Chemical sources and origins: **a:** Emerger S.A., Agentina; **b:** Monband, Hebei, China; **c:** Dahua, China; **d:** Biopack S.A., Argentina.

groups. After completion of the reaction, the polymer obtained was dried at 90 °C for 48 h and finally ground to reach desired granulometry.

For the polymers containing nutrient ions, the same procedure was followed, except that right after the addition of the KOH-HEC solution to the AA, a fertilizer solution was incorporated into the reaction flask, thoroughly mixing it in (salts -137 g-had been dissolved in 150 ml of deionized water and maintained at 90 °C until utilization). For the **SAPH-BAL** composite, the fertilizer salts were selected after analyzing available data on nutrient ratios for improving the growth of *Eucalyptus* seedlings (Dell et al., 1995, 2003; Herbert, 1983, 1990; Knecht and Göransson, 2004). We named this nutrient mix 'BAL', and the components as well as the chemical sources are listed in Table 1a. The amount of BAL salts accounted for 14% (w/w) of the SAPH-BAL polymer. For the **SAPH-2BAL** we doubled the amount of BAL salts added to the polymer. The compounds obtained were dried at 90 °C for 48 h and ground to reach the desired granulometry.

Finally, as controls for the experiments aimed at analyzing the effect of HEC on the polymer's physical properties, we prepared the SAP and SAP-BAL compounds. These were produced in the same manner as the SAPH and SAPH-BAL compounds but without the addition of HEC.

2.3. Characterization of polymers

2.3.1. IR spectroscopy

The composites were characterized by a Fourier-transform infrared (FTIR) spectrophotometer (Thermo iS50 FT-IR, Thermo Fisher Scientific, USA). The dry samples were comminuted and ground with dried KBr powder. The KBr disc was dried again and subjected to the FTIR spectrophotometer.

2.3.2. Scanning electron microscopy (SEM) and energy disperse X-ray (EDS) spectrum analysis

Scanning electron microscopy (SEM) observations were carried out using a Philips XL 30 ESEM scanning electron microscope (Netherlands) at intermediate vacuum, IGP: 1 × E−5 Pa. This equipment was fitted with an EDAX energy dispersive x-ray detector (Super UltraThin Window -detection from Boron- resolution: 130 eV F·W·H.M by MnKα for 50 μsec) through which the EDS spectra of the composites were obtained. This equipment permitted the study of dry as well as hydrated polymer samples.

2.3.3. Water sorption

The swelling capacity (SC) values were obtained as described by Bowman et al. (1990). Briefly, 1 g of the polymer crystals was weighted after 24 h of swelling in 1000 ml deionized water or in NaCl solutions of increasing osmolality (20–200 mM NaCl). The hydrated gels were collected on a fine-mesh (0.25 mm) screen. The SC values were the ratio of the hydrated polymer weight and its corresponding dry weight.

To determine the doses of use of the produced polymers (*i.e.* SAPH, SAPH-BAL, SAPH-2BAL) we added increasing quantities of the composites (0, 4, 8, 12, 16, 20 g) in beakers containing 1000 ml of tap water, and measured the amount of water that the polymers could absorb by weighting the swollen crystals. The selected dose of use was such that each composite was able to retain ~95% of the water in the beaker. SAPH was therefore used at concentration of 6 g.l^{-1}, whereas SAPH-BAL was used at a concentration of 14 g.l^{-1} and SAPH-2BAL at 18 g.l^{-1}. Osmolalities of the obtained composites at these doses were measured using a vapor pressure osmometer (Wescor, model Vapro 5600, UT, USA) 24 h after polymer addition and were 29.0 ± 8.5 mOsm.kg^{-1} (SAPH), 79.7 ± 8.1 mOsm.kg^{-1} (SAPH-BAL) and 127.4 ± 10.8 mOsm.kg^{-1} (SAPH-2BAL).

Reversibility of salt inhibition of SC was measured adding a 6 g sample of SAPH-BAL into 1000 ml of deionized water. After 24 h, the crystals were collected and weighed as above. Bach sample was then transferred to 1000 ml of deionized water for 24 h, then collected and reweighed. The transfer and reweighing was repeated on a daily basis for 6 more days.

2.3.4. Rheological properties

Rheological properties were measured with an oscillatory rheometer (Physica MCR301, Anton Paar GmbH, Germany) having a cone-plate geometry of 50 mm diameter at 25 °C. Viscosity curves were obtained over a shear rate range of 0.1–500 s^{-1}. Amplitude sweep tests were made at constant angular frequency of 10 s^{-1} and a strain range of 0.01–100%. Frequency sweep tests were carried out at an angular velocity range of 0.01–100 s^{-1} and 0.5% of strain (under the linear viscoelastic region). All tests were repeated three times for each sample in order to obtain a representative value and average values were reported.

2.3.5. Nutrient release behavior of SAPH-BAL

Dry SAPH-BAL (0.5 g) was seal-packed in a tea-bag formed using two layers of polypropylene nonwoven fabric (30 g.m^{-2}; Softbond, Argentina) sealed with a hand thermosealer (size: 5 × 5 cm) and placed in a tapered bottle filled with 500 ml distilled water. The nonwoven fabric retains the polymer crystals, but is permeable to water and ions, so the ion concentrations can be measured. Nitrate and phosphate release tests were conducted in triplicate. Four ml of the soaking solution samples were withdrawn at predetermined intervals (0, 15, 30, 60, 120, 720, 1440 and 2280 min) and the bottles were refilled with the same volume of deionized water. Samples were treated with HCl and the nitrate and phosphate concentrations were determined spectrophotometrically (UV-Mini-1240, SHIMADZU, Australia) at 220 nm and 297 nm, respectively. The percentage release was calculated dividing the measured absorbance at each particular time (abs_t) by the maximum absorbance after 2280 min (abs_{max}).

2.4. Experiments in semi-controlled conditions

2.4.1. Plant material and growth conditions

For all greenhouse experiments, we employed three-months-old *Eucalyptus grandis* seedlings grown from seed obtained from a single producer located in Misiones Province, Argentina.

Seedlings were transplanted (one per pot) into 15 cm diameter and 25 cm height perforated plastic pots containing a thoroughly mixed substrate composed of 50% silica sand (medium grade, Arenera Pueyrredon, Argentina) and 50% vermiculite (Intersum, Argentina) forming a central hole. When employed, the dry polymer granules were previously soaked in deionized water (SAPH: 6 g.l^{-1}, SAPH-BAL: 14 g.l^{-1}, and SAPH-2BAL: 18 g.l^{-1}) for 60 min and 500 ml of this mixture were placed in the central hole before transferring the seedling. After inserting the seedling, all pots received an upper layer of substrate, carefully covering the roots. Immediately after planting, plants were well watered by adding 500 ml of tap water.

The pots were arranged in a randomized block design with 4–8 replicates per experiment. All experiments took place at the university campus greenhouse located in Buenos Aires, Argentina (midday irradiance was circa 1300 μmol.m^{-2}.s^{-1}). Pots were rotated twice a week to avoid any possible effect of position on growth. The experiments were carried out during the spring and summer seasons (from September to March) to guarantee optimal light intensity and temperature for *E. grandis* growth. Daytime temperatures ranged from 20 to 40° C during experiments. Relative humidity ranged from 40% to 70%.

Different irrigation schemes were then used as indicated. For continuous irrigation experiments, seedlings were watered daily using 500 ml of tap water. Pots were allowed to drain and the excess water was collected in trays in order to maintain a well-watered condition. In some experiments, watering was interrupted at the indicated times to simulate natural rain cycles. For no-irrigation treatments, no further water was added after the initial watering. After 70 days, the seedlings were harvested to determine their biomass and/or leaf area. Greenhouse experiments were independently repeated three times.

2.4.2. Nutrient/polymer combinations

The following planting conditions were tested:

i) Control: substrate without nutrients or polymers
ii) BAL: substrate mixed directly with 1.06 g of the BAL powdered nutrient mix
iii) SAPH: 500 ml added to the substrate
iv) SAPH-BAL: 500 ml added to the substrate
v) SAPH-2BAL: 500 ml added to the substrate
vi) SAPH-NPK: 500 ml added to the substrate

The SAPH-NPK composite was equivalent to SAPH-BAL except that we replaced the BAL nutrient mix for an NPK nutrient mix featuring a higher P input (Table 1a). This emulates the nutrient proportions of the conventional fertilizer used in *Eucalyptus* plantations but delivered via the hydrogel. The dose of use of SAPH-NPK was equal to that of SAPH-BAL (14 g.l^{-1}), having also an equivalent osmolality at that dose (~80 mOsm.kg^{-1}). The differences in nutrient concentration between both mixes at the dose of use in their respective polymers are shown in Table 1b.

2.4.3. Plant growth parameters

Height (h) measurements were obtained weekly using a metallic tape measure, which was positioned in direct contact with the substrate. Immediately after harvesting, plants were divided into root and aerial parts. To determine the leaf area, fresh leaf blades were excised and photographed with a digital camera. Images were processed with the ImageJ 1.48v software (http://rsb.info.nih.gov/ij/). To determine dry weight (DW), samples were dried at 60 °C during 48 h (constant weight) and weighted. For survival assessment, seedlings were considered 'dead' once the apical leaves had wilted permanently, although occasionally new leaves could be initiated at the apex, or new shoots could form at the base.

2.4.4. Stomatal conductance

Stomatal conductance (g_s) was measured with plants maintained under natural radiation between 11:30 a.m. and 12:30 p.m., under ambient CO_2 concentration, using a portable steady state diffusion leaf porometer (model SC-1, Decagon Devices, Pullman, WA, USA). Before the first measurement, the youngest fully expanded leaf was marked. The g_s was measured thereafter always at the marked leaf. We verified that the upper and lower layers of leaves had similar g_s, as previously reported (Mielke et al., 1999).

2.5. Field experiments

2.5.1. Plant material

For all field trials, we used three-month-old seedlings available at each location. *E. grandis* seedlings were used in 9 out of 11 trials. In the other two trials, we used *E. dunnii* (assay E1) and *E. globulus* (assay E10, Table 2) as these were the species regularly grown at each respective location, where climate incompatibilities prevent the use of *E. grandis*.

2.5.2. Field conditions and site description

All field trials were performed at active production sites covering a range of different environmental conditions (Fig. 7A). The mean annual precipitation (CMAP database; Xie and Arkin, 1997) shows a west-east gradient and a maximum in north-eastern Argentina and southern Brazil of above 4.4 mm day^{-1} (Fig. 7B). The mean annual surface temperature for the region of study (not shown) reveals a maximum to the northwest, with mean annual temperatures of over 23 °C, and decreasing to the southeast, with mean annual temperatures between 19 and 17 °C in southern Brazil, Uruguay and central Argentina. Detailed information on rainfall, temperature and soil types for each trial is shown in Table 2. Cumulative precipitation for the trials is shown in Supp. Fig. 6B. Weather stations located near the assay sites were selected to analyze the rainfall conditions during each assay compared to the climatology (long-term average conditions; see Table 2). Historical daily rainfall between 1980 and 2014 was taken from the weather stations selected for each assay (Suppl. Table 1). The central and northern part of the area of study comprises clay soils (oxisol and alfisol), while loamy clay soils can be found to the south of the region (Supp. Fig. 6A). Information about the soil texture within the region of study was retrieved from the Land Data Assimilation Systems (LDAS) of the National Aeronautics and Space Administration (NASA), which was derived from the dataset of Reynolds et al. (2000) based on the Food and Agriculture Organization (FAO) soil map of the world.

Table 2

Detailed description of the field trials performed. Plantation data (dates, location, duration, soil type, fertilizer used and plant material) as well as environmental data (temperature and precipitation) for each field trial is provided. N/A, not applicable; RBD, randomized block design; pp, precipitation.

Assay	Start date	End date	Duration (days)	Location	Soil type	Plant material	Fertilizer (N-P-K)	RBD Reps	Plants/ treatment/Rep	Plants/ treament	Tmed (°C)	Tmin_ext (°C)	Tmax_ext (°C)	pp_acum (mm)	pp (mm/ day)	pp (mm/ month)	Days with rain
E1	10/25/2008	03/23/2009	150	Tres Arboles, Paysandu, Uruguay	Loamy Clay (Litosol)	*E. dunnii*	11-52-00	5	10	50	21.5	7.1	36.9	220.1	1.5	42	21 (13.8%)
E2	10/31/2008	12/05/2008	36	Santa Clara de Olimar, Rio Negro, Uruguay	Loamy clay	*E. grandis*	11-52-00	5	10	50	20.7	4.2	33.2	52.3	1.5	45	3 (8.3%)
E3	11/05/2008	12/11/2008	37	Sarandi, Fray Bentos, Uruguay	Clay	*E. grandis*	11-52-00	5	10	50	24.0	6.5	39.3	130.8	3.5	105	6 (16.2%)
E4	04/02/2009	11/26/2009	239	Virasoro, Corrientes, Argentina	Clay (Alfisol)	*E. grandis*	02-39-06	4	10	40	17.9	-5	38.1	1543.6	6.5	195	65 (27.1%)
E5	11/18/2009	07/01/2010	225	Garruchos, Corrientes, Argentina	Clay (Alfisol)	*E. grandis*	02-39-06	8	4	32	22.1	2.0	38.7	1706.0	7.5	225	71 (31.1%)
E6	11/18/2009	07/01/2010	225	Garruchos, Corrientes, Argentina	Clay (Alfisol)	*E. grandis*	02-39-06	8	4	32	22.1	2.0	38.7	1706.0	7.5	225	71 (31.1%)
E7	05/02/2010	08/02/2010	93	Guaiba, Porto Alegre, Brasil	Clay (Oxisol)	*E. grandis*	06-30-06	4	100	400	15.5	2.4	30.6	516.0	5.5	165	35 (37.6%)
E8	02/02/2011	06/15/2011	134	Carmelo, Uruguay	Loamy clay	*E. grandis*	14-24-00	3	50	150	17.5	0.3	33.7	238.3	1.8	54	24 (17.9%)
E9	11/04/2011	02/05/2012	94	Hernandarias, Alto Parana, Paraguay	Clay (Oxisol)	*E. grandis*	04-30-10	3	8	24	25.6	11.0	38.0	269.0	2.9	87	16 (17.0%)
E10	12/17/2012	03/17/2013	91	Balcarce, Buenos Aires, Argentina	Loam (Molisol)	*E. globulus*	N/A	5	16	80	19.7	2.7	37.3	454.4	5.0	150	19 (20.9%)
E11	04/08/2013	09/08/2013	154	Hernandarias, Alto Parana, Paraguay	Clay (Oxisol)	*E. grandis*	04-30-10	3	8	24	17.7	0.0	33.2	800.7	5.2	156	29 (18.8%)

2.5.3. Treatment design and preparation

The design adopted at all field trials was one of randomized complete blocks with 3–8 replicates and 4 to 100 seedlings for each treatment per block, depending on the trial (Table 2), with a spacing of 4 m × 2 m (1250 seedlings ha^{-1}). For the polymer treatments, we used a bulldozer tank equipped with hoses to pump the polymer preparation, in hydrated form, into previously made 30 cm deep x 20 cm wide holes. The tree seedlings were afterwards deposited in the holes and covered with soil. Height was measured every 30 or 60 days. Duration of each field experiment ranged from 36 to 239 days, as indicated (Table 2).

The planting conditions tested in the field were mostly the same as for the greenhouse experiments:

i) SAPH: 500 ml in the plant hole
ii) SAPH-BAL: 500 ml in the plant hole
iii) SAPH-2BAL 500 ml in the plant hole
iv) SAPH + $NPK_{pellets}$:500 ml SAPH in the plant hole plus conventional NPK pellets on top soil

This last treatment consisted of 500 ml hydrated SAPH in the plant hole and 75 g of granulated NPK fertilizer added on the surface of the soil surrounding each seedling after transplantation. Although all NPK pellet fertilizers featured a high P input, the actual compounds used in each trial were those used routinely at each production site.

2.5.4. Statistical analysis

One-way analysis of variance (ANOVA) was used to analyze the effects of treatments on seedling growth responses in greenhouse experiments, while two-way ANOVA was utilized in the case of the field trials. Post-hoc Tukey tests were employed for mean comparisons ($P \leq 0.05$). Variable normality and homogeneity of variances were previously verified in order to satisfy ANOVA's assumptions using the Brown–Forsythe test. All statistical analyses were performed with the GraphPad Prism 6 package. Results are presented as mean ± SEM. Each sample size (n) is indicated in the figure legends. Different upper-case letters or asterisks indicate significant differences ($P \leq 0.05$) between means.

3. Results

3.1. Characterization of SAPH-BAL composite

To investigate whether a superabsorbent polymer could effectively carry mineral nutrient ions into tree seedling rhizospheres, we prepared, via dry bulk radical polymerization, a partially neutralized potassium polyacrylate additivated with a fertilizer mix, balanced for the proper growth of *Eucalyptus* seedlings (BAL nutrient mix, Table 1). Additionally, we included in this polymer, 2% hydroxyethyl cellulose (HEC) -an ether colloidal thickener-as it has been reported to act as a stabilizer in polyacrylic acid (PAA) hydrogel systems by reacting with the hydroxyl groups in PAA (Mabrouk et al., 2015) and also due to its nonionic thickener property. The resulting compound was named SAPH-BAL. To chemically characterize this compound, we compared its FT-IR spectrum with that of pure potassium polyacrylate (SAP; Fig. 1A). The characteristic peaks of polyacrylate (2930, 1557 and 618 cm^{-1}) were observed in both samples. However, the SAPH-BAL composite also presented a broad band with a peak at 3337 cm^{-1} attributable to HEC (Mabrouk et al., 2015) and peaks compatible with those of the main fertilizer molecules: NO_3^- (1305 and 813 cm^{-1}), NH_4^+ (1449 cm^{-1}) and PO_4^{3-} (1167 and 947 cm^{-1}). The SAPH-BAL composite was, therefore, the admixture of cross-linked polyacrylate, HEC and the included fertilizer salts, which existed as themselves.

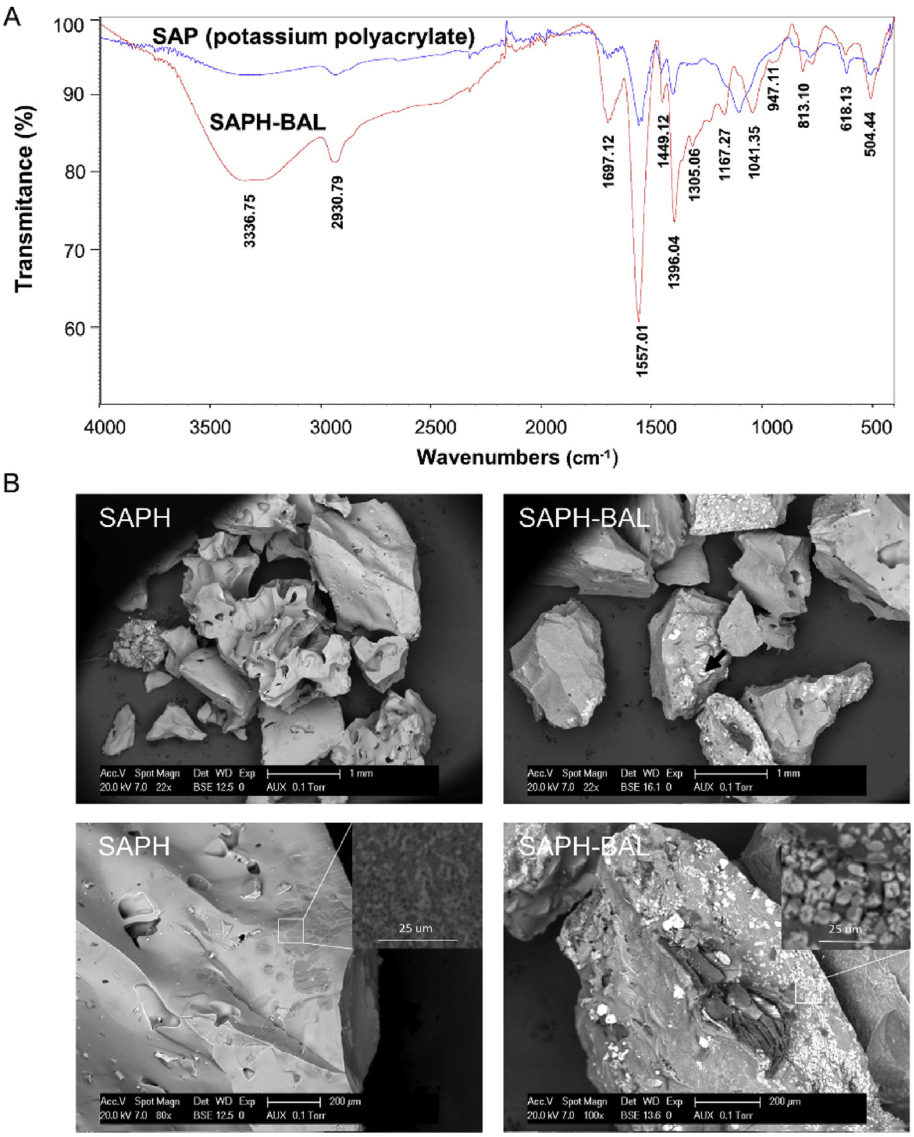


Fig. 1. Chemical characterization of the synthesized SAP composites. A. FT-IR spectrum of SAPH-BAL (SAPH-BAL) and potassium polyacrylate SAP (SAP). B. Scanning electron microscope images of the SAPH composite (left panels) and SAPH-BAL composite (right panels). The arrow indicates the salt crystal deposition that was analyzed by EDS (shown in Suppl. Fig. 1). The insert on the lower left panel shows the porosity of the SAPH compound. The insert on the lower right panel shows the salt particles integrated in the SAPH-BAL polymer.

To evaluate the morphology of the synthesized composite and to investigate how HEC and the fertilizer salts were integrated within the polymer network, scanning electron microscope images were obtained. We compared the SAPH-BAL polymer with a SAPH compound (containing only polyacrylate and HEC). We found that HEC was well integrated within the polyacrylate, both in SAPH and SAPH-BAL, forming a homogenous porous matrix (Fig. 1B). Differently from the SAPH polymer, the SAPH-BAL composite presented salt crystal depositions of variable sizes (ranging from 10 to 200 μm) that were dispersed in the smooth-surfaced framework (Fig. 1B, right panels). Complementary EDS analysis of the SAPH-BAL composite indicated high proportions of C (37.27%), O (35.81%) and K (22.29%) and comparatively lower proportions of N (2.54%) and P (1.84%) (Suppl. Fig. 1A). The salt depositions were enriched in P and K (Suppl. Fig. 1B). Analysis of partially swollen SAPH-BAL showed that many salt microparticles remained in the polymer after 15 min of hydration but fewer particles remained after 30 min of hydration in excess deionized water (Suppl. Fig. 2).

3.2. Water sorption and rheological properties of SAPH-BAL

As water sorption is a key feature for any hydrogel, we analyzed the swelling behavior of the SAPH and SAPH-BAL composites. The SAPH composite had similar swelling capacity (SC) in deionized water (1 g SAPH absorbs ca. 250 g H_2O) compared to a commercially acquired acrylamide/potassium acrylate copolymer (Stockosorb 500 XL, Evonik Industries, Germany), which is a regularly used polymer for agricultural applications (Fig. 2A). Indeed, SAPH showed good water retention capability when we tested it in *Eucalyptus* seedlings under water stress (Suppl. Fig. 3). As expected, the SC of SAPH decreased in response to increasing osmolality of the soaking solution (NaCl; Fig. 2A). In the case of the SAPH-BAL composite, the water retention was considerably reduced (40% of SAPH retention) due to the presence of the fertilizer salts, which increased the osmolality of the soaking solution. While the dose of

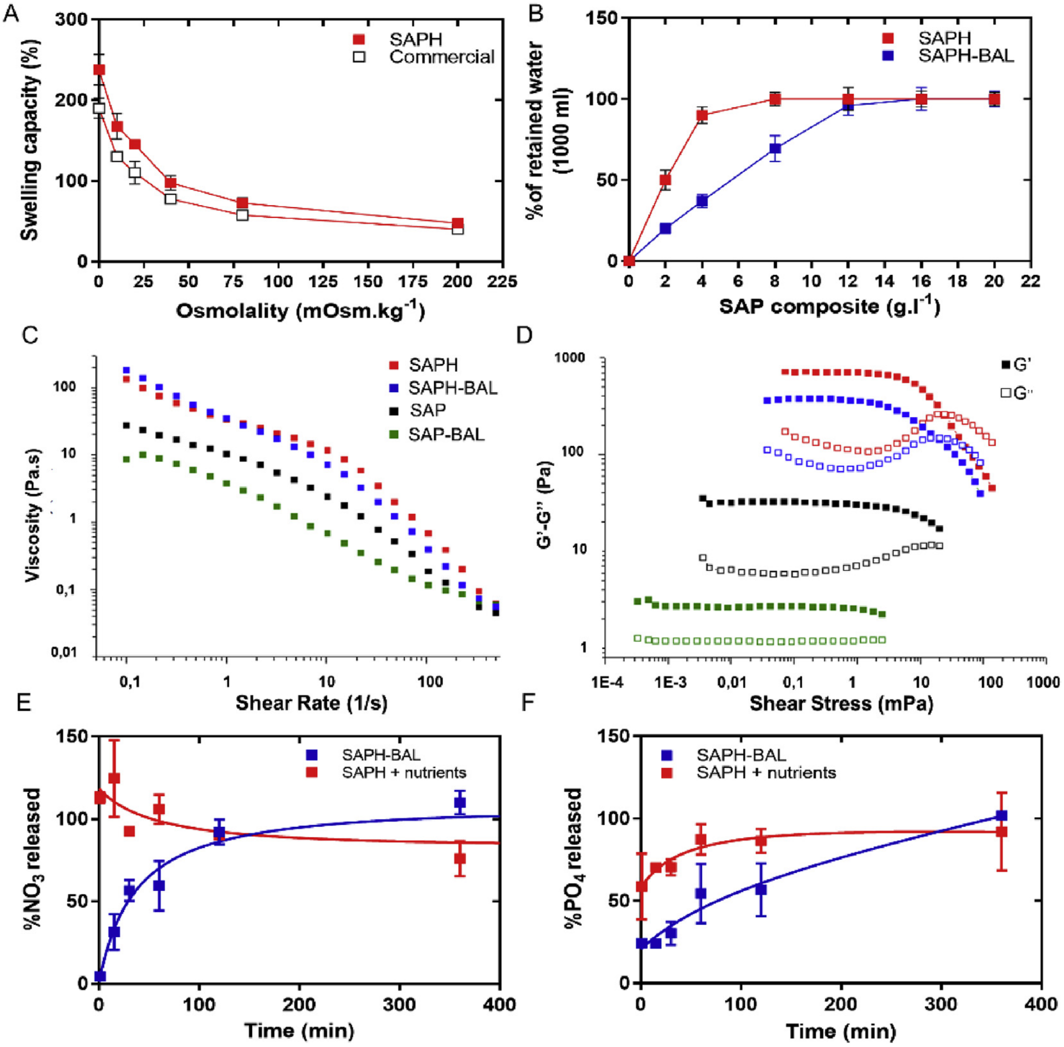


Fig. 2. Swelling capacity, rheological properties and nutrient release behavior of the SAP composites. A. Swelling capacity of SAPH and of a commercial acrylamide/potassium acrylate copolymer in solutions of increasing osmolality. B. Percentage of retained water (1000 ml tap water) by increasing doses of SAPH or SAPH-BAL. C, D. Viscosity and storage modulus values (G′ and G″) of the polyacrylate compounds that feature HEC (SAPH and SAPH-BAL) and of those that do not include it (SAP and SAP-BAL), respectively; color coding is maintained in both figures. E, F. Nitrate and phosphate release curves of the SAPH-BAL composite and of SAPH plus the equivalent BAL powdered nutrients added separately. The release % at each time corresponds to the corrected absorbance (abs$_t$) divided by the maximum absorbance overall (abs$_{max}$). Error bars indicate SEM (n = 3).

SAPH for obtaining a sufficiently viscous hydrogel (without free water) was 6 g l^{-1} in tap water, the SAPH-BAL dose required was 14 g l^{-1} (Fig. 2B).

Chemical additivation (*i.e.* with fertilizer salts) at synthesis of the composite might contribute to distortion in the hydrogel's strength and viscosity. Since the polymer must withstand the pressure imposed by the soil's upper layer, we analyzed the compound's rheological properties using an oscillatory rheometer. We measured these properties for the polymers that included HEC (SAPH and SAPH-BAL) as well as for those without HEC (SAP and SAP-BAL). As seen in Fig. 2C, the addition of HEC markedly increased polymer viscosity. Furthermore, the increase of storage modulus values (G′) indicates higher cohesive strength in the case of SAPH and SAPH-BAL, probably due to the formation of a three-dimensional network that grants rigidity to these hydrogels. Moreover, the flow points of SAPH and SAPH-BAL are shifted to higher shear stress values, indicating that they have higher resistance to flow and behave as a viscous liquid (Fig. 2D). The addition of HEC therefore overcame the negative effect of salt additivation, producing a hydrogel more fitted for agronomic use.

3.3. Nutrient release behavior of SAPH-BAL

The rate at which ions are released by the polymer to the surrounding solution could potentially be a relevant factor affecting plant survival and development. To analyze the rate of ion release from the SAPH-BAL composite we quantified spectrophotometrically the nitrate and phosphate concentrations as a function of time after placing the polymer in deionized water. Fig. 2E and F shows that the speed of release of both nitrate and phosphate was reduced in the case of the SAPH-BAL composite compared to the pure SAPH polymer and the equivalent fertilizer salts (BAL nutrient mix) separately. Furthermore, in experiments where SAPH-BAL crystals were soaked in deionized water and repeatedly washed (also with deionized water), a complete recovery of the swelling capacity (compared to that of the pure SAPH) was observed. (Suppl. Fig. 4).

3.4. Nutrient delivery mediated by SAPH-BAL in *Eucalyptus grandis* seedlings

With the aim of designing an alternative method to conventional pellet fertilization, we tested the ability of SAPH-BAL to deliver mineral nutrients into the seedling's root system. The effect of nutrient delivery mediated by the composite was evaluated by measuring physiological parameters as a function of time in well-watered seedlings. We chose to monitor stomatal conductance (g_s), as a parameter that positively correlates with both the plant water status and photosynthetic performance (Hernandez et al., 2016; Wong et al., 1985).

A group of seedlings was planted into substrate containing SAPH-BAL while another group was planted into substrate mixed with an equivalent amount of the BAL nutrient mix in powdered form (BAL). These two groups were compared with their counterparts which received substrate plus SAPH (SAPH) or substrate only (Control). Our results are summarized in Fig. 3. Nutrient supplementation produced a two-fold increase in g_s values compared to the plants that did not receive nutrients, and the extent and variation with time after transplantation were similar, with a peak around 20 days after transplant (DAT) among the nutrient-treated plants regardless of nutrient source (directly in the substrate or delivered via the SAPH-BAL, Fig. 3A). By 40 DAT, g_s values were low and similar in all four groups, probably reflecting the exhaustion of nutrients. Plant height (h) values increased approximately two-fold in SAPH-BAL-treated plants compared to plants that only received BAL (Fig. 3B). Furthermore, both root and shoot dry matter allocation (DW) were also doubled among the SAPH-BAL-treated plants compared to the BAL-treated group (Fig. 3C and D).

To compare the effect on growth of seedlings supplied with SAPH-BAL to those supplied with a fertilizer similar to the employed at forestry production fields, we prepared an equivalent polymer composite (SAPH-NPK) replacing, in the polymer synthesis, the BAL nutrient mix for a conventional NPK fertilizer mix (NPK nutrient mix) with higher P content but lacking other macro- and all micronutrients (details for this nutrient formulation are given in Table 1a -chemical composition- and Table 1b -nutrient concentrations-). The polymerization procedure was equivalent to that of the SAPH-BAL composite (See Materials and Methods, section 2.4.2). We compared the growth parameters obtained for well-watered seedlings treated with SAPH-NPK to those of plants treated with SAPH-BAL or only with SAPH for a period of 60 days (Fig. 4). Results showed that, whereas the SAPH-NPK composite enhanced biomass (DW) and total leaf area compared to SAPH controls (>50%), the SAPH-BAL-treated group showed a substantial improvement (~40% increase) in those parameters compared to SAPH-NPK-treated plants, suggesting that a balanced nutrient formulation such as BAL, in which part of the P mass is replaced with other nutrients, enhances the efficacy of the polymer fertilizer composite (Fig. 4).

3.5. *Effect of nutrient concentration on g_s and growth parameters*

While a larger initial amount of nutrients available to the roots could accelerate the growth rate of the seedlings, an increased initial osmolality of the soil solution can impair their performance and survival, due to salt stress or ion toxicity (Jacobs et al., 2004; Morabito et al., 1994). To elucidate the effect of increasing the initial nutrient concentration in our superabsorbent compound, we measured g_s and h as a function of time on seedlings subjected to a) SAPH-BAL (the composite used so far, $\text{osmolality}_{24h} \approx 80$ mOsm.kg^{-1}), b) SAPH-2BAL ($\text{osmolality}_{24hs} \approx 130$ mOsm.kg^{-1}) and c) only SAPH ($\text{osmolality}_{24hs} \approx 30$ mOsm.kg^{-1}). All these experiments were carried out in well-watered conditions. Results showed a marked negative effect of the SAPH-2BAL on g_s, h and DW.

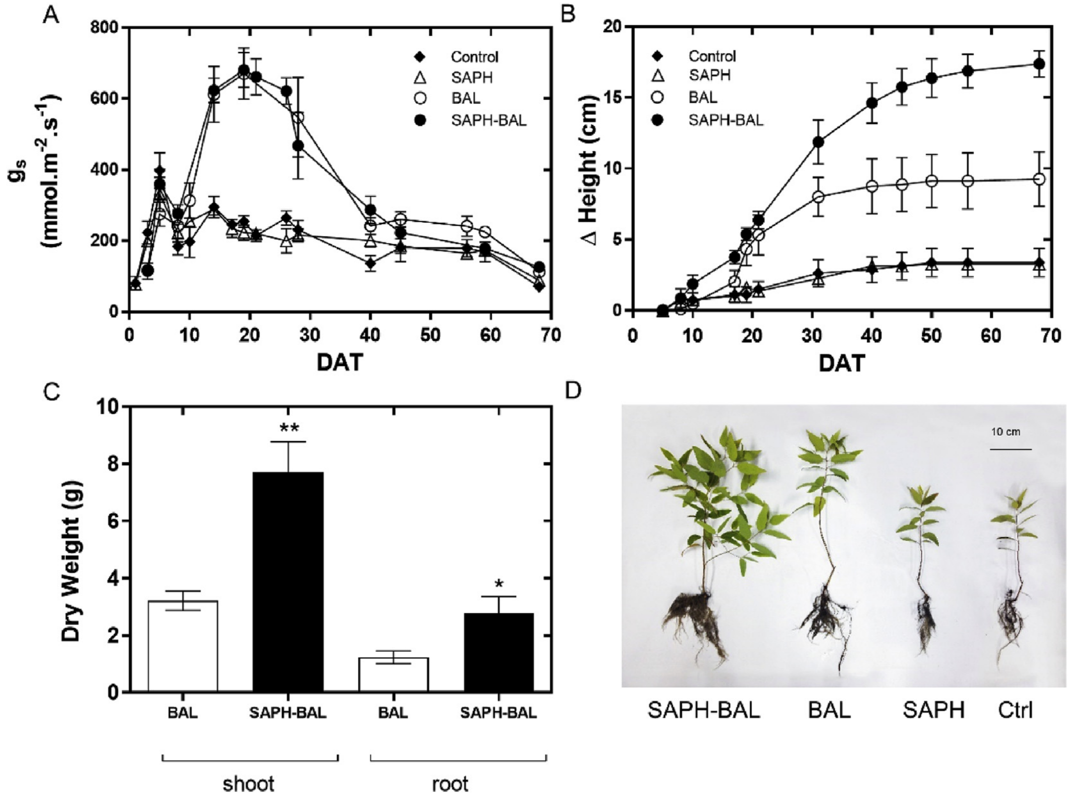


Fig. 3. Effect of mineral nutrients and polymer on stomatal conductance and growth under normal watering. A, B. Stomatal conductance (g_s) and height increment (Δ Height) as a function of time. Control conditions: no SAPH, no BAL, other additions as indicated. C. Shoot and root dry weight of plants treated with BAL or SAPH-BAL, data taken 70 days after transplantation (DAT). D. Plant phenotypes as visualized 70 DAT for each treatment and control (Ctrl) conditions. Error bars indicate SEM ($n = 7$); * = $p < 0.05$; ** = $p < 0.005$.

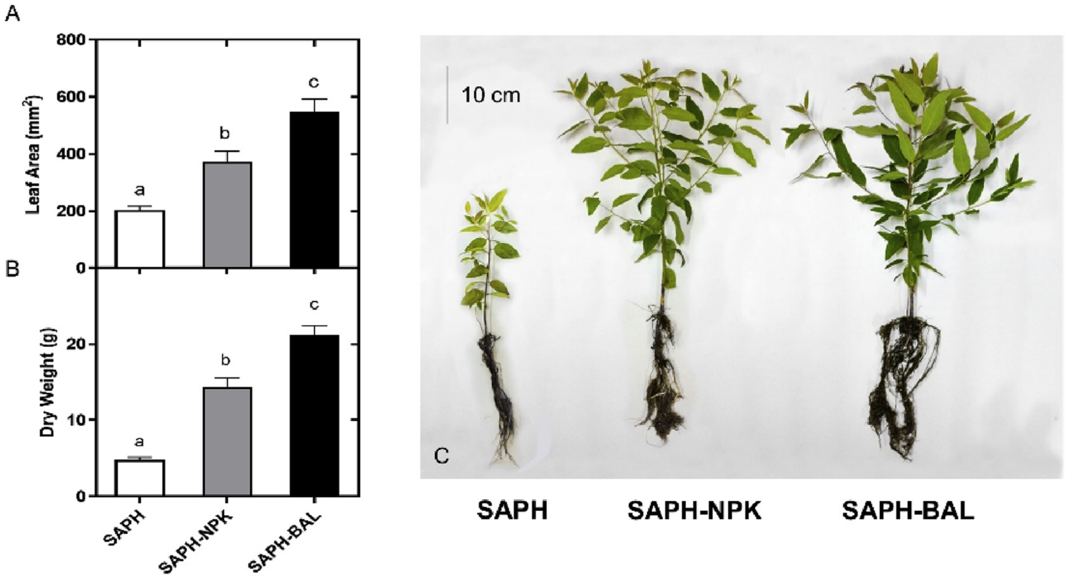


Fig. 4. Effect of two different SAP composites synthetized with different nutrient formulations (SAPH-NPK and SAPH-BAL) on *E. grandis* growth and biomass. A, B. Dry weight of the aerial part and total leaf area, respectively, at 60 DAT. C. Plant phenotypes as visualized 60 DAT. Error bars indicate SEM (n = 8). Different letters indicate significant differences among treatments.

Specifically, it was observed that seedlings subjected to SAPH-2BAL underwent a lag period in which g_s as well as growth (h) remained very low. Only 30 DAT seedlings resumed transpiration and growth, reaching, by 45 DAT, values even greater than those of SAPH-BAL-treated plants (Fig. 5).

3.6. Performance of SAPH-BAL in the greenhouse under water deficit

As already shown, when water availability is not restricted, SAPH-BAL accelerates seedling development. Under extreme water restriction conditions (plants only watered initially) the presence of

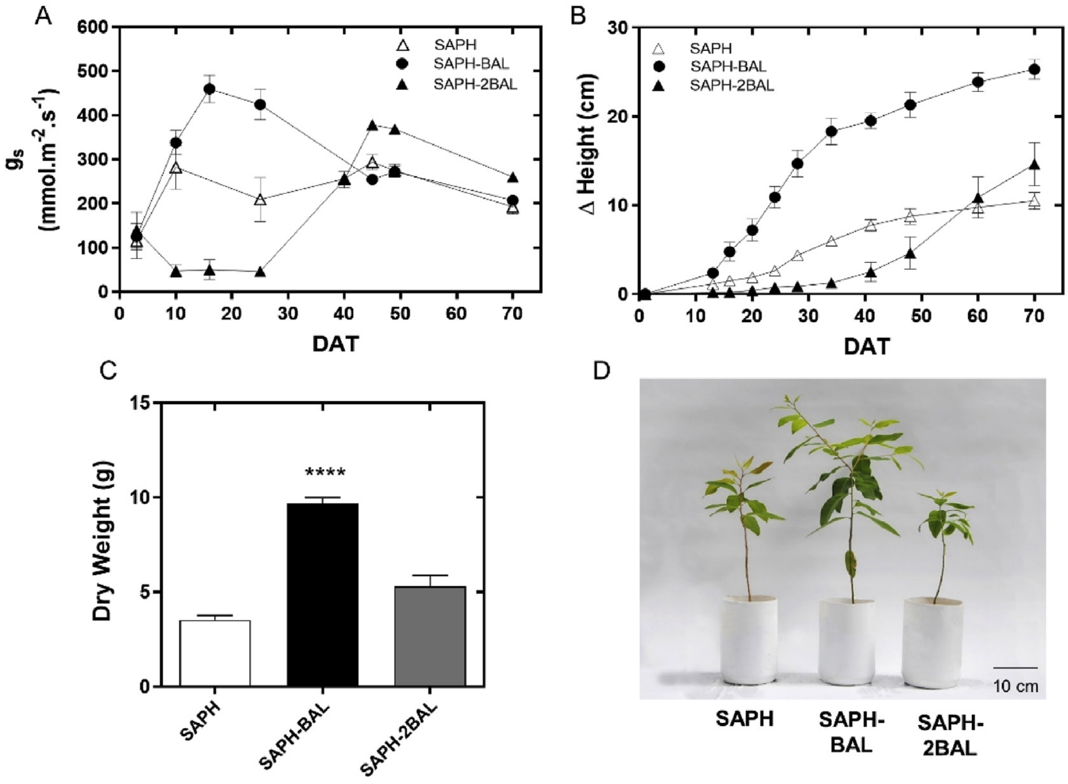


Fig. 5. Effect of SAP mineral nutrient concentration on stomatal conductance and seedling height. A, B, C. Stomatal conductance (g_s), plant height increment and shoot dry weight, respectively, of plants treated with only SAPH, SAPH-BAL or SAPH-2BAL (n = 6). For panel C, plants were harvested 70 DAT. D. Photographs of representative plants 42 days after transplantation. Error bars indicate SEM (n = 6). **** = $p < 0.0001$.

fertilizers markedly reduced g_s and increased the mortality rate, both in the seedlings treated with SAPH-BAL and in the seedlings that only received the BAL nutrient mix in the substrate (Fig. 6A). However, the presence of SAPH-BAL did allow for an increased g_s and an extension of lifespan (ca. 8 days) compared to seedlings that only received the BAL nutrient mix. Height measurements showed no significant differences among groups, possibly because plant growth is interrupted under water restriction (data not shown).

To evaluate how the SAPH-BAL composite affects seedling performance under conditions more similar to a field environment, we also subjected our plants to a discontinuous irrigation regime to simulate rain and drought episodes. This was achieved by maintaining daily watering for 20 days, followed by a period of another 20 days in which watering was suspended, and finally resuming daily watering at 40 DAT. g_s showed a considerable reduction during the water starvation period (Fig. 6B) and, as expected, growth (measured as Δh) was halted (Fig. 6C). After water availability was restored, g_s recovered to the initial values and growth resumed with a rate similar to that of well-watered plants.

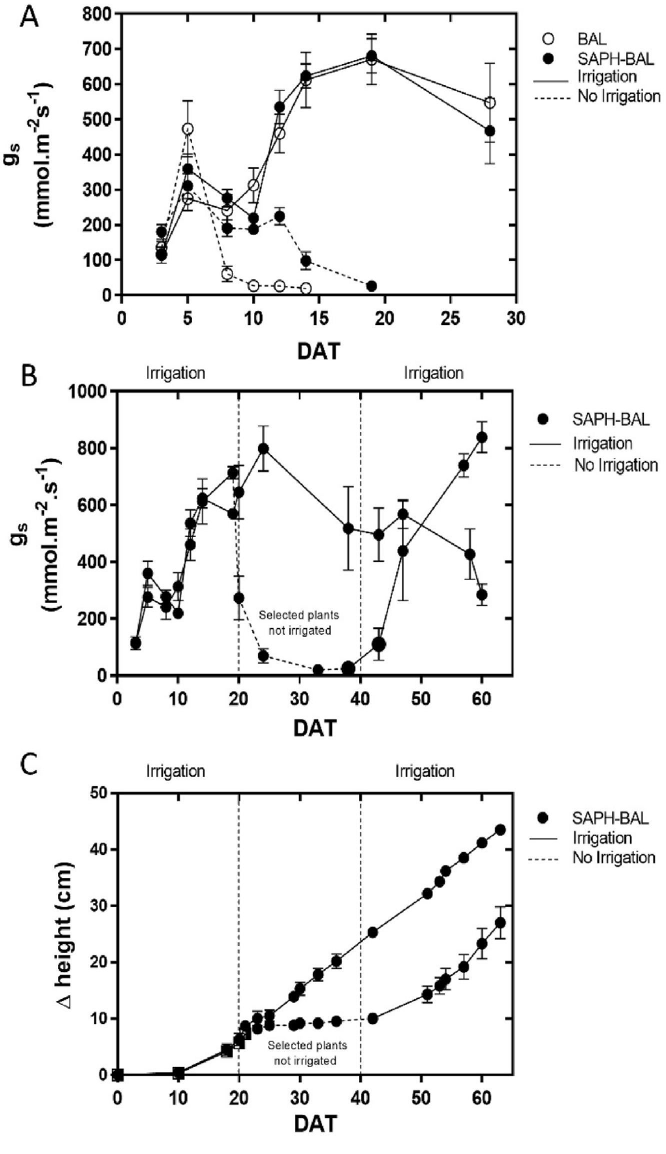


Fig. 6. Effect of water restrictions on stomatal conductance and height of seedlings grown in the presence of mineral nutrients. A. Stomatal conductance (g_s) of plants treated with BAL (open symbols) and SAPH-BAL (closed symbols). One set of plants were watered daily (continuous line) and another set of plants were only watered at the time of transplantation. B, C. Stomatal conductance and height increment, respectively, of plants watered daily for the first 20 days after transplantation and then subjected to watering interruption for a period of another 20 days, followed by a recovery period of daily watering. Error bars indicate SEM (n = 7).

To analyze if the drought protective effect of SAPH-BAL remained during later growing stages of the plantation, we maintained irrigation for 50 days in plants treated with SAPH-BAL and in plants that only received the BAL nutrient mix. At 50 DAT, we interrupted watering to both groups. Seven days later, the group of SAPH-BAL -treated plants still remained turgid while the group that only received the BAL nutrient mix, developed visible water stress symptoms, confirming that SAPH-BAL is able to still protect from water deficit in this temporal window (Suppl. Fig. 5).

3.7. *Performance of SAPH-BAL under field conditions*

So far, we have shown that SAPH-BAL is adequate for delivering nutrients efficiently under semi-controlled greenhouse conditions. To evaluate whether these observations could be replicated under field conditions, we set 11 trials at South American production sites (Fig. 7A). Detailed information on the 11 field trials performed, together with their corresponding precipitation and temperature data are presented in Table 2. Also, Suppl. Fig. 6 shows the cumulative precipitation recorded at each location during the trials. The first objective was to analyze if the SAPH-BAL composite had indeed a beneficial effect when used under different environmental conditions and, if so, to compare it with the traditional fertilization method (superabsorbent plus 75 g of NPK pellets added on the soil surface besides each seedling). The collected treatments included SAPH only, SAPH-BAL, SAPH-2BAL and SAPH + $\text{NPK}_{\text{pellets}}$.

3.8. *Plant mortality assessment*

As initial seedling fertilization of plantations often can cause plant mortality, we tallied the number of wilted plants at 30 DAT. Results showed that the absence of added nutrients favored survival, as judged by the fact that the SAPH treatment -in which exogenous mineral nutrients were absent-presented the lowest mortality range overall (0–14%; Fig. 7C). The next best performance was shown by SAPH-BAL, with mortality rates ranging from 0 to 20%. In the case of the SAPH + $\text{NPK}_{\text{pellets}}$ treatment, mortality rates increased and ranged from 5 to 32%. Finally, the SAPH-2BAL treatment presented the highest mortality rates overall, ranging from 16 to 42% (Fig. 7C). As expected, and in agreement with our greenhouse results, these observations suggest that the initial osmolality of the rhizosphere is critical and has a strong effect on growth and survival under field conditions.

3.9. *SAPH-BAL enhances the early development of seedlings*

To analyze the effect of our treatments on seedling growth, height data from the field trials were pooled into three categories depending on the measurement times: 30–60 DAT, 90–120 DAT and 150–240 DAT. Fig. 7D shows plant height relative to the SAPH control treatment within each assay as a function of time. As observed, the beneficial effect of SAPH-BAL can be detected earlier than that of the conventional method (SAP + $\text{NPK}_{\text{pellets}}$). Specifically, at early stages of the plantation (30–60 DAT), the SAPH-BAL treatment produced taller plants than the SAPH control in all the trials (12–36% taller than the control). Interestingly, at these early stages, the SAPH + $\text{NPK}_{\text{pellets}}$ treatment produced more variation in height among assays and reduced, consistently in half of the independent trials, the height of the seedlings relative to the SAPH control. At later stages (90-120 DAT), both treatments performed similarly, enhancing plant height by up to 40% relative to the SAPH

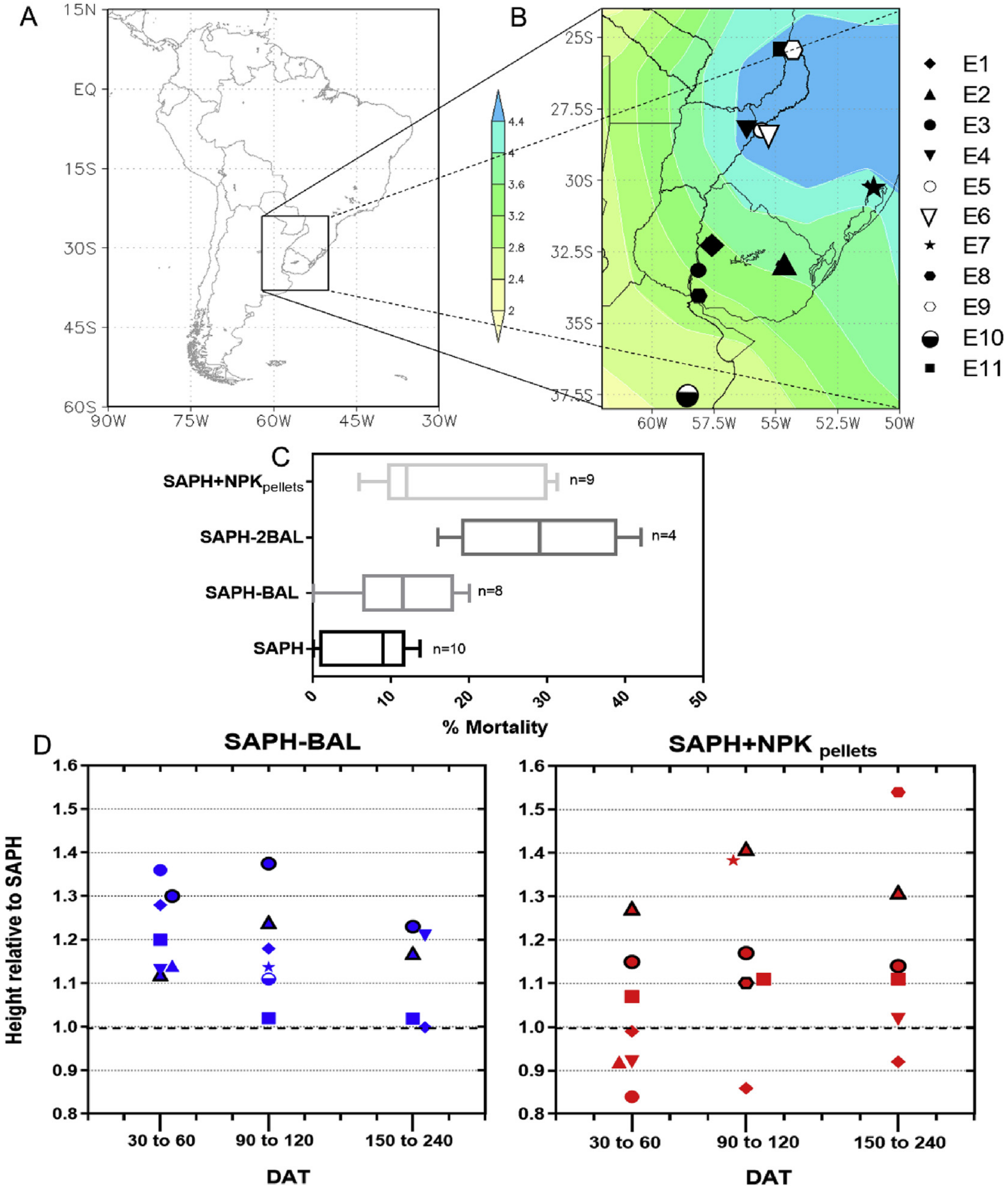


Fig. 7. Effect of SAPH-BAL in field trials at South American sites. A, B. Localization of each trial site in the area of study and annual average precipitation for the region (mm.day^{-1}), respectively. C. Mortality rates of the different treatments tested in the field. Horizontal boxes show the minimum to maximum mortality values (spread), bars show the median mortality rate for each condition, n indicates the number of trials included in the calculations. D. Plant height relative to SAPH as a result of the imposed treatments. Data points indicate the mean height of each treatment (SAPH-BAL or SAP + NPK$_{pellets}$) relative to the effect of SAPH alone for each particular assay.

control. Finally, at even later stages (150–240 DAT), the SAPH + NPK$_{pellets}$ treatment produced very variable results compared to SAPH-BAL, clearly enhancing height in several of the trials (which could indicate a long-term effect on height), but also producing a negative effect in others.

3.10. Effect of precipitation variation on SAPH-BAL performance

As water availability is directly linked to the efficacy of *Eucalyptus* fertilization programs (Jacobs et al., 2004; Weggler et al., 2008), we analyzed to which extent contrasting precipitation regimes (abundant to poor) affected the performance of the treatments. In general, the average precipitation during the field trials (Table 2) followed the expected by the annual climatology (Fig. 7B; Berbery and Barros, 2002), with maximum values in northeastern Argentina and southern Brazil and decreasing to the southwest. Additionally, some assays showed a higher average rainfall during the trials than the annual climatology.

Among the assays in which SAPH-BAL and SAPH-NPK$_{pellets}$ treatments were tested jointly (assays E1-E7 and E11; Table 3), in most of the assays with high precipitation and high proportion of days with rain (assays E4-E7 and E11; Suppl. Fig. 6B, Table 2), the SAPH-BAL alternative outperformed the SAPH control at one or more measurement times, confirming the positive effect of SAPH-BAL on plant height in the absence of water restriction (Table 3). Whereas the conventional scheme (SAPH + NPK$_{pellets}$) worked well

Table 3
Effect of SAPH, SAPH-BAL and SAPH + NPK$_{pellets}$ on plant height in the assays where the three treatments were tested jointly. Assays E1, E2 and E3 presented low rainfall (pp) values (<4 mm.day^{-1}) while assays E4, E5, E6, E7 and E11 showed high rainfall values (>5 mm.day^{-1}). Errors calculated were SEM. Asterisks indicates significant differences compared to SAPH-treated plants. * = $p < 0.05$; ** = $p < 0.005$, *** = $p < 0.001$.

ASSAY		E1	E2	E3	E4	E5	E6	E7	E11
pp (mm.day^{-1})		1.5	1.5	3.5	6.5	7.5	7.5	5.5	5.2
DAT	**Treatment**	**Mean Height (cm)**							
30–60	SAPH	36.2 ± 0.7	27.6 ± 1.2	25.3 ± 1.1	34.5 ± 1.0	33.8 ± 1.2	47.0 ± 2.2	–	27.0 ± 0.7
	SAPH + NPK	35.8 ± 1.3	25.9 ± 1.2	21.7 ± 1.5	35.0 ± 0.9	38.9 ± 3.7	59.8 ± 3.0**	–	29.1 ± 0.8
	SAPH-BAL	46.3 ± 1.1***	31.5 ± 3.7*	34.4 ± 1.4**	42.8 ± 0.9***	44.1 ± 2.9*	52.5 ± 2.5	–	32.4 ± 0.9**
90–120	SAPH	69.2 ± 3.3	–	–	–	67.2 ± 4.1	99.6 ± 6.5	38.41 ± 3.5	44.9 ± 1.2
	SAPH + NPK	59.5 ± 3.6	–	–	–	78.5 ± 10.3	141.2 ± 7.3***	48.92 ± 3.0*	50 ± 1.2*
	SAPH-BAL	81.7 ± 3.2*	–	–	–	92.4 ± 8.5*	123.7 ± 7.8*	43.63 ± 3.6	46.2 ± 1.3
150–240	SAPH	140.8 ± 4.8	–	–	152.7 ± 5.6	135.9 ± 9.2	189.3 ± 11.5	–	70.8 ± 3.0
	SAPH + NPK	129.6 ± 5.7	–	–	155.6 ± 5.3	154.7 ± 17.0	248.9 ± 9.6**	–	78.8 ± 1.5*
	SAPH-BAL	143.4 ± 4.7	–	–	185.6***	171.5 ± 16.1	221.5 ± 12.4	–	72.4 ± 3.1

at certain high rainfall assays enhancing height considerably (*i.e.* E6; Fig. 8A, lower panels), at other assays with high precipitation the SAPH-BAL treatment produced taller plants compared to the SAPH + NPK$_{pellets}$ scheme, mostly at the beginning of the plantation. For example, in a trial performed at the site with the highest precipitation and highest percentage of days with rain (E5; 7.5 mm. day^{-1} on average, 71.0%, respectively; Table 2) the SAPH-BAL-treated plants were taller than the SAPH-treated group (30%, 37.5% and 26% taller compared to SAPH-treated plants at 60, 120 and 225 DAT respectively), while there were no significant

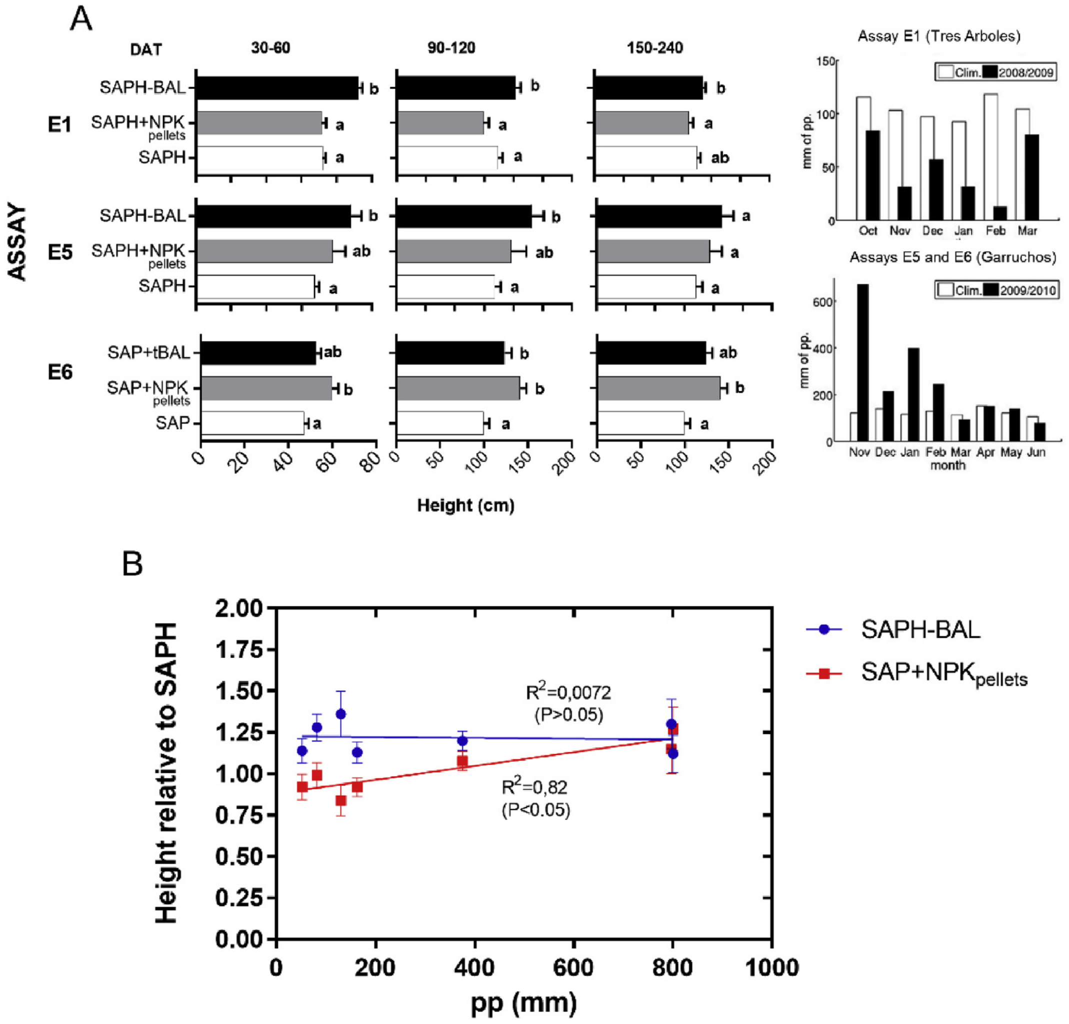


Fig. 8. **Effect of the fertilization method on plant growth in field trials with contrasting precipitation regimes.** A. Top panel: Effect of SAPH-BAL compared to SAP + NPK$_{pellets}$ and SAPH alone at the location with the lowest precipitation (E1, Los Arboles; n = 50). Lower panels: Effect of SAPH-BAL compared to SAP + NPK$_{pellets}$ and SAPH alone in two trials performed at the site with the highest precipitation (E5 and E6, Garruchos; n = 32). Different letters indicate significant differences among treatments. Right panels show the monthly cumulative precipitation corresponding to each site during the months of the assay and the long term mean precipitation for the same months. B. Correlation graph: mean height of the treatments (relative to SAPH) plotted against the cumulative precipitation recorded for each trial at 60 DAT. Error bars indicate SEM.

differences in height among the SAPH-BAL and SAPH + $\mathrm{NPK_{pellets}}$-treated groups ($p < 0.05$; Fig. 8A, middle panels). Similar results were obtained at other high rainfall locations (*i.e.* assay E4, Table 3). Conversely, on the sites with lower precipitation and low proportion of days with rain (assays E1-E3; Suppl. Fig. 6B, Table 2), the SAPH-BAL treatment outperformed both the SAPH and the SAPH + $\mathrm{NPK_{pellets}}$ treatments (Table 3). Indeed, at the site with the lowest precipitation overall (assay E1, 1.5 mm. $\mathrm{day^{-1}}$ on average, Table 2) and a low proportion of days with rain (13,8%), the SAPH-BAL treatment produced taller plants compared to both the SAPH and the SAPH + $\mathrm{NPK_{pellets}}$ treatments throughout most of the trial, with a marked difference at 60 DAT (SAPH-BAL = 46.25 cm, SAPH + $\mathrm{NPK_{pellets}}$ = 35.75 cm, SAPH = 36.15 cm, $p < 0.0001$; Fig. 8A, top panels). Similar results were obtained at other locations with diminished rainfall (*i.e.* assay E2, E3; Table 3).

To evaluate if there was in fact a relationship between precipitation and treatment performance during the first stages of the plantation, a correlation analysis was carried out between precipitation and height in the different assays, computing rain and height data for the first 60 DAT. The data showed a positive correlation of the conventional SAPH + $\mathrm{NPK_{pellets}}$ treatment to precipitation (slope different to zero, $p < 0.05$: $R^2 = 0.82$), whereas no such correlation was found in the case of the SAPH-BAL treatment (slope not different to zero, $p > 0.05$: $R^2 = 0.0001$), suggesting a higher degree of independence from the weather conditions in this latter treatment (Fig. 8B).

4. Discussion

The aim of this work was to design, synthetize and evaluate the efficacy of a composite superabsorbent polymer for nutrient delivery during tree seedling transplantation to the field. By utilizing the dry bulk radical polymerization method (Mikita et al., 1987), we were able to polymerize AA monomers in the presence of nutrient elements to obtain the SAPH-BAL composite. Differently from other polymerization techniques, such as solution polymerization (Liu et al., 2006), this synthesis method is simple and inexpensive, while producing a good quality superabsorbent product. The addition of 2% HEC during polymerization overcame the distortions produced by the addition of the fertilizers and produced a hydrogel with increased viscosity and strength, more suitable for soil improvement applications. The enhancement on these rheological properties was likely due to physical entangling caused by the HEC molecules with PAA residues so that a three-dimensional structure could be properly formed (Mabrouk et al., 2015). This stabilization effect of HEC is consistent with previous reports concerning other modified natural polymers such as carboxymethyl starch in acrylic based hydrogel systems (Gottlieb and Copelle, 2005; Soleimani and Sadeghi, 2012).

Eucalyptus is a very successful wood crop because it is highly efficient in using water and mineral nutrients (Whitehead and Beadle, 2004). However, the use at outplanting of traditional granulated fertilizers with high phosphate content is routine in *Eucalyptus* commercial forests (Attiwil and Adams, 1996). The high nutrient uptake efficiency of *Eucalyptus* led us to question whether, by synthetizing a hydrogel additivated with balanced amounts of specific nutrients, the reliance on solid NPK fertilizers could be decreased. To fulfill the mineral nutritional requirements of *Eucalyptus* seedlings, we developed a balanced nutrient formulation (BAL, Table 1) that was incorporated into the superabsorbent composite during synthesis. The nutrients were chosen so that the main element ratios were compatible with *Eucalyptus* seedlings needs (Herbert, 1990; Schönau and Herbert, 1983) during the two-month settling process into the final terrain. We also included all the other essential macro and micronutrients (Dell et al., 2003, Table 1).

Greenhouse-grown, well-watered plants that received the SAPH-BAL composite increased their stomatal conductance by up to 350% by 20 DAT reaching a peak of similar magnitude to the maximum g_s reported for *E. grandis* (Whitehead and Beadle, 2004). After 30 DAT, g_s started to decrease, and by 45 DAT values were not different from the controls, probably due to nutrient exhaustion. This suggests that the nutritional condition of the *Eucalyptus* seedlings is a factor that strongly impacts g_s, in accordance with previous reports (Battie-Laclau et al., 2013; Franks et al., 2009). Interestingly, in our experimental conditions the increased g_s was obtained regardless of whether the nutrients were delivered through the SAPH-BAL composite or were simply mixed with the substrate without adding hydrogels (BAL treatment). However, seedling height as well as root and shoot biomass were significantly increased among the SAPH-BAL-treated group compared to plants that only received the nutrients (BAL), suggesting an additional role of the composite in relation to efficient nutrient use. The fact that g_s behavior could not explain the increased growth rates observed in SAPH-BAL-treated plants suggests that these differences were not due to an increased photosynthesis per unit leaf area but were the result of an enhanced capacity to form new leaves (Fig. 3). To explain the beneficial effect of SAPH-BAL, one possibility is that the polymer helped maintain a proper local concentration of nutrient molecules in the root surroundings over an extended period. The finding that SAPH-BAL releases nutrients slower compared to placing the fertilizers and hydrogel separately, is compatible with that idea and it agrees with published results that show that hydrogels can significantly diminish the nutrient release rate (Guo et al., 2004; Smith and Harrison, 1991). It has been reported that, besides improving nutrient retention, the hydrogel could also enhance the diffusion of low mobility molecules present in low concentration within the rhizosphere (Bres and Weston, 1993; Ghebru and Steyn, 2007; Henderson and Hensley, 1985; Mikkelsen, 1995). Several superabsorbent polymers have been used in different species to deliver nutrients with favorable results, in agreement with our observations. For example Chen et al. (2004) observed in a study performed in *Populus* that polyacrylamide favors absorption of $\mathrm{Ca^{2+}}$, significantly enhancing growth.

Due to the elevated initial P demand (Barros et al., 1992; Fernandez et al., 2000), traditional NPK fertilizers used to improve *Eucalyptus* outplanting performance are generally rich in P, having a N:P ratio close to 0.5, aimed at compensating the soil's P deficiency. The BAL nutrient mix provides a lower amount of P (N:P = 1.25) in comparison to these NPK fertilizers but still it is higher than nutrient compositions such as the Hoagland's solution (N:P = 6.8; Hoagland and Arnon, 1950). We found that the SAPH-BAL composite outperformed the SAPH-NPK composite on growth parameters (45% average biomass increase). We concluded that reducing P to include other nutrients is beneficial for seedling establishment, in agreement with published results showing that higher N:P and K:P ratios favor *Eucalyptus* growth (Battie-Laclau et al., 2013; Christina et al., 2015; Herbert, 1983, 1990; Knecht and Göransson, 2004). The presence of other nutrients could contribute, as well, to the improved growth that we observed, and in the field, this could help the seedling to outcompete the natural flora, which is critical for success at outplanting. It was reported, in fact, that small amounts of macronutrients such as Ca, S, and Fe, as well as certain micronutrients like B, Cu, Zn, Mn and even Na, can dramatically benefit *Eucalyptus* throughout its field establishment (Battie-Laclau et al., 2013; Dell et al., 2003; Merino et al., 2003; Xu and Dell, 2003). Moreover, adding micronutrients to the initial fertilizer mix could become particularly beneficial, in view of the fact that heavy fertilization with macronutrients has been linked with deficiencies in the uptake of micronutrients (Xu and Dell, 2003).

Similarly to our greenhouse observations, we found that in the field, compared to using only SAPH, the SAPH-BAL composite improved growth in most of the trials, confirming the suitability of this polymer as a nutrient deliverer for field utilization. When comparing the SAPH-BAL to the traditional fertilization scheme (superabsorbent plus 75 g NPK pellets, our SAPH + $NPK_{pellets}$ treatment), we found that both methods increased growth in general terms, despite substantial differences in the amount of nutrients applied (75 g of NPK pellets per seedling vs. 1.06 g of fertilizers if SAPH-BAL is used). Furthermore, compared to SAPH controls or to SAPH-BAL, the traditional fertilization scheme increased the seedling mortality rate and significantly reduced growth in several trials. The fact that SAPH-BAL outperformed the SAPH + $NPK_{pellets}$ on these field trials was likely due to NPK pellets-derived inhibition of root system development and of drought avoidance mechanisms as previously observed (Jacobs et al., 2004; Weggler et al., 2008).

The variability recorded for the treatments at different trials can be explained based on the interaction of genetic, weather and edaphological parameters on each assay (Dell et al., 2003; Goncalves et al., 1997; Laclau, 2003; Merino et al., 2003; Morabito et al., 1994). The SAPH-BAL treatment presented less variation between locations compared to using SAPH + $NPK_{pellets}$. Among the performed trials, rainfall was particularly uneven, covering a wide range (from 1.5 mm. day^{-1} to 7.5 mm. day^{-1} on average). Interestingly, several of the assays in which the SAPH + $NPK_{pellets}$ treatment showed diminished growth or increased mortality presented low rainfall values at the early stages of the plantation. Abundant water seems to be essential to guarantee the correct functionality of P rich fertilizers (Graciano et al., 2006; Weggler et al., 2008) whose excess leads to nutrient toxicity. It has been proposed that this impairs further nutrient uptake as a consequence of regulatory responses, *e.g.* decreasing the expression of root specific transporters (Shen et al., 2011). Reduced rainfall could also decrease g_s, diminishing nutrient uptake through mass flow (Cernusak et al., 2011; Mielke et al., 1999). Notably, in our assays where rainfall was low (*i.e.* trials E1, E2 and E3), the SAPH-BAL alternative not only did not cause growth retardation or seedling mortality, but it enhanced growth compared to SAPH alone, guaranteeing elevated survival rates in a low water availability scenario. Furthermore, a correlation analysis suggested that the growth supported by the SAPH + $NPK_{pellets}$ method was highly dependent on accumulated rainfall during the first 60 DAT, while the SAPH-BAL method was found to be less dependent on rainfall. This is compatible with reports showing that the addition of solid fertilizers can lead to reduced ability of *E. globulus* seedlings to manage water stress (see, for example, Wang et al., 1988).

Contrary to the granulated NPK method, the nutrients present in the hydrated SAPH-BAL are available to the roots as soon as plants are transferred to the soil and allow for a homogeneous distribution of nutrients throughout the soil profile. In this regard, the identity, quantity and bioavailability of elements granted by SAPH-BAL were sufficient to hasten growth during outplanting and showed a benefit even in fertile terrains. In this respect, the SAP's nutrient concentration and osmolality were detrimental to seedling establishment if excessive, and therefore should be tightly controlled to avoid growth retardation and early mortality (this was the case for SAPH-2BAL-treated plants). Increased osmolality of the soil solution was likely the cause of failed attempts to use SAP as a vehicle of fertilizers in previous work, where *Eucalyptus* treated with a superabsorbent mixed with a fertilizer formulation showed poorer growth compared to using only the polymer or granulated NPK pellets (Viero and Little, 2006). The fact that only limited amounts of ions can be incorporated into the polymer would be compensated by improved SAP-mediated nutrient mobilization/delivery and also by the nature of the molecules supplied (*i.e.* key micronutrients) that could complement the nutritional status of the soil. The low amounts of nutrients and the slower release rate observed for the SAPH-BAL composite bring the additional benefit of reducing fertilizer derived ground pollution and virtually eliminate the risk of undesired fertilization of natural flora.

5. Conclusion

In conclusion, we propose a virtuous cycle, in which a polymer composite like SAPH-BAL could sustain early high stomatal conductances and carbon assimilation rates to produce fast growth and enable seedlings to reach ground water and soil nutrients more rapidly. Moreover, in highly weathered soils, where the fertilization schemes aimed at incorporating large volumes of P are fundamental, such a compound could enhance the efficiency of the granulated fertilizers, reducing the amounts needed and allowing for increased independence from rain events. Due to the low planting densities utilized in silviculture, this method of supplying nutrients is compatible with current forestry practices and takes advantage on the already established SAP applications techniques.

Conflicts of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author contributions

ET and GA conceived the idea of this work and designed the experiments. MSA and FAT contributed with the field assays. ET, VAV, IB and GA analyzed the data and discussed the results. ET, IB and GA, planned and wrote the manuscript. All authors approved the final version.

Acknowledgements

We thank Anabella Di Gaudio, Jose María Chain, Andrea Dengis, Mónica Robles, Alejandro Bacigalupe, Santiago Marsili and Conrado Geron for their valuable contribution to this work.

This work was supported by the Agencia Nacional para la Promoción Científica y Técnica [Préstamo BID PICT16-3265] and Universidad de Buenos Aires UBACyT14-17, all grants to G.A.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jenvman.2017.12.062.

References

Abreu-Junior, C.H., Pitol Firme, L., Baca Maldonado, C.A., Pires de Moraes Neto, S., Corrêa Alves, M., Muraoka, T., Enedi Boaretto, A., Gava, J.L., He, Z., Assis Rodrigues Nogueira, T., Capra, G.F., 2017. Fertilization using sewage sludge in unfertile tropical soils increased wood production in Eucalyptus plantations. J. Environ. Manag. 203, 51–58. https://doi.org/10.1016/j.jenvman.2017.07.074.

Albaugh, T.J., Albaugh, J.M., Fox, T.R., Allen, H.L., Rubilar, R.A., Trichet, P., Loustau, D., Linder, S., 2016. Tamm Review: light use efficiency and carbon storage in nutrient and water experiments on major forest plantation species. For. Ecol. Manag. 376, 333–342.

ABRAF - Associaçao Brasileira de Produtores de Florestas Plantadas, 2013. Yearbook Statistical Abraf 2013 Base Year 2012. ABRAF, Brasília. Available at: http://www.ipef.br/estatisticas/.

Attiwil, P.M., Adams, M.A., 1996. In: V. C. P. (Ed.), Nutrition of Eucalyptus. Collingwood CSIRO Publishing.

Barros, N.F., Novais, R.F., Neves, J.C.L., Leal, P.G.L., 1992. Fertilizing eucalypt plantations on the Brazilian savannah soils. In: Intensive Forestry: the Role of Eucalypts (Durban, South Africa: IUFRO Symposium), pp. 7–12. https://doi.org/10.1080/00382167.1992.9630404.

Battie-Laclau, P., Laclau, J.P., Piccolo, M., de, C., Arenque, B.C., Beri, C., Mietton, L., et al., 2013. Influence of potassium and sodium nutrition on leaf area components in *Eucalyptus grandis* trees. Plant Soil 371, 19–35. https://doi.org/10.1007/s11104-013-1663-7.

Berbery, E.H., Barros, V.R., 2002. The hydrologic cycle of the La plata basin in south America. J. Hydrometeorol. 3, 630–645. https://doi.org/10.1175/1525-7541.

Binkley, D., Fisher, R., 2013. Ecology and Management of Forest Soils. Wiley-Blackwell.

Bohlenius, H., Overgaard, R., 2014. Effects of direct application of fertilizers and hydrogel on the establishment of poplar cuttings. Forests 5, 2967–2979. https://doi.org/10.3390/f5122967.

Booth, T.H., 2013. Eucalypt plantations and climate change. For. Ecol. Manag. 301, 28–34. https://doi.org/10.1016/j.foreco.2012.04.004.

Bowman, D.C., Evans, R.Y., Paul, J.L., 1990. Fertilizer salts reduce hydration of polyacrylamide gels and affect physical properties of gel-amended container media. Hortic. Sci. 115, 382–386.

Bres, W., Weston, L.A., 1993. Influence of gel additives on nitrate, ammonium, and water retention and tomato growth in a soilless medium. Hort Science 28, 1005–1007.

Calo, E., Khutoryanskiy, V.V., 2015. Biomedical applications of hydrogels: a review of patents and commercial products. Eur. Polym. J. 65, 252–267. https://doi.org/10.1016/j.eurpolymj.2014.11.024.

Cernusak, L.A., Winter, K., Turner, B.L., 2011. Transpiration modulates phosphorus acquisition in tropical tree seedlings. Tree Physiol. 31, 878–885. https://doi.org/10.1093/treephys/tpr077.

Chapman, N., Miller, A.J., Lindsey, K., Whalley, W.R., 2012. Roots, water, and nutrient acquisition: let's get physical. Trends Plant Sci. 17, 701–710. https://doi.org/10.1016/j.tplants.2012.08.001.

Chen, S., Zommorodi, M., Fritz, E., Wang, S., Hüttermann, A., 2004. Hydrogel modified uptake of salt ions and calcium in *Populus euphratica* under saline conditions. Trees Struct. Funct. 18, 175–183. https://doi.org/10.1007/s00468-003-0267-x.

Christina, M., Le Maire, G., Battie-Laclau, P., Nouvellon, Y., Bouillet, J.P., Jourdan, C., et al., 2015. Measured and modeled interactive effects of potassium deficiency and water deficit on gross primary productivity and light-use efficiency in *Eucalyptus grandis* plantations. Global Change Biol. 21, 2022–2039. https://doi.org/10.1111/gcb.12817.

Davidson, D.W., Verma, M.S., Gu, F.X., 2013. Controlled root targeted delivery of fertilizer using an ionically crosslinked carboxymethyl cellulose hydrogel matrix. SpringerPlus 2, 318. https://doi.org/10.1186/2193-1801-2-318.

Davis, A.S., Jacobs, D.F., 2005. Quantifying root system quality of nursery seedlings and relationship to outplanting performance. New For. 30, 295–311. https://doi.org/10.1007/s11056-005-7480-y.

Dell, B., Malajczuk, N., Xu, D., Grove, T.S., 1995. Nutrient Disorders in Plantation Eucalypts. Australian Centre for International Agricultural Research, Canberra, Australia.

Dell, B., Xu, D., Rogers, C., Huang, L., 2003. Micronutrient disorders in eucalypt plantations: causes, symptoms, identification, impact and management. In: Eucalyptus Plantations: Research, Management and Development: Proceedings of the International Symposium. World Scientific, Guangzhou, China, pp. 241–252.

Diaz-Balteiro, L., Alfranca, O., Gonzalez Pachon, J., Romero, C., 2016. Ranking of industrial forest plantations in terms of sustainability: a multicriteria approach. J. Environ. Manag. 180, 123–132. https://doi.org/10.1016/j.jenvman.2016.05.022.

Erazo, F., 1987. Superabsorbent hydrogels and their benefits in forestry applications 1. In: Landis, T.D. (Ed.), Proceedings, Intermountain Forest Nursery Association. U.S. Department of Agriculture, Oklahoma City, OK.

FAO, 2008. Eucalyptus Universalis. Cultivated Eucalypt Forests Global Map. FAO Department of Forestry, Rome, V. 1.0. .

FAO, 2015. World Fertilizer Trends and Outlook to 2018. FAO.

Fernandez, J.Q.P., Dias, L.E., Barros, N.F., Novais, R.F., Moraes, E.J., 2000. Productivity of *Eucalyptus camaldulensis* affected by rate and placement of two phosphorus fertilizers to a Brazilian Oxisol. For. Ecol. Manag. 127, 93–102. https://doi.org/10.1016/S0378-1127(99)00121-8.

Franks, P.J., Drake, P.L., Beerling, D.J., 2009. Plasticity in maximum stomatal conductance constrained by negative correlation between stomatal size and density: an analysis using *Eucalyptus globulus*. Plant Cell Environ. 32, 1737–1748. https://doi.org/10.1111/j.1365-3040.2009.002031.x.

Forrester, D.I., 2013. Growth responses to thinning, pruning and fertiliser application in *Eucalyptus plantations*: a review of their production ecology and interactions. For. Ecol. Manag. 310, 336–347. https://doi.org/10.1016/j.foreco.2013.08.047.

Ghebru, M.G., Steyn, J.M., 2007. Water and nutrient retention by Aquasoil and Stockosorb polymers. South Afric. J. Plant Soil 24, 32–36. https://doi.org/10.1080/02571862.2007.10634778.

Goncalves, J. L. de M., Barros, N., Nambiar, E.K.S., Novais, R.F., 1997. Soil and stand management for short-rotation plantations. Manag. Soil Nutri. Water Trop. Plant. For. 379–411.

Good, A.G., Beatty, P.H., 2011. Fertilizing nature: a tragedy of excess in the commons. PLoS Biol. 9, 1–9. https://doi.org/10.1371/journal.pbio.1001124.

Gottlieb, K.F., Copelle, A., 2005. Starch Derivatization: Fascinating and Unique Industrial Opportunities. Wageningen Academic Publishers, The Nederlands. https://doi.org/10.3920/978-90-8686-541-3.

Graciano, C., Goya, J.F., Caldiz, D.O., 2004. Acumulacion y distribucion de materia seca en *Eucalyptus globulus* (Labill.) plantado en macetas con tres tipos de suelo y fertilizado con fosforo. Ecol. Austral 14, 53–63.

Graciano, C., Goya, J.F., Frangi, J.L., Guiamet, J.J., 2006. Fertilization with phosphorus increases soil nitrogen absorption in young plants of *Eucalyptus grandis*. For. Ecol. Manag. 236, 202–210. https://doi.org/10.1016/j.foreco.2006.09.005.

Grossnickle, S.C., 2005. Importance of root growth in overcoming planting stress. New For. 30, 273–294. https://doi.org/10.1007/s11056-004-8303-2.

Grossnickle, S.C., Folk, R.S., 1993. Stock quality assessment: forecasting survival or performance on a reforestation site. Tree plant. Notes 44, 113–121.

Guo, M., Liu, M., Hu, Z., Zhan, F., Wu, L., 2004. Preparation and properties of a slow release NP compound fertilizer with superabsorbent and moisture preservation. J. Appl. Polym. Sci. 96, 2132–2138. https://doi.org/10.1002/app.21140.

Henderson, J.C., Hensley, D.L., 1985. Ammonium and nitrate retention by a hydrophilic gel. HortScience 20, 667–668.

Herbert, M.A., 1983. The response of *Eucalyptus grandis* to fertilising with nitrogen, phosphorus, potassium and dolomitic lime on a Mispah soil series. Suid-Afrikaanse Bosboutydskif 124, 4–12. https://doi.org/10.1080/00382167.1983.9628859.

Herbert, M.A., 1990. Fertilizer/site interactions on the growth and foliar nutrient levels of *Eucalyptus grandis*. For. Ecol. Manag. 30, 247–257. https://doi.org/10.1016/0378-1127(90)90140-7.

Herbert, M.A., Schonau, A.P.G., 1989. Fertilising comercial forest species in southern Africa: research progress and problems (Part1). South. Afr. For. J. 151, 58–70.

Hernandez, M.J., Montes, F., Ruiz, F., Lopez, G., Pita, P., 2016. The effect of vapour pressure deficit on stomatal conductance, sap pH and leaf-specific hydraulic conductance in *Eucalyptus globulus* clones grown under two watering regimes. Ann. Bot. 117 (6), 1063–1071. https://doi.org/10.1093/aob/mcw031.

Hoagland, D.R., Arnon, D.I., 1950. The water-culture method for growing plants without soil. Calif. Agric. Exp. Stn. Circ. 347, 1–32.

Hoare, T.R., Kohane, D.S., 2008. Hydrogels in drug delivery: progress and challenges. Polymer (Guildf). 49, 1993–2007. https://doi.org/10.1016/j.polymer.2008.01.027.

Hüttermann, A., Zommorodi, M., Reise, K., 1999. Addition of hydrogels to soil for prolonging the survival of *Pinus halepensis* seedlings subjected to drought. Soil Tillage Res. 50, 295–304.

Jacobs, D., Rose, R., Haase, D., Alzugaray, P., 2004. Fertilization at planting impairs root system development and drought avoidance of Douglas-fir (*Pseudotsuga menziesii*) seedlings Douglass. Ann. For. Sci. 61, 643–651. https://doi.org/10.1051/forest:2004065.

Knecht, M.F., Göransson, A., 2004. Terrestrial plants require nutrients in similar proportions. Tree Physiol. 24, 447–460. https://doi.org/10.1093/treephys/24.4.447.

Kröger, M., 2012. Global tree plantation expansion: a review. ICAS Rev. Pap. Ser. 1–25.

Laclau, J., 2003. Nutrient cycling in a clonal stand of Eucalyptus and an adjacent savanna ecosystem in Congo 1. Chemical composition of rainfall, throughfall and stem flow solutions. For. Ecol. Manag. 176, 105–119. https://doi.org/10.1016/S0378-1127(02)00280-3.

Landis, T.D., Haase, D.L., 2012. Applications of hydrogels in the nursery and during outplanting. For. Conserv. Nurs. Assoc. 53–58. Available at: http://www.fs.fed.us/rm/pubs/rmrs_p068/rmrs_p068_053_058.pdf.

Liang, R., Liu, M., 2006. Preparation and properties of coated nitrogen fertilizer with slow release and water retention. Ind. Eng. Chem. Res. 45, 8610–8616.

Liu, M., Liang, R., Zhan, F., Liu, Z., Niu, A., 2006. Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties. Polym. Adv. Technol. 17, 430–438. https://doi.org/10.1002/pat.

Mabrouk, M., Chejara, D.R., Mulla, J.A.S., Badhe, R.V., Choonara, Y.E., Kumar, P., et al., 2015. Design of a novel crosslinked HEC-PAA porous hydrogel composite for dissolution rate and solubility enhancement of efavirenz. Int. J. Pharm. 14952, 1–9. https://doi.org/10.1016/j.ijpharm.2015.05.082.

Madejón, P., Alaejos, J., García-Álbala, J., Fernández, M., Madejón, E., 2016. Three-year study of fast-growing trees in degraded soils amended with composts: effects on soil fertility and productivity. J. Environ. Manag. 169, 18–26. https://doi.org/10.1016/j.jenvman.2015.11.050.

Merino, A., Lopez, A.R., Branas, J., Rodriguez-Soalleiro, R., 2003. Nutrition and growth in newly established plantations of *Eucalyptus globulus* in northwestern Spain. Ann. For. Sci. 60, 509–517. https://doi.org/10.1051/forest:2003044.

Mielke, M.S., Oliva, M.A., De Barros, N.F., Penchel, R.M., Martinez, C.A., De Almeida, A.C., 1999. Stomatal control of transpiration in the canopy of a clonal *Eucalyptus grandis* plantation. Trees Struct. Funct. 13, 152–160. https://doi.org/10.1007/s004680050199.

Mikita, M., Tanioku, S., and Touda, T. (1987). Process for preparing dry solid water absorbing polyacrylate resin. USA patent 4,703,067. 1–10.

Mikkelsen, R.L., 1994. Using hydrophilic polymers to control nutrient release. Fert. Res. 38, 53–59. https://doi.org/10.1007/BF00750062.

Mikkelsen, R.L., 1995. Using hydrophilic polymers to improve uptake of manganese fertilizers by soybeans. Fert. Res. 41, 87–92. https://doi.org/10.1007/BF00750749.

Munns, R., Tester, M., 2008. Mechanisms of salinity tolerance. Annu. Rev. Plant Biol. 59, 651–681.

Montagu, K.D., Kearney, D.E., Smith, R.G.B., 2003. The biology and silviculture of pruning planted eucalypts for clear wood production - a review. For. Ecol. Manag. 179, 1–13. https://doi.org/10.1016/S0378-1127(02)00579-0.

Morabito, D., Mills, D., Prat, D., Dizengremel, P., 1994. Response of clones of

Eucalyptus microtheca to NaCl in vitro. Tree Physiol. 14, 201–210. Available at: http://www.ncbi.nlm.nih.gov/pubmed/14967714.

Rabat, E.N., Hashim, S., Abdul, R., 2016. Effect of different monomers on water retention properties of slow release fertilizer hydrogel. Process Eng. 148, 201–207. https://doi.org/10.1016/j.proeng.2016.06.573.

Research and Markets, 2015. Global Superabsorbent Polymers (SAP) Market - Industry Analysis, Size, Share, Growth, Trends and Forecast 2014-2021. Dublin Available at: http://www.researchmarkets.com/reports/3398216.

Reynolds, C.A., Jackson, T.J., Rawls, W.J., 2000. Estimating soil water-holding capacities by linking the Food and Agriculture Organization soil map of the world with global pedon databases and continuous pedotransfer functions. Water Resour. Res. 36, 3653–3662. https://doi.org/10.1029/2000WR900130.

Sands, P.J., Cromer, R.N., Kirschbaum, M.U.F., 1992. A model of nutrient response in *Eucalyptus grandis* seedlings. Aust. J. Plant Physiol. 19, 459–470. https://doi.org/10.1071/PP9920459.

Schönau, A.P.G., Herbert, M.A., 1983. Relationship between growth rate, fertilizing and foliar nutrient concentrations for *Eucalyptus grandis*; preliminary investigations. Fert. Res. 380, 369–380.

Sharma, R., Bell, R.W., Wong, M.T.F., 2016. Dissolved reactive phosphorus played a limited role in phosphorus transport via runoff, throughflow and leaching on contrasting cropping soils from southwest Australia. Sci. Total Environ. 1–12. https://doi.org/10.1016/j.scitotenv.2016.09.182.

Shen, J., Li, C., Mi, G., Li, L., Yuan, L., Jiang, R., et al., 2013. Maximizing root/rhizosphere efficiency to improve crop productivity and nutrient use efficiency in intensive agriculture of China. J. Exp. Bot. 64, 1181–1192. https://doi.org/10.1093/jxb/ers342.

Shen, J., Lixing, Y., Junling, Z., Haigan, L., Zhaohai, B., Xinping, C., et al., 2011. Phosphorus dynamics: from soil to plant. Plant Physiol. 156, 997–1005. https://doi.org/10.1104/pp.cgi/www.plantphysiol.org/Turner.

Sitthaphanit, S., Limpinuntana, V., Toomsan, B., Panchaban, S., Bell, R.W., 2009. Fertiliser strategies for improved nutrient use efficiency on sandy soils in high rainfall regimes. Nutrient Cycl. Agroecosyst. 85, 123–139. https://doi.org/10.1007/s10705-009-9253-z.

Smethurst, P.J., 2010. Forest fertilization: trends in knowledge and practice compared to agriculture. Plant Soil 335, 83–100. https://doi.org/10.1007/s11104-010-0316-3.

Smith, J.D., Harrison, H.C., 1991. Communications in Soil Science and Plant Analysis Evaluation of polymers for controlled - release properties when incorporated with nitrogen fertilizer solutions. Commun. Soil Sci. Plant Anal. 22, 559–573. https://doi.org/10.1080/00103629109368437.

Soleimani, F., Sadeghi, M., 2012. Synthesis of pH-sensitive hydrogel based on. J. Biomaterials Nanobiotechnol. 3, 310–314. https://doi.org/10.4236/jbnb.2012.322038.

Stape, J.L., Binkley, D., Ryan, M.G., 2004. Eucalyptus production and the supply, use and efficiency of use of water, light and nitrogen across a geographic gradient in Brazil. For. Ecol. Manag. 193, 17–31. https://doi.org/10.1016/j.foreco.2004.01.020.

Tng, D.Y.P., Janos, D.P., Jordan, G.J., Weber, E., Bowman, D.M.J.S., 2014. Phosphorus limits *Eucalyptus grandis* seedling growth in an unburnt rain forest soil. Front. Plant Sci. 5, 527. https://doi.org/10.3389/fpls.2014.00527.

Ullah, F., Othman, M.B.H., Javed, F., Ahmad, Z., Akil, H.M., 2015. Classification, processing and application of hydrogels: a review. Mater. Sci. Eng. C 57, 414–433. https://doi.org/10.1016/j.msec.2015.07.053.

Viero, P.W.M.I., Little, K.M., Oscroft, D.G., 2000. The effect of a soil-amended hydrogel on the establish- ment of a *Eucalyptus grandis* x *E. camaldulensis* clone grown on the sandy soils of Zululand. South. Afr. For. J. 188, 21–28.

Viero, P.W.M., Little, K.M., 2006. A comparison of different planting methods, including hydrogels, and their effect on eucalypt survival and initial growth in South Africa. South. Afr. For. J. 5–13. https://doi.org/10.2989/10295920609505256.

Wang, D., Bachelard, E.P., Banks, J.C., 1988. Growth and water relations of seedlings of two subspecies of *Eucalyptus globulus*. Tree Physiol. 4, 129–138. https://doi.org/10.1093/treephys/4.2.129.

Weggler, K., Carney, C., Stone, C., 2008. Effect of Fertiliser and Water Supply on the Growth, Nutrient Status and Photochemical Efficiency of Eucalyptus Pilularis Seedlings in a Phosphorus-deficient Soil, vol. 71, pp. 54–63. https://doi.org/10.1080/00049158.2008.10676271.

Whitehead, D., Beadle, C.L., 2004. Physiological regulation of productivity and water use in Eucalyptus: a review. For. Ecol. Manag. 193, 113–140. https://doi.org/10.1016/j.foreco.2004.01.026.

Wong, S.-C., Cowan, I.R., Farquhar, G.D., 1985. Leaf conductance in relation to rate of CO(2) assimilation: III. Influences of water stress and photoinhibition. Plant Physiol. 78, 830–834. https://doi.org/10.1104/pp.78.4.830.

Xie, P., Arkin, P.A., 1997. Global precipitation: a 17-year monthly analysis based on gauge observations, satellite estimates, and numerical model outputs. Bull. Am. Meteorol. Soc. 78, 2539–2558.

Xu, D., Dell, B., 2003. Nutrient management of eucalypt plantations in South China. In: R. W., Xu, D. (Eds.), Eucalyptus plantation. Research, Management and Development. Proceedings of the International Symposium (Singapore). World Scientific, pp. 269–289.

Zhang, X., Davidson, E.A., Mauzerall, D.L., Searchinger, T.D., Dumas, P., Shen, Y., 2015. Managing nitrogen for sustainable development. Nature 528, 51–59. https://doi.org/10.1038/nature15743.