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RESEARCH ARTICLE

Effects of La_2O_3 nanoparticles and bulk-La_2O_3 on the development of *Pfaffia glomerata* (Spreng.) Pedersen and respective nutrient element concentration

Vinicius Machado Neves[1] · Graciela Marini Heidrich[1] · Camila Cavalheiro da Costa[2] · Julia Gomes Farias[3] · Fernando Teixeira Nicoloso[2] · Dirce Pozebon[4] · Valderi Luiz Dressler[1]

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Abstract

Nanoparticles (NPs) have been progressively applied in the last decades, which may impact the environment. Synthesis of pigments, growing, and nutrient element uptake by plants can also be affected by NPs. The influence of lanthanum oxide nanoparticles (La_2O_3 NPs) on growth, pigment synthesis, and nutrient element uptake by *Pfaffia glomerata* (Spreng.) Pedersen, a medicinal plant native in South America, was evaluated in the present study. *P. glomerata* plantlets were cultivated for 28 days in the absence (control) and presence of 100, 200, and 400 mg L^{-1} of La_2O_3 NPs or bulk-La_2O_3 (b-La_2O_3) at the same cultivation conditions. Root development, aerial part growth, and pigment concentration in plants were affected by b-La_2O_3 and La_2O_3 NPs, mainly by La_2O_3 NPs. In spite of alteration of nutrient element concentration observed for the 100 and 200 mg L^{-1} of La_2O_3 NPs or b-La_2O_3 treatments, Ca, Cu, Fe, K, La, Mg, Mn, Mo, P, S, and Zn determination in stems and leaves revealed drastically and similar decrease of these elements in plants cultivated in the presence of 400 mg L^{-1} of La_2O_3 NPs or b-La_2O_3. Element distribution (mapping) determined by using laser ablation inductively coupled plasma mass spectrometry in leaves of plants submitted to treatment with 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs showed differences in the distribution of elements, indicating distinct effects of b-La_2O_3 and La_2O_3 NPs on *P. glomerata*. As such, this study demonstrated that La_2O_3 NPs may impact plant growth. However, more investigations are necessary for better understanding of the effect of La_2O_3 on plants, including a broader range of concentration.

Keywords La_2O_3 nanoparticles · *P. glomerata* · Element mapping · Laser ablation inductively coupled plasma mass spectrometry

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Highlights

- La_2O_3 affect growth, pigment synthesis, and nutrient elements in *Pfaffia glomerata.*
- Changes of nutrient distribution are observed in leaves of *Pfaffia glomerata.*
- The effect of lanthanum oxide on plants depends on lanthanum concentration and form (nanoparticles or bulk).

✉ Valderi Luiz Dressler
vdressler@gmail.com

[1] Department of Chemistry, Federal University of Santa Maria, 97.105-900, Santa Maria, RS, Brazil

[2] Department of Biology, Federal University of Santa Maria, 97.105-900, Santa Maria, RS, Brazil

[3] Arizona State University, Tempe, AZ 480-965-2100, USA

[4] Institute of Chemistry, Federal University of Rio Grande do Sul, 91.501-970, Porto Alegre, RS, Brazil

Introduction

Plants need nutrient elements for growing and development. Elements such as Ca, K, Mg, N, P, S, B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn are required for chlorophyll production, cell structure integrity, enzyme synthesis, metabolic activities, energy storage and its transformation, regulation of the stomata aperture, and ion transport (Aihemaiti et al. 2019; Gupta et al. 2014; Kötschau et al. 2013). On the other hand, toxic elements such as As, Cd, and Pb can affect the absorption of essential elements by plants, causing oxidative stress, growth retardation, leaf necrosis, and plant death (Aihemaiti et al. 2019; Gupta et al. 2013, 2014; Li et al. 2018). In addition to the elements in ionic form, recent studies have shown positive and/or negative influence of metal nanoparticles (NPs) in plant development (Apodaca et al. 2017; García-Gómez et al. 2017; Iavicoli et al. 2017; Su et al. 2019).

Nanoparticles are materials with dimensions ranging from 1 to 100 nm and have been increasingly used in sensors, new materials, medicines, and cosmetics and as antimicrobial agent, catalyst, food additive, fertilizer (nanofertilizers), and pesticide (nanopesticides) (Ebbs et al. 2016; Iavicoli et al. 2017; Malhotra et al. 2020; Musial et al. 2020; Prasad et al. 2017). Nanoparticles of essential elements, for example ZnO NPs, have been used as a controlled source of nutrient for crop improvement (Montanha et al. 2020; Prasad et al. 2017). On the other hand, studies about uptake and toxicity of metal oxide NPs in plants revealed a negative effect of NPs on seed germination, length of root and shoots, and dry biomass, besides alteration of nutrient element concentration (Ebbs et al. 2016; Ma et al. 2010; Prasad et al. 2017). Ullah (Ullah et al.2020) reported that TiO_2 NPs in low concentration improved wheat (*Triticum aestivum*) growth and crop yield. This NP rose the P content in plant tissue even in the absence of phosphate fertilizer. Concentrations of other elements in shoots of plants treated with 50 mg kg^{-1} of TiO_2 NPs increased; Al, Ca, Mg, and Cu increased 171%, 316%, 187%, and 296%, respectively. However, for plants treated with 100 mg kg^{-1} of TiO_2 NPs, a decline of the element content was observed, but it was not lower than that in shoots of control plans. Other studies report positive and negative effects of NPs used in agriculture (Kumar et al. 2019).

There are few studies dealing with the bioavailability and toxicity of lanthanide element NPs. However, in recent studies (Adeel et al. 2021a), it has been observed that La_2O_3 NPs, bulk La_2O_3, or bulk Yb_2O_3 increased earthworm (*Eisenia fetida*) mortality and reduced reproduction. These substances also induced abnormalities in internal organelles, including mitochondria, Golgi apparatus, and chloragosomes; La_2O_3 NPs and Yb_2O_3 significantly reduced earthworm digestive and cast enzymes. Earthworms reduce the toxicity of La_2O_3 and Yb_2O_3 in the soil by minimizing exposure to microbial biomass carbon and soil enzymes. The study revealed that La_2O_3 and Yb_2O_3 beyond 50–100 mg kg^{-1} adversely impact soil microbiota. La_2O_3 NPs, bulk La_2O_3, Yb_2O_3 NPs, and bulk Yb_2O_3 induced neurotoxicity in earthworms by inhibiting acetylcholinesterase, and La_2O_3 NPs proved to be highly detrimental, mainly through oxidative stress and subsequent failure of antioxidant system. La_2O_3 NPs and Yb_2O_3 significantly downregulated the expression of annetocin mRNA in the parental and progeny earthworms, which is crucial for earthworm reproduction. Histological observations showed that these NPs at 200 mg kg^{-1} induced drastic changes in the intestinal epithelium and typhlosole of *E. fetida* (Adeel et al. 2021b).

A comparison study of the photosynthesis between seedlings of C3 (soybean) and C4 (maize) plants upon La_2O_3 NP exposure showed that the photosynthesis of both soybean and maize plants could be inhibited in response to La_2O_3 NPs. However, it was observed that the damage mechanisms are different between the two plants; La_2O_3 NPs can significantly inhibit the photosynthesis of soybean by hindering the light utilization and electron transport, which could further reduce the supply of ATP and NADPH; the inhibition of photosynthesis in maize can be mainly due to restricted carbon fixation. The activity of key enzymes such as rubisco and phosphoenolpyruvate carboxylase (PEPC) was both reduced through the downregulation of their relative gene expression. Excess of electrons was then accumulated, and superfluous reactive oxygen species (ROS) were generated (Liu et al. 2019).

Lanthanum, a lanthanide element (Ln), has not been considered a nutrient for plants. However, it has been observed that lanthanide elements (Lns) can influence seed germination, root size development, total biomass accumulation, production of secondary metabolite, and absorption of minerals. Nevertheless, these effects can be positive or negative, depending on the Ln concentration (Hu et al. 2004; Khan et al. 2017; Zhang et al., 2013). Lanthanum oxide NPs (La_2O_3 NPs), commonly used in paint coatings, catalysts, and luminescent materials, decreased the root length of *Brassica oleracea* L. (cabbage), *Triticum aestivum* L. (wheat), *Cucumis sativus* L. (cucumber), *Raphanus sativus* L. (radish), *Lycopersicon esculentum* Mill. (tomato), *Lactuca sativa* L. (lettuce), and *Brassica napus* L. (rape) when their seeds were soaked in 2000 mg L^{-1} La_2O_3 NP suspension before planting (Ma et al. 2010).

Uptake of La_2O_3 NPs by *Pfaffia glomerata* (Spreng.) Pedersen (also known as ginseng) has been investigated and the presence of La_2O_3 NPs into stems and leaves was observed (Neves et al. 2019). Ma et al. (2011) demonstrated that La_2O_3 NPs were taken by *Cucumis sativus* L. and transformed into needle-like $LaPO_4$ nanoclusters in intercellular regions in *Cucumis sativus* L. roots (Ma et al., 2011). However, a detailed study about La_2O_3 NP effects on absorption of other elements by a plant and their distribution in the plant have not been investigated so far.

Mapping of elements in plants allows to understand changes in element distribution due to external effects, element transport pathways through plants, and storage properties of cells that constitute or border the elemental transport corridor (Conn and Gilliham 2010; Kötschau et al. 2013).

Techniques such as micro-X-ray fluorescence (μ-XRF), secondary ion mass spectrometry (SIMS), and laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) allow element mapping in plants, with high resolution (μm to nm) (Ko et al. 2018; Kötschau et al. 2013; Neves et al. 2019; Pozebon et al. 2014). This possibility has opened new perspectives in studies about physiology, biochemical functions, and metabolism in plants (Ko et al. 2018; Kötschau et al. 2013). In this context, the use of LA-ICP-MS has increased due to the good spatial resolution achieved (in the μm range), sensitivity (limit of detection (LOD) in

ng g^{-1} to μg g^{-1} range), and multi-element determination capability (Nunes et al. 2016; Pozebon et al. 2014). Several calibration procedures have been proposed for quantitative element mapping in plants, mainly calibration with certified reference materials (CRMs), matrix-matched standards, and/or internal standardization (IS) (Ko et al. 2018; Kötschau et al. 2013; Nunes et al. 2016).

Considering the increased use of Lns NPs and the scarce studies already conducted about the effects of these NPs on plant development and nutrient element uptake by plants, the effect of La_2O_3 NPs on *Pfaffia glomerata* (Spreng.) Pedersen was investigated in the present study. To this end, plants were grown in the absence or presence of La_2O_3 NPs and nutrient elements determined in leaves and stems of the cultivated plants. In addition, plant development and pigment synthesis were evaluated. For comparison, plants were also grown in the presence of bulk-La_2O_3 (b-La_2O_3). *Pfaffia glomerata* was chosen for the study because it has medicinal properties and can be easily in vitro cultivated, which facilitates a controlled environment. *Pfaffia glomerata* is a semi-prostrate shrub, with a woody trunk and thin herbaceous branches, which reaches up to 2.0 m in height; its small yellowish-white flowers are grouped in capitula, forming a globular structure. It occurs naturally in Africa and the Americas, being widely distributed in the Brazilian territory. Brazil is considered the most important center of assessment of *Pfaffia glomerata* roots for medicinal, nutritional, and cosmetic purposes. Roots of the plant are used as aphrodisiac and stimulant and in the treatment of diabetes and inflammatory diseases, and extracts of roots possess a central nervous system depressant activity. Several economically important compounds have been isolated and identified from roots of *Pfaffia glomerata* (Spreng.) Pedersen, such as ecdysterone, saponins, glomeric acid, pfameric acid, rubrosterone, oleanolic acid, and beta-glucopyranosyl oleanolate (Neves et al. 2016).

Materials and methods

Reagents and solutions

Ultrapure water (resistivity of 18.2 MΩ cm) was obtained from a Milli-Q system (Millipore Corp., USA) and used for solutions and sample preparation. Nitric acid (65% m m^{-1}, Merck, Germany), used for solution preparation and sample decomposition, was purified by sub-boiling distillation (a Duopur Milistone, Italy, distiller was employed). Calibration solutions were prepared in 5% (v v^{-1}) HNO_3 by serial dilutions of 10 mg L^{-1} multi-element reference solution (SCP 33 MS, SCP Science, Canada) and 1000 mg L^{-1} (Certipur, Merck IV, Merck, Germany), mono-element reference solutions of S (Spex CertiPrep, USA) and P (Merck, Germany). For method accuracy evaluation, the certified reference materials NIST 1515 (apple leaves) from the National Institute of Standards and Technology (NIST, USA) and BCR 670 (aquatic plant) from the Community Bureau of Reference (Belgium) were analyzed. The La_2O_3 NPs (purity of 99.99%, particle size ranging from 15 to 30 nm and with spherical morphology) used for plant treatment were acquired from Nanostructured & Amorphous Materials Inc. (Houston, USA). The b-La_2O_3 (purity of 99.9%) was acquired from Neon Commercial (São Paulo, Brazil). Additional information about morphology, zeta potential, and agglomeration of La_2O_3 NPs and b-La_2O_3 are given elsewhere (Neves et al. 2019). In short, the shape of the particles of both oxides is spherical, most of them are present as agglomerate in the solution used for plant cultivation and the size of La_2O_3 NPs is lower than 30 nm while b-La_2O_3 are higher dimensions (130 nm or higher).

Instrumentation

An inductively coupled plasma optical emission spectrometer (ICP OES) (Optima 4300 DV, Perkin Elmer, Shelton, USA) was employed for Ca, Cu, Fe, K, Mn, Mg, P, S, and Zn determination, whereas emission signals were collected in axially viewed plasma mode. The ICP OES instrument was equipped with a quartz torch with an alumina injector tube (2 mm i.d.), GemCone nebulizer, and cyclonic spray chamber. Lanthanum and Mo were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using an ELAN DCR II instrument (from Perkin Elmer Sciex, Canada). The instrument was equipped with a quartz torch with a quartz injector tube (2 mm i.d.), concentric nebulizer, and baffled cyclonic spray chamber. Argon with 99.998% of purity was used as plasma gas, auxiliary, and nebulizer/carrier gas. A laser ablation system (LSX-266, Teledyne Photon Machines, Bozeman, MT, USA) with a frequency quadrupled Nd:YAG (266 nm) laser was connected to the ICP-MS instrument. The LA-ICP-MS system was employed for element mapping in leaves. The operation parameters of ICP OES, ICP-MS, and LA instruments are summarized in Table 1.

Plant cultivation

Murashige and Skoog (1962) culture medium was prepared and supplemented with equivalent amounts of 30 g L^{-1} sucrose and 0.1 g L^{-1} myo-inositol and the pH adjusted to 5.8. Suspensions containing 2000, 4000, or 8000 mg L^{-1} of La_2O_3 NPs or b-La_2O_3 were prepared in ultrapure water and sonicated in an ultrasonic bath (Transsonic, Elma GmbH & Co., Germany) for 30 s to disperse the particles (Gomez-Garay et al. 2014). Then, 500 μL of each suspension was added to 9.5 mL of nutrient medium in glass tubes (2.5 cm

Table 1 Instrumental parameters of the ICP OES, ICP-MS, and LA instruments

Parameter	ICP-MS	ICP OES
RF power, W	1300	1400
Plasma gas flow rate, L min^{-1}	15	15
Auxiliary gas flow rate, L min^{-1}	1.3	0.20
Nebulizer gas flow rate, L min^{-1}	1.00	0.70
Sampler and skimmer cones	Pt	-
Sweeps per readings	5 or 1*	-
Readings per replicate	5 or variable*	-
Replicates	3 or 1*	-
Dwell time, ms	20	-
Monitored isotopes, *m/z*	^{13}C, ^{44}Ca, ^{63}Cu, ^{56}Fe, ^{139}La, ^{26}Mg, ^{55}Mn, ^{98}Mo, ^{31}P, ^{34}S	-
Wavelength, nm I – atomic line II – ionic line	-	Ca II (317.933), Cu I (327.393), Fe II (238.204), K I (766.490), Mg I (285.213), Mn II (257.610), P I (213.617), S I (181.975), Zn II (206.200)
	LA LSX-266	
Fluency, J cm^{-2}	17.8	
Pulse width, ns	5	
Repetition rate, Hz	20	
Spot size, µm	100	
Scan speed, µm s^{-1}	100	
Ablation mode	Line (standards); multiline (leaves)	
Ablation cell volume, mL	50	
Carrier gas flow rate (Ar), L min^{-1}	1.30	

* denotes instrumental conditions for LA-ICP-MS

i.d. × 16.0 cm height) to obtain cultivation media with 100, 200, and 400 mg L^{-1} of La_2O_3 NPs or b-La_2O_3. The control cultivation medium was prepared by mixing 9.5 mL of nutrient medium and 500 µL of ultrapure water. All tubes containing nutrient medium were closed with an aluminum foil and autoclaved for 30 min at 120 °C and 1.0 atm.

P. glomerata plantlets 25 days old were obtained from the Genetics Germplan Program, Federal University of Santa Maria, Brazil. Nodal segments (1.0 cm length) without leaves were inoculated in the cultivation medium and the flasks closed with an aluminum foil and then placed in a greenhouse where they were kept for 28 days at 25 ± 2 °C, relative humidity between 50 and 60%, and light density of 35 µmol m^{-2} s^{-1}. The light was supplied by a cold white-fluorescent lamp during 16 h per day. Plants were harvested after 28 days of planting.

A total of 126 plants were cultivated, being 18 plants for each group (control, 100, 200, and 400 mg L^{-1} of La_2O_3 NPs or b-La_2O_3). For analysis, the 18 plants were divided into three groups ($n = 3$) with six plants each.

Root analysis

Roots were removed from cultivated plants, washed with distilled water, and frozen (− 5 °C) during 7 days. Subsequently, the roots were thawed at room temperature and scanned (Epson 11,000 XL). The total length, surface area, total volume, and average diameter of roots were determined using the WinRhizo Pro Software (Regent Intruments Canada Inc.). The roots were dried at 60 °C until constant weight for determination of their dry mass.

Determination of pigments

Carotenoid and chlorophyll concentrations were determined following the method of Hiscox and Israelstam (1979) and estimated by means of Lichtenthaler's formula (Hiscox and Israelstam 1979; Lichtenthaler 1987). Briefly, 0.05 g of frozen leaves (− 5 °C) were incubated at 65 °C in concentrated dimethyl sulfoxide (DMSO) until the tissues were completely bleached. The DMSO solution absorbance was then measured at 470, 645, and 663 nm using a molecular absorption spectrometer (Model Bel Spectro S05, Italy) to determine the carotenoids and chlorophyll a and chlorophyll b concentrations, respectively. Total chlorophyll concentration was calculated by summing the chlorophyll a and chlorophyll b contents.

The anthocyanin concentration was determined according to Zhang and Quantick (1997). Anthocyanin was extracted from the leaves using 5 mL of methanol containing 1% v/v HCl and the absorbance of the extract measured at 600 and 530 nm. The anthocyanin concentration was expressed as the

change of 0.1 unit of difference between absorbance measured at 530 nm and 600 nm.

Determination of nutrient elements and lanthanum

Leaves and stems were segmented and dried at 60 °C until constant weight. Then, approximately 50 mg of dried leaves or stem was exactly weighed and decomposed with 1.0 mL of HNO_3 in polypropylene flasks under heating in a water bath at 80 °C for 2 h. Subsequently, the decomposed sample was analyzed by ICP OES and ICP-MS. Instrumental conditions for element determinations by ICP OES and ICP-MS are given in Table 1. The CRMs NIST 1515 and BCR 670 were analyzed in the same way as the plant samples to check the accuracy of the method. The CRM analysis results are given in Supplementary Information.

Plant development analysis

The plant development was evaluated through plant length, number of leaves, sprouts and nodal segments, and dry biomass. Plant length was measured using a measuring tape whereas the number of leaves, sprouts, and nodal segments were visually counted one by one. The aerial part of the plant was dried at 60 °C until constant weight for dry matter (dry biomass) determination.

Analysis of leaves by LA-ICP-MS

Quantitative analysis of *P. glomerata* leaves by LA-ICP-MS was based on the method developed by Nunes et al. (2016). Calibration curves were prepared using filter paper discs (diameter of 17 mm), each one supporting 40 µL of calibration solution. Multi-element calibration solutions (SCP 33 MS) with 0.25, 0.50, 1.25, 2.50, 5.00, and 10.0 mg L^{-1} of Cu, Mn, Mo, and Zn were added to filter paper discs, resulting in 0.50, 1.00, 2.50, 5.00, 10.0, and 20.0 µg g^{-1} of these elements. Multi-element (Ca, Fe, and Mg) and mono-element (P and S) solutions with 100, 250, 375, 500, and 1000 mg L^{-1} of each element were also added, resulting in 0.20, 0.50, 0.75, 1.0, and 2.0 mg g^{-1} of the five elements. A blank was prepared by deposition of 40 µL of 5% (v v^{-1}) HNO_3 on a filter paper disc. Then, the filter paper discs with the deposited solutions were dried under an infrared lamp at 80 °C for 2 min and fixed on quartz slides through polyvinyl acetate glue (PVA, Acrilex, Brazil). Three lines of approximately 10 mm length were ablated on each paper disc. To evaluate the LA-ICP-MS method accuracy, a pellet of certified apple leaves (NIST 1515) was prepared by pressing 350 mg of the powdered material with 5 tons (with a hydraulic press) for 2 min and then ablated in the same way as the filter paper discs. The limit of quantification (LOQ) for each element was estimated by ablating 10 lines of the filter paper disc where the nitric acid solution had been deposited (blank). The LOQ for each element was calculated following the IUPAC (International Union of Pure and Applied Chemistry) recommendations, using B + 10 s, where B is the mean of element concentration of 10 determinations (10 lines ablated in the present case) and s is the respective standard deviation. In all LA-ICP-MS measurements, ^{13}C was used as IS. The CRM analysis results and LOQs for LA-ICP-MS are given in Supplementary Information. For element mapping, leaves removed from *P. glomerata* plants cultivated in the absence (control plant) and presence of 400 mg L^{-1} of La_2O_3 NPs or b-La_2O_3 were analyzed. Prior to analysis, the leaves were kept between two filter papers at 25 °C and 60–70% humidity. Then, the dried leaves were fixed on quartz slides through a PVA glue and analyzed by LA-ICP-MS at the same conditions used for the standards (paper disc where the reference solutions were deposited). The data obtained were exported in .xls format and images of element distribution generated using the MATLAB software (version 7.9.0).

Statistical analysis

The statistical analyses were performed by the Instat software. Data are presented as mean ± standard derivation (1SD) and were tested for statistical significance using analysis of variance (ANOVA) followed by Tukey's pairwise comparison. The data follow a normal distribution, which was tested by the Shapiro–Wilk test using software R (R Core Team, 2021). The default 95% confidence level was considered in all statistical analyses.

Results and discussion

Root morphology

Concerning plants, water and element absorption and synthesis of organic compounds take place in the plant roots. Contaminants in the soil can change the root growth and their physiology, which influence the plant development. Effects of Lns in plants were observed in previous studies (Hu et al. 2004; Khan et al. 2017; Ma et al. 2010; Zhang et al. 2013). In the present study, reduction of total length, dry mass, surface area, total volume, and average diameter of roots of plants cultivated in the presence of 100, 200, and 400 mg L^{-1} of La_2O_3 NPs was observed (Fig. 1). Reduction of dry mass and total volume of roots of plants cultivated in the presence of b-La_2O_3 was also observed for the three treatments. However, the total length and surface area of roots decreased only in the presence of higher b-La_2O_3 concentration (400 mg L^{-1}).

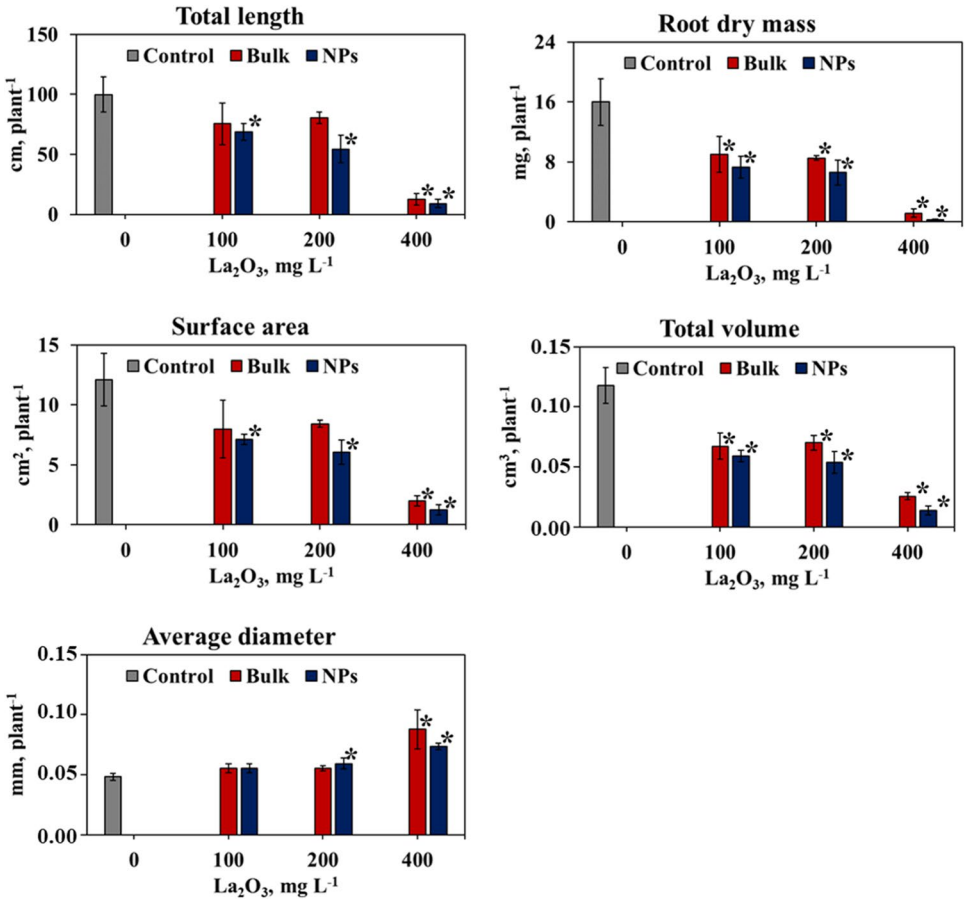

Fig. 1 Effect of b-La_2O_3 or La_2O_3 NPs on root development of *P. glomerata* cultivated in vitro. Results are expressed as the average and standard deviation of six replicates. Bars marked with * denote values significantly different ($p < 0.05$) of control plants

The root diameter increase is usually related to difficulties of root growth, possibly due to toxicity of one or more substances present in the medium where the plant is cultivated (Bernardy et al. 2016). As can be observed in Fig. 1, the average diameter of roots of the plants cultivated in the presence of 200 and 400 mg L^{-1} of La_2O_3 NPs and 400 mg L^{-1} of b-La_2O_3 increased.

Organic acids, amino acids, and other substances are secreted by plant roots and produce Lns complexes that reach the xylem. Phosphorus in high concentration into xylem can precipitate Lns and block the passage of water and minerals into the roots (Ma et al. 2011; Migaszewski and Gałuszka 2015). Physical obstruction caused by La_2O_3 NPs on the roots is also prone to occur; the size of cell wall pores of root ranges from 2 to 20 nm, while the size of La_2O_3 NPs used in this work is in the range of 15–30 nm. Thus, part of La_2O_3 NPs could enter the cells and other parts can be deposited and aggregate on cell wall and block the path of nutrients to plant cells, reducing root growth (Chichiriccò and Poma 2015). Investigations about La_2O_3 NP uptake by roots were also conducted by Zhang (Zhang et al. 2012), and these authors concluded that more investigation would be necessary to demonstrate what really happens with these NPs on root development and uptake of La_2O_3.

Pigment concentration

The photosynthetic pigments (chlorophyll and carotenoids) in leaves are responsible for the capture of light, which is essential to generate the energy necessary for plant development. Changes in the concentrations of these pigments are indicative of some stress caused by elements or substances (Li et al. 2018). Figure 2 shows that the concentration of chlorophyll a, chlorophyll b, total chlorophyll, and carotenoids increased in plants cultivated in the presence of 100 mg L^{-1} of La_2O_3 NPs or 200 mg L^{-1} of b-La_2O_3. Such effect can be related to a catalytic action of La on the pigment production. In a revision about metallic NP influence on plants, Tighe-Neira (Tighe-Neira et al. 2018) mention that the effect of metallic NPs on photosynthetic pigments and other characteristics induced in plants is still controversial; both increase and decrease in photosynthetic activity can occur. This depends on the element or oxide in the NP form, NP concentration, NP size, and NP shape, as well as the type of plant. In the case of CeO_2 NPs, an oxide of a lanthanide element, a wide range of responses of various plant species to CeO_2 NPs was observed and with no clear pattern emerging regarding a structural and/or functional effect. Treatment with 400 mg L^{-1} of La_2O_3

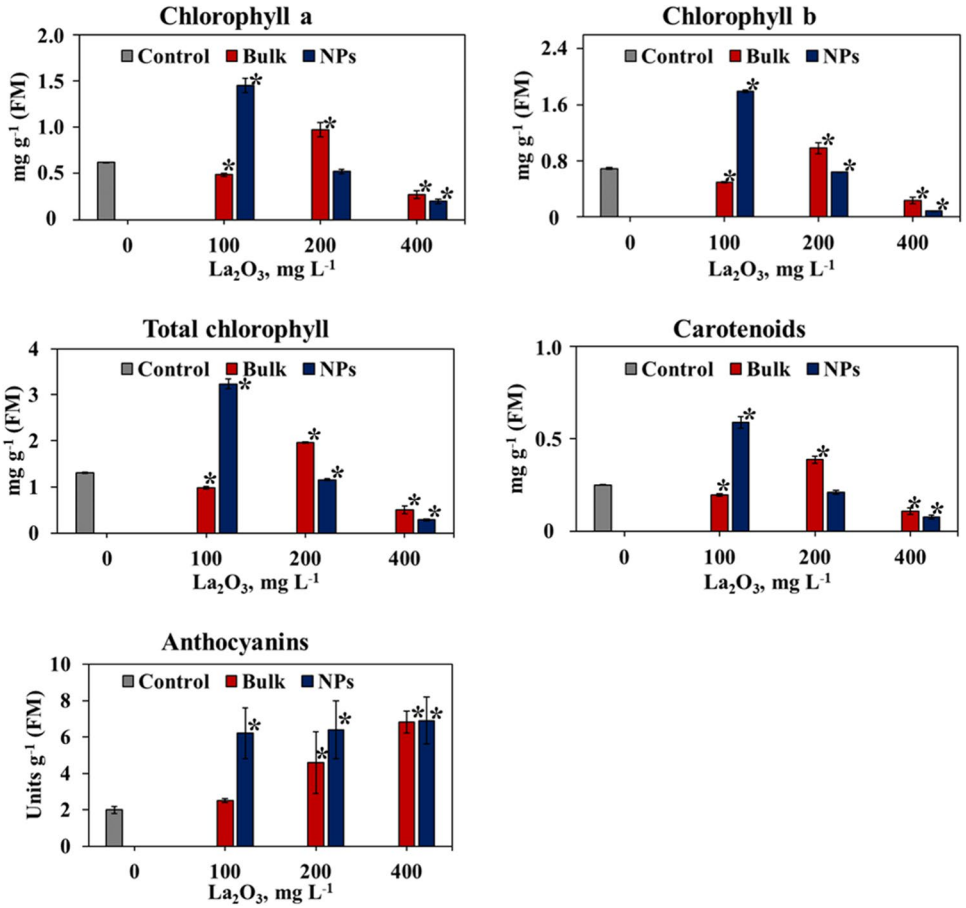

Fig. 2 Effect of b-La_2O_3 or La_2O_3 NPs on pigment concentration in *P. glomerata* cultivated in vitro. Results in fresh matter (FM) are expressed as the average and standard deviation of six replicates. Bars marked with * denote values significantly different ($p < 0.05$) of control plants

NPs or b-La_2O_3 decreased the concentration of these pigments remarkably. The chlorophyll and carotenoid concentration decrease are related to the reduction of photosynthetic activity and dry matter (biomass) and oxidative stress (Khataee et al. 2017; Missaoui et al. 2017). Aggregation of La_2O_3 NPs on the surface of plant roots, which impairs water transport to leaves, may have also affected the pigment production in plants treated with 400 mg L^{-1} of La_2O_3 NPs. Changes of chlorophyll a, chlorophyll b, and carotenoids in leaves were also observed when plants were grown in the presence of TiO_2 NPs (Missaoui et al. 2017). The authors state that higher chlorophyll accumulation at a concentration of 50 mg L^{-1} TiO_2 NPs might be due to complementary effects of other inherent nutrients like Mg, Fe, and S. TiO_2 NPs could improve the structure of chlorophyll, increase light absorbance, facilitate the formation of pigments, allow better capture of sunlight and transfer of light energy to active electrons and chemical activities, and affect photosynthesis. On the other hand, these authors observed significant decreases in chlorophyll a, chlorophyll b, and carotenoids for plants treated with 100 mg L^{-1} TiO_2 NPs. The chlorophyll and carotenoid content decrease might be due to an oxidative process, which is an indicator of tissue aging. The observed chlorosis in leaves and reduction in leaf area were not due to a direct interaction of NPs with the chlorophyll biosynthesis pathway, but most probably caused by a decrease in chloroplast density. In another study (Ullah et al. 2020), it was observed a correlation among TiO_2 NPs on water and nutrient uptake, and a catalytic role of such NPs to trigger the metabolic activities and enhance the growth of plants.

As can be seen in Fig. 2, the anthocyanins concentration increased in plants treated with b-La_2O_3 or La_2O_3 NPs, excepting plants treated with 100 mg L^{-1} of b-La_2O_3. The increase in anthocyanins was naturally due to an antioxidant defense mechanism against overproduction of reactive oxygen species (ROS) that could damage lipids, proteins, and DNA in plants under stress. Anthocyanins actuate as ROS scavenger, hydrogen donor, and metal chelator in plants. The stress caused by b-La_2O_3 or La_2O_3 NPs could induce the production of H_2O_2, triggering anthocyanins biosynthesis by plants. Changes in antioxidative enzyme (glutathione peroxidase, ascorbate peroxidase, and catalase) activity and membrane peroxidation damage were also observed in plants grown in the presence of TiO_2 NPs (Missaoui et al. 2017).

Plant development

The plant length, number of segments, leaves, sprouts, and dry mass of the aerial part of plants under study are illustrated in Fig. 3. According to this figure, plants cultivated in the presence of 400 mg L^{-1} of b-La_2O_3 were noteworthy affected, but the aerial part of plants treated with 100 and 200 mg L^{-1} of b-La_2O_3 were not different of control plants. Plants treated with La_2O_3 NPs were more affected than those treated with b-La_2O_3. However, alike plants treated with b-La_2O_3, the number of sprouts did not decrease in plants treated with 400 mg L^{-1} of La_2O_3 NPs. The plant aerial part development depends on root performance and nutrient absorption. Thus, it can be said that La_2O_3 NPs affected nutrient absorption by plants, and the plant length, number of leaves, and dry biomass were accordingly affected.

Figure 4 shows images of plants that were cultivated in the absence and in the presence of b-La_2O_3 or La_2O_3 NPs to illustrate the root and aerial part of plants. It can be seen in Fig. 4 that both the aerial part and roots of plants treated with La_2O_3 NPs were more affected than plants treated with b-La_2O_3.

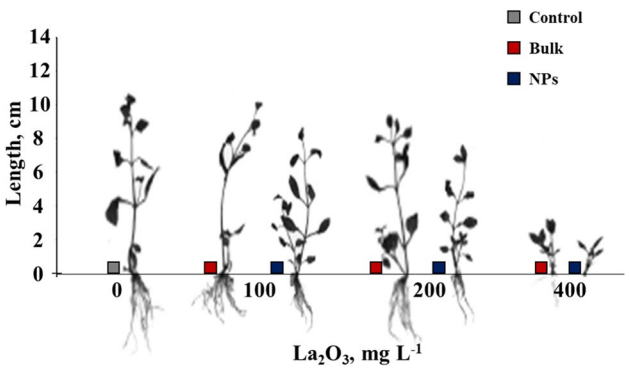

Fig. 4 Images of scanned *P. glomerata* plants cultivated in the absence (control) and presence of b-La_2O_3 or La_2O_3 NPs

Determination of nutrient elements and La

Water-soluble Lns are easily taken by plant roots through complexation with organic acids, which allows the element uptake and their transport to aerial parts of the plant (Khan et al. 2017; Ma et al. 2011). Ma et al. (2011) reported biotransformation of La_2O_3 NPs into La^{3+} and $LaPO_4$ in cucumber roots. However, in another study reported, La_2O_3

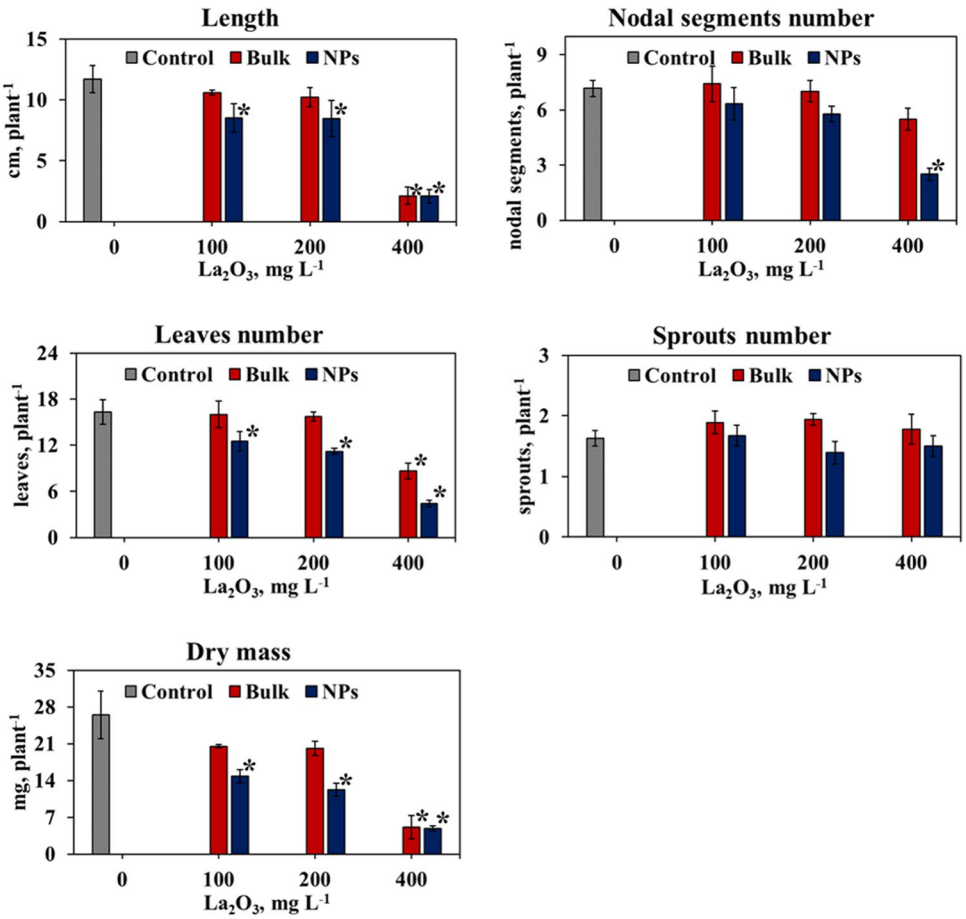

Fig. 3 Effect of b-La_2O_3 or La_2O_3 NPs on the aerial part of *P. glomerata* cultivated in vitro. Results are expressed as the average and standard deviation of six replicates. Bars marked with * denote values significantly different ($p < 0.05$) of control plants

NPs were found in stems and leaves of *P. glomerata* cultivated in the presence of 400 mg L^{-1} of La_2O_3 NPs (Neves et al. 2019). Therefore, different interactions of NPs occur in plants and distinct effects are possible due to differentiated physicochemical properties of NPs (Ma et al. 2011) and the medium where plants are cultivated.

Figure 5 shows the concentration of nutrient elements in stems and leaves of *P. glomerata* plants cultivated in the absence (control) and presence of 100, 200, and 400 mg L^{-1} b-La_2O_3 or La_2O_3 NPs. In general, the nutrient element concentration in stems and leaves of plants cultivated in the presence of La_2O_3 NPs changed more than in the presence of b-La_2O_3 when compared to control plants. Iron and Mn were the most affected elements whose concentrations reduced significantly for all treatments with b-La_2O_3 or La_2O_3 NPs. Other elements very affected were Mg and S whose

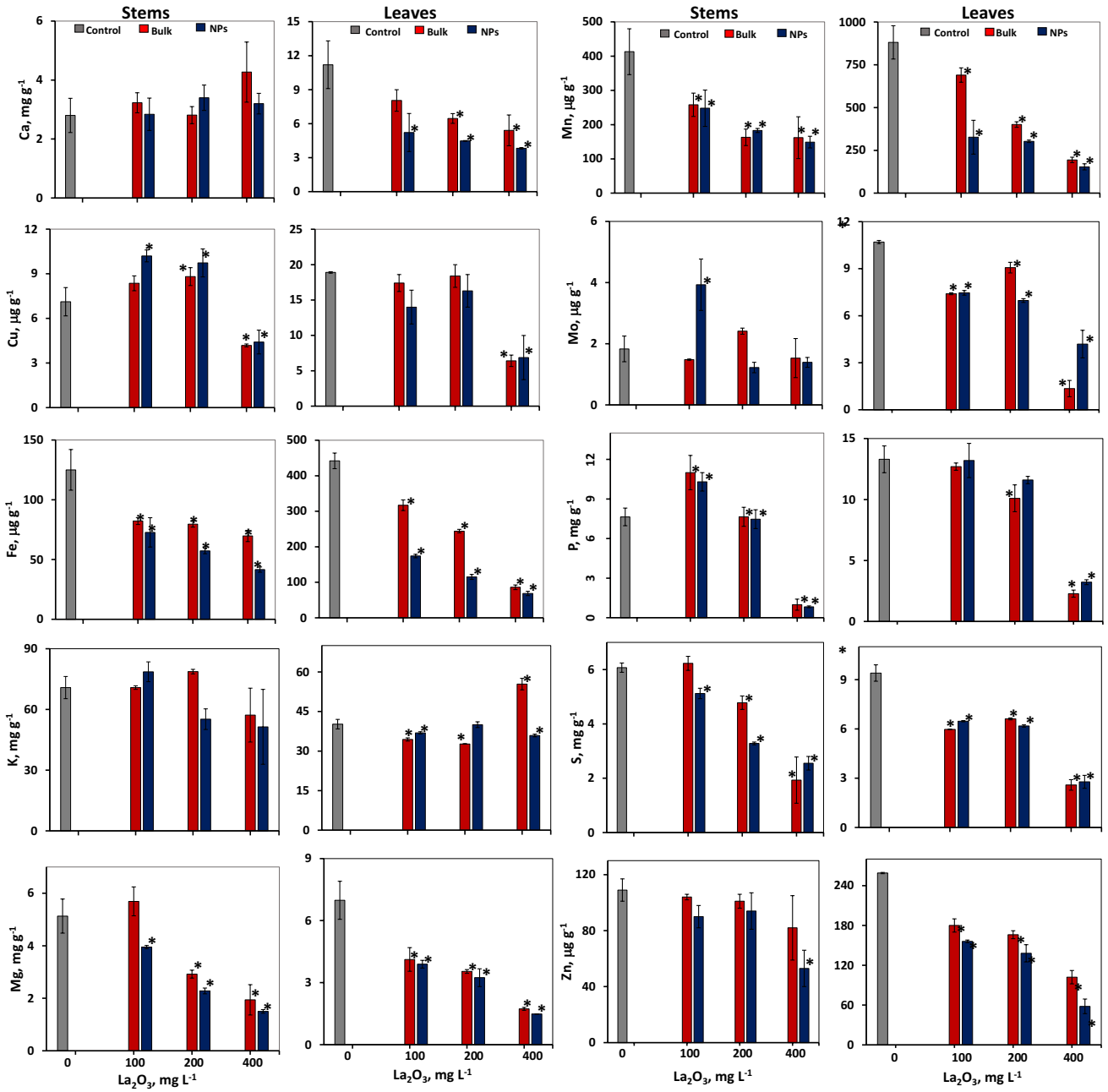

Fig. 5 Effect of b-La_2O_3 or La_2O_3 NPs on nutrient element concentration in stems and leaves of *P. glomerata* cultivated in vitro. Concentrations are expressed as the mean and standard deviation of six replicates by means of ICP OES (Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn) or ICP-MS (Mo) after sample decomposition. Bars marked with * denote concentrations significantly different ($p < 0.05$) of those found in control plants

concentrations decreased significantly in stems and leaves. Nevertheless, in stems of plants cultivated in the presence of 100 mg L^{-1} of b-La_2O_3, the Mg and S concentrations did not change significantly when compared to control plants. The Ca and Zn concentrations decreased significantly in leaves, differently of the stems where the Ca concentration decrease was not significant. Zinc concentration decreased only in the stem of plants cultivated in the presence of 400 mg L^{-1} La_2O_3 NPs. However, the Zn concentration in the leaves of all plants treated with b-La_2O_3 or La_2O_3 NPs decreased. On the other hand, the Ca concentration did not decrease significantly, except in the leaves of plants cultivated in the presence of 100 mg L^{-1} of b-La_2O_3.

Figure 5 shows that in some cases the element concentration increased when plants were treated with b-La_2O_3 or La_2O_3 NPs. The reason might be the beneficial effects of La for plants, which depends on La concentration (Rim 2016; Thomas et al. 2014; Zhang et al. 2013). For example, the Cu, Mo, and P concentrations increased significantly in stems of plants cultivated in the presence of 100 mg L^{-1} of La_2O_3 NPs. Copper concentration increase is also observed in stems of plants treated with 200 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs. On the other hand, in stems of plants cultivated in the presence of 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs, the Cu concentration decreased significantly. The Cu concentration in leaves reduced significantly for 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs, differently of what is observed for the other two treatments. The P concentration increased in the stem of plants treated with 100 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs, whereas the element concentration in stems of plants cultivated in the presence of 200 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs did not change significantly. Contrarily, in the stem of plants treated with 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs, the concentration of P reduced significantly. A decrease of P concentration in leaves was observed for treatments with 200 and 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs. The Mo concentration in leaves and stems of treated plants decreased, except in stems of plants cultivated in the presence of 100 mg L^{-1} of La_2O_3 NPs, where the Mo concentration increased significantly. The K concentration did not change in stems of plants cultivated in the presence of b-La_2O_3 or La_2O_3 NPs. However, the K concentration increased significantly in leaves of plants cultivated in the presence of 400 mg L^{-1} of b-La_2O_3.

The increase or decrease of nutrient element concentration in stems and leaves of the treated plants could be associated with La absorption by the plants (see Fig. 6). A remarkable and similar decrease of investigated elements occurred in stems and leaves of plants treated with 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs. However, the La concentration found in plants cultivated in the presence of b-La_2O_3 was sevenfold higher in their leaves and fourfold higher in their stems when compared to plants grown in the presence of La_2O_3 NPs. This demonstrates that the plants absorbed more La when it was added in the form of b-La_2O_3 to plants. As previously discussed, some La_2O_3 NPs have diameters greater than the cell wall pores, which can obstruct the channels instead of entering the cells and thus reduce the absorption of NPs. The agglomeration of NPs, as shown in Neves et al. (2019), can also influence their absorption by plants.

However, roots of plants grown in periodically waterlogged soil or nutrient solution have the lacunate cortex where there are large intercellular spaces, making possible NP penetration (Su et al. 2019). Moreover, the endodermis has passage cells that can act as a pathway for water

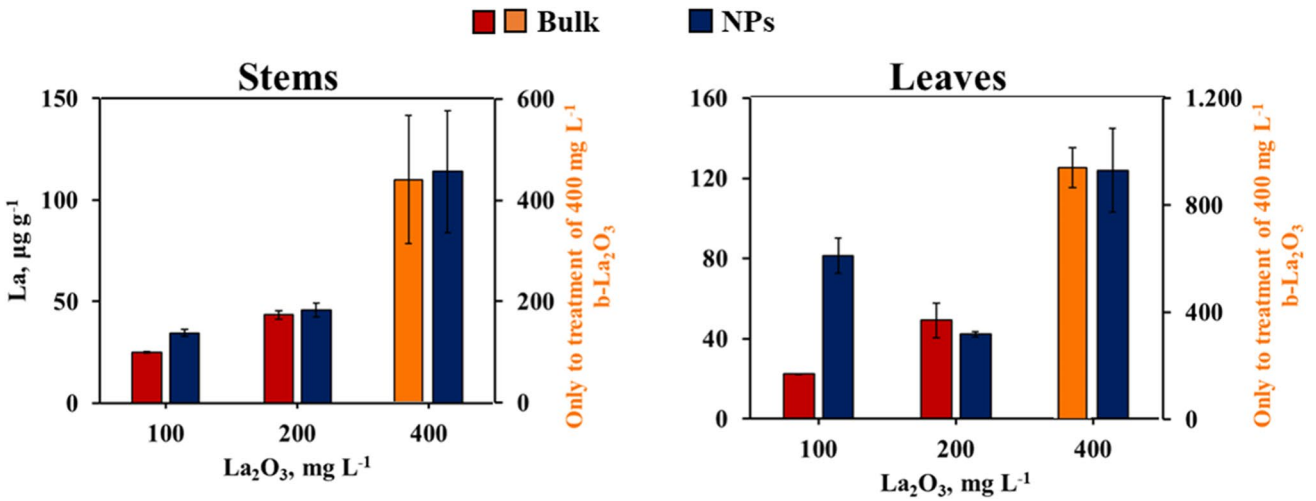

Fig. 6 Lanthanum concentration in stems and leaves of *P. glomerata* cultivated in vitro. Concentration values are mean and standard derivation of six replicates. Lanthanum was not detected in the control plant (results not shown in the figures)

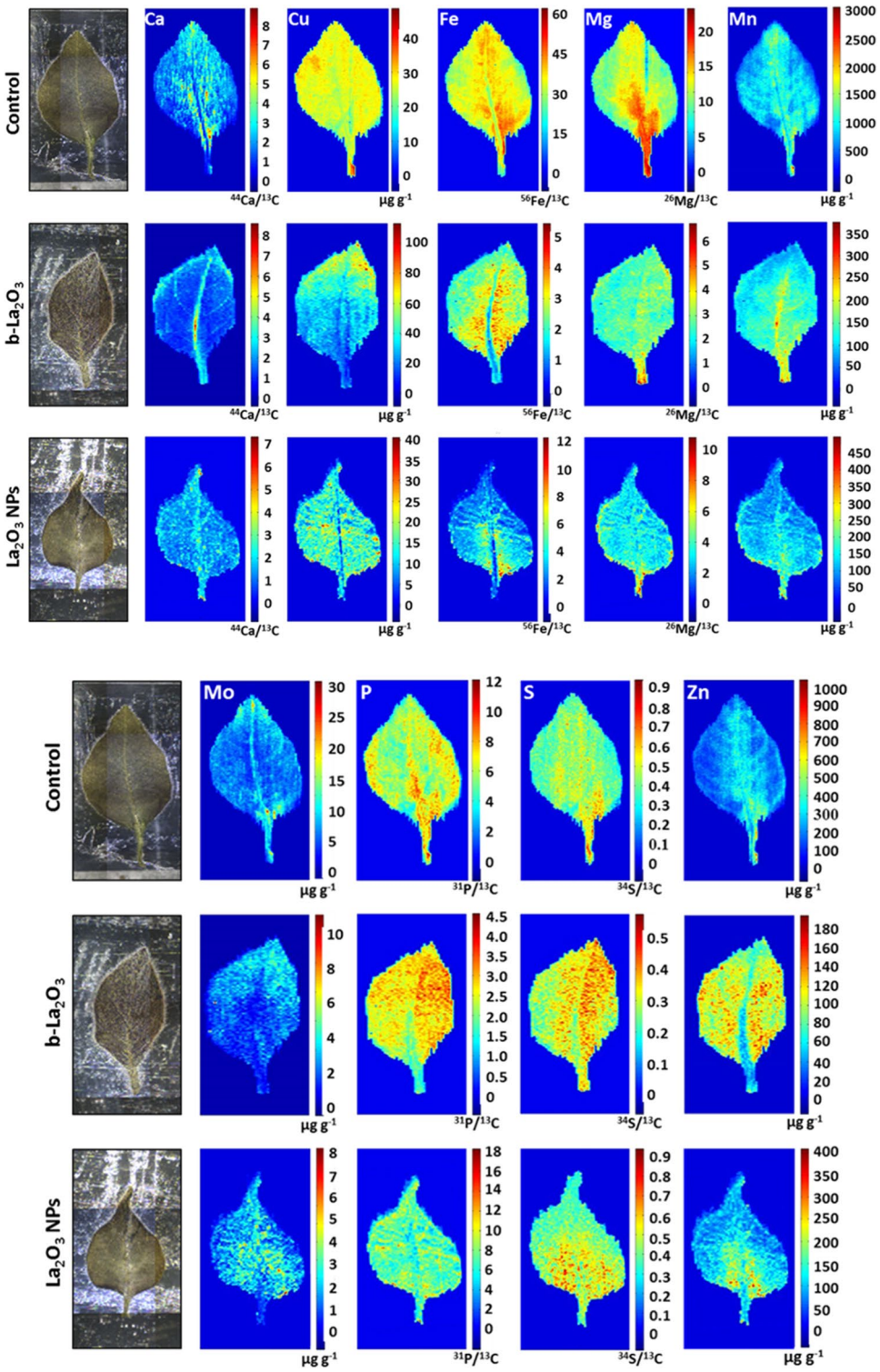

Fig. 7 Distribution of nutrient elements in *P. glomerata* cultivated in the absence (control) and presence of b-La_2O_3 or La_2O_3 NPs. Images on the left are photographs of the leaves fixed on quartz slides. The other images were generated from data obtained in LA-ICP-MS analysis. Copper, Mn, Mo, and Zn (could be quantified, and images are for their concentrations). The ratio element signal/^{13}C signal (internal standard) images are shown for Ca, Fe, Mg, P, and S

and dissolved solutes. Such cells can be the route for NP transport from endodermis to xylem in the root. The NPs can move along the xylem together with bulk water/sap and achieve the superior parts of the plant (Su et al. 2019); the presence of La_2O_3 NPs in stems and leaves has been observed in the previous study (Neves et al. 2019). However, the high ionic strength of the sap (due to the abundant presence of divalent cations) may cause partial NP aggregation and obstruct the pathway to nutrients in the plant. Therefore, NPs not only interact within the plant vascular system, but also impair the absorption of nutrient elements due to physical obstruction (Martínez-Fernández et al. 2016).

According to Fig. 6, for treatment with 100 mg L^{-1} of La_2O_3 NPs or b-La_2O_3, the La amount transported to stems and leaves was higher in plants cultivated in the presence of La_2O_3 NPs (34.7 ± 1.6 µg g^{-1} La in stem and 81.2 ± 8.8 µg g^{-1} La in leaves) than in plants cultivated in the presence of b-La_2O_3 (25.1 ± 0.4 µg g^{-1} La in stem and 22.4 ± 0.2 µg g^{-1} La in leaves). These results demonstrated that when present in low concentration (100 mg L^{-1} in the present case) the La in La_2O_3 NPs is more easily taken by the plant. It should be cited that NP agglomeration is lower when present in lower concentration as already discussed. In addition, the higher reactivity of La_2O_3 NPs in comparison to b-La_2O_3 can increase the bioavailability of La species for plants (Khan et al. 2017). Nevertheless, an opposite effect is observed for stems and leaves of plants grown in the presence of 400 mg L^{-1} of b-La_2O_3. The La concentration increased in stems and decreased in leaves of plants cultivated in the presence of 100 or 200 mg L^{-1} of La_2O_3 NPs, respectively, possibly due to aggregation of NPs in the sap (Su et al. 2019).

Effects of Lns on stabilization and functionalization of cytoplasm membrane, changing of membrane characteristics, and membrane cell fluidity were reported (Hu et al. 2004). Lanthanum could influence several reactions in cells, decreasing the permeability of cell membrane. Therefore, La could influence ionic fluxes and affect several plant processes, including nutrient uptake. These processes are based on complex mechanisms that are not understood and well described yet (Hu et al. 2004; Khan et al. 2017).

Mapping of nutrient elements in leaves

Figure 7 shows the nutrient element distribution in leaves of *P. glomerata* plants cultivated in the presence of 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs and control plants. Leaves of these plants were chosen for element mapping for better visualization of the effects of b-La_2O_3 and La_2O_3 NPs. According to Fig. 5, the Cu, Fe, and Mg concentrations decreased in leaves of plants treated with 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs in relation to control pants. In Fig. 7, it is possible to observe that the distribution of these elements was differently affected; Fe was more concentrated around the main vein in leaves of control plants and in those of plants treated with b-La_2O_3 or La_2O_3 NPs; Mg distribution was similar in leaves of plants treated with b-La_2O_3 or La_2O_3 NPs, whereas the element was more homogeneously distributed when compared to leaves of control plants. Copper concentration was practically homogenous in leaves of control plant or cultivated in the presence of La_2O_3 NPs, but the element was more concentrated in the tip of leaves of plants treated with b-La_2O_3. The Mo, P, and S distribution in leaves of control plants was homogeneous, but more concentrated in the tip of leaves of plants treated with b-La_2O_3; Mo and S were more concentrated in the center of leaves of plants treated with La_2O_3 NPs while P was homogeneously distributed in these leaves. The Zn and Mn concentrations decreased in leaves of plants cultivated in the presence of b-La_2O_3 or La_2O_3 NPs in relation to control plant leaves where Zn was more concentrated in the main vein. Manganese was more concentrated in the main vein in leaves of plants treated with b-La_2O_3 and in the tip of leaves of control plants and more homogenously distributed in leaves of plants treated with La_2O_3 NPs. Calcium is not affected by both species of lanthanum; however, some differences in its distribution can be observed mainly for plants treated with La_2O_3 NPs. Therefore, the images in Fig. 7 make clear the alteration of nutrient element distribution in leaves of *P. glomerata* treated with 400 mg L^{-1} of La_2O_3 NPs or b-La_2O_3. The nutrient element mapping also revealed distinct effects caused by La_2O_3 NPs and b-La_2O_3.

Conclusion

It can be concluded that both La_2O_3 NPs and b-La_2O_3 added to plants can affect their development, pigment synthesis, and nutrient element uptake. However, the La_2O_3 NPs and b-La_2O_3 effects are dissimilar. The reduction of nutrient element concentrations in leaves and stems was dependent on the La_2O_3 form, whereas La_2O_3 NPs affected more than b-La_2O_3. Plants treated with the latter were visible better, denoting that La_2O_3 NPs were more toxic to plants than was b-La_2O_3. The worst root and aerial part development and changes in pigment concentration revealed the more severe effect of La_2O_3 NPs. Although the nutrient element concentrations were similar in stems and leaves of plants treated with 400 mg L^{-1} of b-La_2O_3 or La_2O_3 NPs, the element mapping showed a significant difference of their distribution in leaves. The results obtained in the present study demonstrated that La_2O_3 NPs can exert a negative effect on plants, depending on the La_2O_3 NP concentration. The effect of La_2O_3 NPs at concentration lower than 100 mg L^{-1} is the objective of future studies, to check if their effects would be positive or different from those observed for higher La_2O_3 NP concentration.

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Dirce Pozebon was responsible for the text organization and revision. Valderi Luiz Dressler was responsible for supervising the data and text organization.

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Data availability All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Declarations

Ethics approval Not applicable.

Consent to participate All authors confirm consent to participate in this journal.

Consent for publication All authors accept to publishing.

Competing interests The authors declare no competing interests.

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