

# Silicon Nanoparticles Decrease Arsenic Translocation and Mitigate Phytotoxicity in Tomato Plants

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## Research Article

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# Abstract

In this study we simulate the irrigation of tomato plants with As contaminated water (from 0 to 3.2 mg L<sup>-1</sup>) and investigate the effect of the application of silicon nanoparticle (Si NPs) in form of silicon dioxide (0, 250 and 1000 mg L<sup>-1</sup>) on As uptake and stress. Arsenics concentrations were determined in substrate and plant tissue at three different stratum. Phytotoxicity, As accumulation and translocation, photosynthetic pigments and antioxidant activity of enzymatic and non-enzymatic compounds were also determined. Irrigation of tomato plants with As contaminated water caused As substrate enrichment and As bioaccumulation (roots > leaves > stem) showing that the higher the concentration in irrigation water, the farther the contaminant flowed and translocated through the different tomato stratum. Phytotoxicity was observed at low concentrations of As, while tomato yield increases at high concentrations. Application of Si NPs decreases As translocation, tomato yield, and root biomass. Increased production of photosynthetic pigments and improved enzymatic activity (CAT and APX) suggested tomato plant adaptation at high As concentrations in the presence of Si NPs. Our results reveal likely impacts of As and nanoparticles on tomato production in places where As in groundwater is common and might represent a risk.

## Introduction

Arsenic (As) is considered one of the most toxic elements in the environment (Otero et al. 2016). Irrigation of agricultural soils with As contaminated water causes As soil enrichment as well as As bioaccumulation and toxicity (Ruíz-Huerta et al. 2017). As a result, it can enter the food chain and represent a risk to human health (Islam et al. 2016). Reduced CO<sub>2</sub> fixation, disorganization of the photosynthetic integral processes as well as imbalance in nutrient and water absorption are some of the effects that plants can exhibit under As stress (Ali et al. 2009; Zhao et al. 2009). Arsenic also induces reactive oxygen species (ROS) production that lead to lipid peroxidation and can result in plant death (Finnegan and Chen, 2012). To counteract ROS stress, plants activate their antioxidant defense system in order to protect their cellular system from harmful effects (Gomes et al. 2014).

Most crops, including tomato (*Solanum lycopersicum* L.), are sensitive to As stress exhibiting reduced seed germination, reduced growth, and even modified molecular responses (Beesley et al. 2013; Marmioli et al. 2014; Miteva et al. 2005). Due to its high level of consumption (160 millions tons per year<sup>-1</sup> in 2013) (FIRA, 2017), tomato is economically one of the most important vegetables in the world (Martí et al. 2018). However, safe quality tomato production may be compromised as groundwater contaminated with As has been reported in several countries including India, Vietnam, Mongolia, Greece, Hungary, USA, Thailand, Ghana, Chile, Argentina, Mexico, Bangladesh, Cambodia, China, Nepal, Pakistan, and Taiwan (Singh et al. 2015). In the case of Mexico, the highest concentrations of As appear in alluvial aquifers in arid and semi-arid areas in northern Mexico (Alarcón-Herrera et al. 2020), where greenhouse tomato production is commonly practiced and irrigation with As contaminated water could occur.

Silicon (Si) is the second most abundant element on earth's crust. It is predominantly found as silicon dioxide ( $\text{SiO}_2$ ), a non-available form to be taken up by plants. Plant-available Si forms include silicic acid ( $\text{Si(OH)}_4$ ) or mono silicic ( $\text{H}_4\text{SiO}_4$ ) (Zargar et al. 2019). Within the plants, and depending on the species, Si accumulates in plant tissue at concentrations ranging from 0.1–10% (dry weight) as a polymer of hydrated amorphous silica (Savvas and Ntatsi, 2015). Silicon exerts beneficial effects on plant growth and production by alleviating biotic and abiotic stress (Ma and Yamaji, 2008). Silicon application under metal stress protects plant structures by compartmentation, co-precipitation and/or chelation of heavy metals in different parts of the plants, which in turn results on increased plant growth and biomass (Adrees et al. 2015). In the case of As, it can be absorbed by a subclass of aquaporins that participate in Si transport with mobility efficiencies that depend on the species (Allevato et al. 2019).

Nanotechnology is an innovative, novel and scientific approach that leads to design, manipulation and development of highly useful nanomaterials (ranging in size from 1 to 100 nm), whose main advantages (compared to bulk forms) include increased surface area to volume ratio, improved (bio) chemical reactivity, and unusual and valuable thermal, mechanical, optical, structural and morphological properties (Mali et al. 2020; Tyagi et al. 2018). A variety of nanomaterials like silicon nanoparticles (Si NPs), nanopesticides, nanoinsecticides, and nanoemulsions have been developed using nanotechnology. Currently, Si NPs are fabricated by pulse laser irradiation of single-crystal silicon wafers in water (Momoki et al. 2020). Among their applications, Si NPs have shown a protective and promising preventive strategy against hepatotoxicity and are useful for the fabrication of multifunctional cotton fabrics with enhanced UV protective, durability, antibacterial and thermal properties in combination with silver or zinc nanoparticles (El-Nagaar et al. 2017; Mohamed et al. 2017). Si NPs are also useful as nanofertilizers and pesticides against pests in maize (El-Nagaar et al. 2020).

Si NPs could be also useful to prevent As toxicity and uptake by tomato crops. Studies show that Si NPs prevented Cr accumulation in pea seedlings (Tripathi et al. 2015), increased chlorophyll and carotenoid content as well as plant growth in *Pleioblastus pygmaeus* in the presence of Pb (Emamverdian et al. 2020), improved the components of the glutathione cycle (antioxidant system non-enzymatic) in *Zea mays* plants in the presence of arsenic (Tripathi et al. 2016), and increased antioxidant enzymatic activity in *Triticum aestivum* L. plants in the presence of Cd (Ali et al. 2019). Therefore, while irrigation of tomato plants with As contaminated water might increase the concentrations of As in soil and plant tissue, Si NPs might help to avoid As translocation and to boost the plant's biochemical system. Knowledge is particularly scarce regarding the effect of Si NPs in tomato plants irrigated with As contaminated water and its subsequent phytotoxic effects on the physiological and biochemical properties.

In this study, an experimental design intended to simulate the irrigation of tomato plants with As contaminated water as well as the application of Si NPs has been tested to better understand the antioxidant response of tomato plants against As in the presence of Si NPs. The objectives of this work are: (i) to determine the concentration of As in substrate and plant tissue as a function of the concentration of As in irrigation water, (ii) to evaluate the effect of As contamination on the growth of tomato plants, (iii) to determine the translocation of As at different stratum, and the effect of Si NPs

application in such translocations, (iv) to evaluate As and Si NPs phytotoxicity, and (v) to determine the effect of As and Si NPs on photosynthetic pigments, enzymatic activity and non-enzymatic antioxidant compounds of tomato plants.

## Materials And Methods

A total of 18 treatments intended to simulate the irrigation of tomato plants with As contaminated water at six different concentrations (0.0, 0.2, 0.4, 0.8, 1.6, and 3.2 mg L<sup>-1</sup>) as well as the application of Si NPs at three different doses (0, 250 and 1000 mg L<sup>-1</sup>) were tested in tomato plants in twelve replicates to make a total of 216 experimental units (Table S1, Supplementary Material).

## Greenhouse experiment: As contamination simulation and Si NPs application

Tomato seeds (*Solanum lycopersicum* L.) of the var. Hybrid, "Sun 7705", saladette type and indeterminate growth, were used in this study. Initially, seedlings were placed in a mixture of peat moss and perlite (1:1, v/v), as a growth substrate, in 12 L black polyethylene bags. A direct irrigation system was then implemented to water the crops for 150 days using Steiner nutrient solution for crop nutrition (Steiner, 1961).

Arsenic was supplied by Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O dissolution in irrigation water to simulate contaminated water according to the maximum permissible concentration of As in irrigation water in Mexico (0.2 mg L<sup>-1</sup>) (DOF, 1997). Si NPs from SkySpring Nanomaterials Inc. were applied via substrate at 0, 250 and 1000 mg L<sup>-1</sup> doses every three weeks making a total of 6 applications of 10 mL of solution per plant. Si NPs were spherical, between 10 and 20 nm, presented a surface area of 160 m<sup>2</sup> g<sup>-1</sup>, and a bulk density of 0.08 to 0.1 g cm<sup>-3</sup>. At the greenhouse, active photosynthetic radiation was 1100 μmol m<sup>-2</sup> s<sup>-1</sup> at peak hours, average day temperature was 28°C, and average relative humidity was 61.8%.

## Determining As concentrations in substrate and plant tissue

Arsenic concentrations were determined in substrate, root, stem, leaves, and fruit up to the seventh cluster of each plant after 150 days. 6 out of 12 pots were randomly selected per treatment to sample substrate and roots. Each substrate sample was homogenized and air dried after root removal. Root samples were thoroughly rinsed under running water and air dried. Samples of stem and leaves were collected from the same pots at three different strata, from which fruit was harvested when tomato branches matured. Stratum one (S1) covered up to the first cluster of fruit, stratum two (S2) covered up to the fourth cluster of fruit, and stratum three (S3) covered up to the seventh cluster of fruit.

All samples were oven dried at 80°C for 72 h, grinded with a mortar and pestle, homogenized, weighed, and stored in polyethylene bags until As analysis. Fruit samples were oven dried for 144 h. As concentration was determined in three out of the 6 samples by X-ray fluorescence spectroscopy (XRF) in

a ThermoScientific Niton FXL instrument according to the 6200 USEPA method. Reference samples (NIST 1573a for tomato leaves and NIST 2711, 2710 and 2709 for soil) and triplicate analyses were carried out for quality control to ensure the reliability of the analytical data.

## Measuring tomato growth and yield

Plant height, number of leaves, stem diameter and yield were determined in all tomato plants every 15 days after transplantation and until elimination of the plants. Plant height and stem diameter was measured from the first pair of true leaves to the apex with a flexometer and a digital vernier, respectively. The number of leaves was determined by direct count, while the yield was calculated by the sum of the total number of fruits harvested per plant over the 150 day period.

## Translocation of As and Si NPs in tomato plants

Translocation of As in tomato plants was calculated for each stratum as the concentration of As in shoots (stem and leaves) divided by the concentration of As in roots times 100 (Vaculík et al. 2013).

Additionally, microscopic analyses were carried out by scanning electron microscopy coupled to energy X-ray dispersion spectroscopy (SEM-EDS) to observe the presence of either As or Si NPs in tomato plant tissue using a ESEM-QUANTA FEG-250 from FEI. Root and leaf tissues from the fresh plant were sampled from a  $3.2 \text{ mgAs L}^{-1}$  and  $250 \text{ mgSi NPs L}^{-1}$  treatment rinsed with deionized water, and frozen, until they were mounted in carbon tape in aluminum pins for SEM-EDS analyses.

## Phytotoxicity of As

The relative phytotoxicity index (PRI) was calculated using Eq. (1) adapted from (Alejandro-Córdova et al. 2017) for aerial and radical dry biomass of plants. To measure the effect of the treatments with As, the PRI of each biomass was compared with the values corresponding to the control treatment ( $0 \text{ mgAs L}^{-1}$ ).

$$PRI_{xi} = \frac{CoT}{CT} \quad (1)$$

Where PRI: relative phytotoxicity index;  $x_i$ : i biomass (where i = radical and aerial); CoT: contaminated (arsenic and/or Si NPs) treatment; CT: Control treatment.

Values of  $PRI > 1$  indicate plant adaptation to As and  $\text{SiO}_2$  NPs suggesting the biomass was stimulated while  $PRI < 1$  indicates As and Si NPs plant toxicity suggesting the biomass was inhibited for  $PRI = 1$  plants show tolerance to As and Si NPs, without differences compared to the control suggesting the biomass was not affected.

## Measuring photosynthetic pigments in tomato plants exposed to As and Si NPs

Biochemical parameters Chlorophylls, antioxidants enzymes and non-enzymatic antioxidant compounds were analysed for 6 out of 12 samples. Fully expanded young leaf tissue from stratum S2 was collected from randomly selected plants for biochemical analysis. After collection, samples were stored at  $-20^\circ\text{C}$  in

a freezer, lyophilized (Yamato Scientific Co. Ltd., Model D401, Santa Clara, CA, USA) at -84°C for 72 h, and subsequently ground to fine powder and stored until further analysis.

Photosynthetic pigments (Chl a = chlorophyll a; Chl b = chlorophyll b; and Chl t = total chlorophyll) were determined using a UV-Vis spectrophotometer (UNICO Spectrophotometer Model UV2150, Dayton, NJ, USA) and Equations (2), (3) and (4) using the absorbances measured at 645 (x Abs<sub>645</sub>) and 663 (x Abs<sub>663</sub>) nm (Nagata and Yamashita, 1992):

$$Chla(mg100g^{-1}DW) = 0.999x|Abs_{663}| - 0.0989x|Abs_{645}| \quad (2)$$

$$Chlb(mg100g^{-1}DW) = -0.328x|Abs_{663}| + 1.77x|Abs_{645}| \quad (3)$$

$$Chlt(mg100g^{-1}DW) = Chla + Chlb \quad (4)$$

## Antioxidant activity of enzymes and non-enzymatic compounds

200 mg of lyophilized leaves, 20 mg of polyvinylpyrrolidone and 1.5 mL of phosphate buffer (0.1 M) with a pH of 7–7.2 were located in a 2 mL eppendorf tube. This mixture was then micro-centrifuged at 12,000 rpm for 10 min at 4°C. The supernatant was filtered using a nylon membrane and kept refrigerated until determination of antioxidant enzyme activity (APX, GPX, SOD, and CAT), glutathione, and proteins using a UV–Vis spectrophotometer (UNICO Spectrophotometer Model UV2150, Dayton, NJ, USA) and a microplate (Allsheng, AMR-100 model, Hangzhou, China). In the case of non-enzymatic antioxidant compounds (flavonoids and phenols), another quantity of lyophilized tissue was weighed according to the established methodology for each variable. Six out of 12 plants were analyzed per treatment for all the antioxidant response variables.

Ascorbate peroxidase activity (APX, EC 1.11.1.11) was determined using the methodology described by Nakano and Asada (Nakano and Asada, 1981), glutathione peroxidase (GPX, QE 1.11.1.9) with the methodology described by Xue et al. (2001), catalase (CAT, QE 1.11.1.6) using the methodology of Dhindsa et al. (1981), superoxide dismutase (SOD, QE 1.15.1.1) using a SOD Cayman 706002® kit.

Total protein quantification (mg g<sup>-1</sup> of dry weight (DW)) was carried out according to Bradford's colorimetric technique Bradford, (1976). Glutathione (mmol 100 g<sup>-1</sup> DW) was determined using the method by Xue et al. (2001) by means of a 5,5-dithio-bis-2 nitrobenzoic acid (DTNB) reaction. Flavonoids (mg 100 g<sup>-1</sup> DW) were determined using the method by Arvouet-Grand et al. (1994). Phenols (mg g<sup>-1</sup> DW) were determined with Folin–Ciocalteu reagent as described in Cumplido-Nájera et al. (2019).

All data were analyzed using the InfoStat statistical package, and an analysis of variance and a test of means Least Significant Difference of Fisher ( $p \leq 0.05$ ) were carried out.

## Results And Discussion

# Arsenic in substrate and plant tissue

Arsenic concentrations in substrate are directly proportional to the concentrations supplied in irrigation water (Fig. 1a). Furthermore, As concentration in irrigation water  $> 0.8 \text{ mg L}^{-1}$  causes As levels above  $22 \text{ mg kg}^{-1}$  in the substrate and is considered as contamination by Mexican guidelines for As in agricultural soils (DOF, 2007), and other international guidelines (i.e.  $17 \text{ mg kg}^{-1}$  from Canada) (Canadian Council of Ministers of the Environment, 2001).

Total As concentrations in roots, leaves and stems, at different As exposures, are shown in Fig. 1b. In general, we have found higher As concentrations in the roots than in stems and leaves. Average As concentrations in roots, stems, and leaves are  $25.10$ ,  $0.80$ , and  $1.47 \text{ mg kg}^{-1}$ , respectively. No As was detected in the fruit. According to other studies, roots are the plant organ that tend to accumulate the highest levels of As (Beesley and Marmiroli, 2011; Du et al. 2017; Ruíz-Huerta et al. 2017). Arsenic accumulation in root tissue can cause an inhibition of the root's morphological characters (Pandey et al. 2016). Remodelling of root architecture in response to toxic elements can be used by plants as a strategy to adapt to and/or survive toxic elements (Ronzan et al. 2019). Morphological changes could lead to an increase of As in roots while reducing As translocation to shoots.

Additionally, we have found higher As concentrations in stems and leaves in S1 than in S2 and S3 (Fig. 1c). The higher the concentration of As in irrigation water, the higher the concentration of As in plant tissue (Fig. 1b). However, limited As uptake have been observed at low As concentration in irrigation water ( $\leq 0.4 \text{ mg L}^{-1}$ ), where As was neither found in stems from S2 and S3 at  $0.2$  and  $0.4 \text{ mgAs L}^{-1}$ , nor in leaves from S3 at  $0.2 \text{ mgAs L}^{-1}$ . The strategy developed by tomato plants to tolerate As is avoidance, limiting As transport to shoots, and increasing As accumulation in the root system (Carbonell-Barrachina et al. 1997), which in turn plays a fundamental role on As immobilization within plants. Processes that occur in the rhizosphere influence As concentrations and bioavailability because they involve local changes in redox potential, pH, and organic matter content (Punshon et al. 2017) causing lower As mobility.

## Effect of As on tomato growth and yield

At low As concentrations in irrigation water ( $0.2 \text{ mgAs L}^{-1}$ ) As causes statistically significant reduced growth and lower number of leaves, as compared to tomato plants irrigated with As free water and most of other As doses (Fig. 2a, b and c). Tomato plants irrigated with water containing  $0.2 \text{ mgAs L}^{-1}$  of As exhibit toxicity likely due probably to inactivation of the defense system. Similarly, exposure to low doses of Pb ( $0.05 \text{ mg L}^{-1}$ ) has been reported to decrease root biomass and induced genotoxicity in lettuce (Silva et al. 2017). Furthermore, it has been reported that As affects grafted melon plants by reducing the number of leaves, leaf area and aerial dry biomass, however it did not show to affect fruit biomass (Allevato et al. 2019). In this study, low concentrations of As clearly shows a negative impact on plant growth and number of leaves, but no statistically significant effects are observed in stem diameter and tomato yield (Fig. 2c and d). Compartmentalization of As in tomato root tissue might be minimizing its

impact on plant growth and metabolism (Carbonell-Barrachina et al. 1997), which in turn could help to explain these findings in Fig. 2.

At higher As concentrations in irrigation water ( $0.4 \text{ mgAs L}^{-1}$ ) As was tolerable and promoted stem diameter growth and yield, which were statistically higher than those of tomato plants irrigated with As free water (Fig. 2c, d and e). However, the highest As doses in irrigation water does not show a statistically significant difference in stem diameter and yield compared to the control (Fig. 2c, d and e). Enhanced plant growth at high As doses ( $3.2 \text{ mgAs L}^{-1}$ ) has been observed in *Pteris vittata* (Chen et al. 2016), an As hyperaccumulator (Ma et al., 2001) known to cope with As toxicity due to a balance between As detoxification (by efflux of As(III)) and As accumulation [41]. Arsenic effluxes of the order of *Pteris vittata* have been estimated for tomato plants at relatively low As exposures ( $0.75 \text{ mg L}^{-1}$ ) (Chen et al. 2016), which may help to explain why our tomato plants show higher stem diameter and yield at  $0.4 \text{ mgAs L}^{-1}$  compared to the control. The potential for tolerance to metal toxicity of different plant species varies considerably from one species to another as well as between various genotypes (Chandrakar et al. 2016). Generally, crop yields decrease in the presence of As, however similar to this study, it has also been reported that the yield of potato tubers (*Solanum tuberosum* L.) was significantly higher in soils contaminated with As (Codling et al. 2016).

## Translocation of As and Si NPs in tomato plants

Figure 3 shows As translocation factor through plant strata and tissues. As translocated up to 34.19 % within tomato plants at all As doses (Fig. 3). At  $0.2 \text{ mgAs L}^{-1}$ , As translocates from roots to stratum S1, exhibiting a preferential accumulation within the leaves (Fig. 3a). At  $0.4 \text{ mgAs L}^{-1}$ , As translocates all the way up to stratum S2, exhibiting a preferential accumulation within the leaves as well. At higher As doses, As translocates farther from the roots reaching in some cases stratum S3 with preferential accumulation of As in leaves (Fig. 3a). These results imply the flow of As towards higher strata, which is supported by higher concentrations of As in plant tissue (Fig. 1b).

Arsenic translocation within tomato plants might occur similarly to phosphorus (P), as As could enter cells adventitiously through nutrient uptake systems such as phosphate permeases and aquaglyceroporins (Garbinski et al. 2019). Arsenic translocation within tomato plants seems to be enhanced at high As, a process that seems to occur as P absorption decreases as a result of the contamination (Gomes et al. 2014). Furthermore, it has been shown that As uptake by tomato plants through the root system results in the following accumulation order:  $\text{As}^{\text{root}} > \text{As}^{\text{leaf}} > \text{As}^{\text{stem}} > \text{As}^{\text{fruit}}$  (Stazi et al. 2018). In our study, translocation percentages are:  $\text{As}^{\text{leaf}}$  (31.43%) >  $\text{As}^{\text{stem}}$  (17.07%) >  $\text{As}^{\text{fruit}}$  (not detected). As mentioned previously, no As has been detected in fruits of tomato plants exposed to As (González-Moscoso et al. 2019).

Figure 3b and c show the results from SEM-EDS observations. We found Si NPs in root and leaf tissue from tomato plants, which suggests that tomato plants take up Si NPs through the roots (Fig. 3b) and translocate them to the leaves (Fig. 3c), where they accumulate at least in the trichomes.

Figure 3d and e show the translocation of As in the presence of Si NPs. No clear trends can be observed for the translocation of As to stem with increasing Si NPs. In general, however, the translocation of As seems to decrease towards the leaves with increasing Si NPs. Hence, application of Si NPs results in a decrease of As translocation to tomato aerial parts. Yet the highest translocation of As is occurring towards the leaves at level S1 independent of the Si NPs treatments (Fig. 3a, d and e). Decreased concentrations of As in stem, leaf, husk of brown rice have been reported after the addition of Si (Li et al. 2018). Furthermore, application of Si to tomato plants has resulted in decreased As accumulation in fruit and aerial parts (Marmioli et al. 2014), likely due to stimulation of radical exudates that can chelate metals and reduce their translocation (Kidd et al. 2001). These exudates include amino acids, organic acids, sugars and phenolic compounds (Haichar et al. 2014). Si NPs application has been reported to decrease cadmium translocation up to a 60.8% in rice plants (Chen et al. 2018).

In this study, adhesion of Si NPs to plant roots may have helped to restrict at least partially As translocation to the aerial part of tomato plants. This is likely due to increases of root exudates as it has been reported in other studies using metallic nanoparticles (de Sousa et al. 2019; Ghoto et al. 2020). This hypothesis is supported by high accumulation of As in tomato plant roots (Fig. 1b). On the other hand, it has been reported that trichomes from tobacco plants exposed to Cd actively excrete crystals, which helped to exclude the toxic element through the main cells of the trichomes (Choi et al. 2001), suggesting that trichomes played an important role in the exudation of Cd crystals through crystallization (Choi et al. 2004). Furthermore, Si NPs have been reported to increase trichome size in *Mentha piperita* L. (Ali et al. 2019). In the present study, the presence of Si NPs in tomato leaf trichomes may also have contributed to the As detoxification process in our tomato plants.

## Effect of As and Si NPs on tomato growth and yield and the relative phytotoxicity index

Figure 4 shows the effect of Si NPs on tomato plant height, number of leaves, stem diameter, yield and the relative phytotoxicity index. The application of Si NPs does not show significant differences in plant height, number of leaves and stem diameter (Fig. 4a, b and c). However, the application of Si NPs shows a significant decrease in tomato yield, both in the absence and in the presence of As (Fig. 4d), which accounts for up to 23.31% at 1000 mgSi NPs L<sup>-1</sup> and 0 mgAs L<sup>-1</sup> and up 27.04% at 250 mgSi NPs L<sup>-1</sup> and 3.2 mgAs L<sup>-1</sup>, respectively.

Application of nanoparticles to crops has not shown any clear trend on plant growth. While some studies report positive effects (Elsheery et al. 2020; García-López et al. 2019; Salachna et al. 2019) others report negative effects (Alquraidei et al. 2019; Le et al. 2014; Oukarroum et al. 2013). Nanoparticle geometry and size as well as the type of organic coating seem to induce plant responses that range from biostimulation to toxicity (Joško and Oleszczuk, 2013; Juárez-Maldonado et al. 2019; Zuverza-Mena et al. 2017). While low nanoparticle concentration (< 100 mg L<sup>-1</sup>) has been reported to increase plant growth (Juárez-Maldonado et al. 2019; Tolaymat et al. 2017), high Si NPs concentrations (100, 500 and 2000 mg L<sup>-1</sup>)

have been reported to cause negative effects on plant physiology (Le et al. 2014). In our study, we used high doses of NPs (250 and 1000 mg L<sup>-1</sup>). No significant effects can be observed in plant growth (plant height, number of leaves and stem diameter), but significant negative effects are observed in tomato yield, both in the absence and in the presence of As.

To estimate tomato plant tolerance to the stress induced by As and Si NPs as determined by radical and aerial biomass production, PRI has been estimated. Nearly all PRI values were at all As doses in the absence of Si NPs, suggesting that tomato plants show tolerance to As (Fig. 4e and f). Apparently, under conditions of contamination of As, tomato plants develop a detoxification system that allows them to tolerate As. Similar findings have previously been reported (Carbonell-Barrachina et al. 1997). An interesting observation is the case of aerial dry matter in the presence of Si NPs, which shows higher PRI values than its radical counterparts, suggesting lower toxicity to As in the aerial system which proves tolerance to As at 3.2 mgAs L<sup>-1</sup> and 1000 mgSi NPs L<sup>-1</sup>. It is known that the toxicity of a metal can decrease as the result of the “dilution effect” which accounts for the dilution of the concentration of the toxic metal within the plant by increasing plant biomass (Masood et al. 2012). In this study, the dilution effect might have helped to cope with As. The more generation of biomass, the lower the toxicity. In contrast, in the presence of Si NPs, nearly all PRI value were less to 1 at all As doses suggesting that tomato plants exhibit toxicity in the presence of Si NPs (Fig. 4e and f).

## **Modification of the photosynthetic pigments in tomato plants exposed to As and Si NPs**

Figure 5 shows the concentration of chlorophyll a, chlorophyll b and total chlorophyll in tomato leaves in the presence of As and Si NPs.

All chlorophylls were significantly higher than the control at any As doses in the absence of Si NPs (Fig. 5). Chlorophyll a increased up to 34.55% at 3.2 mgAs L<sup>-1</sup> while chlorophyll b increased up to 63.9% at 0.8 mgAs L<sup>-1</sup> (Fig. 5a and b). No significant differences in chlorophylls were observed with As treatments.

While several studies have shown a decrease in chlorophylls due to effects of As in different plant species (Azeem et al. 2017; Miteva et al. 2005; Pandey and Gupta, 2015), increases in chlorophyll content was also reported in plants of *Borreria verticillata* due to exposure to different As concentrations (Campos et al. 2014). This might be the result of plants stressed by abiotic factors improving leaf photosystem II (PSII) reaction center activity, electron transport, light harvesting complexes, and adequate heat dissipation in order to maintain leaf photosynthetic performance under stress (Jiang et al. 2014).

Regarding the effect of Si NPs, in the absence of As, only the dose of 1000 mgSi NPs L<sup>-1</sup> has shown to have a significant effect on the chlorophyll content, which accounts for up to 76% in total chlorophyll, 48.5% chlorophyll b and 35.5% chlorophyll a (Fig. 5).

Increases in chlorophylls as a result of NPs application were reported elsewhere (Ali et al. 2019; Tripathi et al. 2015). In rice plants, ZnO NPs proved to increase the concentration of chlorophyll a and b by 69% and 44%, respectively, at the highest dose of NPs ( $100 \text{ mg L}^{-1}$ ) compared to the control (Ali et al. 2019). The supply of Si NPs in pea leaves improved the photosynthetic pigments under Cr stress (Tripathi et al. 2015). This can be explained with nanomaterials having the potential to improve functional properties in organelles and photosynthetic organisms which enhances the use of solar energy and biochemical detection (Giraldo et al. 2014). Silicon can increase the chlorophyll content suggesting that more PSII reaction centers are opened which could allow for more excitation energy to be used for electron transport (Zhang et al. 2018).

All chlorophylls are significantly higher than the control ( $0 \text{ mgAs L}^{-1}$  and  $0 \text{ mgSi NPs L}^{-1}$ ) at any As and Si NPs doses (Fig. 5), indicating an improved photosynthetic capacity of our tomato plants. No significant differences are observed among As and Si NPs treatments (Fig. 5), except for chlorophyll b which shows a significant increase at  $3.2 \text{ mgAs L}^{-1}$  and  $250 \text{ mgSi NPs L}^{-1}$  compared to the highest dose of As.

The interaction of As and NPs has been reported to improve the content of chlorophylls and carotenoids in *Brassica juncea* compared to the treatment with only As (Praveen et al. 2018). However, this same interaction decreased the content of chlorophylls compared to the absolute control (Praveen et al. 2018). Chlorophylls have also been reported to increase in *Pisum sativum* plants when they interact with Cr-Si NPs, compared to treatment with only Cr and this interaction is not statistically different than the absolute control (Tripathi et al. 2015). This could indicate that Si NPs can maintain or increase, as in our case, photosynthetic capacity in the presence of metalloids.

## Antioxidant activity of enzymes and non-enzymatic compounds

The antioxidant enzymatic activity shows significant differences among treatments for ascorbate peroxidase (APX), glutathione peroxidase (GPX), catalase (CAT), and superoxide dismutase (SOD) (Fig. 6).

Statistically significant increased enzymatic activity in tomato leaves can be observed for APX and CAT at the lowest ( $0.2$  and  $0.4 \text{ mgAs L}^{-1}$ ) and highest ( $1.6$  and  $3.2 \text{ mgAs L}^{-1}$ ) As doses, respectively (Fig. 6a and c). CAT activity increases up to 137.12% at  $3.2 \text{ mgAs L}^{-1}$  (Fig. 6c). In contrast, statistically significant decreased enzymatic activity is observed, mostly for GPX at higher ( $> 0.4 \text{ mgAs L}^{-1}$ ) As doses, and in some cases for SOD at intermediate ( $0.4$  to  $0.8 \text{ mgAs L}^{-1}$ ) As doses (Fig. 6b and d).

APX activity reportedly increased to nearly 68% in the presence of aluminum ( $100 \text{ } \mu\text{M L}^{-1}$ ) stress in cucumber plants, but that it is inhibited at very high doses ( $1000$  and  $2000 \text{ } \mu\text{M L}^{-1}$ ) (Pereira et al. 2010). GPX activity has been reported to decrease considerably in *Myracrodruom urundeuva* plants when exposed to high As doses ( $100 \text{ mg Kg}^{-1}$ ) (Gomes et al. 2014). In this study, increased CAT activity at high

doses may be due to the fact that CAT production is stimulated in response to trace elements as an important mechanism to prevent oxidative damage (Mittler, 2002). It has been reported that SOD activity decreased in *Cicer arietinum* plants exposed to As concentrations of 30 and 60 mg Kg<sup>-1</sup>, as the As treatment did not cause concentrations of superoxide that could affect the plant (Gunes et al. 2009).

Enzymes are susceptible to oxidative explosions and carbonylation of proteins, when plants are exposed to trace elements (Romero-Puertas et al. 2002). In our study, enzymatic activity shows different responses due to As exposure that ranges from an increase at low doses to inhibition and an increase at high doses. It has been observed that antioxidant activity increases with increasing metal accumulation initially and is gradually inhibited after a few days (Kalita et al. 2018). However, enzyme activity can also be maintained or even increased by exposures to high concentrations of As (500 µM) (Shri et al. 2009).

In the absence of As, application of Si NPs to tomato plants shows stimulatory effects on APX and GPX enzymatic activities in tomato leaves (Fig. 6a and **b**), reaching up to a 94.4% increase of GPX at 1000 mgSi NPs L<sup>-1</sup>. CAT enzymatic activity shows non significant effects as a result of Si NPs application, while SOD shows a decrease down to 49.10% at 1000 mgSi NPs L<sup>-1</sup> (Fig. 6c and **d**). Similar results have been reported where the application of silver nanoparticles to *Brassica juncea* plants increased APX, GPX and CAT enzymatic activity (Sharma et al. 2012). In the present study, improved antioxidant enzymatic activity and reduced production of reactive oxygen species (ROS), as determined by increases of APX and GPX in the presence of Si NPs, may result in less stress to the plant. The decrease in SOD may be due to the fact that it is the first line of defense which may be catalyzing free radicals produced in plants (Gill and Tuteja, 2010) and the excess of these radicals can decrease their activity.

Application of Si NPs to tomato plants irrigated with As enriched water shows a statistically significant increase in APX enzymatic activity at low As concentrations (0.2 and 0.4 mg L<sup>-1</sup>) for any Si NPs doses as compared to the control (Fig. 6a). Increased APX enzymatic activity is also observed at 0.8 mgAs L<sup>-1</sup> and 1000 mgSi NPs L<sup>-1</sup> (Fig. 6a). In contrast, the interaction of As and Si NPs causes a statistically significant decrease in GPX enzymatic activity at any As and Si NPs doses, compared to the control, with the exception of 0.4 mgAs L<sup>-1</sup> and Si NPs application (Fig. 6b) which decrease to undetectable concentrations at 3.2 mgAs L<sup>-1</sup> (Fig. 6b). No significant differences are observed for CAT enzymatic activity among As and Si NPs treatments (Fig. 6c) except at 0.2 mgAs L<sup>-1</sup> and 1000 mgSi NPs L<sup>-1</sup> and 0.4 mgAs L<sup>-1</sup> and 250 mgSi NPs L<sup>-1</sup> where CAT enzymatic activity increases compared to the control. Either non statistically significant or statistically significant decreases are observed for SOD enzymatic activity with no clear trends among the different As and Si NPs treatments (Fig. 6d) although seven out of ten interactions cause decreased SOD activity.

Decreases in SOD and GPX may be the result of high As exposure as well as the result of additional stress imposed to tomato plants by the high doses of the Si NPs applied (250 and 1000 mg L<sup>-1</sup>). It has been reported that the activities of antioxidant enzymes decrease at high concentrations of metals (Adrees et al. 2015). An increase in enzyme activity is generally reported when the NPs interact with a

metal or metalloid, e.g. the application of zinc oxide nanoparticle at relatively low dosis ( $25 \text{ mg L}^{-1}$ ) proved to increase SOD activity in *Leucaena leucocephala* seedlings exposed to cadmium and lead (Venkatachalam et al. 2017). In comparison, our NPs concentrations are much higher which could have influenced the negative effect. More chemical components can bind to the surface of the NPs and consequently their reactivity and toxic effects increase (Madannejad et al. 2019). As for the decrease in GPX, it may also be due to the decrease in glutathione content presented in Fig. 7a, because this compound is a substrate for this enzyme.

In addition to defensive enzyme systems to deal with ROS production, other non-enzymatic antioxidants also exist in plant cells (Cao et al. 2004), such as glutathione, vitamin C, phenolic acids, carotenoids, flavonoids, which are a natural response of plants against stress (Kasote et al. 2015). In this study, the content of non-enzymatic compounds in tomato leaves exposed to doses of As and Si NPs shows significant differences between treatments (Fig. 7).

In general, glutathione decreases significantly compared to the control (Fig. 7a) suggesting that tomato plants antioxidant capacity may be sensitive to the phytotoxic effect of As (Zvobgo et al. 2019), as GSH-related antioxidant defenses may be affected in response to As tolerance (Huang et al. 2012). Flavonoid content decreases when tomato plants are exposed to  $0.4$  and  $1.6 \text{ mgAs L}^{-1}$  but is not significantly different to the control at other As doses (Fig. 7b). It has been reported that As stress can inhibit flavonoid synthesis in *panax notoginseng* plants (Liu et al. 2016). However, many of the biological roles of flavonoids are attributed to their potential cytotoxicity, antioxidant abilities and also prevent the formation of ROS by chelating metals (Pourcel et al. 2007). Regarding the effect of As on the content of phenols, no significant differences can be observed in the presence of As, except at  $1.6 \text{ mgAs L}^{-1}$  where phenol content decreases (Fig. 7c). Plant phenols play an important role in the defensive response of plants including excessive concentrations of toxic metal(lloid)s (Woźniak et al. 2017). It has been reported that exposure of different forms of As and their combinations increases the content of phenols in *Ulmus laevis* Pall (Drzewiecka et al. 2018), but decreases have also been reported in *Ocimum basilicum* plants (Saeid et al. 2014). In our study it seems that tomato plants have adapted to As stress conditions such that phenol content did not change. Total protein content decreases at any As dose (**Fig. 7d**). Biswas et al. (2016) reported that exposure to As in two rice cultivars, at  $4 \text{ mg L}^{-1}$ , decreased total protein content down to 48.56% and 68.34%. Apparently, when trace metal concentrations are high, higher generation of ROS and therefore greater oxidative stress is observed (Gupta et al. 2009) which can cause the reduction in proteins as a result of a greater oxidative damage due to part of the trace elements (Sanal et al. 2014). It has been reported that As causes toxic effects on proteins as a result of binding to sulfhydryl groups and interaction with the catalytic regions of enzymes (Zhao et al. 2009).

The effect of Si NPs in the absence of As shows that the dose of  $250 \text{ mg Si NPs L}^{-1}$  reduces glutathione content (Fig. 7a), although that same dose increases the content of phenols by 25.77% (Fig. 7c). The application of Si NPs has no significant effect on flavonoid content, however Si NPs doses decrease total proteins (Fig. 7b and **d**). It is well known that metallic oxide nanoparticles influence the development of

plants. While some species do not show any physiological change, others show variations in the antioxidant system (Siddiqi and Husen, 2017). The impact can be both positive and negative, which may depend on the type of nanoparticle, their size, and the concentration used (Torrent et al. 2020).

In this study, As-Si NPs interactions show a decrease in glutathione content as a function of the concentration of As and Si NPs (Fig. 7a). Glutathione is a crucial non-enzymatic antioxidant which stabilizes the membrane's structure within the cell and reduces the negative impact of toxic cellular products (Tripathi et al. 2016). However, both As and metallic NPs can decrease their content in plants as observed in this study.

The interaction  $0.2\text{--}1000\text{ mg L}^{-1}$  of arsenic and Si NPs reduces the content of flavonoids. This reduction also occurs when plants are exposed to  $1.6\text{--}3.2$  of arsenic and Si NPs. However, the highest dose of arsenic ( $3.2\text{ mgAs L}^{-1}$ ) in interaction with Si NPs increases the flavonoid content (Fig. 7b). The increased content of flavonoids induced by high doses of As and Si NPs is due to the fact that flavonoids are produced under conditions of severe stress to inhibit the generation of ROS (Ni et al. 2017). On the other hand, it has been reported that flavonoid contents of hyper accumulative plants under conditions of As treatment are higher than the control (Wang et al. 2010).

The phenol content is only reduced when the plants are exposed to the interaction  $0.8\text{--}250\text{ mg L}^{-1}$  of arsenic and Si NPs, respectively, the rest of the interactions show no statistically significant differences to the control (Fig. 7c). Total phenolics, which are a class of compounds that can eliminate reactive oxygen species (ROS) and are indicators of antioxidant stress responses, show no change in their content for any type of NPs (Song et al. 2019). The level of unchanged phenols suggests that the plants show no response to stress after exposure to As-Si NPs.

Proteins decrease significantly in all interactions (Fig. 7d). A decrease in the protein content of both leaves and roots in the *Brassica juncea* plant have been reported when iron oxide nanoparticles are exposed in interaction with arsenic (Praveen et al. 2018).

In conclusion, irrigation of tomato plants with As contaminated water causes As substrate enrichment and As bioaccumulation in roots, stem and leaves showing that the higher the concentration in irrigation water, the farther the contaminant flows and translocates through the different tomato stratum. Furthermore, within each stratum As accumulated preferentially in leaf tissue as compared to stem tissue. Arsenic concentrations in tomato fruit always stay below the detection limit ( $2\text{ mg kg}^{-1}$ ). Low As concentrations in irrigation water ( $0.2\text{ mg L}^{-1}$ ) cause decreased plant growth and number of leaves, while higher As concentrations in irrigation water ( $0.4\text{--}3.2\text{ mg L}^{-1}$ ) seem to not induce a phytotoxic response. In fact, at higher As concentrations tomato yield is observed to increase. We additionally find that application of Si NPs decreases As translocation, tomato yield, and root biomass. Most likely, lower root biomass accounts for lower As uptake and lower yield. Surprisingly, the combined effect of As and Si NPs at high concentrations ( $3.2\text{ mg L}^{-1}$  and  $1000\text{ mg L}^{-1}$ ) suggests adaptation of tomato plants to As according to the relative phytotoxicity index (PRI), increases production of photosynthetic pigments, and

improves activity of CAT and APX. Results from this study show the possible impact that As and nanoparticles could have on tomato production in places where tomato production and the presence of this contaminant in groundwater are both common.

## **Declarations**

### **Ethics approval and consent to participate**

Not applicable

### **Consent for publication**

Not applicable

### **Availability of data and materials**

All data generated or analysed during this study are included in this published article [and its supplementary information files].

### **Competing interests**

The authors declare that they have no competing interests

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### **Authors' contribution**

Magín González-Moscoso: Investigation, Writing – Original draft, writing – review & editing. Antonio Juárez-Maldonado: Investigation, Methodology, editing, supervision. Gregorio Cadenas-Pliego: Investigation, editing, supervision. Diana Meza-Figueroa: Investigation, editing, supervision. Bhaskar SenGupta: Investigation, editing, supervision. Nadia Martínez-Villegas: Conceptualization, writing – review & editing, supervision.

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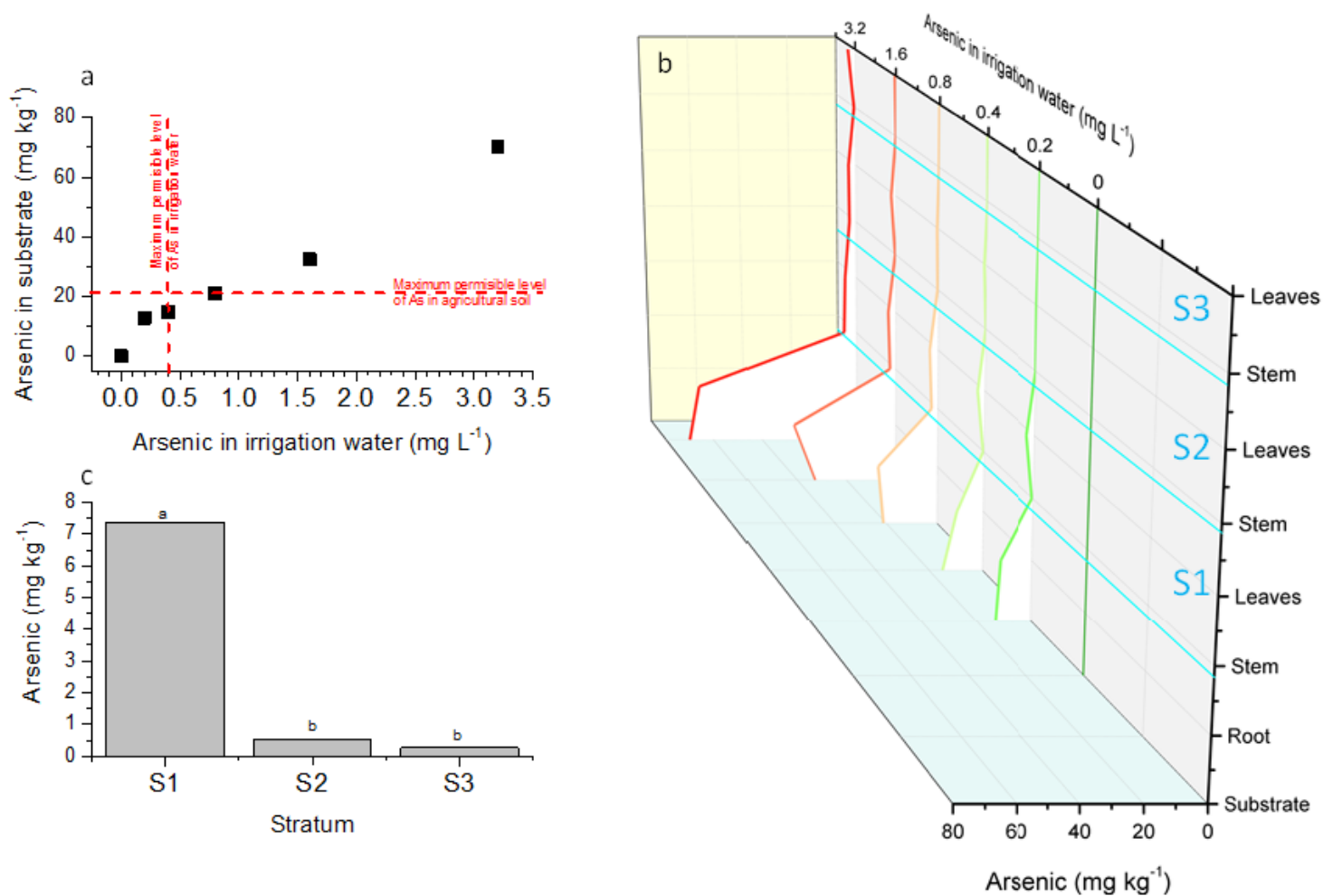
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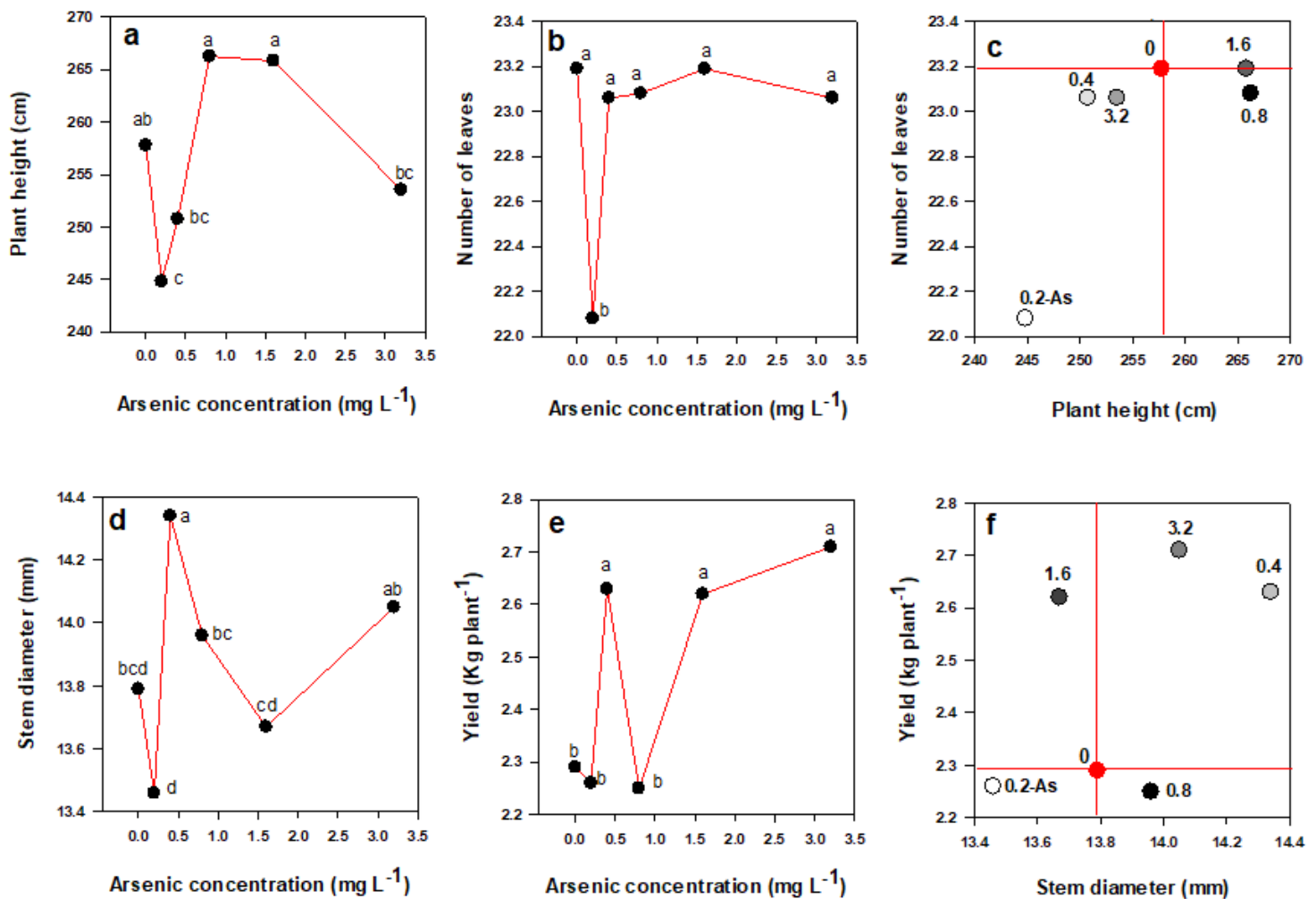
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## Figures



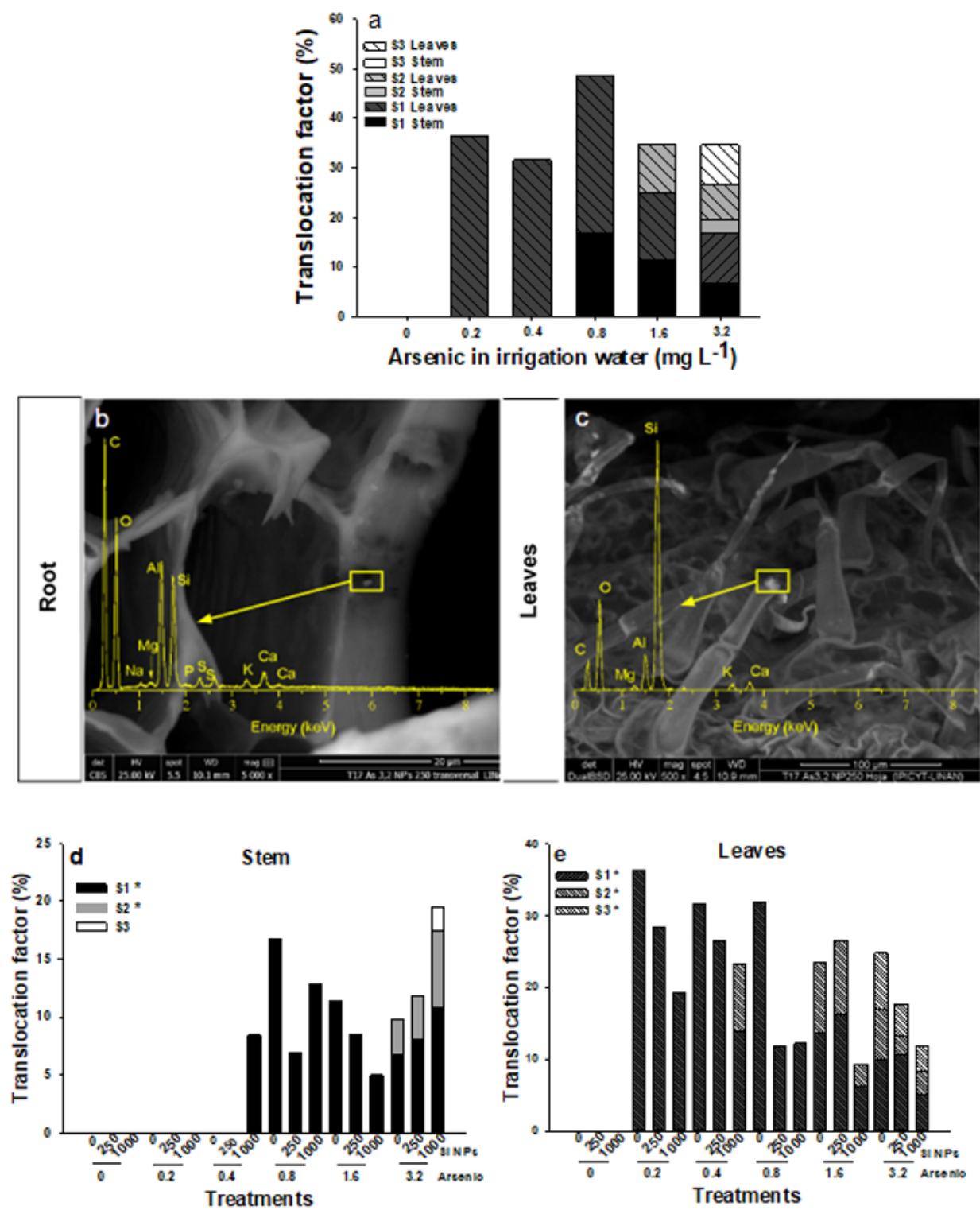
**Figure 1**

Arsenic concentration in irrigation water, substrate, and tomato plant tissue. (a) Arsenic in substrate as a function of As in irrigation water. (b) Arsenic in substrate and plant tissue as a function of As in irrigation water. (c) Average As concentration as a function of aerial stratum. Different letters per bar indicate significant differences according to the Fisher Least Significant Difference test ( $p \leq 0.05$ ,  $n=3$ )



**Figure 2**

Arsenic effect in agronomic variables. (a) Plant height and (b) number of leaves as a function of arsenic concentration in irrigation water (c) Number of leaves as a function of plant height (d) Stem diameter and (e) yield as a function of As concentration in irrigation water (f) Tomato yield as a function of stem diameter (Numbers at each point represent the concentration of arsenic). All values represent the mean of each parameter for n=12. Different letters per point indicate significant differences according to the Fisher Least Significant Difference test ( $p \leq 0.05$ ,  $n=3$ )



**Figure 3**

Translocation of As in tomato plants as a function of As in irrigation water and Si NPs. (a) As translocation to the aerial part (stem and leaf) of tomato plants, (b) Si NPs in the roots of tomato plants and (c) Si NPs in the leaf trichomes. (d) As translocation to stem as a function of As and Si NPs and (e) As translocation to leaves as a function of As and Si NPs and see Table 1 (Supplementary Material) for

statistical differences. \* significant differences were found among different treatments according to Fisher test ( $p \leq 0.05$ ,  $n=3$ )

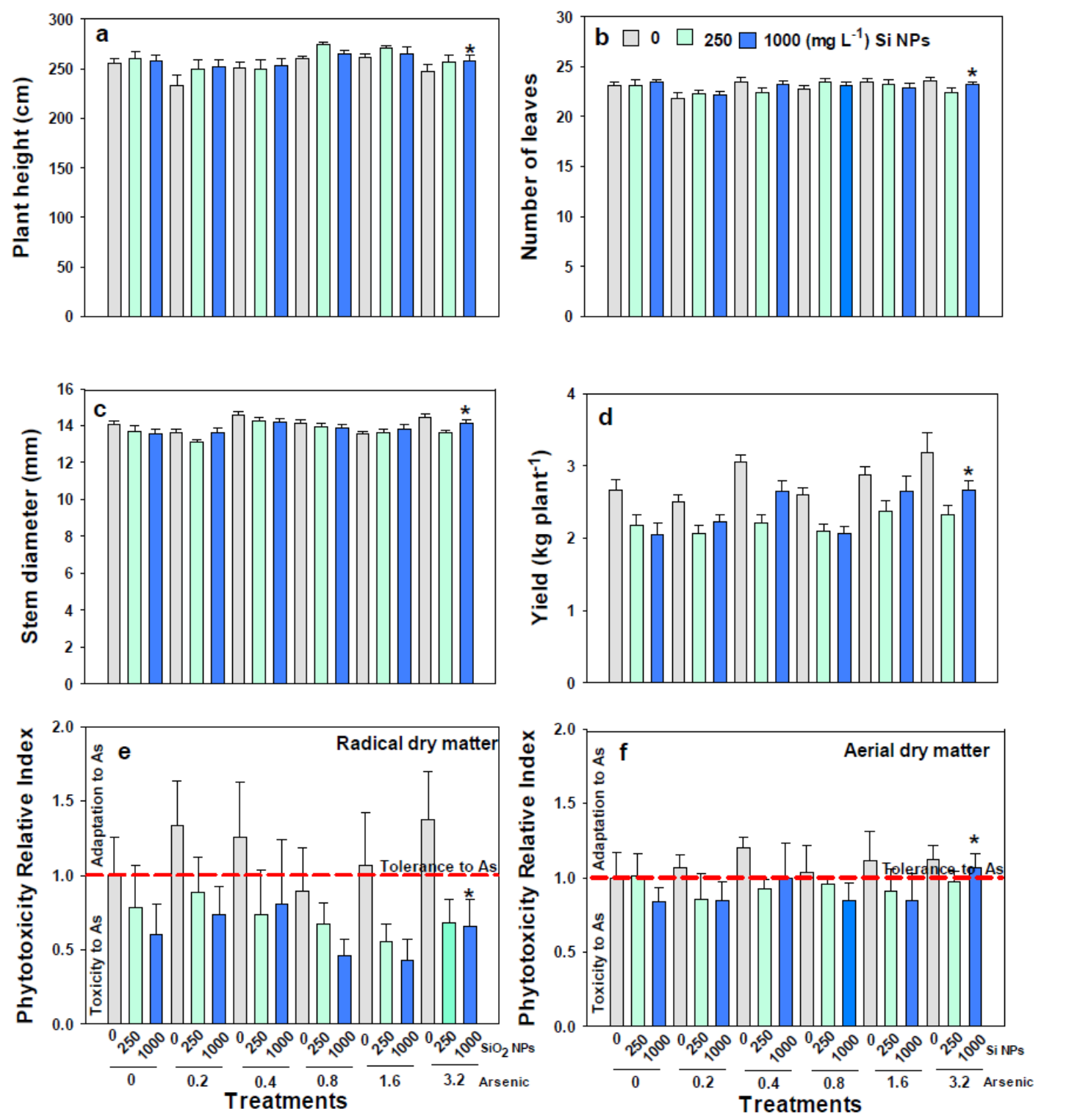
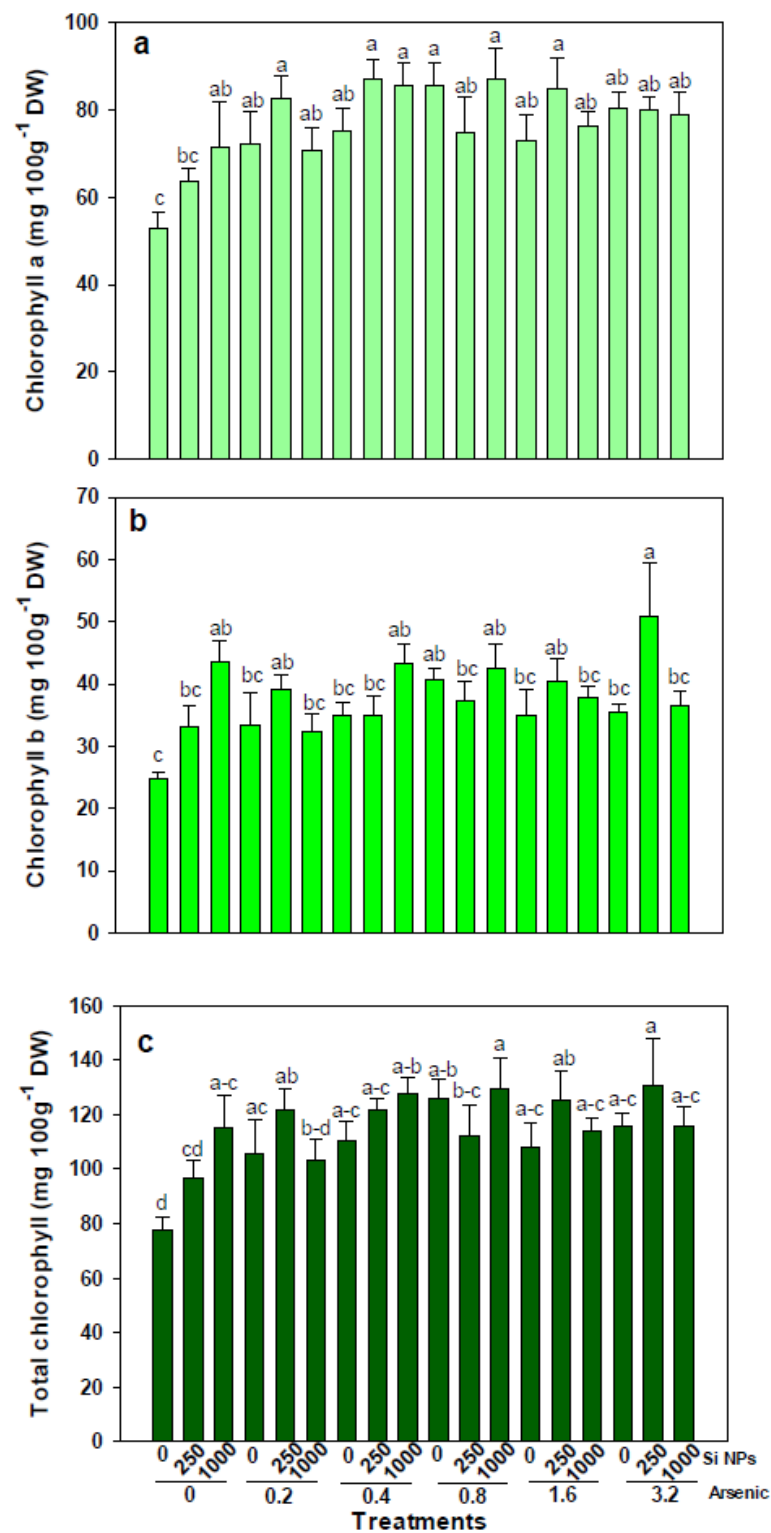


Figure 4

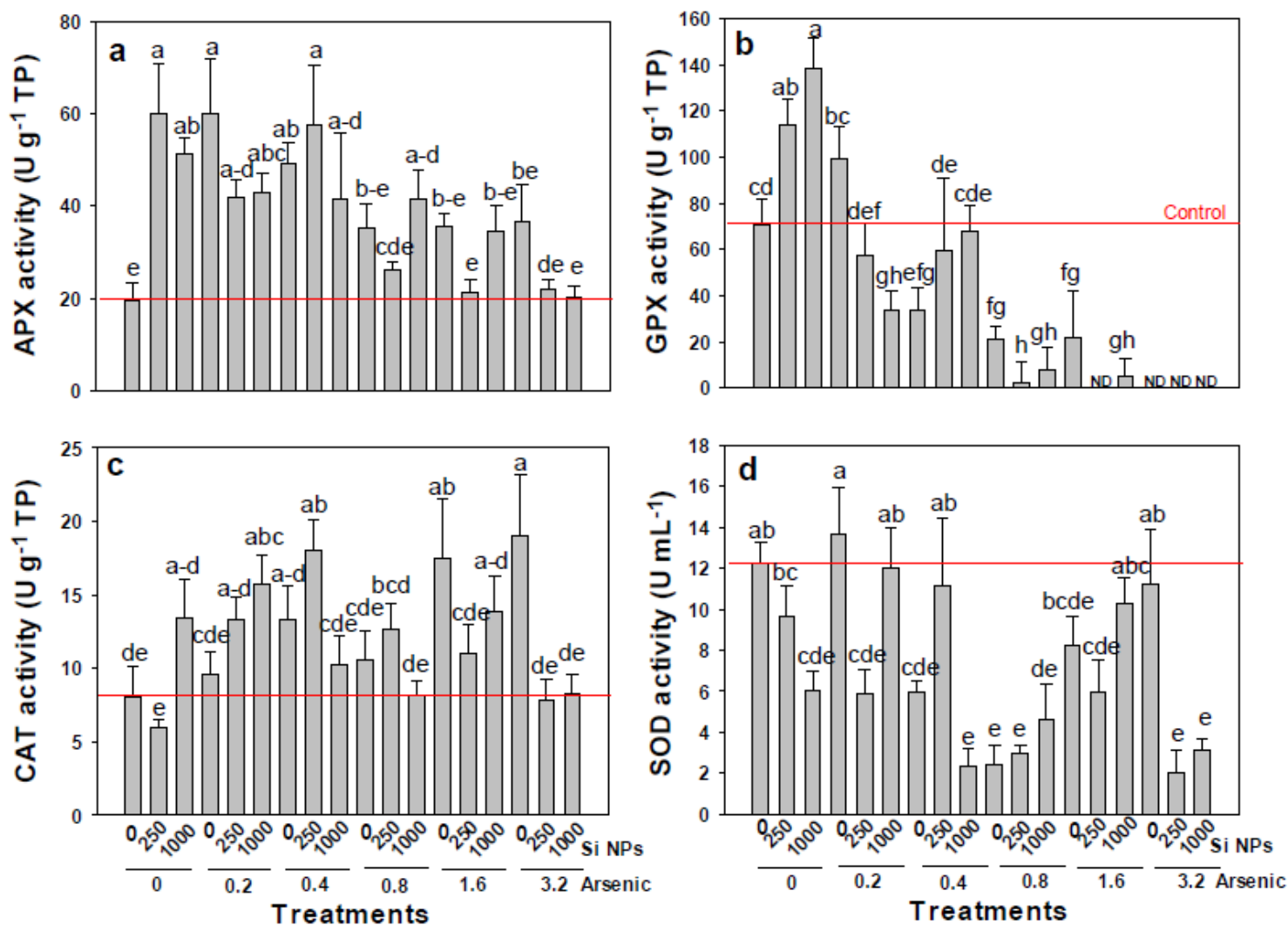
Effect of Si NPs on tomato plant development and the phytotoxicity relative index of arsenic and Si NPs. (a) Plant height, (b) number of leaves, (c) stem diameter, and (d) yield as a function of As and Si NPs. Relative phytotoxicity index in (e) radical and (f) aerial biomass as a function of As and Si NPs. \*

indicates significant differences according to the Fisher's least significant difference test ( $p \leq 0.05$ ,  $n=12$ ). Statistical differences are shown in Table S4 (Supplementary Material)



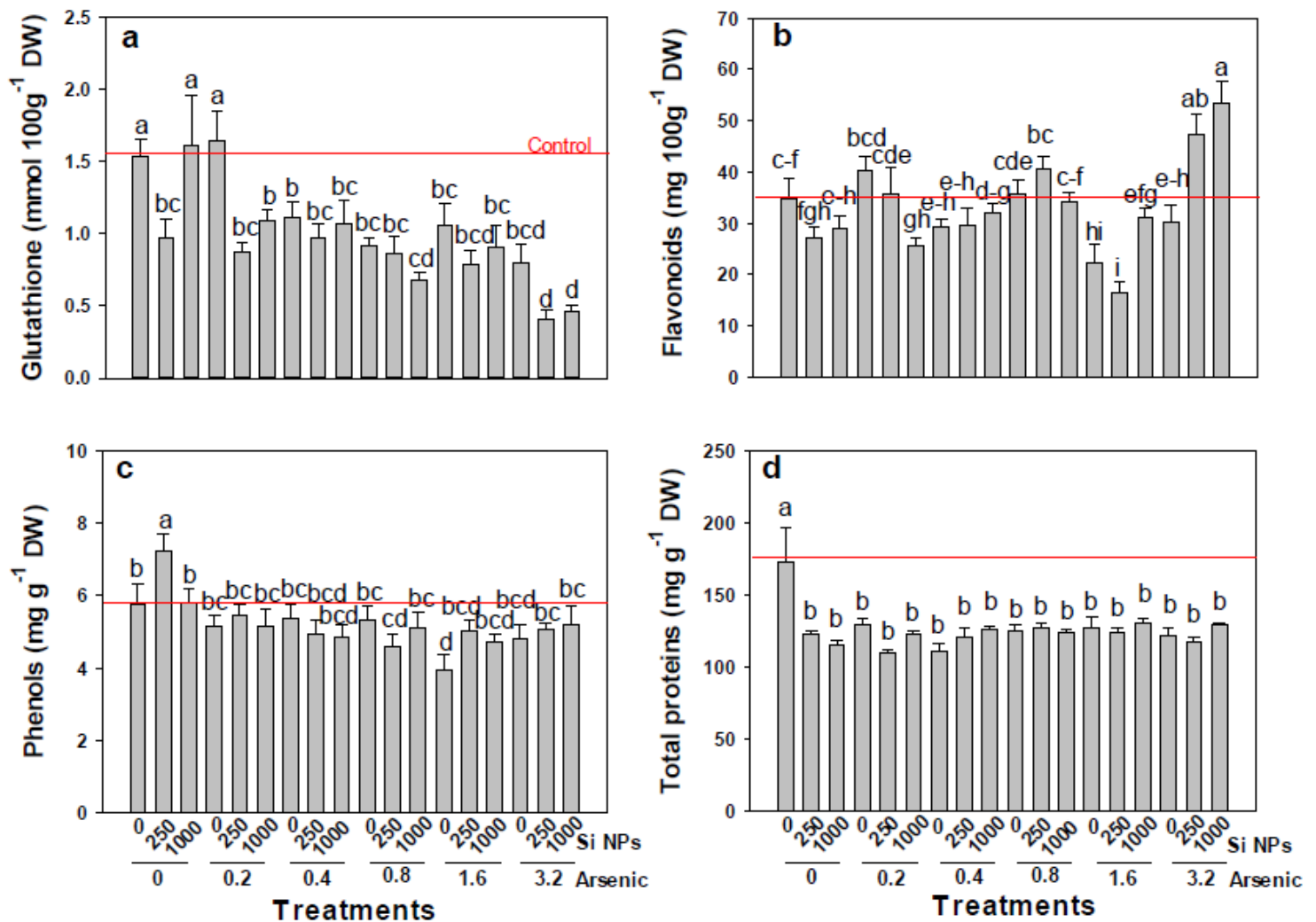
**Figure 5**

Photosynthetic pigments in the leaves of tomato plants. (a) chlorophyll a, (b) chlorophyll b and (c) total chlorophyll increased by exposure to As and Si NPs compared to the control. Different letter per bar indicate significant differences according to the Fisher Least Significant Difference test ( $p \leq 0.05$ ,  $n=6$ )



**Figure 6**

Enzymatic antioxidant compounds in tomato leaves. (a) APX, (b) GPX, (c) CAT, and (d) SOD activities as a function of Si NPs for different levels of Arsenic, TP: Total proteins, ND: not detected. Different letter per bar indicate significant differences according to the Fisher Least Significant Difference test ( $p \leq 0.05$ ,  $n=6$ )



**Figure 7**

Non-enzymatic antioxidant compounds in tomato leaves exposed to As and Si NPs. (a) Glutathione, (b) Flavonoids, (c) Phenols, and (d) Total Proteins as a function of Si NPs for different levels of Arsenic. Different letter per bar indicate significant differences according to the Fisher Least Significant Difference test ( $p \leq 0.05$ ,  $n=6$ )

# Supplementary Files

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