UNIVERSIDAD AUTÓNOMA AGRARIA ANTONIO NARRO
SUBDIRECCIÓN DE POSTGRADO

APLICACIÓN DE NANOPARTÍCULAS DE SILICIO EN PLANTAS DE TOMATE PARA INDUCIR TOLERANCIA AL ESTRÉS POR ARSÉNICO

Tesis

Que presenta MAGÍN GONZÁLEZ MOSCOSO
como requisito parcial para obtener el Grado de
DOCTOR EN CIENCIAS EN AGRICULTURA PROTEGIDA

Saltillo, Coahuila

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Dr. Antonio Juárez Maldonado
Director UAAAN

Dra. Nadia Valentina Martínez Villegas
Directora Externa

Saltillo, Coahuila

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Elaborada por MAGÍN GONZÁLEZ MOSCOSO como requisito parcial para obtener el grado de Doctor en Ciencias en Agricultura Protegida con la supervisión y aprobación del Comité de Asesoría

Dr. Antonio Juárez Maldonado
Asesor Principal

Dra. Nadia Valentina Martínez Villegas
Asesor

Dr. Adalberto Benavides Mendoza
Asesor

Dra. Susana González Morales
Asesor

Dra. María del Carmen Rivera Cruz
Asesor

Dr. Marcelino Cabrera De la Fuente
Subdirector de Postgrado
UAAAN

Saltillo, Coahuila

Diciembre 2020

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DEDICATORIA

A mis padres por su apoyo incondicional y consejos en cada momento de mi vida.

A mis hermanos por ser parte de mi vida y por estar siempre unidos.

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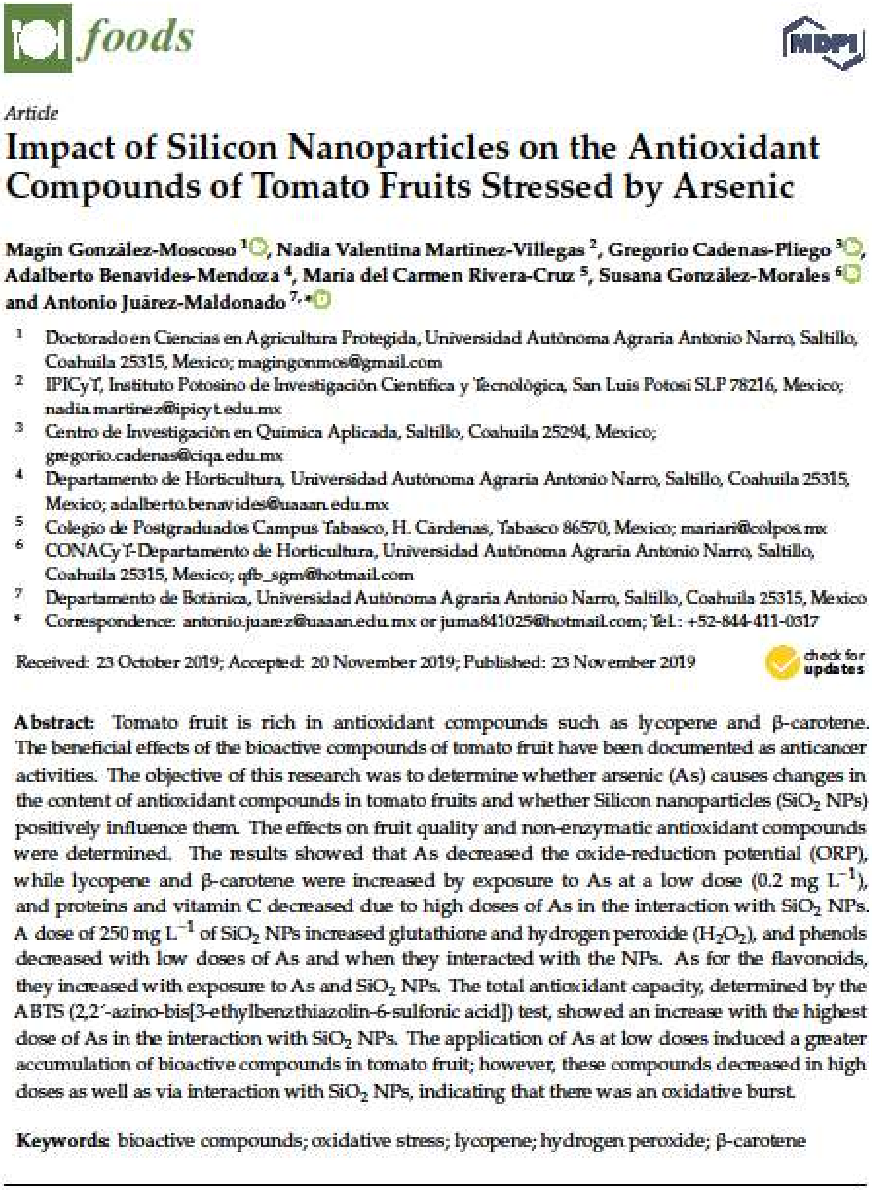

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Article

Impact of Silicon Nanoparticles on the Antioxidant Compounds of Tomato Fruits Stressed by Arsenic

Magín González-Moscoso [1], Nadia Valentina Martínez-Villegas [2], Gregorio Cadenas-Pliego [3], Adalberto Benavides-Mendoza [4], María del Carmen Rivera-Cruz [5], Susana González-Morales [6] and Antonio Juárez-Maldonado [7,*]

[1] Doctorado en Ciencias en Agricultura Protegida, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico; magingonmos@gmail.com

[2] IPICyT, Instituto Potosino de Investigación Científica y Tecnológica, San Luis Potosí SLP 78216, Mexico; nadia.martinez@ipicyt.edu.mx

[3] Centro de Investigación en Química Aplicada, Saltillo, Coahuila 25294, Mexico; gregorio.cadenas@ciqa.edu.mx

[4] Departamento de Horticultura, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico; adalberto.benavides@uaaan.edu.mx

[5] Colegio de Postgraduados Campus Tabasco, H. Cárdenas, Tabasco 86570, Mexico; mariari@colpos.mx

[6] CONACyT-Departamento de Horticultura, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico; qfb_sgm@hotmail.com

[7] Departamento de Botánica, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico

* Correspondence: antonio.juarez@uaaan.edu.mx or juma841025@hotmail.com; Tel.: +52-844-411-0317

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Abstract: Tomato fruit is rich in antioxidant compounds such as lycopene and β-carotene. The beneficial effects of the bioactive compounds of tomato fruit have been documented as anticancer activities. The objective of this research was to determine whether arsenic (As) causes changes in the content of antioxidant compounds in tomato fruits and whether Silicon nanoparticles (SiO_2 NPs) positively influence them. The effects on fruit quality and non-enzymatic antioxidant compounds were determined. The results showed that As decreased the oxide-reduction potential (ORP), while lycopene and β-carotene were increased by exposure to As at a low dose (0.2 mg L^{-1}), and proteins and vitamin C decreased due to high doses of As in the interaction with SiO_2 NPs. A dose of 250 mg L^{-1} of SiO_2 NPs increased glutathione and hydrogen peroxide (H_2O_2), and phenols decreased with low doses of As and when they interacted with the NPs. As for the flavonoids, they increased with exposure to As and SiO_2 NPs. The total antioxidant capacity, determined by the ABTS (2,2′-azino-bis[3-ethylbenzthiazolin-6-sulfonic acid]) test, showed an increase with the highest dose of As in the interaction with SiO_2 NPs. The application of As at low doses induced a greater accumulation of bioactive compounds in tomato fruit; however, these compounds decreased in high doses as well as via interaction with SiO_2 NPs, indicating that there was an oxidative burst.

Keywords: bioactive compounds; oxidative stress; lycopene; hydrogen peroxide; β-carotene

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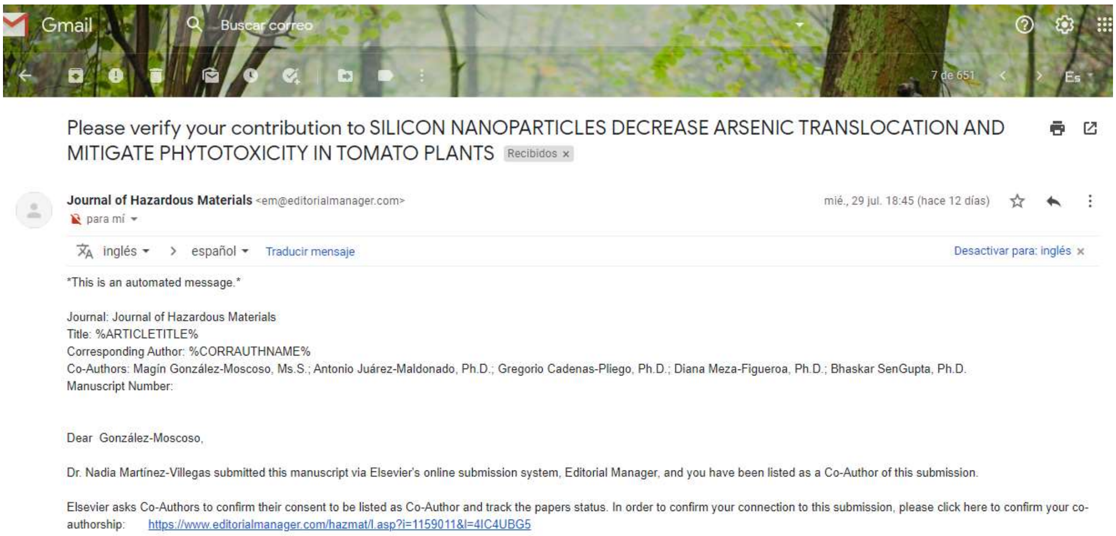

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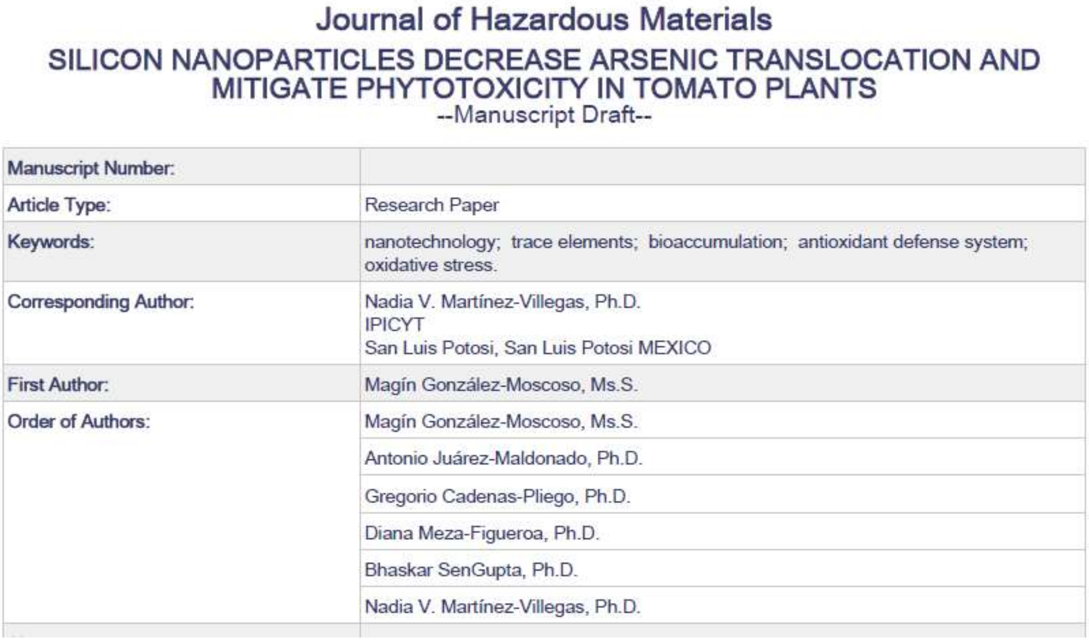

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Article Type:	Research Paper
Keywords:	nanotechnology; trace elements; bioaccumulation; antioxidant defense system; oxidative stress.
Corresponding Author:	Nadia V. Martínez-Villegas, Ph.D. IPICYT San Luis Potosi, San Luis Potosi MEXICO
First Author:	Magín González-Moscoso, Ms.S.
Order of Authors:	Magín González-Moscoso, Ms.S.
	Antonio Juárez-Maldonado, Ph.D.
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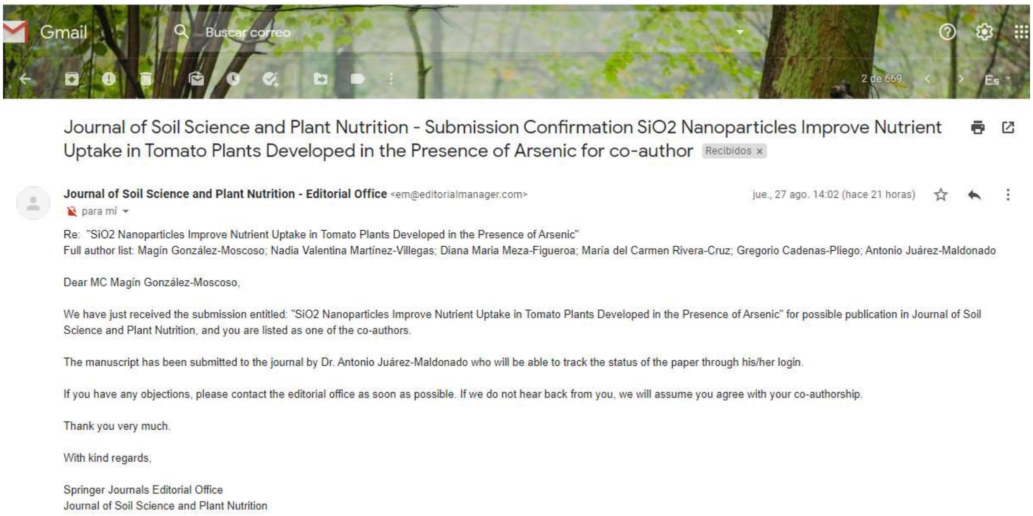

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Dear MC Magín González-Moscoso,

We have just received the submission entitled: "SiO2 Nanoparticles Improve Nutrient Uptake in Tomato Plants Developed in the Presence of Arsenic" for possible publication in Journal of Soil Science and Plant Nutrition, and you are listed as one of the co-authors.

The manuscript has been submitted to the journal by Dr. Antonio Juárez-Maldonado who will be able to track the status of the paper through his/her login.

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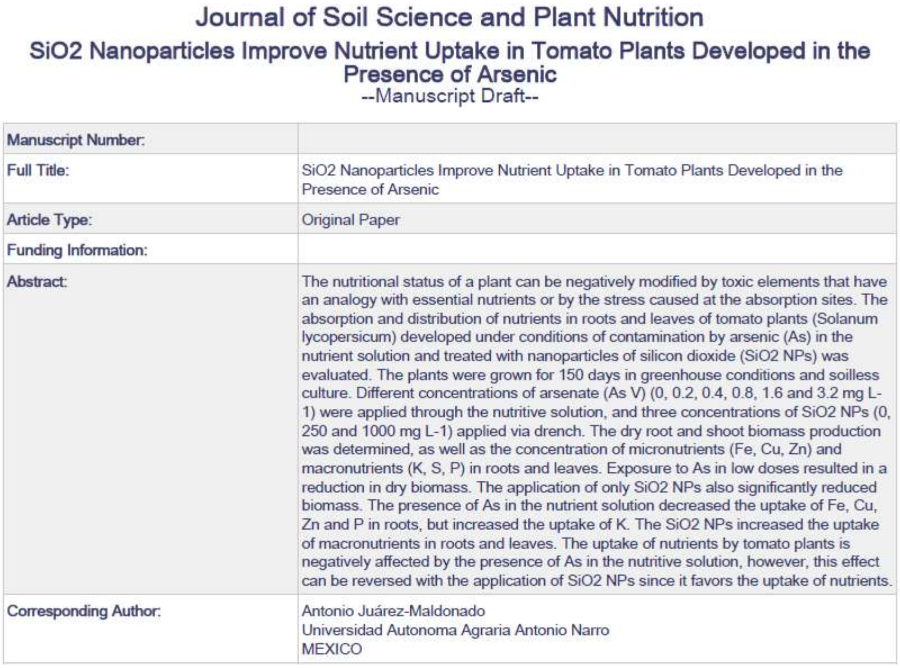

Journal of Soil Science and Plant Nutrition

SiO2 Nanoparticles Improve Nutrient Uptake in Tomato Plants Developed in the Presence of Arsenic

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Manuscript Number:	
Full Title:	SiO2 Nanoparticles Improve Nutrient Uptake in Tomato Plants Developed in the Presence of Arsenic
Article Type:	Original Paper
Funding Information:	
Abstract:	The nutritional status of a plant can be negatively modified by toxic elements that have an analogy with essential nutrients or by the stress caused at the absorption sites. The absorption and distribution of nutrients in roots and leaves of tomato plants (Solanum lycopersicum) developed under conditions of contamination by arsenic (As) in the nutrient solution and treated with nanoparticles of silicon dioxide (SiO2 NPs) was evaluated. The plants were grown for 150 days in greenhouse conditions and soilless culture. Different concentrations of arsenate (As V) (0, 0.2, 0.4, 0.8, 1.6 and 3.2 mg L-1) were applied through the nutritive solution, and three concentrations of SiO2 NPs (0, 250 and 1000 mg L-1) applied via drench. The dry root and shoot biomass production was determined, as well as the concentration of micronutrients (Fe, Cu, Zn) and macronutrients (K, S, P) in roots and leaves. Exposure to As in low doses resulted in a reduction in dry biomass. The application of only SiO2 NPs also significantly reduced biomass. The presence of As in the nutrient solution decreased the uptake of Fe, Cu, Zn and P in roots, but increased the uptake of K. The SiO2 NPs increased the uptake of macronutrients in roots and leaves. The uptake of nutrients by tomato plants is negatively affected by the presence of As in the nutritive solution, however, this effect can be reversed with the application of SiO2 NPs since it favors the uptake of nutrients.
Corresponding Author:	Antonio Juárez-Maldonado Universidad Autonoma Agraria Antonio Narro MEXICO

ÍNDICE

INTRODUCCIÓN

El arsénico (As) es considerado el "rey de los venenos". Debido a su abundancia generalizada en el agua potable, influye en la salud humana a nivel mundial (Rehman et al., 2020). Está presente en bajas concentraciones en el medio ambiente y se origina a partir del impacto antropogénico y las fuentes geogénicas (Kumar et al., 2015). Millones de personas en todo el mundo están crónicamente expuestas a altos niveles de As en los alimentos y el agua potable (Ruíz-Huerta et al., 2017). La exposición crónica a As causa anormalidades de la piel, neuropatía periférica, problemas cardiovasculares, respiratorio, hepático y renal entre otras (Erickson et al., 2018; Mohammed Abdul et al., 2015) así cómo cáncer de piel, hígado y pulmón (Varol and Köse, 2018).

El As en el suelo y en el agua puede representar un riesgo potencial para los organismos del suelo y las plantas (Vašíčková et al., 2016). Las especies inorgánicas de As existen en dos estados de oxidación diferentes, conocidos como arseniato pentavalente completamente oxidado (As V) y arsenito trivalente reducido (As III) (Xu et al., 2015), siendo el As III 100 veces más toxico que el As V (Chandrakar et al., 2016). En las plantas, el As induce la producción de especies reactivas de oxígeno (ROS) que conducen a la peroxidación lipídica que puede causar la muerte de la planta (Finnegan and Chen, 2012). Sin embargo, ante la presencia de As, las plantas activan su sistema de defensa antioxidante (compuestos enzimáticos y no enzimáticos) para proteger al sistema celular de los efectos nocivos de las ROS (Gomes et al., 2014).

La mayoría de los cultivos, entre estos el tomate, son sensibles al estrés por As, cuyos efectos consisten en reducir la germinación de semillas, disminuir su crecimiento y modificar respuestas moleculares (Beesley et al., 2013; Marmiroli et al., 2014; Miteva et al., 2005). Por la extensión de sus sembradíos y alto nivel de consumo, el tomate (*Solanum lycopersicum* L.) es una de las hortalizas de mayor importancia en el mundo (Nicola et al., 2009). No obstante, su producción y consumo pueden verse comprometidos por la contaminación de As. Los campos agrícolas se consideran, inclusive, como una fuente de toneladas de As que entran a la cadena alimentaria, año tras año, mediante el riego de dichos cultivos con agua subterránea con en As y/o su cultivo en suelos cargados de As (Neumann et al., 2011). Cuando el As ingresa a la cadena alimentaria, a través del consumo de cultivos, el asunto se convierte en un motivo de preocupación ambiental y de salud (Praveen et al., 2017).

Por otro lado, la nanotecnología tiene un enorme potencial en la agricultura, desde aumentar el rendimiento, hasta mejorar la calidad de los productos agrícolas (Kumar et al., 2019). En la actualidad la nanotecnología también es útil como una tecnología ambiental. Ésta se usa para proteger al ambiente, ya sea a través de la prevención, el tratamiento o la limpieza de sitios con desechos peligrosos (Karn et al., 2009). Las nanopartículas (NPs) son partículas con dimensiones inferiores a 100 nm que se caracterizan por un área superficial especifica alta y que pueden servir como adsorbentes de metales pesados (Auffan et al., 2009; Xiong et al., 2015). Las NPs modifican significativamente las funciones y el metaboloma de las plantas, aumentan la clorofila, las enzimas antioxidantes, el glutatión y el ácido ascórbico (Jurkow et al., 2020). Se ha reportado que, por ejemplo, la aplicación de NPs de óxido de zinc (NPs ZnO) a cultivos de chile habanero mejoran la calidad de los frutos aumentando el contenido de capsaicina, fenoles totales y flavonoides totales (García-López et al., 2019). En tomate se ha reportado que la aplicación de NPs de cobre induce la producción de frutos con mayor firmeza y aumenta el contenido de licopeno y vitamina C (Lopez-Vargas et al., 2018).

Estudios recientes han demostrado que los adsorbentes a nanoescala tienen una mayor capacidad de adsorción de As que las partículas más grandes (Meng et al., 2005). Se ha reportado también que la aplicación de NPs ZnO reduce la toxicidad de As en plantas de soya al restringir la absorción y modular las enzimas antioxidantes, el ciclo ascorbato-glutatión y el sistema de glioxalasa (Ahmad et al., 2020).

En cuanto a las NPs de silicio (NPs Si), se ha reportado que su aplicación aumenta el crecimiento de plantas bajo toxicidad por plomo (Emamverdian et al., 2020), reduce la acumulación de cromo en plántulas de guisante (Tripathi et al., 2015) y reduce el efecto toxico del arsénico en plantas de maíz (Tripathi et al., 2016). Además, se ha reportado que tienen la capacidad de aumentar el sistema antioxidante en plantas de trigo (Tripathi et al., 2017). La aplicación de NPs Si puede mejorar el contenido de clorofila y disminuir el daño de la pared celular en plantas bajo estrés abiótico (Mahmoud et al., 2020).

Considerando que el enriquecimiento de As en el agua de riego puede aumentar la concentración de As en el suelo y la acumulación en tejidos vegetales, además puede modificar el desarrollo fisiológico y bioquímico de la planta, aunado a los cambios de altas concentraciones de nanopartículas de dióxido de silicio (NPs SiO_2). Por todo lo anterior, el objetivo del presente trabajo de investigación fue conocer el potencial de dosis altas de NPs SiO_2 en la producción de compuestos bioactivos de frutos de tomate en sustrato con As, la acumulación y translocación de As en tejidos vegetales de tomate, la respuesta fisiológica y del sistema de defensa antioxidante, y su efecto en la absorción y acumulación de nutrientes minerales.

REVISIÓN DE LITERATURA

Origen del arsénico en el ecosistema

El As es un metaloide (no metal) que tiene propiedades intermedias entre metales y no metales (Hong et al., 2020). Una vez liberado al medio ambiente por fuentes naturales o antropogénicas, el As es tóxico y cancerígeno, (Alam et al., 2019). Una mayor concentración de As en el suelo puede ser el resultado de actividades humanas, entra las que se encuentran el uso de pesticidas, la minería y operaciones de procesamiento de minerales (Yoshida, 2013). Los suelos naturales generalmente pueden contener un nivel de 0.1–10 mg kg^{-1} de As (Zhao et al., 2010).

El As es un elemento omnipresente y ocupa el puesto 20 en abundancia dentro de la corteza terrestre y el puesto 14 en agua de mar (Flora, 2015). El As y sus compuestos son transportables en ambientes superficiales y subterráneos. Es un elemento tóxico que normalmente se origina en el agua subterránea, siendo uno de los principales contaminantes importantes de ésta (Huq et al., 2020).

El As se puede encontrar de forma inorgánica como Arseniato (As V) ($HAsO_4^{2-}$, $H_2AsO_4^-$, y H_3AsO_3), Arsenito (As III), y arsenopirita. Pero también se puede encontrar en forma orgánica como arsenobetaina (AsB) y arsenocolina (AsC), arsenosugar o metilado como ácido monometilarsonico (MMA), ácido dimetilarsinico (DMA), oxido de trimetilarsina (TMA), y (Abbas et al., 2018; Honma et al., 2016). Los mecanismos y eficiencias de la biotransformación de As varían entre los organismos. En general, se cree que la mayoría de los animales, microorganismos y plantas producen enzimas transformadoras cruciales, como arsenito metiltransferasa codificada por arsénico (estado de oxidación +3) metiltransferasa (AS3MT) (Wang et al., 2020).

La movilidad del As en los suelos, sedimentos y sistemas de aguas subterráneas está fuertemente controlada por la adsorción que se produce en las interfaces de óxido de hierro/agua, el alcance de esta adsorción puede verse influenciado por la presencia de materia orgánica (Xue et al., 2019). La presencia de As en los sedimentos también se ve fuertemente afectada por el pH, lo que resulta en reacciones de desorción y disolución, que moviliza el As de la fase sólida (sedimento) a la fase líquida (agua) (Prakash et al., 2019). Es bien sabido que la solubilidad y la movilidad de As en el sistema del suelo dependen en gran medida de las variaciones potenciales redox. En condiciones oxidantes (valores altos de Eh,100 a + 200 mV), el As inorgánico (V) es la especie predominante de As. A un alto valor de Eh, As (V) se adsorbe y/o coprecipita con diferentes minerales, especialmente óxidos de hierro y manganeso (Khalid et al., 2017).

Arsénico en la cadena alimentaria y su efecto en la salud humana

La ingestión del As en humanos a través de diversas fuentes de alimentos es un problema de salud mundial (Kumarathilaka et al., 2019). Se han reportado concentraciones de hasta 11.7 mg kg^{-1} de As en hojas de maíz, derivadas del cultivo de dicho en suelo contaminado irrigado con agua con altos niveles de As (Ruíz-Huerta et al., 2017). El maíz puede representar el primer producto en la cadena trófica y, como tal, su calidad es importante debido al potencial de acumulación de metales pesados y As (Ding et al., 2011). Lo anterior es preocupante debido a que el maíz se utiliza como forraje en muchos partes del mundo y en el caso del ganado podría afectar tanto a la salud de los animales como la calidad de la leche y carne.

Por otro lado, el arroz es el componente básico más importante de la dieta humana en todo el mundo, especialmente en Asia (Wang et al., 2019). Dicho cultivo acumula 10 veces más As que otros granos resaltando un riesgo potencial de toxicidad para los humanos (Carracelas et al., 2019; Davis et al., 2017). Se ha reportado que el uso de agua potable rica en As para cocinar podría elevar la concentración de As en el arroz cocido hasta un 129% por encima de la muestra cruda, aumentando así la vulnerabilidad de la población a la exposición al As a través del consumo de arroz (Mandal et al., 2019).

En la Tabla 1 se muestran estudios recientes de la concentración de As en alimentos comunes de la población y que se producen en el área agrícola. Si bien las cantidades podrían parecer relativamente pequeñas, de acuerdo con Mondal et al., (2020), 200 µg kg^{-1} podrían contribuir negativamente a la salud humana tras exposición crónica.

Tabla 1. Concentración de As en alimentos agrícolas.

Alimentos de campos agrícolas	Concentración de As (µg kg^{-1})	Referencia
Fresa	220 – 300	(González de las Torres et al., 2020)
Arroz	68.39 – 345.31	(Mondal et al., 2020)
Arroz	93 – 989	(Althobiti et al., 2018)
Pimiento	59.2 – 360	(Yang et al., 2019)
Manzana	0.15 - 0.28	(Rezaei et al., 2019)
Durazno	0.14 - 0.34	(Rezaei et al., 2019)
Uva	0.23 - 1.20	(Rezaei et al., 2019)
Melón	0.186 – 309	(Allevato et al., 2019)
Lechuga	876	(Yañez et al., 2019)
Cebolla	734 – 916	(Funes Pinter et al., 2018)
Mango	0.6 – 50	(Liao et al., 2014)
Tomate	2 – 13	(Marmiroli et al., 2014)
Tomate	1.19 - 2.5	(Beesley et al., 2013)
Maíz	0.02 - 0.016	(Ding et al., 2011)

También se ha reportado la influencia del agua de consumo con As para ganado en los niveles de As en leche cruda de vacas en granjas lecheras de Argentina, los resultados mostraron un bajo nivel de transferencia de As a la leche de vaca por la ingestión de agua contaminada (Sigrist et al., 2010). En China se evaluaron 10 áreas productoras de leche de vaca y se reportó contenidos de As en un rango de 0.13 a 0.80 µg L^{-1} en leche cruda (Zhou et al., 2019). La concentración de As en Pakistán de muestras de leche de vacas, búfalos, ovejas, cabras y camellos se presentó en el rango de 15.1-18.4, 2.6-7.7, 25.7-33.2, 10.5-37.3 y 6.6-13.7 µg L^{-1}, respectivamente, y se correlaciono directamente con los niveles de As en el agua potable del ganado de cada granja, que se encontraron en el rango de 238–2000 µg L^{-1} (Kazi et al., 2016). Los valores presentados son peligrosos sobre todo la leche de oveja y cabras, el consumo de esta leche puede crear efectos adversos para la salud en etapa infantil de acuerdo al estudio antes mencionado.

Los animales están expuestos al As a través del agua potable contaminada, alimentos (forrajes), pastos, incluso el As en animales contamina la carne, la leche y el huevo (Mandal, 2017). En carne de bovinos se ha reportado acumulación de As hasta 0.06 µg g^{-1}, aunque los niveles de As están dentro del rango normal para propósitos de salud animal (Alto: 1-5, tóxico: 7-100 mg kg^{-1}) (Roggeman et al., 2014), no deja de ser un riesgo de salud humana.

Las aportacionesde As a los alimentos son pequeñas en comparación con el agua, a menos que las concentraciones en el agua potable sean bajas (<10 µg L^{-1}), se ha identificado un mayor riesgo de cáncer debido al As en poblaciones con altas concentraciones en el agua potable, generalmente >200 µg L^{-1} (Cohen et al., 2019). Una vez ingerido, se estima que entre el 70 y el 90% del As es absorbido por el tracto gastrointestinal y se distribuye ampliamente a través de la sangre a diferentes órganos, principalmente al hígado, los riñones, los pulmones y la vejiga y, en segundo lugar, al tejido muscular y nervioso (Palma-Lara et al., 2020). También se ha reportado que el As en concentraciones extremadamente bajas en células humanas induce mutagénesis tardía y osteosarcoma humano (Mure et al., 2003).

En cuanto al cáncer de pulmón, también es la causa principal de muerte debido a la exposición al As, y este carcinógeno actúa como el principal agente etiológico en el cáncer que ocurren en las personas que nunca han fumado (Mead, 2005). Mientras que los canceres de piel, entre personas expuestas al As, se puede desarrollar en la población, sin embargo, la variabilidad genética, el sistema inmune y la interacción de ambos pueden diferir, lo que lleva a susceptibilidades diferenciales (Lee et al., 2011). De hecho la enfermedad de Bowen inducida por As, es el cáncer de As más común, se caracteriza por una mayor proliferación, displasia y apoptosis de células individuales, todas las cuales involucran mitocondrias (Lee et al., 2013).

Efectos fisiológicos y bioquímicos del arsénico en las plantas

El As reduce la fijación del CO_2 y desorganiza los procesos integrales fotosintéticos de la plantas (Zhao et al., 2009). Las membranas son muy vulnerables al estrés por As, el daño en las membranas produce un desbalance en la absorción de nutrientes y agua en las células vegetales (Ali et al., 2009). De hecho, estudios previos encontraron que el As(V) afecta principalmente a la pared celular, al metabolismo primario y secundario, al metabolismo del ácido abscísico y a la germinación, mientras que el As(III) afecta principalmente a las hormonas y el proceso de señalización (Sharma, 2012).

La tolerancia de las plantas puede derivar de la capacidad de metabolizar As a formas menos tóxicas, como la reducción de As(V) a As(III) por la enzima arseniato reductasa (AR), que posteriormente se compleja a través de fitoquelatinas (III) (Tripathi et al., 2007) y se almacenan en las vacuolas de las células como complejo As(III)-tris glutatión en los brotes y As(III)-tris tiolato en las raíces (Mallick et al., 2011), lo que permite a la planta acumular el elemento sin toxicidad (Meharg and Hartley-Whitaker, 2002). Para combatir el estrés oxidativo uno de los componentes importantes de la vía redox es el sistema glutatión/glutareoxina que mantiene el estado de proteína tiol/disulfuro (Verma et al., 2020). A nivel molecular los genes que responden a As pueden agruparse en varios procesos biológicos como el estrés oxidativo, el transportador, la homeostasis hormonal y la transducción de señales (Fu et al., 2014).

Impacto del arsénico/metales pesados en el sistema antioxidante

El As y los metales pesados inducen la formación de especies reactivas de oxígeno (ROS), el aumento de las ROS determina el estrés oxidativo en las células vegetales (Piacentini et al., 2020). Sin embargo, las plantas activan el sistema de enzimas antioxidantes como superóxido dismutasa (SOD), catalasa (CAT), ascorbato peroxidasa (APX) y la glutatión peroxidasa (GPX) que permiten que las plantas combatan el efecto de las ROS (Tiwari and Sarangi, 2017). Además, el As induce aumentos de glutatión (GSH), glutamato cisteína (GCL) y la glutatión reductasa, enzimas involucradas en la síntesis de GSH y el reciclaje redox (Lee et al., 2016). Se ha reportado que el metabolismo antioxidante de *Trigonella foenum-graecum* L. aumenta por la exposición a As debido a la inducción de isoformas únicas de Cu/Zn, Fe y Mn de SOD y APX-3, APX-4y o su expresión aumentada en coordinación con CAT (Talukdar, 2013). Las alteraciones de las actividades antioxidantes enzimáticas y no enzimáticas son dependientes de la especie de As, la dosis y del tejido (Song et al., 2020). Incluso el efecto del As en el sistema antioxidante muestra variaciones dentro de cultivares de una misma especie de plantas (Farooq et al., 2015).

El cultivo del tomate y su respuesta al arsénico

El tomate es un cultivo muy importante desde el punto de vista económico y nutricional (Pérez-Labrada et al., 2019). El fruto es importante en la dieta del ser humano ya que puede proporcionar vitaminas y una amplia gama de moléculas bioactivas (Salehi et al., 2019), como vitamina C y E, compuestos fenólicos, licopeno y el β-caroteno (Stajčić et al., 2015; Xie et al., 2019). Estos compuestos parecen desempeñar un papel contra el desarrollo de diferentes tipos de cáncer y enfermedades cardiovasculares, debido a su capacidad antioxidante (Cao et al., 2019) .

Estudiar el movimiento de metales tóxicos y determinar el lugar final donde se acumula el metal son muy útiles para determinar la seguridad de los alimentos (Almaroai and Eissa, 2020). Los altos niveles de As en el suelo provocan algunos cambios en la concentración de pigmento en el tomate (Miteva, 2002). De acuerdo a un estudio realizado por Miteva et al., (2005), el As modifica la actividad peroxidasa, clorofila y pigmentos del cloroplasto ocasionando un efecto tóxico pero no letal. Las plantas de tomate pueden desarrollar estrategias para tolerar este elemento, limitando el transporte a brotes y aumentado la acumulación de As en el sistema raíz, el As en el tejido de raíz de tomate parece estar tan compartimentado que su impacto en el crecimiento y metabolismo de la planta puede ser mínimo (Carbonell-Barrachina et al., 1997). Se ha reportado que el As puede llegar al fruto y acumular 13 $\mu g\ g^{-1}$ en peso seco (Marmiroli et al., 2014), < 3 $\mu g\ kg^{-1}$ (Beesley et al., 2013).

Nanomateriales en la producción de cultivos

Las propiedades únicas de los nanomateriales (NMs) y su utilización en los campos científicos y tecnológicos han enriquecido el área agrícola (Younes et al., 2019). Las aplicaciones de los NMs en la agricultura incluyen fertilizantes para aumentar el crecimiento y el rendimiento de las plantas, pesticidas para el manejo de plagas y enfermedades, y sensores para monitorear la calidad del suelo y la salud de las plantas (Servin et al., 2015). Los NMs también actúan como agentes para estimular el crecimiento de las plantas, debido a sus propiedades mecánicas, térmicas, químicas y eléctricas (Dimkpa, 2018; Singh et al., 2017). En la escala de nanómetros, el área de superficie relativamente grande de los NMs da como resultado una actividad química/biológica mejorada (Deng et al., 2014).

Los NMs incluyen nanotubos de carbono de pared simple y pared múltiple, grafeno, fullerenos (Zaytseva and Neumann, 2016), nanopartículas de hierro magnetizado (Fe), aluminio (Al), cobre (Cu), oro (Au), plata (Ag), silicio (Si), zinc (Zn) y óxido de zinc (ZnO), dióxido de titanio (TiO_2) y óxido de cerio (Ce_2O_3) (Khot et al., 2012).

Los efectos positivos de los distintos NMs, incluyen: mayor porcentaje y tasa de germinación; longitud de la raíz y brote y biomasa vegetativa de muchas plantas de cultivo (Kole et al., 2013). Mejoran el sistema antioxidante de plántulas de tomate (González-García et al., 2019) e incrementan la calidad y el contenido de compuestos bioactivos de frutos de tomate (Lopez-Vargas et al., 2018).

Nanopartículas generan bioestimulación y toxicidad

Las nanopartículas (NPs) son partículas con dimensiones inferiores a 100 nm (Xiong et al., 2015). Tienen excelentes propiedades térmicas, mecánicas, ópticas, estructurales y morfológicas que les permiten ser utilizados en diferentes aplicaciones (Tyagi et al., 2018).

Las NPs no son moléculas simples en sí mismas y, por lo tanto, están compuestas por tres capas: La capa superficial, la capa del caparazón y el núcleo. La capa superficial puede funcionalizarse con una variedad de pequeñas moléculas, iones metálicos, surfactantes y polímeros. La capa del caparazón es químicamente diferente del núcleo en todos los aspectos. Por último, el núcleo es esencialmente la porción central de las NPs y generalmente se refiere a la NPs misma (Shin et al., 2016).

Las NPs pueden considerarse bioestimulantes ya que, en rangos específicos de concentración, generalmente en niveles pequeños, aumentan el crecimiento de las plantas (Juárez-Maldonado et al., 2019). Por otro lado, el tamaño de las partículas también pueden influir en las respuestas estimulantes, de hecho puede pasar que entre tres tamaños diferentes una puede ser más tóxica y las otras dos con tamaño menor en concentración de hasta 60 a 100 más altas sean menos toxicas (Fratoddi et al., 2015).

La disminución en el tamaño de los NPs se asocia con un aumento significativo en el área superficial de las partículas. Por lo tanto, se pueden unir más componentes químicos a la superficie de las NPs y, en consecuencia, su reactividad y efectos tóxicos aumentan (Madannejad et al., 2019). Aunque estas características de las NPs pueden ser tóxicas para algunas especie podrían ser no tóxicas para otras (Dev et al., 2018).

Nanopartículas como método de remediación de metales y metaloides

La nanoremediación o fito-nanoremediación de suelos es prometedora ya que puede minimizar la entrada de contaminantes metálicos en las plantas, reduciendo así la absorción y la toxicidad (El-Ramady et al., 2017). Las NPs son eficientes en el proceso de nanoremediación del suelo debido al hecho de que pueden reducir las fracciones de lixiviados metálicos e inmovilizar metales o metaloides, como Cd, Pb, As y Cr, en el suelo (Mallampati et al., 2013).

Las NPs más utilizadas en la nanoremediación son las compuestas de Fe, en particular, el Fe de nanovalor cero (nZVI) (Fajardo et al., 2020). Sin embargo, nZVI tiende a agregarse rápidamente debido a su magnetismo, propiedad y efecto de pequeño tamaño, que reduce significativamente su reactividad hacia el contaminante (Basnet et al., 2013). Los procesos de inmovilización metal-nZVI pueden resumirse de la siguiente manera: reducción, adsorción, oxidación/reoxidación, coprecipitación y precipitación (Xue et al., 2018).

Se ha reportado que la aplicación de nZVI reduce la disponibilidad de cadmio y cromo en el suelo, además induce una reducción de la fitotoxicidad y una mejora en el desarrollo de las plantas de cebada (*Hordeum vulgare*), que pudieron completar su período de crecimiento (Gil-Díaz et al., 2016). Aunque también se ha reportado que dosis altas de nZVI (1000 y 2000 mg kg^{-1}) disminuye la acumulación de plomo en plantas de *Lolium perenne*, pero también causa la disminución de la biomasa vegetal y la respuesta antioxidante (Huang et al., 2018).

Sin embargo, la fitorremediación en combinación con NPs metálicas, todavía tiene grandes áreas de oportunidad, ya que la publicación de trabajos en esta interdisiplina data de 10 años a la fecha y existen escasos informes en la literatura (Gomes et al., 2016). No obstante, los resultados son muy prometedores y la nanorremediación seguramente se aplicará cada vez más para la solución de problemas de contaminación ambiental.

Nanopartículas de silicio y su efecto en la mitigación del estrés inducido por arsénico

El silicio (Si) es considerado el segundo mineral más abundante en el suelo y es clasificado como nutriente no esencial para la planta (Moghanloo et al., 2019). El Si tiene múltiples funciones en la respuesta de la planta a los factores ambientales, los efectos sobre el rendimiento de la planta y los efectos sobre las comunidades y los ecosistemas (Katz, 2019). El Si mejora el intercambio de gases de las hojas y el sistema de defensa antioxidante en plantas de *Saccharum officinarum* en respuesta a estrés abiótico (Verma et al., 2020). Reduce la peroxidación de lípidos, decrece la absorción de cadmio, modula el nivel de ácido abscísico, ácido salicílico y ácido jasmónico en *Phoenix dactylifera* L. (Khan et al., 2020).

Se ha reportado que el Si disminuye las concentraciones de cadmio al modular el desarrollo de la suberina endodérmica de la raíz en las plantas de trigo y regular la expresión del gen relacionado con el flujo de salida de CdTaTM20 (Wu et al., 2019). Incluso cuando las plántulas de *Oryza sativa* son expuestas al ácido arsanílico una forma de As orgánico, disminuye su crecimiento, sin embargo, la aplicación de Si revierte el efecto negativo al mejorar la actividad antioxidante y el metabolismo de las proteínas (Geng et al., 2018).

Las NPs de silicio (NPs Si) tienen un efecto similar al silicato sobre los parámetros de crecimiento y estructura celular en plantas de avena y en muchos casos incluso más fuerte (Asgari et al., 2018). Además, pueden usarse como nano pesticidas, nano herbicidas y nano fertilizantes (Rastogi et al., 2019). Sin embargo, las concentraciones altas de NPs Si causan efecto negativos en la fisiología de las plantas (Karimi and Mohsenzadeh, 2016; Le et al., 2014). También se ha reportado que el tamaño de las NPs Si influye y manifiesta diferentes respuestas tanto fisiológicas como genéticas en plantas de *Oryza sativa* (Cui et al., 2017).

Las NPs Si mejoran el crecimiento de las plantas, al aumentar el contenido de clorofila y carotenoides y aumentar la actividad enzimática antioxidante, incluso bajo la toxicidad por plomo (Emamverdian et al., 2020). Por otro lado, las NPs Si tienen un efecto protector contra la fitotoxicidad de cromo (VI) en plántulas de guisantes, reduciendo la acumulación de Cr tanto en raíces como en brotes y el estrés oxidativo (Tripathi et al., 2015). Igualmente reducen el efecto toxico del As al mejorar los componentes del ciclo ascorbato-glutatión en plantas de maíz (Tripathi et al., 2016). Tanto el ascorbato como el glutatión, se reconocen como el corazón del metabolismo redox, son antioxidantes abundantes y estables con potenciales redox adecuados que actúan juntos en varias vías y se mantienen en una condición comúnmente reducida (Foyer and Noctor, 2011). Dentro de la célula vegetal, el peróxido de hidrógeno (H_2O_2) es desintoxicado por la APX (Zechmann, 2020).

Además, las NPs Si tienen la capacidad de aumentar el sistema antioxidante tanto enzimático como no enzimático en plantas de trigo (Tripathi et al., 2017). La reducción de la translocación de arsénico y otros metales pesados, además de que las NPs Si aumentan el sistema de defensa como medida de protección, también se debe a que aumentan la acumulación de ácidos orgánicos en raíces como mecanismo de desintoxicación de metales a través del proceso de quelación (de Sousa et al., 2019).

PRIMER ARTÍCULO

Impact of Silicon Nanoparticles on the Antioxidant Compounds of Tomato Fruits Stressed by Arsenic

Article

Impact of Silicon Nanoparticles on the Antioxidant Compounds of Tomato Fruits Stressed by Arsenic

Magín González-Moscoso [1], Nadia Valentina Martínez-Villegas [2], Gregorio Cadenas-Pliego [3], Adalberto Benavides-Mendoza [4], María del Carmen Rivera-Cruz [5], Susana González-Morales [6] and Antonio Juárez-Maldonado [7,*]

[1] Doctorado en Ciencias en Agricultura Protegida, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico; magingonmos@gmail.com
[2] IPICyT, Instituto Potosino de Investigación Científica y Tecnológica, San Luis Potosí SLP 78216, Mexico; nadia.martinez@ipicyt.edu.mx
[3] Centro de Investigación en Química Aplicada, Saltillo, Coahuila 25294, Mexico; gregorio.cadenas@ciqa.edu.mx
[4] Departamento de Horticultura, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico; adalberto.benavides@uaaan.edu.mx
[5] Colegio de Postgraduados Campus Tabasco, H. Cárdenas, Tabasco 86570, Mexico; mariari@colpos.mx
[6] CONACyT-Departamento de Horticultura, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico; qfb_sgm@hotmail.com
[7] Departamento de Botánica, Universidad Autónoma Agraria Antonio Narro, Saltillo, Coahuila 25315, Mexico
***** Correspondence: antonio.juarez@uaaan.edu.mx or juma841025@hotmail.com; Tel.: +52-844-411-0317

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Abstract: Tomato fruit is rich in antioxidant compounds such as lycopene and β-carotene. The beneficial effects of the bioactive compounds of tomato fruit have been documented as anticancer activities. The objective of this research was to determine whether arsenic (As) causes changes in the content of antioxidant compounds in tomato fruits and whether Silicon nanoparticles (SiO_2 NPs) positively influence them. The effects on fruit quality and non-enzymatic antioxidant compounds were determined. The results showed that As decreased the oxide-reduction potential (ORP), while lycopene and β-carotene were increased by exposure to As at a low dose (0.2 mg L^{-1}), and proteins and vitamin C decreased due to high doses of As in the interaction with SiO_2 NPs. A dose of 250 mg L^{-1} of SiO_2 NPs increased glutathione and hydrogen peroxide (H_2O_2), and phenols decreased with low doses of As and when they interacted with the NPs. As for the flavonoids, they increased with exposure to As and SiO_2 NPs. The total antioxidant capacity, determined by the ABTS (2,2′-azino-bis[3-ethylbenzthiazolin-6-sulfonic acid]) test, showed an increase with the highest dose of As in the interaction with SiO_2 NPs. The application of As at low doses induced a greater accumulation of bioactive compounds in tomato fruit; however, these compounds decreased in high doses as well as via interaction with SiO_2 NPs, indicating that there was an oxidative burst.

Keywords: bioactive compounds; oxidative stress; lycopene; hydrogen peroxide; β-carotene

1. Introduction

Tomato is the second most important crop in the world from an economic point of view [1]. However, tomato fruit is also important in the human diet because it can provide vitamins and a wide range of bioactive molecules [2], such as vitamins C and E, flavonoids, and phenols [3]. Lycopene is one of the strongest natural antioxidants known and is the main carotene in ripe tomatoes [4], and together with β-carotene, it is effective in eliminating peroxyl radicals [5]. These compounds seem to play a role against the development of different types of cancer and cardiovascular diseases due to their antioxidant capacity [6,7], which is why they are very important for human health.

There are many biotic and abiotic factors that influence the growth and development of a tomato crop, which can modify the quality of the fruit. One of these is arsenic (As), a highly toxic metalloid for plants and humans [8,9]. It is known that irrigation water contaminated by As causes a gradual and continuous accumulation in the soil that affects the sustainability of agriculture, decreases crop yield, and contaminates the food chain [10,11]. The concentration of As in rice grains has been reported to range from 93 to 989 μg kg^{-1} dry weight [12], in mango fruits from 0.6 to 50 μg kg^{-1} fresh weight [13], and from 2 to 13 μg g^{-1} of dry weight in tomatoes [14]. In addition, the capacity of a tomato plant to absorb and translocate As is of vital importance, since the fruit is the organ of consumption [15].

Arsenic induces the production of reactive oxygen species (ROS), which lead to lipid peroxidation [16,17]. Antioxidant metabolites synthesized by plants to avoid ROS-induced damage during oxidative stress are constitutively present in fruits and at different levels according to their stage of maturation [18]. The oxidative stress in tomato fruit increases in a coordinated manner with the ripening of the fruit and reaches a peak in the final stages, which triggers metabolic changes and softening of the fruit [19].

Currently, nanotechnology is used for different purposes in agriculture for the promotion of plant growth [20]. Nanoparticles (NPs, materials with a dimension of less than 100 nm) are noteworthy and can be considered biostimulants, since in specific ranges of concentration, generally at low levels, they increase plant growth [21]. NPs have been implicated in inducing a better quality of tomato fruit and increasing lycopene under conditions of abiotic stress [22]. Silicon nanoparticles (Si NPs) increase the yield of cucumber fruit [23]. Silicon decreases the toxic effect of heavy metals by reducing uptake and translocation to the aerial parts of plants [24]. It can also inhibit the negative impact of oxidative stress caused by As by restricting the production of ROS, improving the action of various antioxidant compounds, and regulating the osmotic potential of the cell [25]. Considering the above, the objective of the present investigation was to determine the impact of the SiO_2 NPs on the antioxidant content of tomato fruits obtained from plants developed under conditions of arsenic stress.

2. Materials and Methods

2.1. Fruit Sampling

A tomato crop (*Solanum lycopersicum* L.) var. "Sun 7705" (Nunhems Amsterdam Netherlands B.V. Napoleonsweg 152 6083 AB Nunhem Nederland), of type saladette and indeterminate, was grown. A total of 216 plants were established for the experiment. A soil-less culture system was used, which involved placing the plants in 12 L black polyethylene bags containing a mixture of Peat moss and perlite (1:1) as substrate. A Steiner nutrient solution [26] was used for crop nutrition.

Arsenic contamination was simulated in the irrigation water, where different concentrations of the contaminant were applied (0, 0.2, 0.4, 0.8, 1.6, and 3.2 mg As L^{-1} water). In addition, different doses of silicon dioxide nanoparticles (SiO_2 NPs) (0, 250, and 1000 mg L^{-1}) were applied. The SiO_2 NPs (10 mL to each plant) were applied to soil at intervals of three weeks from transplanting, with a total of six applications. In total, 18 treatments were evaluated. SiO_2 NPs of 10–20 nm size had a spherical morphology, a surface area of 160 m^2 g^{-1}, and a bulk density of 0.08–0.1 g cm^{-3} (SkySpring Nanomaterials Inc., Houston, TX, USA). Arsenic was applied as sodium arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) in the irrigation water.

It was verified that the tomatoes selected by treatment did not have damage and were of a homogeneous size. They were harvested as full red according to the USDA scale: red indicates that more than 90 percent of the surface in the aggregate shows a red color [27]. Quality analysis, biochemical analysis, and an arsenic content determination were performed on these fruits.

2.2. Fruit Quality

The parameters that describe a fruit's quality (hydrogen potential (pH), total soluble solids (TSS), fruit firmness, titratable acidity (TA), electrical conductivity (EC), and Oxide-Reduction Potential (ORP)) were determined, as described in López-Vargas et al. [28]. For this, six fruits per treatment (one per plant) of uniform size and in a light red state of maturity were collected from the third cluster.

2.3. Biochemical Analysis

The fruit samples were stored at −80 °C until use. The samples were lyophilized (lyophilizer, Yamato Scientific Co. Ltd., Model D401, Santa Clara, CA, USA). For antioxidant compound determination, 200 mg of lyophilized fruits and 20 mg of polyvinylpyrrolidone were weighed. After this, 1.5 mL of phosphate buffer with a pH of 7–7.2 (0.1 M) was added, and the mixture was then subjected to micro-centrifugation at 12,000 rpm for 10 min at 4 °C. The supernatant was filtered with a nylon membrane. With this extract proteins, glutathione and ABTS (2,2′-azino-bis[3-ethylbenzthiazolin-6-sulfonic acid]) antioxidant capacity in hidrophilic compounds were determined.

The quantification of total protein (mg g^{-1} of dry weight (DW)) was performed using Bradford's colorimetric technique [29]. In a microplate, 5 µL of the extract and 250 µL of Bradford reagent were placed in each well. The mixture was incubated for 10 min at room temperature (26 °C) and then read at a wavelength of 630 nm on a microplate reader (Allsheng, AMR-100 model, Hangzhou, China).

Lycopene and β-carotene (mg 100 g^{-1} DW) were determined according to Nagata and Yamashita [30]. For this, a sample (0.1 g) was mixed with 20 mL of hexane:acetone solution (3:2). An aliquot was taken from the supernatant and measured at absorbance values of 453, 505, 645, and 663 nm, as shown in Equations (1) and (2).

$$\text{Lycopene} = -0.0458 \times \text{Abs}_{663} + 0.204 \times \text{Abs}_{645} + 0.372 \times \text{Abs}_{505} - 0.0806 \times \text{Abs}_{453} \quad (1)$$

$$\beta\text{-carotene} = 0.216 \times \text{Abs}_{663} - 1.22 \times \text{Abs}_{645} - 0.304 \times \text{Abs}_{505} + 0.452 \times \text{Abs}_{453} \quad (2)$$

Vitamin C (mg g^{-1} DW) was determined by the colorimetric method using 2,6 dichlorophenol, 1 g of fresh tissue, and 1 mL of 1% metaphosphoric acid and filtered with Whatman No. 1 filter paper, as described in Hung and Yeng [31].

Glutathione (mmol 100 g^{-1} DW) was determined using the method of Xue et al. [32] by means of a 5,5-dithio-bis-2 nitrobenzoic acid (DTNB) reaction. A mixture of 0.480 mL of the extract, 2.2 mL of sodium dibasic phosphate (Na_2HPO_4 at 0.32 M), and 0.32 mL of the DTNB dye (1 mM) was placed in a test tube. Then, the mixture was vortexed and read on a UV–Vis spectrophotometer (UNICO Spectrophotometer Model UV2150, Dayton, NJ, USA) at 412 nm using a quartz cell.

Flavonoids (mg 100 g^{-1} DW) were determined by the method of Arvouet-Grand et al. [33]. For the extraction, 100 mg of lyophilized tissue was placed in a test tube with 10 mL of reagent-grade methanol and then shaken for 30 s until the mixture was homogenized. The mixture was filtered using No. 1 Whatman paper. For the quantification, 2 mL of the extract and 2 mL of a methanolic solution of aluminum trichloride ($AlCl_3$) 2% were added to the test tube and the mixture was left to rest for 20 min in the dark. The reading was then taken using a UV–Vis spectrophotometer (UNICO Spectrophotometer Model UV2150, Dayton, NJ, USA) at a wavelength of 415 nm using a quartz cell.

Phenols (mg g^{-1} DW) were determined with Folin–Ciocalteu reagent, as described in Cumplido-Nájera et al. [34]. The sample (0.2 g) was extracted with 1 mL of a water:acetone solution (1:1). The mixture was vortexed for 30 s. The tubes were centrifuged (UNICO Spectrophotometer Model UV2150, NJ, USA) at 17,500× *g* for 10 min at 4 °C. In a test tube, 50 µL of the supernatant, 200 µL of the Folin–Ciocalteu reagent, 500 µL of 20% sodium carbonate (Na_2CO_3), and 5 mL of distilled water were added, and the mixture was then vortexed for 30 s. The samples were placed in a water bath at

45 °C for 30 min. Finally, the reading was taken at an absorbance of 750 nm using a plastic cell in a UV–Vis spectrophotometer (UNICO Spectrophotometer Model UV2150, Dayton, NJ, USA).

The antioxidant activity by ABTS was determined using the spectrophotometric method of Re et al. [35], which is based on the discoloration of the ABTS radical cation. This radical was obtained from the reaction of ABTS at 7 mM with potassium persulfate at 2.45 mM (1:1) in the dark at 26 °C for 16 h and then diluted with 20% ethanol to obtain an absorbance of 0.7 ± 0.01 at 750 nm. Afterwards, to determine antioxidant capacity in the hydrophilic compounds, phosphate buffer, 5 μL of extract, and 245 μL of the ABTS radical dilution (7 mM) were placed in a microplate, stirred for 5 s and then allowed to stand for 7 min in darkness. The absorbance was measured by a microplate reader (Allsheng, AMR-100 model, Hangzhou, China) at a wavelength of 750 nm. The blank was prepared with 250 μL of phosphate buffer (pH 7.0–7.2, 0.1 M). For the determination of the same in lipophilic compounds, extraction was carried out with a hexane:acetone solution. The results were expressed as vitamin C equivalents in mg per gram of dry weight (mg g^{-1} DW).

Hydrogen peroxide (μmol g^{-1} DW) levels were determined according to Velikova et al. [36] with slight modifications; 25 mg of lyophilized fruit tissue was weighed and placed in an Eppendorf tube, and 1 mL of cold 0.1% trichloroacetic acid was then added. The mixture was then centrifuged at 12,000× *g* for 15 min and 0.5 mL of the supernatant was taken; 0.5 mL of 10 mM potassium phosphate buffer (pH 7.0) and 1 mL of 1 M potassium iodide was added, and the reading was performed in a UV–Vis spectrophotometer (UNICO Spectrophotometer Model UV2150, Dayton, NJ, USA) at 390 nm. The H_2O_2 content was measured using a standard curve.

2.4. Arsenic Determination

To quantify the arsenic content in the organs of the plant (Root, stem, leaf and fruit), two methods were performed. The method for X-ray fluorescence with miniaturized tubes (ThermoScientific Niton XLt3, Boston, MA, USA) was used in all organs of the plant. The detection capacity of the equipment is 2 μg g^{-1}. Analyses were performed in triplicate. The second method was used only in fruit—for this, acid digestion was performed with HNO_3:H_2O_2. Subsequently, the samples were analyzed by inductively coupled plasma optical emission spectrophotometry ICP-OES (Varian Agilent 730-ES, Santa Clara, CA, USA). The arsenic detection capacity by the equipment is 1 μg L^{-1}.

2.5. Statistical Analysis

Six repetitions per treatment were analyzed, considering a fruit as an experimental unit. An analysis of variance (two-way ANOVA) was performed considering a completely randomized experimental design, and Fisher's Least Significant Difference test was applied to compare the means ($p \leq 0.05$). Additionally, Pearson's correlation analysis was performed. The whole process was carried out using Infostat software (2018v). (https://www.infostat.com.ar).

3. Results

3.1. Arsenic Determination

The X-ray fluorescence analysis showed the accumulation of arsenic only in the root, stem and leaves of tomato plants; however, in fruits, it was not detected by either of the two methods used (Figure 1). Therefore, it is possible that the arsenic has not been translocated to the fruits, or that it has been translocated in negligible amounts.

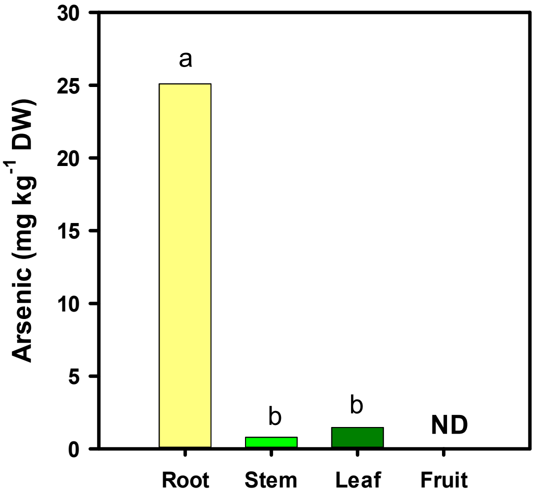

Figure 1. Arsenic concentration in different organs of the tomato plant. Different letters above the bars indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$). ND: not detected.

3.2. Fruit Quality

The quality of tomato fruits exposed to As and SiO_2 NPs showed significant differences (Table 1). The firmness increased by 34.34% in the treatment with 1.6 mg L^{-1} of As and 250 mg L^{-1} of SiO_2 NPs with respect to the control, although they were not statistically different. Regarding total soluble solids, there was a slight increase of 5.76% compared to the control with the treatment of 250 mg L^{-1} of SiO_2 NPs, and also with 0.4 mg L^{-1} of As in the interaction with 1000 mg L^{-1} of SiO_2 NPs. However, none of the treatments were statistically different. On the other hand, the pH decreased according to the exposure of As and SiO_2 NPs alone and when they interacted, the control had the highest pH.

A tendency to increase the EC was observed at high doses of As, and in the interaction with the NPs, the treatment with 3.2 As and 250 SiO_2 NPs mg L^{-1} resulted in an increase of 13.8%, while the low dose of As (0.2 mg L^{-1}) showed a decrease (−4.07%) compared to the control, although they were not statistically different. Regarding the ORP, a decreasing tendency was observed as arsenic and SiO_2 NPs were applied; the dose of 3.2 mg L^{-1} of As decreased the ORP by 72.25%.

Table 1. Quality of tomato fruits with applications of SiO_2 nanoparticles (NPs) and stressed by arsenic.

As	SiO_2 NPs	Firmness	TSS	pH	EC	ORP
(mg L^{-1})		(kg cm^{-1})	(°Brix)		(mS cm^{-1})	(mV)
0	0	4.60 ± 0.26 ^{ab}	5.20 ± 0.28 ^{ab}	4.75 ± 0.04 ^{a}	3.98 ± 0.27 $^{a–d}$	54.83 ± 1.25 ^{b}
	250	4.21 ± 0.85 ^{b}	5.50 ± 0.34 ^{a}	4.57 ± 0.02 ^{bcd}	3.81 ± 0.15 ^{bcd}	61.00 ± 1.79 ^{a}
	1000	4.85 ± 0.46 ^{ab}	5.33 ± 0.33 ^{ab}	4.51 ± 0.02 ^{def}	4.17 ± 0.16 ^{abc}	51.50 ± 1.15 ^{bc}
0.2	0	5.88 ± 0.56 ^{ab}	5.25 ± 0.17 ^{ab}	4.53 ± 0.02 $^{b–f}$	3.42 ± 0.47 ^{d}	50.17 ± 2.09 ^{c}
	250	4.35 ± 0.70 ^{b}	5.17 ± 0.17 ^{ab}	4.52 ± 0.03 $^{b–f}$	3.98 ± 0.24 $^{a–d}$	50.00 ± 1.69 ^{cd}
	1000	5.88 ± 0.47 ^{ab}	5.33 ± 0.21 ^{ab}	4.51 ± 0.02 $^{c–f}$	4.30 ± 0.28 ^{ab}	51.00 ± 0.89 ^{bc}
0.4	0	4.97 ± 1.01 ^{ab}	5.28 ± 0.16 ^{ab}	4.58 ± 0.02 ^{b}	3.51 ± 0.29 ^{cd}	41.00 ± 1.32 ^{e}
	250	5.45 ± 0.89 ^{ab}	5.05 ± 0.03 ^{ab}	4.52 ± 0.02 $^{b–f}$	4.19 ± 0.25 ^{abc}	45.67 ± 0.92 ^{d}
	1000	5.48 ± 0.24 ^{ab}	5.50 ± 0.18 ^{a}	4.51 ± 0.02 ^{def}	3.87 ± 0.48 $^{a–d}$	40.17 ± 1.01 ^{e}
0.8	0	5.27 ± 0.71 ^{ab}	5.37 ± 0.20 ^{ab}	4.47 ± 0.02 ^{f}	4.22 ± 0.11 ^{ab}	38.17 ± 1.96 ^{efg}
	250	5.73 ± 0.57 ^{ab}	5.23 ± 0.09 ^{ab}	4.54 ± 0.02 $^{b–e}$	4.50 ± 0.14 ^{ab}	38.83 ± 0.48 ^{ef}
	1000	5.25 ± 0.54 ^{ab}	5.17 ± 0.29 ^{ab}	4.51 ± 0.01 $^{c–f}$	4.41 ± 0.18 ^{ab}	39.83 ± 1.82 ^{e}
1.6	0	5.31 ± 0.92 ^{ab}	5.42 ± 0.20 ^{ab}	4.52 ± 0.02 $^{c–f}$	4.25 ± 0.10 ^{ab}	36.67 ± 1.87 ^{efg}
	250	6.18 ± 0.39 ^{a}	4.83 ± 0.17 ^{b}	4.55 ± 0.02 $^{b–e}$	4.15 ± 0.13 ^{abc}	37.17 ± 1.19 ^{efg}

	1000	4.78 ± 0.56 ^{ab}	5.33 ± 0.36 ^{ab}	4.55 ± 0.01 $^{b–e}$	4.00 ± 0.36 $^{a–d}$	35.00 ± 2.35 ^{fgh}
3.2	0	4.86 ± 0.57 ^{ab}	5.42 ± 0.20 ^{ab}	4.50 ± 0.04 ^{ef}	4.14 ± 0.12 ^{abc}	31.83 ± 2.15 ^{h}
	250	5.73 ± 0.77 ^{ab}	5.37 ± 0.20 ^{ab}	4.54 ± 0.02 $^{b–e}$	4.53 ± 0.11 ^{a}	36.83 ± 1.47 ^{efg}
	1000	5.72 ± 0.46 ^{ab}	5.03 ± 0.03 ^{ab}	4.58 ± 0.02 ^{bc}	4.15 ± 0.25 ^{abc}	34.17 ± 1.72 ^{gh}
CV (%)		30.05	10.30	1.29	14.92	9.04

As: Arsenic; TSS: Total soluble solids; pH: Hydrogen potential; EC: Electric conductivity; ORP: oxidation reduction potential. Different letters within a column indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$).

3.3. Proteins

Total proteins decreased due to the interaction of the highest dose of As and SiO_2 NPs, reaching up to 31.16% and 22.09% with 3.2–250 or 1000 mg L^{-1} of As and Si NPs, respectively, although the value also decreased by 16.15% with 0.8 and 250 mg L^{-1} of As and SiO_2 NPs. The rest of the treatments were not statistically different from the control (Figure 2).

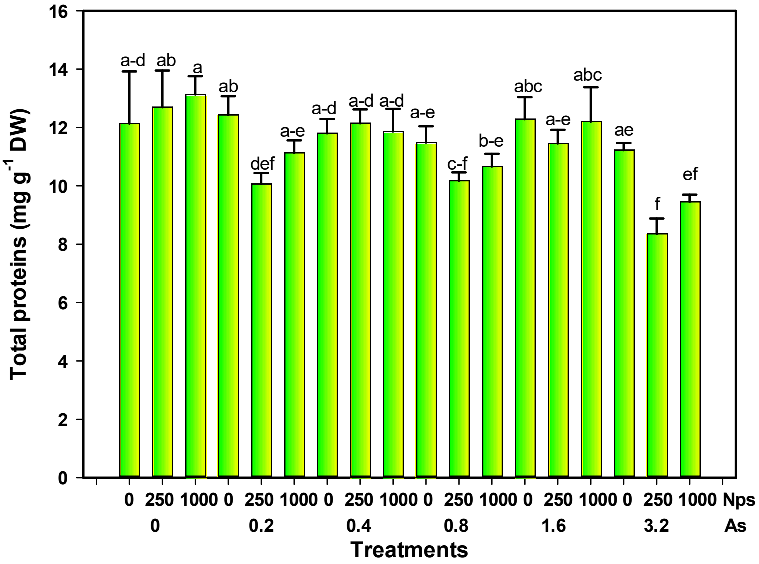

Figure 2. Total proteins in tomato fruits exposed to different doses of arsenic and nanoparticles. Different letters above the bars indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$). NPs: Dose applied of SiO_2 NPs (mg L^{-1}); As: Dose applied of arsenic (mg L^{-1}).

3.4. Antioxidant Compounds

The lycopene content in tomato fruits increased by 34% at the lowest dose of As (0.2 mg L^{-1}). As–SiO_2 NP interactions at 3.2–1000 mg L^{-1} increased lycopene by 40.82%. SiO_2 NPs at 250 mg L^{-1} reduced the lycopene content by 51.30%, and 0.2 and 1000 mg L^{-1} of As–SiO_2 NPs decreased it by 51.88% (Figure 3A).

Regarding the content of β-carotene, there was an increase with exposure to doses of 0.2, 0.8, and 3.2 mg L^{-1} of As without application of SiO_2 NPs (29, 49, and 18%, respectively). An amount of 250 mg L^{-1} of SiO_2 NPs decreased the content by 24%, although it was not statistically different from the control. The interaction between 3.2 and 250 mg L^{-1} As–SiO_2 NPs decreased the β-carotene content by 40%. However, the dose of 1000 mg L^{-1} of SiO_2 NPs without As increased the content of β-carotene by 13% (Figure 3B).

Glutathione increased with the application of 250 mg L^{-1} of SiO_2 NPs (35.48%); however, this dose in combination with 0.2 and 0.8 mg L^{-1} of As decreased glutathione by 32.26% and 35.49%, respectively. The application of 0.8 mg L^{-1} of As decreased glutathione by 45.15%. When the plants were exposed to the two high doses of As and with the interaction with SiO_2 NPs, there was a significant increase in glutathione with respect to the control. However, the greatest increase (45.16%) was in response to 3.2 mg L^{-1} of As without NPs, and 41.13% with 1.6–250 mg L^{-1} of As–SiO_2 NPs (Figure 4A).

Regarding the vitamin C content, there was a 31.09% decrease when 250 mg L^{-1} of SiO_2 NPs was applied. In addition, the three highest doses of As (0.8, 1.6, and 3.2 mg L^{-1}) alone and in combination with the SiO_2 NPs decreased the vitamin C content. The treatment of 0.8–250 mg L^{-1} of As–SiO_2 NPs showed a 45.22% reduction in vitamin C, while treatments consisting of 1.6 and 3.2 mg L^{-1} of As in combination with 1000 mg L^{-1} of SiO_2 NPs resulted in decreases of 42.02% and 36.04%, respectively. Although the doses of 0.2 and 0.4 mg L^{-1} of As alone showed a slight increase in this compound (8.12% and 9.54%, respectively), they were not statistically different from the control (Figure 4B).

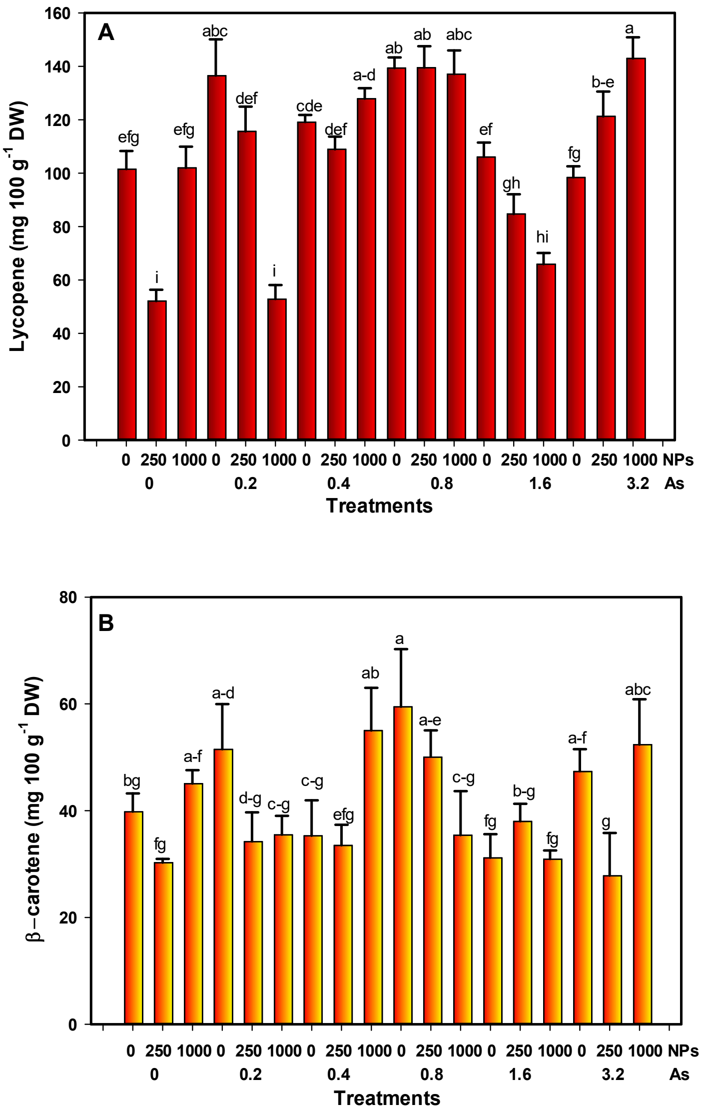

Figure 3. (**A**) Lycopene and (**B**) β-carotene content in fruits under stress conditions. Different letters above the bars indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$). NPs: Dose applied of SiO_2 NPs (mg L^{-1}); As: Dose applied of arsenic (mg L^{-1}).

Phenols decreased with low doses of As alone, as well as in combination with SiO_2 NPs. The treatments with the greatest decrease in phenols were 0.2 mg L^{-1} of As (25.82%), as well as 0.2 and 0.4 mg L^{-1} in combination with 1000 mg L^{-1} of SiO_2 NPs (21.35% and 21.16%, respectively). Regarding the effect of the SiO_2 NPs, the dose of 250 mg L^{-1} showed a slight increase (4.85%); however, it was statistically the same as the control. In contrast, 1000 mg L^{-1} of SiO_2 NPs decreased the phenol content by 21.74% (Figure 4C).

Flavonoids increased upon exposure to As and SiO_2 NPs, although treatments with 1000 mg L^{-1} of SiO_2 NPs alone, as well as 0.2 and 0.4 mg L^{-1} of As in combination with 250 mg L^{-1} SiO_2 NPs were statistically the same as the control The greatest increase in flavonoids was with 0.8 mg L^{-1} of As alone, and in combination with 250 mg L^{-1} of SiO_2 NPs—up to 79.26% and 82.42%, respectively (Figure 4D).

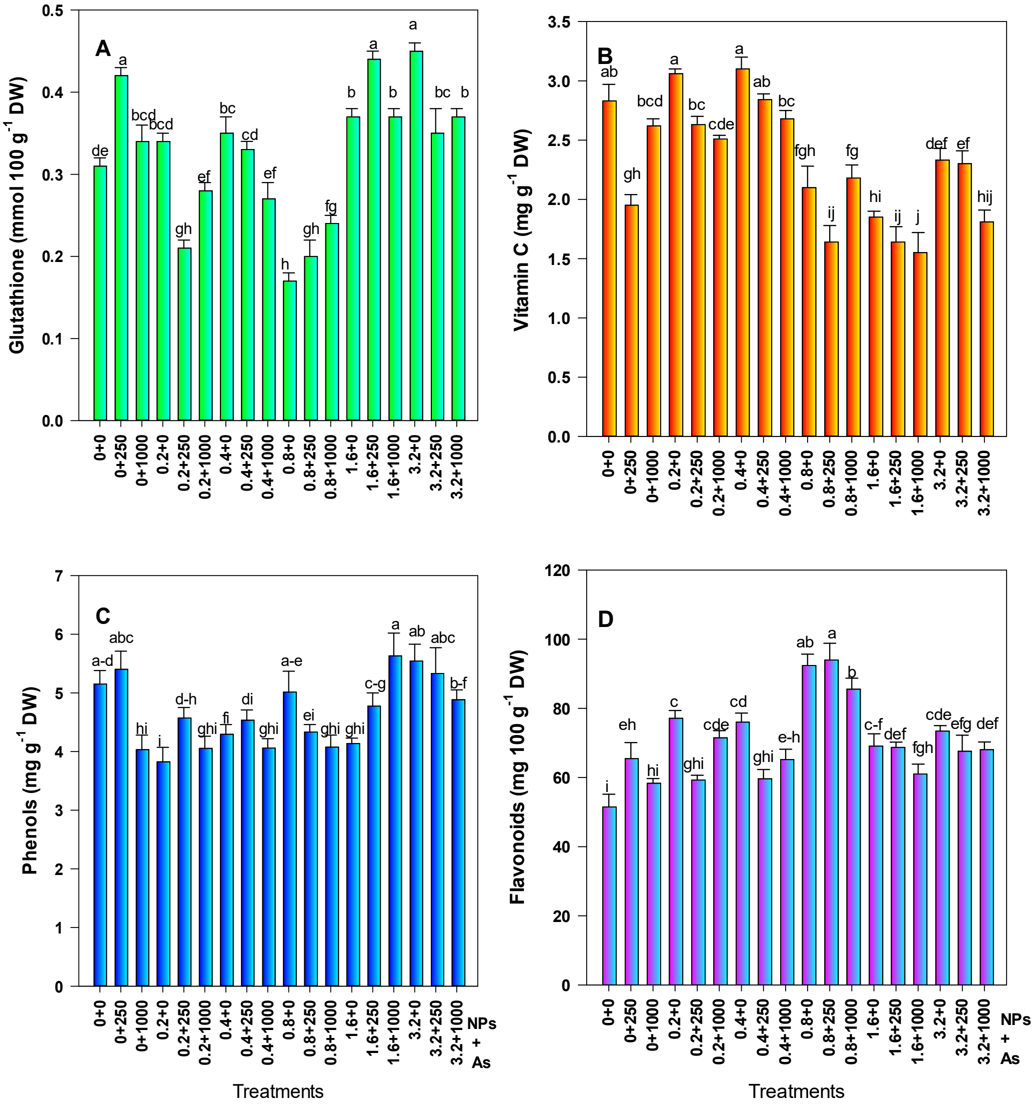

Figure 4. Non-enzymatic antioxidant compounds in tomato fruits. (**A**) Glutathione, (**B**) Vitamin C, (**C**) Phenols, and (**D**) Flavonoids. Different letters above the bars indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$). NPs: Dose applied of SiO_2 NPs (mg L^{-1}); As: Dose applied of arsenic (mg L^{-1}).

3.5. Antioxidant Capacity

The antioxidant capacity determined in tomato fruits showed significant differences between treatments (Figure 5). With respect to hydrophilic compounds, 3.2–1000 and 1.6–250 mg L^{-1} of As–SiO_2 NPs showed an increase of 35.14% and 20.54%, respectively. However, the antioxidant capacity decreased with 0.2–250 mg L^{-1} As–SiO_2 NPs—by up to 34.4%. On the other hand, lipophilic compounds showed a similar trend to hydrophilic compounds; the highest dose of As (3.2 mg L^{-1}) in combination with 250 and 1000 mg L^{-1} of SiO_2 NPs being the treatments that presented respective increases of up to 104.24% and 121.20% in terms of antioxidant capacity.

Regarding the total antioxidant capacity, the highest dose of arsenic in combination with both doses of SiO_2 NPs had the highest values, being 79.59% and 99.17% higher than the control, respectively.

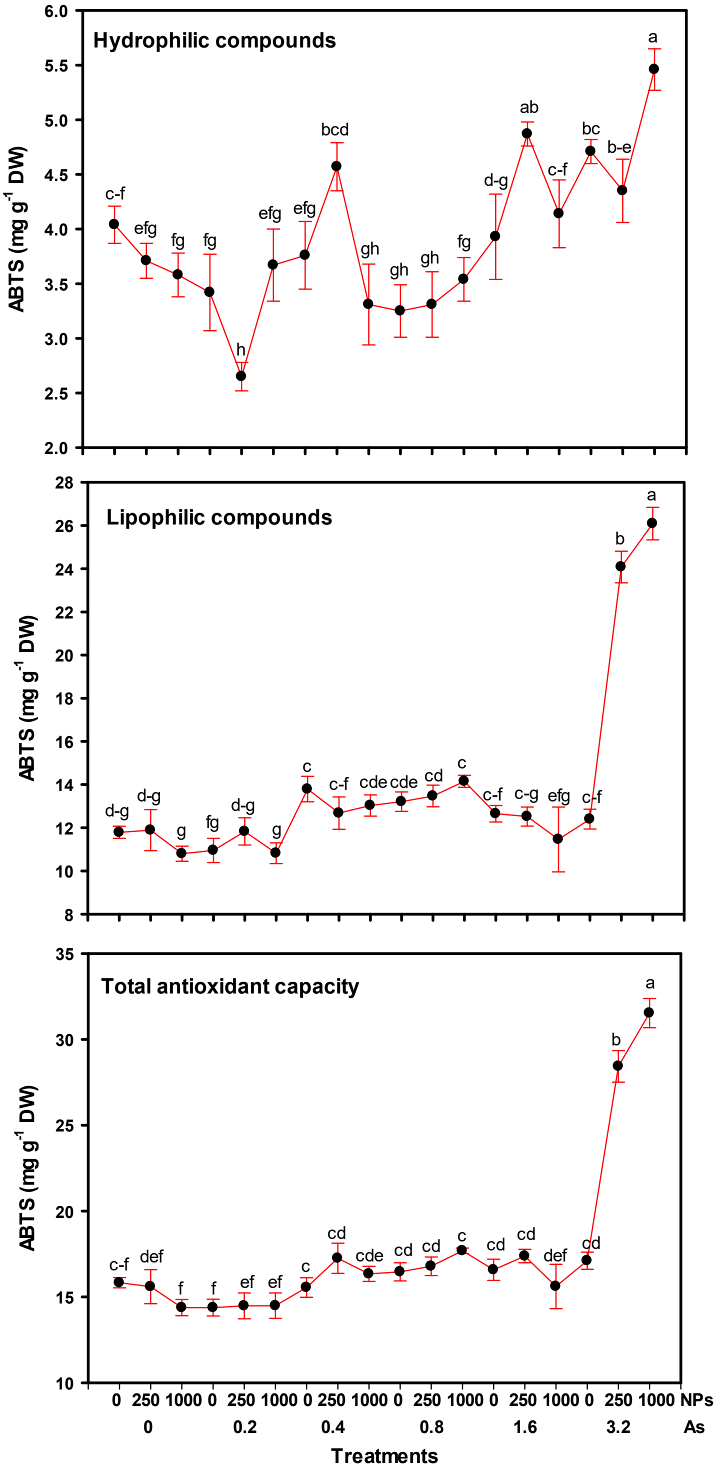

Figure 5. Antioxidant capacity of tomato fruits with applications of SiO_2 NPs and stressed by arsenic. Different letters indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$). NPs: Dose applied of SiO_2 NPs (mg L^{-1}); As: Dose applied of arsenic (mg L^{-1}).

3.6. Hydrogen Peroxide Content

The H_2O_2 level increased by 46.15% with 250 mg L^{-1} of SiO_2 NPs; however, it decreased by 17.05% with 1000 mg L^{-1} of SiO_2 NPs compared with the control. On the other hand, 0.8 mg L^{-1} of arsenic alone increased the H_2O_2 level by 31.31%. Moreover, the interaction of 0.2 mg L^{-1} of As with 250 and 1000 mg L^{-1} of SiO_2 NPs showed a slight increase of 15.93% and 26.92%, respectively (Figure 6).

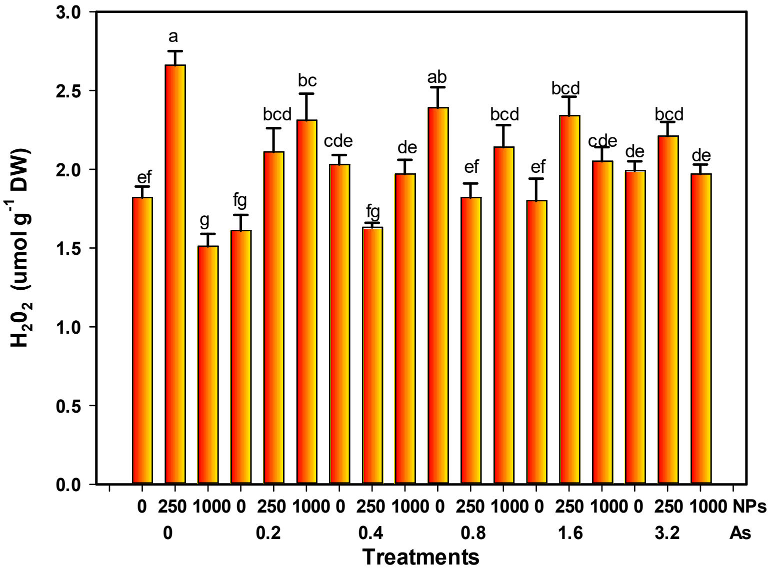

Figure 6. H_2O_2 content of tomato fruits with application of SiO_2 NPs and stressed by arsenic. Different letters above the columns indicate significant differences according to Fisher's Least Significant Difference test ($p \leq 0.05$). NPs: Dose applied of SiO_2 NPs (mg L^{-1}); As: Dose applied of arsenic (mg L^{-1}).

Regarding the correlation between the different compounds evaluated, the results of the Pearson test showed high correlations between some variables, and only the SiO_2 NPs did not show a correlation with any variable (Table 2). A positive correlation of As was observed with the antioxidant capacity of hydrophilic, lipophilic, total, and glutathione compounds (r = 0.53, 0.67, 0.71, and 0.41 ($p \leq 0.01$), respectively); however, As had a negative correlation with proteins, vitamin C and ORP (r = −0.35 ($p \leq 0.05$), −0.42, and −0.71 ($p \leq 0.01$)). This suggests that arsenic is the treatment that most strongly influences the antioxidant content of the tomato fruits.

It was observed that the total antioxidant capacity had a highly positive correlation with the antioxidant capacity of lipophilic compounds (r = 0.99, $p \leq 0.01$), while it was negatively correlated with proteins (r = −0.41, $p \leq 0.01$) and ORP (r = −0.40, $p \leq 0.01$).

Lycopene showed a positive correlation with the antioxidant capacity of lipophilic compounds (r = 0.33, $p \leq 0.05$) and with the content of flavonoids (r = 0.39, $p \leq 0.01$), while glutathione was positively correlated with the antioxidant capacity of hydrophilic compounds (r = 0.52, $p \leq 0.01$). Likewise, it was observed that there was a negative correlation between lycopene and glutathione (r = −0.37, $p \leq 0.05$).

Finally, the ORP had a negative correlation with the antioxidant capacity of hydrophilic compounds (r = −0.27, $p \leq 0.05$), the antioxidant capacity of lipophilic compounds (r = −0.38, $p \leq 0.01$), the total antioxidant capacity (r = −0.40, $p \leq 0.01$), lycopene (r = −0.28, $p \leq 0.05$), and flavonoids (r = −0.33, $p \leq 0.05$); in contrast, it presented a positive correlation with proteins (r = 0.22, $p \leq 0.05$) and vitamin C (r = 0.38, $p \leq 0.01$).

Table 2. Pearson correlations between As, SiO_2 NPs, antioxidant capacity, H_2O_2, antioxidant compounds, proteins and ORP.

	ABTS H	**ABTS L**	**TAC ABTS**	**H_2O_2**	**Lycopene**	**B-Carotene**	**Proteins**	**Vitamin C**	**Glutathione**	**Phenols**	**Flavonoids**	**ORP**
As	0.53 **	0.67 **	0.71 **	0.08 NS	0.14 NS	−0.02 NS	−0.35 *	−0.42 **	0.41 **	0.35 *	0.08 NS	−0.71 **
SiO_2 NPs	0.04 NS	0.14 NS	0.14 NS	−0.04 NS	−0.12 NS	0.02 NS	−0.04 NS	−0.18 NS	−0.11 NS	−0.14NS	−0.13 NS	−0.05
ABTS H		0.37 *	0.53 **	0.04 NS	−0.08 NS	0.01 NS	0.10 NS	−0.19 NS	0.52 **	0.33 *	−0.1 NS	−0.27 *
ABTS L			0.99 **	0.10 NS	0.33 *	−0.03 NS	−0.46 **	−0.22 *	0.07 NS	0.16 NS	0.04 NS	−0.38 **
TAC ABTS				0.10 NS	0.29 *	−0.02 NS	−0.41 **	−0.24 *	0.16 NS	0.20 *	0.02 NS	−0.40 **
H_2O_2					−0.22 *	−0.15 NS	−0.04 NS	−0.21 *	0.05 NS	0.31 *	0.19 NS	0.02 NS
Lycopene						0.19 NS	−0.19 NS	0.17 NS	−0.37 *	0.16 NS	0.39 **	−0.28 *
β–carotene							0.05 NS	−0.03 NS	−0.19 NS	0.01 NS	0.22 *	−0.10 NS
Proteins								0.11 NS	0.18 NS	−0.06 NS	−0.04 NS	0.22 *
Vitamin C									−0.09 NS	−0.22 *	0.17 NS	0.38 **
GSH										0.25 *	−0.28 *	0.11 NS
Phenols											−0.07 NS	−0.12 NS
Flavonoids												−0.33 *
	🟨	Significant Correlation			⬜	No significance						

*, ** Significant correlation at the $p \leq 0.05$ and ≤ 0.01 levels, respectively. NS: no significance. ABTS H, Antioxidant capacity determined in hydrophilic compounds by 2,2′-azino-bis[3-ethylbenzthiazolin-6-sulfonic acid], radical, ABTS L, Antioxidant capacity determined in lipophilic compounds by 2,2′-azino-bis[3-ethylbenzthiazolin-6-sulfonic acid]), radical, As: arsenic, SiO_2 NPs: nanoparticles, H_2O_2: hydrogen peroxide, and ORP: oxidation reduction potential.

4. Discussion

Considering the quality and safety of food products, the determination of toxic elements such as arsenic is important, since food contaminated with this element can cause health risks [37]. In the present study, arsenic was not detected in tomato fruits that were exposed to different concentrations of this element. This is because arsenic accumulates mainly in the root, while only a small portion is translocated to shoots with even smaller quantities to fruits [38]. Several studies have shown the presence of arsenic in fruits at very low concentrations [13,39,40], and so the risk for human consumption is very low.The quality of fruits is indispensable for the market, particularly since fleshy fruits are perishable, and their quality is affected by different types of both abiotic and biotic stresses [41]. The observed effects are different depending on the variety, the phenological stage, the duration of stress, as well as the interaction with other environmental conditions [42]. The quality of the fruit is greatly modified during the ripening process in its different stages, affecting both the taste quality and the nutritional quality [43]. The initial decision to buy fruits and vegetables is usually made based on appearance and firmness [44]. In this sense, the firmness of the fruits increased consistently with the application of SiO_2 NPs, coinciding with reports of other authors [45,46]. This is because silicon can accumulate in the epidermis, making it more rigid [47].

The application of SiO_2 NPs decreased the pH of tomato fruits, which coincides with what was observed in jalapeño pepper with the application of Cu NPs + Cs–PVA [48]. The pH of the fruits directly influences the quality, in addition to the fact that consumers prefer less acidic fruits because they have a better flavor [49]. As for TSS and EC, in some studies, there was a decrease or increase in these parameters, depending on the type of treatment or the conditions to which the fruits were exposed [50,51].

The decrease in ORP observed in the As–SiO_2 NPs interaction indicates a better fruit quality, since it can translate into a higher antioxidant potential [52], as observed in the correlations in this work. This trend has been reported by other authors who have worked with the application of NPs in tomato [28] and observed a decrease in ORP of 5.7% with the application of 250 mg L^{-1} of Cu NPs.

Proteins play an important role in regulating the development and quality of fruit [53]. Most of the regulatory proteins related to ripening in tomatoes have been functionally associated with the climacteric induction of ethylene biosynthesis [54]. Within all proteins, there are metallothioneins, which are proteins that respond to heavy metal stress [55]. Thiol groups in metallothioneins can act as powerful antioxidants, so they can play a role in protecting against oxidative damage [56]. However, when heavy metal concentrations are high, there is a higher generation of ROS, and therefore, greater oxidative stress [57], which can consequently decrease protein production. On the other hand, nanoparticles have been implicated in the increase in proteins in cucumber fruits [58]. However, they do not always have that effect, since it depends on the type of NPs and the dose used.

From the visual perspective, the quality of the fruit is directly related to the amount of carotenoids, mainly lycopene and β-carotene, that accumulate in ripe tomato fruits [59]. In addition, the consumption of carotenoids has beneficial effects on human health, since this can reduce the risk of certain forms of cancer, cardiovascular diseases, macular degeneration, among others [60]. In tomato fruits, ripening involves various morphological, physiological, biochemical, and molecular changes, including the degradation of chlorophyll as well as the synthesis and storage of carotenoids (mainly lycopene) during the transition from the chloroplast to the chromoplast [61]. Another important carotenoid is β-carotene, which is the main precursor of vitamin A; as opposed to β-carotene, lycopene has no pro-vitamin A activity but is a good antioxidant [62]. Lycopene is a powerful antioxidant and has a protective role against cancer [63]. In tomato fruits, the amount of lycopene can vary depending on the species, the stage of maturity, and the environmental conditions under which the fruit ripens [64]. The carotenoids in ripe fruit appear to play an important role in the detoxification of ROS, in particular to relieve the symptoms of stress induced by arsenic exposure [15], which is consistent with the results observed in this work.

Reduced glutathione (γ-glutamyl-cysteinyl glycine, GSH) participates in functional activities in many plants [65]. GSH has unique redox and nucleophilic properties and is involved in the cellular defense against the toxic actions of xenobiotics, oxiradicals, salinity, acidity, and metal cations [66]. Specifically under conditions of metal stress, GSH is a non-enzymatic antioxidant that plays a central role in homeostasis and acts as a precursor to a metal-binding peptide [67]. Therefore, a high concentration of GSH in cells acts as a buffer system against redox imbalance [68]. On the other hand, silicon can counteract the negative impact of oxidative stress by restricting the production of ROS caused by arsenic, in addition to improving the action of various antioxidant compounds and regulating the osmotic potential of the cell [69].

Vitamin C has a main function as an antioxidant and cofactor in redox reactions, in addition to being involved in the activation of epigenetic mechanisms that control cell differentiation [70]. However, vitamin C is highly unstable, and its levels may vary if subjected to stress factors [71]. Additionally, the antioxidants in the fruit can be affected by the intensity of light, temperature, and internal factors such as variety of cultivation, load, and position of the fruit [72]. For human health, sufficient absorption and distribution of vitamin C throughout the body are essential for many biochemical processes, including some that are vital to the growth and spread of tumors [73].

Phenols are antioxidant compounds that trigger the synthesis of a series of secondary metabolites from the shikimic acid pathway or through phenylpropanoids under conditions of abiotic stress [74]. The antioxidant capacity of phenolic compounds is also attributed to their ability to chelate metal ions involved in the production of free radicals [75]. Phenolic compounds can act as antioxidants, since hydroxyl groups donate hydrogen and can react with reactive oxygen species in a termination reaction, which breaks the cycle of generating new radicals [76].

It is known that silicon promotes the production of phenolic compounds that have an antioxidant or structural role. In addition, it can improve toxicity to heavy metals such as aluminum [77].

Flavonoids are among the most abundant phytochemicals in fruits and vegetables and have cancer cell anti-proliferative, antioxidant, anti-inflammatory, and estrogenic activities [78]. Flavonoids have anticancer activity in cellular and preclinical animal models, which makes them potential candidates in cancer prevention and treatment [79]. This is due to their antioxidants, which regulate the homeostasis of ROS [80].Antioxidant capacity represents the ability to inhibit the oxidation process. It is a very desirable property of food since it plays an important role in various diseases [81]. There are different methods to evaluate the antioxidant capacity of a food; the two most commonly used tests are ABTS (2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) and DPPH (2,2-diphenyl-1-picrylhydrazyl) [82]. The ABTS test can react with a wider range of antioxidant compounds [83]. Since the ABTS test is based on the generation of blue/green $ABTS^{\bullet+}$, which is applicable to both hydrophilic and lipophilic antioxidant systems, this method is better for the evaluation of the antioxidant capacity of highly pigmented and hydrophilic compounds compared to DPPH [84]. However, the antioxidant capacity of fruits to inhibit ABTS or DPPH also depends on the type of treatment to which they have been exposed [85].

ROS include free radicals, such as O^{2-} and OH, and non-radicals, such as H_2O_2 and $^1O_2$, which induce oxidative damage in cells [86]. The increase in the H_2O_2 content is a typical plant response to arsenic exposure [87], so much so that when arsenic exposure increases, H_2O_2 levels also increase, being strongly time dependent [15]. One of the most prominent and earliest defense responses is the oxidative burst, generated by ROS, which includes H_2O_2 [88]. In addition to this, fruit ripening is an oxidative phenomenon that raises the level of ROS, a process that is genetically programmed [89].

Thus, the changes in the ROS of tomato fruits can be modified both by environmental and arsenic stress, as well as by the natural ripening process.

5. Conclusions

The results obtained in this research study highlight the importance of the stressful effect that arsenic can have on tomato fruit and how it modifies the antioxidant compounds. Low doses of As (0.2 mg L^{-1}) in irrigation water induce a greater accumulation of antioxidant compounds; however, when exposed to high doses or when they interact with SiO_2 NPs, there appears to be greater stress and oxidative damage that inhibit these compounds. On the other hand, 250 mg L^{-1} of SiO_2 NPs increased glutathione. Flavonoids are the only group of antioxidants that are increased by As and SiO_2 NPs. Total antioxidant capacity shows an increase with the highest dose of As in combination with SiO_2 NPs. Our research shows that As, a highly toxic metalloid, and the SiO_2 NPs, modified the processes of generating antioxidant compounds in ripe tomato fruit, usually with an increasing trend.

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SEGUNDO ARTÍCULO

Silicon Nanoparticles Reduce Arsenic Translocation and Mitigate Phytotoxicity in Tomato Plants

Original submission

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SILICON NANOPARTICLES DECREASE ARSENIC TRANSLOCATION AND MITIGATE PHYTOTOXICITY IN TOMATO PLANTS

Magín González-Moscoso[a], Antonio Juárez-Maldonado[b], Gregorio Cadenas-Pliego[c], Diana Meza-Figueroa[d], Bhaskar SenGupta[e], Nadia Martínez-Villegas[f,*].

*Corresponding autor
Nadia Martínez-Villegas
IPICyT, Instituto Potosino de Investigación Científica y Tecnológica
Camino a la Presa San Jose No. 2055
Col. Lomas 4a Sec., 78216 San Luis Potosi, SLP, Mexico.
E-mail addresses: nadia.martinez@ipicyt.edu.mx, amelieybonita@gmail.com.

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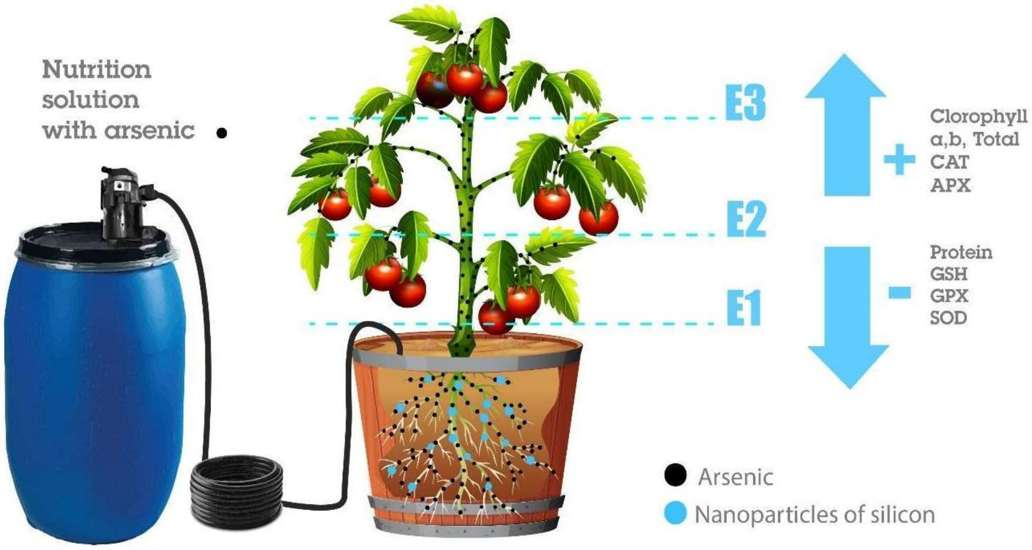
[a]Doctorado en Agricultura Protegida, Universidad Autónoma Agraria Antonio Narro, Calzada Antonio Narro 1923, Buenavista, 25315, Saltillo, Coahuila, México.
[b]Departamento de Botánica, Universidad Autónoma Agraria Antonio Narro, Calzada Antonio Narro 1923, 25315, Saltillo, Coahuila, México.
[c]Centro de Investigación en Química Aplicada, Enrique Reyna H 140, 25294 Saltillo, Coahuila, México. [d]Departamento de Geología, Universidad de Sonora, Blvd. Luis Encinas J, Calle Av. Rosales &, Centro, 83000 Hermosillo, Sonora, México.
[e]School of Energy, Geoscience, Infraestructure & Society, Heriot-Watt University, Water Academy, EGIS 2.02A William Arrol Building, EH14 4AS Scotland, United Kingdom.
[f]IPICyT, Instituto Potosino de Investigación Científica y Tecnológica, Camino a la Presa San José No. 2055, Col. Lomas 4a Sec., 78216 San Luis Potosí, SLP, México.

ABSTRACT

In this study we simulate the irrigation of tomato plants with As contaminated water (from 0 to 3.2 mg L^{-1}) and investigate the effect of the application of silicon dioxide nanoparticle (SiO_2 NPs; 0, 250 and 1000 mg L^{-1}) on As uptake and stress. As concentrations are determined in substrate and plant tissue at three different stratums. Phytotoxicity, As accumulation and translocation, photosynthetic pigments and antioxidant activity of enzymatic and non-enzymatic compounds are also determined. Irrigation of tomato plants with As contaminated water causes As substrate enrichment and As bioaccumulation (roots>leaves>steam) showing that the higher the concentration in irrigation water, the farther the contaminant flows and translocates through the different tomato stratums. Phytotoxicity is observed at low concentrations of As while tomato yield increases at high concentrations. Application of SiO_2 NPs decreases As translocation, tomato yield, and root biomass. Increased production of photosynthetic pigments and improved enzymatic activity (CAT and APX) suggest tomato plant adaptation at high As concentrations in the presence of SiO_2 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.

Keywords: nanotechnology, trace elements, bioaccumulation, antioxidant defense system, oxidative stress.

GRAPHICAL ABSTRACT



HIGHLIGHTS

- Relatively low concentrations of As in irrigation water cause As bioaccumulation and toxicity.
- High concentrations of As in irrigation water induce adaptation of tomato plants.
- Silicon nanoparticles decrease As translocation.
- Tomato plants increase photosynthetic, CAT, and APX activity under As stress and silicon nanoparticle application.

1. Introduction

Arsenic (As) is considered one of the most toxic elements in the environment [1]. Irrigating of agricultural soils with As contaminated water causes As soil enrichment as well as As bioaccumulation and toxicity [2]. As a result, it can enter the food chain and represent a risk to human health [3].

Reduced CO_2 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 [4,5]. Arsenic also induces reactive oxygen species (ROS) production that lead to lipid peroxidation and can result in plant death [6]. To counteract ROS stress, plants activate their antioxidant defense system in order to protect their cellular system from harmful effects [7].

Most crops, including tomato (*Solanum lycopersicum* L.), are sensitive to As stress exhibiting reduced seed germination, reduced growth, and even modified molecular responses [8–10]. Due to its high level of consumption (160 million tons per year^{-1} in 2013) [11], tomato is economically one of the most important vegetables in the world [12]. 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 [13]. In the case of Mexico, the highest concentrations of As appear in alluvial aquifers in arid and semi-arid areas in northern Mexico [14], where greenhouse tomato production is commonly practiced and irrigation with As contaminated water could occur.

The use of Silicon nanoparticles (SiO_2 NPs) could be a useful technology to prevent As toxicity and uptake by tomato crops. Studies show that SiO_2 NPs prevented Cr accumulation in pea seedlings [15], increased chlorophyll and carotenoid content as well as plant growth in *Pleioblastus pygmaeus* in the presence of Pb [16], improved the components of the glutathione cycle (antioxidant system non-enzymatic) in *Zea mays* plants in the presence of arsenic [17], and increased antioxidant enzymatic activity in *Triticum aestivum* L. plants in the presence of Cd [18]. Therefore, while irrigation of tomato crops with As contaminated water might increase the concentrations of As in soil and plant tissue, SiO_2 NPs might help to avoid As translocation and to boost the plant's biochemical system. However, to our knowledge, low concentrations of As may not cause toxicity and even activity hormesis, while high concentrations of As cause harmful effects on crops. Furthermore, we know that low concentrations of nanoparticles modulate plant antioxidant systems, but the effect of high concentrations of SiO_2 NPs interacting with low and high concentrations of As is unknown.

In this study, an experimental design intended to simulate the irrigation of tomato plants with As contaminated water as well as the application of SiO_2 NPs has been tested. 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 stratums, and the effect of SiO_2 NPs application in such translocations, (iv) to evaluate As and SiO_2 NPs phytotoxicity, and (v) to determine the effect of As and SiO_2 NPs on photosynthetic pigments, enzymatic activity and non-enzymatic antioxidant compounds of tomato plants.

2. 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^{-1}) as well as the application of SiO_2 NPs at three different dosis (0, 250 and 1000 mg L^{-1}) were tested in tomato plants in twelve replicates to make a total of 216 experimental units (Table S1, Supplementary Material).

2.1. Greenhouse experiment: As contamination simulation and SiO_2 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 [19]. Arsenic was supplied by $Na_2HAsO_4 \cdot 7H_2O$ 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^{-1}) [20]. SiO_2 NPs from SkySpring Nanomaterials Inc. were applied via substrate at 0, 250 and 1000 mg L^{-1} doses every three weeks making a total of 6 applications of 10 mL of solution per plant. SiO_2 NPs were spherical, between 10 and 20 nm, presented a surface area of 160 m^2 g^{-1}, and a bulk density of 0.08 to 0.1 g cm^{-3}. At the greenhouse, active photosynthetic radiation was 1100 µmol m^{-2} s^{-1} at peak hours, average day temperature was 28 °C, and average relative humidity was 61.8%.

2.2. 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 stratums, from which fruit was harvested when tomato brunches 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.

2.3 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.

2.4 Translocation of As and SiO_2 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 [21].

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 SiO_2 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 mgAs L^{-1} and 250 mgSiO_2 NPs L^{-1} treatment rinsed with deionized water, and frozen, until they were mounted in carbon tape in aluminum pins for SEM-EDS analyses.

2.5 Phytotoxicity of As.

The relative phytotoxicity index (PRI) was calculated using Equation (1) adapted from [22] 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 mgAs L^{-1}).

$$PRIxi = \frac{CoT}{CT} \qquad (1)$$

Where PRI: relative phytotoxicity index; x_i: i biomass (where i=radical and aerial); CoT: contaminated (arsenic and/or SiO_2 NPs) treatment; CT: Control treatment.

Values of PRI>1 indicate plant adaptation to As and SiO_2 NPs suggesting the biomass was stimulated while PRI<1 indicates As and SiO_2 NPs plant toxicity suggesting the biomass was inhibited for PRI=1 plants show tolerance to As and SiO_2 NPs, without differences compared to the control suggesting the biomass was not affected.

2.6 Measuring photosynthetic pigments in tomato plants exposed to As and SiO_2 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 °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_{645}) and 663 (x Abs_{663}) nm [23]:

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

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

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

2.7. 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 [24], glutathione peroxidase (GPX, QE 1.11.1.9) with the methodology described by Xue *et al.* [25], catalase (CAT, QE 1.11.1.6) using the methodology of Dhindsa *et al.* [26], superoxide dismutase (SOD, QE 1.15.1.1) using a SOD Cayman 706002® kit.

Total protein quantification (mg g^{-1} of dry weight (DW)) was carried out according to Bradford's colorimetric technique [27]. Glutathione (mmol 100 g^{-1} DW) was determined using the method by Xue *et al.* [25] by means of a 5,5-dithio-bis-2 nitrobenzoic acid (DTNB) reaction. Flavonoids (mg 100 g^{-1} DW) were determined using the method by Arvouet-Grand *et al.* [28]. Phenols (mg g^{-1} DW) were determined with Folin–Ciocalteu reagent as described in [29].

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.

3. Results and discussion

3.1. Arsenic in substrate and plant tissue.

Arsenic concentrations in substrate are directly proportional to the concentrations supplied in irrigation water (**Fig. 1**a). Furthermore, As concentration in irrigation water >0.8 mg L^{-1} causes As levels above 22 mg kg^{-1} in the substrate and is considered as contamination by Mexican guidelines for As in agricultural soils [30], and other international guidelines (i.e. 17 mg kg^{-1} from Canada) [31].

Total As concentrations in roots, leaves and stems, at different As exposures, are shown in **Fig. 1**b. 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 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 [2,32,33]. Arsenic accumulation in root tissue can cause an inhibition of the root's morphological characters [34]. 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 [35]. 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. 1**c). The higher the concentration of As in irrigation water, the higher the concentration of As in plant tissue (**Fig. 1**b). However, limited As uptake have been observed at low As concentration in irrigation water (≤0.4 mg L^{-1}), where As was neither found in stems from S2 and S3 at 0.2 and 0.4 mgAs L^{-1}, nor in leaves from S3 at 0.2 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 [37], 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 [38] causing lower As mobility.

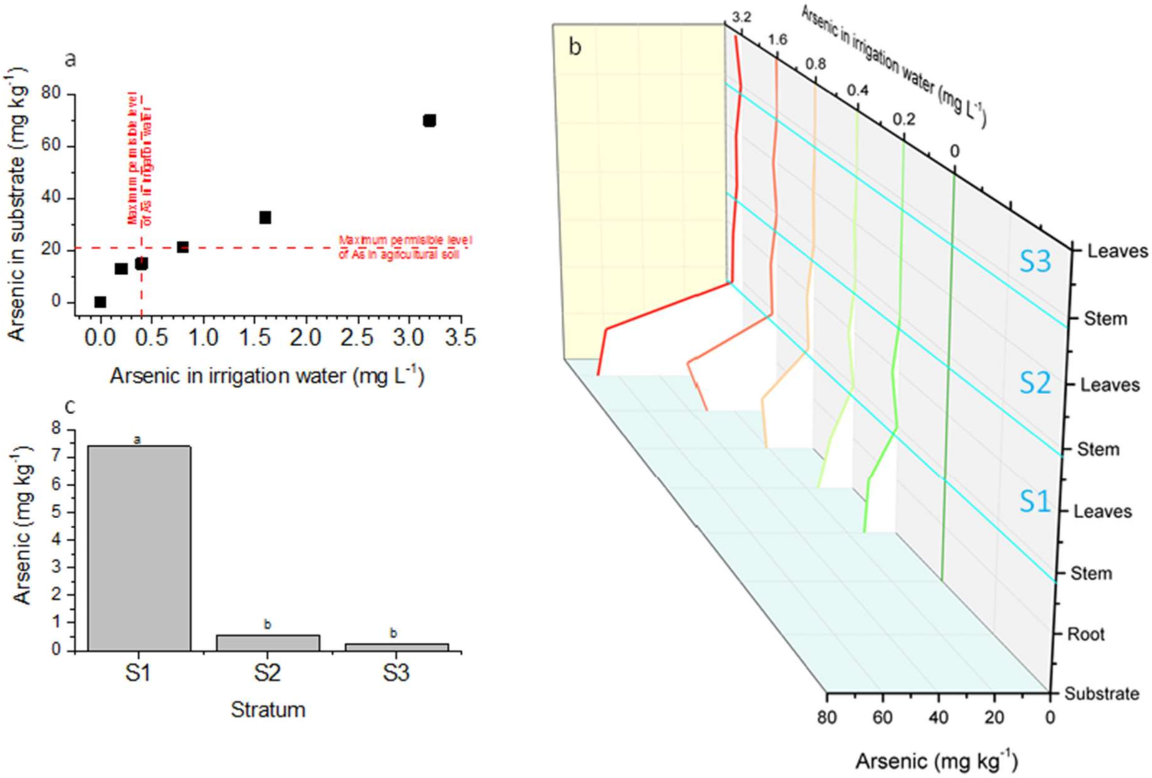


Fig. 1. Arsenic concentration in irrigation water, substrate, and tomato plant tissue. (a) Arsenic in substrate as a function of As in irrigation water. (b) Arsenic in substrate and plant tissue as a function of As in irrigation water. (c) Average As concentration as a function of aerial stratums. Different letters per bar indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$, n=3).

3.2. Effect of As on tomato growth and yield.

At low As concentrations in irrigation water (0.2 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. 2** a, b and c). Tomato plants irrigated with water containing 0.2 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 mg L^{-1}) has been reported to decrease root biomass and induced genotoxicity in lettuce [39]. 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 [40]. 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 steam diameter and tomato yield (**Fig. 2**c and d). Compartmentalization of As in tomato root tissue might be minimizing its impact on plant growth and metabolism [37], which in turn could help to explain these findings in **Fig. 2**.

At higher As concentrations in irrigation water (0.4 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. 2** c, 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. 2** c, d and e). Enhanced plant growth at high As doses (3.2 mgAs L^{-1}) has been observed in *Pteris vittata* [41], an As hyperaccumulator [42] 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 mg L^{-1}) [43], which may help to explain why our tomato plants show higher stem diameter and yield at 0.4 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 [44]. 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 [45].

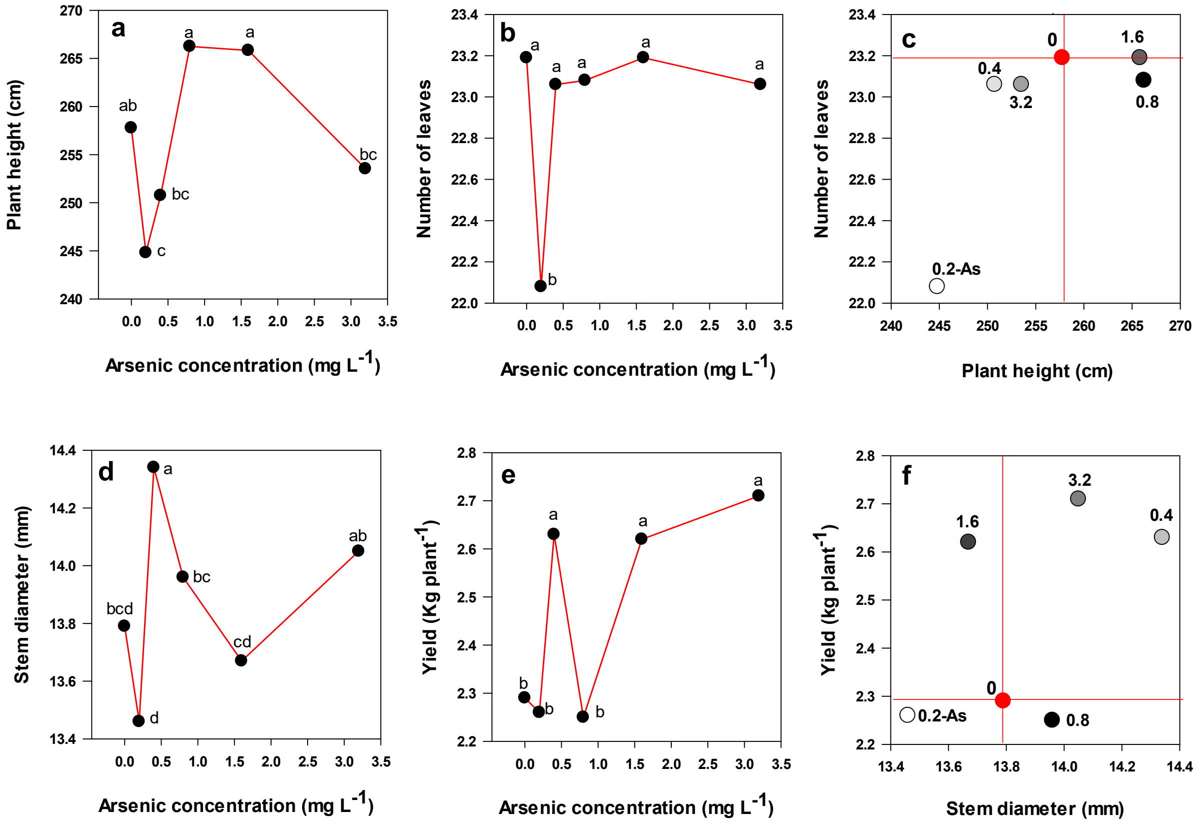


Fig. 2. Arsenic effect in agronomic variables. (a) Plant height and (b) number of leaves as a function of arsenic concentration in irrigation water c) Number of leaves as a function of plant height (d) Stem diameter and (e) yield as a function of As concentration in irrigation water (f) Tomato yield 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≤0.05, n=3).

3.3. Translocation of As and SiO_2 NPs in tomato plants.

Fig. 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 mgAs L^{-1}, As translocates from roots to stratum S1, exhibiting a preferential accumulation within the leaves (**Fig. 3**a). At 0.4 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. 3**a). These results imply the flow of As towards higher strata, which is supported by higher concentrations of As in plant tissue (**Fig. 1**b).

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 [46]. 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 [7]. Furthermore, it has been shown that As uptake by tomato plants through the root system results in the following accumulation order: As^{root} > As^{leaf} > As^{stem} > As^{fruit} [47]. In our study, translocation percentages are: As^{leaf} (31.43%) > As^{stem} (17.07%) > As^{fruit} (not detected). As mentioned previously, no As has been detected in fruits of tomato plants exposed to As [48].

Fig. 3b and c show the results from SEM-EDS observations. We found SiO_2 NPs in root and leaf tissue from tomato plants, which suggests that tomato plants take up SiO_2 NPs through the roots (**Fig. 3**b) and translocate them to the leaves (**Fig. 3**c), where they accumulate at least in the trichomes.

Fig. 3d and e show the translocation of As in the presence of SiO_2 NPs. No clear trends can be observed for the translocation of As to stem with increasing SiO_2 NPs. In general, however, the translocation of As seems to decrease towards the leaves with increasing SiO_2 NPs. Hence, application of SiO_2 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 SiO_2 NPs treatments (**Fig. 3**a, d and e). Decreased concentrations of As in stem, leaf, husk of brown rice have been reported after the addition of Si [49]. Furthermore, application of Si to tomato plants has resulted in decreased As accumulation in fruit and aerial parts [9], likely due to stimulation of radical exudates that can chelate metals and reduce their translocation [50]. These exudates include amino acids, organic acids, sugars and phenolic compounds [51]. Silicon nanoparticle application has been reported to decrease cadmium translocation up to a 60.8% in rice plants [52].

In this study, adhesion of SiO_2 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 [53,54]. This hypothesis is supported by high accumulation of As in tomato plant roots (**Fig. 1**b). 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 [55], suggesting that trichomes played an important role in the exudation of Cd crystals through crystallization [56]. Furthermore, Si NPs have been reported to increase trichome size in *Mentha piperita* L. [18]. In the present study, the presence of SiO_2 NPs in tomato leaf trichomes may also have contributed to the As detoxification process in our tomato plants.

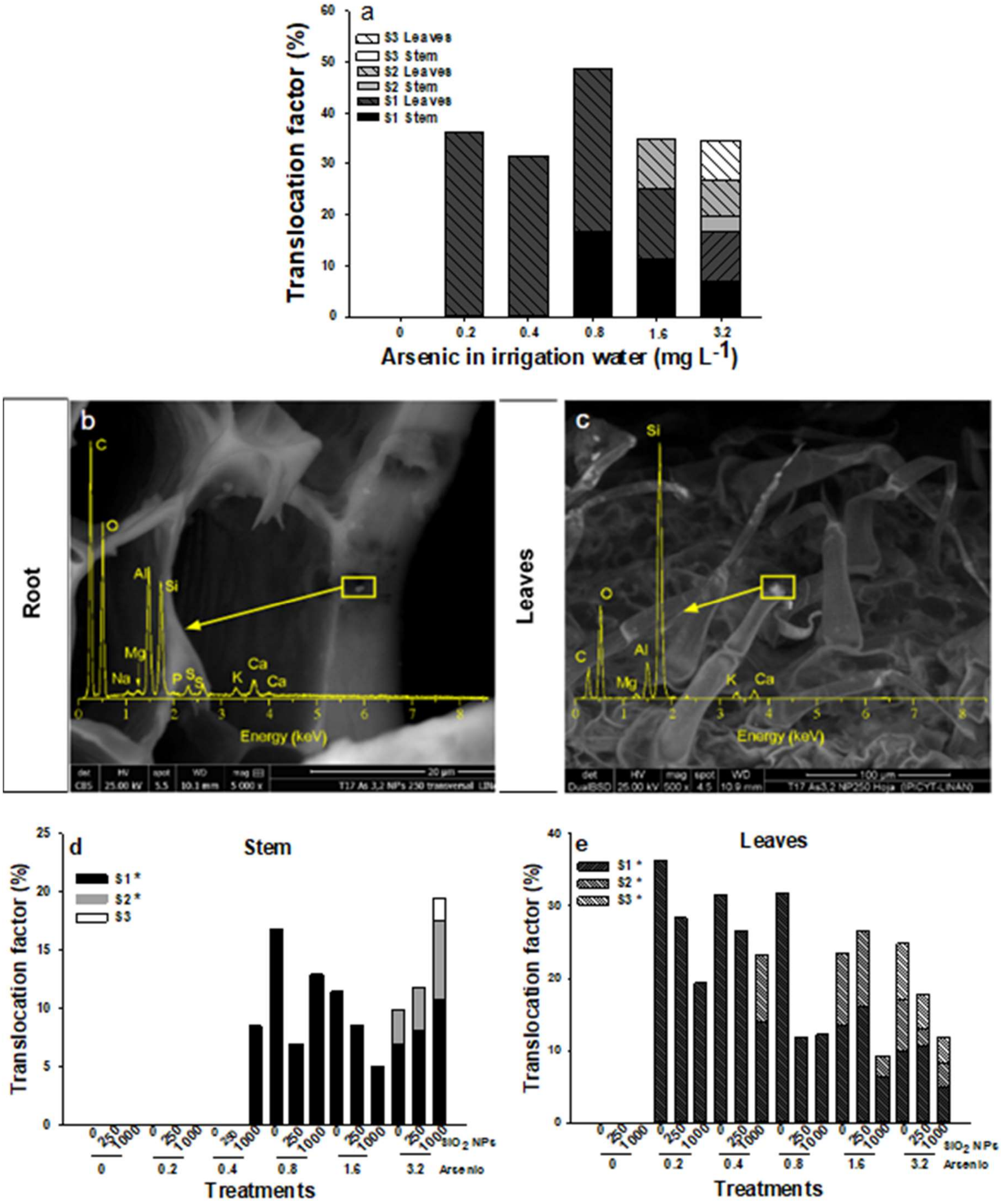


Fig. 3. Translocation of As in tomato plants as a function of As in irrigation water and SiO_2 NPs. (a) As translocation to the aerial part (stem and leaf) of tomato plants, (b) SiO_2 NPs in the roots of tomato plants and (c) SiO_2 NPs in the leaf trichomes. (d) As translocation to stem as a function of As and SiO_2 NP2 and (e) As translocation to leaves as a function of As and SiO_2 NP_2 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).

3.4. Effect of As and SIO_2 NPs on tomato growth and yield and the relative phytotoxicity index.

Fig. 4 shows the effect of SiO_2 NPs on tomato plant height, number of leaves, stem diameter, yield and the relative phytotoxicity index. The application of SiO_2 NPs does not show significant differences in plant height, number of leaves and stem diameter (**Fig. 4**a, b and c). However, the application of SiO_2 NPs shows a significant decrease in tomato yield, both in the absence and in the presence of As (**Fig. 4**d), which accounts for up to 23.31% at 1000 mgSiO_2 NPs L^{-1} and 0 mgAs L^{-1} and up 27.04% at 250 mgSiO_2 NPs L^{-1} and 3.2 mgAs L^{-1}, respectively.

Application of nanoparticles to crops has not shown any clear trend on plant growth. While some studies report positive effects [57–59] others report negative effects [60–62]. Nanoparticle geometry and size as well as the type of organic coating seem to induce plant responses that range from biostimulation to toxicity [63–65]. While low nanoparticle concentration (<100 mg L^{-1}) has been reported to increase plant growth [65,66], high SiO_2 NPs concentrations (100, 500 and 2000 mg L^{-1}) have been reported to cause negative effects on plant physiology [61]. In our study, we used high doses of NPs (250 and 1000 mg L^{-1}). 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 SiO_2 NPs as determined by radical and aerial biomass production, PRI has been estimated. Nearly all PRI values were ≥ 1 at all As doses in the absence of SiO_2 NPs, suggesting that tomato plants show tolerance to As (**Fig. 4**e 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 [37]. An interesting observation is the case of aerial dry matter in the presence of SiO_2 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^{-1} and 1000 mgSiO_2 NPs L^{-1}. 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 [67]. 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 SiO_2 NPs, nearly all PRI value were less to 1 at all As doses suggesting that tomato plants exhibit toxicity in the presence of SiO_2 NPs (**Fig. 4**e and f).

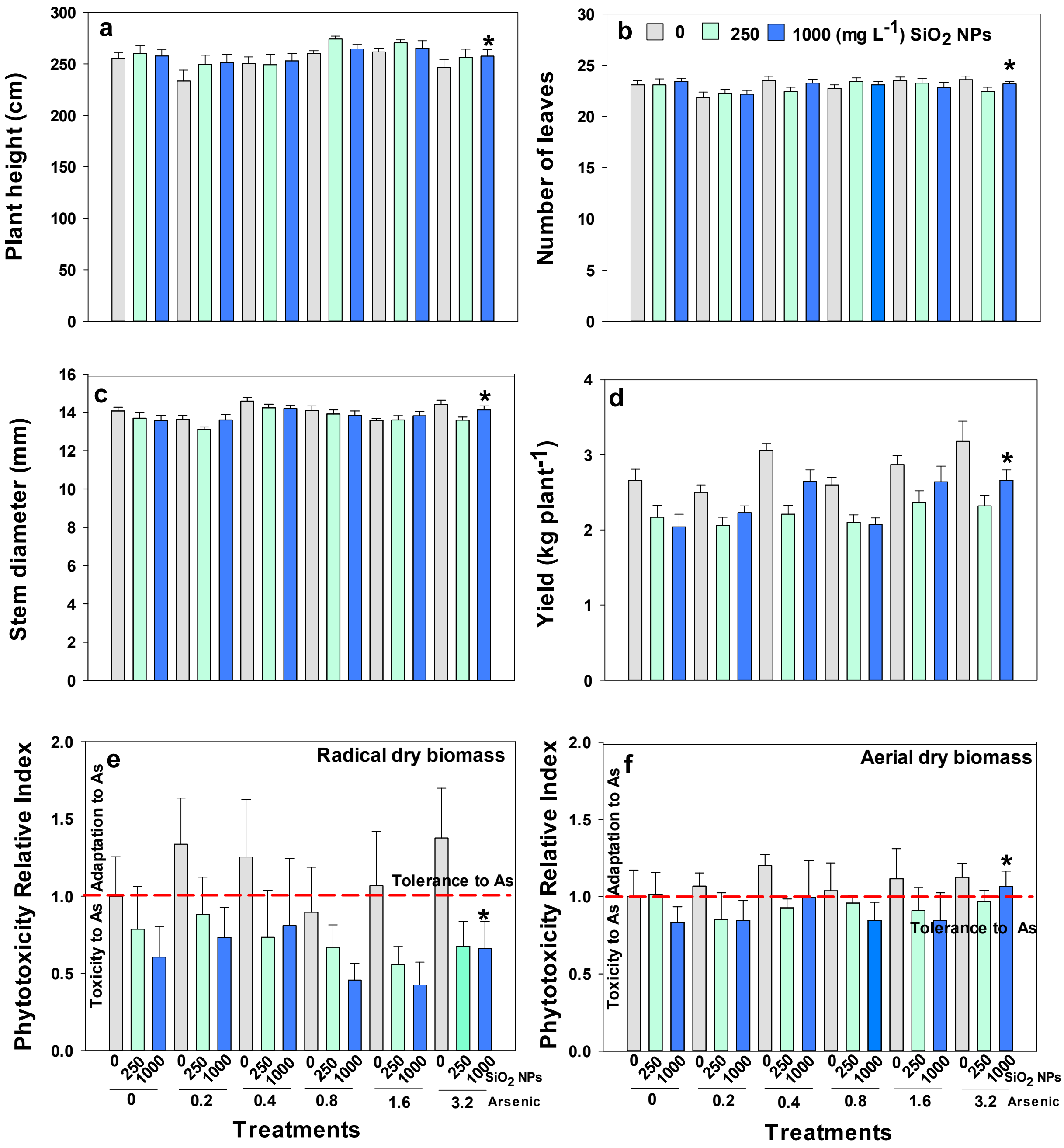


Fig. 4. Effect of SiO_2 NP on tomato plant development and the phytotoxicity relative index of arsenic and SiO_2 NPs. (a) Plant height, (b) number of leaves, (c) stem diameter, and yield as a function of As and SiO_2 NPs. Relative phytotoxicity index in (e) radical and (f) aerial biomass as a function of As and SiO_2 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).

3.5. Modification of the photosynthetic pigments in tomato plants exposed to As and SiO_2 NPs.

Fig. 5 shows the concentration of chlorophyll a, chlorophyll b and total chlorophyll in tomato leaves in the presence of As and SiO_2 NPs.

All chlorophylls were significantly higher than the control at any As doses in the absence of SiO_2 NPs (**Fig. 5**). Chlorophyll a increased up to 34.55% at 3.2 mgAs L^{-1} while chlorophyll b increased up to 63.9% at 0.8 mgAs L^{-1} (**Fig. 5**a 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 [10,68,69], increases in chlorophyll content was also reported in plants of *Borreria verticillata* due to exposure to different As concentrations [70]. 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 [71].

Regarding the effect of SiO_2 NPs, in the absence of As, only the dose of 1000 mgSiO_2 NPs L^{-1} 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 [15,18]. 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 mg L^{-1}) compared to the control [18]. The supply of SiO_2 NPs in pea leaves improved the photosynthetic pigments under Cr stress [15]. 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 [72]. 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 [73].

All chlorophylls are significantly higher than the control (0 mgAs L^{-1} and 0 mgSiO_2NPs L^{-1}) at any As and SiO_2 NPs doses (**Fig. 5**), indicating an improved photosynthetic capacity of our tomato plants. No significant differences are observed among As and SiO_2 NPs treatments (**Fig. 5**), except for chlorophyll b which shows a significant increase at 3.2 mgAs L^{-1} and 250 mgSiO_2 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 [74]. However, this same interaction decreased the content of chlorophylls compared to the absolute control [74]. 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 [15]. This could indicate that SiO_2 NPs can maintain or increase, as in our case, photosynthetic capacity in the presence of metalloids.

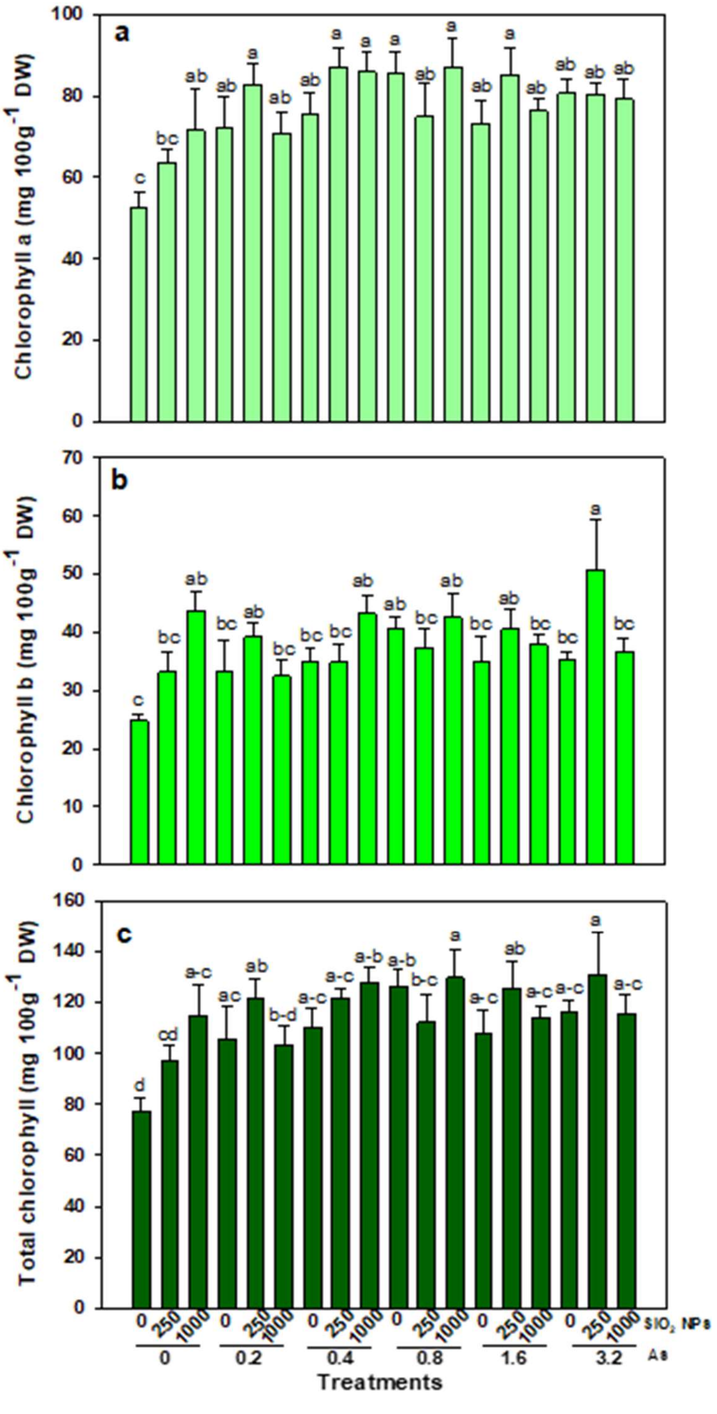


Fig. 5. Photosynthetic pigments in the leaves of tomato plants. (a) chlorophyll a, (b) chlorophyll b and (c) total chlorophyll increased by exposure to As and SiO_2 NPs compared to the control. Different letter per bar indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$, n=6).

3.6. 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 mgAs L^{-1}) and highest (1.6 and 3.2As mg L^{-1}) As doses, respectively (**Fig. 6**a and c). CAT activity increases up to 137.12% at 3.2 mgAs L^{-1} (**Fig. 6c**). In contrast, statistically significant decreased enzymatic activity is observed, mostly for GPX at higher (>0.4 mgAs L^{-1}) As doses, and in some cases for SOD at intermediate (0.4 to 0.8 mgAs L^{-1}) As doses (**Fig.** 6b and d).

APX activity reportedly increased to nearly 68% in the presence of aluminum (100 μM L^{-1}) stress in cucumber plants, but that it is inhibited at very high doses (1000 and 2000 μM L^{-1}) [75]. GPX activity has been reported to decrease considerably in *Myracrodruom urundeuva* plants when exposed to high As doses (100 mg Kg^{-1}) [7]. 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 [76]. It has been reported that SOD activity decreased in *Cicer arietinum* plants exposed to As concentrations of 30 and 60 mg $Kg^{-1,}$ as the As treatment did not cause concentrations of superoxide that could affect the plant [77].

Enzymes are susceptible to oxidative explosions and carbonylation of proteins, when plants are exposed to trace elements [78]. 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 [79]. However, enzyme activity can also be maintained or even increased by exposures to high concentrations of As (500 μM) [80].

In the absence of As, application of SiO_2 NPs to tomato plants shows stimulatory effects on APX and GPX enzymatic activities in tomato leaves (**Fig. 6**a and b), reaching up to a 94.4% increase of GPX at 1000 mgSiO_2 NPs L^{-1} . CAT enzymatic activity shows non significant effects as a result of SiO_2 NPs application, while SOD shows a decrease down to 49.10% at 1000 mgSiO_2 NPs L^{-1} (**Fig. 6**c and d). Similar results have been reported where the application of silver nanoparticles to *Brassica juncea* plants increased APX, GPX and CAT enzymatic activity [81]. 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 SiO_2 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 [82] and the excess of these radicals can decrease their activity.

Application of SiO_2 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^{-1}) for any SiO_2 NPs doses as compared to the control (**Fig 6**a). Increased APX enzymatic activity is also observed at 0.8 mgAs L^{-1} and 1000 mgSiO_2 NPs L^{-1} (Fig 6a). In contrast, the interaction of As and SiO_2 NPs causes a statistically significant decrease in GPX enzymatic activity at any As and SiO_2 NPs doses, compared to the control, with the exception of 0.4 mgAs L^{-1} and SiO_2 NPs application (**Fig. 6**b) which decrease to undetectable concentrations at 3.2 mgAs L^{-1} (**Fig. 6**b). No significant differences are observed for CAT enzymatic activity among As and SiO_2 NPs treatments (**Fig. 6**c) except at 0.2 mgAs L^{-1} and 1000 mgSiO_2 NPs L^{-1} and 0.4 mgAs L^{-1} and 250 mgSiO_2 NPs L^{-1} 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 SiO_2 NPs treatments (**Fig. 6**d) 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 SiO_2 NPs applied (250 and 1000 mg L^{-1}). It has been reported that the activities of antioxidant enzymes decrease at high concentrations of metals [83]. 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 mg L^{-1}) proved to increase SOD activity in *Leucaena leucocephala* seedlings exposed to cadmium and lead [84]. 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 [85]. 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.

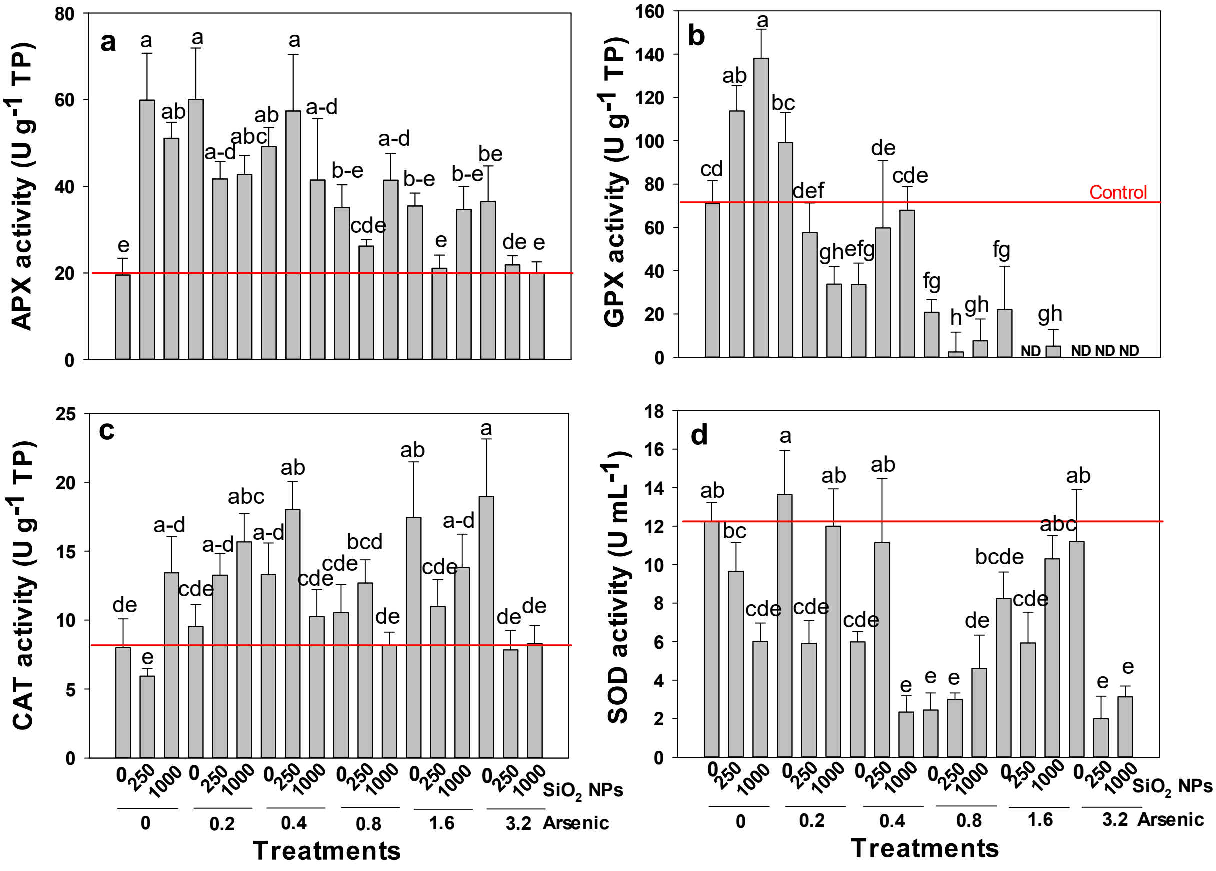


Fig 6. Enzymatic antioxidant compounds in tomato leaves. (a) APX, (b) GPX, (c) CAT, and (d) SOD activities as a function of SiO2 NPs for different levels of Arsenic, TP: Total proteins, ND: not detected. Different letter per bar indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$, n=6).

In addition to defensive enzyme systems to deal with ROS production, other non-enzymatic antioxidants also exist in plant cells [86], such as glutathione, vitamin C, phenolic acids, carotenoids, flavonoids, which are a natural response of plants against stress [87]. In this study, the content of non-enzymatic compounds in tomato leaves exposed to doses of As and SiO2 NPs shows significant differences between treatments (**Fig. 7**).

In general, glutathione decreases significantly compared to the control (**Fig. 7**a) suggesting that tomato plants antioxidant capacity may be sensitive to the phytotoxic effect of As [88], as GSH-related antioxidant defenses may be affected in response to As tolerance [89]. Flavonoid content decreases when tomato plants are exposed to 0.4 and 1.6 mgAs L^{-1} but is not significantly different to the control at other As doses (**Fig 7**b). It has been reported that As stress can inhibit flavonoid synthesis in *panax notoginseng* plants [90]. 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 [91]. 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 mgAs L^{-1} where phenol content decreases (**Fig 7**c). Plant phenols play an important role in the defensive response of plants including excessive concentrations of toxic metal(loid)s [92]. It has been reported that exposure of different forms of As and their combinations increases the content of phenols in *Ulmus laevis Pall* [93], but decreases have also been reported in *Ocimum basilicum* plants [94]. 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 7**d). [95] reported that exposure to As in two rice cultivars, at 4 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 [96] which can cause the reduction in proteins as a result of a greater oxidative damage due to part of the trace elements [97]. 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 [4].

The effect of SiO_2 NPs in the absence of As shows that the dose of 250mg SiO_2 NPs L^{-1} reduces glutathione content (**Fig. 7**a), although that same dose increases the content of phenols by 25.77% (**Fig. 7**c). The application of SiO_2 NPs has no significant effect on flavonoid content, however SiO_2 NPs doses decrease total proteins (**Fig 7**b 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 [98]. The impact can be both positive and negative, which may depend on the type of nanoparticle, their size, and the concentration used [99].

In this study, As-SiO_2 NPs interactions show a decrease in glutathione content as a function of the concentration of As and SiO_2 NPs (**Fig 7**a). 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 [17]. However, both As and metallic NPs can decrease their content in plants as observed in this study.

The interaction 0.2-1000 mg L^{-1} of arsenic and SiO_2 NPs reduces the content of flavonoids. This reduction also occurs when plants are exposed to 1.6-3.2 of arsenic and SiO_2 NPs. However, the highest dose of arsenic (3.2 mgAs L^{-1}) in interaction with SiO_2 NPs increases the flavonoid content (**Fig 7**b).The increased content of flavonoids induced by high doses of As and SiO_2 NPs is due to the fact that flavonoids are produced under conditions of severe stress to inhibit the generation of ROS [100]. 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 [101].

The phenol content is only reduced when the plants are exposed to the interaction 0.8-250 mg L^{-1} of arsenic and SiO_2 NPs, respectively, the rest of the interactions show no statistically significant differences to the control (**Fig 7**c). 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 [102]. The level of unchanged phenols suggests that the plants show no response to stress after exposure to As-SiO_2 NPs.

Proteins decrease significantly in all interactions (**Fig 7**d). 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 [74].

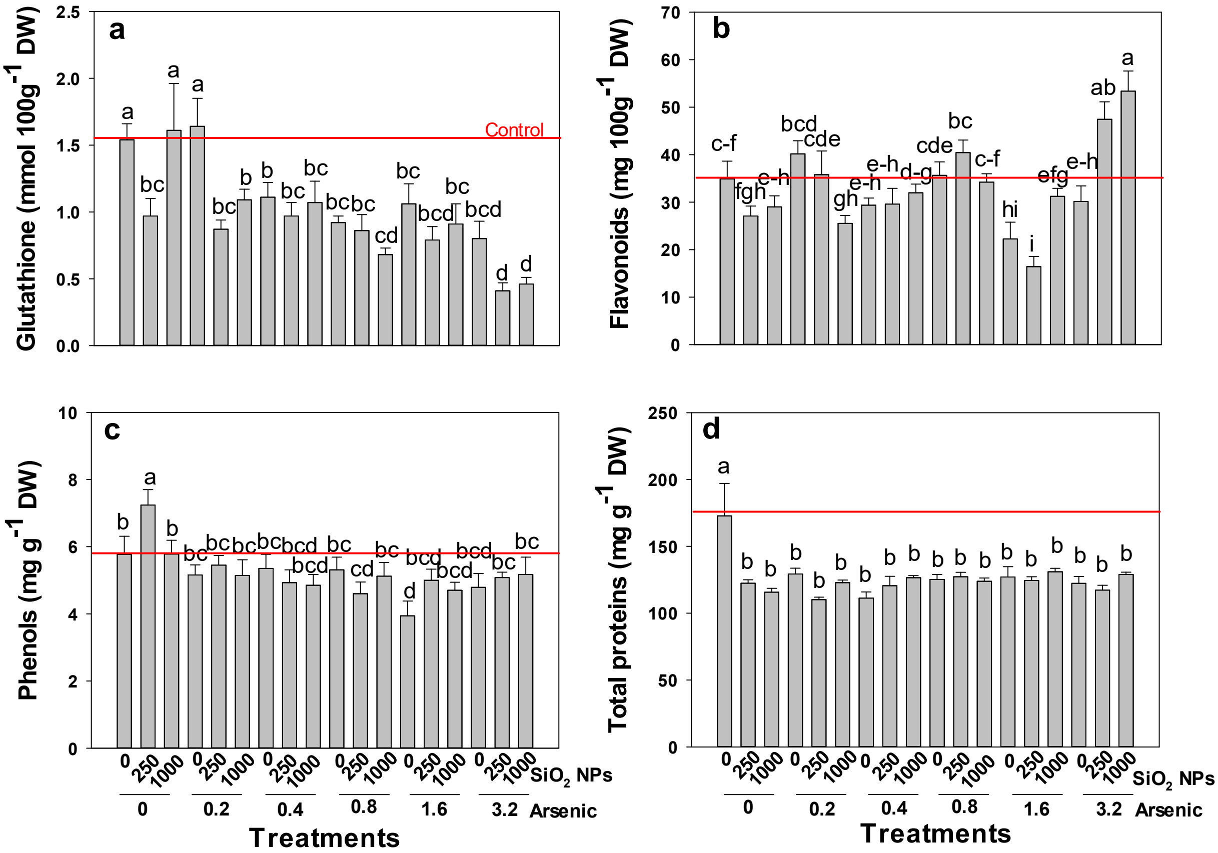


Fig. 7. Non-enzymatic antioxidant compounds in tomato leaves exposed to As and SiO_2 NPs. (a) Glutathione, (b) Flavonoids, (c) Phenols, and (d) Total Proteins as a function of SiO_2 NPs for different levels of Arsenic. Different letter per bar indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$, n=6).

4. Conclusions

Irrigation of tomato plants with As contaminated water causes As substrate enrichment and As bioaccumulation in roots, steam and leaves showing that the higher the concentration in irrigation water, the farther the contaminant flows and translocates through the different tomato stratums. 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 mg kg^{-1}). Low As concentrations in irrigation water (0.2 mg L^{-1}) cause decreased plant growth and number of leaves, while higher As concentrations in irrigation water (0.4-3.2 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 SiO_2 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 SiO_2 NPs at high concentrations (3.2 mg L^{-1} and 1000 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.

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Supplementary Material

SILICON NANOPARTICLES DECREASE ARSENIC TRANSLOCATION AND MITIGATE PHYTOTOXICITY IN TOMATO PLANTS

Magín González-Moscoso[a], Antonio Juárez-Maldonado[b], Gregorio Cadenas-Pliego[c],
Diana Meza-Figueroa[d], Bhaskar SenGupta[e], Nadia Martínez-Villegas[f,*].

4 Tables, 5 Pages including cover

Corresponding author: Nadia Martínez-Villegas
E-mail addresses: nadia.martinez@ipicyt.edu.mx, amelieybonita@gmail.com

[a]Doctorado en Agricultura Protegida, Universidad Autónoma Agraria Antonio Narro, Calzada Antonio Narro 1923, Buenavista, 25315, Saltillo, Coahuila, México.
[b]Departamento de Botánica, Universidad Autónoma Agraria Antonio Narro, Calzada Antonio Narro 1923, 25315, Saltillo, Coahuila, México.
[c]Centro de Investigación en Química Aplicada, Enrique Reyna H 140, 25294 Saltillo, Coahuila, México. [d]Departamento de Geología, Universidad de Sonora, Blvd. Luis Encinas J, Calle Av. Rosales &, Centro, 83000 Hermosillo, Sonora, México.
[e]School of Energy, Geoscience, Infraestructure & Society, Heriot-Watt University, Water Academy, EGIS 2.02A William Arrol Building, EH14 4AS Scotland, United Kingdom.
[f]IPICyT, Instituto Potosino de Investigación Científica y Tecnológica, Camino a la Presa San José No. 2055, Col. Lomas 4a Sec., 78216 San Luis Potosí, SLP, México.

Table S1. A factorial experiment was established in a plot design divided into randomized complete blocks. The large factor were the doses of As (0, 0.2, 0.4, 0.8, 1.6 and 3.2 mg L^{-1}) and the small factor were the doses of SiO_2 NPs (0, 250 and 1000 mg L^{-1}). A total of 18 different treatments were applied in this study, each treatment was replicated twelve times.

Treatments	As	SiO_2 NPs	Plant	Experimental units.
	mg L^{-1}	mg L^{-1}		
1	0	0	*Solanum lycopersicum*	1-12
2	0	250	*Solanum lycopersicum*	13-24
3	0	1000	*Solanum lycopersicum*	25-36
4	0.2	0	*Solanum lycopersicum*	37-48
5	0.2	250	*Solanum lycopersicum*	49-60
6	0.2	1000	*Solanum lycopersicum*	61-72
7	0.4	0	*Solanum lycopersicum*	73-84
8	0.4	250	*Solanum lycopersicum*	85-96
9	0.4	1000	*Solanum lycopersicum*	97-108
10	0.8	0	*Solanum lycopersicum*	109-120
11	0.8	250	*Solanum lycopersicum*	121-132
12	0.8	1000	*Solanum lycopersicum*	133-144
13	1.6	0	*Solanum lycopersicum*	145-156
14	1.6	250	*Solanum lycopersicum*	157-168
15	1.6	1000	*Solanum lycopersicum*	169-180
16	3.2	0	*Solanum lycopersicum*	181-192
17	3.2	250	*Solanum lycopersicum*	193-204
18	3.2	1000	*Solanum lycopersicum*	205-216

Table S2. Translocation factor in tomato stem.

Treatments	As	SiO_2 NPs	Translocation factor (%)		
	mg L^{-1}	mg L^{-1}	S1	S2	S3
1	0	0	0±0c	0±0c	0±0b
2	0	250	0±0c	0±0c	0±0b
3	0	1000	0±0c	0±0c	0±0b
4	0.2	0	0±0c	0±0c	0±0b
5	0.2	250	0±0c	0±0c	0±0b
6	0.2	1000	0±0c	0±0c	0±0b
7	0.4	0	0±0c	0±0c	0±0b
8	0.4	250	0±0c	0±0c	0±0b
9	0.4	1000	8.46±4.23bc	0±0c	0±0b
10	0.8	0	26.86±11.75a	0±0c	0±0b
11	0.8	250	6.96±1.94bc	0±0c	0±0b
12	0.8	1000	12.89±2.05b	0±0c	0±0b
13	1.6	0	11.4±1.64bc	0±0c	0±0b
14	1.6	250	8.49±5.45bc	0±0c	0±0b
15	1.6	1000	5±1.05bc	0±0c	0±0b
16	3.2	0	6.83±1.96bc	3.01±1.04bc	0±0b
17	3.2	250	8.12±2.75bc	3.69±1.39ab	0±0
18	3.2	1000	10.75±5.75bc	6.69±2.31b	2.04±1.09b

Different letters per columne indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$, n=6)

Table S3. Translocation factor in tomato leaves.

Treatments	As	SiO_2 NPs	Translocation factor (%)		
	mg L^{-1}	mg L^{-1}	S1	S2	S3
1	0	0	0 ±0e	0±0c	0±0c
2	0	250	0 ±0e	0±0c	0±0c
3	0	1000	0 ±0e	0±0c	0±0c
4	0.2	0	36.3±6.83a	0±0c	0±0c
5	0.2	250	28.34±11.62a-d	0±0c	0±0c
6	0.2	1000	19.32±1.74a-e	0±0c	0±0c
7	0.4	0	31.56±15.81abc	0±0c	0±0c
8	0.4	250	26.56±13.49a-d	0±0c	0±0c
9	0.4	1000	13.83±0.80b-e	9.48±4.76a	0±0c
10	0.8	0	31.89±7.98ab	0±0c	0±0c
11	0.8	250	11.84±2.38cde	0±0c	0±0c
12	0.8	1000	12.21±2.50b-e	0±0c	0±0c
13	1.6	0	13.58±2.28b-e	9.851.85a	0±0c
14	1.6	250	16.16±8.67b-e	10.39±6.34a	0±0c
15	1.6	1000	6.31±2.13e	2.96±2.03bc	0±0c
16	3.2	0	9.87±3.12de	7.08±2.23ab	7.84±3.92a
17	3.2	250	10.55±3.19de	2.55±1.28bc	4.62±1.65b
18	3.2	1000	4.92±1.35e	3.27±1.03bc	3.65±0.41b

Different letters per columne indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$, n=6)

Table S4. Effect of SiO_2 NP on tomato plant development and the phytotoxicity relative index of arsenic and SiO_2 NPs.

As	SiO_2 NPs	Plant height	Stem diameter	Number of leaves	Yield	PRI Root	PRI Aerial
mg L^{-1}	mg L^{-1}	cm	Mm		Kg $plant^{-1}$		
0	0	255.67±5.06a-d	14.08±0.19a-e	23.08±0.40a-c	2.66±0.15b-d	1±0.25b-d	1±0.17b-f
0	250	260.00±7.56a-d	13.70±0.30c-f	23.08±0.58a-c	2.17±0.16gh	0.78±0.27c-g	1.01±0.14b-e
0	1000	257.67±6.01a-d	13.57±0.27ef	23.42±0.31ab	2.04±0.17h	0.60±0.19e-h	0.83±0.09g
0.2	0	233.42±10.54e	13.65±0.19c-f	21.83±0.55d	2.50±0.10c-g	1.33±0.29a	1.06±0.08a-d
0.2	250	249.58±8.89c-e	13.12±0.12f	22.25±0.37cd	2.06±0.11h	0.88±0.24c-f	0.85±0.17fg
0.2	1000	251.42±7.85c-e	13.61±0.28d-f	22.17±0.37cd	2.23±0.09e-h	0.73±0.19c-h	0.84±0.12fg
0.4	0	250.17±6.56c-e	14.59±0.20a	23.50±0.42ab	3.06±0.09ab	1.25±0.37ab	1.20±0.07a
0.4	250	249.17±10.03c-e	14.24±0.19a-c	22.42±0.43b-d	2.21±0.12f-h	0.73±0.30c-h	0.92±0.05d-g
0.4	1000	252.92±7.08b-d	14.20±0.16a-d	23.25±0.37a-c	2.65±0.15b-d	0.80±0.43c-f	0.99±0.24b-g
0.8	0	260.00±2.82a-d	14.10±0.24a-e	22.75±0.33a-d	2.60±0.10c-f	0.89±0.29c-e	1.03±0.18b-e
0.8	250	274.17±2.88a	13.92±0.21b-e	23.42±0.34ab	2.10±0.10gh	0.66±0.14d-h	0.95±0.04c-g
0.8	1000	264.58±4.24a-d	13.85±0.23b-e	23.08±0.34a-c	2.07±0.09h	0.45±0.10gh	0.84±0.11fg
1.6	0	261.67±3.50a-d	13.58±0.11ef	23.50±0.34ab	2.87±0.12a-c	1.06±0.35a-c	1.11±0.19a-c
1.6	250	270.42±2.98ab	13.61±0.22d-f	23.25±0.43a-c	2.37±0.15d-h	0.55±0.11f-h	0.90±0.14e-g
1.6	1000	265.42±7.11a-c	13.82±0.23c-e	22.83±0.51a-d	2.64±0.21b-e	0.42±0.14h	0.84±0.18fg
3.2	0	246.67±7.70de	14.42±0.22ab	23.58±0.36a	3.18±0.27a	1.37±0.32a	1.12±0.09ab
3.2	250	256.42±7.99a-d	13.60±0.16ef	22.42±0.43b-d	2.32±0.14d-h	0.67±0.16d-h	0.96±0.07b-g
3.2	1000	257.50±6.50a-d	14.13±0.21a-e	23.17±0.24a-c	2.66±0.14bcd	0.65±0.17eh	1.06±0.09a-e
	C.V. (%)	9.06	5.31	5.98	20.90	35.28	14.14

PRI: Relative phytotoxicity index. Different letters per columna indicate significant differences according to the Fisher Least Significant Difference test ($p \leq 0.05$)

TERCER ARTÍCULO

SiO_2 Nanoparticles Improve Nutrient Uptake in Tomato Plants Developed in the Presence of Arsenic

SiO_2 Nanoparticles Improve Nutrient Uptake in Tomato Plants Developed in the Presence of Arsenic

Magín González-Moscoso[1], Nadia Valentina Martínez-Villegas[2], Diana Meza-Figueroa[3], María del Carmen Rivera-Cruz[4], Gregorio Cadenas-Pliego[5], Antonio Juárez-Maldonado[6].

[1] Doctorado en Agricultura Protegida, Universidad Autónoma Agraria Antonio Narro, Calzada Antonio Narro 1923, Buenavista, 25315, Saltillo, Coahuila, México.

[2] IPICyT, Instituto Potosino de Investigación Científica y Tecnológica, Camino a la Presa San José No. 2055, Col. Lomas 4a Sec., 78216 San Luis Potosí, SLP, México.

[3] Departamento de Geología, Universidad de Sonora, Blvd. Luis Encinas J, Calle Av. Rosales, Centro, 83000 Hermosillo, Sonora, México.

[4] Colegio de Postgraduados Campus Tabasco, Km 2 Periférico Carlos A. Molina. 86570, H. Cárdenas, Tabasco, México.

[5] Centro de Investigación en Química Aplicada, Enrique Reyna H 140, 25294 Saltillo, Coahuila, México.

[6] Departamento de Botánica, Universidad Autónoma Agraria Antonio Narro, Calzada Antonio Narro 1923, 25315, Saltillo, Coahuila, México.

Corresponding author: antonio.juarez@uaaan.edu.mx

Abstract

The nutritional status of a plant can be negatively modified by toxic elements that have an analogy with essential nutrients or by the stress caused at the absorption sites. The absorption and distribution of nutrients in roots and leaves of tomato plants (*Solanum lycopersicum*) developed under conditions of contamination with arsenic (As) in the nutrient solution and treated with nanoparticles of silicon dioxide (SiO_2 NPs) was evaluated. The plants were grown for 150 days in greenhouse conditions and soilless culture. Different concentrations of arsenic as As (V) (0, 0.2, 0.4, 0.8, 1.6 and 3.2 mg L^{-1}) were applied through the nutritive solution, while three concentrations of SiO_2 NPs (0, 250 and 1000 mg L^{-1}) were applied via drench. Dry root and shoot biomass production as well as the concentration of micronutrients (Fe, Cu, Zn) and macronutrients (K, S, P) in roots and leaves were determined. Exposure to As in low doses resulted in dry biomass decreases. The application of only SiO_2 NPs also significantly decreased biomass. The presence of As in the nutrient solution decreased the uptake of Fe, Cu, Zn and P in roots, but it increased the uptake of K. The SiO_2 NPs increased the uptake of macronutrients in roots and leaves. The uptake of nutrients by tomato plants was negatively affected by the presence of As in the nutritive solution. However, such an effect could be reversed with the application of SiO_2 NPs, as they favored nutrient uptake.

Keywords: Heavy metals, nanotecnology, nutrient uptake, crop growth.

1 Introduction

At present, anthropogenic activities have caused a series of environmental problems that put the development of agriculture at risk. One of the main problems is the contamination of water and soil with heavy metals and metalloids, which due to their characteristics (toxicity, bioavailability, bioaccessibility, persistence and high solubility) cause various problems in living organisms (Li et al., 2015; Ruíz-Huerta et al., 2017; Thapa et al., 2012; Xian et al., 2015). Arsenic (As) is one of the main pollutants around the world (Sarkar and Paul, 2016). It is a potentially toxic metalloid that is released into the environment as a result of both natural and anthropogenic processes (Kalita et al., 2018). This metalloid has a negative impact on plants, animals and humans (Zvobgo et al., 2019). In plants, most of the

As is retained in the root cells, and, although the translocation to the shoots is relatively low, it varies substantially between species and even within the same species (Finnegan and Chen, 2012). As induces nutritional alterations in plants, since it affects the absorption of nutrients by direct competition with other nutrients, which, in turn, alters metabolic processes (Gomes et al., 2014). Based on their oxidation state, there are two main inorganic species of As, the fully oxidized pentavalent arsenate (AsV) and reduced trivalent arsenite As(III) (Sánchez-Pardo et al., 2015; Xu et al., 2015). As(V) acts as a phosphate analog due to the chemical similarity between them, entering the cell using phosphate transporters and affecting the absorption of phosphate (Panda et al., 2010; Tripathi et al., 2013). In the case of As(III), the transporters that have been reported in rice cultivation are those of silicon and some aquaporins related to silicon (Chen et al., 2017). Arsenic enters cells through nutrient uptake systems such as phosphate permeases (arsenate) and/or aquaglyceroporins (Garbinski et al., 2019). Although As can replace phosphorus, it cannot perform its biological functions (Gunes et al., 2009), triggering a number of problems, such as reduced absorption of nutrients, disturbances in carbohydrate metabolism, reduced photosynthetic rate, and even cell death (Gomes et al., 2012; Panda et al., 2010; Stoeva et al., 2005; Zvobgo et al., 2014).

Silicon (Si) is an element with multiple benefits. It can improve soil conditions and the absorption of nutrients in plants (Zargar et al., 2019). Silicon can increase Ca and K uptake in corn husks under abiotic stress (Kaya et al., 2006). Even low concentrations of silicon can improve K absorption due to the activation of H^+-ATPase in both, hydroponics and soil (Mali and Aery, 2008). Silicon absorption mechanisms vary between different plant species and apparently depend on the presence of specific transporters of this element (Kaur and Greger, 2019). The fundamental mechanisms involved in Si-mediated tolerance to heavy metal stress include reduction of metal ions in the substrate or soil, co-precipitation of toxic metals, chelation, stimulation of antioxidants, and structural alterations in plants (Bhat et al., 2019).

The application of nanotechnology in agriculture and environmental protection has grown in recent years due to the unique chemical and physical properties of the nanomaterials (Cui et al., 2017). Silicon nanoparticles (Si NPs) can decrease the toxic effects of As in plants (Tripathi et al., 2015). For example, the application of Si NPs increased the photosynthesis of the plant in the presence of cadmium, facilitating the transport of nutrients through the xylem (Gao et al., 2018). Si NPs have also been reported to improve the efficiency of water and nutrient use absorption balance (Alsaeedi et al., 2019). Therefore, the objective of this study was to determine the effect of the application of SiO_2 NPs in the uptake of macro and micronutrients in tomato plants irrigated with water contaminated with As(V).

2 Materials and Methods

2.1 Crop Growth

The experiment was carried out in a polycarbonate greenhouse with automatic temperature control at the Antonio Narro Autonomous Agrarian University, Coahuila, Mexico. Tomato seeds (*Solanum lycopersicum* L.) of the hybrid var. "Sun 7705", saladete type and indeterminate growth were used as plant material. The seedlings were transplanted into 12 L capacity black polyethylene bags containing a mixture of Peat most and perlite (1:1) as growth substrate. The crop was handled on a single stem and developed for 150 days after transplantation.

2.2 Experimental Design and Plant Nutrition

Arsenic was added to irrigation water as $Na_2HAsO_4 \cdot 7H_2O$, when the nutritive solution was prepared to obtain arsenic concentrations of 0.2, 0.4, 0.8, 1.6 and 3.2 mg L^{-1}. The SiO_2 NPs were applied via drench from the transplant every three weeks making a total of six applications (10 ml per application to each plant). The crop was established using a design divided in plots and complete random blocks, where the large plot was the concentration of arsenic and the small plot the application of Si NPs (0, 250, and 100 mg L^{-1}), for a total of 18 treatments. SiO_2 NPs are spherical, 10-20 nm size, with a surface area of 160 m^2 g^{-1}, and a bulk density of 0.08-0.1 g cm^{-3} (SkySpring Nanomaterials Inc., USA).

Plant nutrition was managed through a directed irrigation system using Steiner solution (Steiner, 1961). This was applied at different concentrations depending on the phenological stage: 25% in vegetative stage, 50% in flowering, 75% in fruit set, and 100% in fruit filling and harvesting. The pH of the nutrient solution was kept between 6.0 and 6.5 using sulfuric acid.

2.3 Plant Sampling

At 150 days after transplantation, the plants were harvested, and leaf and root samples were collected. The samples were dried in a drying oven at a constant temperature of 80°C for 72 hours until constant weight was reached. The dried material was ground using a porcelain mortar for mineral analysis. Dry root and shoot biomass were also determined.

2.4 Mineral Nutrient Analysis

The concentration of macro and micro nutrients in roots and leaves was determined by X-ray fluorescence spectroscopy (XRF) in a ThermoScientific Niton FXL instrument. Analyzes were carried out in three plicates, and the quality of the results was evaluated using the reference material NIST 1573a for tomato leaves.

2.5 Statistical Analysis

An analysis of variance (ANOVA) was performed to determine differences between the treatments and the Fisher´s Least Significant Differences test ($\alpha = 0.05$) to compare the means. For these analyzes, the statistical package InfoStat (v2019) was used. In addition, regression analyzes were performed to evaluate the relationships between the variables using only the mean values of each factor (As(V) or SiO_2 NPs) and without considering the interactions. SigmaPlot software (V12.0) was used for this process.

3 Results

3.1 Biomass Production

Biomass production was affected by the different concentrations of As and the application of SiO_2 NPs (Fig. 1). The production of root dry weight (RDW) showed a slight increase compared to the control with the low concentrations of As (0.2-0.4 mg L^{-1}). Arsenic concentrations of 0.8-1.6 mg L^{-1} decreased RDW. However, 3.2 mg L^{-1} induced 3.3% more biomass (Fig. 1A). Shoot dry weight (SDW) did not show effect in most concentrations, however, an increasing trend was observed with high doses. The application of SiO_2 NPs presented a similar trend in both RDW and SDW, in both cases the biomass decreased (Fig. 1D). RDW decreased up to 49% compared to the control (Fig. 1B), while SDW only decreased 18% (Fig. 1D).

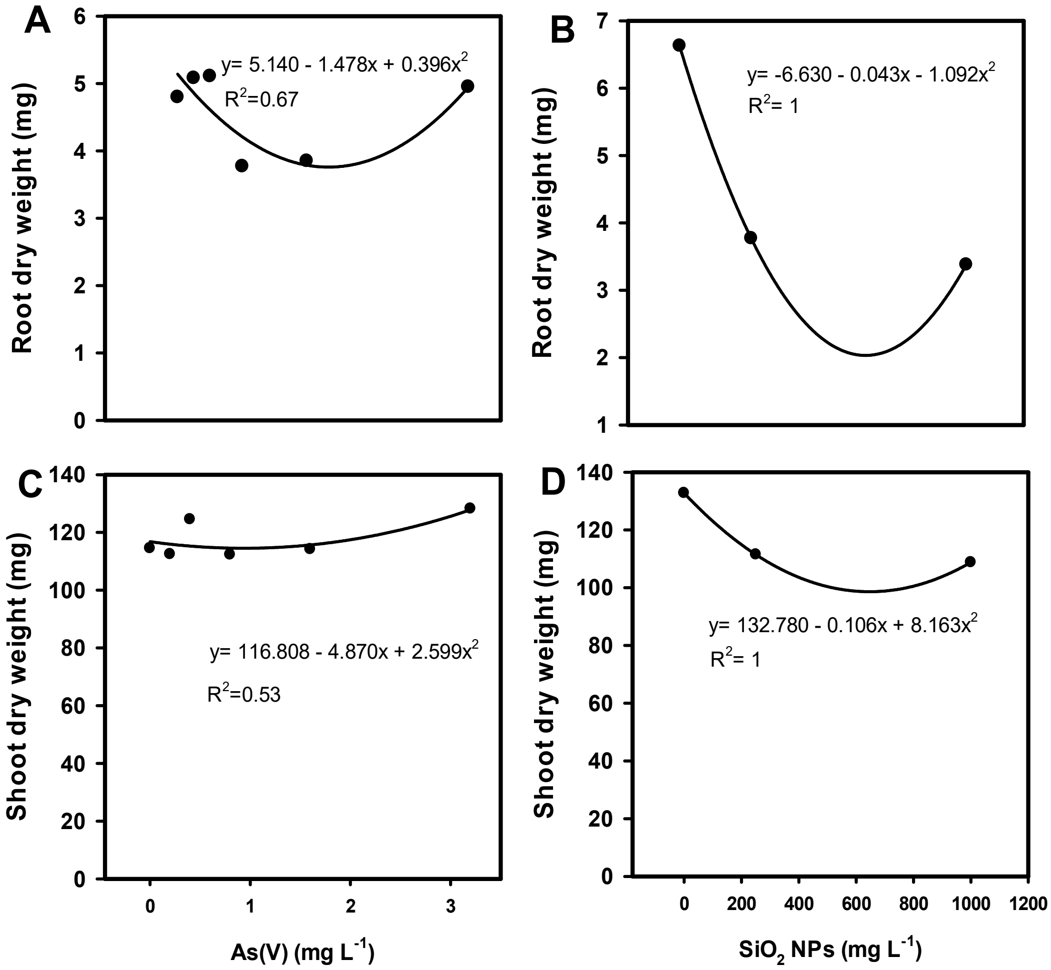

Fig. 1 Relationship between dry biomass production (root [A, B] and shoot [C, D]) of *Solanum lycopersicum* as a function of As and SiO_2 NPs concentrations. The regression curve of As (V) refers to the mean values of three replicates. The regression curve of SiO_2 NPs refers to the mean values of six replicates.

The interaction of As(V) with SiO_2 NPs had a negative effect on biomass production. RDW decreased significantly at 0.8-1.6 mg L^{-1} of As (V) with 1000 mg L^{-1} of SiO_2 NPs (Fig. 2A). The effect of the As(V)-SiO_2 NPs interaction in the production of SDW showed the same decreasing trend, yet to a lower extent. The concentration of 3.2 mg L^{-1} of As (V) with the application of 250 mg L^{-1} of SiO_2 NPs decreased the SDW by 3.1%. However, this same concentration of As (V) together with 1000 mg L^{-1} of SiO_2 NPs increased by 6.89% the production of SDW compared to the control (Fig. 2A).

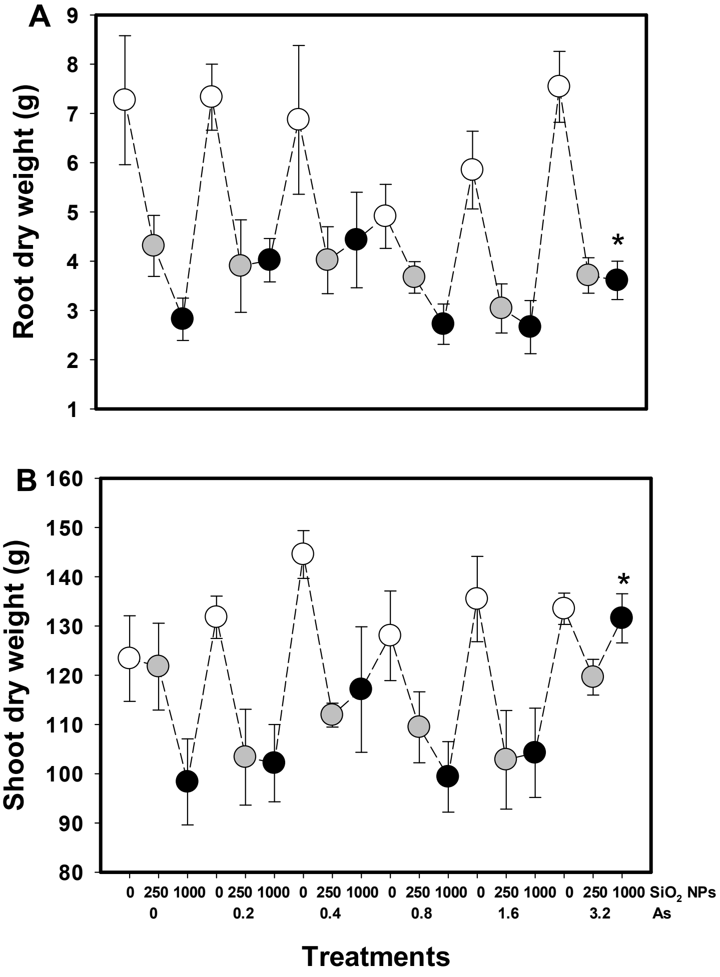

Fig. 2 Effect of the interaction of As(V) and SiO_2 NPs on the production of root and shoot biomass in plants of *Solanum lycopersicum*. N= 6 ± standard error. * indicate significant differences between treatments according to the Fisher´s Least Significant Difference test ($\alpha = 0.05$).

3.2 Effect of Arsenic and SiO_2 NPs on the Uptake of Micronutrients in Root and Leaves

The presence of As(V) in nutritive solution decreased the concentration of Fe and Cu in the root proporcionately (Fig. 3A and 3C). In contrast, low concentrations of As(V) (0.4-0.8 mg L^{-1}) induced higher concentrations of Zn (4.9% and 15.5%, respectively). while hight concentrations of As (3.2 mg L^{-1}) induced lower concentrations of Zn in the root (12.6%) (Fig. 3E). A very similar effect was observed in the concentration of Fe, Cu and Zn in the leaves, at high doses of As(V) (1.6 and 3.2 mg L^{-1}), the concentration of Fe (9.7% and 30.6%), Cu (27.2% and 41.8%), and Zn (23.5% and 22.4%) decreased (Fig. 3E).

SiO_2 NPs modified the Fe concentration. In the root a decrease of 14.4% and 8.7% of the concentration of this micronutrient was observed, due to exposure to 250 and 1000 mg L^{-1} respectively. In contrast, the opposite effect was presented in the leaves, since the Fe concentration increased 45.7% and 27.2% with the application of 250 and 1000 mg L^{-1} of SiO_2 NPs (Fig. 3B). The application of 250 and 1000 mg L^{-1} SiO_2 NPs induced an increase in Cu (10.8% and 14.8%) and Zn (18.5% and 22.5%) in the root; in the leaves no effect was observed (Fig. 3D and 3F).

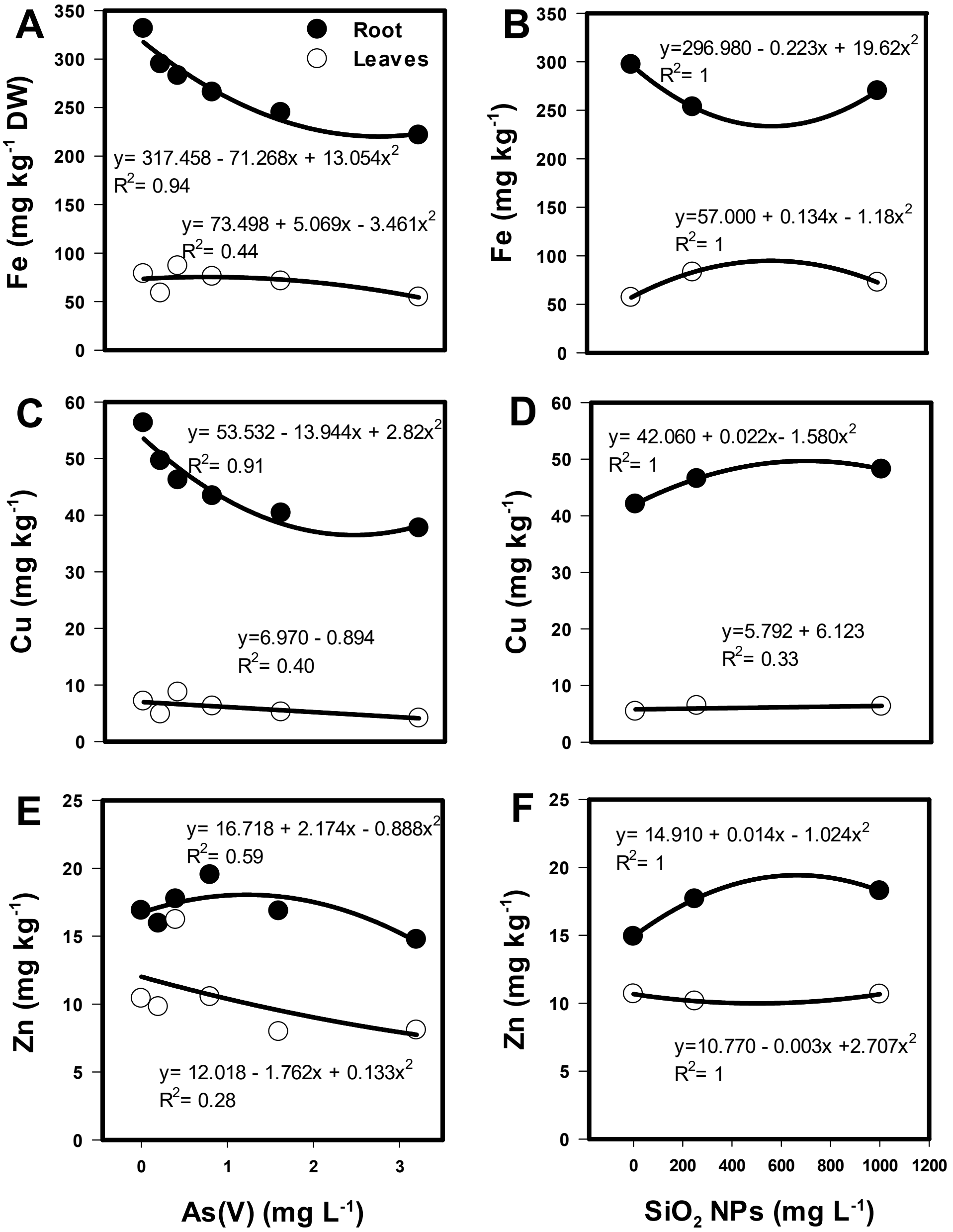

Fig. 3 Relationship between the concentration of Fe (A, B), Cu (C, D), and Zn (E, F) and As (V) and SiO_2 NPs in roots and leaves of *Solanum lycopersicum*. Regression curve of As (V) refers to the mean values of three replicates. The regression curve of SiO_2 NPs refers to the mean values of six replicates.

The interaction of As(V) with the SiO_2 NPs showed a negative effect on Fe concentration in roots, which was more negative (45.7%) at high As and SiO_2 NPs concentrations, (3.2 mg L^{-1} of As and 1000 mg L^{-1} of SiO_2 NPs) (Fig. 4A). However, in the absence of As(V), it was observed that both concentrations of SiO_2 NPs induced a higher concentration of Fe (8.3% and 14.1%) in the leaves. When the concentration of As(V) was 0.2-1.6 mg L^{-1}, the application of 250 mg L^{-1} of SiO_2 NPs induced an increase in the concentration of Fe in the leaves of 13.1%, 49.6%, 37.9% and 20.9%, respectively, compared to the control (Fig. 4B).

Cu concentration in the root was positively affected by the application of SiO_2 NPs in the absence of As(V), presenting an increase of 9.7% and 25.2% at 250 and 1000 mg L^{-1} of SiO_2 NPs, respectively, compared to the control. The presence of As(V), in general, induces a negative effect on the concentration of Cu in the root. However, a positive effect was observed when SiO_2 NPs were applied to each dose of As (V), however at 3.2 mgAs L^{-1} and 250 and 1000 mg L^{-1} of SiO_2 NPs, Cu concentration decreased 19.1% and 32.4% ,respectively (Fig. 4C). The Cu concentration in the leaves only increased 154.6% with the combination of 0.4 mg L^{-1} As(V) and 250 mg L^{-1} SiO_2 NPs, in the rest of the As(V)-SiO_2 NPs interactions the effect was null or negative (Fig. 4D).

The zinc concentration in the root increased by the application of SiO_2 NPs up to 104.5% in relation to the control in the absence of As (V), while in the presence of As (V) increases of up to 58% approximately were observed (Fig. 4E). In the leaves, the zinc concentration increased 94.5% with the concentration of 0.4 mg L^{-1} As (V) with 250 mg L^{-1} SiO_2 NPs. However, also the combination of 0.2 mg L^{-1} As (V) with 1000 mg L^{-1} SiO_2 NPs induced an increase of 55% in relation to the control (Fig. 4F).

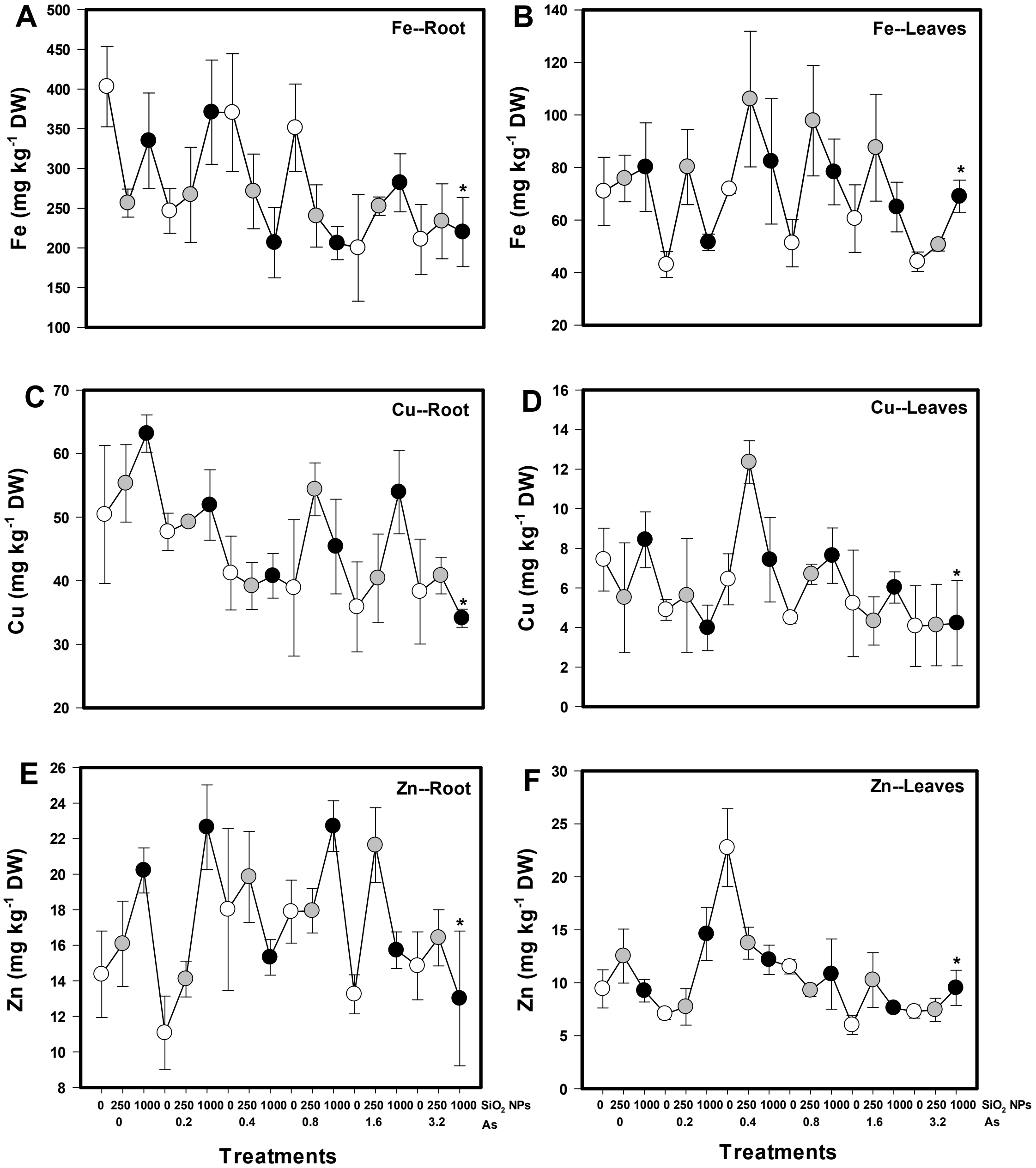

Fig. 4 Effect of the interaction of As (V) and SiO_2 NPs on the concentration of Fe, Cu and Zn in root and leaves of *Solanum lycopersicum*. N= 6 ± standard error. * indicate significant differences according to the Fisher´s Least Significant Difference test (α = 0.05).

3.3 Effect of Arsenic and SiO_2 NPs on Macronutrient Uptake in Root and Leaves

The concentration of K in both root and leaves decreased as the concentration of As(V) in the nutritive solution increased; the decreases were up to 17.8% in root and 22.5% in leaves at the high dose of 3.2 mg L^{-1} of As(V) (Fig. 5A). However, the application of 250 and 1000 mg L^{-1} of SiO_2 NPs induced the opposite effect, since the concentration of K was increased by 46.1% and 68.2% in root, and 23.5% and 33.3% in leaves respectively (Fig. 5B).

The sulfur concentration in the leaves was not affected by the different concentrations of As(V), nor by the application of SiO_2 NPs (Fig. 5C and 5D). However, the sulfur concentration in the root increased 10% with the highest concentration of As(V) (3.2 mg L^{-1}) and 10.5% with the concentration of 0.8 mg L^{-1}. The lowest concentration of As(V) (0.2 mg L^{-1}) induced a decrease of 14.7% in the root sulfur concentration (Fig. 5C). On the other hand, the application of 1000 SiO_2 NPs increased the sulfur concentration in the root 6.7% (Fig. 5D).

The concentration of P was affected by As(V), however the effect was different between the organs of the tomato plant. In the roots, the concentration of P decreased 41.4%, 40.4%, 11.8%, 54.7% and 31.1% with the different concentrations of As(V) (0.2-3.2 mg L^{-1} respectively). In the leaves the P concentration increased 24.6% with the As(V) at concentration of 1.6 mg L^{-1} (Fig. 5E). In the case of the applications of 250 and 1000 mg L^{-1} of SiO_2 NPs, the application induced an increase of 26.9% and 54.9% in the concentration of P in roots and 40.3% and 36.2% in leaves respectively (Fig. 5F).

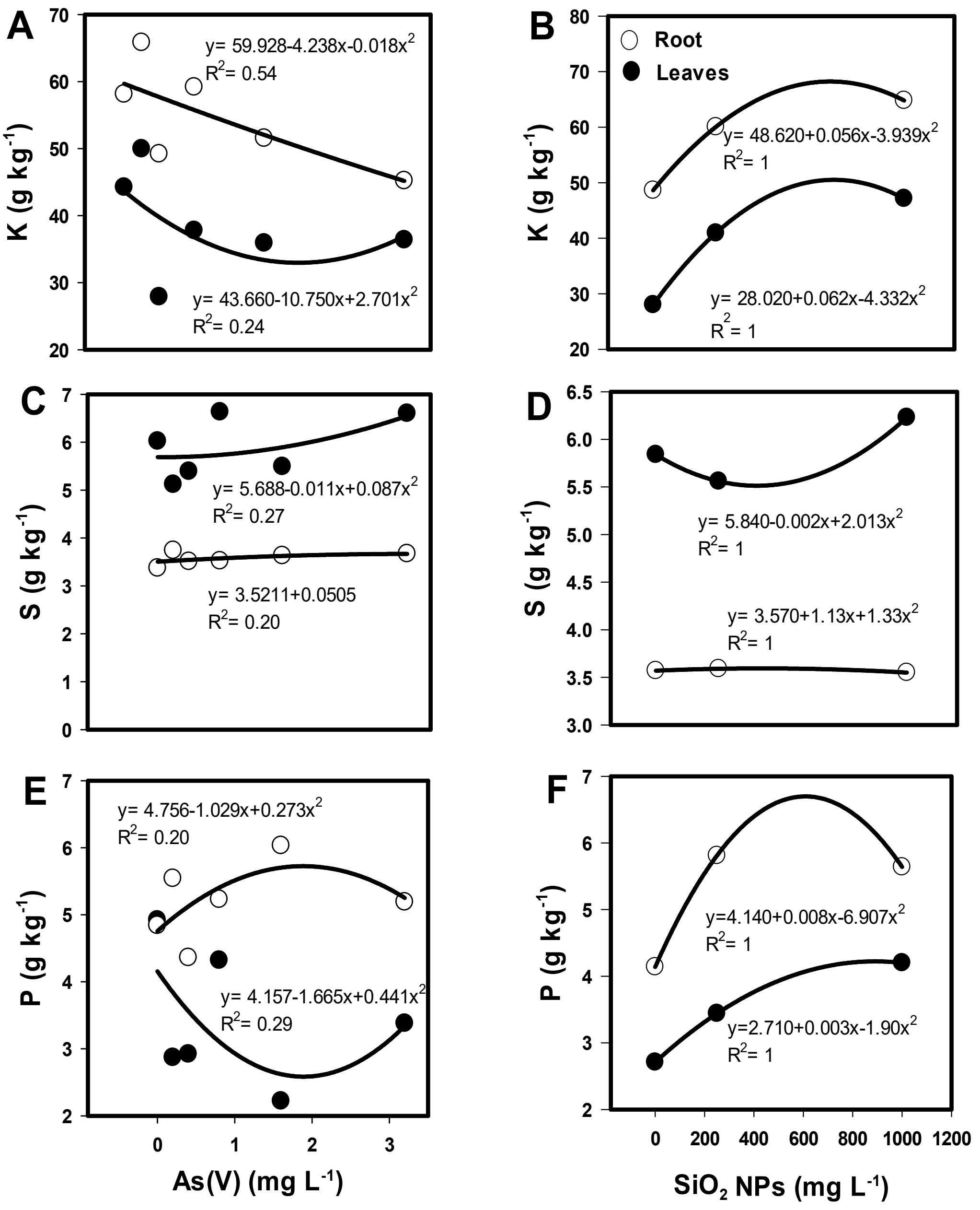

Fig. 5 Relationship between the concentration of K (A, B), S (C, D), and P (E, F) with the concentration of As (V) and SiO_2 NPs in roots and leaves of *Solanum lycopersicum*. The regression curve of As (V) refers to the mean values of three replicates. The regression curve of SiO_2 NPs refers to the mean values of six replicates.

The combination of As(V) with SiO_2 NPs induced changes in potassium concentration both in the root and in the leaves (Fig. 6). In both organs when only SiO_2 NPs were applied, a significant increase in potassium concentration was observed, being 70% in roots and 65.2% in leaves (Fig. 6A and 6B). When SiO_2 NPs were applied in combination with As(V), an increase in potassium was generally observed compared to the application of only As(V), the effect being greater with the concentration of 0.2 mg L^{-1} of As(V) and 1000 mg L^{-1} of SiO_2 NPs the increase was 106.7%.

The sulfur concentration in the root increased 32.5% with the application of 1000 mg L^{-1} of SiO_2 NPs in the absence of As(V). However, the concentration of 0.8 mg L^{-1} of As (V) without application of SiO_2 NPs also increased the content of this element by 43.1% (Fig. 6C). In the leaves, the concentration of 0.8 mg L^{-1} of As(V) without application of SiO_2 NPs increased the sulfur content (44.4%). Furthermore, the combination of 1000 mg L^{-1} of SiO_2 NPs with 1.6 and 3.2 mg L^{-1} of As(V) increased the sulfur concentration by 15.6% and 31.7% respectively (Fig. 6D).

In the absence of As(V), the phosphorus concentration increased significantly in root (37.7% and 117.6%) and leaves (45.5% and 45.1%) with the application of 250 and 1000 mg L^{-1} of SiO_2 NPs (Fig. 6E and 6F). With the presence of As(V) and with the application of 1000 mg L^{-1} of SiO_2 NPs, an increase up to 78.5% was observed in the phosphorus concentration in leaves (Fig. 6F). In the root, the interaction of 1.6 and 3.2 mg L^{-1} of As (V) with 1000 mg L^{-1} of SiO_2 NPs decreased the phosphorus concentration by 12.1% and 17.3% respectively (Fig. 6E).

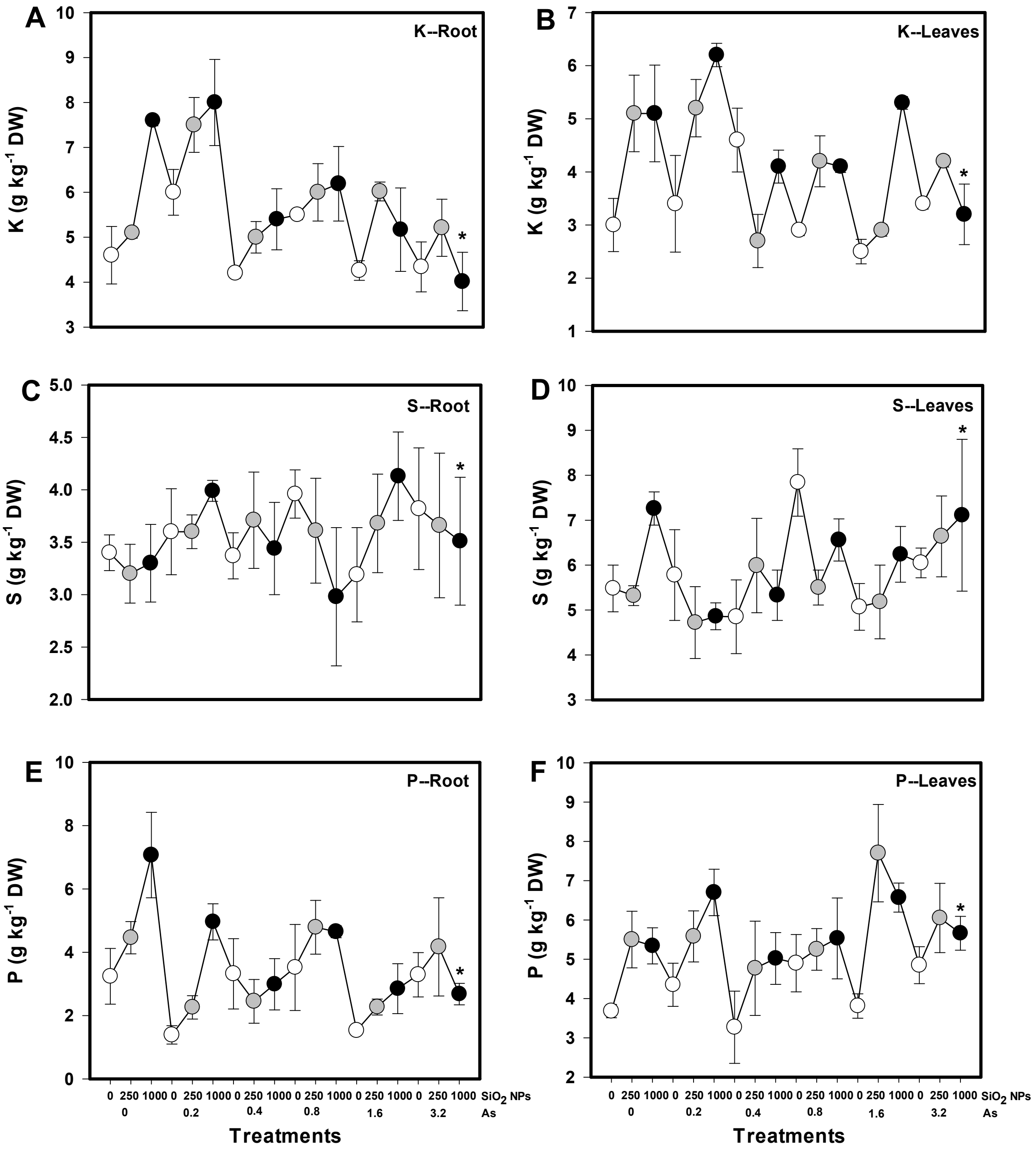

Fig. 6 Effect of the interaction of As (V) and SiO_2 NPs on the concentration of K, S and P in root and leaves of *Solanum lycopersicum*. N= 6 ± standard error. * indicate significant differences according to the Fisher´s Least Significant Difference test ($\alpha = 0.05$).

4 Discussion

4.1 Dry Matter Production

The exposure of plants to As produces growth inhibition, stops the accumulation of biomass and causes physiological disorders in plants, due to the high toxicity of this metalloid (Garg and Singla, 2011; Stoeva et al., 2005). A 50% reduction in dry biomass production has been reported in rice plants grown in nutritive solution with 4.0 mg L^{-1} of As(III) (Wang et al., 2010). Sunflower plants grown in soil contaminated with As(V) reduced root dry weight by up to 60.5% and shoot dry weight by up to 49.2% when exposed to concentrations of 40 and 80 mg kg^{-1} of As(V), respectively (Azeem et al., 2017). However, an increase of 17% of the dry biomass of shoots has also been reported in grafted tomato plants subjected to arsenic stress (100 $\mu g\ L^{-1}$ of As (V) in nutritive solution) (Stazi et al., 2016).

Arsenic can replace phosphate in respiration processes, interrupting cellular metabolism, generating adenosine diphosphate-arsenate (ADP-As) instead of adenosine triphosphate (ATP) (Meharg et al., 1994). Within plant tissue, As(V) is reduced to As(III) by the enzyme arsenate reductase which binds with thiol groups of enzymes and proteins leading to the inhibition of cellular functions (Finnegan and Chen, 2012). There are mechanisms that the plant uses to detoxify itself such as chelation with polypeptides such as glutathione (GSH) and phytochelatins (PC), once chelated, arsenic is stored in the vacuoles of the roots (Liu et al., 2010).

Regardless of the arsenic accumulation and detoxification mechanisms, most of the arsenic in tissue is probably physiologically inert (Santos et al., 2010). In addition, the hormetic effect could be another response caused by arsenic. This is characterized by stimulation at low concentrations and inhibition at high concentrations of heavy metals that takes the form of concentration-response in the form of U or inverted U (Agathokleous et al., 2019). The inverted U shape can be caused by hormesis triggered by non-essential element ions (Poschenrieder et al., 2013).

NPs can be considered biostimulants, since application in small concentrations can increase plant growth (Juárez-Maldonado et al., 2019). This stimulation can be physicochemical in nature through the energy and surface charges of the NPs, which interact with cell walls and membranes, modifying the activity of receptors, transporters and other proteins (Zuverza-Mena et al., 2017). Furthermore, the absorption of NPs is considered as an active transport mechanism that includes other cellular processes such as signaling, recycling and regulation of the plasma membrane (Tripathi et al., 2017a). Once NPs come into contact with plants, they can be absorbed and transported, causing stimulat of antioxidant compounds, improving plant growth, or even causing toxicity (Cox et al., 2016; Pérez-Labrada et al., 2019; Zhang et al., 2018). Ali et al. (2019) reported an increase in root and shoot biomass of 59% and 69% in wheat plants by foliar application of Si NPs at a concentration of 1200 mg L^{-1}. However, it is well known that the effect of NPs on plants will depend on the plant species, route of application, dose, concentration and the physicochemical characteristics of NPs such as type, size and shape (Shalaby et al., 2016; Syu et al., 2014). Regarding SiO_2 NPs, an increase of 25% in dry root biomass and 75% in shoots has been reported in fenugreek plants (*Trigonella foenum-graecum*) (Nazaralian et al., 2017). In *Pisum sativum* plants subjected to chromium stress, the application of 10 µM of Si NPs improves the production of dry biomass (Tripathi et al., 2015). Si NPs have been reported as beneficial, since they can improve the growth of plants subjected to heavy metal stress (Cui et al., 2017; Tripathi et al., 2015). One of the mechanisms of Si NPs is the stimulation of acid exudates through the root such as oxalic acid and polyphenols, which could reduce the toxic effects of aluminum in corn (de Sousa et al., 2019).

4.2 Micronutrients

As can induce stress in the plant due to the impact it generates on the homeostasis of essential elements, by reducing the absorption of some nutrients (D. Kumar et al., 2015). In addition, exposure to As generates anatomical deformations in the root, reduces the cells of the parenchyma, and the size of the xylem cells (Tripathi et al., 2015), which can directly affect nutrient absorption. It can also be attributed to the formation of metal complexes that cannot be absorbed by the root, thus preventing the absorption of essential elements (Khan et al., 2019).

The decrease in micronutrients due to exposure to As is consistent with those reported by (Carbonell-Barrachina et al., 1997). They found that the absorption of B, Cu, Zn and Mg in tomato plants was reduced when they were exposed to arsenite. (Gomes et al., 2012) reported a reduction in Fe that was directly proportional to the increase in As in *Anadenanthera peregrina*.

Radical exudates, such as amino acids, organic acids, sugars, phenolic compounds, and other secondary metabolites (Haichar et al., 2014) can act as natural chelating agents for heavy metals (Kim et al., 2010). It has been reported that under Cd stress the concentration of organic acids (malic, citric, acetic, oxalic, glutamic and formic acids) increases in corn plants as a tolerance mechanism (Javed et al., 2017). It is likely that tomato plants follow this same strategy, since exposure to As induces the exudation of organic acids by the root and the transport of As to the shoots is limited, increasing accumulation in the roots (Carbonell-Barrachina et al., 1997; Madeira et al., 2012; Stazi et al., 2016). Radical exudation may be involved in the stabilization process but could also sequester micronutrients. Under metallic stress (metallic ions, metallic NPs), plants release more low molecular weight substances such as organic acids (oxalate, acetate and malate) as defense against stress (Shang et al., 2019). In particular, citric, oxalic and malic acids form complexes with metals, which affects their fixation, mobility and availability to plants (Xie et al., 2013). The complexation rate between organic acids and Cd has been reported to be significant and can reach 85% with citric acid in the soil solution of *Lupinus* plants (Römer et al., 2000). However, the modification in the exudation of plants under metallic stress can influence the dynamics of soil nutrients and the microbial activity of the rhizosphere (Jia et al., 2014). In addition to the fact that the ability to pump protons by the H^+-ATPases in the plasmalemma of the plant cell decreases under stress by metals, which can affect the assimilation of nutrients (Javed et al., 2017).

4.3 Macronutrients

The decrease in P accumulation probably resulted from phytotoxicity by As (Wang et al., 2002), or because As can replace P (Tu and Ma, 2005). This is due to their analogy, as they both have similar electronic configurations and chemical properties and compete for the same absorption transporters (Meharg and Hartley-Whitaker, 2002). For this reason, P also strongly influences the absorption of As in plants (Anawar et al., 2018). However, although As can replace P in the plant, it cannot perform its biological functions (Tu and Ma, 2005). Tripathi et al. (2015) reported an increase of K and P in root and leaves of *Pisum sativum* seedlings with the addition of Si NPs alone, and also improved absorption even when the seedlings were exposed to Cr(VI). (Alsaeedi et al., 2019) reported an increase in the absorption and concentration of K (52%, 75% and 41% in root, stem and leaves respectively) of *Cucumis sativus* plants with the application of Si NPs. Silicon has the ability to activate H^+-ATPases located in the plasma membrane, which increases cellular absorption of potassium through electrochemical gradients and K^+ channels and transporters (Liang et al., 2006).

NPs are capable of inducing signaling reactions in root cells (Sosan et al., 2016). It is known that the exposure of plants to NPs can modify the growth patterns of roots by altering their morphology (Dimkpa et al., 2015), generating effects such as the proliferation of root hairs that could increase the absorption of nutrients (Adams et al., 2017). On the other hand, the increase in macronutrient concentrations in plants by SiO_2 NPs may be related to a "concentration effect", since shoots and root biomass decreased. (Yang et al., 2020) reported that the concentration of N and P increases in response to the decrease in the height of *Leymus chinensis* and *Stipa krylovii*. The concentration of Mg-Zn in root and K in leaves of *Pfaffia glomerata* increases in response to the decrease in dry root and leaf biomass caused by exposure to 50 µM of As (Gupta et al., 2013).

5 Conclusions

Tomato plants were affected in their growth by both As and SiO_2 NPs, As decreased root and shoot biomass at low concentrations. As stimulated root and shoot biomass at high concentrations. SiO_2 NPs decreaesed them. On the other hand, tomato plants did not show toxicity symptoms, such as chlorosis or necrosis due to the application of As(V) and/or SiO_2 NPs, at any concentrations.

Fe and Cu uptake by roots and root and leaves, respectively, decreased by the presence of As(V) in the nutritive solution, but both nutrients decreased at the highest dose of As(V). The concentration of P decreased in roots dependent of the concentration of As(V); in contrast, the opposite effect occurred in leaves. K and S were not affected by the presence of As(V) in nutritive solution.

The SiO_2 NPs positively influenced the uptake and concentration of Zn and Cu in roots, and Fe in leaves. Also, macronutrients uptake in root and leaves was increased by SiO_2 NPs.

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CONCLUSIONES GENERALES

Los resultados obtenidos en esta investigación resaltan la importancia del efecto estresante que puede tener el arsénico en el fruto del tomate y cómo modifica los compuestos antioxidantes. Dosis bajas de As (0,2 mg L^{-1}) en el agua de riego inducen una mayor acumulación de compuestos antioxidantes; sin embargo, cuando se exponen a altas dosis o cuando interactúan con las NPs SiO_2, parece haber mayor estrés y daño oxidativo que inhiben estos compuestos.

El riego de plantas de tomate con agua contaminada de As provoca un enriquecimiento del sustrato de As y la bioacumulación de As en raíces, tallo y hojas, lo que demuestra que cuanto mayor es la concentración en el agua de riego, más fluye y transloca el contaminante a través de los diferentes estratos de tomate. Las NPs SiO_2 reducen la translocación de As. Además, dentro de cada estrato, el As se acumula preferentemente en el tejido de la hoja en comparación con el tejido del tallo. Las concentraciones bajas de As en el agua de riego (0,2 mg L^{-1}) provocan una disminución del crecimiento de las plantas y del número de hojas, mientras que las concentraciones más altas de As en el agua de riego (0,4-3,2 mg L^{-1}) parecen no inducir una respuesta fitotóxica. El efecto combinado de las NPs SiO_2 y As a altas concentraciones (3,2 mg L^{-1} y 1000 mg L^{-1}) aumenta la producción de pigmentos fotosintéticos y mejora la actividad de CAT y APX.

La absorción de Fe en raíz y Cu en raíz y hojas disminuyó por la presencia de As(V) en la solución nutritiva; La concentración de Zn en la raíz aumentó y la concentración de Fe en las hojas mostró un aumento, pero disminuyó en la dosis más alta de As(V). La concentración de P disminuyó en las raíces de manera dependiente de la concentración de As(V); en cambio, el efecto contrario ocurrió en las hojas. K y S no se vieron afectados por la presencia de As(V) en la solución nutritiva. Los NPs SiO_2 influyeron positivamente en la absorción y concentración de Zn y Cu en raíces y Fe en hojas. Además, la absorción de macronutrientes en la raíz y las hojas aumentó con las NPs SiO_2.

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