CuO nanoparticles modify bioaccumulation of perfluorooctanoic acid in radish (Raphanus sativus L.)

Yang Xu\textsuperscript{a}, Wenchao Du\textsuperscript{b}, Ying Yin\textsuperscript{b}, Yuanyuan Sun\textsuperscript{c}, Rong Ji\textsuperscript{b}, Huan He\textsuperscript{b}, Shaogui Yang\textsuperscript{a}, Shiyin Li\textsuperscript{d}, Jichun Wu\textsuperscript{c} and Hongyan Guo\textsuperscript{b}

*School of Environment, Nanjing Normal University, Nanjing, China; \textsuperscript{b}State Key Laboratory of Pollution Control and Resource Reuse, School of Environment, Nanjing University, Nanjing, China; \textsuperscript{c}State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Surficial Geochemistry, School of Earth Sciences and Engineering, Nanjing University, Nanjing, China

**ABSTRACT**

Research on combined phytotoxicity of perfluorooctanoic acid (PFOA) and nanoparticles is very important for the remediation of PFOA contaminated soil and further assessment for the potential of nano-enhanced phytoremediation. Here, joint effects of PFOA and CuO nanoparticles (nCuO) in plants were studied by exposing radish (Raphanus sativus L.) to PFOA (4 mg/kg) and nCuO (200 and 400 mg/kg) for 30 days, and measuring for contaminant accumulation, radish biomass, photosynthesis profiles and nutrient contents. Results showed that PFOA accumulated highly in radish organs but showed limited effects on radish biomass. nCuO could increase the transfer rate of PFOA from root to shoot and reduce PFOA accumulation in edible root part, but higher nCuO lead to decreased radish biomass. Reversely, PFOA alleviated the adverse effects of nCuO on leaf photosynthesis and root metabolism of vitamins and amino acids. These results provided basics for exploring possibility of nano-enhanced phytoremediation for PFOA soil pollution.

**1. Introduction**

Owing to its neurotoxicity, genotoxicity and development toxicity to endocrine disruption in organisms, perfluorooctanoic acid (PFOA) has been shortlisted in the Stockholm Convention in 2019 [1–3]. However, due to its high stability and unique hydrophilicity, PFOA is still produced for domestic and international demands [4–6]. PFOA has been frequently detected in agricultural soil throughout the world, especially in some hot spots with concentration up to 123.6 µg/kg [2,7]. PFOA can be accumulated in plant’s roots and transported to shoots or other edible parts, posing potential food exposure and threatening human health [3,8–11].

Nano-particles, functioning as regulators, pesticides and fertilizers, have been documented as promising soil amendments in sustainable agriculture [12]. Nanoparticles existing in the soil will alter not only the properties of soil but also the migration, transformation and toxicity of coexisting pollutants [13–16]. Hence, theoretically, it can be assumed that nanoparticles have potential effects on the carryover and bioavailability of PFOA when they coexisting in soil. In particular, metal-based nanoparticles, not only with large surface area but also releasing cations, can interact with PFOA via electrostatic interaction and ligand exchange, and thus affecting PFOA bioavailability [17]. However, there is a lack of research on the interaction between nanoparticles and PFOA in soil-plant system, which is very important for the agricultural product safety and remediation technology development for PFOA contaminated soil.

Here, we conducted an experiment to test the joint effects of PFOA and CuO nanoparticles (nCuO) on radish (Raphanus sativus L.). Radish is a traditionally and widely consumed vegetable in east Asian countries, and nCuO is largely and extensively applied in agriculture as pesticides and biocides [12,18,19]. The uptake and translocation of PFOA and nCuO in radish, and their effects on radish photosynthetic parameters, biomass and nutritional values (total sugar, starch, vitamins and amino acids) were measured.

**2. Experimental**

**2.1. Plant growth and exposure**

Radish (Raphanus sativus L.) seeds were purchased from Wanbang Seed Corporation (Nanjing, China). $^{14}$C-PFOA was purchased from American Radiolabeled Chemicals, Inc. (St. Louis, MO) with a specific radioactivity of 2.035 GBq/mM. Non-labeled PFOA and nCuO were purchased from Sigma-Aldrich Co., St. Louis, MO. According our previous study, nCuO has a primary size at 10–100 nm and zeta potential at $–34.4 \pm 0.5$ mV [19].

**CONTACT** Wenchao Du du@njnu.edu.cn

© 2022 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Commercial soil (potting mix, Miracle Gro* with micromax, Marysville, OH, USA) was thoroughly mixed with PFOA solutions to contain 0 (control) and 4 mg PFOA per kg soil (dry weight). PFOA solutions were prepared by adding $^{14}$C-PFOA and unlabeled PFOA stock solutions to ultrapure water (Milli-Q, Sigma-Aldrich) and homogenized by sonication in a water bath (180 watts x 20°C x 30 min). Subsequently, nCuO suspensions were thoroughly mixed with the spiked soil to contain 0 (control), 200 and 400 mg Cu per kg soil (dry weight). Nanoparticle suspensions were prepared in Millipore water and homogenized using ultrasonic in a 5°C water bath for 30 min. In all, there are six treatments: one for control, soil without any supplementation; one for PFOA treatment, soil amended with PFOA (4 mg kg$^{-1}$); two for nCuO treatments, soil amended with nCuO (200 or 400 mg kg$^{-1}$); two for PFOA+nCuO treatments, soil amended with combination of PFOA (4 mg kg$^{-1}$) and nCuO (200 or 400 mg kg$^{-1}$).

The spiked soil was placed in plastic pots (19 cm diameter x 18 cm height) and seeded 24 h after treatment application. Four replicates for each treatment were allocated in a completely random design. Plants were maintained in a greenhouse with day/night temperatures at 28/20°C, relative humidity at 60%, illumination at 200 µmol·m$^{-2}$·s$^{-1}$ for 14 h photoperiod.

### 2.2. Photosynthetic index analysis

Prior to harvest, chlorophyll contents in cucumber leaves were measured according to the method described by Lichtenthaler and Wellburn [20] at 645 and 663 nm using a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). Net photosynthetic rate (Pn), stomata conductance (Gs), intercellular CO$_2$ concentration (Ci) and transpiration rate (Tr) were measured by a Li-Cor 6800 portable photosynthesis system (Li-Cor Inc., Lincoln, NE). The measurements were carried out at the aforementioned light intensity, with an air flow of 700 µmol s$^{-1}$ through the sample chamber, and a CO$_2$ concentration of 400 µmol mol$^{-1}$ in the sample chamber.

### 2.3. Biomass, copper and PFOA concentration analysis

Thirty days after germination, plants were removed from soil, rinsed with tap water and ultrapure water over 10 times, and separated into root and shoot parts. Plant biomass was then measured after lyophilization. For copper analysis in radish roots and shoots, 100 mg samples of oven dried tissues were digested with HNO$_3$ and HClO$_4$ (4:1, v/v) and adjusted to 10 ml with Millipore water. Element copper was analyzed using an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300 DV, Perkin-Elmer, USA). The recovery for Cu was 94–105%.

Concentrations of PFOA in plants were calculated by the initial $^{14}$C-radioactivity and PFOA concentration in spiked soil. Briefly, 0.1 g plant samples were combusted at 800–900°C in a combustion unit (Ox500 Biological Oxidizer, Zinsser Analytic, Germany), mixed with a scintillation cocktail (Gold Star multipurpose, Meridian Biotechnologies Ltd., UK) and $^{14}$C-activity was quantified by a liquid scintillation counter (LS6500, Beckman Coulter, Brea, CA). The recovery for $^{14}$C-chemicals was tested (79–82%) and subsequently calibrated by radioactivity.

### 2.4. Nutrient contents in radish roots

Amino acid contents were analyzed using external standard method according to 21. Amino acid standards were purchased from Sigma Aldrich Co. St. Samples were ground to a powder in liquid N$_2$ and subsequently dissolved in ultrapure water. Derivatization was performed with an AccQ-Tag Ultra Derivatization Kit (Waters, USA). UPLC-MS analyses were performed using an ultra-performance liquid chromatography (UPLC, U3000 DGLC, Thermo Fisher, USA) containing an ACCQ-Tag TMULTRA C18 column (1.7 µm, 2.1 × 100 mm, Waters, USA).

Vitamin B and C contents were analyzed using external standard method according to 22. Radish root at 200 mg was extracted using 500 µL 80% methanol (containing 1% acetic acid) and ultrasonice for 15 min. The supernatant was centrifuged at 12,000 rpm for 10 min. Repeated extraction for 3 times, and collected the supernatant into a tube for determination. Vitamin contents were extrapolated from a standard curve by Liquid Chromatography Mass Spectrometry (LC-MS, DGLC-QE, Thermo Fisher, USA). Starch contents were analyzed using glucose standard calibration curve at 510 nm according to 23. Total sugar content was quantified from the glucose standard calibration curve at 620 nm according to 24.

### 2.5. Statistical analyses

The data were expressed as mean ± standard deviation (n = 4). Statistical significance of differences among treatments was evaluated by one-way analyses of variance (ANOVA) performed by SPSS (IBM Statistics 22). Reference to a significant difference between treatments was based on a probability of p < 0.05.

### 3. Results and discussion

#### 3.1. PFOA and Cu accumulation

PFOA accumulation in radish roots and shoots is presented in Figure 1. Contents of $^{14}$C-activity chemicals were 1.55–2.18 mg/kg in roots and 3.46–4.44 mg/kg in shoots after PFOA exposure. PFOA in the radish shoots
was approximately 2-fold higher than that in roots, hypothesizing that phytoremediation could be considered for PFOA contaminated soil [8,25]. Generally, the adsorption affinity of long-chain compounds in plant is dependent on compound hydrophobicity, so PFOA was thought more efficiently adsorbed to root but less available for translocation through transpiration stream [26,27]. However, radish roots, unlike a typical dicotyledonous root, are primarily consist of vascular tissue, lacking the Casparian strip as barrier to prevent PFOA’s transport from roots to shoots [8]. Consequently, PFOA was found concentrated in radish shoots.

Notably, nCuO significantly increased the transport of PFOA to shoots by 11% and 28% for 200 mg/kg and 400 mg/kg, respectively. nCuO could remodify the protein receptor that regulate the transport of PFOA or mechanically damage the structure of membranes, promoting the PFOA translocation [12,28]. Besides, PFOA may be transferred to leaves by adsorbing on the surface of nCuO [16]. Although the dissolution of nCuO proceeded all the time, the particles of CuO still existed even after 88 days of culture [15]. nCuO could adsorb PFOA through electrostatic interaction and ligand exchange and thus affect distribution of PFOA in plants [14].

Meanwhile, PFOA also modified Cu accumulation in roots and upward transport to leaves (Figure 2). nCuO alone significantly improved Cu contents, tested 0.29–0.63 mg/kg in roots and 28–72 mg/kg in shoots, but without difference between 200 mg/kg and 400 mg/kg. The periderm, a layer of dead cells covering the radish root, has a clear capacity to adsorb and retain a large amount of nCuO and Cu$^{2+}$ released from nCuO [29]. So, nCuO with high dissolution rate and the translocation could promote Cu accumulation in shoots [28]. Here, PFOA obviously promoted the uptake of Cu in radish roots but not changed Cu upward transfer to leaves, indicating that PFOA may increase Cu bioavailable forms’ proportion via the desorption of Cu from soil, functioning as low-molecular-weight organic acids (LMWOAs) [30,31]. The dissolution and aggregation of nCuO were generally affected by numerous soil conditions such as pH, organic matter, ionic species and colloids [32]. Especially, organic acids may absorb on the surface of nCuO through electrostatic interaction or complex with free Cu$^{2+}$ ions by ligand exchange [31,32]. So, PFOA could adsorb on the nCuO surface by the carboxyl group, or form a complex with Cu through sequestration or ion exchange, decreasing the adsorption of Cu and increasing the availability of Cu in soil [14,33,34]. However, the PFOA-Cu complex may have a different transport behavior from individual Cu, so the limited adsorption sites of radish roots and the finite amount of Cu transporters may restrict the uptake and the translocation of Cu in radish [35,36].

![Figure 1](image.png)

Figure 1. Concentrations of PFOA in shoots and roots of radish plants grown for 30 days in PFOA polluted soil (4 mg/kg) amended with CuO nanoparticles at 0, 200 and 400 mg/kg. Data are means of four replicates ± standard deviation. Different letters among columns indicate statistically significant differences at p < 0.05.

3.2. Effects on radish photosynthetic parameters and final biomass

PFOA alone showed no obvious effect on chlorophyll contents in radish leaves, while nCuO at 400 mg/kg significantly reduced the contents of chlorophyll b (Figure 3A). Further disturbance in chloroplast electron-transport system were reflected by changes in Pn, Tr, and Fv/Fm value as shown in Figure 3. Pn is
Figure 2. Concentrations of Cu in shoots and roots of radish plants grown for 30 days in soil amended with PFOA at 0, and 4 mg/kg and CuO nanoparticles at 0, 200 and 400 mg/kg. Data are means of four replicates ± standard deviation. Different letters among columns indicate statistically significant differences at p < 0.05.

Figure 3. (A) Chlorophyll (Chl, mg/g fresh weight), (B) Net photosynthetic rate (Pn; µmol m⁻² s⁻¹), (C) Transpiration rate (Tr, mmol m⁻² s⁻¹), and (D) Fv/Fm value in leaves of radish plants grown for 30 days in soil amended with PFOA at 0, 4 mg/kg and CuO nanoparticles at 0, 200 and 400 mg/kg. Data are means of four replicates ± standard deviation. Different letters among columns indicate statistically significant differences at p < 0.05. (Not changed: intercellular CO₂ concentration (Ci; µmol mol⁻¹), and stomata conductance (Gs; mmol m⁻² s⁻¹)).
a reliable method for gauging the primary production of plants; Fv/Fm value is a useful way to detect disturbances in the photosynthetic system caused by various stressors [37]. PFOA caused no obvious change in such two indices, while nCuO at 400 mg/kg lead to an obvious reduce. Nanoparticles may generate reactive oxygen species (ROS) and decrease leaves’ chlorophyll contents, subsequently reducing PSII reaction centers and inhibiting electron transport from the water splitting system to Qb reduction [38–40]. In addition, transpiration rate was thought playing an important role in the transport of perfluorinated compounds in plants [8,41]. But, here there was no change observed in transpiration rate, revealing that changed PFOA accumulation in radish shoots were not result from the disturbance of nCuO to plant transpiration. The specific reasons need further research. Still, it demonstrated that nanoparticles have the ability to redistribute organic compounds in plants [16,36,42].

Figure 4 shows the biomass of final harvest radish. nCuO alone caused a significant decrease in root and shoot biomass, while PFOA showed limited effects. Accumulation of Cu in plant could decrease the chlorophyll contents, inhibit the photosynthesis, and finally reduce plant biomass [15]. Notably, PFOA significantly alleviated such reduce in biomass by nCuO, even though PFOA increased the accumulation of Cu in radish roots. PFOA, functioning as LMWOAs, may enhance the bioavailability of metal nutrients in soil [31]. But, as a kind of organic acid, it could also hinder dissolution of nCuO via blocking the active sites of nCuO surface [13]. nCuO assumed to be retained in tissue as PFOA-Cu complex through strong COO-binding group [43].

### 3.3. Changed nutrients in radish

Figure 5 and Table S1 present the summary statistics for changed nutrients in harvest radish roots. PFOA alone showed limited modification in radish nutrient except for an increase in biotin (VB7) when compared with control. Biotin, as an essential cofactor related to carboxylation reactions, was increased by PFOA, indicating that PFOA caused some disturbance in carbon and energy metabolism [44]. While nCuO alone obviously disturbed metabolism of starch, amino acids, and vitamin. Especially, nCuO at 400 mg/kg decreased contents of starch, asparagine (Ser) and VC by 9%, 31% and 16%, but increased those of serine (Ser), alanine (Ala) and VB7 by 19%, 22% and 49%, respectively. It indicated that nCuO could disturbed the metabolism of carbohydrate, amino acid and vitamin, some of which are related to energy status maintenance such as glycolysis and the TCA cycle [38,45]. Decline in starch contents was consistent with the reduction in chlorophyll contents, implying that nCuO has negative effects on the metabolism of carbohydrate [46]. Higher Ala accumulating indicated that excessive accumulation of Cu led to the breakdown of protein synthesis [47,48]. Besides, changes in Ser and Asn contents indicated a reprogramming of nitrogen and sulfur metabolism may occur in radish roots to

![Figure 4. Biomass of shoots and roots of radish plants grown for 30 days in soil amened with PFOA at 0 and 4 mg/kg and CuO nanoparticles at 0, 200 and 400 mg/kg. Data are means of four replicates ± standard deviation. Different letters among columns indicate statistically significant differences at p < 0.05.](image)
modulate carbon, nitrogen and sulfur status [49,50]. Ser, as an important precursor of cysteine (Cys) synthesis, may contribute to the biosynthesis of glutathione (GSH), an essential component of resistance systems to heavy metals [51]. Nicotinic acid (VA5) and ascorbic acid (VC) are associated with the antioxidant systems in plants, so their up-regulation indicated the generation of ROS by nCuO [52,53]. nCuO also inhibited the biosynthesis of folic acid (VB9), a cofactor consisted with one-carbon (C1) biosynthesis, implying an inhibition of cell division and consequent decrease in root biomass [54].

Compared with individual nCuO (400 mg/kg) exposure, combined PFOA and nCuO (400 mg/kg) led to obvious up-regulation in Asn and Ser, and down-regulation in Ala, indicated that PFOA partially alleviated the toxicity of nCuO to radish nutrients. This was contrary to the content trend of Cu in roots, indicated that PFOA might change Cu form in plant, might as PFOA-Cu complex, and thus inhibited copper toxicity [43]. Accumulation of Asn was related to a nitrogen storage pathway and reflected plant response to the abiotic stresses [55]. And recovery in Ser and Ala contents also reflected the restoration of nitrogen metabolism, sulfur metabolism, and protein synthesis [50,56]. PFOA also increased the contents of VB9, indicating the recovery of cell division process, in correspondence with the restoration of radish biomass [54]. PFOA may activate a stress protective strategy in plants or directly interact with nCuO to inhibit the negative effect of nCuO [17]. However, both nCuO (400 mg/kg) alone and its combination with PFOA significantly reduced starch contents in roots, which may ascribe to the disturbance in the starch biosynthesis. In addition, the nutrient value of radish is mainly dependent on the above bio-molecules such as starch, folic acid and ascorbic acid, which are essential for plant and human growth. As the application of nCuO at high concentration slightly inhibited the growth of plants, so it is essential to control dose of nCuO in handling PFOA risk to food safety. Besides, the antagonism between nCuO and PFOA could reduce some adverse effects of nCuO on plant growth and expand the safety concentration of nCuO application.

4. Conclusions

How nanoparticles will affect plant utilization and toxicity of PFOA was assessed, and results confirmed that nCuO at appropriate dose could redistribute PFOA in plant, increasing transport to aboveground part and decreasing accumulation in edible part. This work highlighted that nanoparticles have potential to regulate PFOA risk in agriculture field and enhance phytoremediation, but attention should be focused on the application
concentration and mode in practice. Further studies are needed to expand more kinds of nanoparticles and explore the underlying mechanism.

Acknowledgments

This research work was supported by the National Natural Science Foundation of China (grant nos. 42077116 and 42077109).

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the National Natural Science Foundation of China [42077109,42077116].

References

[1] Lau C, Anitole K, Hodes C, et al. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol Sci. 2007;99(2):366–394.
[2] Li P, Oyang X, Xie X, et al. Perfluorooctanoic acid and perfluorooctane sulfonate co-exposure induced changes of metabolites and defense pathways in lettuce leaves. Environ Pollut. 2020;256:113512.
[3] Zhang M, Wang P, Lu Y, et al. Bioaccumulation and human exposure of perfluoroalkyl acids (PFAAs) in vegetables from the largest vegetable production base of China. Environ Int. 2020;135:105347.
[4] Eun H, Yamazaki E, Taniyasu S, et al. Evaluation of perfluoroalkyl substances in field-cultivated vegetables. Chemosphere. 2020;229:124758.
[5] Liu Z, Lu Y, Wang P, et al. Pollution pathways and release estimation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFQA) in central and eastern China. Sci Total Environ. 2017;580:1247–1256.
[6] Wang YW, Fu JJ, Wang T, et al. Distribution of perfluorooctane sulfonate and other perfluoroochemicals in the ambient environment around a manufacturing facility in China. Environ Sci Technol. 2010;44(21):8062–8067.
[7] Brusseau ML, Anderson RH, Guo B, et al. PFAS concentrations in soils: background levels versus contaminated sites. Sci Total Environ. 2020;740:140017.
[8] Blaine AC, Rich CD, Sedlacko EM, et al. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. Environ Sci Technol. 2014;48(14):7858–7865.
[9] Ghisi R, Vamerali T, Manzetti S, et al. Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: a review. Environ Res. 2019;169:326–341.
[10] Wen B, Li L, Zhang H, et al. Field study on the uptake and translocation of perfluoroalkyl acids (PFAAs) by wheat (Triticum aestivum L.) grown in biosolids-amended soils. Environ Pollut. 2014;184:547–554.
[11] Wen B, Wu Y, Zhang H, et al. The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils. Environ Pollut. 2016;216:682–688.
[12] Zhao L, Lu L, Wang A, et al. Nano-biotechnology in agriculture: use of nanomaterials to promote plant growth and stress tolerance. J Agric Food Chem. 2020;68(7):1935–1947.
[13] Asadishad B, Chahal S, Akbari A, et al. Amendment of agricultural soil with metal nanoparticles: effects on soil enzyme activity and microbial community composition. Environ Sci Technol. 2018;52(4):1908–1918.
[14] Liu J, Simms M, Song S, et al. Physiological effects of copper oxide nanoparticles and arsenic on the growth and life cycle of rice (Oryza sativa ‘Koshihikari’). Environ Sci Technol. 2018;52(23):13728–13737.
[15] Peng C, Xu C, Liu Q, et al. Fate and transformation of CuO nanoparticles in the soil-rice system during the life cycle of rice plants. Environ Sci Technol. 2017;51(9):4907–4917.
[16] Wu X, Wang W, Zhu L, et al. Enhanced organic contaminants accumulation in crops: mechanisms, interactions with engineered nanomaterials in soil. Environ Pollut. 2018;240:51–59.
[17] Deng R, Lin D, Zhu L, et al. Nanoparticle interactions with co-existing contaminants: joint toxicity, bioaccumulation and risk. Nanotoxicology. 2017;11(5):591–612.
[18] Servin A, Elmer W, Mukherjee A, et al. A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield. J Nanopart Res. 2015 17.92.
[19] Wang YJ, Lin YJ, Xu YW, et al. Divergence in response of lettuce (var. ramosa Hort.) to copper oxide nanoparticles/microparticles as potential agricultural fertilizer. Env Pollut Bioavail. 2019;31(1):80–84.
[20] Lichtenthaler Hartmut, K, Wellburn Alan R. Determinations of total carotenoids and chlorophylls a and b of leaf extracts in different solvents. Biochem Soc Trans. 1983;11(5):591–592.
[21] Cohen SA, Michaud DP. Synthesis of a fluorescent derivatizating reagent, 6-aminoinquinoyl-N-hydroxysuccinimidyl carbamate, and its application for the analysis of hydrolysate amino acids via high-performance liquid chromatography. Anal Biochem. 1993;211(2):279–287.
[22] Li KT, Moulin M, Mangel N, et al. Increased bioavailable vitamin B6 in field-grown transgenic cassava for dietary sufficiency. Nat Biotechnol. 2015;33:1029–1032.
[23] Smith AM, Zeeman SC. Quantification of starch in plant tissues. Nat Protoc. 2006;1(3):1342–1345.
[24] Verma S, Dubey RS. Effect of cadmium on soluble sugars and enzymes of their metabolism in rice. Biol Plant. 2001;44(1):117–123.
[25] Lechner M, Knapp H. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant and distribution to the different plant compartments studied in cultures of carrots (Daucus carota ssp. Sativus), potatoes (Solanum tuberosum), and cucumbers (Cucumis Sativus). J Agric Food Chem. 2011;59(20):11011–11018.
[26] Bizakarguenaga E, Zabaleta I, Mijangos L, et al. Uptake of perfluorooctanoic acid, perfluorooctane sulfonate and perfluorooctane sulfonamide by carrot and lettuce from compost amended soil. Sci Total Environ. 2016;571:444–451.
[27] Muller CE, LeFevre GH, Timofte AE, et al. Competing mechanisms for perfluoroalkyl acid accumulation in plants revealed using an arabidopsis model system. Environ Toxicol Chem. 2016;35(5):1138–1147.
[28] Yuan J, He A, Huang S, et al. Internalization and phytotoxic effects of CuO nanoparticles in arabidopsis thaliana as revealed by fatty acid profiles. Environ Sci Technol. 2016;50(19):10437–10447.

[29] Ebbs SD, Bradfield SJ, Kumar P, et al. Accumulation of zinc, copper, or cerium in carrot (Daucus carota) exposed to metal oxide nanoparticles and metal ions. Environ Sci Nano. 2016;3(1):114–126.

[30] Qin F, Shan XQ, Wei B, et al. Effects of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils. Chemosphere. 2004;57(4):253–263.

[31] Zhao S, Fan Z, Sun L, et al. Interaction effects on uptake and toxicity of perfluoroalkyl substances and cadmium in wheat (Triticum aestivum L.) and rapeseed (Brassica campestris L) from co-contaminated soil. Ecotoxicol Environ Saf. 2017;137:194–201.

[32] Rajput V, Minkina T, Sushkova S, et al. ZnO and CuO nanoparticles: a threat to soil organisms, plants, and human health. Environ Geochem Health. 2020;42(1):147–158.

[33] Huang G, You J, Zhou X, et al. Effects of low molecular weight organic acids on Cu accumulation by castor bean and soil enzyme activities. Ecotoxicol Environ Saf. 2020;203:110983.

[34] Rodea-Palomares I, Leganes F, Rosal R, et al. Toxicological interactions of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) with selected pollutants. J Hazard Mater. 2012;201-202:209–218.

[35] Liu J, Wolfe K, Potter PM, et al. Distribution and speciation of copper and arsenic in rice plants (Oryza sativa japonica Koshikihari) treated with copper oxide nanoparticles and arsenic during a life cycle. Environ Sci Technol. 2019;53(9):4988–4996.

[36] Wen B, Huang R, Wang P, et al. Effect of complexation on the accumulation and elimination kinetics of cadmium and ciprofloxacin in the earthworm Eisenia fetida. Environ Sci Technol. 2011;45(10):4339–4345.

[37] Pietrini F, Passatore L, Fischetti E, et al. Evaluation of morpho-physiological traits and contaminant accumulation ability in Lemna minor L. treated with increasing perfluorooctanoic acid (PFOA) concentrations under laboratory conditions. Sci Total Environ. 2019;695:133828.

[38] Hu XG, Lu KC, Mu L, et al. Interactions between graphene oxide and plant cells: regulation of cell morphology, uptake, organelle damage, oxidative effects and metabolic disorders. Carbon. 2014;80:665–676.

[39] Perreault F, Samadani M, Dewez D, et al. Effect of soluble copper released from copper oxide nanoparticles solubilisation on growth and photosynthetic processes of Lemna gibba L. Nanotoxicology. 2014;8(4):374–382.

[40] Saison C, Perreault F, Daigle JC, et al. Effect of core-shell copper oxide nanoparticles on cell culture morphology and photosynthesis (photosystem II energy distribution) in the green alga, chlamydomonas reinhardtii. Aquat Toxicol. 2010;96(2):109–114.

[41] Yu PF, Xiang L, Li XH, et al. Cultivar-dependent accumulation and translocation of perfluorooctanesulfonate among lettuce (Lactuca sativa L.) cultivars grown on perfluorooctanesulfonate-contaminated soil. J Agric Food Chem. 2018;66(50):13096–13106.

[42] Roche RD, Pagano L, Majumdar S, et al. Co-exposure of imidacloprid and nanoparticle Ag or CeO2 to Cucurbita pepo (zucchini): contaminant bioaccumulation and translocation. Nanoimpact. 2018;1:136–145.

[43] Bonilla-Bird NJ, Paez A, Reyes A, et al. Two-photon microscopy and spectroscopy studies to determine the mechanism of copper oxide nanoparticle uptake by sweet potato roots during postharvest treatment. Environ Sci Technol. 2018;52(17):9954–9963.

[44] Smith AG, Croft MT, Moilin M, et al. Plants need their vitamins too.Curr Opin Plant Biol. 2007;10(3):266–275.

[45] Li R, Zhu Y. The primary active components, antioxidant properties, and differential metabolite profiles of radish sprouts (Raphanus sativus L.) upon domestic storage: analysis of nutritional quality. J Sci Food Agr. 2018;98(15):5853–5860.

[46] Turakainen M, Hartikainen H, Seppanen MM, et al. Effects of selenium treatments on potato (Solanum tuberosum L) growth and concentrations of soluble sugars and starch. J Agric Food Chem. 2004;52(17):5378–5382.

[47] Monselise EB, Parola AH, Kost D, et al. Low-frequency electromagnetic fields induce a stress effect upon higher plants, as evident by the universal stress signal, alaline. Biochem Biophys Res Commun. 2003;302(2):427–434.

[48] Pavlikova D, Zemanova V, Prochazkova D, et al. The long-term effect of zinc soil contamination on selected free amino acids playing an important role in plant adaptation to stress and senescence. Ecotoxicol Environ Saf. 2014;100:166–170.

[49] Majumdar S, Pagano L, Wohlschlegel JA, et al. Proteomic, gene and metabolite characterization reveal the uptake and toxicity mechanisms of cadmium sulfate quantum dots in soybean plants. Environ Sci Nano. 2019;6(10):3010–3026.

[50] Watanabe M, Tohge T, Fernie AR, et al. The effect of single and multiple SERAT mutants on serine and sulfur metabolism. Front Plant Sci. 2018;9:702.

[51] Freeman JL, Persans MW, Nieman K, et al. Nickel and cobalt resistance engineered in Escherichia coli by overexpression of Serine Acetyltransferase from the nickel hyperaccumulator plant thlaspi goingense. Appl Environ Microbiol. 2005;71(12):8627–8633.

[52] Berglund T, Wallstrom A, Nguyen TV, et al. Nicotinamide; antioxidant and DNA hypomethylating effects in plant cells. Plant Physiol Biochem. 2017;118:551–560.

[53] Ghosh T, Srivastava SK, Gaurav A, et al. A combination of linalool, vitamin C, and copper synergistically triggers reactive oxygen species and DNA damage and inhibits Salmonella enterica subsp. enterica Serovar Typhi and Vibrio fluvialis. Appl Environ Microbiol. 2019;85(4):e02487–18.

[54] Burguieres E, McCue P, Kwon YH, et al. Effect of vitamin C and folic acid on seed vigour response and phenolic-linked antioxidant activity. Biosensour Technol. 2007;98(7):1393–1404.

[55] Postles J, Curtis TY, Powers SJ, et al. Changes in free amino acid concentration in rye grain in response to nitrogen and sulfur availability, and expression analysis of genes involved in asparagine metabolism. Front Plant Sci. 2016;7:917.

[56] Pavlik M, Pavlikova D, Staszkova L, et al. The effect of arsenic contamination on amino acids metabolism in Spinacia oleracea L. Ecotoxicol Environ Saf. 2010;73(6):1309–1313.