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Differential sensitivity of light-harnessing photosynthetic events in wheat and sunflower to exogenously applied ionic and nanoparticulate silver

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HIGHLIGHTS

- Ag-NPs, unlike Ag^+, do not perturb light harnessing photosynthetic machinery.
- Ag-NPs, unlike Ag^+, do not perturb polyphasic Chl a fluorescence transients.
- Photosynthetic events in wheat than in sunflower are more sensitive to Ag^+.
- Uptake of ionic Ag by plants is significantly higher than nanoparticulate Ag.
- Ag^+ is translocated to leaves in wheat, but detained by the stem in sunflower.

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ABSTRACT

Potential impacts of inevitable leaks of silver nanoparticles (AgNPs) into environment on human beings need attention. Owing to the vitality of photosynthesis in maintaining life and ecosystem functioning, impacts of exogenously applied nanoparticulate and Ag^+ on photosystem (PS)II function, which governs overall photosynthesis, in wheat and sunflower were evaluated. PSII efficiency and related Chl *a* fluorescence kinetics of these two plants remained unaffected by AgNPs. However, Ag^+ caused a significant decline in the PSII activity and related fluorescence steps in wheat, but not in sunflower. Electron flow between Q_A and PQ pool was found most sensitive to Ag^+. Number of active reaction centers, electron transport, trapping of absorbed light for photochemistry, and performance index declined, while dissipation of absorbed light energy as heat significantly increased in wheat exposed to Ag^+. Total antioxidant activity in sunflower was least affected by both Ag and AgNPs. In contrast, in the case of wheat, the antioxidant activity was declined by Ag^+ but not by AgNPs. Further, the amount of silver absorbed by plants exposed to Ag^+ was higher than that absorbed by plants exposed to AgNPs. While wheat retained majority of Ag in its roots, sunflower showed major Ag accumulation in stem. Photosynthetic events in sunflower, unlike wheat, were least affected as no detectable Ag levels was recorded in their leaves. Our findings revealed that AgNPs seemed non/less-toxic to light harnessing photosynthetic machinery of wheat, compared to Ag^+. Photosynthetic events in sunflower were not affected by Ag^+, either, as its translocation to leaves was restricted.

Abbreviations: ABS, absorbed energy flux; Chl, chlorophyll; CSo, cross section or leaf area; DIo, energy flux dissipated as heat; EDX, energy dispersive X-ray; ETo, electron transport; Fv, variable fluorescence; Fm, maximal fluorescence; OJIP, polyphasic fast Chl *a* fluorescence transients, where O and P refer to minimal and maximal fluorescence, and J and I are inflections between O and P; PQ, plastoquinone; PS II, photosystem II; Q_A, Quinone; RC, reaction center; TRo, trapping of absorbed light energy; ϕPo, quantum yield of primary photochemistry (Fv/Fm); ψEo, Quantum yield of electron transport; SAED, selected area electron diffraction; TEM, transmission electron microscope.

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1. Introduction

Silver nanoparticles (AgNPs) are the most widely used engineered NPs. Owing to their exceptional physicochemical and antimicrobial properties, AgNPs find immense applications in engineering, medicine, agriculture and environment (Rai et al., 2009; Fabrega et al., 2011; Yamal et al., 2013; Shabnam et al., 2016). This has led to a rapid and tremendous increase in demand-based production and usage of AgNPs. Indeed, AgNPs have become an integral part of consumer products such as cosmetics, textiles, hospitals, food packaging industries, water purification, paints, etc. that are commonly used in our daily life (Rai et al., 2009; Pardha-Saradhi et al., 2014; Arruda et al., 2015). Release of NPs into the environment from various consumer products has been reported earlier (Benn and Westerhoff, 2008; Kaegi et al., 2010; Gondikas et al., 2014; Kunniger et al., 2014). Based on previous records, Ellis et al. (2018) recently reported that (i) the annual production of nano-products increased from 10 tons in 2011 to 300 tons in 2015; and (ii) estimated levels of AgNPs in sediments, sludge, treated soils and surface water are 30.1 mg kg^{-1}, 2.3 mg kg^{-1}, 2.3 mg kg^{-1} and 2.2 mg L^{-1}, respectively. The inevitable release of AgNPs into our surroundings and apprehensions of its likely negative impact(s) on living beings including humans have drawn attention of scientists, policy makers and regulatory bodies (e.g., World Health Organization, Environmental Protection Agencies, European Commission etc.) (Duvall and Wyatt, 2011). The established findings revealing negative impacts of AgNPs on mammalian cells including human ones further add to the concern on potential leaks of AgNPs into environment; accordingly, impact of metal-NPs on living systems has been being investigated by researchers across the globe for over a decade. AgNPs cause toxicity to mammalian skin, liver, lung, brain, vascular system and reproductive organs (Nel et al., 2006; Ahamed et al., 2010). These AgNPs can induce genes associated with cyclic progression of cells to get damaged, resulting in complete cell apoptosis (Ahamed et al., 2010).

Significant work has been carried out on impacts of AgNPs on both freshwater and marine biota which include daphnids, fish, etc. (Navarro et al., 2008; Chae et al., 2009; Zhao and Wang, 2011; Lapresta-Fernandez et al., 2012; Oukarroum et al., 2012, 2013). Similarly, enormous work has been carried out to evaluate the impact of AgNPs on a variety of microorganisms: in particular, a negative impact on the integrity of plasma membrane (Bao et al., 2015). Although there are numerous studies on impact of AgNPs on plants, most of these are fragmentary or limited to few growth parameters (such as seed germination, length and fresh/dry weight of root/shoot), inadequate anatomical studies, F_v/F_m, Chl content, transpiration and some components of an antioxidant system (Stampoulis et al., 2009; Gubbins et al., 2011; Jiang et al., 2012; Sharma et al., 2012; Yin et al., 2012, 2012; Qian et al., 2013; Yasur and Rani, 2013; Nair and Chung, 2014). Some of these studies showed positive/non-inhibitory effects of AgNPs on growth of a few plant species (Yin et al., 2011; Sharma et al., 2012; Vannini et al., 2014; Yasur and Rani, 2013; Zuverza-Mena et al., 2016). In contrast, there are also reports on negative impacts of AgNPs on plants (Lin and Xing, 2007; Kumari et al., 2009; Stampoulis et al., 2009; Yin et al., 2011; Qian et al., 2013; Thuesombat et al., 2014; Zuverza-Mena et al., 2016). The AgNPs induced negative impact is believed to be mediated through the release of Ag ions (Vannini et al., 2014; Arruda et al., 2015). Ag^+-induced negative impact may be related to its potential to replace Cu from Cu-containing/dependent biomolecules/receptors such as the ethylene (an important and only gaseous key plant growth regulator) receptor (McDaniel and Binder, 2012; Shabnam et al., 2017).

Recently, it was reported that ionic silver (i.e., Ag^+) is more toxic to light harnessing photosynthetic machinery of *Spirodela polyrhiza*, an aquatic plant, than AgNPs (Shabnam et al., 2017). Photosynthesis is the key metabolic event that governs plant growth (or development) and overall productivity (Shabnam and Pardha-Saradhi, 2016; Shabnam et al., 2017). It is well established that the CO_2 fixation and productivity of a plant rely largely on the light harvesting photosynthetic machinery, in particular PS II (Shabnam et al., 2017; Shabnam and Pardha-Saradhi, 2016). Hence, in the present study, the impact of exogenously applied AgNPs and Ag^+ on light harnessing photosynthetic events in two distinct crop plants, namely, wheat (an important cereal crop) and sunflower (an important oil yielding crop) was evaluated. In this communication, we report for the first time that (i) nanoparticle species of Ag do not have any negative impact on the light harnessing photosynthetic machinery and antioxidant potential; and (ii) wheat responds differentially to Ag^+ compared to sunflower based on a significant variation in translocation of Ag ions into their leaves.

2. Materials and methods

Seeds of *Triticum aestivum* L. (cv. 1544) (wheat, Poaceae) were obtained from the Indian Agricultural Research Institute (Delhi, India). Seeds of *Helianthus annuus* L. (DRSF-108) (sunflower, Asteraceae) were obtained from the Directorate of Oil Seeds Research, Hyderabad (Telangana, India).

2.1. Synthesis and harvest of silver nanoparticles

Silver nanoparticles were prepared by autoclaving 0.5 mM $AgNO_3$ supplemented with 0.1% yeast extract at 121 °C under a pressure of 1.06 kg cm^{-2} for 20 min (Yamal et al., 2013). Subsequent to cooling the solution; AgNPs were harvested through centrifugation at 28000 × *g*. The pellet obtained was then washed with deionized. The later was achieved through steps involving resuspension of the pellet in deionized water and centrifugation at least three times. Subsequently, the resultant washed AgNP pellet was dried in a desiccator at room temperature and homogenized to obtain a fine uniform powder. A 1000 ppm (i.e., 1000 mg L^{-1}) stock solution was prepared by sonicating the suspension of fine powder of AgNPs in deionized distilled water through 30 min sonication at 33 khZ in a Metrex ultra-sonic bath sonicator (Metrex Scientific Instruments Pvt., Delhi, India). Investigation with TEM coupled with EDX and SAED revealed that majority of AgNPs were in the size range of 20–30 nm (Fig. 1).

2.2. Exposure of crop plants to Ag^+ and AgNPs

Various concentrations of AgNPs were prepared using 1000 ppm AgNPs stock solution. Grains/seeds of wheat and sunflower were washed with cetrimide, treated with 0.1% $HgCl_2$ for 5 min, washed thoroughly with sterilized double-distilled water, and then were placed in autoclaved glass bottles containing glass beads in double-distilled water, in a laminar hood. These bottles were then incubated under continuous light (with an intensity of 120 μmol photons m^{-2} s^{-1}) at 25 ± 2 °C. 10 days old uniform plants of wheat and sunflower were selected and their root system was washed carefully with sterile distilled water. The selected seedlings were exposed independently to different levels (0, 10, 25, 50 and 100 ppm) of AgNPs and Ag^+ ($AgNO_3$ was used for preparing different levels of Ag^+) by immersing their root system in respective test solutions in Borosil glass test tubes (125 × 12 mm). Then, the plants were incubated under continuous light (with an intensity of 120 μmol photons m^{-2} s^{-1}) at 25 ± 2 °C for 24 h. No agglomeration of AgNPs was noted during these experiments.