Foliar Application of Selenite and Selenate to Potato (*Solanum tuberosum*): Effect of a Ligand Agent on Selenium Content of Tubers

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The effect of a foliar spray of selenium on potatoes was investigated for 2 years. Amounts of 0, 50, and 150 g of Se ha^{-1} were applied both as sodium selenate and as sodium selenite in water, either pure or with the addition of 0.15% of soluble leonardite as a source of humic acids (pH 7). Tuber selenium concentration increased with the application levels, both with sodium selenate and with sodium selenite, when only aqueous solutions were used. When humic acids were added, the tuber selenium level rose more markedly after the application of sodium selenate as compared to the case of the aqueous solutions; however, in the case of sodium selenite, the level showed a large increase only after the application of 50 g of Se ha^{-1}. Kinetics showed that humic acids raised the selenate availability, but no differences were found in the distribution of selenium in the tuber fractions. Foliar application of selenium with humic acids was proven to be a good way to increase the selenium content of potatoes, but the assimilation process of selenium was simpler with selenate than with selenite.

Keywords: *Selenium; potato; Solanum tuberosum; ligand; humic acids*

INTRODUCTION

Selenium is a mineral essential to human beings, and the Recommended Daily Allowances established in the United States are 55 and 70 μg/day for women and men, respectively (Committee on Dietary Allowances, 1989). Food is the main source of selenium for humans. Meat and fish are rich in selenium in the form of selenocysteine, but this has been discovered to be lacking in bioavailability; vegetables and fruits are a poor source of selenium, but they contain selenomethionine, which is more bioavailable. Combs (1988) summarizes the bioavailability of selenium forms as very low in reduced and insoluble inorganic forms, as low to moderate in most animal-derived foods, and as good in most plant-derived foods.

Selenium deficiencies were found in several areas, especially in Finland, New Zealand, and parts of China and the United States, and the supply of this element to livestock through forage and to human beings through vegetables has been a practice adopted to face this problem (Gissel-Nielsen et al., 1984). Several studies were carried out to compare the efficiency of soil application of selenium-containing fertilizers with that of foliar spraying of aqueous solutions of sodium selenite and selenate, and the use of foliar fertilizers was found to be safer and more efficient (Cary and Rutzke, 1981; Ylaranta, 1983). Asher et al. (1977) and Gissel-Nielsen (1982) have shown that plant uptake and translocation of selenite and selenate are different. Selenium is taken up immediately through the roots and translocated to the plant tops, but it is recovered either in the amino acid fraction or as inorganic selenate depending on whether it was present in the nutrition solution either as selenite or as selenate.

The selenium content of potatoes varies according to geographical areas, but most authors report concentrations of ~0.010 ppm (Bratakos et al., 1987; Mejuto-Martì et al., 1988; Diaz-Alarcon et al., 1994). Due to wide consumption, potatoes integration with selenium should be useful for populations subject to deficiency. In Finland, the selenium content of potatoes increased from values <0.010 ppm to average values of 0.070 ppm after the application of Se-integrated fertilizers (Eurola et al., 1989). Some authors found that the application of selenium to potatoes increases both total and protein amino acid contents (Munshi et al., 1990) while decreasing the total glycoalkaloid and nitrate contents of tubers (Munshi and Mondy, 1992).

Foliar spray of selenium in the form of sodium selenite was tested on potatoes (Munshi and Mondy, 1992), but the effect of different forms of selenium and their combination with additional agents is not yet very well-known.

The aims of this study were (i) to determine the selenium content of potatoes after the foliar application of different concentrations of sodium selenite and selenate and (ii) to study the influence that the addition of humic acids as a ligand agent to selenium spray solutions can have on the selenium content and distribution in potatoes.

EXPERIMENTAL PROCEDURES

Potatoes (*Solanum tuberosum*) cv. Primura were grown at a University of Bologna (Italy) research farm; the soil type was Thipic eutrochrep. Plots of ~250 m^2 were organized in a randomized block distribution scheme. Selenium, in the forms of sodium selenite and sodium selenate (Na_2SeO_3 99% and Na_2SeO_4 98%, respectively, both by Sigma-Aldrich), was applied foliarly at rates of 0, 50, and 150 g ha^{-1} in 500 L ha^{-1}

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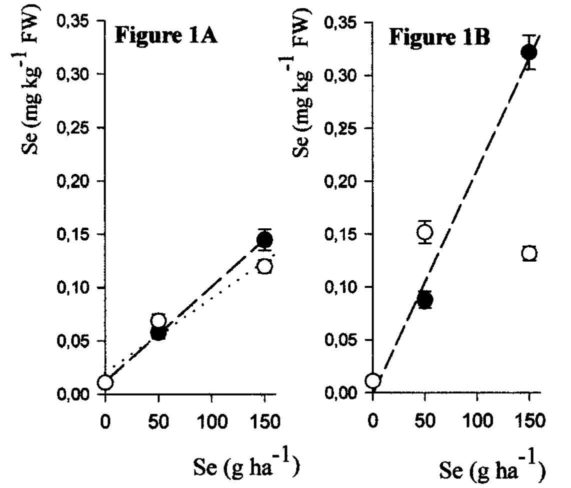

Figure 1. Se concentration in potato after foliar application of sodium selenate (Na_2SeO_4, ●) or sodium selenite (Na_2SeO_3, ○) in aqueous solution (A) or with humic acids (B).

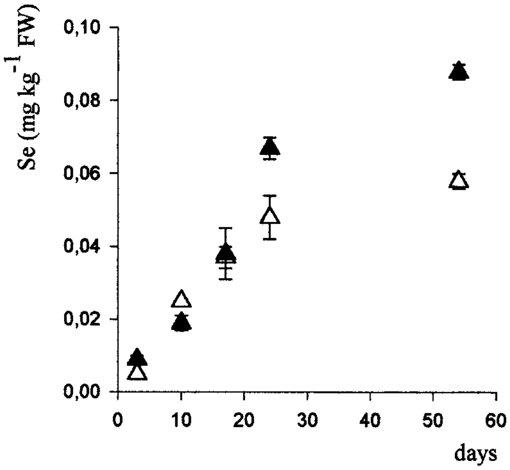

Figure 2. Se concentration in potato as a function of time (days) from the point of the foliar application of 50 g of Se ha^{-1} as sodium selenate (Na_2SeO_4) in aqueous solution (△) or with humic acids (▲) until the harvest.

of water. Both of the selenium forms and each rate were applied through water either pure or with the addition of soluble leonardite (0.15%), as a source of humic acids (HA), at pH 7.0. This study was carried out for 2 years.

Sample Preparation. The tubers were mechanically harvested and stored in bins at 6 °C and at 85% relative humidity. Potato tubers were washed and dried, cut longitudinally, frozen, and lyophilized in a Heto Holten freeze-drier. Parts of these samples were manually cut, forming slices, separated into skin, cortex, and medulla, froze, and lyophilized. All of the lyophilized tissues were ground in a Moulinex grinder and then in a Retsch mill and passed through a 25 mesh screen. Lyophilized powder was used for selenium determination.

Selenium Determination. Samples were analyzed in duplicate for selenium content according to the diaminonaphthalene fluorometric method of Olson et al. (1975). Lyophilized samples were digested with nitric and perchloric acids. Hydrochloric acid was used to reduce selenium to Se^{4+}; this selenium form was complexed with 2,3-diaminonaphthalene (DAN) to produce a fluorescent compound, which was extracted with cyclohexane. Fluorescence measurements were performed using a Perkin-Elmer LS50B spectrofluorometer equipped with a Hamamatsu R928 red-sensitive photomultiplier. The Se fluorescent compound was excited at 378 nm and fluorescence detected at 528 nm. Readings were performed, depending on the sample concentration, using different emission slit widths of the emission monochromator. Fluorescence was linearly related to concentration up to at least 0.1 μg of selenium/mL of cycloexane. The interpolation of the experimental results was performed with the SIGMAPLOT computer program.

RESULTS AND DISCUSSION

The level of the selenium concentration of the solutions sprayed was defined on the basis of a wide range of literature that suggests a high selenium assimilation by plant leaves. Every application tested determined a reproducible increase of the tuber selenium concentration in the two experimentation years.

When pure aqueous solutions were used (Figure 1A), the potato selenium concentration increased linearly with the application levels, both with sodium selenate ($y = 9 \times 10^{-4}x + 1.20 \times 10^{-2}$, $r = 0.9996$) and with sodium selenite ($y = 7 \times 10^{-4}x + 2.03 \times 10^{-2}$, $r = 0.9492$). Sodium selenate was more effective than sodium selenite only at the higher concentration of selenium spray.

When humic acids were added (Figure 1B), the tuber selenium content rose linearly with the application level only if sodium selenate was used; the increase was more marked than that obtained with the aqueous solutions ($y = 2.1 \times 10^{-3}x - 4 \times 10^{-4}$, $r = 0.9913$). In the case of sodium selenite, the content showed a large increase, as compared to the case of the aqueous solutions, only after the spray of 50 g of Se ha^{-1}, whereas a 150 g of Se ha^{-1} spray did not cause a significant variation. The potato selenium concentration increased during plant growth (Figure 2) with a similar trend after the application of both aqueous and humic acid selenate solutions but reached a different maximum level. The results suggest that humic acids raise the selenate availability for the plant. Studies on the chemical structure of humic substances clearly explain their interaction with metal ions giving rise to complexes or ligands for anion species (Shulten, 1994). The HA interaction with both the selenium anions and the plant tissues can extend the time of their contact and the absorption ability of the leaf cells. This is probably true only for selenate ions because, as shown by Asher et al. (1977) and Gissel-Nielsen (1979), selenate is absorbed and translocated without metabolic involvement: in our specific case, when the humic acids protracted the ion availability, the selenate was assimilated in a larger amount. We also studied the relative distribution of selenium in the tuber fractions after sodium selenate spray, and we did not find any difference using either aqueous or humic acid solutions (Figure 3).

The above-mentioned authors have also suggested a metabolic involvement in the uptake and transport of selenium supplied as selenite. This can explain why, when the availability of the selenite for the leaf tissues increased, no more accumulation was observed in the tubers: the metabolic stage can be the limiting step in the absorption process. Similar results were obtained by Munshi and Mondy (1992): when the selenite foliar application level was raised, the tuber selenium concentration did not show any particular increase. In that case, the larger possibility of absorption by plant leaves was due to the higher selenium amount sprayed rather than to the longer time of contact.

Our results prove that foliar application of selenium with humic acids can be a convenient way to increase the selenium content of vegetables such as potatoes but that the complexity of the assimilation processes can influence the final results. More information about the

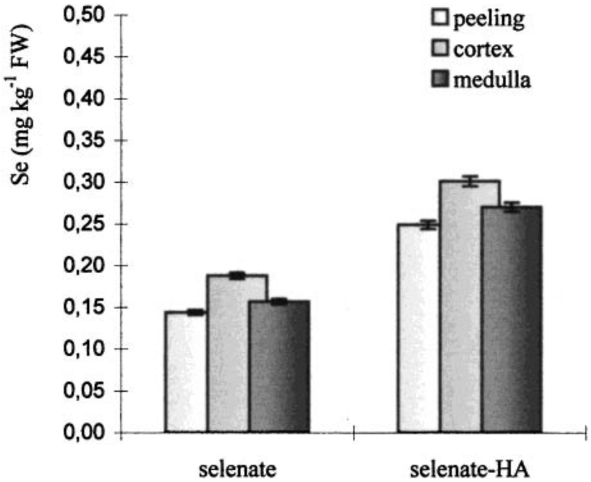

Figure 3. Se concentration as a function of the region of potato tuber after foliar application of 150 g of Se ha^{-1} as sodium selenate (Na_2SeO_4) in aqueous solution (selenate) or with humic acids (selenate-HA).

mechanisms of leaf absorption and translocation of the different forms of selenium in potato plants is necessary to explain the role of the ligand agent: at present we are carrying out a specific study to clarify the relationship between the kind of ion involved, either selenite or selenate, and absorption kinetics.

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