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Analytical Methods

Variations in the accumulation, localization and rate of metabolization of selenium in mature Zea mays plants supplied with selenite or selenate

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ABSTRACT

Quantification of selenium bioavailability from foods is a key challenge following the discovery of the antioxidant role of this micronutrient in human health. This study presents the uptake, accumulation and rate of metabolization in mature Zea mays plants grown in hydroponic solution supplemented with selenate or selenite.

Selenium content was lower in plants supplemented with selenate and accumulated mainly in the leaves compared with selenite-treated plants where the selenium was retained in the roots. Selenite-treated grains accumulated more selenium. Selenate was metabolized less than selenite in whole plants, but in grains selenium was present exclusively as organic selenium compounds.

For humans, the bioavailability of organic selenium was evaluated at 90% compared with only 50% for inorganic forms. Our results show that the potential for selenium bioavailability is increased with selenite treatment.

1. Introduction

Selenium (Se) is an essential micronutrient in human and animal diets. More than 20 selenoproteins or selenoenzymes are involved in normal metabolism and selenium has also been proposed to lower the risk of cardiovascular diseases and cancer (Rayman, 2008; Thomson, 2004). Food is the principal route of selenium intake. Meat and seafood contain the highest amounts of selenium, with 0.4–1.5 μg per gram (Rayman, 2008), but cereals, fruits and vegetables are also good food sources. Selenium enters the food chain through plants and especially crops, which are part of the diet of both primary and secondary consumers.

Selenium concentrations in food, including crops, depend not only on selenium concentrations in agricultural soils (which vary considerably between countries and regions) but also on selenium phytoaccessibility controlled by many abiotic and biotic factors such as soil pH, redox conditions, organic matter content, microbial activities, irrigation and compaction. In some countries or regions, low selenium levels in soil lead to low concentrations in feed or forage, which in turn can result in selenium deficiency in livestock and humans. For example, the average selenium intake is only 36 μg per day in France, 34 μg per day in the UK and 35 μg per day in Sweden (Rayman, 2008); these levels are below the recommended dietary allowance of 40 to 70 μg per day. To increase selenium levels in human and animal diets, several processes have been developed including mineral supplementation, genetic biofortification (plant breeding) and finally, the option chosen here, agronomic biofortification of food or forage.

In contrast to humans, the role of selenium for plants is more ambiguous, although studies on young plants have led to a better understanding of selenium pathways in higher plants (De Souza et al., 1998; Hopper & Parker, 1999; Li, McGrath, & Zhao, 2008; Terry, Zayed, De Souza, & Tarun, 2000; Ximenez-Embun, Alonso, Madrid-Albarran, & Camara, 2004; Zayed, Lytle, & Terry, 1998; Zhang, Pan, Chen, & Hu, 2003). Plant development and selenium metabolism are strongly dependent on the form of supplied selenium. The greater mobility of selenate compared to selenite results in differences in the absorption, translocation and metabolism of selenium within the plant. Indeed, when plants are exposed to selenite, selenium accumulation is less than after selenate treatment (De Souza et al., 1998; Terry et al., 2000; Ximenez-Embun et al., 2004; Zhang et al., 2003), with a greater reduction in biomass

Abbreviations: CRC-ICP-MS, collision/reaction cell-inductively coupled plasma mass spectrometry; ICP-AES, inductively coupled plasma atomic emission spectrometry; GFAAS, graphite furnace atomic absorption spectrometry; DW, dry weight; LOD, limit of detection; SD, standard deviation; FeEDDHA, Iron - Ethylenediamino-N, N'-bis(2-hydroxy-phenyl)acetic acid; IRMM, Institute for Reference Materials and Measurements.

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production (Hopper & Parker, 1999; Ximenez-Embun et al., 2004). After selenate treatment, selenium is almost entirely translocated to the leaves and weakly metabolized as selenoamino-acids, with a selenate concentration in shoots (i.e. stems and leaves) representing more than 90% of the total shoot selenium (De Souza et al., 1998; Hopper & Parker, 1999; Li et al., 2008; Mazej, Osvald, & Stibilj, 2008; Terry et al., 2000; Ximenez-Embun et al., 2004; Zayed et al., 1998; Zhang et al., 2003). In contrast, when supplied as selenite, selenium accumulates principally in roots with little translocation, although selenoamino-acid production (principally selenomethionine, selenocysteine and selenomethylselenocysteine) is greater (De Souza et al., 1998; Hopper & Parker, 1999; Li et al., 2008; Liu & Gu, 2009; Terry et al., 2000; Ximenez-Embun et al., 2004; Zayed et al., 1998) and the selenium volatilization rate is about 2-fold higher from those plants (De Souza et al., 1998).

After ingestion by humans or animals, bioavailable selenium is the fraction that enters the systemic circulation (Thiry, Ruttens, De Temmerman, Schneider, & Pussemier, 2012). As with other micronutrients, selenium bioavailability strongly depends on the chemical form of the element: organic forms (such as Se-methionine and Se-cysteine), mainly from plant and animal sources, have more bioavailability than inorganic forms (selenate and selenite), which are principally found in dietary mineral supplements. Experimental designs used to measure selenium bioavailability vary widely in the literature, making it difficult to compare the results (Knowles, Grace, Wurms, & Lee, 1999; Nicholson, McQueen, & Bush, 1991; Podoll et al., 1992). According to Thomson (2004), the apparent absorbed selenium (i.e. the difference between selenium ingested and selenium excreted in feces and urine) in humans was evaluated at about 90% for Se-met and Se-cys versus 50% for selenite or selenate supplements (Panel on Dietary Antioxidants and Related Compounds, Subcommittee on Upper Reference Levels of Nutrient, Subcommittee on Interpretation and Uses of DRIs, Standing Committee in the Evaluation of Dietary Reference Intakes of the Food and Nutrition Board, Institute of Medicine & the National Academies and Health Canada, 2000). However, due to a lack of data on the bioavailable fraction across all food products, the recommended daily dietary allowances of selenium for humans are based only on the total selenium concentration, without taking into account the speciation. The two percentages (90% and 50%) estimated by Thomson (2004) are a "pseudo reference" value used in the present study to evaluate the selenium bioavailability in our so-called "organic" and "inorganic" fractions in Zea mays plants.

Due to the essential function of selenium in staple foods, a number of recent studies on grains and seeds have been carried out not only in wheat, but also in sesame, buckwheat pumpkin and Zea mays (Broadley et al., 2010; Cubadda et al., 2010; Kapolna, Gergely, Dernovics, Illès, & Fodor, 2007; Mbagwu, 1983; Moore et al., 2010; Smrkolj, Osvald, Osvald, & Stibilj, 2007; Smrkolj, Stibilj, Kreft, & Kapolina, 2005; Stibilj, Kreft, & Smrkolj, 2004). In *Brassica rapa* (Lyons et al., 2009), selenite fertilization increased seed number and weight produced by each plant. Regardless of the enrichment procedures employed in agricultural practice, the development and growth of plants and grains were not affected negatively by selenium supplementation (Broadley et al., 2010; Stibilj et al., 2004). Independently of the selenium concentration added as amendment, grains seem to be an ideal storage tissue, with selenium concentrations higher than in shoots or fruits (Cubadda et al., 2010; Mbagwu, 1983; Stibilj et al., 2004). It has previously been shown that the major selenium species in grains is selenomethionine accounting for 45–90% of total selenium (Cubadda et al., 2010; Kapolna et al., 2007; Smrkolj et al., 2005, 2007), with only very low levels of selenate detected (Cubadda et al., 2010; Lyons, Genc, Stangoulis, Palmer, & Graham, 2005).

In the present study, we investigated selenium enrichment in Zea mays grains grown in a hydroponic system. Cereal grains are rich in phytic acids, known for their antioxidant roles in humans and which strongly bind mineral and trace elements (Hurrel, 2003). Zea mays grains contain more of this compound than wheat grains (Egli, Davidsson, Juillerat, Bearclay, & Hurrell, 2003). Moreover, Zea mays is the most widely cultivated cereal in the world, producing mainly forage and grains for animal feed but also grains as well as derived products for human consumption. In Malawi, for instance, 50% of the diet is derived from Zea mays (Chilimba et al., 2011). Consequently, the limited data available on selenium accumulation in Zea mays grains has been obtained in specific locations (selenium-deficient (Chilimba et al., 2011) or seleniferous areas) or for Se-supplementation, fly-ash for example (Mbagwu, 1983). Furthermore, the influence of the chemical form of selenium in Zea mays plants, on accumulation including location (i.e. roots, stems, shoots and grains), has not been widely studied. The first objective of the present study was, therefore, to quantify the effects of those two inorganic chemical forms (selenate and selenite) on Zea mays growth and seed production. The second aim was to investigate the uptake, translocation and speciation of selenium in different Zea mays tissues: roots, stems, leaves and grains.

2. Materials and methods

2.1. Seed germination and culture conditions

Three weeks after germination, *Zea mays sups.mays* (L.) corn seedlings were cultivated in hydroponic conditions in 20 L plastic tanks filled with a modified Hoagland nutrient solution consisting of KNO_3 (3 mmol l^{-1}), $Ca(NO_3)_2{\cdot}4H_20$ (2.72 mmol l^{-1}), NH_4NO_3 (2 mmol l^{-1}), NaCl (0.2 mmol l^{-1}), KH_2PO_4 (0.98 mmol l^{-1}), $MgSO_4{\cdot}7H_20$ (0.70 mmol l^{-1}), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.04 μmol l^{-1}), H_3BO_3 (24 μmol l^{-1}), $MnSO_4$ (13 μmol l^{-1} M), $ZnSO_4$ (6 μmol l^{-1}), $CuSO_4$ (1.5 μmol l^{-1}) and FeEDDHA (6%) (4 μmol l^{-1}). Two nutrient solutions were supplemented with 12 μmol l^{-1} selenium as either Na_2SeO_4 or Na_2SeO_3 (solutions Se^{VI}-T and Se^{IV}-T), respectively. Under control conditions (C-T), no selenium was added. Five corn seedlings were transplanted in each tank and placed into a RUBIC5 plant growth chamber (Reactor Used for Continental Isotopic Biogeochemistry), a 9 m^3 sealed chamber (Servathin, France) the atmospheric compositions of which are controlled. Lighting was provided by 15 × 400 watt Philips Son-T Agro bulbs over an 8-h photoperiod set at 600 μM m^{-2} s^{-1} photosynthetically active radiation at plant height. Air temperature was set at 25 °C during the day and 18 °C at night. Air humidity was controlled by a dew point condenser in order to maintain a set-point of 70% relative humidity. Beyond this set point, excess water vapor was condensed and collected using an Isco 3700 water sampler (so called "condensates"). The CO_2 concentration was measured using a LI-COR (Lincoln, Nebraska USA) Li620 infrared gas analyzer set at 400 ppmv. The chamber had a slight positive pressure of +20 Pa to avoid entry of outside air. Data were logged by a computer and averaged at 10 min intervals.

The change in aerial biomass production was followed by recording the leaf area five times during the experiments.

At maturity, plants (five for each treatment) were harvested and roots briefly rinsed in deionized water to remove traces of nutrient solution. The selenium concentration in this rinse water fell below the detection threshold of CRC-ICP-MS. The leaves, stems, roots and grains were then separated. Plant samples were freeze-dried,