



## Selenium accumulation by forage and grain crops and volatilization from seleniferous soils amended with different organic materials

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### ABSTRACT

Greenhouse and field experiments were conducted to study the direct and residual effect of applying different organic materials on Se accumulation by crops and volatilization from seleniferous soils of north-western India. Among organic manures, press mud and poultry manures proved 4–5 times more effective in reducing Se accumulation by different crops than farmyard manure. Efficiency of organic manures increased with increase in application rates. Application of both press mud and poultry manures reduced Se accumulation by 44–97% in wheat (*Triticum aestivum*) and rapeseed (*Brassica napus*) shoots in the greenhouse; 85–92% in wheat straw, 45–74% in wheat grains, 45–74% in rapeseed straw and 76–92% in rapeseed grains under field conditions. Both the manures remained highly effective in reducing Se accumulation by the crops following wheat and rapeseed and the extent of reduction varied from 50% to 87% in maize (*Zea mays*) and cowpeas (*Vigna sinensis*) in the greenhouse and 40% to 89% in maize and rice (*Oryza sativa*) crops under field situation. Rate of Se volatilization by wheat and rapeseed crops increased by 1.8–4.0 times; the greatest increase was observed with press mud followed by poultry manure, arhar (*Cajanus cajan*) leaves and farmyard manure. After 134 d of incubation of 500 g soil amended with 2% of plant tissues, the maximum amount of Se was volatilized with cowpea leaves (385 ng) followed by wheat grains, leaves of maize, sugarcane (*Saccharum officinarum*), arhar, poplar (*Populus deltoides*) and the control (91 ng). The results of this study convincingly prove the usefulness of applying press mud and poultry manure in enhancing volatilization and retarding the transfer of Se from soil to plant in seleniferous soils.

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### 1. Introduction

Selenium is not an essential element for plant growth, but its optimum level in plants and plant products has significant bearing on animal and human health. Regular consumption of feed containing less than 0.02–0.10 mg Se kg<sup>-1</sup> can result in deficiency symptoms depending upon the animal species and vitamin E level, whereas concentrations higher than 4–5 mg Se kg<sup>-1</sup> in the diet can cause toxic effects in domestic animals (Underwood and Suttle, 1999). In the natural environment Se occurs primarily in two forms – selenate (SeO<sub>4</sub><sup>2-</sup>) and selenite (SeO<sub>3</sub><sup>2-</sup>) (Adriano, 1986; Elrashidi et al., 1989). Organic Se may also be present in soil solutions (Abrams et al., 1990). While selenate dominates under alkaline and oxidizing conditions, selenite is the dominant form under acidic and reducing conditions (Elrashidi et al., 1989). Selenate is generally the toxic form in soils (Bisbjerg and

Gissel-Nielsen, 1969; van Dorst and Peterson, 1984), whereas selenite can be toxic to plants grown in solution culture (Spencer and Siegel, 1978).

The concentration and bioavailability of different forms of Se depend on soil properties such as pH, organic matter content, texture, microbiological activity and the presence of competing ions and organic compounds. Application of crop residue or animal manure to a selenate treated soil reduced the Se accumulation by canola leaves by 7–10 times (Ajwa et al., 1998). Addition of cattle manure in combination with selenite and selenate reduced the adsorption of both the ions in a loam soil (Øgaard et al., 2006). Ferri et al. (2003) observed significant reduction in Se accumulation by *Lactuca sativa* from a soil amended with selenite or selenate in the presence of a polysaccharide – carboxymethylcellulose. Interaction of carboxymethylcellulose with Se makes it less mobile as indicated by increase in the insoluble Se fractions (Pezzarossa et al., 2007). In a column study with a podzol soil, 77% of the added selenite was retained in the upper 2 cm thick raw humus layer (Gustafsson and Johnsson, 1992). Rapid and efficient Se retention by surface horizon of forest soils was primarily due to microbially mediated reductive process leading to Se reduction to low valence states and then incorporation into low-molecular-weight humic

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fractions (Gustafsson and Johnsson, 1994). Selenium concentration in wheat grains was reduced from 1350 to 160  $\mu\text{g kg}^{-1}$  when the organic matter content in the plough layer increased from 1.4% to 39% (Johnsson, 1991).

Transformation of nonvolatile Se into volatile products may constitute an effective detoxification process for seleniferous soils. Volatilization of Se in soil–plant system can be promoted by stimulating indigenous microorganisms with specific organic amendments. Selenium volatilization potential of a clay loam soil was 2.9% without carbon amendments and it increased to 3.3% by amending the soil with cellulose, to 3.7% with dairy manure, to 5.2% with starch, to 6.6% with maize leaves, and to 8.8% with pectin (Karlson and Frankenberger, 1988). Addition of selenomethionine to a seleniferous sediment resulted in rapid and extensive volatilization of Se as dimethyleneselenide (DMSe), but very limited amount of DMSe was produced from selenocystine additions (Frankenberger and Karlson, 1989). Selenocystine, being very unstable in soil, gets rapidly mineralized to inorganic Se forms in soil (Martens and Suarez, 1997).

Some pockets of seleniferous soils containing total Se from 0.2 to 4.6  $\text{mg kg}^{-1}$  have been identified in northwestern India. Selenium is present in the soil profile up to 2 m depth and the surface layer contains 1.5–6.0 times more Se than the lower layers. Consumption of Se-rich feed based on forage and grain crops grown on these soils has resulted in serious health hazards to animals and humans (Dhillon et al., 1992; Dhillon and Dhillon, 1997). Thus there is need to devise strategies for accelerating loss of Se through volatilization and controlling excessive transfer of Se from soil to plants. Amending the soils with organic materials which enhance volatilization of Se may help in achieving this objective. Greenhouse and field experiments were conducted to assess the direct and residual impact of different organic materials on Se accumulation by grain and forage crops and the efficiency of Se volatilization process from seleniferous soils. Changes in Se fractions with the addition of different organic manures to the seleniferous soil were also investigated.

## 2. Materials and methods

### 2.1. Greenhouse study

The experimental soil was collected in bulk from a seleniferous field located at 31.12986°N and 76.21092°E in village Barwa in Nawanshahar district of the Indian Punjab. The soil was air-dried under shade and ground to pass through 2 mm sieve. The soil was silty loam in texture, alkaline in reaction having a pH of 8.2, electrical conductivity 0.3  $\text{dS m}^{-1}$ , organic carbon 0.5% and total Se content 4.5  $\text{mg kg}^{-1}$ . The treatments consisted of a non-organic material control, four organic materials – press mud, poultry manure, farmyard manure and fresh arhar (*Cajanus cajan*) leaves; two levels of application – 2% and 5% and two crops – wheat (*Triticum aestivum*) and rapeseed (*Brassica napus*). A basal dose of N, P and K was applied to the soil through urea, potassium dihydrogen orthophosphate and potassium chloride, respectively. All the treatments were replicated thrice. The portions (4 kg) of air-dried soil were treated with different materials, placed in polythene lined earthen pots, brought to field capacity moisture level and allowed to equilibrate for 48 h. Thereafter, 20 seeds of rapeseed (as hills comprising of 3–4 seeds) and 10 seeds of wheat were sown in the soil equidistant from each other. The pots were arranged in a completely randomized design (CRD). Within 10 d the plants were well-established and thereafter four plants were retained in each pot. To study the residual effect of different treatments, wheat was followed by maize (*Zea mays*) and rapeseed by cowpeas (*Vigna sinensis*) in the same pots. As far as possible, the roots of each crop were

removed from the soil before sowing the next crop. Each crop was harvested after 60-d of growth. Samples of the above-ground portion were collected, washed free of any contamination and dried in an oven at  $55 \pm 5$  °C to a constant weight. After recording the dry matter yield, the plant samples were ground in a Wiley grinding mill and stored in air-tight plastic containers for estimation of selenium and other nutrients. Soil samples were also collected from each pot after harvesting wheat and rapeseed crops and analyzed for hot water soluble Se.

### 2.2. Field study

The field experiments were conducted during 2006–2008 at a site located in the seleniferous region of northwestern India at 31.12931°N and 76.21197°E. The surface soil layer (0–15 cm) of the experimental field was silt loam in texture, alkaline in reaction having a pH of 8.5, electrical conductivity 0.4  $\text{dS m}^{-1}$ , organic carbon 0.7%,  $\text{CaCO}_3$  3.7% and total Se content 4.3  $\text{mg kg}^{-1}$ . The treatments consisted of a control; three sources of organic manures – press mud, poultry manure and farmyard manure; two rates of application – 15 and 20  $\text{t ha}^{-1}$  in case of press mud and farmyard manure and 10 and 15  $\text{t ha}^{-1}$  in case of poultry manure. The treatments were laid out in a randomized block design with three replications. The organic manures (air-dried) were applied 20-d before sowing of crops and mixed thoroughly with the surface soil layer (0–15 cm). Wheat and rapeseed crops were grown as test crops to assess the effect of direct application of organic manures on Se accumulation. To study the residual effect of different treatments, maize was sown after harvesting wheat and rapeseed which in turn was followed by rice (*Oryza sativa*). Plant samples of wheat and rapeseed crops were collected at two stages of growth – at peak flowering (rapeseed)/ear initiation (wheat) and at maturity. Samples of 50-d old maize plants and that of grain and straw of rice at maturity were collected. After air-drying for 24 h, the samples were oven-dried at  $55 \pm 5$  °C to a constant weight, ground to a fine powder in a Wiley grinding mill and stored in plastic containers for chemical analysis.

### 2.3. Laboratory studies

#### 2.3.1. Se volatilization

- (a) The apparatus used for trapping volatile Se in the laboratory consisted of filtration flasks of 500 mL capacity attached to a pressure pump through a glass tube with multiple outlets. The soil used for this study was the same as described for greenhouse study. The portions (250 g) of the air-dried soil were placed in each flask. The treatments consisted of an unamended control soil (C/N-7.2; 4.5  $\text{mg Se kg}^{-1}$ ) and three organic manures – farmyard manure (C/N-13.6, 2.1  $\text{mg Se kg}^{-1}$ ), poultry manure (C/N-9.0; 1.3  $\text{mg Se kg}^{-1}$ ) and press mud (C/N-12.5, 2.4  $\text{mg Se kg}^{-1}$ ). Each treatment was replicated two times. Portions of the experimental soil were amended with organic manures at 2%. Soil was brought to field capacity moisture regime (27.5% moisture) by adding double-distilled water. The flasks were made air-tight with rubber corks having air inlet and outlet tubes. The inlet tube of each flask was attached to the pressure pump. The test tube containing 7 mL of concentrated  $\text{HNO}_3$  was attached to the outlet tube for collecting volatile Se compounds. Moist air was circulated twice through the flasks for the duration of 1 h every time. Room temperature ranged from 30 to 34 °C. Test tubes containing concentrated  $\text{HNO}_3$  were replaced at fixed time intervals with tubes containing  $\text{HNO}_3$ . The tubes containing Se volatiles were analyzed for Se.

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