# Potential availability of fertiliser selenium in soils during flooding and subsequent aeration

H. M. P. Lakmalie Premarathna[A], Mike J. McLaughlin[A<B], Jason Kirby[B], Ganga Hettiarachchi[B,C], Samuel Stacey[A] and David Chittleborough[A]

[A]Soil and Land Systems, School of Earth and Environmental Sciences, University of Adelaide, SA, Australia,
Email herath.premarathna@adelaide.edu.au
[B]CSIRO Land and Water, SA, Australia; [3]Department of Agronomy, Kansas State University, Manhattan, USA.

## Abstract

The partitioning coefficient ($K_d$) and potential availability of selenite ($SeO_3^{-2}$) or selenate ($SeO_4^{-2}$) as a percentage of Se applied (% $E_{add}$ values) were measured using isotopic dilution techniques in a study under variable redox conditions. Both Se species were added to a soil subjected to prolonged (30 d) submergence (low redox) followed by 7 d oxidising conditions (high redox). Even though applied Se had no effect on the $SeO_3^{-2}$ or $SeO_4^{-2}$ $K_d$ values, time had a significant effect. Selenate $K_d$ values were always lower than $SeO_3^{-2}$ $K_d$ values. Applied Se species had a significant effect on the $SeO_3^{-2}$ %$E_{add}$ values. For both forms of applied Se <20% of applied Se was initially in the available pool as $SeO_3^{-2}$. However, after 14 d of submergence %$E_{add}$ values for $SeO_3^{-2}$ increased to 80%. Then availability decreased and did not increase during oxidation. Applied Se species, time and their interaction had a significant effect on the $SeO_4^{-2}$ %$E_{add}$ values. Selenate applied soils initially had more than 80% in available pool but this decreased with time and did not increase during oxidation. These results clearly show that irrespective of the species of Se applied to the soil, speciation changes depend on the changes in soil redox and pH. Adsorbed $SeO_3^{-2}$ and $SeO_4^{-2}$ were released into the soil solution with the reduction of Fe oxides and we possibly reduced to Se (0). Since there was no increase in the available pool of either Se species during the oxidation phase we can assume that fixed Se, as Se(0), did not oxidise readily during the 7 day oxidation period.

## Key Words

Redox, fortification, isotopic dilution, adsorption.

## Introduction

Sorption and fixation of fertiliser and native selenium (Se) determine the availability for plant uptake. Sorption and desorption of Se in soil is mainly determined by the oxidation-reduction potential, pH, microbial activity, mineralogy and organic matter, and other anions (Dhillon and Dhillon 2000; Goh and Lim 2004). However, most of the information on Se was derived from experiments in aerobic soil systems, and the behaviour of Se in anaerobic soil systems, or those with fluctuating redox, hass not been extensively investigated. Chemical thermodynamic data can be used to predict the most stable Se species in a particular soil environment, but kinetics of the chemical transformations of Se in soils are not well understood (Mikkelsen *et al.* 1989). Moreover it is further complicated by different management practices and type of crops grown. The rate of transformation of fertilizer Se in soil into sorbed or fixed forms is very important for Se accumulation by crops. For paddy rice production systems, in which soils are subjected to variable redox conditions, the kinetics of transformation of fertilizer Se in soil will govern availability for crop uptake. In order to fill this research gap a controlled microcosm study was undertaken with the following objectives:

## Materials and methods

This experiment utilized a controlled-atmosphere ($N_2$ and air) stirred flask technique Patric *et al.* (1973) to gain an understanding of the influence of redox conditions and applied Se species (selenite and selenate) on the availability (potential availability) of fertilizer Se in a rice growing soil. The redox conditions in the cell were periodically adjusted to simulate soil conditions exposed to rice plants. An uncontaminated paddy field soil was spiked with Se (1 mg of Se/kg) in the form of $SeO_3^{-2}$ and $SeO_4^{-2}$. The soils were incubated for 30 d under reduced redox conditions followed by incubation for 7 d under oxidised conditions. Soil suspensions collected at 0, 14, 30, and 37 days were used to measure Se partitioning ($K_d$) and potential Se availability (*E* values) using an isotopic dilution technique. The apparent isotopic $K_d$ values for $SeO_3^{-2}$ or $SeO_4^{-2}$ were calculated using the following equations:

$$K_d\ (\mathrm{L/kg}) = \frac{R-r}{r} \times \frac{v}{m} \qquad (1)$$

where, R is the total activity of $^{75}SeO_3^{-2}$ or $^{75}SeO_4^{-2}$ added to samples in Bq; r is the activity of $^{75}SeO_3^{-2}$ or $^{75}SeO_4^{-2}$ remaining in solution after equilibration in Bq; v is the volume in L and m is mass of soil in kg. The isotopically exchangeable pool of $SeO_3^{-2}$ (*E* $SeO_3^{-2}$ value) or $SeO_4^{-2}$ (*E* $SeO_4^{-2}$ value) in the soil was calculated using the equation:

$$E\ \text{value (mg/kg)} = \frac{S}{r} \times R \times \frac{v}{m} \qquad (2)$$

where, S is the concentration of $SeO_3^{-2}$ or $SeO_4^{-2}$ in solution after equilibration (mg $L^{-1}$); r is the activity of $^{75}SeO_3^{-2}$ or $^{75}SeO_4^{-2}$ remaining in solution after equilibration (Bq); R is the total activity of $^{75}SeO_3^{-2}$ or $^{75}SeO_4^{-2}$ spiked into samples (Bq); v is volume in L and m is mass in kg. Results were expressed as a percentage of Se added (%$E_{add}$ values) by comparing E values in control and Se-amended soils, and dividing by the rate of Se added.

**Results and discussion**

Redox and pH had an inverse relation during the incubation time (Figure 1). Redox decreased with time in the reduced phase and stabilized around -150 and -200 mV and increased quickly with oxidation. On the other hand pH had an increasing trend over the time in reduced soils and decreased within few hours in the oxidized phase before increasing and returning to the initial pH. There was no conversion of $^{75}SeO_3^{-2}$ to $^{75}SeO_4^{-2}$ during the shaking and equilibration time. Applied Se had no effect on the $SeO_3^{-2}$and $SeO_4^{-2}$ $K_d$ values indicating that $SeO_3^{-2}$ and $SeO_4^{-2}$ adsorption was still in the linear range of the sorption isotherm (adsorbed $SeO_3^{-2}$ *versus* equilibrium $SeO_3^{-2}$ concentration) at this rate of applied Se. However time had a significant effect, decreasing the $SeO_3^{-2}$ and $SeO_4^{-2}$ $K_d$ values and 7 d after oxidation the soil had the lowest $K_d$ values. Selenate $K_d$ values were always lower than $SeO_3^{-2}$ $K_d$ values as observed by others (Collins *et al.* 2006).

**Table 1. Characteristics of soil used for the experiment.**

| | Bentota soil (Thionic Histosol) |
|---|---|
| pH (water) | 5.4 |
| Clay (%) | 17.7 |
| Organic C (%) | 4.3 |
| Oxalate Fe (mg/kg) | 6935 |
| Oxalate Al (mg/kg) | 1590 |
| Total Se (µg/kg) | 118 |

Applied Se species had a significant effect on the $SeO_3^{-2}$ %$E_{add}$ values. In both $SeO_3^{-2}$ and $SeO_4^{-2}$ treatments, soil initially had a very low % (<20%) of applied Se in the available $SeO_3^{-2}$ pool . After 14 d of submergence, both Se treatments had much higher percentages (>80%) in the available $SeO_3^{-2}$ pool. However, with time availability decreased and even after 7 d of oxidation availability did not increase. Applied Se species, time, and their combination effect had a significant effect on the $SeO_4^{-2}$ %$E_{add}$ values. Soil amended with $SeO_4^{-2}$ initially had more than 80% in the available $SeO_4^{-2}$ pool. In the soil amended with $SeO_4^{-2}$, labile $SeO_4^{-2}$ decreased with time in the reduced phase and did not increase during the subsequent oxidation period. The pH and redox changes during the reduced phase evidently caused significant changes in Se speciation. By day 14, $SeO_3^{-2}$ was the major Se species in both treatments. These results clearly

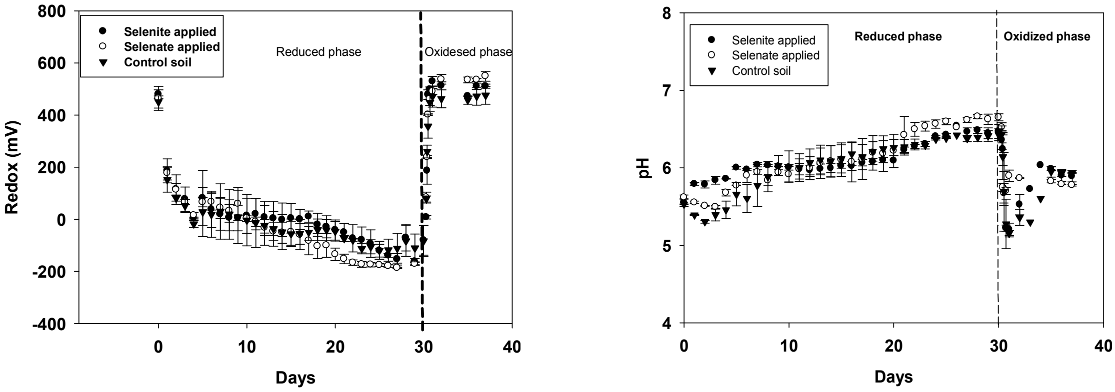

**Figure 1. Redox and pH during the experiment.**

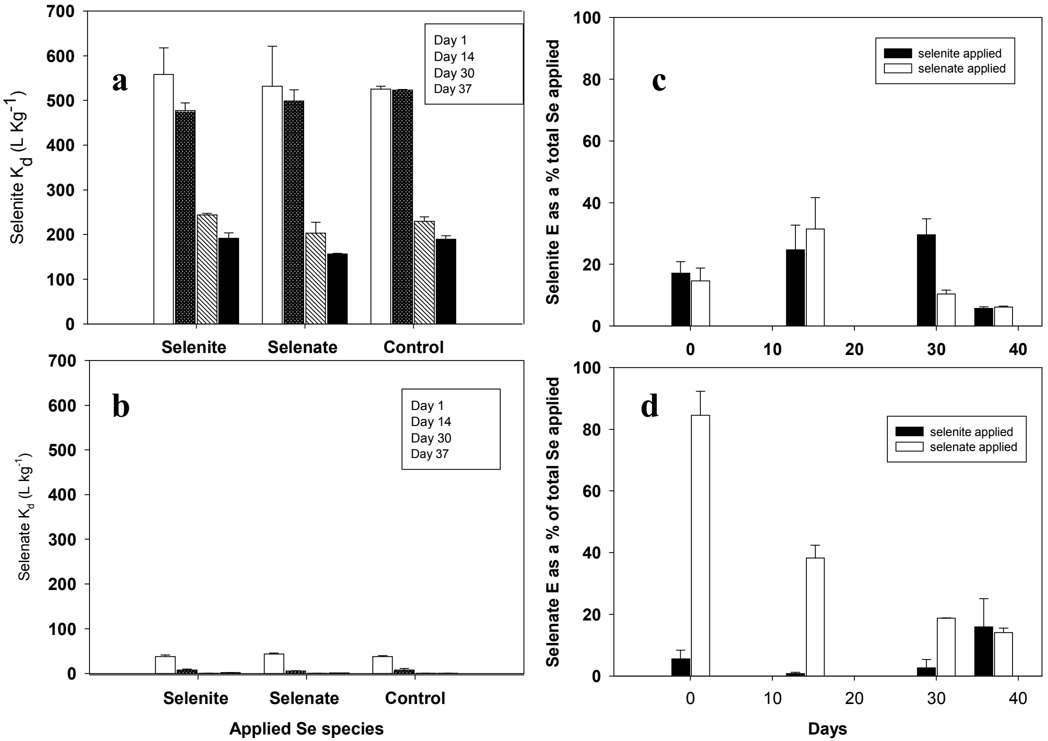

**Figure 2. K$_d$ values for $SeO_3^{-2}$ (a) $SeO_4^{-2}$ (b), $SeO_3^{-2}$ *E* values as a % of total Se applied (c) and *E* value of $SeO_4^{-2}$ as a % of total Se applied (d).**

show that irrespective of the species of Se applied in to the soil, speciation changes depend on the interaction of soil redox and pH conditions. It is highly likely that the Reason for the decrease of available $SeO_3^{-2}$ and $SeO_4^{-2}$ with time was the reduction of these species to Se(0). Since there was no increase in the labile $SeO_3^{-2}$ and $SeO_4^{-2}$ during the oxidation phase, we can assume that the Se(0) formed did not oxidise readily when soils were aerated for one week.

We have shown that if we add Se at pre planting as either $SeO_3^{-2}$ or $SeO_4^{-2}$, by the time of transplanting (14 d after submergence) significant amounts of fertilizer Se would be available for plant uptake as $SeO_3^{-2}$. However, the availability of both fertilizer Se species declined rapidly with time and did not increase on re-oxidation, suggesting that it is not a good practice to add fertilizer Se prior to planting rice, as availability goes down with submergence. However since rice roots have the special ability to oxidise their rhizosphere (Kirk *et al.* 1993) added Se may remain in forms that the plant can absorb. Experiments are underway to investigate the accumulation of Se forms in rice grains under variable redox conditions.

## Conclusions

Irrespective of the species of Se added to soil, partitioning and availability of Se in soil was controlled by soil redox and pH. Long term submergence significantly reduced the availability of fertilizer Se applied possibly by reduction to Se(0). Oxidation of this Se(0) was insignificant.

## References

Collins RN, Tran ND, Bakkaus E, Avoscan L, Gouget B (2006) Assessment of isotope exchange methodology to determine the sorption coefficient and isotopically exchangeable concentration of selenium in soils and sediments. *Environ. Sci. Technol.* **40**, 7778-7783.

Dhillon SK, Dhillon KS (2000) Selenium adsorption in soils as influenced by different anions. *J.plant Nutr. Soil Sci.* **163**, 577-582.

Goh K, Lim T (2004) Geochemistry of inorganic arsenic and selenium in a tropical soil: effects of reaction time, pH and competitive anions on arsenic and selenium adsorption

*Chemosphere* **55**, 849-859.

Kirk GJD, Begg CBM, Solivas JL (1993) The chemistry of the lowland rice rhizosphere. *plant and soil* **155-156**, 83-86.

Mikkelsen R, Mikkelsen. DS, Abshahi A (1989) Effects of soil flooding on selenium transformation and accumulation by rice. *Soil Sci Soc Am J* **53**, 122-127.