

# Dissolution rate of selected sulphur fertilizers; understanding selenate – sulphate competition

RSC 2016  
London  
U.K

\*Jiang L<sup>1</sup>, Young S.D.<sup>1</sup>, Broadley M.R.<sup>1</sup>, Bailey E.H.<sup>1</sup>,  
Graham N.S.<sup>1</sup> and McGrath S.P.<sup>2</sup>

<sup>1</sup> School of Biosciences, University of Nottingham, Sutton Bonington Campus, Loughborough, Leicestershire LE12 5RD, UK.

<sup>2</sup> Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, UK.

The University of  
Nottingham  
UNITED KINGDOM · CHINA · MALAYSIA

\*Corresponding author: [linxi.jiang@nottingham.ac.uk](mailto:linxi.jiang@nottingham.ac.uk)

## INTRODUCTION

A relatively unknown aspect of Se biofortification of crops is the extent to which **sulphur** fertiliser application may suppress selenate uptake by plants. This is caused by competition between sulphate ( $\text{SO}_4^{2-}$ ) and selenate ( $\text{HSeO}_4^-$ ,  $\text{SeO}_4^{2-}$ ) anions for adsorption sites on roots. Selenate added to soil undergoes fixation into unavailable organic forms so plant uptake probably occurs during a 'window of opportunity' shortly after application. The current project aims to assess the use of slower-release **sulphate** fertilisers in minimising suppression of Se uptake during this critical period while still providing sulphur nutrition during the growing season. This poster presents a study of the release characteristics of one such S-compound, **polyhalite** ( $\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ), commercially *Polysulphate*<sup>TM</sup>, compared to some other sulphur fertilisers.

## Materials and Methods



Triplicate soil columns (200 g sandy loam; arable Wick series) were fertilised with three granules of commercial grade Polysulphate,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$  or  $\text{CaSO}_4$ . The granules were covered with 1 cm soil except for a second 'surface-applied' Polysulphate treatment. The soil columns were leached with 1 pore volume of water each day and the leachate collected for analysis by inductively coupled plasma mass spectrometry for sulphur and the constituent cations.

Treatment(6)	Ammonium sulphate, Potassium sulphate, Magnesium sulphate, Anhydrite and Polyhalite (soil covered or surface applied)
Granule	3 (each column)
Water	1 pore volume leached per day
Soil	200 g (each column)
Duration	6 hr leaching
Days	32 days with daily leaching

Table 1. Experiment design of soil column release rate trial

## Results(i): Soil column leaching

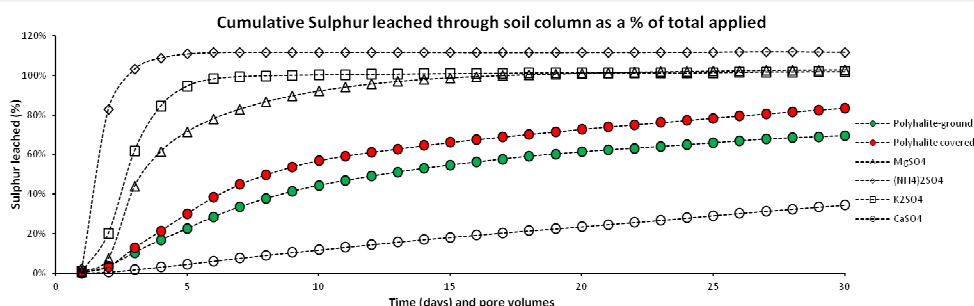


Figure 1. Cumulative release of sulphur through soil column leached daily with 1 pore volume of water

- Ammonium, potassium and magnesium sulphates are dissolved readily and release >80% intrinsic sulphur within 10 d.
- While anhydrite releases sulphur much more slowly, polyhalite shows an intermediate trend suggesting a more evenly paced dissolution which may minimise Se uptake suppression while still providing S nutrition during the growing season.
- These results then lead on to a second trial to test whether sulphur release from polyhalite is the result of purely congruent dissolution of a homogeneous isomorphically substituted crystal or whether there is evidence of incongruent dissolution of independent micro-crystals of Ca, K and Mg sulphate (results below, Figure 2).

## Results(ii): Single rapid polyhalite crystal dissolution

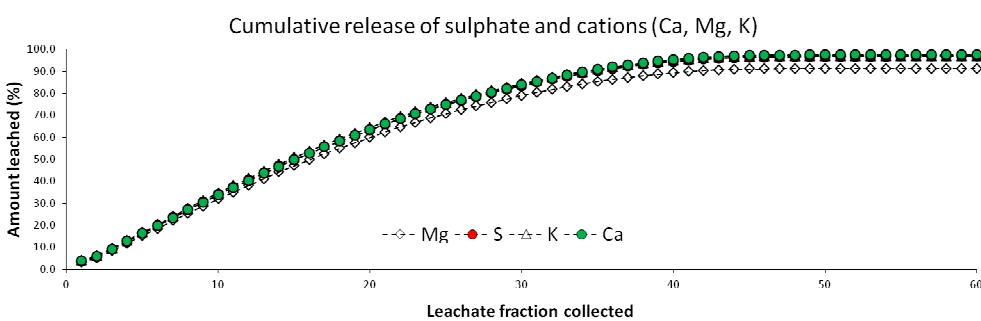


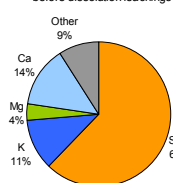
Figure 2. Cumulative release of sulphur and cations (Ca, Mg, K) from a single polyhalite crystal in response to rapid washing

1. The single polyhalite crystal rapid dissolution trial indicates completely congruent dissolution with co-release of all four main constituent ions at a rate dictated only by their stoichiometry.
2. Comparing this trial with soil column dissolution, it seems that the prolonged release of Polysulphate may be explained by *in-situ* crystallisation of calcium sulphate from Ca originating in the Polysulphate.

## CONCLUSIONS

- Polyhalite, as granular Polysulphate<sup>TM</sup>, releases sulphate at a rate which is intermediate between those of readily-soluble salts such as  $\text{NH}_4$ , K and Mg sulphate and that of  $\text{CaSO}_4$ .
- Polysulphate dissolves by congruent dissolution of the homogeneous, isomorphically-substituted polyhalite crystal ( $\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ). However, the concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions around the dissolving granule can lead to an *in-situ* precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which re-dissolves.
- It seems likely that the use of Polysulphate as a sulphate fertiliser may offset suppression of selenium uptake during the limited period of selenate availability in Se biofortification of crops; this is the next phase of this work with Polysulphate.

Ionic composition of granule before dissolution leachings



Ionic composition of 'skeleton' after 30 daily pore volume leachings

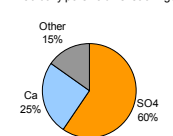


Figure 3 shows a comparison of surface-applied polyhalite granule composition before and after partial leaching in the soil column experiment.

After partial dissolution over 32 days, the polyhalite composition shows that K and Mg (and Na and B) have all been dissolved and what remains for subsequent dissolution is essentially a  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  skeleton which has apparently precipitated *in-situ* in response to the high  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations during dissolution. The ratio of  $\text{Ca}^{2+}$  to  $\text{SO}_4^{2-}$  in the skeletal granule is that of  $\text{CaSO}_4$ . The mass of the skeletal granule is significantly less than the original, resulting in a greater proportion of 'other', mostly insolubles.

This work was supported by ICL Fertilizers and the UoN China Scholarship scheme. Project participants are named as co-authors. We gratefully thank Rory Hayden and Lolita Wilson for help in setting up the dissolution rate trial.

Figure 3. Polyhalite composition before and after daily leaching for 30 days.