Supplemental Material

Oxidation of elemental sulfur in granular fertilizers depends on the soil-exposed surface area

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1) Solid/liquid partition coefficient at trace level

The adsorption coefficient of SO\(_4\)-S at trace level was determined. Five g of soil was weighed out into a 50-mL centrifuge vial and 20 mL of carrier-free \(^{35}\)SO\(_4\)-S spiked water (25 Bq mL\(^{-1}\)) was added. The samples were shaken overnight on an end-over-end shaker, centrifuged (15 minutes at 3000 g) and a subsample of the supernatant was filtered through a 0.45-\(\mu\)m membrane filter. The \(^{35}\)S activity in the filtered subsample was determined and the solid/liquid partition coefficient (\(K_d\), L kg\(^{-1}\)) was calculated as:

\[
K_d = \left(\frac{a_{ini} - a_{fin}}{a_{fin}}\right) \cdot \frac{V}{W}
\]

where \(a_{ini}\) and \(a_{fin}\) are the initial (added) and final activities (Bq) in the total solution, \(W\) the weight of soil (kg) and \(V\) the volume of solution (L). The \(K_d\) in the Brazilian soil was 3.2 L kg\(^{-1}\). The \(K_d\) in the Beardstown and Edmonton soils was <0.1 L kg\(^{-1}\) – no exact value could be determined because the difference between initial and final activity in solution was too small.

2) Breakthrough curves

The breakthrough of a sulfate pulse (as (NH\(_4\))\(_2\)SO\(_4\)) was determined in a preliminary column experiment. The soils were packed in the same way as for the column experiments described in the manuscript and pre-leached for 2 hours with 1 mM CaCl\(_2\) at a flow rate of 10 mL h\(^{-1}\). A sulfate pulse was added to the column by using 0.1 M (NH\(_4\))\(_2\)SO\(_4\) as influent at a flow rate of 3 mL h\(^{-1}\) for 1 h, after which the columns were leached with 1 mM CaCl\(_2\) at a flow rate of 3 mL h\(^{-1}\). The effluents were collected at regular time intervals and analyzed for S by ICP-OES (inductively-coupled plasma optical emission spectroscopy).

Figure S1 shows the breakthrough curves determined for the Edmonton or Beardstown soils (70 g soil per column). For both soils, almost all added SO\(_4\)-S was leached out after 35 mL. Therefore, 35 mL was used as leaching volume in the main column experiment.

Figure S2 shows the breakthrough curves for the Brazilian soil (60 g soil per column). Because of the stronger retention of sulfate in this soil, more solution was required to fully remove the added sulfate from the soil column. A leaching volume of 220 mL was selected because the sulfate concentrations in the effluent reached background level after 220 mL water had percolated through the column. Calculations with STANMOD (Šimůnek et al.) confirmed that 220 mL is sufficient to remove all SO\(_4\)-S from the column even at low sulfate levels, based on the \(K_d\) of 3.2 L kg\(^{-1}\) determined at trace level.
Fig. S1. Column breakthrough curves of a sulfate pulse for (A) Edmonton or (B) Beardstown. The red curve shows the concentration in the influent and the blue symbols the concentrations in the effluent. The soil columns contained 70 g dry soil.

Fig. S2. Column breakthrough curves of a sulfate pulse for the Sorisso soil. The red curve shows the concentration in the influent (left y-axis) and the blue symbols the concentrations in the effluent (right y-axis). The soil column contained 60 g dry soil.

Reference

3) Fitted and observed leaching curves

Figure S3 illustrates the observed sulfate-S leaching (also shown in Figure 3) and ES remaining in the column at the end of the experiment (for Exp. 1), and the fitted curves using the parameters given in Table 5.

**Fig. S3.** Cumulative recoveries of elemental S (ES)-derived S in the leachates (black) and %ES remaining in soil (orange) as a function of time, for powdered ES (panels A-B), MES10 (MAP-based fertilizer with 5% ES; panels C-D) and Tiger90 (ES:bentonite pastilles; panels E-F) in the Edmonton (left) or Beardstown soil (right). The symbols give measured values and the lines the predicted values (Eq. 7) with parameter values for the oxidation as given in the graphs and parameter values for the immobilization as follows: $I_{\text{max}} = 0.04 \text{ mg kg}^{-1} \text{ d}^{-1}$ and $K_{m} = 0.50 \text{ mg kg}^{-1}$ for Edmonton; $I_{\text{max}} = 0.31 \text{ mg kg}^{-1} \text{ d}^{-1}$ and $K_{m} = 0.59 \text{ mg kg}^{-1}$ for Beardstown.