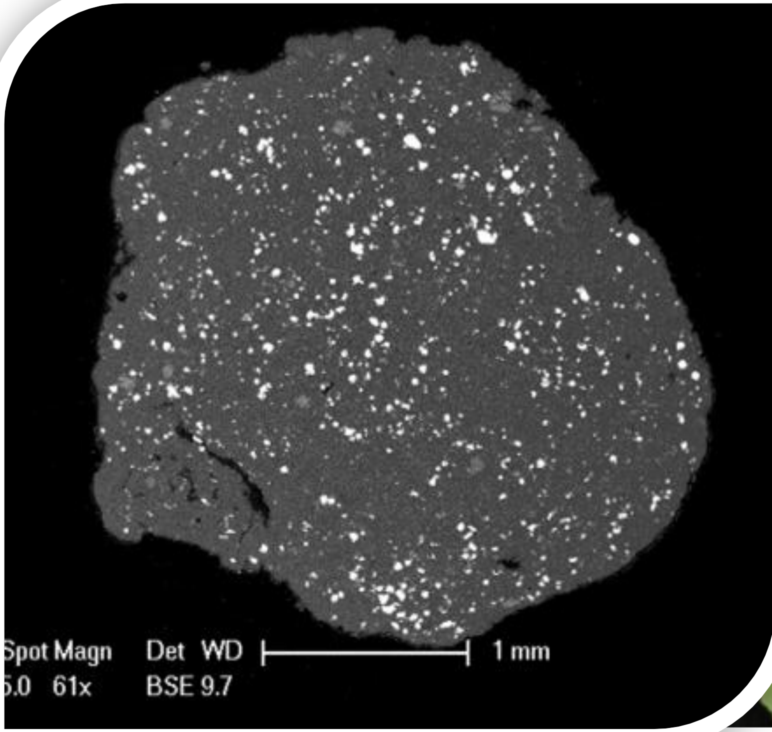

Transformations of sulfate and elemental sulfur in soil

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Introduction

- Sulfur is an essential major plant nutrient, but has received relatively little attention.

- Removal (kg/ha/y) | Input (kg/ha/y)

Removal (kg/ha/y)	Input (kg/ha/y)
Crops: 5-20	Atmospheric: 2-20
Leaching: 0-50	Mineral weathering: 0-5

$\Rightarrow$ Removal > input (especially in high-rainfall areas) without any other S input

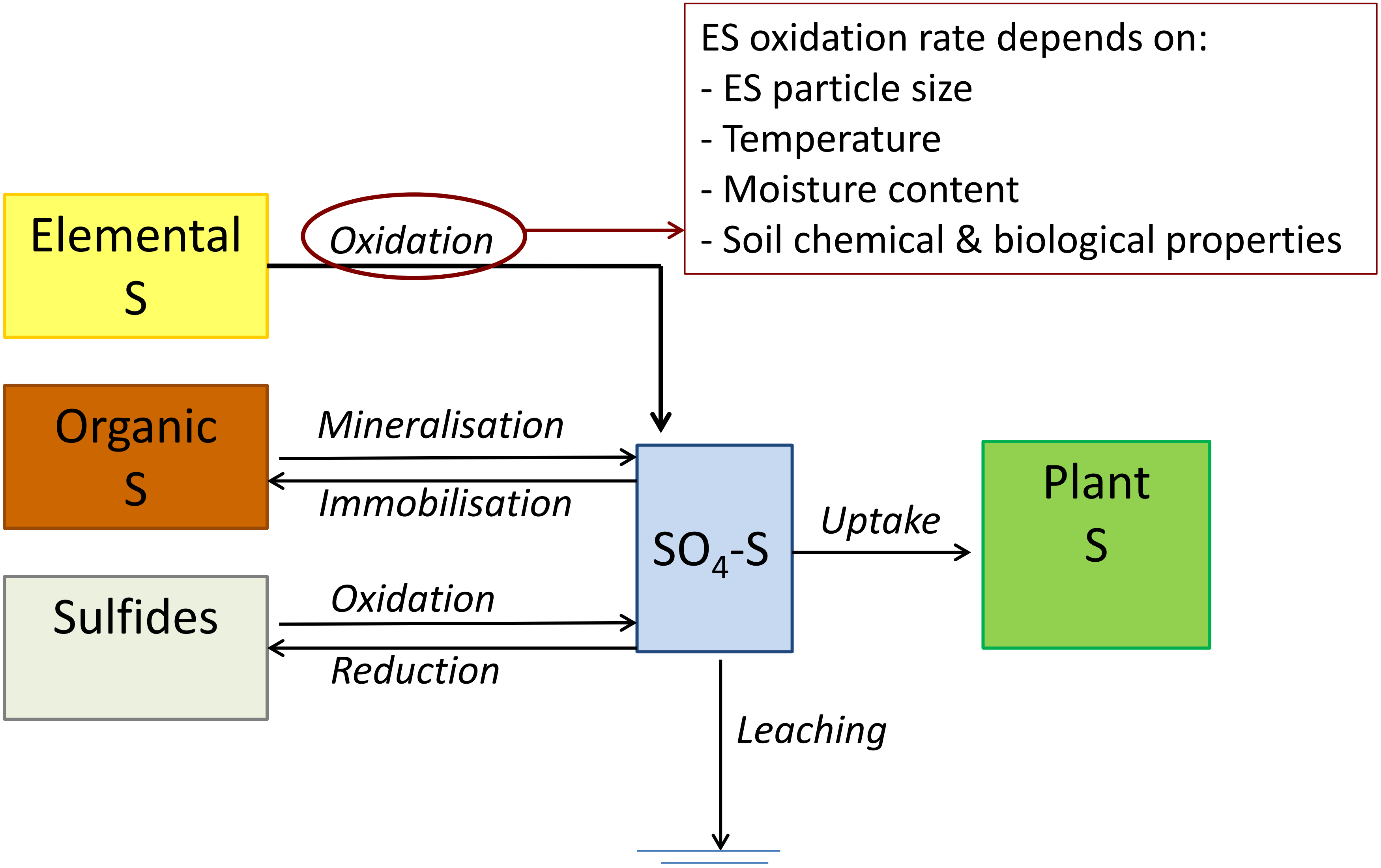
Stevenson & Cole, 1999

- S deficiency has become more common, because of the use of high-analysis S-free fertilizers and reduced atmospheric S deposition

Introduction: inorganic sulfur fertilisers

S form	(Dis)advantages	Fertilisers (%S)
Sulfate	+ Readily available - Susceptible to leaching losses High transport/application cost on a nutrient basis (SO_4^{2-})	$(NH_4)_2SO_4$ (24%) KMag ($K_2SO_4.2MgSO_4$, 21%) Gypsum (18%) K_2SO_4 (18%) SSP (11%)
Elemental S 	+ Lower transportation/application cost Sustained release - Only available when oxidised	ES pastilles/prills (~90%) ES cogranulated with TSP, MAP, urea etc.

Introduction: the S cycle in soil

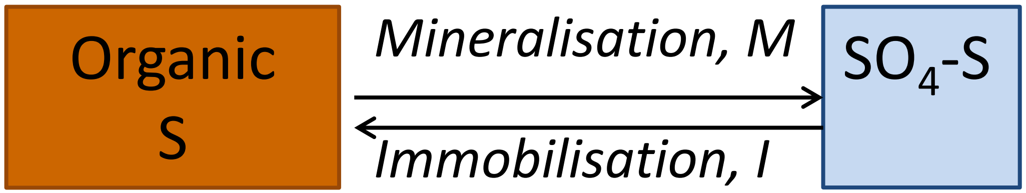


Outline

- Incubation experiment 1 (mineralisation/immobilisation):
  – 10 Australian soils
  – Incubated without or with 50 mg S/kg as $(NH_4)_2SO_4$
- Incubation experiment 2 (oxidation):
  – 10 (N and S-)American and Australian soils
  – Incubated with 100 mg S/kg elemental S (ES)
- Pot experiment:
  – S-Australian soil
  – Without or with 20 mg S/kg in different forms
  – 2 Canola crops

- (Field trials)

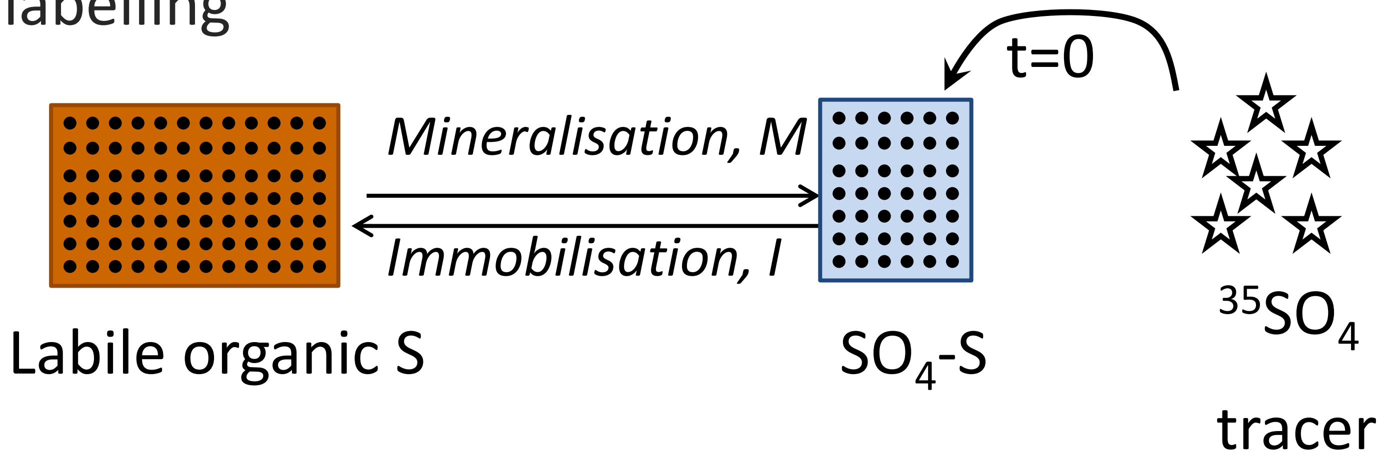
1. Mineralisation/Immobilisation



- Concurrent processes:
  - Net immobilisation= I-M
  - Steady state if I=M
  - Changes in SO_4-S concentrations indicate the net immobilisation (or mineralisation), but not the gross immobilisation and mineralisation rates.

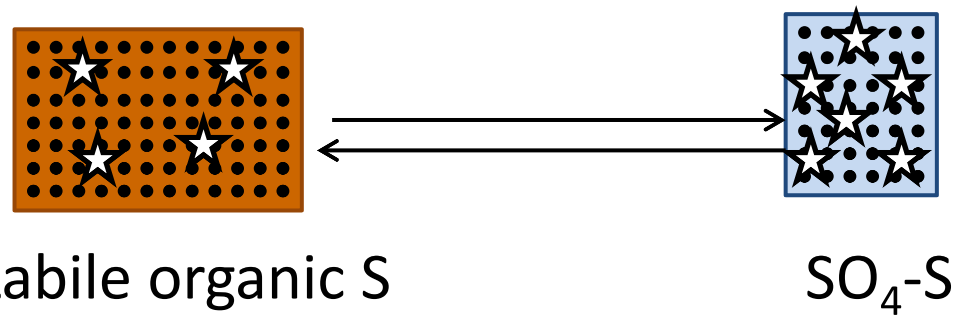
1. Mineralisation/Immobilisation

- Isotopic labelling



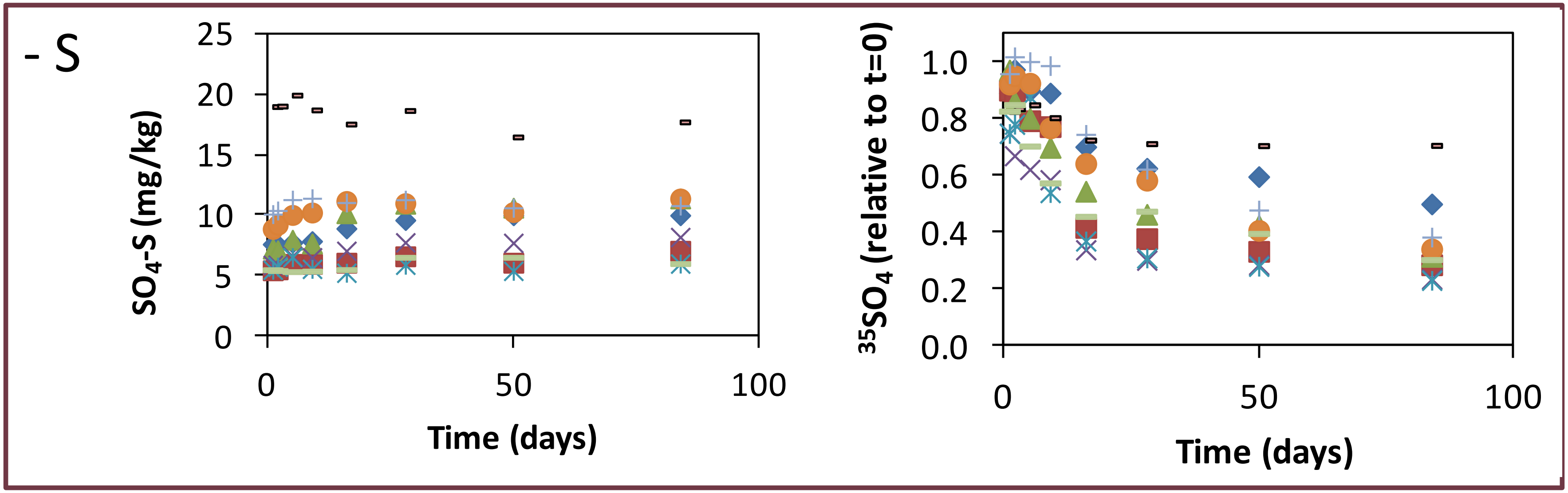
1. Mineralisation/Immobilisation

- Isotopic labelling



- Method:
  - 10 soils, pre-incubated for 1 week
  - Addition of $^{35}SO_4$, with or without 50 mg S/kg as $(NH_4)_2SO_4$
  - Sulfate extraction with 0.01 M $Ca(H_2PO_4)_2$. Stable S and ^{35}S in extract determined, at day 1, 2, 5, 9, 16, 28, 50 and 84.

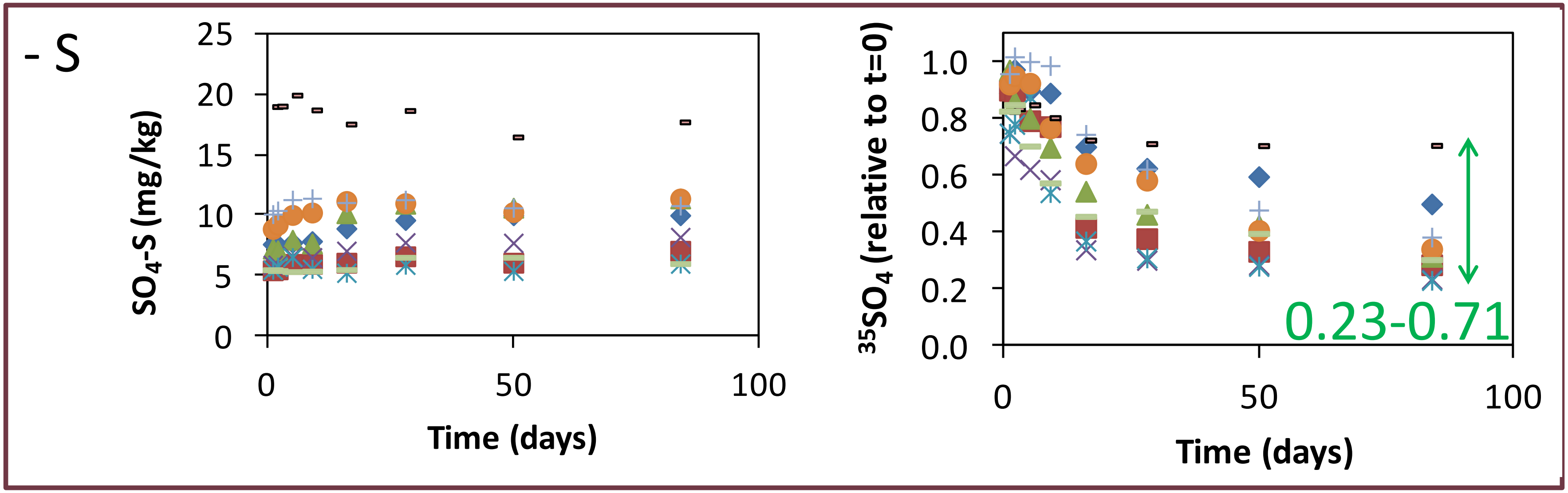
1. Mineralization/Immobilization – no added S



- Little change in sulfate concentrations

  ⇐ Steady state: Mineralisation = Immobilisation

1. Mineralization/Immobilization – no added S



- Little change in sulfate concentrations

  $\Leftarrow$ steady state: Mineralisation = Immobilisation

- Solution for $^{35}SO_4$ (f, relative to t=0; f=1 at t=0) if steady state:

$$f = f_{eq} + (1 - f_{eq}).\exp(-kt) \quad \text{with} \quad \begin{cases} f_{eq} = \dfrac{SO_4\text{-}S}{SO_4\text{-}S + LOS} \\ k = \dfrac{M}{LOS} + \dfrac{I}{SO_4\text{-}S} \end{cases}$$

(Fitting parameters: LOS and M=I)

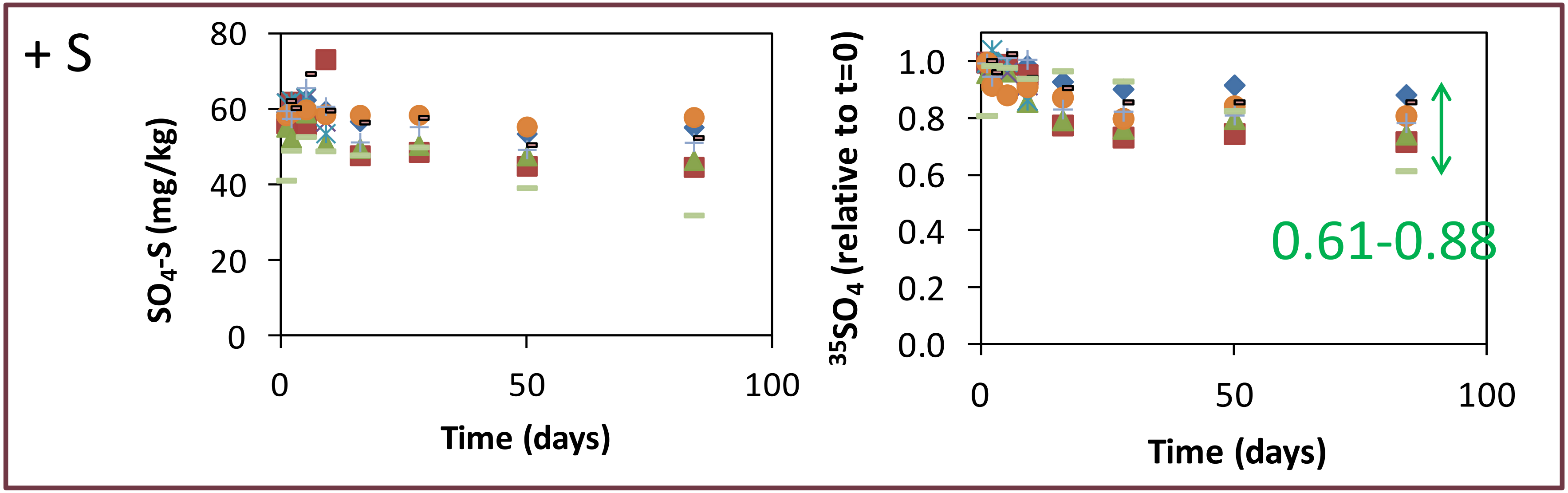
1. Mineralization/Immobilization – no added S

	pH ($CaCl_2$)	Total S (mg/kg)	SO_4-S (mg/kg)	LOS (mg/kg)	M=I (mg/kg/d)	Turnover t (days)
SA4	7.3	182	8	7	0.17	43
SA6	6.2	205	5	13	0.28	49
SA8	7.5	279	7	13	0.34	38
V1	5.1	224	6	14	0.68	21
V2	7.3	83	5	16	0.40	41
N1	5.2	128	9	19	0.24	78
N4	4.6	133	10	16	0.20	80
WA1	4.0	64	19	8	0.98	8
Q2	6.7	52	5	11	0.38	28
MIN	**4.0**	**52**	**5**	**7**	**0.17**	**8**
MAX	**7.5**	**279**	**19**	**19**	**0.98**	**80**

Crop removal: 5–20 kg/ha ~ 2–7 mg/kg (2 dm depth)

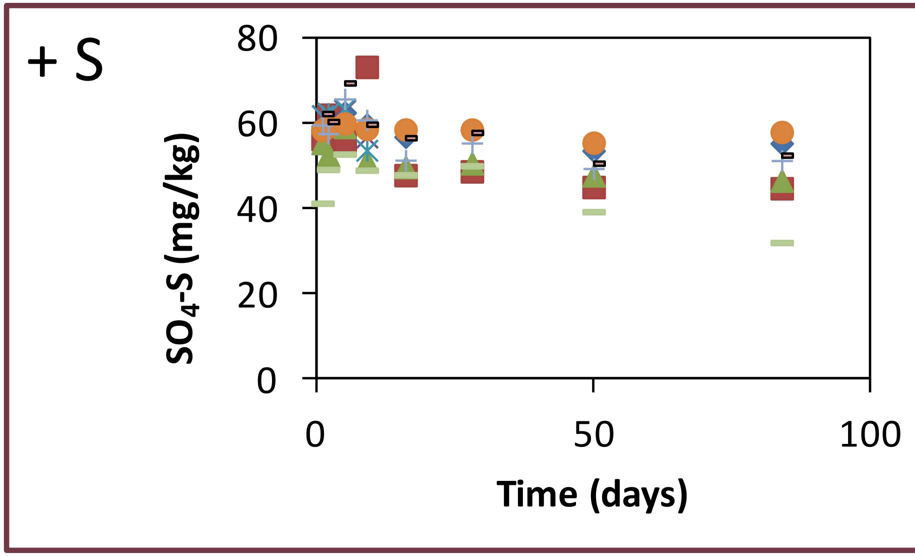
S uptake by crops: up to circa 0.3 mg/kg/day

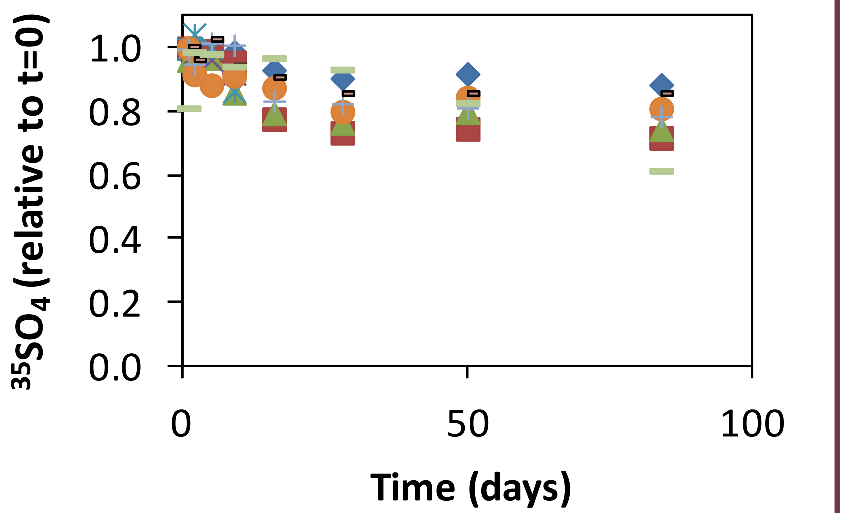
1. Mineralization/Immobilization - with added S

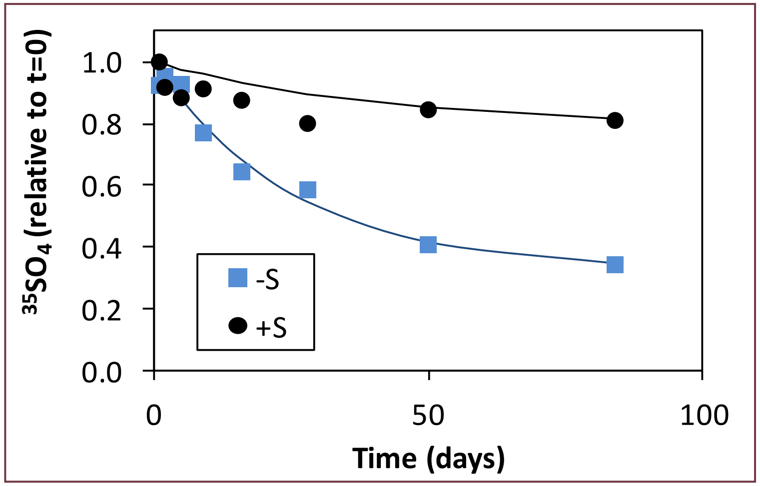


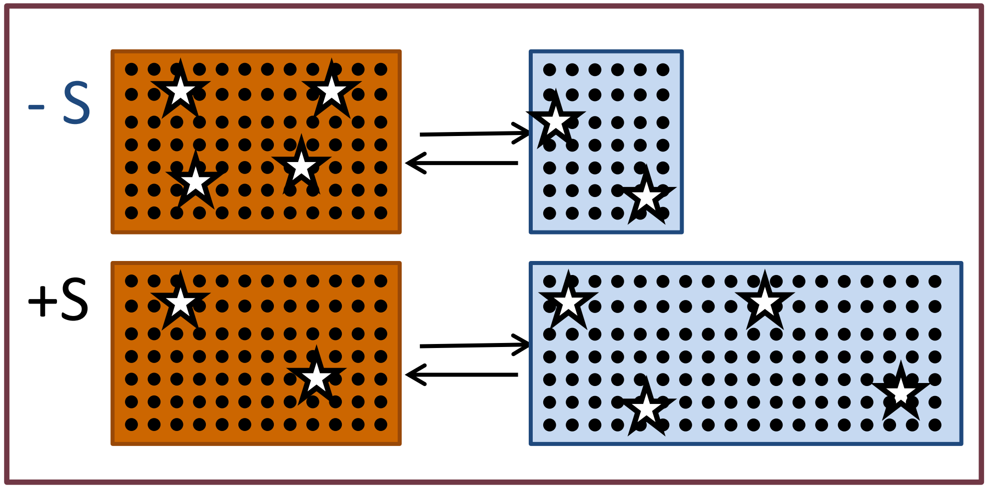
- Net immobilisation: 0.5-16 mg/kg in 84 days
- High sulfate levels result in relatively less incorporation of $^{35}SO_4$-S into the organic S pool

1. Mineralization/Immobilization - with added S

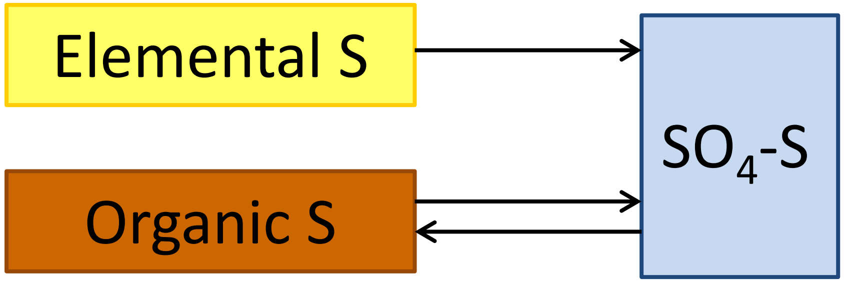






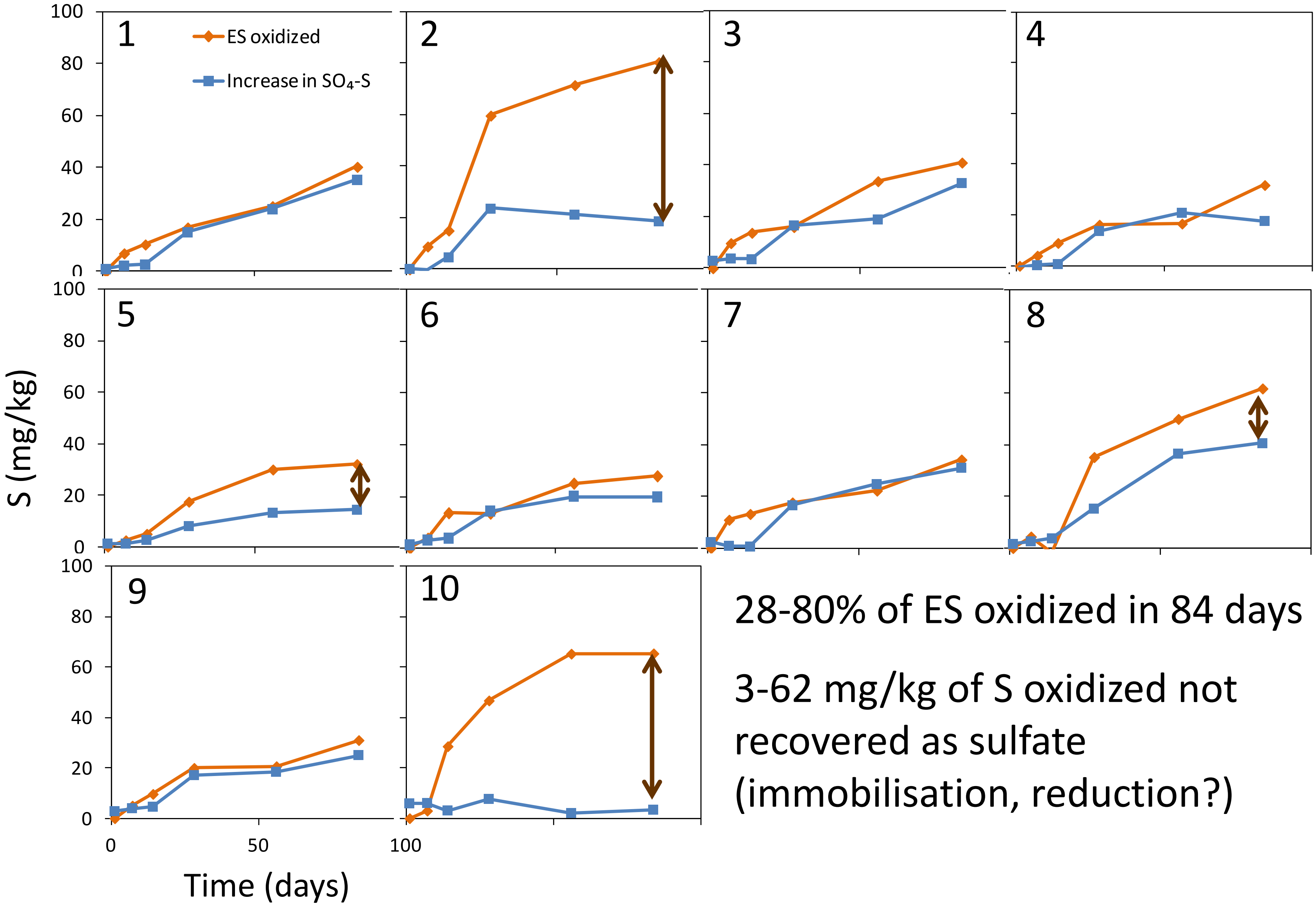


2. Oxidation experiment



- Method:
  - 10 soils, pre-incubated for 1 week
  - Addition of 100 mg ES/kg (d_{av} 40 µm) (+ $^{35}SO_4$ tracer)
  - At day 1, 7, 14, 28, 56 and 84:
    - Sulfate extraction with 0.01 M $Ca(H_2PO_4)_2$; stable S and ^{35}S in extract determined
    - Chloroform extraction and determination of elemental S with HPLC

2. Oxidation experiment



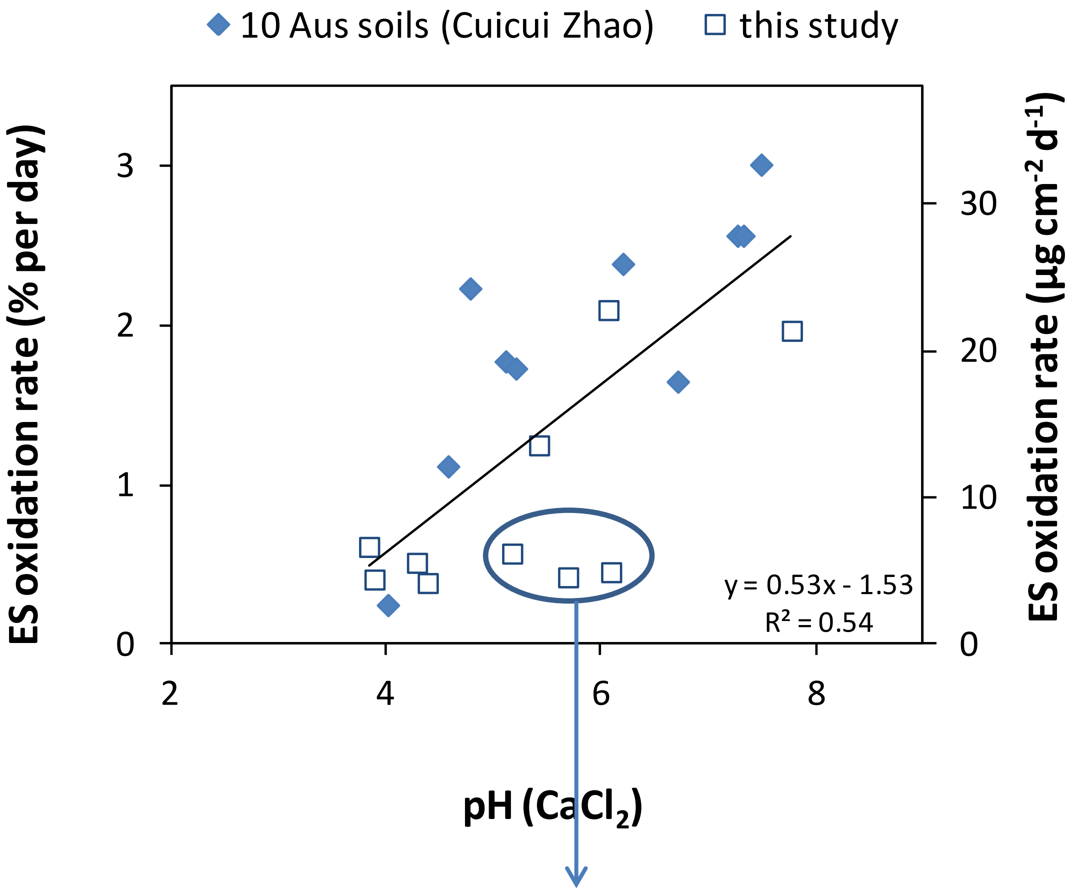
28-80% of ES oxidized in 84 days

3-62 mg/kg of S oxidized not recovered as sulfate (immobilisation, reduction?)

2. Oxidation experiment

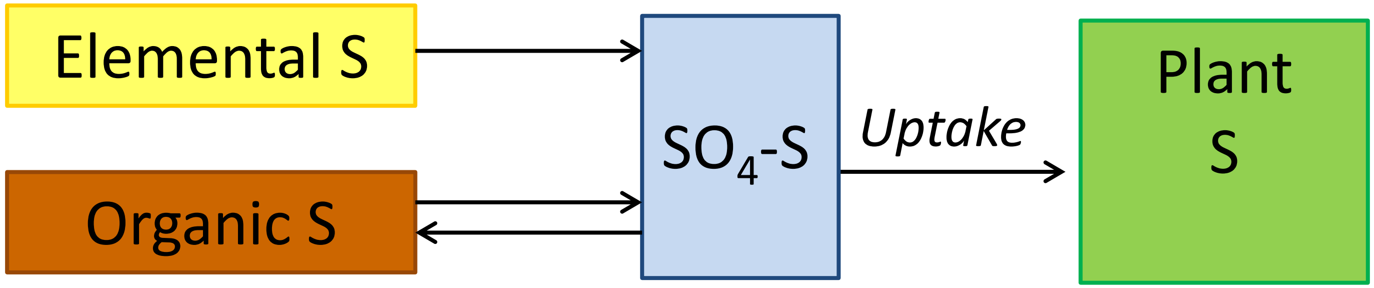
		pH ($CaCl_2$)	OC (%)	Total S (mg/kg)	SO_4-S (mg/kg)	LOS (mg/kg)	Oxidation rate (%/day)
1	USA1	5.2	0.4	36	9	2	0.6
2	USA2	6.1	2.0	182	16	74	2.1
3	Brazil1	3.8	0.9	99	13	3	0.6
4	Brazil2	3.9	2.2	322	49	10	0.4
5	Brazil3	4.3	0.8	99	23	2	0.5
6	Brazil4	4.4	1.1	97	17	5	0.4
7	Chile	5.7	3.8	301	55	4	0.4
8	Argentina	5.4	2.9	287	12	20	1.3
9	Aus1	6.1	0.8	99	5	14	0.5
10	Aus2	7.8	2.0	196	9	nd	2.0
	MIN	**3.8**	**0.4**	**36**	**5**	**2**	**0.4**
	MAX	**7.8**	**3.8**	**322**	**55**	**74**	**2.1**

2. Oxidation experiment



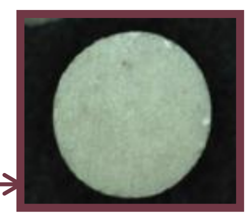
Soils with relatively low oxidation rate: two sandy soils and an Andisol with high sulfate concentration.

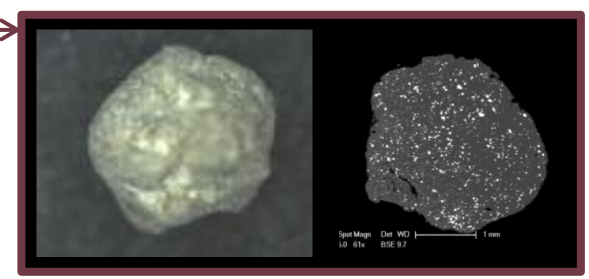
3. Pot experiment



Methods:

- Sandy soil (South Australia, pH 7.0)
- Labelled with $^{35}SO_4$ and pre-incubated for 50 days
- Fertilizer added (20 mg S per kg):
  - $(NH_4)_2SO_4$ (=SoA)
  - Elemental S pastille (90% ES)
  - MAP+5%ES+5%SO_4-S fertiliser

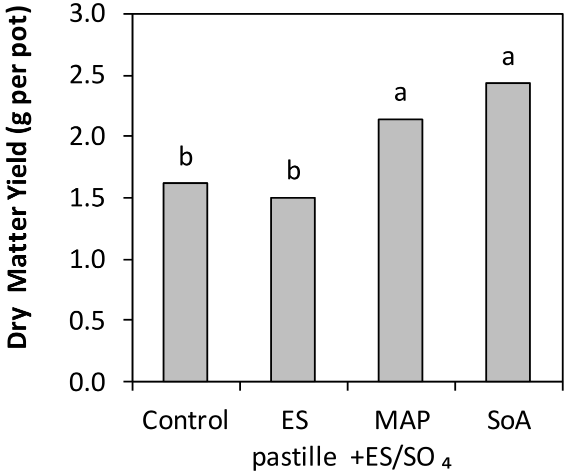


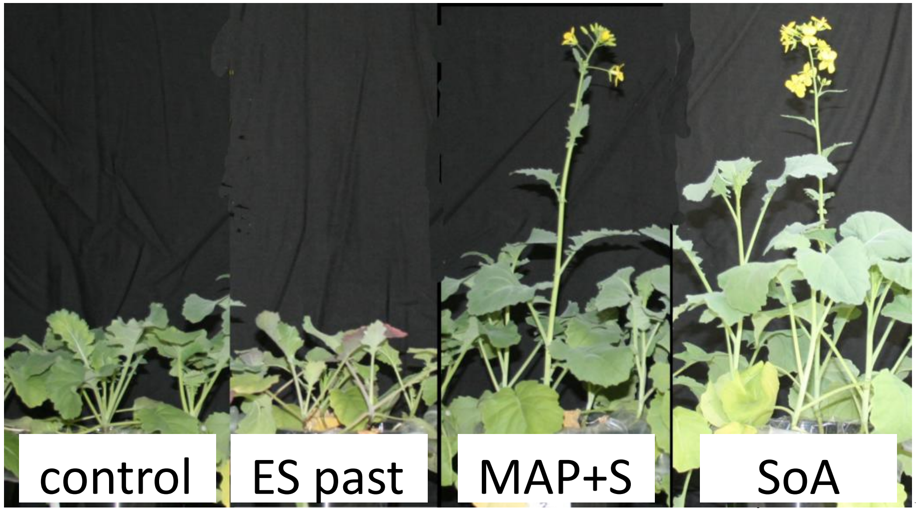


- Two Canola crops:
  - Crop 1: day 1–42
  - Soil mixed
  - Crop 2: day 80 – 125

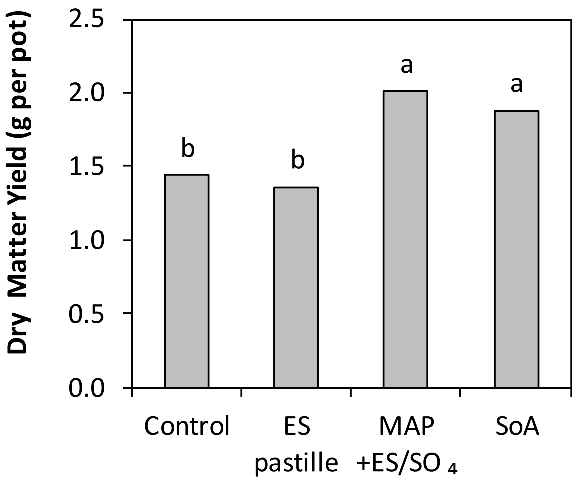
3. Pot experiment

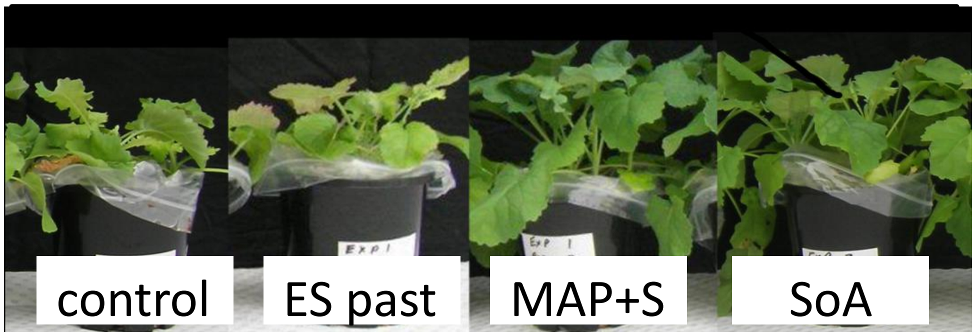
Crop 1





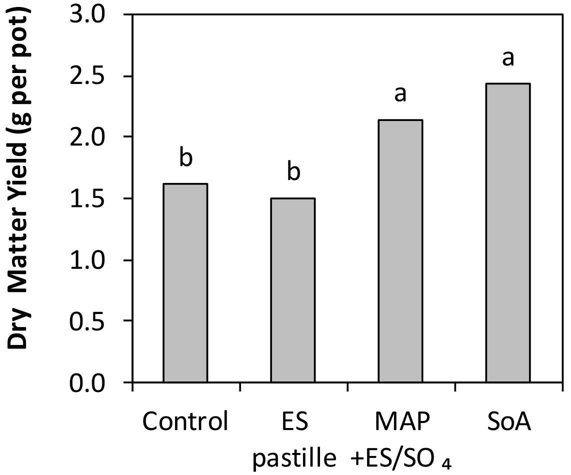
Crop 2

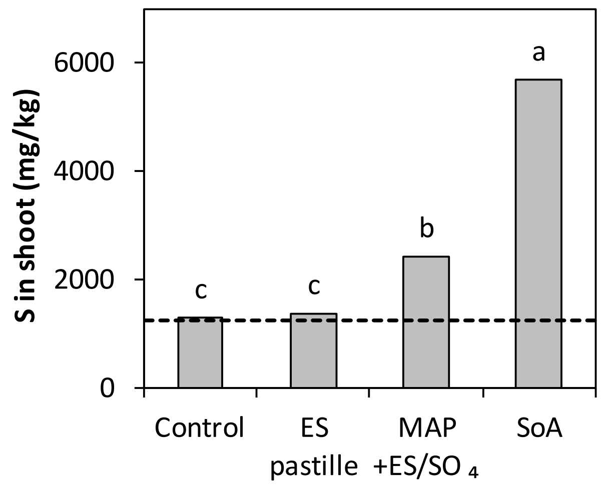


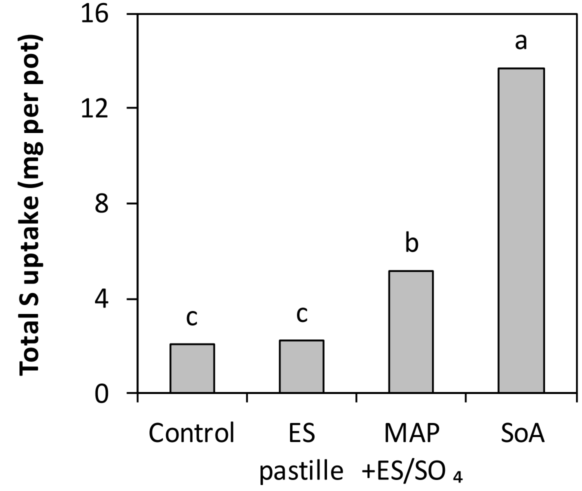


3. Pot experiment

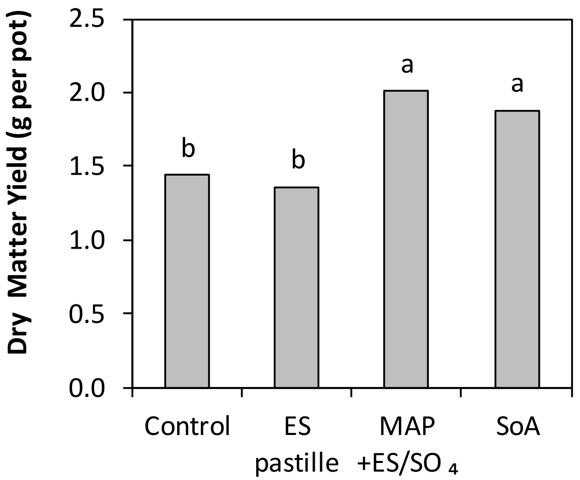
Crop 1

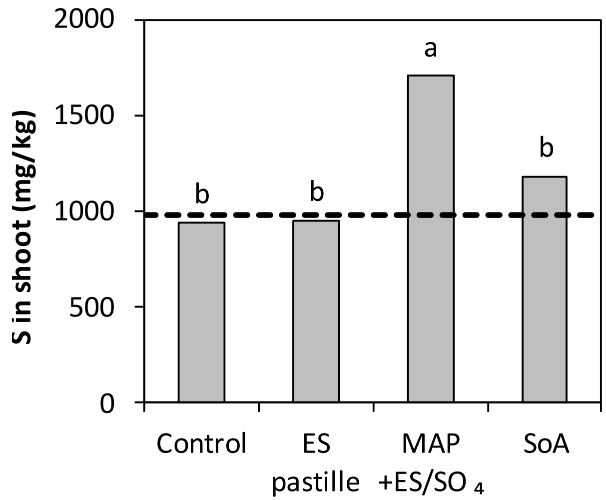


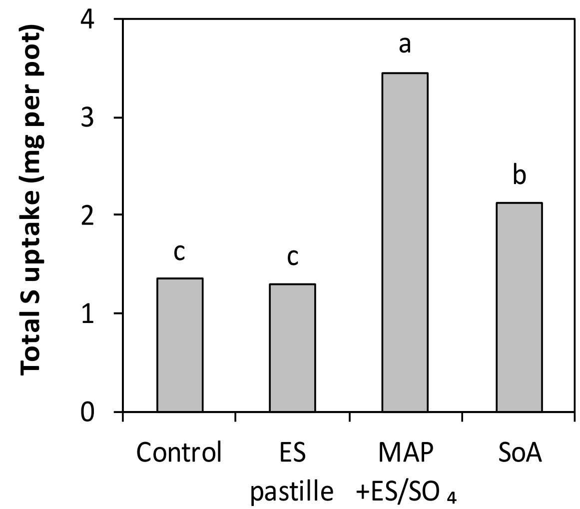




Crop 2







Conclusions

- Labile organic S pool in 20 soils ranged from 2-74 mg/kg (1-40% of total S). The turnover of LOS was fast (turnover time of 8-80 days).
- Elemental S oxidation range at 25°C ranged from 3 to 37 μg/cm^2/day (~ 0.2–3% per day for ES with d=40 μm). Soil properties (pH, others) affect the oxidation rate.
- The cycling of S in organic matter is important to understand soil S availability and fertiliser S fate.
- Sulfate fertilisers are susceptible to leaching and luxury uptake. The slow release from elemental S allows for a supply later in the season or in subsequent seasons.

Acknowledgements

Mosaic

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Thank you for your attention!