Electronic Supplementary Information for

Sulfur Polymer Composites as Controlled-Release Fertilisers

Maximilian Mann,†[a,b] Jessica E. Kruger,†[a,b] Firas Andari,[a,b] Joshua McErlean,[b] Jason R. Gascooke,[a,b] Jessica A. Smith,[c] Max J. H. Worthington,[a,b] Cheylan C. C. McKinley,[a,b] Jonathan A. Campbell,[a,b] David A. Lewis,[a,b] Tom Hasell,[c] Michael V. Perkins,[b] and Justin M. Chalker*[a,b]

Affiliations:

a. Institute for NanoScale Science and Technology, Flinders University, Sturt Road, Bedford Park South Australia, Australia

b. College of Science and Engineering, Flinders University, Sturt Road, Bedford Park, South Australia, Australia.

c. Department of Chemistry, University of Liverpool, Crown Street, Liverpool, United Kingdom

To whom correspondence should be addressed: justin.chalker@flinders.edu.au

Web: www.chalkerlab.com

Table of Contents

General Considerations

^{1}H NMR spectra were recorded on a 600 MHz or 400 MHz Bruker spectrometer with pyridine-D5, $CDCl_3$, or D_2O as the solvent, as indicated. Samples were filtered using PTFE 0.45 µm syringe filters before acquiring spectra. Spectra were referenced to residual solvent peaks (δ_H = 8.74 for pyridine and δ_H = 7.26 for $CDCl_3$).

Infrared (IR) spectra were recorded (neat film or ATR) using a FTIR Perkin Elmer spectrophotometer between 4000 and 500 cm^{-1}.

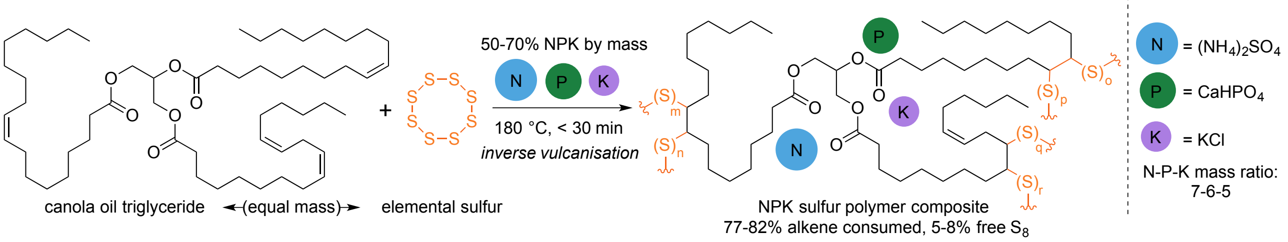
SEM and EDX images were obtained using an FEI Inspect F50 SEM fitted with a EDAX energy dispersive X-Ray detector. Samples were sputter coated silver metal (20 nm thickness) before analysis.

Differential Scanning Calorimetery (DSC) was carried out using a Perkin Elmer DSC 8000 with the nitrogen furnace purged at 20 mL / min. A heating rate of 5 ºC / min was used to measure phase changes in the composites.

Conductivity of water was measured using a Sper Scientific Benchtop Water Quality Meter. The meter was calibrated before each use using a 0.02 M KCl standard solution with a conductivity of 2.76 mS.

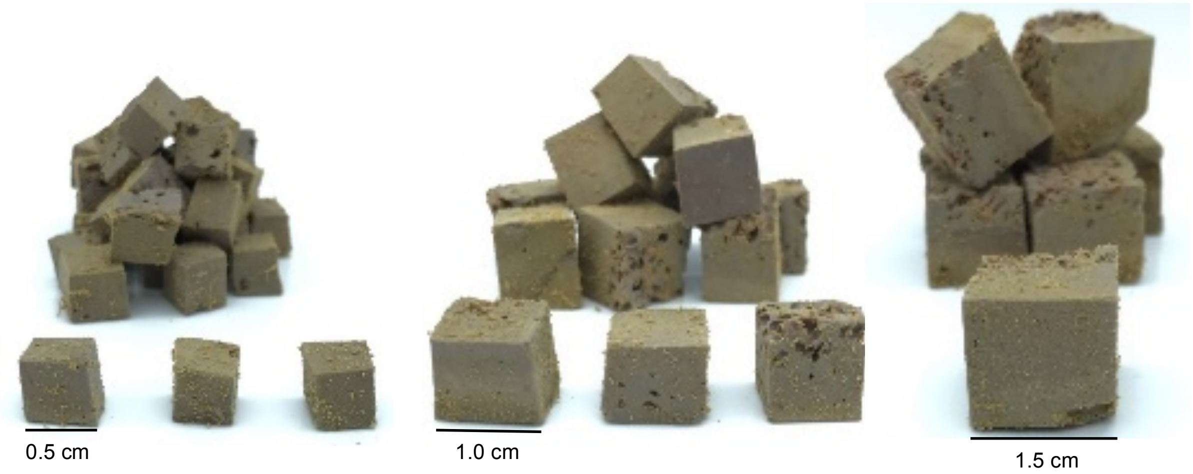
Ion Chromatography was conducted using a Dionex ICS-1500 ion chromatograph fitted with a Dionex AS 40 automated sampler. The column used was a Dionex Ion Pac^{TM} AS14A, RFIC^{TM}, 4 x 250 mm. The eluent was 0.8 mM sodium carbonate / 1.0 mM sodium bicarbonate.

Synthesis of the canola oil polysulfide and the NPK sulfur polymer composites



An NPK nutrient mixture was prepared by mixing ammonium sulfate ($(NH_4)_2SO_4$, Chem Supply, analytical reagent), calcium phosphate dibasic ($HCaO_4P$, Sigma-Aldrich, 98.0-105.0%) and potassium chloride (KCl, Chem Supply, laboratory reagent) in a mass ratio of 7:6:5, respectively. These NPK components were used as received.

The synthesis of the polymer and NPK-polymer composite was adapted from a procedure described previously.[1,2] Briefly, equal masses of sulfur and canola oil were added to a reactor with the desired amount of the NPK mixture. For example, the 50% NPK sulfur polymer composite was prepared by adding 50 g sulfur, 50 g of canola oil and 100 g of the NPK mixture to a 300 mL reactor equipped with an overhead stirrer. The reaction was heated with stirring to 180 ºC. The stirring rate was increased after the sulfur melted (~120 ºC) to ensure efficient mixing. After 30 minutes of total reaction time, the reaction mixture became viscous and lightened in colour. At this point, the stirring was stopped and the reactor removed from the hotplate. Upon cooling the sulfur polymer composite was cut from the reactor to provide cubes with widths of 0.5 cm, 1.0 cm or 1.5 cm. A control sample of polymer without NPK was also prepared by the same protocol. Images of the polymer and the NPK polymer composites are shown below and on page S5.



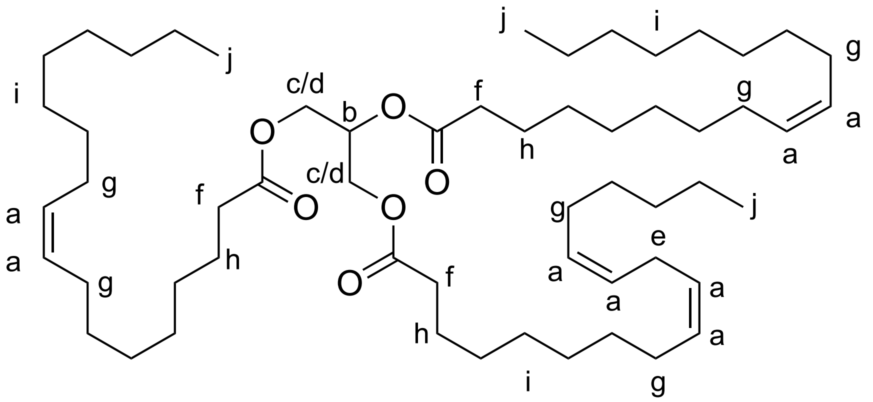
0.5 cm, 1.0 cm and 1.5 cm cubes of the canola oil polysulfide with **0% NPK fertiliser**

0.5 cm, 1.0 cm and 1.5 cm cubes of sulfur polymer composite containing **50% NPK fertiliser**

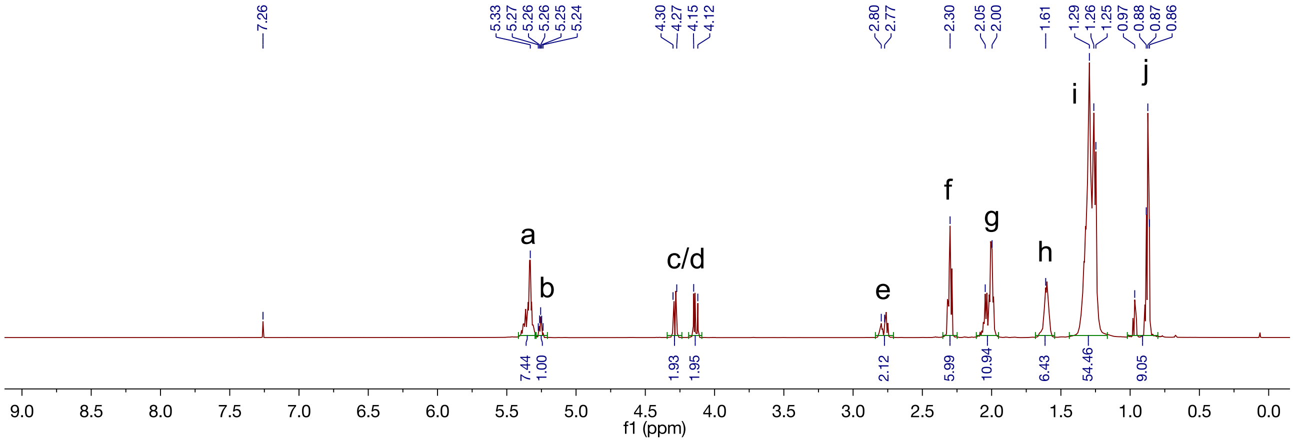
0.5 cm, 1.0 cm and 1.5 cm cubes of sulfur polymer composite containing **60% NPK fertiliser**

0.5 cm, 1.0 cm and 1.5 cm cubes of sulfur polymer composite containing **70% NPK fertiliser**

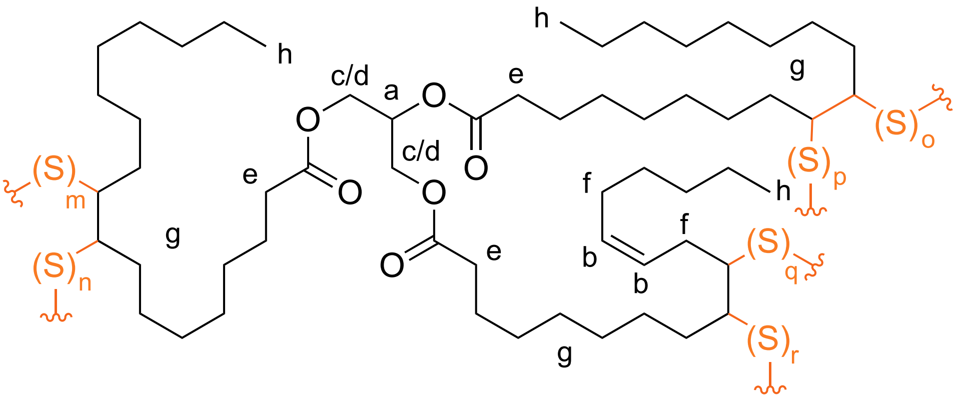
NMR data for canola oil, canola oil polysulfide, and NPK sulfur polymer composites



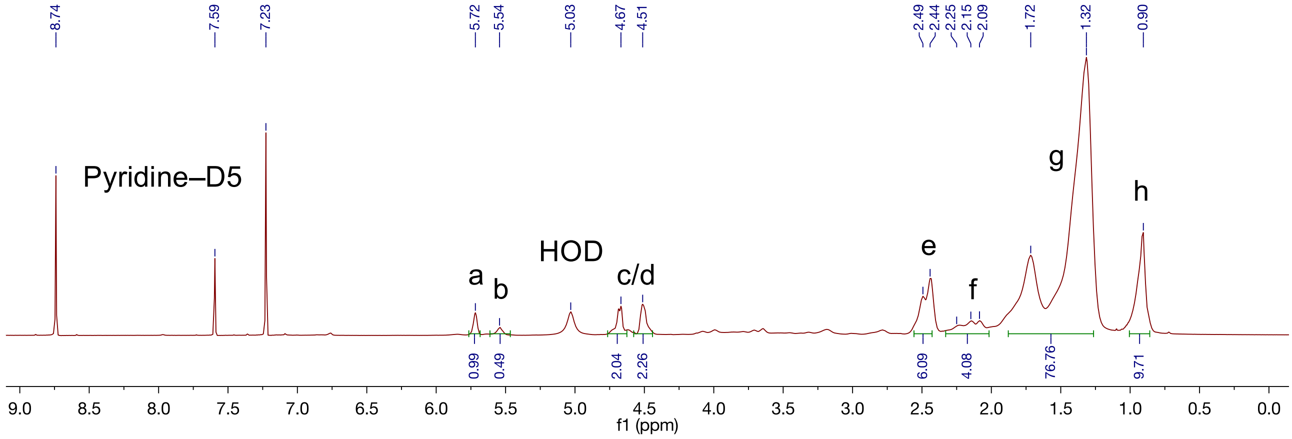
Canola oil triglyceride (approximate structure, based on fatty acid composition analysis)[1,2]



^{1}H NMR spectrum for canola oil (600 MHz, CDCl$_3$): $\delta = 0.87$ and 0.97 (proton j, 9H, t, $J = 6.9$, CH$_3$), 1.25-1.36 (proton i, 54H, all non-allylic, non-α/β CH$_2$), 1.58-1.66 (proton h, 6H, β CH$_2$), 1.97-2.08 (proton g, ~11H, allylic CH$_2$), 2.29-2.32 (proton f, 6H, α CH$_2$), 2.74-2.81 (proton e, 2H, doubly allylic CH$_2$), 4.12-4.15 and 4.27-4.30 (protons c/d, 2H each, glycerol CH$_2$), 5.26 (proton b, 1H, glycerol CH), 5.29-5.41 (proton a, CH=CH).



Canola oil polysulfide (50% canola oil, 50% sulfur, 0% NPK)

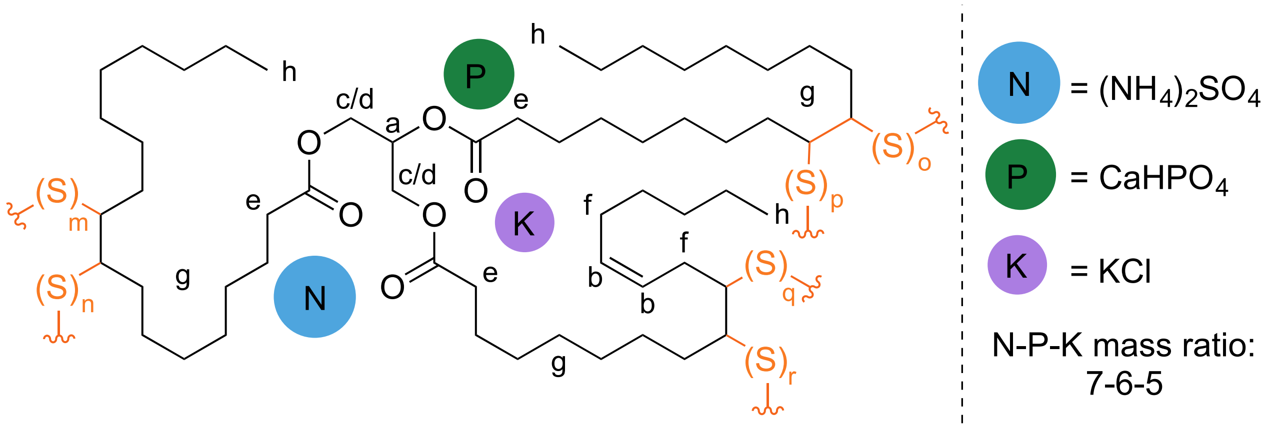


^{1}H NMR spectrum for polysulfide prepared from canola oil and sulfur (no NPK) (600 MHz, pyridine-D5): δ = 0.90 (proton h, CH_3), 1.31 and 1.72 (proton g, all CHS and non-α CH_2), 2.09-2.25 (proton f, allylic CH_2), 2.44-2.50 (proton e, α CH_2), 4.51 and 4.67 (proton c/d, glycerol CH_2), 5.54 (proton b, unreacted HC=CH), 5.72 (proton a, glycerol CH).

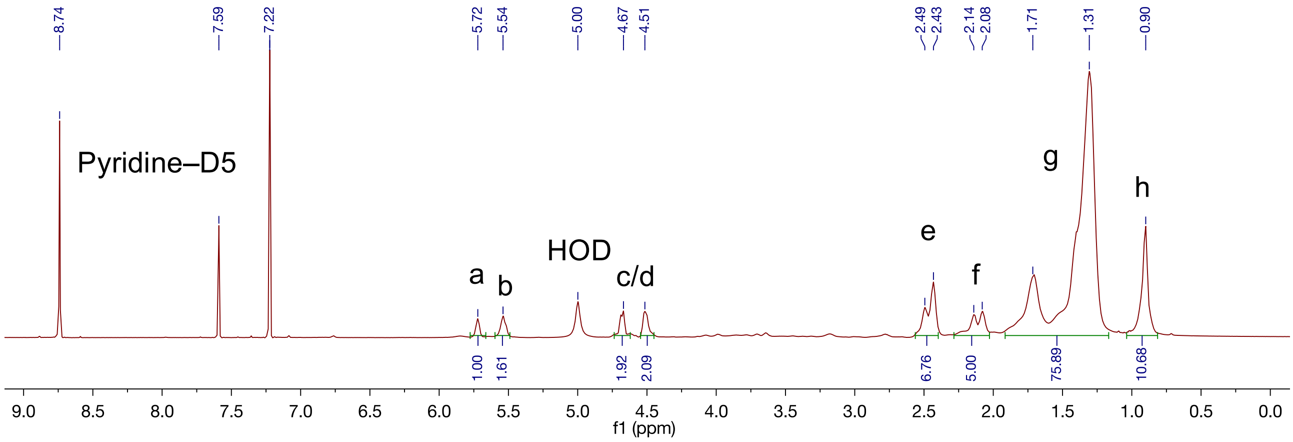
The ratio of the unreacted alkene to the CH_3 groups in the canola oil polysulfide (no NPK) is 0.49 / 9.71 = 0.05

The ratio of the alkene signals to the CH_3 groups in the canola oil starting material is 7.44 / 9.05 = 0.82

This means that 94% of the alkenes have reacted in the polymerisation.



NPK sulfur polymer composite (50% NPK)

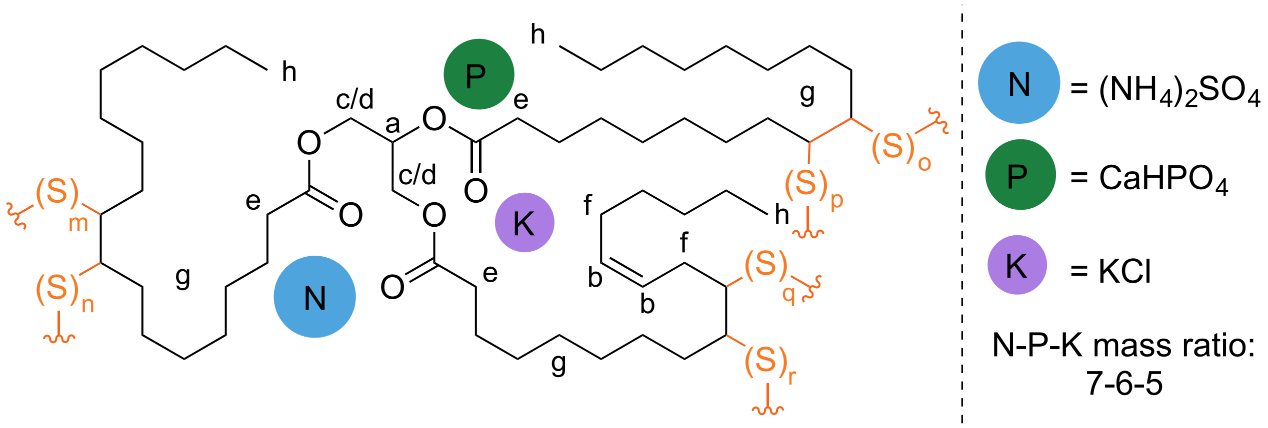


^{1}H NMR spectrum for sulfur polymer composite (50% NPK) (600 MHz, pyridine-D5): $\delta = 0.90$ (proton h, CH_3), 1.31 and 1.72 (proton g, all CHS and non-α CH_2), 2.08-2.25 (proton f, allylic CH_2), 2.43-2.50 (proton e, α CH_2), 4.51 and 4.67 (proton c/d, glycerol CH_2), 5.54 (proton b, unreacted HC=CH), 5.72 (proton a, glycerol CH).

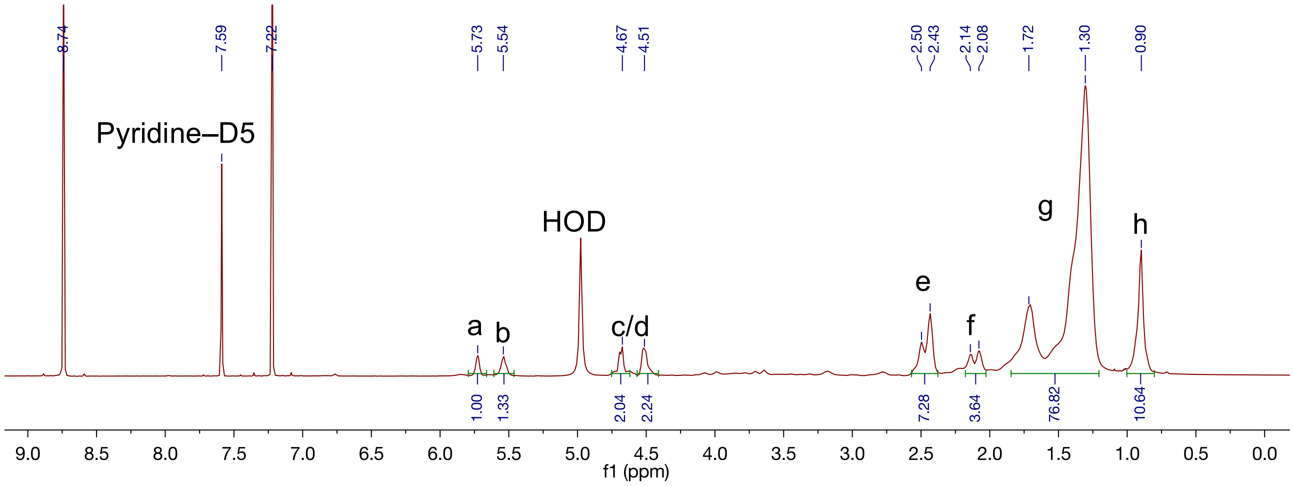
The ratio of the unreacted alkene to the CH_3 groups in the NPK sulfur polymer composite (50% NPK) is 1.61 / 10.68 = 0.15

The ratio of the alkene signals to the CH_3 groups in the canola oil starting material is 7.44 / 9.05 = 0.82

This means that 82% of the alkenes have reacted in the polymerisation.



NPK sulfur polymer composite (60% NPK)

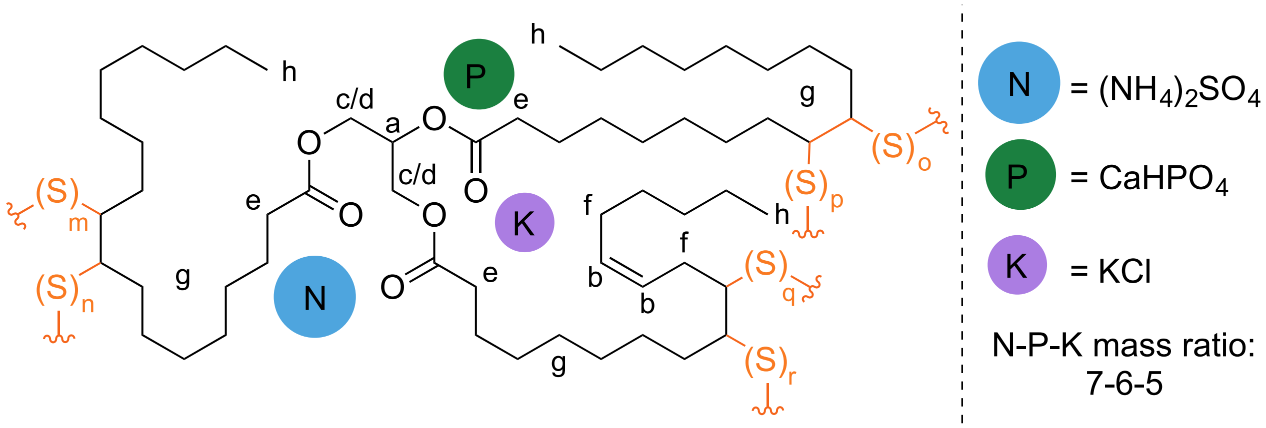


^{1}H NMR spectrum for sulfur polymer composite (60% NPK) (600 MHz, pyridine-D5): δ = 0.90 (proton h, CH_3), 1.30 and 1.72 (proton g, all CHS and non-α CH_2), 2.08-2.25 (proton f, allylic CH_2), 2.43-2.50 (proton e, α CH_2), 4.51 and 4.67 (proton c/d, glycerol CH_2), 5.54 (proton b, unreacted HC=CH), 5.72 (proton a, glycerol CH).

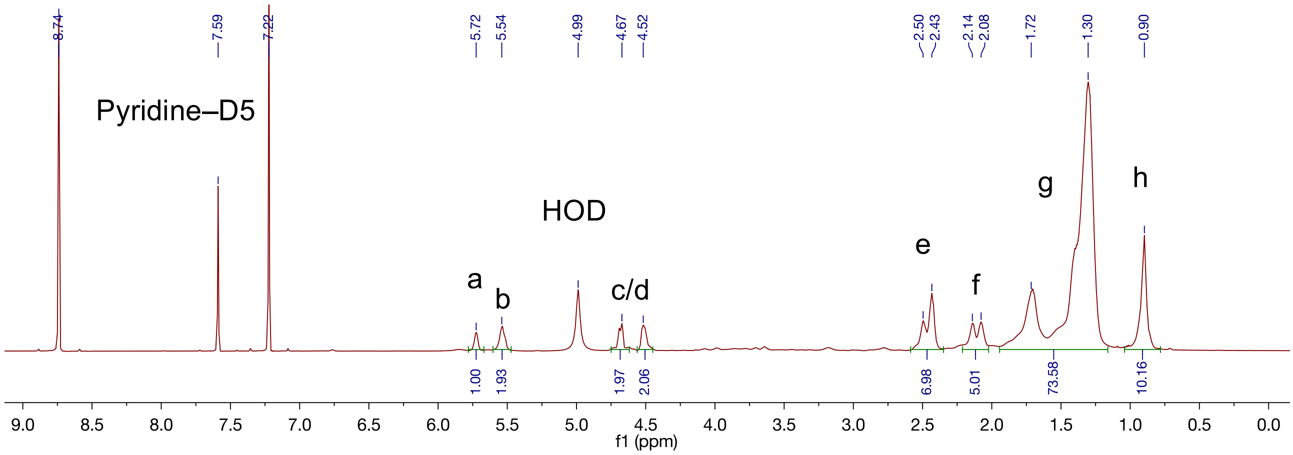
The ratio of the unreacted alkene to the CH_3 groups in the NPK sulfur polymer composite (60% NPK) is 1.33 / 10.64 = 0.16

The ratio of the alkene signals to the CH_3 groups in the canola oil starting material is 7.44 / 9.05 = 0.82

This means that 81% of the alkenes have reacted in the polymerisation.



NPK sulfur polymer composite (70% NPK)



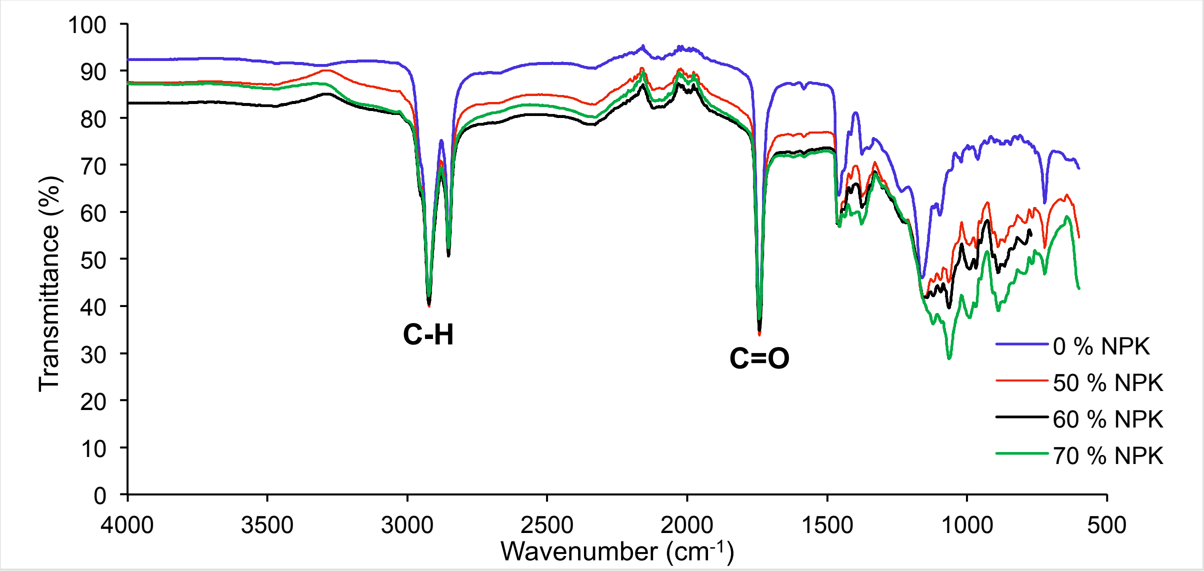
^{1}H NMR spectrum for sulfur polymer composite (70% NPK) (600 MHz, pyridine-D5): δ = 0.90 (proton h, CH_3), 1.30 and 1.72 (proton g, all CHS and non-α CH_2), 2.08-2.25 (proton f, allylic CH_2), 2.43-2.50 (proton e, α CH_2), 4.51 and 4.67 (proton c/d, glycerol CH_2), 5.54 (proton b, unreacted HC=CH), 5.72 (proton a, glycerol CH).

The ratio of the unreacted alkene to the CH_3 groups in the NPK sulfur polymer composite (60% NPK) is 1.93 / 10.16 = 0.19

The ratio of the alkene signals to the CH_3 groups in the canola oil starting material is 7.44 / 9.05 = 0.82

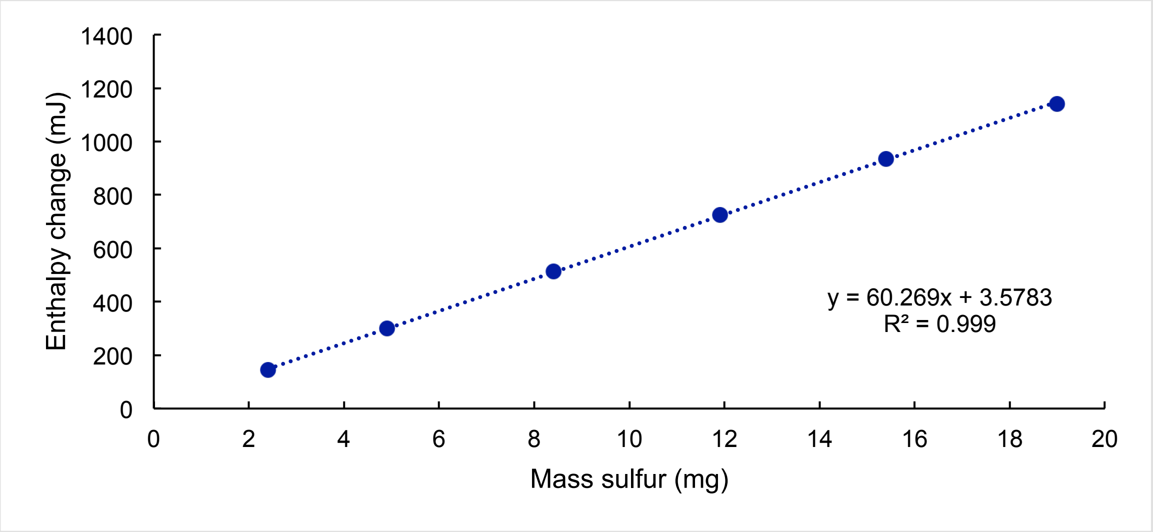
This means that 77% of the alkenes have reacted in the polymerisation.

IR spectra of canola oil polysulfide, and NPK sulfur polymer composites

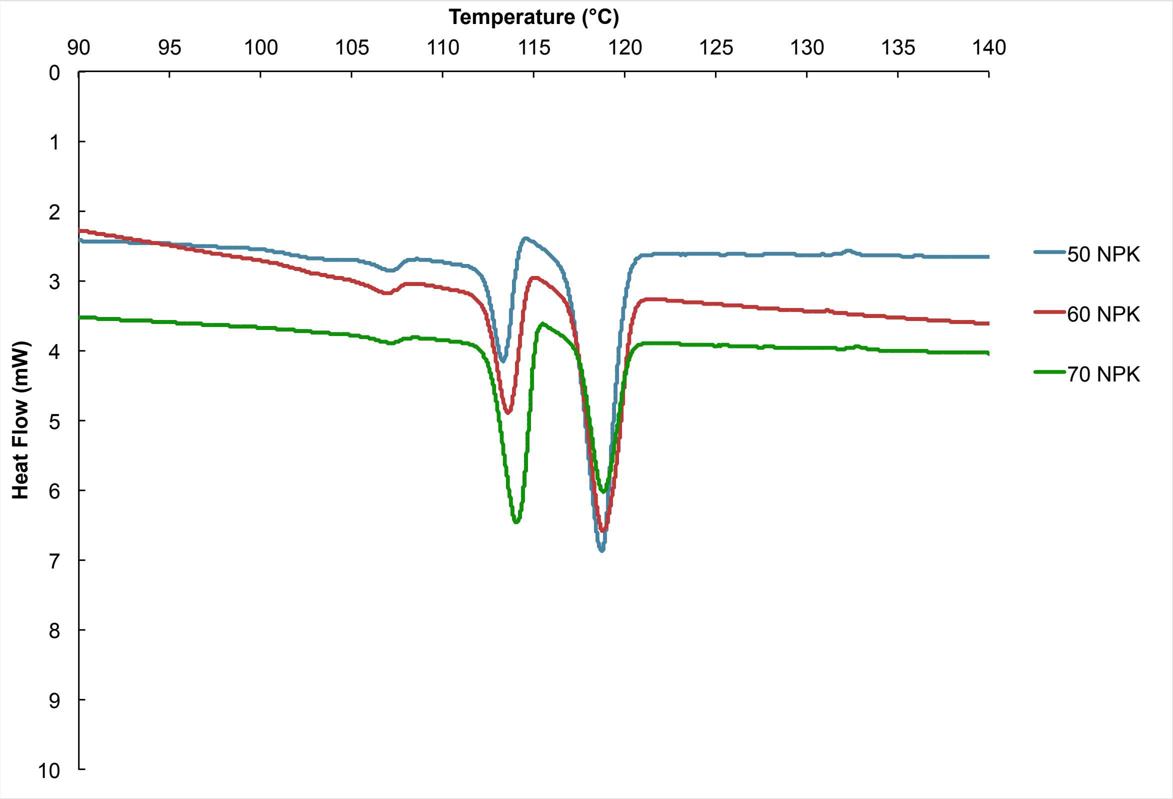


DSC analysis of sulfur polymer composites

DSC was used to estimate the amount of free sulfur (unreacted S_8) in the sulfur polymer composites. First, a calibration curve was constructed using measured amounts of elemental sulfur and the associated enthalpy change for the melting transition (calculated by integrating under the peak from 100 ºC to 130 ºC). The enthalpy change for the melting transition of sulfur vs mass of sulfur is plotted below:



This calibration curve was used to estimate the amount of free sulfur in the sulfur polymer composites by integrating the area under the peak from 100 ºC to 130 ºC in the DSC trace. The DSC traces and calculated free sulfur are shown on page S12.

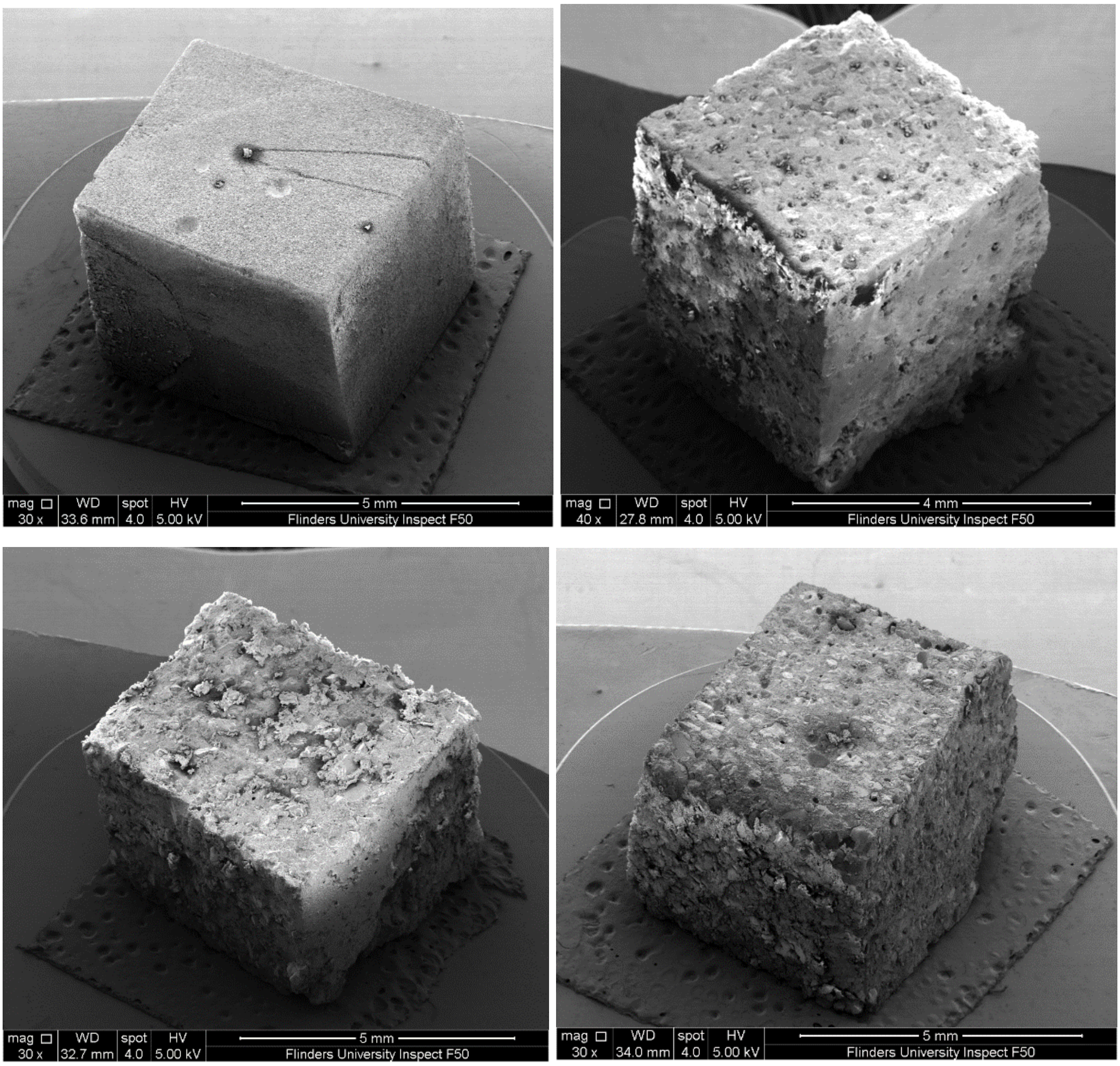


DSC trace showing the melting transition of free sulfur in the NPK-polymer composites. Integrating the area under these melting transitions allows an estimate of the free sulfur in the NPK-polymer composites:

Sample	**Composite mass (mg)**	**Peak Area (mJ)**	**Free sulfur (mg)**	**Free sulfur (mass %)**
50% NPK	25.0	125.2	2.0	8.1
60% NPK	24.9	126.4	2.0	8.2
70% NPK	25.0	92.1	1.5	6.0

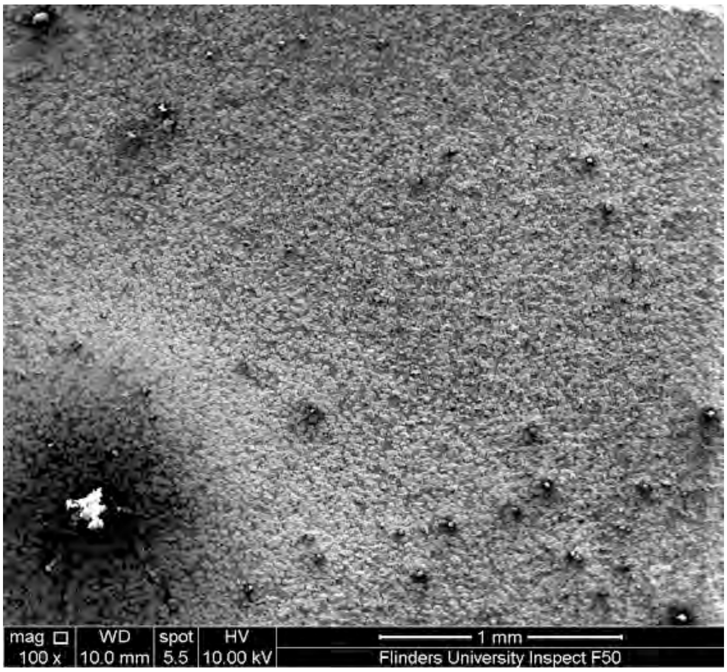
SEM and EDX analysis

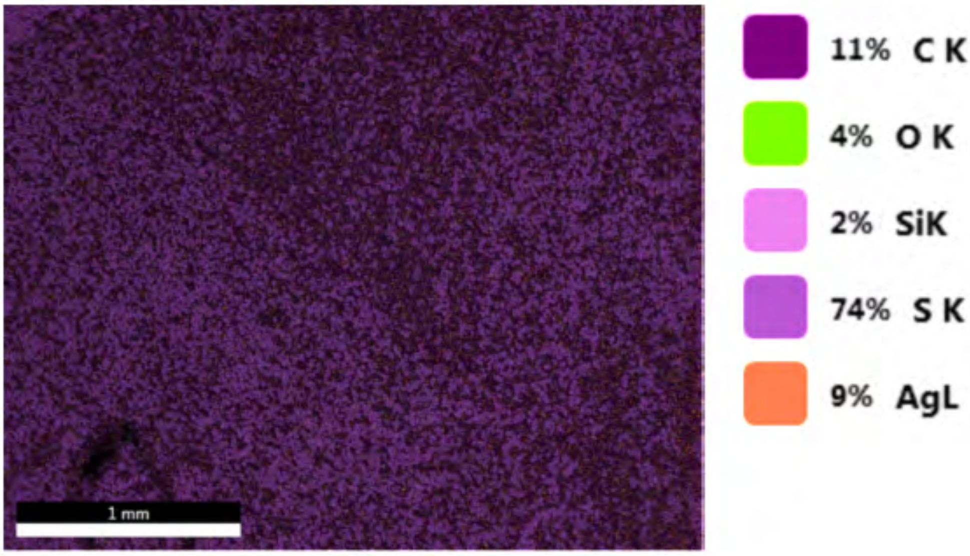
SEM images and EDX analysis were performed on a 0.5 cm cube of each polymer and polymer composite.

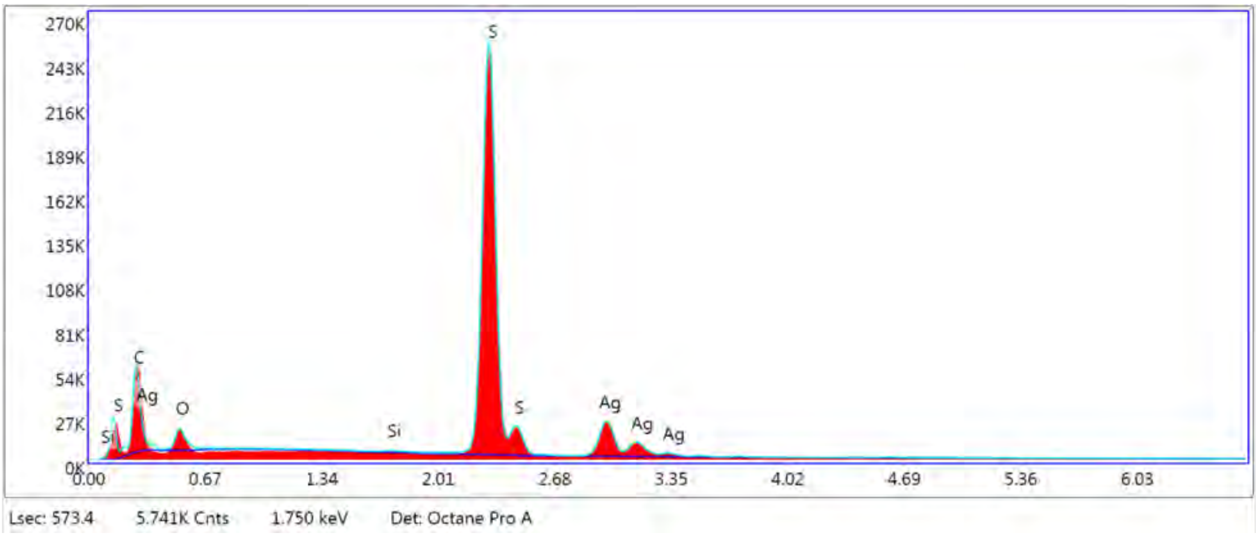


SEM images of canola oil polysulfide containing 0% NPK (top left), 50% NPK (top right), 60% NPK (bottom left), and 70% NPK (bottom right)

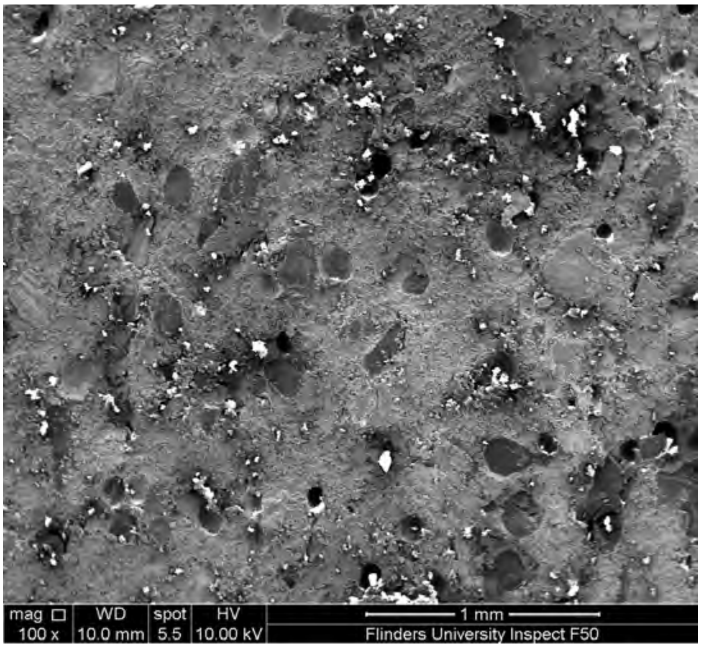
SEM and EDX: Canola oil polysulfide with 0% NPK fertiliser

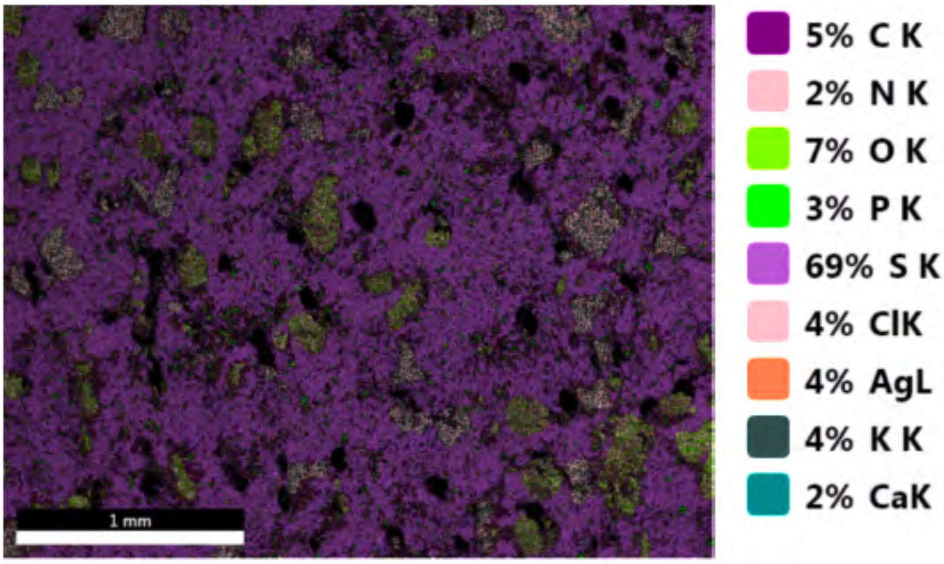


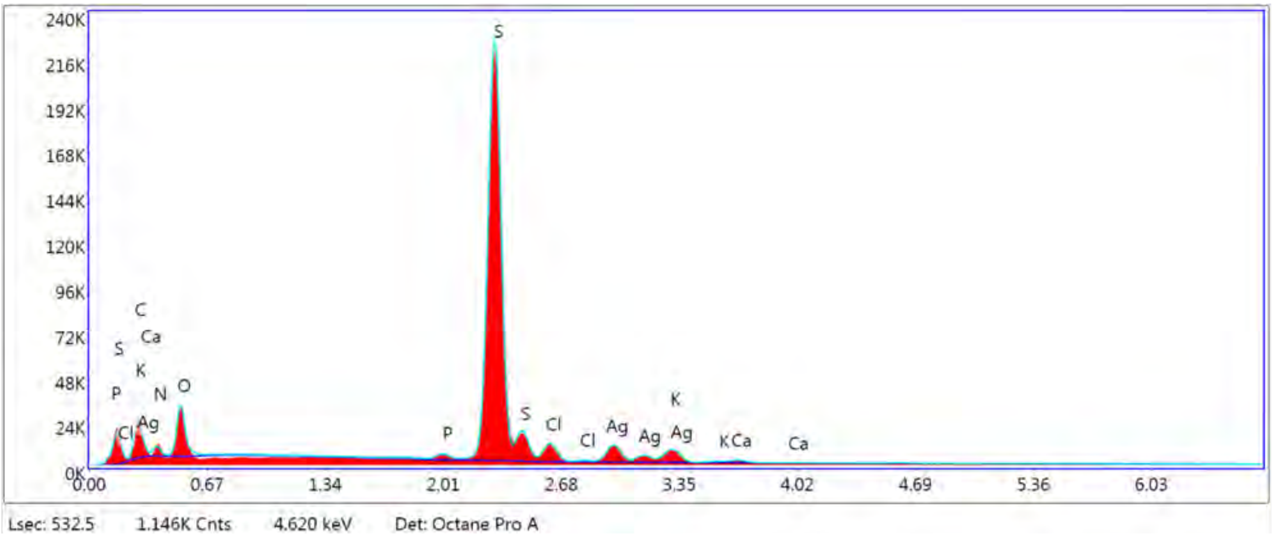




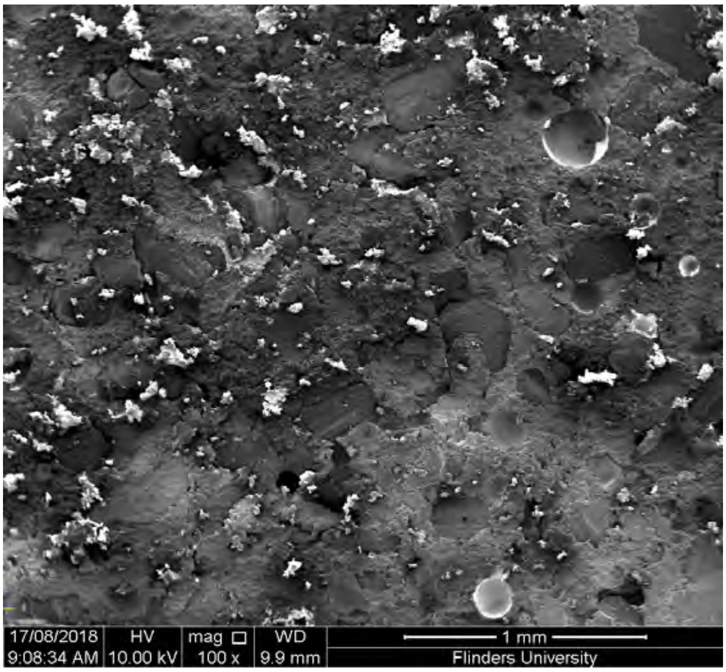
SEM and EDX: Sulfur polymer composite containing 50% NPK fertiliser

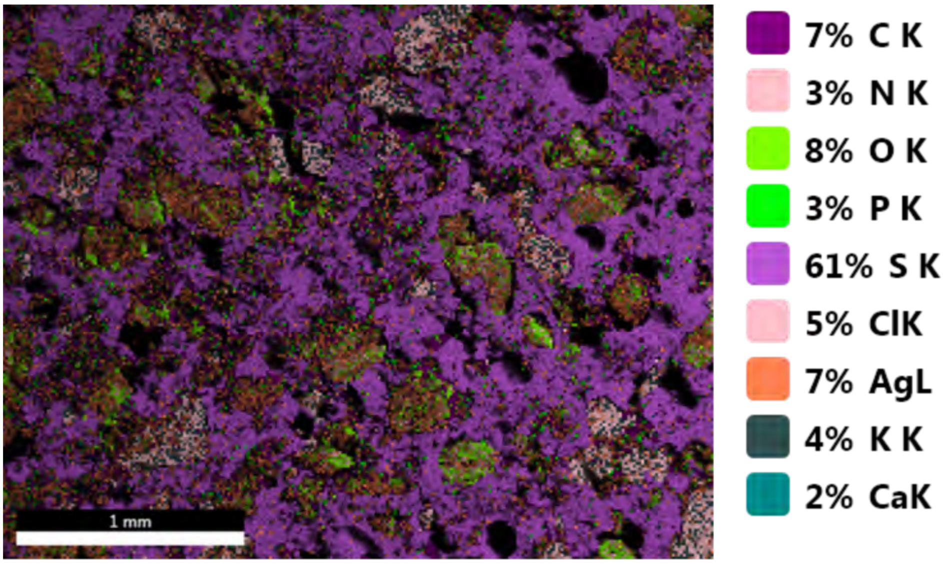


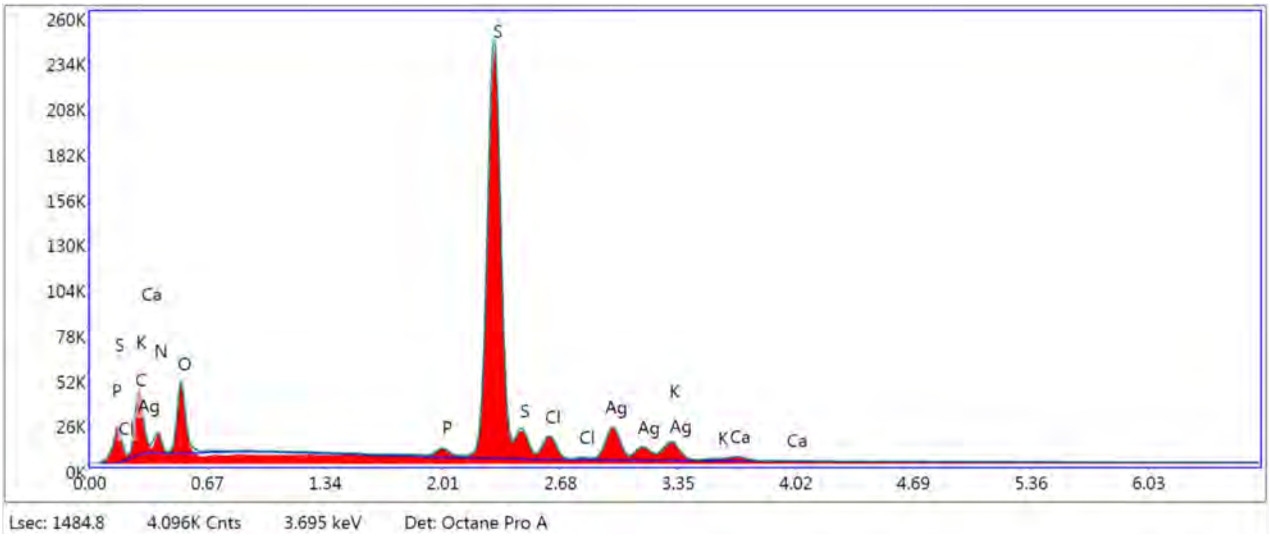




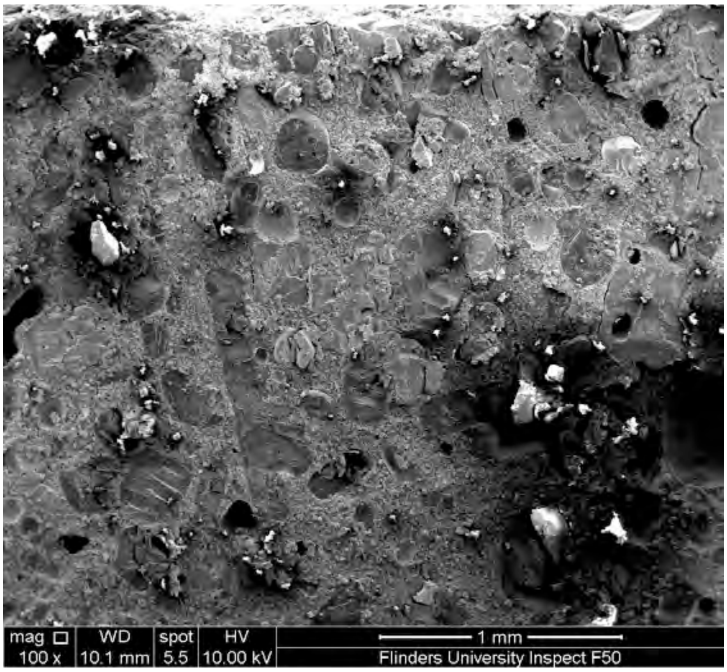
SEM and EDX: Sulfur polymer composite containing 60% NPK fertiliser

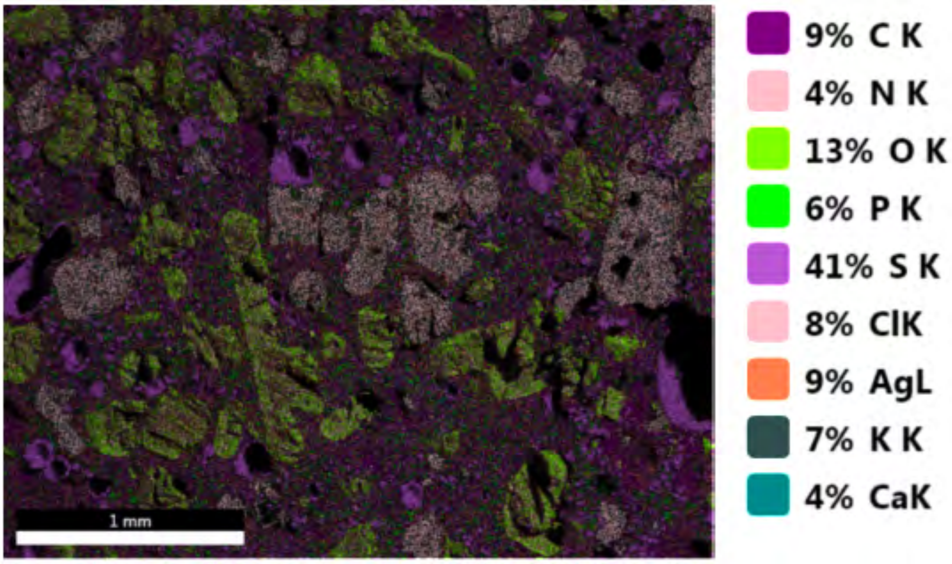


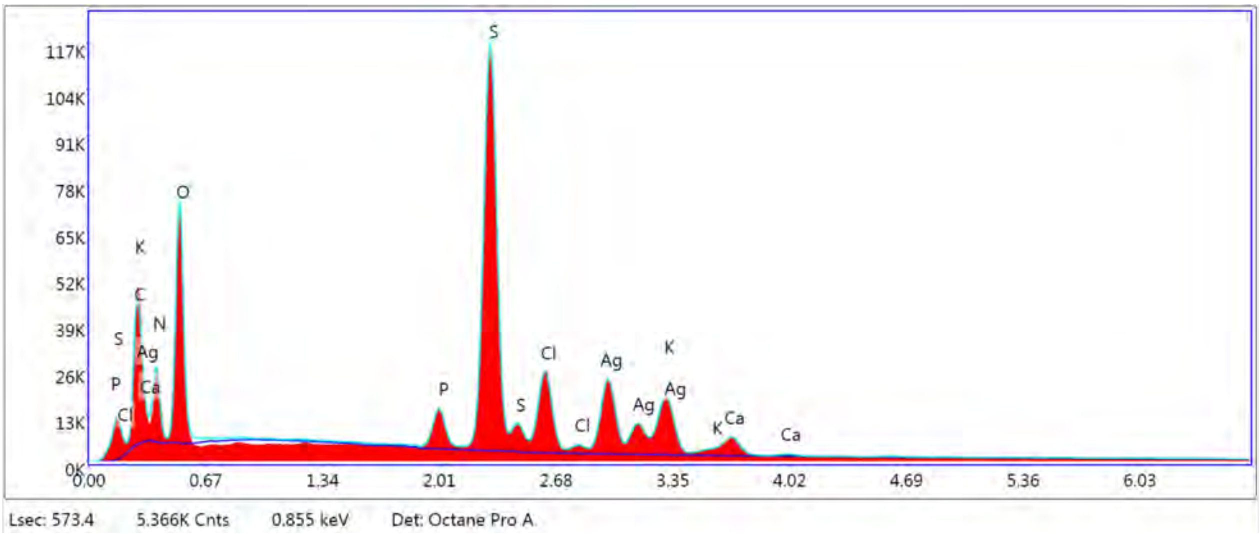




SEM and EDX: Sulfur polymer composite containing 70% NPK fertiliser





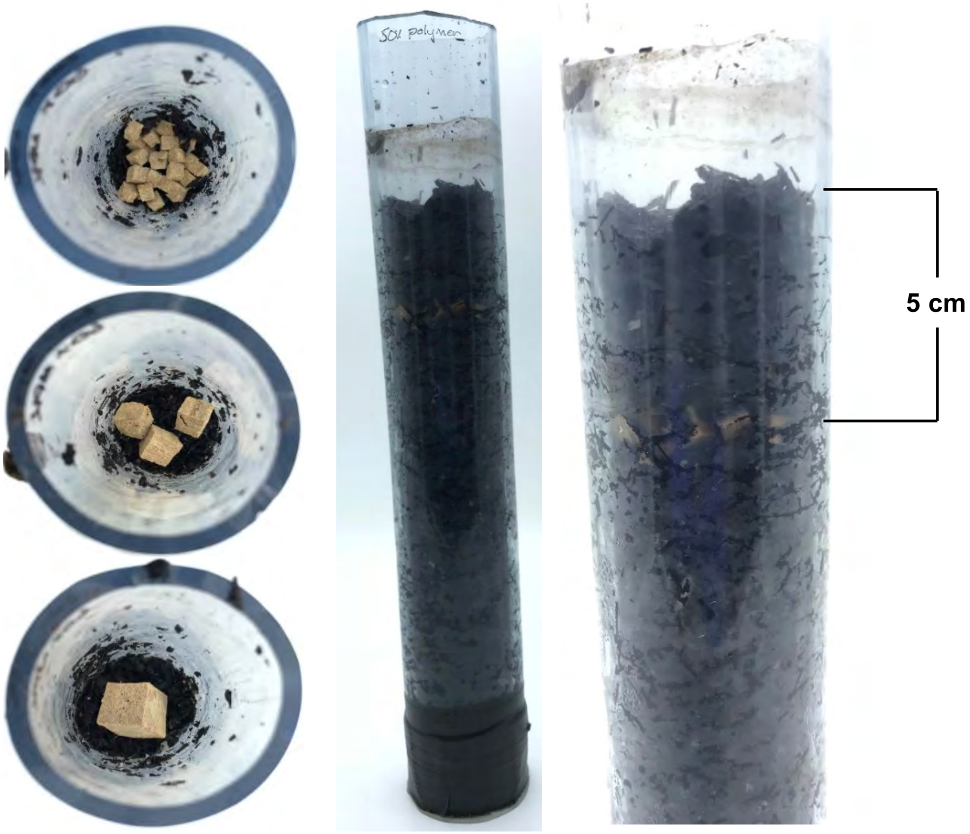


Soil Preparation

Hortico Garden Soil (2 kg) was added to 5 L of deionised water and soaked for 1 hour. The water was then drained and the process repeated up to 6 times. After washing, 2 L of water was passed over the soil and the conductivity of the outflow was measured to ensure it was consistently below 100 µS. If the conductivity was not below 100 µS, the washing process was repeated. This soil was used for both the column elution studies and the potted plant studies.

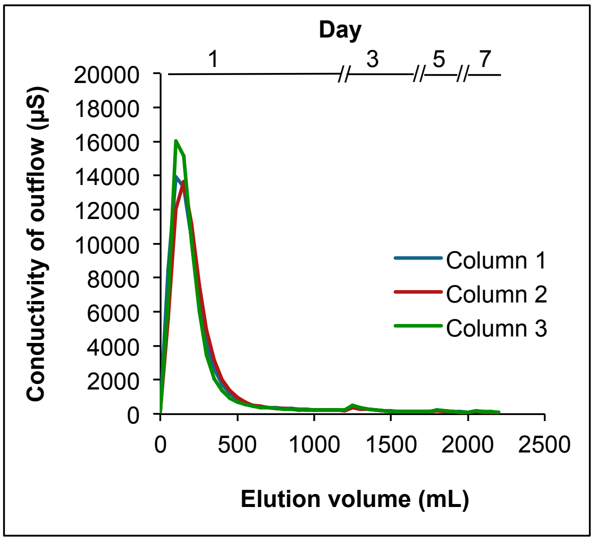
Elution Studies

15 PVC tubes (300 mm in length and an internal diameter of 38 mm) were filled with 150 g of washed soil. A plastic mesh was fastened at one end of the tube to hold the soil in place. 100 mL of deionised water was added to each column to pack and wet the soil. Free NPK fertiliser or the NPK sulfur polymer composites were then buried at a 5 cm depth in the soil. The total NPK content for all of these samples was 2.9 g. A control column with the canola oil polysulfide (0% NPK) was prepared in which 5.8 g of the polymer was buried at a 5 cm depth. All polymer or NPK polymer composite samples were prepared as cubes with widths of 0.5 cm, 1.0 cm and 1.5 cm. To elute the NPK salts, the column was first fastened to a retort stand and then 50 mL portions of water were added. The outflow was collected for 3 minutes before the conductivity was measured. The initial conductivity was typically between 80-100 µS. As NPK was dissolved and eluted, the conductivity increased. The elution process was continued, in 50 mL portions, until the conductivity of the outflow returned to below 100 µS. This elution process was repeated after 3, 5, and 7 days. Plots of outflow conductivity are shown on pages S19-21 (this is the same data shown in Figure 2).

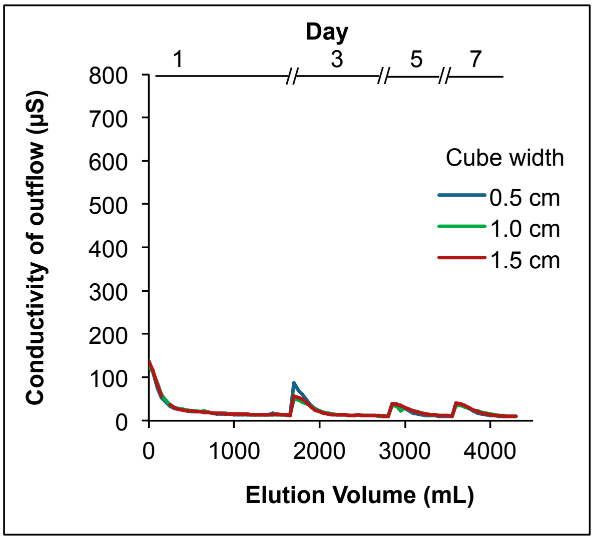


Above: NPK sulfur polymer composite (0.5 cm, 1.0 cm and 1.5 cm cubes) containing 2.9 g total NPK salts were buried at a 5 cm depth in the elution study.

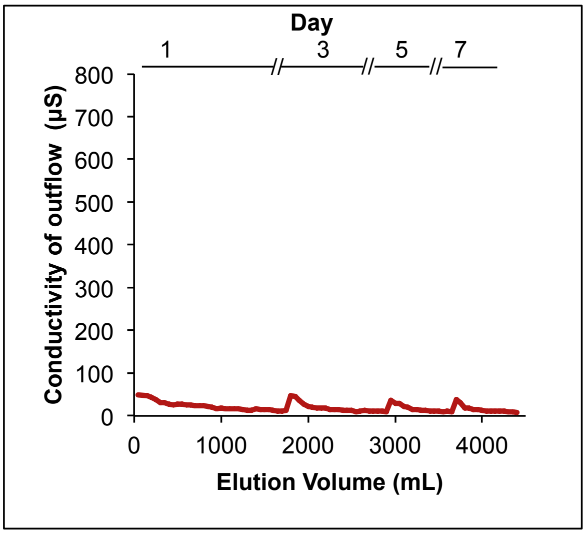
Free NPK control (no polymer, triplicate experiment):



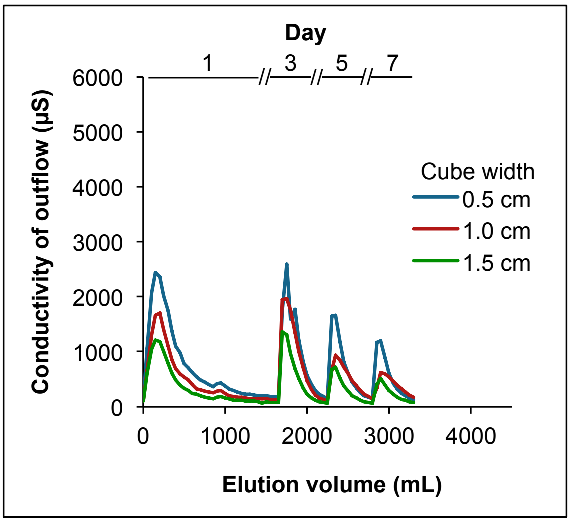
Sulfur polymer control (no NPK):



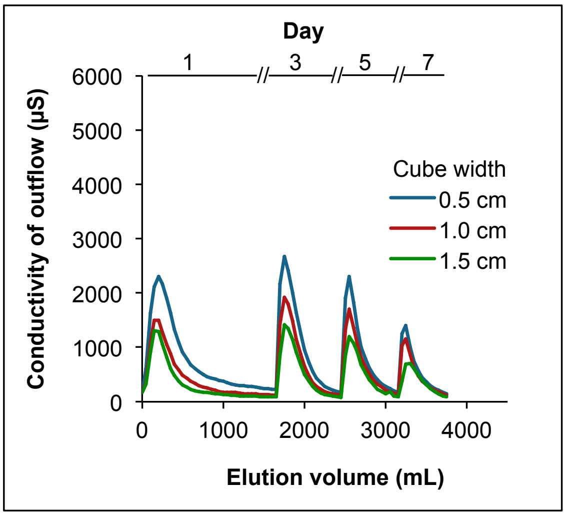
Soil only control (no polymer, no NPK, average of triplicate columns):



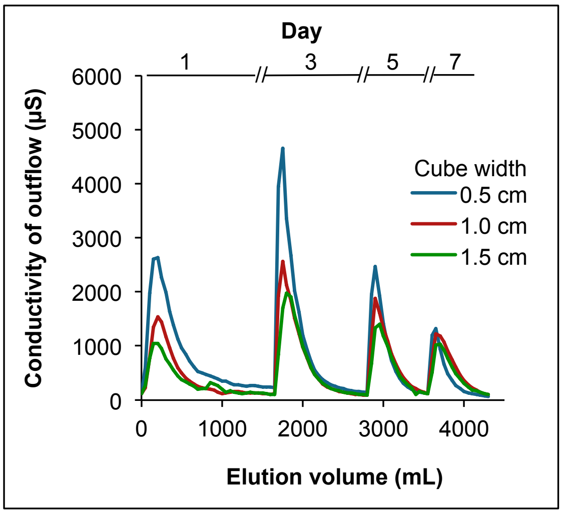
50% NPK sulfur polymer composite:



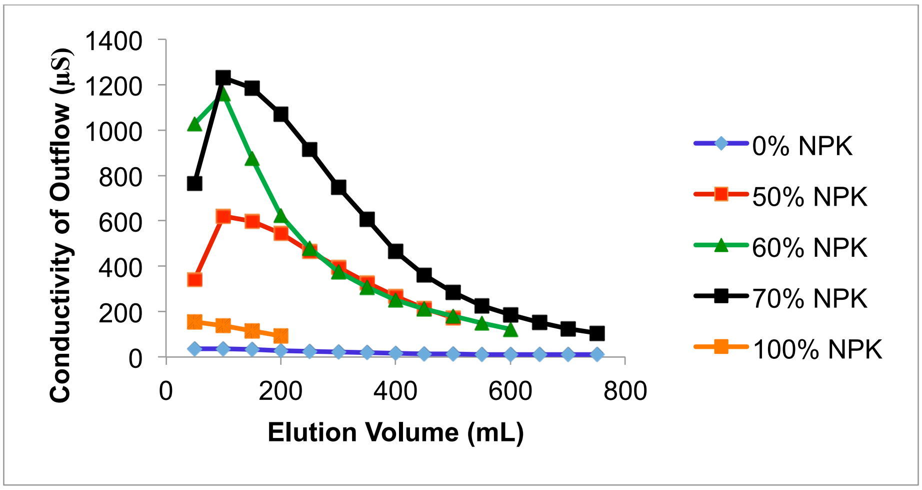
60% NPK sulfur polymer composite:



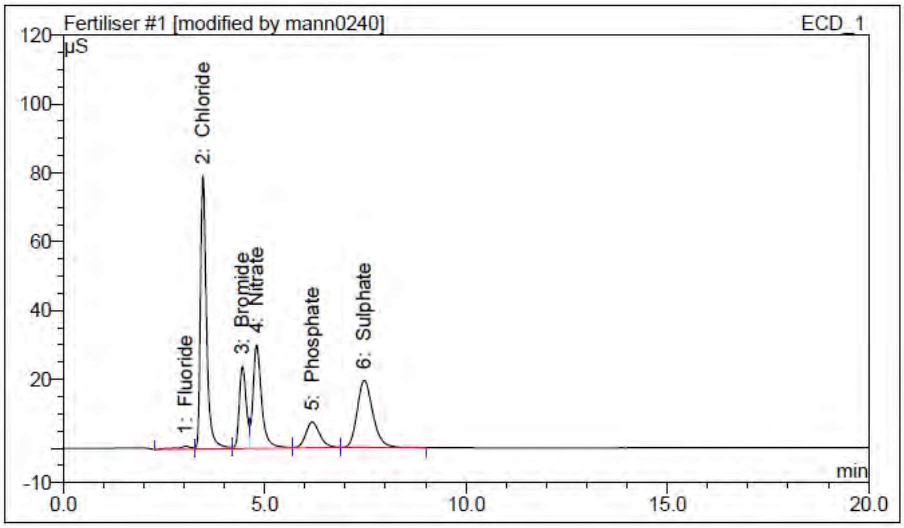
70% NPK sulfur polymer composite:



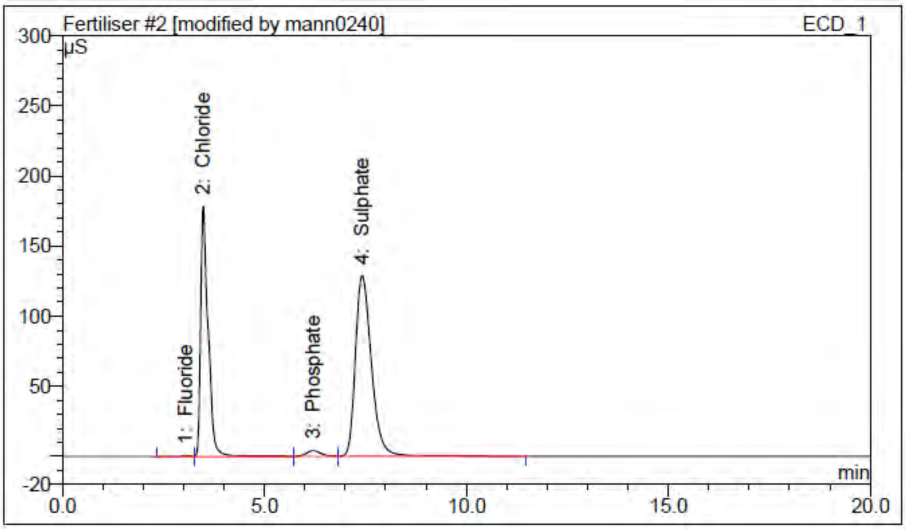
Day 7 elution for 1 cm cubes of the NPK sulfur polymer composite (50, 60 and 70% NPK) and comparison to the sulfur polymer (0% NPK) and free NPK (100% NPK). This plot illustrates how the NPK sulfur polymer composites are still releasing nutrients on the day 7 elution, while the free NPK sample has already lost most nutrients in the outflow.



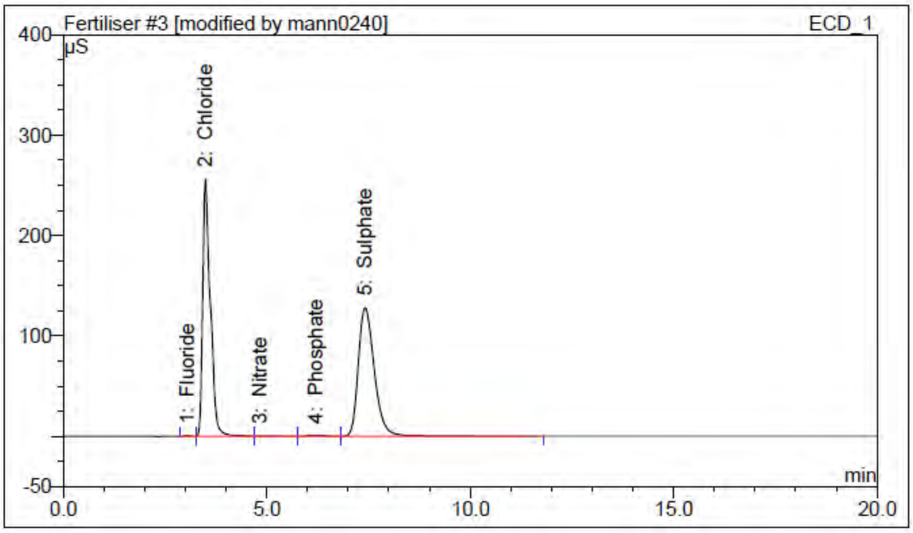
Ion chromatography of soil column outflow



Reference standard: 100 ppm mixture of fluoride, chloride, bromide, nitrate, phosphate and sulfate anions.



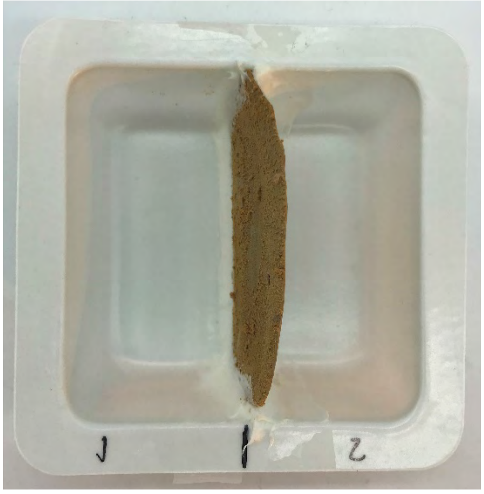
Reference NPK solution, diluted to same conductivity as outflow sample from soil column.



Outflow of soil column for 0.5 cm cube of the 70% NPK sulfur polymer composite (Day 5).
This experiment confirms that the conductivity in the outflow arises from NPK release from the polymer.

Ion permeability experiment

In order to determine if dissolved ions can migrate through the polymer the following experiment was conducted: A polysulfide polymer (50 wt% canola oil / 50 wt% sulfur) was synthesised. From that polymer a thin (1-2 mm) piece was cut to the dimension to fit in a plastic weighing tray (6.5 cm x 6.5 cm). The strip of polymer was fixed to the centre of the tray with a silicon sealant. Next 37 mL of a 1000 ppm KCl solution was added to compartment 1 and the same volume of deionised water was added to compartment 2. The initial conductivity of the KCl solution was 7700 µs and 3 µs for the conductivity water. Over a 7 day period, the difference in conductivity between the two chambers did not change, indicating that ions could not pass through the polymer at this thickness. This result implies that the release of the NPK from the NPK sulfur polymer composite is due to leaching through channels in the polymer and not direct passage through the polymer.



Growth study with potted tomato plants (*Lycopersicom esculentum*)

Plants were housed in two grow boxes constructed of an aluminium frame (120 cm length, 60 cm width and 100 cm height). The sides and back of the grow houses were covered in one layer of aluminium foil. A 600 W high pressure sodium lamp with a 600 mm reflector was suspended from the top of the grow box. This lamp was equipped with a timer.

1.5 kg of washed soil was added to each of 12 pots. 500 mL of DI water was added to each pot and allowed to drain. Tomato plants, *Lycopersicom esculentum*, were soaked for 1 hour in warm water (approximately 25 °C) before removing from packaging. The plants were allowed to soak for an additional hour to loosen the soil from roots. Tomatoes were then transplanted into the pots with canola oil polysulfide polymer (no NPK, 1 cm cubes), 60% NPK sulfur polymer composite (1 cm cubes), or free NPK fertiliser buried at a 2 cm depth. For samples with NPK (free NPK or the NPK sulfur polymer composite), the total NPK mass was 5 g.

Image of washed *Lycopersicom esculentum* before transplanting (left), image of potted plant with 60% NPK sulfur polymer composite fertiliser (centre) and 100% NPK fertiliser (right).

Twelve plants were planted in total (four groups with three plants each):

A) Negative control group with no polymer and no fertiliser

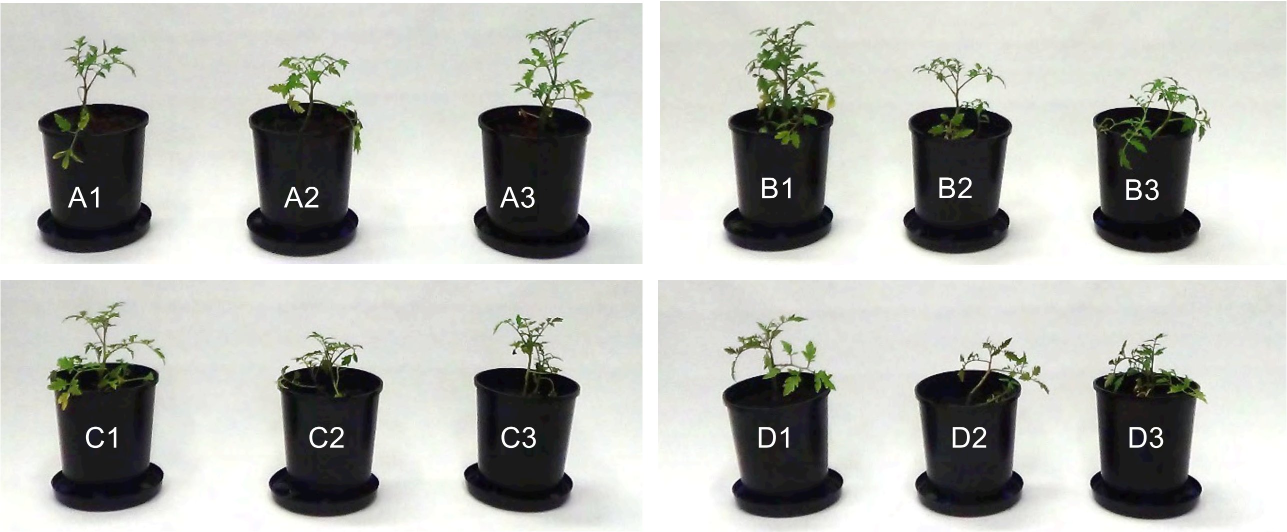
B) Negative control group with the sulfur polymer (3.3 g, 1.0 cm cubes) but no NPK

C) Experimental group treated with the 60% NPK sulfur polymer composite (1.0 cm cubes, 5 g total NPK)

D) Free NPK (5 g), no polymer.

The plants were watered three times a week (Monday, Wednesday and Friday) with 200 mL of deionised water. After five weeks the water was increased in frequency to 200 mL of DI water twice per day, five days per week (Monday-Friday).

Conductivity was measured and recorded after the first watering on Monday, Wednesday and Friday. Photographs were taken weekly. Plants were exposed to light for 10 hours every day between 7am – 5pm by 600 W HPS lamp with a 600 mm reflector. In order to support the plants, stakes were used for groups C and D in week 7.

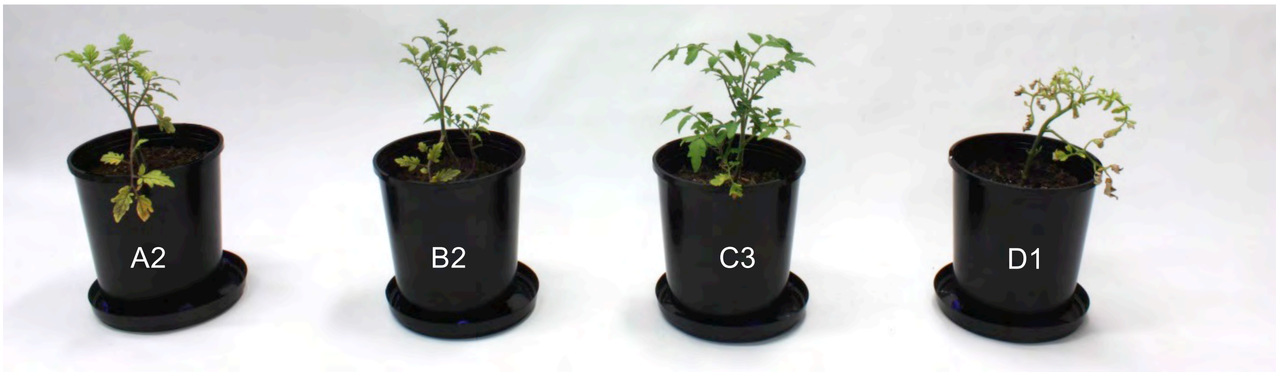


Day 1 images of all 12 plants in growth study. A1-A3) Negative control group with no polymer and no fertiliser; B1-B3) Negative control group with the sulfur polymer but no NPK Polymer; C1-C3) 60% NPK sulfur polymer composite (1.0 cm cubes, 5 g total NPK); D1-D3) Free NPK (5 g), no polymer.

To illustrate the difference in growth between the different groups a representative sample from each group was selected and photographed together over 70 days. The plants were selected for these images because they were approximately the same height at day one.

Day 1: All plants approximately the same size and colour

Day 7:
A2) Negative control group with no polymer and no fertiliser: slow growth, leaf yellowing
B2) Negative control group with the sulfur polymer but no NPK: slow growth, leaf yellowing
C3) 60% NPK sulfur polymer composite: leaf growth, additional leaves, green colour
D1) Free NPK, no polymer: leaf yellowing, nutrient burn



Day 14:
A2) Negative control group with no polymer and no fertiliser: slow growth, leaf yellowing
B2) Negative control group with the sulfur polymer but no NPK: slow growth, leaf yellowing
C3) 60% NPK sulfur polymer composite: stem growth, leaf growth, additional leaves, green colour
D1) Free NPK, no polymer: leaf yellowing, nutrient burn, slow growth

Day 21:
A2) Negative control group with no polymer and no fertiliser: slow growth, leaf yellowing
B2) Negative control group with the sulfur polymer but no NPK: slow growth, leaf yellowing
C3) 60% NPK sulfur polymer composite: stem growth, leaf growth, additional leaves, darker green colour
D1) Free NPK, no polymer: leaf yellowing, nutrient burn, slow recovery from nutrient burn

Day 28:

A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: stunted growth, leaf yellowing, leaf loss
C3) 60% NPK sulfur polymer composite: stem growth, leaf growth, additional leaves, darker green colour
D1) Free NPK, no polymer: leaf yellowing, slow recovery from nutrient burn

Day 35:

A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: stunted growth, leaf yellowing, leaf loss
C3) 60% NPK sulfur polymer composite: stem growth, blossoms, green but wilted leaves (restricted water did not meet demands of rapid plant growth, so the amount of water applied to all plants was increased on day 35).
D1) Free NPK, no polymer: slow recovery from nutrient burn, stem growth, greener leaves

At day 35, watering was increased in frequency to 200 mL of DI water twice per day, five days per week for all plants

Day 42:

A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: stunted growth, leaf yellowing, leaf loss
C3) 60% NPK sulfur polymer composite: stem growth, additional blossoms, green turgid leaves due to increased irrigation from day 35.
D1) Free NPK, no polymer: recovery from nutrient burn, stem growth, greener leaves (facilitated by increased irrigation from day 35)

Day 49:

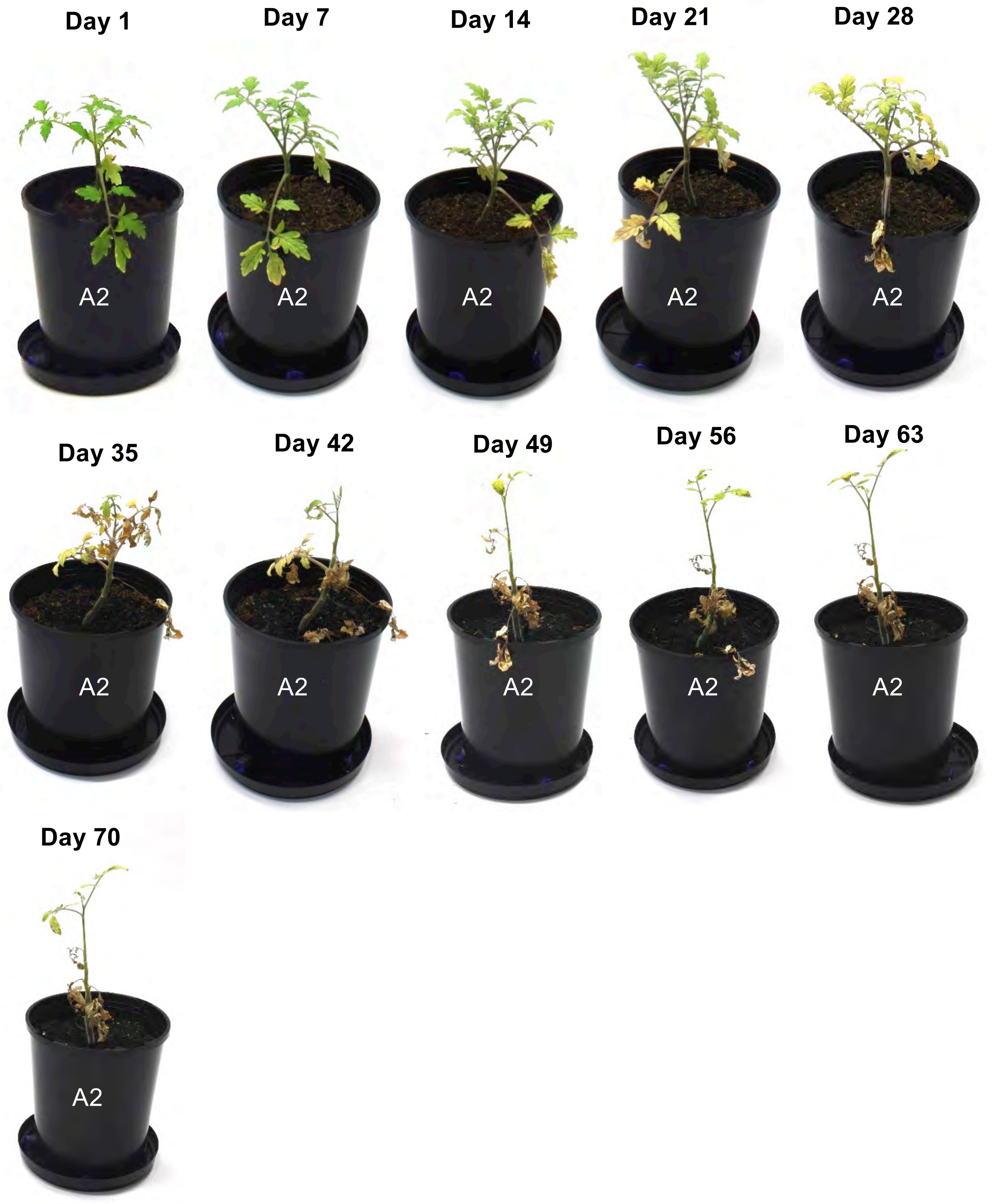
A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: stunted growth, leaf yellowing, leaf loss
C3) 60% NPK sulfur polymer composite: stem growth, green leaves, first fruit
D1) Free NPK, no polymer: slowed growth, leaf yellowing

Day 56:
A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: stunted growth, leaf yellowing, leaf loss
C3) 60% NPK sulfur polymer composite: stem growth, green leaves, additional and larger fruit
D1) Free NPK, no polymer: slowed growth, leaf yellowing, blossoms

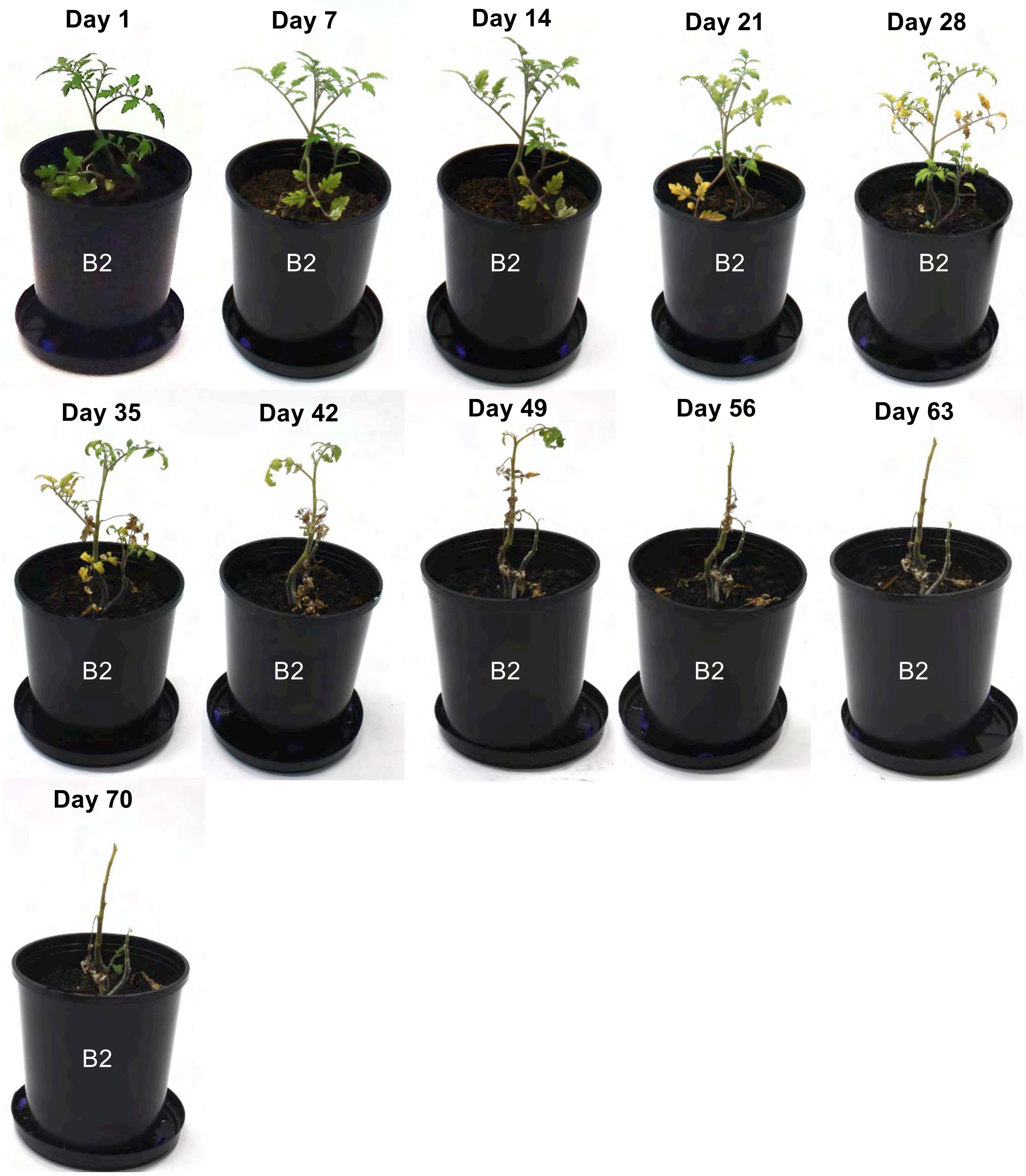
Day 63:
A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: stunted growth, plant death
C3) 60% NPK sulfur polymer composite: additional fruit, leaf loss
D1) Free NPK, no polymer: slowed growth, leaf yellowing

Day 70:

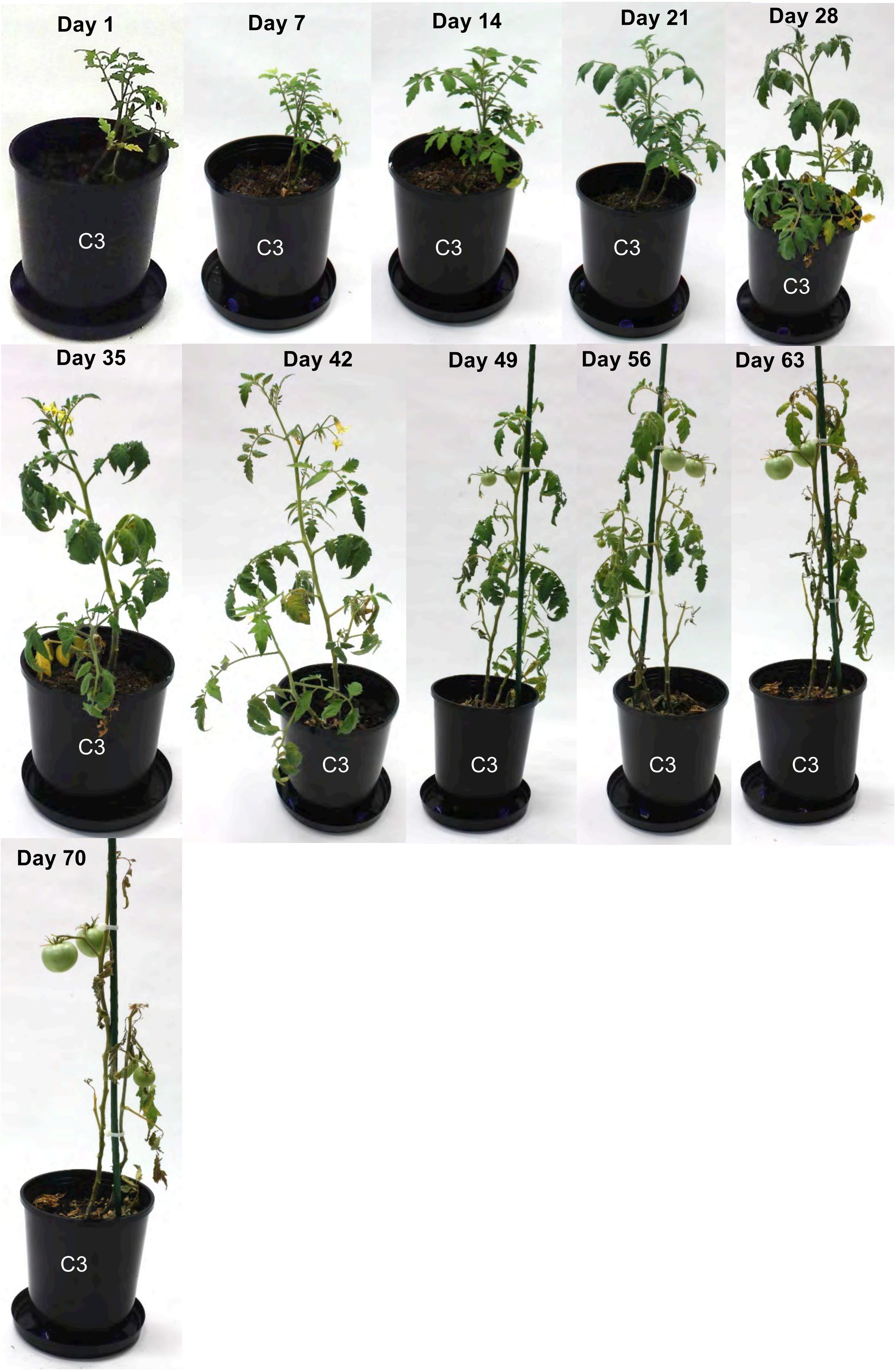
A2) Negative control group with no polymer and no fertiliser: stunted growth, leaf yellowing, leaf loss
B2) Negative control group with the sulfur polymer but no NPK: plant death
C3) 60% NPK sulfur polymer composite: additional fruit, leaf loss
(restricted nutrients allocated to fruit development)
D1) Free NPK, no polymer: slowed growth, leaf yellowing, small fruit



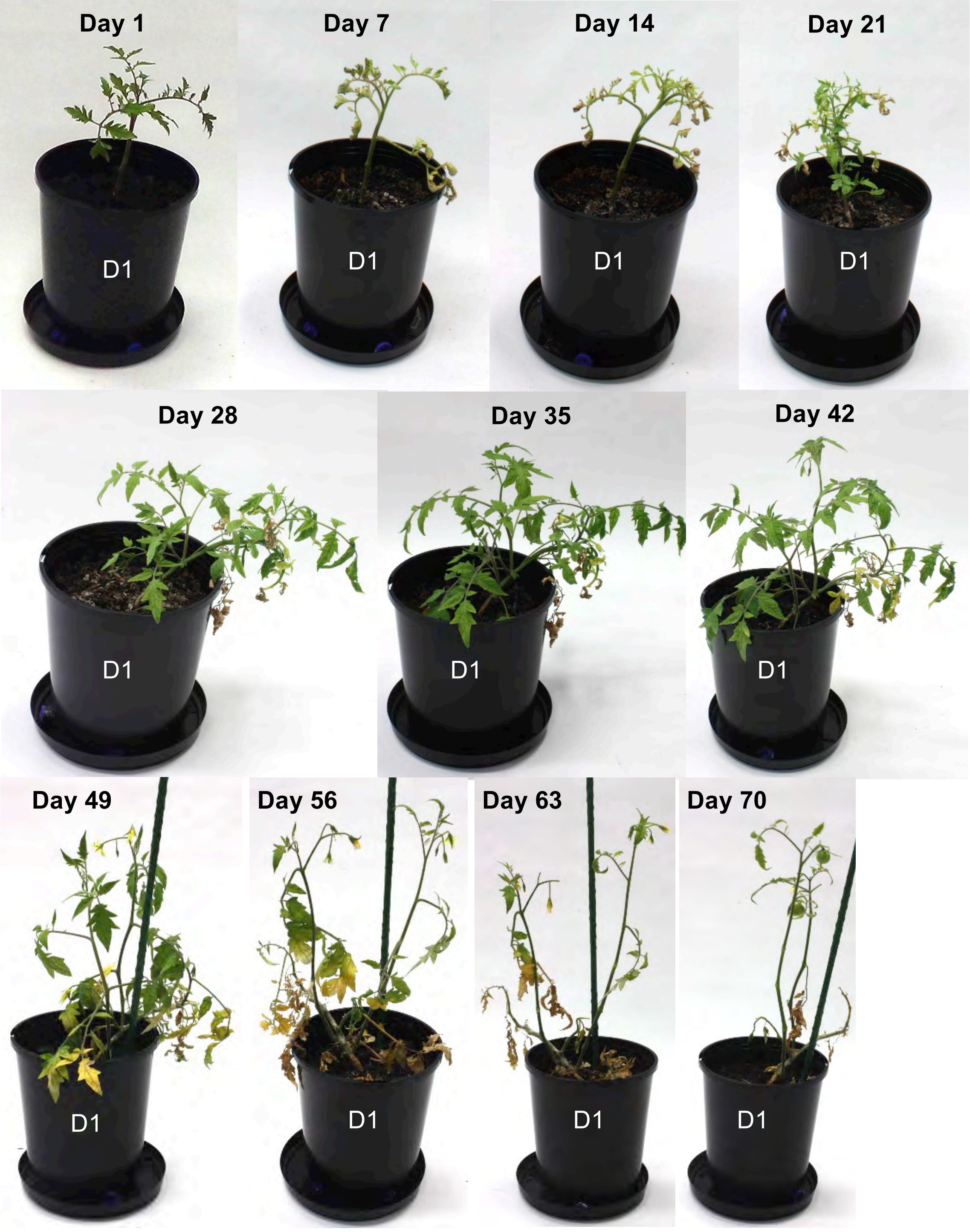
Plant A2) Representative plant for negative control group: no polymer and no fertiliser



Plant B2) Representative plant for negative control group: sulfur polymer but no NPK

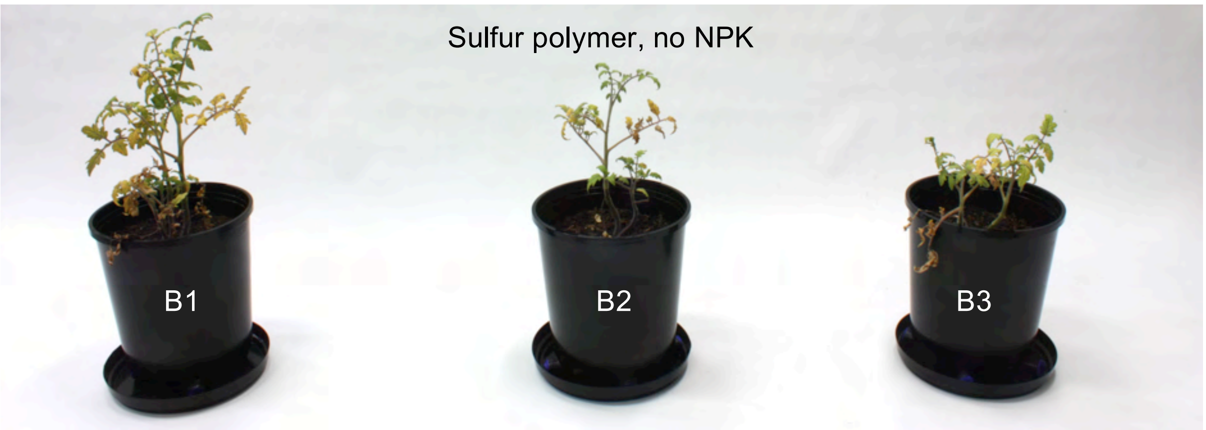


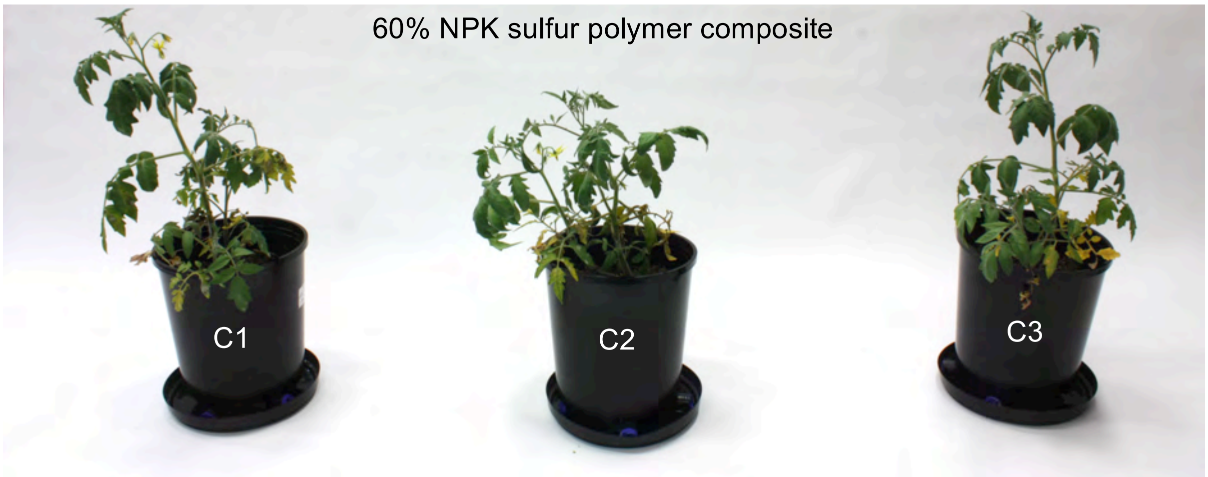
Plant C3) Representative plant from group treated with 60% NPK sulfur polymer composite



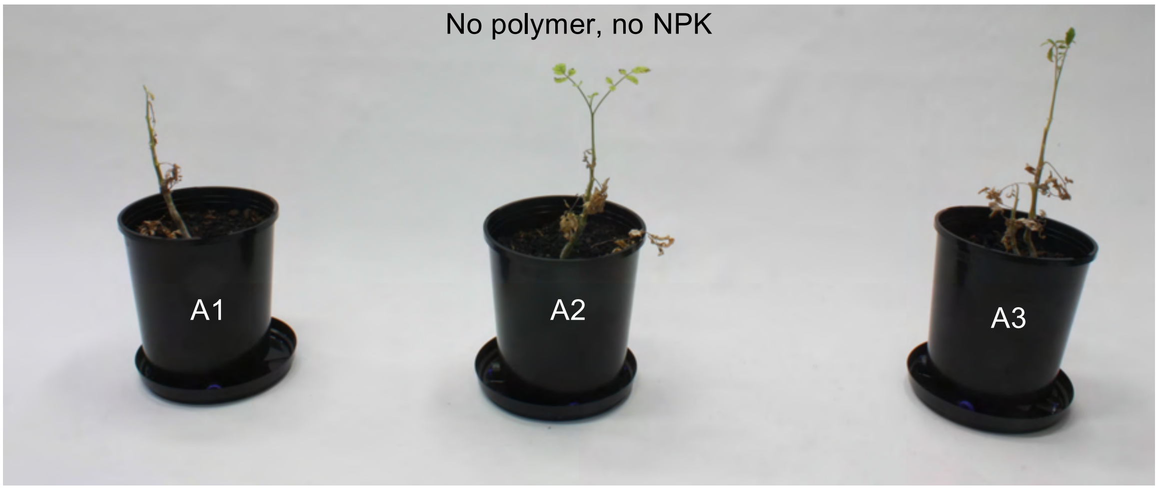
Plant D1) Representative plant from group treated with free NPK

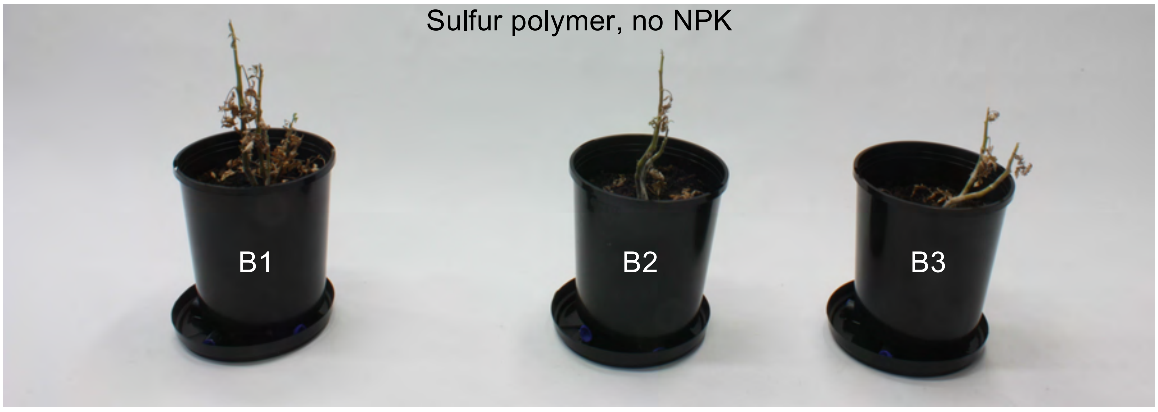
All plants at day 28





All plants at day 56 (negative controls)

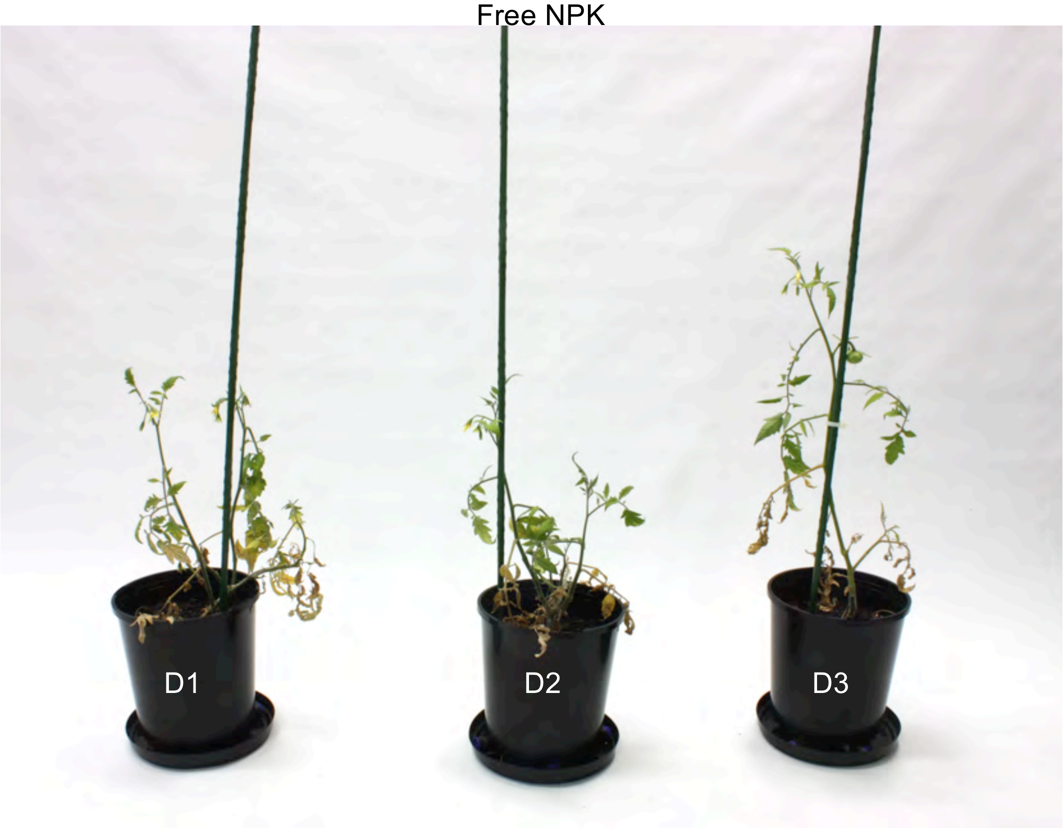




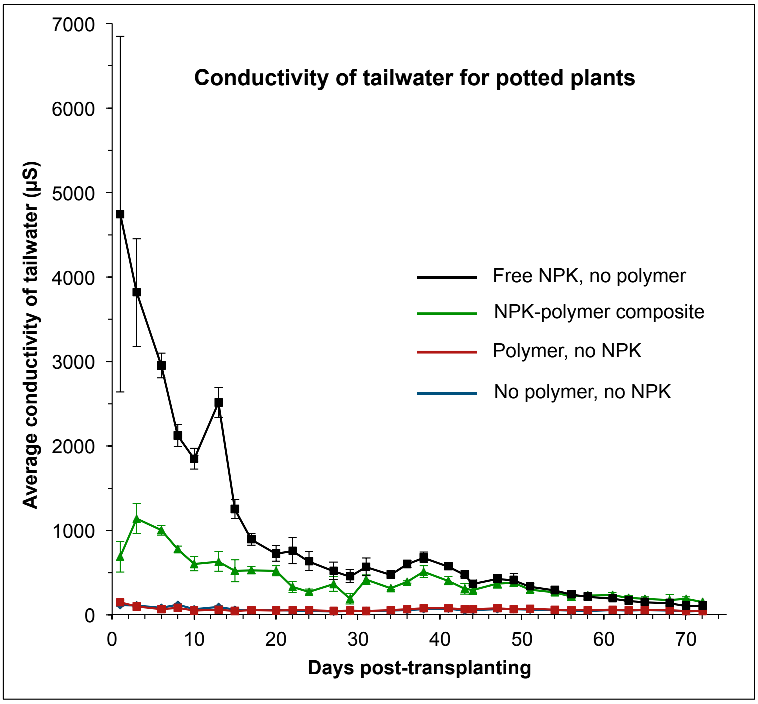
All plants at day 56 (NPK sulfur polymer composite and free NPK)

60% NPK sulfur polymer composite

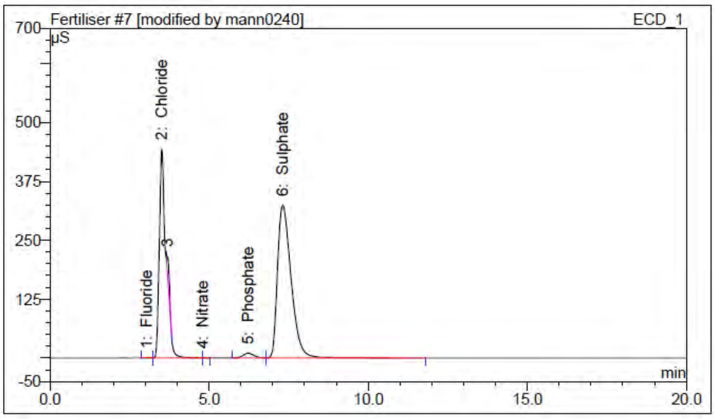
Free NPK



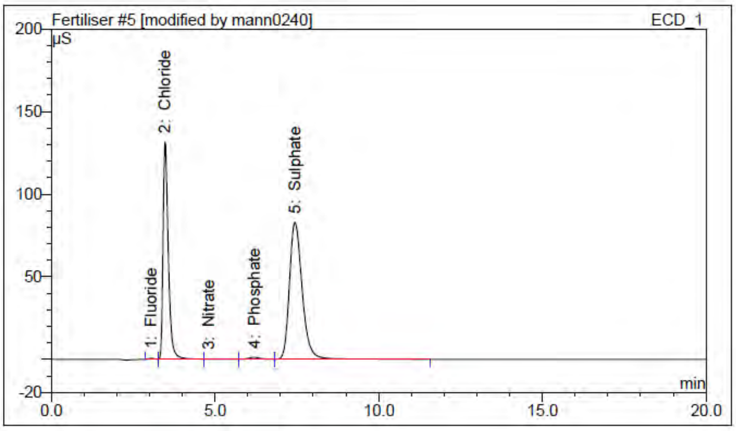
Average conductivity of tailwater for all plants in growth study



Ion chromatography of tailwater for selected samples



Ion chromatogram of tailwater from plant D3 (Free NPK), Day 3. This data indicates that the chloride, phosphate and sulfate from the free NPK is washed off of the soil in the potted plant.



Ion chromatogram of tailwater from plant C1 (60% NPK sulfur polymer composite), Day 3. This data confirms that chloride, phosphate and sulfate are released from the sulfur polymer composite. Note the amount of NPK lost in the tail water is less than observed for the free NPK (both by conductivity and IC).

NPK sulfur polymer composite hydrolysis experiment

A sample of the 60% NPK sulfur polymer composite was cut into a 5 mm × 5 mm × 1 mm piece and added to 1 mL of a 1M NaOH solution in D_2O. The solution was clear, but gradually turned dark yellow and then brown over several days. After 50 days at room temperature, the solution was sampled and analysed by ^1H NMR, which revealed the presence of glycerol. Glycerol is the expected water-soluble product of hydrolysis of the canola oil triglyceride that makes up the polymer backbone. This experiment suggests that the polymer component of the fertiliser composite can degrade slowly by hydrolysis under basic conditions.

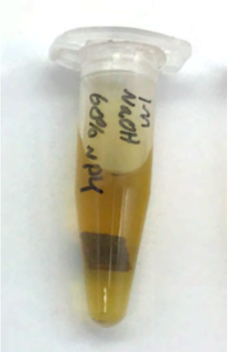
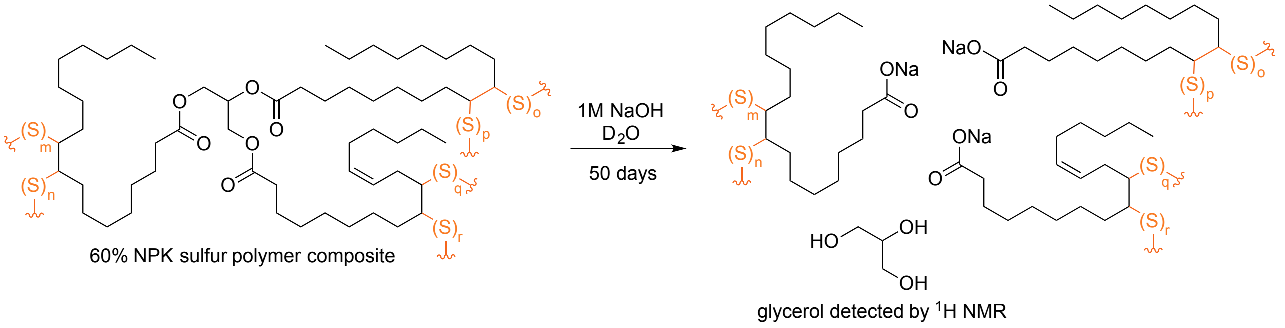
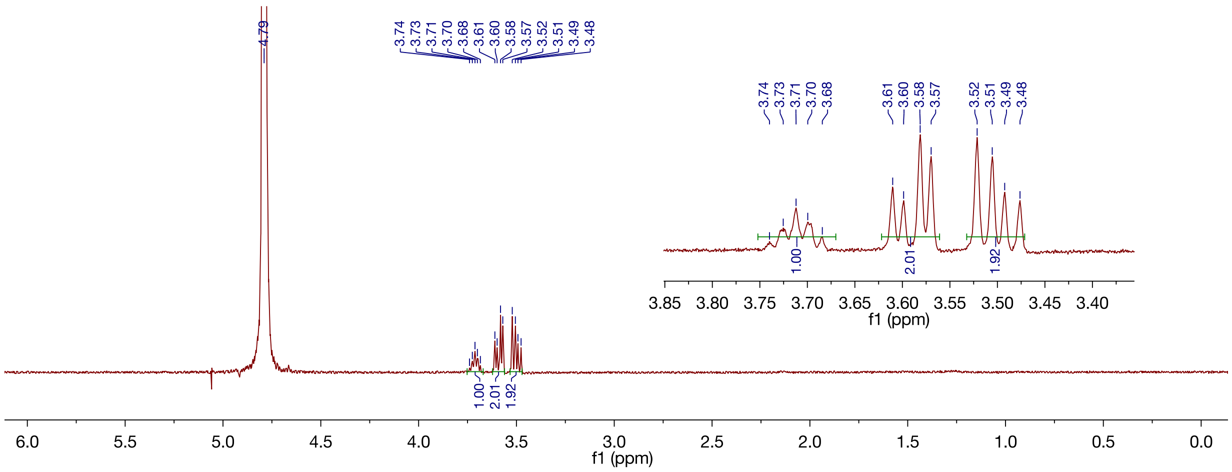


Image of 60% NPK sulfur polymer composite after 50 days in a 1M solution of NaOH in D_2O





^1H NMR of glycerol product (400 MHz, D_2O)—the water soluble organic product of the sulfur polymer hydrolysis. The spectrum was identical to an authentic sample of glycerol added to 1M NaOH in D_2O.

References

1. M. J. H. Worthington, R. L. Kucera, I. S. Abuquerque, C. T. Gibson, A. Sibley, A. D. Slattery, J. A. Campbell, S. F. K. Alboaiji, K. A. Muller, J. Young, N. Adamson, J. R. Gascooke, D. Jampaiah, Y. M. Sabri, S. K. Bhargava, S. J. Ippolito, D. A. Lewis, J. S. Quinton, A. V. Ellis, A. Johs, G. J. L. Bernardes and J. M. Chalker, *Chem. Eur. J.*, 2017, **23**, 16219-16230.

2. M. J. H. Worthington, C. J. Shearer, L. J. Esdaile, J. A. Campbell, C. T. Gibson, S. K. Legg, Y. Yin, N. A. Lundquist, J. R. Gascooke, I. S. Albuquerque, J. G. Shapter, G. G. Andersson, D. A. Lewis, G. J. L. Bernardes and J. M. Chalker, *Adv. Sustainable Syst.*, 2018, 1800024.