FeSO$_4$/lime mixtures – an alternative to mineral sulfur and lime fertilizer for summer rape

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ABSTRACT

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Sulfur (S) is one of six important macronutrients and due to the strong reduction of atmospheric S, it has to be fertilized to cover the S demand of plants – especially of those with a high S demand. In addition to regular S fertilizers, FeSO$_4$ × 7 H$_2$O was tested as a compound for a new S fertilizer. A pot experiment was conducted in order to test if FeSO$_4$ × 7 H$_2$O, a by-product in TiO$_2$ production from ilmenite (FeTiO$_3$), can be used in mixtures with limestone (CaCO$_3$) or hydrated lime [Ca(OH)$_2$] as an S fertilizer for summer rape (*Brassica napus* L). The results showed that S fertilization in the form of FeSO$_4$ × 7 H$_2$O/lime mixtures resulted in the same effects on the S and phosphorus (P) availability to summer rape as a gypsum/CaCO$_3$ mixture. Application of S as FeSO$_4$ × 7 H$_2$O/lime mixtures resulted in the same seed yields of summer rapes as compared to S application as a gypsum/CaCO$_3$ mixture. These results indicate that FeSO$_4$ × 7 H$_2$O/lime mixtures can be used as a combined mineral S and lime fertilizer.

Keyword: macroelement; extractability; phosphorus bioavailability; iron oxides; phosphate; sulfate

It is well known that the sulfur (S) input from atmospheric deposition is less than 10 kg S/ha/year in most of the Western European countries (Hu et al. 2005). One reason for the strong decrease in S deposition is the reduction in SO$_2$ emissions due to cleaning the exhaust fumes of coal-fired power stations. Another reason is the use of fuels with a low S concentration. The strong reduction in S deposition results in a reduction of S concentration in soils so that S fertilization is necessary for plants with a relatively high S demand such as canola, cabbage species (kohlrabi, cauliflower), field garlic, false flax, legumes and common wheat (Lošák et al. 2008, 2010, Scherer 2009, Čekey et al. 2011, Leithold et al. 2015). The S demand can be met by S application in the form of organic or inorganic fertilizers. The total S concentration of organic fertilizers such as compost, cattle slurry and organic manure is in the range of 0.14, 0.20 and 0.37% S on a dry matter basis (Pape et al.

1997). The mineralization of organic S depends mainly on S retention, the C:N:S ratio, soil pH and microbial activity in soil (Scherer 2009). Several S containing fertilizers can be applied such as elemental S, gypsum, ammonium sulfate, ammonium sulfate nitrate, potassium sulfate, sulfate of potash magnesia and magnesium sulfate. Recently, S has also been applied as a mixture of limestone and gypsum referred to as Granukal-S with 4% S (Vereinigte Kreidewerke Dammann GmbH & Co. KG, Germany).

In the production of TiO$_2$ from ilmenite (FeTiO$_3$), melanterite (FeSO$_4$ × 7 H$_2$O) occurred as a co-product. This salt can be used as an iron fertilizer in vineyards or as a feedstock for iron oxide pigment production. On peat bog soils, Scheffer et al. (1985) applied FeSO$_4$ × 7 H$_2$O to reduce phosphorus (P) leaching. Applied Fe^{2+}SO$_4$ × 7 H$_2$O is oxidized to Fe^{3+}SO$_4$ which is then transformed to Fe^{3+} ocher that sorbs P, resulting in the reduc-

tion of P leaching, while P uptake in grass is not affected. However, the question arises if $FeSO_4 \times 7 H_2O$ can be used as an S fertilizer. $FeSO_4 \times 7 H_2O$ from TiO_2 production contains a small amount of sulfuric acid, so that its application as top dressing could cause plant damage. Therefore, in this study, $FeSO_4 \times 7 H_2O$ was mixed with lime in the form of $CaCO_3$ or $Ca(OH)_2$. It was assumed that the oxidized iron could be converted to amorphous Fe oxide able to adsorb sulfate or P to decrease the S and P availability. Zhu et al. (2014) reported that sulfate is adsorbed on Fe oxyhydroxide surfaces. The Fe-S interatomic distance of the Fe-oxide sulfate complex is 0.322 to 0.325 nm. The findings of Zhu et al. (2014) demonstrate that sulfate adsorption involves a similar process as phosphate adsorption on Fe-oxide surfaces. The process of P adsorption decreases P bioavailability (Mengel 1997). However, little is known about mixing of $FeSO_4 \times 7 H_2O$ with limestone in terms of regeneration of amorphous iron oxides and adsorption of sulfate and P, which may decrease S and P bioavailability. Based on this, a pot experiment was conducted in order to investigate the S and P availability related to $FeSO_4 \times 7 H_2O$/lime mixtures. For this pot experiment, the following hypothesis was proposed: $FeSO_4 \times 7 H_2O$/lime mixtures applied to summer rape have the same effects on the S and P availability to summer rape as a gypsum/$CaCO_3$ mixture.

MATERIAL AND METHODS

Pot experiment. The experiment, which contained five treatments (Trt.), was conducted in the Mitscherlich pots (6 kg soil/pot) under natural conditions in a greenhouse. Following variants were conducted: Trt. 1: Control without S and lime; Trt. 2: Limestone ($CaCO_3$); Trt. 3: $FeSO_4 \times 7 H_2O$/$CaCO_3$ mixture; Trt. 4: $CaSO_4$/$CaCO_3$ mixture; Trt. 5: $FeSO_4 \times 7 H_2O$/$Ca(OH)_2$ mixture. Lime in the form of $CaCO_3$ or $Ca(OH)_2$ was mixed with $FeSO_4 \times 7 H_2O$ or $CaSO_4$ in a ratio of 1:1 so that the total S concentration was 6% S in all lime/sulfate mixtures. Each treatment contained four replications. The experimental design of the pot experiment was completely randomized and was changed twice a week.

For the pot experiment, subsoil (depth 40–80 cm) from a brown soil derived from loess was selected (45% sand, 35% silt, 20% clay, 0.17% total C, 0.03% total N, 0.027% total S, 6.3 mg CAL-P/kg soil, pH in 0.01 mol/L $CaCl_2$ of 6.4). The soil was air-dried and sieved through a 4 cm sieve for the pot experiment. Pots were filled with 3 kg soil plus 3 kg quartz sand. The soil was mixed with sand in a ratio of 1 + 1 in order to have a substrate low in S availability. The soil/sand mixture in the pots was treated with 167 mg N (NH_4NO_3, $Mg(NO_3)_2$), 300 mg K (K_2HPO_4, KCl), 100 mg P (K_2HPO_4), 50 mg Mg ($Mg(NO_3)_2$), 0.5 mg B (H_3BO_3), 0.1 mg Mo (NH_4-molybdate), 20 mg Mn ($MnCl_2$), 10 mg Zn 89 ($ZnCl_2$) and 5 mg Cu ($CuCl_2$)/kg soil. Sulfur was applied only to the Trt. 3–5 in the dose of 50 mg S/kg soil. The macronutrients were applied as salts and the micronutrients in liquid form. After mixing the fertilizers with the soil/sand mixture, the soil was filled into the pots and moistened to 60% of the water holding capacity. After seven days of incubation, soil samples were collected with a small soil sampler from each pot and dried at 40°C. Summer rape seeds (*Brassica napus* L. cv. Belinda) were sown with 15 seeds/pot and then thinned to 10 plants five days after germination. Twenty-four days after sowing the plants were thinned to three plants/pot and the harvested plants were dried at 80°C for further analyses.

After this harvest and before flowering of rape, 0.5 g N (NH_4NO_3)/pot in liquid form was applied. Senescent rape leaves were collected from the plants of each pot during the vegetation and were dried at 80°C. This plant material was then mixed with the harvested stems and hulls of rape. At harvest time, the hulls were collected carefully from the rape plants and were treated with an experimental thresher. Seeds were dried at 40°C and the vegetative plant mass (straw = leaves, stems, hulls) was dried at 80°C. After drying, the dry weight of seeds and of straw of rapeseed was recorded.

Analyses of soil and plant samples. Soil samples were dried at 40°C and ground to pass a < 2 mm sieve. Sulfur and P were extracted as described by Houba et al. (1986). 10 g soil was extracted for 2 h with 100 mL 0.01 mol/L $CaCl_2$ in a 200 mL PVC flask on a rotation shaker. Then the soil extracts were filtered (Filter Papers MN 615 ¼ Ø 110 mm from Macherey-Nagel). The S and P concentrations in the extracts were analysed by the ICP-OES using an ES 720 from Varian Inc. (Palo Alto, USA). All plant samples were analysed, except for the

Table 1. Effect of lime, lime/FeSO$_4$ × 7 H$_2$O mixtures and lime/CaSO$_4$ mixture on 0.01 mol/L CaCl$_2$ extractable sulfur (S) and phosphate in soil and pH before sowing of summer rape

Treatment	Sulfur (mg S/kg)	Phosphate (mg P/kg)	pH$_{CaCl_2}$
Control	7.6 ± 0.4[a]	9.1 ±1.3[a]	6.4 ± 0.1
CaCO$_3$	7.6 ± 0.8[a]	8.8 ± 1.4[a]	6.8 ± 0.1
FeSO$_4$ × 7 H$_2$O/CaCO$_3$	64.5 ± 10.9[b]	10.3 ± 3.0[a]	6.7 ± 0.1
CaSO$_4$/CaCO$_3$	66.8 ± 6.8[b]	6.4 ± 1.4[a]	6.8 ± 0.1
FeSO$_4$ × 7 H$_2$O/Ca(OH)$_2$	70.4 ± 6.0[b]	7.2 ± 0.5[a]	7.0 ± 0.1

Different letters within a column indicate a significant difference at the 5% level

seeds, at 80°C dried and ground to < 1 mm samples. Total N and total S in plants were analysed with an elemental analyser whereas total N and S in seeds were analysed with the NIRS technique. The P concentration in plants was analysed by ashing of 1 g dry matter at 550°C. The ash was boiled in 5 mol/L HNO$_3$, and after filtration the P concentration was measured at 450 nm wavelength as an NH$_4$- molybdo-vanado-complex (Gericke and Kurmies 1952).

Statistical analyses. Experimental data were statistically analysed with Microsoft Excel 2010. SPPS was used for an ANOVA and a Tukey's test.

RESULTS AND DISCUSSION

Sulfur extractability was not affected by the form of sulfate and the form of lime. Extractable S in soil was increased due to the application of either gypsum and lime/FeSO$_4$ × 7 H$_2$O mixtures. In general, all lime/sulfur mixtures resulted in the same concentration of 0.01 mol/L CaCl$_2$ extractable soil S. This documents that the S extractability was not affected by the form of sulfate and the form of lime (Table 1). Furthermore, the values of

0.01 mol/L CaCl$_2$ extractable phosphate show that the assumed synthesis of amorphous Fe oxide, which could have adsorbed sulfate and phosphate, did not occur.

Sulfur fertilization increases the plant growth. The concentrations of S and P and the N/S ratio in the young rape shoots are presented in Table 2. Application of S resulted in a strong increase in S concentrations of the rape shoots whereas the concentrations of P were not affected due to the addition of the lime/FeSO$_4$ × 7 H$_2$O mixtures. The relatively high P concentration in the rape shoot in the control treatment is related to a concentration (dilution) effect since the rape growth was limited by S deficiency. Haneklaus et al. (2007) reported that rape plants suffer from S deficiency at the S concentration of 1.6 mg S/g DM (dry matter) and that adequate nutritional status of S is 4.8 mg S/g DM. S deficiency of rape in the control and the lime treatments is documented by a very wide N/S-ratio in the rape shoots (Table 2).

Very strong S deficiency in the control treatments (no S, no S plus lime) is also evident from the plant growth documented in Figure 1. This deficiency of the control plants was so severe that they could not be harvested in the generative

Table 2. Effect of lime, lime/FeSO$_4$ × 7 H$_2$O mixtures and lime/CaSO$_4$ mixture on the S- and P-concentration and the N/S ratio in young summer rape plants

Treatment	S concentration (mg S/g DM)	P concentration (mg P/g DM)	N/S ratio
Control	1.8 ± 0.1[a]	5.9 ± 0.1[a]	32:1
CaCO$_3$	1.5 ± 0.1[a]	5.0 ± 0.2[b]	53:1
FeSO$_4$ × 7 H$_2$O/CaCO$_3$	11.1 ± 1.1[b]	4.3 ± 0.2[c]	5:1
CaSO$_4$/CaCO$_3$	11.5 ± 1.1[b]	4.5 ± 0.2[c]	5:1
FeSO$_4$ × 7 H$_2$O/Ca(OH)$_2$	11.1 ± 0.1[b]	4.1 ± 0.5[c]	5:1

Different letters within a column indicate a significant difference at the 5% level. DM – dry matter

Figure 1. Effect of lime, lime/$FeSO_4 \times 7 H_2O$ mixtures and lime/$CaSO_4$ mixture on the growth of summer rape. The sulfur fertilization was 0.3 g S/pot in form of the various lime sulfate mixtures, where the number denotes 1 – S0 (no S fertilization); 2 – $CaCO_3$ + S0; 3 – $CaCO_3$ + $FeSO_4 \times 7 H_2O$; 4 – $CaCO_3$ + $CaSO_4$; 5 – $Ca(OH)_2$ + $FeSO_4 \times 7 H_2O$

phase (Figure 2). Fertilization with the $FeSO_4 \times 7 H_2O/CaCO_3$ mixture and $FeSO_4 \times 7 H_2O/Ca(OH)_2$ mixture achieved the same seed and straw yield and S uptake as the $CaSO_4/CaCO_3$ treatment. The S uptake in the rape shoot increased due to S application from 5.4 mg S/pot (control) to 71.4, 66.9 and 73.0 mg S/pot in the $CaCO_3/FeSO_4 \times 7 H_2O$, $CaCO_3/CaSO_4$ – and $Ca(OH)_2/FeSO_4 \times 7 H_2O$ mixture, respectively (Table 3). The differences between treatments fertilized with S are not statistically significant, demonstrating that the $FeSO_4 \times 7 H_2O$ lime/mixtures have the same effects on S nutrition as the $CaSO_4$/lime mixture. There are only significant differences to the control treatments. On the other hand, these results prove that mixing of lime either as $CaCO_3$ or $Ca(OH)_2$ with $FeSO_4 \times 7 H_2O$ had no effect on sulfate adsorption on amorphous iron oxides from the $FeSO_4 \times 7 H_2O$/lime mixtures. It was further concluded that the $FeSO_4 \times 7 H_2O$/lime mixtures had no effect on the P bioavailability because the seed P concentration was the same as in the lime/$CaSO_4$ mixture (Table 3).

For the experiments, the following hypothesis was proposed: $FeSO_4 \times 7 H_2O$/lime mixtures applied to summer rape have the same effects on S and P availability to summer rape as a gypsum/

$CaCO_3$ mixture. The achieved results confirm these hypothesis, as mixtures from $FeSO_4 \times 7 H_2O$ with lime either in the form of $CaCO_3$ or $Ca(OH)_2$ resulted in the same seed yield as a mixture from gypsum and $CaCO_3$. On the other hand, these results prove that mixing of lime either as $CaCO_3$ or $Ca(OH)_2$ with $FeSO_4 \times 7 H_2O$ had no effect on sulfate adsorption on amorphous iron oxides from the $FeSO_4 \times 7 H_2O$/lime mixtures. Furthermore, the results show that the $FeSO_4 \times 7 H_2O$/lime mixtures had no effect on the P bioavailability because the young shoot and seed P concentrations were the same as in the lime/$CaSO_4$ mixture (Tables 2 and 3). An adsorption of inorganic anions (phosphate, molybdate, borate, and sulfate) depends on pH and oxides and hydroxides. The capacity of adsorption is increased with a decreasing pH of soil and the concentration of oxides and hydroxides (Schinner and Sonnleiter 2013). The strongest sulfate adsorption was observed at pH of 3.0 (Scott 1976), whereas no specific sulfate adsorption was
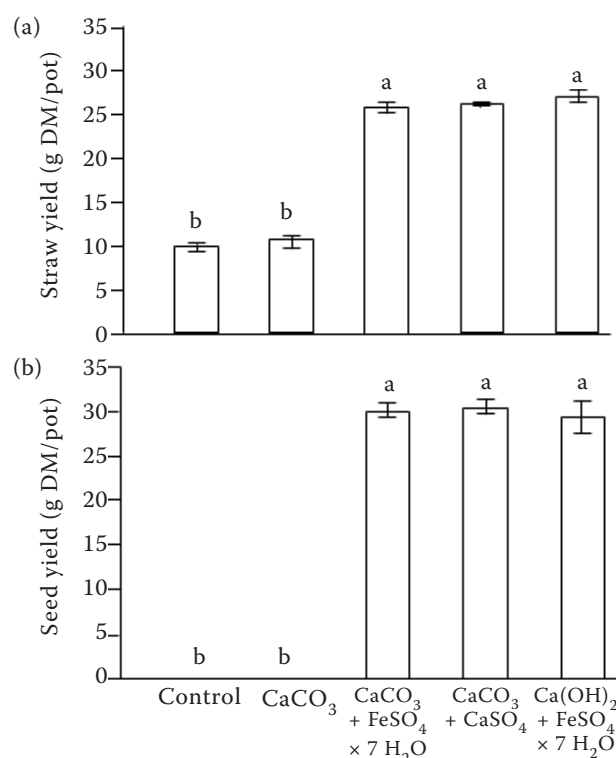

Figure 2. Effect of lime, lime/$FeSO_4 \times 7 H_2O$ mixtures and lime/$CaSO_4$ mixture on (a) the straw yield and (b) seed yield of summer rape. The sulfur fertilization was 0.3 g S/pot in form of the various lime sulfate mixtures. Mean of 4 replications, ± standard error. Different letters within a column indicate a significant difference at the 5% level

Table 3. Effect of lime, lime/$FeSO_4 \times 7\ H_2O$ mixtures and lime/$CaSO_4$ mixture on the sulfur (S) uptake in rape shoots and the phosphorus (P) concentration in seed

Treatment	S uptake in shoots (seeds plus straw) (mg S/pot)	P concentration in seeds (mg P/g seed)
Control	5.4 ± 0.5^a	–
$CaCO_3$	8.9 ± 3.5^a	–
$FeSO_4 \times 7\ H_2O/CaCO_3$	71.4 ± 6.0^b	6.9 ± 0.5^b
$CaSO_4/CaCO_3$	66.9 ± 7.2^b	6.9 ± 0.4^b
$FeSO_4 \times 7\ H_2O/Ca(OH)_2$	73.0 ± 7.8^b	6.9 ± 0.5^b

Different letters within a column indicate a significant difference at the 5% level

analysed at pH of 6.5 (Curtin and Syers 1990). In this study, soil pH of 6.4 was recorded in the control treatment and 6.7–7.0 in the $FeSO_4 \times 7\ H_2O$/lime mixtures (Table 1). Hence, it is assumed that the sulfate adsorption did not occur.

The assumption is that due to mixing of $FeSO_4 \times 7\ H_2O$ with lime, especially with $Ca(OH)_2$, synthesis of amorphous Fe oxide was not obtained. If amorphous Fe oxides were generated in the $FeSO_4 \times 7\ H_2O$/lime mixtures a decrease in $CaCl_2$ extractable soil S and P concentrations would occur. Neither the $CaCl_2$ extractable S nor the $CaCl_2$ extractable P concentrations were affected by $FeSO_4 \times 7\ H_2O$ fertilization compared to the $CaSO_4$ application (Table 1). The $CaCl_2$ method was chosen for soil analyses in order to analyse the intensity of S and P availability. One reason for the lack of amorphous Fe oxides synthesis could be the soil pH measured after fertilization. The soil pH increased in the control from 6.4 to 6.7 in the $FeSO_4 \times 7\ H_2O/CaCO_3$ treatment and to 7.0 in the $FeSO_4 \times 7\ H_2O/Ca(OH)_2$ treatment. For synthesis of goethite from $Fe(NO_3)_3$ mixed with KOH, pH above 10 is needed (Schwertmann and Cornel 1991). For this, a relatively quick synthesis of amorphous Fe oxides can be obviated that could have fixed sulfate and phosphate during the experimental time. Therefore, the fertilization in the form of $FeSO_4 \times 7\ H_2O$/lime mixtures achieved the same S and P concentrations in the young shoots of summer rape as in the gypsum/$CaCO_3$ treatment (Table 2). An effect of the residence time on synthesis of amorphous Fe oxides did not occur during the cultivation of summer rape, since the S uptake and the P concentration in rape seeds were not influenced by mixing $FeSO_4 \times 7\ H_2O$ with lime neither as $Ca(OH)_2$ nor as $CaCO_3$. It may be further concluded that the $FeSO_4 \times 7\ H_2O$/lime

mixtures had no effect on the P bioavailability because the seed P concentration was the same as in the lime/$CaSO_4$ mixture (Table 3). The first results from the field experiment with winter rape confirm the positive effect of $FeSO_4 \times 7\ H_2O$/lime mixtures on the S and P availability.

In conclusion, the results indicate that mixing $FeSO_4 \times 7\ H_2O$ with lime ($CaCO_3$ or $Ca(OH)_2$) is a promising new S fertilizer because the $FeSO_4 \times 7\ H_2O$/lime mixtures applied to summer rape have the same effects on the S and P availability for summer rape in comparison to a gypsum/$CaCO_3$ mixture.

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REFERENCES

Čekey N., Šlosár M., Uher A., Balogh Z., Valšíkova M., Lošák T. (2011): The effect of nitrogen and sulphur fertilization on the yield and content of sulforaphane and nitrates in cauliflower. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis, 59: 17–22.

Curtin D., Syers J.K. (1990): Extractability and adsorption of sulphate in soils. European Journal of Soil Science, 41: 305–312.

Gericke S., Kurmies B. (1952): The colorimetric phosphoric acid determination by ammonium-vanadate-molybdate and its application in plant analysis. Zeitschrift für Pflanzenernährung und Bodenkunde, 104: 235–247. (In German)

Haneklaus S., Bloem E., Schnug E., de Kok L.J., Stulen I. (2007): Sulfur. In: Barker A.V., Pilbeam D.J. (eds.): Handbook of Plant Nutrition. Boca Raton, CRC Press, Taylor & Francis Group, 183–238.

Houba V.J.G., Novozamsky I., Huybregts A.W.M., van der Lee J.J. (1986): Comparison of soil extractions by 0.01 M $CaCl_2$, by EUF and by some conventional procedures. Plant and Soil, 96: 433–437.

Hu Z.Y., Zhao F.J., McGrath S.P. (2005): Sulphur fractionation in calcareous soils and bioavailability to plants. Plant and Soil, 268: 103–109.

Leithold G., Becker K., Riffel A., Schulz F., Schmid-Eisert A., Brock C. (2015): Nitrogen and Sulfur in Organic Farming. Guidebook to Better Nutrient Supply in Arable Crops. Berlin, Verlag Dr. Köste. (In German)

Lošák T., Hlušek J., Kráčmar S., Varga L. (2008): The effect of nitrogen and sulphur fertilization on yield and quality of kohlrabi (*Brassica oleracea*, L.). Revista Brasileira de Ciencia do Solo, 32: 697–703.

Lošák T., Vollmann J., Hlušek J., Peterka J., Filipčík R., Prášková L. (2010): Influence of combined nitrogen and sulphur fertilization on false flax (*Camelina sativa* [L.] Crtz.) yield and quality. Acta Alimentaria, 39: 431–444.

Mengel K. (1997): Agronomic measures for better utilization of soil and fertilizer phosphates. Developments in Crop Science, 25: 277–289.

Pape H., Brough D., Steffens D. (1997): S- and N-mineralization of bio-compost in comparison to farm fertilizer. Mitteilung Deutsche Bodenkundliche Gesellschaft, 83: 359–362. (In German)

Scheffer B., Bartels R., Blankenburg J. (1985): Possible usage of red mud and green salt on high moor soils. Zeitschrift für Pflanzenernährung und Bodenkunde, 148: 527–535. (In German)

Scherer H.W. (2009): Sulfur in soils. Journal of Plant Nutrition and Soil Science, 172: 326–335.

Schinner F., Sonnleitner R. (2013): Bodenökologie: Mikrobiologie und Bodenenzymatik Band III. Anorganische Schadstoffe. Berlin, Heidelberg: Springer-Verlag.

Schwertmann U., Cornell R.M. (1991): Iron Oxides in the Laboratory – Preparation and Characterization. Weinheim, VCH Verlagsgesellschaft.

Scott N.M. (1976): Sulphate contents and sorption in scottish soils. Journal of the Science of Food and Agriculture, 27: 367–372.

Zhu M.Q., Northrup P., Shi C.Y., Billinge S.J.L., Sparks D.L., Waychunas G.A. (2014): Structure of sulfate adsorption complexes on ferrihydrite. Environmental Science and Technology Letters, 1: 97–101.