

Sulphate leaching through two contrasting New Zealand soils

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Abstract

Despite the fact that substantial sulphur/sulphate leaching losses have been reported in New Zealand and overseas, little work has been done on the mechanisms involved and the modelling of sulphate leaching. Retention of sulphate in soils is highly dependent on pH and mineralogy, and some studies have shown that the accompanying cation can also be important. The implications of these various factors on sulphate leaching, however, have not yet been well explored. Detailed studies of sulphate movement in different soils, in tandem with model refinement or development are thus needed to gain better understanding of the sulphur dynamics in soils. We performed a number of leaching experiments with repacked and undisturbed columns of two contrasting New Zealand soils, a high anion retaining allophanic Egmont soil, and a low retaining pumice Taupo soil. Three different concentrations of CaCl₂ followed by CaSO₄, and a single concentration of KCl followed by K₂SO₄ were used. Anions, cations, pH and EC were measured in the leachate to describe sulphate transport in soils. The results show high correlations among pH, EC, and cation concentration changes in the leachate. Sulphate adsorption was low in Taupo soil. In the Egmont soil adsorption was dependent on the accompanying cation, with significant higher adsorption with calcium compared to potassium. Differences in the shape of the breakthrough curves and the results of pH, EC and cations were consistent with the assumption of calcium-sulphate paired adsorption. It is concluded that the accompanying cation cannot be neglected when studying sulphate adsorption/leaching in this soil.

Key Words

Sulphur Balance; Modelling; Ion exchange; Disk permeameter; BTC; co-adsorption.

Introduction

Sulphur is one of the most important nutrients for plants. Its deficiency can cause yield losses (Booth *et al.* 1991, Schnug and Haneklaus 1994), and may have a great influence on crop quality parameters such as protein content and composition (Eppendorfer and Eggum 1994). Also, sulphur supply can affect the efficiency of nitrogen utilisation by plants (Schnug *et al.* 1993), and the susceptibility of crops to certain diseases (Schnug *et al.* 1995, Bourbos *et al.* 2000, Klikocka *et al.* 2004). Sulphur deficiency in New Zealand and overseas has been reported (Nguyen and Goh 1994, Moncaster *et al.* 2000), whilst the ever-increasing use of non-sulphur containing nitrogen and phosphate fertilizers, and the introduction of new high yielding and sulphur-demanding cultivars, tends to intensify the problems of sulphur deficiency for plants. Hence, improved understanding of the dynamics of sulphur in the soil-plant system has become an important issue for sustainable production.

Sulphate is the most important form of inorganic sulphur in soils and is the most readily available form to plants (Alves and Lavorenti 2003). The fate of sulphate in the soil is influenced by many chemical, biological and physical factors. Therefore the concentration of sulphate in natural soils can be very variable in both space and time (Schnug and Haneklaus 1998, Bloem *et al.* 2001), making it very difficult to assess sulphate availability for soil fertility management purposes. Soil hydraulic properties and ion adsorption are two main soil characteristics affecting sulphate leaching-storage processes in soils (Clothier *et al.* 1998). Both characteristics can be described in leaching experiments or separately in specific experiments.

Performing miscible displacement or leaching experiments and analysing the resulting breakthrough curves (BTC) is a common way of studying solute movement in the soil. This procedure simplifies the interpretation of data as the imposed hydraulic regime and ion concentration are controlled. The BTC's can be used to either validate and parameterize an existing transport model, or for developing a more

refined model. The model can then be used as a decision support tool for land management practices by farmers. However, care should be taken when results from controlled experiments are transferred into the field, as the hydraulic regime imposed in the laboratory is much steadier than in the natural environment. Furthermore, leaching studies focus on certain ions, while others are generally neglected. Nevertheless, this procedure is still useful for studying the important processes involved in the fate of nutrients in the soil, as well as for estimating model parameters, since field trials are difficult to accomplish and analyse.

Concerns still remain about the best way to describe ion adsorption. For modelling results from leaching experiments, empirical adsorption isotherms are commonly used (Bolan *et al.* 1993, Martinson *et al.* 2003, Selim *et al.* 2004). Adsorption is often assumed to occur instantaneously and to be completely reversible and independent of other ions. This assumption has been found to be an oversimplification in some mineral soils, (Selim *et al.* 2004), where hysteresis in adsorption isotherms (Gobran 1998), and paired adsorption of sulphate and calcium may occur (Marcano-Martinez and McBride 1989, Bolan *et al.* 1993). Furthermore, the adsorption of sulphate is not always instantaneous (Sparks, 1989). But as the factors influencing adsorption are not yet well understood, and seem to depend on the soil and the soil solution composition, the use of simple empirical isotherms is still justified. The hydraulics of the leaching process also need to be addressed, given some transport models assume the entire soil solution takes part in the leaching process, while in others only a mobile fraction is assumed to be active (Clothier *et al.* 1998).

Despite these and other issues, solute leaching models have been developed and used successfully for various cations and anions. In recent years more attention has been paid to sulphur/sulphate dynamics in the soil, and some specific modelling has been presented (Fumoto and Sverdrup 2000, Martinson *et al.* 2003, Selim *et al.* 2004). The authors suggested however, that the processes involved need to be better understood, particularly in relation to sulphate behaviour in soils with different chemical and physical characteristics.

In order to study some of the processes involved in the dynamics of sulphur in New Zealand soils, several miscible displacement experiments were carried out. Results from these experiments using two contrasting New Zealand soils are presented here. Comparisons between measurements from the two different soils, and also when using different accompanying cations in the input solutions, are discussed. Evidences of paired adsorption of sulphur and calcium are presented as well.

Methods

Soils

Two contrasting New Zealand soils were used: undisturbed and repacked columns of pumice Taupo soil (Typic Vitrandept); and repacked columns of Egmont soil (Typic Dystrandept), an allophanic soil with variable charge (Marsh *et al.* 1987). The lesser weathered and well-drained pumice Taupo soil has almost no structure, a bulk density between 600 and 800 kg m⁻³ and a moderate to low anion exchange capacity (Molloy 1998). The allophanic Egmont soil is more weathered, has a higher clay content and also a higher anion exchange capacity. This soil also has a well-developed structure and the bulk density is usually below 900 kg m⁻³ (Molloy 1998). Soil samples were collected from 0.05 m to 0.20 m depth.

Leaching experiments

A series of leaching experiments were conducted using equipment and procedures similar to those described by Magesan *et al.* (1995). All experiments were conducted under unsaturated conditions, - 0.1 kPa was applied to both the top and the bottom of the column. The columns were first pre-leached with a CaCl₂ solution to eliminate indigenous sulphate and cations other than calcium, and then leached with three different concentrations of a CaSO₄ solution (

Table 1). One column was used for each treatment. The leaching solutions were applied until the effluent concentration reached the same concentration as the influent solution. Pre-leaching and leaching solutions had the same ionic strength. In addition, one column of the Egmont soil was pre-leached with 0.03M KCl and then leached with 0.01M K₂SO₄ to examine the influence of the accompanying cation on sulphur adsorption. Basic description of experiments and information on column characteristics are also presented in

Table 1.

Table 1. Leaching experiments: Soil type and concentration of influent solutions, soil bulk density, water-filled pore volume (WFPV), mean water flux density during leaching and the number of water filled pore volumes of flow (PVs) during each stage of the experiment. R means repacked column and U undisturbed.

Soil		Solution concentration		Soil density (kg m ⁻³)	WFPV (cm ³)	Water flux density (mm h ⁻¹)	PVs	
		Pre-leaching CaCl ₂ (M)	Leaching CaSO ₄ (M)				Pre-leaching	Leaching
Egmont	R	0.0067	0.005	755	819	44.1	7.55	7.27
	R	0.0133	0.01	754	763	29.9	5.11	6.77
	R	0.03*	0.01*	770	789	20.5	6.36	6.73
	R	0.0033	0.0025	795	578	58.4	7.46	8.48
	U	0.0033	0.0025	879	608	46.0	6.35	8.61
Taupo	R	0.0067	0.005	840	579	33.2	6.22	7.20
	U	0.0067	0.005	683	511	72.9	7.63	7.71
	R	0.0133	0.01	860	581	41.9	4.55	4.55
	U	0.0133	0.01	885	581	46.6	4.35	5.07

*For this column KCl was used for pre-leaching and K₂SO₄ for leaching

Analyses

Leachate solutions were analysed for sulphur, chloride and the major cations (calcium, magnesium and potassium). The pH and the electrical conductivity (EC) of the leachate aliquots and soil columns were also measured. Sulphur was determined by the methylene blue method (Johnson and Nishita 1952), chloride by the mercury thiocyanate-iron method (Florence and Frarrer 1971) and cations using atomic absorbance spectroscopy.

Results

The behaviour of leachate pH was distinctly different for the two contrasting soils (Figure 1). In general, leachate pH was higher for the Taupo soil than the Egmont one. However, the Egmont soil exhibited a distinct peak in pH at about two liquid-filled pore volumes after the CaSO₄ solution had been applied, just before the breakthrough of sulphate (Figure 1a). For the Taupo soil the changes in pH also occurred prior to the sulphate breakthrough, although they were smaller than in the Egmont soil and without the pronounced peak. Taupo repacked columns exhibited sharper increases than the undisturbed ones (Figure 1b). For both soils the shapes of the pH curves were very similar for all the three solution concentrations, thus are not all presented here.

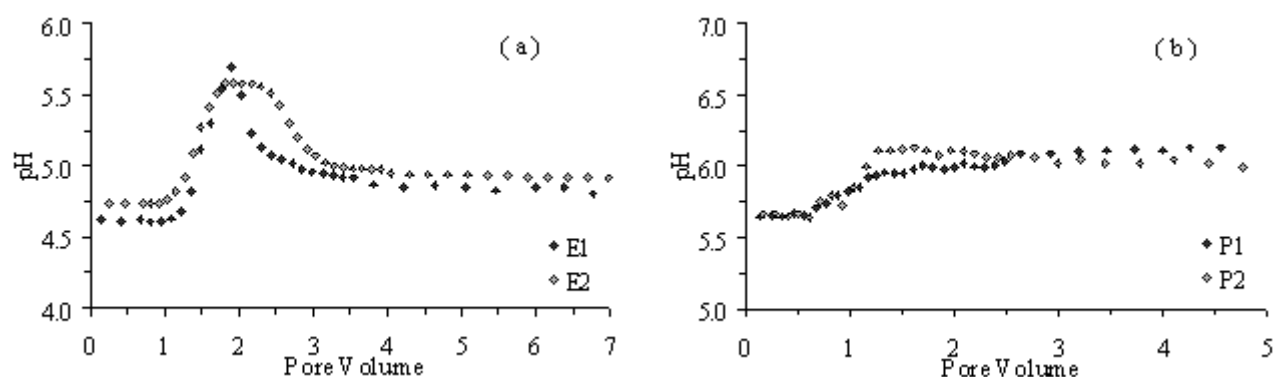


Figure 1. pH of leachate for columns with repacked Egmont soil (a) – E1: 0.01 M CaSO₄, E2: 0.005 M CaSO₄, – and Taupo Pumice soil (b) with 0.01 M CaSO₄ – P1: undisturbed, P2 repacked.

The peak in the leachate pH for Egmont soil columns coincided with a drop in the leachate EC. The EC of the leachate was also highly correlated with the cation concentration in the solution (Figure 2). Similar correlations were also found for Taupo columns, but no noticeable peak in pH or drop in EC occurred, especially in the leachates from the undisturbed columns.

Calcium was the only significant cation present in the effluent, except at the very beginning of the pre-leaching, where potassium and magnesium made up almost half of the initial peak in the Egmont columns. However, K and Mg were rapidly leached thereafter. This early peak was not observed in the

Taupo columns, and the concentrations of potassium and magnesium collected in the leachate were much lower than those from the Egmont soil.

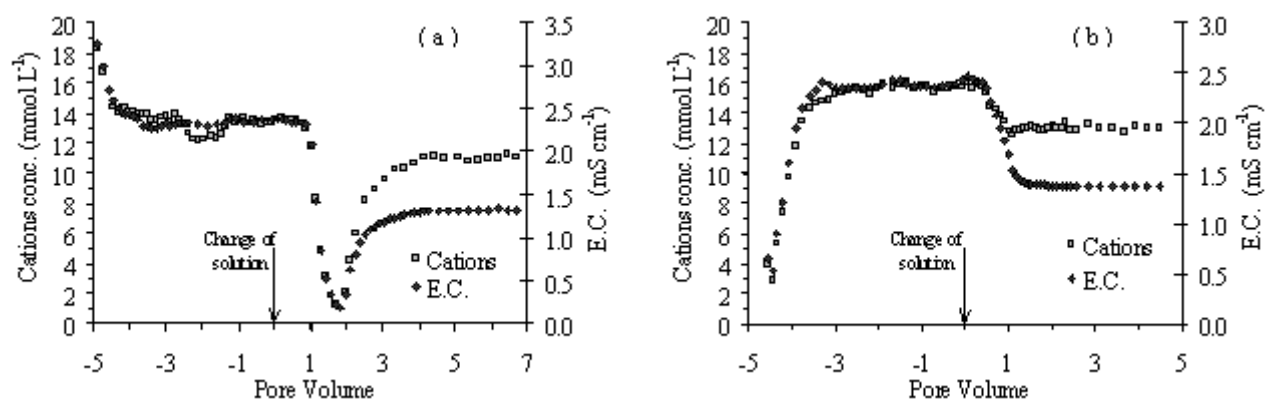


Figure 2. Comparison of EC and cations measurements in the leachate for the column with Egmont soil (a) and Taupo soil (b), leached with 0.01 M CaSO₄ solution.

The contrasting behaviour of the Egmont and Taupo soils can be seen even more clearly, in Figure 3, which shows the sulphate and calcium concentrations in the effluent following the application of 0.01 M CaSO₄. For the Taupo soil, the calcium concentration dropped from the pre-leaching solution's concentration to the leaching one, and there was a corresponding rise in the sulphate concentration from zero to the concentration of the input solution, both as expected. There were no significant differences between the three different leaching solution concentrations. However the leachate from the Egmont columns showed a large but temporary drop in calcium concentration, which almost reached zero. This drop lasted longer at the lower the influent concentration. After this drop, both the calcium and sulphate concentrations rose to reach the concentration of the input solution, as expected.

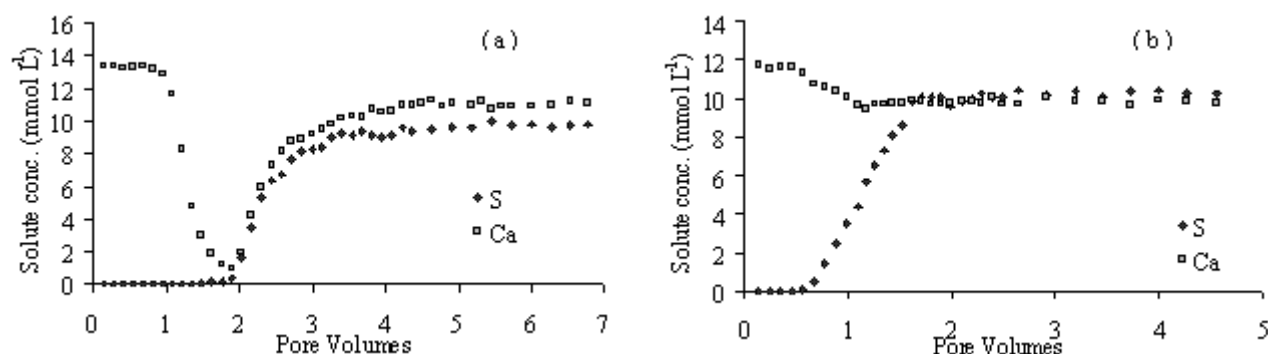


Figure 3. Breakthrough curves for calcium and sulphur of leachate from Egmont soil (a) and from Taupo soil (b); solution of 0.01 M CaSO₄.

This drop of calcium in the leachate can be explained by the phenomenon of paired adsorption of sulphate and calcium (Marcano-Martinez and McBride 1989, Bolan *et al.* 1993). When a calcium sulphate solution is added to a soil, which is already saturated with calcium chloride solution from pre-leaching, sulphate adsorption can induce an extra amount of calcium to be adsorbed at the same time. This occurs in order to preserve charge balance in the effluent solution. This phenomenon of paired adsorption can explain the shape of the calcium and sulphate curves. The temporary absence of solutes in the leachate, due to this extra adsorption, is consistent with the temporary drop in EC in Figure 2a.

In contrast to the Egmont soil columns very little sulphate adsorption was observed in the Taupo soil columns, confirming the low anion adsorption capacity of this pumice soil (Figure 4). Also there was no clear evidence of paired adsorption in most of the columns (see Figure 2b and Figure 3b). Only the results from the repacked column at the lowest concentration (0.0025 M CaSO₄) exhibited a very small drop/peak (data not shown).

In the column with repacked Egmont soil, where the cation in the influent solution was changed from calcium to potassium, leachate pH exhibited a much smaller peak, whilst the corresponding drop in EC and cations was also much smaller. This suggests that some paired adsorption can also occur between potassium and sulphate, though to a much lower extent, or alternatively the results found for the Egmont soil have an explanation other than only paired adsorption. Further studies must be done to properly understand these interactions. Clear differences were also found in the shape of the sulphate breakthrough curves, in the case where potassium was the accompanying cation. The BTC was similar to the ones found for the Taupo soil, where almost no sulphate adsorption occurred, (Figure 4). Sulphate adsorption capacity is therefore almost the same as in the Taupo soil if paired adsorption with calcium is avoided. These results demonstrate that sulphate breakthrough curves are significantly altered by the dominant cation in the soil solution, but it also depends on the soil type. For the Egmont soil the accompanying cation must be considered when describing sulphate adsorption and transport, while it can be ignored for the Taupo soil. The reasons for these differences are not clear, and specific studies are needed to better describe the process of paired adsorption of cations and sulphate. Nevertheless our results have clearly shown that paired adsorption cannot be ignored when modelling sulphate dynamics. Further studies are also needed to determine the influence of this different adsorption behaviour on sulphate uptake by plants, and its implications on sulphur dynamics in the field.

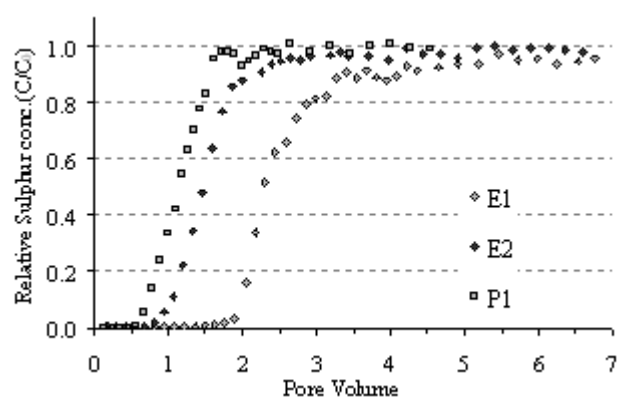


Figure 4. Sulphur breakthrough curves for columns with Egmont soil leached with 0.01 M CaSO₄ solution (E1) and 0.01 M K₂SO₄ (E2) and Taupo pumice soil with 0.01 M CaSO₄ (P1).

Conclusion

Significant differences between sulphate transport in the two contrasting soils were found. The Taupo soil exhibited, as expected, almost no sulphate adsorption, and the behaviour of pH, EC and calcium concentration in the effluent reflected this. In the Egmont soil, sulphate adsorption was significantly higher when calcium, instead of potassium, was the accompanying cation. Considerable differences on the shape of breakthrough curves were found, and agreed with the calcium-sulphate paired adsorption approach. The study showed that cation and anion interactions need to be considered when studying and predicting sulphate dynamics in the soil.

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