Measurement and simulation of soluble, exchangeable, and non-exchangeable ammonium in three soils

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1. Introduction

The quest for improved N efficiency in agricultural systems is recognised worldwide. Important to cropping system management are the proper amount and timing of N applied that considers local weather, pedological factors, and crop characteristics. A more rational use of N fertilisers can be obtained using cropping system models that support the evaluation of different N management options.

Ammonium fixation in its non-exchangeable form is defined as “the adsorption or absorption of ammonium ions by the mineral or organic fraction of the soil in a manner that they are relatively unexchangeable by the usual methods of cation exchange” (Osborne, 1976b, as cited by Nieder et al., 2011).

Fixation occurs mostly in the interlayer regions of 2:1 clay minerals, such as illite, vermiculite, and montmorillonite. “Native fixed” is the term for ammonium present during mineral forma-tion while “recently fixed” is fixed later, and located in the outermost areas of the minerals. Recently fixed ammonium comes typically from fertilisation; in fact, fertiliser-N fixed can represent as much as 50% of applied ammonium (Kowalenko and Cameron, 1976; Kowalenko, 1978). Fixation becomes problematic when fertiliser-based ammonium is sequestered and not available to the crop, as opposed to the resource it becomes when it is slowly released into the soil solution. Furthermore, a potential for water pollution arises when soluble ammonium is nitrified outside relevant crop N uptake periods.

The rate of ammonium fixation is diffusion-controlled and decreases over time until equilibrium is reached between non-exchangeable and exchangeable ammonium, and between non-exchangeable and soluble ammonium (Nõmmik, 1965). Fixation is fast and occurs within the first few hours after fertiliser application (e.g., Kowalenko, 1978; Sowden, 1976). On the other hand, its release, which normally concerns only a fraction of the fixed ammonium, is slower and longer-lasting, taking up to several weeks (Osborne, 1976a; Smith et al., 1994; Steffens and Sparks, 1997).

The amount of fixed ammonium and the fixation capacity of a soil depend on many factors: parent material, clay content (Opuwaribo and Odu, 1974; Moyano and Gallardo, 1988), type of clay minerals (Feigin and Yaalon, 1974; Sparks et al., 1979), concentration of potassi-um in the soil solution, saturation of potassium on exchange sites, saturation of 2:1 clay minerals (Hinman, 1966; Doram and Evans,

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1983), and soil water content (Black and Waring, 1972). The myriad factors involved and their importance in clay soils mostly, make it rare to find models that simulate ammonium fixation and release in soils.

Isotherms can be used to represent the static adsorption of an ion (e.g., ammonium) onto a surface (Hamdaoui and Naffrechoux, 2007; Salarirad and Behnamfard, 2011) as a function of ion concentration. The most used non-linear isotherms are those of Freundlich and Langmuir, in which the percentage of adsorbed ion decreases as ion concentration increases. Soil science employs widely used phosphorus, zinc, selenium, and cadmium ion representations (Rennie and McKercher, 1959; Weir and Soper, 1962; John, 1972; Al-Kanani and MacKenzie, 1991; Dhillon and Dhillon, 1999; Lewis and McGechan, 2002; Mesquita and Vieira e Silva, 2002; Wang and Harrell, 2005; Bolster, 2008) while on the contrary, few isotherm representations exist in agricultural models to simulate ammonium exchange and fixation, and only in a few cases do they account for soil water content and temperature effects (e.g., Cameron and Kowalenko, 1976; Kowalenko and Cameron, 1976; Stöckle and Nelson, 2014). Frissel and Van Veen (1978) used a different approach and represented fixation using a reversible first-order kinetic reaction between fixed and soluble forms; however, no exchangeable form representation was done.

The calibration of isotherm-based models requires measurement of soluble, exchangeable, and clay-fixed ammonium pools at increas-ing concentrations of applied ammonium. Several ammonium fixation studies are found in the literature at the laboratory, greenhouse, and field scales (e.g., Doram and Evans, 1983; Kowalenko, 1978; Scherer and Mengel, 1986). However, in only a few cases (Kowalenko and Cameron, 1976; Nõmmik, 1957) were two or three pools measured at increasing concentrations of applied ammonium, whereas more frequently, fixation was measured with only a single dose application. The data reported by Nõmmik (1957) showed that the ammonium fixation percentage decreased as applied ammonium concentrations increased and then plateaued at the low fixation rate of 11% when 5600 mg NH_4–N kg^{-1} soil were applied. This implies that for the calibration of non-linear isotherm-based models, experiments should be conducted over a wide range of applied ammonium concentrations in order to enable the maximum fixation capacity of the soil. If concentrations of 5000 mg NH_4–N kg^{-1} soil seem unrealistic for normal field practice (where only 10–100 mg NH_4–N kg^{-1} soil is expected), then consider that localised application of ammonium fertilisers have yielded far higher soil concentrations of ammonium locally. For example, 45 days after injection of anhydrous ammonia, Sanchez (1986) measured up to 300 mg NH_4–N kg^{-1} soil near the injection point when nitrapyrin (a nitrification inhibitor) was applied as a treatment. Blue and Eno (1954) also measured local concentrations along the injection line as high as 628 mg NH_4–N kg^{-1} after application of 292 kg NH_4–N ha^{-1}, and went on to demonstrate that even higher concentrations can be reached under higher fertilisation rates. In such cases, a spatially-heterogeneous N model (e.g., Masse et al., 2007) must be adopted to account for concentration differences between the injection point and surrounding soil.

The objective of our work was to design a simulation model to describe the partitioning of applied ammonium among soluble, exchangeable, and clay-fixed pools, using Langmuir isotherms. Characterisation of the parameters was the result of measurements specifically performed to support our model, which included ammonium pools, but included neither nitrate nor organic N pools. For this reason, the experiment was conducted by inhibiting nitrification and microbial immobilisation — two processes the model could not represent. Therefore, the application domain of our model is, in its present form, restricted to fixation occurring after ammonium application under constant and controlled laboratory conditions.

2. Materials and methods

2.1. Experiments

Three soils of different textural classes (Table 1) were used, of which none had received organic amendments during the prior three years. After sampling, soils were air dried, crushed to pass through a 0.5 mm sieve, and then stored until experimental start.

We conducted two experiments. The first was to assess fixation kinetics and the second was to determine the response curve of non-exchangeable ammonium to increasing ammonium concentrations.

2.1.1. Kinetics experiment

The first experiment measured the rate of fixation at lengthening time intervals. We used the Nõmmik (1957) method, adopting a completely randomised design of four replicates, two treatments, and six destructive measurements. Six experimental unit sets, equal in num-ber to destructive sampling dates and each composed of eight experi-mental units, were prepared for each soil. Each experimental unit consisted of 10 g of dry soil in a 175-mL conical centrifugal tube that received one of two treatments: addition of 10 mL of water (control), or addition of 10 mL of a solution of $(NH_4)_2SO_4$ (280 mg N L^{-1}). Immediately after the water or ammonium addition, 20 μL DMPP (3,4-dimethyl pyrazole phosphate, 0.024% dilution) to inhibit nitrification (Zerulla et al., 2001) and three drops of $CHCl_3$ to kill soil microorganisms were added and the tube was then sealed. The $CHCl_3$ was added again every 12 h.

Soil soluble and exchangeable ammonium concentrations were measured after 0.8, 1.6, 6.7, 24.5, 48.6, and 144.7 h; each experimental set (six in total) received water/ammonium one time only, after which it was destroyed at the dedicated measurement time. Air temper-ature was held at 25 °C during the experiment as were dark conditions.

2.1.2. Response curve experiment

The experiment to ascertain the response curve of non-exchangeable ammonium to increasing concentrations of added ammonium used the same method as in the Kinetics experiment. As increasing concentrations of ammonium (0, 70, 140, 280, 700, 1400 and 2800 mg NH_4–N kg^{-1} soil) were added, a constant soil to solution ratio of 1:1 was maintained. For each concentration, soluble and exchangeable ammonium levels were measured after 48 h, per the re-sults obtained in the first experiment.

2.2. Analytical techniques

To verify that nitrate concentrations were stable during the experiment, we analysed NO_3–N on Soil 1 supernatants (sulphanilamide–

Table 1
Experimental soils.

	Soil 1	Soil 2	Soil 3
Sand, g kg^{-1}	450	440	100
Silt, g kg^{-1}	250	350	560
Clay, g kg^{-1}	300	210	340
Texture class	Clay loam	Loam	Silty clay loam
Cation exchange capacity, cmol kg^{-1}	24.0	20.4	54.7
Maximum fixation capacity, cmol kg^{-1}	2.31	0.97	0.68
pH (H_2O)	6.8	6.7	6.6
Organic carbon, g kg^{-1}	11.6	14.9	18
Total nitrogen, g kg^{-1}	1.4	1.66	1.84
Quartz, g kg $soil^{-1}$	210	380	80
K-Feldspar, g kg $soil^{-1}$	60	110	120
Plagioclase, g kg $soil^{-1}$	120	180	210
Amphibole, g kg $soil^{-1}$	0	30	0
Chlorite, g kg $soil^{-1}$	180	130	50
Mica, g kg $soil^{-1}$	150	90	40
Smectite, g kg $soil^{-1}$	160	80	500
Kaolinite, g kg $soil^{-1}$	120	0	0

naphtylethylendiamine dihydrochloride method), after preliminary re-duction of NO_3^- to NO_2^- by a copper–cadmium reductor column (ISO 13395 procedure, 1996). No net nitrate increase occurred in the ammonium-amended treatments.

To measure the soluble and exchangeable ammonium concentration, 100 mL of water were added to each experimental unit, which were hand-shaken for 2 min and then centrifuged for 10 min at 3500 rpm (2120 relative centrifugal force). After centrifugation, the supernatant was taken to measure the concentration of soluble ammonium. To the remaining soil was added 100 mL of 1 M KCl and agitated on a rotary shaker for 2 h. After agitation, the soil was centrifuged for 10-min at 3500 rpm, and the supernatant taken to measure the ammonium concentration, which corresponded to the exchangeable ammonium fraction plus residual soluble ammonium. We performed a preliminary test using samples from Soil 1 to check the increase in exchangeable NH_4–N after a second extraction with KCl. After finding the increase was not relevant, we used one extraction to quantify the fraction of NH_4–N present on the exchange complex.

Concentrations of NH_4–N in the supernatants were determined by flow injection analysis and spectrometric detection (FIAstar 5000 Ana-lyzer, Foss Tecator, Denmark) using the gas semi-permeable membrane method per the ISO 11732 procedure (1997).

Soil samples were analysed according to Italian official soil chemical analysis methods (Italian Ministry for Agriculture and Forestry Policy, 2000), briefly described below. Soil pH was potentiometrically-determined in a 1:2.5 soil/water suspension. Particles concentrations (sand, silt, and clay) were measured by Na hexametaphosphate disper-sion and then with the pipette method. Organic C and total N were de-termined by dry combustion using a ThermoQuest NA1500 elemental analyser (Carlo Erba, Milano, Italy). The cation exchange capacity (CEC) was established by the $BaCl_2$ (pH 8.2) method, according to the ISO 11260 procedure.

Mineralogical analyses were performed on soil samples dried at 40 °C and finely ground by an Agatha mortar. X-ray powder diffraction analyses were completed on three differently-treated samples: untreat-ed, treated at 550 °C for 3 h, and treated with ethylene glycol. Following the methodology proposed by Biscaye (1965) and Moore and Reynolds (1997), a semi-quantitative estimate of the clay minerals was obtained.

The maximum ammonium fixation capacity of soil was determined according to Nõmmik (1957) with some slight modifications. Five grams of soil were added with 25 mL of a 1 N ammonium sulphate so-lution and held at 25 °C for 48 h (same treatment as in Kinetics experiment). Then, the soil samples were washed with 100 mL water, centrifuged, then the exchangeable ammonium was extracted twice with 100 mL 1 M KCl (first extraction after 2 h of agitation; second extraction after hand shaking for 2 min), followed by two 100 mL water washings. Soil pellets were oven-dried (25 °C), hand ground (0.5 mm), and analysed for non-exchangeable ammonium content using the Silva and Bremner (1966) method (but without further grinding at a size less than 100 mesh as reported in the original method). Samples were treated with an alkaline potassium hypobromite solution to remove exchangeable ammonium and organic N. Soil residues from this pre-treatment were washed three times with 0.5 M KCl and shaken for 20 h with an acid solution (5 M HF:1 M HCl) to decompose silicates. The ammonium concentration in the acid extract was then determined by steam distillation and titration. Distillation was performed using a Büchi K-350 distillation unit (BÜCHI Labortechnik AG, Switzerland) after preliminary alkalisation of the extracts with a 32% NaOH solution. The distillate, collected in a beaker containing a 4% H_3BO_3 solution, was titrated with 0.005 M HCl using a G20 Compaq Titrator (Mettler-Toledo AG, Analytical, Switzerland). Maximum ammonium fixation capacity was calculated as the difference between non-exchangeable ammonium content in ammonium-saturated samples and samples treated using the same procedure, but with water added rather than the am-monium sulphate solution.

2.3. Calculations

We define “soluble ammonium” ($NH_4–N_{soluble}$) as the fraction of applied ammonium recovered after water extraction. We calculated exchangeable ammonium ($NH_4–N_{exchangeable}$) as ammonium quantity in 1 M KCl extract minus residual soluble ammonium in the pel-let after the first centrifugation to eliminate soluble ammonium. Finally, we estimated the ammonium fixed in non-exchangeable form ($NH_4–N_{fixed}$) as:

$$NH_4–N_{fixed} = NH_4–N_{added}–NH_4–N_{soluble}–NH_4–N_{exchangeable} \qquad (1)$$

where $NH_4–N_{added}$ is the added ammonium, and soluble and exchangeable ammonium concentrations are net of control. For this calculation, we assumed ammonium did not undergo transformations (nitrification, volatilisation, or microbial immobilisation) in the time interval between soil addition and measurement.
The Silva and Bremner (1966) method was used only for determination of the maximum fixation capacity, while ammonium fixation in the

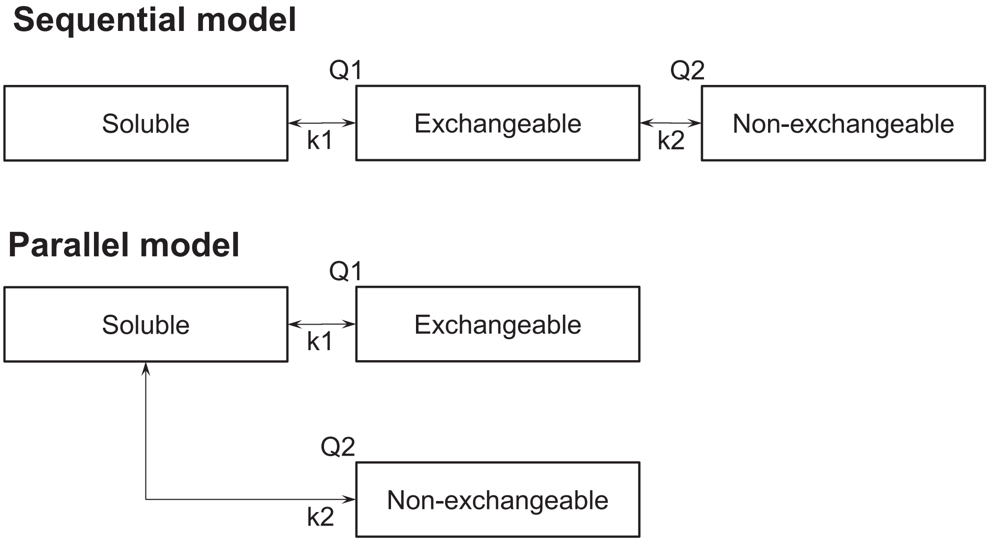

Fig. 1. Sequential and parallel models used to simulate the equilibria between soluble, exchangeable, and non-exchangeable ammonium in the soil. *Q*1, cation exchange capacity. *Q*2, maximum fixation capacity. *k*1 and *k*2, equilibrium constants regulating the exchange between pools. Model parameters are also described in Table 2.

Kinetics experiment and in the Response curve experiment was estimated as described in Eq. (1).

2.4. Statistical analysis

For the first experiment we performed an analysis of variance (ANOVA) using the Tukey test for post-hoc comparison among time measures, while in the second experiment, we used ANOVA to evaluate differences among applied ammonium concentrations. Due to heteroscedasticity, the Dunnet T3 test was employed in both experi-ments. All tests utilised SPSS, Version 21 (UNIANOVA procedure) (IBM Inc., Armonk, New York).

2.5. Modelling

2.5.1. The two models

The Langmuir equation can be used to depict the equilibrium of an ion between the adsorbed (N_A) and non-adsorbed (N_{NA}) fractions:

$$N_A = Q\,kN_{NA}/(1 + kN_{NA}) \qquad (2)$$

where Q is the maximum attainable value for N_A, and k is the ratio be-tween $k_{A\text{-}NA}$ and $k_{NA\text{-}A}$, where $k_{A\text{-}NA}$ is the rate constant of N_A flowing into N_{NA} and $k_{NA\text{-}A}$ is the rate constant of N_{NA} flowing into N_A (Bolster and Hornberger, 2007).

We used the Langmuir equation to build two plausible models of ammonium in the soil (Fig. 1). In the parallel model, the soluble fraction is in equilibrium with the exchangeable and non-exchangeable frac-tions, with no interaction between the exchangeable and non-exchangeable fractions. This model, in which soluble ammonium can be fixed quickly without passing through the exchangeable form, is sup-ported by the rapid fixation observed in our preliminary experiment (Fig. 2). Rapid accumulation of ammonium in the non-exchangeable form from the soluble form might also arise from fast transit through the exchangeable pool, which also validates sequential model (pro-posed by Nommik and Vahtras, 1982) adoption. In this model, the solu-ble fraction is in equilibrium with the exchangeable fraction, and the exchangeable fraction is in equilibrium with the non-exchangeable fraction.

Next, we solved the system of equations obtained for each model by combining the two Langmuir equilibrium equations with the ammonium mass conservation. In this way, the amount of ammonium in each fraction at equilibrium (soluble, exchangeable, and non-exchangeable) was expressed as a function of model parameters ($Q1$, $Q2$, $k1$, and $k2$). Model parameters are described in Table 2.

2.5.2. Model parameterisation using the linearised forms of the Langmuir equation

The four linearised forms of the Langmuir equation are reported in Table 3, resulting in four parameterisation strategies called A1, A2, A3, and A4. These formulae allowed us to find the optimal values of two parameters at a time (e.g., $Q1$ and $k1$ when soluble and exchangeable ammonium measurements are used). Values for parameters Q and k were obtained through linear regression (Microsoft Excel 2010) using experimental y and x to obtain a and b (Table 3) from which parameters Q and k were derived. Uncertainties on a and b (named S_a and S_b, respec-tively) were finally calculated as (Taylor, 1997):

$$S_a = \sqrt{S_y^2\left(\frac{\sum x_i^2}{n\sum(x_i-\overline{x})^2}\right)}$$

$$S_b = \sqrt{\frac{S_y^2}{\sum(x_i-\overline{x})^2}}$$

where $S_y^2 = \frac{\sum(y_{i,m}-y_{i,s})^2}{n-2}$, n is the number of concentrations tested, $y_{i,m}$ and $y_{i,s}$ are measured and simulated y.

2.5.3. Sensitivity analysis

Sensitivity analysis (SA; Saltelli et al., 2004) explores parameter effects on model outputs. During SA, many parameter combinations are generated, and for each of them, a simulation is performed. Thereafter, model output variations are related to model input variations, by quantifying the contribution of each parameter and of parameter interactions on model output variation. Therefore, SA helps select the most important parameters requiring variation during parameter optimisation for a comprehensive understanding of model behaviour.

Sensitivity analysis was carried out for the four parameters of the two models using the Sobol' method (Sobol' and Kucherenko, 2005), which is based on output variance decomposition from different sources of variation (the partial variances due to single parameters and to all possible interactions among model parameters). The Sobol' method outputs sensitivity indices, given by the ratios between the con-ditional variances and the total unconditional variance; these indices represent contributions to the total output variance of individual pa-rameters (first-order indices) or in combination with other parameters. “Conditional” variance is the variance obtained after having fixed the value of a parameter at its true value.

The calculation of SA was implemented in C++, following Saltelli et al. (2010). The number of parameter combinations generated in our case was 2^{16}. The sensitivity analysis was repeated at increasing concen-trations of added ammonium (35, 70, 140, 280, 700, 1400, 2800, 5600, and 11,200 mg N kg^{-1}). Sensitivity analysis evaluated a wider range of concentrations of added ammonium (0–11,200 mg N kg^{-1}) than considered in the experiment (0–2800 mg N kg^{-1}) to develop a complete representation of model parameter effects and of their interactions.

The lower boundary for $k1$ and $k2$ was defined as one-tenth of their lowest values estimated using procedures A1, A2, A3, and A4. Similarly,

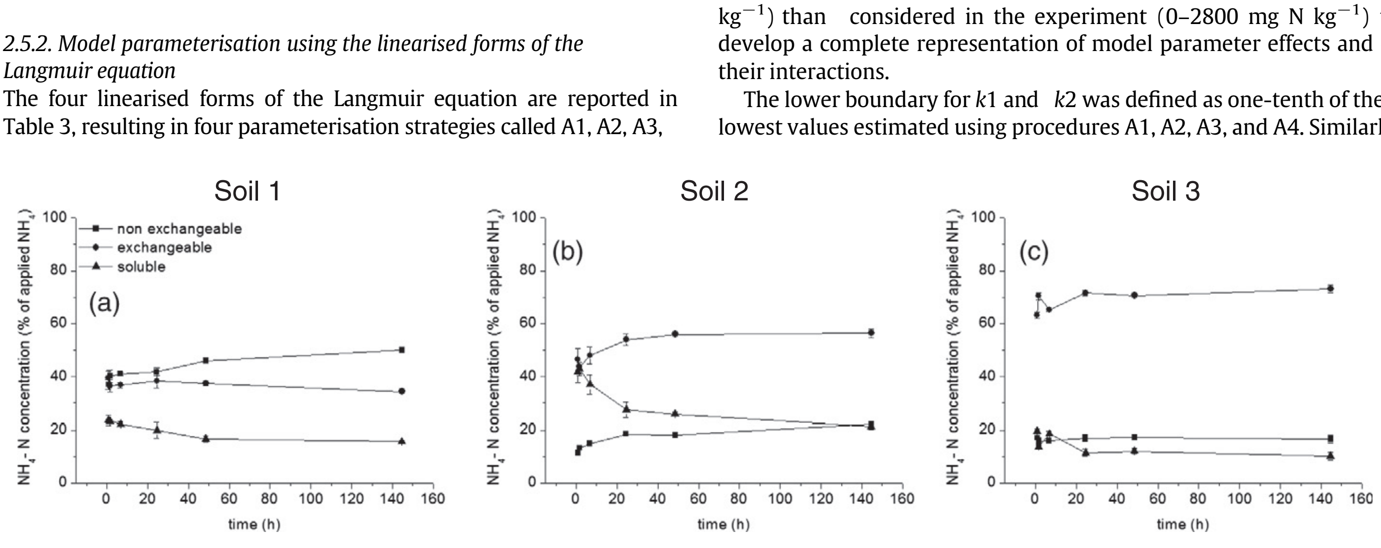

Fig. 2. Dynamics of soluble, exchangeable, and non-exchangeable ammonium, expressed as a percentage of applied ammonium.

Table 2
Names and meanings of model parameters.

Model	Flow	Q	Equilibrium constant
Parallel	Soluble ↔ Exchangeable	Cation exchange capacity ($Q1$)	$k1$
	Soluble ↔ Non-exchangeable	Maximum fixation capacity ($Q2$)	$k2$
Sequential	Soluble ↔ Exchangeable	Cation exchange capacity ($Q1$)	$k1$
	Exchangeable ↔ Non-exchangeable	Maximum fixation capacity ($Q2$)	$k2$

the upper boundary for $k1$ and $k2$ was defined as ten-fold their highest values estimated using procedures A1, A2, A3, and A4. The boundaries for $k1$ and $k2$ were defined separately by modelling (sequential and par-allel). For $Q1$ and $Q2$, a literature review was conducted to find CEC and maximum fixation capacity values (Hinman, 1966; Doram and Evans, 1983; Sahrawat, 1995; Paramasivam and Breitenbeck, 2000; Zhang et al., 2007). The found minimum and the maximum values for CEC and maximum fixation capacity were then used as the lower and upper boundaries for $Q1$ and $Q2$ during SA (Table 4). We did not describe the plausible correlation between $Q1$ and $Q2$ for lack of exper-imental data.

2.5.4. Model parameterisation using the downhill simplex

The two models were also optimised in three additional procedures (procedures B, C, and D), using the downhill simplex (Nelder and Mead, 1965). In procedure B we optimised $k1$, $k2$, $Q1$, and $Q2$. In procedure C we calibrated $k1$, $k2$, and $Q2$, after having fixed $Q1$ equal to the mea-sured cation exchange capacity. In procedure D we optimised $k1$ and $k2$, after having fixed $Q1$ equal to the measured cation exchange capac-ity and $Q2$ equal to the measured maximum fixation capacity. Model pa-rameter boundaries for procedures B, C, and D were the same as those used in SA. The objective function to be minimised was the average relative root mean squared error (RRMSE) of the three ammonium frac-tions (soluble, exchangeable, and non-exchangeable). With the sim-plex, we also estimated the uncertainties of model parameters using a Monte Carlo approach. For this purpose, we generated 10,000 random sets of relationships between added ammonium solution concentration and soluble and exchangeable ammonium concentration after 48 h. Each set was obtained (Motulsky and Christopoulos, 2003) by adding to the original measured value a random number taken from a normal distribution with average equal to zero and standard deviation S_{xy}:

$$S_{xy} = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{i,s} - y_{i,m}\right)^2}{n-p}},$$

where n is the number of data points available in each data set, y is the measured soluble or exchangeable ammonium concentration (simulat-ed: s; measured: m), and p is the number of model parameters. The simplex was applied to the 10,000 generated sets to obtain 10,000 combinations of model parameters. The frequency distribution of each model parameter was cut at 2.5 and 97.5% to obtain uncertainties. We reported the performance of each parameterisation strategy using the RRMSE, the modelling efficiency (ME), the coefficient of determination (CD), and the coefficient of residual mass (CRM) (Loague and Green, 1991).

3. Results

3.1. Measurements

The experiment to assess kinetics (Fig. 2) showed that the concen-tration of non-exchangeable ammonium increased until 48.6 h after ap-plication and then did not change substantially. Adsorption of added ammonium ion to both exchangeable and non-exchangeable sites oc-curred mainly within 0.8 h after application of ammonium sulphate for all soils. The ANOVA indicated that the concentrations of soluble am-monium and exchangeable ammonium at 48.6 h did not differ signifi-cantly ($P < 0.05$) from the concentrations at 144.7 h, with the single exception of exchangeable ammonium on Soil 3. After 48.6 h, Soils 1, 2, and 3 fixed 92%, 82%, and 104%, respectively, of the ammonium fixed after 144.7 h.

The results of the experiment to determine the response curve of non-exchangeable, exchangeable, and soluble ammonium versus the concentration of added ammonium are reported in Fig. 3. As con-centrations of applied ammonium were increased from about 70 to 2800 mg N kg^{-1} soil, both soluble and exchangeable ammonium increased significantly ($P < 0.05$). While applied ammonium concentra-tion increased by two orders of magnitude, non-exchangeable ammoni-um concentration increased by one order only and soluble fraction concentration increased two-fold. Exchangeable ammonium concentra-tion increased proportionally to the applied ammonium concentration, suggesting that the exchange sites were not saturated with ammonium.

3.2. Sensitivity analysis

Sensitivity analysis results (Sobol' sensitivity indices) are reported in Fig. 4. Their interpretation should consider that most of the $Q1$ and $Q2$ explored range lies outside amounts normally used by farmers in field applications. In most cases, field applied ammonium is lower than 100 mg NH_4–N kg^{-1}, or 360 kg NH_4–N ha^{-1}, with an assumed bulk density of 1.2 t m^{-3} and a fertiliser mixing depth of 30 cm.

3.2.1. Sensitivity of the simulated ammonium concentration in the soluble fraction

In the parallel model, the values of Sobol' first-order sensitivity indi-ces indicated that at low concentrations of added ammonium (0–700 mg N kg^{-1}), the soluble fraction was mostly sensitive to $k1$ (Fig. 4a) and not sensitive to $Q1$. This occurred because the allowed range of variation for $Q1$ (980–9800 mg kg^{-1}; Table 4) was much larger than the added concentration. Therefore, $Q1$ was acting as an infinite re-ceiving pool, which left $k1$ as the only parameter regulating the soluble concentration. Added ammonium equal or higher than 2800 mg kg^{-1}

Table 3
Linearised forms of the Langmuir equation used.

Name	Strategy	Equation[a]	y[b]	x	a[c]	b
Lineweaver–Burke	A1	$1 / N_A = 1 / Q + 1 / (k\, N_{NA})$	$1 / N_A$	$1 / N_{NA}$	$1 / Q$	$1 / k$
Eadie–Hofstee	A2	$N_A = Q - N_A / (k\, N_{NA})$	N_A	N_A / N_{NA}	Q	$-1 / k$
Scatchard	A3	$N_A / N_{NA} = Q\,k - k\,N_A$	N_A / N_{NA}	N_A	$Q\,k$	$-k$
Hanes–Woolf	A4	$N_{NA} / N_A = 1 / (Q\,k) + N_{NA} / Q$	N_{NA} / N_A	N_{NA}	$1 / (Q\,k)$	$1 / Q$

[a] N_A, N_{NA}, Q, and k are defined in Eq. (1).
[b] y is estimated based on x, fitting a and b.
[c] a and b, as used in the estimation of parameters and of their uncertainty.

Table 4
Boundaries of model parameters imposed during sensitivity analysis and during parameter optimisation with the downhill simplex (procedures B, C, and D).

	$k1$ (both models)	$k2$ (parallel model)	$k2$ (sequential model)	Q1 (mg N kg^{-1}) (both models)	Q2 (mg N kg^{-1}) (both models)
Lower boundary	0.0000962	0.000887	0.000122	980	30
Upper boundary	0.074	0.289	0.06813	9800	650

demonstrated that most sensitivity was due to $Q1$, which, depending on the values assumed within its range of variation, could or could not accept the applied ammonium. Therefore, above 2800 mg kg^{-1}, soluble ammonium concentration depended mostly on $Q1$ and not on $k1$ anymore. The parameters governing ammonium fixation in exchangeable form ($k2$ and $Q2$) had only a modest impact on soluble ammonium at low concentrations of added ammonium, and no impact above 2800 mg kg^{-1}. Due to the low values allowed for $Q2$ (30–650 mg kg^{-1}), only part of the applied ammonium was fixed; most of it was allocated to the soluble or exchangeable fractions. Below 2000 mg kg^{-1} of added ammonium, interactions among parameters have a non-negligible importance; in particular, the interaction between $k1$ and $Q2$ was the second source of sensitivity after $k1$ at 280 mg kg^{-1} of added ammonium. The same occurred for the $k1 \times k2$ interaction at 35 and 70 mg kg^{-1}.

Very similar findings were obtained in the sequential model (Fig. 4b), albeit with less importance of interactions among parameters.

3.2.2. Sensitivity of the simulated ammonium concentration in the exchangeable fraction

In the parallel model at low concentrations of applied ammonium (0–1400 mg kg^{-1}), the exchangeable fraction was mostly sensitive to $k1$, while $k2$, $Q1$, and $Q2$ had more important roles than on the soluble fraction. Exchangeable fraction sensitivity to $Q1$ and $k1$ may be attributable to the phenomenon put forth for the soluble fraction ($Q1$ much greater than application and not limiting exchange site accumulation). $Q2$ sensitivity can be explained by its small size, which can limit ammonium accumulation in non-exchangeable form. Therefore, as the exchangeable ammonium in this model is fed through the soluble form, the exchangeable form was sensitive to $Q2$. At added ammonium concentrations equal or higher than 2800 mg kg^{-1}, sensitivities for the exchangeable and soluble concentrations were similar for the same reasons.

While the sequential model was very similar to the parallel model above 2800 mg kg^{-1}, it was very different below this threshold. Up to 1400 mg kg^{-1} of added ammonium, neither the large $Q1$, nor $k1$ limited the exchangeable fraction. $Q2$ on the contrary—depending on the value assumed within its variation range (30–650 mg kg^{-1})—either could or could not accept all the applied ammonium. Therefore, the ammonium concentrations of the exchangeable and non-exchangeable pools were sensitive to $Q2$ between 0 and 1400 mg kg^{-1} where their values depended on the fact that $Q2$ was in its lower or upper variation range.

3.2.3. Sensitivity of the simulated ammonium concentration in the non-exchangeable fraction

The sequential model showed a clear trend; increased concentrations of added ammonium tend to increase sensitivity of non-exchangeable ammonium to $Q2$ and decrease sensitivity to $k2$. This means that at very high added ammonium concentrations, the size of the non-exchangeable pool matters (as expressed by $Q2$), rather than the exchangeable ammonium fixation rate (expressed by $k2$). At concentrations equal to or higher than 2800 mg kg^{-1}, the values allowed for $Q2$ (30–650 mg kg^{-1}) are much lower than the applied concentration, and therefore strongly limit accumulation in the non-exchangeable form. This clarifies the high sensitivity to $Q2$ of the non-exchangeable ammonium concentration. To understand why $k1$ and $Q1$ are not important in the sequential model, we recall that ammonium must pass through the exchangeable pool to reach the non-exchangeable pool. The $Q1$ passage size is large, fails to limit ammonium transit towards the non-exchangeable pool, and therefore results in low model sensitivity to $Q1$.

In the parallel model, the situation below 5600 mg kg^{-1} differs from that of the sequential model because $k1$ and $Q1$ are more important. In the parallel model the values allowed for $k2$ (0.000887–0.289) are much higher than in the sequential model (0.000122–0.06813). This drives the parallel model to fill the non-exchangeable pool, and leaves the soluble pool relatively emptier compared to the sequential model. Therefore, parameters governing the soluble concentration ($Q1$ and $k1$) are of higher importance in the parallel model. Moreover, $k1$ is more important than $k2$ because $Q1$ is larger than $Q2$; therefore, ammonium preferentially flows to $Q1$.

3.3. Parameter calibration

Parameter calibration yielded very similar simulation errors for both models (Table 5). The following comments, therefore, apply to both models. Among linearisation methods, Hanes–Woolf (Strategy A4) per-formed better than other methods on all soils. This is made evident through several measures: RRMSE < 15%, ME and CD close to 1, and CRM near 0. The four linearisation methods gave rather similar results on Soil 1, while they were more differentiated on Soils 2 and 3. Specifi-cally, RRMSE ranged from 10 to 26% on Soil 1, from 5 to 53% on Soil 2, and from 14 to 68% on Soil 3. The best linearised solution for each soil had an RRMSE of 10%, 5%, and 14% on Soils 1–3, respectively, and

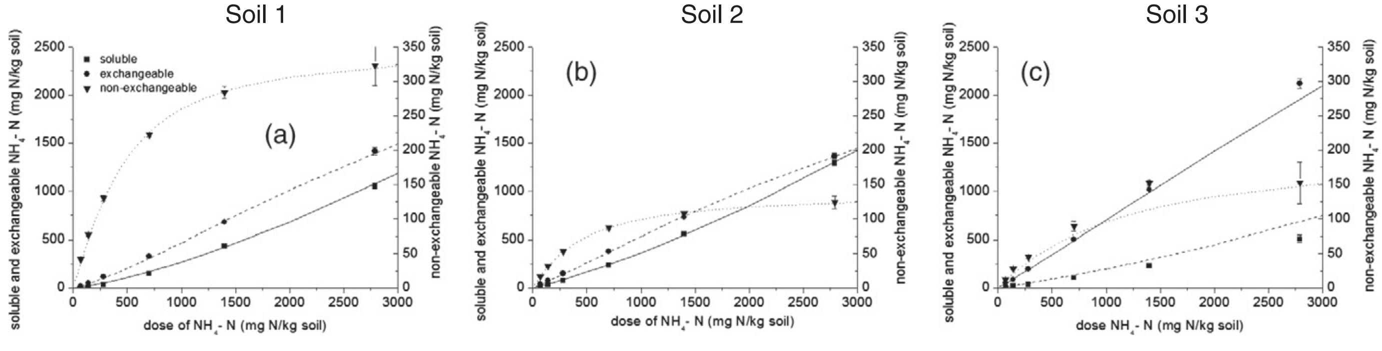

Fig. 3. Measured and simulated concentrations of soluble, exchangeable, and fixed (non-exchangeable) ammonium in three soils. Lines = simulated values obtained with the sequential model parameterised using procedure B.

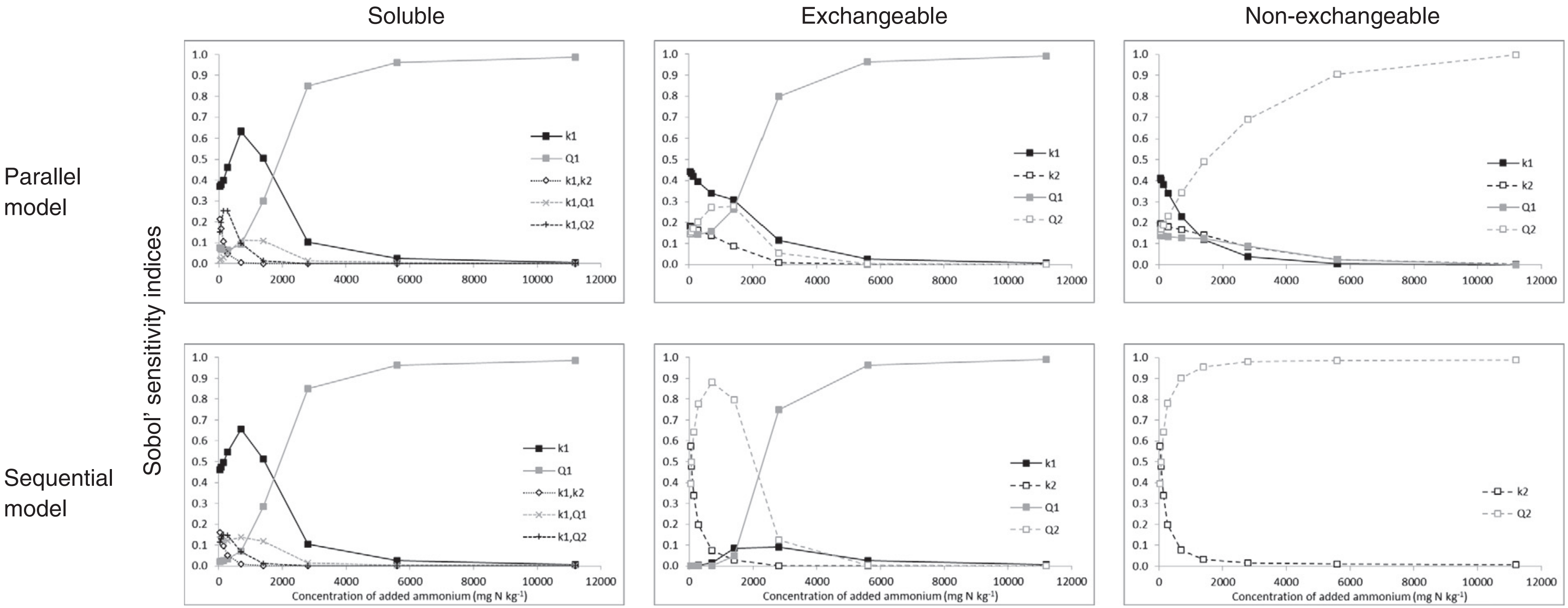

Fig. 4. Sobol' sensitivity indices of three ammonium fractions (soluble, exchangeable, and non-exchangeable) to changes in model parameters at increasing concentrations of added ammonium in sequential and parallel models. *k*1, *k*2, *Q*1, and *Q*2: first-order sensitivity indices. "*k*1, *k*2", "*k*1, *Q*1", and "*k*1, *Q*2": second-order sensitivity indices.

Table 5

Results of the parameterisation with four procedures of sequential and parallel ammonium equilibrium models: model parameters, their uncertainties, and indices of model performance (RRMSE = relative root mean squared error; ME = modelling efficiency; CD = coefficient of determination; CRM = coefficient of residual mass).

Sequential model	$Q1$ (mg N kg^{-1})	$Q2$ (mg N kg^{-1})	$k1$ [a]	$k2$ [a]	RRMSE	ME	CD	CRM
Soil 1, Strategy A1	1722 (0–4729)	314 (283–345)	2.30 (0.00–6.30)	6.81 (6.11–7.52)	0.19	0.97	1.07	−0.01
Soil 1, Strategy A2	1424 (1079–1769)	350 (334–366)	2.82 (1.91–3.73)	5.70 (5.25–6.15)	0.25	0.94	1.05	0.01
Soil 1, Strategy A3	1834 (1207–2461)	354 (321–387)	1.99 (1.35–2.63)	5.56 (5.12–6.00)	0.14	0.98	0.99	0.00
Soil 1, Strategy A4	2090 (1643–2537)	368 (363–373)	1.58 (1.16–2.00)	5.04 (4.78–5.30)	0.10	1.00	0.97	0.00
Soil 2, Strategy A1	758 (458–1058)	172 (153–191)	3.91 (2.35–5.47)	2.77 (2.46–3.00)	0.53	0.44	1.93	−0.07
Soil 2, Strategy A2	1667 (1296–2038)	154 (148–160)	1.54 (1.09–1.99)	3.30 (3.10–3.50)	0.14	0.98	1.03	0.00
Soil 2, Strategy A3	2077 (1443–2711)	155 (144–166)	1.15 (0.81–1.49)	3.25 (3.05–3.45)	0.07	1.00	0.98	0.00
Soil 2, Strategy A4	2341 (1930–2752)	151 (149–153)	0.96 (0.77–1.15)	3.43 (3.31–3.55)	0.05	1.00	0.99	0.00
Soil 3, Strategy A1	1234 (873–1595)	158 (130–186)	7.39 (5.22–9.56)	1.82 (1.49–2.15)	0.68	0.54	1.65	0.00
Soil 3, Strategy A2	2014 (1547–2481)	190 (174–206)	4.15 (2.85–5.45)	1.43 (1.25–1.61)	0.32	0.92	1.01	0.03
Soil 3, Strategy A3	2554 (1704–3404)	198 (171–225)	2.98 (2.05–3.91)	1.34 (1.17–1.51)	0.18	0.97	0.96	0.01
Soil 3, Strategy A4	2853 (2197–3509)	209 (196–222)	2.43 (1.73–3.13)	1.22 (1.11–1.33)	0.14	0.98	0.95	0.01
Strategy B								
Soil 1	4323 (3046–7854)	363 (345–384)	0.46 (0.22–0.79)	5.38 (4.32–6.70)	0.03	1.00	1.01	0.00
Soil 2	3554 (3030–4383)	146 (142–149)	0.48 (0.35–0.62)	4.00 (3.68–4.35)	0.02	1.00	1.00	0.00
Soil 3	7367 (3952–9800)	214 (185–260)	0.53 (0.36–1.37)	1.14 (0.76–1.63)	0.05	1.00	1.01	−0.01
Strategy C								
Soil 1	3361[b]	366 (350–383)	0.67 (0.63–0.72)	5.10 (4.26–6.10)	0.04	1.00	1.01	0.00
Soil 2	2854[b]	147 (144–150)	0.68 (0.65–0.72)	3.76 (3.52–4.02)	0.03	1.00	1.00	0.00
Soil 3	7660[b]	214 (189–248)	0.51 (0.47–0.55)	1.14 (0.84–1.54)	0.05	1.00	1.01	0.00
Strategy D								
Soil 1	3361[b]	324[b]	0.68 (0.64–0.72)	7.75 (5.81–10.53)	0.06	0.99	0.97	0.00
Soil 2	2854[b]	136[b]	0.68 (0.65–0.72)	4.64 (4.09–5.28)	0.04	1.00	0.97	0.00
Soil 3	7660[b]	95[b]	0.52 (0.48–0.55)	7.71 (1.29–104.89)	0.18	0.88	0.79	0.03
Strategy E								
Soil 1	3361[b]	324[b]	0.63[c]	6.7[c]	0.07	0.99	0.97	0.00
Soil 2	2854[b]	136[b]	0.63[c]	6.7[c]	0.08	0.98	0.98	−0.03
Soil 3	7660[b]	95[b]	0.63[c]	6.7[c]	0.24	0.87	0.75	0.07
Parallel model	$Q1$ (mg N kg^{-1})	$Q2$ (mg N kg^{-1})	$k1$	$k2$[a]	RRMSE	ME	CD	CRM
Soil 1, Strategy A1	1722 (0–4729)	292 (264–320)	2.30 (0.00–6.30)	28.89 (25.88–31.90)	0.18	0.97	1.06	−0.01
Soil 1, Strategy A2	1424 (1079–1769)	303 (284–322)	2.82 (1.91–3.73)	27.10 (23.91–30.29)	0.26	0.94	1.07	0.00
Soil 1, Strategy A3	1834 (1207–2461)	310 (266–354)	1.99 (1.35–2.63)	25.68 (22.66–28.70)	0.15	0.98	1.02	0.00
Soil 1, Strategy A4	2090 (1643–2537)	337 (329–345)	1.58 (1.16–2.00)	17.75 (14.36–21.14)	0.10	1.00	0.97	0.00
Soil 2, Strategy A1	758 (458–1058)	118 (111–125)	3.91 (2.35–5.47)	11.97 (11.19–12.75)	0.52	0.45	1.92	−0.07
Soil 2, Strategy A2	1667 (1296–2038)	126 (121–131)	1.54 (1.09–1.99)	10.56 (9.85–11.27)	0.15	0.98	1.05	0.00
Soil 2, Strategy A3	2077 (1443–2711)	127 (117–137)	1.15 (0.81–1.49)	10.37 (9.68–11.06)	0.08	1.00	1.03	0.00
Soil 2, Strategy A4	2341 (1930–2752)	134 (132–136)	0.96 (0.77–1.15)	8.87 (8.18–9.56)	0.05	1.00	0.99	0.00
Soil 3, Strategy A1	1234 (873–1595)	110 (94–126)	7.39 (5.22–9.56)	24.00 (20.26–27.74)	0.68	0.54	1.65	0.00
Soil 3, Strategy A2	2014 (1547–2481)	134 (119–149)	4.15 (2.85–5.45)	17.50 (14.18–20.82)	0.33	0.91	1.05	0.03
Soil 3, Strategy A3	2554 (1704–3404)	144 (112–176)	2.98 (2.05–3.91)	15.30 (12.40–18.20)	0.19	0.97	1.00	0.01
Soil 3, Strategy A4	2853 (2197–3509)	165 (154–176)	2.43 (1.73–3.13)	10.31 (7.96–12.66)	0.14	0.98	0.95	0.01
Strategy B								
Soil 1	4324 (3045–8156)	348 (332–365)	0.46 (0.21–0.79)	11.16 (8.82–14.33)	0.03	1.00	1.01	0.00
Soil 2	3556 (3032–4384)	136 (134–139)	0.48 (0.35–0.62)	7.30 (6.67–8.01)	0.02	1.00	1.00	0.00
Soil 3	7158 (3911–9800)	191 (167–220)	0.55 (0.35–1.40)	5.07 (3.49–8.05)	0.05	1.00	1.01	0.00
Strategy C								
Soil 1	3361[b]	346 (333–359)	0.67 (0.63–0.72)	12.17 (10.25–14.52)	0.04	1.00	1.01	0.00
Soil 2	2854[b]	135 (133–137)	0.68 (0.65–0.72)	8.00 (7.49–8.56)	0.03	1.00	1.00	0.00
Soil 3	7660[b]	192 (174–215)	0.51 (0.47–0.55)	4.93 (3.72–6.50)	0.05	1.00	1.01	0.00
Strategy D								
Soil 1	3361[b]	324[b]	0.68 (0.64–0.72)	15.39 (12.45–19.12)	0.05	1.00	0.99	0.00
Soil 2	2854[b]	136[b]	0.68 (0.65–0.71)	7.71 (7.34–8.10)	0.03	1.00	1.01	0.00
Soil 3	7660[b]	95[b]	0.52 (0.48–0.55)	27.85 (4.65–288.93)	0.18	0.89	0.79	0.03
Strategy E								
Soil 1	3361[b]	324[b]	0.63[c]	16.98[c]	0.06	0.99	0.99	−0.01
Soil 2	2854[b]	136[b]	0.63[c]	16.98[c]	0.12	0.94	1.04	−0.06
Soil 3	7660[b]	95[b]	0.63[c]	16.98[c]	0.25	0.88	0.79	0.10

[a] The values of $k1$ and $k2$ were multiplied by 1000 before being reported in the table.

[b] These parameters were not optimised, but fixed equal to the measured value (CEC for $Q1$; maximum fixation capacity for $Q2$).

[c] These parameters were not optimised, but fixed equal to the average of the optimised values on the three soils with Strategy D.

were characterised by narrow confidence intervals, especially for $Q2$, $k1$, and $k2$. Optimised $Q1$ values were smaller than the corresponding measured values (CEC). For $Q2$, the optimised values agreed with the measured values (maximum fixation capacity) on Soils 1 and 2, and were twice those measured on Soil 3. Optimised $k1$ values were similar across soils (on the order of 10^{-3} d^{-1}) as was for $k2$. Optimised $Q1$ and $k1$ in the parallel model were identical to those obtained in the sequential model.

Among the optimisation strategies based on the simplex, the RRMSE was lower for strategy B compared to C, and for C compared to D. Sim-plex strategies B and C always performed better than the linearisation methods, as indicated by the performance indexes (RRMSE, ME, CD, and CRM). Compared to the linearisation methods, strategy B provided higher $Q1$ estimate—and correspondingly lower values for $k1$ (on the order of 10^{-4} d^{-1})—while other parameters were similar. The perfor-mance indexes for the Simplex strategy D were less satisfying compared to B and C, in particular for Soil 3. This was due to the markedly different $Q2$ value used in strategy D (measured value) *versus* strategies B and C (optimised value). One possible reason for the inadequate measured value for $Q2$ might relate to the portion of applied ammonium held by the soil in a form not extractable by the KCl 1 M solution (during the measurement of soluble and exchangeable ammonium used to calcu-late the difference in non-exchangeable ammonium), while in the case of the Silva and Bremner (1966) method used during determina-tion of maximum fixation capacity, it was less strongly fixed and unable to resist KOBr–KOH attack. While strategies B and C provided similar values of $k2$, strategy D $k2$ values were higher on all three soils, and in particular on Soil 3, where a much larger confidence interval was obtained.

4. Discussion

4.1. Dynamics and percentage of ammonium fixation

Our results confirmed that fixation is a rather fast process, with most of the fixation occurring within hours or days (Nieder et al., 2011). Moreover, we verified that ammonium fixed and amount added were not linearly proportional; instead, the percentage of fixation decreased with increasing addition concentrations. Specifically, we found that over the wide range (70–2800 mg NH_4–N kg^{-1}) of added ammonium, percentage fixation was 60–12% on Soil 1, 24–4%on Soil 2, and 17–5% on Soil 3. Moreover, when only agronomic applications (70 mg NH_4–N kg^{-1}) were considered, fixation was 60, 24, and 17% on Soils 1, 2 and 3, respectively. The literature shows similar fixation percentages have been measured in other soils. For example, Nõmmik (1957) has observed fixation of 16–83% in the 0–20 cm layer of soils added with 140 mg NH_4–N kg^{-1} (1 meq NH_4–N 100 g^{-1}) under laboratory conditions. At higher concentrations of added ammonium, Sowden (1976) measured 38–48% fixation after adding 250 mg NH_4–N kg^{-1}, while Doram and Evans (1983) measured 5–29% in six soils after 500 mg NH_4–N kg^{-1} were added.

The maximum fixation capacity of the three soils (Table 1) was well correlated with the concentration of mica ($R^2 = 0.91$). However, we did not find that the other minerals were useful in interpreting measured ammonium fixation.

4.2. Modelling

4.2.1. Linearisation vs. simplex

The models used in this study allowed two algorithmic classes to be evaluated for identifying optimal parameter values (linearised solutions versus simplex) and soil ammonium partitioning solutions (parallel vs. sequential).

Several examples of application of linearised solutions of the Langmuir equation using adsorbates different from ammonium exist in the literature (Subramanyam and Das, 2009). The Lineweaver–Burke solution is often reported to yield the best results. In our case, the Hanes–Woolf solution performed better than the other methods on all soils. We found the iterative simplex procedure always performed better for parameter optimisation than did linearisation methods, as many solutions were evaluated within the allowed parameter space. Others have reported the same findings (Bolster and Hornberger, 2007). Of note, is the easy use of linearised forms (procedures A1–A4) as param-eters and standard errors are calculable with a spreadsheet or statistical package, as opposed to the ad-hoc optimisation software required for simplex (procedures B–D).

4.2.2. Sequential vs. parallel model

We also compared the sequential and parallel model performance. Our aim was to find which model showed a better fit to the experimen-tal results, an issue not discussed in the literature. We expected that one of the two models would have clearly better performance indices (such as, lower RRMSE) and could better represent ammonium flows among the three pools. On the contrary, the performance indices of the two models (Table 5) were similar after optimisation. Both model optimised parameter values for $Q1$ and $k1$ were almost identical, $Q2$ was very sim-ilar, while $k2$ was different. The similar performance may result from there being no substantial change whether two (strategy D) or four (strategy B) parameters were optimised with the simplex using only eighteen data points. In this regard, the parallel model performed slight-ly better than the sequential model.

The two models provided markedly different results when studied with the sensitivity analysis, in particular for the fixed and exchangeable fractions. The reason for this is the different structures of the two models.

Both models simulated applied ammonium partitioning shortly after reaching equilibrium well. Our work is innovative because it simulated equilibrium among three, rather than two, pools, which allowed NH_4–N fertiliser partitioning to be described completely.

4.2.3. Sensitive parameters

Practically it is helpful to know to which parameters the two models are most sensitive when ammonium is applied at rates commonly used in farm practice. When 200 kg NH_4–Nha^{-1} is applied on a soil with a bulk density of 1.2 t m^{-3} and incorporated to a depth of 0.3 m, the expected soil ammonium concentration is 55 mg N kg^{-1}. This suggests that sensitivities in the range of 0 and 70 mg N kg^{-1} be considered.

In the parallel model (Fig. 4), the most important parameter for the 0 to 70 mg N kg^{-1} concentration range on all fractions was $k1$ (Sobol' in-dices of 0.37–0.44: Fig. 4). Only on the soluble fraction were interactions between $k1$ and $k2$ and between $k1$ and $Q2$ important (Sobol' indices of 0.15–0.21). The second most important parameter was $k2$, which had effects of 0.18–0.20 on the exchangeable and non-exchangeable frac-tions. Third were $Q1$ and $Q2$, which had effects of 0.14–0.17 on the ex-changeable and non-exchangeable fractions. In the sequential model (Fig. 4), $k1$ was important only for the soluble fraction (Sobol' index of 0.46–0.47), while $Q2$ and $k2$ were important for the exchangeable and non-exchangeable fractions (Sobol' index = 0.48–0.58 for $k2$, and 0.39–0.50 for $Q2$). The interactions of $k1 \times k2$, $k1 \times Q1$, and $k1 \times Q2$ were important for soluble fraction alone.

The fact that the two models are very sensitive to $k1$ and $k2$ and less sensitive to $Q1$ and $Q2$ complicates model application because while $Q1$ and $Q2$ can be measured relatively quickly, $k1$ and $k2$ (which have higher sensitivities) can only be estimated after measuring ammonium fixation at increasing ammonium concentrations, as done in this work. It should be noted, however, that $k1$ variation among the three soils is relatively limited, and to a lesser extent, so is $k2$. For this reason, we evaluated the change in simulation results when the two models used $Q1$ and $Q2$ measures (soil-specific) as opposed to the three-soil average optimised values of $k1$ and $k2$. The results (Table 5: Strategy E) show model performance was only slightly inferior with this latter approach. This suggests that the size of the two sinks (cation exchange capacity and maximum fixation capacity) is best when measured by experiment, while the two kinetic constants can be adequately approximated by av-eraging values from many situations.

5. Conclusions

We confirmed the importance of ammonium fixation after application to soil of ammonium fertilisers. The percentage fixation strongly varied by soil type (from 17 to 60% in the three soils used in this experiment). Therefore, when making decisions about N management, fixation cannot be estimated using a constant percentage, but needs to be adjusted according to the soil. To calculate percentage fixation, an equilibrium model like the ones presented in this paper need to be parameterised. Due to the multiplicity of factors involved (clay concentration and type; potassium concentration; water content), it is likely that parameters need to be measured with support of the model in mind. Our research suggests that two of these measurements are the cation exchange capacity and the maximum fixation capacity of the soil. More research is needed to evaluate if kinetic parameters can be averaged by soil groups. The effect of other variables (such as temperature, soil moisture content, and pH) on model performance and on model parameter values should also be studied. Finally, to fully incorporate this partitioning model into a dynamic soil model, the kinetic release of fixed ammonium and the effect of other ions (such as K and Ca) on the fixation/release process should also be modelled.

References

Al-Kanani, T., MacKenzie, A.F., 1991. Sorption and desorption of orthophosphate and pyrophosphate by mineral fractions of soils, goethite, and kaolinite. Can. J. Soil Sci. 71, 327–338. http://dx.doi.org/10.4141/cjss91-032.

Biscaye, P.E., 1965. Mineralogy and Sedimentation of Recent Deep-Sea Clay in the Atlantic Ocean and Adjacent Seas and Oceans. Geol. Soc. Am. Bull. 76, 803–832. http://dx.doi. org/10.1130/0016-7606(1965)76[803:MASORD]2.0.CO;2.

Black, A., Waring, S., 1972. Ammonium fixation and availability in some cereal producing soils in Queensland. Soil Res. 10, 197–207.

Blue, W.G., Eno, C.F., 1954. Distribution and retention of anhydrous ammonia in sandy soils. Soil Sci. Soc. Am. J. 18, 420–424. http://dx.doi.org/10.2136/sssaj1954. 03615995001800040017x.

Bolster, C.H., 2008. Revisiting a statistical shortcoming when fitting the Langmuir model to sorption data. J. Environ. Qual. 37, 1986–1992. http://dx.doi.org/10.2134/jeq2007.0461.

Bolster, C.H., Hornberger, G.M., 2007. On the use of linearized Langmuir equations. Soil Sci. Soc. Am. J. 71, 1796–1806. http://dx.doi.org/10.2136/sssaj2006.0304.

Cameron, D.R., Kowalenko, C.G., 1976. Modelling nitrogen processes in soil: mathematical development and relationships. Can. J. Soil Sci. 56, 71–78.

Dhillon, K.S., Dhillon, S.K., 1999. Adsorption–desorption reactions of selenium in some soils of India. Geoderma 93, 19–31. http://dx.doi.org/10.1016/S0016-7061(99)00040-3.

Doram, D.R., Evans, L.J., 1983. Native fixed ammonium and fixation of added ammonium in relation to clay mineralogy in some Ontario soils. Can. J. Soil Sci. 63, 631–639. http://dx.doi.org/10.4141/cjss83-063.

Feigin, A., Yaalon, D.H., 1974. Non-exchangeable ammonium in soils of Israel and its relation to clay and parent materials. J. Soil Sci. 25, 384–397.

Frissel, M.J., Van Veen, J.A., 1978. Critique of computer simulation modeling for nitrogen in irrigated croplands. Nitrogen in the Environment. Academic Press, New York, pp. 145–162.

Hamdaoui, O., Naffrechoux, E., 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon: part I. Two-parameter models and equations allowing determination of thermodynamic parameters. J. Hazard. Mater. 147, 381–394. http://dx.doi.org/10.1016/j.jhazmat.2007.01.021.

Hinman, W.C., 1966. Ammonium fixation in relation to exchangeable K and organic matter content in two Saskatchewan soils. Can. J. Soil Sci. 46, 223–225. http://dx.doi.org/10.4141/cjss66-036.

Italian Ministry for Agriculture and Forestry Policy, 2000. Analytical Methods for Chemical Analyses of Soils. Franco Angeli, Milano, Italy.

John, M.K., 1972. Cadmium adsorption maxima of soils as measured by the Langmuir isotherm. Can. J. Soil Sci. 52, 343–350. http://dx.doi.org/10.4141/cjss72-046.

Kowalenko, C.G., 1978. Nitrogen transformations and transport over 17 months in field fallow microplots using ^{15}N. Can. J. Soil Sci. 58, 69–76.

Kowalenko, C.G., Cameron, D.R., 1976. Nitrogen transformations in an incubated soil as affected by combinations of moisture content and temperature and adsorption-fixation of ammonium. Can. J. Soil Sci. 56, 63–70.

Lewis, D.R., McGechan, M.B., 2002. SW—soil and water: a review of field scale phosphorus dynamics models. Biosyst. Eng. 82, 359–380. http://dx.doi.org/10.1006/bioe.2002.0102.

Loague, K., Green, R.E., 1991. Statistical and graphical methods for evaluating solute transport models: overview and application. J. Contam. Hydrol. 7, 51–73. http://dx.doi.org/ 10.1016/0169-7722(91)90038-3.

Masse, D., Cambier, C., Brauman, A., Sall, S., Assigbetse, K., Chotte, J.-L., 2007. MIOR: an individual-based model for simulating the spatial patterns of soil organic matter microbial decomposition. Eur. J. Soil Sci. 58, 1127–1135. http://dx.doi.org/10.1111/j. 1365-2389.2007.00900.x.

Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, Oxford.

Mesquita, M.E., Vieira e Silva, J.M., 2002. Preliminary study of pH effect in the application of Langmuir and Freundlich isotherms to Cu–Zn competitive adsorption. Geoderma 106, 219–234. http://dx.doi.org/10.1016/S0016-7061(01)00125-2.

Motulsky, H., Christopoulos, A., 2003. Fitting models to biological data using linear and nonlinear regression. In: GraphPad Software, Inc. (Ed.), A Practical Guide to Curve Fitting. GraphPad Software, Inc., San Diego, CA.

Moyano, A., Gallardo, J.F., 1988. Fixed ammonium determination in some clay soils.Commun. Soil Sci. Plant 19, 225–238. http://dx.doi.org/10.1080/ 00103628809367934.

Nelder, J.A., Mead, R., 1965. A simplex method for function minimization. Comput. J. 7, 308–313. http://dx.doi.org/10.1093/comjnl/7.4.308.

Nieder, R., Benbi, D.K., Scherer, H.W., 2011. Fixation and defixation of ammonium in soils: a review. Biol. Fertil. Soils 47, 1–14. http://dx.doi.org/10.1007/s00374-010-0506-4.

Nõmmik, H., 1957. Fixation and defixation of ammonium in soils. Acta Agric. Scand. 7, 395–436. http://dx.doi.org/10.1080/00015125709434240.

Nõmmik, H., 1965. Ammonium fixation and other reactions involving a nonenzymatic immobilization of mineral nitrogen in soil. Soil Nitrogen, Monograph. American Society of Agronomy, pp. 198–258.

Nommik, H., Vahtras, K., 1982. Retention and fixation of ammonium and ammonia in soils. Nitrogen in Agricultural Soils, Agronomy Monograph. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, pp. 123–171.

Opuwaribo, E., Odu, C.T.I., 1974. Fixed ammonium in Nigerian soils I. Selection of a method and amounts of native fixed ammonium. J. Soil Sci. 25, 256–264.

Osborne, G., 1976a. The significance of intercalary ammonium in representative surface and subsoils from southern New South Wales. Soil Res. 14, 381–388.

Osborne, G., 1976b. The extraction and definition of non-exchangeable or fixed ammonium in some soils from southern New South Wales. Soil Res. 14, 373–380.

Paramasivam, S., Breitenbeck, G.A., 2000. Quantitative Determination of Recently Fixed Nonexchangeable Ammonium in Soils. Soil Sci. Soc. Am. J. 64, 1859–1866. http://dx. doi.org/10.2136/sssaj2000.6451859x.

Rennie, D.A., McKercher, R.B., 1959. Adsorption of phosphorus by four Saskatchewan soils. Can. J. Soil Sci. 39, 64–75. http://dx.doi.org/10.4141/cjss59-009.

Sahrawat, K.L., 1995. Fixed ammonium and carbon-nitrogen ratios of some semi-arid tropical Indian soils. Geoderma 68, 219–224. http://dx.doi.org/10.1016/0016-7061(95)00031-I.

Salarirad, M.M., Behnamfard, A., 2011. Modeling of equilibrium data for free cyanide adsorption onto activated carbon by linear and non-linear regression methods. Present-ed at the International Conference on Environment and Industrial Innovation, Malaysia.

Saltelli, A., Tarantola, S., Campolongo, F., Ratto, M., 2004. Sensitivity Analysis in Practice: A Guide to Assessing Scientific Models. John Wiley & Sons Inc.

Saltelli, A., Annoni, P., Azzini, I., Campolongo, F., Ratto, M., Tarantola, S., 2010. Variance based sensitivity analysis of model output. Design and estimator for the total sensitivity index. Comput. Phys. Commun. 181, 259–270. http://dx.doi.org/10.1016/j.cpc. 2009.09.018.

Sanchez, C.A., 1986. ^{15}N-Tracer Studies of the Transformations, Movement, and Recovery of Anhydrous Ammonia-derived N in the Rooting Zone of Corn (PhD thesis). Iowa State University.

Scherer, H.W., Mengel, K., 1986. Importance of soil type on the release of nonexchangeable NH_4^+ and availability of fertilizer NH_4^+ and fertilizer NO_3^-. Fertil. Res. 8, 249–258. http://dx.doi.org/10.1007/BF01048626.

Silva, J.A., Bremner, J.M., 1966. Determination and isotope-ratio analysis of different forms of nitrogen in soils: 5. Fixed ammonium. Soil Sci. Soc. Am. J. 30, 587–594.

Smith, S.J., Power, J.F., Kemper, W.D., 1994. Fixed ammonium and nitrogen availability indexes. Soil Sci. 158, 132–140.

Sobol', I.M., Kucherenko, S.S., 2005. Global sensitivity indices for nonlinear mathematical models. Review 2, 2–7.

Sowden, F.J., 1976. Transformations of nitrogen added as ammonium and manure to soil with a high ammonium-fixing capacity under laboratory conditions. Can. J. Soil Sci. 56, 319–331.

Sparks, D.L., Blevins, R.L., Bailey, H.H., Barnhisel, R.I., 1979. Relationship of ammonium nitrogen distribution to mineralogy in a Hapludalf soil. Soil Sci. Soc. Am. J. 43, 786–789. http://dx.doi.org/10.2136/sssaj1979.03615995004300040034x.

Steffens, D., Sparks, D.L., 1997. Kinetics of nonexchangeable ammonium release from soils. Soil Sci. Soc. Am. J. 61, 455–462.

Stöckle, C.O., Nelson, R., 2014. CropSyst — simulation chemical: nitrogen. http://sites. bsyse.wsu.edu/cs_suite/CropSyst/manual/simulation/chemical/nitrogen.htm (accessed 9.8.14).

Subramanyam, B., Das, A., 2009. Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil. Int. J. Environ. Sci. Technol. 6, 633–640.

Taylor, J.R., 1997. Introduction to Error Analysis, The Study of Uncertainties in Physical Measurements. 2nd ed. University Science Books, Sausalito, CA.

Wang, J.J., Harrell, D.L., 2005. Effect of ammonium, potassium, and sodium cations and phosphate, nitrate, and chloride anions on zinc sorption and lability in selected acid and calcareous soils. Soil Sci. Soc. Am. J. 69, 1036–1046. http://dx.doi.org/10.2136/sssaj2004.0148.

Weir, C.C., Soper, R.J., 1962. Adsorption and exchange studies of phosphorus in some Manitoba soils. Can. J. Soil Sci. 42, 31–42. http://dx.doi.org/10.4141/cjss62-006.

Zerulla, W., Barth, T., Dressel, J., Erhardt, K., von Locquenghien, K.H., Pasda, G., Rädle, M., Wissemeier, A., 2001. 3,4-Dimethylpyrazole phosphate (DMPP) — a new nitrification inhibitor for agriculture and horticulture. Biol. Fertil. Soils 34, 79–84. http://dx.doi. org/10.1007/s003740100380.

Zhang, Y., Huang, S., Wan, D., Huang, Y., Zhou, W., Zou, Y., 2007. Fixed Ammonium Content and Maximum Capacity of Ammonium Fixation in Major Types of Tillage Soils in Hunan Province, China. Agric. Sci. China 6, 466–474. http://dx.doi.org/10.1016/S1671-2927(07)60071-6.