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

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ABSTRACT

Clay minerals can fix high amounts of ammonium in non-exchangeable form, which can be of management importance when some ammonium applied with fertilisers is sequestered and not available to the crop. Non-exchangeable ammonium can be released slowly and increase soil N availability. The percentage of ammonium fixed depends, among other factors, on the ammonium dose applied. We applied increasing amounts of ammonium to three soils and then measured (after 48 h) the soil equilibrium concentration of non-exchangeable, exchangeable, and soluble ammonium. At a 70 mg NH_4–N kg^{-1} dose, non-exchangeable ammonium measured 60, 24, and 17% on the three soils, while at 2800 mg NH_4–N kg^{-1} the fixation percentage decreased non-linearly to 12, 4, and 5%. Ammonium equilibrium concentrations in non-exchangeable, exchangeable, and soluble fractions as a function of ammonium applied were simulated with two innovative analytically-solved models using two Langmuir equations, one for each pair of pools. Both models predicted well the three ammonium fractions in all soils, with average relative root mean squared errors ranging from 2 to 5%. Sensitivity analysis demonstrated the importance of all four model parameters; however, to extend the model to other soils requires measurement of two parameters — cation exchange capacity and maximum fixation of ammonium in non-exchangeable form. The other two parameters are equilibrium constants that vary little among soils, according to our preliminary results. Therefore, to simplify model use, averaged optimised constant values on multiple soils might suffice. Additional experiments on more soils are needed to verify this hypothesis.

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 formation 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 potassium 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 increasing 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 number to destructive sampling dates and each composed of eight experimental 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 temperature 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 results 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