INVITED

Combining Physico-chemical, Biological and Behavioural Processes for Modelling Nitrogen Dynamics in the Urine Patch (NDUP)

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Abstract The intense aggregation of nitrogen (N) in urine patches from grazing ruminants can lead to an inefficient use of N on-farm and a point source of leached nitrate, which can contaminate water supplies. Three stages or submodels (*NDUP1,2,3*) are described for simulating the N dynamics of the urine patch and for predicting the long-term consequences of this aspect of grazing behaviour on the stability of the grazing resource. Field observations on biological responses and the mass balance of patch N are proceeding in parallel with model development and the work is also being supported by laboratory experiments. *NDUP1* (0-6 days) is based on rapid hydrolysis of urine components and losses from the volatilization of ammonia. Knowledge of enzyme dynamics and ionic equilibria is reasonably well established for modelling this phase. We have included a potentially rapid microbial response based on labile carbon in the surface soil and this can provide a useful sink and source for retaining and recycling N. The addition of a generic relationship between ammonium adsorption and the cation exchange capacity of pasture soils provides some basis for extrapolating *NDUP1* to a range of soils. The nitrification phase is included in *NDUP2* (6-200 days) where plant uptake can become a significant sink and source for N. Nitrate leaching can become critical and hence a sufficient hydrological section is a key component for *NDUP2*. Patchiness, in a general sense, can contribute to biological diversity. However, the intense aggregation of N imposed at the micro-scale of the patch may create instability in the resource from an inefficient use of the nutrient and its loss from the system. Further, the stability outcome of grazing preference for or against the patch has not been examined and this can be done best by modelling (*NDUP3*). The first modelling stage is completed along with the hydrological component of the second stage. Features of the approach to *NDUP3* are outlined.

1. INTRODUCTION

The economies of nitrogen (N) and water are inter-related and critical for sustained animal production from sown temperate pastures. The nitrogen economy of Australian pastures is almost exclusively dependent on the biological fixation of N by the legume-rhizobial association. In good rainfall years, the N fixed can be in substantial excess of the systems requirement for high production and this excess can provide a source of ground water contamination (eg Dillon 1988). The potential for N loss is exacerbated by grazing, which is attended by an aggregation of N at high concentration within the urine patch. The fate of this N involves physico-chemical, soil biological and hydrological (leaching) processes along with potential longer term consequences of sheep excretal behaviour and foraging preferences. The development of a three-stage simulation model is reported. The model aims to evaluate the effect of the urine patch on the stability of the N economy in Australian temperate pastures which are subject to variable rainfall distribution and leaching events. The model is being developed in parallel with experiments which span pasture types ranging from productive perennials to degraded annuals.

2. FIRST STAGE (*NDUP1*)

The first stage of the model (*NDUP1*) is constrained to the short-term dynamics of nitrogen (N) in the urine patch (0 to *ca.* 6 days) and uses a time step of 6 minutes. Nitrogenous components of sheep urine hydrolyse rapidly to ammonium, which can be a significant source of N loss as volatilized ammonia. *NDUP1* is based on established chemical parameters for ionic equilibria (NRC 1979) and on equations developed by Sherlock and Goh (1985a). We have added the potential for by-pass flow of urine, soil adsorption of ammonium and its enhanced short-term uptake by micro-organisms in moderately grazed pastures where there can be substantial particulate organic matter in the soil surface (authors unpubl.).

2.1 Structure

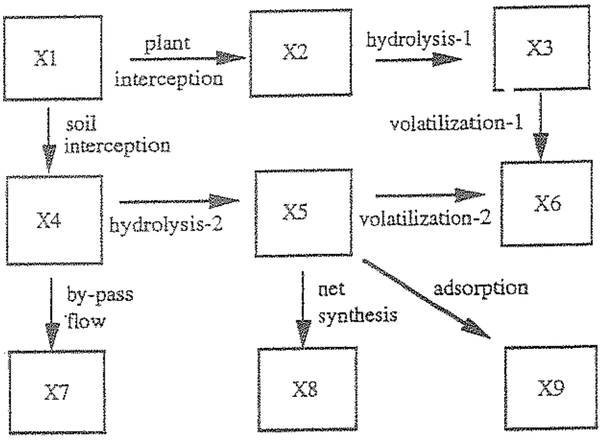

Figure 1: Structure of NDUP1.

State variables (X1..9), illustrated in Figure 1, are defined as follows:-

X1: A single urination (sheep) of mean volume and specified N concentration, which reflects grazing intake from a defined pasture type.
X2: Urinary-N constituents intercepted by plant tops and residues and subject to rapid hydrolysis by ureases.
X3: Ammoniacal-N formed from the hydrolysis of urine intercepted by plant cover (tops and residues) and subject to rapid volatilization as ammonia gas.
X4: Urinary-N constituents intercepted by soil in a patch of measured dimensions, corrected for by-pass flow and subject to enzymatic hydrolysis.
X5: Ammoniacal-N present in the patch as the balance between hydrolysis, volatilization, formation of net biological sinks and adsorption by soil.
X6..9: Nitrogen accounted for by volatilization, by-pass flow, biological uptake (mainly microbial in *NDUP1*) and net soil adsorption of ammonium ions.

2. Governing Equations

The description of *NDUP1* will be centred on flows from the state variables, with each flow representing a process, which is dealt with below.

Plant interception: Voided urinary N is intercepted by plant tops and litter lying on the soil surface. The interception may vary from 1 to 20% depending mainly on the mass of plant material. The latter depends on pasture type, season, stocking rate and grazing practice (eg continuous *versus* rotational). Percent interception is a required input for *NDUP1* and a prediction relationship based on plant mass is being developed in parallel field experiments.

Soil interception and by-pass flow: The remaining urine enters the soil. The dimensions of the surface urine patch are required inputs for the model. However, by-pass flow to soil below the patch through macropores and voids can be significant and its extent will be estimated in the field. Dye applications and soil profile analysis will be used for estimating patch dimensions and by-pass flow. We assume that by-pass flow does not participate in the complex transformations in the patch *per se* but it will be accounted for in the mass balance for N in the system as a whole.

Hydrolysis ($H_{1,2}$): Equations for hydrolysis of urinary N are based on established parameters for urea, which is the major constituent of urinary N (*ca.* 80%). Other N compounds, with the exception of hippuric acid (3%) and creatine (1%), are moderately hydrolysable (Whitehead *et al* 1989). H is calculated from a rate constant (k_1) for the action of the enzyme urease, which is then scaled for an *in situ* factor for field performance (F) and for absolute temperature (TK) using a Q_{10} value of 2.0.

$$H_{1,2} = k_1 * F * \mathit{exp}\ (0.0693*[TK-273]) \qquad (1)$$

In the field, H is sensitive to diurnal changes in TK. For *NDUP1*, a sinusoidal function has been developed to include the amplitude (AMPL) of the diurnal rise in TK and the time of day for a specified urinary event (EVENT). EVENT is the number of hours from 0900h (Time = 0), which is the standard time for daily meteorological recording.

$$T^{o}K = AMPL * \mathit{sin}\ (2\Pi * EVENT/ 24) + TK_{(0900h)} \qquad (2)$$

Moisture can influence H. However, initial moisture conditions in urinary films on the surfaces of plant tops (H_1) and their residues and within the patch (H_2) are high and rates of hydrolysis are rapid. From a simulation run of *NDUP1*, which produced the losses of ammonia gas shown in Figure 3 (a mild summer), the predicted half-lives for urea N were about 3 hours. Hence, unless drying rates are very rapid, the influence of moisture on the hydrolytic process can be overlooked. We are planning summer experiments at Armidale, when hot dry conditions may negate this assumption for the patch soil.

Adsorption: Some ammoniacal N (X5) can be held in the patch soil by adsorption of ammonium ions. The cation exchange capacity (CEC) of soil appears to be a good predictor of adsorption of ammonium ions and thus reducing losses of N as volatilized ammonia. We have fitted a linear function (Figure 2) to data from 14 grassland soils in the UK (Whitehead and Raistrick 1993). Values for CEC in these soils range from 108 to 443 mmol/kg and this is likely to include most grassland soils. Within this range, there is a rectilinear relationship between CEC and the fraction of N that is volatilized. Outside this range, there is some evidence that the relationship is curvilinear and this is indicated by the dotted lines (Figure 2).

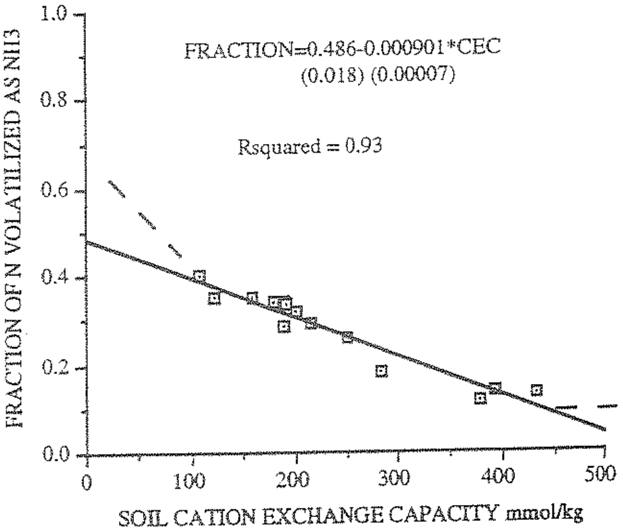

Figure 2: Prediction of the effect of soil CEC on the fraction of N that will be volatilized as ammonia gas. Standard errors for the two coefficients of the equation are given in brackets.

Reduction in ammonia volatilization between CEC values 108 and 433 mmol/kg is calculated by applying the following multiplier (REDN) to volatilization from X5 and allocating the reduction to X9. This provides a conservative estimate for the amount of adsorbed N and a first step towards accommodating variation in adsorption of ammonium for a range of soils. REDN represents an empirical approach to accommodating the adsorption process.

$$REDN = 0.000901 * (CEC - 108) \qquad (3)$$

A mechanistic approach to the adsorption of ammonium ions would be the application of a partitioning coefficient (D) between aqueous ammonium and soil adsorption sites (Parton *et al* 1980). However, estimation of an appropriate value for D is difficult.

Net microbial synthesis: There is growing evidence for the role of microbial synthesis in providing a significant biological sink for ammonium in the nutrient rich environment of the urine patch. Currently for *NDUP1*, we have set a conservative value of 5% for net microbial N synthesis (SYN = 0.05). Synthesis in the patch will be limited by accessibility of micro-organisms to carbon sources of relatively high quality (*sensu* metabolizability). In moderately grazed permanent pastures, these sources are concentrated in the surface soil as are the mineral nutrients in the patch. These conditions would favour microbial growth. However, any increase in free-living nematodes, which graze micro-organisms would result in an enhanced mineralization of N. These biological processes and interactions are being examined in current experiments.

Volatilization: Exogenous ureases present on plant tops, litter and soil can be assumed to be non-limiting and aqueous ammonium (NH_4^+) is the nitrogenous product of hydrolysis. While some NH_4^+ will be adsorbed, the aqueous ammonium rapidly establishes a new equilibrium with aqueous ammonia (NH_3) with the two entities combined termed ammoniacal-N .

Ammonia volatilization (V_1) from the surface of plant tops and their residues is extremely rapid. Aqueous ammonia is assumed to be present as a free water surface from which a rate constant (k_2) for the initial volatilization of ammonia of 72.8 /hr has been measured (Sherlock and Goh 1985b). If X3 and X5 are combined as one space with a combined interface with air, which is in equilibrium, then a value Mv_1 can be calculated from the ratio of plant interception volume and patch volume. Kh is an application of Henry's law which expresses the condition that the equilibrium constant of a solute in solution must exceed the vapour pressure of the solute in air for volatilization to occur.

$$V_1 = k_2 / (Kh*Mv_1) \qquad (4)$$

Kh needs to be adjusted for TK as:-

$$Kh = 10^{(-1.69 + 1477.7 / TK)} \qquad (5)$$

V_1 is a very rapid process. In the simulation run for *NDUP1* presented in Figure 3, the half-time for V_1 was about 2.4 hours.

Volatilization (V_2) from the urine patch is more complex and its underlying theory is reviewed. V_2 occurs at the soil to air interface and is a function of the difference in partial pressure between the aqueous (soil) and gas (air) phases of ammonia. Given that mixing (turbulence) is adequate, V_2 is related to the concentration of ammoniacal-N in X_3. During the volatilization phase, aqueous ammonia can be replenished by the upward diffusion of ammoniacal-N. Protons (H^+) deposited diffuse downwards and bicarbonate (HCO_3^-) ions diffuse upwards and may be augmented by the CO_2 profile from soil respiration (Rachpal-Singh and Nye 1986). A rapid rise of 2 to 3 pH units in the surface soil is attributed to bicarbonate and its slow decline is related reciprocally to the time course for volatilization (V_2). The V_2 phase modelled in *NDUP1* finishes as the pH falls towards 7.5 when the equilibrium between protons (H^+) and bases, notably $HCO3^-$ has been re-established. These mechanisms governing V_2 and pH rise in the urine patch have been confirmed by a number of studies.

The application of established equilibria constants and the effect of pH have been incorporated in a quotient Q (Sherlock and Goh 1985a).

$$Q = (1 + 10^{[0.0908 + 2729.92 / TK - pH]}) \qquad (6)$$

whence volatilization-2 (V_2) becomes

$$V_2 = k_3 / (Kh*Q*Mv_2) \qquad (7)$$

and Mv_2 is the volume of water in the patch. Immediately after the urine is voided the moisture status of the patch would be in excess of field capacity. Drying of the patch reduces the value of Mv_2 and hence increases V_2 (7) by increasing the concentration of ammoniacal N.

2.3 Inputs for *NDUP1*

For the present study the values of the required inputs will be obtained from concurrent field experiments and the focus in this submodel is on the magnitude of by-pass flow, the operation of soil and microbial sinks, and the prediction of losses of N from ammonia volatilization. Losses of other volatiles (oxides of N), are considered to be minor in this early phase (Sherlock and Goh 1983).

The required inputs for *NDUP1* are as follows:-
- The mean volume per urination and the concentrations of total N and urea.
- The volume of urine intercepted by plant tops and litter.
- The dimensions of the urine patch, from which the soil, microbial and nematode sampling routines are optimised.
- Analyses for total N and its components (urea, ammonium, nitrite and nitrate) by depth to *ca.* 60 cm.
- The extent of by-pass flow.
- CEC of the patch soil.
- Absolute temperature (TK), particularly at the interface of

soil and air (0-3mm) and its diurnal amplitude.
- The time of the urine application.
- Changes in pH (1:2.5 water) at the soil-air interface.

2.4 Sample Output

Data from a summer application of sheep urine (Sherlock and Goh 1984,1985b) are used to demonstrate predicted output of ammonia volatilization from the current version of *NDUP1*. The experiment involved a perennial ryegrass (*Lolium perenne*)/white clover (*Trifolium repens*) New Zealand pasture. The NZ authors measured the rates of ammonia volatilization using ventilated enclosures. There is good agreement between their observations and the output of *NDUP1* (Figure 3).

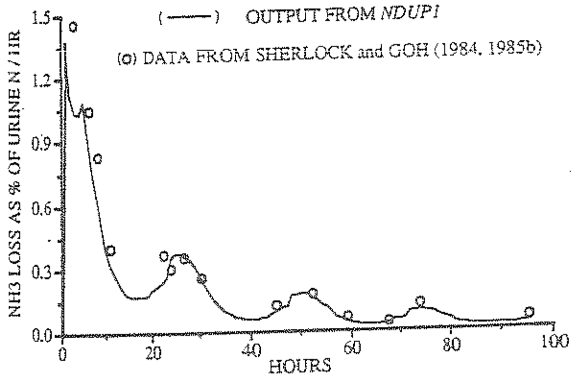

Figure 3: Agreement between predicted losses of volatilized ammonia and observations from a NZ experiment

2.5 Summary of *NDUP1*

Losses of volatilized ammonia can be measured directly at the pasture scale by integrating the flux of ammonia gas within and above the pasture canopy (Freney and Black 1988). Enclosures are often used at a urine patch scale but their use involves a substantial risk of changing the field environment. We have preferred the use of measurements of pH change, temperature and moisture as surrogate predictors of ammonia volatilization from a model that is based on well established theory of ionic equilibria. By-pass flow of urine, soil adsorption of ammonium and short term microbial sinks are also included.

Field and laboratory experiments are concurrently supporting this phase. The criterion for success will be the ability of the submodel to predict the rapid flows and transformations that occur (0-6) days after urine application. Testing is over seasons (winter, spring, summer and autumn) and a range of urine and pasture types.

3. SECOND STAGE (*NDUP2*)

The simulation period for *NDUP2* is *ca.* 6-200 days, with a one day time step. Nitrification proceeds early in this phase of urine patch dynamics. Plant uptake becomes a significant sink and source for N, the other soil biota continue to be active and the potential for leaching of nitrate becomes critical for the mass balance of N. Water flow provides the carrier for nitrate drainage and hence an adequate hydrological submodel is required to provide the mechanism for movement of the ion (NO_3^-).

3.1 Hydrological Sub-model for *NDUP2*

Daily rainfall and tank evaporation data provide climatic inputs. The latter are based on records from an Australian Tank evaporimeter (90 cm diameter ; 90 cm deep), with a pan coefficient (Kp) of 1.0 (Doorenbos and Pruitt 1984). Pan evaporation (ET_o) represents the rate of evaporation from "an extensive surface of green grass of uniform height, growing actively, shaded to ground level and with unlimited water". Grazed, permanent pasture seldom fully meets these criteria and hence ET_o is reduced by a factor (k_c). This factor can be varied seasonally and with changes in plant cover. However, to provide an estimate of potential evapotranspiration (PET), we have set k_c at a constant value of 0.8.

$$PET = 0.8*ET_o \qquad (8)$$

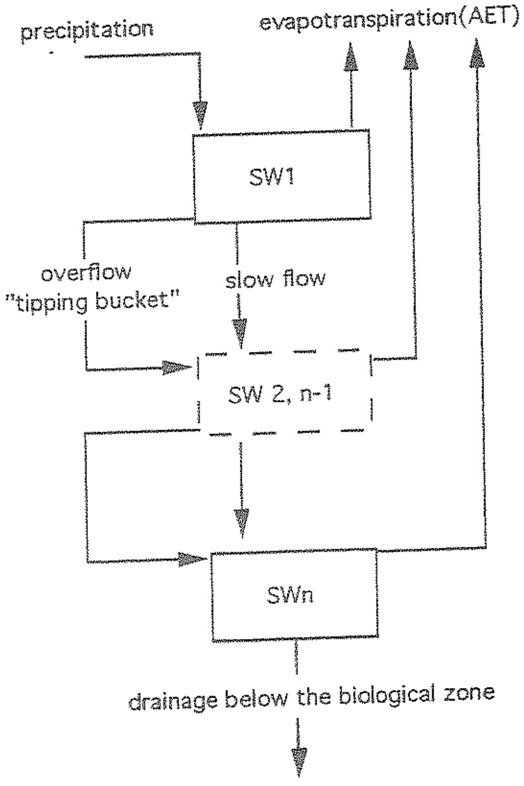

Figure 4: Structure of the hydrological sub-model

3.2 State Variables

Geometrically, the model is based on one-dimensional vertical flow through a layered soil profile, with A and B horizons differing in their hydrological properties. The profile is divided into horizontal layers (state variables $SW_{i=1,n}$), which are not necessarily of the same thickness. However, they are chosen to accommodate major differences in their soil moisture characteristics. The boundary for the system is the biological zone which is set by information on the distribution of root length density (RLD). RLD also provides a surrogate estimate for the distribution of the presence of other biota ie. micro-organisms and invertebrate fauna. Drainage below the biological zone is considered to be a loss from the system.

3.3 Downward Water Flows

All water data are expressed in linear measure (cm). We assume that subsequent to a rainfall input, the infiltration process is completed within 1 day. Following infiltration, the downward redistribution of water between the compartments is also largely accomplished within 1 day time steps with the use of a set of conditional statements, which is analogous to a tipping bucket instrument for measuring flow:-

$$\text{overflow}_{[i=1,n]} = \text{IF } (SW_{[i=1,n]} > \text{field capacity}_{[i=1,n]}) \text{ THEN } (SW_{[i=1,n]} - \text{field capacity}_{[i=1,n]}) \text{ ELSE } 0 \qquad (9)$$

A slow flow of water down the profile may continue for a period up to 10 days or more assuming that drainage (cm/day) is an exponential function of water storage (Black *et al* 1969). The amounts of water involved are not great but they vary with soil type reflecting hydraulic properties (eg Hillel and van Bavel 1976); at this stage we are using a multiplier (sf) which provides additional flexibility to the model

$$\text{slow flow} = sf_{[i=1,n)]} * SW_{[i=1,n]} \qquad (10)$$

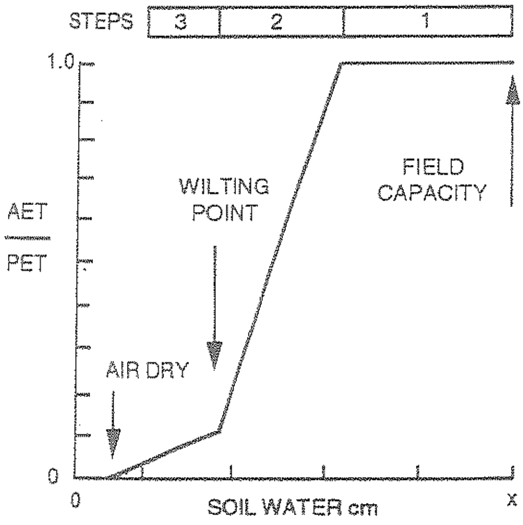

Figure 5: Schematic diagram showing the form of the ratio of actual to potential evapotranspiration (AET/PET) used for the compartments SWi=1,n

3.4 Actual Evapotranspiration (AET)

In permanent pastures with good plant cover, the transpiration component of AET is dominant and the vertical movement of water upward is proportional to the RLD distribution in the soil profile. A stepped regression relationship for change in the relation between the ratio of AET/PET and current soil water is given in Figure 5. Different relationships for the soil compartments ($SW_{i=1,n}$) are based on their soil moisture characteristics ie. moisture (cm) at field capacity (*ca.* -0.10 to -0.30 bars) and at plant wilting point (*ca.* -15 bars). Step 1 of the regression (Figure 5) ranges from field capacity to a moisture level at which AET starts to decline (ratio<1). Step 2 produces a declining AET due to rate limiting diffusion of water to the root surface (uniform soil) and/or an increasing proportion of dry microsites surrounding the roots (small scale heterogeneity). Step 3 is initiated at wilting point where transpiration effectively stops. The soil compartments $SW_{i \text{ to } n}$ continue to dry slowly by evaporation until an air dry state is reached.

$$\text{ratio} = \text{AET/PET} \qquad (11)$$

and for each compartment $SW[_{i=1,n}]$ the mass balance for water is determined as :-

$$SW_i=SW_{i-1}+\text{overflow}_{i-1}+\text{slow flow}_{i-1}-\text{overflow}_i-\text{slowflow}_i-\text{aet}_i \qquad (12)$$

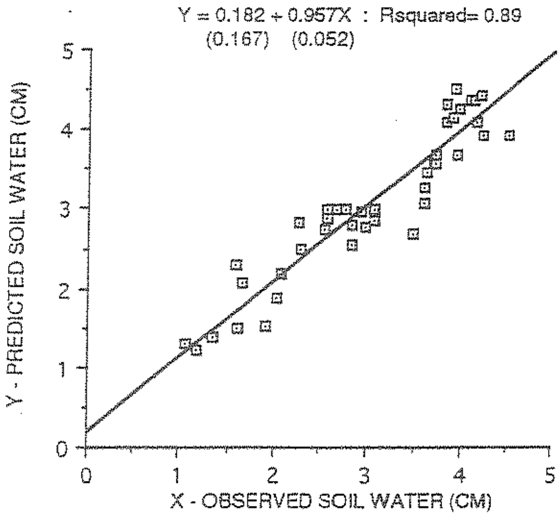

Figure 6: Agreement between observed soil moisture-cm and soil moisture-cm predicted by the submodel

3.5 Model Output *versus* Observation and Future Development

Model output for the 6 compartments (0-15, 15-25, 25-35, 35-45 and 45-55 cm soil depth) has been compared with neutron probe data (K.L.Greenwood *unpubl. data*), for winter and summer, in a neighbouring site of similar soil to the current parallel experiments. Reasonable agreement was obtained (Figure 6). However, we are dealing with a layered soil and a major objective of *NDUP2* is to predict nitrate leaching. We will be examining the extent, if any, of lateral movement of the nitrate ion particularly at the junction of the layers. If this occurs we will have to amend the model to incorporate lateral flow. This would also have considerable significance for *NDUP3*.

3.6 Nitrogen Submodel for *NDUP2*

Nitrate production can be calculated as a first order kinetic function of the concentration of ammoniacal N; the process is usually restricted to the upper soil layer(s). Because nitrite is oxidized rapidly, the process can be considered as a single step (NH_4^+ to NO_3^-). The rate of nitrification will be modified according to water status and to temperature for the nitrifying compartments ($SW_{i=1 \text{ to } n}$) with the rate of oxygen diffusion assumed to be non-limiting. It is expected that nitrification will be attended by a return in the pH of the patch soil to the level prior to urine addition. Potential loss of nitrate by denitrification will not be included in the submodel unless mass balance calculations, under conditions where denitrification is likely, point to the potential for this loss process. Biological uptake of both ammonium and nitrate is strongly seasonal and is expected to have an important influence in determining the potential for nitrate loss by leaching. Season also affects AET and hence the balance for downward water flow. Mobile nitrate will be assumed to be completely soluble in water moving through the soil profile and influenced strongly by the pattern and size of rainfall events. Soil adsorption of nitrate will be taken as zero.

Integration of the two submodels, which will use the same layers ($SW_{i=1 \text{ to } n}$) will provide inputs for the size and timing of drainage events. The soil solution nitrate in each SW_i will be divided into mobile and immobile portions with the mobile component only to be displaced during water movement. When each flow ceases, an equilibrium is re-established between the mobile and immobile phases. Both water and nitrate are lost by drainage below the soil biological zone (one-dimensional flow). However there may be lateral flow at the boundary between the soil layers and the model must accommodate this possibility (see 3.5). The upper and lower limits of mobile water are to be set arbitrarily according to the soil moisture characteristics of the layers (Addiscott 1977).

4. THIRD STAGE (*NDUP3*)

Passage of ingesta through the ruminant gut enhances mineralization (eg. action of rumen microbes) and this has been widely accepted as contributing to improving fertility. However, it is now generally recognized that the ensuing process of excretion is inefficient because the spatial distribution of excreta results in an intense aggregation of nutrients. *NDUP3* is planned as a temporally and spatially explicit model, which can predict the aggregation of N produced by urine patches and its consequences on the nitrogen economy of sown, temperate pastures. Plants, microbiota and soil (ammonium adsorption) have a role in the retention of patch N. Rainfall events provide potential for leaching losses at the macro-scale, but small amounts of lateral flow would enable dilution, particularly of nitrate, and better opportunity for the retention of N by foraging roots (Gross *et al* 1993) and microbial uptake. At the system level, inefficiency in the retention and use of patch N, will ultimately be reflected by the degree of spatial aggregation along with gaseous and leaching losses of the element.

4.1 Animal Behaviour

The distribution of pasture soil N and its components is commonly lognormal (eg. Bramley and White 1991) and this is due mainly to excretal patches. We are using Merino sheep as the large herbivore. The breed exhibits a strong flocking behaviour, forming night camps on high ground where they can deposit 40% of their excreta on 5% or less of the grazing area. This results in a major aggregation of N (urine and faeces) at the *meso*-scale. Grazing activity radiates out from the camp resulting in discrete patches of faeces and urine (micro-scale) with the latter as the focus of the present study. Stocking level and dietary N intake will be the major determinants of the mean N concentration per patch.

In natural grasslands, patchiness is considered beneficial by providing a variety of habitat types for maintaining species diversity (Huston 1979) and this patchiness has been associated with urine deposition (Jaramillo and Detling 1992). However, in a sown grasslands an increase in species diversity is not an objective. Urine patches may be neglected by herbivores for a short period but the patch herbage then becomes preferred (Norman and Green 1958). Preference has been associated with an enhanced amount and level of N in the patch (Day and Detling 1990).

4.2 Planned Modelling Approach

The first-pass in the development of *NDUP3* will use a spatial matrix with appropriate densities of randomly voided urine patches. These will be weighted by an index of sheep spatial grazing behaviour with the camp as a reference point (authors unpubl.). Varying levels of urinary N concentrations, stocking rates, and levels of preference for patch herbage will provide sets of initial conditions. Use of approximate "decay" parameters for the presence of patch N should generate a range of aggregated spatial distributions for N. When the system has stabilised, the differences between patch N presence and their initial values should represent system losses and provide a measure of destabilizing effects on the N economy. Solutions might be translatable into mathematical shorthand for summarising the spatial and temporal dynamics of N in the system.

5. CONCLUSIONS

The development of the *NDUP* model in parallel with field and laboratory experiments is providing substantial research benefits. At this stage, the modelling component is based largely on published data. The current modelling is being used to optimise limited experimental resources eg sampling times for field experiments.

As the project proceeds, local experimental data can play a greater role in optimising the model in a site-specific sense. This stage should provide valuable clues on where the model can be made more generic in its application without loss of significant predictive power.

The ultimate goal is to provide a synthesis, which is temporally sound and spatially explicit. This will be used to assess the destabilizing effects of grazing on the nitrogen economy of temperate pastures and examine ways by which management might address the problems that have been defined.

6. ACKNOWLEDGMENTS

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