



Modeling Apparent Nitrogen Mineralization under Field Conditions Using Regressions and Artificial Neural Networks

Roberto Alvarez* and Haydée S. Steinbach

ABSTRACT

Soil N mineralization is an important source of N for grain crops, but its estimation under field conditions is usually very difficult. Our objective was to develop models suitable for predicting N mineralization during the growing seasons of wheat (*Triticum aestivum* L.) and corn (*Zea mays* L.) under field conditions. Fifty-eight field experiments were performed with wheat, and 35 with corn, along three growing seasons, in which soil apparent N mineralization was estimated by the mass balance approach. Apparent nitrogen mineralized from decomposing residues (ANMR) or soil humic substances (ANMH) were estimated separately. Two empirical modeling techniques were tested, linear regression and artificial neural networks, using as independent variables or inputs some environmental variables. Both techniques allowed the development of suitable models for N mineralization prediction ($R^2 > 0.68$), but neural networks gave slightly better results. The ANMR ranged from -42 to 64 kg N ha^{-1} , increasing as residue mass and N concentration increased. An average ANMR of 15 to 16 kg N ha^{-1} was produced both during wheat and corn growing seasons. The ANMH ranged from -80 to 328 kg N ha^{-1} , being on average four times greater during corn growing cycle than during wheat season (127 vs. 34 kg N ha^{-1}). The ANMH decreased as initial mineral N content of the soil, remaining residue mass or fine particles content of the soil increased, and it was greater in soils of higher organic matter level and mineralization potential, as determined by an incubation test. Increases in temperature and rainfall also determine greater ANMH. The methodology developed for apparent N mineralization estimation may be applied to other crops and production regions.

ADEQUATE FERTILIZATION STRATEGIES are of economical and environmental concerns. The balance sheet method may be used for determining N fertilization requirements in cases where yield response functions are not available (Vanotti and Bundy, 1994). For applying this methodology, N mineralization during residue decomposition and from soil organic matter degradation must be known, which, combined with measured soil mineral N, allows estimation of total N supply capacity of the soil. This estimation is contrasted with crop N demand to calculate fertilizer rate for non-N-fixing crops (Brye et al., 2003):

$$N_{\text{fertilizer}} = (N_{\text{crop}} + N_{\text{residual}}) - (N_{\text{mineral}} + N_{\text{mineralization}} - N_{\text{losses}}) \quad [1]$$

where $N_{\text{fertilizer}}$ represents the rate of fertilizer nitrogen, N_{crop} is the amount of nitrogen absorbed to attain a yield goal, N_{residual} is remaining mineral nitrogen in the soil at harvest, N_{mineral} is mineral nitrogen content of the soil at sowing, $N_{\text{mineralization}}$ is the net nitrogen mineralization and represents the difference between gross nitrogen mineralization and immobilization, and N_{losses} integrates the possible losses of nitrogen from the agroecosystem, mainly by volatilization, denitrification, and leaching.

The balance equation may be rearranged to estimate net N mineralization when the other terms are known:

$$N_{\text{mineralization}} = (N_{\text{crop}} + N_{\text{residual}} + N_{\text{losses}}) - (N_{\text{mineral}} + N_{\text{fertilizer}}) \quad [2]$$

As direct determination of all N losses is rather difficult and subjected to uncertainties (Brye et al., 2003), many times the balance sheet methodology is used for N mineralization estimation by the equation:

$$N_{\text{mineralization}} - N_{\text{losses}} = (N_{\text{crop}} + N_{\text{residual}}) - (N_{\text{mineral}} + N_{\text{fertilizer}}) \quad [3]$$

where the term $N_{\text{mineralization}} - N_{\text{losses}}$ is the so-called apparent N mineralization (Engels and Kuhlmann, 1993), and represents the difference between net N mineralization and N losses from the agroecosystem.

Apparent N mineralization may be not correlated to net mineralization, but makes a better picture of the real availability of N for the crop (Blankenau et al., 2000). It is an important source of N for grain crops and may contribute with much of the N requirements of graminaceous crops (Delphin, 2000, Campbell et al., 2008). In-season prediction of apparent N mineralization under field conditions is usually very difficult, but some empirical models had been developed using linear regression methods (Rohde, 1996, Egelkraut et al., 2003).

Facultad de Agronomía, Univ. de Buenos Aires-CONICET, Av. San Martín 4453 (1417) Buenos Aires, Argentina. Received 8 June 2010. *Corresponding author (ralvarez@agro.uba.ar).

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Abbreviations: ANMR, apparent nitrogen mineralized from decomposing residues; ANMH, apparent nitrogen mineralized from soil humic substances; ANN, artificial neural network.

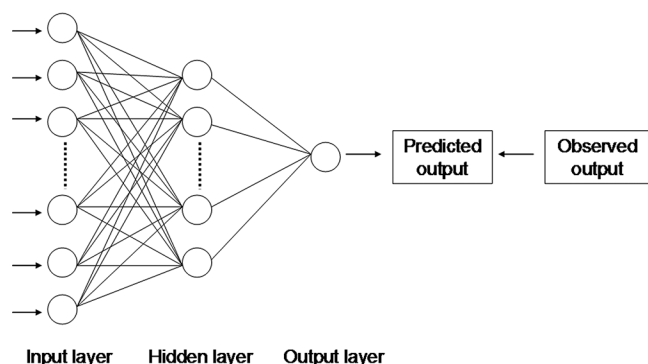


Fig. 1. Representation of an artificial neural network showing layers and connections.

Artificial neural networks (ANNs) are empirical modeling techniques simpler than process-based models, with great predictive quality, and becoming popular in biological sciences during recent years (Joergensen and Bendoricchio, 2001, Özemi et al., 2006). Their architecture and functioning has been described elsewhere (Fausett, 2008, Gupta et al., 2003). They are adaptive analytical methodologies with a structure and processing similar to the neural architecture and functioning of the brain, capable of extracting hidden information from data (Joergensen and Bendoricchio, 2001). Over other empirical modeling techniques, ANNs have the advantage that they do not assume an a priori structure for the data and are well suited for fitting nonlinear relationships and complex interactions (Batchelor et al., 1997) but, as with all modeling techniques, they cannot extrapolate outside the range of data inputs. The most common ANN structure is the multilayer perceptron structured in three neuronal layers: the input layer with a number of neurons corresponding to the number of input variables, the hidden layer with a complexity determined empirically during ANN fitting, and the output layer with a neuron for each output variable (Fig. 1). Information flows from the input layer through the hidden layer to the output layer and the learning process consists of adjusting the weights associated to the transfer functions between neurons comparing ANN outputs with observed data by an iterative procedure (Joergensen and Bendoricchio, 2001). Back propagation is the most common algorithm used to perform the learning process during which the weights from the output layer through the input layer are adjusted (Kaul et al., 2005). This type of ANN is known as feed forward neural network. Transfer functions connect neurons passing information from one layer to the next. Usually, the linear function is used between the input layer and the hidden layer, and the sigmoid function between the hidden layer and the output layer (Kaul et al., 2005). Good results have been obtained using an ANN as modeling technique in areas as diverse as environmental correlation (Park and Vlek 2002), soil organic C prediction (Somaratne et al., 2005), fertilizer recommendation (Broner and Comstock, 1997), soil hydraulic properties estimation (Nemes et al., 2003), crop development assessment (Elizondo et al., 1994), epidemic severity evaluation (Batchelor et al., 1997), and yield forecasting (Kaul et al., 2005, Alvarez, 2009).

The Pampas is a vast plain of around 50 Mha, which runs from 28 to 40° S latitude in Argentina, and is considered one of the World's best regions for grain crop production (Satorre and Slafer, 1999). Climate is humid temperate, the relief flat or slightly rolling with Mollisols as predominant soils (Alvarez and Lavado,

1998), and its natural vegetation consists of grasslands in which graminaceous species dominate (Hall et al., 1992). Agriculture is performed on well drained soils and areas with hydromorphic soils are devoted to pastures (Hall et al., 1992). The Rolling Pampa, in the central portion of the region, is the main agricultural area of the country (Hall et al., 1992), with wheat, corn, and soybean [*Glycine max* (L.) Merr.] as main crops, with 70 to 80% of seeded surface conducted under no-till (MinAgri, 2010).

Adequate N management is essential for obtaining high wheat and corn yields in pampean agroecosystems (Alvarez, 2007). Mineralization of N from soil organic pools during the growing seasons meets 30% of wheat (González Montaner et al., 1997) and 60% of corn (Steinbach et al., 2004) demands for N of medium to high yielding crops. In average, 50 and 150 kg N ha⁻¹ are mineralized, respectively. Difference in N mineralization between the growing cycles of wheat and corn may be attributed to temperature conditions but this has not been deeply studied.

In pampean soils, N mineralization is extremely variable from one site to another, depending on soil conditions (González Montaner et al., 1997) and management (Alvarez et al., 2004). Estimation under field scenarios is necessary as the balance sheet method has become widespread for N fertilizer recommendation (Alvarez, 2007). Our objectives were (i) to develop models suitable for predicting N mineralization rate which may be used as helping tools when applying the balance sheet methodology in soils of the Rolling Pampa, and (ii) to determine the main climate, soil, and management factors controlling mineralization during wheat and corn growing seasons.

MATERIALS AND METHODS

Study Area

The Rolling Pampa (32–35° S to 58–61° W) is a vast plain of around 10 Mha (Hall et al., 1992) with slightly rolling relief and long slopes varying from 0.5 to 1%. Mean annual rainfall ranged from 900 to 1000 mm (1900–2010 period), depending on the site, with 35% received during wheat growing season of June to November and 60% falling during corn growing season of September to March. Mean annual temperature is 16 to 17°C, with an average monthly maximum of 24°C in January and a minimum of 10°C in July. Typic Argiudolls, developed over aeolian sediments, are predominant soils, with illite as the most common clay mineral and usually of a silty clay loam texture. Typic Hap-ludolls of coarser textures are also present (Hall et al., 1992).

Experimental Design and Sampling

Fifty-eight field experiments were performed with wheat between 1997 and 1999 and 35 with corn between 2000 and 2002, under a broad range of variation of climate, soil, and management conditions, representing some common scenarios founded in the region (Table 1). Experiments were installed within production fields and managed as commercial crops. Wheat experiments have been described previously (Alvarez et al., 2004). Briefly, 26 of these experiments were managed with tillage and 32 were no-tilled. Previous crop was soybean at 26 sites and corn at 32 sites. Nitrogen fertilization, usually at sowing or immediately after, ranged from 25 to 97 kg N ha⁻¹. All sites received phosphorus fertilization with rates ranging 15 to 20 kg P ha⁻¹. Each experiment consisted of one single plot of 20 by 20 m in which, at the growth stage of two expanded

leaves, soil samples were collected by compositing at least six cores (8 cm diameter, 0- to 30-cm depth) taken on the row and at different distances on the furrow, for soil fertility evaluation, root biomass production and buried residue quantification. Soil was dispersed in water and buried residues + roots washed on 500 microns mesh size and dried. Residues were separated from roots by hand and both weighed. Surface residue was collected from six microplots of 25 by 25 cm each, and were also washed and weighed. At physiological maturity, aboveground biomass was harvested in at least six microplots of 17 × 100 cm by plot, dried (70°C), grain separated from straw, and soil and surface residue sampling was repeated. Corn experiments were performed 18 under tillage, and 17 under no-till, with soybean as previous crop in all cases. Each experiment had a control (zero N) plot and N fertilized plot, with rates varying from 32 to 106 kg N ha⁻¹, applied at the two-four expanded leaf growth stage. This design allowed generating a wide range of soil + fertilizer N availability. Phosphorus fertilizer was received in all cases at rates ranging 15 to 20 kg P ha⁻¹. Plots had 400 m² each. At the stage of four expanded leaf, soil cores and surface residue were collected as indicated for wheat. When the crop reached physiological maturity, 10 microplots of 22 by 70 cm each were harvested by treatment plot for aboveground biomass and yield evaluation. Soil and surface residue was sampled again at this time. Rainfall was recorded during the crops growing cycles at all sites. Air temperature records were obtained from observatories under 50 km from the experiments.

Analytical Methods and Estimations

Soil ammonium and nitrate were determined on fresh samples from the 0- to 30-cm depth by steam distillation (Mulvaney, 1996). On dried 500-μm-mesh sieved soil, organic N was determined by wet digestion (Bremner, 1996), extractable P by the Bray method (Kuo, 1996), pH in a soil/water ratio 1:2.5, and texture by the hydrometer method (Gee and Bauder, 1986). The mass of soil in the extracted cores was weighed for bulk density assessment to calculate results on areal bases. Mineral N in the 0- to 60-cm soil layer was estimated using data from the 0- to 30-cm layer by a regression model locally developed (Alvarez et al., 2001). Soil N mineralization potential was estimated using samples of 100-g dry soil incubated in 400-mL flasks at 30°C and 50% soil water holding capacity for 17 d. Ammonium plus nitrate were determined by steam distillation at the end of the incubations. Carbon in the soil light fraction was determined by centrifuging (1000 × g) 5 g soil in 30 mL of a bromoform-ethanol mixture having a density of 2 g mL⁻¹ (Alvarez and Alvarez, 2000). Nitrogen content of crop grain, straw and roots and decomposing residues was analyzed by the Kjeldahl digestion (Jackson, 1960, p. 183–204).

Crop N uptake was calculated as the sum of N in aboveground biomass, roots, and rhizodeposition. Total root biomass to the 100-cm depth was estimated taking into account that roots in the 0- to 30-cm layer represented 70% of that biomass (Jackson et al., 1996). We assumed that rhizodeposition was equivalent to 6% of the aboveground + root N at harvest (Merbach et al., 1999). Nitrogen released from decomposing residues, available for crop utilization, was estimated as the difference in the N content of residues on an areal basis between the two- to four-leaf growth stage and maturity. This N content was estimated by taking into account measured residue

Table 1. Main characteristics of the experiments in which apparent nitrogen mineralization from residues (ANMR) and humic substances (ANMH) was estimated.

Crop	Clay + silt†	pH‡	Mineral N§	Organic N‡	Organic C†	Light fraction C†	N mineralized§	Mg DM ha ⁻¹	Residue N‡	Total N in residue	Rainfall#	Temp.#	Yield	ANMR	ANMH
	g kg ⁻¹		kg ha ⁻¹	kg ha ⁻¹	Mg ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹	Mg DM ha ⁻¹	g kg ⁻¹ DM	kg ha ⁻¹	mm	°C	Mg DM ha ⁻¹	kg ha ⁻¹	kg ha ⁻¹
Wheat															
Mean	620	6.1	153	6.1	65.1	6.8	167	9.5	10.5	96	260	16.0	3.8	16	34
Max.	790	6.5	260	9.0	87.2	12.6	326	20.0	16.4	200	450	16.4	6.3	64	220
Min.	470	5.9	68	4.7	49.6	3.4	51	3.4	4.6	37	194	15.5	2.1	-42	-80
Corn															
Mean	670	6.0	91	7.1	75.2	10.6	123	5.3	14.6	74	492	21.4	9.4	15	127
Max.	880	6.4	188	10.4	109	16.1	303	13.0	18.3	178	740	22.4	14.5	49	328
Min.	430	5.7	20	5.0	48.4	5.5	16	2.1	10.7	33	306	20.5	4.6	-3.9	2.0

† In the 0- to 30-cm soil layer.

‡ Nitrate + ammonium N in the 0–60 cm soil layer at two leaf growth stage of crops.

§ N mineralized in vitro from samples taken from the 0–30 cm soil layer.

¶ Dry mass of previous crop residues present on soil surface summed to buried residues in the 0–30 cm layer at the two leaf growth stage of crops.

Total rainfall and mean air temperature during crops growing seasons.

mass and its N concentration. It was assumed that 30% of the N mineralized from surface residue and 70% from buried residue became microbial biomass (Parton et al., 1993). The total remaining amount of N released to the soil solution by surface and buried residue was considered the ANMR. Apparent N mineralization was calculated with Eq. [3], using measured values for soil, plant, and fertilizer inputs. The ANMH was the difference between apparent N mineralization and ANMR. Means and ranges of climate, soil, and crop variables, with their corresponding units, are presented on Table 1.

Modeling Techniques

Polynomial regression and ANNs were compared as modeling techniques. The regression model used incorporated linear, quadratic, and interaction terms of independent variables on the dependent variable (Colwell, 1994):

$$y = a_0 + a_1v_1 - a_2v_1^2 + a_3v_2 - a_4v_2^2 + a_5v_1v_2 + \dots + a_{n-2}v_x - a_{n-1}v_x^2 + a_nv_xv_{x-1} \quad [4]$$

where y = ANMR or ANMH, a_0 to a_n = regression coefficients, and v_1 to v_x = independent variables.

The data set was randomly partitioned into 70% for training and 30% for validation. Models were fit using the training set and their ability to generalize was evaluated with the validation set. The forward stepwise method was used for variable selection. Only terms significant at $P = 0.05$ by the F test were maintained in the models. Categorical variables, tillage system and previous crop, were included as dummy variables in models. The soil and climate variables presented in Table 1 (clay + silt, pH, mineral N, organic N, organic C, light fraction C, mineralized N in vitro, residue dry matter, residue N concentration, residue N mass, rainfall, and temperature) were also considered as independent variables for ANMR and ANMH estimation. Linear and interaction terms were only included for assessing categorical variable effects. Additional, independent variables were created by calculating ratios or products of the original random variables in Table 1 (organic C/organic N, organic C/clay+silt, organic N/clay+silt, rainfall \times temperature). Combined variables which produced better predictions than the original variables were incorporated in the final model. Multicollinearity was checked by the variance inflator factor (Neter et al., 1990).

The ANN models were estimated using the back propagation algorithm for weights fitting by a supervised learning procedure (Rogers and Dowla, 1994). Linear transfer functions connected the input layer with the hidden layer and the output layer with the network output; meanwhile, the sigmoid function, described by Lee et al. (2003), connected the hidden layer with the output layer. To make data suitable for better network performance, continuous input variables were scaled (Somaratne et al., 2005, Specht, 1991). The minimax procedure was applied. Network outputs were de-scaled to original units. Categorical variables, previous crop or tillage system, were taken as nominal variables and encoded for neural networks fitting (Brouwer, 2004). All the same independent variables tested for regression analysis were initially used as inputs in ANN development. The hierarchical approach of Schaap et al. (1998) was implemented during variable selection, testing variables or combination of variables as inputs. In a first step,

sensitivity analysis was performed to weigh the effect of different inputs on ANMR and ANMH by calculating a sensitivity ratio (SR) (Miao et al., 2006). The higher this ratio, the greater the impact of the input on the output. Only variables with $SR > 1$ were preselected because a lower value indicates no impact of the variable on the ANN output (Miao et al., 2006). Selected variables were then tested as inputs by a stepwise procedure (Gevrey et al., 2003). Maximum simplification of ANN architecture was achieved by reducing input variables as much as possible without reducing R^2 and taking into account that the SR of all variables in the final models were >1 . The learning rate, which controls the magnitude of weights changes during each iteration made by the back propagation algorithm (Kaul et al., 2005), was set at a low value of 0.1, as large learning rates may lead to faster convergence but also to local minimum (Lee et al., 2003). The epoch size represents the number of iterations during which the back propagation algorithm runs. On each epoch, the training data set is fed through the network and weights adjusted (Somaratne et al., 2005). Usually, 50 epochs are enough for convergence (Schaap et al., 1998), so an epoch size of 100 was used. Increasing ANN complexity, using a higher number of neurons in the hidden layer, leads to better fits to the training data but it also increases the problem of overlearning, decreasing the ANN ability to generalize (Özesmi et al., 2006). Methods describe by Somaratne et al. (2005) were used for setting initially the number of neurons in the hidden layer, being deleted one at a time, till model simplification reduced their prediction ability as judged by R^2 . The number of data in the training set was at least five times the number of connections in the ANN to prevent overlearning (Gupta et al., 2003). Cross-validation was also implemented to avoid overlearning (Özesmi et al., 2006), fitting models using the training set and testing them against the validation set, stopping weights adjustment on the training set when R^2 from the validation set becomes lower than from the training set (Park and Vlek, 2002). The same training and validation sets as those used for regression fitting were used. Alternative, data were partitioned into 50% for training, 25% for validation and 25% for testing, and results compared with the 70:30 partition method when developing ANN models. Models were fit using the training and validation sets as described above and tested against the test sets. The ANN models were fit using Statistica (StatSoft, Inc., Tulsa, OK). The RMSE of models were calculated (Kobayashi and Salam, 2000). The determination coefficients of training, validation, and test sets were contrasted (Kleinbaum and Kupper, 1979). Modeling methods were compared testing the coefficients of determination on the same validation data set. Intercepts and slopes of regressions of observed vs. estimated data were compared by the t using IRENE (Fila et al., 2003). In all cases, $P = 0.05$. RESULTS

The ANMR ranged from -42 to 64 kg N ha^{-1} , with similar averages for wheat and corn, which ranged 15 to 16 kg N ha^{-1} (Table 1). As a mean, 15% of total N in residues was released during the crops' growing seasons. Residues were, in most of the cases, sources of N for crops. Only in four cases, during wheat growing season, they immobilized a quantity of N of agronomic significance ($>10 \text{ kg N ha}^{-1}$). This immobilization was observed in sites when great amounts of corn residues were present in the soil. Average ANMR was similar during the growing season of

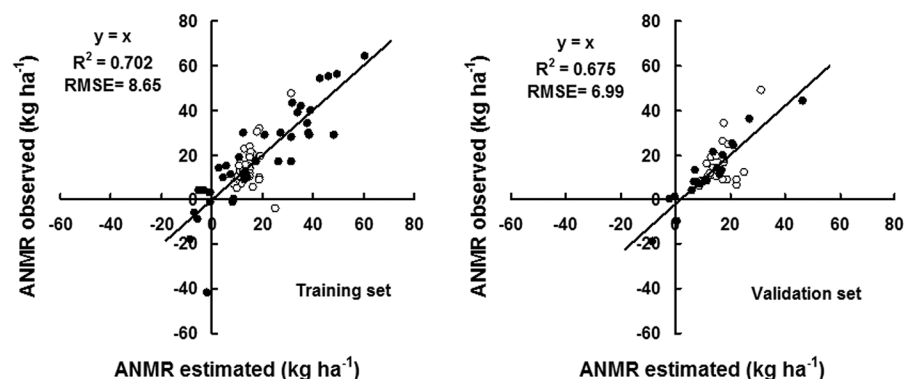


Fig. 2. Observed vs. estimated apparent nitrogen mineralization from residues (ANMR) estimated by a polynomial regression method. Full circles: during wheat growing season, empty circles: during corn growing season.

wheat independently of corn or soybean as the previous crop. The higher residue mass of corn as previous crop in comparison to soybean (11.2 vs. 7.5 Mg DM ha⁻¹) compensated its lower N concentration (0.90 vs. 1.22%) leading to similar ANMR averages. ANMR was higher in sites under no-till than under tillage (23.6 kg N ha⁻¹ vs. 8.4 kg N ha⁻¹, respectively). This result was attributed to the greater amount of remaining residues from previous crops under no-till at the initial stages of the growing season of wheat (12.6 vs. 7.0 Mg DM ha⁻¹) and corn (7.0 vs. 3.5 Mg DM ha⁻¹), which may compensate for the lower mineralization rate of surface residue. As a mean, under no-till, 38% of residue mass was buried at the initial phases of crops growing seasons; meanwhile, under tillage, 90% of residue mass was founded belowground. On the soil surface, residue mass decreased on average by 17% during the wheat growing season and 29% during the corn growing season. Meanwhile, buried residue lost 49 and 48% of their mass, respectively.

The ANMR could be modeled using both linear regression and ANN (Fig. 2, 3). The two modeling techniques fit data with similar performance, despite the R^2 was slightly greater and the RMSE lower for the ANN model. No significant differences were detected between the R^2 of the training and validation sets in any case. Also, the R^2 of both modeling techniques did not differ significantly when compared on the same validation data set. Both models had an ordinate not different from 0 and slope equal to 1. When the data was partitioned into training ($R^2 = 0.68$), validation ($R^2 = 0.71$), and testing ($R^2 = 0.68$) sets, the performance of the ANN was not significantly

affected, indicating that the ANN model developed using early stopping of weight fitting did not led to overlearning.

The best ANN fit had six neurons in the hidden layer and showed that ANMR was controlled by three factors, the crop during which the processes occurs (wheat or corn, SR = 1.25), the initial mass of remaining decomposing residues (SR = 2.29) and its N concentration (SR = 2.22) (Fig. 4). Crop effect was small (~10%) on ANMR, and its tendency depended on the range of data taken into account. Generally, it was higher during corn than during wheat growing season. The ANMR increased as residue mass increased, with an average mineralization of 4.3 kg N Mg DM⁻¹ residues. Below a N concentration of approximately 0.9%, the ANN model predicted immobilization; meanwhile above this threshold, mineralization prevailed. A strong interaction between these two variables was described by the ANN model, which allowed the estimation of ANMR under contrasting scenarios. The ANN models with similar performance to those described here were fit using as inputs crop type and total initial N in residues (residue mass × N concentration). As these simplified models would not allow assessment of the effects of residue mass and its N concentration separately, the more complex ANN was selected for understanding the effects of control factors on ANMR. Other variables had no impact on ANMR and were dropped from models. The best regression model was fit using crop type and total initial N in residues as independent variables. The ANMR predicted by the regression model was higher for corn than wheat and increased as the amount of N in residues at the beginning of crops growing seasons was greater.

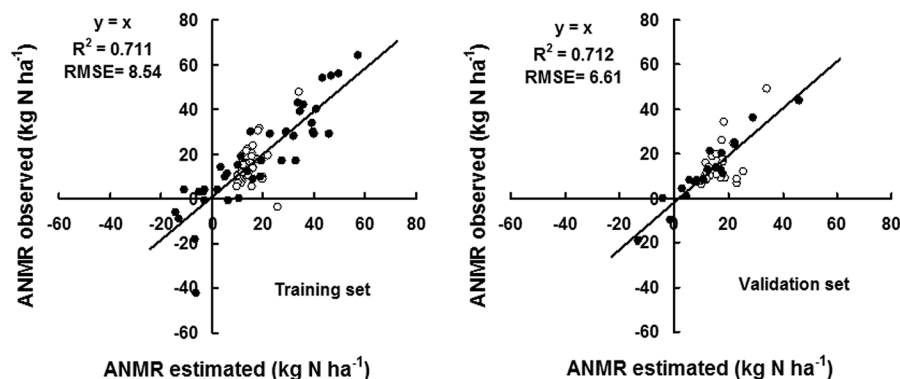


Fig. 3. Observed vs. estimated apparent nitrogen mineralization from residues (ANMR) estimated by an artificial neural network. Full circles: during wheat growing season, empty circles: during corn growing season.

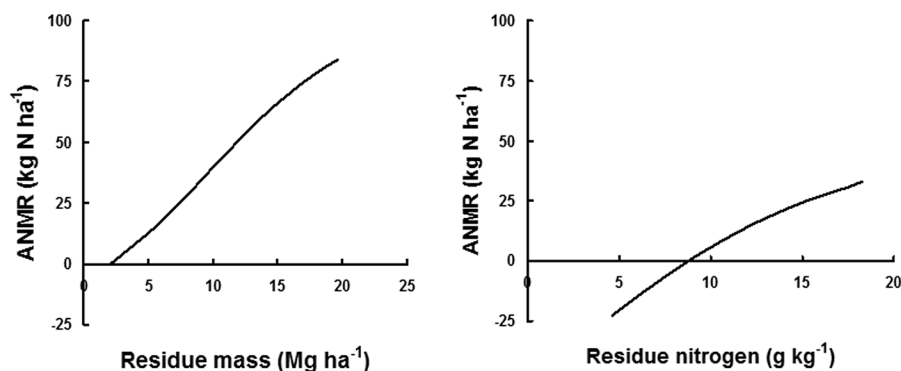


Fig. 4. Average impact of residue mass and composition on apparent nitrogen mineralization from residues (ANMR) as estimated by an artificial neural network.

The ANMH showed a broad range from -83 to 328 kg N ha^{-1} (Table 1), averaging 34 kg N ha^{-1} during wheat growing cycle and 127 kg N ha^{-1} during corn growing cycle. In $\sim 20\%$ of sites, ANMH had negative values in wheat; meanwhile, no negative values were estimated in corn. The ANMH was an important N source for wheat, doubling the average flux of N generated from residues, and it was the main source of the nutrient for corn, being ~ 10 times the magnitude of ANMR.

Modeling of ANMH using regression or ANN could be performed with good results (Fig. 5, 6). Intercepts and slopes of observed vs. estimated data were not different from 0 and 1, respectively, both for training and validation data sets, and there were no detectable differences in R^2 of training and validation. The ANN model had six neurons in the hidden layer and a little better performance than regression, but not significant. Partitioning data into training ($R^2 = 0.77$), validation ($R^2 = 0.77$), and test ($R^2 = 0.74$) indicated that the model fit using only two data sets did not lead to overlearning. The ANMH was controlled by soil mineral N level (soil + fertilizer N) (SR = 1.17), the amount of initial remaining residues from previous crop (SR = 1.23), the N mineralization potential of soil determined in an incubation test (SR = 1.16), the ratio of organic N to clay + silt soil content (SR = 1.01), and the interaction of rainfall \times temperature (SR = 1.51) (Fig. 7). The ANMH decreased in soils with higher initial mineral N level, residue mass present and fine particles content, and increased as soil organic N, mineralization capacity, rainfall, and temperature during the crop growing season were greater. Many strong interactions existed between all these variables, so the ANN model must be used for ANMH estimation under specific site conditions. The selected regression model included

the same independent variables as those used by the ANN as inputs, with similar effects. When mineral N content of the soil was dropped from the ANN model a small reduction of the determination coefficient was observed (R^2 changed from 0.78 to 0.73). Consequently, a simplified ANN model could be fitted that allowed ANMH prediction without using soil N + fertilizer N rate as input. This simplified model was suitable for ANMH estimation when applying the balance sheet methodology for calculating a fertilizer N rate under some common scenarios founded in the Pampas (Fig. 8).

DISCUSSION

In the pampean agroecosystems of our study, residues acted as sources of N for crops in most of the cases. Despite in some sites where ANMR was $>30 \text{ kg N ha}^{-1}$ (12% of sites), the average N mineralization was 15 kg N ha^{-1} , which may be considered a small nutrient source. Wheat and corn N demands for high yields in the region are much higher, ranging 200 and 300 kg N ha^{-1} , respectively (Alvarez, 2007).

Our methodology for ANMR estimation assumed that the change in N content of decomposing residues between harvest and initial growth stages of crops, was the amount of N mineralized; based on surface or buried fraction, this amount of N was allocated to the soil solution or microbial biomass pools. In cases when net immobilization occurred (N in residues at harvest was greater than initial content), a partitioning coefficient was not applied for ANMR calculation, and results are not considered biased by it. If different partition coefficients were used, for example, 50% of N released both for buried or surface material, estimations of ANMR would suffer only a small change, averaging $16.5 \text{ kg N ha}^{-1}$ during the crops'

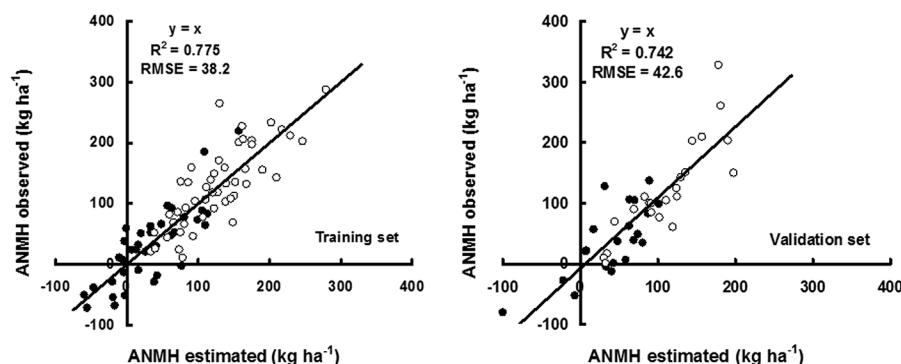


Fig. 5. Observed vs. estimated apparent nitrogen mineralization from humic substances (ANMH) estimated by a polynomial regression method. Full circles: during wheat growing season, empty circles: during corn growing season.

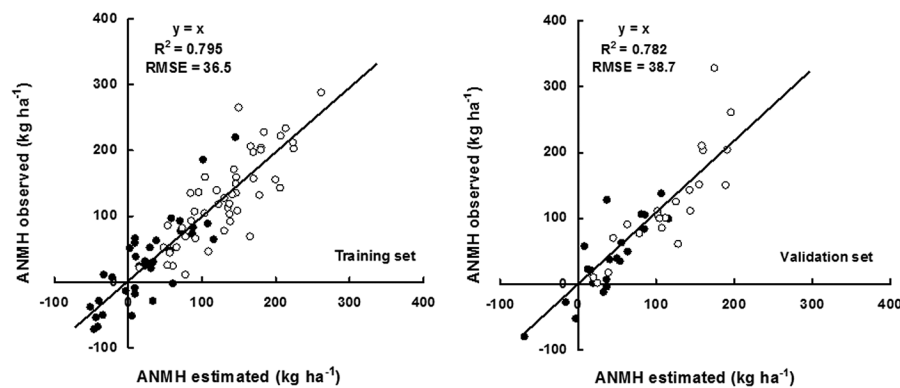


Fig. 6. Observed vs. estimated apparent nitrogen mineralization from humic substances (ANMH) estimated by an artificial neural network. Full circles: during wheat growing season, empty circles: during corn growing season.

growing cycles. Extreme possible partition coefficients (0.3 vs. 0.7 for the whole residue material) would lead to changes in mean ANMR estimation of only $\pm 8 \text{ kg N ha}^{-1}$, and would have a minor impact on the estimation ANMH calculated by difference between apparent N mineralization and ANMR.

The ANMR did not differ between the growing seasons of wheat and corn. Temperature and water are important environmental control factors that regulate decomposition rate (Zhou et al., 2008) and N release (Quemada and Cabrera, 1997). In the Pampas, soil temperature is lower but water content higher during the wheat growing cycle than during the corn cycle (Alvarez, 2006), so compensation effects of these two factors on decomposition could exist.

Under no-till management, ANMR was three-fold greater than under tillage. Usually, buried residue decomposes faster than on the soil surface, releasing its N (Lachnicht et al., 2004; Lupwayi et

al., 2006). As a consequence of this phenomenon, in the pampean experiments, remaining residues were greater in no-till sites than in tilled ones during the initial phases of the crops' growing seasons. Additionally, as decomposition proceeds, labile components are degraded and the remaining residue mass is enriched in recalcitrant ones which may release N slowly (Leblanc et al., 2006; Nakhone and Tabatabai, 2008). As the sum of these two processes, the mineralization of labile components from the abundant and less-degraded residue initially present when the experiments started likely contributed to the observation of greater ANMR under no-till than that observed under tillage management.

The ANN model fit allowed the estimation of the residue mass effect on ANMR with a minimum estimation of zero and a maximum possible release of around 80 kg N ha^{-1} . The mass effect on N release from residues under field conditions has been scarcely studied. Most works focus mainly on residue type

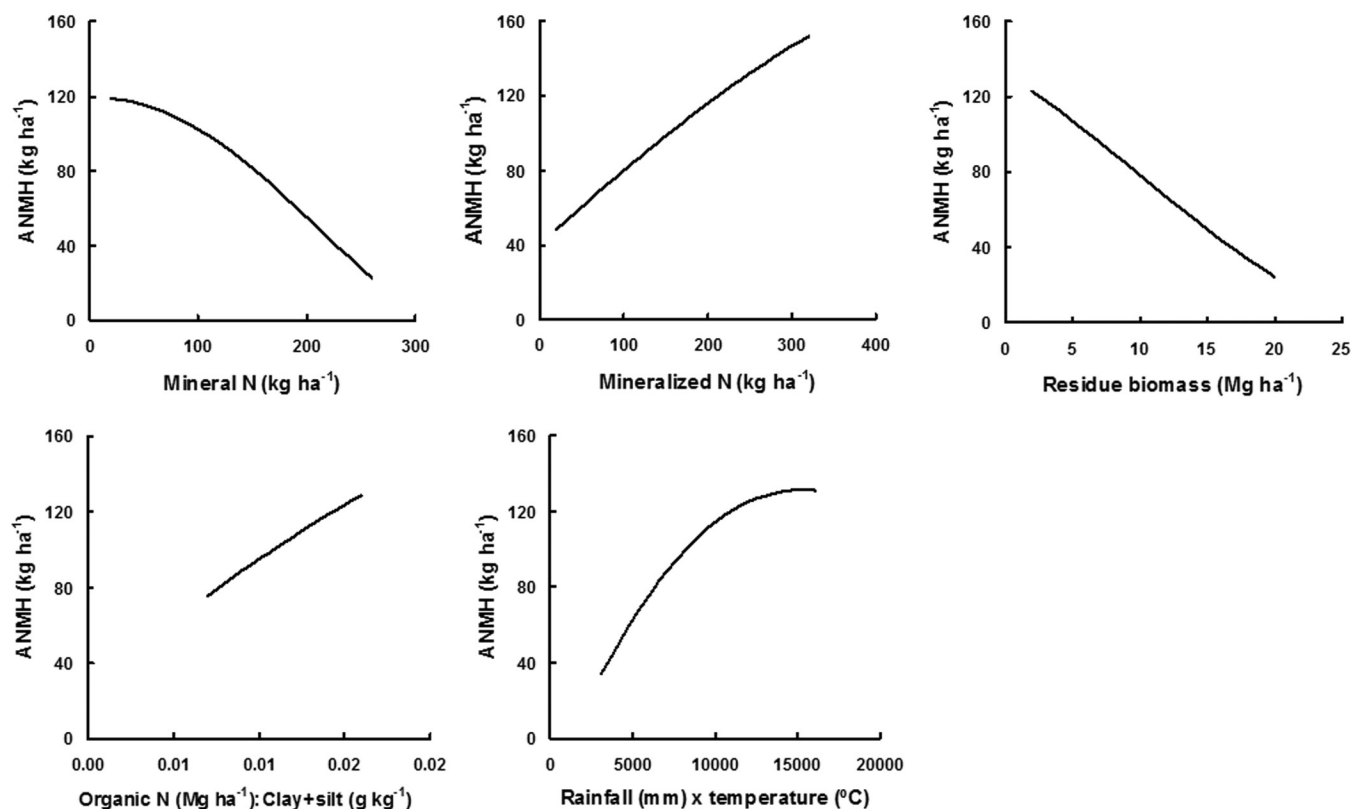


Fig. 7. Impact of soil properties and climate on apparent nitrogen mineralization from humic substances (ANMH) as estimated by an artificial neural network.

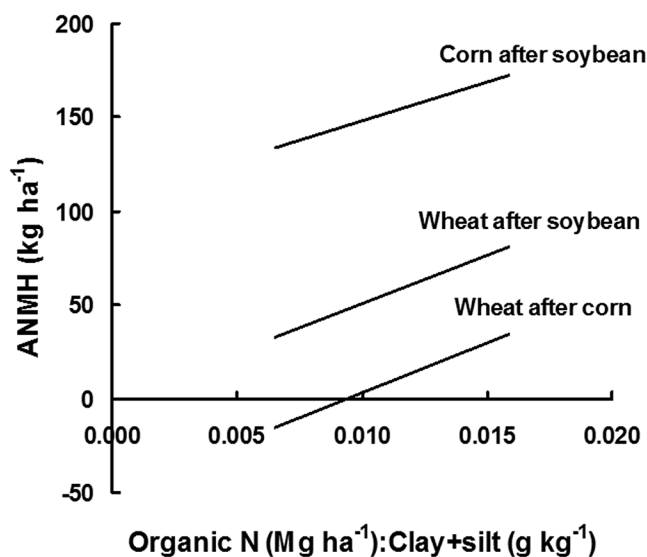


Fig. 8. Apparent nitrogen mineralization from humic substances (ANMH) as estimated by an artificial neural network model for some common scenarios founded in the Pampas. Estimations were performed for (i) average climatic conditions during wheat and corn growing cycles, (ii) average remaining residues biomass from previous crops under no-till management, and (iii) average mineralization potential of soils as determined by an incubation test.

impacts on mineralization. Results from different experiments showed that N mineralization from decomposing residues is extremely variable, ranging from 2 to 5 kg N ha⁻¹ during the following crop growing cycle in the case of poor N residues of some graminaceous crops (Bremer and van Kessel, 1992, Beare et al., 2002) to >100 kg N ha⁻¹ when legume residues had an initially high N concentration (Gentry et al., 2001, Sarrantonio, 2003). Our results showed that the residue mass initially present in soil is a variable useful for predicting N mineralization.

Above a N concentration of 0.9%, the ANN model predicted mineralization; meanwhile, below this threshold, immobilization on residues occurred. This N concentration is equivalent to a C/N of approximately 44. Results from the review of numerous experiments had shown that a C/N from 20 to 30 is a common threshold for immobilization to mineralization (Seneviratne, 2000, Jensen et al., 2005), but this threshold is regulated by the polyphenol and lignin content of the material (Janssen, 1996), reaching values as high as 40 (Janssen, 1996, Kumar and Goh, 2003). Our field results fall near this upper limit. Nitrogen mineralization from corn and soybean residues during the wheat growing season averaged similar values, which can be attributed to the compensation of greater corn residue mass with a higher N concentration in soybean material. The ANN model could estimate ANMR from different combinations of residue mass and N richness under field conditions and be used as a helping tool when using the balance sheet method.

The ANMH was more important as a N source for crops than ANMR, especially for corn, representing on average around half of the N requirements of this later crop. The ANMH decreased as soil mineral N content increased. Taken into account that ANMH represented the difference between gross mineralization, immobilization, and losses, different causes could produce this result. A possible inhibition of gross mineralization due to a feedback process caused by high mineral N had been described for some soils (Sierra, 1992, Carpenter-Boggs et al., 2000). An increase of

the immobilization process in organic pools had also been detected under high mineral N content scenarios (Engels and Kuhlmann, 1993, Blankenau et al., 2000). Finally, N losses from the agroecosystem are expected to be greater under highly fertilized conditions (Ma et al., 1999, Blankenau et al., 2000). Previous studies reported that, usually, apparent N mineralization is inhibited as soil mineral N or fertilizer rate increased (González Montaner et al., 1997, Blankenau et al., 2000), with even negative values when total mineral N content of the soil (soil + fertilizer N) is very high (Engels and Kuhlmann, 1993, Delphin, 2000). Conversely, in some cases, N mineralization evaluated using ¹⁵N methods (Blankenau et al., 2000) or determined by field incubation techniques (Ma et al., 1999) increased with soil mineral content. These results can be attributed to an activation of gross mineralization by mineral N. If this process occurred in our experiments, instead of inhibition of mineralization, it was overwhelmed by immobilization or losses, leading to a decrease of ANMH when N level became greater.

As in other studies (Delphin, 2000, Curtin and McCallum, 2004), we observed the estimation of soil N mineralization potential using an incubation test was related to apparent N mineralization assessed by the balance sheet method. Regression techniques (Egelkraut et al., 2003) and heuristic methods (Rohde, 1996) allowed development of models for apparent N mineralization estimation. These models included as explaining variables, soil water and temperature and the results of incubation tests, but they had only a moderate capacity (R^2 approximately 0.40) of explaining apparent mineralization variability. Our regression or ANN models, using the results of an incubation test, joined to soil and climate data, allowed a good prediction of ANMH.

As remaining residue mass increased in soil, ANMH decreased. Despite in some sites net N immobilization was detected on residues, generally they released N. Nevertheless, even in sites where residues released N, immobilization may have occurred in other organic pools. Some experiments showed that incorporation of residues led to an increase of soil microbial biomass N by immobilization of mineral N (Ibewiro et al., 2000, Korsæth et al., 2001). Additionally, the soil light fraction (Whalen et al., 2000), or the soil fraction > 200 microns (Recous et al., 1998) may be acting as a N sink. Immobilization was a potential cause of the decrease in ANMH observed as residue mass increased. We calculated an immobilization rate of 5.3 kg N Mg⁻¹, using the ANN model, which falls between other reported immobilization rates. The rate of N immobilization caused by residue addition to the soil is very variable, ranging from 1.4 kg N Mg⁻¹ DM residues (Trinsoutrot et al., 2000) to 16 kg N Mg⁻¹ DM (Recous et al., 1995). Another possible reason for ANMH decrease as residue mass increased in some sites is that, under no-till management, residues can reduce soil temperature, which may impact N mineralization (Andraski and Bundy, 2008).

The organic N pool size regulates N mineralization rate in many soils (Wang et al., 2001, O'Connell et al., 2003, Li et al., 2008) despite that some studies reported that the C/N ratio (Springob and Kirchmann, 2003), or the amount of labile soil components may be better predictors (Mishra et al., 2005). Apparent mineralization assessed by the balance approach had been observed to be curvilinearly-correlated to soil organic C with a net release of 4.8 kg N Mg⁻¹ organic C in some subtropical Indian soils (Benbi and Chand, 2007). The ANN model developed for pampean agroecosystems predicted

a mean ANMH of approximately 8 kg N Mg⁻¹ organic N, a much lower mineralization rate, for these soils with a mean C/N of approximately 10 for soil organic matter (Table 1).

Textural effects on N mineralization are well known. Incubation experiments, in which the mineralization rate of different soils with varying textural composition were contrasted, showed that as the clay + silt content increased it also increased the total amount of organic N of the soil and the rate of N mineralization, but a strong decrease of the N mineralization by unit of organic N mass was produced (Hassink, 1994, Bechtold and Naiman, 2006). This effect of fine particles, protecting organic matter from microbial attack, had been described previously in soils of the Southern Pampa, a portion of the Pampas southwest from the region where we performed our experiments, with coarser soils of higher organic matter content (González Montaner et al., 1997). In this study, regression methods were tested for developing models suitable for apparent N mineralization estimation. The best model fit explained 50% of the variation of the mineralization during the wheat growing season using as independent variables soil mineral N level and the ratio of organic matter/clay. As in our regression and ANN models for ANMH prediction, in that regression model soil fine particles controlled mineralization of organic pools by reducing the rate of the process as clay rose. Our ANN model estimated that if the clay + silt soil content doubled, for a certain organic N level, ANMH decreased on average by 40%.

The interaction of rainfall and temperature described by the ANN model was the main reason which determined that mineralization during the corn growing cycle was around four times that produced during wheat cycle. Soil temperature, water content and their interaction controls net N mineralization in soils as determined in laboratory tests (O'Connell and Rance, 1999, Wang et al., 2004). Apparent N mineralization assessed by the balance method is also controlled by soil temperature and water content (Campbell et al., 2008) and had been modeled by regression methods using temperature, water content and other soil variables with moderate success, as stated above (Egelkraut et al., 2003). We had no available records of soil water content during crop growing seasons in the pampean experiments, so rainfall was taken into account to subrogate that variable. Under similar temperature scenarios it may be expected that more rainfall led to higher soil water content. The regression and ANN models may be used for modeling ANMH under production conditions, using past records for defining some expected climatic conditions and determining the soil variables used as inputs experimentally.

Both modeling techniques tested, linear regression and ANNs, gave good results when developing tools for N mineralization estimation under field conditions. As ANN models had a slightly better performance, they are recommended for mineralization prediction when the balance sheet method is used. Monograms or tables can be generated with the ANN models, and by using site values of the ANN inputs as initial information, future users may estimate apparent N mineralization under average climatic scenarios. The methodology developed may be applied in different areas and for other crops.

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