Estimating nutrient release from soil organic matter using ion exchange membranes

P. Qian, J. J. Schoenau and A. Braul

Department of Soil Science, University of Saskatchewan

Abstract

A simple method was developed to assess mineralizable soil organic N and S using anion exchange membrane (AEM) burial. With this method, strips of AEM were buried in the soil and used to absorb nitrate and sulfate ions released from organic matter during the incubation of field-moist soil in plastic vials. An index of mineralization was obtained by subtracting initial AEM extractable ion from the ion absorbed on an AEM strip removed at the end of incubation. The mineralization index was compared to a reference method using the same incubation system but with 0.001M $CaCl_2$ solution to extract nitrate and sulfate. A total of 67 soil samples were used which provided a range of soil properties. Results showed the AEM incubation to be simple and to be more closely correlated with plant N and S uptake (r^2 = 0.862**** for N and 0.920**** for S) than the reference method (r^2 = 0.602**** for N and 0.682**** for S).

Introduction

The determination of residual profile nitrate is widely used as the criteria for fertilizer N recommendations in Western Canada and the USA in regions where limited leaching occurs before planting (Smith, 1966; Spencer *et al.*, 1966; Herron *et al.*, 1971 Soper *et al.*, 1971; Ward, 1971; Carson, 1975). However, mineralization of organic N during the growing season can provide a certain amount of inorganic N as NH_4-N and NO_3-N, which cannot be neglected because of its easy access for plants. Carter *et al.* (1974; 1976) and Stanford *et al.* (1977) suggested that use of a mineralization index in conjunction with residual profile NO_3-N would improve the degree of prediction of N fertilization needs. To that end, a new nitrogen recommendation procedure was adopted by Saskatchewan Soil Testing Laboratory. The mineralization estimate is based on the typical soil N level in the soil zone multiplied by an approximation of percentage N mineralized over a growing season in that soil zone. The factor used to multiply typical soil N mineralized is derived from soil moisture based on the rainfall probabilities for the growing season. The proportion of mineralized N is not only influenced by soil moisture but may also be influenced by different inherent soil properties which affect the composition of the soil organic matter and the ease by which it is mineralized. For this reason, fertilizer recommendations might be improved if the actual contribution in a farmer's own field could be indexed, and the recommendation adjusted if it deviates widely from the "average" for an area. This approach could also be applied to S recommendations since organic S mineralization is usually the main input into plant available sulfate pool (Schoenau & Germida, 1992). The objective of this study was to develop and evaluate a simple method to account for the contribution of N and S mineralization to the total amount of nutrient available to a crop over a growing season.

Materials and Methods

Soils

Sixty-seven soil samples (0-15 cm) were obtained from the major soil zones in Saskatchewan to provide a wide range of chemical and physical properties. Of these soils, different management histories with contrasting tillage, cultivation periods, rotation, and slope positions were also represented. All soils were analyzed for mineralizable N and 44 of the samples were also measured for mineralizable S. Of the 67 samples, 23 and 28 samples were selected for use for minus N and minus S treatments, respectively, in a growth chamber study .

Incubation Procedure

The procedure used in this study to measure N and S mineralization was an aerobic incubation. Fifty grams of each air-dried soil sample was transferred to a 65-ml polyethylene vial. After the sample was brought to field capacity, the vial was sealed with parafilm to avoid dryness of samples and 5 small holes punctured on the parafilm to allow aeration. 23 samples were incubated for one week for N mineralization. In a second experiment for N and S mineralization, 44 samples were incubated for two weeks. The incubation experiment was designed as a randomized block with three replicates and conducted at 30°C. Two methods were used: 1). anion exchange membrane burial and incubation and 2). calcium chloride extraction at the end of the incubation. In the AEM burial, a strip of AEM (2 x 4 cm) was inserted directly into the soil before adding water, and then retrieved from the soil after incubation and washed free of adhering soil with deionized water. The ions sorbed on the strip during incubation were eluted using 0.5M HCl (Qian, *et. al.*, 1992). The reference method was a standard closed system in which soils were brought to field capacity and incubated. At the end of the incubation, soils were air-dried and ground and mixed thoroughly for 0.001M $CaCl_2$ extraction . Nitrate in the 0.5M HCl eluent and in the 0.001M $CaCl_2$ extract was determined using Technicon automated colorimetry. Sulfate was determined using inductively coupled plasma (ICP) emission.

Growth Chamber Experiment

Canola plants were grown to the late flowering stage in a growth chamber set at 26°C daytime and 12°C at night. Plants were grown in 200 g styrofoam pots with 6 mg P, 40 mg K and 10 mg S per pot for - N treatment and with 20 mg N, 6 mg P and 40 mg K per pot for - S treatment. All soils were also given a blanket micronutrient treatment of Cu, Zn, Mn, Mo and B at rate of 0.12, 0.8, 1.0, 0.12 and 0.3 mg per pot. All pots were watered twice a day to maintain the moisture level at about 90 % of field capacity during the experimental period.

After harvesting, all plants were oven-dried at 60°C, weighed to determine dry matter yield, and ground in a stainless steel mill. Total N in the plant tissue was determined using a sulfuric acid-peroxide digestion in a temperature-controlled digestion block (Thomas, *et. al.*, 1967), followed by determination of the ion concentrations in the digest using automated colorimetry. Total plant S was determined by sodium hypobromite oxidation (Tabatabai, 1982), followed by measurement of sulfate in the digest using ICP emission.

Results and Discussion

N mineralization is the process by which N in the organic form is converted into the inorganic form of NH_4^+. With adequate aeration, soil-derived NH_4^+ can be easily oxidized to NO_3^- by nitrifiers. Some workers (Vlassak, 1970; Normmil, 1976) have indicated the importance of measuring both NO_3-N and NH_4-N as total mineralized N. Others (Smith, 1966; Rixon,1969) assumed the measurement of NO_3-N to be sufficient because NH_4-N accumulation is negligible. In our experiment, the proportion of inorganic N comprised of NH_4-N in the 2 week incubation study was only 0.04 - 0.47%. Therefore, NO_3-N accumulation was used as the measure of soil N mineralization and the accumulation of SO_4-S was used as the measure of soil S mineralization.

In this study, the net N and S mineralization is represented by subtracting initial nitrate and sulfate present in the samples from the respective values present at the end of incubation. For the reference method, the initial NO_3-N and SO_4-S is determined by $CaCl_2$ extraction before incubation. For the AEM method, it is difficult to obtain a quantitative measure of the actual initial N and S because we cannot predict how long it will take for all NO_3-N and SO_4-S in the soil to be completely absorbed by the membrane. Since the nitrate and sulfate extracted by 3 different burial times (1 hr, 6 hrs and 16 hrs) were all highly correlated with those extracted by 0.001M $CaCl_2$ (Table 1), the level of nitrate and sulfate extracted by 1 hour (the shortest time tested) was selected to represent the index of residual profile NO_3-N and SO_4-S .

Table 1. Coefficients of determination (r^2) for correlations between 0.001M $CaCl_2$ extraction and AEM burial for different times.

Time of AEM burial	Nos. of samples	NO3-N extracted	SO4-S extracted
First experiment			
1 hour	23	0.970****	
6 hours	23	0.912****	
Second Experiment			
1 hour	18	0.998****	0.993****
16 hours	18	0.953****	0.941****

****Significant at $P < 0.0001$ level.

The relationship of mineralized N and S as determined by the AEM method to the reference method ($CaCl_2$ extraction).

The mineralized NO_3-N and SO_4-S from the AEM method showed good relationships with those obtained from the reference method both in a 1 week incubation experiment and in a 2 week incubation experiment (Table 2). The correlations for net N mineralization between two methods were higher in the 2 week incubation than in 1 week incubation, but with the same level of significance.

Table 2. Coefficients of determination for correlation between AEM method and 0.001M $CaCl_2$ extraction for measuring net N and S mineralization in two experiments

Period of incubation	No. of samples	Mineralized NO_3-N r^2	Mineralized SO_4-S r^2
one week	23	0.283**	
two weeks	18	0.445**	0.278*

*Significant at the < 0.05 probability level
**Significant at the < 0.01 probability level

The relationship of mineralized N and S with total and organic N and S concentrations.

The correlation of mineralized N using 0.001M $CaCl_2$ extraction with either total N and organic N was highly significant (Table 3). This result is similar to that obtained by Nyborg and Hoyt (1978): r =0.63** for 40 soils. When using the AEM burial method to estimate the mineralized N, the correlation was also significant, but only at $p < 0.05$ level. For the S mineralization measurement, the correlations for both AEM burial and 0.001M $CaCl_2$ extraction were similar with the correlation between mineralized S and total and/or organic S significant at $p < 0.05$ level. The difference in correlation between NO_3-N extracted by AEM and calcium chloride with organic N may be because the mineralization index as provided by AEM burial (2 wk - 1 hr) includes a portion of the initial NO_3-N in the sample, since not all of the NO_3-N initially present is accounted for in the 1 hr burial. A better estimate of the amount of N derived from mineralization alone might be obtained by subtracting the initial $CaCl_2$ extractable NO_3-N from the AEM 2 wk burial.

Table 3. Coefficients of determination (r^2) for linear relationship between net N and S mineralization and total and/or organic N and S.

Incubation method	Coefficient of determination (r^2) Total N	Organic N	Total S	Organic S
One week§				
mineralized N from $CaCl_2$	0.801****			
mineralized N from AEM	0.253*			
Two week¶				
ralized N & S from $CaCl_2$	0.714****	0.739****	0.217*	0.249*
alized N & S from AEM	0.359**	0.354**	0.312*	0.266*

§ Twenty three soil samples were used in one week experiment
¶ Eighteen soil samples were used in two week experiment
*Significant at $p < 0.05$ level
**Significant at $p < 0.01$ level
****Significant at $p < 0.0001$ level

Ability of AEM and $CaCl_2$ methods to predict N and S availability to canola.

The relationship between N and S uptake by canola and the predicted availability as given by the AEM burial and $CaCl_2$ extraction are provided in Table 4. Both methods showed very good relationships with N and S uptake by canola. Since AEM-extractable N and S after 2 week burial was more closely correlated with plant N and S uptake (r^2 = 0.862**** and 0.920****) than the amount of NO3-N and SO4-S removed by $CaCl_2$ after 2 week incubation (r^2 = 0.602**** and 0.682****), the AEM burial may be a superior method to account for residual nitrate and sulfate plus the contribution from mineralization. The ability of the AEM to continually absorb the released nitrate and sulfate and thereby mimic a plant root may explain the apparent better relationship with plant uptake. Conventional closed incubations, where the nitrate and sulfate is allowed to accumulate in soil solution, have been criticized because of cumulative inhibitory effects (Stanford and Smith, 1972). Inconsistencies in behavior of S and N mineralization observed in conventional closed incubation systems led Roberts (1985) to suggest that closed incubation systems may be of limited value in estimating the long-term N and S supplying power of the soil. Reflecting possible problems, some of the net N and S mineralization as measured by incubation followed by $CaCl_2$ extraction was obtained as negative values.

The relationships between canola N and S uptake and NO_3-N and SO_4-S levels after 2 week incubation were better than for initial NO_3-N and SO_4-S. Cook *et al.* (1957) and Stanford *et al.* (1965) found similar results with good agreement between mineralizable N and plant N uptake.

Table 4. Coefficients of determination (r^2) for relationship between total uptake of N and S (y) by canola and individual measurement of NO3-N and SO4-S in soil.

Nutrient extraction	Coefficient of determination (r^2) N-uptake (n = 23)	S-uptake (n = 28)
1 hr AEM burial (initial)	0.688****	0.712****
2 wk AEM burial (initial plus mineralization)	0.862****	0.920****
Initial $CaCl_2$ extraction	0.586****	0.477***
$CaCl_2$ extraction after 2 wk incubation (initial plus mineralization)	0.602****	0.682****

****P < 0.0001
***P < 0.001

Conclusion

Combining a N and S mineralization index with residual profile nitrate and sulfate proved to give a better prediction of N and S plant uptake than using residual nutrients alone. This is not surprising since crop uses both residual nutrients and mineralized nutrients during the growing season. There are many methods available to estimate mineralized N and S but few are easy enough to be adapted in routine testing for a large amount of soil samples in a short period of time. The AEM burial test may be a better method than standard incubations not only because of its ability to act as a sink for

mineralized N and S, but also because of its simplicity.

Acknowledgements

The authors thank the Saskatchewan Agriculture Development Fund and Saskatchewan Environmental Technology Development Program for financial support.

Reference

Carson, P. L. 1975. Recommended nitrate-nitrogen tests. P. 13-15. *In* W. C. Dahnke (ed.) Recommended chemical soil test procedures for the north-central region. North Dakota Agric. Exp. Stn. Bull 499, North Dakota State Univ. Fargo.

Carten, J. N., M. E. Jensen, and S. M. Bosma. 1974. Determining nitrogen fertilizer needs for sugar beets from residual nitrate and mineralizable nitrogen. Agron. J. 66:319-323.

Carter, J. N., D. T. Westerman, and M. E. Jensen. 1976. Sugar yield and quality as affected by nitrogen level. Agron. J. 68:49-55.

Cook, F. D., F. G. Warder and J. L. Doughty. 1957. Relationship of nitrate accumulation to yield response of wheat in some Saskatchewan soils. Can. J. Soil Sci. 37:84-88.

Herron, G. M., A. F. Dreier, A. D. Flowerday, W. L. Colville, and R. A. Olsen. 1971. Residual mineral N accumulation in soil and its utilization by irrigated corn (*Zea mays* L.). Agron. J. 63:322-327.

Nommik, H. 1976. Predicting the nitrogen-supplying power of acid forest from data on the release of CO2 and NH3 on partial oxidation. Commun. Soil Sci. Plant Anal. 7:569-584.

Nyborg, M. and P. B. Hoyt. 1978. Effects of soil acidity and liming on mineralization of soil nitrogen. Can. J. Soil Sci. 58:331-338

Qian, P., J. J. Schoenau, and W. Z. Huang. 1992. Use of ion exchange membranes in routine soil testing. Commun. Soil Sci. Plant Anal. 23:1791-1804.

Rixon, A. J. 1969. The influence of annual and perennial irrigated pastures on soil fertility as shown by the yield and quality of a subsequent wheat crop. Aust. I. Agric. Res. 20:243- 255.

Roberts, T. L. 1985. Sulfur and its relationship to carbon, nitrogen and phosphorus in a climo- toposequence of Saskatchewan soils. Ph. D. thesis. University of Saskatchewan.

Schoenau, J. J. and J. J. Germida. 1992. Sulphur cycling in upland agricultural systems. pp. 261- 277. *In*: Howarth, R. W. *et al.* (eds), Sulphur Cycling on the Continents. John Wiley & Sons Ltd.

Smith, J. A. 1966. An evaluation of nitrogen soil test method for Ontario soils. Can. J. Soil Sci. 46:185-194.

Soper, R. J., G. J. Racz, and P. I. Fehr. 1971. Nitrate nitrogen in the soil as a means of

predicting the fertilizer nitrogen requirements of barley. Can. J. Soil Sci. 51:45-49.

Spencer, W. F., A. J. MacKenzie, and F. G. Viets, Jr. 1966. The relationships between soil tests for available nitrogen and nitrogen uptake by various irrigated crops in the western states. Soil Sci. Soc. Am. Proc. 30:480-485.

Stanford, G., A. S. Ayers and M. Doi. 1965. Mineralizable soil nitrogen in relation to fertilizer needs of sugarcane in Hawaii, Soil Sci. 99:132-137.

Standford, G. and S. J. Smith. 1972. Nitrogen mineralization potentials of soils. Soil Sci. Soc. Am. Proc. 36:465-472.

Stanford, G., J. N. Carter, D. T. Westerman, and J. J. Meisinger. 1977. Residual nitrate and mineralizable soil nitrogen in relation to nitrogen uptake by irrigated sugar beets. Agron. J. 69:303-308

Tabatabai, M. A. 1982. Sulfur. pp. 501-538. *In*: Pace, A. L. *et al.* (eds), Method of soil analysis Part 2. ASA Inc.. and SSSA Inc., Madison.

Thomas, R. L., R. W. Sheard, and J. P. Moyer. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorus and potassium analysis of plant material using a single digest. Agron. J. 99:240-243.

Vlassak, K. 1970. Total soil nitrogen and nitrogen mineralization. Plant Soil 32:27-32.

Ward, R. C. 1971. NO_3-N soil test - approaches to use and interpretation. Commun. Soil Sci. Plant Anal. 2:61-71.