



Encapsulated mixed-bed ion-exchange resins : practical uses monitoring nitrate movement and nitrogen soil fertility

by John Howard Miller

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Soils
Montana State University

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Abstract:

Leaching and cost of N-fertilizer concern agriculturalists and environmentalists. Proper management of N must be based on soil test results that account for N dynamics. This study involved different N rates to compare chemical-extraction soil testing with resin capsule methodology. The study was conducted at three different regions of Montana, involving three different crops. Irrigated and dry-land conditions were represented. Three approaches to soil testing were involved 1) the standard chemical extraction method used on dried field samples, 2) resin capsule tests on field-fresh soil samples made into saturated paste, and 3) in situ resin capsule tests placed at selected depths by means of an access tube. The latter approach allows continuous monitoring of N dynamics as influenced by field conditions. Small grains were analyzed for total N, and mint stems were analyzed for NO₃. Soil test results were compared to plant data. Studies on peppermint in the Flathead Valley involved N and irrigation variables. Br was included to obtain additional data on its value as a tracer for NO₃. Br breakthrough curves (BTC) generally occurred one to two weeks earlier than NO₃ at the 0.15 m depth, indicating resin capsule sensitivity to N dynamics under field conditions. Higher incremental N rates, compared to an initial application of the same amount of total N, resulted in a buildup of NO₃ in the upper 0.15 m of soil. Winter monitoring with resin capsules showed continued N dynamics at the deeper sampling points, even after the upper soil profile froze. Mint stem N data regressed on resin soil test data was better in 1994 than 1993, probably reflecting seasonal differences. Standard soil test data for NO₃ did not regress well on 1993 resin capsule test data, but this relationship was better in 1994. Golden Triangle studies were on dry-land spring wheat. Soil cores were collected from two depths, composited, and split. Half of each sample was tested by standard soil test. The other half was used for resin capsule testing in a saturated paste. Resin adsorbed NO₃ remained unchanged after two days in Golden Triangle soils, probably due to low quantities of available NO₃. When compared to 1993, spring wheat concentration of N and soil NO₃ tended to be higher in 1994. Neither soil test worked well to predict spring wheat N. Standard soil test data regressed well on resin saturated paste data. Studies at Sidney were on irrigated sugar beets. At Sidney soil cores were collected from three depths and handled like the Golden Triangle soil cores. In 1993 the NO₃ continued to be adsorbed to the resin capsule for seven days, probably due to higher initial soil concentrations of NO₃. Standard soil test data regressed better on 1993 resin data than for 1994 data. Resin data from the saturated paste method may be additive, but more research is needed. Based on results of this study, resin capsules provided a useful methodology for testing soil in the laboratory, as well as to allow in situ monitoring of the dynamic soil system.

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MONTANA STATE UNIVERSITY-BOZEMAN
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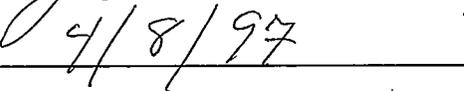
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ABSTRACT

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CHAPTER 1

INTRODUCTION

Nitrogen (N) fertilizer applied to agricultural land is a growing concern due to risks of polluting groundwater. A related concern of agricultural producers is the increasing cost of N-fertilizer. The cost of petroleum relates directly to the price of N-fertilizer, because oil and natural gas are the energy and H sources for fixing atmospheric dinitrogen (N_2) into ammonia (NH_3) in the energy-intensive Haber-Bosche process. As a result of the above factors, the rancher and farmer would like to be as efficient as possible when using applied N fertilizer. It is important to manage N so that plants take up applied N before it leaches beyond the root zone of agronomic crops. This reduces the cost to the agriculturalist and is good for the environment. Proper management, however, must be based on results from an accurate, rapid, and reliable N soil test that predicts each soil's N-supplying capacity in relation to plant requirements during the growing season.

Current N soil tests are based on chemical extraction procedures that are labor and energy intensive, and they take several days to complete. Soil samples must be collected from the field, dried, ground, sieved, and weighed before the extraction can be done. The time required for the chemical extraction and analysis is also considerable. Finally, the results provide only a "snapshot" of conditions at the time of sampling. Test results do not

reveal the processes that occur in the soil systems that control nutrient bioavailability, which are biologically active, dynamic, and constantly changing throughout the growing season. Furthermore, even though the extraction may account for all of the soil nitrate (NO_3) in the sample, it does not account for other forms of available N (eg, NH_4 and organic forms). For this type of soil test to be highly useful, results from field experiments must be available so that lab results can be correlated to crop response to applied fertilizer. Such field results are very limited and mostly out-dated for today's farming practices and cropping systems.

Accurate N management must account for N dynamics in the soil-plant system. Depending on the nature of the fertilizer, potential fates include: 1) denitrification, 2) volatilization, 3) mineralization, 4) immobilization, 5) nitrification, 6) plant uptake, and 7) leaching. Denitrification is a microbial process that converts NO_3 to N_2 gas, mostly under conditions of poor aeration. Volatilization is the loss of NH_3 gas to the atmosphere. When organic fertilizers are applied, mineralization of the organic compounds must occur to provide plant-available ammonium (NH_4) or NO_3 . Microorganisms also use these forms of N for their own metabolism. When this happens, some N is immobilized in microbial tissues and not available for plants. If NH_4 -forms of fertilizer are applied (or become available from mineralization), this is converted to NO_3 by the process of nitrification. All of these are microbial processes, and their rates are regulated by factors affecting microbial activity. The NO_3 form is the quasi-endpoint of the N cycle. This is the form in which plants take up most of their N, and due to its high solubility in water it is the form most susceptible to loss by leaching. From the standpoint of crop N management and environmental protection, the key is to have a good prediction of quantities of NO_3 at

various stages of crop growth. We conducted this study to address problems of soil testing, plant uptake of NO_3 and leaching.

The soil testing segment of the study was conducted to compare chemical-extraction soil testing (a static test) with a dynamic soil test using resins capsules. The chemical-extraction soil test will hereafter be referred to as standard soil testing or the standard soil test. The capsules are spherical (19 mm diam.) and contain a mixture of strongly acidic (H^+) and strongly basic (OH^-) ion exchange resins held within a molded porous polyester mesh fabric. For a review of how resins have been used in soil and environmental studies, the reader is referred to Skogley and Dobermann (1996). In our study, field-fresh soil was collected and transported to the laboratory for testing using both methods. Plant uptake of N (total) was measured in plants from each treatment area of experimental plots so that plant use of N could be accounted for.

The leaching segment of the research was conducted by comparing two methods of measuring NO_3 movement. Resin capsules were placed at selected soil depths to monitor movement of NO_3 . Br^- , which is commonly used as a tracer for NO_3^- , was surface applied to plots so that its movement could also be tracked. Capsules were emplaced by means of access tubes that allowed repeated "point" sampling at the same location. This system provides continuous monitoring of N dynamics. Results from this system were compared to those obtained by periodic soil sampling (a non point-specific, periodic, destructive methodology).

In this thesis, the capsule system is referred to as MBIER (mixed-bed ion-exchange resin). Its use for soil testing was described by Skogley (1992, 1994), who called this

methodology The Universal Bioavailability Environment/Soil Test (UNIBEST). Li et al. (1993) used this method to study Br leaching, showing it to be effective for describing solute movement under unsaturated water flow in a soil column as well as under irrigated conditions in the field. In this study we measured NO_3 and Br simultaneously in the MBIER to obtain additional data on Br as a conservative tracer for NO_3 under natural conditions. A major advantage of the resin capsule system is its capacity to capture "event based transport" of ions as water moves through the soil profile.

A major objective of this study was to determine the efficacy of MBIER to monitor plant-available NO_3 quantities, sensitivity to plant uptake, and leaching under field conditions. Farmers could benefit greatly if they had a simple, convenient method to reveal relationships between total N applied, plant uptake of N, and leaching of excess N. An important aspect of such a methodology would be the capability to detect "event based transport" that could reveal what happens during irrigation or heavy rainfalls.

Another aspect of the study was to investigate the relationship between total plant N and NO_3 adsorbed by resin capsules. If a strong relationship occurred, this would suggest the possibility of using capsules to predict plant nutrient needs under varying conditions, such as variable irrigation.

Field studies were conducted at three locations in Montana, and the major objectives at each location were:

1) Creston

- a) Monitoring NO_3 and Br leaching simultaneously under natural conditions;
- b) relationship between mint plant N and soil NO_3 under varying irrigation treatments and N rates;

- c) determination of MBIER to predict the amount of N needed by the plant over the growing season;
- d) winter time monitoring of NO_3 with MBIER.

2) Golden Triangle and Sidney

- a) Comparison of standard soil NO_3 test and saturated paste MBIER NO_3 ;
- b) relationship between total spring wheat N and saturated paste MBIER NO_3 under varying N fertilizer rates.

CHAPTER 2

LITERATURE REVIEW

This study involves several basic concepts of soil science. Dynamics of N fertilizers in soils is of utmost importance to development of appropriate management practices. Solute transfer, adsorption of ions by soil solids, diffusion (as it affects N availability), and various aspects of measuring nutrient availability (sampling, testing, etc.) are additional concepts that are involved. Each of these topics are briefly reviewed here.

Sampling and Testing for Nitrate in Soils

Nitrogen fertilizer applied to agricultural land is a growing concern due to potential groundwater contamination and health risks associated with NO_3 levels in the groundwater (Torbert and Elkins, 1992). On the other hand, application of N fertilizers has been shown to have many highly important environmental benefits, such as increased crop cover and decreased soil erosion. Applying N to more productive land allows less suitable crop land to be removed from production or not cultivated at all. The economic impact of crop response to N fertilizer is of utmost importance to the farmer, and a careful balance must be found between adopting management practices that reduce the potential for NO_3 leaching and rates that do not allow economic crop yields (Schnabel et al., 1993). For this reason, it

is necessary to have an accurate, cost effective, and simple method for measuring NO_3 flux through the soil profile (Barbee and Brown, 1986; Schnabel et al., 1993).

Techniques for Measuring Nitrate Movement in Soils

Techniques used to measure NO_3 leaching in the soil profile include 1) porous cup soil solution samplers, 2) zero-tension lysimeters (pan or free-drainage samplers), and 3) direct soil sampling (Barbee and Brown, 1986; Haines et al., 1982; Hansen and Harris, 1975; Torbert and Elkins, 1992). Each methodology has serious limitations that prevent any one of them to be used across a broad range of environmental studies.

Porous cup soil solution samplers are useful for sampling and evaluating soil water held under low tension in the soil matrix (Jemison and Fox, 1992). Disadvantages include 1) the soil must be quite moist for the sampler to collect enough soil solution for analysis; 2) it is difficult to collect enough soil solution for analysis even at low hydraulic potentials in clay soils (Li et al., 1993); 3) the porous cup may become plugged, thereby influencing the intake rate (Hansen and Harris, 1975; 4) in structured soils the sampler may be circumvented by channeling of water and chemicals (Shaffer et al., 1979; Shufford et al., 1977); 5) applying suction can cause higher seepage rates compared to free drainage rates; 6) suction can cause lowered pressure resulting in degassing with resultant pH and solubility changes (van der Ploeg and Beese, 1977); 7) new porous cup samplers tested in solution show a wide range of intake rates (Hansen and Harris, 1975); 8) error is introduced due to estimation of the water flux values and interpolation of ion movement between sampling (Schnabel et al., 1993); 9) solution extraction must be continuous for continuous sampling

in a dynamic system (Barbee and Brown, 1986; Li et al., 1993); and 10) the volume of the soil sampled is not known (Carlyle and Malcolm, 1986).

Pan samplers have the advantage of collecting the total volume of soil solution being leached through the soil profile (Schnabel et al., 1993). Disadvantages of zero tension samplers include: 1) low collection efficiency (Jemison and Fox, 1992; Russel and Ewel, 1985); 2) flow of the soil solution may be diverted due to textural changes, such as a sand lens in a fine textured soil (Jemison and Fox, 1992); 3) installation and maintenance costs are high (Schnabel et al., 1993); and 4) the soil profile and its environment are generally highly disturbed during installation.

The greatest advantage to direct soil sampling is the amount of research that has been completed using this methodology for sampling, nevertheless this does not make it the best method to use in environmental testing. Disadvantages of direct soil sampling include: 1) destructive sampling, meaning that the point can only be sampled once; 2) the data are a "snapshot" of the soil system; 3) water flux must be estimated; and 4) interpolation of data between samples introduces error, especially if water movement has occurred since the last sampling. Knowing that these sampling methodologies are suspect in measuring ion movement in the environment, another method must be found for measuring ion movement in the soil profile (Carlyle and Malcolm, 1986), especially where NO_3 is concerned.

An alternative methodology that eliminates most of these limitations is based on resin capsules. Mixed-bed ion exchange resins (MBIER) can serve as a continuous sink for ions in the soil solution to indicate quantities present as soluble ions as well as their movement due to diffusion or water transfer toward the resin (Lajtha, 1988; Skogley et al.,

1990; Somasiri and Edwards, 1992; Li et al., 1993). When the MBIER is introduced to the soil system, amounts of ions initially adsorbed relate closely to soil solution concentrations, giving a direct indication of ions that could be transferred by mass flow. With extended time, capsule results indicate ion diffusion relationships (if no water is moving), or a combination of mass flow and diffusion (if water is moving). Sensitivity to these processes that regulate ion availability to plants provides a methodology that can be developed to provide a better prediction of nutrient dynamics during plant growth (Binkley, 1984; Skogley et al., 1990). In addition, MBIER can be placed at multiple depths within and below the plant rooting zone to provide three-dimensional data on NO_3 transfer. Due to its negative charge, NO_3 will move with soil water. It will, however, remain plant available as long as it does not leach below the crop rooting zone. Once it reaches this depth, it is generally on a one-way trip to the groundwater. Using MBIER as a sampling method for measuring ion movement in the soil would eliminate the need to estimate water flux, because the samples would be collected at the same point over time (Schnabel, 1983; Schnabel et al., 1993), giving a direct measure of ion transfer at that point.

Nitrate movement in the soil is mostly due to mass flow and does not follow diffusion isotherms (Binkley, 1984; Yang and Skogley, 1992). Binkley and Matson, 1983, indicated that ion exchange resins demonstrated a sensitivity to on-site factors that other methods do not measure. Bromide has been used as a tracer for anion movement in soils in many studies. Smith and Davis, 1974, showed that "Br has utility for following the potential path of NO_3 movement through soils." Differences in the movement of the two ions can be attributed to microbial activity involving NO_3 (Smith and Davis, 1974) and plant uptake of

Br (Li et al., 1993). Li et al., 1993, indicated that the quantity of Br accumulated on MBIER were a function of sampling duration, water and Br movement, water content near the capsule, and Br plant uptake. From their results they reported that "resin capsule technology may provide an alternative (*in situ* solid-phase-extraction) to the vacuum extraction method for measuring Br transport under conditions of unsaturated flow."

Soil Testing

Soil testing is a prerequisite to a good soil fertility program (Brusko, 1992; Francis et al., 1987; Granatstein and Bezdicsek, 1992). Soil tests have been developed during the past several decades to provide a basis for predicting crop nutrient needs for specific fields. These tests are based on chemical extraction of nutrients from soil samples that have been greatly modified from natural conditions. Results from this type of test are useful only when accompanied by results from field experiments that provide correlation and calibration data to validate the approach. Unfortunately, little has been done over the past couple decades to provide field correlation results for new cropping systems and changes in soil fertility status. An accurate soil test must be able to test for the plant nutrients that are available to the plant (Karlen and Sharpley, 1994). This would also help to develop a sustainable soil fertility program that minimizes nonpoint pollution from fields (Karlen and Sharpley, 1994). Chase et al. (1991) suggested using the "sufficiency approach," where fertilizers should not be used if the soil test level of nutrients is above a predetermined level. This is a very simple approach to the problem and would not allow for appropriate N management in most instances.

Current soil tests reveal little about the complex chemical, biological, and physical interactions of various nutrients in the soil (Granatstein and Bezdicek, 1992). Research results indicate, however, that the resin capsule methodology provides the basis for development of a soil test to assist in achieving sustainable soil fertility, while supplying appropriate amounts of all essential nutrients at the proper time during the plant growth cycle (Karlen and Sharpley, 1994; Skogley, 1994; Dobermann et al., 1994).

It is clear that there is a large window of opportunity to improve the soil test foundation on which to base a sustainable agriculture system. Improved methods for laboratory soil testing must be developed, and additional research must be conducted *in situ* to understand the variety of chemical, biological, and physical factors of the soil system. The basic concepts on which the MBIER system is based include ion adsorption and exchange. The following review is presented to provide a historical view of these concepts.

Absorption

The first indications of chemical adsorption by soils were reported as absorption phenomena. In his paper presented to the Royal Society, Way (1850) mentioned several anecdotes relating to the absorptive power of sand or soil. Salt was removed from sea water during Lord Bacon's lifetime by digging a hole starting above the high water mark to a depth below the low water mark. The hole then filled with fresh water when the water raised due to the tide. Dr. Stephen Hales in 1739 had reported to the Royal Society that the first pint of water filtered through a stone cistern was like pure water. Berzelius found that solutions of salt filtered through sand were free of salinity. Professor Matteucci filtered a salt solution

through sand several times and found that for each successive time the salt solution became less concentrated. About 1848 a Mr. Huxtable stated to Mr. Way that he filtered liquid manure through a loam soil. After passage through the soil the liquid manure effluent was clear and no longer smelled. At about the same time a Mr. Anderson told Mr. Way that soil had the ability to separate ammonia from solution. Way himself (1852) found that soil had the ability to separate from solution the different earthy and alkaline metals in manure, reporting that when solution containing salts of ammonia, potash, and magnesia were first filtered through soil five or six inches deep, the effluent no longer contained the salts. He further stated that the power of soil to absorb the salt was not extended to the whole salt, but only to the alkali itself. Way (1852) further stated that the absorbent power of the soil did not exist in sand or organic matter, but only in the clay fraction of the soil.

To further his knowledge of the process, Way manufactured "double silicates of soda, lime, and potash." He added a solution of ammonia salts to the manufactured "double silicates" and found that the ammonia replaced the bases of soda, lime, and potash. He went on to show that water made acid with carbon dioxide and dissolved the ammonia from the "double silicate" in a quantity much greater than did pure water.

These findings provided the beginning of understanding for the phenomenon of cation exchange capacity of soil clays, but about 50 years passed before more significant work was reported on the ability of soil to absorb ions.

In 1905, Cameron and Bell defined absorption as "the phenomenon of the difference existing between the concentration or density of the liquid film adjacent to a bounding medium and the concentration or density of the mass of the liquid," and they defined

absorption as a selective process, i.e., "the solid material has the power of preferring some substances to others."

Cameron and Bell (1905) reported that a number of experiments had been tried using different dyes on soils. Methylene blue was completely retained by the soil, while eosine could be removed by washing. It was also noted that various soils had a definite absorption limit, in that when the dye was filtered slowly through the soil, it would eventually cease removing the dye from solution. They also stated that certain dyes may be held so tightly by the soil that a large amount of the dye could not be removed with water, but could be washed out with a different absorbent material.

Cameron and Bell (1905) concluded that: 1) colloidal substances have the power of absorption, 2) the soil solution is physiologically of the greatest importance as it is the source of plant nutrients, 3) the base carrying minerals are generally true salts that readily dissolve in water, 4) that the salts that dissolved in water and are readily absorbed by soils are prominent fertilizer constituents, and 5) that "the chemistry of the soil is not the ordinary chemistry of the beaker."

Cameron and Patten (1906-1907) reported different absorptive capacities for different solutes. Somewhat later, Miyake (1916) reported that other chlorides decreased the absorption of ammonia from ammonium chloride solution.

By 1917, McBeth stated that it is well known that a soil's ability to act as a reservoir for plant nutrition depended in part on its ability to absorb such substances as potash, phosphoric acid, and ammonia against leaching. The fixation of ammonia was rapid for the first few minutes, but the process of fixation was not complete after 96 hours. Results of

other experiments performed by McBeth indicated that Ca, Mg, or Na salts added to semiarid soils prior to adding ammonia had little effect on the ability of the soil to fix ammonia, but the addition of Al, Fe, or K salts prior to adding ammonia to the soil decreased the soil's ability to fix ammonia. McBeth (1917) also concluded that anions had little or no influence on the soil's ability to fix ammonia.

Up until the 1920s, the general school of thought was that 95% of the absorptive capacity of the soil was due to organic matter and soil colloids (called zeolites) that were made up of inorganic gels (Anderson et al., 1922; Kerr, 1928). In highly micaceous soil the noncolloidal absorption was reported to reach 10 to 20% of the total absorption. Anderson et al. (1922), used a centrifuge to separate the colloidal material or "ultra clay" from the rest of the soil constituents, and Whitney (1921) showed that "ultra clay" had absorptive capacities two to twenty times higher than the original soil. Anderson et al. (1922) were the first to indicate that the ability of colloidal material to absorb ions was probably due to its different structure than that of the rest of the soil constituents.

Hissink (1923) was one of the first to use acid to remove all of the bases and a base salt for exchangeable bases. He reported that part of the bases occur in the clay-humus complex in a replaceable or exchangeable form, and they could be leached with a solution of salts that contained one of the bases.

Because the exchange process happens quickly, Hissink (1923) reasoned that the bases must be on the surface of the clay-humic complex. This led him to conclude that the bases are adsorbed instead of absorbed. This is the first reference stating that soil colloids adsorb ions, and research on this process expanded rapidly thereafter.

Adsorption

Hans Jenny (1936) was the first researcher to introduce a simple model for ion exchange at the surface of soil colloids, stating that Na ions "wander at random as a consequence of Brownian movement." He further stated:

"Now, if it so happens that by chance a migrating sodium ion slips between the wall and an oscillating potassium ion which has momentarily moved away from the surface, an exchange reaction will occur. The positive sodium ion is electrically attracted by the negative wall, and the potassium ion is left in the solution or even pushed into it by the electrical repulsion forces of the sodium ion."

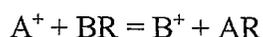
An important contribution of Jenny's work was that the proposed mechanism of adsorption of cations or anions could not happen without equivalent release of a corresponding surface ion.

Selectivity of ion exchange was first introduced by Bray (1942), stating that "In as far as one exchangeable cation has a greater ease of release than another it will be present in the intermicellar water layer in proportions relative to the amount of each present." He suggested that cations in soil solution are influenced by their ease of release from the soil exchange complex.

Diffusion

Ion diffusion is known to be a major process controlling the availability of nutrients at the plant root surface (Barber, 1962). The sensitivity of ion exchange resins to diffusion is one of the major benefits in using them for soil testing (Skogley and Dobermann, 1996). In this regard, however, it is critical that ion diffusion within the resin bead itself must not

be rate-limiting, allowing ion diffusion through the soil to be measured. For example, the diffusional process for two monovalent ions can be represented by the law of conservation of mass, as follows:



where A and B are cations and R is an anion associated with the cation in solution. Boyd et al. (1947) reported that the rate of ion exchange adsorption of alkaline metal cations by resin are diffusion controlled processes. They showed that diffusion in the solution surrounding the resin bead was rate-limiting (rather than diffusion within the resin) when concentrations were weak (as in soil solutions). This was verified for soil-resin systems by Yang and Skogley (1992).

Nye (1979) reported that ion diffusion could even occur within a crystal lattice. Ions in the lattice do not readily exchange, due to the ionic bonding, but they can diffuse through the lattice if a vacancy exists in the lattice structure, and the ion encounters high activation. In such cases, an ion can diffuse along fracture planes within the crystal.

Jardine and Sparks (1984) suggested three distinct kinds of diffusion in soils. The first is intraparticle diffusion, described as the "transport of the adsorbing ion through the liquid associated with difficultly accessible exchange sites of the soil." Surface diffusion is "the movement of the adsorbing ion along the walls of the difficultly accessible spaces", and film diffusion is "the transport of the adsorbing ion through the static liquid film that surrounds the constituents of the soil." Accumulation of ions by resins placed in soils has

been shown to be well represented by various equations used to describe ion diffusion to plant roots (Yang, et al., 1990; Yang and Skogley, 1992).

Resin Capsule Methodology

There are different methodologies for using resins as a soil test medium (Skogley and Dobermann, 1996). The most commonly used resin methodologies are batch, membrane, bag, and encapsulated. Each of these methodologies have limitations for use in soil testing.

The batch method involves mixing a certain mass of soil and resin in excess water and shaking the mixture for a period of time. Using the batch method, van Raij et al., 1986, reported that simultaneous extraction of P, K, Ca, and Mg was possible with ion-exchange resins. A major problem with the batch system is the separation of resin beads from the soil suspension (van Raij, 1994). The theoretical limitation of batch methods is that they do not provide ions an opportunity to diffuse to the resins (Skogley and Dobermann, 1996), so the contribution of this important phenomenon to ion availability is not measured. Another limitation of the batch method is that it is not adaptable for use in *in situ* solid phase extraction studies.

The resin membrane method for soil testing consists of placing sheets of membrane in the soil, which simplifies the problem of separating the resin from the soil. The major problem with membranes is their limited adsorption capacity with respect to the soils ability to supply nutrients to the membrane (Bernardo et al., 1985; Kawate et al., 1991).

Sibbesen, 1977, put ion-exchange resins in a porous polyester bag to facilitate separation of resins from the soil after shaking. Binkley and Matson, 1983, first used the bag

method for an *in situ* study of soil N. These hand-made bags, however, generally do not have a constant, uniform surface area exposed to the medium being tested. A variation in surface contact between the resin and soil may cause errors in values obtained because ion adsorption is directly related to area of contact.

Based on personal studies dating from 1957, plus related research by others, Dr. Skogley began detailed research to develop the encapsulated resin method in 1988. The process for encapsulation and methods of using capsules were patented in 1994 (personal communication). When the encapsulated resin method is used in the laboratory for soil testing the method is called The Phytoavailability Soil Test (PST). The PST methodology is based on the hypothesis that a uniformly shaped and sized capsule of mixed-bed cation/anion exchange resin placed in direct contact with the soil solution will accumulate ions from the soil by exchange processes similar to those of living roots (Skogley et al., 1990; Yang et al., 1991a).

The PST addresses the major problems with the batch, bag, and membrane methodologies of soil testing. The currently used capsule has a uniform, spherical, total surface area of 11.4 cm² and is filled with a 1:1 mixture of strongly acidic cationic (H⁺) and strongly basic anionic (OH⁻). H and OH are counterions that exchange with other ions in the soil solution. Exchange capacity of the capsule is 2.2 meq of cationic and anionic exchange capacity (Dobermann et al., 1995). The exchange capacity is large enough to act as an ion sink for long periods of time in soil. The capsule design allows for ease of handling during use and analysis.

CHAPTER 3

MATERIALS AND METHODS

Objectives of this research relate to improving and simplifying methods for detecting NO_3 in soils, and in particular to follow its movement. Another objective was to relate mint stem NO_3 to MBIER adsorbed NO_3 . To minimize costs, we arranged cooperation with several researchers who were already conducting projects involving N fertilizer management, both under irrigation and dryland, and for different crops. Each of these projects differed, so we describe major aspects of each one, along with specific activities included for our study.

Creston

Field experiments were conducted during 1993 and 1994 seasons at the Northwest Agricultural Experiment Station, at Creston, MT, on the Flathead soil series, (coarse-loamy, mixed, Pachic Udic Haploboroll). The experiment was designed to study fertility and irrigation management of Peppermint (*Piper mentha* cv. Black Mitcham) under direction of Dr. Mal Wescott, Professor of Soil Science, Western Agricultural Research Center, Montana State University. Rootstock of 'Black Mitcham' peppermint was planted in April of 1992. Five N management (rate and timing) treatments and one Br treatment were included. Urea was the form of N fertilizer used, and the experimental design for the N treatments was a

randomized complete block. Br was included in the study to provide an independent measure of anion movement, and was surface-applied as a solution of KBr at a rate equivalent to 112 kg Br ha⁻¹. Initial fertilization was applied as urea prills and incremental treatments were applied as a urea solution. Three N treatments were applied incrementally, while one treatment was applied as the total N rate at the beginning of the growing season, the fifth treatment was a control or 0 kg N ha⁻¹ (Table 1). Br was applied as a total rate the first week of each field season, and within one day of the N treatments. In 1993 incremental treatments involved applying 6.5% of the total amount of N the week immediately prior to the first irrigation. The balance of the total N was applied in six equal weekly treatments immediately prior to irrigation. In 1994 the treatments were the same except that all N was applied as six equal treatments immediately prior to each irrigation.

Table 1. Nitrogen and Br treatments in the fertility and leaching study at Northwest Agricultural Research Center, 1993 and 1994 field seasons.

N rate (kg ha ⁻¹)	Application procedure to reach the total	Sampling method using resins ¹
0 (control)	none	<i>in situ</i> and saturated paste
134.5	incremental	<i>in situ</i> and saturated paste
403.5	total	<i>in situ</i>
403.5	incremental	<i>in situ</i>
672.6	incremental	<i>in situ</i>
Br rate (kg ha ⁻¹)		
112.1	total	<i>in situ</i>

¹ The *in situ* and saturated paste methods of sampling are described in the materials and methods section.

Our component of this study involved use of resin capsules as ion adsorbers to compare with standard measures. Resin capsules contained Amberlite IRN-150^{®1} (Rohm and Haas Co., Philadelphia, PA), a 1:1 mixture of strongly acid cationic and strongly basic anionic resin, initially saturated with H⁺ and OH⁻ (UNIBEST, Inc., Bozeman, Mt). The capsule is a 19 mm diameter sphere, making it large enough to handle easily and with enough MBIER to function as an effectively infinite sink for ions in a soil system. Using the scheme developed by Skogley and Dobermann (1996), all resin studies in this thesis are classified as I.L.D.U.m.c.-H/OH.

Irrigation was supplied by a line source system with 0.6 m risers spaced at 6.1 m along the line. Two irrigation timings and two irrigation levels were selected for use in the *in situ* MBIER study. Irrigation levels were determined by the distance from the line source. The medium level was 6.1 m from the line source and the low level was 10.7 m from the line source. The target amount of water from irrigation and precipitation was 51 mm per week at the medium level (Table 2). Irrigation timing was either once or twice per week.

Precipitation records are weekly totals, meaning that all of the precipitation for a one week period are added together (Table 2). Precipitation records were done in the same manner for both 1993 and 1994. Records for 1993 started on June 13 and continued to the last week of the field season, which ended on August 6. For the 1994 growing season, records were kept from June 19 to July 30, the last week of the field season.

¹ Mention of a specific brand, trade, or chemical name does not imply endorsement of that product over others of a similar nature or function.

Table 2. Irrigation and precipitation for peppermint experiment, 1993 and 1994 field seasons.

Date		Irr. timing	Medium (mm)		Low (mm)		Precipitation (mm)	
1993	1994		1993	1994	1993	1994	1993	1994
6/15	6/21	1	8	51	2	25	6/13-6/19	6/19-6/25
		2	7	24	1	11	26.70	10.16
6/23	6/24	1	30	0	14	0	6/20-6/26	
		2	7	27	1	17	19.80	
6/25	6/28	1	0	40	0	19	6/26-7/2	
		2	18	16	3	8	0	
6/29	7/1	1	43	0	9	0	6/27-7/3	
		2	18	26	4	18	38.10	
7/2	7/5	1	0	50	0	27	7/3-7/9	
		2	11	26	4	11	0	
7/6	7/8	1	0	0	0	0	7/4-7/10	
		2	0	25	0	20	98.30	
7/9	7/12	1	0	50	0	25	7/10-7/16	
		2	0	25	0	17	0	
7/13	7/15	1	38	0	22	0	7/11-7/17	
		2	14	26	6	17	13.46	
7/16	7/19	1	0	50	0	30	7/17-7/23	
		2	16	25	4	15	0	
7/21	7/22	1	22	0	10	0	7/18-7/24	
		2	0	25	0	19	33.78	
7/23	7/26	1	0	51	0	30	7/24-7/30	
		2	23	26	9	16	0	
7/27		1	34		18		7/25-7/31	
		2	9		4		14.73	
7/30		1	0		0			
		2	25		9			
8/3		1	50		30		8/1-8/6	
		2	26		16		2.03	
8/6		1	0		0			
		2	25		12			
Total		1	225	293	104	156	246.89	10.16
		2	196	273	75	169		

Table 3 summarizes the total amount of water (irrigation plus precipitation) for the 1993 and 1994 field seasons.

Table 3. Total water applied (irrigation+precipitation) to the peppermint plots for 1993 and 1994 field seasons.

Irr. Timing	Total water applied (mm)			
	Medium		Low	
	1993	1994	1993	1994
1	472	303	351	166
2	443	283	322	179

Access tubes for resin capsule insertion and retrieval were placed at three depths (0.15, 0.61, and 1.22 m) in each of three replications of plots selected for the *in situ* resin study. Five N treatments were compared at 0.15 m depth, but only three were studied at the 0.61 and 1.22 m depths. Two sampling methods were compared, these being 'field fresh' soil cores made into saturated paste and *in situ* sampling with encapsulated MBIER.

Each fall prior to the study year (October 1992 and 1993), plots were fertilized with 24.7 kg N, 51.3 kg P, and 139.6 kg K ha⁻¹. In October 1993, an additional 49.3 to 71.7 kg S ha⁻¹ was applied through fertigation. Weed control during 1993 involved use of Sinbar®, Basagran®, and Assure II®, and for 1994 Sinbar®, Poast®, and Basagran® were used. Installation of access tubes for the MBIER study took place in June 1993, before the growing season N-treatments were applied, and the same tubes were used for studies both years.

Access tubes were polyvinyl chloride (PVC, 38 mm OD) pipe cut to length and installed after boring holes with a pickup-mounted hydraulic soil sampler. Tubes were

placed at a 30° angle from vertical so that the tube would not interfere with vertical transport of ions. Soil was removed from about 50 mm beyond the lower end of the access tube, and a cavity made to accommodate the size and shape of the resin capsule. A smaller PVC tube (19 mm ID), with a capsule held in place at its end, was inserted into the access tube. Capsules were held in place by hooking a barbless fishhook attached to carpet thread, and running the thread through the insertion tube where it was held in place by a rubber stopper. The access system was covered with a PVC cap to prevent entrance of water. Sampling was done by uncapping, removing the insertion tube, and exchanging the used resin capsule with a fresh capsule. At the time of changing capsules, soil samples were collected from the 0.15 m soil depth. Sampling interval was seven days throughout both growing seasons, with the exception of a 12-day period for the first sampling in 1994. After retrieval, capsules were rinsed with distilled water to remove any adhering soil particles and placed individually in 5-ml snap-cap cups. They were then frozen and packed in dry ice for shipping to the laboratory in Bozeman, MT. Soil cores taken for saturated paste studies were immediately mixed with distilled water, divided into three portions, and each portion placed in 60 ml containers. A resin capsule was inserted into the center of each soil paste. The three capsules, for the 1993 growing season, were allowed to sit at room temperature for either 24, 96, or 168 h (2, 4, and 7 days). After the prescribed time period, capsules were removed from the paste, rinsed thoroughly with distilled water, and handled the same as the *in situ* capsules. During the 1994 growing season, only the 24 h capsule adsorption period was used.

Plant N data were collected using an ion specific electrode procedure by Dr. Mal Westcott. These data were regressed against the MBIER data. Data were analyzed using Quattro Pro, version 5.00, Borland International, for calculation of the Standard Error of the Mean (SEM). The results were graphed using Sigma Plot, version 1.02, Jandel Corporation.

Golden Triangle

Three N fertility experiments, conducted by Dr. Grant Jackson, Soil Scientist, Western Triangle Agricultural Research Center, Montana State University, were included in this study. Specific locations, all in Montana, were: 1) east of Ledger on the Bob Inabnit farm, 2) northeast of Loma on the farm of Lyle McKeever, and 3) southwest of Fort Benton on the Ron Long farm. At Ledger the soil was the Joplin series (fine-loamy, mixed, Aridic Argiboroll); at Loma the Scobey series (fine, montmorillonitic, Aridic Argiboroll); and at Fort Benton the Vida series (fine-loamy, mixed, Typic Argiboroll) in 1993 and the Bearpaw series (fine, montmorillonitic, Typic Argiboroll) in 1994.

The experimental design was a randomized complete block. The 1993 Ledger and Fort Benton plots were planted with a plot drill with 0.15 m row spacing. The Loma plot was planted by the farmer using the same row spacing. Plots were planted with Amidon spring wheat (*Triticum aestivum* L. EM. thell.) into no-till recrop at the Ledger and Fort Benton sites, and variety Newana at the Loma site. Amidon spring wheat was planted at all three locations in 1994, using a plot drill adjusted to 0.15 by 0.36 m paired rows.

Rates of N were the same for all experimental plots in 1993 and 1994, except at Loma (Table 4). A blanket application of 24 P- 33.6 K- 31.4 Cl (kg ha^{-1}) was added during

or before seeding for the 1993 growing season. The KCl fertilizer was broadcast in front of the drill openers and the P fertilizer placed with the seed at the Ledger and Fort Benton sites. All fertilizers were broadcast prior to seeding in 1993 at the Loma site. At all locations in 1994 P was placed with the seed and other fertilizers were banded at a depth of 0.05 m between paired rows. Blanket applications of P-K-Cl were different for each plot, and were as follows (kg ha^{-1}): 1) Ledger, 12.2-33.6-30.3, 2) Loma, 9.7-22.4-20.2, and 3) Fort Benton, 9.7-33.6-30.3.

Roundup® was used on stubble for weed control at the Ledger site in 1993, but no weed control measures were used for 1994. Bronate® was used at the Loma site to control broadleaf weeds both years and Hoelon® was used as needed to control wildoats (*Avena loci*). At the Fort Benton site Roundup® was used both years.

Table 4. Nitrogen rates applied on Golden Triangle field experiments, 1993 and 1994.

Location	Year	N-treatment (kg ha^{-1})
All	1993	0, 56.0, 112.1, and 168.1
Loma	1994	0, 33.6, 67.3, and 100.9
Ledger and Ft. Benton	1994	0, 56.0, 112.1, and 168.1

Soil sampling was done in 1993 with an Oakfield® step sampler and with a 'King tube' in 1994. The dry growing season during 1994 (Table 5) caused very hard soil conditions that did not allow sampling with the step sampler. In each plot at Ledger and Loma, eight core samples were taken to 0.15 m depth and four at 0.15 to 0.61 m depth. Cores were combined to obtain a representative subsample of the soil. Due to rockiness at the Fort Benton site, samples were collected only to 0.15 m. Samples were collected at two

times during the growing season each year. Immediately after collection, soil samples were placed in plastic-lined paper bags and kept in a cooler with dry ice for transporting to the laboratory to maintain field-fresh condition. Upon arrival at the laboratory, each sample was divided into two portions. One portion was made into a saturated paste for resin capsule analysis and the other portion oven-dried at 50° C for standard analysis.

For resin capsule analysis, three portions of saturated paste (50-60 ml each) were placed in separate cups and a capsule inserted into each one. One capsule was removed after either 2, 4, or 7 days, rinsed in distilled deionized water, and analyzed for NO₃. Soil that had been dried was ground and sieved to < 2 mm for standard testing of extractable NO₃.

Table 5. Precipitation during 1993 and 1994 growing seasons at Golden Triangle sites.

Location	Year	Precipitation (mm)
Ledger	1993	274
	1994	32
Loma	1993	290
	1994	112
Fort Benton	1993	212
	1994	124

Plant samples were collected from the same soil areas at the time of soil sampling. Plant samples included the entire above-ground portion and were collected at approximately the three to four leaf stage and again prior to maturity. To allow estimation of plant uptake of N, the sampling area was measured. Plants were dried at 50° C, weighed, ground, and

combined. A subsample of the combined material was analyzed for total N. MSUSTAT 5.1 (Lund, 1992), was used to analyze data using ANOVA with means separation by LSD.

Sidney

A N fertility project conducted at the Eastern Agricultural Research Center, under the direction of Dr. Joyce L.A. Eckhoff, Research Agronomist, was also included in this study. Three rates of N (124.5, 166, and 207.5 kg ha⁻¹) were applied on April 13, 1993, prior to planting sugar beets (*Beta vulgaris* cv. Monohikari) on April 23, 1993. The experimental soil was the Farnuf series, (fine-loamy, mixed, Typic Argiboroll) in 1993 and the Savage series, (fine, montmorillonitic, Typic Argiboroll) in 1994. Fertilizer N was applied as 18-46-0 on September 22, 1993 at the rate of 40.4 kg N ha⁻¹, with the remainder applied as liquid, 28-0-0 on October 27, 1993 for a total of 84.9, 113.2, and 141.5 kg N ha⁻¹. Sugar beets, cv. Monohikari, were planted on May 5, 1994.

Petiole samples were collected at various times by Dr. Joyce Eckhoff and analyzed for NO₃ by Holly Sugar Corporation. These data were used for comparison with results of soil analyses of samples collected at three times during the growing season. Soils were collected from three depths (0 to 0.15, 0.15 to 0.61, and 0.61 to 1.22 m) using a tractor-mounted hydraulic core sampler. At least two soil cores per sample were combined, and the samples handled in the same manner as those from the Golden Triangle.

Desorbing the MBIER

Resin capsules were desorbed using 2 N HCl or 2 N H₂SO₄. Each MBIER capsule was placed in the mouth of a 60 ml widemouthed plastic bottle under a drip tube fed by a

peristaltic pump. Acid was metered at a rate 1 ml per minute for 50 minutes, which has been shown to remove nearly 100% of adsorbed NO_3 . The desorption solution serves as the analyte for all target elements, and was capped and stored at room temperature until analysis.

Resin capsules from the peppermint study at Creston were stripped using H_2SO_4 so that Br could be analyzed by ion-selective electrode, in which case Cl would interfere. Br analysis of stripping solutions was conducted by Dr. Jon Wraith who shared the data for use in this thesis.

Analysis of Desorbing Solution

Cadmium (Cd) reduction colorimetric procedure, developed by Doner et al. (1973) and West and Ramachandran (1966), was used to analyze NO_3 . Modifications for resin solution analysis include neutralization of an aliquot with 2 N NaOH to raise the pH to about 10, which is required for color development. If needed, the sample is diluted with deionized water to within the analytical range. A standard curve (in the 0 to 8 ppm range) was made using reagent grade KNO_3 , with either 2 N HCl or H_2SO_4 as the background, depending on the samples being analyzed. Nitrate analysis was done with a Technicon Autoanalyzer.

Standard Soil Nitrate

The method developed by Sims and Jackson (1971) and the solution described by Doner et al. (1973) and West and Ramachandran (1966) were used for soil NO_3 analysis, using the same standard curve range as that for analysis of the MBIER desorbing solution.

Spring Wheat Analysis for Total N

Total N in plant samples was determined using the procedure developed by Cataldo et al. (1974), in which heat and 30% H₂O₂ are used to digest plant material. A colorimetric procedure developed by Nelson and Sommers (1973) was used to analyze for total N by measuring % transmittance in a Spectronic 21 after color development.

CHAPTER 4

RESULTS AND DISCUSSION FOR CRESTON

With environmental laws and public opinion getting stronger about non-point source pollution, agricultural practices are under increasingly close scrutiny. The main objective of research at Northwestern Agricultural Research Center was to monitor NO_3 and Br movement in the soil profile. This was to determine sensitivity of the MBIER to monitor NO_3 under varying environmental conditions and to further determine if Br was a good conservative tracer in a 'natural system' with urea fertilizer as the N source. A natural system was maintained by using access tubes installed at an angle so they would not interfere with normal vertical movement of solutes. This also allowed repeated point sampling over time and provided a continuous record of NO_3 and Br in the soil system. The field site was ideal for monitoring the movement of NO_3 and Br, due to high N and high water applications used to grow peppermint.

Irrigation Effects

Data used for NO_3 and Br accumulation have units of μg (NO_3 or Br) capsule⁻¹ day⁻¹. The first sampling with capsules for 1993 was seven days from the date of the initial N treatment, while for 1994 it occurred 12 days later. To account for this difference, data were converted to a daily basis by dividing the total uptake per capsule by the number of days

