



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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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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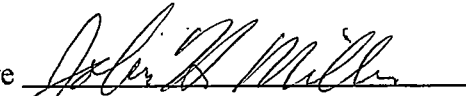
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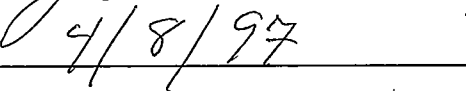
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VITA

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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 NO_3 . 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 NO_3 . Br breakthrough curves (BTC) generally occurred one to two weeks earlier than NO_3 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 NO_3 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 NO_3 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 NO_3 remained unchanged after two days in Golden Triangle soils, probably due to low quantities of available NO_3 . When compared to 1993, spring wheat concentration of N and soil NO_3 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 NO_3 continued to be adsorbed to the resin capsule for seven days, probably due to higher initial soil concentrations of NO_3 . 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.

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 Bezdicsek, 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."

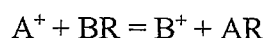
An important contribution of Jenny's work was that the proposed mechanism of adsorption of cations or anions could not happen without equivalent release of a corresponding surface ion.

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

between capsule insertion and retrieval. Based on these data, there was no difference in NO_3 adsorption due to irrigation treatments for 1993 (Table 6) at the 0.15 m sampling depth. This may have been due to the exceptionally wet growing season in 1993, when 164 mm more rainfall occurred than during 1994 (Table 4). This excess rainfall may have eliminated differences in amounts of solutes moving to and beyond the sampling depth, regardless of quantity of irrigation water applied. During the drier 1994 season, there were differences in NO_3 accumulation by capsules, within some N treatments, due to irrigation timing and level (Table 7). No differences occurred due to irrigation during 1994 for the single application of $403.5 \text{ kg N ha}^{-1}$, but irrigation timing did cause a difference at the 0.15 m depth (Table 8).

Table 6. Quantities of NO_3 in MBIER capsules from *in situ* measurement as influenced by irrigation timing and levels for 1993 and 1994 at all depths.

Year	Irr. timing	n	$\mu\text{g cap}^{-1} \text{ d}^{-1}$	Difference ¹	Irr. level	n	$\mu\text{g cap}^{-1} \text{ d}^{-1}$	Difference ¹	
1993	1 wk ⁻¹	486	93.21	A	low	486	93.26	A	
	2 wk ⁻¹	486	85.40	A	medium	486	85.35	A	
			LSD = 48.86				LSD = 44.09		
1994	1 wk ⁻¹	270	52.09	A	low	270	28.60	A	
	2 wk ⁻¹	270	22.53	A	medium	270	46.03	A	
			LSD = 42.89				LSD = 36.22		

¹ Different letters indicate significant differences based on LSD @ $p \leq 0.05$.

Table 7. Quantities of NO₃ in MBIER from *in situ* measurements for each treatment as influenced by irrigation timing and levels for 1994 at 0.15 m depth.

Treatment kg N ha ⁻¹	Irr. timing	n	µg cap ⁻¹ d ⁻¹	Difference ¹	Irr. level	n	µg cap ⁻¹ d ⁻¹	Difference ¹
403.5 incremental	1 wk ⁻¹	90	32.93	A				
	2 wk ⁻¹	90	16.25	B				
LSD = 8.28								
672.6 incremental	1 wk ⁻¹	90	39.14	A	low	90	19.25	A
	2 wk ⁻¹	90	20.31	B	medium	90	40.19	B
LSD = 17.73				LSD = 14.43				

¹ Different letters indicate significant differences based on LSD @ $p \leq 0.05$.

Table 8. Quantities of NO₃ in MBIER from *in situ* measurements, across all treatments at the 0.15 m depth, during 1994.

Irr. timing	n	µg cap ⁻¹ d ⁻¹	Difference ¹
1 wk ⁻¹	90	55.57	A
2 wk ⁻¹	90	22.77	B
LSD = 24.73			

¹ Different letters indicate significant differences based on LSD @ $p \leq 0.05$.

Soil Water Content

Soil water content data were collected with a neutron probe, and analyzed, by Dr. Jon Wraith. Because the neutron probe data were collected the same day the MBIERs were changed, capsule data was expressed as µg NO₃ capsule⁻¹ (with no requirement for conversion to a daily basis). Soil water content data from only the twice week⁻¹ (medium irrigation regime) are presented (Figures 1 through 4), as this represents what occurred for each irrigation and nitrogen treatment. The longer error bar caps are associated with the soil water content.

Peaks in soil water content during 1993 at 28 and 49 days after initial N treatments (Figure 1) were a result of a combination of irrigation and precipitation during the previous week. Total precipitation for the week preceding the 28-day measurement was 64 mm, and that prior to the 49-day reading was 18 mm (NOAA, July 1993). This information will also help explain differences in amounts of NO_3 adsorbed by capsules during the two years.

The soil maintained an overall higher water content during 1993 than during 1994. Little or no soil water depletion was recorded during the middle of the growing season in 1993, but water depletion was obvious during 1994 (Wraith, unpublished data). The quantity of NO_3 adsorbed by MBIER from the 0.15 m depth during both years reflected measured water contents at the 0.20 m depth (Figures 1a and 2a).

The quantities of NO_3 and Br adsorbed by MBIER during 1994 were considerably less, at all depths, than during 1993. During 1994 the soil water content was probably high enough to facilitate ion diffusion, but little mass flow; whereas during 1993 the increased soil water content probably caused ion movement due to water transfer to lower depths.

Nitrate and Bromide Movement

0.15 m Depth

In 1993, highest quantities of Br were recovered at the 14-day sampling with the twice per week irrigation and at 28 days with once per week irrigation (Figure 5). For 1993 once week⁻¹ low irrigation level, single application NO_3 (Figure 6) and Br (Figure 5) peaks occurred 28 days after fertilization and then both decreased throughout the growing season.

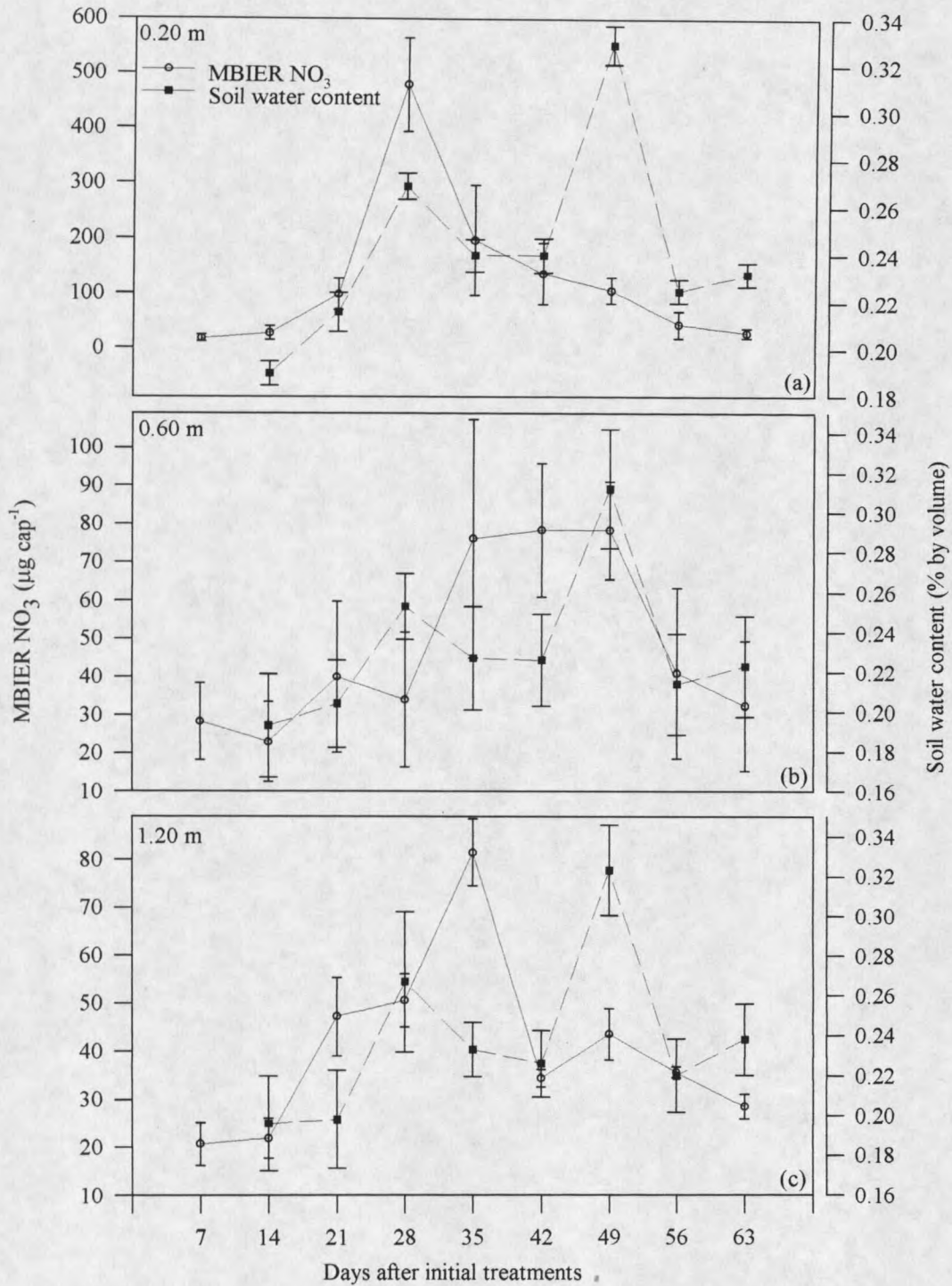


Figure 1. NO₃ measured using MBIER under single application N rate, 403.5 kg N ha⁻¹, compared with representative soil water contents for the 1993 field season. Irrigation treatment was twice weekly at the medium level.

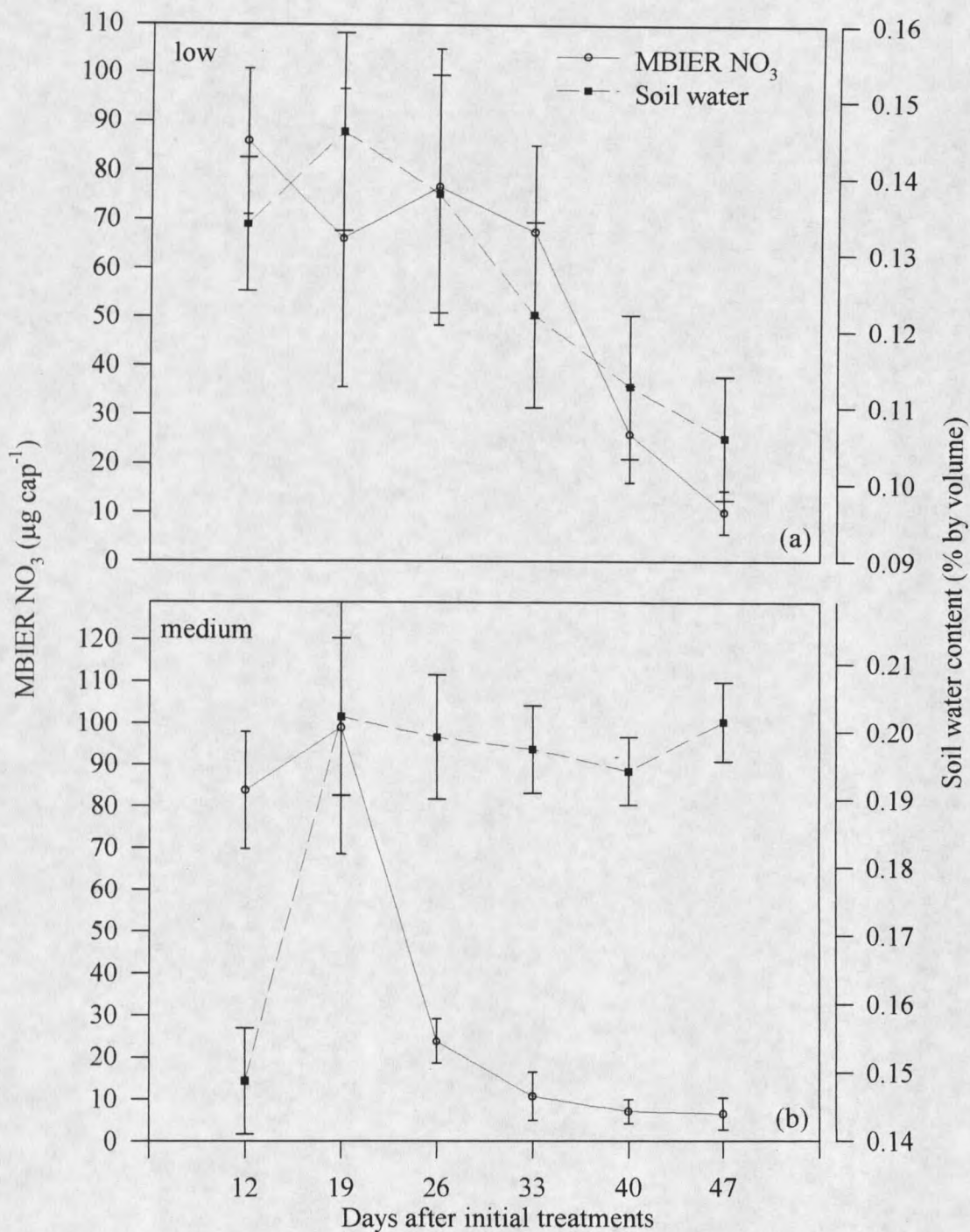


Figure 2. NO₃ measured using MBIER under single application N rate, 403.5 kg N ha⁻¹, compared with representative soil water contents, 0.20 m depth, for the 1993 field season. Irrigation treatment was twice weekly at the low and medium level.

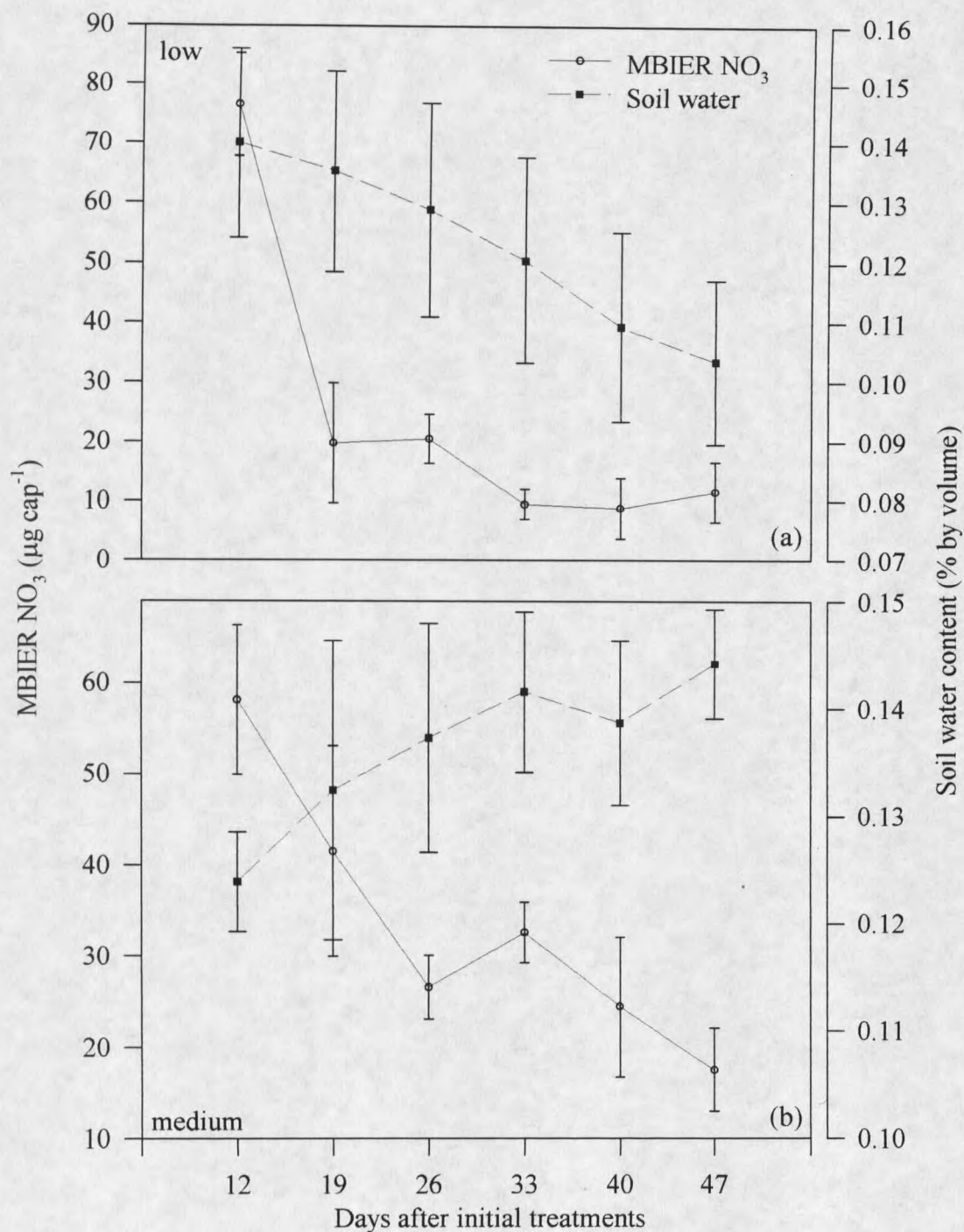


Figure 3. NO₃ measured using MBIER under single application N rate, 403.5 kg N ha⁻¹, compared with representative soil water contents, 0.60 m depth, for the 1993 field season. Irrigation treatment was twice weekly.

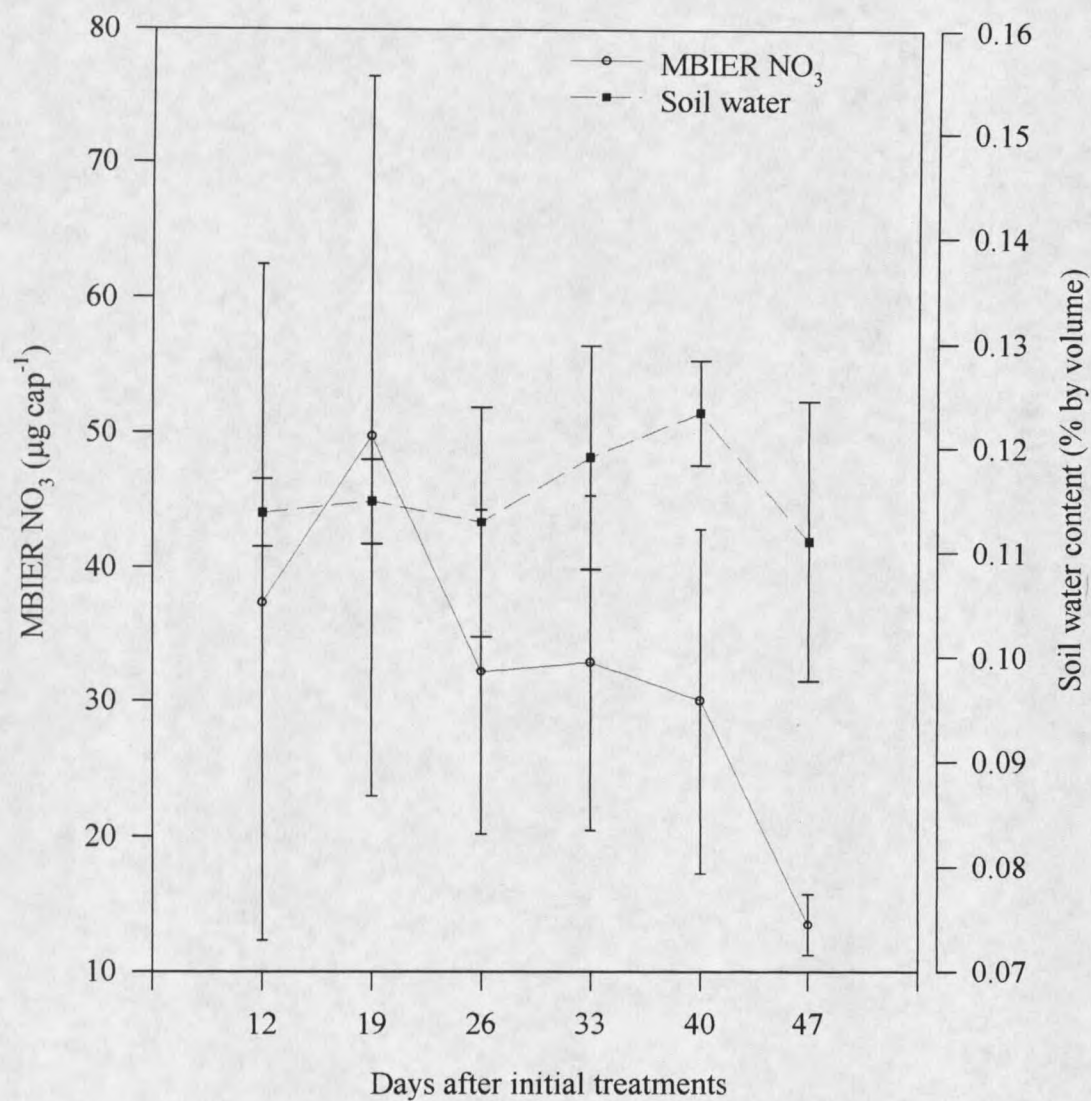


Figure 4. NO₃ measured using MBIER under single application N rate, 403.5 kg N ha⁻¹, compared with representative soil water contents, 1.20 m depth, for the 1993 field season. Irrigation treatment was twice weekly at the medium level.

Bromide from a single application of KBr moved through the soil profile more rapidly than the single application of urea for the 1993 field season. The Br breakthrough curve (BTC), in general, was about two weeks ahead of the NO_3 -BTC for the 0.15 m depth. This further indicates the generation of NO_3 during this period, and that MBIER capsules are sensitive to this component of N dynamics, as well as to NO_3 transfer by water.

The generation of NO_3 could be from mineralization of applied urea or the organic matter present in the soil. Mineralization of urea is carried out by bacteria that are present in the soil. The mineralization of urea to NH_3 is a hydrolysis process. The NH_3 is further reduced to NH_4 . After NH_4 is formed it undergoes nitrification. Nitrification is the microbial oxidation of NH_4 to nitrite (NO_2) then to NO_3 .

The 1994 medium irrigation level resulted in the highest quantities of Br recovered by capsules at the first (12-day) sampling (Figure 7). Quantities rapidly decreased throughout later sampling periods, indicating that breakthrough occurred sometime during the first 12 days. Transfer of Br, as measured by MBIER, appeared to precede that of NO_3 by a week or two for both the low (Figure 5a vs Figure 6a) and medium (Figure 8b vs Figure 7b) irrigation levels during both years.

The highest incremental N rate ($672.6 \text{ kg N ha}^{-1}$) resulted in increased accumulation by MBIER after 21 to 35 days for all irrigation levels and timings (Figure 6a and 6b). The $403.5 \text{ kg N ha}^{-1}$ incremental treatment, with once per week (medium) irrigation, resulted in increased NO_3 accumulation toward the end of the growing season, while this occurred after 35 days with the once week⁻¹ (low) irrigation treatment.

During 1993, *in situ* MBIER NO_3 levels increased throughout the growing season when high rates of N were applied incrementally, suggesting that more NO_3 became available than the mint took up, and NO_3 accumulated in the soil. The same effect was not evident during 1994 from *in situ* MBIER NO_3 data, but data from soil samples analyzed by MBIER in saturated paste indicated that soil NO_3 did increase at the 0.15 m depth (Figure 9) with the two highest N rates. The difference in quantities of NO_3 adsorbed by the *in situ* and saturated paste MBIER is an indication that MBIERs are sensitive to ion movement due to soil water content and movement.

In 1994 the only N treatment that had an obvious NO_3 -BTC was $403.5 \text{ kg N ha}^{-1}$ single application (Figure 7a and 7b). The peak occurred 26 days after urea was applied, then decreased throughout the growing season. The decrease was much slower than the decrease in Br over the same period for the twice week⁻¹ medium irrigation level (Figure 8b), suggesting that considerable urea-N was being nitrified during this period.

Incremental N applications did not result in a definite BTC in 1994 (Figure 7). The control and $134.5 \text{ kg N ha}^{-1}$ incremental treatments resulted in essentially no change in capsule accumulation of NO_3 throughout both growing seasons (Figure 6b and 7b).

0.61 m Depth

For 1993 at the 0.61 m depths, the breakthrough curves for Br generally began at 35 days for all treatments, irrigation levels, and irrigation timings, Figure 10a. The exception was the one time week⁻¹ low irrigation level, where there was never any indication of Br reaching this soil depth (data not shown).

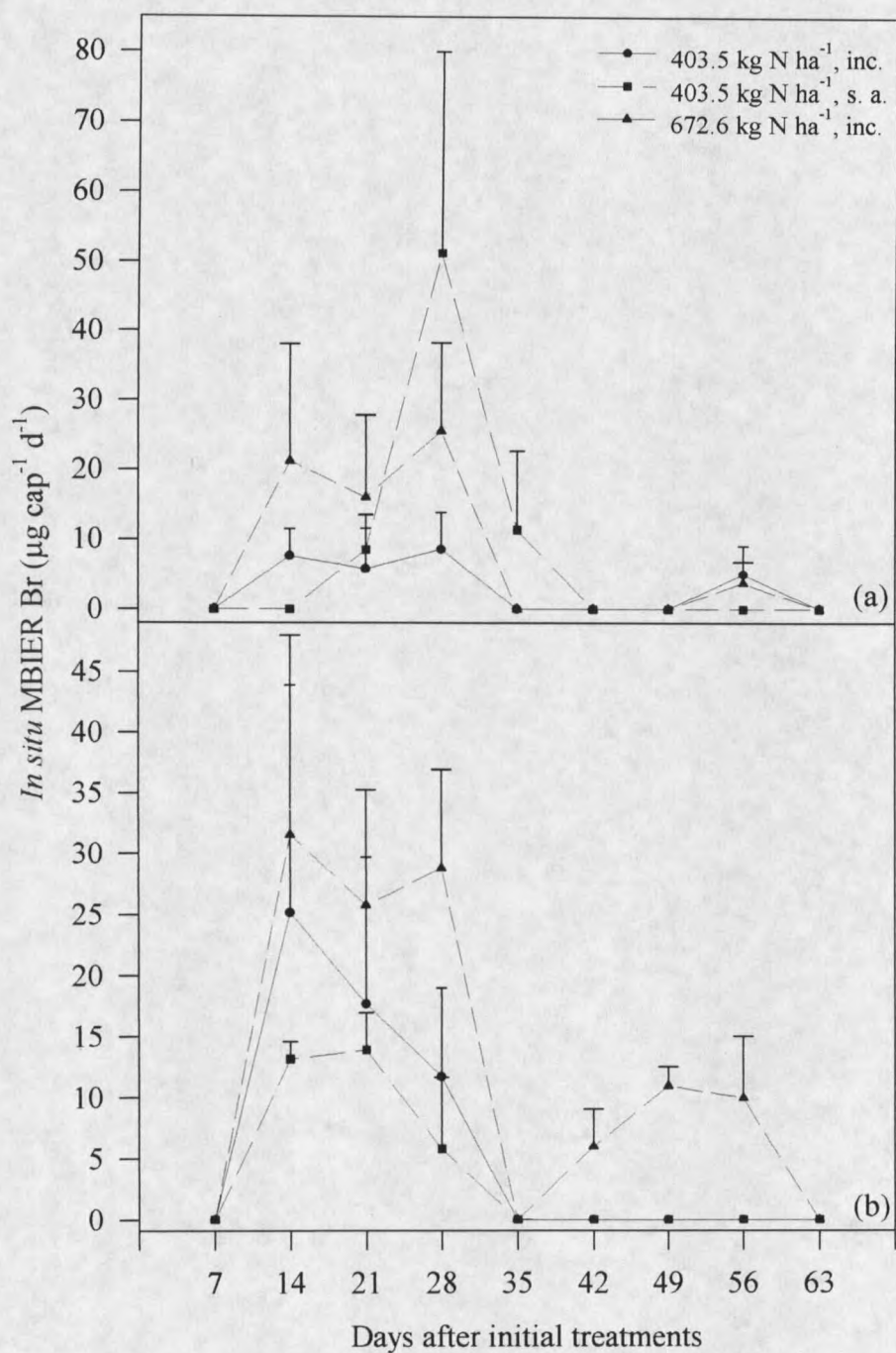


Figure 5. Br BTC for the 1993 field season at the 0.15 m depth. Graph (a) is once wk⁻¹ low, and graph (b) is twice wk⁻¹ medium irrigation.

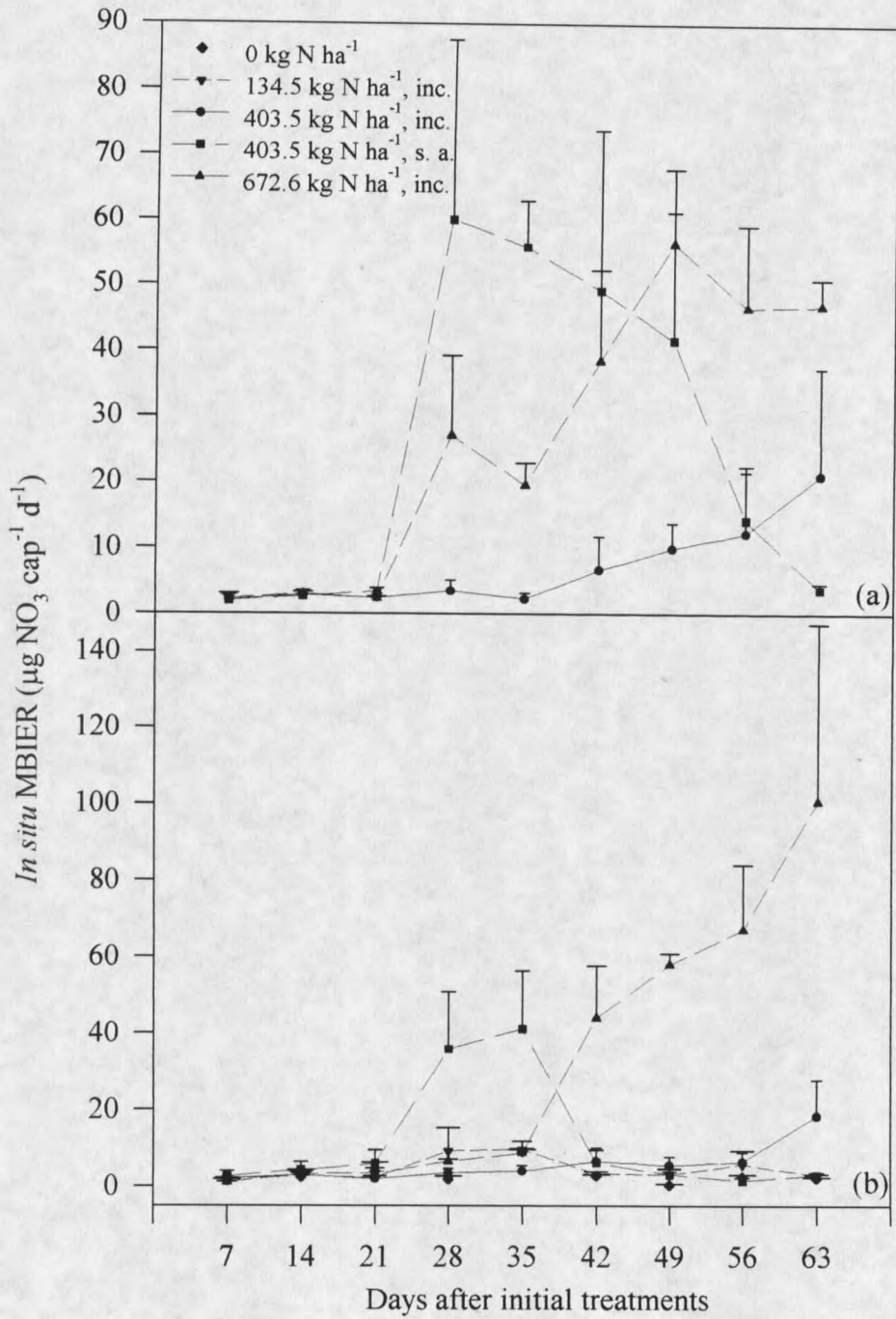


Figure 6. NO₃ BTC for the 1993 field season at the 0.15 m depth. Graph (a) is once wk⁻¹ low, and graph (b) is once wk⁻¹ medium irrigation.

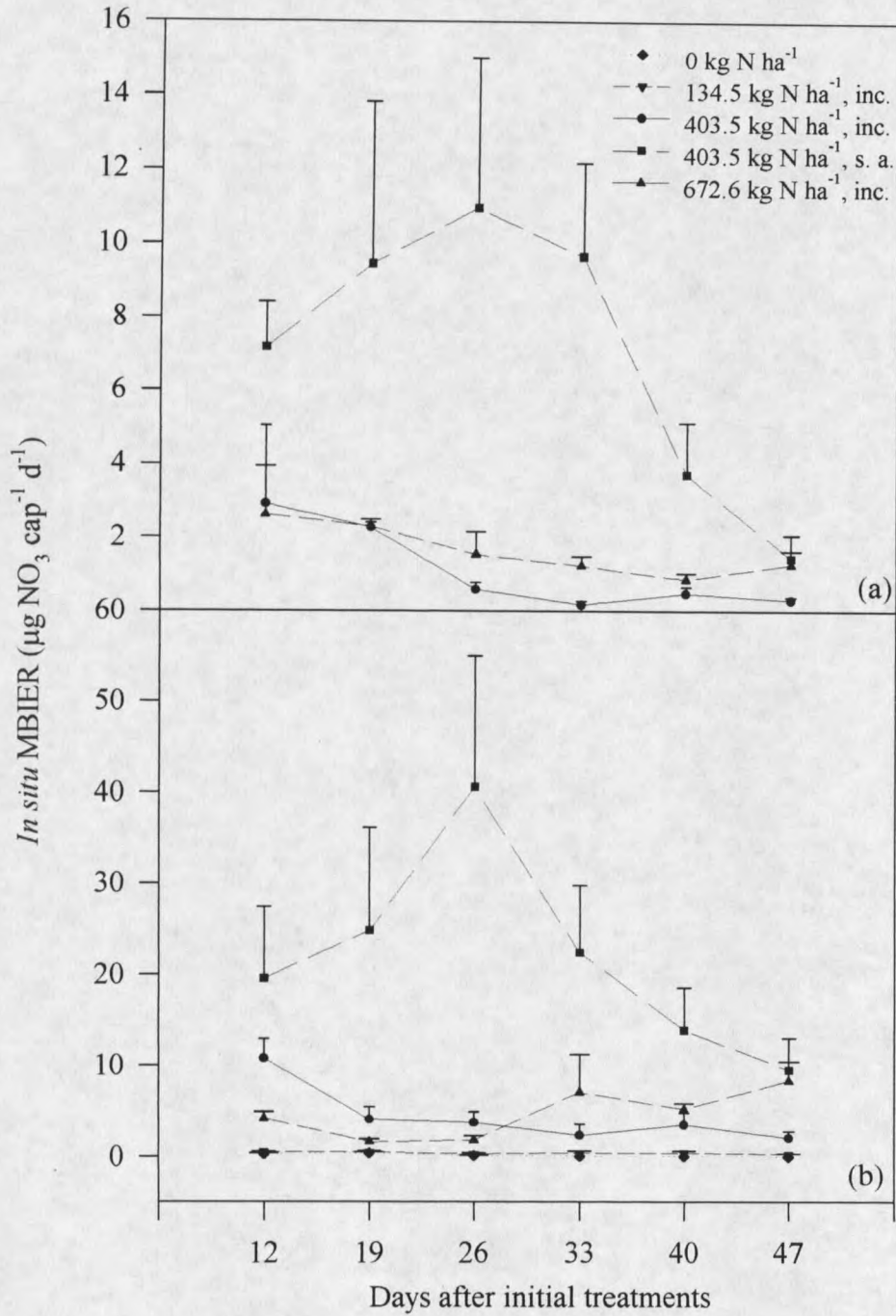


Figure 7. NO_3 BTC for the 1994 field season at the 0.15 m depth. Graph (a) is twice wk^{-1} low, and the graph (b) is once wk^{-1} medium irrigation.

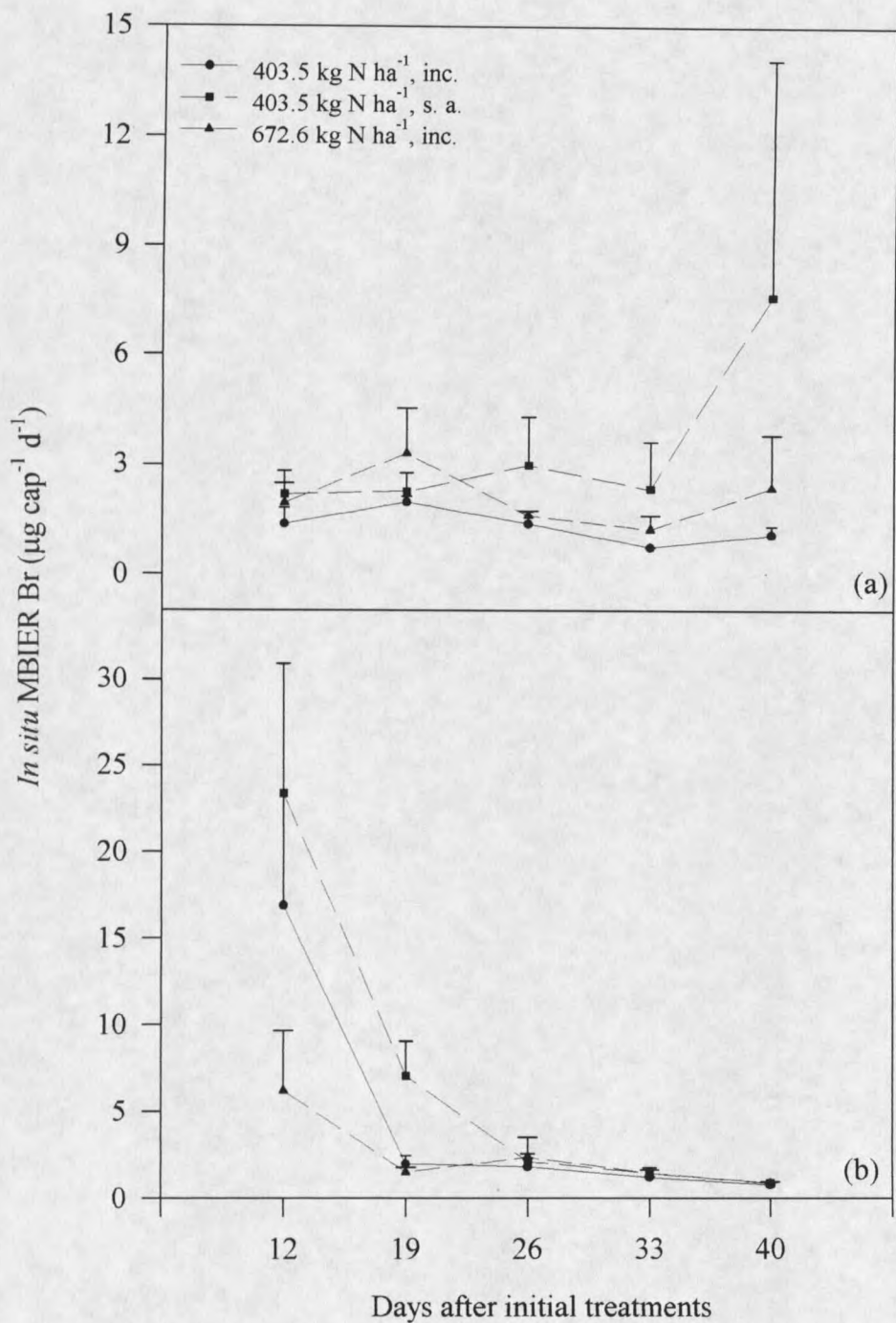


Figure 8. Br BTC for the 1994 field season at the 0.15 m depth. Graph (a) is once wk⁻¹ low, and graph (b) is twice wk⁻¹ medium irrigation.

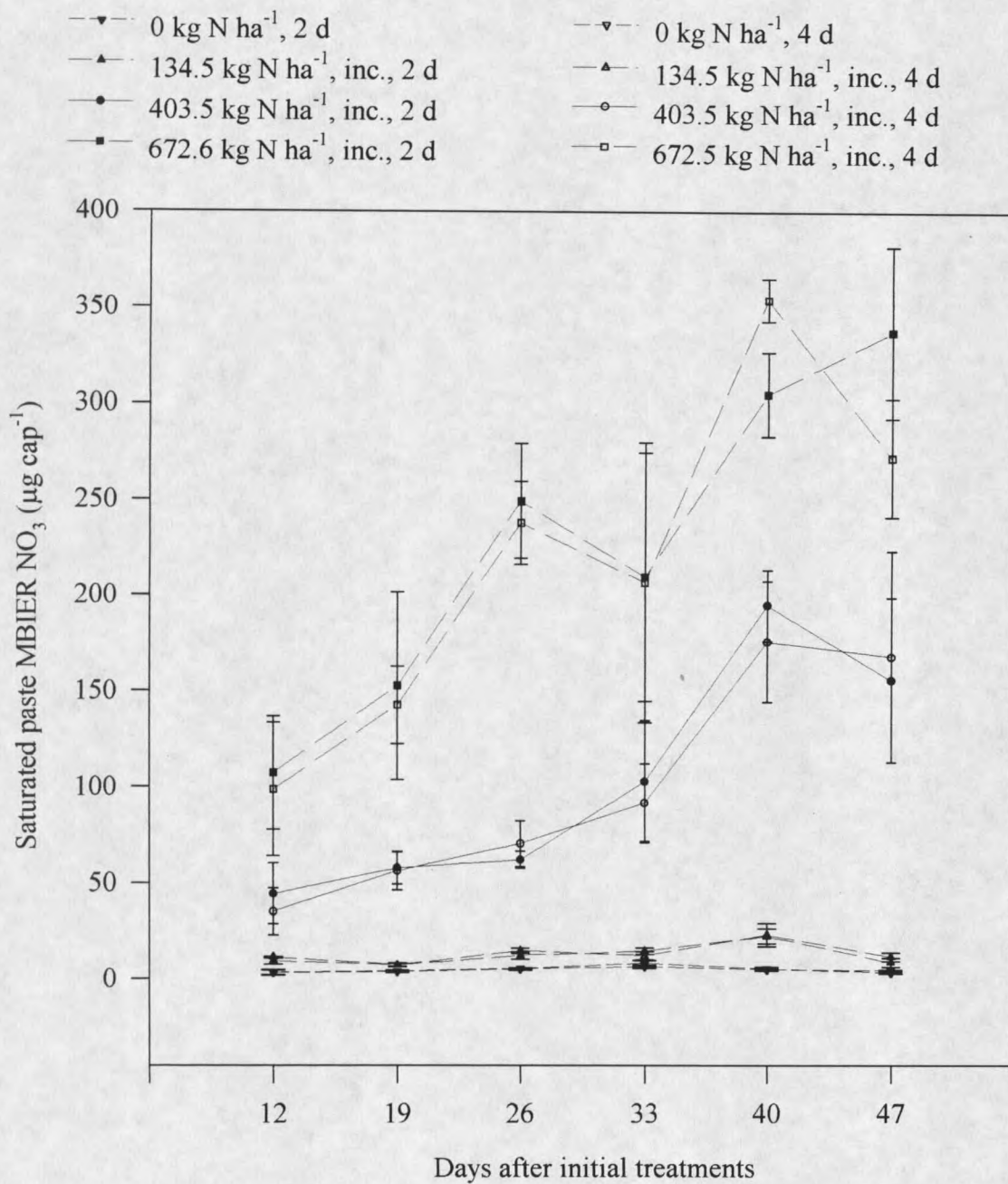


Figure 9. 1994 field season MBIER saturated paste, 2 and 4 d data, from 0.15 m depth soil samples.

At the 0.61 m depth, the BTC for NO_3 associated with the single application of $403.5 \text{ kg N ha}^{-1}$ began 35 days after the initial treatment, increased until 56 days, then rapidly declined with both the low and medium irrigation levels (Figure 11). At this depth the Br BTC (Figure 10a) coincided with that for NO_3 with the single application of urea. The $672.6 \text{ kg N ha}^{-1}$ incremental treatment resulted in development of a breakthrough curve beginning about 49 days after the initial treatment (Figure 11b).

In 1994 there was a slight increase in Br accumulation 19 days after KBr was applied (Figure 10b). It is questionable that this was due to leaching of the Br, as the quantities detected were very small, and commensurate with quantities measured with 0 and $134.5 \text{ kg N ha}^{-1}$ applied, but where no KBr was applied (data not shown). The quantities detected in 1994 are probably due to an artifact of measurement in the laboratory.

At the 0.61 m depth during 1994, maximum NO_3 accumulation by capsules occurred about 19 days after the initial treatments (Figure 12). These peaks are probably not related to N applied at the beginning of the 1994 growing season, but more likely are due to the N applied in October of 1993, and finally reaching this soil depth.

1.22 m Depth

During 1993, maximum NO_3 accumulation at the 1.22 m depth occurred 35 days after initial treatment (Figure 13a), while in 1994 this occurred after 19 days (Figure 13b). Quantities detected then generally decreased throughout both sampling periods. It is suggested that these peaks, for both years, may also be due to residual N in the soil profile, rather than N leaching to this depth. The timing of the NO_3 increase at the 1.22 m depth

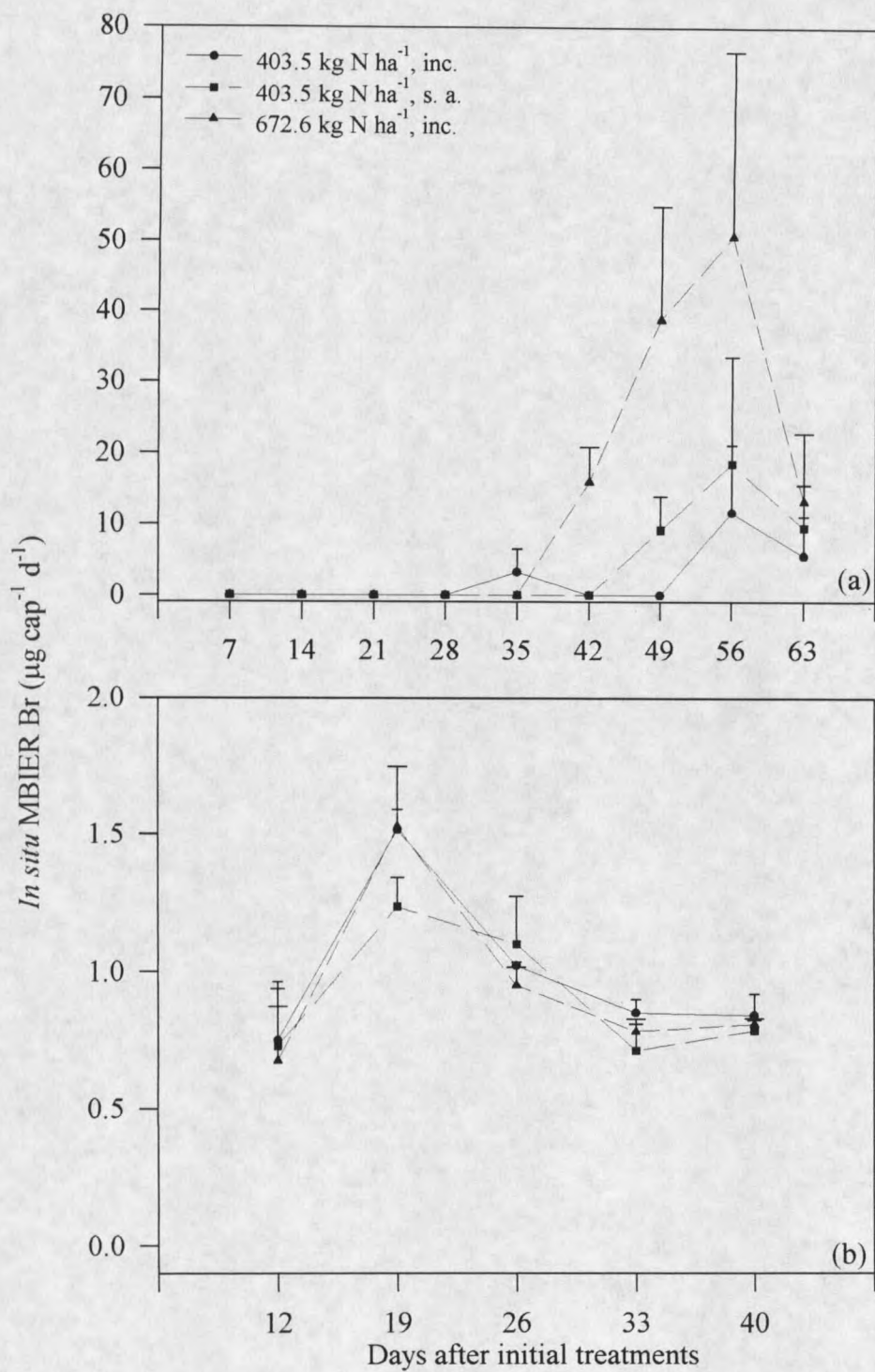


Figure 10. Br BTC for the 1993 and 1994 field seasons at the 0.61 m depth. Graph (a) is 1993 twice wk⁻¹ low, and graph (b) is 1994 once wk⁻¹ low irrigation.

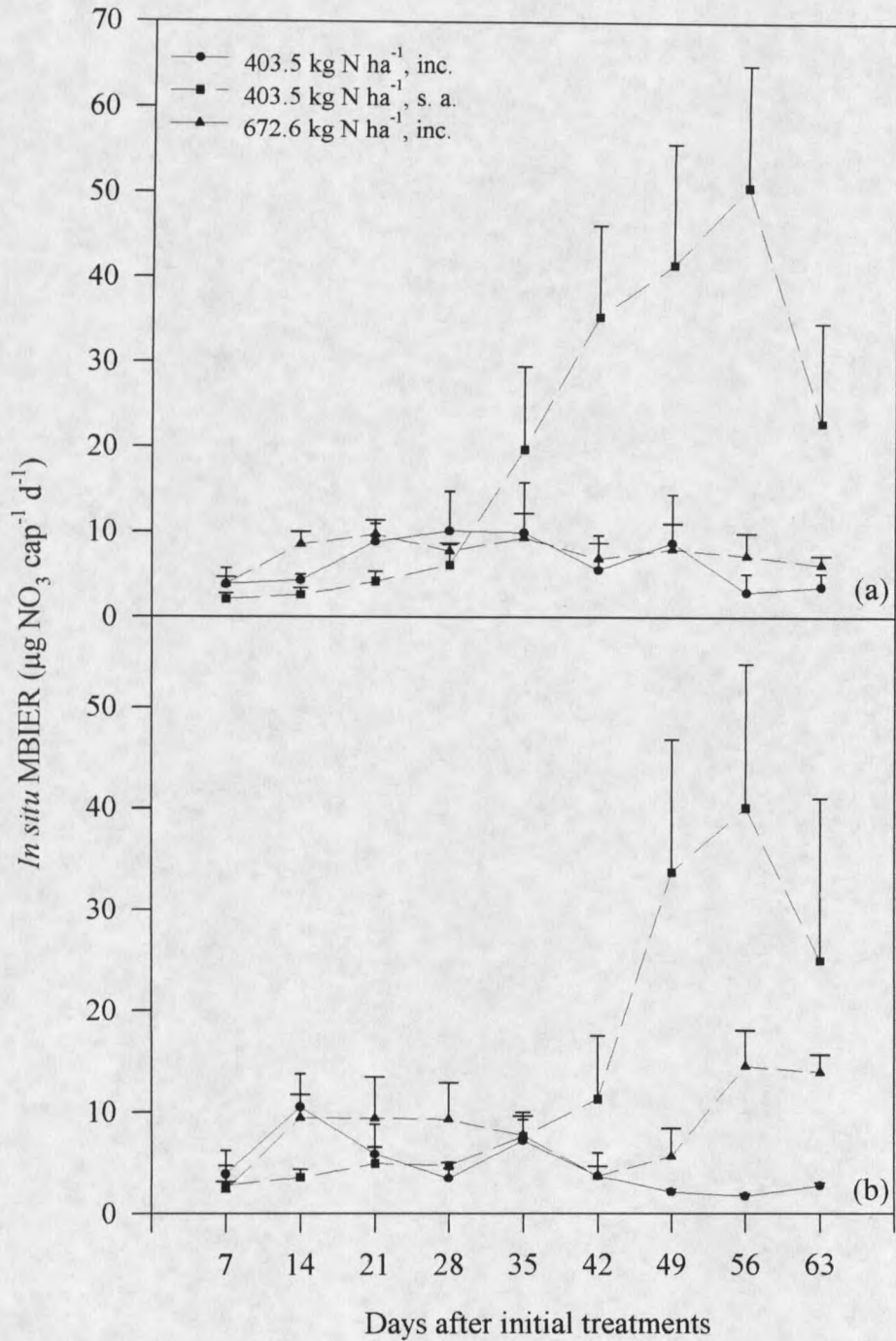


Figure 11. NO_3 BTC for the 1993 field season at the 0.61 m depth. Graph (a) is once wk^{-1} low, and graph (b) is once wk^{-1} medium irrigation.

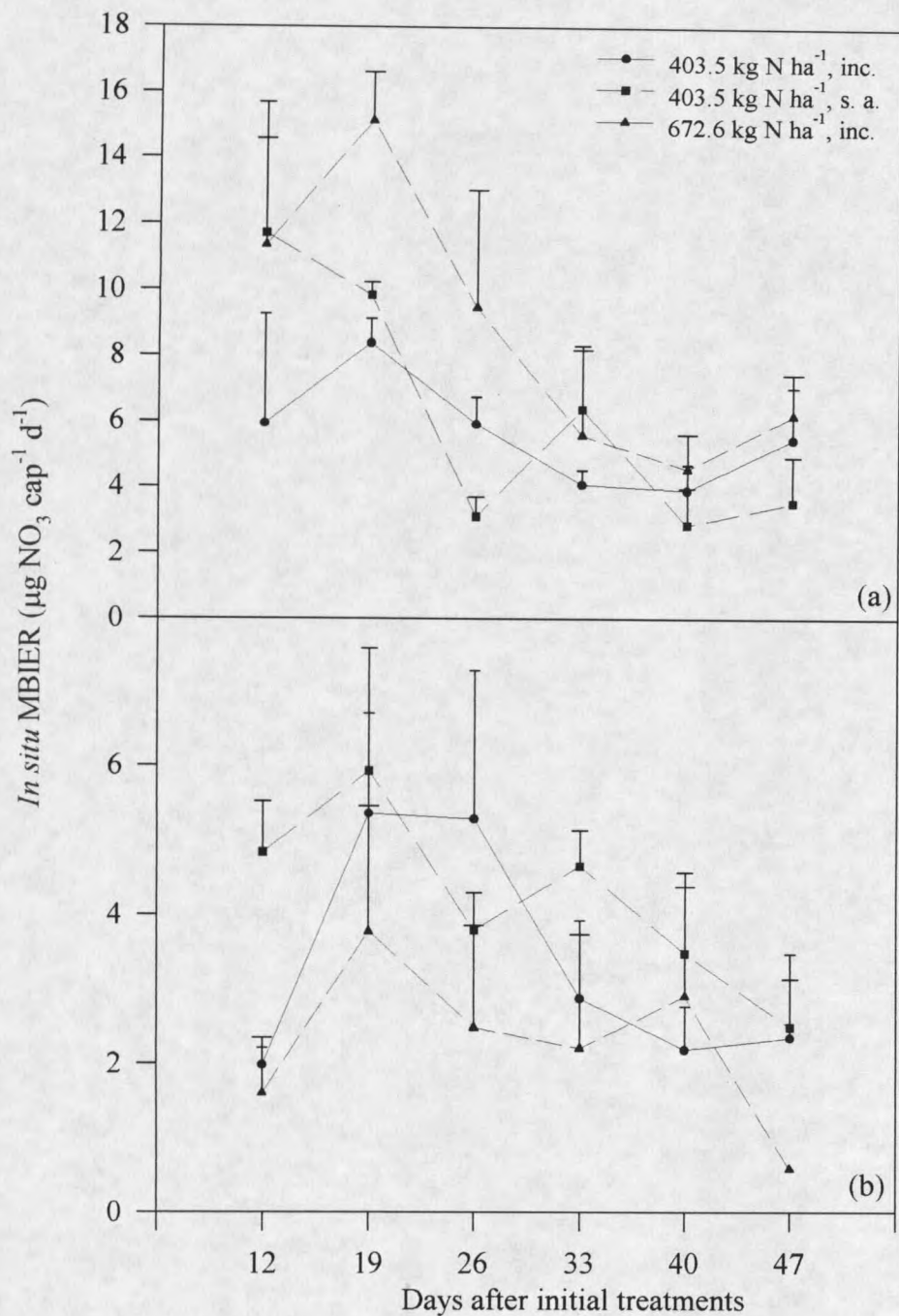


Figure 12. NO₃ BTC for the 1994 field season at the 0.61 m depth. Graph (a) is once wk⁻¹ medium, and graph (b) is twice wk⁻¹ medium irrigation.

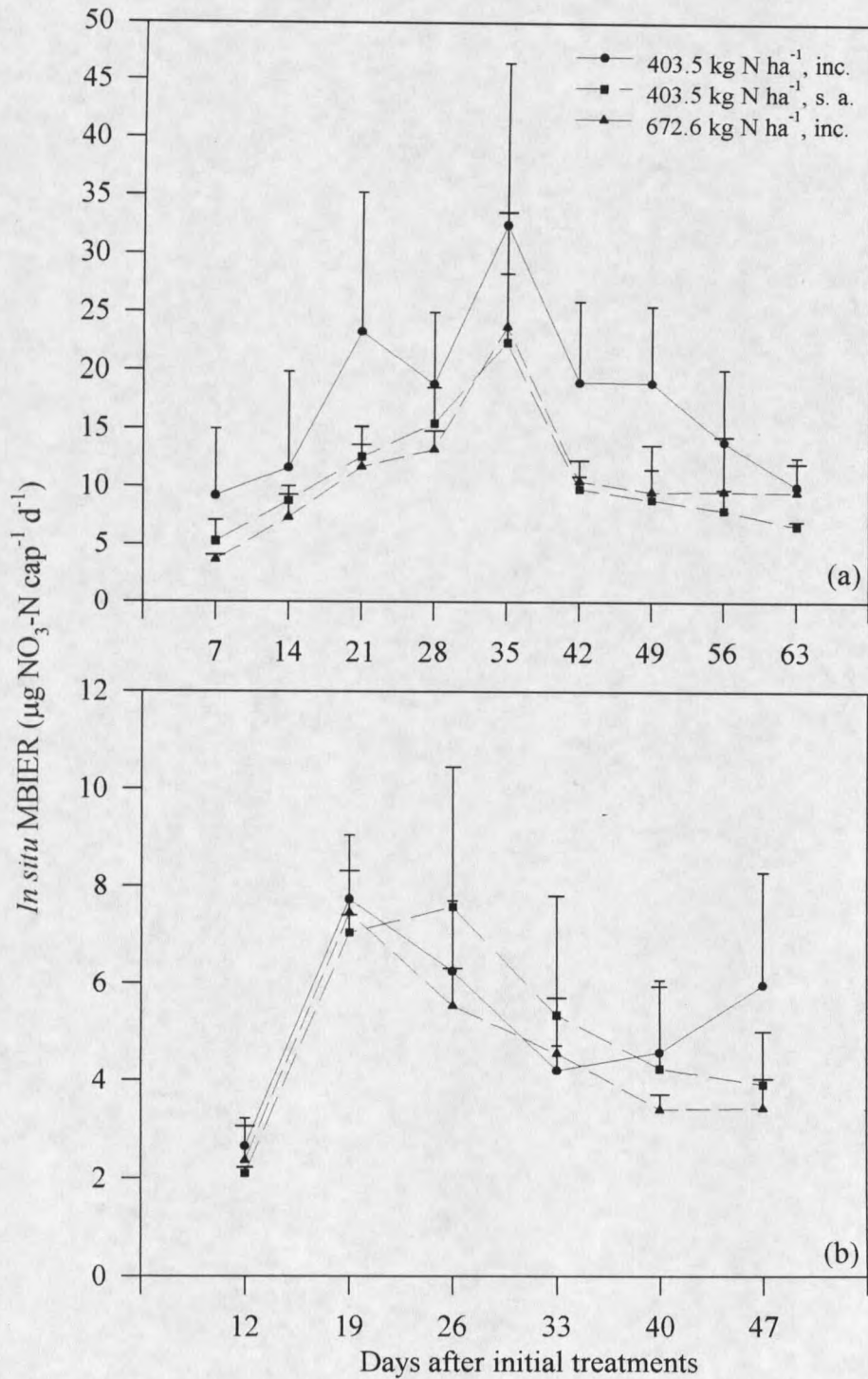


Figure 13. NO₃ BTC for the 1993 and 1994 field seasons at the 1.22 m depth. Graph (a) is 1993 once wk⁻¹ medium, and graph (b) is 1994 once wk⁻¹ low irrigation.

does not lag behind the BTC at the 0.61 m depth, indicating that there was no downward movement of NO_3 between these depths. This is supported by the lack of correspondence to soil water relations for the two years.

Winter NO_3 Monitoring

Movement of NO_3 throughout the winter period was monitored on plots that had received the once weekly low or medium irrigation treatments. If NO_3 was detected by MBIER at the 1.22 m depth during the growing season, it is likely on a one-way trip to the groundwater, dependent on the amount of water moving through the soil profile between growing seasons. Figures 14, 15, and 16 illustrate NO_3 dynamics as measured by MBIER capsules retrieved during the period between growing seasons. It can be clearly seen that NO_3 moved between the 0.15 m and 0.61 m depth, particularly associated with the higher incremental N treatment, during the months following the growing season. Nitrate present at the two lower depths at the beginning of the growing season is unlikely to be intercepted by the roots of mint and would be expected to move through the soil profile as more water is applied to the soil surface during the growing season.

The NO_3 peak at 0.15 m depth and associated with $672.6 \text{ kg N ha}^{-1}$ incremental treatment occurred in August, 12 days after harvest (Figure 14a and 14b), then decreased during winter months. This is likely a function of little soil water movement due to a likely decrease in soil water content. Precipitation for September and October of 1993 was 41 and 26 mm, respectively (NOAA, Sept. and Oct., 1993). Little or no nitrification would occur at this depth as well.

At the 0.15 m depth, little or no NO_3 was recovered by resin capsules from both irrigation levels throughout the winter and spring months (Figure 14). The soil was observed to be frozen at this depth during the February 1994 sampling, and resin capsule results reflected the lack of N dynamics under these conditions. At the two deeper soil depths, however, capsules continued to accumulate NO_3 throughout the winter. At these depths the soil remained unfrozen and NO_3 continued to diffuse to capsules.

Figure 15a and 15b illustrate the movement of N, as influenced by water level, when the highest rate of N ($672.6 \text{ kg N ha}^{-1}$) was applied. With medium irrigation the NO_3 peak at 0.61 m depth occurred in late September, but not until October under low irrigation. The lag time in NO_3 movement between the 0.15 and 0.61 m depths, as revealed by capsule data, can be seen by comparing Figures 14, 15, and 16. It is obvious that diffusion of NO_3 to the MBIER was still occurring two and one-half months after the last application of urea.

Effects of split applications of urea are also apparent from these data. For example, during 1993-1994 under medium irrigation, and at the 0.61 m depth (Figure 15b), single application of $403.5 \text{ kg N ha}^{-1}$ resulted in maximum NO_3 accumulation by capsules in the fall, whereas incremental application of the same rate did not peak until April and early May the next year. There was obviously much more NO_3 remaining in the soil at the end of the wet 1993 growing season when urea applications were extended throughout the season, whereas much of the initial single application apparently leached beyond these soil depths.

The peak that occurred at the 1.22 m depth in September, for both irrigation regimes and associated with the $672.6 \text{ kg N ha}^{-1}$ treatment (Figure 16a and 16b) may be an anomaly.

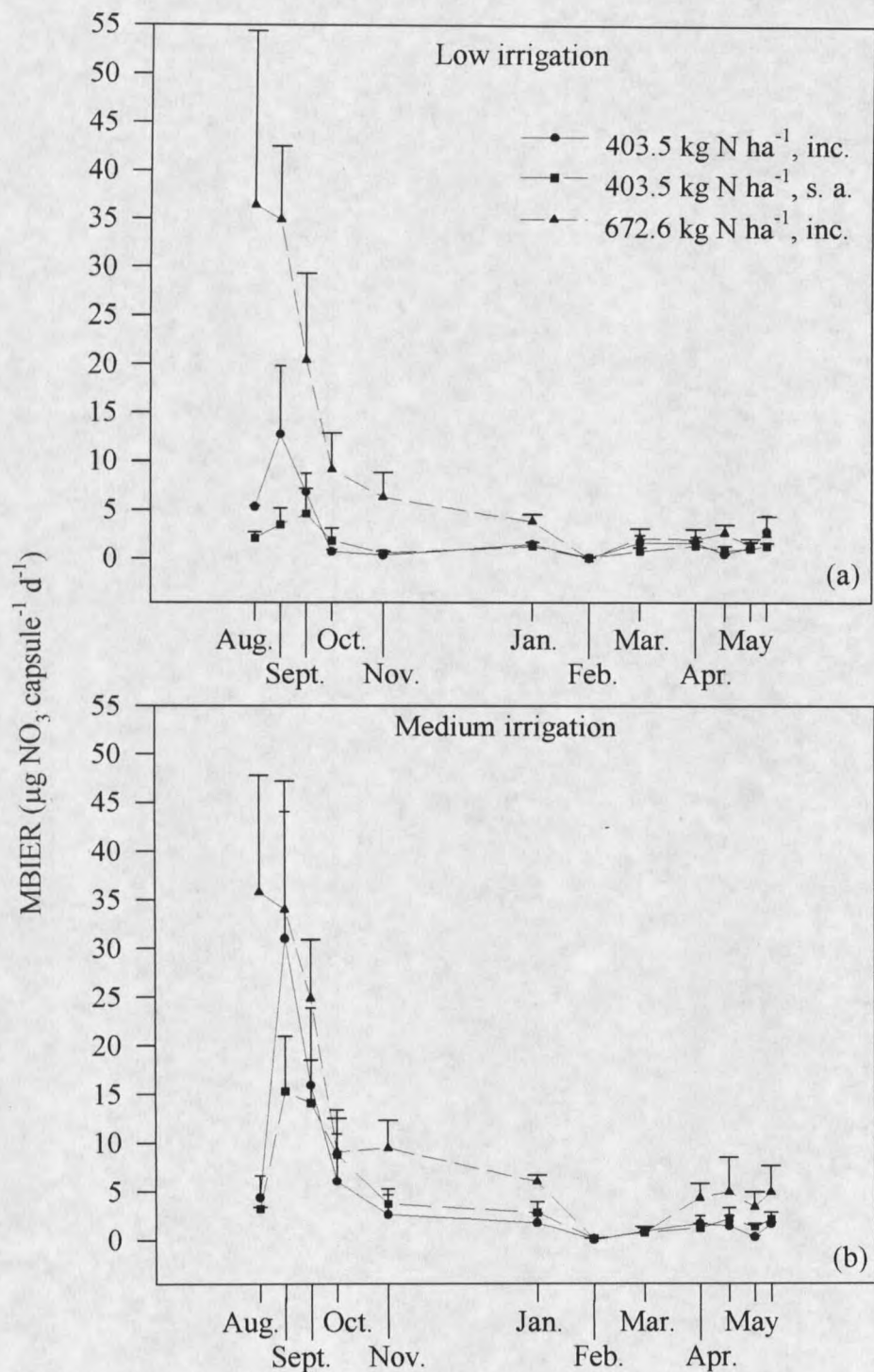


Figure 14. Graphs a and b illustrate NO_3 dynamics from 1993 harvest to the beginning of the next cropping season at the 0.15 m depth.

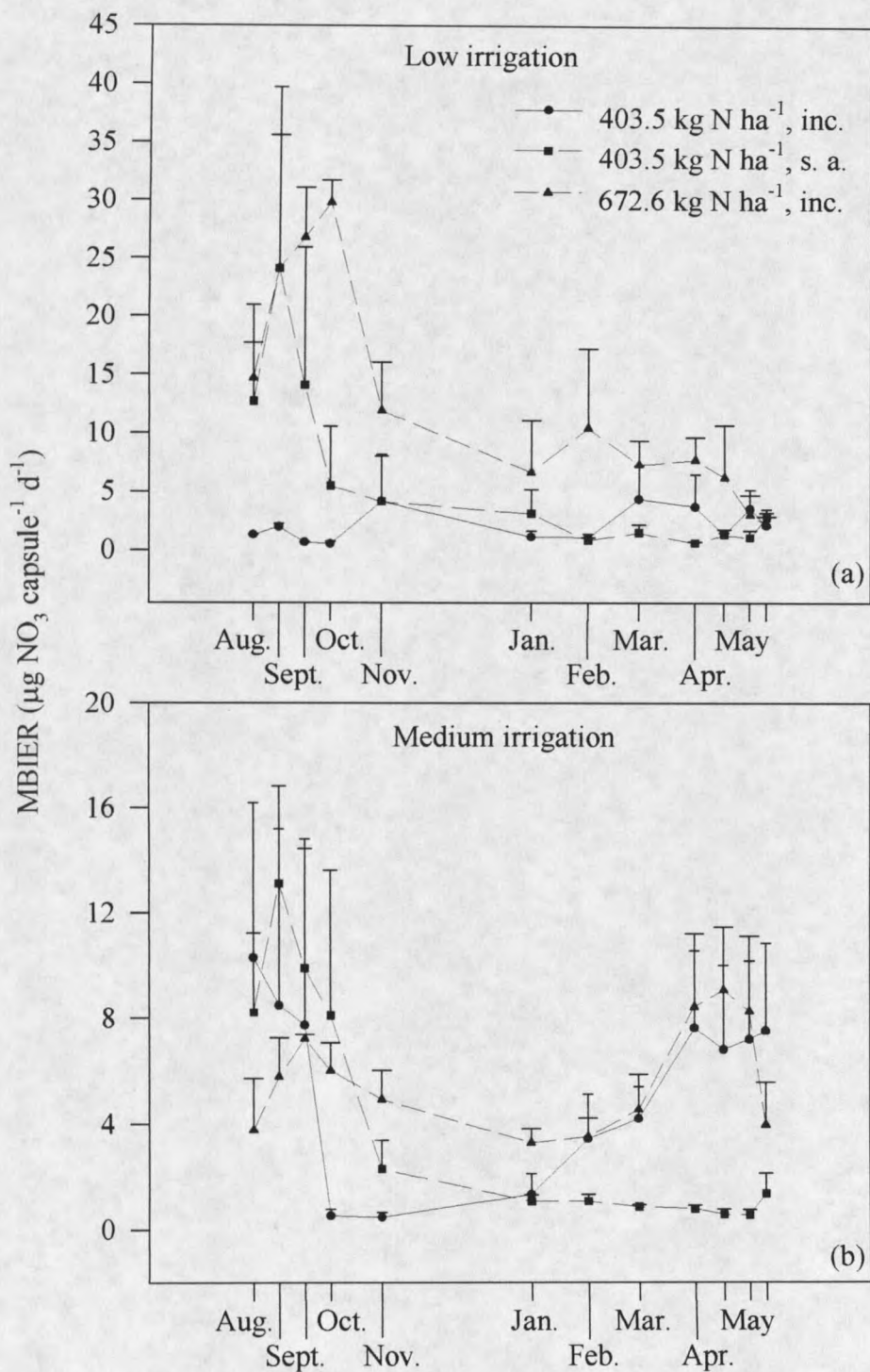


Figure 15. Graphs a and b illustrate NO_3 dynamics from 1993 harvest to the the beginning of the next cropping season at the 0.61 m depth.

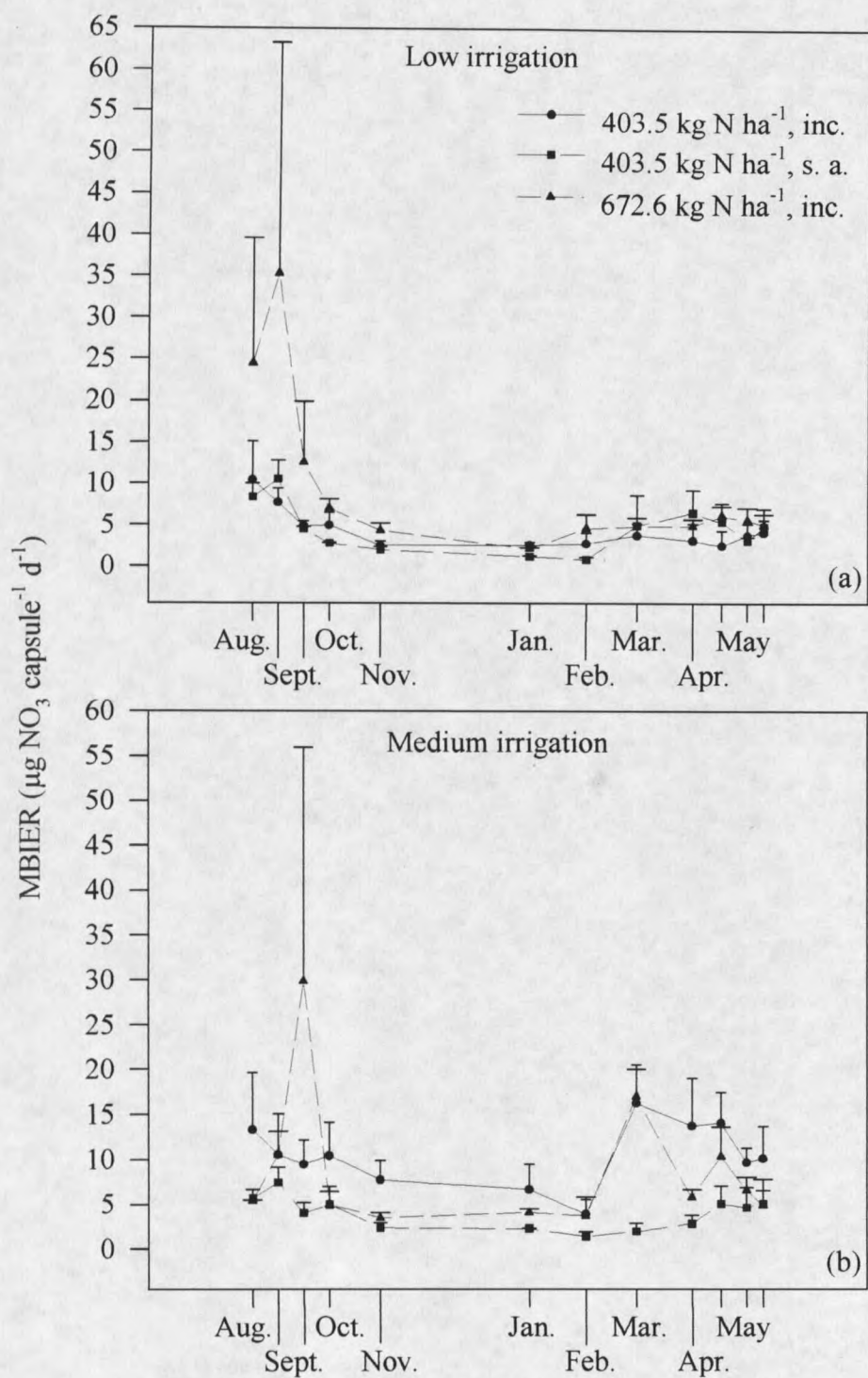


Figure 16. Graphs a and b illustrate NO_3 dynamics from 1993 harvest to the beginning of the next cropping season at the 1.22 m depth.

Prior to harvest, access tubes had to be cut at ground level to allow harvesting of the mint. This cutting caused some soil disturbance around the tube and may have resulted in erroneous values.

The data collected using access tubes and MBIER capsules during the fall, winter, and spring months indicate clearly that this system provides a simple, convenient method of sampling soils, even when surface soils are frozen.

Average Mint Stem NO₃ Regressed on Average *In Situ* MBIER NO₃

Mint grown in 1993 had higher stem NO₃ concentrations than that grown in 1994 (Table 9). The high stem NO₃ for 1993 is attributed to below normal temperatures and cloudy weather (Brown, 1983). Mint plants were sampled for stem NO₃ analysis at the same time that soil or capsule data were collected. For 1993 samples were obtained from the third to the eighth sampling, and from the first to the last sampling for 1994. Figure 17 presents the regression relationship between mint stem NO₃ content and MBIER capsule values for each year. The relationship was much better during 1994 than during 1993. The difference between the two years is, again, probably related to soil water relations and plant physiology as influenced by climatic conditions between the two years. In 1994, both the mint crop and the capsule would have been influenced by actual rates of applied N which remained in the rooting and sampling soil depths.

During 1993, the only significant regression between mint stem NO₃ and *in situ* MBIER NO₃ occurred with the 403.5 kg N ha⁻¹ applied weekly, and at the medium level

irrigation (Figure 17a). This same relationship was significant during 1994, in addition to several others. Single application N fertilizer treatments resulted in higher regression values

Table 9. Mint stem NO₃ concentrations and LSD for 1993 and 1994 as influence by N treatments, averaged across all irrigation regimes.

Year	Treatment ¹ kg N ha ⁻¹	n	mg NO ₃ kg ⁻¹	Difference ²
1993	403.5 inc.	72	7619	A
	403.5 s.a.	72	8761	B
	672.6 inc.	72	8819	B
			LSD = 606.2	
1994	403.5 inc.	72	2859	A
	403.5 s.a.	72	3960	B
	672.6 inc.	72	4778	C
			LSD = 474.9	

¹ s. a. = A single application of urea. inc. = Incremental applications of urea.

² Different letters indicate significant differences based on LSD @ $p \leq 0.05$.

between plant and MBIER data than did any of the incremental treatments (Figure 18). The only incremental N treatments that yielded significant regressions between mint stem NO₃ and *in situ* MBIER NO₃ was the 403.5 and 134.5 kg N ha⁻¹ during the 1994 growing season (Figure 19).

Ion Probe NO₃ Regressed on MBIER *In Situ* Data

Soil samples taken from the 0 to 0.25 meter soil depth were analyzed for NO₃ using an ion-selective electrode. To determine whether these values were similar to those obtained from *in situ* MBIER capsules, the data were regressed against each other. When

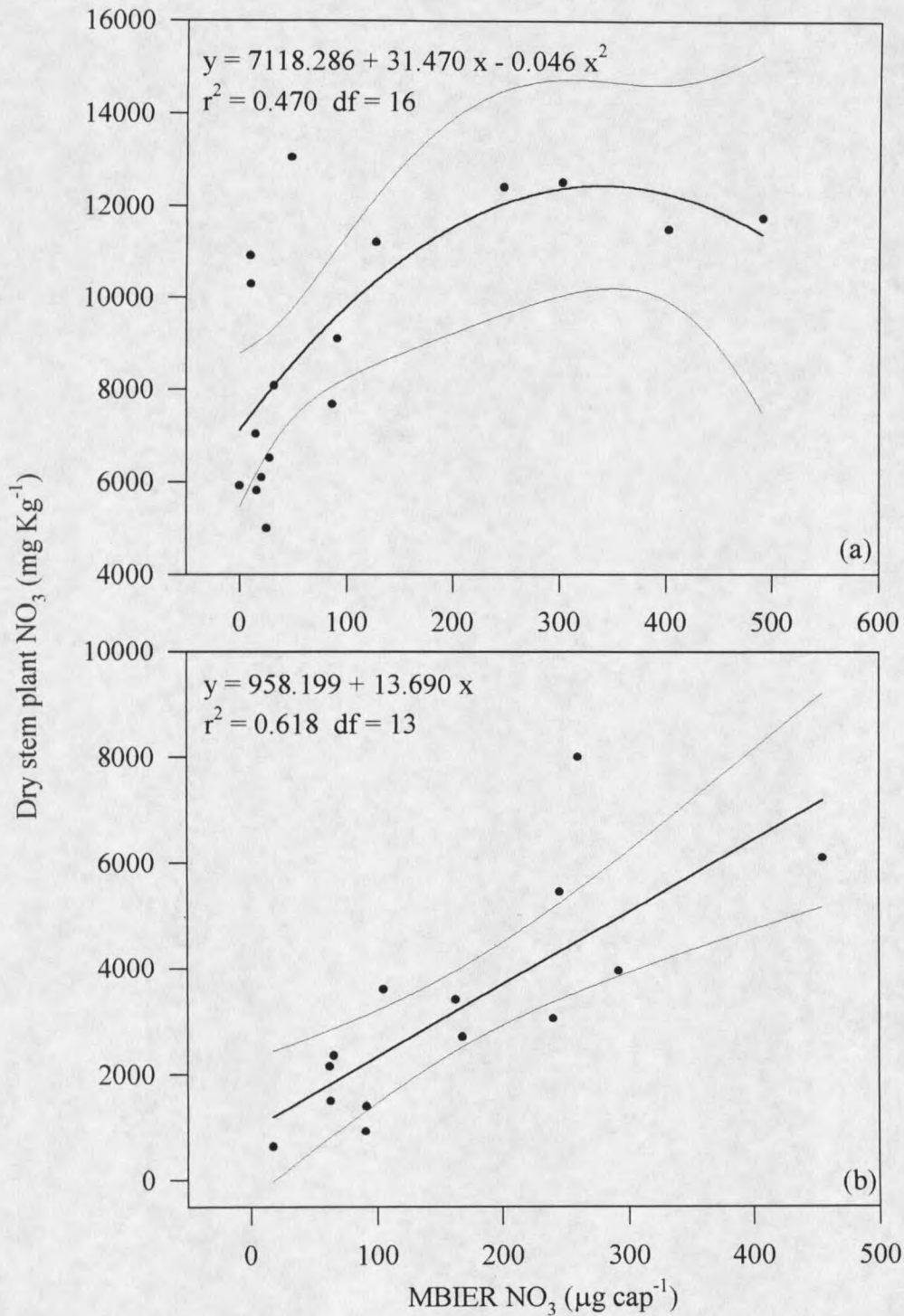


Figure 17. Regression of 1993 and 1994 mint stem NO₃ on 0.15 m *in situ* MBIER NO₃. Graph a is from 1993 and graph b is from 1994. Treatments were 403.5 kg N ha⁻¹ single application, at once wk⁻¹ medium irrigation.

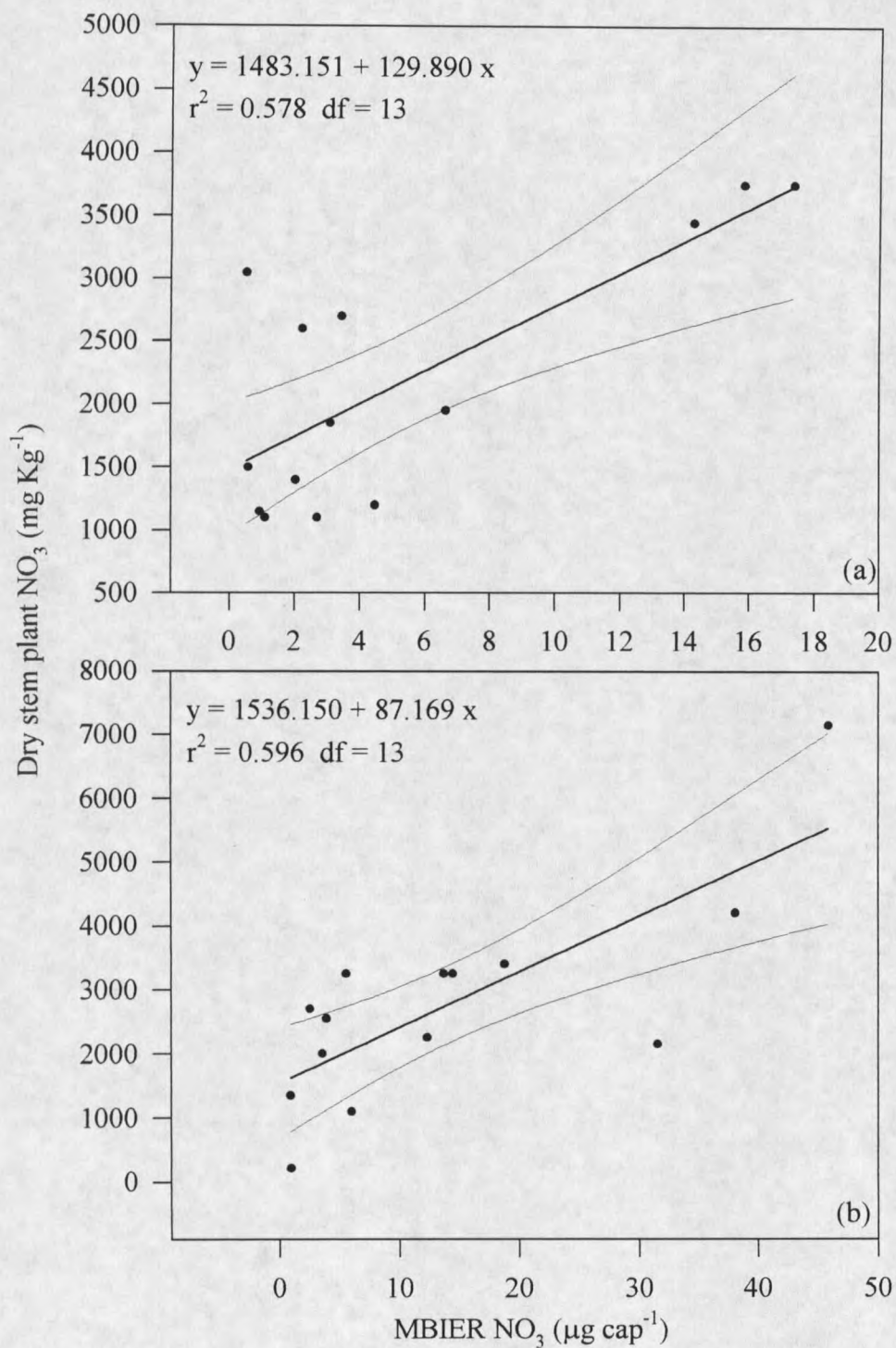


Figure 18. Regression of 1994 mint stem NO_3 on 0.15 m *in situ* MBIER NO_3 . Treatments were 403.5 kg N ha^{-1} applied incrementally with twice wk^{-1} irrigations. Graph a is the low level and graph b is the medium level.

data for all treatments and both years were combined, there was no significant relationship (data not shown). There were, however, significant regressions within treatments and for individual years, with regressions tending to be better for 1994. The best correlations, in general, occurred with the once per week medium irrigation level. A typical regression between standard soil test (ion probe for NO_3) and MBIER data is illustrated in Figure 20, and that for other incremental treatments is shown in figure 21.

These results indicate that, under certain conditions, resin capsules will provide data similar to standard soil test analysis. Differences would be expected under many conditions, however, because of the different mechanisms involved in resin capsule accumulation of solutes as compared to chemical extraction of soil samples.

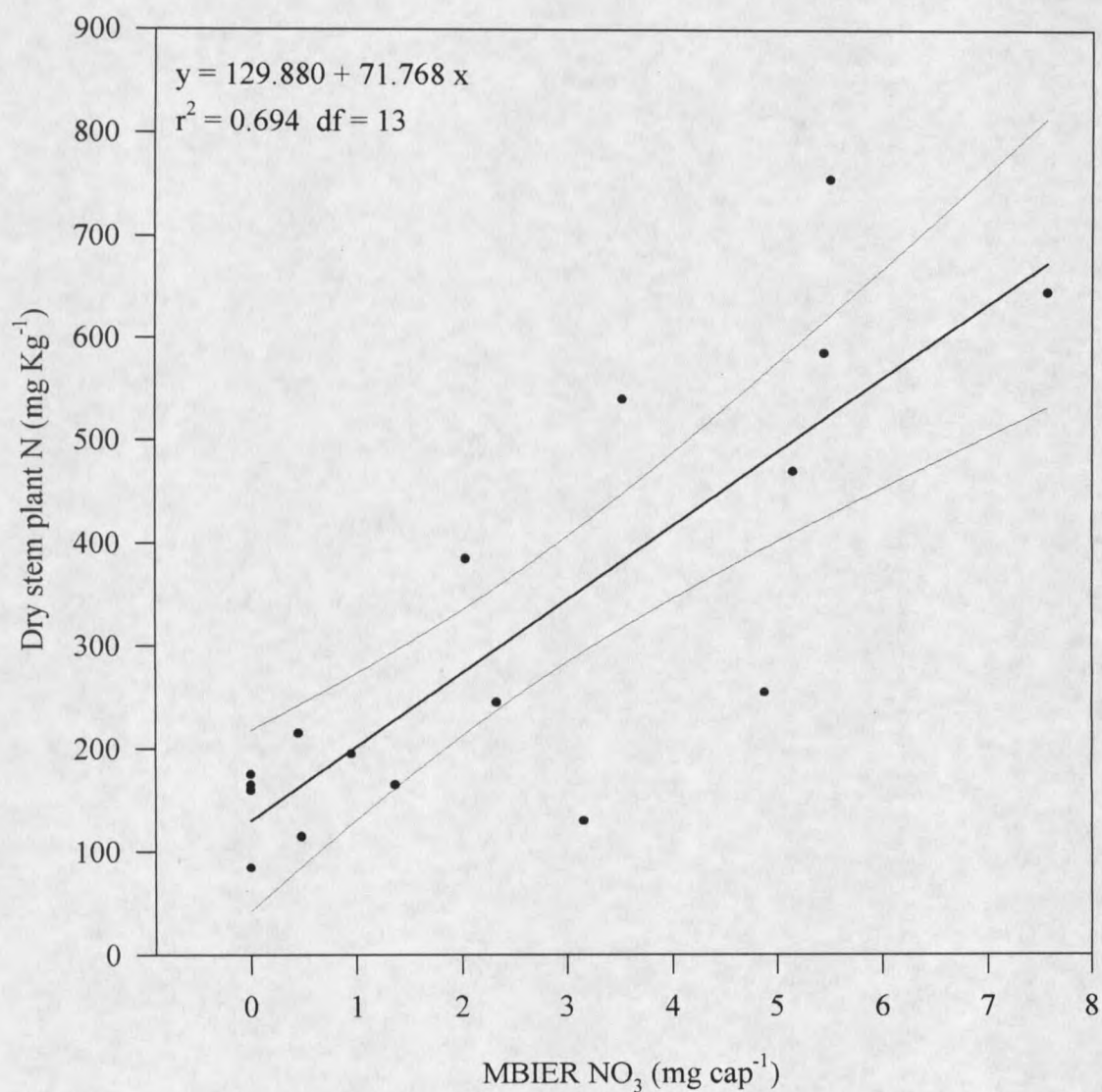


Figure 19. Regression of 1994 mint stem NO₃ on 0.15 m *in situ* MBIER NO₃. Treatments were 134.5 kg N ha⁻¹ incremental, with once wk⁻¹ medium irrigation level.

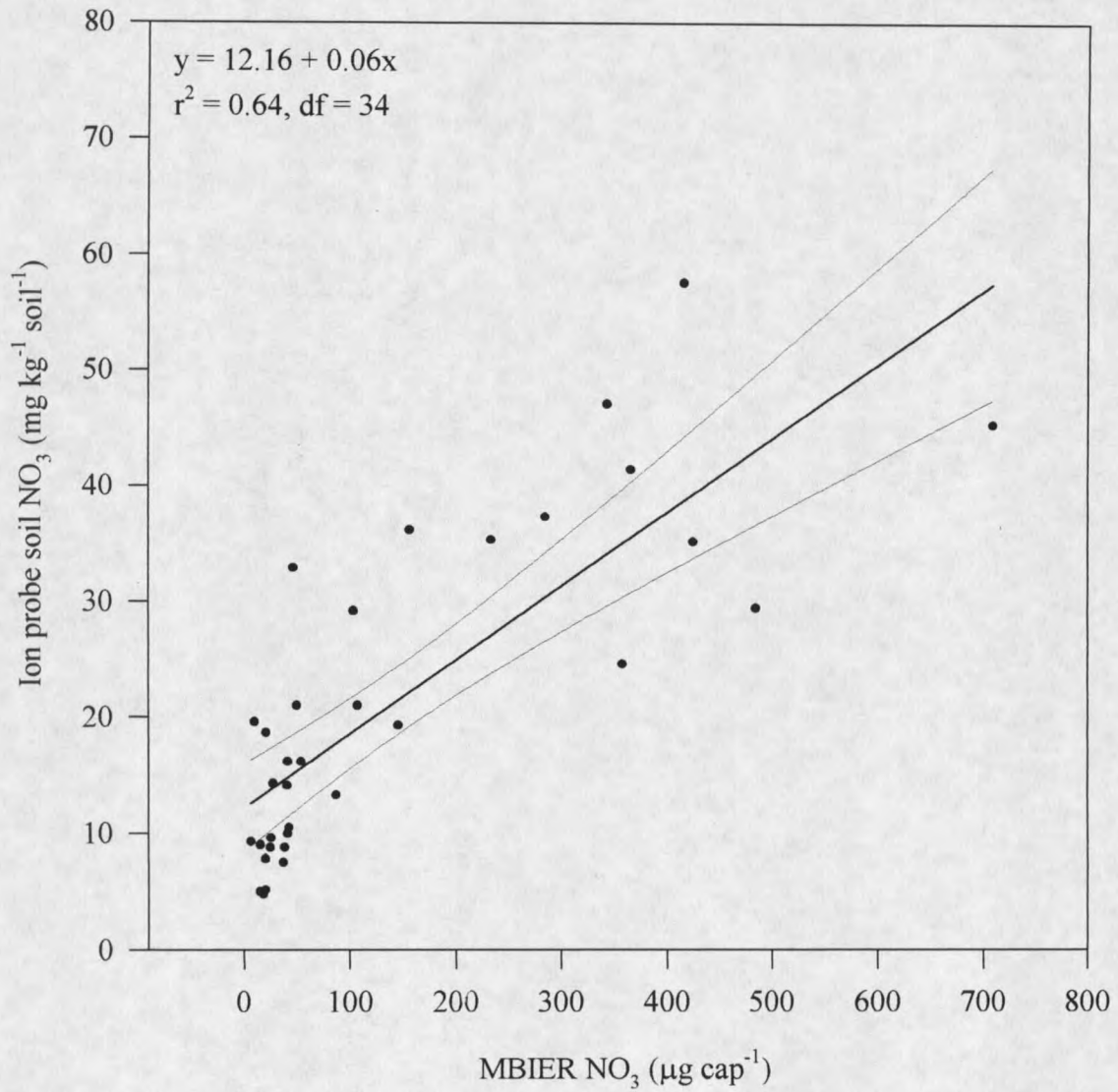


Figure 20. Standard soil NO₃, ion probe method, regressed on MBIER NO₃ for the 672.6 kg N ha⁻¹ incremental treatment for the 1993 and 1994 growing season.

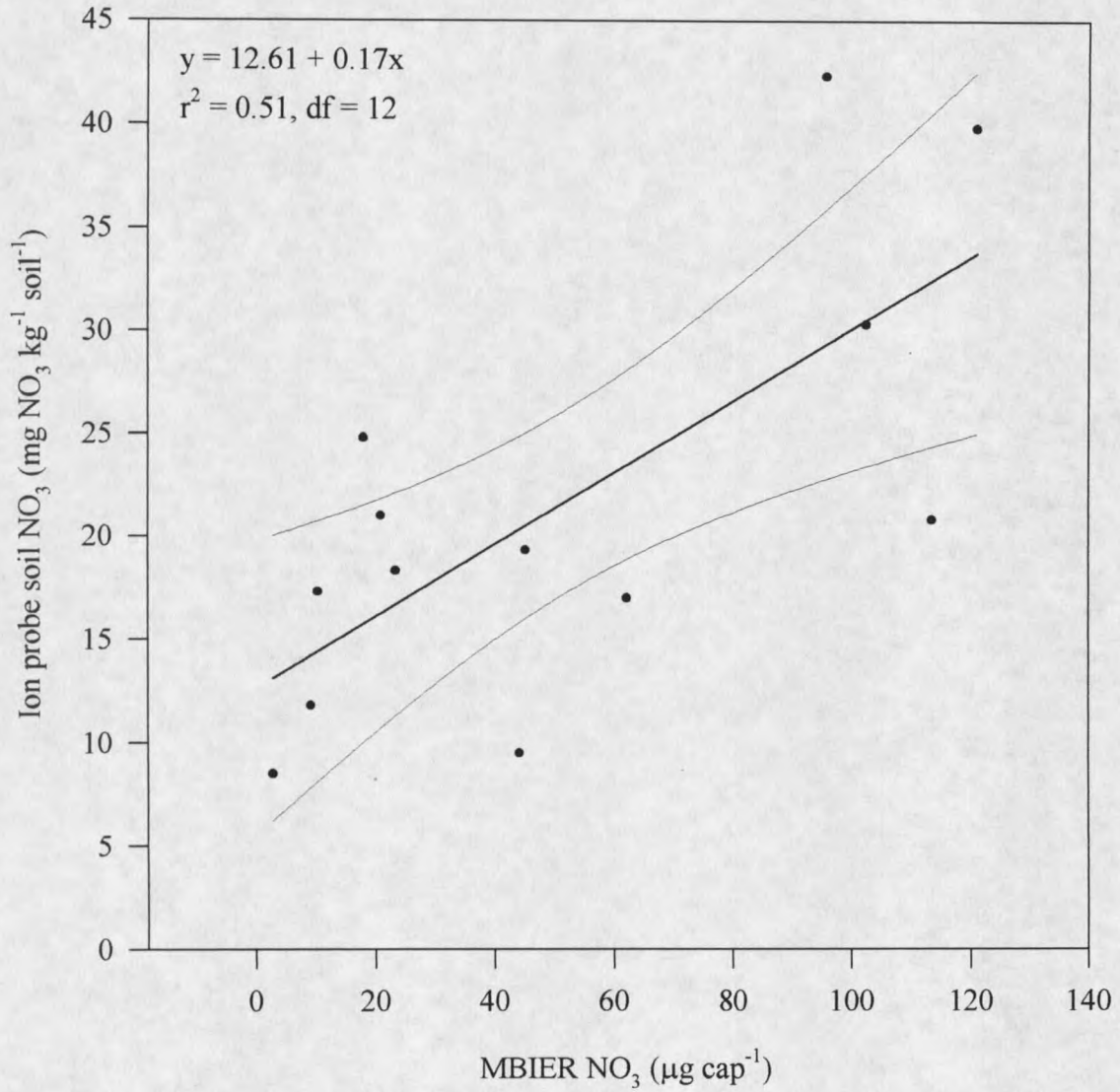


Figure 21. Standard soil NO₃, ion probe method, regressed on MBIER NO₃ for the 403.5 kg ha⁻¹ incremental treatment for the 1994 growing season.

CHAPTER 5

RESULTS AND DISCUSSION FOR THE GOLDEN TRIANGLE AND SIDNEY SITES

Saturated Paste NO_3 Adsorption by MBIER

There were no differences in the quantity of NO_3 adsorbed over time (2, 4, or 7 days) by MBIER capsules in saturated pastes from soil samples taken at the 0 to 0.15 m depth in 1993 at the Golden Triangle sites (Figure 22). This occurred whether sites were analyzed individually or combined, using the standard error of the mean (SEM) to denote statistical significance. Dynamics in the N system probably occur during the 2 to 7 day period as the saturated paste sample creates anaerobic conditions. Apparently, at these sites, such changes yielded neutral effects on NO_3 adsorption by capsules. With one exception, the same results occurred with samples collected from the 0.15 to 0.61 m depth (data not shown). In the one case where a difference did occur, there was a decline in the quantity of NO_3 adsorbed over time (Table 10). It is not clear what caused this decline, but it is possible that the anaerobic conditions in the saturated paste resulted in denitrification and actual loss of resin-adsorbed NO_3 as the solution concentration declined over time.

Based on 1993 results, samples were subjected to only the 2d capsule adsorption period in 1994. Nevertheless, some of the data from 1993 illustrate that capsules will reflect

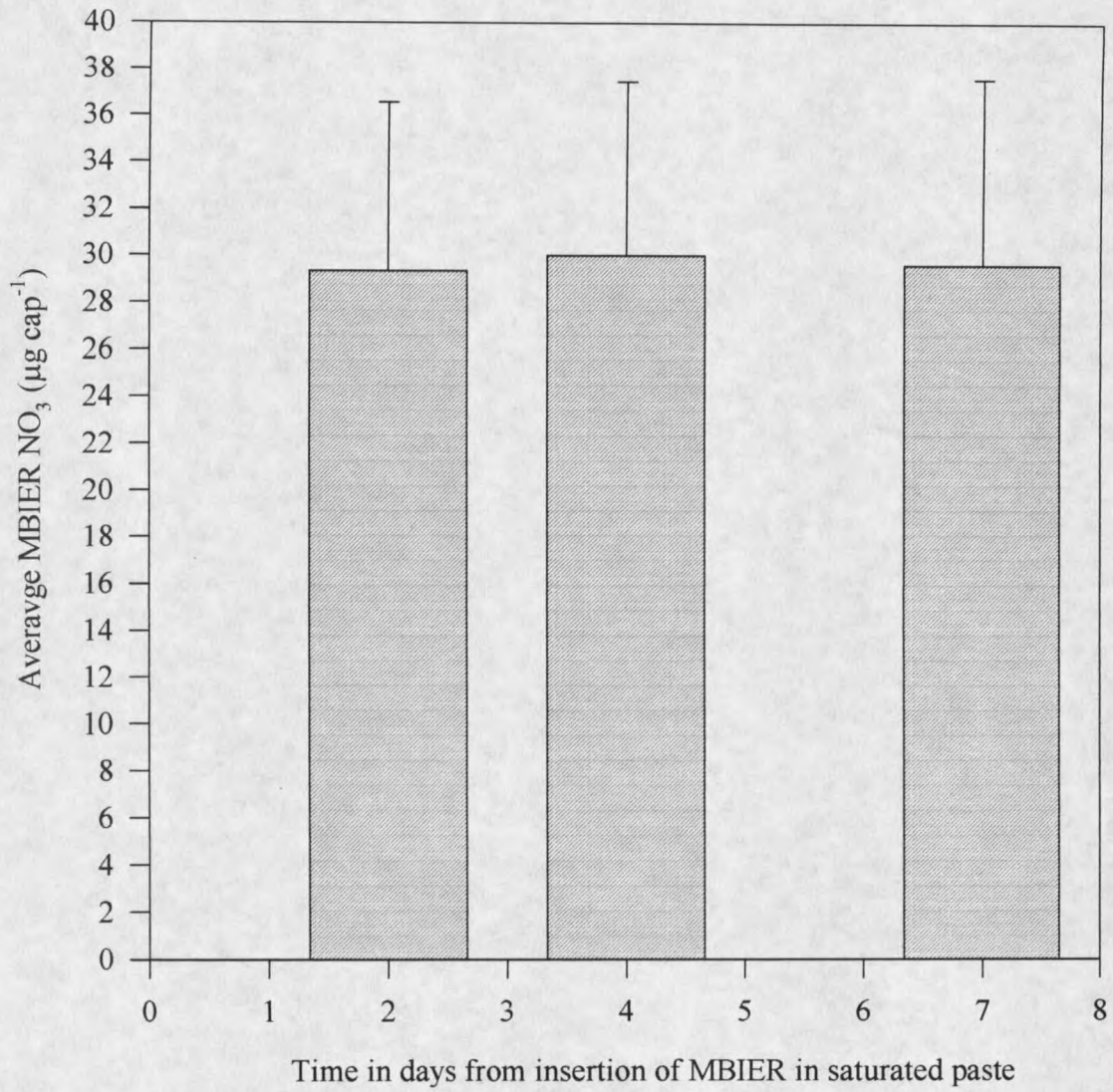


Figure 22. Two, four, and seven day MBIER standard error of the mean for the Ledger, Ft. Benton, and Loma 1993 field season, across both sampling dates and all treatments.

Table 10. LSD for MBIER at the 0.15 to 0.61 m depth for 2, 4, and 7d data across both sampling times and all treatments for the 1993 field season.

Day	n	$\mu\text{g NO}_3 \text{ capsule}^{-1}$	Difference ¹
2	24	9.317	B
4	24	6.504	AB
7	24	3.871	A
		LSD = 3.666	p \leq 0.05

¹ Different letters indicate significant differences based on LSD @ p \leq 0.05.

soil N dynamics under certain conditions. Figure 23 illustrates that the MBIER continued to adsorb NO_3 over the seven day period in samples collected at Sidney. This difference in response to time may be due to the level of NO_3 available, as the amounts adsorbed by capsules were about 10 times greater from soils at Sidney than from those from the Golden Triangle. These results do suggest, however, the possibility to develop the MBIER capsule system to diagnose differences in solution concentrations of NO_3 , as well as an indicator of various system components or dynamics. It may be possible to reveal effects of soil organic matter content, form of N fertilizer used, or the amount of mineralization taking place in various soils.

Average quantities of NO_3 adsorbed by MBIER capsules from Golden Triangle samples (0.15 m depth) were much lower during 1993 than for 1994 (Figure 24). In 1993 the Loma site had the greatest quantity of NO_3 adsorbed and Ledger had the least, while this was reversed in 1994. These differences do not correspond to those from standard soil test analysis of samples taken from the top 0.30 m prior to seeding. These analyses for 1993 from figure 24 clearly indicate that differences in available NO_3 occurred between the two

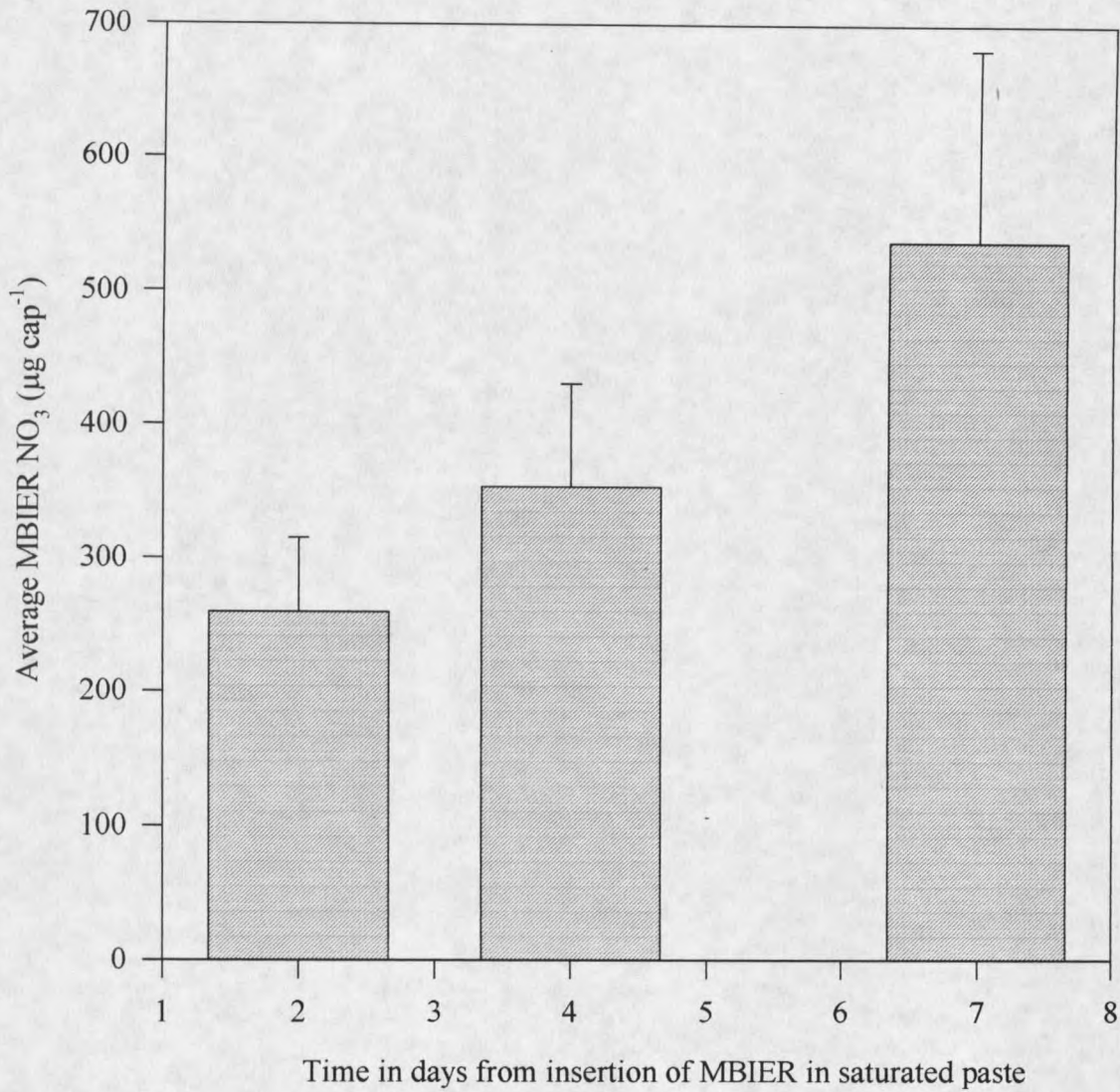


Figure 23. Two, four, and seven day MBIER standard error of the mean for the Sidney 1993 field season, across three sampling dates and all treatments.

growing seasons. The cool wet growing season during 1993 probably resulted in considerable NO_3 leaching to below the 0.15 m depth, as reflected by small amounts of resin-adsorbed NO_3 during the growing season.

Soil and Plant Relations

Differences in N accumulation by plants at the three sites at two sampling times and for the two years are shown in Figures 25 and 26. It is clear that seasonal precipitation, as well as other site variables, can result in large differences in N accumulation by the crop. The Ft. Benton and Loma sites were not statistically different, at either sampling, for 1993 even though there was a difference in the amount of NO_3 present for the initial soil test (data not shown; Jackson et al., 1993). Plant N accumulation for 1993 was significantly less at Ledger than at the other two sites. Plant accumulation of N, at all three sites, increased between sampling times, corresponding to a decrease in soil NO_3 (table 11) as measured either by standard or capsule methods. The decrease in soil NO_3 can be attributed to plant uptake and possibly leaching of the ion.

In 1994 the Loma site had less applied N than it did in 1993, but plant accumulation of N was statistically greater during the first sampling than for the other two sites (Fig. 26). There were no differences between the Ft. Benton and Ledger sites at the first sampling, but by the second sampling the Ft. Benton site had significantly greater N accumulation than the Loma site. These data also illustrate that there was virtually no uptake of N between sampling times for the Ledger and Loma sites. This was probably due to the extremely dry soil conditions during this period in 1994.

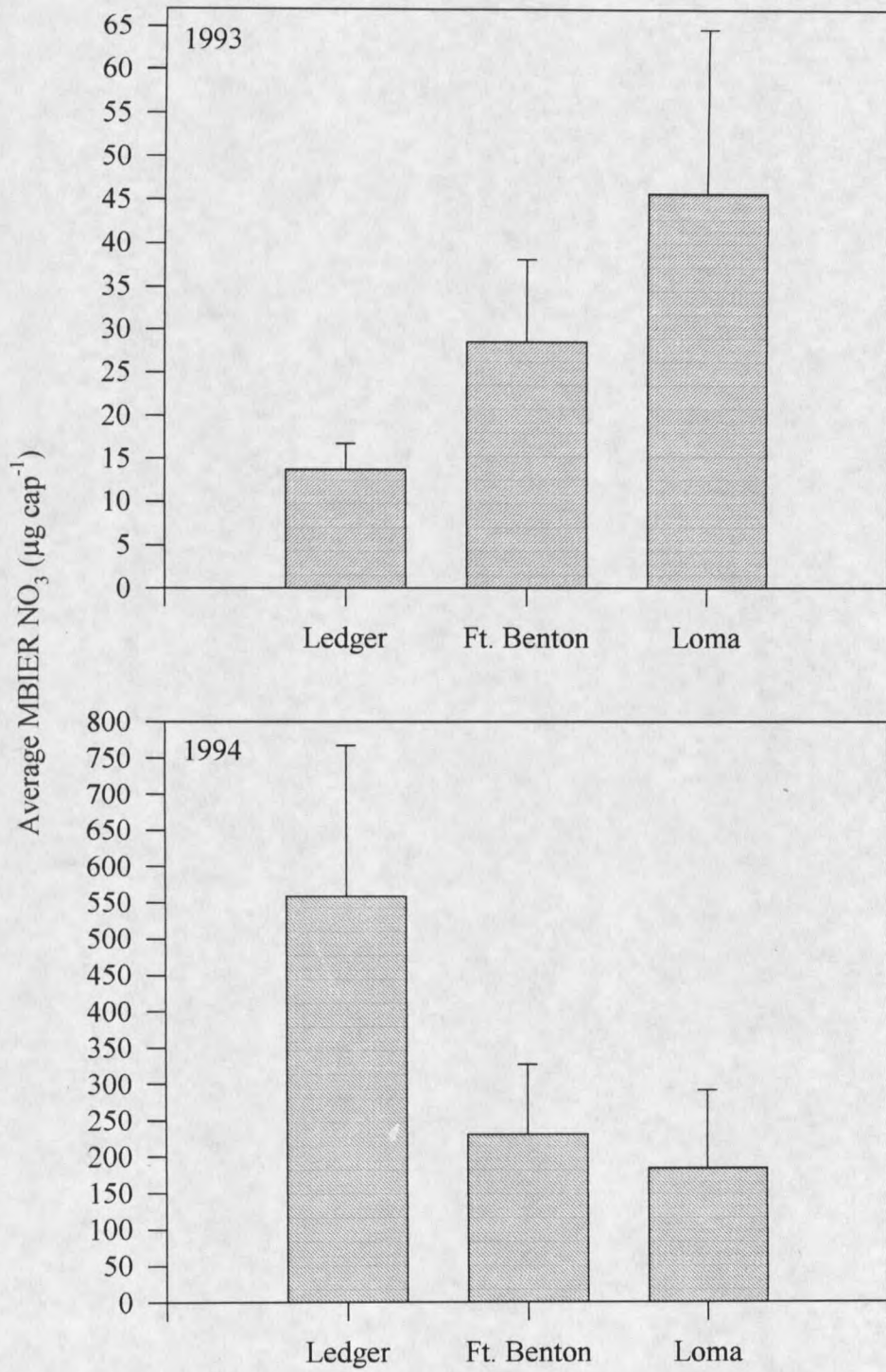


Figure 24. Average MBIER NO₃, separated by year, for Ledger, Ft. Benton, and Loma at the 0.15 m depth across both sampling times and all treatments.

Table 11. Soil NO₃ levels for the 0.15 m depth of Golden Triangle sites at two sampling times for 1993 as measured by resin capsules or standard soil test.

Location	Depth (m)	Time	n	µg NO ₃ -N cap ⁻¹	Difference ¹	mg NO ₃ -N kg ⁻¹	Difference ¹
Ledger	0.15	1	12	19.08	A	4.468	A
	0.15	2	12	8.3	B	3.59	B
				LSD = 9.434		LSD = 0.8167	
Loma	0.15	1	12	74.83	A	5.842	A
	0.15	2	12	16.66	B	3.863	B
				LSD = 54.65		LSD = 1.768	
Ft. Benton	0.15	1	12	44.75	A	6.183	A
	0.15	2	12	12.31	A	4.325	A
				LSD = 33.09		LSD = 2.360	
Ledger	0.61	1	12	11.21	A	1.911	A
	0.61	2	12	7.425	A	1.601	B
				LSD = 5.010		LSD = 0.2478	
Loma	0.61	1	12	59.78	A	3.083	A
	0.61	2	12	15.5	B	2.021	B
				LSD = 20.29		LSD = 0.9963	

¹ Different letters indicate significant differences based on LSD @ $p \leq 0.05$.

In contrast to 1993 results, NO₃ soil test levels increased between sampling times at Ledger and Loma in 1994 (Table 12). This indicates that the lack of N accumulation by plants during this period was not related to N availability, but probably due to the extreme dryness. Although soil water was limiting for plant growth, N mineralization would still proceed and there would have been no leaching of this N to lower depths.

Total plant N accumulation was regressed against soil test results from the two methods (Figure 27). It is clear that neither soil test method worked well to predict plant N uptake. During 1993 some NO₃ may have leached beyond the plant root zone before the

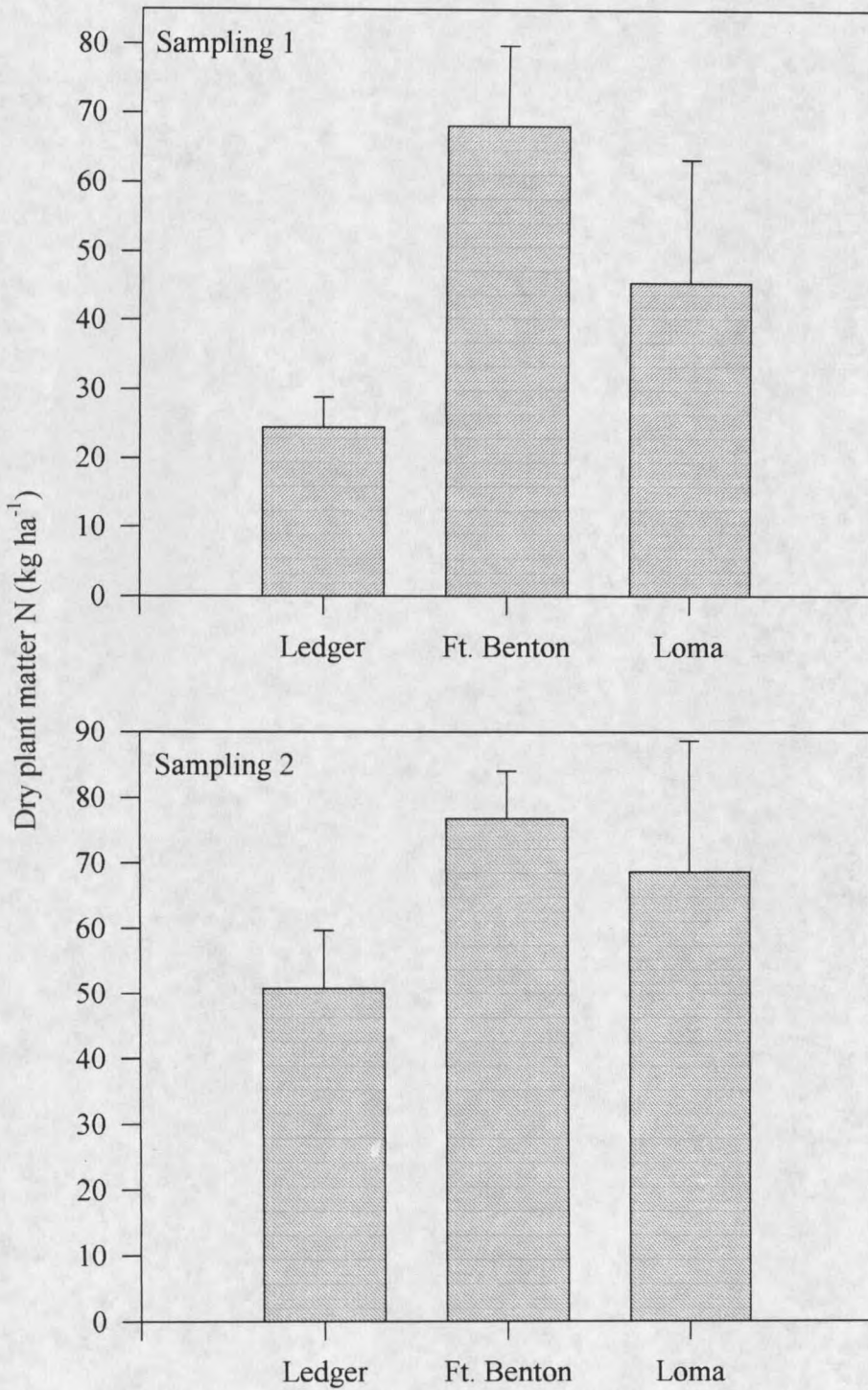


Figure 25. Spring wheat accumulation of N, separated by sampling and location, across all treatments for the 1993 growing season.

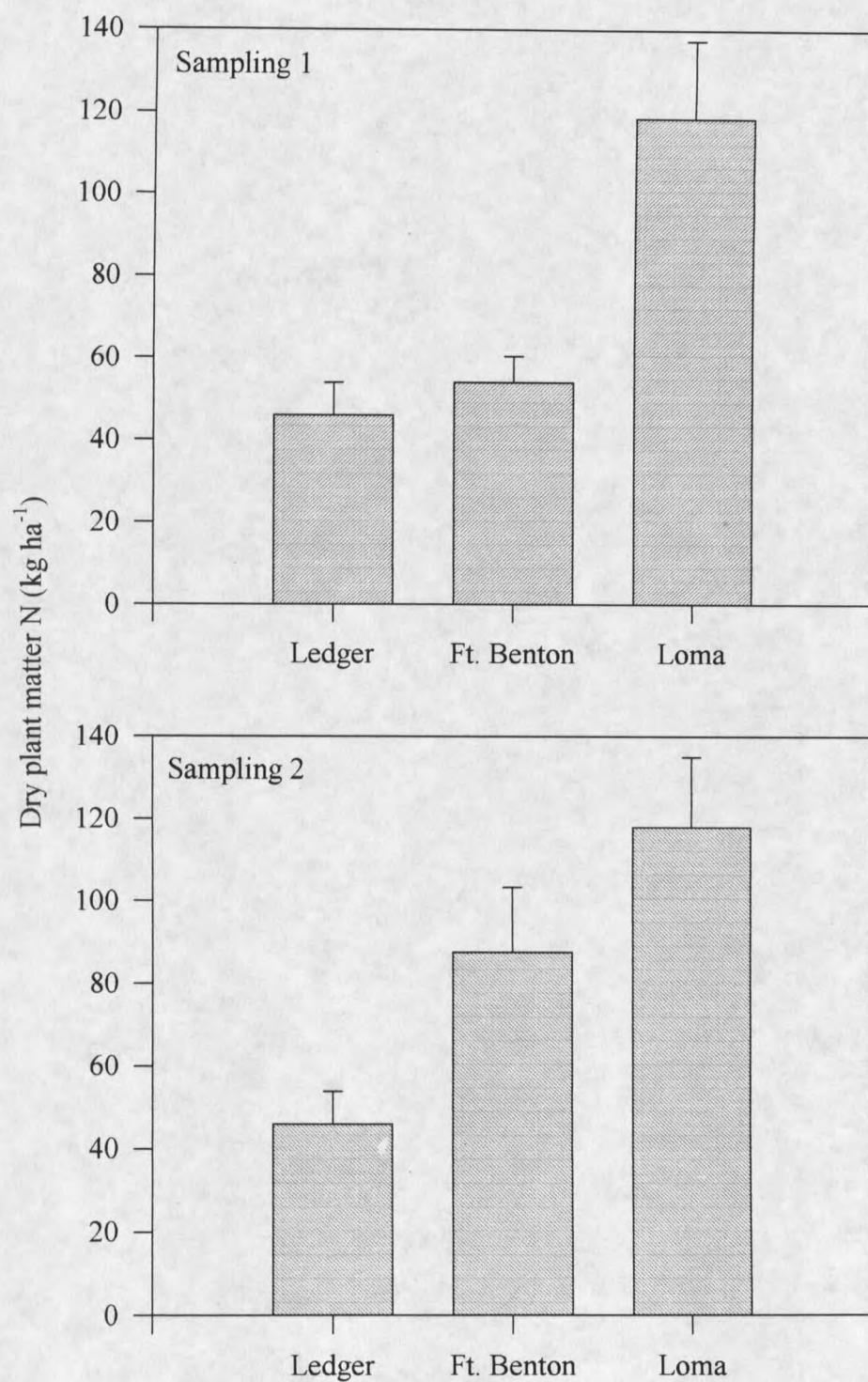


Figure 26. Spring wheat accumulation of N, separated by sampling and location, across all treatments for the 1994 growing season.

Table 12. Soil NO₃ levels for the 0.15 m depth at Ledger and Loma at two sampling times for 1994 as measured by resin capsules or standard soil test.

Location	Time	n	µg NO ₃ -N cap ⁻¹	Difference ¹	mg NO ₃ -N kg ⁻¹ soil	Difference ¹
Ledger	1	12	134.4	A	16.08	A
	2	12	982.6	B	56.77	B
			LSD = 655.5	LSD = 36.00		
Loma	1	12	37.55	A	12.70	A
	2	12	647.5	B	40.67	B
			LSD = 191.2	LSD = 11.12		

¹ Different letters indicate significant differences based on LSD @ $p \leq 0.05$.

plant could take it up, while in 1994 it seems obvious that water, and not N, was the limiting factor for crop growth.

Plant regressions on the MBIER data from Sidney were not practical, as the sampling dates for sugar beets were out of our control and different from the soil sampling dates. We feel these differences in sample dates to be great enough to invalidate comparisons.

Soil Test Comparisons

One objective of this research was to compare results from MBIER capsule soil test results with standard soil testing for NO₃. Most of the soil test data from the Golden Triangle sites were grouped near zero for both the MBIER and standard soil test, with only a few data points in higher ranges. Figure 28 presents the regression of MBIER against the standard laboratory soil test for NO₃ at selected sites and combinations. Graph (a) data were from the 0 to 0.15 m depths at Ledger, and across both growing seasons, sampling times, and all treatments. Graph (b) data were from the same site, but for the 0.15 to 0.61 m depth. Graph (c) data were from Loma at the 0 to 0.15 m depth. Graph (d) includes data from all

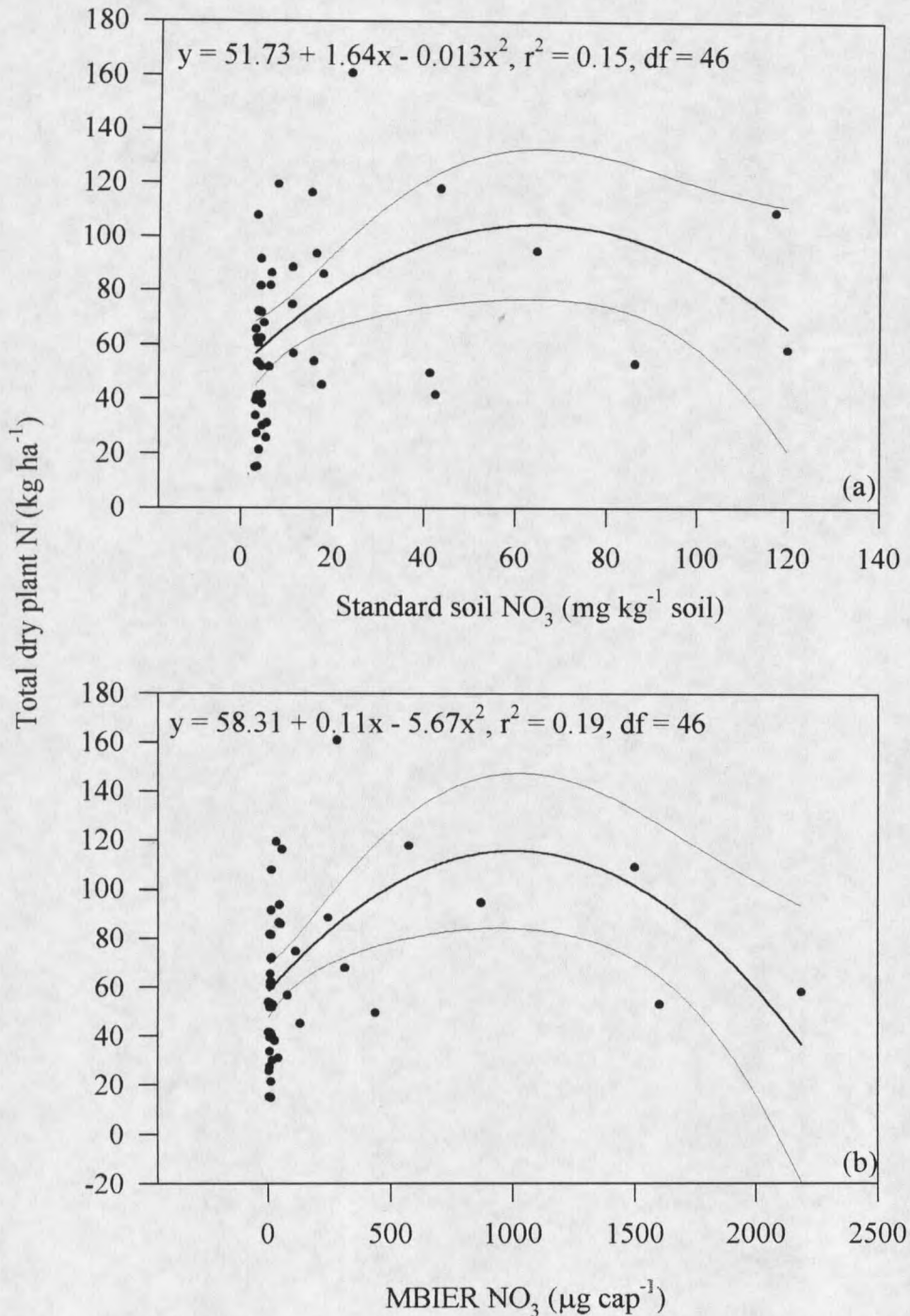


Figure 27. Regressions of accumulated spring wheat N on the upper 0.15 m of soil, using different methods of soil testing. Regressions are across all treatments, samplings and locations for the 1993 and 1994 growing seasons.

three sites at the 0 to 0.15 m depth for both years, and across all sampling dates and treatments. The highly significant correlations between soil test results suggests that the MBIER capsule method could be developed as an alternative to the standard method. The combined regression of the three sites is significant at $p \leq 0.05$ (Figure 28, graph d), with an r^2 of 0.90 and with 47 degrees of freedom. The capsule test is much simpler, quicker and more energy efficient than the standard test, and if it provides similar data there would be no need to conduct years of additional field trials for correlation with crop response. Data from the MBIER, saturated paste method of laboratory testing, could be used for the balance sheet approach (by correlation with standard test values) for determining the rate of N-fertilizer needed by the producer. This potential is encouraging considering the difference in field sites as well as the vastly different moisture conditions for the two field seasons (Table 5) in this study. One additional requirement for this to be possible, however, would be for soil test data from different depths to be additive.

Additivity of MBIER Soil Test Data

Data from the standard soil test are additive for the different depths sampled, as the units for the test are based on soil mass. MBIER test results are expressed as mass of nutrient accumulated by the capsule, and the mass of soil contributing the accumulated nutrient is soil-specific (and generally not known). If, however, the good relationship between standard and MBIER methods that occurred for the surface soil layer (Fig. 28) is also expressed for results for lower soil depths, it may be possible to add results from the MBIER in the same way as for standard tests. Standard soil testing for NO_3 , in theory,

removes all of the NO_3 from the sample being extracted. This is not the case for MBIER, even where there were no changes in resin-adsorbed NO_3 after 2 days. The lack of change probably means that the dynamics occurring during the change from aerobic to anaerobic in the saturated paste sample resulted in neutral effects on NO_3 adsorption. This was different at Sidney, where NO_3 continued to be adsorbed beyond the two day time period. These different results suggest, however, that the 2-day results from MBIER would likely be the most appropriate for comparison with the standard test to determine additivity.

When testing the soil for NO_3 , the total amount available in the plant rooting depth is of interest. Soil samples are generally taken at 0.30 m intervals to the approximate rooting depth, or to a root-limiting soil layer. Quantities of NO_3 in each soil depth are added to determine total available NO_3 . Data to compare the additive properties of MBIER over different depths are available only from the Ledger, Loma, and Sidney sites for all sampling times and treatments, so these were used for comparison with the standard test results.

Evidence for additivity can be seen in Figure 28(b), where the regression of standard soil and MBIER averaged data for the 0.15 to 0.61 m soil depths is shown. Figure 29 presents the regression of the standard soil test raw data on the MBIER raw data, with the MBIER not adjusted for depth, but the standard soil adjusted for depth. The r^2 value of 0.90, with 95 degrees of freedom, and over a rather broad range of test values, suggests that this approach may be feasible to develop. When the MBIER raw data were adjusted for depth, there was a slight increase in the r^2 value (Fig. 30).

Figures 31 and 32 present similar regression for the data collected at Sidney in 1993 and 1994. The relationship for 1993 (Fig. 31) was much better than for 1994 (Fig. 32). Reasons for this discrepancy are not clear.

Figure 33 presents the regression of all of the raw standard soil data combined over both years, including dryland and irrigated plots. The data from the dryland plots included two depths, while that for irrigated plots were from three soil depths. The r^2 for this relationship was 0.62 with 172 degrees of freedom and $p \leq 0.05$. These are significant relationships, but they are such that they leave questions concerning using this statistical approach as a means of proving the additivity of MBIER capsule data for NO_3 . Much more research must be conducted, specifically on this relationship, to elucidate the potential for additivity of MBIER capsule results.

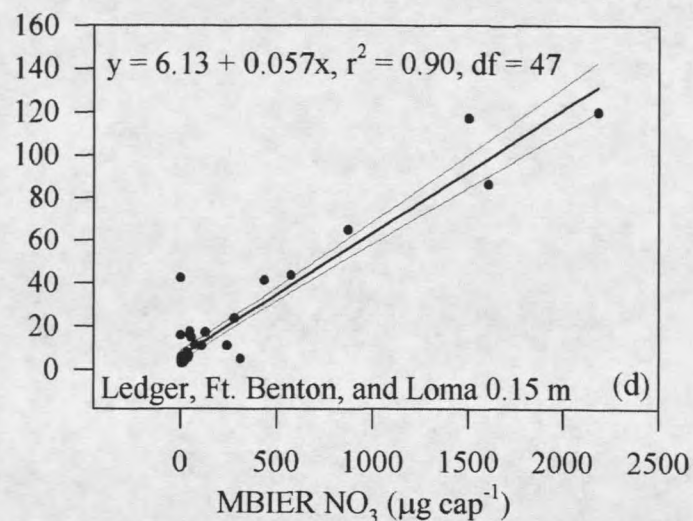
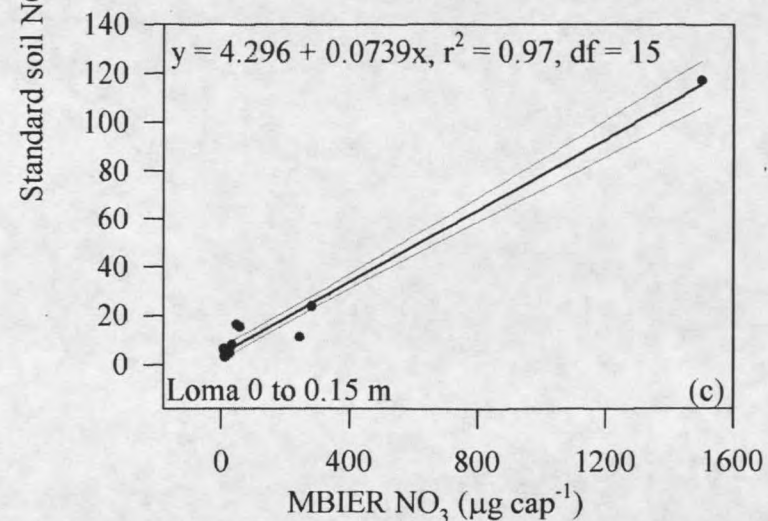
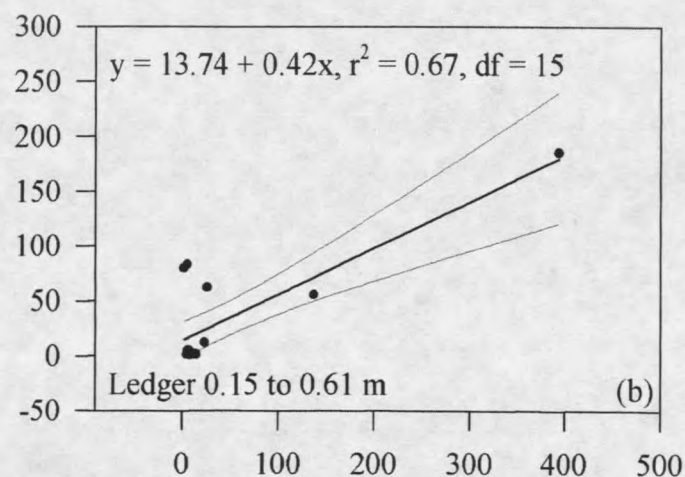
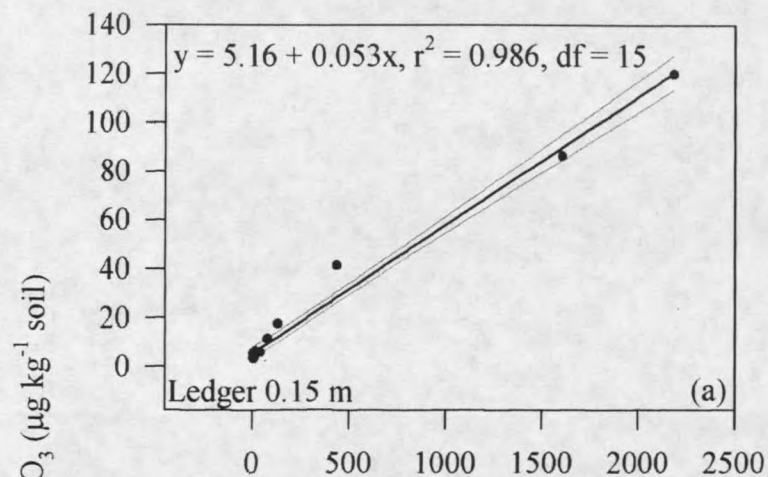


Figure 28. Regression of standard soil test NO₃ on two day MBIER NO₃ from chosen sites and depths on the Golden Triangle. For graphs a through d 1993 and 1994 soil data are combined.

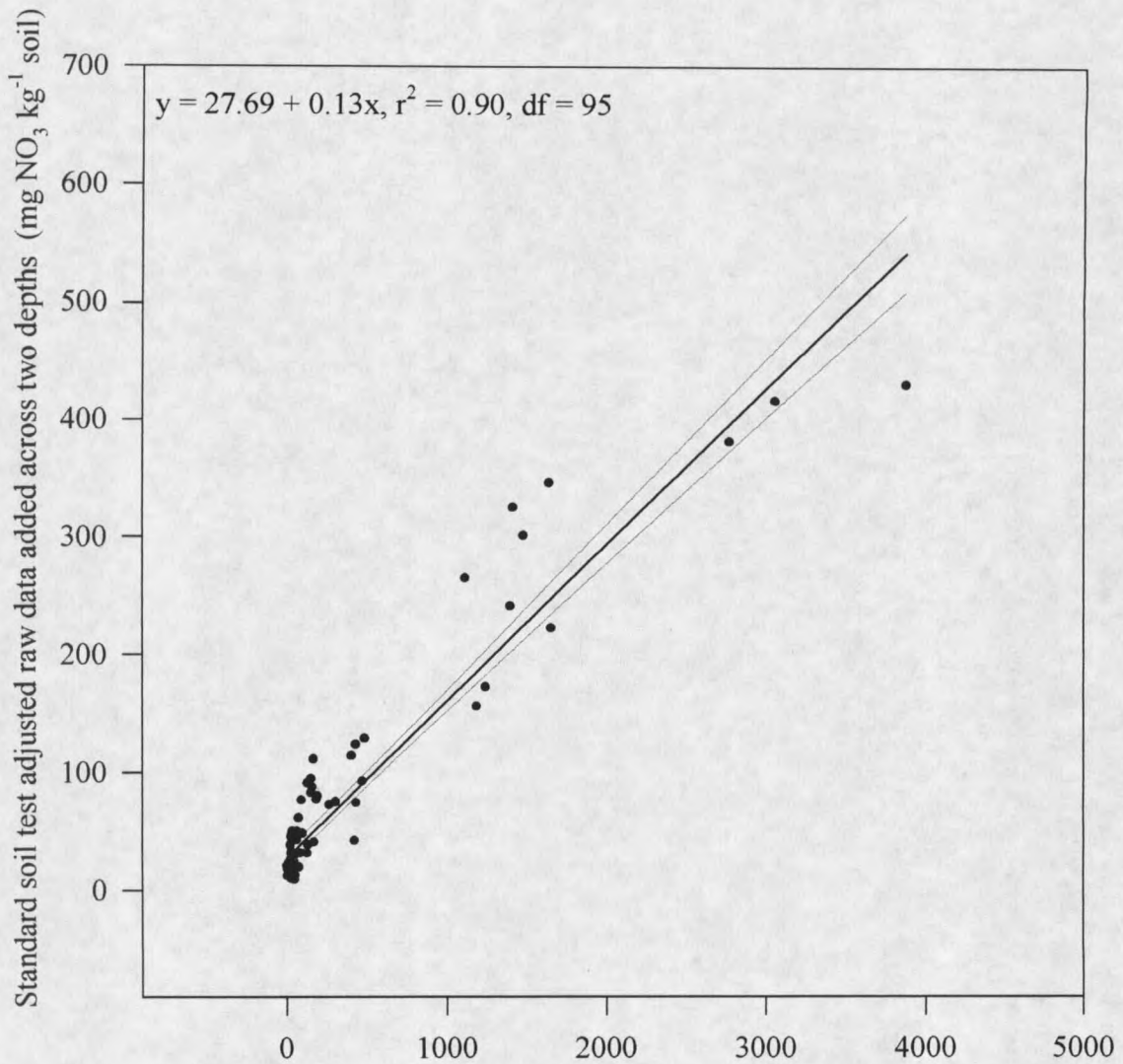


Figure 29. Possible additive properties for two methods of soil testing for NO₃. The standard soil test data has been adjusted for depth and the MBIER data has not been adjusted for depth. The regression is on raw data from Ledger and Loma across the 1993 and 1994 field seasons.

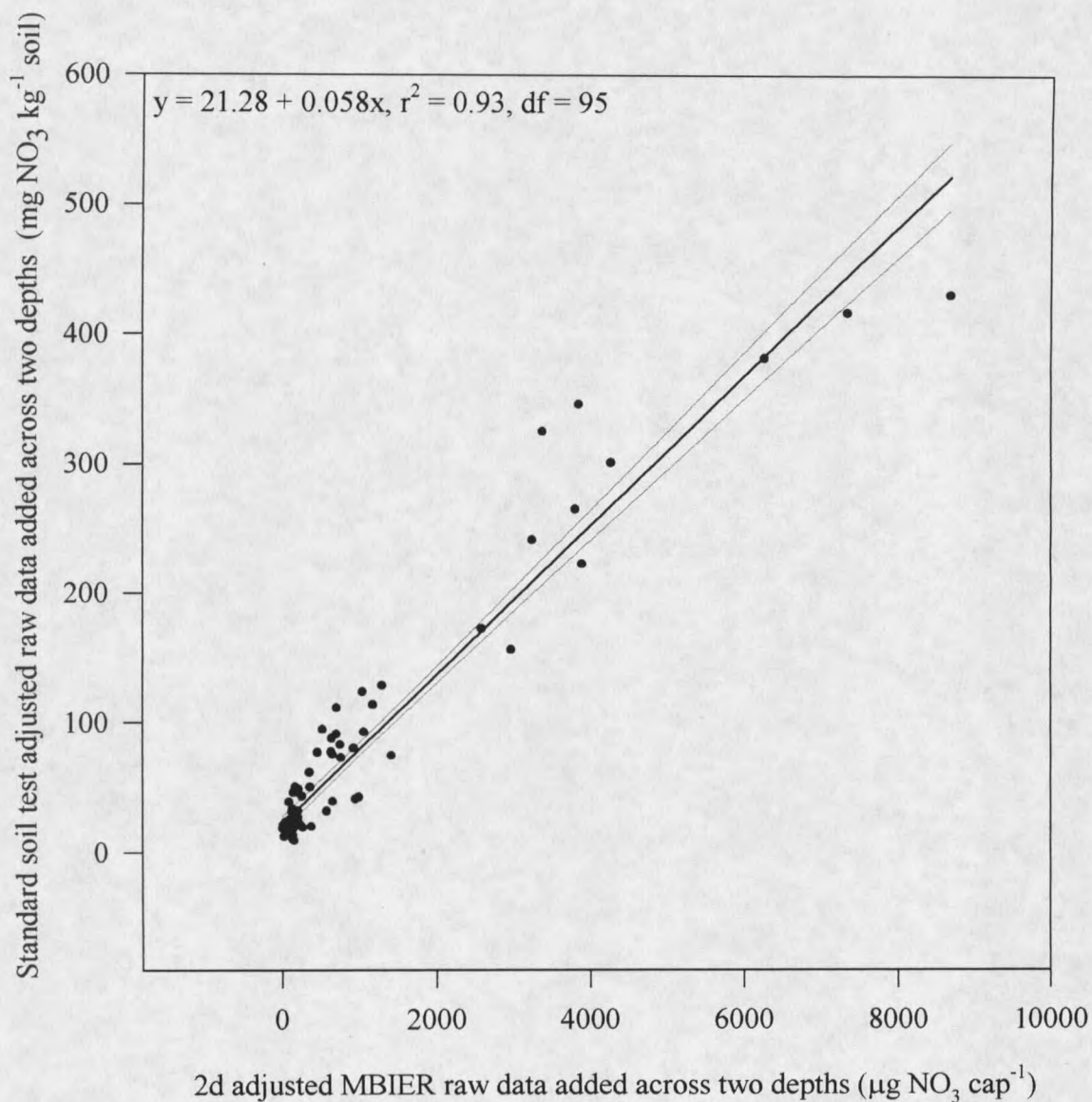


Figure 30. Possible additive properties for two methods of soil testing for NO_3 . The standard soil test and MBIER data were adjusted for depth. The regression is on raw data from Ledger and Loma across the 1993 and 1994 field seasons.

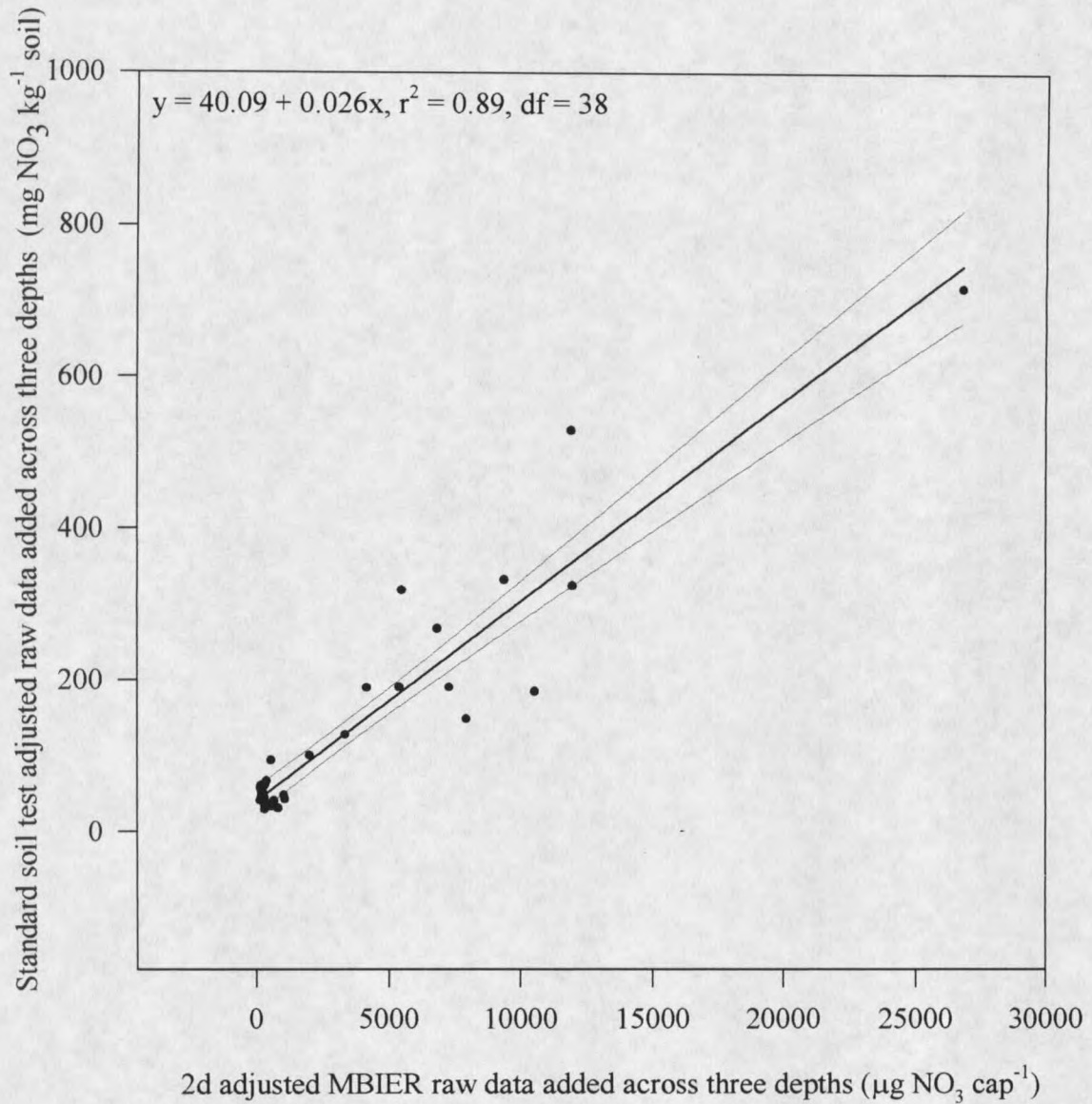


Figure 31. Possible additive properties for two methods of soil testing for NO_3^- . The standard soil test and MBIER data were adjusted for depth. The regression is on raw data from Sidney for the 1993 field season.

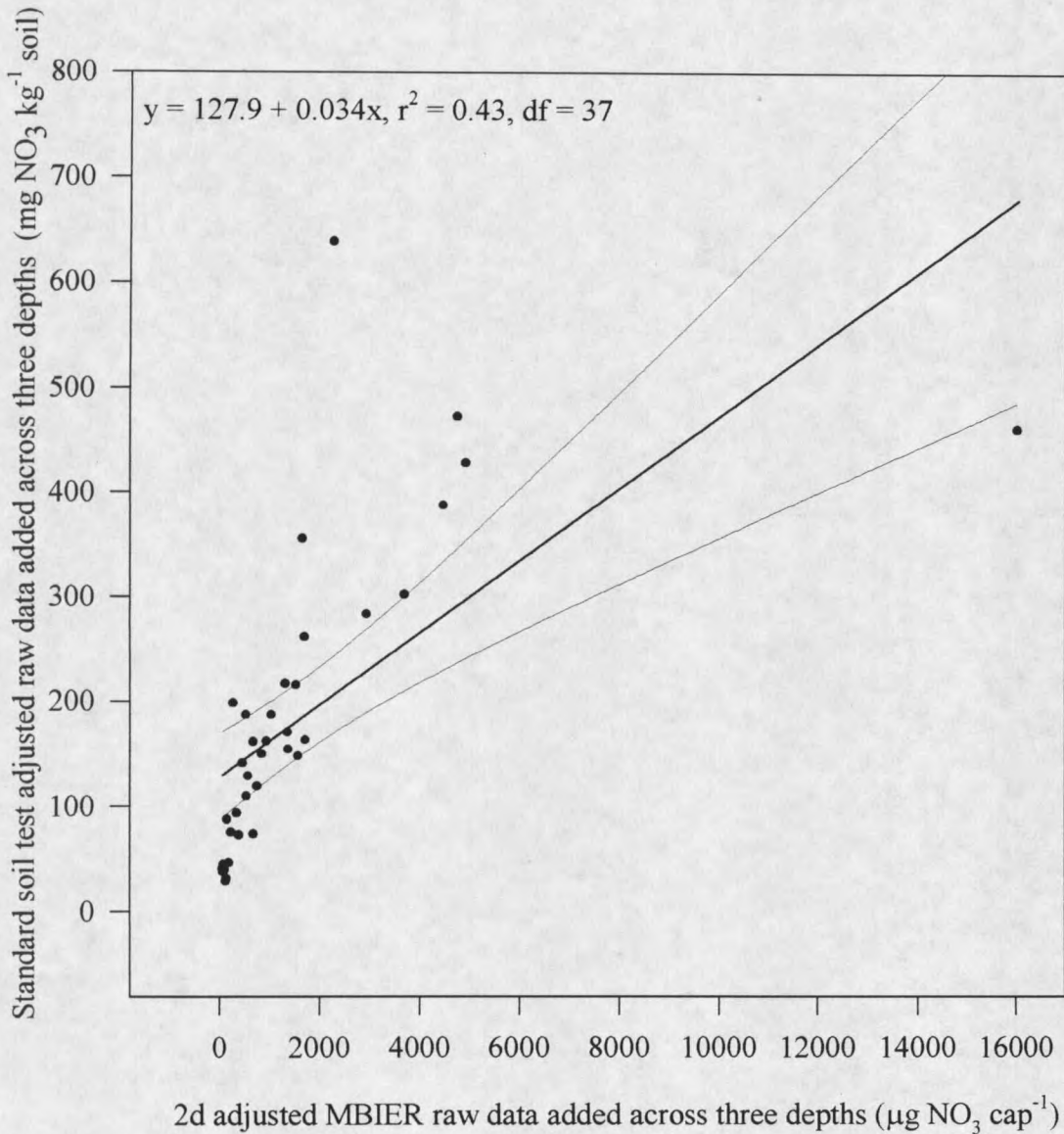


Figure 32. Possible additive properties for two methods of soil testing for NO_3 . The standard soil test and MBIER data were adjusted for depth. The regression is on raw data from Sidney for the 1994 field season.

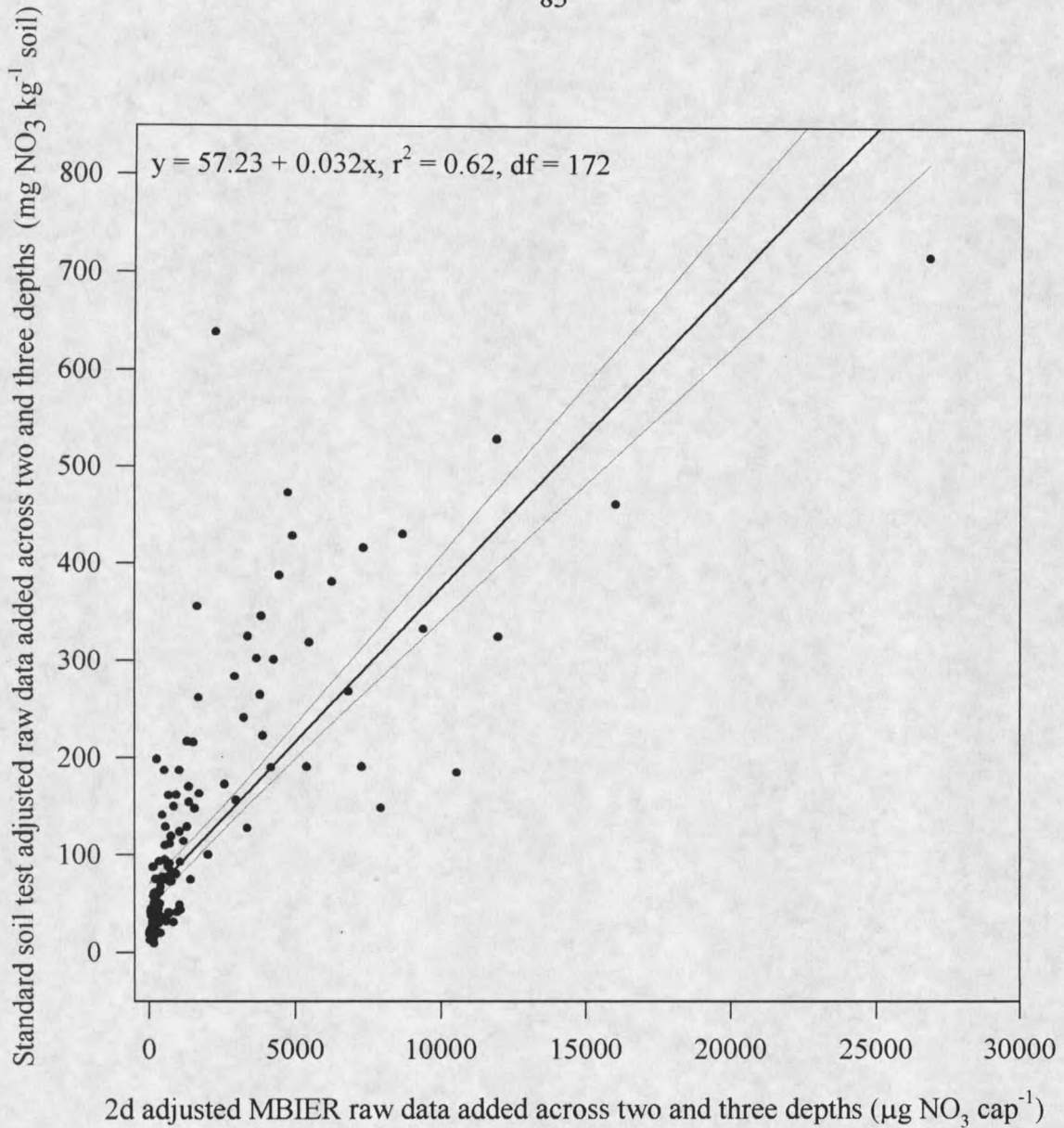


Figure 33. Possible additive properties for two methods of soil testing for NO_3 . The standard soil test and MBIER data were adjusted for depth. The regression is on raw data from Sidney, Ledger, and Loma for the 1993 and 1994 field seasons.

CHAPTER 6

CONCLUSIONS

Creston

There is no long term baseline for the *in situ* study. The data from the first sampling period, for each year, was used as a baseline for this study. The winter *in situ* study was the exception, the baseline was from the summer study of NO_3 and Br movement.

The irrigation treatment for 1993 had no effects on results, due probably to the greater than normal precipitation, whereas, irrigation treatments had an effect during the drier 1994 season. The greater soil water content of the 1993 growing season probably facilitated mass movement of NO_3 and Br past the *in situ* MBIER. Lower soil water content for 1994 probably allowed diffusion to have an influence on the quantity of nutrient and tracer adsorbed to the MBIER. The difference in soil water content did not interfere with the MBIERs ability to monitor 'event based transport.' In other words, during a specific time lapse, when a presumably higher quantity of NO_3 or Br moved past the MBIER, a larger quantity of NO_3 and Br was adsorbed to the capsule.

MBIER capsule technology is a good method of repeated measures in an environment of varying soil water contents. We suggest that the different quantities of NO_3 and Br adsorbed between the two seasons at Creston are due, in large part, to differences in

soil water content. This was indicated by results from the saturated paste method on incremental treatments which showed that the upper 0.15 m of the soil had increasing NO_3 for 1994, but this increase was not reflected by the *in situ* MBIER quantities adsorbed. Because the soil water content is much higher in the saturated paste the ions can diffuse to the capsule more freely than in the natural soil system that has a soil water content of between 0.10 and 0.14 % by volume. If the soil water content had been like that of 1993, NO_3 would probably have moved more readily to the *in situ* capsules showing the build up of NO_3 . Such a build up was noted with the 1993 *in situ* capsules. This indicates that the mint was not using all of the NO_3 from the soil pool, thereby allowing the NO_3 to build up in the shallow soil profile. Soil water content plays a critical role in the quantity of nutrients a plant will uptake and in the quantity of NO_3 and Br that the MBIER will adsorb. Again this is an indicator that the MBIER imitates a plant root in the soil system. Dobermann et al., 1994 and Qian et al., 1992, state that ion exchangers remove ions from the soil in a manner analogous to a plant root.

There was generally a lapse of about one to two weeks between the Br and NO_3 BTC at 0.15 m, and the NO_3 BTC generally declined more slowly than the Br BTC. Both of these results suggest that NO_3 was being generated from the applied urea over a period of several weeks. On the other hand, only one quantity of Br (that which was initially applied) was available for leaching, and its BTC was clear and distinct.

The applied single application of Br better modelled the single application rather than incremental applications of urea, as is expected. The single application of urea had enough nitrogen applied to allow for a quick surplus of NO_3 in the soil. This surplus of NO_3

moved much like Br. On the other hand, incremental treatments did not have a like amount of quickly available NO_3 , but over the course of the growing season this treatment resulted in a build-up of NO_3 in the upper 0.15 m of soil. Results from MBIERs that reflect these differences further illustrate their capability to monitor a dynamic system. This is consistent with Binkley and Matson, 1983, who state that the resins demonstrated a sensitivity to on-site factors that other laboratory methods do not test.

Winter monitoring of NO_3 movement was on plots that received the once weekly low and medium irrigation treatments. For medium and low irrigations at the 0.61 m depth, NO_3 peaks occurred in September and October. It was clear that NO_3 continued to diffuse to the MBIER two and one half months after the last urea treatments. This is an indication that the soil water content was still sufficient for ion diffusion to occur.

Results from continued monitoring of NO_3 after harvest showed clearly that N dynamics in the upper and lower depths continued to function. At the 0.15 m depth N dynamics continued until the soil froze. At the deeper depths NO_3 continued to diffuse to the MBIER throughout the winter. The MBIER results during this period, however, reflected decreased N dynamics due to minimal soil water movement and decreased soil temperatures. This is consistent with findings by Binkley, 1984, and Lajtha, 1988.

The NO_3 present in the lower depths after the growing season is not likely to be intercepted by the mint roots when a new growing season begins. As the water is applied and starts to move through the soil profile the NO_3 will be pushed even deeper and move beyond the plant roots. In the case of mint (a shallow-rooted crop), any of the NO_3 detected by MBIER at 1.22 m is likely to leach eventually into the groundwater. It would have been

preferable to continue studies at the same location over the two-year span, but plots had to be reestablished at a different location in 1994 due to road construction. To determine long-term effects on NO_3 and Br ion movement, it would have been better to leave the plot in the same location for at least two years and possibly longer.

The only significant mint stem NO_3 regression on the *in situ* MBIER NO_3 occurred with the $403.5 \text{ kg N ha}^{-1}$ single application and at the once per week medium level irrigation. The same relationship was significant in 1994, along with some incremental treatments.

Mint stem NO_3 was higher in 1993 than 1994. The regressions between plant stem and MBIER NO_3 tended to be better in 1994 than 1993. The relationship could have been influenced by different factors. Between the years plants were subjected to much different light, temperature, and water conditions, some of which probably influenced metabolic activities involving nutrient translocation and assimilation. Soil factors which were different between the two seasons include soil water relations and nitrification rates.

The regression of values obtained from ion-selective electrode and *in situ* MBIER across both years and all treatments did not have a significant relationship. There were some significant regressions within treatments for individual years. This is an indication that under certain conditions resin capsules provide data similar to the ion-selective probe, but more importantly, it suggests that capsules are capable of capturing N dynamics occurring over time, whereas periodic soil sampling and analysis did not.

The resin capsule proved to be a highly useful tool for simultaneous, *in situ* monitoring of NO_3 and Br movement. The MBIER was sensitive to 'event based transport' of NO_3 and Br. The capsule was sensitive to generation of NO_3 over time, indicating the

capsule's capability to monitor a dynamic system. The MBIER also proved to be sensitive to changing N dynamics as influenced by soil water content and soil temperature.

Golden Triangle and Sidney

In soil from the Golden Triangle the MBIER adsorbed about the same quantity of NO_3 when it was left in the saturated paste for two, four, or seven days. In soil from Sidney the MBIER continued to adsorb NO_3 throughout the seven day period. The magnitude of NO_3 in soils from the two regions was, however, much different, suggesting that time effects on resin capsule accumulation of NO_3 may provide an additional parameter for correlating results with actual field conditions.

Combined standard soil test NO_3 data regressed well on combined MBIER NO_3 data from the dryland plots, $r^2 = 0.90$. The 0 to 0.15 m sampling depth tended to have the best regressions of the standard soil test on the MBIER saturated paste method. Similar regressions for the Sidney data did not turn out as well.

The standard soil test data regressed well on the MBIER saturated paste data, but for the MBIER results to be most useful for prescribing N fertilizer management, data from multiple soil depths should be additive. Preliminary results suggest that the MBIER data may be additive, but experiments with this as a main objective will need to be conducted to further elucidate this relationship. Nevertheless, results from this study are encouraging. More research is needed to compare the standard soil test with the MBIER methodology to establish a relationship between the different methodologies. If a strong relationship can be established, the balance sheet approach for N fertilizer prediction could be used. This is an

approach familiar to producers, and relying on it would be a less time-consuming approach to developing the resin capsule technology for soil testing, as compared to conducting years of field research under a broad range of conditions to directly correlate the capsule approach.

A number of approaches could be used with resin capsules for soil testing. For example, a producer could use the MBIER saturated paste methodology directly at the sampling location. The freshly taken sample could be made into a saturated paste and the capsule inserted into the sample for a prescribed time period. The capsule could then be removed from the saturated paste, rinsed, and sent to the laboratory for analysis, thereby reducing shipping and handling costs. Also, by using the MBIER saturated paste system of soil testing, the soil, a precious resource, can be left in the field. The soil used for the saturated paste could be returned to the field, as there are no harsh or toxic chemicals involved.

Average quantities of NO_3 adsorbed by MBIER capsules from the Golden Triangle samples (0.15 m depth) were much lower during 1993 than for 1994. Saturated paste MBIER quantities, between years, were opposite for irrigated vs dryland. The MBIER adsorbed large quantities of NO_3 from irrigated plots for the 1993 growing season, whereas, the adsorption was low from dryland plots. The opposite was true for the 1994 growing season. Differences in precipitation during the two years may have been responsible for these results. Because 1993 was quite wet and cool, there was a greater possibility of NO_3 leaching with each precipitation event.

At Sidney during 1993 the increased precipitation and cloud cover probably decreased photosynthesis and evaporative demand of sugar beets, thereby decreasing the uptake of NO_3 , and leaving a pool of NO_3 in the soil, as detected by soil tests.

Plant uptake for N was higher in 1994 than in 1993 on dryland plots, with the Ledger site being the exception. The difference, between years, in the amount of plant N at Ledger was small. The drier and warmer summer of 1994 would have resulted in less movement of NO_3 out of the rooting zone, increasing that available for plant uptake.

Neither soil test method worked well to predict spring wheat uptake of NO_3 . During 1993 the NO_3 may have leached beyond the sampling depths before soil sampling commenced. In 1994, water, not N, was the limiting factor for crop growth, so quantities of N measured by soil testing would not be expected to relate well to amounts actually taken up.

Suggestions for Further Research

Further research should include working with all major irrigated crops in Montana. The studies on irrigated land should involve an *in situ* component. Along with the *in situ* component, the saturated paste method should be employed as a monitor of ion availability in a saturated system. The encapsulated resin could be used to study *in situ* solid phase N-dynamics of the soil system. When further *in situ* research is performed a collar should be installed around the access tube to prevent possible preferential flow down the outside of the tube.

The next step for dryland would be a verification of the balance sheet approach for N-fertilizer recommendations based on the MBIER system of soil testing. With the usage of the MBIER soil test system the costs for soil testing could be reduced. In conjunction with more research into the N-fertility aspect, studies should involve the field availability of P and K (and perhaps other nutrients) for both dryland and irrigated agriculture. Because the resin capsule is a "universal" adsorber, the only additional cost of including other nutrients would be analytical.

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