The development and characterization of the phytoavailability soil test for potassium, sulfur, and phosphorus

by Stuart James Georgitis

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Crop and Soil Science
Montana State University

Abstract:

Results of research in Montana have shown that standard soil tests for P, K, and S were unsuitable for accurate prediction of fertilizer requirements on many Montana agricultural soils. Results of research in Montana and elsewhere have shown improved soil test accuracy from procedures which account for diffusion rate processes inherent to individual soils. The objective of this research was to develop and characterize a multielement extraction procedure for soil phytoavailable P, K, and S that would be an improvement over current standard methods for use as an index of soil phytoavailable nutrient supply.

The Phytoavailability Soil Test, PST, was developed as a multielement extraction procedure which uses a mixed bed ion exchange resin bag as a sink to the diffusible soil ions of saturated soil paste. The method simulates the root absorption process and was shown to be a better assay of phytoavailable K and S than standard methods. The method was found to be less reliable than P standard methods because of poor affinity toward phosphate of the resins used in this research. The extractable quantity and extraction rate of the PST method was influenced by ion charge species of the mixed bed resin, soil-resin contact time, temperature, mineralization, and the concentration equilibria of the soil solid and solution phase. The PST extraction process was shown to operate in accordance with Pick's laws of diffusion. Physical chemistry descriptive model terms of flux and coefficient of diffusion were normal with respect to the moisture and temperature conditions of the experiments.

These results suggest that the further development of the PST method can be pursued to the point of adoption as an improved standard soil test method for K and S. The PST extraction procedures used in this research are also suitable for use as a standard quantitative method for measurement of S mineralization on saturated soils.

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APPROVAL

of a thesis submitted by

Stuart James Georgitis

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.

May 26, 1989 — Earl O. Skogley
Date — Chairperson, Graduate Committee

Approved for the Major Department

May 26, 1989 — Charles F. McGuire
Date — Head, Major Department

Approved for the College of Graduate Studies

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Date 5/26/89

DEDICATION

The author dedicates this thesis to William James Georgitis whose dream of completion of a Doctoral degree is finally fulfilled and shared in all aspects with his devoted son.

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The author thanks God for sustaining him and his family throughout this experience.

I would like to recognize all of the classroom teachers who have worked so unselfishly for my benefit and shall now know that I am deeply appreciative.

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ABSTRACT

Results of research in Montana have shown that standard soil tests for P, K, and S were unsuitable for accurate prediction of fertilizer requirements on many Montana agricultural soils. Results of research in Montana and elsewhere have shown improved soil test accuracy from procedures which account for diffusion rate processes inherent to individual soils. The objective of this research was to develop and characterize a multielement extraction procedure for soil phytoavailable P, K, and S that would be an improvement over current standard methods for use as an index of soil phytoavailable nutrient supply.

The Phytoavailability Soil Test, PST, was developed as a multielement extraction procedure which uses a mixed bed ion exchange resin bag as a sink to the diffusible soil ions of saturated soil paste. The method simulates the root absorption process and was shown to be a better assay of phytoavailable K and S than standard methods. The method was found to be less reliable than P standard methods because of poor affinity toward phosphate of the resins used in this research. The extractable quantity and extraction rate of the PST method was influenced by ion charge species of the mixed bed resin, soil-resin contact time, temperature, mineralization, and the concentration equilibria of the soil solid and solution phase. The PST extraction process was shown to operate in accordance with Fick's laws of diffusion. Physical chemistry descriptive model terms of flux and coefficient of diffusion were normal with respect to the moisture and temperature conditions of the experiments.

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INTRODUCTION

Soil tests are chemical assays of a soil sample to determine or index the quantity of plant available nutrient. The indexed amount is considered a reserve or resource quantity that must be amended by additions of fertilizer to supply a given crop with ample nutrient to attain the desired yield. The service desired by users of soil tests is the recommendation of fertilizer and the ultimate value of a soil test is judged by the field performance of a crop managed on the basis of that recommendation.

Duplicative analytical procedures are accepted by various scientific societies as "standard methods." Individual standard methods were developed on a regionally specific basis because the geographic distribution of soil types is broadly regional as a function of the five factors of soil formation.

The highly intensive and specific nature of agricultural management today demands commensurately accurate and specific soil analysis, but there has been little success in refinement of the current standard methods to adequately meet this demand. The result is that the value of soil testing to today's user is generally low, except in specific instances where the particular method used was developed for a region of very similar soils, climate, and crop management.

The standard soil tests of neutral ammonium acetate extractable K and acid ammonium acetate extractable S are the unanimous methods of choice for soil testing laboratories serving Montana. The predominant methods of choice for P are the sodium bicarbonate extractable P and the dilute acid-fluoride soluble P method. None of these methods were specifically developed for Montana, but each has been scientifically evaluated in the state for the purpose of deriving appropriate fertilizer recommendation algorithms based on the results of each method. Despite the efforts that have been made, each test remains an unreliable assay of phytoavailable nutrient reserve for some of the soils in the state.

The key to the failure of these tests is the fact that they are all based on a simple extraction procedure and as such they only index their respective chemically extractable quantity. Research aimed at identifying a standard K method more appropriate to Montana did not meet that goal (Haby 1975). However, this work and additional research by others has continuously improved the definition of the problem and consistently shown that a successful method would have to account for ion diffusion as a critical component of the phytoavailable reserve estimate (Barber 1962, Massee 1973, Phillips 1973, Haby 1975, Wang

1975, Skogley 1975, Schaff 1979, Veeh and Skogley 1986, and Miller 1988). A method which could assay any nutrient's phytoavailable quantity as a function of ion diffusion would theoretically be more accurate than any present method, and also could be a geographically universal standard method.

The primary goal of this research was to fundamentally develop a standard soil test (the Phytoavailability Soil Test - PST) method which would assay phytoavailable quantity of P, K, and S in a manner sensitive to the ion diffusion process. Secondary goals included: 1) designing the method as a multielement extraction to simplify the overall standard soil testing process, 2) to design the method as simply as possible to minimize loss of accuracy and precision by multiple and complex steps, and 3) to design the process such that the analytical equipment commonly used by soil testing laboratories would be appropriate for use with the PST method.

These goals actually require a sustained research effort involving many regional and extra-regional participants. Therefore, the objective of this work was to establish a scientifically sound foundation for continuance of the research to attain all of the stated goals sometime in the future. The specific objectives of this work pertain to the elements of P, K, and S, and they are:

1. Design a multielement extraction method using

mixed bed cationic and anionic exchange resin that would be sensitive to the diffusive ion quantity and rate of nutrient supply from source to sink for representative Montana agricultural soils.

2. Conduct a limited characterization of the system with respect to affecting factors of time, temperature, and microbiological activity.

3. Investigate the relationship of diffusive ion quantity and rate with physical and chemical properties of the Montana soils.

4. Test the predictive value of the PST method in comparison with standard methods by use of controlled environment fertilizer rate response experiments.

Each objective was addressed by formal experiments which are presented and discussed in this dissertation. Each formal experiment was supported by numerous pilot experiments, which in all cases serve as the underlying basis for the techniques described in the materials and methods sections. The pilot experiments are not presented but are noted where necessary.

Development of a new soil testing methodology is by necessity an evolutionary process within a scientific research framework. The refinements of the method throughout the course of this project are noted in appropriate context.

LITERATURE REVIEW

Standard Methods

Phosphorus, K, and S represent three of the four most commonly applied fertilizer elements in Montana. Each of these elements is evaluated by standard soil testing methods that do not accurately assess the phytoavailable quantity in all the different types of soil in Montana.

The standard methods used predominantly in Montana for P are the sodium bicarbonate exactractable P, or Olsen test, (Olsen et al., 1954) and the dilute acid-fluoride soluble P, or Bray 1, method (Bray and Kurtz, 1945). Both methods provide an index of P availability, not a total quantitative assay of phytoavailable P.

The Olsen method was specifically designed to be a better assay of available P in alkaline soil because the 0.5 M $NaHCO_3$ at a near constant pH of 8.5 decreases the concentration of Ca in solution by causing precipitation of Ca as $CaCO_3$ (Olsen and Sommers, 1982). The result in calcareous, alkaline or neutral soils containing calcium phosphates, is an increase of P in the extraction solution due to Ca precipitation. The combination of HCL and NH_4F in the Bray 1 method was designed to remove the acid soluble forms of P, primarily calcium phosphate, and also remove a portion of the iron and aluminum phosphates (Olsen and Sommers, 1982). The NH_4F dissolves aluminum and iron phosphates by its complex ion formation with these metal ions in the acid solution. The method is most successful on acid soils, but yields low estimates in calcareous soils because the acid solution is rapidly neutralized by calcium carbonate and thereby rendered ineffective.

The standard method for K is the neutral 1.0 N ammonium acetate extractable procedure. It is also an index procedure which is basically a simple equilibrium extraction method where NH_4 displaces K on the cation exchange sites of the soil in a manner yielding 80 to 95% of the exchangeable K (Knudsen et al., 1982). Although this is the most popular soil testing method for K in the United States, it has been shown to be particularly poor for prediction of fertilizer response to Montana soils ranked high in available K by the method itself (Skogley, 1975).

There are numerous standard methods for phytoavailable S. These methods are generally categorized as readily soluble sulfate, readily soluble and portions of adsorbed sulfate, and readily soluble and portions of adsorbed sulfate and portions of organic sulfate (Reisenauer et al., 1973). Organic sulfate is recognized as an important contributing source of phytoavailable S, but the quantity available is largely the function of mineralization. As such, a simple laboratory procedure capable of accounting for this fraction has yet to be developed (Tabatabai, 1982).

The most popular standard test for S in Montana is the acid ammonium acetate soluble sulfate method (Bardsley and Lancaster, 1960). This indexing method was developed to assess phytoavailable S by extraction of the soluble phase plus a fraction of the adsorbed phase (Tabatabai, 1982). The adsorbed sulfate is displaced by the acetate anion which has a greater coordinating ability according to the series hydroxyl > phosphate > sulfate = acetate > nitrate = chloride (Bingham et al., 1965; Chang and Thomas, 1963; Chao et al., 1964). This method of inorganic S evaluation was found to be incapable of predicting S deficiency in Montana soils but was able to identify incremental applications of spring applied S fertilizer (Gavlak, 1982).

Ion Exchange Resin Methods

Anion exchange resins remove phosphate from the soil by a simple exchange reaction which, theoretically, does not alter the pH of the soil (Olsen and Sommers, 1982). The use of anion exchange resin as a P soil test method was introduced by Amer et. al., 1955, and has been the subject of much investigation since that time. The method commonly used is the batch procedure where a 1:1 ratio of soil to resin is shaken in a water supersaturated state for a given period of time. The method has not been shown to be consistently or greatly superior to standard extraction methods, except in terms of simplicity and in the theoretical mode of action, which approximates the P uptake mechanism of roots (Olsen and Sommers, 1982). The method is sensitive to the anionic form of the resin and has been proven to be best in correlation to plant indexes of P when the resin is charged with bicarbonate (Sibbesen, 1978). The use of the chloride anion for the resin has been shown to be superior to standard methods, but the amount of P desorbed and the change of soil suspension pH varies with the type of resin used and the soil-water ratio, when chloride is the charged anion (Sibbesen, 1978).

The introduction of cation exchange resin for soil testing use was made by Arnold, 1958, where he reported sodium saturated resin desorbed approximately the same amount of K as was NH_4 exchangeable. Later research revealed that Na or Ca saturated resin did not adsorb K from nonexchangeable sources, but H saturated resin adsorbed K from both exchangeable and nonexchangeable sources (Pratt, 1951; Haagsma and Miller, 1963).

Research based on Montana soils has revealed that a neutral mixture of H and OH charged ion exchange resin was valuable for predicting short term uptake of K by plants (Massee, 1973) and a soil test using strongly acidic H saturated ion exchange resin showed promise as a method for predicting crop response to K fertilizer (Haby, 1975).

A thorough search of the literature failed to identify any published research where ion exchange resin was used for the purpose of soil S extraction.

Ion Exchange Resin Bag Methods

The use of a netted bag for holding ion exchange resin was introduced by Sibbesen in 1977 as a technique which would simplify the retrieval of the resin in the batch P method. The use of resin bags was distinctly modified by Binkley and Mateson, 1983, by their use of the resin bags as an in-situ ion exchange resin sink assessment of available nitrogen. They employed their technique of burying the mixed bed exchange resin bags in the soil on field plots in three different forested stands. Resin bags were also buried in greenhouse pots filled with mixed soils collected from the field sites. The results of the two resin bag procedures were compared to six standard methods of chemical and incubation N availability analyses. The results showed that the greenhouse resin bag incubation correlated well with the traditional indices of N availability but the field plot resin bags yielded different availability estimates. The latter estimates were consistent with forest floor development in the stands. The researchers concluded that the in-field technique was sensitive to on-site factors that other laboratory methods did not test.

Binkley followed this work with a project comparing clear cut and un-cut forest stands at three elevations on Vancouver Island in British Columbia (Binkley, 1984). The resin bags that were buried in the soil of the clear cut extracted 7 to 20 times more inorganic N than the paired un-cut site resin bags. The difference was attributed to increased mineralization rates, reduced plant uptake, or increased mobility of N ions associated with the wetter soil of the clear cut sites.

Research based on Binkley's work was conducted in England where mixed bed ion exchange resin bags were buried at 10 cm intervals along two transects representing grassland and dune slack soils (Gibson et al., 1985). Although the experiment was intended to be investigation of spatial variability of nutrient supply, it was concluded that the in-situ resin bag method assessed the actual supply rate of plant available nutrients. This is in direct contrast to data from conventional methods which provide only an index of potential plant-available nutrient.

The technique of in-situ mixed bed resin bag analysis allows nutrient supply to be measured for any cation or anion (Gibson et al., 1985). The mode of extraction is similar to a plant root in both uptake mechanism and capacity (Sibbesen 1978; Smith 1979). As long as an excessive exchange sink is provided by the exchange resin, the technique is sensitive to organic and inorganic nutrient supply rates and ion movement rate in the soil (El-Nennah, 1978; Binkley 1984).

These principles support the theoretical basis for the Phytoavailability Soil Test and these techniques were adapted to the purpose of developing the phytoavailability laboratory method.

PST AND STANDARD METHODS

It was necessary to conduct pilot experiments using different combinations of mixed bed resins in order to choose one mixture capable of serving as a relatively infinite sink toward exchangeable P, K, and S.

Pilot experiments were also conducted to determine quantity of resin, minimum duration of contact time to collect an assayable quantity of P, K, and S, and type of stripping solution necessary for a minimum of 99 % recovery of resin adsorbed ions. The soil used was always prepared as a saturated paste to provide a "standard" soil water condition and to maximize the diffusive properties of the soil, while still allowing characteristics of the chemical and physical processes of the equilibrium dynamics and diffusion pathway to be influential. The parameters derived from these pilot experiments continued to be modified throughout the course of study, and such changes will be noted where appropriate.

The Bozeman silt loam bulk soil sample was the only soil used in the methods development experiments. The method described for determination of saturation moisture content on the Bozeman silt loam was used for all the soils of this research. The determination involved supersaturating 100 g. of soil with distilled-deionized water, hereafter referred to as ddw, followed by equilibration for 24 hours. This process was repeated until removal of free water was necessary and the soil reached a static state of saturation. The quantity of water present in the saturated paste was gravimetrically determined and an equivalent amount was used for 50 g. samples of soil in the replications of all experiments.

The mixed bed ion exchange resin bag, used as the effectively infinite sink for exchangeable ions, contained 2.5 mls of wet, Dowex 50W-X8 H^+ charged cationic resin, mixed with 2.5 mls of wet, Dowex 1-X8 Cl^- charged anion exchange resin. The resins were separately prepared by degassing under water by applying a vacuum. The resins were then combined 1:1 volumetrically, mixed, and loaded into columns for repeated washing with reagent grade, concentrated hydrochloric acid. The resins were then repeatedly rinsed with ddw and packed into 100 % polyester cloth and tightly tied with braided polyester string to form a tight "sphere." The resin bags were trimmed of excess cloth and string and rewashed with acid and ddw as per the prior loose resin procedure. The resin bags were then stored in sealed containers filled with ddw until moments before being buried in the soil samples.

Soil samples were prepared by transfer of 50 g. dry soil into acid washed, 60 ml. screw cap jars. Immediately prior to interment of the resin bags, the soil samples were mixed with the appropriate amount of ddw required to produce the saturated paste status. The resin bags were then inserted into the center of the sample and covered with soil sample material from the container itself. The jars were tightly sealed and placed into a controlled temperature chamber at 30 ^{o}C, unless otherwise stated.

Sample units were removed from the temperature chamber after predetermined time had elapsed and the resin bags were immediately removed from the soil. Resin bags were thoroughly washed with ddw to remove any adhering soil particles. The clean resin bags were placed in acid washed snap-cap containers and frozen. Freezing was necessary to standarize handling and avoid variable standing time due to an inefficacious stripping process.

The standard stripping process was also developed from numerous pilot experiments and later refined by employment of a Centurion Model 24 Vacuum Extractor. Resin bags were retrieved from the freezer and allowed to thaw at room temperature. They were again rinsed with ddw and placed in a device which allowed the resin to be steadily flushed with a total of 50 mls of 2 N HCl extracting solution at an approximate rate of 1 ml. per minute. The eluent was collected and sealed in acid washed screw cap bottles. This extract solution was analyzed for P, K, and S concentration by plasma emission on a Perkin Elmer Model

5500 Sequential Inductively Coupled Argon Plasma Emission Spectrophotometer, hereafter referred to as ICP.

The samples were always run in triple replication and means of the three replications were used as data, except in analysis of variance statistical procedures.

General Materials and Methods

The entire study included 22 different bulk soil samples collected from former field fertilizer rate response experiment locations in Montana. The Gallatin and Bozeman Series soils were used for Phytoavailability Soil Test (PST) methods development and influencing factor experiments. The remaining 20 soils were used for correlative experiments and controlled environment fertilizer rate response experiments.

Soils

All soils were air dried soon after collection, sieved to retain the less than or equal to 2 mm. fraction, and stored in bulk in an air dried condition. Subsamples were subjected to the following test procedures:

(1) particle size analysis by hydrometer method (Gee and Bauder, 1986);

(2) percent $CaCO_3$ by gravimetric loss (U.S. Salinity Lab, 1954);

(3) percent organic matter (Sims and Haby, 1970);

(4) soil pH and conductivity by 2:1 dilution (U.S. Salinity Lab, 1954);

(5) extractable K, Na, Ca, and Mg by 1.0 N NH_4OAc extraction and atomic adsorption analysis (Bower et al., 1952);

(6) extractable K by 0.5 N $MgCl_2$ and 0.5 NH_4OAC (Rich, 1964);

(7) extractable K by sodium tetraphenyl boron (Scott and Reed, 1960);

(8) extractable K by 1.0 N HNO_3 (Mclean and Simon, 1958);

(9) saturated paste K, Ca, and Mg extraction and atomic adsorption analysis (U.S. Salinity Lab, 1954);

(10) extractable P by sodium bicarbonate (Olsen et al., 1954).

(11) extractable P by dilute acid-fluoride (Bray and Kurtz, 1945).

(12) sulfate by acetate soluble SO_4 (Bardsley and Lancaster, 1960);

(13) nitrate extraction (Sims and Jackson, 1971) and analysis by Cd reduction (Willis, 1980);

(14) clay mineralology (Jackson, 1958);

(15) resin extraction of P, K, and S by PST method (Georgitis and Skogley, 1988) and analysis by ICP.

Taxonomic names, and tables of data from the analyses of the 20 soils are presented in Appendix A.

Plants

Plant material collected from the controlled environment fertilizer rate experiments consisted of the entire above ground portion of the plants per pot. The tissue was dried at 65 °C and ground to pass a 40 mesh screen. Samples were weighed and then analyzed by the following procedures:

(1) plant tissue K, P, and S by dry ash (Olsen and Dean, 1965) and analysis by ICP;

(2) plant tissue total nitrogen by modified semi-micro kjeldahl (Bremner, 1965);

Statistical Analyses

Statistical analysis procedures included analysis of variance, least significant difference T tests, linear and maxr multiple linear regression (SAS Institute, 1987). Independent and dependent variables were direct concentration values from the previously stated methods. Variables created from this data base included:

PAR = Potassium Adsorption Ratio;

OTHERCLAY = 100 -(vermiculite + illite + montmorillonite);

iBETA = Slope from linear regression line of concentration of the ith ion (Y) with log time (X).

CHARACTERISTICS OF THE PST METHOD

The Phytoavailability Soil Test (PST) method is fundamentally based on the hypothesis that a quantity of mixed bed ion exchange resin placed in direct contact with the solution phase of the soil will extract ions from the soil by a process similar to a living plant root in a natural soil system.

Theoretically, both systems would be identical with respect to the removal of ions from solution by an exchange process. Both systems would continuously procure ions by establishing a chemical concentration gradient whereby ions would diffuse toward the net zero concentration sink from the net positive concentration soil solution. The amount of ions adsorbed by the sink would be a function of the quantity and intensity factors of the soil's equilibrium process, the diffusion pathway, time, and the effect of counter diffusion of anions and cations departing from the sink as a result of the resin ion exchange-extraction process.

Given the similarity of the two systems, the PST method should act as a quantitative index of soil phytoavailable quantity and supply rate of nutrients. The PST method cannot act as a total quantitative assay of phytoavailability because, the resin sink has a relatively fixed capacity to modify the source of nutrient ions, while the root has a dynamic ability to modify the rhizosphere.

The objective of this series of experiments was to determine whether the PST method operated in a manner consistent with the theorized characteristics.

Materials and Methods

The PST procedure was employed for these experiments using Bozeman Silt Loam soil. The elapsed time period of resin bag—soil contact was the treatment in the first experiment. The treatment times used were 0.5, 1, 2, 3, 6, 12, 24, 48, 72, and 96 hours at 30 °C.

The second experiment was identical to the first except the treatments were repeated under temperature conditions of 10 °C and 50 °C.

Results and Discussion

Charting the resin extract concentration of P, K, and S with time revealed a rapid initial increase in RAQ (resin adsorption quantity) which eventually tapered (Figure 1). The different line slope and concentration for each element illustrate the independent sensitivity of the process with respect to the individual elements.

The short term phenomenon can be described as a rapid adsorption of the ions in direct contact and near the resin. This action extends the chemical concentration

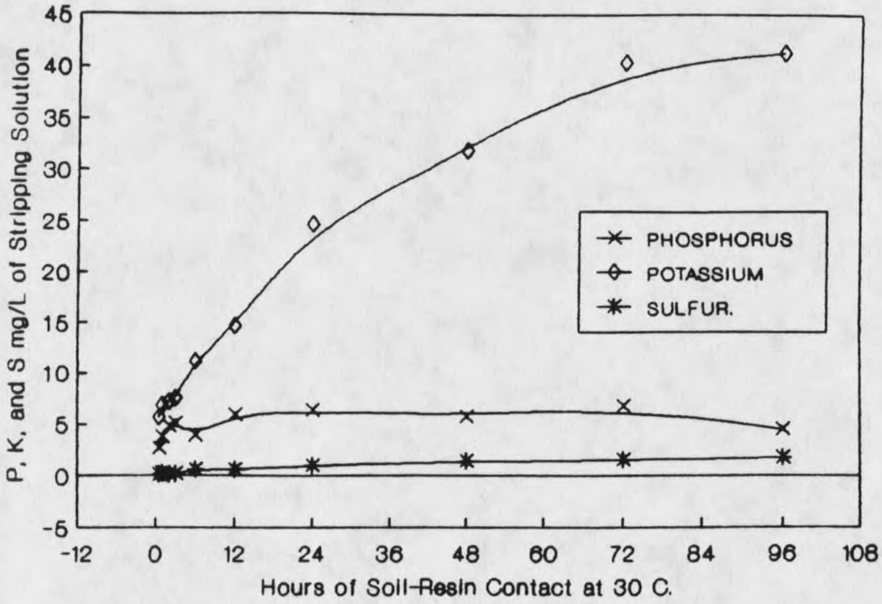

Figure 1. Resin stripping solution concentration of P, K, and S for the Bozeman Silt Loam soil.

gradient into the bulk soil and thereby sustains the increase in RAQ at a diminishing rate with respect to time. This is consistent with diffusion dominated processes in soil, where the concentration gradient itself is greatest at the sink but diminishes with distance from the sink. Given enough time, the rate of adsorption (slope of the concentration line) will become fixed as the chemical gradient potential reaches equilibrium with the soil's intensity and rate reductive forces of pathway tortuosity. These data evidence an approach to equilibrium status by the declining RAR, resin adsorption rate, but insufficient time was allowed for establishment of a stable equilibrium.

The temperature treatments were used to further test the description of the system as a diffusion dominated process. Diffusion rate is a function of temperature as it is a kinetic process. Theoretically, increased temperature would cause increased RAQ and RAR.

The K RAQ did increase with temperature and time after the first 0.5 hour (Figure 2). Phosphorus did not respond in any dependable manner related to temperature (Figure 3). Sulfur results were mixed, showing RAQ increase from 10 °C to 30 °C but then a decrease from 30 °C to 50 °C (Figure 4).

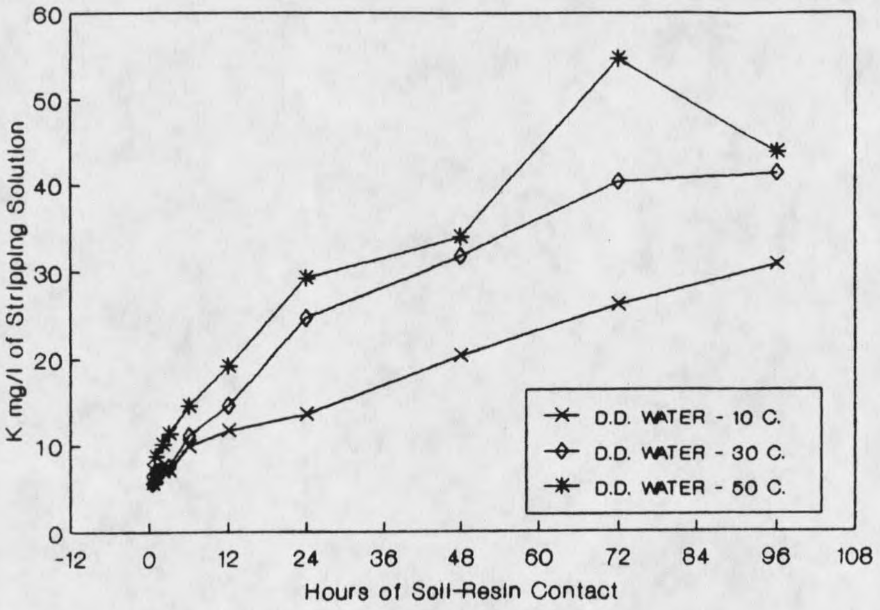

Figure 2. Resin stripping solution concentration of K for Bozeman Silt Loam at 3 temperatures.

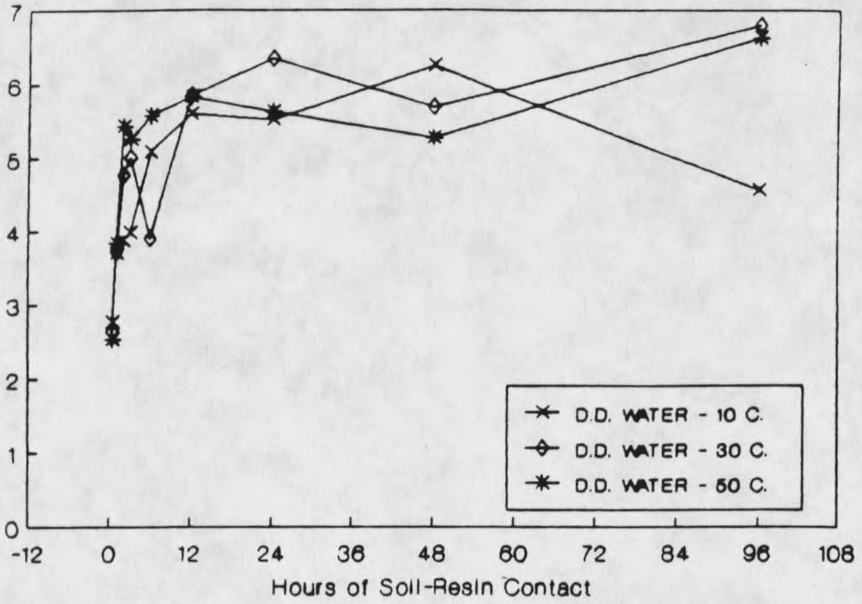

Figure 3. Resin stripping solution concentration of P for Bozeman Silt Loam at 3 temperatures.

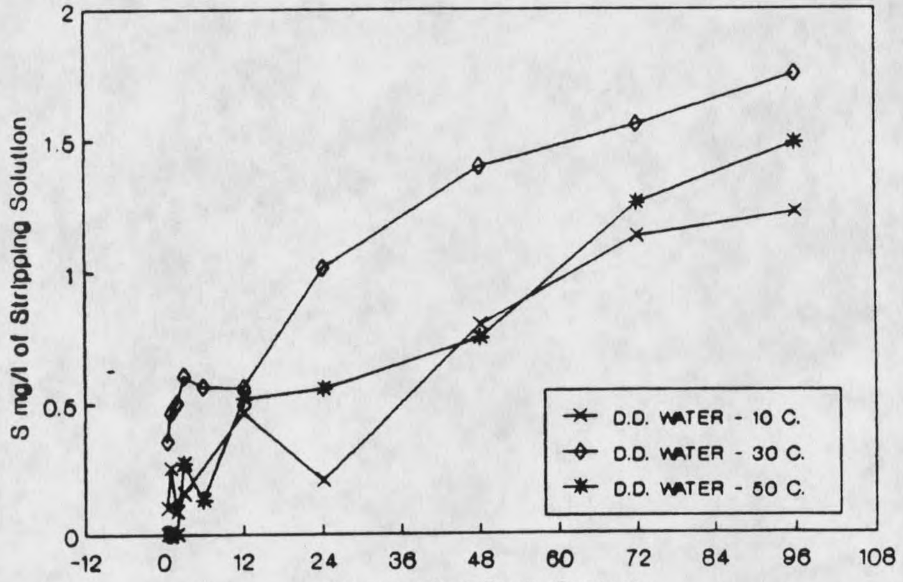

Figure 4. Resin stripping solution concentration of S for Bozeman Silt Loam at 3 temperatures.

The lack of distinct K and P concentration differences at the shorter time points was attributed to the fact that the samples were at room temperature when placed in the temperature chamber. The samples certainly were not equilibrated to the chamber temperature immediately and so were subject to some lag period for the actual treatment effect. Unfortunately, measurements were not taken to document this effect.

The relationship of K to temperature was an obvious increase in RAQ as a function of temperature, which verified the dominance of diffusion for that element. The relationship of P and S to temperature was not clearly an indication of a diffusion dominated process.

The lack of continuous increase in RAQ P, after the short term, suggested simply that the adsorption of P by the resin was weak and a stable chemical gradient was not established. The short term RAQ illustrated the expected relationship to time but valid statements regarding diffusion in the long term were negated by the variability of the data. The variability was probably due to the weakness of the resin in performance as an infinite ion sink and the imprecision of the resin stripping process at this point in the research.

The effect of time on RAQ S did indicate that a normal diffusion rate process was driving the system at each temperature. However, the decreased RAQ at 50 ^{o}C suggested that the quantity of S in soil solution was reduced by the higher temperature treatment. The amount of S in soil solution is influenced by anaerobic bacterial mineralization. The influence of temperature probably decreased mineralization at the 10 ^{O}C and 50 ^{O}C level and enhanced mineralization at the more biologically optimal temperature of 30 ^{O}C. This explanation is plausible but was not directly tested in this experiment.

Conclusions

The PST method was shown to be independently sensitive to P, K, and S in terms of RAQ, RAR, and temperature effects. The data trends for K consistently followed principles attributable to a diffusion dominated system. There was sufficient evidence for conclusion that S was a diffusion dominated system, but the amount of S available in solution appeared to be a function of a temperature sensitive, possibly biologically mediated process. The data trends for P offered only weak evidence of a diffusion dominated system. The severe problems associated with P indicated a clear need for modification of the method.

TEMPERATURE AND BIOLOGICAL EFFECTS ON THE PST EXTRACTION

A pilot study evaluating different anion exchange resins in combination with the same hydrogen cation resin resulted in the choice of Amberlite IRN 150 mixed bed H^+ saturated cation and OH^- saturated anion resin for these experiments. This resin has better P selectivity than H/Cl resin.

A series of experiments was designed to test the hypothesis that microbial mineralization of S does contribute to RAQ. Treatments of phosphatase enzymes and sucrose were used to test for possible influences of other biological effects on RAQ.

Materials and Methods

The Gallatin Silt Loam bulk soil sample was collected at the Montana Agricultural Experiment Station at Fort Ellis variety trial site adjacent to Rocky Creek in Bozeman, Montana. This sample was necessary because the remaining quantity of Bozeman Silt Loam was insufficient for these experiments. The methods employed for these experiments were identical to the basic PST method except that the new mixed resin was not cleaned with hydrochloric acid. Pilot work did verify that the resin as provided by the supplier was free of P, K, and S contamination.

To test the hypothesis that temperature effects on S mineralization rates are related to RAQ S differences, it was necessary to design treatments for experiment I that would eliminate microbial mineralization. A pilot study was conducted to establish minimum separate threshold concentrations of $HgCl_2$ and Tetracycline necessary for prevention of anaerobic bacterial activity. Mercuric chloride was chosen for its extreme biological toxicity, and tetracycline (a broad spectrum antibiotic) was chosen for its destructive effect on anaerobic bacteria and its human innocuousness. Both treatments were added as prepared solutions in place of ddw for preparation of saturated paste. Both solutions were tested and found to be free of P, K, and S contamination.

The treatments of experiment I included:

1) 3 different saturated paste preparations of either ddw, or 15 mg l^{-1} Tetracycline, or 15 mg l^{-1} HgCl;
2) 5 temperature treatments of 10, 20, 30, 40, and 50 ^{o}C;
3) 5 time periods of 1, 3, 5, 7, and 15 days.

The materials and methods of experiment II were consistent with those of experiment I, except for the treatments and use of one temperature, 30 ^{o}C. This experiment was intended to test for an enhancement effect of common root exudates on the RAQ of P, K, and S. The treatments of experiment II included:

1) Soil pretreated by autoclaving and mixed to saturated

paste with ddw;

2) Soil pretreated by autoclaving and made to saturated paste with 50 mg l^{-1} acid phosphatase solution;
3) Soil pretreated by autoclaving and made to saturated paste with 50 mg l^{-1} alkaline phosphatase solution;
4) Soil not pretreated and made to saturated paste with 50 mg l^{-1} sucrose solution.

The levels of these treatments were designed to be higher than naturally occurring concentrations to accentuate any possible effects. The autoclaving pretreatment of the soil was necessary as bacteria would consume the enzyme as a carbon source if left unchecked. The process of autoclaving can change the physical and chemical character of the soil, so treatment 1 was designed to serve as a check against treatments 2 and 3.

The ddw 30 °C treatment of experiment I served as the check against the sucrose treatment of experiment II. The hypothesis tested with this treatment was that presence of a readily utilized carbon source would enhance microbiological mineralization activity. This enhancement should be measurable as RAQ change.

Time and Temperature Effects

The analysis of variance table for experiment I reveals significant single term effects of day and temperature for all elements, and an additional significant effect of treatment in the case of S (Table 1).

Table 1. The analysis of variance table for experiment I P, K, and S on Gallatin Silt Loam soil.

Dependent Variables: P, K, and S concentration of stripping solution in mg l^{-1}. Alpha = 0.05.

Source	DF	P Mean Square	K Mean Square	S Mean Square
REP	2	0.4	21.9	0.8
TRT[a]	2	8.4	17.3	2.2**
DAY[b]	4	1545.5**	8897.9**	71.4**
TEMP[c]	4	33.4**	4146.2**	37.0**
TRT*DAY	8	4.6	33.6**	0.6**
TRT*TEMP	8	7.2**	7.4	0.4**
TEMP*DAY	16	10.5**	252.9**	2.0**
TRT*TEMP*DAY	32	5.9**	10.1	0.1
Error	148	2.3	12.7	0.11

** Denotes significance at or beyond the 0.01 level.

a : Saturated soil paste made as ddw, or 15 mg l^{-1} HgCl, or 15 mg l^{-1} Tetracycline.

b : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

c : Temperature during soil-resin contact time of 10, 20, 30, 40, and 50 °C.

The significance of the treatment effect for only S was verified by the least significant difference T grouping, hereafter referred to as LSD, (Table 2). The effect of the antibiotic was a significant reduction in mean RAQ S, insignificant reduction of K and slight differences in P. These results imply that P was not released by mineralization, and that the K release was not directly a function of mineralization. The clear effect of the treatments on S suggest that S released by mineralization contributed to RAQ. Sulfur was also significantly higher by the HgCl treatment than by

Table 2. T groupings by least significant difference for the experiment I treatments on Gallatin Silt Loam soil.

Dependent Variables: P, K, and S concentration in stripping solution in mg l^{-1} across all times and temperatures. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	TRT	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	14.75	Tet[a]	A	29.71	H_2O	A	2.26	H_2O
AB	14.59	H_2O[b]	A	29.20	Tet	B	2.11	HgCl
B	14.11	HgCl[c]	A	28.75	HgCl	C	1.92	Tet
LSD	0.4872			1.1483			0.1071	

a : Saturated soil paste made 15 mg l^{-1} Tetracycline.
b : Saturated soil paste made with ddw.
c : Saturated soil paste made with 15 mg l^{-1} HgCl.

tetracycline, indicating that the chloride anion may have promoted release or conversion of S to a diffusible form.

The significant effect of DAY in the ANOVA table was supported by LSD (Table 3). The progression of mean RAQ was consistent with the diffusion dominated system for all elements. This trend and the clear separation of each day indicated that the H+/OH- mixed bed resin was operating as a relatively infinite exchangeable ion sink to each of the three elements for the 15 day duration of this study.

The significant TEMPERATURE effect of the ANOVA table was elucidated by LSD analysis (Table 4). These data illustrate a steady increase in RAQ under the influence of increasing temperature for K and S but not for P. The P data were not clearly different for 20 and 30 °C and the 40 °C mean was not ranked in a normal progressive order.

Table 3. T groupings by least significant difference of experiment I soil-resin contact time in days for P, K, and S on Bozeman Silt Loam soil.

Dependent Means: Mean concentration of stripping solution in mg l^{-1} across all temperatures. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	DAY[a]	T GROUP	MEAN	DAY	T GROUP	MEAN	DAY
A	22.68	15	A	49.14	15	A	3.80	15
B	16.84	7	B	33.35	7	B	2.67	7
C	14.21	5	C	27.98	5	C	2.10	5
D	11.75	3	D	21.65	3	D	1.48	3
E	6.93	1	E	11.97	1	E	0.44	1
LSD	0.629			1.4825			0.1383	

a : Soil-resin contact time in days.

Table 4. T groupings by least significant difference of experiment I temperature on Gallatin Silt Loam soil. Alpha = 0.05.

Dependent Means: Mean concentration of stripping solution in mg l^{-1} across all days. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	TEMP[a]	T GROUP	MEAN	TEMP	T GROUP	MEAN	TEMP
A	15.60	50	A	41.82	50	A	3.46	50
B	14.87	30	B	35.73	40	B	2.37	40
BC	14.50	20	C	27.28	30	C	1.99	30
C	14.23	40	D	23.49	20	D	1.67	20
D	13.26	10	E	17.78	10	E	1.01	10
LSD	0.629			1.4825			0.1383	

a : Temperature during soil-resin contact time in °C.

These data indicate that temperature does not have a simple effect of enhancement of RAQ P, but that indirect effects may be contributory. The overall effect of temperature was consistent with diffusion enhancement when the lowest and highest temperature treatments were compared. The confusion in the mid range may have been the result of microbial activity, or enhanced rate of reaction of calcium phosphate formation as a function of temperature, or unknown influences which cannot be determined from these experiments.

Any interaction term involving DAY is a test of the RAR process. When a treatment allows an increase of RAQ S it indicates that the solution S available for diffusion to the resin has increased. When a similar tendency is evident as a function of time it is an indication that the rate of diffusion to the resin has been enhanced by the influencing force.

The significant ANOVA table interaction effect of TRT by DAY for K and S was an indication that the rate of both K and S was affected by biological activity, even though the RAQ for K was not significantly increased by the treatment. This apparent influence on K intensity may be explained by release of K from soil exchange sites to aid in balancing the net negative soil solution charge generated by increased S concentration.

The significant ANOVA table interaction of DAY by TEMP for all elements was a clear indication that rate was enhanced by temperature. The much stronger expression of this interaction for K and S verses P was the result of the unclear single term effect of temperature for P. However, this DAY by TEMP interaction supports the contention that the entire system is diffusion dominated. Dynamics of P within this context are not clearly shown.

The significant ANOVA interaction of TEMP by TRT for S was based on the consistent increase in S by temperature across all treatments. The relative RAQ difference between treatments remained unchanged as ddw > HgCl > tetracycline across all times and all temperatures. The significant interaction of TEMP by TRT for P was the result of the significant concentration rise as a function of temperature and the treatment effects by HgCl and tetracycline. Potassium data did not show significance for a two way interaction because there was no treatment effect. The cause of the significant three way interaction for P are not clear and cannot be reasonably described.

Sucrose Treatment Effects

The ddw treatment of experiment I was most appropriately comparable as a control for the 50 mg/L sucrose treatment of experiment II. The treatments of experiment I tested for microbiological influence on the system by prevention of bacterial activity, while the addition of sucrose was intended to test for microbial influence by enhancement of activity.

The ANOVA table of this comparison indicated that there was a significant effect of sucrose on RAQ S but not on K or P (Table 5). The addition of sucrose clearly caused a substantial increase in S release as a direct result of the treatment (Table 6). The non significant increase of K was identical to the experiment I results, indicating that the explanation of K release for solution charge balance was valid and applicable to both experiments. The decrease of P that resulted from added sucrose may be evidence that the sucrose did increase microbiological activity, in that P otherwise available for diffusion was also readily available for microbial utilization in the flush of population growth and activity that accompanied the sucrose addition.

Table 5. The analysis of variance table for experiment II P, K, and S sucrose treatment with experiment I ddw treatment on Gallatin Silt Loam soil at 30 °C.

Dependent Variables: P, K, and S concentration of stripping solution in mg l^{-1}.

Source	DF	P Mean Square	K Mean Square	S Mean Square
REP	2	0.49	19.95	1.38
TRT[a]	1	10.60	23.34	561.40**
DAY[b]	4	133.40**	715.28**	39.39**
TRT*DAY	4	1.55	49.33**	9.95**
Error	18	2.04	8.04	0.39

** Denotes significance at or beyond the 0.01 level.
a : Saturated soil paste made with ddw or 50 mg l^{-1} sucrose.
b : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

Table 6. T groupings by least significant difference for P, K, and S, sucrose treatment of experiment II and ddw treatment of experiment I on Gallatin Silt Loam at 30 °C. Alpha = 0.05.

Dependent Variables: Mean P, K, and S concentration of stripping solution in mg l^{-1} across all days. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	TRT	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	14.73	ddw[a]	A	29.44	Suc.	A	7.60	Suc.
B	13.54	Suc.[b]	A	27.67	ddw	B	2.17	ddw
LSD	1.0947			2.1756			0.4818	

a : Saturated soil paste made with ddw.
b : Saturated soil paste made with 50 mg l^{-1} sucrose.

The significant effect of DAY for all elements in the ANOVA analysis was supported by the separation and normal progression of means in the LSD analysis (Table 7). The

Table 7. T groupings by least significant difference of P, K, and S experiment II sucrose treatment with ddw treatment of experiment I on Gallatin Silt Loam soil at 30 °C. Alpha = 0.05.

Dependent Means: Mean P, K, and S concentration of stripping solution in mg l^{-1} across both treatments. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	DAY[a]	T GROUP	MEAN	DAY	T GROUP	MEAN	DAY
A	20.39	15	A	43.63	15	A	6.33	15
B	16.71	7	B	34.25	7	AB	6.05	7
C	13.94	5	C	28.35	5	B	5.32	5
D	11.51	3	D	21.91	3	C	4.40	3
E	8.12	1	E	15.00	1	D	2.34	1
LSD	1.7309			3.4400			0.7618	

a : Soil-resin contact time in days.

rate of S release increased most dramatically in the first 5 days and then abruptly tapered off. This progression suggests that activity was enhanced up to 5 days and that something may have become limiting after that point.

The significant TRT by DAY interaction terms of the ANOVA table for K and S represent the fact that K and S increased both with time and with sucrose addition. The lack of significance for P was due to the fact that sucrose caused an overall decrease in RAQ P, while time produced the normal trend of increase.

Phosphatase Treatment Effects

The autoclaved ddw treatment resulted in a slight increase in RAQ S in comparison to the nonautoclaved ddw treatment. The difference between autoclaving treatments was negligible for P and K. Data in the ANOVA table for this experiment illustrate a significant effect for treatment on S, but not for P or K (Table 8). The LSD analysis of the treatment term showed that all elements were increased by the phosphatase treatments, but the increase for P was far from significant (Table 9). The strongest effect of the treatment was on S where alkaline phosphatase caused the greatest release, but either phosphatase caused the release of more than twice the ddw amount.

The mode of action of the phosphatase enzyme is

Table 8. The analysis of variance table for experiment II P, K, and S on autoclaved Gallatin Silt Loam soil at 30 °C.

Dependent Variables: P, K, and S concentration of stripping solution in mg l^{-1}.

Source	DF	P Mean Square	K Mean Square	S Mean Square
REP	2	0.57	4.03	0.09
TRT[a]	2	0.50	56.21	88.94**
DAY[b]	4	212.62**	1820.74**	61.99**
TRT*DAY	8	1.48	9.66	2.70**
Error	28	1.75	12.30	0.62

** Denotes significance at or beyond the 0.01 level.

a : Saturated soil paste made with ddw, or 50 mg l^{-1} acid phosphatase, or 50 mg l^{-1} alkaline phosphatase.

b : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

Table 9. T groupings by least significant difference for P, K, and S experiment II treatments on autoclaved Gallatin Silt Loam soil at 30 °C. Alpha = 0.05.

Dependent Variables: Mean P, K, and S concentration of stripping solution mg l^{-1} across all days. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	TRT	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	14.25	AlPt.[a]	A	32.82	AlPt.	A	8.00	AlPt.
A	14.02	AcPt.[b]	A	32.08	AcPt.	B	7.14	AcPt.
A	13.89	ddw[c]	B	29.16	ddw	C	3.42	ddw
LSD	0.9907			2.6231			0.5902	

a : Saturated soil paste made with 50 mg l^{-1} alkaline phosphatase.

b : Saturated soil paste made with 50 mg l^{-1} acid phosphatase.

c : Saturated soil paste made with ddw.

cleavage of ester bonded phosphate, and it is capable of attacking ester bonded sulfate. It was evident from these data that ester bonded phosphate was a small portion of the inorganic P pool, but ester bonded sulfate apparently occurred in an amount equal to that normally available for diffusion. The treatment amount of S released by the phosphatase was very nearly identical to the treatment mean amount released by addition of sucrose (Table 6). This suggests that the sterically exposed ester bonded sulfate may have been the primary source utilized by bacteria in the mineralization process. However, this would have to be tested directly to be conclusive.

Perhaps the clearest indication of a trend for K release as a function of S release was exhibited by the parallel increases from ddw to acid phosphatase to alkaline phosphatase. The parallel relationship is clear, but the lesser increase of K relative to S suggests K probably contributes to solution charge balance yet does not itself satisfy all of the positive charge requirement.

The significant term of DAY in the ANOVA table was the result of the normal progression of RAQ increase with time in a diffusion dominated system (Table 10). The mean values for P were relatively identical to experiment I, while the values of K and S were higher due to the enzymatic release of S (Table 3).

The significant interaction term of TRT by DAY for S was a result of the coincident effects of a doubling of soil solution concentration due to the phosphatase

Table 10. T groupings by least significant difference for P, K, and S experiment II days on autoclaved Gallatin Silt Loam soil at 30 ^{o}C. Alpha = 0.05.

Dependent Means: Mean P, K, and S concentration of striping solution in mg l^{-1} across all treatments. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	DAY[a]	T GROUP	MEAN	DAY	T GROUP	MEAN	DAY
A	20.48	15	A	52.11	15	A	9.95	15
B	16.16	7	B	36.47	7	B	6.88	7
C	14.04	5	C	30.36	5	C	6.51	5
D	12.27	3	D	23.46	3	D	4.61	3
E	7.30	1	E	14.35	1	E	2.98	1
LSD	0.629			1.4825			0.1383	

a : Soil-resin contact time in days.

treatment and a consistent concentration increase with time. The lack of significance for P and K resulted from the total lack of treatment effect on P and the discrimination of only phosphatase verses non-phosphatase for K.

Conclusions

The effect of time under all conditions was shown to be consistent with a diffusion dominated system. Temperature directly influenced RAQ S and K in a manner consistent with a diffusion dominated system. Phosphorus was influenced in a normal manner by the extremes of temperature, but was complicated by unknown processes in the middle range of treatments.

The treatments of tetracycline and mercuric chloride dampened RAQ K and S but did not affect P. The sucrose treatment enhanced mineralization which resulted in increased RAQ K and S and decreased P. The S RAQ was shown to be directly related to microbiological activity while K was weakly related to solution S changes, and not directly related to mineralization.

Sulfur release was caused by phosphatase enzyme cleavage of ester bonded S in a quantity parallel to enhancement of mineralization by sucrose addition. Sulfur release was also caused by the HgCl treatment.

A COMPARISON OF PST AND STANDARD TEST EXTRACTION PROCESSES ON TWENTY SOILS

The objective of these experiments was to characterize the sensitivity of each extraction process to soil solid and solution phase concentration dynamics.

Three different PST procedures and standard soil test method extractions of P, K, and S were comparatively related to soil properties of 20 representative Montana agricultural soils to meet the objective.

Materials and Methods

The twenty bulk soil samples identified in chapter 1 were subjected to the standard PST method with mixed bed resin treatments of: A. resin bags made with H+ charged cationic resin (Dowex 50W-X8) mixed with anionic Cl^- charged resin (Dowex 1-X8) and used in soil samples brought to saturated paste by ddw addition, B. resin bags made of Amberlite IRN 150 H^+/OH^- charged mixed bed resin and used in soils brought to saturated paste by ddw addition, C. resin bags made of Amberlite IRN 150 H^+/OH^- charged mixed bed resin and used in soils brought to saturated paste by 15 ug/L tetracycline solution addition. Hereafter, these treatments will be referred to simply as HCL, HOH, and HOHT, respectively. The equilibration temperature was 30

°C and equilibration times were reported as 1, 3, 5, 7, and 15 days in all cases. The actual times for HCL were 1, 2, 3, 4, 5, 6, 7, and 14 days for 15 of the soils and 1, 2, 3, 4, 7, and 14 days for 5 of the soils. The actual times for HOH and HOHT were 1, 3, 5, 7, and 15 days. A valid statistical approach was used to generate values for 5 and 15 days when necessary to balance the overall data base.

Many independent and dependent variables were used for statistical analysis by regression, but full reporting of all results would be tediously redundant. The two reported dependent variables for each soil and for each element were 1) the concentration mean as derived from the sum of all replications of days 1, 3, 5, 7, and 15, and 2) the slope of a linear regression line calculated from a plot of concentration (y) with the log of time (x). The time-phase data of PST method were not appropriate for calculation of dependent variables representing "Quantity" and "Intensity" as described by Beckett 1964. However, the concentration mean was clearly a term dominated by a quantity relationship, while the slope of the concentration as a function of log-time was a term dominated by intensity. In order to avoid confusion with the accepted terms of "Quantity" and "Intensity", the terms Resin Adsorption Quantity (RAQ) and Resin Adsorption Rate (RAR) were used throughout this text.

Results and Discussion

Analysis of variance was performed using the data base of the 20 soils in a randomized complete block design. The RAQ of each element was used as the dependent variable (Table 11). The anova table revealed that all the factors of the model were significant except replications.

Table 11. The analysis of variance table for P, K, and S RAQ on 20 soils.

Dependent Variables: Mean P, K, and S concentration of stripping solution in mg l^{-1}.

Source	DF	P Mean Square	K Mean Square	S Mean Square
REP	2	0.1	97.8	1.5
TRT[a]	2	555.7**	91364.4**	175.7**
DAY[b]	4	649.3**	121312.7**	294.2**
SOIL[c]	19	464.6**	20665.5**	414.5**
SOIL*TRT	38	33.1**	2384.4**	60.5**
SOIL*DAY	76	14.3**	1148.1**	12.8**
TRT*DAY	8	92.7**	6883.3**	23.5**
SOIL*TRT*DAY	152	3.4**	221.3**	3.6**
ERROR	598	0.80	65.5	0.59

** Denotes significance at or beyond the 0.01 level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation, or HOH resin with ddw saturated soil paste preparation, or HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

b : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

c : Twenty Montana agricutural soils.

An LSD statistical procedure was conducted for the term SOIL (Table 12). The separation of soils into a large number of individual T groupings was a broad indication of the sensitivity of the PST method toward resin available quantities of the element. This procedure

Table 12. T groupings by least significant difference for P, K and S soil means for 20 soils.

Dependent Means: P, K, and S concentration of stripping solution in mg l^{-1} across all days and treatments. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	SOIL[a]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	14.48	6	A	116.18	15	A	9.37	19
B	13.15	10	B	84.45	17	B	7.30	20
C	12.27	4	C	77.64	20	B	7.14	12
D	10.49	20	C	77.03	3	C	6.46	9
E	9.97	3	D	72.04	8	D	5.24	15
E	9.63	8	ED	71.51	1	E	4.19	8
F	9.07	14	EF	68.66	5	E	3.87	3
G	8.49	15	EF	68.62	11	F	3.25	7
H	8.03	12	F	67.40	6	F	3.17	17
H	7.91	9	G	61.99	9	F	3.00	16
I	7.50	5	HG	61.29	7	G	2.53	6
J	6.07	11	HI	57.96	18	H	2.17	14
KJ	5.90	1	I	56.85	10	IH	1.99	13
KL	5.55	18	J	52.75	12	IH	1.94	5
L	5.48	13	J	51.60	4	IH	1.93	10
M	4.80	7	K	47.18	16	JIH	1.87	4
NM	4.58	16	L	35.31	19	KJI	1.81	18
NM	4.47	17	M	31.65	13	KJ	1.59	2
N	4.29	2	M	31.01	2	K	1.51	11
O	2.76	19	N	23.41	1	K	1.50	1
LSD	0.370			3.352			0.317	

a : Soil number, taxonomic name listed in Appendix Table 69.

was the most conservative approach for testing sensitivity because the individual treatments do not directly affect the separation of soil RAQ means. The different ranked order and T groupings exhibited for each element was also a most conservative test that indicated the mixed bed ion exchange resin was sensitive to P, K, and S individually. Within each element, it was noted that the separation was best in the higher concentration ranges and less distinct in the lowest third of the concentration range.

An LSD statistical procedure was conducted on the treatment means (Table 13).

Table 13. T groupings by least significant difference for the P, K, and S concentrations of the HCL, HOH, and HOHT treatments on 20 soils.

Dependent Variables: Mean P, K, and S concentration of stripping solution in mg l^{-1} across all soils and days. Alpha = 0.05.

PHOSPHORUS			POTASSIUM			SULFUR		
T GROUP	MEAN	TRT	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	8.834	HOHa	A	80.68	HCL	A	4.667	HCL
B	8.178	HOHTb	B	53.20	HOH	B	3.622	HOH
C	6.218	HCLc	C	48.30	HOHT	C	3.176	HOHT
LSD	0.1433			1.2982			0.1228	

a : PST procedure using HOH resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
c : PST procedure using HCL resin with ddw saturated soil paste preparation.

The HCL mixed bed resin showed the lowest overall mean quantity of P because Cl^- charged anion resin has been determined to have a substantially lower exchange affinity toward P than OH^- charged resin (Table 14).

The ratio of resin selectivity for the phosphate ion to the hydroxyl ion is 5 which indicates adsorption of phosphate would be favored. The ratio of resin selectivity for the phosphate ion to the chloride ion was less than 1, which indicates adsorption of phosphate would not be

Table 14. Relative selectivities of Type I strong base anion exchange resin for adsorption of phosphate ions.

Ion	Relative Selectivity
OH^-	1
HSO_4^-	85
NO_3^-	65
NO_2^-	24
Cl^-	22
HPO_4^-	5

Goltz 1989.

favored in this resin. The higher mean P concentrations for the HOH resin treatments supports this characteristic.

The lower mean concentration for HOHT versus HOH across all elements indicates that microbiological activity did affect RAQ. Whether this was a direct effect of mineralization in each element's case was not tested directly and therefore remains speculative.

The HCL resin bags caused a noticeable fizzing of the soil when first buried in the sample, but the HOH resin bags did not cause such a reaction. The fizzing clearly indicates an acid-base reaction of carbonates to free acid in the resin. The relative selective advantage of divalent calcium for cation exchange sites in the soil would have caused a subsequent release of potassium. The higher mean K concentration for HCL probably resulted from this assumed increased calcium concentration in soil solution from dissolved calcium carbonate.

The higher mean S concentration for the HCL resin was consistent with other experimental data previously presented. The solution chloride provided by the resin may have released sulfate from organic sources by S_N2 organic displacement reaction. Solution chloride may have promoted sulfate release by inorganic reactions of substitution for S occurring as solution ion pair and/or mass action displacement of exchangeable sulfate. Whatever the true cause, the effect of the sulfate release by chloride was strong enough to override the fact that the relative selectivity toward sulfate is poorer for CL^- charged anion exchange resin than for OH^- charged resin.

The SOIL, DAY and TRT factors are individually strong in the anova models and are therefore likely to generate significant interactions. Both P and K exhibited the TRT by DAY interaction term as the strongest, which suggests that RAQ for a given treatment is influenced by a rate process. The strongest interaction term of soil by TRT for S indicated that the quantity of S adsorbed by the particular resin treatment was dependent on the treatment's specific interaction with a given soil. The SOIL by DAY interaction is also significant, indicating the rate factor was important across different soils.

The data set was split into individual treatments to more specifically address RAQ relationships and to incorporate RAR relationship evaluation.

Phosphorus Treatment Responses

The results of the analysis of variance for mean P concentration by each treatment indicated that all factors of the model have a significant effect except replications (Table 15).

Table 15. The analysis of variance table for P RAQ by treatment on 20 Soils.

Dependent Variable: P concentration of stripping solution in mg l^{-1}.

Source	DF	HCL[a] Mean Square	HOH[b] Mean Square	HOHT[c] Mean Square
REP	2	0.2	0.9	1.2
DAY[d]	4	43.7**	495.7**	260.1**
SOIL[e]	19	200.7**	178.8**	133.3**
SOIL*DAY	76	4.0**	9.2**	6.9**
ERROR	299	0.41	0.84	1.14

** Denotes significance at or beyond the 0.01 level.
a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
d : Soil-resin contact time of 1, 3, 5, 7, and 15 days.
e : Twenty Montana Agricultural soils.

SOIL is the strongest factor affecting the model for HCL, and DAY is the strongest factor affecting the HOH and HOHT treatments. The significance of the soil factor in each model restates the fact that PST is soil sensitive. This sensitivity was further supported by the LSD separation into T groupings (Table 16).

Table 16. T groupings by least significant difference of P concentration for soils by treatment on 20 soils.

Dependent Means: P concentration of stripping solution in mg l^{-1} across all days. Alpha = 0.05.

	HCL[a]			HOH[b]			HOHT[c]	
T GROUP	MEAN	SOIL[d]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	14.26	6	A	14.96	6	A	14.23	6
B	13.03	10	B	13.91	10	B	12.50	10
B	12.74	4	C	12.57	20	C	11.65	4
C	9.00	3	C	12.42	4	C	11.37	20
D	7.53	20	D	11.71	3	DC	10.99	8
D	7.27	8	D	11.52	9	DE	10.43	14
D	7.26	11	ED	11.13	15	E	10.20	15
E	6.57	14	EF	10.65	8	FE	9.75	9
F	5.76	5	GF	10.20	14	FG	9.19	3
F	5.64	12	G	9.62	12	G	8.83	12
G	5.08	1	H	8.30	5	G	8.43	5
HG	4.78	13	I	7.01	18	H	6.64	18
HI	4.51	17	I	7.01	16	H	6.58	1
JI	4.25	7	J	6.03	1	I	5.68	13
JI	4.15	15	J	5.98	13	I	5.49	11
J	3.83	2	J	5.53	7	J	4.63	7
K	3.01	18	J	5.47	11	J	4.60	2
L	2.52	16	K	4.66	17	J	4.26	17
L	2.45	9	K	4.46	2	J	4.22	16
M	0.74	19	L	3.53	19	J	3.90	19
LSD	0.4605			0.6618			0.7674	

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

d : Soil number, taxonomic name listed in Appendix Table 69.

Close scrutiny of the T Groupings shows that HOH and HOHT rankings are similar, with only soil 16 displaying a dramatic shift between the two treatments. The prevention of microbiological activity (HOHT) caused all soils to have a lower P concentration than HOH. The HCL order is markedly different from the HOH treatments for soils 3, 11, 17, 9, and 15 in particular. The order rearrangement and the lower HCL concentrations are related to the difference in relative selectivity for phosphate between the two types of anion resin and differing responses to this altered affinity.

The most distinct evidence of the different behavior of P for HCL compared to HOH treatment was exhibited by the least significant difference separation of DAY means (Table 17).

Table 17. T groupings by least significant difference of P concentration for days by treatment on 20 soils.

Dependent Means: P concentration of stripping solution in mg l^{-1} across all soils. Alpha = 0.05.

	HCL[a]			HOH[b]			HOHT[c]	
T GROUP	MEAN	DAY[d]	T GROUP	MEAN	DAY	T GROUP	MEAN	DAY
A	6.83	7	A	12.71	15	A	11.19	15
BA	6.69	5	B	10.13	7	B	9.13	7
BC	6.48	3	C	8.95	5	C	8.28	5
C	6.36	15	D	7.28	3	D	7.00	3
D	4.73	1	E	5.10	1	E	5.29	1
LSD	0.2302			0.3309			0.3837	

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

d : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

The fallibility of depending on significance from an

ANOVA table as a single criterion for understanding experimental effects was illustrated by the HCL treatment separation of DAY means. The HCL treatment order and separation of DAY means is not logical, even though the ANOVA test is significant for the HCL day term. The data show the expected jump in concentration from time zero to 3 days, but concentration remains static and variable with additional time. Again, this is related to the poor relative selectivity of the Cl^{-1} resin. The HOH treatments, in contrast, are normally ordered and totally separated with respect to time.

The significant interaction term of SOIL by DAY for the HCL treatment was discounted as unimportant because of the obviously undependable nature expressed by DAY mean separation data. The SOIL by DAY interaction is significant for the HOH and HOHT treatments. This interaction is the most direct test of RAR (resin adsorption rate) significance available within the analysis of variance statistical format. Although the interaction term is not strong in comparison with the separate term effects, it does indicate that rate was an important factor in the system.

A maxr stepwise linear regression analysis technique was employed to further compare the treatment differences and to illuminate possible relationships. The two dependent variables used for the regression were the mean resin concentration, RAQ, and RAR as the beta or slope of the linear regression line of resin extract concentration (Y) with the log of time in days (X).

The maxr regression procedure was restricted to a best 3 independent variable model. The independent variable pool included soil physical and chemical measurements, standard soil test method variables for P, K, and S, and those PST variables for P, K, and S not directly related to the dependent variable (for instance HOHP as a dependent variable would have HOHK and HOHS in the independent variable pool but not HOHP or HOHTP).

The maxr method proceeds on a sampling with replacement basis to generate a single, then double, then triple variable linear model equation of maximum r-square without regard to probability value of the individual variables in a given final equation. The HOHT treatment P regression illustrates the fact that a 3 variable model can be developed which has unacceptably poor probability value associated with one or more of the terms. An acceptable probability level of P > F of 0.01 or lower was adopted and used to select the optimally valid model equation in such cases. As a result, some of the regression model equations reported had less than three independent variables. All model equations reported were significant at the 0.01 P>F level with respect to the overall equation.

The RAQ models for P were not generally strong in predictive value (magnitude of r-square) which suggests weakness in the trend relationships (Table 18).

Table 18. Maxr regression model equations for mean resin adsorption quantity of P across all days by treatment on 20 soils.

Dependent Variables: Mean P concentration of stripping solution in mg l^{-1} across all days.

Dependent Variable	Equation	R^2
HCL^a	$= 8.84 - 2.20*CAEX - 1.03*OM + 0.16*MONT$	.690
HOH^b	$= 35.21 + 0.13*KSAT - 3.54*PH - 0.21*OTHERCLAY$	.655
$HOHT^c$	$= 8.03 - 1.98*CAEX + 0.14*MONT$	.550

All terms were significant at the 0.01 P>F level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

CAEX : Ammonium acetate extractable Ca in cmol kg^{-1}.
OM : Soil organic matter in g cg^{-1}.
MONT : Montmorillonitic clay in g cg^{-1}.
KSAT : Saturated extract K in mg l^{-1}.
PH : Soil pH 2:1 procedure.
OTHERCLAY : Clay total - vermiculite, illite and montmorillonite in g cg^{-1}.

The HCL P is negatively related to ammonium acetate extractable Ca (CAEX) and percent organic matter (OM). The formation of calcium phosphate minerals is favored in alkaline soils where Ca is available for the reaction. All twenty soils were calcareous to some degree, therefore, it was normal to see some measure of Ca or carbonate appear in negative relation to soil mean RAQ P. The contribution of the CAEX variable to the equation was far greater than either the negatively related OM term or the positively related montmorillonite clay (MONT).

The negative OM relation may relate to the fact that organic matter contributes greatly to the anion exchange capacity of most soils and is in direct competition with the anion exchange resin as a sink for soluble P. The appearance of a negatively related OM with a positively related montmorillonite within the same model for P is not considered a statistical anomaly because the same relation is expressed in part for the HOHT P model (negative Ca term, positive montmorillonite term).

The positive relationship of montmorillonite literally indicates that labile P available for diffusion and resin exchange is increased by montmorillonite. The silicate clays of kaolinite, montmorillonite and illite are known to "fix" phosphates as a surface reaction between exposed -OH groups and H_2PO_4 ions at the mineral surface. Part of the P bound in this manner is subject to a replacement reaction, anion exchange, with other anions such as hydroxyl or chloride. The release of hydroxyl or chloride by the resin as it adsorbs other anions would necessarily increase the concentration of hydroxyl or chloride in soil solution, thereby promoting release of silicate clay bound phosphate.

The initial binding reaction of the phosphate to the montmorillonite occurs in a pH range of approximately 4.8 to 7.8 (Brady, 1974). Nine of the 20 soils were within this pH range in their natural state and 11 were above this level. However, the tendency for cation resin to cause acidification of the soil by free acid reaction and by emigration of H^+ from cation adsorption, dictates that the 11 other soils would be subject to these reactions in the near proximity of the resin where the acidification occurred. These explanations were not tested directly and further research, particularly with a number of acidic soils, would be necessary to define these reactions and the role they play in resin adsorption quantity or phytoavailable supply of phosphate.

The positive relation of saturated extract K in the equation for P by HOH treatment is understood as an expression of soil solution K acting as an ion pair to P . The negative pH relation is consistent with the reduction of labile P associated with calcium phosphate precipitation at higher pH levels. The negative relation of OTHERCLAY is ambiguous due to the imprecise definition of "OTHERCLAY", but may be indicative of increased pathway tortuosity due to increased clay. It should be understood that the poor r-square exhibited for the SOIL mean RAQ related equations negates definitive explanation.

The r-square values for the RAR dependent variable equations were somewhat stronger than those for the soil mean RAQ (Table 19).

Table 19. Maxr regression model equations for resin adsorption rate P by treatment on 20 soils.

Dependent variable: Slope of linear regression line of stripping solution P concentration, Y, with the log of time, X.

Dependent Variable	Equation	R^2
HCL[a]	$= 1.10 - 0.74 * CAEX - 0.03 * OP + 0.06 * MONT$	.834
HOH[b]	$= 12.86 + 0.06 * OP - 1.49 * PH - 0.40 * OM$	.762
HOHT[c]	$= 11.26 - 1.26 * PH$	.610

All terms were significant at the 0.01 P>F level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
CAEX : Ammonium acetate extractable Ca in cmol kg^{-1}.
OP : Sodium bicarbonate extractable P in mg kg^{-1}.
MONT : Montmorrillonitic clay in g cg^{-1}.
PH : Soil pH 2:1 procedure.
OM : Soil organic matter in g cg^{-1}.

The equation for resin adsorption rate of HCL exhibited the same negative relationship for Ca and positive relationship for montmorillonite as in the soil mean RAQ model. The third term, negatively related sodium bicarbonate extractable P (OP), would literally indicate that the greater the amount of sodium bicarbonate extractable P, the slower the rate of movement to and adsorption by the resin. The opposite and more acceptable principle was exhibited by a strong positive relationship of OP to the HOH resin adsorption rate. The discrepancy was probably related to the weak selectivity for P by the Cl resin.

The equation for HOH P RAR was most strongly based on the positive relationship with OP and augmented by negative relationships with pH and OM. This model would imply that rate was primarily a function of a supply (+ OP) that was limited by loss to calcium phosphate mineral formation (-pH) and loss to competitive exchange sites (- OM).

The equation for HOHT expressed significant relation to only one variable, pH. The negative relation was attributed again to the increased precipitation of P by Ca as pH increases.

All of the equations utilized terms in a manner indicative of a system dominated by inorganic reactions regardless of the resin treatment. The dominant influence on both resin adsorption quantity (RAQ) and resin adsorption rate (RAR) was attributable to the precipitation of P as calcium phosphate. Secondary influences were expressed as competition for exchangeable P by organic matter and increase of exchangeable P by montmorillonite.

Maxr regressions were also performed using the standard soil test variables of Olsen P (OP) and Bray P (BP) as dependent variables (Table 20).

The OP dependent variable is negatively related to pH. The pH relation was understandable for the same reasons

Table 20. Maxr regression model equations for standard P methods of sodium bicarbonate extraction, OP, and hydrochloric acid with sodium fluoride extraction, BP, on 20 soils.

Dependent variable: P concentration in soil in mg kg^{-1}.

Dependent Variable	Equation	R^2
OP	= 32.86 - 5.82*PH + 0.38*SAND + 1.00*CLAY	.508
BP	= 0.54 + 0.34*OM	.458

All terms were significant at the 0.01 P>F level.
PH : Soil pH 2:1 procedure.
SAND : Sand percent in soil in g cg^{-1}.
CLAY : Clay percent in soil in g cg^{-1}.
OM : Soil organic matter in g cg^{-1}.

explained in the soil mean RAQ and RAR discussions. The Olsen P dependent is positively related to both SAND and CLAY within the model, but in simple correlation OP has a very weak, negative relation to SAND (r= -.049) and weak positive relation to CLAY (r= +.464). The weak r-square of the model and contrary direct relations of OP to Sand, and CLAY suggests that an understanding of the true relation of SAND and CLAY to Olsen P is not possible from these data.

The positive relationship of Bray P to percent organic matter may reflect an extraction of P from organic exchange sites, or that the acid promoted dissociation of organo-phosphate complexes. The latter reaction is not a mode of extraction specifically intended by the Bray method. The most valid statement with respect to the OP and BP equations is that they were not sensitive to phosphate equilibrium variables in the same manner as PST. There is a need for further research aimed toward improved definition of the sources of P extracted by these soil tests when Montana agricultural soils are used.

Potassium Treatment Responses

The results of the analysis of variance for mean K concentration by each treatment indicate all factors of the model had significance except replications (Table 21).

Table 21. The analysis of variance table for K RAQ by treatment on 20 Soils.

Dependent Variable: K concentration of stripping solution in mg l^{-1}.

Source	DF	HCL[a] Mean Square	HOH[b] Mean Square	HOHT[c] Mean Square
REP	2	60.9	54.6	27.6
DAY[d]	4	87866.0**	22459.8**	24753.5**
SOIL[e]	19	15650.3**	4385.3**	5398.7**
SOIL*DAY	76	861.0**	226.3**	503.4**
ERROR	299	113.61	37.1	46.8

** Denotes significance at or beyond the 0.01 level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

d : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

e : Twenty Montana Agricultural soils.

The term DAY is consistently the strongest factor across all treatments. The least significant difference T grouping shows clear separation between each day and the ranked order for day is logical (Table 22).

Table 22. T groupings by least significant difference of K concentration for days by treatment on 20 soils.

Dependent Means: K concentration fo stripping solution in mg l^{-1} across all soils. Alpha = 0.05.

HCL[a]			HOH[b]			HOHT[c]		
T GROUP	MEAN	DAY[d]	T GROUP	MEAN	DAY	T GROUP	MEAN	DAY
A	130.1	15	A	79.2	15	A	74.8	15
B	99.7	7	B	62.4	7	B	58.9	7
C	83.1	5	C	54.3	5	C	49.2	5
D	61.6	3	D	41.4	3	D	36.7	3
E	28.9	1	E	28.8	1	E	21.9	1
LSD	3.8377			2.1926			2.4627	

a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
d : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

The difference in magnitude between the treatments was consistent with previous statements regarding the competitive release of K due to calcium provided from free acid reaction by the HCL resin bags.

The means for the antibiotic treatment (HOHT) were again lower than means for HOH. The most plausible explanation for that difference is the release of exchangeable K to maintain the charge balance of soil solution under the influence of increased soil solution sulfate via mineralization in the anaerobic conditions of the PST extraction procedure. The average difference between DAYS for HOH versus HOHT was 4.92 ug/l or HOHT concentration was approximately 98.2 percent of the HOH concentration. The small 1.8 percent difference between these two treatments suggests that the inorganic K pool dominated soil mean RAQ.

The term of SOIL was also strong for all treatments and the least significant difference T group separations supported the previous statement of the powers of PST towards discrimination between different soils (Table 23). The ranked order across all treatments is identical for the highest mean (soil 15) and the lowest 4 means (soils 19, 13, 2, and 14). The remaining 15 soil means show more order rearrangement between the HCL treatment and the HOH treatment than between HOH and HOHT (see soils 20 and 18 of Table 23). A valid discussion of causes for individual soils that appear high in ranked order by one treatment and low in another would require additional experimentation. The key point is the illustration of the existing treatment differences from the perspective of the SOIL term. The general causes are assumed to be identical to those discussed for the DAY term.

The significant interaction between SOIL and DAY for all treatments reflects the importance of K RAR in the PST system, as well as the strength of the single term effects. This significant interaction was expected, as K has been shown to be dominantly supplied to plants by a diffusion process (Barber, 1962; Skogley, 1975). The fact that RAR

Table 23. T groupings by least significant difference of K concentration for soils by treatment on 20 soils.

Dependent Means: K concentration of stripping solution in mg l^{-1} by across all days. Alpha = 0.05.

	HCL[a]			HOH[b]			HOHT[c]	
T GROUP	MEAN	SOIL[d]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	165.7	15	A	91.9	15	A	90.9	15
B	119.6	3	B	72.0	20	A	86.3	17
C	104.9	8	B	71.7	17	B	68.1	20
DC	99.6	6	C	65.0	5	CB	63.6	5
DC	99.5	1	C	64.5	1	C	61.0	7
DC	98.8	11	DC	60.8	3	D	55.9	8
D	95.4	17	DE	57.8	11	E	50.7	3
D	95.3	9	DE	57.3	18	E	50.5	1
D	92.8	20	DE	57.3	16	E	49.3	11
E	81.6	4	FE	55.9	7	E	49.1	18
E	79.2	10	FE	55.3	8	FE	47.2	6
E	77.3	5	FE	55.3	6	FG	43.0	9
F	67.9	12	FE	52.1	10	G	40.1	12
F	67.5	18	G	50.3	12	HG	39.3	10
F	67.0	7	G	47.7	9	HI	34.8	16
G	49.5	16	H	40.4	4	I	32.8	4
HG	44.2	19	I	30.0	19	JI	31.8	19
HI	38.5	2	I	29.3	13	JK	27.9	13
HI	37.8	13	I	28.5	2	K	26.1	2
I	31.5	14	J	21.0	14	L	17.7	14
LSD	7.6753			4.3853			4.9255	

a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
d : Soil number, taxonomic name listed in Appendix Table 69.

in this test was significant implies that the hypothesis of PST sensitivity to the diffusion rate process is correct.

The reliability, r-square magnitude, exhibited by the maxr regression generated models for K RAQ were generally much stronger than those previously presented for P (Table 24).

Table 24. Maxr regression model equations for mean resin adsorption quantity of K across all days by treatment on 20 soils.

Dependent Variables: Mean K concentration of stripping solution in mg l^{-1} across all days.

Dependent Variable	Equation	R^2
HCL[a]	= 4.76 + 2.31*KSAT + 12.95KNEX - 5.87*CAEX	.916
HOH[b]	= 0.85 + 66.03*PARSAT + 16.10*KEX + 0.12*N	.925
HOHT[c]	= 2.07 + 1.75*KSAT - 0.08*CASAT + 10.83*KEX	.928

All terms were significant at the 0.01 P>F level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

KSAT : Saturated extract K in mg l^{-1}.

KNEX : Sodium tetraphenyl boron extractable K in cmol kg^{-1}.

CAEX : Ammonium acetate extractable Ca in cmol kg^{-1}.

PARSAT : Potassium adsorption ratio of saturated extract.

KEX : Ammonium acetate extractable K in mg kg^{-1}.

N : Soil calcium hydroxide extractable nitrate-nitrogen in mg kg^{-1}.

CASAT : Saturated extract CA in mg l^{-1}.

The HCL K is positively related to the K concentration of soil solution (KSAT) and nonexchangeable K (KNEX) of the mineral soil. These two K fractions are in equilibrium with each other in the natural state of soil and both serve as sources of phytoavailable K. Their positive relation to soil mean RAQ simply stated that the higher the overall K equilibrium, the higher the concentration of soil solution

K available for diffusion to the resin.

The negative relation of ammonium acetate exchangeable Ca (CAEX) was consistent with the prior two variables because the cation concentration in soil solution will be in equilibrium with exchangeable and nonexchangeable sources. The Ca measured by ammonium acetate represents both the exchangeable and the carbonate sources. Soil solution Ca will increase as a result of a larger ammonium acetate Ca supply. Therefore, the model illustrates that the concentration of K in solution available for diffusion to the resin was depressed by the influence of a higher equilibrium concentration of calcium and conversely enhanced by the influence of an increasing equilibrium concentration of K.

The model for HOH K exhibits similar equilibrium relationships. The K adsorption ratio for soil solution (PARSAT) reflects the equilibrium status of soil solution K and again shows that the quantity of K in the resin was a result of the equilibrium status of K with inclusion of the influence by Ca. This solution-solid phase equilibria relationship is supported in the equation, again, by inclusion of another K equilibrium status indicator, KEX, ammonium acetate exchangeable K.

The positive influence of nitrogen on the equation could be accounted for by either a charge balance relationship with K in soil solution, or release of K from organic sources as nitrogen exists in greater supply for promotion of mineralization. The former explanation was nonexclusively favored because of agreement with the RAR models yet to be discussed.

The model for HOHT also placed importance on the solution concentration of K (KSAT) with support from contributing equilibrium sources of Ca (CASAT, negative influence) and exchangeable K (KEX, positive influence). The explanations presented for HCL and HOH previously are pertinent to this model as well.

The relationships exhibited by the RAR models for K are somewhat weaker than the soil mean RAQ models and fewer variables met the criteria of significance (Table 25).

The K resin adsorption rate by the HCL treatment is positively related to the solution K adsorption ratio (PARSAT) and negatively related to calcium carbonate (CACO3). The non-solution K equilibrium indicators such as non-exchangeable K or exchangeable K did not contribute to the model. This suggests the diffusion rate of K to the resin is somewhat independent of soil mean RAQ and reasonably well related to classic intensity principles. The negatively related CACO3 appears only in this HCL treatment model for rate, while no other Ca related variable appears in the other rate models. Since the HCL resin causes an acid base reaction in the soil, the release of Ca from dissolved calcium carbonate may slow the rate of

Table 25. Maxr regression model equations for resin adsorption rate of K across all days by treatment on 20 soils.

Dependent variable: Slope of linear regression line of stripping solution K concentration, Y, with the log of time, X.

Dependent Variable	Equation	R^2
HCL[a]	= 15.85 + 64.10*PARSAT − 2.65*CACO3	.772
HOH[b]	= 7.14 + 31.02*PARSAT − 1.19*S + 0.08*N	.901
HOHT[c]	= −4.76 + 53.26*PARSAT + 0.07*N	.782

All terms were significant at the 0.01 P>F level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

PARSAT : Potassium adsorption ratio of saturated extract

CACO3 : HCL reactable soil calcium carbonate in g cg^{-1}.

S : Acid ammonium acetate extractable S in mg kg^{-1}.

N : Soil calcium hydroxide extractable nitrate-nitrogen in mg kg^{-1}.

adsorption of K on the resin by both competitive selectivity for the resin exchange and repulsion of the like charged K in the near proximity of the resin where the acid base reaction takes place. This possibility is consistent with the fact that the only solid phase Ca variable utilized in the soil mean RAQ equations appeared in the HCL model, while all other variables were derived directly from soil solution analyses.

The adsorption rate for the HOH and HOHT treatments were identically influenced by the positively related PARSAT. The consistent appearance of PARSAT in each RAR model indicates rate is primarily a solution K-Ca equilibrium function, while soil mean RAQ includes solid phase equilibria influences.

The inclusion of the positively related nitrogen (N) variable in both the HOH and the antibiotic HOHT rate models provides evidence that the influence of nitrogen on K supply and rate is not primarily biologically derived. The relationship is considered as evidence of ion pairing of nitrogen and K in soil solution.

The negative relation of S to HOH rate for K probably relates to the fact that solution S will react with Ca to form a solid, gypsum. Calcium should be released from soil exchange sites under the influence of the gradient established by the depletion of solution S through gypsum formation. Depletion of exchangeable calcium dampens the release of K to soil solution from the soil exchange complex. The rate of K movement to the resin is also likely to be reduced by the increased pathway tortuosity from more diffuse double layers as a result of less Ca saturation of the soil cation exchange complex.

A broad view of the RAR and soil mean RAQ K relationships reveal that the increase of soil Ca in the system was consistently detrimental to both quantity and rate of resin adsorbtion K. This influence is counter balanced by K's own equilibrium between solid and solution phases. All of the relationships expressed by the models indicate that soil mean RAQ and RAR were dominated by inorganic processes.

The maxr regression of the standard soil test for ammonium acetate extractable K shows a positive relationship to both soil cation exchange capacity (CEC) and HOH treatment mean quantity of K (HOHK), (Table 26).

Table 26. Maxr regression model equation for the standard K method of Normal ammonium acetate extractable K on 20 soils.

Dependent Variable: Soil ammonium acetate extractable K in mg kg^{-1}.

Dependent Variable	Equation	R^2
K	$= -21.42 - 6.35*OTHERCLAY + 14.06*CEC + 7.75*HOHK$	.941

All terms were significant at the 0.01 P>F level.

OTHERCLAY : Clay total - vermiculite, illite and montmorrilionite in g cg^{-1}.

CEC : Soil cation exchange capacity in cmol kg^{-1}.

HOHK : PST procedure soil mean RAQ stripping solution concentration of K across all days in mg l^{-1}.

The HOH relation suggests the PST method is more relevant to the standard assay than the other equilibrium K tests available in the independent variable pool. The former models illustrate the fact that PST was a sensitive assay of K dynamics because of its relation to several important direct and indirect measures of the K equilibrium. The lack of relation of ammonium acetate K to other K fraction variables indicates that it is a rather strictly independent test of soil K which only infers sensitivity to K equilibria through the final entered term of HOHK.

The positive relationship to CEC was expected because the standard method chemistry is a mass action displacement of exchangeable soil ions which means, normally, a higher CEC soil naturally yields a greater amount of K in the extract solution. The negative relation to the ambiguous term of OTHERCLAY cannot be interpreted beyond the statement that the sum of the types of clays not analyzed directly was actually the most important component related to the index of available K by ammonium acetate. The critical importance of the most ill-defined variable available in the independent pool suggests that the strong r-square of the ammonium acetate extractable K model was built from a very weak foundation.

Sulfur Treatment Responses

The results of the analysis of variance for mean S concentration, RAQ, by each treatment indicate that all factors of the model have significant effect except replications (Table 27).

The effect of the single term DAY is the strongest factor for the HCL treatment, while the effect of the SOIL term was the greatest single factor in the HOH and HOHT treatments.

Table 27. The analysis of variance table for S RAQ by Treatment on 20 Soils.

Dependent Variable: S concentration of stripping solution in mg l^{-1}.

Source	DF	HCL[a] Mean Square	HOH[b] Mean Square	HOHT[c] Mean Square
REP	2	0.3	1.1	0.7
DAY[d]	4	228.0**	70.1**	43.1**
SOIL[e]	19	188.7**	178.7**	168.1**
SOIL*DAY	76	13.1**	3.2**	3.8**
ERROR	299	0.81	0.42	0.54

** Denotes significance at or beyond the 0.01 level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

d : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

e : Twenty Montana Agricultural soils.

The least significant difference T grouping shows clear separation between each day, and the ranked order for DAY means is normal (Table 28).

All treatments means show a relatively similar S concentration at day 1 but the HCL surpassed the other treatments in terms of concentration rise for each subsequent day. This steady increase exceeds the least significant difference value by a consistently wide margin and thereby accounts for the greater strength of the DAY term displayed for the HCL treatment in the analysis of variance table.

The HOH treatment shows a smaller but significant and consistent increase in concentration by day. The HOHT

Table 28. T groupings by least significant difference of S concentration for days by treatment on 20 soils.

Dependent Means: S concentration of stripping solution in mg l^{-1} across all soils.

Alpha = 0.05.

	HCL[a]			HOH[b]			HOHT[c]	
T GROUP	MEAN	DAY[d]	T GROUP	MEAN	DAY	T GROUP	MEAN	DAY
A	7.27	15	A	4.78	15	A	3.89	15
B	5.54	7	B	4.24	7	A	3.80	7
C	4.74	5	C	3.90	5	B	3.48	5
D	3.71	3	D	3.21	3	C	2.89	3
E	2.07	1	E	1.98	1	D	1.83	1
LSD	0.3231			0.2341			0.2640	

a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
d : Soil-resin contact time of 1, 3, 5, 7, and 15 days.

treatment data show continuous increase, which diminished with time until the final two points (Day 7 and Day 15) do not significantly differ from each other. This contrast gives rise to the possibility that the inorganic supply of S is somewhat limited, and mineralization is a critical intensity component. The much higher concentrations for the HCL versus both HOH resin treatments supports the previously identified phenomenon of sulfate release under the influence of increased soil solution chloride concentration increase.

The single term effect of SOIL is strong and practically equal across all treatments (Table 29).

Table 29. T groupings by least significant difference of S concentration for soils by treatment on 20 soils.

Dependent Means: S concentration of stripping solution in mg l^{-1} across all days by treatment. Alpha = 0.05.

HCL[a]			HOH[b]			HOHT[c]		
T GROUP	MEAN	SOIL[d]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	12.33	9	A	15.47	19	A	15.37	19
B	11.06	19	B	8.61	20	B	8.00	20
C	10.39	15	C	8.07	12	C	5.92	12
D	9.54	8	D	4.30	3	D	3.37	3
E	7.43	12	ED	3.93	7	D	3.23	9
F	6.06	16	EF	3.82	9	D	3.21	7
G	5.30	20	F	3.37	17	ED	2.92	17
H	3.95	3	G	2.76	15	EF	2.59	15
I	3.22	17	H	2.28	6	GF	2.19	5
I	3.14	6	IH	2.25	13	GF	2.15	6
JI	2.62	7	JIH	2.24	14	G	2.03	13
JI	2.58	1	KJIH	1.99	10	GH	1.94	18
J	2.47	14	KJIH	1.99	5	GH	1.81	14
J	2.36	10	KJIH	1.99	16	IGH	1.70	4
JK	2.31	11	KJIH	1.99	18	JI H	1.46	2
JKL	2.11	4	KJI	1.81	4	JI H	1.42	10
KL	1.69	13	KJ	1.78	8	JI	1.25	8
L	1.65	5	K L	1.68	2	J	1.08	1
L	1.64	2	ML	1.28	11	J	0.95	16
L	1.50	18	M	0.83	1	J	0.94	11
LSD	0.6463			0.4682			0.5279	

a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
d : Soil number, taxonomic name listed in Appendix Table 69.

This again implies that the PST system is sensitive to individual soils. Although this statement is valid, there is a distinct difference between this element and P and K statistics of a similar nature.

There is a clear delineation of individual soil means in the upper third of the concentration range, but the separations in the lowest third are poor across all treatments. There is no reason to suspect that this was due to anything more than the inherent range in S for these twenty soils.

There is dramatic switching in soil mean ranked order between the HCL treatment and the HOH treatment (see soils 9, 15, 8, 16, and 1). The switching between rankings for HOH and HOHT soils was nominal, which points out a difference between HCL resin influence on soil versus the HOH resin. The relative affinity of each anion resin type toward sulfate would strongly favor the OH^- charged resin (ratio of sulfate affinity to hydroxyl = 85) over the CL^- charged resin (ratio of sulfate affinity to chloride = 3.9) yet the concentrations indicate the opposite (Table 14). This supports the possibility that the release by chloride is substantial enough to override the selectivity advantage of the OH^- resin.

Lower mean values for the HOHT treatment versus the HOH treatment were found in all soils except for soils 5 and 1. The actual differences for those soils are half of the concentration value derived for the least significant difference criteria statistically generated for either treatment and therefore considered insignificant.

The maxr regression models generated for RAQ S were much more reliable for the HOH resin treatments than for the HCL resin treatment (Table 30). The fact that the first entered variable of soil solution calcium (CASAT) was positively related to RAQ S by HCL treatment indicates a probability of calcium-sulfate ion pairs present in soil solution and thereby available for substitution by chloride. The positive relation of nonexchangeable K (KNEX) may be explained by the fact that in any pH range, less sulfate adsorption occurs on clay when the presence of

Table 30. Maxr regression model equations for mean resin adsorption quantity of S across all days by treatment on 20 soils.

Dependent Variables: Mean S concentration of stripping solution in mg l^{-1}.

Dependent Variable	Equation	R^2
HCL[a]	= −3.547 + 0.04*CASAT + 1.57*KNEX	.690
HOH[b]	= 1.32 − 0.95*CAEX + 1.25*S	.923
HOHT[c]	= 0.92 − 0.84*CAEX + 1.18*S	.904

All terms were significant at the 0.01 P>F level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.

b : PST procedure using HOH resin with ddw saturated soil paste preparation.

c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.

CASAT : Saturated extract CA in mg l^{-1}.

KNEX : Sodium tetraphenyl boron extractable K in cmol kg^{-1}.

CAEX : Ammonium acetate extractable Ca in cmol kg^{-1}.

S : Acid ammonium acetate extractable S in mg kg^{-1}.

K on the clay surface increases. A higher nonexchangeable K concentration would be somewhat indicative of a higher overall exchange saturation by potassium. Under high K saturation conditions sulfate would be more likely to exist in soluble salt or organic complex forms away from the sources of cation exchange. This possible relationship is suggested by these trends, but the data are not strongly definitive of this process. Specific research including fractional assay of soil S would better define this possibility.

Although this explanation may relate well to the HCL treatment, it is not evident in the much stronger two-variable models for HOH and HOHT. An alternative hypothesis would be that nonexchangeable K is indicative of the relative net negative character of the system. The positive relation of both terms in the model implies that higher nonexchangeable K occurs coincidentally with higher Ca in solution. The chloride substitution reaction would release sulfate into a strongly net negative clay system that would offer the least resistance in terms of pathway tortuosity. Either or both mechanisms could be involved, but further clarification was not possible from this data base.

The HOH and HOHT equations are identical to each other showing negative relation to exchangeable Ca (CAEX) and positive relation to acidic ammonium acetate extractable S.

This was viewed as an expression of positive response of soil mean RAQ to a greater supply of S in concert with a reduction of S supply by gypsum formation.

The RAR equations for HCL and HOH are near mimics of their associated soil mean RAQ equations (Table 31). The only discernible difference from these comparisons is the numerical corrective cofactors for each RAR variable were smaller than for RAQ. This suggests the natural fit of the rate data was better than soil mean RAQ. This does not

Table 31. Maxr regression model equations for resin adsorption rate of S across all days by treatment on 20 soils.

Dependent variable: Slope of linear regression line of stripping solution K concentration, Y, with the log of time, X.

Dependent Variable	Equation	R^2
HCL^a	$= -1.87 + 0.02*CASAT + 0.04*KNEX$	.761
HOH^b	$= 0.68 - 0.36*CAEX + 0.34*S$	.918
$HOHT^c$	$= -0.40 + 7.11*NAEX + 0.06*HOHP$	.610

All terms were significant at the 0.01 P>F level.

a : PST procedure using HCL resin with ddw saturated soil paste preparation.
b : PST procedure using HOH resin with ddw saturated soil paste preparation.
c : PST procedure using HOH resin with 15 mg l^{-1} tetracycline saturated soil paste preparation.
CASAT : Saturated extract CA in mg l^{-1}.
KNEX : Sodium tetraphenyl boron extractable K in cmol kg^{-1}.
CAEX : Ammonium acetate extractable Ca in cmol kg^{-1}.
S : Acid ammonium acetate extractable S in mg kg^{-1}
NAEX : Ammonium acetate extractable Na in cmol kg^{-1}.
HOHP : PST HOH resin treatment procedure mean soil P concentration across all days in mg l^{-1}.

necessarily imply any greater validity on behalf of the RAR equations.

The distinctly different relationship expressed for HOHT rate versus HOHT quantity is difficult to explain. The positive relation of exchangeable Na (NAEX) to RAR S may indicate co-diffusion of sulfate with Na present in soil solution. This possibility is questionable because all of the soils have minimal concentrations of exchangeable Na.

The positive relationship of HOHP in the model would indicate that soils not under the influence of microbial activity express the inorganic processes in a much stronger manner. Here, the normally elusive principle of pathway tortuosity is illuminated by the positive relation of HOHP to HOHT S. Any soil providing a stronger net negative pathway would enhance anion diffusion for both the P and S anion.

The maxr regression equation for the standard acid ammonium acetate extractable S procedure consists of a positive relation of the dependent to both pH and EC (Table 32).

The pH term relates to available S quantity existing as gypsum, which should occur in greater quantities as pH rises due to the coincident rise in available Ca. The positive relationship EC is due to the fact that sulfate commonly occurs as an anion in soluble soil salts. It is

Table 32. Maxr regression model equations for the standard S method of acid ammonium acetate extractable S on 20 soils.

Dependent Variable: S concentration of soil in mg kg^{-1}.

Dependent Variable	Equation	R^2
S	= 0.02 + 0.86*PH + 18.54*EC	.844

All terms were significant at the 0.01 P>F level.

PH : Soil pH from 2:1 extraction.

EC : Soil electrical conductivity in saturated paste in mmhos cm^{-1}.

then expected that sulfate abundance increases in harmony with increasing soluble salts. All of the soluble salts of the soil would be readily leachable by the extraction process of the standard method.

Although the explanation of this model is a relatively straight forward argument based on sulfate abundance in the system, the underlying importance of the model is the fact that it is not directly similar to any of the PST models. The PST system is definitely sensitive to a different expression of soil S equilibria than the standard method.

Conclusions

The results from the three resin treatments studied in this experiment were significantly different from each other with respect to each element.

The antibiotic treatment, HOHT, was significantly lower in RAQ for each element, supporting the hypothesis that microbiological activity did contribute to RAQ.

The dominant influence on RAQ for each element was the inorganic equilibrium which consistently depended on the dynamics of Ca in conjunction with quantity and intensity of the element under consideration.

The acidifying action, chloride substitution activity, and relative exchange selectivity of the HCL treatment caused profound effects on RAQ and RAR. The HCL treatment resin did not act as a passive exchangeable ion sink.

The PST method was more sensitive to the broad range of quantity and intensity related principles than the standard soil tests.

CONTROLLED ENVIRONMENT EXPERIMENTS

Fertilizer rate response experiments were conducted to develop a data base suitable for determining the predictive value of the PST method and the standard soil test procedures. The objectives were to directly compare PST with standard tests for prediction of P, K, and S phytoavailability and to describe each method's relation to phytoavailability.

Materials and Methods

The first experiment, "Greenhouse K" was conducted in a greenhouse bay of the Montana State University Plant Growth Center. In this experiment 10 treatments were imposed with 4 replications on the 20 soils. Other nutrient variables were included, but only the K treatment results were used for this study. Treatments were randomized within blocks, forming 4 sections along the length of the greenhouse bench.

The 5 inch square, 500 ml pots used in the study were filled with 750 g of soil. The treatments were applied as a single 50 ml solution aliquot per pot, prior to seeding. The treatment rates were calculated as actual elemental K with respect to the mineral soil weight per pot. The 5 K treatments were 0, 100, 200, 400, and 800 kg ha^{-1} actual K in the form of dissolved reagent grade KCl. The treatment solutions were amended with appropriate concentrations of reagent grade ammonium nitrate, phosphoric acid and calcium sulfate to form a blanket treatment of 100 kg ha^{-1} N, 50 kg ha^{-1} P and 30 kg ha^{-1} S. Subsequent 100 kg ha^{-1} N applications were applied throughout the growing period as needed. Pesticides were applied to control aphid infestations as needed.

Each pot was seeded with 25 spring wheat (Triticum aestivum L. cv. Pondera) seeds. The seeds were barely inserted into the soil then covered by smoothing the soil surface. The soil was then moistened with ddw to promote germination. The seedlings were thinned to 17 per pot after emergence. Water was applied as 50 ml aliquot surface applications of ddw throughout the growth period as needed.

The entire above ground portion of the plants per pot was harvested, and a population count per pot was taken when 85 % of the plants completed the heading growth stage. The plant material was dried at 35 °C, weighed to obtain dry matter yield, and then ground for the chemical analyses as previously described.

Later experiments were conducted in a growth chamber of the same facility. These separate experiments were designed to test rate response to K (Growth Room K Experiment), P (Growth Room P Experiment), and S (Growth

Room S Experiment). Each experiment had 5 treatments and 4 replications on 7 soils.

The soils for each experiment were selected from the 20 soils on the basis of the broadest available range in standard soil test results applicable to the experiment. The Bray P test was used for selection on the P experiment. The soils chosen reflected an evenly distributed range from low to high standard soil test levels. This selection method biased each experiment toward an optimal correlation of the standard soil test with the response parameters. The bias causes the correlative relations of PST to be more conservatively tested than the standard methods.

The soils for each experiment were diluted 1:1 by weight with coarse silica sand and mixed in bulk in a clean cement mixer. Each pot was filled with 650 g of soil mixture and amended by treatment prior to seeding.

The treatment concentrations were calculated on the basis of actual mineral soil weight rather than on the mixture weight. The 5 treatments were added as single 50 ml solution aliquots of 0, 50, 100, 200, and 400 kg ha^{-1} K as dissolved reagent grade KCl (growth room K experiment); 0, 10, 20, 40, and 80 kg ha^{-1} P as diluted reagent grade phosphoric acid (growth room P experiment); and 0, 15, 30, 60, and 120 kg ha^{-1} S as dissolved reagent grade calcium sulfate (growth room S experiment). The solutions were adjusted in the same manner as the greenhouse experiment to deliver appropriate blanket treatments of 100 kg ha^{-1} actual N, 20 kg ha^{-1} actual P, and 30 kg ha^{-1} actual S. Subsequent 100 kg ha^{-1} N applications were applied throughout the growing period as needed.

All pots were seeded by placing 25 spring wheat (Triticum aestivum L. cv. Pondera) seeds on the soil surface. The surface was then covered by smoothing 100 g of pure coarse silica sand over the seeds. The pots were placed in a large tray that held all the randomized pots of one replication for one experiment. Watering was done by adding ddw to the tray, which allowed water to move from the bottom of the pots to the top under the influence of capillarity and hydraulic head. Water was allowed to stand in the tray until the sand surface was moist and then the tray was drained. Water was delivered throughout the growth period in this manner as needed. Pesticides were applied for aphid control as needed.

The plants were thinned to approximately 15 plants per pot after emergence. Plants were harvested and stand counts taken when 80 % of the population had completed the heading stage. The plant samples were handled in the same manner as per the greenhouse experiment.

The dependent variables used for these experiments included dry weight, percent P, K, or S and total milligrams of P, K or S (uptake). Simple linear regression analyses were used to compare the trueness of prediction of standard soil test method results and RAQ terms for HOH, HOHT, and HCL PST methods. The check plot data, 0 treatment, was used as the dependent variable in all linear regression analyses.

In the S growth room experiment an additional RAQ variable called MINS was developed. This variable was generated by simple subtraction of HOHTS from HOHS. The MINS variable represents mineralized S supply in the given soil.

Results and Discussion

Greenhouse K Experiment Results

The initial watering of the pots after seeding caused the soil surface to crust which prevented seedling emergence on some soils. The greenhouse bay was found to have a severe temperature and air movement gradient which influenced plant growth. The leaf tips of all plants showed signs of desiccation after the first fourteen days of growth. This was probably caused by the turbulent air circulation system of the greenhouse bay and the low humidity of the circulating air. Three soils were dropped from the 20 soil data set of the experiment because they had severe seedling emergence problems.

The effect of the adverse growth conditions was particularly expressed in the data pertaining to replications and dry matter yield (Table 33). The

Table 33. The analysis of variance table for greenhouse K experiment on 17 soils.

Dependent Variables: Dry weight per pot in g, K uptake per pot in mg, and K percent per pot in g cg^{-1}.

Source	DF	G/Pot[a] Mean Sq.	K Uptake[b] Mean Sq.	K Pct[c] Mean Sq.
REP	3	4.04**	16900.0**	9.36**
TRT[d]	4	0.68	6750.0**	6.06**
SOIL[e]	16	1.59**	6514.0**	1.89**
TRT*SOIL	64	0.13	361.3	0.20**
Error	252	0.205	381.5	0.088

** Denotes significance at or beyond the 0.01 level.

a : Dry weight yield per pot in g.

b : K uptake per pot in mg.

c : K percent per pot in g cg^{-1}.

d : Fertilizer additions of 0, or 100, or 200, or 400, or 800 kg ha^{-1} per pot.

e : Seventeen Montana agricultural soils.

replication results of the ANOVA table show significance across all dependent variables. The significance of the replication data was attributed to greenhouse gradient effect because the replications were not randomized and were physically aligned in parallel with the gradient. The dry matter yield was not significantly affected by the treatments.

There was a significant treatment effect for the dependent variables of milligrams of K uptake per pot and percent K. The treatment means were separated by the LSD statistical procedure to aide in defining the significance of the treatment effect (Table 34). The ranked order of

Table 34. T groupings by least significant difference for the greenhouse experiment treatments for K by response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, K uptake per pot in mg, and K percent per pot in g cg^{-1} across 17 soils.

Dry Wt. g^{-1}			K Uptake mg^{-1}			K %		
T GROUP	MEAN	TRT[a]	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	3.59	200	A	137.8	0	A	3.59	0
AB	3.66	400	A	140.6	100	B	3.78	100
ABC	3.74	800	A	143.6	200	C	3.91	200
BC	3.80	100	B	151.1	400	D	4.14	400
C	3.84	0	C	162.6	800	E	4.35	800
LSD	0.1530			6.597			0.1004	

[1] Treatment units are kg ha^{-1}.

dry weight means is not normal with respect to increasing application rates of K. The K uptake and percent K treatment mean ranked order is normal with respect to applied K rates. The K uptake means are not different in the 0 to 200 kg ha^{-1} rate range.

The K percent means are clearly separated over the entire range of treatments. The highly significant data for K percent shows the strongest response relation to treatments of all the dependent variables. Percent K is not correlated with dry matter ($r= +.09$).

The SOIL term of the ANOVA table is significantly related to all dependent variables. The soil means were separated by the LSD procedure to elucidate the significant relationship (Table 35).

Both the dry weight and uptake soil means are

Table 35. T groupings by least significant difference for the greenhouse experiment soils for K by response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, K uptake per pot in mg, and K percent per pot in g cg^{-1} across all treatments.

Dry Wt. g^{-1}			K Uptake mg^{-1}			K %		
T GROUP	MEAN	SOIL[a]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	3.24	12	A	109.1	14	A	3.27	14
AB	3.30	6	AB	120.8	9	B	3.54	9
ABC	3.34	14	BC	131.9	12	B	3.59	16
ABC	3.42	9	C	133.0	6	CB	3.72	7
BCD	3.55	10	C	133.9	10	C	3.79	10
BCD	3.57	18	D C	138.0	16	CD	3.83	13
E CD	3.62	4	DEC	141.4	18	CDE	3.89	11
EF D	3.76	15	DE	146.2	4	DEF	3.97	2
EFGD	3.81	3	EF	151.7	11	DEF	3.99	18
EFGD	3.81	16	EF	151.7	7	G EF	4.03	6
EFG H	3.85	2	EF	152.9	2	G EF	4.05	4
EFG H	3.89	17	EF	153.2	13	GH F	4.10	12
FG H	3.91	11	G F	160.7	15	GHI	4.19	5
FG H	4.01	13	GHF	161.5	3	HIJ	4.26	1
G H	4.05	5	GH	169.7	5	HIJ	4.27	3
G H	4.07	1	GH	172.9	1	IJ	4.30	15
H	4.11	7	H	173.1	17	J	4.43	17
LSD	0.2822			12.16			0.1852	

a : Soil numbers, taxonomic soil names are listed in Appendix Table 69.

separated into 8 overall T groups, while K percent is separated into 10 T groups. The T group delineation is more distinct in the high range of the K uptake and percent K means than the high range of the dry weight means. However, the overall strength of the percent K dependent variable is not as well expressed by the soil mean separation.

The significant soil by treatment interaction for the percent K dependent variable is linked to relatively contrasting responses shown by individual soils. This point is evident in the ranked order of soil number 14 across each dependent variable, versus order position shown by soil number 12. Soil 12 is low in dry matter yield, low in K uptake, but quite high in K percent. The quantity of K obtained by the plants grown in soil number 12 was not efficiently translated into biomass and thus the high concentration value. Soil 14 is consistently ranked low among the 17 soils for each dependent variable. The plants grown in soil number 14 were efficient in translating obtained K into biomass.

Soil 12 readily provided K to the plant but growth was limited by undefined outside factors. Soil 14 did not provide K adequately to the plants and K nutrition was the most limiting growth factor.

These contrary relationships of limiting factors pertain to the weak but significant SOIL by TRT two way interaction listed in the ANOVA table. Lack of consistency in treatment response was expected because the soils were all **high** in extractable K to start with.

Greenhouse K Soil Test Relationships

Single variable linear regression equations were derived for the standard soil test method of ammonium acetate K and the PST extraction methods of HOH, HOHT, and HCL. The dependent variables were the means for each soil of plant K percent at 0 kg ha^{-1} K treatment rate and the plant K uptake per pot at the 0 kg ha^{-1} K treatment rate. This format was considered appropriate because the foundation of an accurate soil test method is the power to index the phytoavailable K supply prior to amendment of the soil with fertilizer. The dry weight yield data were too erratic to warrant consideration by this approach.

The predictive value of K uptake by the ammonium acetate K soil test is slightly less than that for HOH or HOHT (Table 36). The HCL resin method is much weaker in

Table 36. Simple linear regression model equations for the greenhouse experiment, K uptake (Kup) for 17 soils.

Dependent Variable: Kup = Mean K uptake per pot in mg at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
Kup =	93.35 + 0.09K[a]	.460	.003
Kup =	89.41 + 0.93*HOHK[b]	.465	.002
Kup =	97.72 + 0.84*HOHTK[c]	.471	.002
Kup =	108.53 + 0.36*HCLK[d]	.255	.003

a : Soil ammonium acetate extractable K in mg kg^{-1}.
b : PST procedure soil mean extractable K across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
c : PST procedure soil mean extractable K across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable K across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

predictive value than any other procedure. The predictive value of the PST method is clearly different from ammonium acetate K when considered in relation to percent K in the plant (Table 37). The HOH method is clearly an improvement over the standard within the context of this experiment.

Table 37. Simple linear regression model equations for the greenhouse experiment, K percent (K%) for 17 soils.

Dependent Variable: K% = Mean K percent per pot in g cg^{-1} at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
K% =	$2.75 + 0.01*K^a$	.326	.017
K% =	$2.33 + 0.24*HOHK^b$	.627	.001
K% =	$0.92 + 2.62*HOHTK^c$	.551	.001
K% =	$2.72 + 0.01*HCLK^d$	.448	.003

a : Soil ammonium acetate extractable K in mg kg^{-1}.
b : PST procedure soil mean extractable K across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
c : PST procedure soil mean extractable K across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable K across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

A further test of the predictive strength of the methods was performed by conducting maxr regression analysis. The independent variable pool included all soil test methods, physical, and chemical soil parameters for a total of 47 independent variables. Selection of reliable equations was made by eliminating models that contained variables poorer than .01 probability.

The maxr equation for percent K contains the negatively related OM variable (Table 38). Organic matter is a dominant source of cation exchange capacity in the soil and increases pathway tortuosity for diffusion of K. The positive relation of HOHK indicates that HOHK was a direct measure of phytoavailable K. Organic matter and HOHK are the critical components of both the K uptake and percent K models.

Table 38. Maxr regression model equations for the greenhouse experiment K response variables at 0 fertilizer rate for 17 soils.

Dependent Variables: K% = Mean percent K per pot in g cg^{-1}.
Kup = Mean K uptake per pot in mg.

Dependent Variable	Equation	R^2
K%	= 2.90 − 0.25*OM + 0.02*HOHK + 0.10HOHTS	.938
Kup	= 124.59 − 7.95*OM + 0.98*HOHK − 7.41*TPBETA	.946

All terms were significant at the 0.01 P>F level.

OM : Soil organic matter in g cg^{-1}.

HOHK : PST procedure soil mean extractable K concentration across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

HOHTS : PST procedure extractable soil mean S concentration across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.

TPBETA : The linear regression slope of PST procedure extractable P concentration using HOH resin with 15 mg l^{-1} solution saturated soil paste preparation, Y, and log time, X.

The positive relation of HOHTS to percent K reflects the charge balance relationship between K and S in soil solution. This was consistent with trends presented in prior chapters. The contribution of HOHTS to the K uptake r-square is much weaker than OM and HOHK. Therefore, strength of prediction for this model is understood to be an expression of the importance of combining a measure of phytoavailable supply with a modifying term related to the diffusion pathway.

The third term of the K uptake model, TPBETA (the RAR measure as the slope of HOH tetracycline P as the dependent with log time as the independent, is negatively related to K uptake. This inorganic P RAR term contributes strongly to the model but is positively and very weakly correlated to both OM (r= .27) and HOHK (r= .21). These conflicting relationships are evidence that the data were not suitable for a clear understanding of the relationship of RAR P to K uptake.

Growth Room K Experiment Results

The use of the growth room eliminated the environmental gradient problem experienced in the greenhouse room. The change in soil preparation and watering method eliminated the soil crusting problem. The tip burn of the plants persisted as a problem in the growth room and was again attributed to turbulent air despite the higher relative humidity provided by evaporation of water from buckets.

The success of the modifications was evident from the lack of significance for replication data in the ANOVA (Table 39). The treatment effect is, again, significant for both K uptake and K percent. The treatment effect is substantially weaker in this experiment as compared to the greenhouse. The data for the LSD separation of treatment means reveal that the first level of added K caused an increase of both K uptake and K percent (Table 40).

Table 39. The analysis of variance table for growth room K on 7 soils.

Dependent Variables: Dry weight per pot in g, K uptake per pot in mg, and K percent per pot in g cg^{-1}.

Source	DF	G/Pot[a] Mean Sq.	K Uptake[b] Mean Sq.	K Pct[c] Mean Sq.
REP	3	0.21	73.67	0.04
TRT[d]	4	0.09	231.34**	0.31**
SOIL[e]	6	10.78**	4588.67**	9.56**
TRT*SOIL	24	0.19	40.19	0.04
Error	102	0.12	40.52	0.04

** Denotes significance at or beyond the 0.01 level.
a : Dry weight yield per pot in g.
b : K uptake per pot in mg.
c : K percent per pot in g cg^{-1}.
d : Fertilizer additions of 0, or 50, or 100, or 200, or 400 kg ha^{-1} per pot.
e : Seven Montana agricultural soils.

Higher treatment rates caused a reduction in K uptake and percent K. These responses to the treatments are probably related to the overall high K status of the soils.

The K uptake ranked order and separation of the higher treatment rates means is not normal. The ranked order of

Table 40. T groupings by least significant difference for the growth room K experiment treatment means for K response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, K uptake per pot in mg, and K percent per pot in g cg^{-1} across 7 soils.

Dry Wt. g^{-1}			K Uptake mg^{-1}			K %		
T GROUP	MEAN	TRT[a]	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	2.88	400	A	31.42	50	A	1.19	50
A	2.84	50	AB	29.49	0	A	1.17	0
A	2.81	100	BC	27.90	100	AB	1.11	100
A	2.79	200	C	25.10	400	BC	1.02	200
A	2.73	0	C	24.66	200	C	0.94	400
LSD	0.1810			3.3746			0.1061	

[a] Treatment units are kg ha^{-1}.

the percent K treatment means reveal that plants responded positively to the 50 kg ha^{-1} rate but higher rates caused a progressively negative effect. Some K cofactor is more likely to be the causal agent of this response rather than a K toxicity, but investigation of this trend is not pertinent to the objectives of this experiment. It is clear from these data that this experiment was not as reliable as the greenhouse experiment.

The SOIL term in the ANOVA table was significant across all dependent variables. The ANOVA F value is an order of magnitude greater than the greenhouse results for each dependent variable. Part of the improved strength of the ANOVA analysis SOIL term results from the built in, evenly distributed range of soils in terms of extractable K.

The separation of soil means by LSD illustrated that the range of the means was relatively consistent between K uptake and K percent with soils 15 and 20 as high, soils 14, 7, and 8 in the mid range and soils 16 and 2 in the low range (Table 41). The data of this table show slightly better separation for K percent than the other dependent variables. Dry matter means were not the same as the ranked order expressed for K uptake and K percent.

Table 41. T groupings by least significant difference of the growth room K experiment soil means for K response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, K uptake per pot in mg, and K percent per pot in g cg^{-1} across all treatments.

	Dry Wt. g^{-1}			K Uptake mg^{-1}			K %	
T GROUP	MEAN	SOIL[a]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	3.54	16	A	57.42	15	A	2.34	20
A	3.39	15	B	38.21	20	B	1.71	15
B	3.12	14	C	23.90	14	C	0.99	8
B	3.09	2	C	23.54	17	D	0.79	17
B	2.96	17	D	18.91	8	D	0.76	14
C	1.91	8	D	16.69	16	E	0.51	2
D	1.64	20	D	15.34	2	E	0.47	16
LSD	0.2142			3.9929			0.1256	

a : Soil numbers, taxonomic soil names are listed in Appendix Table 69.

The significance of the SOIL term indicates that soil type did affect dry weight, K uptake, and K percent. However, the strongest expression of response for this experiment is exhibited by the K percent data. The treatment effects are not strong and as a result there was no significant SOIL by TRT interaction.

Growth Room K Soil Test Relationships

Single variable linear regression equations were derived for the standard soil test method of ammonium acetate K and the PST extraction methods of HOH, HOHT, and HCL. The dependent variables were the means for each soil of the plant K percent at the 0 kg ha^{-1} K treatment rate and the plant K uptake per pot at the 0 kg ha^{-1} K treatment rate. The dry weight yields were considered to be too erratic to warrant further consideration.

The predictive value of the standard soil test method of ammonium acetate K and the PST HCL method are closely aligned with the HOH and HOHT methods in this experiment (Tables 42 and 43). The standard test exceeds PST in the prediction of percent K, while the HOH treatment is the best predictor of K uptake. The probability value of all equations was unacceptably low. This suggests the growth room experiment is a poorer forum for testing predictive value of a soil test than the greenhouse experiment, in spite of the efforts to improve problematic environmental influences. The reduced number of soils used in the growth room may also have contributed to poorer reliability.

The maxr regression equations describing K percent did utilize the KBETA rate term as a finite line adjustment term in the three variable equation (Table 44). All of

Table 42. Simple linear regression model equations for the growth room experiment, percent K in the plant for 7 soils.

Dependent Variable: K% = Mean K percent per pot in g cg^{-1} at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
K%	$= -0.25 + 0.0024*K^a$	.498	.077
K%	$= 0.24 + 0.0172*HOHK^b$	.484	.083
K%	$= 0.44 + 0.0133*HOHTK^c$	.352	.161
K%	$= 0.54 + 0.0076*HCLK^d$	.302	.202

a : Soil ammonium acetate extractable K in mg kg^{-1}.

b : PST procedure soil mean extractable K across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

c : PST procedure soil mean extractable K across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.

d : PST procedure soil mean extractable K across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

the terms of the equation are positively related to K percent (r= +.57 KSAT, r= +.76 CL, r= +.58 KBETA). The positive correlation of the percent clay variable is possibly an indication that clay serves as a source of nonexchangeable K and as a source of exchangeable K. The more specific measures of these sources did not come out of the variable pool because they were not consistently related to all of the 7 soils.

The KSAT and KBETA terms are strongly related to each other (r= +.95). Their relation to percent K is identical

Table 43. Simple linear regression model equations for the growth room experiment, K uptake (Kup) per pot for 7 soils.

Dependent Variable: Kup = Mean K uptake per pot in mg at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
Kup =	$0.56 + 0.05K^{a}$	.521	.067
Kup =	$7.83 + 0.40*HOHK^{b}$	.665	.025
Kup =	$11.93 + 0.32*HOHTK^{c}$	.522	.067
Kup =	$11.29 + 0.22*HCLK^{d}$	.636	.032

a : Soil ammonium acetate extractable K in mg kg^{-1}.
b : PST procedure soil mean extractable K across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
c : PST procedure soil mean extractable K across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable K across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

Table 44. Maxr regression model equations for the growth room experiment K response variables at 0 fertilizer rate for 7 soils.

Dependent Variables: K% = Mean percent K per pot in g cg^{-1}.
Kup = Mean K uptake per pot in mg.

Dependent Variable	Equation	R^2
K% =	$0.003 + 0.07*KSAT + 0.06*CLAY - 0.06*KBETA$	.992
Kup =	$0.006 - 223.38*EC + 1.43*KBETA$	.950

All terms were significant at the 0.01 P>F level.
KSAT : Saturated soil extract K in mg l^{-1}.
CLAY : Percent clay in soil in g cg^{-1}.
KBETA : The linear regression slope of PST RAQ K using HOH resin with ddw saturated soil paste preparation, Y, and log time, X.
EC : Saturated soil electrical conductivity in mmhos cm^{-1}.

but their function in the model is an expression of the statistical best fit process and little else. The real statement of the equation is that the combined solution K and solid phase K terms account well for the percent plant K in the check plots of this experiment.

The K uptake model is constructed from the weak, negative relation of EC to Kup (r= -.21) and the strong positive relation of KBETA (r= +.85). The latter term in a single variable equation has a strong predictive value (R^2 = .70) and thereby illustrates the importance of diffusion rate toward the overall K quantity that the plants absorbed. The KBETA variable is positively correlated to EC (r= +.32) so resin adsorption of K rate does increase with increasing soluble salts even though K uptake decreases with increasing soluble salts. The EC of the 7 soils ranged from .09 to .18, indicating that the negative relation to K uptake was not due to a salt effect. A possible explanation is that a competing cation from soluble salts affects uptake rate by plants but does not influence adsorption rate by resin in the same manner. This possibility was not made clear by these data but it would be an interesting topic for further study.

Growth Room P Experiment Results

The REP effect for the dry weight data of this experiment is significant. There was no apparent gradient related to light, temperature, or air turbulence, so the cause remains unknown (Table 45). These data show

Table 45. The analysis of variance table for the growth room P experiment on 7 soils.

Dependent Variables: Dry weight per pot in g, P uptake per pot in mg, and P percent per pot in g cg^{-1}.

Source	DF	G/Pot[a] Mean Sq.	P Uptake[b] Mean Sq.	P Pct[c] Mean Sq.
REP	3	0.76**	0.80	0.003
TRT[d]	4	0.05	21.51**	0.029**
SOIL[e]	6	6.16**	128.27**	0.245**
TRT*SOIL	24	0.12	0.92	0.002
Error	102	0.08	0.70	0.0015

** Denotes significance at or beyond the 0.01 level.
a : Dry weight yield per pot in g.
b : P uptake per pot in mg.
c : P percent per pot in g cg^{-1}.
d : Fertilizer additions of 0, or 15, or 30, or 60, or 120 kg ha^{-1} per pot.
e : Seven Montana agricultural soils.

significant SOIL and TRT effects for percent P and P uptake, but not for dry weight. The negative relation of percent P to dry matter (r= -.43) and lack of relation between P uptake and dry matter (r= +.06) indicate that some other factors were limiting biomass production in this experiment.

The TRT effect was elucidated by LSD treatment mean separation (Table 46). The ranked order of the T groups is normal with respect to treatment levels. The separation of the TRT means for P uptake shows no difference between the 10 and 20 kg ha^{-1} rate. The separation of means for percent P indicates a split in the

Table 46. T groupings by least significant difference for the growth room P experiment treatment means for P response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, P uptake per pot in mg, and P percent per pot in g cg^{-1} across 7 soils.

Dry Wt. g^{-1}			P Uptake mg^{-1}			P %		
T GROUP	MEAN	TRT[a]	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	2.60	40	A	6.67	80	A	0.264	80
A	2.59	80	B	6.19	40	A	0.254	40
A	2.57	20	C	5.28	20	B	0.211	20
A	2.57	10	C	4.98	10	B	0.203	10
A	2.50	0	D	4.54	0	B	0.193	0
LSD	0.1470			0.4447			0.0206	

[a] Treatment units are kg ha^{-1}.

treatment effect where only the highest fertilizer rates produced a definitive response in P uptake and percent P.

The SOIL effect is significant for all response variables (Table 47), and is much stronger than the TRT effect. The soil mean separation is slightly better for percent P versus P uptake. Percent P and P uptake means both show soil 9 to be highest and soils 11 and 17 to be lowest in ranked order. The dry weight mean ranked order is opposite to both P uptake and percent P for these three soils.

The strength of the SOIL effect is a reflection of the evenly distributed range of soils in terms of residual P as indexed by the Bray P test. The weaker treatment effect is a reflection of the fact that even the low end of the range

Table 47. T groupings by least significant difference of the growth room P experiment soil means for P response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, P uptake per pot in mg, and P percent per pot in g cg^{-1} across all treatments.

T	Dry Wt. g^{-1}		T	P Uptake mg^{-1}		T	P %	
GROUP	MEAN	SOIL[a]	GROUP	MEAN	SOIL	GROUP	MEAN	SOIL
A	3.28	14	A	9.27	9	A	0.427	9
B	2.87	17	B	8.36	14	B	0.283	12
B	2.85	11	C	6.45	12	C	0.257	14
B	2.83	6	D	4.74	6	D	0.211	19
C	2.34	12	E	3.37	19	E	0.170	6
C	2.18	9	E	3.36	11	F	0.117	11
D	1.62	19	E	3.16	17	F	0.110	17
LSD	0.1739			0.5262			0.0244	

a : Soil numbers, taxonomic soil names are listed in Appendix Table 69.

of soils is above deficiency levels. Therefore, it is not surprising to see a lack of dry matter response to the treatments, given the fact that the range is from adequate to very high native P. There is no significant two way interaction because of the weakness of the treatment response.

Growth Room P Soil Test Relationships

Single variable linear regression equations were derived for the standard soil test methods of sodium bicarbonate extractable P, or Olsen P (OP) and dilute acid-fluoride soluble P, or Bray P (BP). Similar equations were also derived for the PST extraction methods of HOH, HOHT, and HCL. The dependent variables were the means for each soil of the plant percent P at the 0 kg ha^{-1} K treatment rate and the plant P uptake per pot at the 0 kg ha^{-1} P treatment rate.

The predictive value of the standard soil test methods of Bray P and Olsen P are well correlated and significant for both percent P and P uptake (Tables 48 and 49). All of the PST methods are weakly correlated and not significant. All methods except HCL show stronger predictive value for P uptake than percent P. This was

Table 48. Simple linear regression model equations for the growth room experiment, percent P in the plant for 7 soils.

Dependent Variable: P% = Mean P percent per pot in g cg^{-1} at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
P% =	0.005 + 0.12*BP[a]	.756	.011
P% =	−0.132 + 0.01*OP[b]	.692	.020
P% =	0.106 + 0.01*HOHP[c]	.174	.351
P% =	0.121 + 0.01*HOHTP[d]	.112	.463
P% =	0.245 − 0.01*HCLP[e]	.143	.403

a : Dilute acid fluoride soluble soil P in mg kg^{-1}.
b : Sodium bicarbonate extractable soil mg kg^{-1}.
c : PST procedure soil mean extractable P across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable P across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
e : PST procedure soil mean extractable P across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

Table 49. Simple linear regression model equations for the growth room experiment, P uptake (Pup) per pot for 7 soils.

Dependent Variable: Pup = Mean P uptake per pot in mg at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
Pup =	$0.16 + 2.89*BP^{a}$	.880	.002
Pup =	$-2.82 + 0.23*OP^{b}$	.758	.011
Pup =	$1.74 + 0.33*HOHP^{c}$	.396	.130
Pup =	$1.82 + 0.34*HOHTP^{d}$	.346	.165
Pup =	$4.85 - 0.04*HCLP^{e}$	.008	.853

a : Dilute acid fluoride soluble soil P in mg kg^{-1}.
b : Sodium bicarbonate extractable soil mg kg^{-1}.
c : PST procedure soil mean extractable P across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable P across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
e : PST procedure soil mean extractable P across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

related to the ANOVA and LSD analysis data which show stronger treatment response and soil effects for P uptake.

The maxr regression models for P uptake and percent P are dominated by the strong relation of the Bray P test to the dependents (Table 50). The additional variables of KSAT and VERM for percent P were positively but very weakly correlated to percent P, (r= +.08 KSAT, r= +.002 VERM). The additional variable of MGEX in the P uptake model was also weakly correlated to the dependent variable, (r= -.33

Table 50. Maxr regression model equations for the growth room experiment P response variables for 7 soils at the 0 fertilizer rate.

Dependent Variables: P% = Mean percent P per pot in g cg^{-1}.
Pup = Mean P uptake per pot in mg.

Dependent Variable	Equation	R^2
P%	= −0.24 + 0.05*KSAT + 016*BP + 0.01*VERM	.997
Pup	= 0.01 − 0.44*MGEX + 2.89*BP	.992

All terms were significant at the 0.01 P>F level.
KSAT : Saturated soil extract K in mg l^{-1}.
BP : Dilute acid fluoride soluble soil P in mg kg^{-1}.
VERM : Vermiculite clay in g cg^{-1}.
CLAY : Percent clay in soil in g cg^{-1}.
MGEX : Ammonium acetate extractable Mg in cmol kg^{-1}.

MGEX). The additional variables could be explained in terms of their relation to the dependents but they are more likely to be statistical modifiers of the strongly related BP and nothing more.

The data suggest clearly that the Bray test was a very good predictor of check plot P availability for plant uptake within the context of this experiment and for these 7 soils. However, the experiment had a built in bias toward the Bray test because this test was the criterion for selection of the 7 soils. Both the Bray and Olsen tests are known to perform poorly for some Montana soils, so this experiment apparently is not based on a representative sample of soils. Therefore, broad conclusions regarding the comparative worth of either the Olsen or the Bray test are not applicable beyond the context of this experiment. However, it is clear that both tests were more reliable than the PST method within the context of this experiment.

The poor performance of the PST method is probably a function of the weak affinity of the anion resins toward phosphate. Even though the OH^- charged resin was shown to be better than Cl^{-1} for P assessment, it still has vastly weaker affinity for phosphate versus nitrate, sulfate, or carbonate.

Pilot studies not reported have shown HOH performance equal to Olsen P when soils actually deficient in available P were included in the experiment. However, the goal of producing a better soil test for phytoavailable P will require much additional research to seek out a resin with high phosphate affinity.

Growth Room S Experiment Results

There was a significant replication effect expressed in the ANOVA analysis for the dry weight data, but the cause was unknown (Table 51). The simple correlation of TRT, SOIL, and two way interaction effects for all dry matter to S uptake (r= +.33) and percent S (r= -.20) does not indicate a negative influence by an outside factor as strongly as in the growth room P experiment. This experiment differs from the other growth room experiments because it shows much stronger effects for TRT than for SOIL. The separation of treatment means by LSD reveals

Table 51. The analysis of variance table for the growth room S experiment on 7 soils.

Dependent Variables: Dry weight per pot in g, S uptake per pot in mg, and S percent per pot in g cg^{-1}.

Source	DF	G/Pot[a] Mean Sq.	S Uptake[b] Mean Sq.	S Pct[c] Mean Sq.
REP	3	0.59**	0.65	0.001
TRT[d]	4	3.07**	95.02**	0.114**
SOIL[e]	6	4.82**	8.07**	0.053**
TRT*SOIL	24	0.27**	1.14**	0.007**
Error	102	0.08	0.34	0.0008

** Denotes significance at or beyond the 0.01 level.
a : Dry weight yield per pot in g.
b : S uptake per pot in mg.
c : S percent per pot in g cg^{-1}.
d : Fertilizer additions of 0, or 15, or 30, or 60, or 120 kg ha^{-1} per pot.
e : Seven Montana agricultural soils.

that the dry weight response was not normal because the middle treatment rate of 30 kg ha^{-1} is ranked highest (Table 52). There is no separation between the upper three treatment levels.

The S uptake and percent S response data are normal in ranked order and perfectly separated. The strong response to treatment is an indication that the 7 soils did fall within the range of S deficiency. The separation of soil means by LSD shows again that dry weight was the least reliable dependent variable (Table 53). The dry weight soil means are not well separated in the mid through upper range. The percent S means are slightly better separated than S uptake across the entire range.

There is good agreement between S uptake and percent S

Table 52. T groupings by least significant difference for the growth room S experiment treatment means for S response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, S uptake per pot in mg, and S percent per pot in g cg^{-1} across 7 soils.

Dry Wt. g^{-1}			S Uptake mg^{-1}			S %		
T GROUP	MEAN	TRT[a]	T GROUP	MEAN	TRT	T GROUP	MEAN	TRT
A	2.95	30	A	6.13	120	A	0.234	120
A	2.93	120	B	5.09	60	B	0.182	60
A	2.92	60	C	4.12	30	C	0.146	30
B	2.64	15	D	2.66	15	D	0.105	15
C	2.18	0	E	1.53	0	E	0.071	0
LSD	0.1483			0.3086			0.0148	

[a] Treatment units are kg ha^{-1}.

Table 53. T groupings by least significant difference of growth room S experiment soil means for S response variables. Alpha = 0.05.

Dependent Means: Dry weight per pot in g, S uptake per pot in mg, and S percent per pot in g cg^{-1} across all treatments.

Dry Wt. g^{-1}			S Uptake mg^{-1}			S %		
T GROUP	MEAN	SOIL[a]	T GROUP	MEAN	SOIL	T GROUP	MEAN	SOIL
A	3.17	7	A	4.84	12	A	0.223	9
AB	3.05	3	B	4.30	3	B	0.217	12
BC	2.98	13	B	4.16	7	C	0.138	3
BC	2.96	17	B	4.08	9	D	0.129	7
C	2.83	2	C	3.70	17	D	0.122	17
D	2.24	12	D	3.30	2	E	0.112	2
E	1.84	9	D	2.96	13	E	0.092	13
LSD	0.1755			0.3652			0.0175	

a : Soil numbers, taxonomic soil names are listed in Appendix Table 69.

with respect to the the entire sequence of ranked order except for soil number 9. Soil 9 yielded the lowest dry matter but showed the highest percent S in the plant tissue. The high percent S could well be the result of a third limiting factor that prevented the translation of available S to biomass for that soil. There does not seem to be any strong trends of suppression of response due to an outside factor for the other soils.

The significant two-way interaction for each of the dependent variables is fundamentally a reflection of good soil mean separation and good, to excellent treatment mean separation. The statistical strength of the interaction is an expression of the fact that the 7 soils of this experiment did respond individually under the influence of the treatments and that the plants responded positively to fertilizer S on all soils. This indicates the materials and methods of this experiment were well suited for testing the predictive value of the soil test methods.

Growth Room S Soil Test Relationships

Single variable linear regression equations were derived for the standard soil test method of acetate soluble sulfate (S) and the PST extraction methods of HOH, HOHT, HCL and MINS. The dependent variables were the means for each soil of the plant dry weight yield, the percent S of the plant, and the plant S uptake per pot. Each dependent variable represents the 0 kg ha^{-1} S treatment for that soil.

The dry matter models have poor predictive value and poor probability associated with all soil test methods (Table 54). The lack of fit for each soil test is

Table 54. Simple linear regression model equations for the growth room S experiment, dry weight (Sdw) as grams per pot for 7 soils.

Dependent Variable: Sdw = Mean S dry weight per pot in g at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
Sdw =	$2.40 - 0.05*S^a$	.069	.570
Sdw =	$2.07 + 0.03*HOHS^b$	.027	.779
Sdw =	$2.07 + 0.03*HOHTS^c$	.012	.819
Sdw =	$2.41 - 0.05*HCLS^d$	.219	.290
Sdw =	$2.09 + 0.12*MINS^e$	.032	.703

a : Ammonium acetate extractable S in mg kg^{-1}.
b : PST procedure soil mean extractable S across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
c : PST procedure soil mean extractable S across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable S across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
e : HOHS - HOHTS in mg l^{-1} of stripping solution.

related to the fact that an undefined environmental factor caused a significant difference in the replications and the air turbulence caused a visible effect on the plant.

The better test of predictive value of the variables is regression of the concentration dependents (Tables 55 and 56). Both the standard soil test method and the HCL PST method have poor correlation and poor probability

Table 55. Simple linear regression model equations for the growth room experiment, percent S in the plant for 7 soils.

Dependent Variable: S% = Mean S percent per pot in g cg^{-1} at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
S% =	$0.03 + 0.01*S^{a}$	.579	.047
S% =	$0.03 + 0.01*HOHS^{b}$	.830	.004
S% =	$0.02 + 0.02*HOHTS^{c}$	.848	.003
S% =	$0.05 + 0.004*HCLS^{d}$	.406	.124
S% =	$0.05 + 0.03*MINS^{e}$	.742	.013

a : Ammonium acetate extractable S in mg kg^{-1}.

b : PST procedure soil mean extractable S across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

c : PST procedure soil mean extractable S across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.

d : PST procedure soil mean extractable S across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

e : HOHS - HOHTS in mg l^{-1} of stripping solution.

toward the percent S and S uptake dependents. The HOHS, HOHTS, and MINS variables are equal in predictive value toward S uptake. The MINS variable is not as strongly related to percent S, the most reliable response parameter of this experiment. The similarity of these three PST measures is a function of the fact that they were each HOH resin sink systems, and organic S is strongly correlated with inorganic S for these 7 soils (r= +.95 for HOHTS to MINS).

Table 56. Simple linear regression model equations for the growth room experiment, S uptake (Sup) per pot for 7 soils.

Dependent Variable: S% = Mean S percent per pot in g cg^{-1} at the 0 fertilizer rate.

Dependent Variable	Equation	R^2	Prob>F
Sup	= 0.87 + 0.16*S[a]	.395	.131
Sup	= 0.56 + 0.25*HOHS[b]	.892	.001
Sup	= 0.39 + 0.36*HOHTS[c]	.879	.002
Sup	= 1.34 + 0.04*HCLS[d]	.100	.490
Sup	= 0.98 + 0.75*MINS[e]	.862	.003

a : Ammonium acetate extractable S in mg kg^{-1}.
b : PST procedure soil mean extractable S across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
c : PST procedure soil mean extractable S across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.
d : PST procedure soil mean extractable S across all days using HCL resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.
e : HOHS - HOHTS in mg l^{-1} of stripping solution.

The maxr regression procedure for percent S and S uptake failed to identify any significant variable that would improve the predictability beyond the amount provided by HOHS or HOHTS individually (Table 57).

The dry weight model includes a negative relation of EC with positive correction of the line by the rate variable TSBETA. Both variables are not strongly related to dry weight on an independent basis (r= -.66, EC, r= +.43, TSBETA). Although the rate term seems relevant to

Table 57. Maxr regression model equations for the growth room experiment S response variables for 7 soils at the 0 fertilizer rate.

Dependent Variables: S% = Mean percent S per pot in g cg^{-1}.
Sup = Mean S uptake per pot in mg.
Sdw = Mean dry weight per pot in g.

Dependent Variable	Equation	R^2
S% =	0.02 + 0.02*HOHTS	.848
Sup =	0.56 + 0.25*HOHS	.892
Sdw =	2.44 - 4.33*EC + 1.06*TSBETA	.939

All terms were significant at the 0.01 P>F level.

HOHTS : PST procedure extractable mean S concentration across all days using HOH resin with ddw saturated soil paste preparation in mg l^{-1} of stripping solution.

HOHTS : PST procedure extractable mean S concentration across all days using HOH resin with 15 mg l^{-1} tetracycline solution saturated soil paste preparation in mg l^{-1} of stripping solution.

TSBETA : The linear regression slope of PST procedure extractable S concentration using HOH resin with 15 mg l^{-1} solution saturated soil paste preparation, Y, and log time, X.

EC : Saturated soil electrical conductivity in mmhos cm^{-1}.

the model, it is secondary to the EC term. The actual EC values for the 7 soils were low, ranging from .12 to .36 mmhos/cm, indicating little likelihood of a salt effect on growth. These arguments, coupled with the previously indicated erratic nature of the dry weight in the experiment, preclude a valid explanation of this model.

Summary and Conclusions

Each experiment was compromised by environmental conditions. The K and P growth room experiments were further compromised by the naturally high levels of K and P in the soils used. The response variables of nutrient concentration and uptake were much more reliable indicators of nutrient relationships than was dry weight. The percent response variable was most consistently shown to be the most sensitive variable for plant-soil nutrient relationships.

The growth room experiments did represent an improvement over the greenhouse in terms of the negative influence of environmental factors on growth. The greenhouse experiment was considered more reliable than the growth room for K evaluation because the treatment effect was strong and normal in the greenhouse, versus the weak growth room treatment-response relationship.

The comparison of soil testing methods was valid because it was based on the 0 rate of treatment in all cases. The problems of plant growth and response performance in these experiments primarily serves to limit the applicability of the results to a narrow range in most cases.

The PST extraction method using H^+/OH^- resin was superior to standard methods for the prediction of K uptake, percent K, S uptake and percent S. It was shown to be inferior to both the Bray and Olsen P tests for P uptake and percent P.

The greenhouse K experiment data clearly indicated that HOHK was a direct measure of phytoavailable K quantity but this term alone did not totally explain the amount of K obtained by the plants from the soil. The incorporation of OM in the model improved the prediction by adjusting the relationship to include a factor related to diffusion pathway tortuosity. The equal predictive value between HOHK and K for the growth room experiment was supportive of the superiority of the PST method because the experiment contained a built in bias in favor of high correlation for the standard method.

The HOHS and HOHTS methods were equivalently strong in predicting S uptake and percent S. Both methods were certainly superior to the standard soil test method for S. The strong treatment effect shown throughout the range of treatment rates by the growth room S experiment suggests that a high blanket S rate should be used in any fertilizer rate-controlled environment experiments that use similar soils to those used in this study.

The PST method was not a good predictor of any P parameter. This was a function of the weak affinity of the resins used toward phosphate, and the statistical bias favoring correlation of the Bray P test. The HOHP variable would probably show improved predictive power in an experiment using soils low in P, but the success of the PST method for P probably will hinge on the use of a differently charged resin or a resin of a different nature.

The PST method should be evaluated by use of soils that allow more emphasis toward the low, and deficient range prior to suggestion of use as a new standard method for K analysis on Montana soils. These results clearly warrant continuation of research toward that end. The PST method should be evaluated by use of additional soils to verify the strength of this method.

These results clearly indicate that PST should be adopted as a new standard soil test method for S once an adequate body of support experiments using different soils verifies these results.

The PST method should not be recommended for P analysis until a suitable anion resin is found and thoroughly evaluated.

A DESCRIPTIVE MODEL OF SOIL-RESIN FLUX

Introduction

The PST method can be viewed in terms of physical chemistry as a measurement of nutrient flux. Flux is the rate of flow of ions through a cross sectional surface area. These terms are related to the PST method as the rate is represented by the concentration of ions in the resin at a given time, and the cross sectional surface area is the resin bag surface area.

Flux is a function of time, temperature and the soil factors of concentration, electrochemical potential and diffusion resistance. According to Fick's first law of diffusion, flux of ions may be mathematically written as:

$J_i = -D_i \times (dC_i\ dD^{-1})$.

where:

J_i = Flux of the ith ion = Quantity per time per surface area, umol $cm^{-2}\ s^{-1}$.

D_i = Diffusion coefficient for ith ion in $cm^2\ s^{-1}$.

$dC_i\ dD^{-1}$ = Driving Force = delta soil concentration in umol cm^{-3} divided by delta distance in cm.

The driving force of the ion flux is established by the net zero concentration of the resin sink in contact with net positive concentration soil. There is no flux at time zero but at an infinitely small time elapse, flux commences and a chemical concentration gradient as a function of distance and electrochemical potential exists.

The dC_i term of the equation relates to the soil concentration at time zero minus the soil concentration at a specific distance (net removal by the sink), for a time greater than zero. At any moment, the soil has an infinite number of electrochemical potentials over a given distance. Each specific electrochemical potential term is a function of the concentrations of soil and soil solution on each adjacent side. This infers that an infinite number of diffusion coefficients may be derived in specific relation to the electrochemical potentials, but the overall relation is reflected in the measured concentration gradient.

A careful sequential sampling of soil at a sufficient number of distances from the ion sink is necessary to characterize the soil's overall chemical concentration gradient. If the relationship of soil concentration to distance is a linear function within the bounds of actual gradient existence, then a single value can adequately describe the chemical concentration gradient of the overall system. Several mathematical approaches may then be employed to derive a general diffusion coefficient for the entire system.

If the concentration to distance relationship is nonlinear, an infinite number of gradient terms and diffusion coefficients would be necessary for specific description of the system.

Theoretically, experiments can be designed to identify the flux and gradient terms to derive the diffusion coefficient when moisture and buffering capacity effects are included. The diffusion coefficient for each soil would then be descriptive of the pathway resistance with respect to diffusion. However, the buffering capacity of the soil serves to release ions to the diffusion pathway as a response to the reduced equilibrium concentration, dC_i, at any point along the gradient. This confounding influence cannot be eliminated or specifically accounted for along the entire gradient. Therefore true soil gradients, and true soil diffusion coefficients are impossible to measure or to derive. It is for these reasons terms such as "effective" diffusion coefficient are used in a soil context.

Objectives

An experiment was designed to measure ion flux to a resin sink and chemical concentration gradients on saturated soil in order to identify the diffusion coefficients applicable to the PST method. This relates to phytoavailability because flux to either a resin sink or a plant root sink is a function of the gradient, diffusion coefficient, surface area and buffering capacity influences relevant to individual soils.

The objectives of this experiment include:

1. design a model for identification of the chemical concentration gradients, resin flux, and diffusion coefficients for P, K, and S in the saturated paste condition of 20 agricultural soils from Montana;
2. compare standard soil test extraction methods with a resin batch extraction method in relation to measured flux of P, K, and S from saturated soil paste;
3. Compare the flux, concentration gradient, and diffusion coefficients of the experiment to plant uptake data from the greenhouse and growth room experiments of chapter 5.

Materials and Methods

The spherical shape of the resin sink in the PST method would require sequential removal of soil as a series of shells away from the resin in order to sample soil concentration by distance in a manner related to the vector of the chemical concentration gradient of the PST method. A suitable technique for soil removal at exact distances in this manner is physically very difficult.

The design of an experiment on a linear basis would allow for accurate removal of the soil by distance and should be reasonably equivalent to the PST method as long as the cross sectional surface area of the resin sink was the same as the resin sphere. The actual design and methods of this experiment represent a modification of the techniques described by Kuchenbuch and Jungk, 1982. The modifications include adaptation for the use of the 20 Montana agricultural soils in the form of saturated paste.

Polyester cloth was glued to one end of a Plexiglas cylinder, 5.1 cm inner diameter (ID) and 2.0 cm in height. Two such cylinders, A and B, were exactly filled with saturated paste soil and a Plexiglas plate was placed on the open side.

The cylinders were inverted and a third Plexiglas cylinder, hereafter referred to as the center ring, of identical ID but 0.6 cm in height was placed on the cloth surface of one cylinder. The center ring was exactly filled with wet H/OH resin. The second ring was then placed cloth side down on the center ring and the entire apparatus was secured with rubber bands (Figure 5).

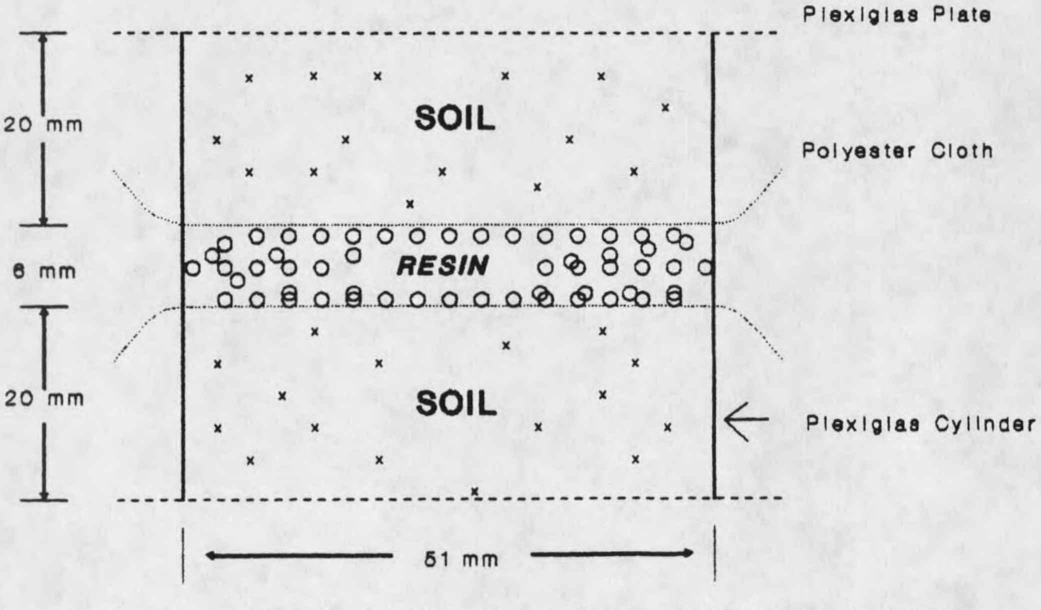

Figure 5. A schematic illustration of the soil ion extraction device used in this experiment.

The entire apparatus, or extraction device, was placed into a plastic bag. One to 2 mls of ddw were added to the bag to prevent any possibility of evaporation from the soil or resin. The evaporative process would influence the extraction by mass flow, therefore, extra steps for prevention of that possibility were required.

The bagged extraction device was placed into a controlled temperature chamber at 30 °C. Three extraction devices were made for each soil thereby providing three replications for the experiment. The reported data are the means of these replications unless stated otherwise.

The extraction devices were removed from the temperature chamber after 96 hours. The device was taken from the bag and soil cylinder A was carefully separated from the center ring. The resin of the center ring was then carefully transferred to a clean beaker.

An additional Plexiglas plate was placed on the cloth face of soil cylinders A and B, and secured there with rubber bands. The cylinders were then placed in clean, labeled whirl pack bags and placed in a freezer. Freezing was necessary for accurate removal of soil at specific distances.

The resin was washed with ddw to remove any soil particles, tied into a resin bag sphere, stripped and analyzed as per standard PST methodology.

The frozen soil cylinders were removed from the freezer in groups of 18 so they would not thaw before completion of the soil removal. A single cylinder was handled at a time in the following steps.

1. The Plexiglas ring was carefully warmed just until the still frozen soil core could be removed.
2. The core was inserted into a plexiglas cylinder that was fixed to a micrometer with a plunger the size of the soil core.
3. The core was aligned such that the soil face that had been adjacent to the resin in the extraction device was flush with the open end of the micrometer cylinder. The core was then pushed out 1 mm and the soil was sliced off with a sharp stainless steel french knife. The removed soil was caught in a pre-weighed, clean, labeled plastic pan. This step was repeated until a total of 5 mm of soil had been removed as 5 individual slices.
4. The soil core was removed, turned around, reinserted, and an approximately 2 mm slice was removed, hereafter referred to as the 6th slice.
5. The micrometer cylinder was then wiped clean prior to insertion of the next core.
6. The micrometer device was dismantled and washed with ddw between each new soil.

The soil slices were allowed to air dry under a covering of paper towels. The pans were then weighed and the soil was crushed and mixed.

The side A samples were analyzed by the standard soil testing methods for P, K, and S. The side B samples were analyzed by the following batch extraction procedure.

1. A 1g aliquot of air dry soil was placed into a 50 ml screw cap tube.
2. A resin bag containing the volume equivalent of 1 g dry weight of H/OH resin was added to each tube.
3. A 45 ml aliquot of ddw was added to each tube and then the tubes were capped and shaken end to end for 2 hours.
4. The resin bags were then removed and rinsed with ddw. They were immediately stripped with 50 mls of 2 M HCl and analyzed as per standard PST procedure.

Calculations

Three terms representing soil flux were calculated from these data. The most accurate flux term was based on the concentration of the center ring resin as per:

J_r = Flux = resin concentration of P, K, or S in umol cm^{-2} s^{-1} divided by 2. Division by 2 represents flux resulting from a single side of the device.

The batch method and the standard soil test method analyses of the thin slices do not directly relate to the sink extraction process of the center resin ring. Therefore a flux term for each analytical method was created as per:

J_{std} = Flux calculated from standard soil extraction method as Q in umol cm^{-2} divided by time in s.

J_{bat} = Flux calculated from batch resin extraction method as Q in umol cm^{-2} divided by time in s.

where Q is derived from standard or batch as per:

$$Q = \frac{(C_i)_{6th} \times \Sigma(dw)_n - \sum_{n=1}^{5}\left\{(C_i)_n \times \frac{\sum_{n=1}^{5}(dw)_n}{5}\right\}}{(MW)_i \times \text{unit area } (cm^2)}$$

where:

$(C_i)_n$ = concentration of the ith ion as ug g-1 in nth slice.
$(dw)_n$ = dry weight of soil in nth slice.
$(MW)_i$ = Molecular Weight of ith ion.
Q = umol cm^{-2}.
s = 345600.

In other words, the total amount of K from 0 to .5 cm at time zero is referenced to the 6th slice (at 1.9 cm distance from the resin sink this soil portion was assumed to be beyond the influence of diffusion within a 96 hour time frame). The time zero total concentration minus the concentration remaining after 4 days represents the flux as measured by a particular soil testing method.

The diffusion gradient was derived by linear regression where umol per unit volume by a given soil test as the dependent variable (Y) was regressed with cm distance as the independent variable (x). The slope of the line then represents the chemical concentration gradient term at any point along the line. The soil test method that generally showed best fit for the linear regression across all 20 soils was used to calculate the diffusion coefficient for each soil by using Fick's first law as:

$J_i = -D_i \times dC_i\ dD^{-1}$.

where:

Ji = Flux of the ith ion, umol $cm^{-2}\ s^{-1}$.

D_i = Diffusion coefficient for ith ion in $cm^2\ s^{-1}$.

$dC_i\ dD^{-1}$ = Concentration Gradient, slope from linear regression, umol $cm^{-3}\ cm^{-1}$.

Linear and quadratic regression equations were executed for all soils, elements, and soil test methods using umol per unit volume as Y and cm as X. Soil data of concentration by distance should normally express a trend relation in accordance with Fick's Laws of Diffusion, where changes of concentration (moving away from the resin sink) diminish with distance. The trend should be described reasonably well by a quadratic equation. The soils of this study which cannot be described well by quadratic regression should be considered to have high experimental error.

Results and Discussion

The Linear Resin Sink Device Versus the PST Method

The similarity of the linear extraction device of this experiment to the spherical device of the PST method was tested by regressing the center ring resin concentration against the mean concentration of the 3 and 5 day PST extraction (Table 58). The high correlation of the K and S equations indicate similarity between a linear extraction and a spherical extraction device.

Table 58. Mean center ring resin concentration of P, K, and S, divided by 2, in linear regression to the 4 day calculated mean concentration of PST P, K, and S for 20 soils.

All Variables = Concentration in the stripping solution in mg l^{-1}.

Element	Equation	R^2	Prob>F
K_r	$= -0.007 + 0.871*HOHK^a$	.877	.0001
S_r	$= 1.029 + 0.750*HOHS^b$	.949	.0001
P_r	$= 1.240 + 0.438*HOHP^c$	.603	.0001

Kr, Sr, Pr : Center ring resin concentration of K, S, and P respectively at 96 hours.
a : PST HOH resin K concentration mean at 96 hours.
b : PST HOH resin S concentration mean at 96 hours.
c : PST HOH resin P concentration mean at 96 hours.

The modifying coefficient for the PST concentrations (HOHP, HOHK, and HOHS) are less than 1.0 for two reasons. First, the increase in concentration from 3 to 5 days (actual measurement times) for PST is curvilinear, therefore, a simple mean taken from day 3 and 5 concentrations is an overestimate of PST concentration at 96 hours. Second, the amount of soil involved in the supply of ions to the spherical sink is greater than the linear sink at equal linear distances away from the respective surfaces. Therefore, a larger volume of soil is under the influence of the peak potential near the resin surface in a spherical system.

The reason the concentration difference between linear and spherical is greatest for P may be related to the lower mobility of P in soil verses K and S. The magnitude of difference between linear system P and spherical system P was not consistent from soil to soil. This accounts for the weaker r-square value of the P model. Considering the weak affinity of OH^- charged anion resin to phosphate it is not surprising to see a device that forces more soil into a zone of peak potential difference to obtain a greater concentration of P.

Although differences between the two extraction techniques are evident, the relation of linear to spherical is strong for K and S. The two systems are not parallel for P extraction ability.

Chemical Concentration Gradient Derivation Results

Identification of the chemical concentration gradient term required a regression of concentration per slice area to distance from the resin sink. The initial trial of linear regressions of P, K, and S umol cm^{-3} as Y with cm as X showed such poor correlation that the entire experiment was potentially worthless.

Inspection of the regression data set revealed that the cause of poor linear regression correlation was due to abnormally high umol values for the 0 to 0.1 cm slice. Close scrutiny of the raw data revealed the dry weight for the first slice was often greater than the second slice, while the concentration of the first slice was consistently lower than the second. The small amount of weight obtained per slice made the calculation of umols extremely sensitive to experimental errors regarding soil dry weight.

The sampling process assumes that a 0.1 cm slice is an exact distance, but the dry weight data indicated that the first slice was often slightly more than 0.1 cm. Therefore, the mean weight of 0.1 cm was calculated from all of the 0.1 cm slices of side A per soil and all of the slices of side B per soil, respectively. The side A and B mean slice weight was then respectively applied to the calculation of umol per slice. This improved the linear regression correlation coefficients for K and P (Tables 59 and 60).

The correlation coefficients for S were still unacceptably low and indicated the experimental method was not appropriate for characterization of S diffusion dynamics (Table 61).

The P, K, and S data for every soil were better described by a quadratic equation. The improvement of r-square from linear to quadratic equations for K and P standard methods was largely a reflection of the characteristic diminishment of chemical concentration with

Table 59. Linear regression equations of K_{std} and K_{bat} (Y) with distance (X) of 0.1 to 0.5 cm for 20 soils.

SOIL	K_{std}			K_{bat}		
	EQUATION	R^2	P>F	EQUATION	R^2	P>F
1	Y^{a}= 13.67 + 7.15*cm	.95	.01	Y= 12.23 + 6.34*cm	.60	.01
2	Y= 7.56 + 4.52*cm	.76	.05	Y= 8.10 + 7.02*cm	.94	.01
3	Y= 10.54 +13.09*cm	.75	.06	Y= 7.92 +14.39*cm	.82	.03
4	Y= 6.32 + 5.66*cm	.81	.04	Y= 7.31 + 3.60*cm	.52	.17
5	Y= 10.26 +10.00*cm	.92	.01	Y= 13.45 + 5.09*cm	.68	.08
6	Y= 6.80 + 7.72*cm	.78	.05	Y= 7.16 + 4.69*cm	.50	.18
7	Y= 5.46 + 6.14*cm	.94	.01	Y= 5.38 + 6.87*cm	.63	.10
8	Y= 9.96 + 9.13*cm	.65	.10	Y= 12.13 + 5.10*cm	.40	.25
9	Y= 3.78 + 4.84*cm	.90	.01	Y= 3.16 + 5.93*cm	.95	.01
10	Y= 6.34 + 8.57*cm	.80	.04	Y= 4.05 +12.02*cm	.97	.01
11	Y= 10.21 +10.72*cm	.94	.01	Y= 8.08 +10.37*cm	.88	.02
12	Y= 10.32 + 6.08*cm	.74	.06	Y= 10.25 + 3.40*cm	.83	.03
13	Y= 6.37 + 7.14*cm	.95	.01	Y= 7.60 + 6.19*cm	.90	.01
14	Y= 5.51 + 4.32*cm	.93	.01	Y= 3.79 + 5.33*cm	.86	.02
15	Y= 14.13 +15.84*cm	.93	.01	Y= 12.31 +12.86*cm	.83	.03
16	Y= 9.49 + 3.03*cm	.37	.28	Y= 9.17 + 4.36*cm	.62	.11
17	Y= 10.74 + 8.93*cm	.95	.01	Y= 6.16 + 0.75*cm	.01	.85
18	Y= 4.53 + 5.46*cm	.91	.01	Y= 6.41 + 3.91*cm	.65	.10
19	Y= 5.52 + 3.41*cm	.86	.02	Y= 6.11 + 3.67*cm	.69	.08
20	Y= 10.57 + 5.74*cm	.87	.02	Y= 13.34 + 0.43*cm	.00	.93

[a] : K umol cm^{-3}.

Table 60. Linear regression equations of P_{std} and P_{bat} (Y) with distance (X) of 0.1 to 0.5 cm for 20 soils.

SOIL	P_{std}			P_{bat}		
	EQUATION	R^2	P>F	EQUATION	R^2	P>F
1	Y^{a}= 1.02 + 0.84*cm	.78	.05	Y = 3.44 + 2.10*cm	.54	.16
2	Y = 0.84 + 0.45*cm	.69	.08	Y = 3.75 + 0.14*cm	.00	.91
3	Y = 1.26 + 0.78*cm	.58	.13	Y = 2.31 + 2.75*cm	.51	.18
4	Y = 0.71 + 0.20*cm	.59	.13	Y = 2.47 + 1.02*cm	.37	.28
5	Y = 0.62 + 0.35*cm	.61	.12	Y = 3.61 + 3.64*cm	.66	.10
6	Y = 0.91 + 0.81*cm	.83	.03	Y = 1.92 + 2.02*cm	.68	.09
7	Y = 0.71 + 1.26*cm	.81	.04	Y = 1.74 + 2.76*cm	.70	.08
8	Y = 1.16 + 0.72*cm	.84	.03	Y = 5.26 + 3.23*cm	.50	.19
9	Y = 0.88 + 1.54*cm	.84	.03	Y = 1.30 + 3.79*cm	.93	.01
10	Y = 0.74 + 0.54*cm	.85	.03	Y = 1.40 + 1.93*cm	.77	.05
11	Y = 0.74 + 0.77*cm	.84	.03	Y = 1.71 + 1.78*cm	.76	.05
12	Y = 1.69 + 2.10*cm	.80	.04	Y = 4.34 + 3.41*cm	.83	.03
13	Y = 1.13 + 0.92*cm	.64	.10	Y = 4.47 + 4.35*cm	.77	.05
14	Y = 1.54 + 1.51*cm	.77	.05	Y = 1.63 + 3.68*cm	.97	.01
15	Y = 1.68 + 1.79*cm	.83	.03	Y = 3.00 + 3.73*cm	.89	.02
16	Y = 0.52 + 0.23*cm	.20	.45	Y = 4.04 - 1.62*cm	.17	.50
17	Y = 1.69 + 0.33*cm	.31	.33	Y = 4.40 - 0.46*cm	.31	.33
18	Y = 0.78 + 0.96*cm	.84	.03	Y = 1.28 + 1.86*cm	.81	.04
19	Y = 0.65 + 1.37*cm	.85	.03	Y = 1.74 + 2.20*cm	.91	.01
20	Y = 2.11 + 1.44*cm	.81	.04	Y = 5.17 + 1.89*cm	.87	.02

[a] : P umol cm^{-3}.

Table 61. Linear regression equations of S_{std} and S_{bat} (Y) with distance (X) of 0.1 to 0.5 cm for 20 soils.

SOIL	S_{std}			S_{bat}		
	EQUATION	R^2	P>F	EQUATION	R^2	P>F
1	Y^{a} = 0.21 + 0.06*cm	.35	.29	Y = 0.51 + 0.14*cm	.72	.07
2	Y = 0.28 + 0.37*cm	.88	.02	Y = 0.81 + 0.21*cm	.94	.01
3	Y = 0.30 + 0.38*cm	.31	.33	Y = 0.59 + 0.24*cm	.33	.31
4	Y = 0.21 − 0.16*cm	.54	.16	Y = 0.80 − 0.09*cm	.13	.56
5	Y = 0.30 + 0.16*cm	.61	.12	Y = 0.90 − 0.06*cm	.00	.89
6	Y = 0.19 − 0.01*cm	.00	.98	Y = 0.77 − 0.22*cm	.36	.29
7	Y = 0.20 + 0.18*cm	.39	.26	Y = 0.68 − 0.02*cm	.01	.86
8	Y = 0.59 − 0.54*cm	.54	.16	Y = 0.67 + 0.15*cm	.12	.57
9	Y = 0.21 + 0.12*cm	.42	.24	Y = 0.66 − 0.31*cm	.38	.27
10	Y = 0.21 + 0.03*cm	.04	.75	Y = 0.61 + 0.45*cm	.86	.02
11	Y = 0.21 + 0.17*cm	.75	.06	Y = 0.73 − 0.09*cm	.06	.70
12	Y = 0.41 + 0.60*cm	.84	.03	Y = 0.80 + 0.59*cm	.60	.12
13	Y = 0.62 + 0.73*cm	.93	.01	Y = 1.48 − 0.83*cm	.11	.58
14	Y = 0.18 + 0.08*cm	.30	.34	Y = 0.53 + 0.22*cm	.67	.09
15	Y = 0.13 + 0.22*cm	.74	.06	Y = 0.60 + 0.14*cm	.33	.31
16	Y = 0.62 − 0.26*cm	.36	.29	Y = 0.73 + 0.25*cm	.97	.01
17	Y = 1.62 + 0.23*cm	.55	.15	Y = 1.52 − 0.08*cm	.55	.15
18	Y = 0.36 + 0.19*cm	.58	.13	Y = 0.98 − 0.83*cm	.78	.05
19	Y = 0.65 + 1.72*cm	.97	.01	Y = 1.21 + 0.56*cm	.41	.25
20	Y = 0.28 + 0.64*cm	.98	.01	Y = 0.67 + 0.35*cm	.45	.22

[a] : S umol cm^{-3}.

distance in a manner consistent with Fick's Laws of diffusion. This trend of the raw data was not applicable to S, which had few well related linear trends, some of which had negative slope terms.

In one sense, the better fit for the quadratic equations would indicate a discussion of the chemical concentration gradient for the majority of soils should be based on the quadratic regression equation. The quadratic equation can be expressed as per:

$$Y = AX^2 + BX + C.$$

where:

$Y = \text{umol} \times \text{cm}^{-3}$.

$X = \text{cm}$.

A, B, and C are constants.

The first derivative of the equation allows for calculation of the driving force as per:

$$dY \times dX^{-1} = 2AX + B.$$

This equation produces reasonably accurate values for the chemical concentration gradient at exact distance points along the line from approximately 0.05 cm to 0.45 cm. It is not appropriate for derivation of a single term which represents an "overall" chemical concentration gradient. A calculation and discussion of several specific concentration gradient values for each soil, for several distance points from 0.05 cm to 0.45, for each element, for each soil test method, would be valid but is not necessary to meet the objectives of the experiment. The slope term of the linear regression is valid and applicable estimate of the overall gradient so it was used in this study.

The linear correlation coefficients for the standard methods were superior to those of the batch method. Therefore, linear regression slope terms for the standard soil test extraction methods were used with the center resin ring flux values, Table 62, to calculate diffusion coefficients for the 20 soils (Table 63).

The listed diffusion coefficients for P are in the range of 10^{-6} to 10^{-7}. This range is one order of magnitude higher than effective diffusion coefficient range of 10^{-7} to 10^{-8} published for corn (Zea mays L.) grown in pots under controlled environment conditions (Anghinoni and Barber, 1980; Schenk and Barber, 1979).

The order of magnitude difference is very appropriate because this experiment was conducted under conditions of high temperature relative to greenhouse conditions, high moisture relative to their greenhouse soils, and the 20 soils were generally high in residual P. Also, the diffusion coefficient of P in water is $.89 \times 10^{-5}$ cm^2 sec^{-1} (Schenk and Barber, 1979). All of these experimental conditions favor diffusion and the coefficients would therefore be expected to fall between values published for

Table 62. The measured values of K, P, and S center ring resin flux at 96 hours on 20 soils.

Flux units are umol cm^{-2} s^{-1}.

SOIL	K FLUX[a]	P FLUX[a]	S FLUX[a]
		10^{-6}	
1	9.92	0.73	0.52
2	4.64	0.64	0.41
3	9.60	1.85	0.88
4	5.24	1.23	0.58
5	11.14	0.88	0.66
6	6.78	1.55	0.60
7	7.72	0.76	0.78
8	8.50	1.10	0.62
9	4.70	1.62	0.66
10	6.89	1.47	0.68
11	8.04	0.90	0.51
12	6.45	0.97	1.37
13	5.08	0.65	0.48
14	2.47	1.38	0.57
15	13.95	1.39	0.76
16	5.55	0.56	0.38
17	10.95	0.46	0.70
18	7.38	1.50	0.56
19	5.47	0.81	3.03
20	8.58	1.46	1.41

[a] : Center ring resin K, P and S flux, respectively.

water and soils used in actual plant growth studies.

The range for K diffusion coefficient range for soil was listed as 10^{-7} to 10^{-8} by Barber in 1974. The diffusion coefficient for K in water is 1.98 x 10^{-5}. The range for K data from this experiment, 10^{-6} to 10^{-7} is also generally one order higher than greenhouse soil and one order below pure water.

The diffusion coefficient values for S were not calculated because the regression data were weak and any chemical concentration gradient term used for calculation

Table 63. The measured linear regression derived values of K and P chemical concentration gradient, (effective distance from .5 to 4.5 mm) and K and P derived diffusion coefficients for 20 soils.

	Potassium		Phosphorus	
SOIL	D_k	dC dD^{-1}	D_p	dC dD^{-1}
	10^{-6}	10^{1}	10^{-6}	10^{1}
1	1.39[a]	7.15[b]	0.87[c]	0.84[d]
2	1.03	4.52	1.43	0.45
3	0.73	13.09	2.36	0.78
4	0.93	5.66	6.41	0.19
5	1.11	10.00	2.48	0.35
6	0.88	7.72	1.91	0.81
7	1.26	6.14	0.61	1.26
8	0.93	9.13	0.22	5.11
9	0.97	4.84	1.05	1.54
10	0.80	8.57	2.69	0.54
11	0.75	10.71	1.17	0.77
12	1.06	6.08	0.46	2.09
13	0.72	7.14	0.70	0.92
14	0.57	4.32	0.91	1.51
15	0.88	15.84	0.77	1.79
16	1.83	3.03	2.48	0.23
17	1.23	8.93	1.39	0.33
18	1.35	5.46	1.55	0.96
19	1.61	3.41	0.59	1.37
20	1.50	5.74	1.02	1.44

a : Dk diffusion coefficient derived from ammonium acetate K gradient term and center ring resin flux, in cm^2 s^{-1}.

b : dC dD-1 or KBETA, ammonium acetate K linear regression slope, in umol cm^{-3} cm^{-1}.

c : Dp diffusion coefficient derived from sodium bicarbonate P gradient term and center ring resin flux, in cm^2 s^{-1}.

d : dC dD^{-1} or PBETA, sodium bicarbonate extractable P linear regression slope, in umol cm^{-3} cm^{-1}.

of D_s would be invalid. The S flux values are in the range of 10^{-7} which is approximately one order of magnitude below the P flux and two orders below the K flux values for this experiment. Soil concentrations of available K, P, and S normally fall into a similar relative scale. So, although the D_s was not calculable, the flux values appear to be reasonable.

These comparisons indicate that the experimental method yielded data normal for the conditions of the experiment and comparable to outside research.

The Analytical Method Relation to Resin Flux

The center resin ring flux in umol cm^{-2} s^{-1} represents the actual amount of ion moved from both soil side A and B into the sink. When the center resin flux is divided by 2 it represents the truest measure of flux of a single side by assuming equal contribution from either side. The linear regression of center ring flux with both the flux calculated from standard soil test extraction, and the flux calculated from the batch extraction allowed for direct comparison of the two soil extraction methods (Table 64).

The only method that was even reasonably close to approximating center ring resin flux was the standard ammonium acetate K. All other methods showed poor correlative value and/or poor probability.

The batch method accounted for more quantity removed from the soil in every case, but the modifying coefficients for batch P (0.02) and S (-0.03) flux indicate the batch method severely overestimated true flux. The modifying coefficient for each standard method flux was in excess of 1.0 which indicates an underestimation of true flux.

Table 64. Linear regression equations for flux as taken directly from center ring resin concentration and as calculated from standard and batch method concentrations for 20 soils.

Flux units are umol cm^{-2} s^{-1}.

Equation	R^2	Prob>F
Potassium		
$J_r = 4.99E{-}7 + 3.37 * J_{std}$	.807	.001
$J_r = 2.95E{-}6 + 2.41 * J_{bat}$	.363	.005
Phosphorus		
$J_r = 8.02E{-}7 + 1.34 * J_{std}$	.095	.186
$J_r = 1.04E{-}6 + 0.02 * J_{bat}$	.002	.847
Sulfur		
$J_r = 3.04E{-}7 + 5.61 * J_{std}$	.477	.001
$J_r = 8.92E{-}7 - 0.03 * J_{bat}$	.003	.831

J_r : Flux of center ring resin.
J_{bat} : Flux calculated from batch extraction.
J_{std} : Flux calculated from the standard methods of ammonium acetate K, sodium bicarbonate P, and ammonium acetate S, respectively.

The poor correlation of standard P flux to resin flux fosters doubt regarding the applicability of the chemical concentration gradient term and the diffusion coefficient term generated from the standard P data.

Linear regression analysis was performed using the check plot, percent P of 7 soils from the growth room experiment of the previous chapter as the dependent variable. Independent variables included center resin ring flux, standard test method flux, batch test method flux, the diffusion coefficient, and the dC dD^{-} term called PBETA (Table 65).

Table 65. Linear regression equations for relation of growth room check treatment percent P with flux, D_p, and dC dD^{-1} terms.

Flux units are μmol cm^{-2} s^{-1}.
D_p units are cm^2 s^{-1}.
dC dD^{-1} units are umol cm^{-4}.

Equation	R^2	Prob>F
$P\ \% = 0.049 + 130486 * J_r$	.309	.195
$P\ \% = 0.047 + 580582 * J_{std}$	.235	.270
$P\ \% = 0.278 + 37075 * J_{bat}$	.103	.482
$P\ \% = 0.025 + 0.139 * PBETA$	.678	.023
$P\ \% = 0.300 - 100764 * D_e$	.240	.265

J_r : Flux of center ring resin.
J_{bat} : Flux calculated from batch extraction.
J_{std} : Flux calculated from sodium bicarbonate P.
PBETA : Linear slope of sodium bicarbonate P umol cm^{-3} (Y) with cm (X).

The percent P in the check plot treatment of the growth room experiment is not predictable by the flux terms or diffusion coefficient terms. The PST method using H/OH resin was shown to be a poor predictor of percent P in the previous chapter. Since the flux and D^p terms are directly related to the removal of soil P by HOH resin, the lack of relation of all flux terms and D_p to percent P indicated that the HOH resin in linear or spherical form does not mimic a plant root sink very well and is not a good index of phytoavailable P. It should be noted that the conditions chosen for this experiment were not intended to simulate plant uptake directly.

The good correlation for the chemical concentration gradient term, PBETA, to percent P indicates that an experiment such as this probably can be used to develop diffusion terms related to plant uptake if an appropriate inorganic P test is used to derive the chemical concentration gradient term and a more suitable resin or actual plant root sink is used for the experiment.

A maxr regression analysis was performed using PBETA as the dependent with 26 soil physical and chemical measurement variables, including Olsen and Bray P, as independents (Table 66). A single variable equation using the saturated water content of the soil, MLS, was highly significant and positively related (r-square = .671). This means the chemical concentration gradient is steeper with respect to distance on soils with higher moisture contents. The additional model terms of percent clay, CL, and sodium bicarbonate phosphorus, OP, were both positively correlated to PBETA in simple correlation. Saturated water content is positively related to clay content so the CL term of the model is a redundant expression. The OP data relation

Table 66. Maxr regression analysis with the chemical concentration gradient term, PBETA, as (Y) and 26 independent soil chemical and physical measurement variables as (X) for 20 soils.

Dependent Variable	Equation	R^2	P>F
PBETA	= −2.87 + 0.04*OP − 0.04*CL + 0.21*MLS	.817	.0001

PBETA : Linear regression slope of thin slice concentration in umol cm^{-3}, Y, and distance in cm, X, final units are umol cm^{-3} cm^{-1} = dC dD^{-1}.
OP : Sodium bicarbonate extractable soil P in ug g^{-1}.
CL : Clay percent in soil in g cg^{-1}.
MLS : Absolute ddw mls used in 50 g of soil.

indicates that the greater supply of sodium bicarbonate extractable P the steeper the gradient.

The general message of the model is steep gradients result primarily from soils which require more water for saturation (high clay, high organic matter) and secondarily from soils with high extractable P.

Regressions were conducted for K flux, D_e, and the chemical concentration gradient term, KBETA, of the check plot greenhouse experiment percent K rate (Table 67).

Table 67. Linear regression equations for relation of greenhouse check treatment percent K with flux, D_k, and dC dD^{-1} terms for 20 soils.

Flux units are umol cm^{-2} s^{-1}.
D_k units are cm^2 s^{-1}.
dC dD^{-1} units are umol cm^{-4}.

Equation	R^2	Prob>F
$K\ \% = 2.47 + 151005*J_r$	.670	.001
$K\ \% = 2.57 + 492052*J_{std}$	.489	.002
$K\ \% = 2.91 + 38467*J_{bat}$	.208	.066
$K\ \% = 2.80 + 0.184*KBETA$	.421	.005
$K\ \% = 3.36 + 226238*D_k$	.017	.615

J_r : Flux of center ring resin.
J_{bat} : Flux calculated from batch extraction.
J_{std} : Flux calculated from ammonium acetate K.
KBETA : Linear slope of ammonium acetate K umol cm^{-3} (Y) with cm (X).

The percent K in the check plot treatment greenhouse experiment plants was most strongly predicted by the center ring resin flux equation. The center resin ring flux was a much better predictor of percent K than either ammonium acetate or batch extraction methods. This result supports the conclusion that an H/OH resin based soil test is superior for assessment of phytoavailable K.

Inspection of the modifying coefficient values for the flux terms reveals that ammonium acetate extracts the least amount of total K from the soil while the batch extraction removes an order of magnitude more than the other two methods. These modifying values are in relation to plant uptake in percent so they are not absolute quantities. However, as plant uptake related terms, the difference between the methods shows the H/OH center resin ring extracts more of the actual phytoavailable K than the other methods. The H/OH resin sink appeared to be a much better substitute for a plant root sink for experimental characterization of K diffusion than was shown for P because of the resin sink's sensitivity to phytoavailable K dynamics.

The chemical concentration gradient term, KBETA, is not as strongly related to percent K as the PBETA term was to percent P. KBETA does account for 42 % of the variability about the percent K line as a single term and it is highly significant in probability.

The gradient term, KBETA, was used as the dependent variable for maxr regression with 26 soil chemical and physical measurement independent variables (Table 68).

This equation is identical to the K by PST HOH extraction concentration equation presented in the previous

Table 68. Maxr regression analysis with the chemical concentration gradient term, KBETA, as (Y) and 26 independent soil chemical and physical measurement variables as (X) for 20 soils.

Dependent	Equation	R^2	P>F
KBETA	$= -0.49 + 30.5*PARSAT - 1.14*KNEX + 0.02*N$	.670	.0004

KBETA : Linear regression slope of thin slice concentration in umol cm^{-3}, Y, and distance in cm, X, final units are umol cm^{-3} cm^{-1} = dC dD^{-1}.
PARSAT : Saturated extract K X $((Ca + Mg)/2)^{-.5}$, where K, Ca, and Mg units are cmol l^{-1}.
KNEX : Nonexchangeable soil K in cmol kg^{-1}.
N = Extractable soil nitrate in ug g^{-1}.

chapter. This is a strong indication that even though ammonium acetate extractable K was used for direct calculation of the dC_k term, the gradient relationship is a function of HOH extraction by the resin sink. Ammonium acetate K can be appropriately used for identification of a chemical concentration gradient. However, this method limits the direct applicability of the gradient and diffusion coefficient terms to true phytoavailability relationships.

The diffusion coefficient term was not well correlated to percent K in the plant. This may be related to the conditions of the experiment which optimize diffusion of K via high temperature and high water content. It may also be related to the fact that 96 hours may not be sufficient for sampling the chemical concentration gradient in order to derive a diffusion gradient term representative of greenhouse plant uptake of K. It may also be related to the possibility that buffering capacity is more important than the diffusion coefficient under experimental conditions which optimize diffusion. These possibilities cannot be offered as concrete explanations because the experiment was not designed to produce data for in depth investigation of this derived term. However, considering the positive relations of resin flux and KBETA to phytoavailability, the lack of D_k relation would be a worthwhile topic for further study.

The S data were not used for similar regressions because the SBETA derivation from either the standard or the batch data would not be valid. The failure of this experiment with respect to S was attributed in part to the poor relation of the standard S procedure to phytoavailable or resin adsorption available quantities. The low concentration of S relative to P or K may require more sensitive analytical techniques in order to appropriately investigate S diffusion dynamics.

The flux, concentration gradient, and diffusion coefficient terms were introduced into the independent variable pools of the percent and uptake maxr regression models presented in the previous chapter. In all cases the new terms did not change the resultant equations except for a direct substitution for HOH resin concentration mean values by related flux values. These substitutions did not improve the r-square significantly in any case.

Similar trials using maxr regression with the flux terms as dependents resulted in identical equations to those of the previous chapter where HOH RAQ variables were used as dependents. Diffusion coefficients were not significantly correlated with any soil variables.

Conclusions

The linear extraction device was found to extract less P, K, and S than the spherical extraction device used in the PST method. Despite the difference, the relation of the linear system extraction to PST was strong for K and S. The linear system was not as well related to PST P. The different quantities of P, K, and S extracted were the probable result of the calculations involved and the different volume of soil in the region of the peak chemical potential, nearest the resin sink surface.

The data for S were not suitable for characterization of diffusion dynamics by this experimental method. The data for P and K were suitable for this purpose but their reliance on standard method assays for determination of chemical concentration gradients limited the applicability of the diffusion terms to phytoavailability.

The batch method for P and K was an overestimation of center resin flux, while the standard methods were an underestimation of resin flux. The data for P and K diffusion coefficients did fall into a reasonable range for the conditions of the experiment.

The P chemical concentration gradient was related to water holding capacity and sodium bicarbonate extractable P. The K chemical concentration gradient was related to K equilibrium dynamics in identical manner as the PST method extraction concentration.

Linear extraction center resin ring flux was as good a predictor of plant percent concentration as the spherical extraction by the PST method. The PST method was previously shown to be superior to standard methods for prediciton of K and S phytoavailability. This improvement is probably due to the similarity of resin sink flux dynamics to root flux for these two nutrients in Montana soils.

GENERAL SUMMARY

Characteristics of PST

The Phytoavailability Soil Test, PST, is a simple multielement soil test which measures the quantity of nutrient ions diffusing to an effectively infinite ion exchange resin sink under saturated soil conditions.

The PST method was shown to be independently sensitive to P, K, and S in terms of resin adsorption quantity, RAQ, and resin adsorption rate, RAR. The RAQ of each element increased with time in a manner consistent with the diffusion dominated extraction process. Potassium and S increased with temperature in a manner consistent with the diffusion dominated extraction, but RAQ P increased only in the extreme range of temperature treatments. The dominant influence on RAQ for each element was the inorganic concentration equilibrium which consistently depended on the dynamics of Ca in conjunction with quantity and intensity of the element under consideration.

Diffusible S increase resulted from release of S to soil solution by a variety of mechanisms including mineralization, soil solution chloride concentration increase, and soil solution phosphatase enzyme presence. Increases of RAQ K were consistently coincident to increases of RAQ S. The trend relationships of RAQ K and S suggests a release of K to soil solution probably caused by the attractive force of excess net negative solution charge. The use of tetracycline solution in the PST extraction was found to be an easy and effective method for study of mineralization concentration dynamics in saturated soil.

The PST method was successfully characterized for K in terms of physical chemistry by an experiment specifically designed to measure flux and chemical concentration gradient in order to derive diffusion coefficients. A Plexiglas ring filled with H^+/OH^- resin, held there by polyester cloth covered rings of soil on either side, allowed for ion extraction where the chemical concentration gradient could be estimated by chemical concentration assay of thin slices of the soil at specific distance intervals.

The flat resin sink procured less P, K, and S than the spherical resin bag sink of the standard PST method. The RAQ K and S data of the two sink shapes were highly correlated. The RAQ P of the two sink shapes was not as well correlated due to soil volume differences within the zone of peak potential of the sink which resulted in greater extracted quantity by the sphere.

The P, K, and S flat resin sink concentration data calculated as flux were compared to outside research data for ion flux to plants grown under controlled environment conditions. The center resin flux data were comparatively within a reasonable range with respect to the standard conditions of this experiment that optimized diffusion by using water saturated soil and 30 °C temperature. The diffusion coefficients for P and K were also within a reasonable range for the conditions of experiment. The linear extraction RAQ data were equal to PST data with respect to relation with plant uptake, plant nutrient concentration, and soil property models.

Comparative Value of PST and Standard Soil Tests

The PST extraction method using H^+/OH^- resin was superior to standard methods for the prediction of plant K uptake, percent K, S uptake, and percent S. It was found to be inferior to both the Bray and Olsen P tests for plant P uptake and percent P. The use of H+/Cl- resin is not recommended because of confounding effects of acid base reactions with calcareous soils, release of S by chloride, and extremely weak affinity of Cl- charged anion resin toward phosphate adsorption. The use of tetracycline solution for preparation of the saturated paste does not significantly improve or decrease relations of P, K, or S to plant nutrient uptake, but can be used effectively to assay mineralization conversion of S to diffusible forms.

The data clearly indicated that the H^+/OH^- resin PST procedure was a direct measure of phytoavailable K quantity, but this measure alone did not totally explain the amount of K obtained by plants from the soil. Incorporation of terms related to diffusion pathway resistance improved the prediction value to 94 % for K uptake and percent K on 17 soils.

The data clearly indicated that the H^+/OH^- resin PST procedure was a direct measure of phytoavailable S quantity. The RAQ S term alone has a predictive value of 89 % for plant S uptake and 84 % for plant percent S on 7 soils.

The PST method was not a good predictor of any plant P response parameter. This was a function of the weak affinity of the resins used toward phosphate. The Bray P test result alone has a predictive value of 76 % for plant percent P and 88% for P uptake on 7 soils. The parameters of the experiment contained a built in bias in favor of high correlation by the standard methods.

The superiority of the PST method versus the standard method for K and S is due to the fact that PST extraction adsorbs all the diffusible ion forms of a nutrient and is sensitive to influence by factors of soil concentration equilibria and diffusion rate in a manner similar to plant roots. The standard methods are not sensitive to these influences and are extractions of specific element fractions representing a variable portion of the soil's phytoavailable nutrient pool.

Applicability of the PST Method

The PST method does assay soil phytoavailable K and S in a manner consistent with Fick's laws of diffusion. As such, this method could be universally successful in any region, but it must first be tested on soils of those regions to verify improvement over current procedures and to calibrate the method to regional factors of soils, climate, and crop management practice.

The PST method is an improvement over standard methods for indexing phytoavailable K and S on representative Montana agricultural soils. It needs to be calibrated to field fertilizer rate response data in both cases, but it should first be tested for S relations to plant uptake on additional soils in a controlled environment setting. Duplication of controlled environment experiments relating PST RAQ of K and S to soils of different regions should be attempted as soon as feasibly possible because a true need for an improved K soil test exists now in the western United States, and a desperate need exists in the entire United States for an improved S soil test.

Research must be continued to identify and characterize a mixed bed ion exchange resin which has stronger affinity to phosphate than those used in this research. Soils low in labile P should be found for use in this work but the final product must serve as an accurate soil index to phytoavailable P on soils both high and low in residual supply.

Methods research should be continued to develop a spherical or cylindrical mixed bed resin bag which can be easily and completely cleaned of attached soil particles.

Until such a process is developed, great care must be taken to avoid soil particle contamination of the stripping solution.

Selection of the spherical or planar form of the effectively infinite exchangeable ion sink was not critical to the success of PST toward P, K and S plant availability but the effect of shape was strongly evident in the P data. Phytoavailable quantity of low mobility or low concentration nutrient elements (such as P, micro-nutrients and trace elements, respectively) may be better estimated by a resin sink which has the ability to simulate the root's tendency to maximize soil volume in the area of high potential as a function of cylindrical shape.

Reduction-oxidation reactions were not studied but are assumed to be important factors involved with RAQ S and should be an interesting topic for future research.

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APPENDIX

APPENDIX

Table 69. Soil number, series name, and taxonomic classification of Montana soils used in this research.

Number	Series:	Soil Classification
1	Gerber:	fine, montmorillonitic Vertic Argiborall.
2	Tanna:	fine, montmorillonitic Aridic Argiboroll.
3	Evanston:	fine-loamy, mixed Aridic Agriboroll.
4	Edgar:	fine-loamy, mixed Ustollic Camborthid.
5	Manhatten:	coarse-loamy, mixed Typic Calciboroll.
6	Fort Collins:	fine-loamy, mixed, Ustollic Haplargid.
7	Flathead:	coarse-loamy, mixed Pachic Haploboroll.
8	Bozeman:	fine-silty, mixed Pachic Argiboroll.
9	Creston:	coarse-silty, mixed Udic Haploboroll.
10	Chanta:	fine-loamy over sand, mixed Aridic Haploboroll.
11	Cherry:	fine-silty, mixed, frigid Typic Ustochrept.
12	Rothiemay:	fine-loamy, mixed Aridic Calciboroll.
13	Varney:	fine-loamy, mixed Aridic Argiboroll.
14	Beaverton:	loamy-skeletal, mixed Typic Agriboroll.
15	Kevin:	fine-loamy, mixed Aridic Argiboroll.
16	Amsterdam:	fine-silty, mixed Typic Haploboroll.
17	Chinook:	coarse-loamy, mixed Aridic Haploboroll.
18	Round Butte:	fine, mixed Borollic Natragids.
19	Stryker:	fine-silty, mixed Aquic Eutroboralf.
20	Bear Paw:	fine, montmorillonitic Typic Argiboroll.
*	Gallatin:	fine-loamy, mixed Pachic Cryoboroll.

Table 70. Resin adsorption quantity (RAQ) and resin adsorption rate (RAR) of P on 20 Montana soils.

RAQ in mg l^{-1} of stripping solution.
RAR in mg l^{-1} of stripping solution x DAYS^{-1}.

	RAQ[a]			RAR[b]		
SOIL	HOHP[c]	HOHTP[d]	HCLP[e]	HOHP	HOHTP	HCLP
1	6.03	6.58	5.08	1.939	1.217	0.682
2	4.46	4.60	3.83	0.126	-0.144	-0.045
3	11.71	9.19	9.00	4.772	2.396	1.446
4	12.42	11.65	12.74	4.033	3.303	2.558
5	8.30	8.43	5.76	0.875	1.370	0.228
6	14.96	14.23	14.26	5.745	4.836	3.423
7	5.53	4.63	4.25	1.835	1.298	0.603
8	10.65	10.99	7.27	1.925	1.806	0.741
9	11.52	9.75	2.45	5.611	4.341	0.119
10	13.91	12.50	13.03	4.183	3.331	1.205
11	5.47	5.49	7.27	1.387	0.926	0.370
12	9.62	8.83	5.64	3.043	1.277	0.107
13	5.98	5.68	4.78	1.426	0.922	0.109
14	10.20	10.43	6.57	3.324	3.564	1.129
15	11.12	10.20	4.15	3.184	3.608	0.472
16	5.51	4.22	2.52	0.749	0.626	0.294
17	4.66	4.26	4.51	1.042	0.877	-0.206
18	7.01	6.64	3.01	3.260	2.817	0.089
19	3.53	3.83	0.74	1.283	1.411	-0.184
20	12.57	11.37	7.53	4.130	3.344	-0.243

a: RAQ is the mean of the sum of all replications across all days.

b: RAR is the linear regression line slope of stripping solution concentration (Y) and the log of DAYS (X).

c: HOH stands for H/OH mixed bed resin with soil pastes made with ddw.

d: HOHT stands for H/OH mixed bed resin with soil pastes made with tetracycline solution.

e: HCL stands for H/CL mixed bed resin with soil pastes made with ddw.

Table 71. Resin adsorption quantity (RAQ) and resin adsorption rate (RAR) of K on 20 Montana soils.

RAQ in mg l^{-1} of stripping solution.
RAR in mg l^{-1} of stripping solution x DAYS^{-1}.

	RAQ[a]			RAR[b]		
SOIL	HOHK[c]	HOHTK[d]	HCLK[e]	HOHK	HOHTK	HCLK
1	64.48	50.52	97.70	17.816	10.067	40.758
2	28.45	26.12	38.47	8.363	7.000	15.137
3	60.83	50.70	119.56	26.039	21.451	54.077
4	40.38	32.83	81.57	16.576	15.613	48.138
5	65.04	63.62	77.32	15.657	19.975	27.529
6	55.32	47.04	99.63	23.304	25.789	49.747
7	55.90	59.61	67.03	26.628	34.723	36.338
8	55.32	55.85	104.94	16.133	17.979	48.015
9	47.69	43.01	95.25	18.406	20.195	45.869
10	52.08	39.26	79.20	20.691	18.130	40.637
11	57.78	49.31	98.77	24.946	18.543	49.536
12	50.98	40.07	67.87	17.689	5.381	28.131
13	29.30	27.90	37.74	8.358	6.020	17.187
14	21.01	17.68	31.53	6.966	7.589	15.345
15	91.94	90.88	165.71	32.356	46.656	79.584
16	35.45	34.78	49.53	12.523	16.012	22.981
17	71.67	86.33	95.35	24.697	40.540	40.829
18	57.25	49.11	67.52	25.377	27.490	36.806
19	29.96	31.75	44.24	2.667	5.931	20.612
20	71.99	68.14	92.04	20.589	27.954	34.267

a: RAQ is the mean of the sum of all replications across all days.

b: RAR is the linear regression line slope of stripping solution concentration (Y) and the log of DAYS (X).

c: HOH stands for H/OH mixed bed resin with soil pastes made with ddw.

d: HOHT stands for H/OH mixed bed resin with soil pastes made with tetracycline solution.

e: HCL stands for H/CL mixed bed resin with soil pastes made with ddw.

Table 72. Resin adsorption quantity (RAQ) and resin adsorption rate (RAR) of S on 20 Montana soils.

RAQ in mg l^{-1} of stripping solution.
RAR in mg l^{-1} of stripping solution x DAYS^{-1}.

	RAQ[a]			RAR[b]		
SOIL	HOHS[c]	HOHTS[d]	HCLS[e]	HOHS	HOHTS	HCLS
1	0.83	1.08	2.58	0.086	-0.017	0.902
2	1.68	1.46	1.64	0.329	0.132	0.437
3	4.30	3.37	3.95	1.565	0.827	1.597
4	1.81	1.69	2.11	1.037	1.086	0.988
5	1.99	2.19	1.65	0.309	0.026	0.635
6	2.28	2.15	3.14	0.919	0.809	1.072
7	3.93	3.21	2.62	1.251	0.976	1.319
8	1.84	1.25	9.54	0.575	0.482	3.959
9	3.82	3.23	12.33	1.557	0.792	7.407
10	1.99	1.42	2.36	0.771	0.452	0.634
11	1.28	0.94	2.31	0.697	0.286	0.672
12	8.07	5.92	7.43	2.543	0.818	3.399
13	2.25	2.03	1.69	0.532	0.306	0.300
14	2.24	1.88	2.48	0.727	0.610	0.812
15	2.76	2.59	10.39	0.918	0.742	3.775
16	0.92	1.05	6.06	0.472	0.512	2.439
17	3.37	2.92	2.56	0.733	0.490	0.828
18	1.99	1.92	1.49	0.658	0.724	0.956
19	15.47	15.37	11.06	4.362	4.895	5.597
20	8.61	7.99	5.30	1.068	1.294	1.821

a: RAQ is the mean of the sum of all replications across all days.
b: RAR is the linear regression line slope of stripping solution concentration (Y) and the log of DAYS (X).
c: HOH stands for H/OH mixed bed resin with soil pastes made with ddw.
d: HOHT stands for H/OH mixed bed resin with soil pastes made with tetracycline solution.
e: HCL stands for H/CL mixed bed resin with soil pastes made with ddw.