



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  
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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 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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MONTANA STATE UNIVERSITY  
Bozeman, Montana

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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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## 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.

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.

## 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, Masee 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 extractable 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  $\text{NaHCO}_3$  at a near constant pH of 8.5 decreases the concentration of Ca in solution by causing precipitation of Ca as  $\text{CaCO}_3$  (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  $\text{NH}_4\text{F}$  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  $\text{NH}_4\text{F}$  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  $\text{NH}_4$  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  $\text{NH}_4$  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 (Masse, 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 °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  $\text{CaCO}_3$  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  $\text{NH}_4\text{OAc}$  extraction and atomic adsorption analysis (Bower et al., 1952);
  - (6) extractable K by 0.5 N  $\text{MgCl}_2$  and 0.5  $\text{NH}_4\text{OAc}$  (Rich, 1964);
  - (7) extractable K by sodium tetraphenyl boron (Scott and Reed, 1960);
  - (8) extractable K by 1.0 N  $\text{HNO}_3$  (McClean 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  $\text{SO}_4$  (Bardsley and Lancaster, 1960);
  - (13) nitrate extraction (Sims and Jackson, 1971) and analysis by Cd reduction (Willis, 1980);
  - (14) clay mineralogy (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

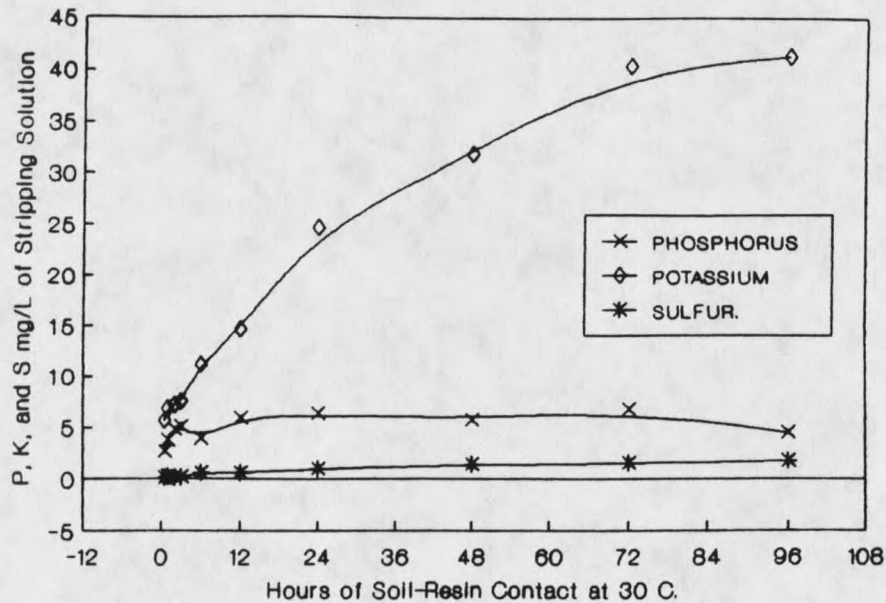


Figure 1. Resin stripping solution concentration of P, K, and S for the Bozeman Silt Loam soil.

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

































































































































































































































































































































