Characterization of soil K availability by chemical and thermodynamic parameters
by Jae Eui Yang

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Crop and Soil Science
Montana State University
© Copyright by Jae Eui Yang (1987)

Abstract:
Contemporary soil tests for K often do not predict K supply characteristics of the soil which influence K phytoavailability, such as K in solution# K buffering capacity, rate of K supply, and K exchange equilibria. The major challenge in elucidating the soil-solution-plant system has been extracting the unaltered soil solution at soil water contents under which plants grow. Procedures have only recently been developed and can now be used to help elucidate this system.

Immiscible liquid displacement and K adsorption isotherm techniques were employed to characterize K supply characteristics of the soil by chemical and thermodynamic indices. Treatments consisted of seven rates of K (0 to 800 mg/Kg), three rates of Cu and Cd (0 to 400 mg/Kg), two soil moisture contents (19 and 25%) and temperatures (5 and 200, and six equilibration times (.25 to 336 hr) applied in complete factorial combinations. The soil used was the Ap horizon of Bozeman silty clay loam (Typic Argiborolls). Concentrations of K, Ca, Mg, Cu and Cd in the soil solution and on the exchange sites were determined and various relationships were calculated.

A schematic description of soil-solution system in relation to soil K availability was developed in response to each treatment. Adding K increased K availability by increasing the K activity and buffering capacity but decreased the role of diffusion to supply K to crop and the affinity of the soil for K. Increasing Cu and Cd additions increased the activity of K in the solution and selectivity for K, but decreased K adsorption# buffering capacity and role of diffusion in supplying K to roots. Thus, larger applications of K fertilizer would be required for a soil contaminated by Cu and Cd to maintain the availability of labile K in the solution. Increasing soil water contents decreased the activity of K in solution, but increased K adsorption; thus, buffering capacity# the role of diffusion to supply K, and selectivity for K. Increasing soil temperature increased the activity of K in the solution but decreased the K adsorption; thus, buffering capacity, and selectivity for K. The adsorption-exchange equilibria were established rapidly.

The immiscible liquid displacement technique proved to be a convenient and precise method to characterize the soil-solution system with respect to soil K availability.

CHARACTERIZATION OF SOIL K AVAILABILITY BY CHEMICAL AND THERMODYNAMIC PARAMETERS

by

Jae Eui Yang

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Crop and Soil Science

MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1987

D378
Y165
Cop. 2

APPROVAL

of a thesis submitted by

Jae Eui Yang

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.

Mar. 31, 1987 — Earl O. Skogley
Date — Chairperson, Graduate Committee

Approved for the Major Department

April 1, 1987 — Dwane G Miller
Date — Head, Major Department

Approved for the College of Graduate Studies

April 1, 1987 — Henry L Parsons
Date — Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirement for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "Fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute copies of the dissertation in and from microfilm and the right to reproduce and distribute by abstract in any format."

Signature

Date Mar. 31, 1987

ACKNOWLEDGEMENTS

I express my most sincere appreciation to Dr. Earl O. Skogley, my major professor, for the project, assistance, encouragement, kindness, and advice during my period of study and research for the Doctorate and the preparation of this dissertation. I thank the members of my committee, Dr. A. Hayden Ferguson, Dr. Paul O. Kresge, Dr. Dwane G. Miller, and Dr. Ralph A. Olsen for their advice, guidance and encouragement lending a great contribution to this dissertation. Thanks also to Dr. Norman D. Reed, who served as a representative of the College of Graduate Studies on my thesis committee.

My wife, Kyungsook, and children deserve my special thanks for providing inspiration and a warm and happy home. Special thanks to my parents and family in Korea for their spiritual and financial support during the period of my staying in a foreign country.

I thank many graduate colleagues, staff, and faculty members for their cameraderie and help.

TABLE OF CONTENTS

APPROVAL..... ii

STATEMENT OF PERMISSION TO USE..... iii

VITA..... iv

ACKNOWLEDGEMENTS..... v

TABLE OF CONTENTS..... vi

LIST OF TABLES.....viii

LIST OF FIGURES..... xv

ABSTRACT.....xvii

INTRODUCTION..... 1

LITERATURE REVIEW..... 4

- Extraction of soil solution..... 4
- Soil K availability..... 7
- Soil solution K and exchangeable K..... 9
- Potassium adsorption isotherm..... 10
- Q/I relation for soil K..... 11
- Potassium potential..... 12
- Fractional saturation of cation..... 13
- Thermodynamic parameters for ion exchange: Selectivity coefficients and preferential adsorption isotherm..... 14

MATERIALS AND METHODS..... 19

- Soil sample..... 19
- Immiscible liquid displacement (ILD) study..... 20
- Potassium adsorption isotherm (KADS) study..... 21
- Chemical analysis of extracted soil solution and soil sample... 22
- Calculations..... 23
  - Activity of cations in soil solution..... 23
  - Adsorption of heavy metal on the soil by Freundlich equation..... 23
  - Potential buffering capacity by Q/I relation..... 24
  - Soil potassium potential..... 25
  - Fractional saturation..... 25
  - Selectivity coefficient..... 26
  - Preferential adsorption isotherm..... 27

TABLE OF CONTENTS-CONTINUED

Page

RESULTS AND DISCUSSION..... 28

Soil solution K..... 28
Exchangeable K..... 44
Heavy metals in the soil and solution..... 50
Estimations of relative contribution of diffusion and mass flow to total crop K demands..... 52
Potassium adsorption isotherm..... 60
Quantity/Intensity relations for soil K..... 69
Soil K potential..... 82
Fractional saturation of cations..... 94
Selectivity coefficients..... 106
Preferential adsorption isotherm..... 117

SUMMARY AND CONCLUSIONS..... 133

LITERATURE CITED..... 141

APPENDIX..... 150

LIST OF TABLES

Table		Page
1.	General properties of experimental soil sample.	19
2.	Cation activity and activity ratio of the soil solution extracted by the immiscible liquid displacement (ILD) technique from the Cu- and Cd-treated soils as affected by K treatments.	29
3.	The percentage of added K recovered and the changes of cations over initial levels in the soil solution of Cu- and Cd-treated soils in the ILD study.	30
4.	Effects of K or Cu and Cd interactions on the cation activities and activity ratio in the ILD study.	31
5.	Regression equations between aK (Y) and K additions (X) and the effects of Cu and Cd additions on this relationship. ..	33
6.	Changes of K, Ca, and Mg and activity ratios over those at no-K added in the soil solution as influenced by K and Cu and Cd interactions.	35
7.	Effect of temperature on the cation activities and activity ratio in the soil solution of Cu- and Cd-treated soils in the ILD study.	37
8.	Effect of soil temperature and K addition interactions on the changes of cations in the soil solution of Cu- and Cd-treated soils of the ILD study.	38
9.	Regression equations between aK (Y) and K additions (X) and the test of temperature effects on this relation.	39
10.	Effect of soil moisture contents on the cation activities and activity ratio in the soil solution of Cu- and Cd-treated soils in the ILD study.	41
11.	Effects of interactions of K addition and soil moisture on the changes of cations in the solution over those at no-K treatment of Cu- and Cd-treated soil in the ILD study.	42
12.	Regression equations between aK (Y) and K addition (X) and test of soil moisture effects on this relation.	44

LIST OF TABLES-CONTINUED

Table | Page

13. Exchangeable cations and their summation in the soil as affected by K additions, soil moisture content, temperature and equilibration time in Cu- and Cd- treated soil of the ILD study. 46

14. Changes of exchangeable cations over those at no-K treatment as influenced by K-Cu and K-Cd interactions in the ILD study. 47

15. Changes of exchangeable cations over those at no-K additions of Cu- and Cd-treated soil as influenced by K additions in the KADS study. 48

16. Existing level (K_{EL}) and sufficiency level (K_{SL}) of soil K and recovery % of the added K in the ILD study. 49

17. Concentrations of Cu and Cd in the soil solution extracted by the ILD method and those of extractable Cu and Cd by DTPA solution as affected by Cu and Cd additions. 50

18. Concentration of soluble and DTPA-extractable Cu and Cd as affected by interaction of heavy metal additions with temperature in the ILD study. 51

19. Regression equations between ln X (Y) and ln C (X) and tests of treatment effects on this relation in the ILD study. ... 52

20. Data for total dry matter production, total crop K demand, and total water use by a winter wheat crop in Montana under moderate-yielding and nonirrigated conditions. 53

21. Soil solution K, exchangeable K, and quantity of K supplied by diffusion and mass flow as influenced by K additions in the ILD study. 54

22. Estimation of relative contributions of diffusion and mass flow to total crop K demands as influenced by K and Cu addition interactions in the ILD study. 57

23. Regression equations between exchangeable K, K supplies by diffusion, and mass flow and K additions (X) and significance test of Cu effects on these relationships in the ILD study. 60

24. Mean values of the amount of K in solution and K adsorbed as influenced by K additions in Cu- and Cd-treated soils of the KADS study. 62

LIST OF TABLES-CONTINUED

Table		Page
25.	Regression equations between amount of K adsorbed (Y) and K in solution (X) as mg-K/kg and significance test of Cu and Cd effects on this relation in the KADS study.	64
26.	Regression equations between amounts of K adsorbed (Y) and K in solution as mg-K/kg and significance test of temperature effect on this relation in Cu- and Cd-treated soil of the KADS study.	67
27.	Mean values of K adsorbed as affected by K addition and soil moisture interaction in Cu- and Cd-treated soil of the ILD study.	67
28.	Parameters defining Q/I relation between ΔK (Y) and KRL (X) and influences of Cu and Cd on this relation in the KADS study.	73
29.	Parameters defining Q/I relation between ΔK (Y) and KRL (X) and effect of temperature on this relation in Cu- and Cd-treated soil of the KADS study.	79
30.	Parameters defining Q/I relation between ΔK (Y) and activity ratio (AR) (X) and influences of soil moisture content on this relation in Cu- and Cd- treated soil of the ILD study.	82
31.	Effect of interactions of K and Cu or Cd additions on the K potential (ΔF) at 5C and 20C in the ILD study.	85
32.	Regression equation between ΔF (Y) as Kcal/mol.K and K addition (X) as mg/kg and significance test of Cu and Cd addition effects on this relation at 20C in the ILD study.	86
33.	Potassium potential (ΔF) values of Cu- and Cd-treated soil as affected by K additions at 5C and 20C in the KADS study.	88
34.	Regression equations between the K adsorption (Y) as mg-K/kg and the K potential (X) as cal/mol.K and significance test of Cu and Cd effects on this relation at 5C in the KADS study.	90
35.	Regression equations between the K potential (Y) and K additions (X) at each soil moisture level and significance test of soil moisture effect on this relation in the ILD study.	92

LIST OF TABLES-CONTINUED

Table		Page
36.	Regression equations between the amounts of K adsorbed as mg-K/kg (Y) and soil K potential as cal/mol.K (X) and significance test of soil moisture effect on this relation in the ILD study.	93
37.	Values for the F statistics and probability greater than F, testing the signifiance effect of time on the relation between ΔF and K addition.	93
38.	Values for F statistics and probability greater than F, testing the significance effect of time on the relation between ΔK and ΔF.	94
39.	Fractional saturation of K, Ca, and Mg in the solution (FSL) and on the exchange phase (FSX) as influenced by K additions in Cu- and Cd-treated soil of the ILD study.	95
40.	Effect of Cu and Cd additions on the percentage of fractional saturation of cations in the soil solution (FSL) and on the exchange site (FSX) in the ILD study.	96
41.	Regression equations between FSL K (Y) or FSX K (Y') and K addition (X) as affected by Cu treatment and significance test of Cu effect on this relation in the ILD study.	99
42.	Effect of soil moisture contents on the percentage of fractional saturation of cations in the solution phase (FSL) and on the exchange phase (FSX) in Cu- and Cd-treated soils of the ILD study.	101
43.	Effect of temperature on the percentage of fractional saturation of cations in solution phase (FSL) and on the exchange phase (FSX) in Cu- and Cd-treated soils of the ILD study.	102
44.	Regression equations between FSX K (Y) and FSL K (X) as affected by Cu and Cd additions and significance test of Cu and Cd effects on this relation in the ILD study.	104
45.	Regression equations between FSX K (Y) and FSL K (X) as influenced by soil temperature and moisture and significance test of their effects on this relation in Cd-treated soil of the ILD study.	106
46.	Selectivity coefficients for each of the cation exchange systems as affected by K additions in Cu- and Cd-treated soils of the ILD study.	108

LIST OF TABLES-CONTINUED

Table		Page
47.	Effect of Cu and Cd additions on cation selectivity coefficients for each of the exchange systems in the ILD study.	110
48.	Effect of soil temperature on cation selectivity coefficients in Cu- and Cd-treated soils of the ILD study.	112
49.	Effect of soil moisture content on cation selectivity coefficients in Cu- and Cd-treated soils of the ILD study.	114
50.	Equivalent ratio of K in the K-Ca exchange system in the solution phase (ERL K) and on the exchange phase (ERX K) as affected by K and Cu interactions in the KADS study.	118
51.	Equivalent ratio of K in the K-Mg exchange system in the solution phase (ERL K) and on the exchange phase (ERX K) as affected by K and Cu interactions of the KADS study.	124
52.	Equivalent ratio of K in the K-CaMg exchange system in solution phase (ERL K) and on the exchange phase (ERX K) as influenced by K and Cu addition interactions of the KADS study.	130
53.	Mean values (n=6) for the electrical conductivity (EC), ionic strength (I), and cation activity coefficients (f_K, f_{Ca}, and f_{Mg}) of soil solution in Cu treatments of the ILD study.	151
54.	Mean values (n=6) for the electrical conductivity (EC), ionic strength (I), and cation activity coefficients (f_K, f_{Ca}, and f_{Mg}) of soil solution in Cd treatments of the ILD study.	152
55.	Mean values (n=6) for the cation (K, Ca, and Mg) concentration in the soil solution and exchangeable cations (Exc K, Exc Ca, and Exc Mg) on the exchange phase in Cu treatments of the ILD study.	153
56.	Mean values (n=6) for the cation (K, Ca, and Mg) concentration in the soil solution and exchangeable cations (Exc K, Exc Ca, and Exc Mg) on the exchange phase in Cd treatments of the ILD study.	154
57.	Mean values (n=18) for the cation (K, Ca, and Mg) concentration in the soil solution, potassium ratio law (KRL), and exchangeable cations (Exc K, Exc Ca, and Exc Mg) in Cu treatments of the KADS study.	155

LIST OF TABLES-CONTINUED

Table		Page
58.	Mean values (n=18) for the cation (K, Ca, and Mg) concentration in the soil solution, potassium ratio law (KRL), and exchangeable cations (Exc K, Exc Ca, and Exc Mg) in Cd treatments of the KADS study.	156
59.	Analysis of variance table for the activity of K (aK), in the soil solution as influenced by K addition (K), Cu addition (Cu), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	157
60.	Analysis of variance table for the activity of K (aK), in the soil solution as influenced by K addition (K), Cd addition (Cd), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	158
61.	Analysis of variance table for the activity ratio (AR), in the soil solution as influenced by K addition (K), Cu addition (Cu), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	159
62.	Analysis of variance table for the activity ratio (AR), in the soil solution as influenced by K addition (K), Cd addition (Cd), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	160
63.	Analysis of variance table for the exchangeable K (Exc K) as influenced by K addition (K), Cu addition (Cu), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	161
64.	Analysis of variance table for the exchangeable K (Exc K) as influenced by K addition (K), Cd addition (Cd), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	162
65.	Analysis of variance table for the amount of K adsorbed (KADS) as influenced by K addition (K), Cu addition (Cu), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	163
66.	Analysis of variance table for the amount of K adsorbed (KADS) as influenced by K addition (K), Cd addition (Cd), temperature (T), moisture (M), and equilibration time (D) in the ILD study.	164

LIST OF TABLES-CONTINUED

Table		Page
67.	Estimation of relative contributions of diffusion and mass flow to total crop K demands as influenced by K and Cd addition interactions at each moisture potential in the ILD study.	165
68.	Regression equations between K additions (X) as Kg/ha and exchangeable K (Exc K), K supply by mass flow (M.F. K) and that by diffusion (Diff K) and significance test of Cd effects on these relationships in the ILD study.	166
69.	Regression equations between K supplies by mass flow (M.F. K) and diffusion (Diff K) and K additions (X) as Kg/ha and significance test of moisture or temperature effects on these relations in Cu- or Cd-treated soils of the ILD study.	167

LIST OF FIGURES

Figure		Page
1.	Typical Q/I relations for soil K.	25
2.	Effects of Cu additions and Cd additions on the relationship between aK and K additions.	34
3.	Response of aK to K addition and Cu and Cd additions.	36
4.	Effects of temperature on the relations between aK and K additions in Cu- and Cd-treated soils.	40
5.	Effect of soil moisture contents on the relations between aK and K additions in the solution of Cu- and Cd-treated soils.	43
6.	Relationship of K additions with exchangeable K and K supply by diffusion and mass flow to meet the total K demands by 50 bu/A winter wheat. Soil solution K data from the ILD study.	56
7.	Effects of Cu additions on the relationships of K additions with exchangeable K and K supply by diffusion and mass flow to satisfy the total K demands by 50 bu/A winter wheat. Soil solution K data from the ILD study.	58
8.	Diagrams for the changes of % of mass flow K and diffusion K as affected by K and Cu additions.	59
9.	Potassium adsorption isotherm as influenced by Cu and Cd additions in the KADS study.	63
10.	Response surface of K adsorption to K and Cu or Cd additions in the KADS study.	65
11.	Effect of temperature on K adsorption isotherm in Cu- and Cd-treated soil of the KADS study.	66
12.	Effect of Cu additions on the relation between the amounts of K adsorbed and the equilibration time in the KADS study.	69
13.	Q/I relations for soil K in the KADS study.	71
14.	Effects of Cu and Cd additions on Q/I relations for soil K.	72
15.	Effect of temperature on Q/I relations in Cu- and Cd-treated soil of the KADS study.	78
16.	Q/I relations for soil K as influenced by soil moisture content in Cu- and Cd-treated soil of the ILD study.	81

LIST OF FIGURES-CONTINUED

Figure		Page
17.	Effect of Cu addition and Cd addition on the relationship between the K potential (ΔF) and K addition at 20C in the ILD study.	84
18.	Effects of Cu and Cd additions on the relations between the amount of K adsorbed (ΔK) and the soil K potential (ΔF) at 5C in the KADS study.	89
19.	Effect of Cu addition on the relation between fractional saturation of K and K addition in solution phase and on the exchange phase in the ILD study.	98
20.	Response surfaces of FSL K and FSX K to the K and Cu interactions in the ILD study.	100
21.	Effect of Cu additions and Cd additions on the fractional K adsorption isotherm in the ILD study.	103
22.	Effects of soil temperature and soil moisture on the fractional K adsorption isotherm in Cd-treated soil of the ILD study.	105
23.	Preferential adsorption isotherm for the K-Ca exchange system as influenced by Cu and Cd additions of the KADS study.	119
24.	Effect of temperature on the preferential K adsorption isotherm of K-Ca exchange system in Cu- and Cd-treated soils of the KADS study.	123
25.	Preferential K adsorption isotherm for the K-Mg exchange system as influenced by Cu and Cd additions of the KADS study.	125
26.	Effect of temperature on the preferential K adsorption isotherm of K-Mg exchange system in Cu- and Cd-treated soils of the KADS study.	128
27.	Preferential K adsorption isoterm for the K-CaMg exchange system as influenced by Cu and Cd additions of the KADS study.	129
28.	Effect of temperature on the preferential K adsorption isotherm of K-CaMg exchange system in Cu- and Cd-treated soil of the KADS study.	132

ABSTRACT

Contemporary soil tests for K often do not predict K supply characteristics of the soil which influence K phytoavailability, such as K in solution, K buffering capacity, rate of K supply, and K exchange equilibria. The major challenge in elucidating the soil-solution-plant system has been extracting the unaltered soil solution at soil water contents under which plants grow. Procedures have only recently been developed and can now be used to help elucidate this system.

Immiscible liquid displacement and K adsorption isotherm techniques were employed to characterize K supply characteristics of the soil by chemical and thermodynamic indices. Treatments consisted of seven rates of K (0 to 800 mg/Kg), three rates of Cu and Cd (0 to 400 mg/Kg), two soil moisture contents (19 and 25%) and temperatures (5 and 20C), and six equilibration times (.25 to 336 hr) applied in complete factorial combinations. The soil used was the Ap horizon of Bozeman silty clay loam (Typic Argiborolls). Concentrations of K, Ca, Mg, Cu and Cd in the soil solution and on the exchange sites were determined and various relationships were calculated.

A schematic description of soil-solution system in relation to soil K availability was developed in response to each treatment. Adding K increased K availability by increasing the K activity and buffering capacity but decreased the role of diffusion to supply K to crop and the affinity of the soil for K. Increasing Cu and Cd additions increased the activity of K in the solution and selectivity for K, but decreased K adsorption, buffering capacity and role of diffusion in supplying K to roots. Thus, larger applications of K fertilizer would be required for a soil contaminated by Cu and Cd to maintain the availability of labile K in the solution. Increasing soil water contents decreased the activity of K in solution, but increased K adsorption; thus, buffering capacity, the role of diffusion to supply K, and selectivity for K. Increasing soil temperature increased the activity of K in the solution but decreased the K adsorption; thus, buffering capacity, and selectivity for K. The adsorption-exchange equilibria were established rapidly.

The immiscible liquid displacement technique proved to be a convenient and precise method to characterize the soil-solution system with respect to soil K availability.

INTRODUCTION

Soil potassium can be divided into four categories: (1) Soil solution K; (2) exchangeable K; (3) difficultly exchangeable K; and (4) mineral K. Most soils have relatively large contents of total K but relatively small amounts of phytoavailable K. Potassium ions move from one category to another at greatly different rates and availabilities whenever equilibrium is disturbed by plant K uptake and K fertilization.

Throughout Montana crops have frequently responded to K fertilizers on soils testing "high" in NH_4OAc-extractable K. Worldwide, contemporary soil tests for K do not perform well for the purpose of predicting crop response to K fertilizers under many soil and climatic conditions. This is probably partly due to the underestimation of the true magnitude of crop demands for K, which differs greatly from that amount of K actually removed by a mature crop. Additionally, soil test procedures do not account for mechanisms of K movement in soils, some of which can limit K availability. Better ways of testing soil to evaluate true soil K availability are clearly needed.

Phytoavailability of soil nutrients can be determined by understanding the nutrient supply characteristics of soils and the nutrient absorption characteristics of plant roots. Soil parameters influencing cation nutrient availability are (1) the activity (or concentration) of nutrients in soil solution, (2) the buffering capacity of the soil for a given nutrient ion, (3) exchange equilibria among ions, and (4) diffusion and mass flow rates through the soil. Plant

parameters depend on root system sizes, characteristics, transport mechanisms, and physiology.

Many studies have been reported relative to plant parameters of nutrient availability as well as methodologies for measuring soil aspects of nutrient availability. The soil-K-plant system is highly complex and influenced by numerous conditions. One of the major limitations to our knowledge in this area probably derives from the complexities of understanding the soil-solution-plant relations. A major challenge in elucidating chemistry of soil nutrient availability is the removal of soil solution, equilibrated with soil, without altering the solutions' chemical compositions. Numerous methods have been proposed based on the principles of suction, pressure, compaction, column displacement, and centrifugation. However, separating the unaltered soil solution from the solid phase of soil has been difficult due to the several limitations involved in each procedure. Establishment of chemical indexes for soil aspects of nutrient availability based on a reliable method of solution extraction would represent significant progress in better understanding soil-solution-plant relations with respect to soil K availability. Procedures for extracting the real representative soil solution without changing its chemical compositions have only recently been developed.

The immiscible liquid displacement (ILD) method, which combines the principles of simple centrifuge method with immiscible displacement, is one of the most convenient and reliable techniques to extract the representative soil solution with a minimum of errors and is a promising

technique from which to characterize the soil as a medium for plant growth.

Several factors are known to affect soil K availability and exchange equilibria with Ca and Mg. Potassium addition, moisture content, temperature, and equilibration time are some of the more important factors. An additional environmental factor which has evoked much attention recently is contamination of agricultural soils with heavy metals. The effects of heavy metals on physiological interferences to crop growth are generally well known, but little is known relative to their influence on chemical properties of soil-solution-plant relations and, hence, on cation nutrient availability and exchange equilibria.

The objectives of this study were to (1) develop chemical indices for characterizing soil K availability, and (2) determine thermodynamic parameters for evaluating K exchange equilibria with Ca and Mg between soil and solution. Both the ILD technique and K adsorption isotherm method were employed, and heavy metal additions were included as treatments. Soil K availability was characterized chemically by determining (1) activity (conc) of K in soil solution, (2) exchangeable K by NH_4OAc at pH 7.0, (3) K adsorption isotherm, (4) Q/I relations and potassium buffering capacity, (5) potassium nutrient potential, and (6) potassium fractional saturations. Potassium exchange equilibria were evaluated thermodynamically by determining (1) selectivity coefficients and (2) preferential K adsorption isotherm.

LITERATURE REVIEW

Extraction of Soil Solution

Soil solution is the aqueous liquid phase of the soil and its solutes consist of ions dissociated from the surfaces of soil particles and other soluble materials. Because soil solution is the medium in which soil chemical reactions occur and from which plants obtain mineral nutrients, there has been a long-time interest in knowing its chemical composition. Numerous methods to extract soil solution have been proposed based on the principles of suction, pressure, displacement, and centrifuge. However, separating unaltered soil solution from solid-phase soil has been difficult.

The column displacement method (Parker, 1921) has been used successfully for many years (Adams, 1974), but the major disadvantage for this method is that operator skill and experience are required in packing columns. The method works well only on limited ranges of soil textures and moisture contents, and it requires constant attention during solution collection (Adams, et al., 1980).

The suction method has survived primarily in the form of the pressure membrane or pressure plate method (Richards, 1941). The major disadvantages of this method are (1) the pressure membrane or plate effectively removes phosphate from the solution, (2) excess water must be added to the soil-membrane or soil-plate interface so that water films will be contiguous from membrane to soil particles, and (3) high

atmosphere of gas pressure within the chamber will alter CO_2 solubility and, hence, solution pH. Therefore the suction method is not suitable for extraction of the real soil solution. The most successful application of the suction method has been not in collecting soil solution composition data but in defining moisture retention curves for soils at moisture contents between field capacity and permanent wilting percentage (Adams, 1974; Faber and Nelson, 1984).

The suction principle also applies to porous ceramic cup method (Wagner, 1962; Hansen and Harris, 1975) and porous plastic filter method (Hossner and Phillips, 1973) in which ceramic cup or plastic filter are embedded in moist soil to obtain soil solution. Solutions obtained in these methods probably have been altered from the true soil solution by (1) the sieving action of the ceramic clay and filter, (2) the altered gas pressure, (3) sorption of elements, (4) leaching of soil solution, and (5) diffusion (Adams, 1974; Faber and Nelson, 1984).

A successful centrifuge method was developed later (Davies and Davies, 1963) and recent improvements in this method suggest that it can be used with fewer problems than the other methods (Edmunds and Bath, 1976; Gillman, 1976; Mubarak and Olsen, 1976a; Reynolds, 1984). Centrifuge method requires no special skills and is easy to use. It works on all soils, but it is particularly good on coarse-textured soils. It has the additional advantage of being nondestructive on the sample, and the soil can be used subsequently for other studies.

While the centrifuge method offers a method for extracting unaltered bulk solution over a desired range of moisture tensions, this