

1987

## **Metal Availability and Rice Growth Under Controlled Redox Potential and pH in Acid Sulfate Soils of Thailand.**

Jirapong Prasittikhet  
*Louisiana State University and Agricultural & Mechanical College*

Follow this and additional works at: [https://digitalcommons.lsu.edu/gradschool\\_disstheses](https://digitalcommons.lsu.edu/gradschool_disstheses)

---

### **Recommended Citation**

Prasittikhet, Jirapong, "Metal Availability and Rice Growth Under Controlled Redox Potential and pH in Acid Sulfate Soils of Thailand." (1987). *LSU Historical Dissertations and Theses*. 4470.  
[https://digitalcommons.lsu.edu/gradschool\\_disstheses/4470](https://digitalcommons.lsu.edu/gradschool_disstheses/4470)

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact [gradetd@lsu.edu](mailto:gradetd@lsu.edu).

## **INFORMATION TO USERS**

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the original text directly from the copy submitted. Thus, some dissertation copies are in typewriter face, while others may be from a computer printer.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyrighted material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is available as one exposure on a standard 35 mm slide or as a 17" × 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. 35 mm slides or 6" × 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.



300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA



**Order Number 8811431**

**Metal availability and rice growth under controlled redox  
potential and pH in acid sulfate soils of Thailand**

**Prasittikhet, Jirapong, Ph.D.**

**The Louisiana State University and Agricultural and Mechanical Col., 1987**

**U·M·I**  
300 N. Zeeb Rd.  
Ann Arbor, MI 48106





**PLEASE NOTE:**

In all cases this material has been filmed in the best possible way from the available copy.  
Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages \_\_\_\_\_
2. Colored illustrations, paper or print \_\_\_\_\_
3. Photographs with dark background ✓
4. Illustrations are poor copy \_\_\_\_\_
5. Pages with black marks, not original copy \_\_\_\_\_
6. Print shows through as there is text on both sides of page \_\_\_\_\_
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements \_\_\_\_\_
9. Tightly bound copy with print lost in spine \_\_\_\_\_
10. Computer printout pages with indistinct print \_\_\_\_\_
11. Page(s) \_\_\_\_\_ lacking when material received, and not available from school or author.
12. Page(s) \_\_\_\_\_ seem to be missing in numbering only as text follows.
13. Two pages numbered \_\_\_\_\_. Text follows.
14. Curling and wrinkled pages \_\_\_\_\_
15. Dissertation contains pages with print at a slant, filmed as received ✓
16. Other: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

U·M·I



Metal Availability and Rice Growth  
Under Controlled Redox Potential and pH  
in Acid Sulfate Soils of Thailand

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

in

The Department of Agronomy

by  
Jirapong Prasittikhet  
B.S., Kasetsart University, Bangkok, Thailand, 1970  
M.S., University of Arkansas, 1977  
December, 1987

To Thai farmers

## ACKNOWLEDGMENTS

I wish to express my sincere appreciation and gratitude to Dr. Robert P. Gambrell, my major advisor, who for nearly five years untiringly assisted and advised me throughout the course of this study.

I am especially grateful to Dr. William H. Patrick, Jr. Boyd Professor of Marine Sciences, for providing the opportunity, encouragement, and guidance which made the completion of this research possible.

Special thanks is also extended to my committee: Dr. Edward P. Dunigan, Dr. Sam E. Feagley, Dr. Edward N. Lambremont, and Dr. Jesse M. Jaynes for their academic expertise and critical review of the manuscript.

I would also like to thank Mr. R. D. DeLaune, Dr. C. W. Lindau, Dr. Chris J. Smith, and Dr. Irving A. Mendelsohn for providing invaluable technical support for this research. Special thanks are extended to D. Leach, M. Christian, W. Boyd, G. Jones, H. Ghane, J. Wiesepepe, J. Pardue and J. Whitcomb for their help with technical analysis.

Dr. Nico van Breemen of the Agricultural University, Wageningen, The Netherlands was most helpful by discussing several concepts on the solution chemistry of acid sulfate soils with me. A special note of thanks is also extended to Dr. P. Moore, Dr. T. Feijtal, Mrs. J. Kotuby-Amacher for helpful discussion and assistance. I would also like to thank Dr. A. Saxton, and Dr. P. Shao for suggestions regarding statistical analyses of this research. Special thanks are also extended to G. Chmura, Dr. B. J. Good, Mr. D. Burdick, M. Koch, and Mr. Mark Hester for computer assistance.

Special thanks goes to R. McClain for her help over the years, and for always maintaining a cheerful and helpful attitude. I would also like to thank Mrs. Rita Roberts, Mrs. Carol McClain, Ms. Lisa Grayson, and Ms. Elizabeth Fitzgerald for their help in various aspects of secretarial services.

Dr. Chob Kanareugsa, Dr. Aroon Jugsujinda, Dr. Sunchai Satawathananont, Ms. Laddawan Laowhaprasithpon, Mr. Wiwat Ingkapradit, Dr. C. Nammeuang, Mr. S. Glaewwikagrom, Mr. S Viriyasiri, Mr. W. Sritanandana, Mr. P. Songmeuang, Mr. P. Sawatdee, Dr. T. Nagara, Mr. W. Hiranyupakorn, Mrs. Y. Tasathon, Ms. H. Kunathai, Mrs. J. (Somboondamrongkul), Mr. P. Mongkolporn, Mr. S. Wattanapayapkul, Miss N. Supakamnerd, Ms. S. Konthasuwan, Dr. T. Attanandana, Mr. C. Charoenchamratcheep, Mr. J. Yuwaniyom, Dr. S. Arunin, Mr. N. Krairapanond, Mrs. A Krairapanond, and a number of my colleagues in several locations helped with various aspects of this study. The support of Dr. Ben R. Jackson, the former Rockefeller representative to Thailand is also appreciated.

I would like to thank Mrs. Pam Shriver, Mrs. Geraldine Newman, and Ms. Brenda Henning for guiding me through the university bureaucracy. I also acknowledge the help from the following persons: R. Kuttalam T., P. Jnyaneshwar, U. R. Khond, Dr. T. Jamjanya, N. Vaisayanunt, Liannah Sa, U. Tanchotikul, Y. Limnithithum, M. D. Tolley, G. Siragusa, A. Toure, K. McKee, S. Patterson, Dr. Hong Yang, X. Y. He, C. Hongprayoon, P. Nisamaneephong, P. Chantanahom, and A. Yusuf. My acknowledgement is also extended to the many Thai students and many colleagues in Laboratory for Wetland Soils, who over the years, have contributed moral support throughout my stay at Louisiana State University.

I gratefully acknowledge the USAID, and the Rockefeller Foundation for financial support on the Redox Chemistry of Acid Sulfate Soils L.S.U.-Thailand Joint Project. I also acknowledge the Department of Agriculture of Thailand for granting my study leave.

Finally, I would like to express my heartfelt thanks to my parents, my brothers, my sisters and my relatives for their support, cooperation, and understanding without which my study could have been impossible.



## TABLE OF CONTENTS

	Page
Dedication.....	ii
Acknowledgments.....	iii
List of Tables.....	vii
List of Figures.....	x
List of Plates.....	xv
Abstract.....	xvi
Chapter One - Introduction.....	1
Chapter Two - Literature Review: Acid sulfate soil.....	6
Chapter Three - Characterization of Soil Materials.....	56
Chapter Four - Rice Growth in Acid Sulfate Soils Under Controlled Redox Conditions.....	70
Chapter Five - Rice Growth in Acid Sulfate Soil Under Controlled pH and Redox Conditions.....	109
Chapter Six - Iron and Manganese Availability to Rice in Acid Sulfate Soils Under Controlled pH and Redox Potential Conditions.....	135
Chapter Seven - Aluminum Availability to Rice in Acid and Non-acid Sulfate Soils Under Controlled pH and Redox Potential Conditions.....	192
Chapter Eight - Summary and Conclusions.....	225
Appendix.....	230
References.....	236
Vita.....	263

## List of Tables

### Chapter Two

Table 1 - Distribution of acid sulfate soils in Southeast and East Asia.....	10
Table 2 - Classification and area in hectares of the acid sulfate soils in the Central Plain of Thailand.....	13
Table 3 - Yields ( $\text{hg ha}^{-1}$ ) of rice as affected by water control at the Rokupr Research Farm, Sierra Leone.....	51

### Chapter Three

Table 1 - General descriptions of the five soils studied.....	58
Table 2 - Selected chemical properties of the five soil materials.....	63
Table 3 - Concentrations of water soluble constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials.....	64
Table 4 - Concentrations of exchangeable constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials.....	65
Table 5 - Concentrations of easily reducible Fe, Mn and some other constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials extracted by 0.25 M $\text{NH}_2\text{OH.HCl}$ - 0.25 M $\text{HCl}$ ....	66
Table 6 - Concentrations of DTPA-extractable constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials extracted by 0.05 M $\text{NaDTPA}$ .....	67
Table 7 - Particle size distribution and textures of the five soils.....	68

### Chapter Four

Table 1 - Selected chemical properties of the soils in the air-dry state.....	75
Table 2 - Variables used in model building and their abbreviations.....	80
Table 3 - Variable and their linear correlations with weight gain of sensitive (IR26) rice grown in non-acid and acid sulfate soils over all redox levels.....	81
Table 4 - Variable and their linear correlations with weight gain of sensitive (IR46) rice grown in non-acid and acid sulfate soils over all redox levels.....	82
Table 5 - Effect of controlled redox potential (Eh) on soil pH and $\text{pe}+\text{pH}$ at harvest in acid and non-acid sulfate soils.....	84
Table 6a - Differences in weight gain of the sensitive rice variety (IR26) grown for 3 weeks between acid and non-acid sulfate soils over all redox potential conditions.....	85

Table 6b - Differences in weight gain of the tolerant rice variety (IR46) grown for 3 weeks between acid and non-acid sulfate soils over all redox potential conditions.....	85
Table 7 - Models and the subset of models for predicting weight gain of rice varieties (IR26 and IR46) in non-acid and acid sulfate soils over all redox conditions.....	90
Table 8 - Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of the IR26 rice variety in non acid sulfate soils.....	92
Table 9 - Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of the IR46 rice variety in non acid sulfate soils.....	93
Table 10 - Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of the IR26 rice variety in acid sulfate soils.....	95
Table 11 - Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of the IR46 rice variety in acid sulfate soils.....	97
Table 12 - Analysis of weight gain and pe+pH over two rice varieties in all soils.....	99
 Chapter Five	
Table 1 - Variables used in model building and their abbreviations.....	114
Table 2 - Variables used in model building and their linear correlations with log <sub>10</sub> weight gain of the sensitive (IR26) rice grown in non-acid and acid sulfate soils over all controlled pH-Eh levels.....	115
Table 3 - Variables used in model building and their linear correlations with log <sub>10</sub> weight gain of the tolerant variety (IR46) rice grown in non-acid and acid sulfate soils over all controlled pH-Eh levels.....	116
Table 4 - Model parameters selected for predicting log <sub>10</sub> weight gain of rice varieties (IR26 and IR46) grown in non-acid and acid sulfate soils over all controlled pH and redox potential conditions.....	117
Table 5 - Analysis of variance, regression coefficients and statistics of fit for dependent variable log <sub>10</sub> weight gain of the IR26 rice variety in non-acid sulfate soils.....	119
Table 6 - Analysis of variance, regression coefficients and statistics of fit for dependent variable log <sub>10</sub> weight gain of the IR46 rice variety in non-acid sulfate soils.....	121
Table 7 - Analysis of variance, regression coefficients and statistics of fit for dependent variable log <sub>10</sub> weight gain of the IR26 rice variety in acid sulfate soils.....	122
Table 8 - Analysis of variance, regression coefficients and statistics of fit for dependent variable log <sub>10</sub> weight gain of the IR46 rice variety in acid sulfate soils.....	124
Table 9 - Weight gain of both rice varieties over all acid and non-acid sulfate soils under controlled pH and redox potential conditions.....	125

Table 10 - Regression analysis of weight gain and pe + pH over two rice varieties and all soils.....	125
--	-----

## Chapter Six

Table 1 - Distribution of various fractions of Fe under controlled redox potential and pH conditions in acid sulfate soils.....	143
---	-----

Table 2 - Distribution of various fractions of Fe under controlled redox potential and pH conditions in non-acid sulfate soils.....	144
---	-----

Table 3 - Weight gain of two rice varieties grown over all non-acid and acid sulfate soils under controlled pH and redox potential conditions.....	148
--	-----

Table 4 - Concentration of selected Mn forms under controlled redox potential and pH conditions in acid sulfate soils.....	161
--	-----

Table 5 - Concentration of selected Mn forms under controlled redox potential and pH conditions in non-acid sulfate soils.....	162
--	-----

Table 6 - Fe uptake and Fe content in the shoot tissue (Shoot Fe) in IR26 and IR46 rice varieties grown over 3 weeks on acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	169
---	-----

Table 7 - Mn uptake and Mn content in the shoot tissue (Shoot Mn) in IR26 and IR46 rice varieties grown over 3 weeks on acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	183
---	-----

## Chapter Seven

Table 1 - Percent Al saturation of the CEC in acid and non-acid sulfate soils over all redox potential and pH conditions.....	
---	--

Table 2 - Percent Al saturation of the CEC in acid and non-acid sulfate soils over all redox potential conditions.....	
--	--

## Appendix

Table A1 - Preparations of stock solutions for nutrient culture solution.....	235
---	-----

## List of Figures

### Chapter Two

Figure 1 - The major steps during the course of pyrite oxidation .....	21
--	----

### Chapter Three

Figure 1 - Map showing approximate locations of soil sample sites.....	59
--	----

### Chapter Four

Figure 1 - Relative weight gain of rice shoot tissue for both varieties as affected by over all controlled redox of the five soils.....	86
Figure 2 - Relative weight gain of rice root tissue for both varieties as affected by over all controlled redox of the five soils.....	86
Figure 3 - Relative weight gain of IR26 shoot tissue as affected by over all controlled redox of the five soils.....	87
Figure 4 - Relative weight gain of IR26 root tissue as affected by over all controlled redox of the five soils	87
Figure 5 - Relative weight gain of IR46 shoot tissue as affected by over all controlled redox of the five soils.....	88
Figure 6 - Relative weight gain of IR46 root tissue as affected by over all controlled redox of the five soils.....	88
Figure 7 - Predicted weight gain of IR26 in non-acid sulfate soils.....	92
Figure 8 - Predicted weight gain of IR46 in non-acid sulfate soils.....	93
Figure 9 - Predicted weight gain of IR26 in acid sulfate soils.....	95
Figure 10 - Predicted weight gain of IR46 in acid sulfate soils.....	97

### Chapter Five

Figure 1 - Predicted log <sub>10</sub> weight gain for IR26 in non-acid sulfate soils.....	119
Figure 2 - Predicted log <sub>10</sub> weight gain for IR46 in non-acid sulfate soils.....	121
Figure 3 - Predicted log <sub>10</sub> weight gain for IR26 in acid sulfate soils.....	122
Figure 4 - Predicted log <sub>10</sub> weight gain for IR46 in acid sulfate soils.....	124
Figure 5 - Relative weight gain for IR26 shoot as affected by over all controlled pH-Eh	

of the five soils.....	127
Figure 6 - Relative weight gain for IR46 shoot as affected by controlled pH-Eh of the five soils.....	127
Chapter Six	
Figure 1 - Concentration of water-soluble Fe in acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	141
Figure 2 - Levels of exchangeable Fe in acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	146
Figure 3 - Distribution of reducible Fe in acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	149
Figure 4 - Relationship between measured $\text{Fe}^{2+}$ activities and pe+pH with theoretical solubility of selected Fe solid species over all pH-Eh levels of acid and non-acid sulfate soils planted to rice.....	154
Figure 5 - Plot of $\text{Fe}^{2+}$ activity as a function of exchangeable Fe in acid and non-acid sulfate soils over all pH-Eh levels.....	154
Figure 6 - Relationship between water soluble Fe and exchangeable Fe in acid and non-acid sulfate soils over all controlled redox potential and pH conditions.....	157
Figure 7 - Relationship between the divalent charge fraction due to Fe and exchangeable Fe in the soil solution ( $E'\text{-Fe}$ ) and the divalent charge fraction due to Fe on the CEC ( $E\text{-Fe}$ ).....	157
Figure 8 - Concentration of water-soluble Mn in acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	159
Figure 9 - Levels of exchangeable Mn in acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	163
Figure 10 - Distribution of reducible Mn in acid and non-acid sulfate soils under controlled redox potential and pH conditions.....	165
Figure 11 - Relationship between measured $\text{Mn}^{2+}$ activities and pe+pH with theoretical solubility of selected Mn solid species over all pH-Eh levels of acid and non-acid sulfate soils.....	167
Figure 12 - Relationship between the divalent charge fraction due to Mn in the soil solution ( $E'\text{-Mn}$ ) and the divalent charge fraction due to Mn on the CEC ( $E\text{-Mn}$ ).....	167
Figure 13 - Relationship between Fe uptake and Fe content in the shoot tissue for the IR 26 rice variety	171
Figure 14 - Relationship between Fe uptake and Fe content in the shoot tissue for the IR 46 rice variety.....	171

Figure 15 - Relationship between Fe content in the shoot tissue and $\text{Fe}^{2+}$ activity in the soil solution for the IR 26 rice variety.....	173
Figure 16 - Relationship between Fe content in the shoot tissue and $\text{Fe}^{2+}$ activity in the soil solution for the IR 46 rice variety.....	173
Figure 17 - Relationship between Fe content in the shoot tissue and water-soluble Fe in the soil solution for the IR 26 rice variety.....	174
Figure 18 - Relationship between Fe content in the shoot tissue and water-soluble Fe in the soil solution for the IR 46 rice variety.....	174
Figure 19 - Relationship between Fe content in the shoot tissue and the divalent charge fraction due to Fe in the soil solution ( $\text{E}^{\text{'}}\text{-Fe}$ ) for the IR 26 rice variety.....	175
Figure 20 - Relationship between Fe content in the shoot tissue and the divalent charge fraction due to Fe in the soil solution ( $\text{E}^{\text{'}}\text{-Fe}$ ) for the IR 46 rice variety.....	175
Figure 21 - Relationship between weight gain and Fe:Mn ratio in the shoot tissue for the IR 26 rice variety.....	177
Figure 22 - Relationship between weight gain and Fe:Mn ratio in the shoot tissue for the IR 46 rice variety.....	177
Figure 23 - Relationship between Fe:Mn ratio in the plant tissue and $\text{Fe}^{2+}$ activity in the soil solution for the IR 26 rice variety.....	179
Figure 24 - Relationship between Fe:Mn ratio in the plant tissue and $\text{Fe}^{2+}$ activity in the soil solution for the IR 46 rice variety.....	179
Figure 25 - Relationship between Fe:Mn ratio in the shoot tissue and $\text{pe}+\text{pH}$ for the IR 26 rice variety.....	180
Figure 26 - Relationship between Fe:Mn ratio in the shoot tissue and $\text{pe}+\text{pH}$ for the IR46 rice variety.....	180
Figure 27 - Relationship between Fe:Mn ratio in the shoot tissue and Fe:Mn activity ratio in the soil solution for the IR 26 rice variety.....	181
Figure 28 - Relationship between Fe:Mn ratio in the shoot tissue and Fe:Mn activity ratio in the soil solution for the IR 46 rice variety.....	181
Figure 29 - Relationship between Mn uptake and Fe:Mn activity ratio in the soil solution for the IR 26 rice variety.....	185
Figure 30 - Relationship between Mn uptake and Fe:Mn activity ratio in the soil solution for the IR 46 rice variety.....	185

## Chapter Seven

Figure 1 - Relationship between $\text{Al}^{3+}$ activity and the theoretical solubility of Al solid
--

species in acid and non-acid sulfate soils over all controlled redox conditions.....	199
Figure 2 - Relationship between $Al^{3+}$ activity and the theoretical solubility of Al solid species in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.....	199
Figure 3 - Relationship between water soluble Al and pH in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.....	202
Figure 4 - Relationship between $Al^{3+}$ activity and pH in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.....	202
Figure 5 - Relationship between percent Al saturation of the CEC and pH in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.....	203
Figure 6 - Relationship of water-soluble Al and pH in acid sulfate soils over all controlled redox conditions.....	203
Figure 7 - Relationship between the negative log of $Al^{3+}$ activity and pH in acid sulfate soils over all controlled redox conditions.....	205
Figure 8 - Relationship between percent Al saturation of the CEC and pH in acid sulfate soils over all controlled redox conditions.....	205
Figure 9 - Relationship between the negative log of $Al^{3+}$ activity and pH in non-acid sulfate soils over all controlled redox conditions.....	206
Figure 10 - Relationship between the negative log of $Al^{3+}$ activity and percent Al saturation of the CEC acid sulfate soils over all controlled redox conditions.....	206
Figure 11 - Relationship between $Al^{3+}$ activity and percent Al saturation of the CEC in non-acid sulfate soils over all controlled redox conditions.....	207
Figure 12 - Relationship of water-soluble Al and percent Al saturation of the CEC in acid sulfate soils over all controlled pH and redox conditions.....	210
Figure 13 - Relationship of water-soluble Al and percent Al saturation of the CEC in acid sulfate soils over all controlled redox conditions.....	210
Figure 14 - Relationship between Al uptake and the negative log of $Al^{3+}$ activity for both rice varieties in acid and non-acid sulfate soils over all controlled redox conditions..	212
Figure 15 - Relationship between Al uptake and Al content for both rice varieties in acid and non-acid sulfate soils over all controlled redox conditions.....	212
Figure 16 - Relationship between Al uptake and percent Al saturation of the CEC for both rice varieties in acid sulfate soils over all controlled redox conditions.....	214
Figure 17 - Relationship between the negative log of ion activity product of variscite and pH in acid sulfate soils over all controlled redox conditions.....	214
Figure 18 - Relationship between Al uptake and percent Al saturation of the CEC for IR26	



variety in acid sulfate soils over all controlled pH and redox potential conditions.....	216
Figure 19 - Relationship between root dry weight and the negative log of $Al^{3+}$ activity for both varieties in acid and non-acid sulfate soils over all controlled pH and Eh....	216
Figure 20 - Relationship between shoot weight gain and the negative log of $Al^{3+}$ activity for both varieties in acid and non-acid sulfate soils over all controlled pH and Eh....	217
Figure 21 - Relationship between shoot weight gain and the negative log of $Al^{3+}$ activity for the IR26 variety in acid and non-acid sulfate soil over all controlled pH and Eh.....	217
Figure 22 - Relationship between shoot weight gain and the negative log of $Al^{3+}$ activity for the IR46 variety in acid and non-acid sulfate soil over all controlled pH and Eh.....	218
Figure 23 - Relationship between Ca uptake and the negative log of $Al^{3+}$ activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH and Eh.....	218
Figure 24 - Relationship between K uptake and the negative log of $Al^{3+}$ activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH and Eh....	219
Figure 25 - Relationship between Mg uptake and the negative log of $Al^{3+}$ activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH and Eh....	219
Figure 26 - Relationship between Mn uptake and the negative log of $Al^{3+}$ activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH and Eh....	220
Appendix	
Figure A1 - The apparatus for incubation of the soil suspension at controlled pH and redox at controlled pH and redox potential conditions.....	231
Figure A2 - Diagram of plant growth/soil incubation apparatus after transplanting rice (a), and plexiglass plate (b) designated for use in supporting rice seedlings in controlled system.....	232
Figure A3 - Apparatus for filtering supernatant solutions under a $N_2$ atmosphere.....	233

## List of Plates

### Appendix

Plate 1 - Differences in growth of tolerant and sensitive rice varieties (IR46 and IR26, respectively) grown over a 3-week period in an acid sulfate soil (Sulfic Tropaquept, Rangsit very acid) and a non-acid sulfate soil (Typic Tropaquept, Ratchaburi) under controlled redox conditions.....	234
--	-----

## ABSTRACT

The effects of controlled pH and redox potential (Eh) conditions on transformations of several metals and their effects on rice growth were studied in laboratory microcosms using acid sulfate (Sulfic Tropaquept) and non-acid sulfate (Typic Tropaquept) soil materials from Thailand. Some microcosms were incubated at selected controlled Eh conditions (500, 250, 50, and -150 mV). Others were incubated at controlled pH and Eh levels (3.5, 4.5, and 5.5 and redox potential levels  $\geq 500$ , 250, and 50 mV respectively). Acid sulfate soil-tolerant and sensitive rice varieties (IR 46 and IR 26, respectively) were used in this study. Results indicated water-soluble Fe and exchangeable Fe were inversely related to both pH and Eh, and reducible Fe was positively related. Redox potential and pH had the same effect on water-soluble Mn as Fe. However, Eh had less of an effect on Mn than on Fe.

Water-soluble Al and percent Al saturation of the CEC was negatively related to pH in both soil types under controlled pH and Eh conditions, but was negatively related to pH in only acid sulfate soils under controlled Eh conditions. Aluminum activity was negatively correlated with pH in both soil types and over all controlled conditions.

Rice uptake of Fe increased with decreasing Eh and pH. Iron uptake was significantly correlated with water-soluble Fe,  $\text{Fe}^{2+}$  activity, and  $\text{E}^{\text{h}}\text{-Fe}$ . The IR 26 accumulated Fe more than the IR 46.

The Mn content in shoot tissue was positively correlated with Eh and pH. Iron possibly had an antagonistic effect on Mn uptake.

Aluminum uptake of both rice varieties correlated best with  $\text{Al}^{3+}$  activity in both soil types under controlled Eh conditions. Under controlled pH and Eh conditions, IR 26 uptake of Al was positively related to percent Al saturation of the CEC in only acid sulfate soils whereas no relationship was observed for IR 46 uptake of Al in both soil types.

In general, growth of rice was negatively related to the Fe:Mn ratio in shoot tissue and  $\text{Al}^{3+}$  activity but positively related to pe + pH and  $\text{Zn}^{2+}$  activity.

Iron solubility was probably controlled by amorphous  $\text{Fe}(\text{OH})_3$  at high pe + pH and goethite at low pe + pH levels. Manganese solubility was regulated by cation exchange processes. Jurbanite and amorphous  $\text{Al}(\text{OH})_3$  may control Al solubility at low and high pH conditions, respectively.

## **Chapter One**

### **Introduction**

## INTRODUCTION

Acid sulfate soils are a serious problem because of their adverse effect on crop production and their abundance in regions of the world where additional food production is especially important. These soils are world-wide in distribution and occupy an area of about 12.5 million ha (FAO/UNESCO, 1979). They occur mainly in the tropics, but are found in temperate zones as well (Kawalec, 1973). Acid sulfate soils are found in low lying coastal areas and developed from recent or sub-recent marine sediments (Pons, 1973), although some are also found in inland areas (Kawalec, 1973; Poelman, 1973).

Acid sulfate soils develop from potential acid sulfate soils which are characterized by the accumulation of pyrite ( $\text{FeS}_2$ ). Pyrite formation requires: a) sulfide derived from reduction of dissolved sulfate from seawater by sulfate-reducing bacteria (i.e. Desulfovibrio desulfuricans) in anaerobic environments, b) ferrous iron from the reduction of insoluble ferric compounds in sediments, c) organic matter as an energy source for bacteria and, d) a predominately anaerobic environment and, e) periods of limited aeration for oxidation of all sulfide to disulfide. Pyrite oxidizes upon long-term soil drainage producing sulfuric acid. If the acid exceeds the acid-neutralizing capacity of the soil, the soil then becomes acidic. In acid sulfate soils, the excess acid often decreases the soil's pH to less than 4. The acid produced has a major effect on chemical and microbial processes in these soils. Plant toxins such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{S}$ , and  $\text{CO}_2$ , are often generated in amounts beyond the critical toxic levels for normal

plant growth. Also, these soils usually contain low levels of available essential nutrients which also limits crop production.

Apart from their acidic nature acid sulfate soils possess at least a few characteristics making them suitable for rice production. They are located in areas well suited for flooded rice cultivation. This is important in densely populated areas in developing countries where rice is the main diet, especially in the coastal areas of southeast Asia and west Africa.

Thailand, one of the major rice-growing countries in southeast Asia, has about 1.5 million ha of actual and potential acid sulfate soils (Pons, and Van der Kevie, 1969) of which approximately 0.8 million ha occurs in the Bangkok Plain (Kevie, and Yenmanas, 1972). The rest are located around the coastal areas in the Southeastern and Southern region of the country. Most acid sulfate soils in the Bangkok Plain are used for rice cultivation, often with limited production success. The Thai government has supported an intensive research effort to improve acid sulfate soils for many years and this effort continues. The genesis and chemistry of acid sulfate soils of Thailand has been described by van Breemen (1976), and a number of research papers on the adverse effects of acid sulfate soils to rice in Thailand have been published (Jugsujinda et al., 1971; Sombatpanit, 1975; Attanandana and Vacharotayan, 1983; Charoenchamratcheep et al., 1982; Maneewon et al., 1982; Kanareugsa et al., 1972; Uwaniyom and Charoenchamratcheep, 1983; Osborne, 1984). A common finding of this work is that the application of low rates of lime plus N and P fertilizer is an important means of improving rice yield on certain classes of acid sulfate soils.

A review of published papers on acid sulfate soils indicate a lack of research on certain aspects of these soils. There is little information on the role of physicochemical parameters such as redox potential on the transformations of both nutrients and materials toxic to plants. Flooded rice cultivation offers a benefit of retarding pyrite oxidation to some degree. However, flooding soils will affect the plant availability of several soil components due to changes in both pH and redox potential conditions of the soils. Reducing conditions (low redox potential) may render toxic metals more soluble in the soil solution, thereby aggravating the adverse effects of acid sulfate soils on plant growth. Oxidized conditions (high redox potential), on the other hand, often creates a deficiency of essential nutrients. Similarly, the rather wide range of pH occurring during flooding and drying cycles can cause either high or low concentrations of both toxic and beneficial substances. Thus, there is a great need to study the effects of various pH and redox potential conditions on the transformations and plant availability of several soil components on rice growth in acid sulfate soils.

Fortunately, research on the role of physicochemical parameters such as pH and redox potential in acid sulfate soils can be done in the laboratory. The laboratory microcosm that has been developed in the Laboratory for Wetland Soils and Sediment (LWSS) at Louisiana State University is ideally suited for this type of research in that pH and redox potential of the soil can be closely controlled or monitored during the period of rice growth (Patrick et al., 1973; Reddy, Jugsujinda, and Patrick, 1976). This system has been utilized for the study of redox chemistry of acid sulfate soils of Thailand, a project



that was funded by USAID and initiated in 1982 at Louisiana State University.

The main objective of this research was to study the activity and transformations of the important components of acid sulfate soils and their effects on rice growth under various controlled pH and redox potential conditions. Hopefully, the findings of research such as this will identify the adverse factors affecting growth of rice in acid sulfate soils of Thailand and ultimately contribute to management practices that will improve the productivity of these soils.

## Chapter Two

### Literature Review: Acid Sulfate Soils

## LITURATURE REVIEW: ACID SULFATE SOILS

### THE OCCURRENCE, GENESIS AND CHEMISTRY

#### Definition of acid sulfate soils

Acid sulfate soils are soils that have the following characteristics: a) a pH below 4 within the 50-cm depth due to sulfuric acid formed by oxidation of pyrite (cubic  $\text{FeS}_2$ ) (van Breemen, 1982), b) a sulfuric horizon that is composed of mineral or organic soil material with a pH  $< 3.5$  and yellow jarosite mottles (USDA, 1975), and, c) waterlogged soils that contain mineral or organic materials with  $\geq 0.75\%$  sulfur and less than three times as much carbonate ( $\text{CaCO}_3$  equivalent) as sulfide sulfur (USDA, 1975).

Van Breemen (1982) proposed to define sulfidic material and a sulfuric horizon as follows: "Sulfidic material is waterlogged mineral, organic, or mixed soil material with a pH of 3.5 or higher, containing oxidizable sulfur compounds, which, if incubated as a 1-cm thick layer under moist, aerobic conditions (field capacity at room temperature), shows a drop in pH of at least 0.5 unit to a pH below 3.5 within 4 weeks."

"A sulfuric horizon is composed of mineral, organic, or mixed soil material, generally containing yellow jarosite mottles with a hue of 2.5Y or yellower, and a chroma of 6 or more, that has a pH  $\leq 3.5$  (1:1 in water) and contains at least 0.05% water soluble sulfate".

Para or pseudo acid sulfate soils are soils that are influenced by sulfuricization, but which are not sufficiently acid (pH is not below 4) to be classified as sulfic subgroups (Pons, 1973). They may either

develop due to relatively small amounts of pyrite in the parent material, or represent the post-sulfuricization stage of soils that were once acid sulfate soils. They can normally be classified in other taxons, often as Tropaquepts or Haplaquepts.

Potential acid sulfate soils are either Sulfaquepts (Aquepts with sulfidic material within 50 cm of the mineral soil surface), Sulfic Fluvaquepts (Fluvaquepts with sulfidic material between the 50 and 100-cm depth), or Sulfihemists (Histosols with sulfidic material within the 100-cm depth) (van Breemen, 1982).

Acid sulfate soils can be classified as Sulfaquepts (Aquepts with a sulfuric horizon that has its upper boundary within 50 cm of the soil surface), Sulfic Tropaquepts (Tropaquepts with jarosite mottles and a pH 3.5 to 4 somewhere within the 50-cm depth, or with jarosite mottles and a pH  $<4$  in some part between 50 to 150 cm depth), or Sulfic Haplaquepts (comparable to Sulfic Tropaquept, but under a more temperate climate) (van Breemen, 1982).

#### Occurrence of acid sulfate soils in the world

Acid sulfate soils are worldwide in distribution in nearly all climatic zones. Most acid sulfate soils are located in coastal areas where they developed in recent or sub-recent marine sediments. However, the sulfidic materials, capable of producing acid sulfate on oxidation, are not exclusively located in recent marine sediments, but are also found in many inland sedimentary rocks. If these pyritic rocks are brought to the surface, acidification may become a serious problem to vegetation, or may cause pollution of streams with sulfuric acid (Pons, 1973). Inland acid sulfate materials are reported in several areas,

i.e. the pyritic papayrus peats of Uganda (Chenery, 1954), pyritic sands in a few valleys in the eastern Netherlands (Poelman, 1973; van Wallenberg, 1973), the Solfatara muds of Java (Chenery, 1954), deposits in a lake bed in the Taiga region of the USSR (Chenery, 1954), papyrus peat in the Kigezi District of Uganda (Chenery, 1954), in Germany (Buurman et al., 1973), Canada (Clark et al., 1961; Pawluk and Dudas, 1978), and in various places in the USA such as North Carolina (Furbish, 1963), Maryland (Wagner et al., 1982), and Texas (Carson and Dixon, 1983).

Pons and van Breemen (1982) reported that acid sulfate soil areas, based on the FAO/UNESCO Soil Map of the World 1971-1979, occupied a total of about 12.6 million ha. These acid sulfate soils occur in Asia and the Far East, Africa, Latin America, and North America in areas of 6.7, 3.7, 2.1, and 0.1 million ha respectively.

#### Distribution of acid sulfate soils in Southeast and East Asia

Van Breemen and Pons (1978) summarized the known occurrence of actual and potential acid sulfate soils in Southeast and East Asia as shown in Table 1. The data do not include millions of ha of shallow peat land in Indonesia underlain by potentially acid sediments.

#### Acid sulfate soils in the Central Plain of Thailand

The soils in the Central Plain of Thailand are classified into four suitability classes for rice cultivation according to soil mapping units and soil productivity potential (Kevie and Yenmanas, 1972) as listed below.

Table 1. Distribution of acid sulfate soils in Southeast and East Asia ( after van Breemen and Pons,1978).

Country	Area (thousand ha)	Reliability	Soil Classification
Bangladesh			
Chittagong	200 <sup>b</sup>	-	Sulfaquents, Sulfaquepts
Khulna Sunderbans	200 <sup>b</sup>	-	Sulfaquents
Burma	180 <sup>b</sup>	-	Sulfaquents
China			
Coastal Areas	67	+	Sulfaquepts, Sulfic
Haplaquepts			
South of Fukien			
India			
Kerala	110	+	highly organic Sulfaquepts, partly (26,000 ha) affected by salinity
W. Bengal	280 <sup>b</sup>	-	Sulfaquents
Indonesia			
Kalimantan and Sumatra	2,000	-	mainly highly organic Sulfaquents and Sulfaquepts and Sulfihemists
Khmer	200	+	mainly Sulfaquepts
Japan	4	++	Sulfaquepts, Sulfic
	17	++	Haplaquepts potentially acid shallow sea bottom
Malaysia			
W. Maiaysia	150	+	highly organic Sulfaquents and Sulfaquents,perhaps also Sulfihemists
Sarawak	10		mangrove marshes acidified due to lobster mounds
Philippines			
Luzon, Mindanao	7	-	Sulfic Tropaquepts Sulfaquepts,highly organic Sulfaquepts
South Korea	3	+	Sulfic Haplaquepts,Sulfaquents
Thailand			
Bangkok Plain	600	++	Sulfic Tropaquepts (55,000 ha) Sulfaquents ( $\pm 10,000$ ha), Sulfaquepts (50,000 ha)
Southeast Coast	20	+	Sulfaquepts, Sulfaquents
Peninsula	50	+	Sulfaquepts, partly highly organic
Vietnam			
Mekong Delta	1,000	-	mainly Sulfaquepts (partly organic), smaller areas of Sulfic Tropaquepts and highly organic Sulfaquents

a. Reliability of hectarage estimate: - = poor, + = fair, ++ = good.

b. These figures are probably gross overestimates ( van Breemen and Pons, 1978 ).

1. P-I - Soils very well suited for rice, having no limitation due to acidity.

2. P-IIa - Soils well suited for rice, having slight limitations due to moderate acidity that restrict their use for rice production. The term "Moderately Acid Soil" is assigned to this group and the area represented is about 0.3 million ha (P=paddy, a=acid in the suitability nomenclature).

3. P-IIIa - Soils moderately suited for rice, having moderate limitations due to severe acidity that restricts their use for rice production, and, which also require special management. The term "Severely Acid Soils" is assigned to this group and the area affected is about 0.2 million ha.

4. P-IVa - Soils poorly suited for rice, having a high limitation due to extreme acidity that restricts their use for rice production, and which require special management. The term "Extremely Acid Soils" is assigned to this group, and the area affected is 70,000 ha.

Kevie and Penmanas (1972) described 16 non-acid marine soil series (including one potential acid sulfate soil) and 20 acid sulfate soil series in the Bangkok Plain.

The soils in Class P-I are nonacid sulfate marine and riverine soils or brackish water deposit para acid sulfate soils (Pons, 1973). Most of these soils fall into the Typic Tropaquept subgroup. The soils in Class P-IIa are mature acid sulfate soils and most are classified into the Sulfic Tropaquept subgroup. The soils in Class P-IIIa are very mature acid sulfate soils and most are classified into the Sulfic Tropaquept subgroup. The soils in Class P-IVa are somewhat mature to young acid sulfate soils and are classified primarily in the Sulfic

Tropaquept subgroup with a few in the Typic Sulfaquept subgroup as shown in Table 2. In addition, acid sulfate peat soils found in the Southern Peninsular are thought to be in the Sulfihemist Great Group. The acid sulfate soils (Sulfic Tropaquepts) produce rice yields of 0.6 to 1.5 t ha<sup>-1</sup> compared to the average yield of 2.5 t ha<sup>-1</sup> for Typic Tropaquepts (Fukui, 1973; Komes, 1973a, 1973b; Rojanasoonthon, 1978). The acid sulfate soils in the Central Plain of Thailand are generally well developed physically, but they are unproductive because of low availability of phosphate, retarded microbial activities, as well as several other growth-inhibiting factors.

#### Genesis of acid sulfate soils

The essential requirements for acid sulfate soils formation are: 1) a physiography or favorable environment that provides the potential for acid sulfate soils development, 2) the formation of pyrite in those locations, and subsequently, 3) the oxidation of pyrite following natural or artificial drainage. Pons and van der Kevie (1969) summarized the genesis of acid sulfate soils as two main processes: a geogenetic process and a pedogenetic process. Formation of pyrite (sulfidization or pyritization) is the main geogenetic process, whereas oxidation of pyrite, acid neutralization, and formation of products due to pyrite oxidation are the important steps of the pedogenetic process.

#### Physiography and formation of potential acidity

Three land systems constitute environments that are suitable for the formation of potential acidity (Pons et al., 1982)

- a) saline and brackish swamps and marshes;



Table 2. Classification and area in hectares of the acid sulfate soils in the Central Plain of Thailand.\*

Soil Series	pH (0-30 cm depth)	Area (hectares)
Well suited for paddy land (P IIa)		
1. Maha Phot(Ma)	4.5-5.5	62,664
2. Ayutthaya(Ay)	4.5-7.0	78,205
3. Ay/Ma complex	4.5-7.0	7,475
4. Sena(Se)	4.5-5.0	147,814
5. Tha Khwang	4.5-5.0	419
Total of P IIa		296,577
Moderately suited for paddy land (P IIIa)		
6. Se/Rs complex	4.5-5.0	13,062
7. Rangsit(Rs)	4.5-5.0	180,222
8. Rangsit high phase	4.5-5.0	168
9. Thanyaburi	4.5-5.0	26,518
Total of P IIIa		219,970
Poorly suited for paddy land (P IVa)		
10. Rangsit very acid phase	3.5-4.5	51,240
11. Ongkharak	4.0-4.5	12,323
12. Cha-am	3.0-4.4	8,811
Total of P IVa		72,374

\* modified from van der Kevie and Yenmanas (1972).

Soil series 1-11 are Sulfic Tropaequept.

Soil series 12 is Typic Sulfaquept.

- b) saline and brackish lagoons and lakes;
- c) poorly drained inland valleys with an influx of sulfate-rich water.

The most important environment is the saline and brackish swamp and marsh areas under herbaceous vegetation such as mangrove swamps (Rhizophora sp. and Avicennia sp.). The dense vegetation serves as a source of metabolizable organic matter needed for pyrite formation. The tidal cycles supply sediment, dissolved sulfate, and removes soluble by-products.

Coastal land formation and the development of potential acidity in the sediment of those areas is affected by relative sea level changes. Following the last glaciation period, the sea level rose rapidly (Blackwelder et al., 1979) and leveled off at a maximum some 5,500 years B. P. This high sea level has remained fairly stable with perhaps only a slight drop after reaching its maximum. The rise in sea level was approximately balanced by the sediment supply, resulting in a vertical build-up of sediments. Lateral coastal accretion started after the late Holocene stabilization of the sea level (Pons et al., 1982).

Pons et. al. (1982) indicated that the rapid lateral coastal accretion after stabilization of the sea level cause rapid shifting of the intertidal zone and mangrove and reed marshes within a relatively short time, and thus limited the suitable period for pyrite formation. The rapid aggrading coast also provides an unfavorable chemical environment for pyritization. They also suggested that rapid coastal accretion in many area increased with increasing upstream erosion and downstream sedimentation due to heavy deforestation within the last 1,000 to 2,000 years.

Pons et. al. (1982) summarized the effect of sedimentation rate with several examples in many parts of the world. Rapid rises in relative sea level, as after the last glaciation, caused deposition of extensive, thick and highly pyritic sediments (examples: interior parts of the Chao Phraya, Mekong and Orinoco deltas, parts of Sumatra, and old sea clays of Holland). After stabilization of the sea level, some 5000 years B. P., pyrite contents remained low where high rates of sedimentation and coastal accretion caused a rapid shift of the intertidal zone (Irrawaddy and Mekong deltas, Guyana coast). High pyrite contents in the most recent sediments are associated with low sedimentation rates (e.g., along the Saigon, Niger, and Gambia rivers), or with regions with a high density of tidal creeks. In humid climates, very low sedimentation rates result in the formation of pyritic peaty material on top of older pyritic clay (the Niger delta and western Netherlands).

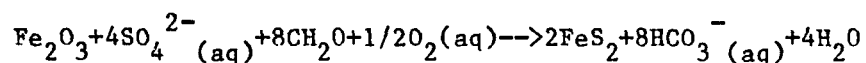
#### Pyrite formation (Geogenetic process)

The genesis of potential acid sulfate soils is a result of the formation of pyrite, a mineral that is commonly 2-10% of the mass of these soils (van Breemen and Pons, 1978). Sedimentary pyrite formation involves:

- a) reduction of sulfate to sulfides by sulfate reducing bacteria decomposing organic matter,
- b) partial oxidation of sulfides to polysulfides or to elemental sulfur, and,
- c) either formation of FeS (from Fe-oxides or Fe-silicates) followed by combination of FeS and S to  $\text{FeS}_2$  (pyrite) (Rickard, 1973;

Goldhaber and Kaplan, 1974; van Breemen, 1976), or direct precipitation of pyrite ( $\text{FeS}_2$ ) from dissolved  $\text{Fe}^{2+}$  and polysulfides (Roberts et al., 1969; Goldhaber and Kaplan, 1974).

Regardless of the actual pathway, the following overall reaction describes complete pyrite formation (pyritization or sulfidization) with ferric oxide in a sediment as the source of iron:



The essential ingredients for pyrite formation are:

- a) a source of dissolved sulfate continuously supplied over an appreciable period. Usually this source will be seawater, brackish tidal water, or sometimes sulfate-rich ground waters (Thompson, 1972; Poelman, 1973),
- b) iron-containing minerals (iron oxides and hydroxides) present in the sediments,
- c) metabolizable organic matter ( $\text{CH}_2\text{O}$ ) to serve as the energy source for sulfate-reducing bacteria,
- d) sulfate-reducing bacteria, (which are almost always present),
- e) a predominately anaerobic environment which is provided by waterlogged sediments that are rich in organic matter, and,
- f) periods of limited aeration (in space or time) for oxidation of all sulfide to disulfide.

As acid sulfate soils are subjected to prolonged submergence, it is believed that Desulfovibrio desulfuricans (a sulfate reducing bacterium) takes part in the formation of pyrite from ferric sulfates (Ivarson et al., 1982). Sulfate reduction results in the production of dissolved sulfide ( $\text{H}_2\text{S}$  aq. and  $\text{HS}^-$  aq.). Dissolved sulfide reacts with sedimentary iron and forms an intermediate metastable iron sulfide such

as mackinawite (tetragonal FeS). In the presence of oxidants, such as oxygen or ferric iron, part of the dissolved or solid sulfide can be oxidized to elemental sulfur. Elemental sulfur reacts with dissolved sulfide to form aqueous polysulfide, which in turn reacts with FeS to form pyrite, FeS<sub>2</sub>, either directly or with greigite (cubic Fe<sub>3</sub>S<sub>4</sub>) that is formed as an intermediate metastable sulfide (Goldhaber and Kaplan, 1974). The pathway that includes greigite requires atmospheric oxygen to yield framboidal pyrite. In the absence of oxygen, the non-framboidal pyrite is formed (Rickard, 1975; Sweeny and Kaplan, 1973). Carbonate alkalinity (mainly HCO<sub>3</sub><sup>-</sup>) arising from oxidation of organic matter by sulfate reducing bacteria leads to supersaturation and precipitation of alkaline earth carbonates (Berner, 1966, 1971; Presley and Kaplan, 1968). However, the carbonate alkalinity (HCO<sub>3</sub><sup>-</sup>) produced during sulfate reduction is normally not conserved in the sediment by precipitation of calcium carbonate (although groundwater in tidal marshes is commonly supersaturated with calcite), but is carried away by tidal action. This separation between immobile potential acidity and mobile alkalinity (HCO<sub>3</sub><sup>-</sup>) is an important process for later acidification (van Breemen, 1973).

Little is known about the mechanism of pyrite formation in situ (Pons et al., 1982). Pyrite has been produced in the laboratory by several workers, and they indicated pyrite formation from the reaction shown acid-volatile sulfide (FeS) with excess solid elemental sulfur as of below (Roberts et al., 1969; Berner, 1970).



The rate of this reaction is slow for forming measurable amounts of pyrite (Goldhaber and Kaplan, 1974). Roberts et. al. (1969) noted more

than seven days were required to form pyrite by the above reaction. However, the production of pyrite is quite rapid through direct precipitation between aqueous ferrous ions and polysulfide ions according to a report of Rickard (1975).



In general, pyrite formation occurs preferentially under low pH conditions. For instance, Berner (1964) produced pyrite in 14 hours at pH 4 and room temperature by direct precipitation. Roberts et. al. (1969) obtained similar results at pH 4 to 6.

#### Pedogenetic process

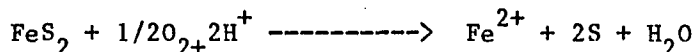
The pedogenetic process consists of three primary steps: a) oxidation of pyrite, b) neutralization of acidity, and, c) formation of products obtained from oxidation and neutralization.

#### Pyrite oxidation

Pyrite oxidation is a complicated process which includes several types of oxidation-reduction reactions, hydrolysis, complex ion formation, solubility controls, and kinetic effects (Nodstrom, 1982). Drainage plays an important role in initiating the oxidation of pyrite and the generation of acidity. Drainage may occur naturally, as a result of a fall in relative sea level or reduced frequency of tidal flooding, or by some combination of deliberate exclusion of tidal action and lowering of the water table (Dent, 1986). Appreciable aeration of potential acid sulfate soils and subsequent acidification start only after the water table stays below the upper part of the highly pyritic zone for several weeks. This is brought about either gradually by

natural processes (coastal accretion or a relative decrease in sea level) or, more abruptly, by impoldering (van Breemen and Pons, 1978). In many of the mangrove areas in Southeast Asia still under tidal influence, acidification takes place as subsoil is brought to the surface by the mound building mud lobster Thalassina anomala (Andriess et al., 1973).

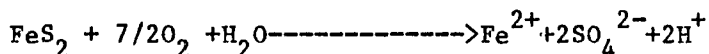
There are several stages of pyrite oxidation involving both chemical and microbiological processes. Dissolved oxygen reacts slowly with pyrite, producing ferrous iron, and sulfur:



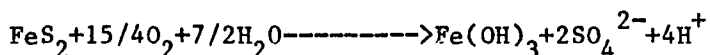
Sulfur is further oxidized by oxygen:



The above equations demonstrate that pyrite exposed to the atmosphere oxidizes chemically giving  $\text{Fe}^{2+}$ , sulfate, and sulfuric acid. The summary reaction is :

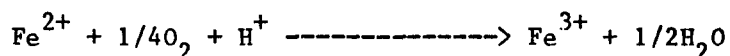


Complete oxidation and hydrolysis of iron to ferric oxide yields two moles of sulfuric acid per mole of pyrite (van Breemen, 1982):

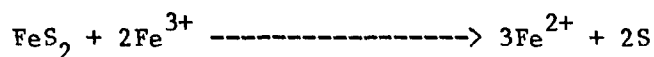


The above reaction is sulfuricization (Fanning, 1978). At a near neutral soil pH, the process is relatively slow, but it becomes faster as acidity increases. In the presence of oxygen, the ferrous iron ( $\text{Fe}^{2+}$ ) produced by these reactions is oxidized to ferric iron which is normally a slow reaction at low pH (Singer and Stumm, 1970). However, Thiobacillus ferrooxidans, which is optimally active between pH 2.5 and 5.8 (Goldhaber and Kaplan, 1974), is effective in oxidizing reduced

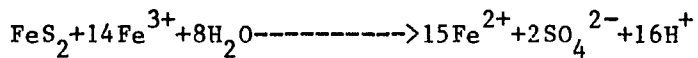
sulfur species and also ferrous iron (Temple and Colmer, 1951) at these low pH levels and thus returns ferric iron to the system:



When the pH of an oxidized system is low enough for  $\text{Fe}^{3+}$  to exist in solution,  $\text{Fe}^{3+}$  may catalyse the oxidation of pyrite. Especially as the pH of an oxidized system is brought below 4, the soluble  $\text{Fe}^{3+}$  present promotes rapid oxidation of pyrite according to the reaction below:



The half time of this reaction is on the order 20-100 minutes (Stumm and Morgan, 1981). The oxidation of pyrite with dissolved ferric iron is very rapid and the overall oxidation may be described as:

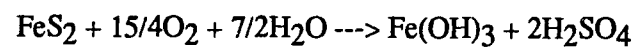


The oxidation of pyrite by  $\text{Fe}^{3+}$  ions is limited by high pH because  $\text{Fe}^{3+}$  is appreciably soluble only at low pH (pH~4), and Thiobacillus ferrooxidans does not function at a higher pH. In soils of high pH, ferric oxides and pyrite may be in close association, but the rate of oxidation by this mechanism will be limited by the insolubility of ferric iron. Nodstrom (1982) summarized the oxidation of pyrite as shown in Figure 1. Oxidation rates are pH dependent for pH levels higher than 4. Below pH 3, the oxidation rates are independent of pH. Elemental sulfur and ferrous iron are produced initially. At higher pH levels, ferrous iron is oxidized to ferric hydroxide.

Following the initiation phase is the acid-generating phase where sulfuric acid is formed from elemental sulfur. Once the pH of the system is brought below 3, ferric iron rapidly oxidizes pyrite and this is called the catalytic phase. Thiobacillus ferrooxidans catalyzes the



### Overall Stoichiometry



ACID MEDIA ( $\text{pH} \leq 3$ )

---

SLIGHTLY ACID TO BASIC MEDIA ( $\text{pH} \geq 4$ )

---

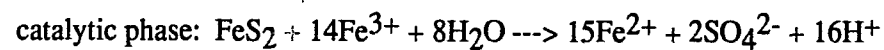
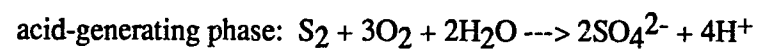
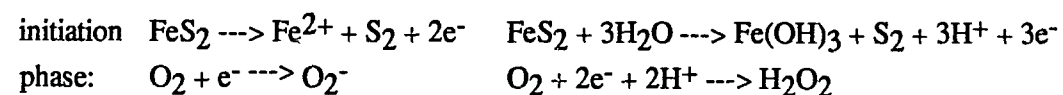


Figure 1. The major steps during the course of pyrite oxidation (after Nordstrom, 1982).

oxidation of ferrous to ferric iron providing the supply of ferric iron to the system.

#### Neutralization of acidity

Acid sulfate soils form where the quantity of sulfuric acid, formed by oxidation of reduced S compounds, exceeds the acid-neutralizing capacity of the soil. The neutralizing capacity of the soil consists of:

a) carbonates, b) exchangeable bases, and, c) easily-weatherable silicates.

Calcium carbonate is an effective neutralizing component, especially at pH levels close to neutrality (Pons et al., 1982). If one mole of pyrite is equivalent to four moles of  $H^+$  upon oxidation, the acidity from the oxidation of 1 percent by mass of pyrite sulfur is approximately balanced by 3 per cent of  $CaCO_3$  (Pons et al., 1982; Dent, 1986). Calcium carbonate contents are low in most marine sediments of the humid tropics, but may be appreciable in sediments of arid and humid temperate regions. If seawater is entrapped in a sediment and all dissolved sulfate is reduced to sulfide, the increase in  $HCO_3^-$  would lead to supersaturation with calcium carbonate. However, calcium carbonate rarely precipitates due to an inhibiting effect of dissolved organic matter (Berner, 1970). Van Breemen (1973) noted the alkalinity of interstitial waters in non-alkaline soils rarely exceeds  $10 \text{ meq L}^{-1}$ , and, a moisture contents up to 100%, the dissolved alkalinity is estimated to contribute to the neutralization of 1 meq of acid per 100 g of soil. Sea-water contains low alkalinity (2 to  $2.5 \text{ mmol L}^{-1}$ ) which cannot be considered an effective buffering agent, even if large

quantities are available. It has been noted that in the eastern part of the Central Plain of Thailand, both the influx of somewhat alkaline floodwater from the riverine part of the delta, and a long period of seasonal flooding with moderately alkaline water (2 to 5 mmol  $\text{HCO}_3^- \text{ L}^{-1}$ ) might have increased the pH of the upper horizons of acid sulfate soils to near neutrality in certain areas (van Breemen, 1976).

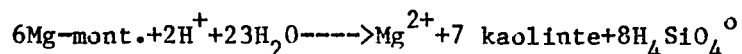
#### Exchangeable bases

In soils with high organic matter and/or clay, the sorption of  $\text{H}^+$  associated with the formation of non-exchangeable acidity can contribute significantly to the neutralization of strong acid under neutral to slightly acid conditions. For instance, between 5 and 10 meq of acid per 100 g of soil is immobilized by the exchange complex of typical acid sulfate soils in Thailand when the pH drops from 7.5 or 7 to about 5 (van Breemen, 1973). Van Breemen (1973) also noted that at a lower pH, more  $\text{H}^+$  can be immobilized because exchangeable  $\text{Al}^{3+}$  enters the solution. The total amount of acid immobilized by the exchange complex of an acid soil is approximately equivalent to the difference between the CEC at pH 7 and the amount of exchangeable bases at a soil pH of 3.5 to 4. These amounts have been shown to be 10 to 30 meq /100 g of acid sulfate soils (pH 3.5 to 4) from Thailand (Sombatpanit, 1970). Most marine-derived heavy clay soils have appreciable amounts of smectites and their exchange complex, when fully saturated with bases, is capable of inactivating most of the acidity released by the oxidation of up to 0.5% pyrite-S so that the pH will not drop below 4.0. If the clay fraction is predominantly kaolinitic, or if clay contents are low, less

than 0.5% pyrite-S may make the soil potentially acid (Pons et al., 1982).

#### Weatherable mineral

Because of their large specific surface area and associated negative charge, clay minerals in soil can be important  $H^+$  consumers. Of all the clay minerals, kaolinite is the end product of most weathering processes under acid conditions, and occurs widely in acid sulfate soils (van Breemen, 1973). At pH levels less than 4, the dissolution of silicate clays with a concurrent consumption of  $H^+$  is observed, though the rate of reaction is slow, and, in most cases, appears unlikely to prevent the development of acid sulfate conditions. However, the severity of acidity is certainly reduced to a degree. As an example, the transformation of Mg montmorillonite to kaolinite can be written as below (Van Breemen, 1973).



#### Products from oxidation and neutralization

##### (a) Jarosite

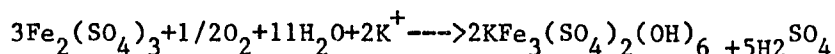
Jarosite is a mixture of basic sulfates with the general formula  $AB_3(SO_4)_2(OH)_6$  in which A is K, Na,  $H_3O$ ,  $1/2Pb$ ,  $NH_4$  or Ag, and B represents Fe (III) (jarosites) or Al (alunites) (van, Breemen, 1973). The most important members of the jarosite group are jarosite ( $KFe_3(SO_4)_2(OH)_6$ ), natrojarosite ( $NaFe_3(SO_4)_2(OH)_6$ ) and hydronium jarosite ( $H_3OFe_3(SO_4)_2(OH)_6$ ).

Typically, jarosite precipitates as pale yellow deposits (2.5-5Y 8/3-8/6), as fillings in biopores, or as efflorescences on ped faces and

pore walls. Individual particles are often smaller than 1  $\mu\text{m}$  and their diameter rarely exceeds 5  $\mu\text{m}$  (Andriess et al., 1973). Jarosite occurs under strongly oxidizing, severely acid conditions. (Eh greater than 400 mV, pH of 2 to 4). Jarosite may occur as natrojarosite and hydronium jarosite due to  $-\text{Na}^+ - \text{H}_3\text{O}^+$  substitution for  $\text{K}^+$ , but the potassium form predominates (van Breemen, 1976). Its formation from pyrite may be expressed by several reactions such as:

$$\text{FeS}_2 + 15/4\text{O}_2 + 5/2\text{H}_2\text{O} + 1/3\text{K}^+ \longrightarrow 1/3\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 4/3\text{SO}_4^{2-} + 3\text{H}^+$$

(Dent, 1986), and

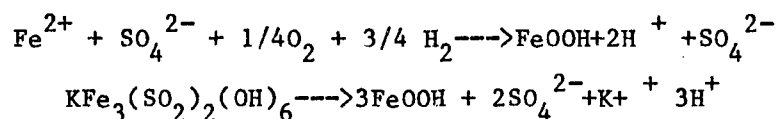


(Bloomfield and Coulter, 1973; Ivarson et al., 1982; Ross et al., 1982).

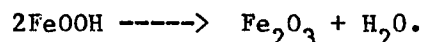
In acid sulfate soils, jarosite is metastable and ultimately is hydrolysed to goethite.

#### (b) Iron oxides

As the pH of the soil remains above 4, ferric-oxides and hydroxides precipitate directly by oxidation of dissolved  $\text{Fe}^{2+}$ . Fine-grained goethite may form, either directly and quickly upon oxidation of the dissolved ferrous sulfate released during pyrite oxidation, or more slowly by hydrolysis of jarosite. The reactions are acidic and part of the sulfuricization process (van Breemen, 1982):



During oxidation of pyrite in drainage water, goethite ( $\text{FeOOH}$ ) is the most commonly identified iron oxide. Sometimes it may be slowly transformed to hematite ( $\text{Fe}_2\text{O}_3$ ) (van Breemen, 1982):

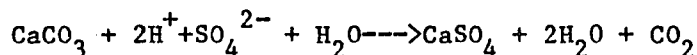


In developed acid sulfate soils, part of the ferric-oxides in the B horizon may exist as hematite as indicated by conspicuous red mottles. In Thailand, these red mottles are used as a field indicator of moderately to strongly acidic conditions (Kevie and Yenamamas, 1972).

### (c) Sulfates

Most of the iron mobilized by oxidation of pyrite remains in the soil profile. A small portion of the sulfate may remained as jarosite or gypsum. Drainage tends to leach most soluble sulfur forms from the oxidized soil profile. At a greater depth where reducing conditions still prevail, some sulfur is reduced once again to sulfide (Dent, 1986).

Gypsum has been observed in coastal marine soils over a wide pH range (3.5 to 7). The upper limit of the calcium sulfate activity product in such soils is clearly regulated by precipitation as gypsum. Gypsum is observed in the dryer soils or in those with some supply of calcium carbonate because gypsum is easily solubilized (van,Breemen, 1982). Gypsum is formed in acid sulfate soils by the neutralization of acidity by calcium carbonate:



The other minerals that are likely formed in pyrite-rich soils or acid sulfate soils are basic aluminum sulfate ( $\text{AlOH}\text{SO}_4$ ), sodium alum ( $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), tamarugite ( $\text{NaAl}(\text{SO}_4)_2(\text{H}_2\text{O})_6$ ), pickeringite ( $\text{MgAl}_2(\text{SO}_4)_4(\text{H}_2\text{O})_{22}$ ), rozenite ( $\text{FeSO}_4(\text{H}_2\text{O})_2$ ), copiapite ( $\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2(\text{H}_2\text{O})_{20}$ ), melanterite ( $\text{FeSO}_4(\text{H}_2\text{O})_7$ ), coquimbite ( $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_9$ ), and szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) (Nodstrom, 1982).

### Profile development of acid sulfate soils

Harmsen and van Breemen (1975) described a hypothetical chronosequence of seasonally flooded acid sulfate soils. These sequences or processes are strongly determined by the external conditions that affect drainage and leaching. For instance, profile development of acid sulfate soils in the Bangkok Plain contains three different stages. A Sulfaquent represents an undrained mangrove soil, and a Sulfaquept and Sulfic Tropaquept represent the increasingly older and deeper developed acid sulfate soils. The more developed an acid sulfate soil, the deeper the pyritic substratum is found (usually well below 1 m from the soil surface under the brown and yellow mottled (jarosite deposit) B horizon and the black A horizon). Sulfaquepts develop brown and yellow mottled surface soils with the gray pyritic substratum at about 50 cm depth, whereas Sulfaquents exhibit the least developed profile having few brown mottles at the surface with the unmottled gray pyritic substratum near the surface. Van Breemen (1982) noted that as the soils become older (in terms of pedological maturity, not absolute age) and better drained, the different horizons are found at progressively greater depths. More details of acid sulfate soil profile development are presented by Dent (1986).

### PROBLEMS OF ACID SULFATE SOILS ASSOCIATED WITH RICE PRODUCTION

Generally, acid sulfate soils show characteristics unfavorable to agricultural production. The value of these soils is largely dependent on the real or the potential acidity of the soil material and the

availability of affordable and feasible management practices to overcome the problems. The lower the sulfur content in these soils, the less serious is the problem posed to the farmer (Moormann, 1963). Problems of acid sulfate soils have been investigated by various workers. Several production limiting factors are discussed here in the following sequence:

1. Soil acidity
2. Aluminum toxicity
3. Iron toxicity
4. Sulfide toxicity
5. Salinity
6. Toxicity of organic acids and carbon dioxide
7. Phosphorus deficiency
8. Nutrient deficiency

#### Soil acidity

The direct adverse effect of  $H^+$  on plants has been observed at an acidity stronger than pH 3.5-4.0 (Arnon and Johnson, 1942; Ponnampetuma et al., 1973; Thawornwong and van Deist, 1974). The evidence was obtained mostly from plants grown in solution culture media. The probability of soil acidity directly resulting in plant growth problems grown on some acid sulfate soils has been reported (Moormann, 1963; Brinkman and Pons, 1973; Ponnampetuma et al., 1973).

Occasionally, pH values of approximately 1 to 2 have been observed in oxidized horizons of acid sulfate soils (Tanaka and Yoshida, 1970). In young acid sulfate soils (Sulfaquepts) and rapidly oxidized potential



acid sulfate soils (Sulfaquents), pH levels as low as 3 or even lower are found (Van Breemen and Pons, 1978). Rice crop damage has been reported when flood water of pH 2.5 to 3.5 from acid sulfate soils has flowed to adjacent, normal fields (Pons and Kevie, 1969).

#### Aluminum toxicity

Aluminum toxicity to various type of plants has received much attention in the past, i.e. in wheat and barley (Foy et al., 1965, 1974; Kerridge et al., 1971; Macleod and Jackson, 1967; Mugiwarra et al., 1976; Sloodmaker, 1974), in rice plants (Howeler and Cadavid, 1976; Cate and Sukhai, 1964), and in general for several other plants (Brown et al., 1972; Foy, 1974; Rorison, 1972; Conner and Sears, 1922; Hartwell and Pember, 1918; Miyake, 1916).

In most of the cereal crops, including rice, the symptoms of aluminum injury are first apparent on the roots. Injured roots are slower to elongate. Later, the roots thicken and do not branch normally. The root tips disintegrate and turn brown while the adventitious roots proliferate as long as the crown is alive (Clarkson, 1969; Fleming and Foy, 1968; Lafever et al., 1977; Reid et al., 1971). In most crops, sufficiently high concentrations of aluminum over a period of time will frequently damage even the most tolerant varieties. Symptoms also appear in the plant tops at a later seedling stage (MacLean and Chiasson, 1966; Reid et al., 1969; Sloodmaker and Arzadum, 1969).

A disease of rice known as "bronzing" was found to be caused by aluminum in combination with calcium deficiency (Ota, 1968). Root development was markedly retarded, similar to that in other crops

mentioned above. Differential aluminum tolerance has been reported among rice varieties grown in nutrient solution. Tanaka and Navasero (1966a) described the aluminum toxicity symptoms of rice plants grown in culture solution as follows: the leaves turned yellowish from the tip and along the margins, and interveinal orangish mottling and scattered brown spots and streaks developed.

The mechanism of aluminum toxicity has been attributed to several factors. It may be due to either the precipitation of the insoluble aluminum phosphate in the soil outside the roots (Blair and Prince, 1923; McLean and Gilbert, 1927; Rorison, 1972; Tanaka and Navasero, 1966b), or the disturbance of phosphate utilization within the plant (Magistad, 1925; Pirre and Stuart, 1933). The latter problem has been attributed to the precipitation of aluminum phosphate within the root (De Kock and Mitchell, 1957; Wright, 1943) which may physically block sorption sites for phosphate (Hackett, 1962). Woolhouse (1970) pointed out that aluminum disrupts the activities of proteinaceous enzymes existing in the cell wall. The direct effect of aluminum has been related to total or partial cessation of cell division (Clarkson, 1969).

Tomlinson (1957) reported that an aluminum level in the soil higher than 250 ppm may be harmful to plant growth (the aluminum content extracted with 1M ammonium acetate buffered at the pH of the soil). Gate and Sukhai (1964) observed that aluminum toxicity symptoms of rice growing in nutrient solution developed within 3 weeks at aluminum concentrations as low as 25 ppm where no other nutrient cations are present. Tanaka and Navasero (1966a) reported the critical concentration of aluminum ion in a culture solution was about 25 ppm for rice plants receiving a normal supply of other nutrients. They found

that above  $300 \text{ mg kg}^{-1}$  of aluminum in the shoot aluminum toxicity symptoms often developed. However these critical levels varied with the phosphate status of the plant and the ion concentration and pH of the culture solution. For instance, the critical content of aluminum in phosphorus-deficient plants was lower than that of phosphorus sufficient plants. With no phosphorus at pH 4, aluminum toxicity symptoms developed at soluble Al level of 15 ppm in the culture solution, but, with 30 ppm P at pH 4, mild aluminum toxicity symptoms developed at the soluble Al level of 61 ppm. Yoshida (1981) listed  $300 \text{ mg kg}^{-1}$  of aluminum in shoot as the critical content for aluminum toxicity to rice plants. Aluminum toxicity appeared in older rice leaves as an orangish yellow interveinal chlorosis. In severe cases, the chlorotic portions may become necrotic. Fageria and Carvalho (1982) observed the critical toxic level of aluminum in the tops of 21 day-old rice plants varying from 100 to  $417 \text{ mg kg}^{-1}$ , depending on the cultivars.

In a large number of studies on aluminum toxicity, aluminum phosphate interactions are often cited (Clarkson, 1967; McCormick and Borden, 1974; White, 1977). Many of the specific effects of aluminum on mineral element uptake and utilization have recently been reviewed (Brown et al., 1972; Foy et al., 1974; Grime and Hodgson, 1969; Andrew et al., 1973). Aluminum has been found to interfere with uptake, transport, and utilization of Ca, Mg, P, K, and water, and with enzyme activity in the root (Foy et al., 1978). Aluminum has an effect on the uptake and absorption of phosphorus (Clarkson, 1965; Rorison, 1965), and of several essential cations, including Ca (Clarkson and Sanderson, 1971; Munns, 1965, Lance and Pearson, 1969) and Mg (Clark, 1977). Excess aluminum in the soil decreases the plant availability of

phosphorus due to precipitation of phosphorus in the soil or immobilization of P in the root (Wright 1937, 1943; Pierre and Stuart, 1933; Jones and Fox, 1978; Clarkson, 1967; Attanandana, 1982). The inverse relationship between plant uptake of aluminum and calcium or iron has been shown for several plants (Magistad, 1925; Tanaka and Navasero, 1966a; Awad et al., 1976). Soluble aluminum depresses the uptake and translocation of calcium (Awad et al., 1976; Lance and Pearson, 1969; Soileau, 1969). Other modes of aluminum toxicity are evident as interference with: calcium and potassium utilization, cell division, water uptake, root respiration, and with the deposition of polysaccharides in cell walls (Foy et al., 1978; Lance and Pearson, 1969). Lee and Pritchard (1984) reported that calcium ions do not alleviate the inhibition of root growth caused by aluminium ions. On the contrary, IRRI (1985) reported that excess calcium can compete with aluminum for exchange sites in the rice roots and hence reduce aluminium toxicity. Calcium, magnesium, and nitrate can each act to suppress the aluminum toxicity effect at low levels of aluminium. The presence of sufficient calcium and magnesium have been reported to permit normal root growth if they are present in amounts sufficient to lower the percentage of aluminum in solution to about 20 (on an equivalent basis) (Cate and Sukhai, 1964). Studies in Brazil have shown the inhibiting effect of aluminum on the concentrations and plant contents of N, P, K, Ca, Mg, S, Na, Zn, Fe, Mn, B and Cu. The inhibition was more effective for macronutrients in the plant tops in following order; Mg>Ca>P>K>N>S>Na. For micronutrients it was in the order of Mn>Zn>Fe>Cu>B (Fageria and Carvalho, 1982; Fageria, 1985).

Aluminum toxicity in acid sulfate soils occurs at pH levels below 4.5-5 for seedlings, and below 3.5-4.2 for older plants. But these levels also depend on other factors, ie., the low availability and high fixation of phosphorus in acid sulfate soils may aggravate aluminum toxicity (Hesse, 1963; Watt, 1969; van Breemen and Pons, 1978).

Aluminum is probably harmful in most acid sulfate soils just after flooding, and aluminum toxicity may persist in soils showing little or no increase in pH after flooding (van Breeman and Pons, 1978). Poor growth and low rice yields in acid sulfate soils have been correlated with excess aluminium in the soil solution, especially at the early growth stages (Moormann, 1963; Beye, 1971; Hesse, 1963). Excess aluminum in acid sulfate soils was also observed under dryland conditions which severely affected the rice growth (Jugsujinda et al., 1978).

#### Iron toxicity

#### Mechanisms of iron toxicity

Several reviewers reported the problem of iron toxicity of wetland rice can be classified into two categories:

(a). Single nutritional soil stress associated with low pH and excess water-soluble iron in the soil (Ponnamperuma et al., 1955; De and Mandal, 1957; Tanaka et al., 1966; Tanka and Yoshida, 1970; Howeler, 1973).

(b). Multiple nutritional soil stress due to a lack and/or unbalanced supply of P, K, Ca, and Mg relative to iron triggering an uncontrolled influx and excessive uptake of iron (Howeler, 1973; van

Breeman and Moormann, 1978; Benckiser et al., 1982, 1984a, 1984b; Ottow et al., 1982, 1983).

#### Iron toxic soils

In acid sulfate soils, iron toxicity is an important growth limiting factor (Nhung and Ponnampuruma, 1966; Tanaka and Navasero, 1966; Ponnampuruma et al., 1973). Iron toxic soils are widely distributed in tropical and subtropical areas (Tanaka and Yoshida, 1970). There are at least three groups of iron toxic soils (van Breeman and Moormann, 1978):

(a). Young acid sulfate soils (Sulfaquepts), eg. in Kalimantan and Sumatra (Indonesia), Vietnam, western Malaysia, Kerala (India), Sierra Leone;

(b). Poorly drained colluvial and alluvial sandy soils (Hydraquents, Tropaquents, Fluvaquents) in valleys receiving interflow water from adjacent higher land with plinthite, weathering igneous or sedimentary rocks, or with acidic sediments, e.g. in Sri Lanka (Panabokke, 1975), Keria and Orissa (India) (Sahu, 1968), Sierra Leone (Virmani, 1978); and,

(c). Alluvial or colluvial clayey soils, mainly acid, kaolinitic Tropaquepts and Tropaquents, in sediments derived from Ultisols or banded and leveled fields in Ultisols, e.g. in Malaysia, Orissa (India), Columbia (Howeler, 1973), Sierra Leone.

#### Iron toxicity symptoms

"Bronzing" and "Yellowing" or "Oranging" are characteristics of iron toxicity in rice plants. Small brown spots appear on the lower

leaves starting from the tips. As the disorder becomes severe, purplish or reddish-brown mottling (bronzing), or sometimes a yellowish (yellowing) or orange discoloration, spreads downward from the tip of the older leaves followed by drying of the leaves. Growth and tillering are depressed and the root system is poorly developed (coarse, short, and darkbrown) while white roots are few or absent (Ponnamperuma et al., 1955; Tanaka and Yoshida, 1970; van Breemen and Moormann, 1978).

Iron toxicity symptoms may appear at any growth stage, but often develop at the maximum tillering and panicle initiation stages (Baba, 1958). Low yields from iron toxicity are associated with a high percentage of unfilled grains (van Breeman and Moorman, 1978). Yield reduction may range from 10 to 90% depending on soil, variety, and growth stage at the appearance of symptoms (Gunawardena, 1979; Virmani, 1978).

#### Quantifying iron toxicity

Criteria used for evaluating the degree of iron toxicity include growth, appearance, foliar symptoms, plant iron content, iron concentration in rooting media, and grain yield.

Several reviews have described toxic iron concentrations in the rooting media in very broad ranges as summarized below:

- (a). a 30-80 mg L<sup>-1</sup> Fe in pot experiments with soils from Sri Lanka (Ponnamperuma, 1958),
- (b). a 100-500 mg L<sup>-1</sup> Fe in culture solution (Okuda and Takahashi, 1965; Tanaka et al., 1966; Tanaka and Navasero, 1966a).
- (c). a 300-400 mg L<sup>-1</sup> Fe in soils well supplied with other nutrients (IRRI, 1973).

(d). a 350-500 mg L<sup>-1</sup> Fe in soils well supplied with other nutrients (IRRI, 1964).

In both field and pot experiments, a relationship between bronzing symptoms of certain varieties and plant iron content exists, and the degree of bronzing also correlates well with grain production (IRRI, 1965).

On the other hand, it has been observed that severe orangizing of rice leaves have appeared at a relatively low iron content in the leaves (170 mg kg<sup>-1</sup>) whereas moderate symptoms appeared in rice plants that had accumulated an iron content of 400 mg kg<sup>-1</sup> in the leaves. These studies indicated the content of P, K, Ca, and Mg in the leaves of the least affected plants were considered normal (Tanaka and Yoshida, 1970), while the severely affected plants were considered deficient (or nearly deficient) in these elements (Howeler, 1973). It has been reported that plants sometimes developed bronzing symptoms only at a very high content of leaf Fe (955 mg kg<sup>-1</sup>) (Haque, 1977). Thus, it appears that no simple relationship exists between bronzing, yellowing or orangizing symptoms and iron content in plant tissue. To confirm suspected iron toxicity, a comparison of the iron contents in leaf blades of affected and healthy plants from the same field should be made (van Breeman and Moorman, 1978) at a specified general nutrient composition (Howler, 1973).

#### Tolerance of rice to high iron concentration

Rice tolerance to high iron concentration has been hypothesized to be due to three functions of rice roots which counteract iron toxicity (Yoshida and Tadano, 1978):

(a) oxidation of iron in the rhizosphere,



- (b) exclusion of iron at the root surface, and,
- (c) retention of iron in the root tissue, which prevents the translocation of iron from root to shoot.

Rice is one of the few plant species with a high rate of oxygen diffusion into the roots. Air enters rice plants through stomates of leaf blades and leaf sheaths and moves downward through air passages known as aerenchyma tissue (Kordan, 1974). Thus, oxygen moves down to the roots where it is used primarily for respiration. After root metabolism requirements are met, extra oxygen may diffuse out from the roots and create an oxidized rhizosphere (Armstrong, 1967) allowing oxidation and immobilization of several potentially toxic ions including iron (Jensen et al., 1967; Armstrong, 1971,; Joshi et al., 1973; Ando et al., 1983). Yamada and Ota, (1958) demonstrated that rice root extracts converted ferrous iron to the ferric form indicating the oxidizing power of rice roots may be attributed partly to enzymatic oxidation. Deposits of ferric iron compounds have been observed on the surface of rice roots (Sturgis, 1936; Bacha and Hossner, 1977; Green and Etherinton, 1977; Chen, Dixon and Turner, 1980).

Rice roots also have the capacity to exclude iron at the surface, and this appears to be associated with respiration. Exclusion of iron at root surface is defined as iron-excluding power (IEP) which is calculated as:

$$\text{Iron-excluding power (IEP)\%,} = ((a-b)/a) \times 100$$

where "a" is the amount of iron, in milligrams, contained in the same volume of culture solution as that of water absorbed by the plant, and "b" is the amount of iron, in milligrams, actually absorbed by the plant (Yoshida, 1981). The IEP of rice roots appears to be associated with

the metabolic activity of rice roots and this mechanism may operate only when the concentration of iron in the rooting media is high. It is interesting to note that deficiencies of phosphorus, potassium, calcium, magnesium, and manganese decrease the IEP of rice roots (Yoshida and Tadano, 1978).

#### Varietal tolerance of rice

Differential responses of rice varieties to excess iron has been reported by many workers (IRRI, 1971; Ikehashi and Ponnamperuma, 1978; Virmani, 1978; Gunawardena, 1979). The majority of the tolerant varieties take up less iron in the tissues compared to the sensitive varieties. Virmani (1978) screened 1,400 rice lines and observed the tolerant varieties contained  $560 \text{ mg kg}^{-1}$  iron in the leaves at maximum tillering compared with 1,650 to  $1,720 \text{ mg kg}^{-1}$  in the leaves of sensitive varieties. His results also indicated yield reduction ranged from a mean of 29% for moderately tolerant varieties to a mean of 74% for the sensitive varieties. Yield reduction of the sensitive varieties ranged from 40% to 60% when iron toxicity was mild, but was almost 100% when iron toxicity was severe as compared with yield of the relatively tolerant varieties (Ponnamperuma and Solivas, 1982b). It is not clear whether varietal differences are due mainly to exclusion of iron in the oxidizing rhizosphere, to reduced translocation of iron, to tolerance for high iron levels in the plant tissue, or to a combination of these factors (Yoshida and Tadano, 1978).

### Sulfide Toxicity

Sulfate is reduced under strongly anaerobic conditions in submerged soils. Sulfate may be reduced to sulfites, hydrogen sulfide, elemental sulfur, and to other reduction products. When an acid sulfate soil is allowed to be reduced too long before rice is sown, the young seedlings may die due to  $H_2S$  toxicity (Brinkman and Pons, 1973). The rate of sulfate reduction in flooded soil depends on soil properties.

Ponnamperuma (1972) reported that in the neutral and alkali soils they studied, concentrations of sulfate as high as  $1,500 \text{ mg kg}^{-1}$  may be reduced to zero within 6 weeks of submergence. The rate of sulfate reduction may be several hundred times slower in acid soils than in alkaline soils. Peak concentrations of hydrogen sulfide were found to vary with soil reaction, organic matter, Fe, and Mn (IRRI, 1973). Hydrogen sulfide levels tend to be greater in soils low in iron or high in organic matter (IRRI, 1973). Generally, the addition of organic matter to a wetland soil accelerates sulfide accumulation (Connell and Patrick, 1968). Tian-ren (1985) demonstrated that in acid sulfate soils, hydrogen sulfide concentrations increased rapidly after one day's submergence, especially when organic matter has been added. The peak value of hydrogen sulfide concentration for the organic matter treatment was higher than for the control treatment. Coulter (1973) suggested more sulfides could be formed in the rooting zone from the accumulated sulfate that moved from the subsoil by diffusion.

Sulfide inhibits the respiration and the oxidizing power of rice roots, hence retarding the uptake of various nutrients and causing poor growth (Vamos, 1967). Tanaka et al. (1968) proposed that iron toxicity

is likely to occur more frequently under high levels of both sulfide and ferrous iron because sulfide destroys the oxidizing power of the roots, and more iron enters the rice plant. However, since high concentrations of soluble ferrous iron tend to precipitate dissolved sulfide by the formation of  $\text{FeS}$ , this mechanism should somewhat protect the toxic effects of dissolved sulfide (Patrick and Reddy, 1978).

Pitts (1971) found toxicity of hydrogen sulfide to rice at levels below 1 ppm in Louisiana rice soils. In Japan, a physiological disorder of rice associated with sulfide injury was reported by Osugi and Kawaguchi in 1938. It was found to be caused by free hydrogen sulfide injury. In acid sulfate soils in Thailand, indirect evidence of sulfide toxicity in rice was noted (Vangnai et al., 1974). Ayotade (1977) observed significant amounts of dissolved sulfide may form within weeks after flooding, especially in highly reduced pockets associated with easily decomposable organic matter. Mitsui et al. (1951) demonstrated by solution culture that a hydrogen sulfide concentration as low as  $0.07 \text{ mg kg}^{-1}$  is toxic to rice. In situ measurement of free hydrogen sulfide with an ion selective electrode in Louisiana rice soils revealed that the average concentration of water-soluble hydrogen sulfide for 53 sites was  $0.104 \text{ mg kg}^{-1}$  (Allam et al., 1972).

The concentration of water-soluble hydrogen sulfide is often very low due to the formation of insoluble sulfides, chiefly  $\text{FeS}$  (Ponnamperuma, 1972). On the other hand, measurements have been made indicating that  $\text{Fe}^{2+}$  concentration had no appreciable effect on hydrogen sulfide accumulation (Allam, 1971). Because soil is chemically heterogeneous, and if reduction of ferric iron is the rate limiting process for the formation of ferrous sulfide (Bloomfield, 1969),

probably at least some parts of rice roots are exposed to a toxic level of free hydrogen sulfide when submerged soils are subjected to a rapid reduction.

Sulfide formation is strongly dependent on pH, the range of 6.5 to 8.5 is most favorable at a redox potential of about - 150 mv and lower (Connell and Patrick, 1968, 1969). In suspensions of Crowley soil, and under conditions of controlled pH and redox potential, they reported sulfide formation occurred in the pH range 5.5 to 8.5 and in the redox potential range -175 to -350 millivolts. The optimum pH for sulfide formation has been reported to be 6.7 in one study (Jakobsen et al., 1981). Thus, liming to raise the soil pH above 5 tends to increase sulfide formation (van Breemen, 1975). Komes (1973a) also pointed out that care should be taken when liming acid sulfate soils of Thailand to avoid accelerating sulfate reduction at a higher pH. Bacterial reduction of sulfate is much less in acid soils, thus sulfide toxicity only develops after the soil pH has been raised to about 5 by prolonged flooding or liming (Dent, 1986). Even at low pH, harmful concentrations of hydrogen sulfide may be present if the dissolved levels of iron are low (IRRI, 1966; Park and Tanaka, 1968). To lessen the problem of sulfide formation, chemical oxidants such as nitrate or manganic oxides can be added to retard sulfide formation (Ponnamperuma, 1965; Engler and Patrick, 1973), probably by stabilizing the redox potential or by competing with organic acid fermentation for molecular hydrogen. Possible management practices might include drainage to prevent development of strongly reducing conditions, or applying low amounts of lime. Yoshida (1981) claimed that varietal differences in tolerance for

hydrogen sulfide toxicity exists and appears to be related to the oxygen-release capacity of roots.

### Salinity

In general, salinity refers to the presence of excessive concentrations of soluble salts in the soil (Yoshida, 1981).

Electrical conductivity of either the saturation extract (ECe) or soil solution collected from the rhizosphere is normally measured to quantify the degree of salinity. For rice growing in flooded soils, the two conductivities can be considered comparable (Yoshida, 1981). Rice and other crops are affected by salinity (ECe or electrical conductivity of soil saturation extract in  $\text{mS cm}^{-1}$  at  $25^{\circ}\text{C}$ ) higher than  $4 \text{ mS cm}^{-1}$ , and this value has been considered as the criteria for identifying saline soils (USDA, 1954).

Major ionic species of salts are sodium, calcium, magnesium, chloride, and sulfate. Among these, sodium and chloride usually predominate. Salinity is expected to occur in acid sulfate soils of coastal regions where the salinity is associated with inundation or intrusion of sea water. In this type of soil, salinity is often associated with low soil pH. Acid sulfate soils in tidal areas are often affected by salinity. Salinity aggravates other toxicities, both by weakening the plants and by increasing iron, and probably aluminum, in solution (Pasricha and Ponnampuruma, 1976). In many young acid sulfate soils, total electrolyte content increases strongly upon reduction and reaches harmful levels (Ponnampuruma et al., 1973; Toure, 1982). As the salt levels increase, pH decreases and the concentration of several cations increase.

Salinity in excess of  $4 \text{ mS cm}^{-1}$  indicate electrolyte quantities in the soil solution that may affect normal growth of rice (IRRI, 1967). Salinity affects the uptake of water and nutrients. High soluble salts impair growth and depress grain yields of rice. Growth of rice is initially retarded between salinity levels of 4 and  $11 \text{ mS cm}^{-1}$ , and rice germination does not occur at a salinity greater than  $11 \text{ mS cm}^{-1}$  (Pearson, 1959, 1961). In one study, the IRRI (1967) reported the relative rice yields of 100, 60, and 19 at salinity values of 1.2, 4.3, and  $7.3 \text{ mS cm}^{-1}$  respectively.

Nhung and Ponnampetuma (1966) and Ponnampetuma et al. (1973) reported specific conductance values of  $8$  to  $10 \text{ mS cm}^{-1}$  or greater in some acid sulfate soils. Very high levels of salinity have been recorded in acid sulfate soils of the mangrove area of Senegal and Gambia where electrical conductivity in the 0-20 cm zone ranged from 27 to  $100 \text{ mS cm}^{-1}$  (Marius, 1982). However, those areas having very high salinity are normally under mangrove forest. In Thailand, van Breemen (1976) analysed water samples and reported salinity values were frequently found between  $15$  to  $30 \text{ mS cm}^{-1}$  in saline acid sulfate soils of the tidal coast,  $8 \text{ mS cm}^{-1}$  in non-acid marine soils, and generally less than  $5 \text{ mS cm}^{-1}$  in older acid sulfate soils and para acid sulfate soils. Salinity toxicity presumably occurs only in saline acid sulfate soils because rice is moderately tolerant to salinity (USDA, 1954). High water levels during the rainy season, as a result of dilution, helps alleviate soluble salt effects in the Bangkok Plain area (van Breeman, 1976).

### Toxicity of organic acids, phenols, and carbon dioxide

Considerable amounts of carboxylic acids are known to occur in submerged soils. These include formic, acetic, propionic, and butyric acids. Acetic acid is generally the most abundant (Motomura, 1962; Takai and Kamura, 1966; Yamane and Sato, 1967; Gotoh and Onikura, 1971). Soil incorporation of organic matter, such as rice straw, promotes the production of organic acids in submerged soils (Yoshida and Tadano, 1978; Chandrasekaran and Yoshida, 1973). Rao and Mikkelsen (1977) detected only acetic acid in the incubated soil they amended with rice straw. The peak production occurred between 15 and 20 days after incubation. Organic acids were not found in sufficient amounts to affect the growth of rice plants grown in soils that were not previously in a reduced state. These carboxylic acids are toxic to rice seedlings at concentrations of  $10^{-2}$  to  $10^{-3}$  mole  $L^{-1}$  (Yoshida and Tadano, 1978).

Reducing, dissolved organic substances in the solution of submerged soils generally consists of phenolic compounds, which are perhaps related to fulvic acids (Takijima, 1964; IRRI, 1971; Okazaki and Wada, 1976). These compounds may be more important than the many better known alcohols, aldehydes, carboxylic acids, and organic sulfur compounds that generally occur in small concentrations in reduced soils, and that may inhibit rice growth at levels greater than 0.1-10 mmole  $L^{-1}$  (van Breemen and Moorman, 1978).

Organic acids retard the uptake of nutrients by rice. Chandrasekaran and Yoshida (1973) reported the uptake of nutrients is retarded in the presence of butyrate and propionate, though acids of higher molecular weights are more toxic to rice growth. Organic acids



not only have a direct effect on rice growth, but also enhance soluble levels of ferrous iron in the soil solution (Motomura, 1961). Thus they may aggravate iron toxicity in some soils (Tanaka and Navasero, 1967).

The pH of the culture media can markedly affect the toxic effect of organic acids on rice. At the same concentrations, organic acids affect rice to a greater degree under low pH conditions compared to near neutral or alkaline conditions. As soil pH decreases, the proportion of injurious undissociated acid increases (Yoshida, 1981). This suggests that the undissociated form of organic acids may be of particular concern in soils low in pH such as in some acid sulfate soils (Ponnamperuma, 1965). Van Breemen (1973) also noted that in flooded acid sulfate soils, undissociated weak acids and stronger acids may be harmful to rice.

Soil temperature has a significant influence on the kinetics of organic acid production. Low soil temperature leads to an accumulation of organic acids (Cho and Ponnamperuma, 1971) which suggests that organic acid toxicity is more likely to occur at low temperatures. Low temperature may also aggravate the harmful effects of organic acids by retarding the increase in soil pH.

The toxicity of carbon dioxide to rice in submerged acid sulfate soils has been noted (Ponnamperuma, 1972). Acid soils accumulated high concentrations of carbon dioxide (IRRI, 1965). Carbon dioxide concentrations exceeding 0.15 percent retard water and nutrient uptake by plants. Excess carbon dioxide restricts the root growth of rice and causes wilting of rice (Ponnamperuma, 1965).

### Phosphorus deficiency

In acid sulfate soils, phosphorus is strongly fixed in unavailable forms such as iron and aluminum phosphates (Moormann, 1963), or phosphate adsorbed to clay surfaces. With time, the phosphate may be converted to the more insoluble ferric phosphate ( $\text{FePO}_4$ ) (Patrick et al., 1985), and even occluded with iron oxide (Patrick and Mahapatra, 1968). At low soil pH, iron and aluminum play a major role in phosphorus fixation (Cole and Jackson, 1950; Kittrick and Jackson, 1955; Yuan et al., 1960). High contents of Fe-bound phosphorus and occluded phosphorus in paddy soils have been shown to exist by Cholitkul and Tyner (1971), using the Chang and Jackson fractionation method.

Under reducing conditions, some of the iron and aluminum phosphate becomes available (Patrick, 1964), but the degree of mobilization by flooding will gradually be reduced by aging and crystallization of the oxide forms (Dent, 1986). Acid sulfate soils which contained low available phosphorus, showed a slight increase in availability of phosphorus with flooding (Patrick et al., 1985). Patrick and Khalid (1974) observed that anaerobic soils released more phosphorus to soil solutions low in soluble phosphorus and sorbed more P from soils high in soluble phosphorus than did aerobic soils. The poorly crystalline and amorphous oxides and hydroxides of iron play a primary role in P retention by flooded soils and sediments (Khalid et al., 1977).

For the older acid sulfate soils of Thailand which have been amended with lime and fertilizer, it appears that phosphorus is the most important limiting factor for rice production (Attanandana and Vacharotayan, 1982; Charoenchamratcheep et al., 1982; Maneewon et al.,

1982). Application of lime and phosphate resulting in improved rice yields may be due to an increased supply of nitrogen by stimulation of ammonification and microbial fixation of nitrogen. These processes are normally retarded in unamended acid sulfate soils (Kawaguchi and Kyuma, 1969; Matsuguchi et al., 1970; Motomura et al., 1975). Application of rock phosphate with a high level of citrate solubility showed satisfactory results in term of increased rice yield in some acid sulfate soils of Thailand (Engelstad et al., 1973). The residual effect of Lao Cai rock phosphate applied in acid sulfate soils of the Red River Delta in Vietnam lasted for only three seasons (Can, 1981), whereas the residual effect of native rock phosphate applied in some acid sulfate soils in Thailand lasted for five consecutive crops (Jugsujinda and Suwanwong, 1973). In the absence of iron and aluminum toxicity and salinity effects, phosphorus deficiency may be the most important growth limiting factor for rice in acid sulfate soils (Koyama et al., 1973; Sombatpanit, 1975; van Breemen and Pons, 1978).

#### Nutrient deficiencies

Acid sulfate soils in their oxidized state show very low base saturation. Nitrogen also is present in short supply (Moormann, 1963). The availability of nitrogen is restricted by the slow mineralization of organic matter and by unfavorable conditions for processes of nitrogen fixation (Dent, 1986). After a long period of leaching, acid sulfate soils contain low quantities of bases, and the exchange complex becomes saturated with aluminum. Acid sulfate soils are thus likely to be deficient in calcium and potassium (Bloomfield and Coulter, 1973). Turner and Bull (1967) reported that oil palms of acid sulfate soils

frequently show symptoms of severe magnesium deficiency. Several other workers have reported somewhat low amounts of bases in acid sulfate soils compared to the amounts of the bases in non-acid sulfate soils from the same area. For instance, Sombatpanit (1970) found 3.5-5.0  $\text{cmol}(+)\text{kg}^{-1}$  exchangeable calcium and 3.0-3.2  $\text{cmol}(+)\text{kg}^{-1}$  exchangeable magnesium in the top 35 cm of acid sulfate soils in Thailand. Nhung and Ponnampetuma (1966) also reported similar amounts in Vietnam soils. Almost twice these amounts were found in non-acid sulfate soil. Andriesse et al. (1973) reported the exchange complex of an acid soil was primarily saturated with aluminum. Oxidized acid soil samples have low contents of exchangeable bases and high values of exchangeable acidity. Bloomfield and Coulter (1973) suggested that under high rainfall and virtually continuous leaching, very small amounts of exchangeable bases will be retained. Where there is a prolonged and intense dry season, as in Thailand and Vietnam, there is less leaching of bases. However some acid sulfate soils of Thailand are generally low in potassium, and they release less than 5 percent of their total nitrogen during anaerobic incubation (Kawaguchi and Kyuma, 1969), compared with 10 to 20% for other tropical soils. In extremely acid sulfate soils, extractable potassium, calcium, and copper are very low and extractable aluminum is very high (Attanandana and Vacharotayan, 1982). This suggests the replacement of exchangeable bases on the exchange complex by aluminum.

## RECLAMATION AND MANAGEMENT OF ACID SULFATE SOILS TO IMPROVE RICE YIELD

Acid sulfate soils are world-wide in distribution, therefore major differences in several conditions associated with these soils exist such as topography, hydrology, climatology, vegetation, and agro-ecological zones. Management of acid sulfate soils to enhance yields must consider these factors, specific soil chemical conditions, and also the local communities i.e., resources available and the people who make decisions concerning utilization of acid sulfate soils. A decision to attempt improvement of acid sulfate soils depends on the resources available and costs vs. the expected economic benefit. In general, a long-term effort will be required to accomplish this task. A multidisciplinary approach is needed in planning, conduct of research and field experimentation, and evaluation of the results. In particular, governmental assistance is usually important in countries needing to develop acid sulfate soils.

In the past, several methods have been applied to improve acid sulfate soils. Development of reclamation and management practices that have been applied to improve rice yield in acid sulfate soils are reviewed below.

### Rice cultivation in tidal marshes

Potential acid sulfate soils (Sulfaquents, physically unripe) will not acidify as long as tidal flooding is sufficiently frequent to prevent prolonged aeration. In most of these areas, soils are strongly saline and rice can only be grown along river banks where tides back up fresh water everyday in the wet season (van Breemen and Pons, 1978). In Indonesia, Bandjarese farmers developed a specific wet rice cultivation

technique in acid sulfate soils in tide-influenced, freshwater areas to cope with the lack of water level control. Normal tillage would inevitably lead to oxidation of pyrites exposed to the air upon plowing. Farmers transplant rice three times, the last transplanting at about 6 weeks after sowing. The seedlings are large enough to cope with deep flooding at the time of final transplant. The advantage of this is that the potential acid sulfate soil is not given an opportunity to oxidize (Driessen and Ismangun, 1973). An example of the effect of tidal rice cultivation was demonstrated in Sierra Leone at Rokupr Rice Research Station. Table 3 gives the yield of rice for 8 years prior to the bunding, for 4 years during the bunding to prevent tidal intrusion, and for 5 years after the restoration of the tidal influence during the dry season. This work demonstrates the detrimental effects of dry season desiccation, and the rapid restoration to a relatively good yield once waterlogging is restored (Bloomfield and Coulter, 1973).

#### Flooded rice cultivation

In some acid sulfate soil areas of Thailand, farmers use small power tillers to puddle the fields, then broadcast pre-germinated seeds just before flooding starts in order to reduce the risk of aluminum toxicity that is normally present with the traditional practice of broadcasting on dry land (van Breemen and Pons, 1978). The introduction of high yielding, non-sensitive-to-photoperiod varieties offers the opportunity of transplanting seedlings into flooded soils after the floodwaters recede, thereby avoiding the period of low pH and aluminum toxicity that normally exist under dry conditions (Dent, 1986). Xuan et al. (1982) reported rice yields often reached as high as 4.5 to 6 tons

Table 3. Yields ( $\text{kg ha}^{-1}$ ) of rice as affected by water control at the Rokupr Research Farm, Sierra Leone (after Bloomfield and Coulter, 1973).

Block No.	Average under Tidal regime 1935-1943	Flooding excluded				Flooding restored				
		1944	1945	1946	1947	1948	1949	1950	1951	1952
22	1850	860	10	30	0	800	1955	1670	2625	3270
23	2310	1170	200	0	35	1255	2670	2435	2570	2960
24	2545	2035	655	200	145	1120	3010	2970	2670	-
25	1900	1735	135	65	235	1980	3280	2735	2910	3525
26	2560	755	235	10	0	955	2070	3160	1910	3870
27	3160	1135	620	35	35	935	2280	2625	2535	3425

$\text{ha}^{-1}$  on acid sulfate soils in the Mekong Delta where the crop is transplanted after the period of deep flooding. However, there is a big risk if a drought occurs before ripening of the rice plant.

#### Intensive shallow drainage

In empolder areas of the Mekong Delta where the soils are typically young acid sulfate soils with jarosite present at 30 to 50 cm below the surface, rice is grown successfully on raised beds (about 9 m wide and 36 m long) drained by an intensive network of broad, shallow ditches (about 1 m wide and 0.3 to 0.6 m deep). During the dry season, oxidation and acidification occur. Leaching commences with the first heavy rains. Since the acid sulfate horizon occurs around a depth of 30 to 60 cm in the raised beds where oxidation takes place during the dry season, the toxic products are then leached out through the drainage network. Drainage water is allowed to collect in the ditches until it reaches the surface of the raised beds. Then, with the next rain, the accumulated acid water is allowed to drain to the river at low tide. This leaching cycle is repeated two or three times until the whole region is flooded by the river. Local yields on undrained acid sulfate soils are only 0.2 to 0.5 tons  $\text{ha}^{-1}$ , but under this system of shallow drainage and leaching, yields of about 4 tons  $\text{ha}^{-1}$  are obtained (Dent, 1986). After the soil is flooded, reduction processes will raise soil pH and further reduce the level of soluble aluminum prior to transplanting. The use of saline- and acid-tolerant varieties, and the transplanting of large seedlings will also counteract toxicity. However, the reclamation of large areas of acid sulfate soils by this



method has led to increased acidity of the floodwaters affecting crops in downstream areas (Xuan et al., 1982).

#### Drainage and leaching

The idea of flooding acid sulfate soils with seawater to displace the aluminum was developed since using large amounts of limestone is not economical. It has been suggested that the seawater acts in the same way as a neutral salt in laboratory experiments so that exchangeable aluminum is displaced from the soil by the bases in the seawater (Bloomfield and Coulter, 1973). Laboratory and field trials in British Guiana on leaching out toxic materials with seawater have been carried out and have been proved effective (Evans and Cate, 1962). However, flooding with diluted seawater is considerably less efficient than leaching with seawater. Nevertheless, it has been shown that the aluminum contents have been reduced to below the percentage of exchangeable cations at which it causes toxicity. Cate and Sukhai (1964) recommended that leaching with seawater may be useful in improving acid soils, both by removing exchangeable aluminum through displacement and by improving the nutrient status of the soil. Also, leaching has given good results in pot experiments (Nhung and Ponnampuruma, 1966; Ponnampuruma et al., 1973). However, in the field, unfavorable hydrology and poor hydraulic conductivity often preclude leaching as a feasible reclamation measure. Because large amounts of fresh water must be available later for desalinization, the utilization of seawater often requires considerable capital and would rarely be economical (van Breemen, 1976). Leaching with seawater has been used with some success in Sierra Leone (Bloomfield and Coulter, 1973). In

Sierra Leone, yields of 2 tons  $\text{ha}^{-1}$  were obtained with a 5 tons  $\text{ha}^{-1}$  lime application in the absence of seawater leaching, and with 2.5 tons  $\text{ha}^{-1}$  lime rate in conjunction with seawater leaching at the end of the dry season (Hart et al., 1963), thus the technique can sometimes be used successfully.

Regarding with the idea of drainage and leaching to improve acid sulfate soil conditions, van Breemen (1976) recommended maximum feasible draining to achieve oxidation, then leaching with water or seawater to remove most of the dissolved acidity. But the time required for complete oxidation of the pyrite in the rooting zone and the environmental impact of the acid drainage water should be kept in mind (Dent, 1986). For example, Dent and Raiswell (1982) have modelled the rate of oxidation in undisturbed, drained soils on the basis of the rate of diffusion of dissolved oxygen into the system and the initial content of pyrite. They found an initial oxidizable sulfur content of 3.5 percent will be reduced to about half over 50 years.

#### Liming and fertilization

Liming is effective in raising soil pH and thus reducing levels of plant-available toxic aluminum. Ponnampetuma et al. (1973) noted that aluminum toxicity is averted by liming and that the buildup of high concentrations of water-soluble iron is prevented by liming. The Tropaepts and Sulfic Hapaquepts in nontidal coastal plains that are commonly used for rice, and moderate yields ( $0.5 - 2 \text{ tons ha}^{-1}$ ) are obtained with large quantity of applied lime (van Breemen and Pons, 1978). However, if this measure alone is implemented, the amount of lime required could easily amount to 10 tons  $\text{ha}^{-1}$  or more and this is

not economical. Moreover, the difficulty of transporting the lime to wet land is a problem (Kawaguchi and Kyuma, 1977). Liming should be carried out after the effect of oxidation and leaching becomes apparent. In Thailand, liming is recommended in amounts just sufficient to inactivate aluminum (Komes, 1973a). Further liming to produce higher pH is observed to have the adverse effect of causing sulfate reduction in the rooting zone. Other reasons for adverse effects of overliming of are obscure, but may be due to temporary alkalinity and formation of sparingly soluble calcium-phosphate compounds (Sombatpanit and Wangpaiboon, 1973; Park et al., 1972). Toure' (1982) found leaching more beneficial than liming and any other amendments in a Typic Sulfaquent rich in organic matter with a high C/N ratio and a high content of fulvic acids. Liming apparently stimulated bacterial activity, caused strong reduction leading to a large release of reduced mineral and organic compounds, and contributed directly or indirectly to an increase in electrical conductivity of the soil solution (Toure', 1982). Ponnampetuma, et al. (1973) noted liming lowered the concentration of water-soluble  $\text{Fe}^{2+}$  substantially and the  $\text{SO}_4^{2-}$  concentration slightly, but increased the partial pressure of carbon dioxide.

Chapter Three  
Characterization of Soil Materials

### Characterization of Soil Materials

Acid sulfate and non-acid sulfate soil materials were collected from Thailand to be used in this study. The five soils selected were Rangsit Very Acid (Rsa), Rangsit (Rs), Mahaphot (Ma), Bangkok (Bk), and Ratchaburi (Rb). These soils are common rice soils of the Central Plain of Thailand. The first three are acid sulfate soils, the fourth soil is a non-acid sulfate, marine-deposited soil, and the last is a non-acid sulfate, freshwater deposited soil. All soils are strongly hydromorphic. General descriptions of the five soils are shown in Table 1.

#### Location and sample preparation

The soil sampling sites in Thailand are shown in Figure 1. All samples except Ratchaburi and Bangkok Soil were collected in the early rainy season of 1981. A 100 kilogram composite sample of each soil was collected from the plow layer (20 cm deep) of approximately a half hectare of land. The samples were shipped to the Rice Division in Bangkok where the soils were air-dried and a 20-kilogram sample of each composite soil was shipped to the Laboratory for Wetland Soil and Sediments, Louisiana State University (LSU). At LSU, the samples were ground, sieved through a 40-mesh screen, and thoroughly mixed on a mechanical roller (Satawathananont, 1986). Bangkok and Ratchaburi Soils were collected, shipped to LSU, and processed similarly in 1983.

The five soils were collected from different locations as described below:

Table 1. General descriptions of the five soils studied.

Soil Series	Acidity	Deposit	Great Soil Group	pH	Suitability class
Rangsit Very Acid (Rsa)	Extremely	Marine	Sulfic Tropaquept	3.7-3.9	P-IV a
Rangsit (Rs)	Severely	Marine	Sulfic Tropaquept	4.0-4.4	P-III a
Mahaphot (Ma)	Moderately	Marine	Sulfic Tropaquept	4.1-4.6	P-II a
Bangkok (Bk)	Non-acid	Marine	Typic Tropaquept	4.5-5.0	P-I
Ratchaburi (Rb)	Non-acid	Freshwater	Typic Tropaquept	5.0-5.5	P-I

P-IV a----Rice production is severely limited due to acidity constraints and requires special management.

P-III a----Rice production is moderately limited due to acidity constraints and requires special management.

P-II a-----Rice production is slightly limited due to the acidity constraints .

P-I-----There is no significant limiting factor for rice production.

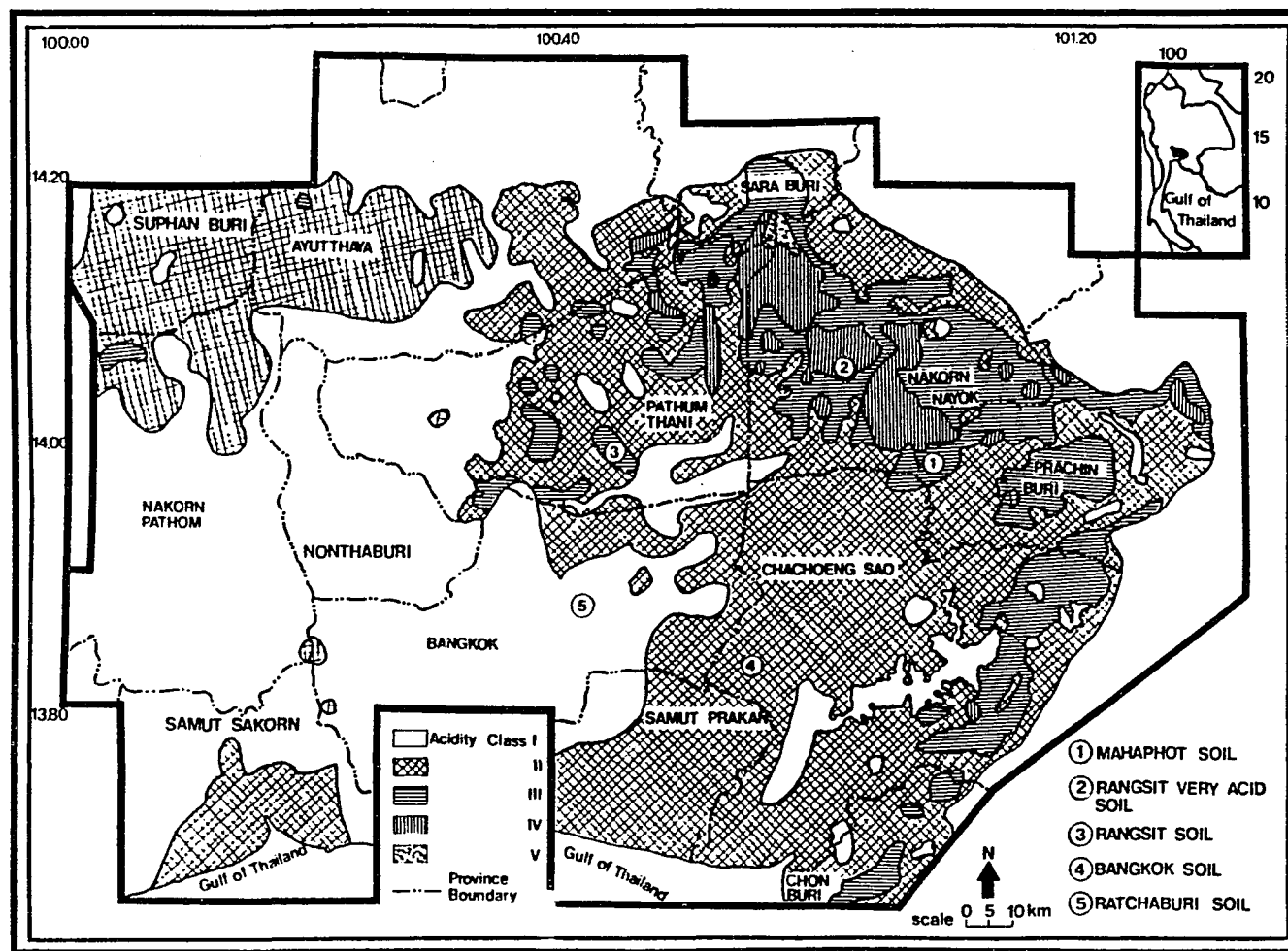


Figure 1. Map showing approximate locations of soil sample sites (adapted from Satawathananont, 1986, and based on the map of Southern Central Plain, Soil Analysis Survey, Report on ASSIP, Department of Land Development, Thailand, 1985).

- a) Mahaphot soil, from Mou 5, Ban Haopai, Thambol Bangpluang, Ban Sang, Prachin Buri,
- b) Rangsit very acid soil, from the Ongkharak Experiment Station, Nakhon Nayok,
- c) Rangsit soil, from Land Development Center, Thanyaburi, Pathum Thani,
- d) Bangkok soil, from Thambol Nhuangkhet, Amphoc Muang, Chachoengsao,
- e) Ratchaburi soil from Thambol Min Buri, Amphor Nong Chok, Bangkok.

#### Chemical properties of the five aerated soils

Soil properties were determined using duplicate soil samples for each of the analyses. Properties and methods of analyses used are described as follows.

pH : determined in 1:1 soil/water suspension, and in 1:2 soil:0.01 M  $\text{CaCl}_2$  suspension using a combination glass/calomel electrode (Attanandana, 1982).

Organic matter: determined by the Walkley-Black method (Black, 1965).

Cation exchange capacity (CEC): Determined by the ammonium saturation-distillation method (Chapman, 1965).

Exchangeable bases: 1M ammonium acetate extraction using the method described by Black (1965); extractable K, Ca, Mg, and Na were measured by by an ICP.



Total exchangeable base: Summation of extractable K, Ca, Mg, and Na.

Titratable acidity: Barium chloride/triethanolamine extraction at pH 8.1 (Peech, 1965).

Exchangeable Aluminum: 1M KCL extract (Black, 1965), and extractable Al measured by an ICP.

Available P: Determined by the Bray II procedure (Bray and Kurtz, 1945).

Active Fe and Mn: Determined by extraction with EDTA and sodium dithionite (Van Breemen, 1976); active Fe and Mn measured by an ICP.

Water soluble sulfate: Extracted with the procedure described by van Breemen (1971); water soluble sulfate determined by ion chromatography.

Iron, Mn, Al, Ca, Mg, K, Na, Mo, P,  $\text{SO}_4^{2-}$ , Cd, Pb, Cr, Ni, and As were fractionated into various forms as described below:

Water soluble: A water extraction using a 1:5 ratio of dry soil to deionized water was made where the soil suspension was then shaken on a mechanical shaker for 30 minutes and centrifuged for 20 minutes at 6000 rpm in a Dupont Sorvall Superspeed Centrifuge equipped with a GS-3 head. The supernatant was filtered through a 0.45 um millipore filter.

$\text{NH}_4\text{OAc}$  extractable: This fraction was obtained by shaking a 200 ml portion of 1 M  $\text{NH}_4\text{OAc}$  (pH 4.0) with the residual soil following the water extraction. The soil suspension was shaken for 2 hours, centrifuged, and filtered as described above.

Reducible (Amorphous iron fraction): The residual soil following  $\text{NH}_4\text{OAc}$  extraction was added with 100 ml of 0.25 M  $\text{NH}_2\text{OH.HCl}$  - 0.25 M  $\text{HCl}$  (Chao and Zhou, 1983). The soil suspension was shaken for 30 minutes in a  $50^\circ\text{C}$  water bath, centrifuged and filtered.

EDTA extractable: The residual soil following the reducible fraction was amended with 100 ml 0.05 M EDTA and 0.2 M  $\text{NaOAc}$  at pH 7.0, and the resulting suspension shaken for 18 hours, centrifuged, and filtered.

The results of the soil characterization work are shown in Tables 2, 3, 4, 5, and 6. The amorphous hydrous oxide fraction is believed to be one of the major immobilization mechanisms and occluding a large portion of some other metals. Several metals recovered largely in the reducible (amorphous) fraction indicating coprecipitation of these elements. In general, Fe, Al, Si, Cu, Zn, Pb, Cr, and Ni were recovered in greatest levels in the reducible (amorphous) fraction. Manganese, Ca, Mg, and As levels recovered in the exchangeable fraction was highest. Sodium,  $\text{SO}_4^{2-}$ , and Si were highest in the water soluble fraction.

Iron, Cu, and Zn levels recovered in the EDTA fraction was relatively high indicating metal chelation of these metals with organics.

#### Particle size distribution

Particle size determination was done using the method described by Attanandana (1982). The percentages of clay, silt, and coarse to very fine sands and texture identification are tabulated in Table 7. All the acid sulfate soils had clay textures with a range of clay content at

Table 2. Selected chemical properties of the five soil materials.

Parameter	Soil				
	Rsa	Rs	Ma	Bk	Rb
Organic matter (%)	4.4	3.3	1.9	1.3	1.5
Soil pH (1:1, water)	3.9	4.3	4.5	4.9	5.2
Soil pH (1:2, 0.01 M CaCl <sub>2</sub> )	3.6	4.0	4.1	4.7	4.7
CEC (cmol (+) kg <sup>-1</sup> )	21.8	20.8	19.9	24.9	14.0
Total exchangeable base (cmol (+) kg <sup>-1</sup> )	5.6	13.7	15.7	20.9	5.9
Exchangeable K (cmol (+) kg <sup>-1</sup> )	0.2	0.5	0.3	1.0	0.1
Exchangeable Ca (cmol (+) kg <sup>-1</sup> )	1.1	5.9	8.2	5.1	3.9
Exchangeable Mg (cmol (+) kg <sup>-1</sup> )	2.7	6.1	6.5	11.6	1.6
Exchangeable Na (cmol (+) kg <sup>-1</sup> )	1.6	1.2	0.6	3.1	0.3
Exchange acidity (cmol (+) kg <sup>-1</sup> )	10.5	2.9	3.2	1.2	2.2
Exchangeable Al (cmol (+) kg <sup>-1</sup> )	10.1	2.0	2.3	1.1	1.9
Available P (mg kg <sup>-1</sup> )	6.5	5.5	3.2	19.2	3.5
Active Fe (%)	1.2	0.5	1.4	0.7	1.4
Active Mn (mg kg <sup>-1</sup> )	33.6	31.3	349.0	67.5	326.0
Water-soluble SO <sub>4</sub> <sup>2-</sup> (mg kg <sup>-1</sup> )	114.0	518.0	504.0	96.4	174.0

Table 3. Concentrations of water-soluble constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials.

Metal	Soil				
	Rsa	Rs	Ma	Bk	Rb
Fe	1.58	1.12	2.98	1.48	1.41
Mn	6.75	1.03	12.00	3.45	7.18
Al	10.50	4.67	3.68	3.55	4.56
Ca	56.30	48.50	64.90	64.80	39.50
Mg	87.60	37.00	38.30	108.00	11.90
K	9.91	16.10	11.40	59.40	5.60
Na	424.00	310.00	232.00	703.00	147.00
Cu	0.42	0.33	0.39	0.39	0.47
Zn	1.57	0.62	1.09	0.65	0.61
Mo	0.05	0.04	0.03	0.02	0.03
P	0.68	0.44	0.43	0.81	0.57
$\text{SO}_4^{2-}$	1114.00	518.00	504.00	96.40	174.00
Cd	0.01	0.01	0.01	0.01	0.05
Pb	0.17	0.07	0.07	0.03	0.08
Cr	0.04	0.03	0.05	0.03	0.03
Ni	0.82	0.06	0.15	0.12	0.11

Table 4. Concentrations of exchangeable constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials.

Metal	Soil				
	Rsa	Rs	Ma	Bk	Rb
Fe	43.20	57.60	46.90	98.00	94.80
Mn	19.00	20.90	251.00	49.00	101.00
Al	713.00	226.00	178.00	91.10	132.00
Ca	150.00	962.0	1271.00	800.00	760.00
Mg	226.00	663.00	681.00	1107.00	205.00
K	Tr*	38.00	<0.02	125.00	<0.02
Na	222.00	231.00	192.00	356.00	53.60
Cu	1.95	0.51	0.92	0.90	1.36
Zn	1.79	2.78	3.33	1.74	1.97
Mo	2.0	1.78	1.83	1.80	1.85
P	6.01	5.07	5.68	7.78	6.05
SO <sub>4</sub> <sup>2-</sup>	74.40	318.00	454.00	40.60	29.80
Cd	0.03	0.05	0.13	0.09	0.06
Pb	2.90	3.58	4.23	3.70	3.67
Cr	0.74	0.69	0.58	0.71	0.55
Ni	1.02	1.88	2.46	1.28	1.36

\* Trace amount

**Table 5. Concentrations of easily reducible Fe , Mn and some other constituent (mg kg<sup>-1</sup>) in the five aerated soil materials extracted by 0.25 M NH<sub>2</sub>OH.HCl-0.25 M HCl.**

Metal	Soil				
	Rsa	Rs	Ma	Bk	Rb
Fe	1413.00	2178.00	4158.00	4311.00	5656.00
Mn	7.10	8.51	79.70	13.80	110.00
Al	2145.00	2001.00	1734.00	1538.00	1440.00
Ca	41.90	115.00	111.00	114.00	59.40
Mg	35.30	40.00	52.80	76.20	60.40
K	25.00	<0.02	<0.02	<0.02	<0.02
Na	67.40	87.90	84.90	93.80	82.30
Cu	4.22	16.30	18.70	10.10	14.10
Zn	7.56	13.60	13.10	8.95	12.40
Mo	1.91	1.85	1.82	1.84	2.03
P	13.50	16.50	15.50	48.20	22.00
Si	794.00	1078.00	974.00	1204.00	832.00
Cd	0.18	0.42	0.56	0.52	0.59
Pb	8.79	9.30	9.85	8.28	10.00
Cr	2.37	3.43	3.14	3.43	2.88
Ni	1.76	2.99	2.90	4.05	1.93

Table 6. Concentrations of DTPA-extractable constituents ( $\text{mg kg}^{-1}$ ) in the five aerated soil materials extracted by .05 M NaDTPA.

Metal	Soil				
	Rsa	Rs	Ma	Bk	Rb
Fe	180.00	222.00	436.00	455.00	411.00
Mn	0.74	0.82	5.90	1.25	5.48
Al	281.00	245.00	187.00	199.00	142.00
Ca	14.60	19.20	19.20	18.70	15.20
Mg	2.82	3.46	4.74	4.79	5.46
K	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	2.86	4.84	3.83	5.38	2.46
Zn	2.81	3.04	4.14	2.75	3.75
Mo	0.48	0.61	0.37	1.01	0.36
P	3.28	3.58	3.64	8.26	5.13
Si	248.00	236.00	213.00	283.00	228.00
Cd	0.01	0.02	0.04	0.04	0.03
Pb	1.35	1.53	1.31	1.60	1.25
Cr	0.95	1.10	0.80	0.97	0.65
Ni	0.36	0.36	0.40	0.47	0.30

Table 7. Particle size distribution and textures of the five soils.\*

Soil	Clay	Silt	Coarse Sand	Medium Sand	Fine Sand	Very fine Sand	Texture
-----%							
Rsa	63	27	--	3	5	2	clay
Rs	70	25	--	1	1	3	clay
Ma	65	26	1	1	2	5	clay
Rb	27	55	--	5	11	2	silty clay loam
Bk	67	30	--	--	1	2	clay

\* Pipette and wet-seiving method.



62% to 70%. For the non-acid sulfate soils, the Bangkok soil was a clay whereas the Ratchaburi was a silty clay loam.

#### Clay mineral composition

X-ray diffraction was used to determine the clay mineral composition of the five soils studied. Preparation of the soil samples followed the procedure used by Jackson (1958). It was observed that the major clay minerals present were kaolinite, illite, and smectite. More quantitative and qualitative composition details of the clay mineralogy in four of the five soils were discussed by Satawathananont (1986).

#### Rice Varieties Used

IR 46 and IR 26 rice varieties, from the International Rice Research Institute, were classified as varieties relatively tolerant and sensitive to acid sulfate soils, respectively. Yield trials on acid sulfate soils in a farmer's field in the Philippines confirmed the tolerance and the sensitivity of these two rice varieties (Ponnamperuma and Solivas, 1982). Other data are available indicating IR 46 is relatively tolerant to saline soils, alkali soils, and acid sulfate soils (IRRI, 1985).

#### Fertilizers Used

Nitrogen, P, and K were added as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , and KCl respectively.

## Chapter Four

### Rice Growth in Acid Sulfate Soils Under Controlled Redox Conditions

## Rice Growth in Acid Sulfate Soils Under Controlled Redox Conditions.

### ABSTRACT

The effects of controlled redox conditions on the growth of rice were studied in laboratory microcosms using acid sulfate (Sulfic Tropaeup) and non-acid sulfate (Typic Tropaeup) soil materials from Thailand. Rice seedlings of acid sulfate soil-tolerant and sensitive varieties (IR 46 and IR 26, respectively) were grown for 3 weeks in soil suspensions incubated at four different Eh levels (500, 250, 50, and -150 mV). Growth of both varieties was generally lower in the acid sulfate soil and under low redox and pH conditions (a range of  $pe + pH$  from 2.82 to 4.57) in both soil types. Growth of IR 26 was more affected than IR 46 by strongly reduced conditions (-150 mV) of acid sulfate soils.

Regression analyses were employed to determine the relationship between soil factors and/or nutrient content in plant tissue (independent variables) and growth of the rice plants (dependent variable) in both acid and non-acid sulfate soils. Prediction models were selected using the stepwise regression technique and the maximum  $R^2$  improvement procedure.

Results indicate ( $pe + pH$ ) is the most important variable positively associated with weight gain of both rice varieties under all soil conditions. The Fe:Mn ratio in the plant tissue is an important variable negatively associated with weight gain of the IR 26 variety in all soils and the IR 46 variety in non-acid sulfate soils. The weight gain of IR 46 in acid sulfate soils was more strongly associated with

the Fe:K+Ca+Mg ratio than the Fe:Mn ratio. Activity of  $Zn^{2+}$  in the soil solution was a variable positively associated with weight gain of both rice varieties in acid sulfate soils and associated with weight gain of IR 46 in non-acid sulfate soils. The other variables examined negatively associated with weight gain included Fe concentration in the plant tissue and in the soil, and Al concentrations in the plants. Regression equations for predicting rice weight gain of both varieties in non-acid and acid sulfate soils are also reported. Soil association model for each variety in each soil type are also included.

#### INTRODUCTION

Large areas in the Central Plain of Thailand are used for rice cultivation. The yield of rice in this area is quite low due to the extensive presence of acid sulfate soils (~800,000 ha). The low productivity of acid sulfate soils has been attributed to: 1) low pH, 2) Al toxicity, 3) Fe toxicity, 4) sulfide toxicity, 5) low nutrient status especially P and N, and, 6) adverse effects of carbon dioxide and organic acids. Numerous studies have been conducted on the adverse effects of acid sulfate soils on the growth of wetland rice (Tanaka and Navasero, 1966; Nhung and Ponnampuruma, 1966; Ponnampuruma et al., 1973; Ponnampuruma and Solivas, 1982; Toure, 1982; Vo-Tong Xuan et al., 1982; Yin and Chin, 1982; L. J. van den Eelaart, 1982). The genesis and solution chemistry of Thailand acid sulfate soils has been described by van Breemen (1976), and, a number of research papers on problems of acid sulfate soils to rice in Thailand have been published (Jugsujinda et al., 1971; Sombatpanit, 1975; Attananadana and Vacharotayan, 1982; Charoenchamratcheep et al., 1982; Maneewon et al.,

1982; Kanareugsa et al., 1983; Uwaniyom, 1983; Satawathananont, 1986; Moore, 1987). A common finding of this work is that application of low rates of lime plus N and P fertilizer is an important means of improving rice yield on certain classes of acid sulfate soils.

Flooding soils influences chemical and microbial transformations as well as plant availability of several important nutrients due to changes in the oxidation-reduction status of the soils. Several studies report the effect of flooding on growth and nutrient uptake by rice (Ponnamperuma et al., 1955; Chaudhry and McLean, 1963; Senewiratne and Mikkelsen, 1961). The effects of pH and soil redox conditions on early growth and nutrient uptake of rice has also been reported (Patrick and Fontenot, 1976; Jugsujinda and Patrick, 1977; Schwab and Lindsay, 1983; Sajwan and Lindsay, 1986). However those studies have examined only the effects of soil pH and/or redox conditions of non 'adverse' soils on nutrient transformation and nutrient uptake by rice.

The object of this study was to attempt to identify the adverse conditions affecting rice growth under controlled redox conditions of both acid sulfate and non-acid sulfate soils of Thailand. Soil pH was allowed to vary as influenced by redox potential and other soil properties.

#### MATERIALS AND METHODS

The soils used in this study were collected from the surface layer at different locations within Thailand. They represented two soils types: 1) Sulfic Tropaquepts (acid sulfate soils) of which three soils series were included [Mahaphot (Ma), Rangsit (Rs), and Rangsit very acid (Rsa)], and, 2) Typic Tropaquepts (non-acid sulfate soils) of which two

soil series were studied [Bangkok (Bk) and Ratchaburi (Rb)]. The soil materials were air-dried and ground to pass through a 2-mm sieve. Characteristics of these soils are given in Table 1.

The soil materials were amended with finely ground rice straw (40 mesh) on a roller mixer to provide an energy source to promote microbial activity (0.5% on oven dry soils basis). The equivalent of 200 g of oven-dry soil mixed with rice straw and 1600 mL of high purity deionized water were placed in a 2 L desiccator base (Pyrex 412230), kept in suspension using a continuously operating magnetic stirrer, and allowed to become reduced to the desired redox level before rice seedlings were transferred. The microcosm consisted of a desiccator base with a plexiglas plate fitted with openings for the rice plants and two platinum electrodes, air and argon inlets, a gas outlet, a pH electrode, and a salt bridge. The treatments included four redox potential (Eh) levels (+500, +250, +50, and -150 mV). The redox potential was controlled at the preselected level by an automatic addition of air (oxygen) to the soil suspension when the potential fell below the set value. The laboratory microcosm used in this study to grow plants in soil suspensions under controlled redox conditions (Eh) has been described by Patrick et al. (1973) and Reddy et al. (1976).

Rice seedlings of acid sulfate soil tolerant and sensitive varieties (IR 46 and IR 26, respectively) were grown for 21 days in a nutrient solution similar to that described by Tanaka and Navasero (1966), Jugsujinda and Patrick (1977), and Yoshida et al. (1976), and then the seedlings were transferred to the laboratory microcosms containing soil suspension. Two seedlings were placed in each opening for plants and then sealed with an inert RTV silicone rubber (RTV 162

Table 1. Selected chemical properties of the soils in an air-dry state.

Parameter	Soil				
	Rsa	Rs	Ma	Rb	Bk
pH (1:1, water)	3.9	4.3	4.5	5.2	4.9
Organic matter(%) <sup>a*</sup>	4.4	3.3	1.9	1.5	1.3
CEC (cmol(+) kg <sup>-1</sup> ) <sup>b</sup>	21.8	20.8	19.9	14.0	24.9
Exchangeable K (cmol(+) kg <sup>-1</sup> ) <sup>c</sup>	0.2	0.5	0.3	0.1	1.0
Exchangeable Ca (cmol(+) kg <sup>-1</sup> ) <sup>c</sup>	1.1	5.9	8.2	3.9	5.1
Exchangeable Mg (cmol(+) kg <sup>-1</sup> ) <sup>c</sup>	2.7	6.1	6.5	1.6	11.6
Exchangeable Na (cmol(+) kg <sup>-1</sup> ) <sup>c</sup>	1.6	1.2	0.6	0.3	3.1
Total exchangeable base (cmol(+) kg <sup>-1</sup> ) <sup>d</sup>	5.6	13.7	15.7	5.9	20.9
Exchangeable Al (cmol(+) kg <sup>-1</sup> ) <sup>e</sup>	10.1	2.0	2.3	1.9	1.1
Exchangeable acidity (cmol(+) kg <sup>-1</sup> ) <sup>f</sup>	10.5	2.9	3.2	3.5	19.2
Available P (mg kg <sup>-1</sup> ) <sup>g</sup>	6.5	5.5	3.2	3.5	19.2
Active Fe(%) <sup>h</sup>	1.2	0.5	1.4	1.4	0.7
Active Mn (mg kg <sup>-1</sup> ) <sup>h</sup>	33.6	31.3	349.0	326.0	67.5
Water-soluble SO <sub>4</sub> <sup>2-</sup> (mg kg <sup>-1</sup> ) <sup>i</sup>	371.0	173.0	168.0	174.0	32.1

\*Method of analyses.

a Walkely-Black (Black, 1965).

b Ammonium saturation-distillation (Chapman, 1965).

c 1 M NH<sub>4</sub>OAC pH 7.0

d Sum of exchangeable K, Ca, Mg, and Na.

e 1 M KCl

f BaCl<sub>2</sub>-Triethanolamine (Peech, 1965).

g Bray II (Bray and Kurtz, 1945).

h Dithionite-EDTA extractable (van Breemen, 1976).

i Water-soluble sulfate (van Breemen, 1971).

WHITE DH 768). The suspensions were amended with  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{KCl}$  so that the rates of N, P, and K were 250, 50, and  $50 \text{ mg L}^{-1}$  respectively. Plants were grown for 21 days with light intensities of  $10^{-4} \text{ E m}^{-2} \text{ sec}^{-1}$  at plant level (measured by a Lambda Instruments quantum sensor). Distilled, deionized water was added frequently to replace that lost by transpiration. At the end of the growth period, root and shoot tissues were harvested separately, washed with tap water, 0.1 M HCL, and distilled deionized water. Plant tissue was placed in perforated paper bags and dried in a forced draft oven at  $65^\circ\text{C}$  until constant weights were obtained. Growth was estimated by determining the weight gain during the 21-day period (final dry weight-initial dry weight). The plant tissue was then finely cut with stainless steel scissors and mixed thoroughly to make a homogenous sample. Shoot and root samples were digested with distilled concentrated nitric acid. Reagent blanks were used to determine contamination, if any, from glassware, and other sources. The plant digests were analyzed for Cu, Zn, Cd, Pb, Cr, Ni, Fe, Mn, Mo, P, Al, K, and Na using an ICP (inductively coupled argon plasma emission spectrometer, Jarrell-Ash, Fisher Scientific Co., Atom Comp Series 800.

On the harvest date, 100 mL of the soil suspension from each treatment was transferred sampled to polycarbonate centrifuge bottles under a  $\text{N}_2$  atmosphere (Gambrell et al., 1975). The soil suspension was centrifuged at 6,000 rpm for 30 min in a Sorvall GS 3 rotor and filtered under a  $\text{N}_2$  atmosphere through a 0.45  $\mu\text{m}$  filter. The samples were preserved with sufficient distilled nitric acid to lower pH to at least 2 and were then stored in polyethylene bottles at  $4^\circ\text{C}$  until analysis for water-soluble metals. The exchangeable fraction of metals was obtained



from the residual solids following the removal of the water-soluble fraction. A 100 mL quantity of 1 M deoxygenated  $\text{NaC}_2\text{H}_3\text{O}_2$ , which was buffered to the soil pH, was added to the centrifuged bottles. The bottles were then shaken on a mechanical shaker for an hour. The samples were centrifuged and filtered as described for the water soluble fractions. Analysis of water-soluble and exchangeable metals in each filtrate was done by means of an ICP. Anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) in soil solution were analyzed by ion chromatography.

#### Determination of the activity of chemical species

Calculation of the activity of chemical species was carried out using the chemical equilibrium computer program Geochem (Sposito and Mattigod, 1979). Attempts have been made here to relate plant uptake and plant growth to ion activity in the soil solution as has been reported before by several authors (Adams, 1974; Khasawneh, 1971; Moore and Patrick, 1987). The input data are total molar concentrations of water-soluble metals,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , pH, pe, an estimate of carbonate at  $\text{pCO}_2$  of 0.001 MPa (Ponnamperuma, 1967; Lindsay, 1979; Schwab and Lindsay, 1983), an estimate of ionic strength. Ionic strength is the summation of  $1/2 m_i z_i^2$ , where  $m_i$  is the species molality (species) and  $z_i$  is the charge of the ion in the solution. The ions considered for computation of ionic strength are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  according to Garrels and Christ (1965). Ionic strength corrections are determined in the Geochem program. The Davies equation is employed to compute activity coefficients (at 25°C). Free metal output from Geochem and activity coefficients were used for calculation of the metal activities. Activities of ionic (metal) species were

transformed into negative  $\log_{10}$  units to facilitate tabulating and presenting the experimental data. Metal activity values were also used for determination of the other soil parameters such as the divalent charge fraction in soil solution or on CEC due to each divalent metal as discussed in the next section.

#### Exchangeable fraction of metals

Moore (1987) presented data on the divalent charge fraction in the exchangeable phase (E-Mi) and in the soil solution phase (E'-Mi). Several equations were employed to obtain the divalent charge fraction as follows:

$$q_i = Z_i X_i$$

This equation is used for calculation of the amount of metal charge on the CEC attributed to each metal, where  $q_i$  is the metal charge on the CEC accounted for by metal  $i$ ,  $Z_i$  is the valence of metal  $i$ , and  $X_i$  is the amount of metal on the CEC in  $\text{cmol (+)} \text{ kg}^{-1}$  soil. The sum of all  $q$  of divalent metal charges produced total divalent metal charge on the CEC ( $q_T$ ). The equation described by Sposito et al. (1983) was then used to calculate the divalent charge fraction in the exchanger phase (EMi) as follows:

$$\text{E-Mi} = q_i / q_T$$

where  $q_i$  is the metal charge on the CEC accounted for by metal  $i$  and  $q_T$  is the sum of all  $q$  of divalent metal charge. The divalent charge fraction in the soil solution was calculated similarly as follows:

$$\text{E'-Mi} = a_i / a_T$$

where  $a_i$  is activity of metal  $i$  and  $a_T$  is the sum of all activities of divalent metals considered (i.e., Fe, Mn, Ca, Mg, Cu, and Zn).

#### Regression analysis procedure

Regression analysis was the statistical tool employed to determine the relationship between nutrient levels in the soil and plant tissue, and rice weight gain. Analyses were done separately for varieties and non-acid and acid sulfate soils to provide a better fit for the curves, and decrease variation. The independent variables consisted of the physicochemical parameters, the concentration of mineral nutrients in shoot tissue, redox potential conditions, soluble nutrient concentration in the soil solution, nutrient concentration in the exchangeable fraction, activities of nutrients in soil solution, divalent charge fraction on CEC, divalent charge fraction in soil solution, and selected nutrient concentration ratios in shoot tissue. Table 2 summarizes all variable used in the model building and their abbreviations. The simple correlations of these variables with rice weight gain (dependent variable) were significant at the 0.15 level or greater (Tables 3 and 4). Regression models were selected based on a combination of the stepwise regression procedure (Draper and Smith, 1966), the maximum  $R^2$  improvement procedure (SAS, 1985) and other considerations of the independent variables based on findings of several published reports. The stepwise procedure is of much benefit to explore the relationship between the multiple independent variables and the dependent or response variable.

Table 2. Variables used in model building and their abbreviations.

Variables	Abbreviations
<b>Physicochemical Parameter</b>	
Acidity	pH
Redox potential	Eh
Redox potential and pH	pe+pH
<b>Nutrient Content of the Plant Tissue</b>	
Fe, Mn, Zn, etc.	Fep, Mnp, Znp, etc.
<b>Nutrient Content of Water-Soluble Fraction in the Soil Solution</b>	
Fe, Mn, Zn, etc.	Fe <sub>s</sub> , Mn <sub>s</sub> , Zn <sub>s</sub> , etc.
<b>Nutrient Content of Exchangeable Fraction in the Soil Solution</b>	
Ca, Mg, K, Fe, Mn, etc.	ExCa, ExMg, ExK, ExFe, ExMn, etc.
<b>Negative log of Activity of Nutrient Species in the Soil Solution</b>	
Fe <sup>2+</sup> , Ca <sup>2+</sup> , Al <sup>3+</sup> , Mn <sup>2+</sup> , etc.	pFe <sup>2+</sup> , pCa <sup>2+</sup> , pAl <sup>3+</sup> , pMn <sup>2+</sup> , etc.
<b>Divalent Charge Fraction on CEC due to Each Divalent Metal</b>	
Fe, Ca, Mg, etc.	E-Fe, E-Ca, E-Mg, etc.
<b>Divalent Charge Fraction in the Soil Solution due to Each Divalent Metal</b>	
Fe, Mn, Ca, Mg, etc.	E'-Fe, E'-Mn, E'-Ca, E'-Mg, etc.

Table 3. Variables and their linear correlations with weight gain of sensitive (IR26) rice grown in non-acid and acid sulfate soils over all redox levels.

	Non-acid (n=16)		Acid sulfate soils (n=24)	
	r*	P#	r	P
	physicochemical parameter			
pe+pH	0.63	0.009	0.79	0.001
	plant nutrient concentration			
Ca	---		0.49	0.01
Mg	---		0.46	0.02
Mn	---		0.56	0.004
Cu	---		0.62	0.001
Zn	---		0.58	0.002
Fe:Mn	-0.62	0.01	-0.80	0.0001
Fe:K+Ca+Mg	---		-0.61	0.001
	water-soluble nutrient concentration			
Ca	---		0.39	0.05
Mg	---		0.44	0.03
Fe	-0.57	0.02	-0.43	0.04
Zn	---		0.48	0.002
	exchangeable nutrient concentration			
Fe	---		-0.69	0.0001
	negative log of activity of nutrient species			
Ca <sup>2+</sup>	---		-0.40	0.05
Mg <sup>2+</sup>	---		-0.37	0.07
Fe <sup>2+</sup>	0.46	0.07	0.69	0.0002
Zn <sup>2+</sup>	---		-0.41	0.04
	divalent charge fraction on CEC			
Fe	---		-0.70	0.0001
Mg	---		0.60	0.002
	divalent charge fraction in the soil solution			
Fe	-0.54	0.02	-0.74	0.0001
Mn	---		0.40	0.05
Ca	---		0.61	0.001
Mg	---		0.50	0.01

\* linear correlation

# The probability level of significance.

\$ Blanks indicate linear correlation was not significant at the 0.15 probability level and these values were not included in the stepwise regression analysis.

Table 4. Variables and their linear correlations with weight gain of tolerant (IR46) rice grown in non-acid and acid sulfate soils over all redox levels.

	Non-acid (n=16)		Acid sulfate soils (n=24)	
	r*	P#	r	P
pe+pH	0.60	0.002	0.64	0.0007
	physicochemical parameter plant nutrient concentration			
Ca	0.46	0.07	---	---
Fe	0.45	0.08	---	---
Zn	0.57	0.02	---	---
Al	---	---	-0.18	0.38
Fe:Mn	-0.69	0.003	-0.49	0.01
Fe:K+Ca+Mg	---	---	-0.46	0.02
	water-soluble nutrient concentration			
Ca	0.45	0.08	0.41	0.04
Mg	---	---	0.41	0.04
	exchangeable nutrient concentration			
Fe	---	---	-0.38	0.06
	negative log of activity of nutrient species			
Ca <sup>2+</sup>	-0.44	0.08	-0.48	0.01
Mg <sup>2+</sup>	---	---	-0.44	0.02
Fe <sup>2+</sup>	---	---	0.34	0.10
Zn <sup>2+</sup>	-0.57	0.02	-0.70	0.0001
	divalent charge fraction on CEC			
Fe	---	---	-0.53	0.008
Mg	---	---	0.35	0.10
	divalent charge fraction in the soil solution			
Fe	---	---	-0.43	0.04
Ca	---	---	0.47	0.02

\* Linear correlation.

# The probability level of significance.

\$ Blanks indicate linear correlation was not significant at the 0.15 probability level and these values were not included in the stepwise regression analysis.

## RESULTS AND DISCUSSION

The data in Table 5 illustrate the effect of controlled redox potential (Eh) on suspension redox and pH (pe + pH) properties among acid and non-acid sulfate soils. Soil suspension pH was inversely related to redox potential whereas redox was positively correlated because pe is calculated directly from Eh ( $pe = Eh(mV)/59.2$  according to Lindsay, 1979). The difference between soils and/or varieties on growth is shown in Tables 6a and 6b. In both the non-acid and acid sulfate soils, the rice weight gains generally decreased as soils became more reducing. Tables 6a and 6b illustrate the differential effects among each soil on weight gain of tolerant and sensitive rice varieties. Growth of both varieties were generally lower in acid sulfate soils except that at an Eh of 50 mV the opposite results were observed. The effect of controlled redox potential on weight gain was demonstrated when the relative weight gain of both shoot and root of rice varieties were plotted against pe + pH levels (Figures 1, 2, 3, 4, 5, and 6)

The regression model for rice growth

For this experiment, the independent variables considered were soil physicochemical properties, various fractions of soil nutrients, and nutrient concentrations in the shoot tissue of the relatively tolerant (IR 46) and sensitive (IR 26) rice varieties at different controlled redox conditions in both non-acid and acid sulfate soils. In order to determine which of these independent variables influenced the weight gain of the rice plants, the multiple regression analysis was used to identify significant relationships. The different soils were

Table 5. Effect of controlled redox potential (Eh) on soil pH and pe+pH at harvest in acid and non-acid sulfate soils.\*

Eh (mV)	Acid sulfate soils						Non-acid			
	Mahaphot		Rangsit		Rangsit Very Acid		Bangkok		Ratchaburi	
	pH	pe*+pH	pH	pe+pH	pH	pe+pH	pH	pe+pH	pH	pe+pH
500	3.7	12.14	3.6	12.04	3.5	11.94	4.5	12.54	4.6	13.04
250	4.1	8.32	3.8	8.02	3.6	7.82	4.3	8.52	4.7	8.92
50	5.2	6.04	5.2	6.04	4.8	5.64	5.2	6.04	5.4	6.24
-150	6.2	3.67	6.2	3.67	5.2	2.67	6.9	4.37	7.2	4.67

\*pe = Eh(mV)/59.2 (Lindsay, 1979)



Table 6a. Differences in weight gain (g) of the sensitive rice variety (IR26) grown for 3 weeks between acid and non-acid sulfate soils under controlled redox potential conditions\*.

Eh(mV)	Acid sulfate soils			Non-acid	
	Ma	Rs	Rsa	Bk	Rb
500	1.56 a	1.36 a	1.46 a	1.52 a	1.45 a
250	1.59 a	1.21 a	1.35 a	1.63 a	1.62 a
50	1.09 a	0.80 a	0.66 a	0.92 a	0.98 a
-150	0.81 ab	0.67 ab	0.37 b	1.07 a	1.02 a

\*Means within each row followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

Table 6b. Differences in weight gain (g) of the tolerant rice variety (IR46) grown for 3 weeks between acid and non-acid sulfate soils under controlled redox potential conditions\*.

Eh(mV)	Acid sulfate soils			Non-acid	
	Ma	Rs	Rsa	Bk	Rb
500	2.62 a	2.71 a	2.58 a	3.25 a	2.75 a
250	2.46 a	2.62 a	1.73 a	3.34 a	3.11 a
50	2.92 a	3.21 a	1.77 a	2.07 a	2.84 a
-150	0.80 ab	0.93 ab	0.34 b	1.09 a	0.94 ab

\*Means within each row followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

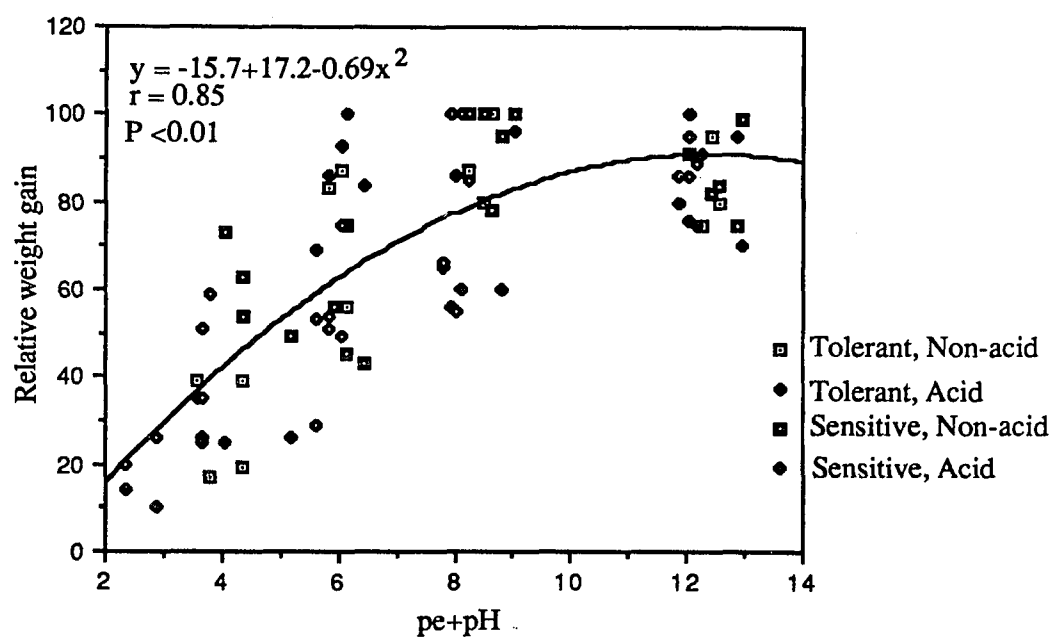


Figure 1. Relative weight gain of rice shoot tissue for both varieties as affected by controlled redox of the five soils.

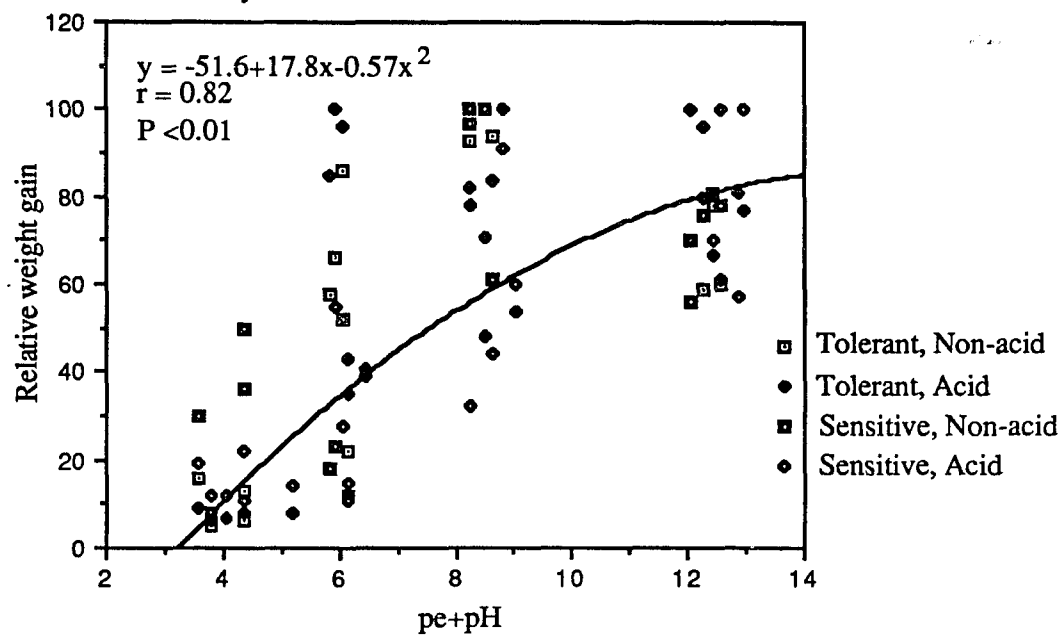


Figure 2. Relative weight gain of rice root tissue for both varieties as affected by controlled redox of the five soils.

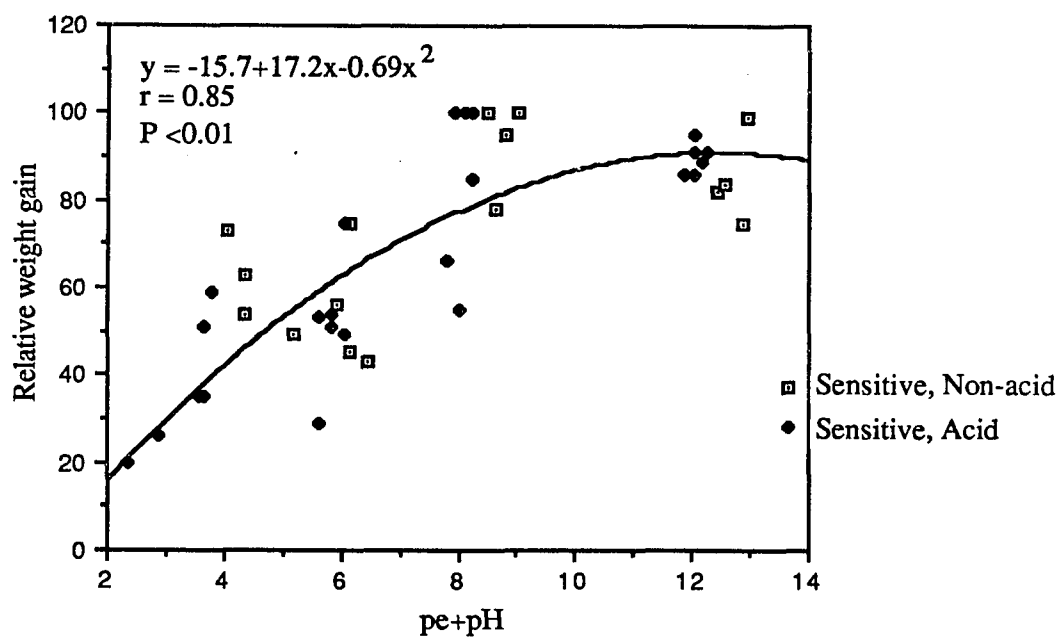


Figure 3. Relative weight gain of IR26 shoot tissue as affected by controlled redox of the five soils.

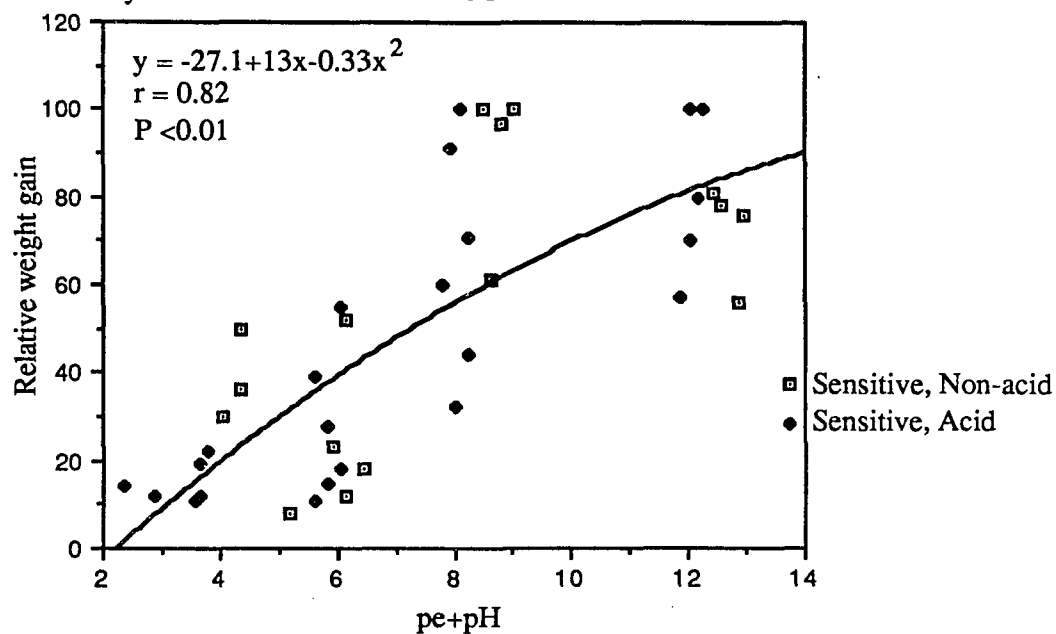


Figure 4. Relative weight gain of IR26 root tissue as affected by controlled redox of the five soils.

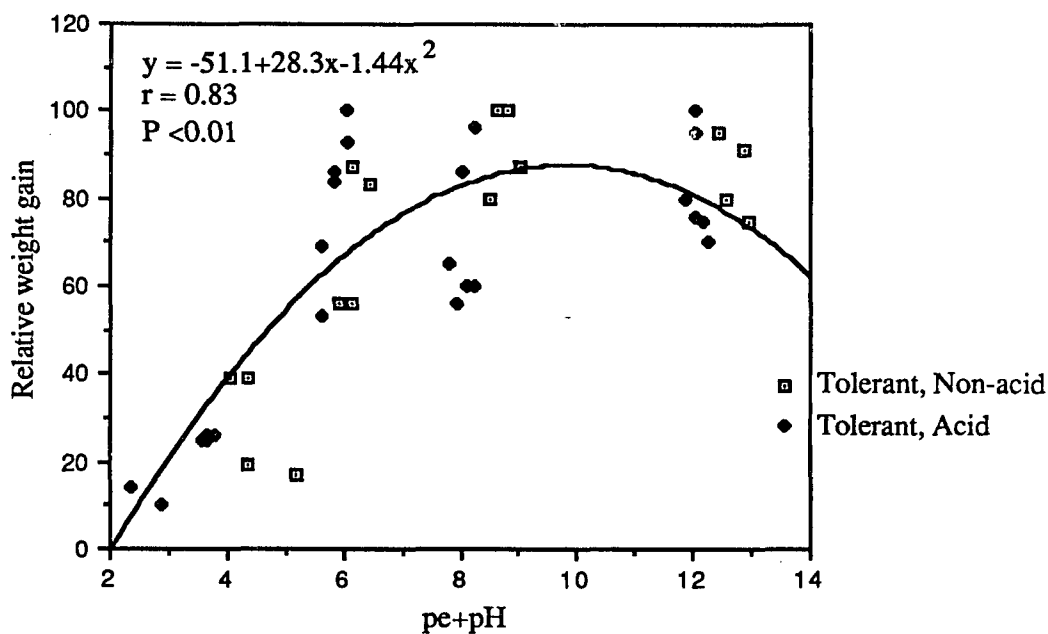


Figure 5. Relative weight gain of IR46 shoot tissue as affected by controlled redox of the five soils.

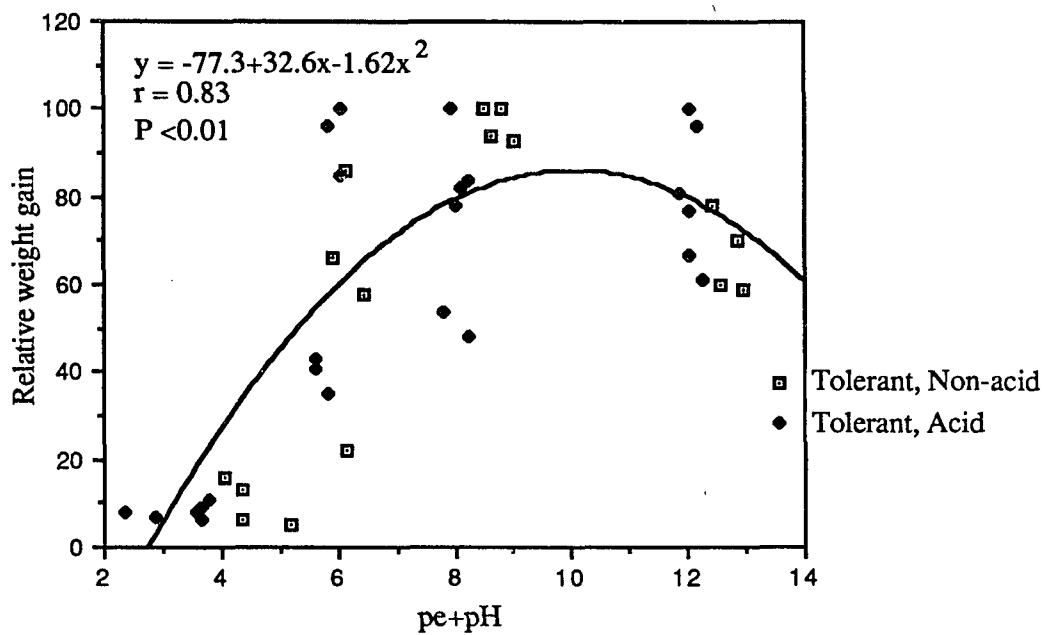


Figure 6. Relative weight gain of IR46 root tissue as affected by controlled redox of the five soils.

considered separately as were the different varieties since the average height of the IR 46 is much greater than that of the IR 26 variety due to genetic differences. The independent variables must correlate with the rice weight gain at significance level of 0.15 or greater to be included in the regression analysis. These variables were then selected to enter into the maximum  $R^2$  improvement statistical procedure. With the aid of both the stepwise technique and the maximum  $R^2$  improvement procedure, four sets of variables most likely to be related to weight gain in each variety were determined (Table 7).

#### Interpretation of the regression model

The rice plants grown in acid sulfate soils were provided with complete N-P-K fertilization as described previously. Thus, moderately well-nourished conditions were provided in order to avoid any limiting factors arising from major soil nutrient deficiencies, and N, P, and K, were omitted from the model building process so that major nutrient status was not included in the regression analysis. While this may be a major omission from some perspectives, it is a reasonable approach from other points of view since some liming with moderate N and P additions is frequently recommended to increase production on acid sulfate soils. Weight gain was used as the most suitable dependent variable representing growth conditions of the laboratory microcosms studies here.

#### Prediction model in non-acid sulfate soils (Bangkok and Ratchaburi)

##### IR 26 variety

Regression analysis with a combination of the Stepwise technique and

Table 7. Models and the subset of models for predicting weight gain of rice varieties (IR26 and IR46) in non-acid and acid sulfate soils over all controlled redox conditions

Model	R <sup>2</sup>
IR 26 Variety	
Non-acid	
pe+pH	0.39
pe+pH, Fep	0.77
pe+pH, Fep, Fep:Mnp	0.82*
pe+pH, FeS, pZn <sup>2+</sup>	0.63#
Acid sulfate soils	
pe+pH	0.64
Fep:Mnp	0.64
pe+pH, Fep:Mnp	0.73
pe+pH, Fep:Mnp, Fep:(Kp+Cap+Mgp)	0.76
pe+pH, E'-Mn, Fep:(Kp+Cap+Mgp)	0.80
pe+pH, Fep:Mnp, Fep:(Kp+Cap+Mgp), pZn <sup>2+</sup>	0.80*
pe+pH, FeS:MnS	0.71#
IR 46 variety	
Non-acid	
pe+pH	0.48
pe+pH, Fep:Mnp, pZn <sup>2+</sup>	0.82*
pe+pH, E'-Fe	0.57#
Acid sulfate soils	
pe+pH	0.42
pe+pH, pCa <sup>2+</sup>	0.50
pZn <sup>2+</sup>	0.49
Fep:(Kp+Cap+Mgp), pZn <sup>2+</sup>	0.71
Fep:(Kp+Cap+Mgp), pZn <sup>2+</sup> , Alp	0.78*
pe+pH, pZn <sup>2+</sup> , Als	0.71#

\* Model selected to represent each variety in each soil type.

# Soil association model for each variety in each soil type which is the best model containing only soil independent variables.

the Maximum  $R^2$  Improvement procedure produced three prediction models relating IR 26 weight gain on non acid sulfate soils to the independent variables (Table 7). The best model contained three variables with an  $R^2$  of 0.82 indicating about 82% of total variation in weight gain can be explained by the three variables in the model (Table 8 and Figure 7). Three variables pe + pH, plant Fe, and Fe:Mn ratio in plant tissue, entered into the model. Plant Fe showed no significant relationship with weight gain if considered separately by the linear correlation, but plant Fe entered into a predictive model containing pe + pH and plant Fe:Mn ratio. Predicted weight gain from the regression equation and the experimental data are plotted as shown in Figure 7. A soil association model which is the regression model yielding the highest  $R^2$  including only soil variables contained pe + pH, water-soluble Fe ( $Fe_s$ ), and  $Zn^{2+}$  activity which yielded an  $R^2$  of 0.63.

#### IR 46 variety

Independent variables best describing weight gain of IR 46 on non-acid sulfate soils are shown in Table 7. The model with the analysis of variance obtained from a regression analysis is shown in Table 9. The best three variable model accounted for 82% of the total variation of weight gain for IR 46. Figure 8 depicts the plot of predicted weight gain vs actual weight gain obtained from the regression model for the IR 46 variety on non-acid sulfate soils. It was observed that 57% of the total variation in weight gain was explained by the soil factors of pe + pH and the divalent charge fraction due to Fe in the soil solution ( $E'-Fe$ ).

Table 8. Analysis of variance, regression coefficients and statistics of fit for dependent variable weight gain of the IR26 rice variety in non acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV, %
Regression	3	1.5103	18.12	0.01	0.82	12.65
Error	12	0.2244				
Total	15	1.7347				

Source	Regression coefficient (b)	Partial sum of squares	F-value	P
Intercept	0.9726			
pe+pH	0.1216	0.6426	24.59	0.01
Fe <sub>p</sub> :Mn <sub>p</sub>	-0.3355	0.0875	3.35	0.10
Fe <sub>p</sub>	-0.0025	0.6290	24.07	0.01

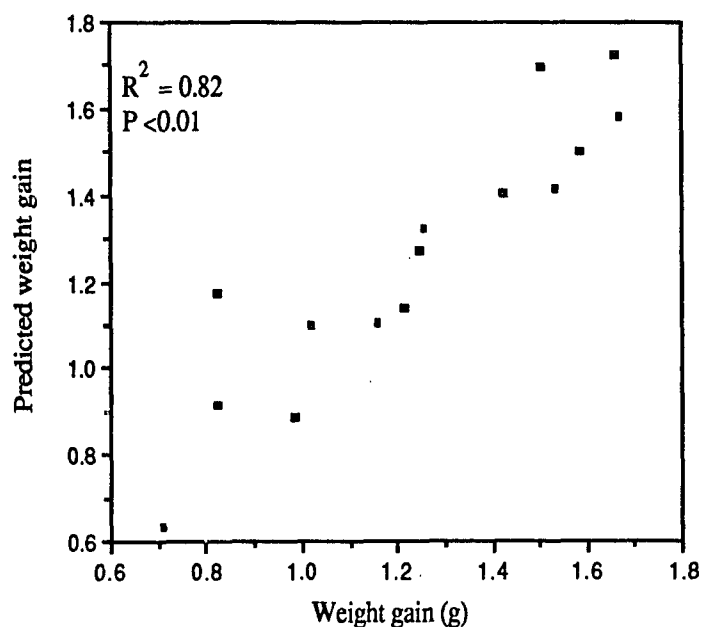


Figure 7. Predicted weight gain for IR26 in non-acid sulfate soils.

$$(\text{Predicted} = 0.97 + 0.12(\text{pe} + \text{pH}) - 0.34\text{Fe}_p : \text{Mn}_p - 0.002\text{Fe}_p)$$



Table 9. Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of IR46 rice variety in non-acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV, %
Regression	3	11.4348	18.01	0.01	0.82	18.9
Error	12	2.5397				
Total	15	13.9746				

Source	Regression coefficient(b)	Partial sum of squares	F-value	P
Intercept	10.3497			
pe+pH	0.1180	0.4818	13.02	0.05
Fe:p:Mnp	-1.0174	0.0711	4.69	0.05
pZn <sup>2+</sup>	-1.4029	0.2654	13.65	0.05

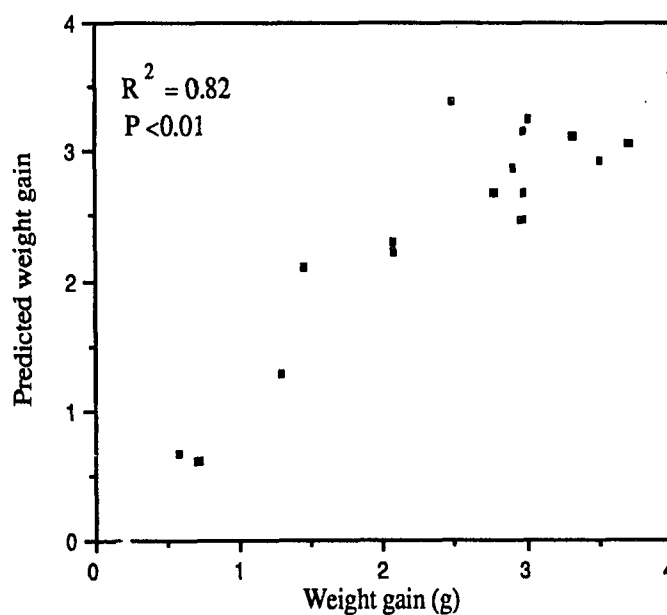


Figure 8. Predicted weight gain for IR46 in non-acid sulfate soils.

$$(\text{Predicted} = 10.4 + 0.12(\text{pe} + \text{pH}) - 1.02\text{Fe p:Mn P} - 1.40\text{pZn}^{2+})$$

Prediction model in acid sulfate soils (Mahaphot, Rangsit, and Rangsit Very Acid)

IR 26 variety

The model selected for IR 26 on acid sulfate soils consisted of 4 variables with an  $R^2$  of 0.80 (Table 7). The statistics of fit for the dependent variable weight gain are described in details in Table 10. The ratio of Fe to Mn in plant tissue accounted for 64% of the total variation in weight gain. The ratio of Fe to the sum of K, Ca, and Mg in plant tissue also entered the model, but its contribution to the model was lower than for the Fe:Mn ratio based on the simple linear correlations (Table 4) and on the results from the maximum  $R^2$  improvement procedure. Redox potential and pH conditions ( $pe + pH$ ) and activity of  $Zn^{2+}$  appeared in the model and these two variables probably correlated to each other. Several soil properties of Fe were negatively correlated with weight gain such as soil solution Fe ( $r=-0.43$ ,  $P=0.04$ ), exchangeable Fe ( $r=-0.69$ ,  $P=0.0001$ ), solution activity of  $Fe^{2+}$  ( $r=-0.69$ ,  $P=0.0002$ ), divalent charge fraction on CEC due to Fe ( $E-Fe$ ) ( $r=-0.70$ ,  $P=0.0001$ ), and divalent charge fraction in soil solution due to Fe ( $E'-Fe$ ) ( $r=-0.74$ ,  $P=0.0001$ ). However all soil properties of Fe may have been deleted from the model because the ratio of Fe to Mn in plant tissue yielded the highest simple correlation with rice weight gain ( $r=-0.80$ ,  $P=0.0001$ ). Predicted weight gains calculated from the model are plotted against true weight gain for the IR 26 rice on acid sulfate soils as depicted in Figure 9. In this soil type/variety combination,  $pe + pH$  and Fe:Mn ratio of the water-soluble fraction in soil solution

Table 10. Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of IR26 rice variety in acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV,%
Regression	4	3.4581	18.55	0.01	0.80	20.02
Error	19	0.8853				
Total	23	4.3434				

Source	Regression coefficient (b)	Partial sum of squares	F-value	P
Intercept	3.0866			
pe+pH	0.0399	0.1219	2.62	0.15
pZn <sup>2+</sup>	-0.3287	0.1505	3.23	0.15
Fep:(Kp+Cap+Mgp)	-14.9234	0.2596	5.57	0.15
Fep:Mnp	-0.1242	0.1400	3.01	0.15

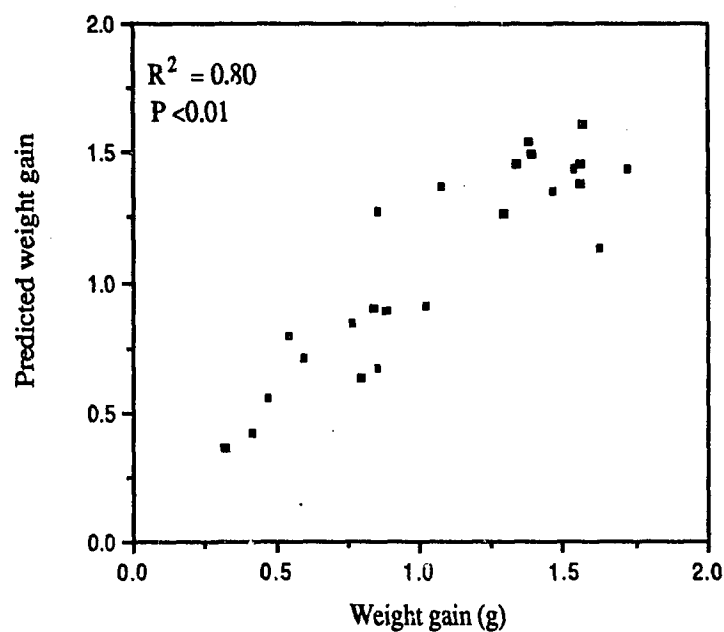


Figure 9. Predicted weight gain for IR26 in acid sulfate soils.

$$(\text{Predicted} = 3.09 + 0.04(\text{pe} + \text{pH}) - 0.33\text{pZn}^{2+} - 14.9\text{Fe p} : (\text{K p} + \text{Ca p} + \text{Mg p}) - 0.12\text{Fe p} : \text{Mn p})$$

comprises the best soil association model that accounted for 71% of the total variation in weight gain of IR 26 in acid sulfate soils.

IR 46 variety

The prediction model for IR 46 on acid sulfate soils included three variables with an  $R^2$  of 0.78 (Table 7). Activity of  $Zn^{2+}$  ( $pZn^{2+}$ ), the ratio of Fe: K+Ca+Mg in plant tissue, and plant content of Al ( $Al_p$ ) were the variables entered into the prediction model. The negative correlation between  $Al_p$  and rice weight gain was not statistically significant at the 0.15 level, but  $Al_p$  may have entered into the model due to its relationship with other variables. There was a highly significant correlation between  $Fe_p:Mn_p$  ratio and rice weight gain ( $r=-0.49$ ,  $P=0.01$ ) as shown in Table 7, but the  $Fe_p:Mn_p$  ratio did not appear in the models as the best model with 1, 2, or 3 independent variables. The  $pe + pH$  had an  $R^2$  of 0.42 while  $pZn^{2+}$  had an  $R^2$  of 0.49, thus  $pZn^{2+}$  was selected as the best one-variable model found by the regression technique. Several soil properties of Fe were significantly correlated with rice weight gain but they did not enter into the model. However, independent variables of high correlation with weight gain may not necessarily be the ones entered into the regression model (Little and Hills, 1978). The predicted value of weight gain and the true weight gain are plotted in Figure 10 and their statistics of regression analysis are illustrated in Table 11. The  $pe + pH$ ,  $Zn^{2+}$  activity, and water-soluble Al were soil variables that appeared in the best soil association model giving an  $R^2$  of 0.71.

Table 11. Analysis of variance, regression coefficients and statistics of fit for the dependent variable weight gain of IR46 rice variety in acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV, %
Regression	3	16.4175	23.77	0.01	0.78	23.3
Error	20	4.6046				
Total	23	21.0221				

Source	Regression coefficient (b)	Partial sum of squares	F-value	P
Intercept	16.8733			
Fep:(Kp+Cap+Mgp)	-63.6665	2.6238	11.40	0.01
pZn <sup>2+</sup>	-2.3409	11.9379	51.85	0.01
Alp	-0.0072	1.5666	6.80	0.01

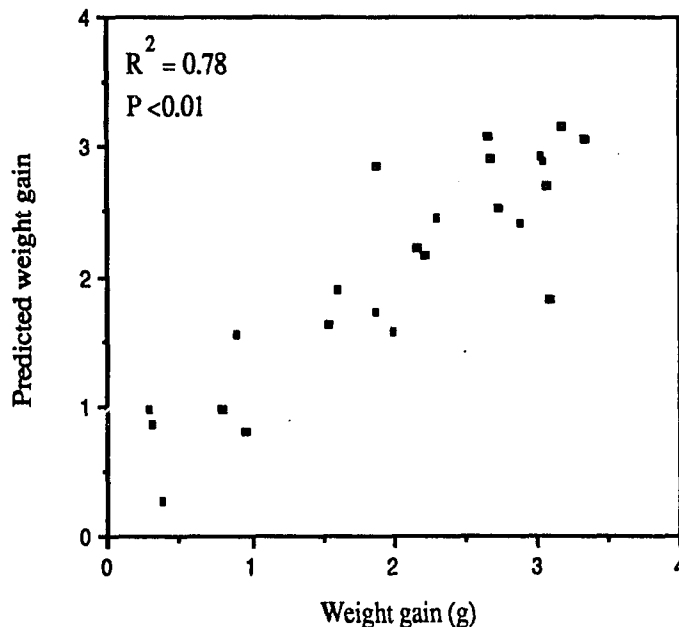


Figure 10. Predicted weight gain for IR46 in acid sulfate soils.  
(Predicted=16.9-63.7Fep:(Kp+Cap+Mgp)-2.34pZn<sup>2+</sup>-0.007Alp)

### Summary of the model for rice growth

Rice weight gain of the tolerant (IR 46) and sensitive (IR 26) varieties on non-acid and acid sulfate soils were explained by several independent variables such as plant tissue composition and soil properties by using regression techniques. Broome et al. (1975) suggested predictive models obtained from multiple regression analyses are not necessarily practical, but can provide a guide to identifying relationship. The multiple regression technique provides information for further investigation, indicating important variables affecting the independent variables of interest (Draper and Smith, 1966).

These results indicate that  $pe + pH$  is an important factor explaining the variation of rice weight gain for all variety/soil type combinations. Weight gain generally increased with an increase of  $pe + pH$  (Table 6a and 6b). Regression analyses showed that the response of rice weight gain to redox was curvilinear (Table 12). Plots of relative weight gain as a function of  $pe + pH$  (Figures 1,3,5) clearly illustrated that the relationship is not linear over the whole range of redox and  $pH$  studied here ( $pe + pH$  of 2.37 to 12.94). The rate of weight gain of rice increased with an increase of  $pe + pH$  to a value of approximately 10, then started to level off or decline. Data in Tables 6a, and 6b indicate a marked effect of redox on weight gain. Growth of both rice varieties was generally lower in the acid sulfate soil, and under low  $pe + pH$  level conditions ( $pe + pH$  at 2.82 to 4.57) in both soils. The sensitive (IR 26) rice variety was more affected than the tolerant (IR 46) variety only in acid sulfate soils, while they both were similarly affected in non-acid sulfate soils. Jugsujinda and Patrick (1977)

Table 12. Analysis of weight gain and pe+pH over two rice varieties and all soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>
Regression	2	23.3864	21.81	0.01	0.36
Error	77	41.2883			
Total	79	64.6747			

Regression	Parameter	Regression coefficient (b)	Partial sum of squares	F-value	P
Linear	Intercept	-1.0994			
	pe+pH	0.6367	9.7338	18.15	0.01
Quadratic	(pe+pH) <sup>2</sup>	-0.0303	5.9548	11.11	0.01

observed that at pH 5.0, plants grown under  $pe + pH = 4.07$  gave lower dry weights than plants grown under aerobic conditions  $pe + pH = 15.7$  which corresponded well with the results found in this study where high redox usually produced weight gain. That the growth of rice is affected by redox potential (Eh) and pH as has been reported by several workers (Tolley et al., 1986; Jugsuginda and Patrick, 1977; Chaudhry and McLean, 1963). Recently, the effect of  $pe + pH$  on the growth of paddy rice has been reported (Schwab and Lindsay, 1983; Sajwan and Lindsay, 1986) on soils of high initial pH values ( $pH > 8$ ). These authors also found growth of rice is affected by  $pe + pH$ .

Following the importance of soil  $pe + pH$  is the ratio of Fe to Mn in plant tissue in the prediction models. Only the prediction model for IR 46 on acid sulfate soils did not include Fe:Mn ratio since the ratio of Fe: K + Ca + Mg was an entry selected for the model despite the fact that a simple correlation of the latter with weight gain was lower than that of the former. The Fe:Mn ratio played an important role. The data suggests a decrease of rice weight gain was accompanied by an increase in the Fe:Mn ratio. Knezek and Greinert (1971) found a decrease of growth with an increase in the Fe:Mn ratio in tissue of Navy beans. Shieve (1941) reported Fe:Mn ratios of 1.5 to 2.5 is required for normal plant growth. Tanaka and Navasero (1966) found the Fe:Mn ratio in plant tissue varied from 0.01 to 25.8 with a very low production of rice growth under the high Fe:Mn ratio conditions. They attempted to correlate Fe:Mn ratio in plant tissue with leaf iron toxicity symptoms but failed to observe a significant relationship. Using their data to determine the simple correlation between plant weight (g/plant) and Fe:Mn ratio in plant tissue, it was found that the Fe:Mn ratio was



significantly related to plant weight ( $r=-0.56$ ,  $P=0.01$ ,  $n=20$ ). Yoshida (1981) listed the critical contents of various elements for deficiency and toxicity in rice at several stages of growth, but for Fe, critical contents information was provided only for the tillering stage. It is interesting to note here that the Fe:Mn ratio in shoot tissue of rice at tillering stage may be used to predict the adverse effect of Fe on the growth status of rice at subsequent stages. The Fe:(K+Ca+Mg) ratios in plant tissue were correlated to rice weight gain only in acid sulfate soils, for both IR 46 and IR 26 varieties, and the simple correlation coefficient was higher for sensitive rice (IR 26) than for tolerant rice (IR 46). Thus, the data may indicate the tendency of multiple nutritional stress due to a deficiency of and/or an unbalanced supply of K, Ca, and Mg versus Fe in these acid sulfate soils as suggested by several authors (Howeler, 1973; van Breemen and Moorman, 1978; Benckiser et al., 1982; Ottow et al., 1982; Ottow et al., 1983; Benckiser et al., 1984).

Under moderate fertilized conditions as provided in this study, the results indicate the positive effect of some micronutrients such as Zn. For micronutrients being entered into the prediction model, activity of  $Zn^{2+}$  appeared for both varieties in acid sulfate soils and for the IR46 variety in non-acid sulfate soils. Activity of  $Zn^{2+}$  in soil solution increased under high pe + pH which was partly due to a decrease in pH associated with the higher Eh levels. Gambrell et al. (1977) noted more Zn appeared in sediment solutions at low pH and high redox potential. Sajwan and Lindsay (1986) reported the Zn concentration was high at high pe + pH and decreased as the pe + pH level decreased. The IRRI (1970) reported soil reduction depresses both the concentration of Zn in the

soil solution of flooded soils and Zn uptake by rice plants. Zinc deficiency has been reported when soils are flooded and when crop residues are actively undergoing decomposition (Mikkelsen and Brandon, 1975). The above findings corresponded well with the results of this experiment where activity of  $\text{Zn}^{2+}$  increased under low pH and high Eh. Soil reduction may permit the formation of insoluble zinc sulfide and the complexing of zinc with large molecular weight humic materials resulting in low zinc in soil solution. Activity of  $\text{Zn}^{2+}$  is clearly related to rice weight gain, especially on acid sulfate soils which normally contain higher zinc in soil solution than soils with higher pH (non-acid sulfate soils studied here). Uptake of Zn increased as redox was increased in this experiment. Attanandana and Vacharotayan (1982) also found a positive relationship between Zn in soil solution and dry matter production of rice plants on both non-acid and acid sulfate soils, but the correlation was significant only in non-acid sulfate soils. Jugsujinda and Patrick (1977) reported the uptake of Zn by rice plants was higher under aerobic than under anaerobic conditions at pH 4.5, 6.0, and 7.5. Those findings indicate the probable beneficial effect of added Zn on rice grown in flooded soils. The results in this study here also showed activity of  $\text{Zn}^{2+}$  was one of the variables positively associated with rice weight gain.

Soil solution Fe was negatively associated with the IR 46 weight gain on non-acid sulfate soils due to the influence of low redox such as at an Eh of 50 mV where soil solution Fe tends to be at the maximum level compared to the other Eh levels (Eh 500, 250, and -150 mV). Soil solution Fe at Eh -150 mV was lower than that of Eh 50 mV but still higher than at other Eh levels. Precipitation of soil solution Fe may

have occurred at Eh -150 mV due to increased pH or formation of FeS that might have been produced at the lowest Eh level of this experiment.

### CONCLUSIONS

The results obtained with a multiple regression analyses indicated several variables were significantly associated with the variation in weight gain of the two rice varieties (IR 46, and IR 26) in both non-acid and acid sulfate soils. The pe + pH was the most significant single variable found for all soil type/variety combinations. Redox potential and pH are important factors associated with transformations of Fe, Mn, and Zn in soils affecting their plant availability. The Fe:Mn ratio in plant tissue appeared to play an important role second to pe + pH. Plant Fe and soil solution Fe also appeared to be important factors. The Fe:K+Ca+Mg ratio appeared in the model for acid sulfate soils implying the balance between Fe availability and these other minerals (K, Ca, and Mg) influence Fe stress to rice plants. Zinc activity seemed to positively associated with growth of both rice varieties in acid sulfate soils and associated with growth of IR 46 rice in non-acid sulfate soils.

### REFERENCES

- Adams, F. 1974. Soil solution. p. 441-481. In E. W. Carson (ed.) The plant root and its environment. University Press of Virginia. Charlottesville.
- Attanandana, T., and S. Vacharotayan. 1982. Chemical characteristics and fertility status of acid sulfate soils of Thailand, p. 118-130. In H. Dost and N van Breemen (ed). Proc. Bangkok Symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Attanandana, T., and S. Vacharotayan. 1983. Rock phosphate utilization on acid sulfate soils of Thailand. Paper No. 12. In KU/FFTC (ed.)

- Ecology and management of problem soils in Asia. Kasetsart Univ., Bangkok, Thailand.
- Benckiser, G., J.C.G. Ottow, I. Watanabe, and S. Santiago. 1984. The mechanism of excessive iron-uptake (iron toxicity) of wetland rice. *J. Plant Nutrition*. 7(1-5):177-185.
- Benckiser, G., J.C.G. Ottow, S. Santiago, and I. Watanabe. 1982. Physicochemical characterization of iron-toxic soils in some Asian countries. *IRRI Res. Paper Series* 85:1-11.
- Broome, S.W., W.W. Woodhouse, Jr., and E.D., Seneca. 1975. The relationship of mineral nutrients to growth of Spartina alterniflora in North Carolina: I. Nutritional Status of plants and soils in natural stands. *Soil Sci. Soc. Am. Proc.* 39:295-301.
- Charoenchamratcheep, C., B. Tantisira, P. Chitnusun, and V. Sin-Aiem. 1982. The effects of liming and fertilizer applications of acid sulfate soils for improvement of rice production in Thailand. p. 157-171. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Chaudhry, M.S., and E.O. McLean. 1963. Comparative effects of flooded soils conditions and nitrogen application on growth and nutrient uptake by rice plants. *Agron. J.* 55, 565-567.
- Draper, N.R., and H. Smith. 1966. *Applied regression analysis*. John Wiley & Sons, Inc., New York.
- Gambrell, R.P., R.A. Khalid, M.G. Verloo, and W.H. Patrick, Jr., 1975. Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Part II. Materials and Methods, Results and Discussion, Contract Report, Office of Dredged Material Research, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., Contract report D-77-4.
- Garrels, R.M., and C.L. Christ. 1965. *Solutions, minerals, and equilibria*. Harper and Row, New York.
- Howeler, R.H. 1973. Iron-induced orange disease of rice in relation to physico-chemical changes in a flooded oxisol. *Soil Sci. Soc. Am. Proc.* 37:898-903.
- IRRI, Int. Rice Res. Inst., Annual Report. 1970. Los Banos, Philippines.
- Jugsujinda, A., and W. H. Patrick, Jr. 1977. Growth and nutrient uptake by rice in a flooded soil under controlled aerobic-anaerobic and pH conditions. *Agron. J.* 69:705-710.
- Jugsujinda, A., P. Duangpattra, S. Suwanwaong, and B.R. Jackson. 1971. Sources of rock phosphate and their residual effects on flooded rice.

Paper presented at the 3rd TVA Meeting of the Advisory Committee on Rice Fertilization, Muscle Shoal, Alabama, U.S.A.

- Kanareugsa, C., J. Somboondumrongkul, and J. Takahashi. 1983. Attempt at improving the productivity of acid sulfate soils. Paper No. 9. In KU/FFIC (ed.) Ecology and management of problem soils in Asia. Kasetsart Univ., Bangkok, Thailand.
- Khasawneh, T.E. 1971. Solution ion acitivity and plant growth. Soil Sci. Soc. Am. Proc. 35:426-436.
- Knezek, B.D., and H. Greinert. 1971. Influence of soil iron and manganese chelate interactions upon the iron and manganese nutrition of bean plants (Phaseolus vulgaris L.). Agron. J. 63:617-619.
- Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley, New York.
- Little, M.T., and Hills, F.J. 1978. Agricultural experimentation: Design and analysis. Wiley, New York.
- Maneewon, M., N. Thawornwong, and B. Tantisira. 1982. Study on rates of marl for rice production on acid sulfate soils in Thailand. p. 172-186, In H. Dost and N. van Breemen (ed.) Proc. Bangkok Symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Mikkelsen, D. S. and D. M. Brandon. 1975. Zinc deficiency in California rice. California Agric., September, 1975.
- Moore, P.A., Jr. 1987. Metal behavior in acid sulfate soils of Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Nhung, M. M., and F.N. Ponnampuruma. 1966. Effect of calcium carbonate, manganese dioxide, ferric hydroxide, and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulfate soil. Soil Sci. 102:19-41.
- Ottow, J.C.G., G. Benckiser, and I. Watanabe. 1982. Iron toxicity of rice as a multiple nutritional stress. Trop. Agric. Res. Ser. (Japan) 15:167-179.
- Ottow, J.C.G., G. Benckiser, and I. Watanabe, and S. Santiago. 1983. Multiple nutritional stress as the prerequisite for iron toxicity of wetland rice (Oryza sativa L.). Trop. Agric. (Trinidad) 60:102-106.
- Patrick, W.H., Jr., B. G. Williams, and J.T. Moraghan. 1973. A simple system for controlling redox potential and pH in soil suspensions. Soil Sci. Soc. Am. Proc. 37:331-332.
- Patrick, and W. J. Fontenot. 1976. Growth and mineral composition of rice at various soil moisture tensions and oxygen levels. Agron. J. 68:325-329.

- Ponnamperuma, F.N. 1965. Dynamic aspects of flooded soils and the nutrition of the rice plant. p. 295-328, 461-462. In *The mineral nutrition of the rice plant*. John Hopkins Press, Baltimore, Md.
- Ponnamperuma, F.N. 1967. A theoretical study of aqueous carbonate equilibria. *Soil Sci.* 103:90-100.
- Ponnamperuma, F.N. 1972. Chemistry of submerged soils. *Adv. Agron.* 24: 29-95.
- Ponnamperuma, F.N., T. Attanandana, and G. Beye. 1973. Amelioration of three acid sulfate soils for lowland rice. p. 391-406. In H. Dost (ed). *Acid sulfate soils*. Proc. Int. Symp. ILRI Pub. 18, Vol. II, Wageningen, The Netherlands.
- Ponnamperuma, F.N., and J.L. Solivas. 1982. Field amelioration of acid sulfate soil for rice with manganese dioxide and lime. p. 213-220. In H. Dost and N. van Breemen (ed). *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Reddy, C. N., Aroon Jugsujinda, and W.H. Patrick, Jr. 1976. A system for growing plants under controlled redox potential-pH conditions. *Agron. J.* 68:987-989.
- Sajwan, K.S., and W.L. Lindsay. 1986. Effects of redox on zinc deficiency in paddy rice. *Soil Sci. Soc. Am. J.* 50:1264-1269.
- SAS. 1985. SAS user's guide: Statistics, Version 5 edition. SAS Institute Inc., Cary, NC, USA.
- Satawathananont, S. 1986. Redox, pH, and Ion Chemistry of Acid Sulfate Rice Soils in Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Schwab, A.P., and W.L. Lindsay. 1983. Effect of redox on the solubility and availability of iron. *Soil Sci. Soc. Am. J.* 47:201-205.
- Senewiratne, S.T., and D. S. Mikkelsen. 1961. Physiological factors limiting growth and yield of *Oryza sativa* under unflooded conditions. *Plant Soil* 14:127-146.
- Shive, J.W. 1941. Significant roles of trace elements in the nutrition of plants. *Plant Physiology* 16:435-445.
- Sombatpanit, S. 1975. Improvement of acid sulfate soils in Thailand. *Int. Rice Res. Conf. 1975. Contrib.* 26. 3 p.
- Sposito, G., C. Jouany, K.M. Holtzclaw, and C.S. LeVesque. 1983. Calcium-magnesium exchange on Wyoming bentonite in the presence of adsorbed sodium. *Soil Sci. Soc. Am. J.* 47:1081-1085.
- Sposito, G., and S.V. Mattigod. 1979. GEOCHEM: A computer program for the calculation of chemical equilibria in soil solution and other

- natural water systems. Kearney Foundation of Soil Science, Univ. of Calif., Riverside.
- Tanaka, A., and S.A. Navasero. 1966a. Interaction between iron and manganese in the rice plant. *Soil Sci. Plant Nutr.* 12:197-201.
- Tanaka, A., and S.A. Navasero. 1966b. Chlorosis of the rice plant induced by high pH of culture solution. *Soil Sci. Plant Nutr.* 12:213-219.
- Tolley, M.D., R.D. Delaune, and W.H., Patrick, Jr. 1986. The effect of sediment redox potential and soil acidity on nitrogen uptake, anaerobic root respiration, and growth of rice (*Oryza sativa*). *Plant and Soil* 93:323-331.
- Toure, M. 1982. Improvement of acid sulfate soils: effects of lime, wood ash, green manure, and preflooding. p. 223-236. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Uwaniyom, J., and C. Charoenchamratcheep. 1983. Liming of acid sulfate paddy soils of Bangkok Plain. Paper No. 10. In KU/FFIC (ed.) *Ecology and management of problem soils in Asia*. Kasetsart Univ., Bangkok, Thailand.
- van Breemen, N. 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. *Agric. Res. Rep.* 848. PUDOC, Wageningen, The Netherlands.
- van Breemen, N., and F. R. Moorman. 1978. Iron toxic soils. p. 781-800. In F. N. Ponnampetuma (ed.) *International Rice Research Institute*. Los Banos, Laguna, Philippines.
- van den Eelaart, L.J. 1982. Problems in reclaiming and managing tidal lands of Sumatra and Kalimantan, Indonesia. p. 272-290. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Vo-Tong Xuan, Nguyen Kim Quang and Le Quang Tri. 1982. Rice cultivation on acid sulfate soils in the Vietnamese Mekong Delta. p. 251-259. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Yin Toh Penq and Poon Yew Chin. 1982. Effect of water management on field performance of oil palms on acid sulphate soils in Peninsular Malaysia. p. 260-271. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Yoshida, S. 1981. *Fundamental of rice crop science*. Int. Rice Res. Inst., Los Banos, Philippines. 269 p.

Yoshida, S., D. A. Forno, J. H. Cock, and K.A. Gomez. 1976. Laboratory manual for physiological studies of rice. Int. Rice Res. Inst., Los Banos, Philippines. 83 p.



## Chapter Five

### Rice Growth in Acid Sulfate Soils Under Controlled pH and Redox Potential Conditions

Rice Growth in Acid Sulfate Soils Under Controlled pH and Redox  
Potential Conditions.

ABSTRACT

Two rice varieties were selected for this study. One (IR46) is relatively tolerant to acid sulfate soil conditions and the other is relatively sensitive (IR26). Seedlings of these two varieties were grown for 3 weeks under controlled pH and redox potential (Eh) conditions in acid sulfate (Sulfic Tropaquept) and non-acid sulfate (Typic Tropaquept) soil materials in laboratory microcosms. Soil suspensions were controlled at three pH levels (3.5, 4.5, and 5.5) and three redox potential levels (500, 250, and 50 mV). A curvilinear relationship was observed between  $p_e + pH$  and growth of both rice varieties. A decrease in  $p_e + pH$  from 8.72 to 4.34 resulted in a decrease in rice weight gain while the rice weight gain tended to decrease to a smaller degree as the  $p_e + pH$  increased from 8.72 to 13.94.

Results from a multiple regression analysis indicated the Fe:Mn ratio in plant tissue was the most important plant property associated with the variation in weight gain of both rice varieties over all soil treatment conditions. Plant properties negatively associated with rice weight gain included the Fe:Mn ratio, Fe content, Fe:K+Ca+Mg ratio, and the Fe:Al ratio in the plant tissue. Activity of  $Al^{3+}$  in the soil solution was also negatively associated with rice weight gain. Divalent charge fraction in the water-soluble fraction due to  $Fe(E-Fe)$  was negatively associated with IR46 weight gain in non-acid sulfate soils.

Variables positively correlated with rice weight gain included the Mg content in the plant tissue, and the divalent charge fraction in the soil solution due to Mg ( $E'-Mg$ ). Regression equations for predicting rice weight gain of both varieties in non-acid and acid sulfate soils are given.

## INTRODUCTION

The influence of soil pH and Eh on transformations of several nutrients affecting both plant uptake of nutrients and growth of plants has been reported (Patrick, 1964; Gotoh and Patrick, 1972, 1974; Gambrell et al., 1977; Patrick and Fontenot, 1976; Reddy and Patrick, 1977; Jugsujinda and Patrick, 1977; Schwab and Lindsay, 1983; Sajwan and Lindsay, 1986; Tolley et al., 1986; Satawathananont, 1986; Moore, 1987). Schwab and Lindsay (1983) and Sajwan and Lindsay (1986) used the parameter  $pe + pH$  to describe rice growth in their experiments with controlled redox potential (Eh). They found an effect of  $pe + pH$  on the growth of rice.

The results of Chapter 4 revealed that as the two rice varieties were grown under only controlled redox potential conditions in acid and non-acid sulfate soils where soil pH was not adjusted, growth of the rice plants was affected by  $pe + pH$  and several other soil and plant properties. In addition, a study on ion chemistry in suspensions of acid sulfate soils has recently been conducted in this Laboratory under controlled pH and redox potential conditions and the results indicated a strong effect of both of these two parameters, either combine or individually on transformations of several nutrients in these soils (Satawathananont, 1986). However, the question yet to be consider is

the degree of impact the two parameters might have on growth and yield of rice where both are controlled in laboratory studies. Thus study was initiated to investigate the interaction between pH and redox potential in affecting both toxic materials and nutrient availability on the growth of two rice varieties in acid and non-acid sulfate soil materials from Thailand.

#### MATERIALS AND METHODS

The acid and non-acid sulfate soil materials used in this study were described for previous experiment (Characterization of Soil Materials section). The treatments studied were three different redox potential levels ( $E_h = +500, +250, \text{ and } +50 \text{ mV}$ ) and three pH levels (3.5, 4.5, and 5.5). Redox potential was maintained at the desired level by an automatic addition of air (oxygen) when  $E_h$  fell below the pre-selected value. The pH was controlled by manually adding either 1 M HCl or 1 M  $\text{Ca(OH)}_2$  to obtain the desired level, and the adjustment of pH was done twice daily if necessary. Addition of acid or alkali was achieved by injecting solutions with a syringe through the serum cap in the laboratory microcosm. The laboratory microcosm used for incubating the soil suspension at controlled pH and redox potential conditions is similar to that described by Patrick et al. (1973) and Reddy et al. (1976). Two rice varieties were used. One is relatively tolerant to acid sulfate soil conditions (IR 46) and the other is sensitive (IR 26). They were grown for 21 days under controlled pH and redox potential conditions. The soil and plant analyses procedures used are described in Chapter 4 as are additional details of the procedures used.

The regression analysis employed a combination of the stepwise regression procedure (Draper and Smith, 1966), the maximum  $R^2$  improvement procedure (SAS, 1985) and a critical consideration of the independent variables based on an agronomic viewpoint. The regression procedure was the same as that described in Chapter 5.

In this study, the independent variables were soil physico-chemical parameters, plant elemental content in shoot tissue, and selected elemental measurements of soil fractions as listed in Table 1. The dependent variable was the weight gain of the rice plants. Weight gain data were transformed to logarithm 10 to obtain a better fit for the regression curves, reduce random variation, and normalize the mean square error (Broome et al., 1975; Steel and Torrie, 1980). Regression analyses were done separately for varieties and non-acid and acid sulfate soils to provide more meaningful interpretation.

## RESULTS AND DISCUSSION

The list of independent variables and their linear correlation to weight gain are presented in Tables 2 and 3. These independent variables were entered into the model building process for each variety for each of the non-acid and acid sulfate soils. The N, P, and K were omitted from the model building process so that major nutrient effects were removed from the regression analysis. Results obtained from the regression analysis indicated several independent variables were associated with rice weight gain. The four sets of variables most likely to be related to rice weight gain were selected from those sets of variables as listed in Table 4.

Table 1. Variables used in model building and their abbreviations.

Variables	Abbreviations
Physicochemical Parameter	
Acidity	pH
Redox potential	Eh
Redox potential and pH	pe+pH
Elemental Content in the Plant Tissue	
Fe, Mn, Zn, etc.	Fep, Mnp, Znp, etc.
Elemental Content of Water-Soluble Fraction in the Soil Suspension (rooting medium)	
Fe, Mn, Zn, etc.	Fe <sub>s</sub> , Mn <sub>s</sub> , Zn <sub>s</sub> , etc.
Elemental Content of Exchangeable Fraction in the Soil Suspension (rooting medium)	
Ca, Mg, Fe, Mn, etc.	ExCa, ExMg, ExFe, ExMn, etc.
Negative log of Activity of Elemental Species in the Water-Soluble Fraction	
Fe <sup>2+</sup> , Ca <sup>2+</sup> , Al <sup>3+</sup> , Mn <sup>2+</sup> , etc.	pFe <sup>2+</sup> , pCa <sup>2+</sup> , pAl <sup>3+</sup> , pMn <sup>2+</sup> , etc.
Divalent Charge Fraction on CEC due to each Divalent Metal	
Fe, Ca, Mg, etc.	E-Fe, E-Ca, E-Mg, etc.
Divalent Charge Fraction in the Water-Soluble Fraction due to each Divalent Metal	
Fe, Mn, Ca, Mg, etc.	E'-Fe, E'-Mn, E'-Ca, E'-Mg, etc.

Table 2. Variables used in model building and the linear correlations with  $\log_{10}$  weight gain of the sensitive (IR26) rice grown in non-acid and acid sulfate soils over all controlled pH-Eh levels.

	Non-acid (n=36)		Acid sulfate soils (n=54)	
	r*	P#	r	P
Physicochemical Parameters				
pH	---	---	0.22	0.14
Eh	0.52	0.001	0.61	0.0001
pe+pH	0.55	0.0005	0.64	0.0001
Elemental Content in the Plant Tissue				
Mn	0.39	0.02	0.40	0.003
Fe	-0.65	0.0001	-0.58	0.0001
Zn	0.30	0.08	0.47	0.0003
Al	-0.31	0.06	-0.33	0.01
Fe:Mn	-0.68	0.0001	-0.58	0.0001
Fe:K+Ca+Mg	-0.68	0.0001	-0.59	0.0001
Fe:Al	-0.69	0.0001	-0.42	0.0001
Elemental Content of Water-Soluble Fraction in the Soil Suspension (rooting medium)				
Fe	-0.68	0.0001	-0.61	0.0001
Mn	-0.45	0.006	-0.24	0.07
Al	-0.28	0.09	---	---
Elemental Content of Exchangeable Fraction in the Soil Suspension (rooting medium)				
Fe	-0.62	0.0001	-0.53	0.0001
Ca	0.43	0.0001	---	---
Negative log of Activity of Elemental Species in the Water-Soluble Fraction				
Fe <sup>2+</sup>	0.51	0.001	0.56	0.0001
Mn <sup>2+</sup>	0.44	0.006	0.28	0.04
Al <sup>2+</sup>	0.35	0.03	0.33	0.01
Zn <sup>2+</sup>	0.28	0.09	0.31	0.02
Divalent Charge Fraction on CEC due to each Divalent Metal				
Fe	-0.65	0.0001	-0.59	0.0001
Ca	0.56	0.0004	0.38	0.004
Mg	---	---	0.33	0.01
Divalent Charge Fraction in the Water-Soluble Fraction due to each Divalent Metal				
Fe	-0.64	0.0001	-0.64	0.0001
Ca	0.48	0.003	0.37	0.005
Mg	0.36	0.03	0.42	0.002

\*Linear correlation.

#The probability level of significance.

\$Blanks indicate linear correlation that is not significant at the 0.15 probability level which these values are not included in the stepwise regression analysis.

Table 3. Variables used in model building and the linear correlations with  $\log_{10}$  weight gain of the tolerant variety (IR46) rice grown in non-acid and acid sulfate soils over all controlled pH-Eh levels.

	Non-acid (n=36)		Acid sulfate soils (n=54)	
	r*	P#	r	P
Physicochemical Parameters				
pH	---	---	0.14	0.31
Eh	0.51	0.001	0.44	0.0008
pe+pH	0.52	0.001	0.46	0.0004
Elemental Content in the Plant Tissue				
Ca	---		0.37	0.006
Mg	---		0.48	0.0003
Fe	-0.64	0.0001	-0.38	0.004
Mn	0.29	0.08	0.24	0.07
Al	-0.25	0.14	---	---
Fe:Mn	-0.61	0.0001	-0.39	0.003
Fe:K+Ca+Mg	-0.63	0.0001	-0.40	0.002
Fe:Al	-0.56	0.0004	-0.47	0.0005
Elemental Content of Water-Soluble Fraction in the Soil Suspension (rooting medium)				
Fe	-0.61	0.0001	-0.52	0.0001
Mn	-0.37	0.02	-0.38	0.004
Elemental Content of Exchangeable Fraction in the Soil Suspension (rooting medium)				
Fe	-0.65	0.0001	-0.50	0.0001
Ca	0.44	0.007	---	---
Negative log of Activity of Elemental Species in the Water-Soluble Fraction				
Fe <sup>2+</sup>	0.53	0.0009	0.42	0.001
Mn <sup>2+</sup>	0.47	0.003	0.39	0.003
Zn <sup>2+</sup>	0.21	0.22	0.24	0.08
Al <sup>3+</sup>	0.37	0.03	0.20	0.15
Divalent Charge Fraction on CEC due to each Divalent Metal				
Fe	-0.64	0.0001	-0.51	0.0001
Ca	0.54	0.0008	0.46	0.005
Mg	0.26	0.13		
Divalent Charge Fraction in the Water-Soluble Fraction due to each Divalent Metal				
Fe	-0.66	0.0001	-0.55	0.0001
Ca	0.46	0.004	0.46	0.004

\*Linear correlation.

#The probability level of significance.

\$Blanks indicate linear correlation that is not significant at the 0.15 probability level which these values are not included in the stepwise regression analysis.



Table 4. Model parameters selected for predicting  $\log_{10}$  weight gain of rice varieties (IR26 and IR46) in non-acid and acid sulfate soils overall controlled pH and redox potential conditions

Model#	R <sup>2</sup>
<b>IR26 Variety</b>	
Non-acid	
Fep:Mnp	0.65
Fep:Mnp, FeS	0.74
Fep:Mnp, E'-Mg, AlS	0.76*
Acid sulfate soils	
Fep:(Kp+Cap+Mgp)	0.49
Fep:(Kp+Cap+Mgp), pe + pH	0.62
Fep:Mnp, pe+pH, pAl <sup>3+</sup>	0.64*
<b>IR46 Variety</b>	
Non-acid	
Fep	0.64
Fep, Fep:Mnp	0.68
Fep:Mnp, FeS	0.69
Fep:Mnp, E'-Fe	0.73*
Acid sulfate soils	
FeS	0.34
FeS, Mgp	0.44
Fep:Alp, Mgp, pAl <sup>3+</sup>	0.49
Fep:Mnp, Fep:Alp, Mgp	0.51
Fep:Mnp, Fep:Alp, Mg, pAl <sup>3+</sup>	0.53*

\*Model parameters selected for predicting  $\log_{10}$  weight gain of each variety in each soil type according to their highest value of R<sup>2</sup> (coefficient of determination).

#Model is the set of the independent variable(s) used as the regressor to form regression equation for predicting the value of the dependent variable.

## Predicted model in non-acid sulfate soils (Bangkok and Ratchaburi)

### IR 26 variety

Regression analyses combined with the stepwise technique and the Maximum  $R^2$  Improvement procedure indicated 3 subsets of independent variables relating to IR 26 weight gain in non-acid sulfate soils (Table 4). The best model for the IR 26 variety consisted of 3 variables with an  $R^2$  of 0.76, indicating that about 76% of the variation in weight gain of IR 26 in non-acid sulfate soils was explained by the independent variables in the regression equation (Table 5). All of these independent variables entered into the model according to their relationship with weight gain as described by simple correlations in Table 2. The Fe:Mn ratio in plant tissue had a large negative effect on the variation of rice weight gain ( $R^2 = 0.65$ ) as shown in Table 4. If the variables were ordered on the basis of the partial sum of squares which is believed to be a measure of the relative significance of the variables in the predicted model (Draper and Smith, 1966) then the Fe:Mn ratio in the plant tissue would be ranked the most important. The second would be the divalent fraction in the soil solution due to Mg ( $E'-Mg$ ). The water-soluble concentration of Al (SA1) is the least significant variable in the regression equation. Predicted values of  $\log_{10}$  weight gain are plotted as shown in Figure 1 vs actual weight gain.

### IR 46 variety

Several subsets of variables describing the variation in weight gain of IR 46 variety in non-acid sulfate soils are shown in Table 4.

Table 5. Analysis of variance, regression coefficients and statistics of fit for dependent variable  $\log_{10}$  weight gain of IR26 rice variety in non-acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV,%
Regression	3	1.0023	33.66	0.01	0.76	3.20
Error	32	0.3177				
Total	35	1.3200				

Source	Regression coefficient (b)	Partial sum of squares	F-value	P
Intercept	3.1067			
Fe:P:Mnp	-0.0244	0.7451	75.05	0.01
E'-Mg	0.3497	0.0992	9.99	0.01
AlS	-0.0073	0.0519	5.23	0.05

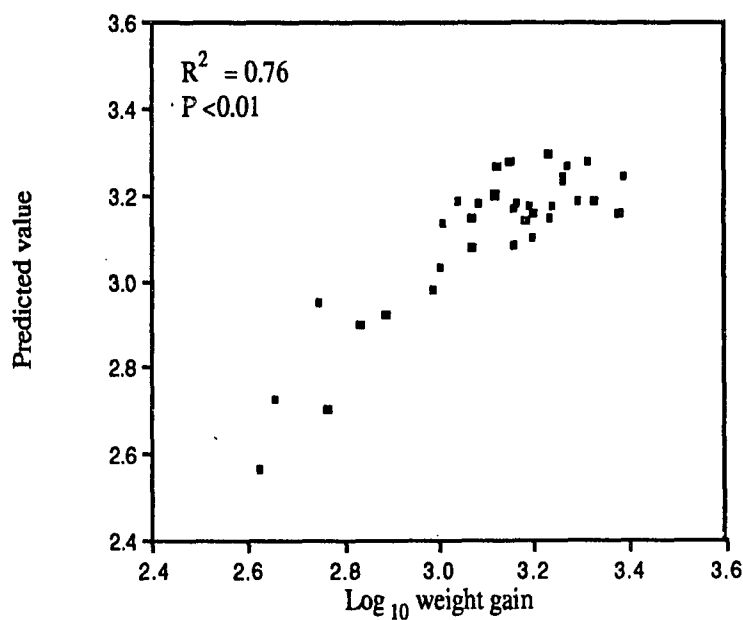


Figure 1. Predicted  $\log_{10}$  weight gain for IR26 in non-acid sulfate soils.

$$\text{Predicted} = 3.11 - 0.02(\text{Fe}_P:\text{Mn}_P) + 0.35(\text{E}'\text{-Mg}) - 0.007\text{AlS}$$

A model with analysis of variance produced by regression is shown in Table 6. Two variables accounted for 73% of the total variation in weight gain ( $R^2=0.73$ ); they were the Fe:Mn ratio in plant tissue and the divalent charge fraction in the water-soluble fraction due to Fe ( $E'-Fe$ ). These variables entered into the prediction model according to their relationship with the rice weight gain as shown by their linear correlation data in Table 3. Both variables were negatively correlated with the rice weight gain. A plot of predicted  $\log_{10}$  weight gain and  $\log_{10}$  weight gain of IR 46 in non-acid sulfate soils is given in Figure 2.

Predicted model in acid sulfate soils (Mahaphot, Rangsit, and Rangsit very acid)

IR 26 variety

The model selected for the IR26 variety in acid sulfate soils contained 3 variables with an  $R^2$  of 0.64, indicating that about 64% of the variation in weight gain was explained by the independent variables in the regression equation (Table 7). The pe + pH, Fe:Mn ratio in plant tissue, and the negative log activity of Al ( $pAl^{3+}$ ) were variables that can be ranked as the most to the least in relative importance, respectively, in this regression equation based on the value of the partial sum of squares. The pe + pH and the  $pAl^{3+}$  were positively related to weight gain. The Fe:Mn ratio in plant tissue was negatively related to weight gain. Predicted value and  $\log_{10}$  weight gain are plotted in Figure 3.

Table 6. Analysis of variance, regression coefficients and statistics of fit for dependent variable  $\log_{10}$  weight gain of IR46 rice variety in non-acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV,%
Regression	3	1.3102	28.77	0.01	0.73	3.72
Error	32	0.4858				
Total	35	1.7960				
<u>Source</u>	<u>Regression coefficient (b)</u>		<u>Partial sum of squares</u>	<u>F-value</u>	<u>P</u>	
Intercept	3.3789					
Fe <sub>p</sub> :Mn <sub>p</sub>	-0.0141		0.0644	24.77	0.01	
E <sup>+</sup> -Fe	-0.0001		0.1283	14.36	0.01	

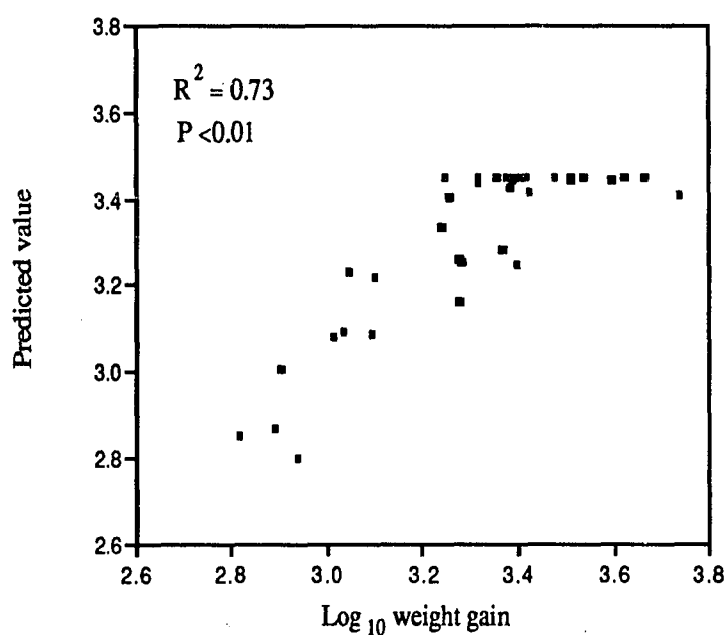


Figure 2. Predicted  $\log_{10}$  weight gain for IR46 in non-acid sulfate soils.

$$\text{Predicted} = 3.45 - 0.02(\text{Fe}_p : \text{Mn}_p) - 0.37(\text{E}^+ - \text{Fe})$$

Table 7. Analysis of variance, regression coefficients and statistics of fit for the dependent variable  $\log_{10}$  weight gain of the IR26 rice variety in acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV, %
Regression	3	0.6602	30.09	0.01	0.64	2.72
Error	50	0.3656				
Total	53	1.0258				

Source	Regression coefficient (b)	Partial sum of squares	F-value	P
Intercept	2.8383			
pe+pH	0.0208	0.1664	22.75	0.01
Fe:p:Mn:p	-0.0094	0.0737	10.08	0.01
pAl <sup>3+</sup>	0.0199	0.0660	9.03	0.01

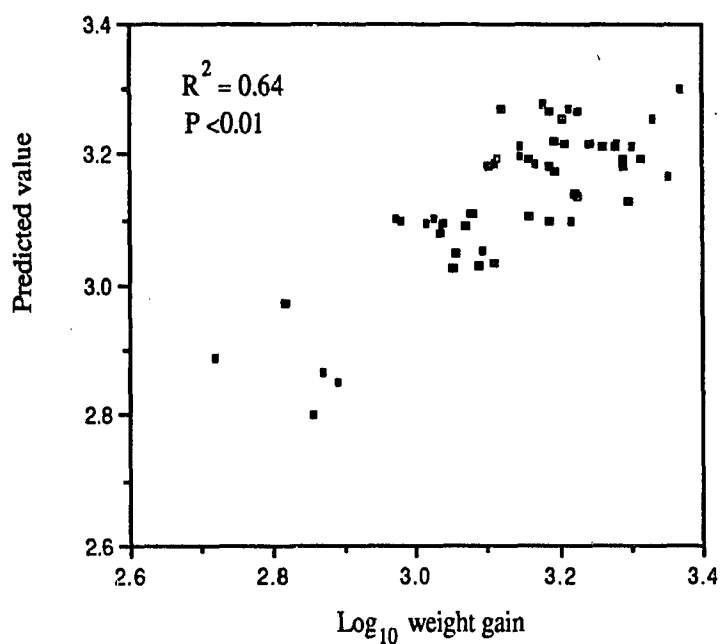


Figure 3. Predicted  $\log_{10}$  weight gain for IR26 in acid sulfate soils.

$$\text{Predicted} = 2.84 + 0.02(\text{pe} + \text{pH}) - 0.009(\text{Fe} : \text{p} : \text{Mn} : \text{p}) + 0.02\text{pAl}^{3+}$$

#### IR 46 variety

The prediction model for IR 46 weight gain in acid sulfate soils included 4 variables with an  $R^2$  of 0.53 (Table 8). These four variables entered the regression equation with either positive or negative signs according to their relationship with weight gain as shown in Table 3. It is not clear why the divalent charge fraction of metal due to Fe on CEC and in the soil solution (E-Fe and E'-Fe respectively) did not enter the model despite their high relationship with weight gain. This was thought to be due to the fact that either E-Fe and E'-Fe are not correlated with the other variables in the model, or E-Fe and E'-Fe were less related with weight gain as compared to the relationship of the Fe:Mn and/or Fe:Al ratio in plant tissue with weight gain. Predicted values obtained from the model are plotted against  $\log_{10}$  weight gain for IR 46 variety in acid sulfate soils as shown in Figure 4.

#### Interpretation of the Prediction Models for Rice Growth

Regression analysis with a combination of the stepwise technique and the maximum  $R^2$  improvement procedure indicates several independent variables affected weight gain of the rice varieties in non-acid and acid sulfate soils over all controlled pH and redox potential conditions. Redox potential (Eh) and  $pe + pH$  showed a significant correlation with weight gain according to data in Tables 2 and 3, but only  $pe + pH$  entered the prediction model for IR 26 in acid sulfate soils. The  $pe + pH$  was found to affect rice weight gain significantly ( $P < 0.01$ ) as indicated by analysis of variance (AOV) and the Duncan's New Multiple Range test procedure (Table 9). Regression analysis indicated the

Table 8. Analysis of variance, regression coefficients and statistics of fit for dependent variable  $\log_{10}$  weight gain of the IR46 rice variety in acid sulfate soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>	CV,%
Regression	4	0.6952	13.46	0.01	0.53	3.39
Error	47	0.6068				
Total	51	1.3021				

Source	Regression coefficient (b)	Partial sum of squares	F-value	P
Intercept	3.1154			
Mgp	0.0001	0.2082	16.13	0.01
Fep:Alp	-0.0010	0.1364	10.56	0.01
Fep:Mnp	-0.0078	0.0517	4.00	0.05
pAl <sup>3+</sup>	0.0148	0.0345	2.68	0.10

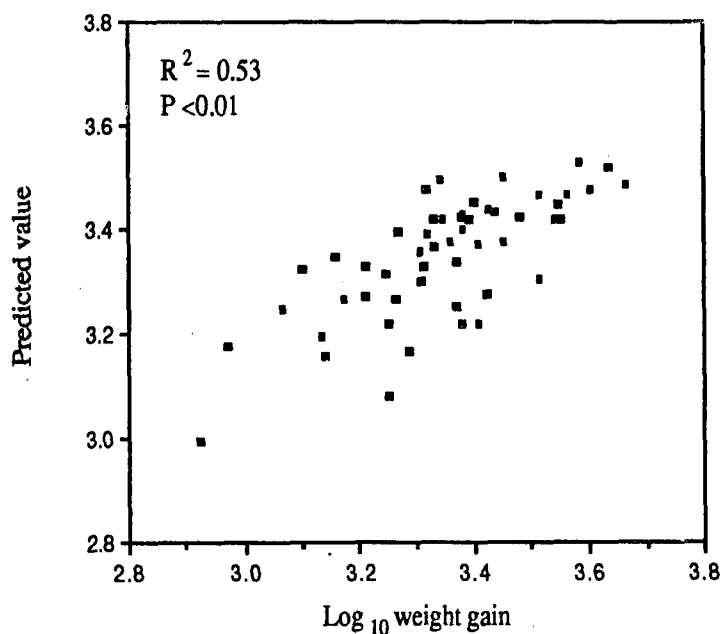


Figure 4. Predicted  $\log_{10}$  weight gain for IR46 in acid sulfate soils.  
 Predicted =  $3.12 - 0.008(\text{Fep:Mnp}) - 0.001(\text{Fep:Alp}) + 0.015\text{pAl}^{3+} + 0.0001\text{Mgp}$



Table 9. Weight gain of both varieties over all acid and non-acid sulfate soils under controlled pH and redox potential conditions.

Eh	pH	pe+pH	Weight gain (g)	
			IR26	IR46
50	3.5	4.34	0.71	1.17
	4.5	5.34	1.21	1.71
	5.5	6.34	1.23	1.58
250	3.5	7.72	1.23	2.22
	4.5	8.72	1.83	3.91
	5.5	9.72	1.62	2.69
500	3.5	11.94	1.70	2.34
	4.5	12.94	1.90	3.27
	5.5	13.94	1.48	2.31
LSD (0.05)			0.62	0.62

Table 10. Regression analysis of weight gain and pe + pH over two rice varieties and all soils.

Source	df	Sum of Squares	F-value	P	R <sup>2</sup>
Regression	2	39.8559	36.06	0.01	0.29
Error	177	97.8075			
Total	179	137.6634			
<u>Regression</u>	<u>Parameter</u>	<u>Regression coefficient (b)</u>	<u>Partial sum of Squares</u>	<u>F-value</u>	<u>P</u>
Linear	Intercept	-1.7328	21.4382	43.49	0.01
	pe+pH	0.7592			
Quadratic	(pe+pH) <sup>2</sup>	-0.0351	15.8212	28.63	0.01

response of weight gain to pe + pH was curvilinear with an  $R^2$  of 0.29 significant at the 0.01 level (Table 10). Results of a previous study where rice varieties were grown under only controlled redox potential (Chapter 4) also showed that the relationship between pe + pH and rice weight gain was curvilinear with an  $R^2$  of 0.36. The response of rice weight gain to the controlled conditions studied here was somewhat scattered as depicted in plots of relative weight gain as a function of pe + pH in Figures 5 and 6.

The data indicate that the Fe:Mn ratio in the plant tissue was the most important independent variable appearing in every prediction model. There was a consistent decrease in rice weight gain associated with an increase in the Fe:Mn ratio. The effect of Fe:Mn ratio in the plant tissue on rice weight gain observed in this study corresponded well with the findings in Chapter 4. Tanaka and Navasero (1966) reported a study in which the Fe:Mn ratio in plant tissue varied from 0.01 to 25.8 with lower growth at high Fe:Mn ratios. The ratio of Fe:Mn observed here varied from 0.01 to 26.4. A ratio of Fe:Mn around 1.5 to 2.5 may be required for normal plant growth (Shive, 1941). The Fe:K+Ca+Mg ratio in the plant tissue also entered in some prediction models for IR 26 weight gain acid sulfate soils with high negative correlations (Table 2). This was thought to be related to the multiple nutritional stress due to an imbalance of K, Ca, and Mg to Fe in the soil and subsequently in the plant tissue. For instance, Ottow et al. (1983) reported the soils of Sri Lanka commonly associated with rice bronzing symptoms are all uniformly deficient in P, K, Ca, Mg as well as Zn. They also indicated that rice leaves exhibiting Fe-toxicity symptoms showed P and K deficiencies and low Zn also. Howeler (1973) also observed that the

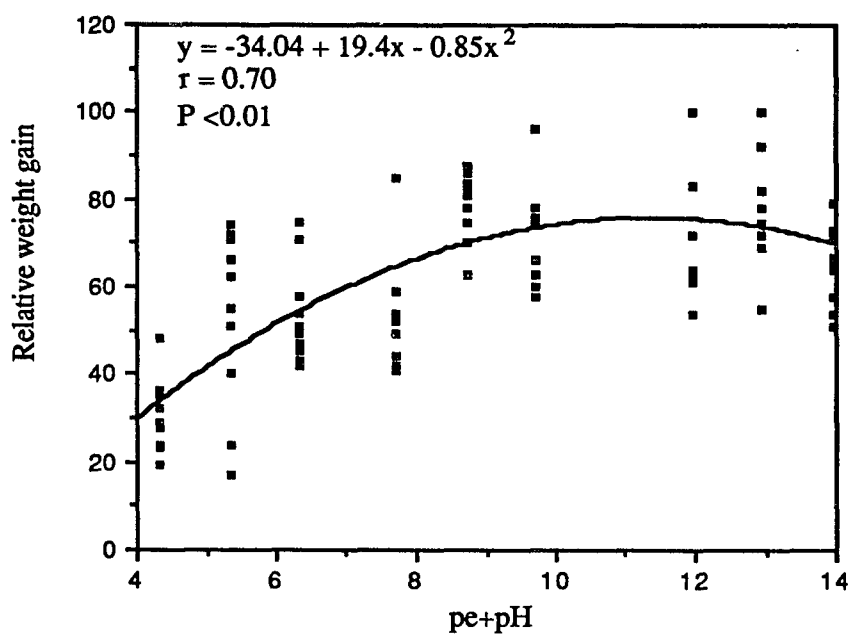


Figure 5. Relative weight gain of IR26 shoot as affected by controlled pH-Eh of the five soils.

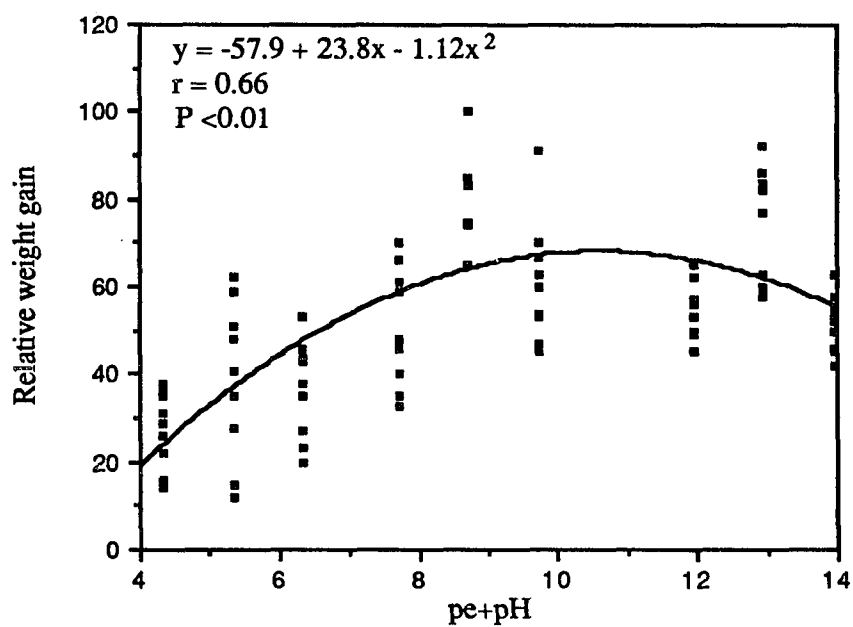


Figure 6. Relative weight gain of IR46 shoot as affected by controlled pH-Eh of the five soils.

severely affected (Fe-toxicity) rice plants had the deficient (or nearly deficient) levels of P, K, Ca, and Mg in the leaves. The ratio of Fe:K+Ca+Mg in the plant tissue of this study may indicate the toxicity effect of Fe is increased as the content of K+Ca+Mg in rice leaf tissue decreased.

The Fe:Al ratio in the plant tissue appeared in the prediction model for IR 46 in acid sulfate soils. The effect of the Fe:Al ratio can not be readily explained and it may enter the regression equation because of the relationship with other independent variables in the model.

The  $pAl^{3+}$  activity was positively associated with rice weight gain as shown by the data in Tables 7 and 8. However, data from Tables 2 and 3 reveal that the correlation between  $pAl^{3+}$  and rice weight gain was significant ( $P=0.01$ ) only for IR 26 variety. The  $Al^{3+}$  entered the prediction model for IR 46 variety with the lowest level of significance ( $P=0.10$ ) suggesting that the stepwise regression picked  $Al^{3+}$  as an additional variable necessary for improving the maximum  $R^2$  (the stepwise technique use the 0.15 significance level as a criteria for variables entering the regression model). This significance level is believed to be appropriate to obtain the model that provides the best prediction using the sample estimates (SAS, 1985). Therefore,  $Al^{3+}$  is indicated to have some predictive value for rice weight gain in case of IR 46 in acid sulfate soils. The adverse effect of Al on the rice plant has been indicated by several authors (Tomlinson, 1957; Hesse, 1963; Cate and Sukhai, 1964; Nhung and Ponnampuruma, 1966; Tanaka and Navasero, 1966; Ota, 1968; Beye, 1971; Watts, 1969; Thawornwong and Van Diest, 1974; Howeler and Cadavid, 1976; Jugsujinda et al., 1978; van Breemen and

Pons, 1978; Attanadana, 1982; Fageria and Carvalho, 1982; IRRI, 1985).

These authors normally used concentration of Al in soil solution when referring to Al. However, the relationship between plant growth and activity of  $Al^{3+}$  was mentioned by some workers. For example, Pavan et al. (1982) found a reduction in root growth of coffee plants more associated with the activity of  $Al^{3+}$  than with other forms of Al. The result of this study suggested high activity of  $Al^{3+}$  in acid sulfate soils is inversely related to rice weight gain.

Plant content of Fe in the shoot tissue ( $Fe_p$ ) entered the model for IR 46 in non-acid sulfate soils and  $Fe_p$  was the single variable best describing the total variation in weight gain. The reason for this is that the non-acid sulfate soils released large quantities of Fe into the soil solution once they were acidified. As Fe in the soil solution increased,  $Fe_p$  increased (data not shown). Van Breemen (1976) noted that in acid sulfate soils which have undergone strong (natural) acidification, these soils may have lost much of their Fe due to leaching. Non-acid sulfate soils never subjected to natural acidification still have a large quantity of potentially reactive Fe (i.e. reducible and precipitated forms of Fe) that can be released as a result of acidifying them to very low pH (pH=3.5). This point is supported by the result of these studies for the non-acid sulfate soils and the IR 26 variety where Fe in the soil solution ( $Fe_s$ ) entered certain prediction models as shown in Table 4. It was seen in acidified non-acid sulfate soil, either Fe content in plant tissue ( $Fe_p$ ) or Fe content in soil solution ( $Fe_s$ ) played an important role as a factor adversely affecting growth of the rice plant.

Other variables entering prediction models with positive effects were  $E'-Mg$  (divalent charge fraction due to Mg in the soil solution), and  $MgP$  (Mg content in the plant tissue). The variable that was negatively associated with rice growth was Al content in the soil solution ( $Al_s$ ). These variables entered the prediction models according to their relationship with the rice weight gain as shown in Tables 2 and 3.

### CONCLUSIONS

Results from multiple regression analysis utilizing the stepwise technique and the maximum  $R^2$  improvement procedure showed several independent variables were significantly associated with the variation in  $\log_{10}$  weight gain of the two rice varieties (IR 26, and IR 46 respectively) in both non-acid and acid sulfate soil conditions under controlled pH and redox potential conditions. Fe:Mn ratio in the plant tissue ( $Fe_p:Mn_p$ ) was indicated to be a very important variable as it appeared in every prediction model. The  $Fe_p:Mn_p$  was negatively correlated with rice weight gain suggesting the interaction effect between the two metals may be an important factor regulating growth of the rice plant. The Fe:K+Ca+Mg ratio in the plant tissue also entered some prediction models. The Fe:K+Ca+Mg ratio was thought to be an index of the nutrient imbalance in both the soil and in the plant tissue with respect to Fe stress. Several soil and plant Fe parameters entered into the prediction models (plant content of Fe ( $Fe_p$ ), soil content of Fe ( $Fe_s$ ), divalent charge fraction in the water-soluble fraction due to Fe ( $E'-Fe$ )) and they were negatively associated with the rice weight gain. But the combination of  $Fe_p:Mn_p$  and  $E'-Fe$  forms the prediction model with

the largest  $R^2$  value. Divalent charge fraction in the water-soluble fraction soil due to  $Mg(E'-Mg)$  was a variable positively associated with rice weight gain. Activity of  $Al^{3+}$  consistently adversely affected weight gain of both rice varieties in acid sulfate soils.

The relationship between  $pe + pH$  and rice weight gain was significant but not as strong as expected. The  $R^2$  was low, but a curvilinear relationship existed between rice weight gain and  $pe + pH$  as that discussed in Chapter 4.

The results of Chapter 4 and Chapter 5 indicated the strong relationship between Fe:Mn ratio in the plant tissue and rice weight gain over all plant and soil types. The  $pe + pH$  may be used for describing either stimulatory or inhibitory effects of several factors on growth of rice because  $pe+pH$  is intimately associated with the transformation of Fe, Mn, and Al in acid sulfate soils studied here.

#### REFERENCES

- Attanandana, T. 1982. Fertility problems of acid sulfate soils of Thailand. Unpublished D. Agr. Thesis, Kyoto Univ. 210 p.
- Beye, G. 1971. Amelioration of two acid sulfate soils for rice. IRRI Saturday seminar. Int. Rice Res. Inst. Los Banos, Laguna, Philippines. p. 19.
- Broome, S. W., W. W. Woodhouse, Jr., and E. D. Senecia. 1975. The relationship of mineral nutrients to growth of Spartina alterniflora in North Carolina: I. Nutrient Status of plants and soils in natural stands. Soil Sci. Soc. Am. Proc. 39:295-301.
- Cate, R. B., Jr. and A. P. Sukhai. 1964. A study of aluminum in rice soils. Soil Sci. 98:85-93.
- Draper, N. R., and H. Smith. 1966. Applied regression analysis. John Wiley & Sons, Inc., New York.
- Fageria, N. K. and J. R. P. Carvlho. 1982. Influence of aluminum in nutrient solution on chemical composition in upland rice cultivars. Plant and Soil 69:31-44.

- Gambrell, R. P. G., R. A. Khalid, M. G. Verloo, and W. H. Patrick, Jr. 1975. Transformation of heavy metals and plant nutrients indredged sediments as affected by oxidation-reduction potential and pH. Vol. II. Materials and methods-results and discussion. Off. of Dredged Material Res., U. S. Army Eng. Waterways Exp. Stn., Vicksburg, Miss. Contract no. D-77-4.
- Gotoh, S., and W. H. Patrick, Jr. 1972. Transformation of manganese in a waterlogged soil as influenced by redox potential and pH. *Soil Sci. Soc. Am. Proc.* 36:738-742.
- Gotoh, S., and W. H. Patrick, Jr. 1974. Transformation of iron in a waterlogged soil as influenced by redox potential and pH. *Soil Sci. Soc. Am. Proc.* 38:66-71.
- Hesse, P. R. 1963. Phosphorus relationships in a mangrove swamp mud with particular reference to aluminum toxicity. *Plant and Soil.* 19:205-218.
- Howeler, R. H. 1973. Iron-induced orangng disease of rice in relation to physico-chemical changes in a flooded Oxisol. *Soil Sci. Soc. Am. Proc.* 37:898-901.
- Howler, R. H., and L. E. Cadavid. 1976. Screening of rice cultivars for tolerance to Al toxicity in nutrient solutions as compared with a screening method. *Agron. J.* 68:551-555.
- International Rice Research Institute. 1985. Annual Report 1972. Los Banos, Philippines. 265 p.
- Jugsujinda, A. and W. H. Patrick Jr. 1977. Growth and nutrient uptake by rice in a flooded soil under controlled aerobic-anaerobic and pH conditions. *Agron. J.* 69, 705-710.
- Jugsujinda, A., Y. Tadashi, and N. van Breemen. 1978. Aluminum toxicity and phosphorus deficiency in acid sulfate soils of Thailand. *International Rice Research Newsletter, IRRI.* (3) 1.
- Little, M. T., and Hills, F. J. 1978. *Agricultural experimentation: Design and analysis.* Wiley, New York.
- Moore, P. A., Jr. 1987. Metal behavior in acid sulfate soils of Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Nhung, M. M., and F. N. Ponnampuruma. 1965. Effects of calcium carbonate manganese dioxide, ferric hydroxide, and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulfate soil. *Soil Science* 102:29-41.
- Ota, Y. 1968. Studies on the occurrence of the physiological disease of rice called "bronzing" (In Japanese with English summary). *Bull. Natl. Inst. Agric. Sci. Nishighara.* Tokyo. Japan. Series D. No. 18:97-100.



- Ottow, J. C. G., G. Benckiser, I. Watanabe, and S. Santiago. 1983. Multiple nutritional stress as the prerequisite for iron toxicity of wetland rice (*Oryza sativa* L.). *Trop. Agric. (Trinidad)* 60:102-106.
- Patrick, W. H., Jr. 1964. Extractable iron and phosphorus in submerged soil at controlled redox potential. *Int. Congr. Soil Sci., Tans.* 8th, Bucharest, Romania. IV:605-608.
- Patrick, W. H., Jr. and W. J. Fontenot. 1976. Growth and mineral composition of rice at various soil moisture tensions and oxygen levels. *Agron. J.* 68:325-329.
- Pavan, M. A., F. T. Bingham, and P. F. Pratt. 1982. Toxicity of aluminum to coffee in ultisols and oxisols amended with  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ . *Soil Sci. Soc. Am. J.* 46:1201-1207.
- Reddy, C. N., and W. H. Patrick, Jr. 1977. Effect of redox potential and pH on the uptake of cadmium and lead by rice plants. *J. Environ. Qual.* 6:259-262.
- Sajwan, K. S., and W. L. Lindsay. 1986. Effects of redox on zinc deficiency in paddy rice. *Soil Sci. Soc. Am. J.* 50:1264-1269.
- SAS Institute. 1985. SAS user's guide: Statistics, Version 5th ed. SAS Institute Inc., Cary, NC, USA.
- Satawathananont, S. 1986. Redox, pH and ion chemistry of acid sulfate rice soils in Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge, Louisiana.
- Schwab, A. P., and W. L. Lindsay. 1983. Effect of redox on the solubility and availability of iron. *Soil Sci. Soc. Am. J.* 47:201-205.
- Shive, J. W. 1941. Significant roles of trace elements in the nutrition of plants. *Plant Physiology* 16:435-445.
- Steel, R. G. D., and J. H. Torrie. 1980. Principles and procedures of statistics. McGraw-Hill, New York.
- Thawornwong, N., and A. van Diest. 1974. Influence of high acidity and aluminium on the growth of lowland rice. *Plant and Soil* 41:107-114.
- Tanaka, A., and S. A. Navasero. 1966a. Aluminium toxicity of the rice plant under water culture conditions. *Soil Sci. Plant Nutr.* 12:55-60.
- Tanaka, A. and S. A. Navasero. 1966b. Interaction between iron and manganese in the rice plant. *Soil Sci. Plant Nutr.* 12:197-201.
- Tolley, M.D., R. D. Delaune, and W. H. Patrick, Jr. 1986. The effect of sediment redox potential and soil acidity on nitrogen uptake, anaerobic root respiration, and growth of rice (*Oryza sativa*). *Plant and Soil* 93:323-331.

- Tomlinson, T. E. 1957. Changes in a sulphide-containing mangrove soil on drying and their effect upon the suitability of the soil for the growth of rice. *Empire J. Exp. Agr.* 25:108-118.
- van Breemen, N. 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. *Agric. Res. Rep.* 848. PUDOC, Wageningen, Netherlands.
- van Breemen, N., and L. J. Pons. 1978. Acid sulfate soils and rice. p. 739-762. In F. N. Ponnampereuma (ed). *Soils and Rice*. International Rice Research Institute, Los Banos, Philippines.
- Watts, J. C. D. 1969. Phosphate retention in acid sulfate pond muds from the Malacca area. *Malays. Agric. J.* 14:187-202.

## Chapter Six

### Iron and Manganese Availability to Rice in Acid Sulfate Soils Under Controlled Redox Potential and pH Conditions

# Iron and Manganese Availability to Rice in Acid Sulfate Soils Under Controlled Redox Potential and pH Conditions

## ABSTRACT

Suspensions of acid sulfate (Sulfic Tropaeup) and non-acid sulfate (Typic Tropaeup) soils were incubated at various controlled redox potential (500, 250, and 50 mV) and pH conditions (3.5, 4.5, and 5.5) to study the distribution of soil Fe and Mn and their availability to rice. After 3 weeks, the solution phase and plant samples were analyzed. The activities of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the soil solution were determined by the computer program (GEOCHEM).

The results suggest that both redox potential and pH governed the soil chemistry and plant uptake of various fractions of Fe. Redox potential has less effect on Mn. The relationship of activity and  $\text{pe} + \text{pH}$  indicated that amorphous  $\text{Fe}(\text{OH})_3$  probably controlled Fe solubility at  $\text{pe} + \text{pH}$  of around 12.95 and above, whereas  $\text{FeOOH}$  (goethite) may influence the solubility of Fe around  $\text{pe} + \text{pH}$  11.95 and below. The Mn solubility was not controlled by any solid phase species that could be identified and was likely regulated by cation exchange reactions.

The Fe content in shoot tissue was negatively related to both redox potential and pH. Water-soluble Fe,  $\text{Fe}^{2+}$  activity, and  $\text{E}'\text{-Fe}$  were found to be significantly correlated with Fe uptake. The critical level of the minimum  $\text{pFe}^{2+}$  and  $\text{E}'\text{-Fe}$  that triggers excessive uptake of Fe was considered to be at  $\text{pFe}^{2+}$  of 3, and  $\text{E}'\text{-Fe} = 0.45$ . Acid sulfate soil sensitive rice (IR 26) accumulated more Fe in the shoot tissue than occurred in a tolerant variety (IR 46). An Fe:Mn ratio of 4.5 and higher in the shoot tissue was associated with an Fe content in shoot

tissue greater than  $300 \text{ mg kg}^{-1}$  ( the critical level of Fe toxicity in shoot tissue ).

The Mn content in shoot tissue was positively correlated with redox potential and pH. Plots of Mn uptake as a function of  $\text{Mn}^{2+}:\text{Fe}^{2+}$  activity ratio suggested that Fe may be antagonistic to uptake of Mn.

## INTRODUCTION

Iron and Manganese chemistry in soils have been studied extensively (Adams and Wear, 1957; Ponnamperuma et al., 1966; Patrick and Turner, 1968; Williams and Patrick, 1971; Gotoh and Patrick, 1972, 1974; Patrick and Henderson, 1981a, 1981b; Mandal and Mitra, 1982).

Transformations of Fe and Mn in a flooded soil under wide ranges of controlled redox potential and pH conditions have been studied by Gotoh and Patrick (1972, 1974). They noted that the redox potential and pH of flooded soils strongly influence Fe and Mn transformations. Similar results were observed in acid sulfate soils (Satawathananont, 1986).

Interest in Fe and Mn solubility in soils has increased in recent years. Several reviews have been published on Fe and Mn solubility in aqueous systems. A number of reviews referred to the  $\text{Fe}(\text{OH})_3\text{-Fe}^{2+}$  system controlling the solubility of  $\text{Fe}^{2+}$  (Barnes and Back, 1964; Ponnamperuma et al., 1967; Doyle, 1968; Van Breemen, 1969; Langmuir and Whittemore, 1971; Gotoh and Patrick, 1974; Pasricha and Ponnamperuma, 1976). Many of these authors were able to relate the solution  $\text{Fe}^{2+}$  to near equilibrium with theoretical solubility in the  $\text{Fe}(\text{OH})_3\text{-Fe}^{2+}$  system. Recently, Schwab and Lindsay (1983a) have reported the solubility of  $\text{Fe}^{2+}$  was controlled by  $\text{FeCO}_3$  (siderite) below  $\text{pe}+\text{pH}$  8.5 and by  $\text{Fe}_3(\text{OH})_8$  (ferrosic hydroxide) above  $\text{pe}+\text{pH}$  8.5 in studies of high pH soils (pH

8.2). Ponnampetuma (1972) has suggested that  $\text{FeCO}_3$  probably controls Fe solubility in many soil solutions. However, Moore (1987) found no indication of an equilibrium between  $\text{Fe}^{2+}$  activity and pure Fe solid phases in acid sulfate rice fields of Thailand.

The Mn solubility has also received much research interest in recent years. Ponnampetuma et al. (1969) suggested that various manganese oxides and  $\text{MnCO}_3$  are involved in redox equilibria in soils that undergo seasonal oxidation-reduction. Bohn (1970) was unable to relate  $\text{Mn}^{2+}$  concentrations between observed and theoretical values calculated from ideal redox couples. Collins and Buol (1970) did not succeed in attempting to relate measure Eh and pH values and  $\text{Mn}^{2+}$  concentrations to the theoretical equilibrium values of  $\text{MnO}_2$ - $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$ - $\text{Mn}_3\text{O}_4$  systems. Gotoh and Patrick (1972) did not find an agreement between observed and theoretical  $\text{Mn}^{2+}$  values in soils under controlled redox potential and pH conditions. This supports the contention that Eh and pH levels in acid sulfate soil usually fall in the  $\text{Mn}^{2+}$  field suggesting that  $\text{Mn}^{2+}$  is mainly present in exchangeable and dissolved forms (Van Breemen, 1976). Pasricha and Ponnampetuma (1976) did report that the  $\text{MnCO}_3$  (rhodocrosite)- $\text{H}_2\text{O}$ - $\text{CO}_2$  systems regulated the solubility of  $\text{Mn}^{2+}$  in some of their work. Schwab and Lindsay (1983b) reported Mn solubility was controlled by  $\text{MnCO}_3$  only below  $\text{pe}+\text{pH} = 16$ . Later, Boyle and Lindsay (1986) proposed that Mn phosphates may control solubility of Mn in some soils.

The uptake of toxic levels of Fe to rice plants has been attributed to excess water soluble Fe associated with low soil pH (Ponnampetuma et al., 1955; De and Mandal 1957; Tadano and Yoshida, 1978; Tanaka et al., 1966a). However, it has been recently hypothesized that Fe toxicity is

probably due to multiple nutritional stress associated with an unbalanced supply of Fe to P, K, Ca, and Mg in the soil contributing to an excess uptake of Fe (Howeler, 1973; Van Breemen and Moorman, 1978; Benckiser et al., 1982, 1984; Ottow et al., 1982, 1983).

The relationship between soil Fe and Mn parameters and plant uptake has been a subject of investigation in several studies. Tanaka and Navasero (1966a) found high Fe in the plant tissue at an early growth stage (3 weeks after transplanting) correlated to high soluble Fe in flooded acid sulfate soils (pH 3.5-4). They observed the highest Fe in plant tissue was  $3630 \text{ mg kg}^{-1}$  which resulted in Fe toxicity and the death of the plant. Tanaka and Navasero (1966b) noted that Mn content in the leaf tissue decreased as soil Fe in the growth media increased. Recently, Schwab and Lindsay (1983a, 1983b) have reported the relationship between uptake of Fe and Mn and activity of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the soil solution under controlled redox conditions. They found plant uptake of Fe and Mn was significantly influenced by their activities in the soil solution phase.

Few studies have examined Fe and Mn interactions in rice. Van Der Vorm and Van Diest (1979a) observed that Mn uptake increased with increasing pH. It was believed that excess Mn uptake induced by high pH may hamper uptake of Fe. Later, Van Der Vorm and Van Diest (1979b) studied growth of rice grown in a sand media and reported that an antagonistic effect of Fe on the uptake of Mn was unlikely. In contrast, Tanaka and Navasero (1966b) found decreases in Fe uptake accompanied by increases in uptake of Mn. They also found the Mn content in rice tissue decreased as soil Fe in the growth media increased.

The experiments reported in this chapter were conducted to: 1) define the relationship between redox potential and pH parameters and the distribution of various form of Fe and Mn in acid and non-acid sulfate soils, 2) compare the measured  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  activities to the theoretical equilibrium solubility of their solid phase species, 3) determine the relationship between soil parameters (Fe and Mn) and plant uptake of Fe and Mn and, 4) study the interaction between Fe and Mn uptake in tolerant and sensitive rice varieties.

#### MATERIALS AND METHODS

Materials and Methods used for the work described in this chapter are the same as that described in Chapter 4 with additional information on pH and redox potential control presented in Chapter 5.

#### RESULTS AND DISCUSSION

Effect of controlled redox potential and pH on the distribution of various fractions of Fe in non-acid and acid sulfate soils.

The levels of total water-soluble Fe in non-acid and acid sulfate soils under controlled redox potential and pH conditions are illustrated in Figure 1. Both redox potential and pH markedly influenced the dissolution of Fe. The concentration of total water-soluble Fe in the solution may represent a balance between reduction processes in reduced conditions that renders iron soluble and the precipitation reactions in oxidized conditions that remove iron from solution. The mixtures of Fe oxides and hydroxides are largely responsible for the solution-reduction or redox reaction of Fe. Several authors proposed equations that can describe the dissolution of Fe in most mineral soils. They suggested



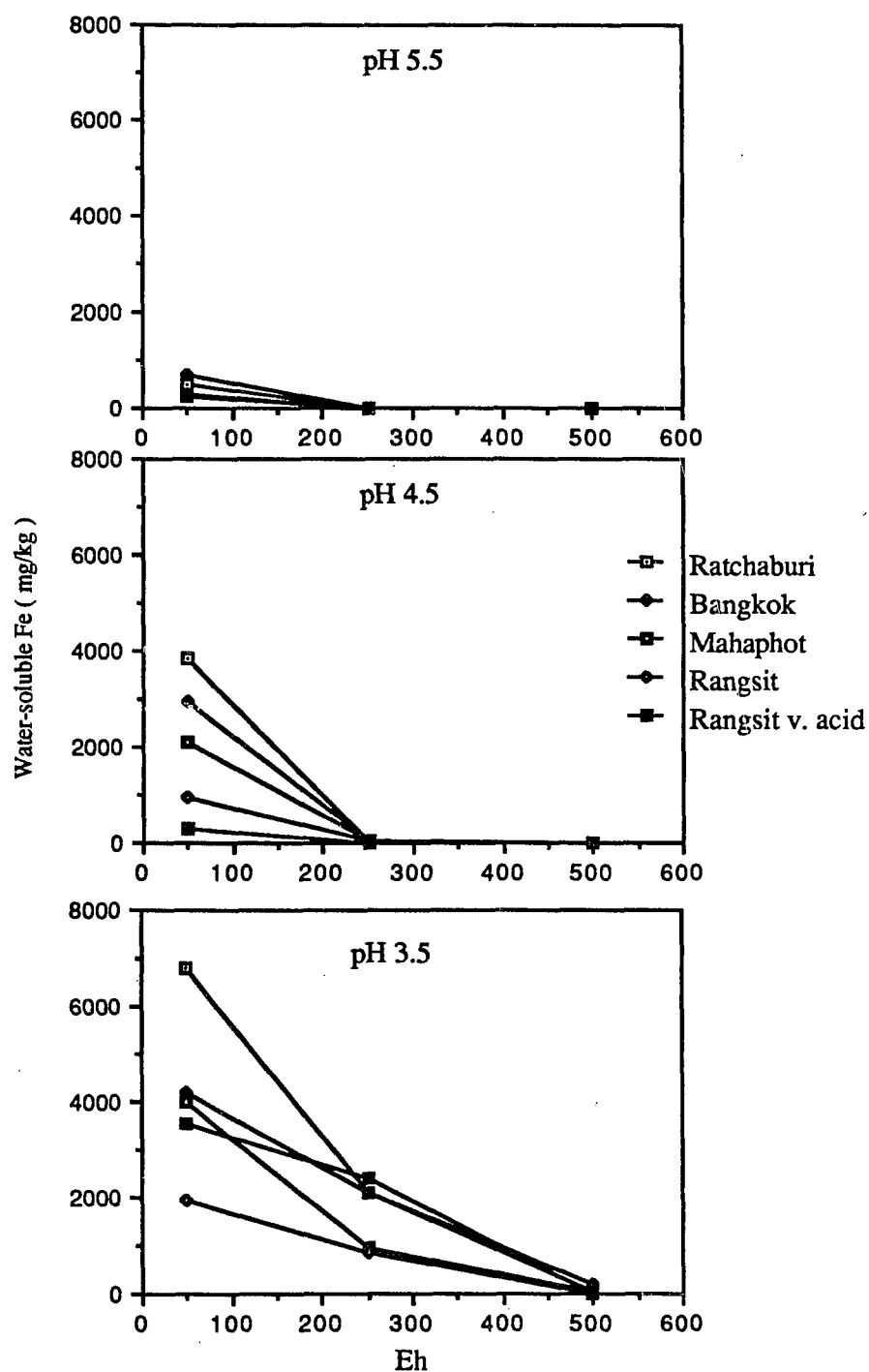
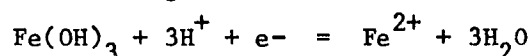


Figure 1. Concentration of water-soluble Fe in acid and non-acid sulfate soils under controlled redox potential and pH conditions.

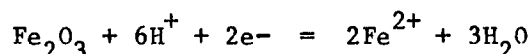
the redox equilibria equations of several systems that can be written based on the Nernst equation as shown below (Ponnamperuma et al., 1967; Langmuir and Whittemore, 1971; Gotoh and Patrick, 1974; Schwab and Lindsay, 1983).

1.  $\text{Fe}(\text{OH})_3\text{-Fe}^{2+}$  system



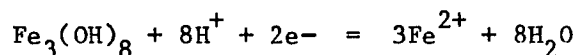
$$\text{for which Eh} = 1.057 - 0.059 \log \text{Fe}^{2+} - 0.177 \text{ pH}$$

2.  $\text{Fe}_2\text{O}_3\text{-Fe}^{2+}$  system



$$\text{for which Eh} = 0.728 - 0.059 \log \text{Fe}^{2+} - 0.177 \text{ pH}$$

3.  $\text{Fe}_3(\text{OH})_8\text{-Fe}^{2+}$  system



$$\text{for which Eh} = 1.373 - 0.0885 \log \text{Fe}^{2+} - 0.236 \text{ pH}$$

According to these equations, redox potential and pH evidently influence Fe dissolution in the soil solution. These redox reactions in general are biologically mediated (Bromfield and Williams, 1963; Takai and Kamura, 1966).

Significant correlation between pH, Eh, and pe+pH parameters with total water-soluble Fe were found in this study with r values of -0.48, -0.56, and -0.66 respectively, indicating that redox potential and pH are important parameters affecting Fe transformations. The levels of water-soluble Fe were greatest at low redox potential and pH. The means among all combinations of Eh-pH were statistically different (Table 1 and 2). Regression analysis of water-soluble Fe as a function of pH and Eh yielded an  $R^2$  of 0.54 which was significant at the 1% level. This

Table 1. Distribution of various fractions of Fe under controlled redox potential and pH conditions in acid sulfate soils.

Eh (mV)	pH	pe+pH	Mahaphot			Rangsit			Rangsit very acid		
			Ws-Fe*	Ex-Fe\$	Rd-Fe#	Ws-Fe	Ex-Fe	Rd-Fe	Ws-Fe	Ex-Fe	Rd-Fe
			mg kg <sup>-1</sup>								
500	5.5	13.94	3.50	2.90	1930	0.50	2.40	980	0.39	11.2	2550
	4.5	12.94	11.0 c	44.9	3510	2.00	59.5	2460	1.00	13.6	1180
	3.5	11.94	59.5	136	2460	4.50	118	1520	1.50	65.2	784
250	5.5	9.72	2.00	15.4	2900	2.00	24.8	2190	1.50	12.9	762
	4.5	8.72	28.5	108	4090	39.0	112	4110	20.5	56.7	1910
	3.5	7.72	942	596	1660	870	1130	753	2400	1310	1040
50	5.5	6.34	292	452	2240	292	500	1280	248	338	1100
	4.5	5.34	2120	2440	2340	972	1850	1430	286	498	931
	3.5	4.34	4060	2530	1680	1966	1640	936	3530	1760	830
LSD (0.05)			743	399	1538	743	399	1538	743	399	1538

\*Ws-Fe : Water-soluble Fe

\$Ex-Fe : Exchangeable Fe

#Rd-Fe : Reducible Fe

Table 2. Distribution of various fractions of Fe under controlled redox potential and pH conditions in non-acid sulfate soils.

Eh (mV)	pH	pe+pH	Bangkok			Ratchaburi		
			Ws-Fe*	Ex-Fe\$	Rd-Fe#	Ws-Fe	Ex-Fe	Rd-Fe
			----- mg kg <sup>-1</sup> -----					
500	5.5	13.94	1.50	18.2	5100	1.50	3.90	4400
	4.5	12.94	8.50	200	8630	2.50	33.9	5180
	3.5	11.94	182	645	5720	37.5	231	5130
250	5.5	9.72	2.50	95.1	7320	2.00	16.3	6760
	4.5	8.72	45.5	268	6610	2.50	63.4	6270
	3.5	7.72	2100	2089	1660	2110	995	2660
50	5.5	6.34	716	1290	2640	495	726	5070
	4.5	5.34	2964	3323	2030	3840	4130	2070
	3.5	4.34	4100	2860	1320	6820	2590	1280
LSD (0.05)			743	399	1538	743	399	1538

\*Ws-Fe : Water-soluble Fe

\$Ex-Fe : Exchangeable Fe

#Rd-Fe : Reducible Fe

suggests that the effects of redox potential and pH interactions are additive. Based on the linear correlations of the two parameters with redox appeared to be more important than pH in affecting water-soluble Fe. Little water-soluble Fe was detected at 250 and 500 mV at pH 5.5 and at 500 mV at pH 4.5 in all soils (Figure 2). DeLaune, et al. (1981) found little soluble Fe at 250 and 500 mV at pH 5.0 estuarine sediment. They suggested the conversion of soluble Fe into insoluble ferric forms under oxidized conditions may account for the low soluble levels. Gambrell et al. (1975) also noted a decrease of water-soluble Fe at higher pH. Water-soluble Fe was somewhat low under reduced conditions (Eh=50mV) at high pH (pH 5.5). DeLaune et al. (1981) suggested that the Fe would be precipitated as ferrous oxyhydroxide under reduced conditions at high pH. Satawathananont (1986) studied the effects of redox potential and pH in stirred suspensions of Ma, Rs, and Rsa soils without rice plants. Similar low values of water-soluble Fe was observed under high redox potential levels (Eh=250 and 500 mV) and high pH values ( $\text{pH} \geq 5.5$ ), which corresponds well with the results this study here. Although the criteria used for deficient concentrations of Fe in the growth media are not established for these soils, the concentrations of water-soluble Fe at the highest redox potential and pH combinations (at 500 mV and pH 5.5) are low. Ponnamperuma (1978) claimed that a concentration of water-soluble  $\text{Fe}(2+)$  in the growth media at  $0.7 \text{ mg L}^{-1}$  is a deficient concentration and at  $400 \text{ mg L}^{-1}$  is a toxic concentration. The low water-soluble Fe observed herein ranged from 0.05 to  $0.45 \text{ mg L}^{-1}$  (or 0.4 to  $3.6 \text{ mg kg}^{-1}$  soil) which are even lower than Ponnamperuma's Fe deficient concentration. In support of this, plant shoot Fe levels of both rice varieties grown under these conditions (250 mV and 500 mV at

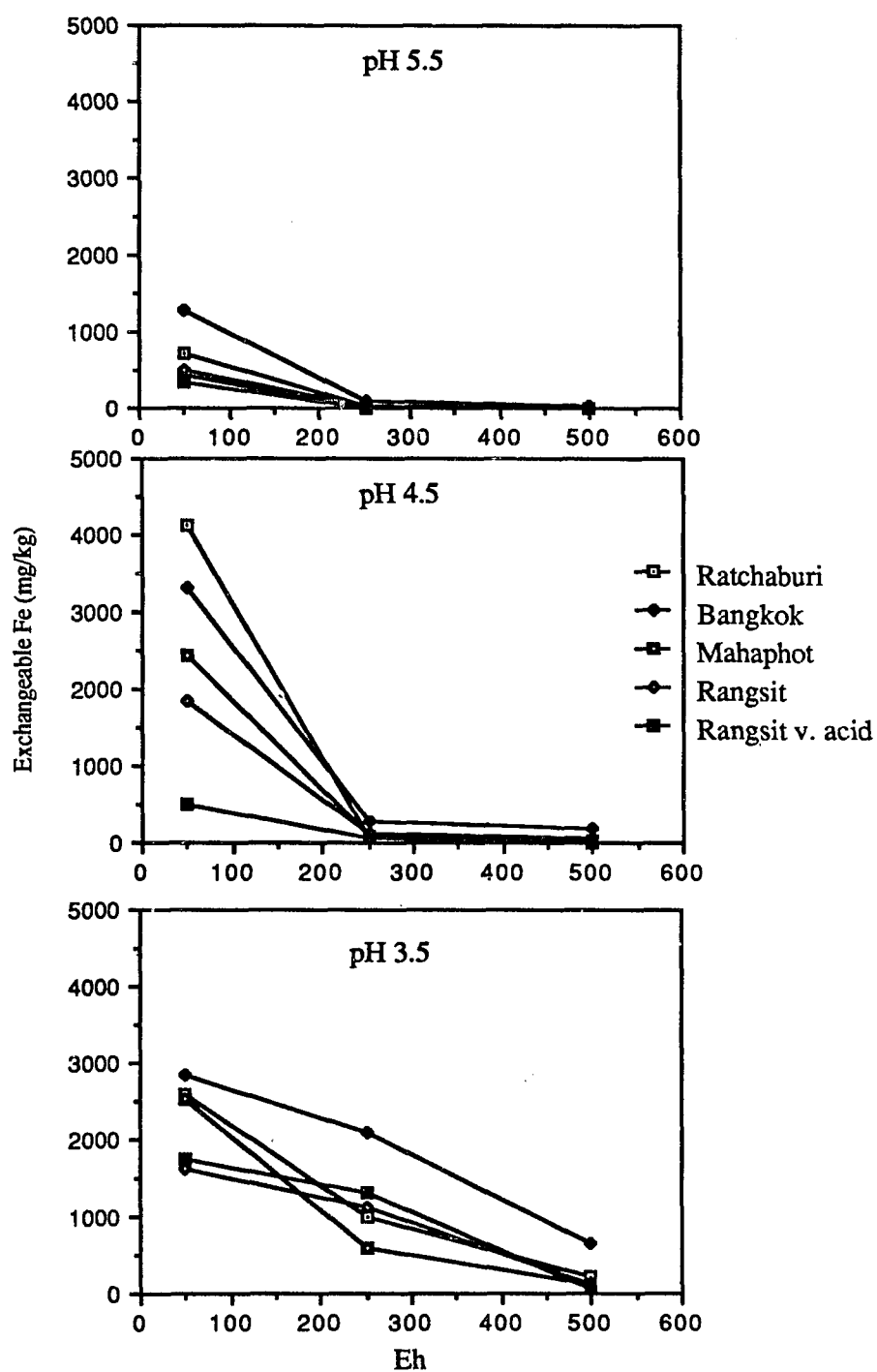


Figure 2. Levels of exchangeable Fe in acid and non-acid sulfate soils under controlled redox potential and pH conditions.

pH 5.5) ranged from 59 to 63 mg kg<sup>-1</sup> which is just below the critical level of Fe deficiency (70 mg kg<sup>-1</sup> Fe in the leaf blade) at the tillering rice stage of (Yoshida, 1981). Rice plants grown under these Eh/pH conditions possibly suffered from the low levels of Fe resulting in relatively low and very low weight gain as shown in Table 3.

Relatively high concentrations of water-soluble Fe at low redox potential and pH levels were reported by Gotoh and Patrick (1974). They suggested the high soluble Fe is due to iron transformations including the reduction of Fe<sup>3+</sup> compounds to the more soluble Fe<sup>2+</sup> forms. In general, the water-soluble Fe increased for each stepwise decrease in redox potential at a given pH. Water-soluble Fe ranged from minimum concentrations at high redox potential and pH levels to maximum concentrations of Fe around 6,000 and 4,000 mg kg<sup>-1</sup> at lowest redox potential and pH levels (50 mV and pH 3.5) of non-acid and acid sulfate soils respectively.

It is interesting to note that the results show a much larger water-soluble Fe concentration in non-acid than in acid sulfate soils. According to van Breemen (1976), the well developed acid sulfate soils, i.e. the three acid sulfate soils used in this study, normally attain concentrations of dissolved Fe (2+) roughly the same as non-acid sulfate soils assuming equivalent physicochemical conditions. The acid sulfate soils had undergone natural acidification for a long period and had probably lost substantial amounts of amorphous Fe and easily reducible Fe oxides and/or hydroxides from the surface horizon and perhaps at a deeper depth due to acid dissolution of solid phases. The data in Figure 3 indicate that the non-acid (Bk and Rb) soils have more amorphous or reducible Fe than the acid sulfate soils (Ma, Rs, and Rsa)

Table 3. Weight gain of two rice varieties grown over all non-acid and acid sulfate soils under controlled pH and redox potential conditions.

Eh (mV)	pH	pe+pH	Weight gain (g)	
			IR26	IR46
50	3.5	4.34	0.71	1.17
	4.5	5.34	1.21	1.71
	5.5	6.34	1.23	1.58
250	3.5	7.72	1.23	2.22
	4.5	8.72	1.83	3.91
	5.5	9.72	1.62	2.69
500	3.5	11.94	1.70	2.34
	4.5	12.94	1.90	3.27
	5.5	13.94	1.48	2.31
LSD (0.05)			0.62	0.62



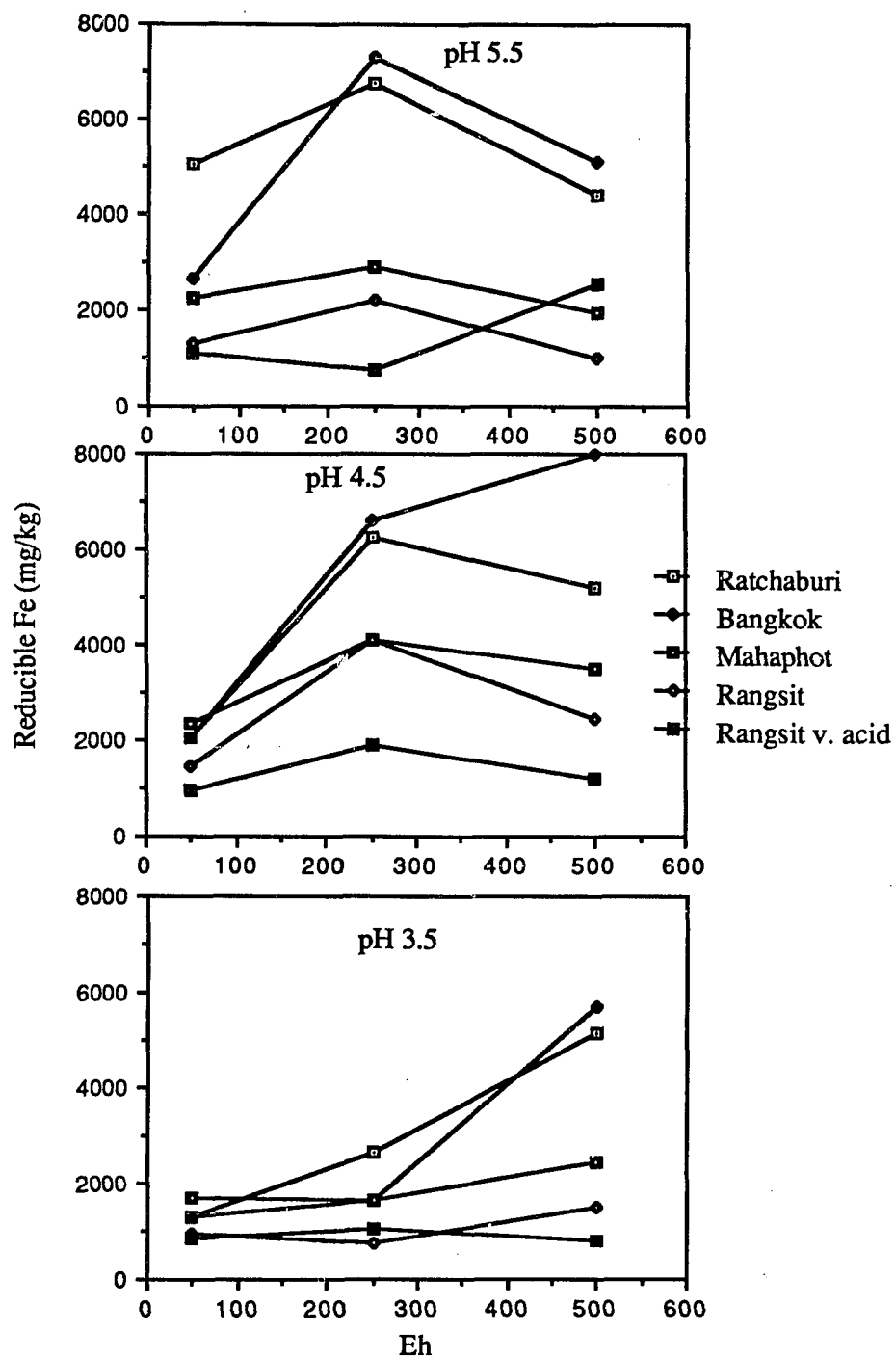


Figure 3. Distribution of reducible Fe in acid and non-acid sulfate soils under controlled redox potential and pH conditions.

under every redox potential and pH condition. Other workers have also reported that acid sulfate soils contain lower fractions of easily decomposable organic matter and lower contents of easily reducible ferric oxide (Ponnamperuma et al., 1973).

Several workers claimed that  $\text{Fe}(2+)$  in the soil solution is oxidized upon contact with the oxidized rhizosphere and deposits of  $\text{Fe}(3+)$  compounds have been observed on the surface of rice roots (Bacha and Hossner, 1977; Green and Etherington, 1977; Chen, Dixon and Turner, 1980) and on the roots of other plant species (Mendelssohn and Postek, 1982). Therefore, under these experimental conditions which combine plants and soils, it would be appropriate to assess the critical redox potential at which dissolution of iron is initiated. Soil with plants may have soluble iron concentrations lower than otherwise equivalent soils without plants due to the influence of rhizosphere oxidation and perhaps plant uptake.

In general, the results suggest that at pH 3.6, the initiation of Fe transformations affecting soluble levels took place near an Eh of 500 mV. At pH 4.5, the Fe conversion started near Eh 250 mV, and at pH 5.5, the conversion of Fe occurred around Eh 50 mV (Tables 1 and 2).

In all varieties and soil types, a statistically significant decrease in growth was accompanied by a marked increase of water-soluble Fe concentrations along the pH/Eh regimes of pH 5.5/Eh 50 mV, pH 3.5/Eh 250 mV, pH 4.5/Eh 50 mV, and pH 3.5/Eh 50 mV respectively (Table 3). This evidence supports the previous results in Chapters 4 and 5 that Fe plays a significant role as one of the factors negatively associated with growth of both rice varieties.

The effects of redox potential and pH on exchangeable Fe concentrations in non-acid and acid sulfate soils are presented in Figure 2. The response of exchangeable Fe to Eh and pH apparently followed a similar pattern as that observed for water-soluble Fe. Statistical analysis indicated a significant difference among means of exchangeable Fe concentrations measured under various Eh-pH levels (Tables 1 and 2). Multiple linear regression of exchangeable Fe as a function of pH and Eh resulted in an  $R^2$  of 0.56, which was significant at the 0.01 level. In addition, the linear correlations of exchangeable Fe with pH, Eh, and pe+pH were highly significant with  $r$  values of -0.39, -0.64, and -0.72, respectively. These results suggest that Eh may be more important than pH in regulating the concentration of exchangeable Fe. At 50 and 250 mV and pH 3.5 for Rb, Ma, and Rsa soils, it was observed that the concentrations of exchangeable Fe was higher than that of water-soluble Fe. Whereas in Bk and Rs soils, exchangeable Fe was higher than water-soluble Fe only at 50 mV and pH 3.5.

Since relatively large amounts of 1M HCl had been used for adjusting to pH 3.5/50 mV, Fe on the exchange complex and/or associated with the solid Fe compounds may have been desorbed or solubilized by the influence of  $H^+$  ions and reduction reaction during a long periods as a stirred suspension. Sidhu et al. (1981) noted that HCL may dissolve Fe' oxides due to the formation of Fe-Cl complexes on the oxide surface which tend to decrease the surface positive charge and increase  $H^+$  (solutions became more acid) to bring about the dissolution. Other workers also reported that metal ion adsorbed on inorganic and materials can be released by HCl (Maynard and Fletcher, 1973). With no plants in the system, Satawathananont (1986) found that water-soluble Fe exceeded

extractable levels of Fe at 400 mV/pH 3.5 and at -50 mV/pH 4.5 in the Rs and Ma soils. At other pH-Eh levels, he found extractable Fe higher than water-soluble Fe which he attributed to his pH 4.0  $\text{NH}_4\text{OAc}$  dissolving some newly precipitated Fe and insoluble Fe-organic matter complexes other than Fe on the exchange complexes alone. Results of this experiment indicate at the lowest pH (3.5) and Eh (50 mV), relatively high concentrations of water-soluble Fe could be accounted for by the reduction of amorphous Fe compounds plus displacement of Fe from the exchange complex by  $\text{H}^+$  ions of the acid used to adjust pH and/or by the  $\text{Al}^{3+}$  ions in the soil solution. At any given pH, exchangeable Fe markedly increased with a decrease of redox potential. At Eh 250 and 500 mV, an increase of exchangeable Fe was accompanied by a decrease in pH in all soils whereas at 50 mV, a progressive increase of exchangeable Fe as pH decreased was observed only in Ma and Rsa soils. On the contrary, at 50 mV, little increase of exchangeable Fe was observed as pH decreased from 4.5 to 3.5 in Bk, Rb, and Rs soils.

Hydroxylamine hydrochloride extractable Fe (reducible Fe, mostly amorphous iron oxide) was also affected by redox potential and pH as depicted in Figure 3. Redox potential, pH, and  $\text{pe}+\text{pH}$  were significantly but somewhat weakly correlated with reducible Fe with  $r$  values of 0.23 ( $P<0.05, n=90$ ), 0.32 ( $P<0.01, n=90$ ), and 0.35 ( $P<0.01$ ) respectively. In general, the pattern of reducible Fe levels in response to pH and Eh changes was opposite to that of water-soluble and exchangeable Fe and increased with an increase of both redox potential and pH. In Bk and Rb (non-acid sulfate soils), reducible Fe was higher than that of acid sulfate soils (Ma, Rs, Rsa) at equivalent pH-Eh levels. In both soils (Bk and Rb), the lower amounts were found at 50 mV and pH 3.5 with

concentrations of 1325, and 1280 mg kg<sup>-1</sup>, while the higher concentrations measured were detected at 250 and 500 mV at pH 4.5 and 5.5. The reducible Fe in these two soils progressively increased with an increase of pH or Eh (holding the other constant) except that at 500 mV and pH 5.5, reducible Fe concentrations declined. In acid sulfate soils (Ma, Rs, and Rsa), an increase in reducible Fe was associated with an increase of both redox potential and pH, but the increase was scattered. Both Ma and Rs soils had the highest concentrations of reducible Fe at 250 mV and pH 4.5 whereas the Rsa soil had the highest reducible Fe at 500 mV and pH 5.5. Thus, the results indicate reducible Fe was high where water-soluble and exchangeable forms were low or vice versa, indicating the transformations between these three fractions under various conditions of redox potential and pH. Gotoh and Patrick (1974) also found the increase in the water-soluble plus exchangeable fraction was accompanied by a decrease in the reducible fraction (dithionite-citrate extractable based on the procedure of Mehra and Jackson, 1960). They pointed that Fe was probably being solubilized by the conversion of insoluble Fe<sup>3+</sup> compounds to the more soluble Fe<sup>2+</sup> forms through the Fe-reduction processes as the soil pH or Eh decreased.

#### Iron solubility

In order to determine which solid species may be involved in controlling solubility of Fe<sup>2+</sup> in the solution phase of the soil suspension under controlled redox potential and pH conditions of both non-acid and acid sulfate soils, Fe<sup>2+</sup> activities in log (Fe<sup>2+</sup>) + 2pH units of the soil solution were plotted as a function of pe+pH as shown in Figure 4. This plot was obtained by the method of Schwab and Lindsay

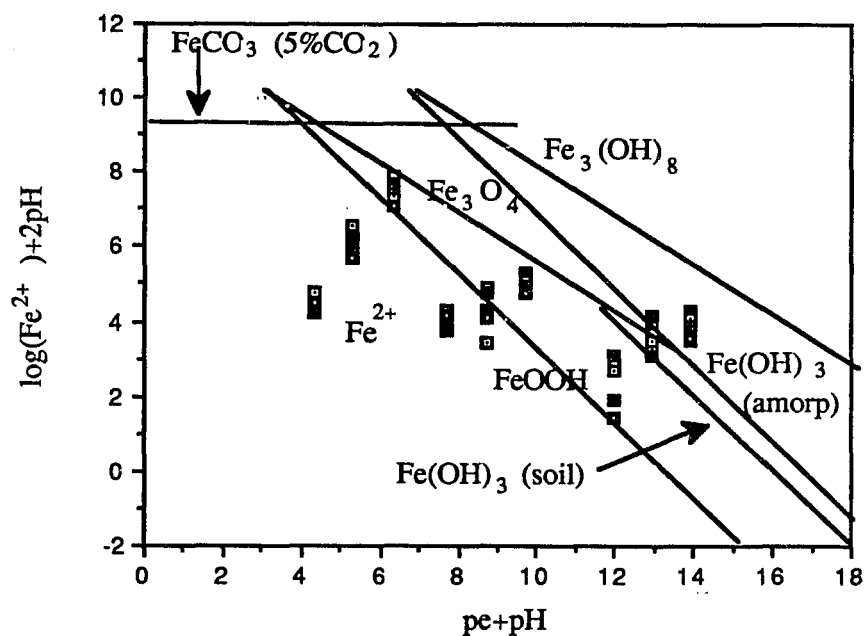


Figure 4. Relationship between  $\text{Fe}^{2+}$  activities and  $\text{pe}+\text{pH}$  with theoretical solubility of selected Fe solid species over all pH-Eh levels of acid and non-acid sulfate soils.

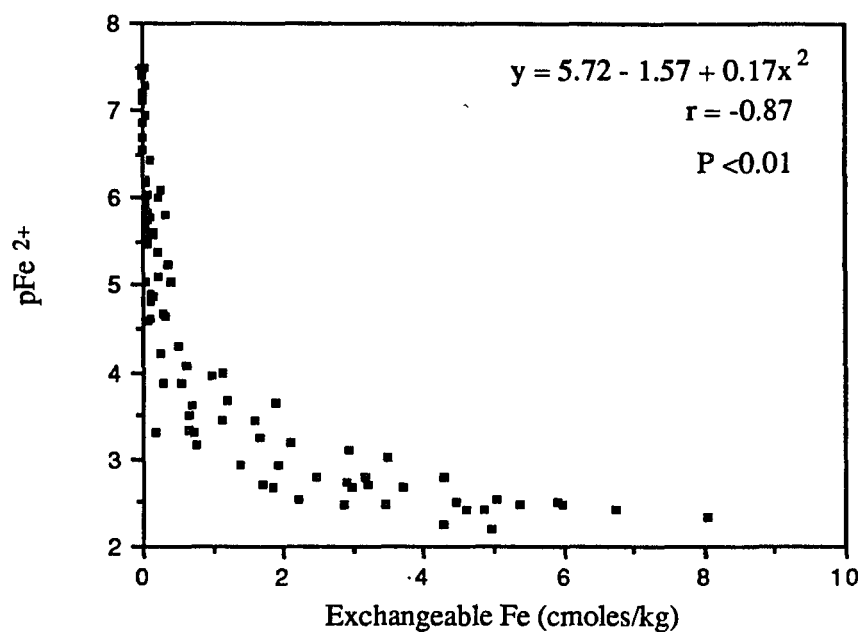


Figure 5. Plot of  $\text{Fe}^{2+}$  activity as a function of exchangeable Fe in acid and non-acid sulfate soils over all pH-Eh levels.

(1983). Points that lie above the line or to the right represent supersaturation with respect to theoretical equilibrium of each solid species, whereas points appear below or to the left of a line indicate undersaturation. At  $pe+pH$  from 12.95 to 13.95 or at redox potential of 500 mV and pH 5.5 to 4.5, most of data points lie above  $Fe(OH)_3$  (amorphous) and  $Fe(OH)_3$  suggesting that Fe solubility was probably controlled by these two solid species. At  $pe+pH$  of 11.95 or just below 12.95, it appeared that most  $Fe^{2+}$  activities are supersaturated with respect to  $FeOOH$  (goethite). Though the solid phases of Fe are not known with certainty, these mechanism are possibly reflected in that water-soluble Fe levels were very low under 500 mV/pH 5.5 to 4.5 conditions and was somewhat low at 500 mV/pH 3.5. The  $Fe(OH)_3-Fe^{2+}$  system is thought to be one of the principal redox systems in reduced soils (Ponnamperuma et al., 1967). Gotoh and Patrick (1974) noted that water-soluble Fe was largely controlled by the  $Fe(OH)_3-Fe^{2+}$  system in which the solid phase ferric oxyhydroxide ranged from amorphous to crystalline (goethite) in form. Van Breemen (1969) reported soluble  $Fe^{2+}$  was controlled by ill-defined ferric oxides that ranged between amorphous  $Fe(OH)_3$  and goethite. Schwab and Lindsay (1983) reported the metastable  $Fe_3(OH)_8$  controlled solution Fe at the highest redox and pH levels (above  $pe+pH$  8). In this study, all of the data points never reached the  $Fe_3(OH)_8$  equilibrium line. The literature mentioned above indicates amorphous  $Fe(OH)_3$  could control Fe solubility. At lower redox and pH levels (between  $pe+pH$  4 and  $pe+pH$  10), the experimental points tended to gather near the theoretical equilibrium line of the crystalline form of ferric oxyhydroxide (goethite).

It was assumed that  $\text{CO}_2$  and carbonate levels were low under the pH range of 3.5 to 5.5, thus all the experimental data points would be understaturated with respect to a carbonate system. Moore (1987) found soluble Fe was in equilibrium with solid phase  $\text{FeCO}_3$  at a pH above 6.8, and found the formation of ferrous bicarbonate complex ion ( $\text{FeHCO}_3^+$ ) occurred above pH 6.0 in the flooded acid sulfate rice fields. This might explain the minimal role of the carbonate system in controlling Fe solubility at pH 5.5 and below in this study.

The results suggest that there was a significant relationship between  $\text{Fe}^{2+}$  activity and exchangeable Fe. The data in Figure 5 showed a highly significant correlation ( $r=0.77$ ,  $P<0.01$ ,  $n=90$ ) between these two parameters. Moore (1987) recently reported similar results. However, the chemical relationship between  $\text{Fe}^{2+}$  and exchangeable Fe can not be readily explained. In an attempt to define the possible effect of exchangeable Fe, water-soluble Fe is plotted as a function of exchangeable Fe which yielded an  $r$  value of 0.86 ( $P<0.01$ ,  $n=90$ ) as shown in Figure 6. The relationship between water-soluble Fe and exchangeable Fe was even stronger than that between  $\text{Fe}^{2+}$  activity and exchangeable Fe. The strong relationship between water-soluble Fe and exchangeable Fe is likely related to the significant relationship between Fe activity and exchangeable Fe. Moore (1987) suggested that exchange reactions may play important role in controlling the solubility of Fe in acid sulfate soils based on the relationship between  $E'-\text{Fe}$  (the divalent charge fraction in the soil solution due to  $\text{Fe}^{2+}$ ) and  $E-\text{Fe}$  (the divalent charge fraction on the CEC accounted for by Fe) which yielded the thermodynamic non-preference exchange isotherm, a term that has been defined by Sposito (1981). The relationship between  $E'-\text{Fe}$  and  $E-\text{Fe}$  in the study



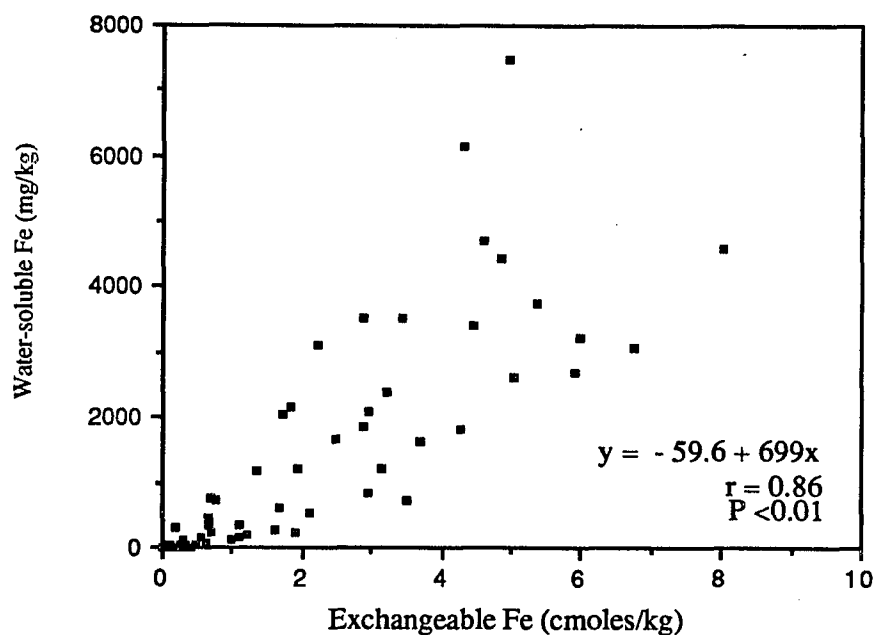


Figure 6. Relationship between water-soluble Fe and exchangeable Fe in acid and non-acid sulfate soils over all controlled redox potential and pH conditions.

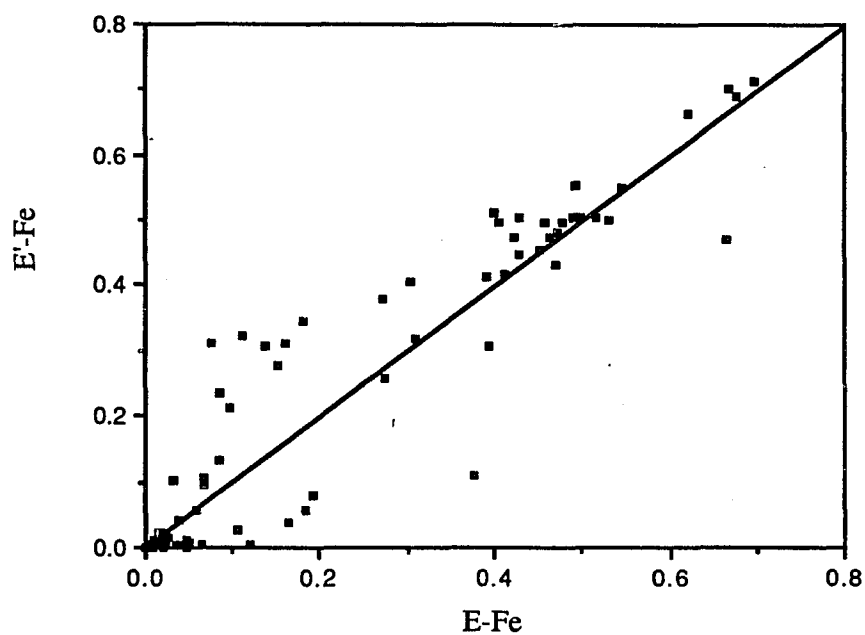


Figure 7. Relationship between the divalent charge fraction due to Fe ( $E'-Fe$ ) in soil solution and the divalent charge fraction due to Fe on the CEC ( $E-Fe$ ).

here are also close to the thermodynamic non-preference exchange isotherm as shown in the plot of Figure 7. The  $45^\circ$  angle solid line which is considered to be the line representing the thermodynamic non-preference exchange isotherm was also drawn through the experimental data points. The experimental data points were somewhat scattered from the  $45^\circ$  line. Part of this scatter may be due to the fact that separation of soluble organic bound metals was not considered in contributing to total soluble metals. In this case, using the data of total soluble metals may not be accurate in describing the relationship between  $E'-Fe$  and  $E-Fe$ .

Effect of redox potential and pH on various fractions of Mn in non-acid and acid sulfate soils planted to rice.

The effect of redox potential and pH on the levels of total water-soluble Mn are shown in Figure 8. The pattern of Mn dissolution is similar to that of water-soluble Fe. Both metals were negatively related to redox potential and pH. Regression analysis revealed that water-soluble Mn increased with decreasing pH ( $r = -0.30$ ,  $P < 0.01$ ,  $n=90$ ). While there was no significant correlation between water-soluble Mn and Eh ( $r = -0.05$ ,  $P = 0.51$ ,  $n=90$ ). This suggests that pH was more important than redox potential in regulating Mn dissolution which is opposite to the results found for water-soluble Fe. Multiple regression of water-soluble Mn as a function of pH and Eh resulted in an  $R^2$  value of 0.25, significant at the 1% level, indicating the effect of both pH and Eh on Mn dissolution. Satawathonanont (1986) noted the similar results as he observed the effect of both pH and Eh on water-soluble Mn dissolution but that Mn was affected more by pH than by redox potential.

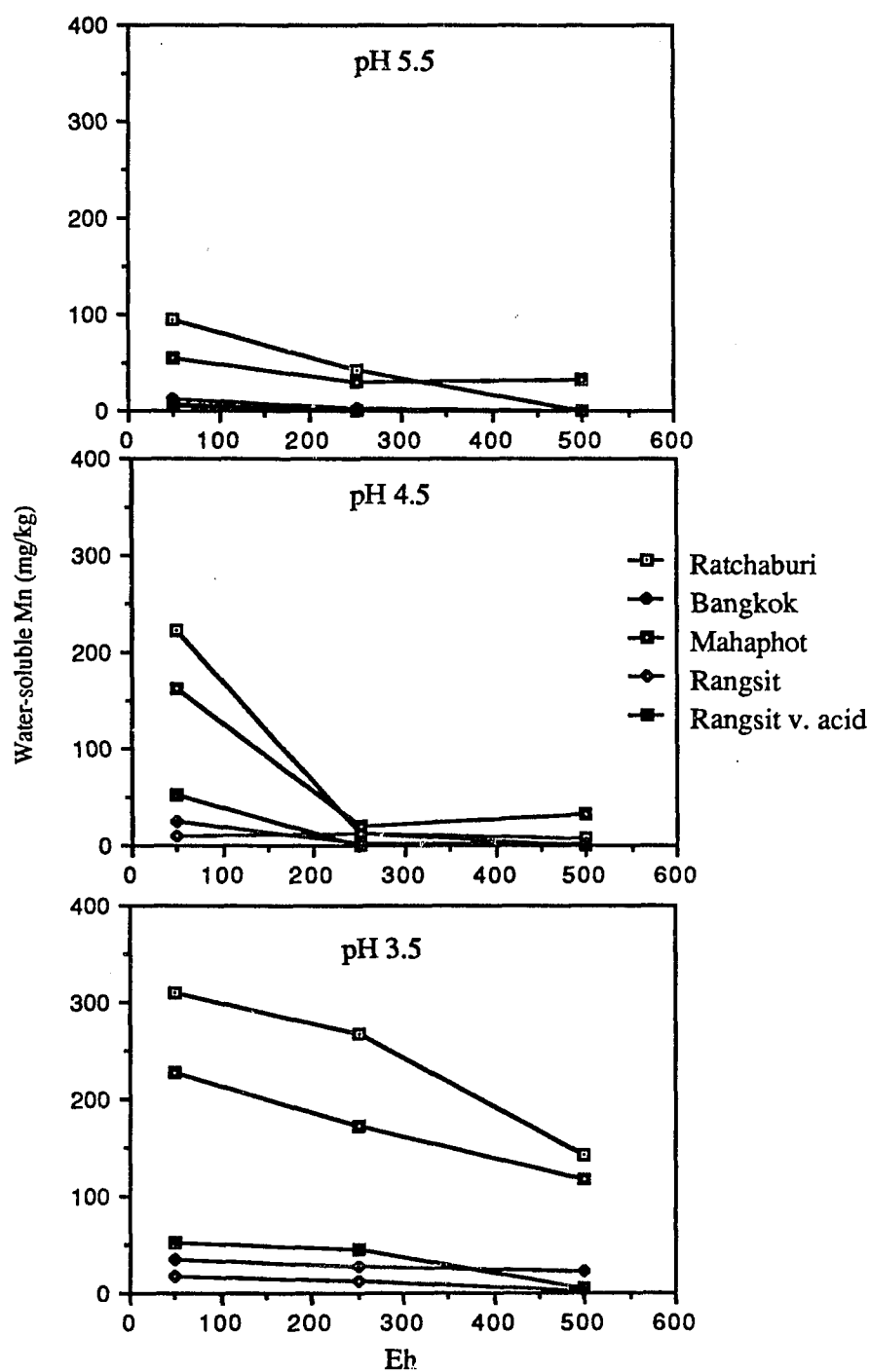


Figure 8. Concentration of water-soluble Mn in acid and non-acid sulfate soils under controlled redox potential and pH conditions.

Gambrell et al. (1975) reported the total water-soluble Mn considerably decreased as pH increased from 5 to 8. Delaune et al. (1981) found the pH strongly affected soluble Mn concentrations. They observed that soluble Mn increased with decreases in redox potential and pH. Similar results had been reported by other workers (Gotoh and Patrick, 1972; Sims and Patrick, 1978; Collins and Buol, 1970).

In all soils, water-soluble Mn concentrations ranged from as low as  $0.05 \text{ mg kg}^{-1}$  to maximum of  $309 \text{ mg kg}^{-1}$  under the lowest redox potential and pH levels (Table 4 and 5). Very low soluble Mn was detected under high pH and high redox potential. For instance, at 500 Mv/pH 4.5 and 5.5, the concentrations of Mn in nearly all soils were in the range of  $0.05 \text{ mg kg}^{-1}$  to  $7.1 \text{ mg kg}^{-1}$  except in the Ma soil where the concentrations of Mn was in the range of 31.1 to  $33.2 \text{ mg kg}^{-1}$ .

The distribution of exchangeable Mn as affected by pH and redox potential is depicted in Figure 9. Exchangeable Mn increased with decreasing pH ( $r=-0.26$ ,  $P<0.05$ ,  $n=90$ ) in all non-acid and acid sulfate soils. Redox potential had little effect on exchangeable Mn distribution. Multiple regression of exchangeable Mn as a function of redox potential and pH resulted in a low  $R^2$  value (0.070). This indicates that the interaction effect of redox potential and pH may be very small on regulating exchangeable Mn. Satawathananont (1986) found his  $\text{NH}_4\text{OAc}$  (pH 4.0) extractable Mn in Ma, Rs, and Rsa soils was positively affected by pH. The possible reason is that  $\text{NH}_4\text{OAc}$  (pH 4.0) might have dissolved Mn from newly precipitated Mn compounds. Other workers found their exchangeable Mn (extracted by 1M NaOAc adjusted to pH of the soils suspension) in Mississippi River sediment decreased as redox potential and pH increased (Gambrell, et al., 1975). Gotoh and

Table 4. Concentration of selected Mn forms under controlled redox potential and pH conditions in acid sulfate soils.

Eh (mV)	pH	pe+pH	Mahaphot			Rangsit			Rangsit very acid		
			Ws-Mn*	Ex-Mn\$	Rd-Mn#	Ws-Mn	Ex-Mn	Rd-Mn	Ws-Mn	Ex-Mn	Rd-Mn
			mg kg <sup>-1</sup>								
500	5.5	13.94	32.6	112	128	0.10	0.00	1.50	0.10	1.50	24.0
	4.5	12.94	33.2	109	100	0.10	1.50	3.00	0.05	2.00	1.50
	3.5	11.94	119	170	70.0	1.70	5.50	3.00	4.90	4.50	3.00
250	5.5	9.72	31.1	86.5	85.0	0.15	7.50	2.00	0.25	3.50	1.00
	4.5	8.72	20.7	110	188	11.6	12.0	16.0	0.20	4.50	2.50
	3.5	7.72	173	156	61.5	13.6	15.0	5.00	46.2	23.0	12.0
50	5.5	6.34	55.2	94.5	113	5.50	10.0	8.00	8.39	8.50	9.00
	4.5	5.34	162	118	67.5	9.10	18.0	7.50	8.15	15.5	6.50
	3.5	4.34	227	141	32.0	17.10	13.0	4.00	52.9	24.5	6.50
LSD (0.05)			45	24	127	45	24	127	45	24	127

\*Ws-Mn : Water soluble Mn.

\$Ex-Mn : Exchangeable Mn.

#Rd-Mn : Reducible Mn

Table 5. Concentration of selected Mn forms under controlled redox potential and pH conditions in non-acid sulfate soils.

Eh (mV)	pH	pe+pH	Bangkok			Ratchaburi		
			Ws-Mn*	Ex-Mn\$	Rd-Mn#	Ws-Mn	Ex-Mn	Rd-Mn
			mg kg <sup>-1</sup>					
500	5.5	13.94	0.65	2.50	16.0	0.10	2.50	417
	4.5	12.94	2.60	11.5	15.0	7.10	75.5	294
	3.5	11.94	23.4	24.5	16.0	142	154	59.5
250	5.5	9.72	1.95	8.00	10.5	41.4	70.0	300
	4.5	8.72	1.60	17.5	9.50	11.8	84.5	129
	3.5	7.72	26.8	23.5	10.5	268	131	25.5
50	5.5	6.34	11.5	17.5	16.5	94.9	77.0	330
	4.5	5.34	25.2	17.5	12.5	222	87.0	39.5
	3.5	4.34	35.5	23.0	8.00	309	102	21.0
LSD (0.05)			45	24	127	45	24	127

\*Ws-Mn : Water-soluble Mn

\$Ex-Mn : Exchangeable Mn

#Rd-Mn : Reducible Mn

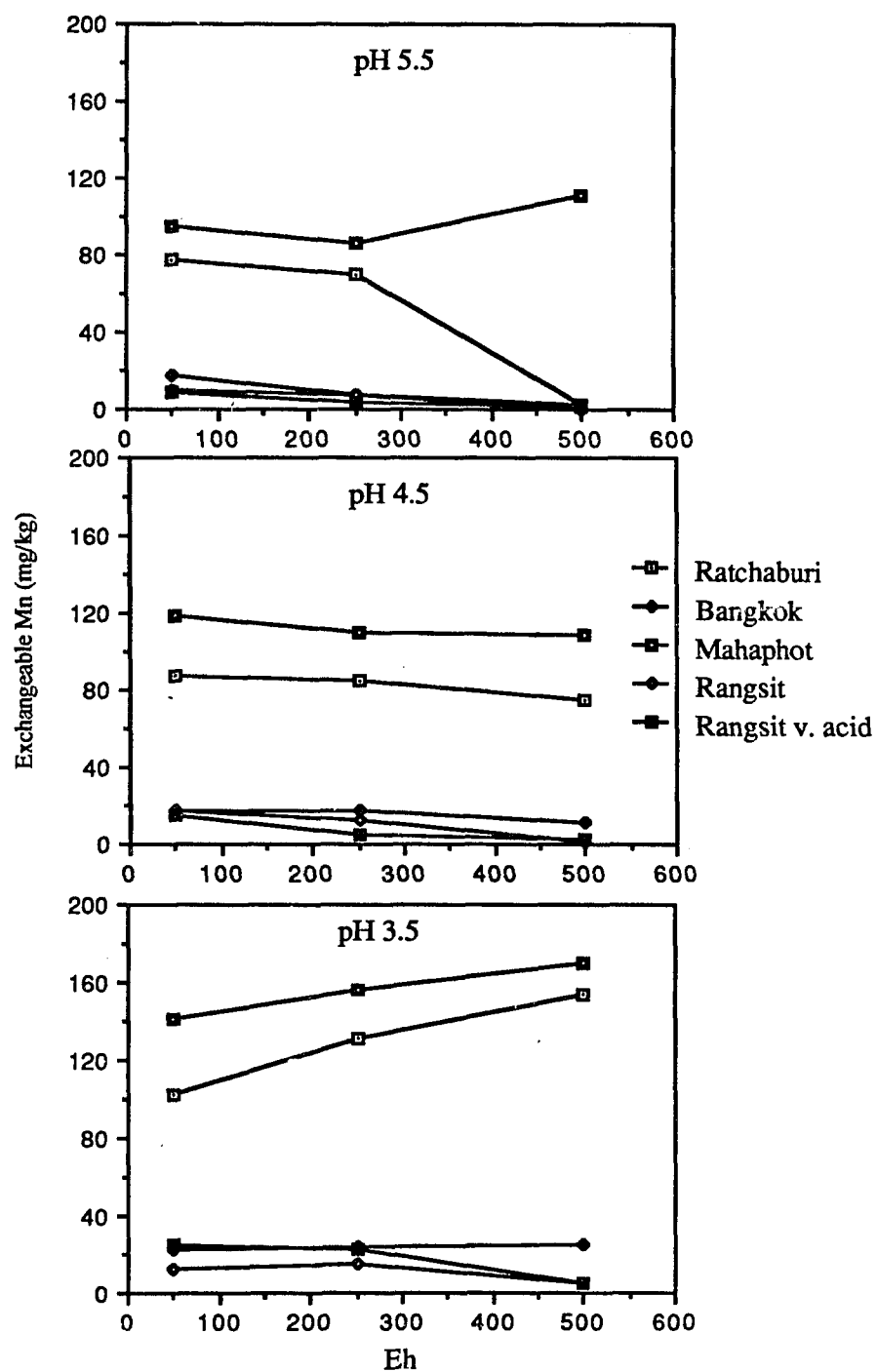


Figure 9. Levels of exchangeable Mn in acid and non-acid sulfate soils under controlled redox potential and pH conditions.

Patrick (1972) found both redox potential and pH influenced the transformations of Mn in a suspension of Crowley rice soil. They indicated that at low redox potential and pH, there was a large conversion of the higher oxides of Mn to the water-soluble plus exchangeable form. Water-soluble Mn apparently increased at the expense of the exchangeable form. They also suggested that cation exchange equilibria involving H, Al, and Mn ions on the exchange complex may be involved in driving Mn into the soil solution at low pH. This is probably the case in this study where large amounts of both water-soluble Mn and Fe are present together. The relatively greater amounts of water-soluble Fe compared to Mn would permit Fe to occupy a larger proportion of the exchange sites driving Mn out. More (1987) also suggested that cation exchange reactions is the probably mechanism regulating Mn distribution in flooded acid sulfate soils.

Reducible Mn (0.25M  $\text{NH}_2\text{OH}\cdot\text{HCL}$ -0.25M HCL extractable) levels under various redox potential and pH conditions are presented in Figure 10. Reducible Mn was also affected by pH, but unlike water-soluble or exchangeable Mn, reducible Mn was positively correlated with pH ( $r=0.28$ ,  $p<0.01$ ,  $n=90$ ). The effect of redox potential on reducible Mn distribution was not statistically significant. The concentrations of reducible Mn were approximately of the same magnitude as that of water-soluble Mn in all of the five soils. The average amount of reducible Mn in Rb and Ma soils was generally higher than that in the Bk, Rs, and Rsa soils. Van Breemen (1976) reported that dissolved and exchangeable levels of  $\text{Mn}^{2+}$  were considered as the majority part of Mn in older acid sulfate soils. This is reflected in this study by relatively low concentrations of reducible Mn in both Rs and Rsa soils.



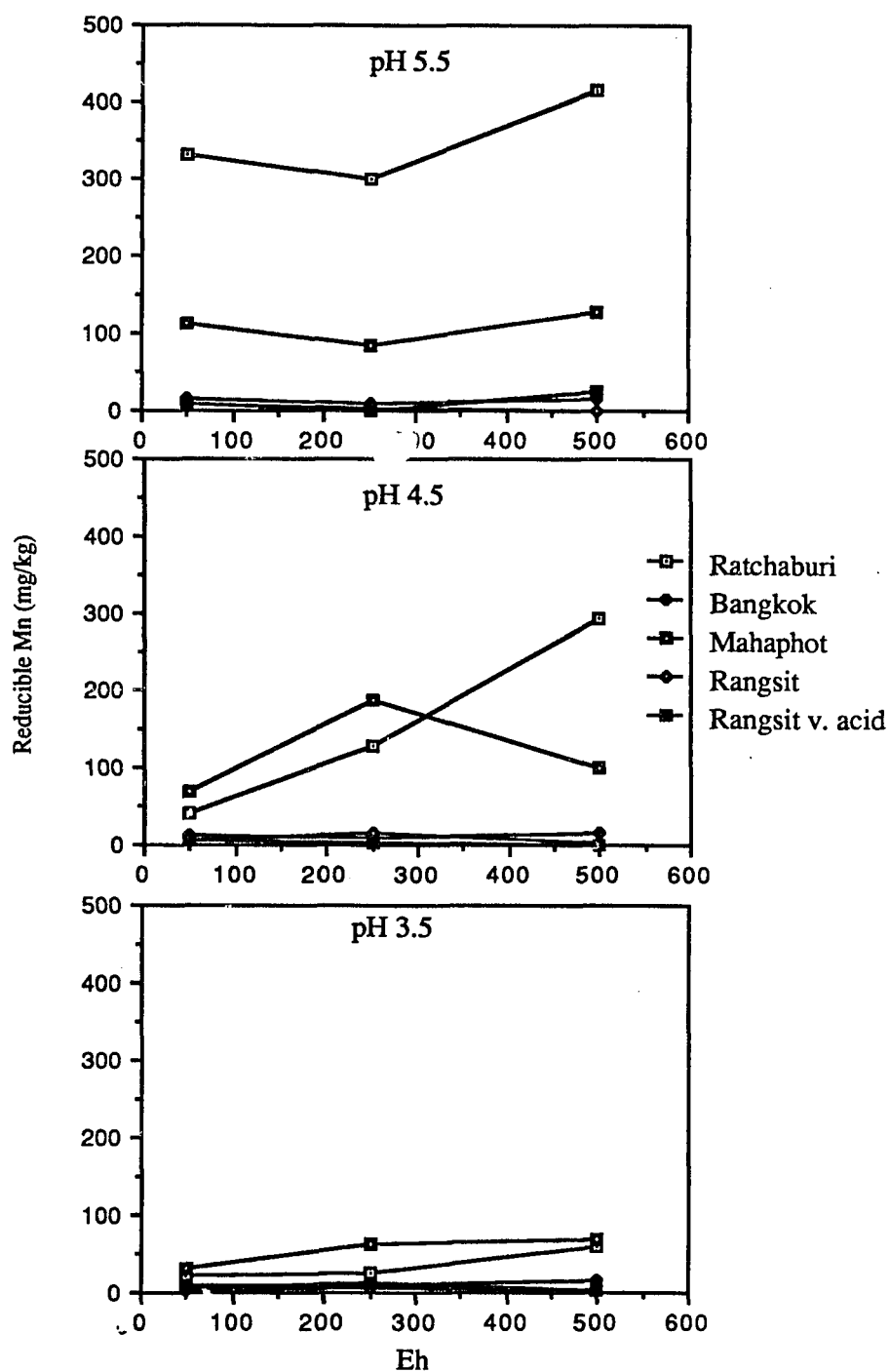


Figure 10. Distribution of reducible Mn in acid and non-acid sulfate soils under controlled redox potential and pH conditions.

### Manganese solubility

The experimental data for  $\text{Mn}^{2+}$  activity as  $\log \text{Mn}^{2+} + 2\text{pH}$  are plotted in Figure 11 using the same procedure as Schwab and Lindsay (1983). The lines indicate the theoretical equilibrium with respect to each of the stable solid phases of Mn as that described by Lindsay (1979). It is apparent that  $\text{Mn}^{2+}$  activities in these suspensions of non-acid and acid sulfate soil under various redox potential and pH conditions were undersaturated with regard to all of the stable solid phases presented here. Van Breemen (1976) reported that his Eh-pH data in acid sulfate soils always fell in the  $\text{Mn}^{2+}$  field. He observed near-equilibrium or slight supersaturation with rhodocrosite ( $\text{MnCO}_3$ ) only in substrata of certain young acid sulfate soils, and in samples of mangrove muds. Moore (1987) observed near equilibrium with  $\text{MnCO}_3$  in some high pH soils ( $\text{pH} > 7.0$ ). Ponnampetuma et al. (1969) also found that the  $\text{MnCO}_3\text{-H}_2\text{-CO}_2$  system regulated the solubility of  $\text{Mn}^{2+}$ . In this study, the highest pH was only 5.5, therefore, equilibrium with  $\text{MnCO}_3$  would not be expected. At the lowest Eh (50 mV), MnS would not precipitate at any pH level. The pH levels here are in the range of slightly acid to strongly acid, thus after reduction, the  $\text{Mn}^{2+}$  ions may remain in solution or enter the exchange complex according to the balance of ion exchange equilibrium. Moore (1987) used the relationship between E-Mn (the divalent charge fraction on the CEC due to Mn) and E'-Mn (the divalent cation charge fraction in the soil solution due to Mn) to provide evidence that  $\text{Mn}^{2+}$  activity in flooded acid sulfate soils is regulated by cation exchange reactions. The relationship between E-Mn and E'-Mn was determined by the plot of their values as depicted in

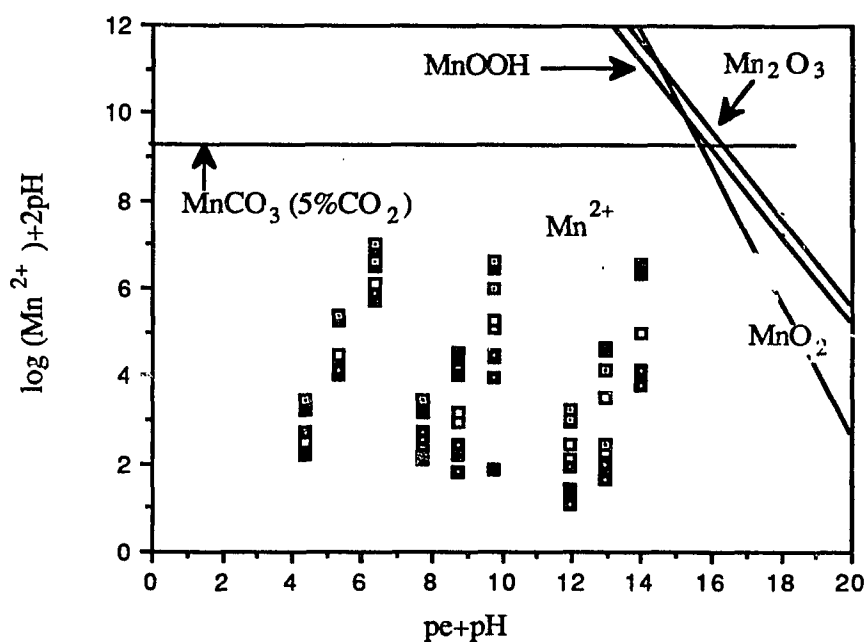


Figure 11. Relationship between  $\text{Mn}^{2+}$  activities and  $\text{pe}+\text{pH}$  with theoretical solubility of Mn solid species over all pH-Eh levels of acid and non-acid sulfate soils.

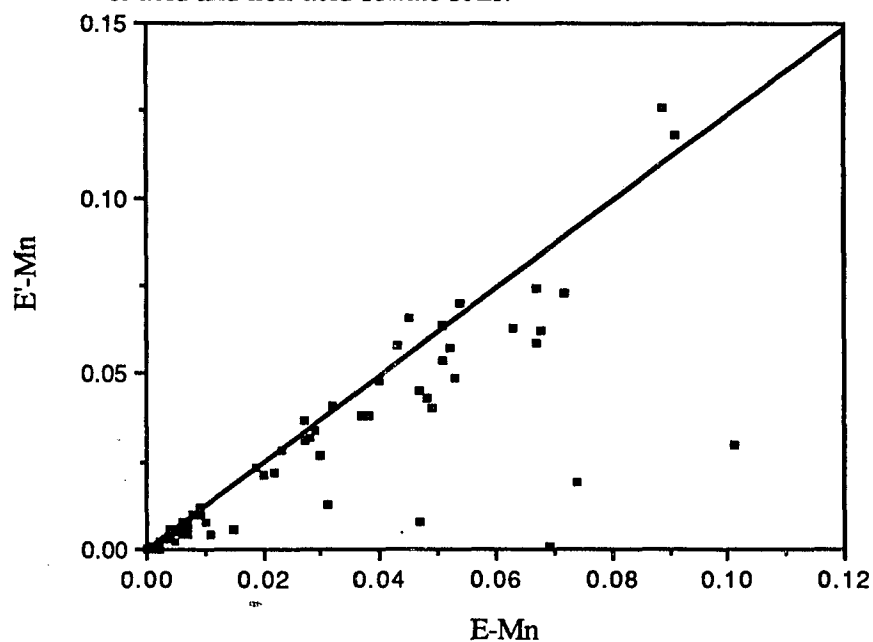


Figure 12. Relationship between the divalent charge fraction due to Mn in the soil solution ( $E'\text{-Mn}$ ) and the divalent charge fraction due to Mn on the CEC ( $E\text{-Mn}$ ).

Figure, 12. The  $45^\circ$  angle solid line which is considered to be the line representing the thermodynamic non-preference exchange isotherm was also drawn through the experimental data points. It was observed that there are many points that lie beyond the line of the thermodynamic non-preference isotherm. Because the majority of data points were clustered along the line, it is believed that the relationship between E-Mn and E'-Mn is still close to the theoretical of nonpreference isotherms as described by Sposito (1981). Thus, it is possible that cation exchange reactions are an important means of regulating the Mn solubility under various controlled redox potential and pH conditions of non-acid and acid sulfate soils in this study.

#### Iron availability to rice

The uptake of Fe and the Fe content in shoot in both tolerant (IR46) and sensitive (IR26) varieties was significantly affected by pe+pH ( $P<0.01$ ) as shown in Table 6. There was a significant correlation between pH, Eh, and pe+pH parameters and Fe uptake with r values of -0.38 ( $P<0.01$ ), -0.48 ( $P<0.01$ ) and -0.56 ( $P<0.01$ ) respectively. The interaction effects of redox potential and pH are additive as the regression analysis of Fe uptake as a function of redox potential and pH gave an  $R^2$  value of 0.31 ( $P<0.01$ ). The results illustrate that shoot levels of the sensitive rice variety ( $690 \text{ mg kg}^{-1}$  average) are higher than for the tolerant rice variety ( $512 \text{ mg kg}^{-1}$  average) suggesting a differential response to Fe in the growth media between the two varieties existed. Virmani (1977) observed that at high levels of soluble Fe in his study, the iron tolerant variety contained  $560 \text{ mg kg}^{-1}$

Table 6. Fe uptake and Fe content in the shoot tissue (Shoot Fe ) in IR 26 and IR 46 rice varieties grown over 3 weeks on acid and non-acid sulfate soils under controlled redox potential and pH conditions.

pH-Eh	pe+pH	Uptake Fe (mg/pot)		Shoot Fe (mg kg <sup>-1</sup> )	
		IR26	IR46	IR26	IR46
3.5-50	4.34	2217	2664	3068	2650
3.5-250	5.34	381	450	325	219
3.5-500	6.34	112	162	71.3	69.9
4.5-50	7.72	1287	1237	2127	1129
4.5-250	8.72	420	646	250	159
4.5-500	9.72	226	335	125	113
5.5-50	11.94	151	250	121	152
5.5-250	12.94	97.2	157	62.9	60.4
5.5-500	13.94	88.4	136	59.1	58.9
LSD (0.05)		973	973	1651	1651

Fe in the leaf tissue while the sensitive variety contained 1650 mg kg<sup>-1</sup>.

The above results are similar to earlier findings (Jugsujinda and Patrick, 1977; Van Der Vorm and Van Deist, 1979a). Increasing Fe uptake was associated with decreases of both redox potential and pH. The highest uptake of Fe was obtained at 50 mV and pH 3.5 while the lowest uptake was observed at 500 mV and pH 5.5. The Fe uptake is plotted as a function of Fe concentration in the plant tissue (shoot Fe) as shown in Figures 13 and 14. For IR 46 variety, shoot Fe ranged from 20 to 10,500 mg kg<sup>-1</sup> and Fe uptake ranged from 29.4 to 4,430 mg/pot. In the IR 46 variety, shoot Fe ranged from 6.1 to 4930 mg kg<sup>-1</sup> and Fe uptake ranged from 17.8 to 5807 mg kg<sup>-1</sup>. At 500 mV and 250 mV at pH 5.5, the average shoot Fe (around 50 mg kg<sup>-1</sup>) was lower than the published critical level for Fe deficiency of 70 mg kg<sup>-1</sup> in the leaf blade tissue at tillering stage (Yoshida, 1981). This suggests that the rice plants may have been Fe deficient at high redox potential and pH.

The results in Chapters 4 and 5 indicated Fe levels in plants and soil forms are important variables negatively associated with growth of both rice varieties in terms of weight gain. The relationship between plant and soil Fe is important to the availability of Fe to rice.

The results of multiple regression analyses produced several prediction models for the variation in weight gain of each variety in each soil type. The model explained the relationship between weight gain and several factors by means of a regression equation. It was observed that the Fe:Mn ratio in the plant tissue and shoot Fe levels are among the most important variables negatively associated with weight gain of rice. Shoot Fe levels of both rice varieties are plotted as a

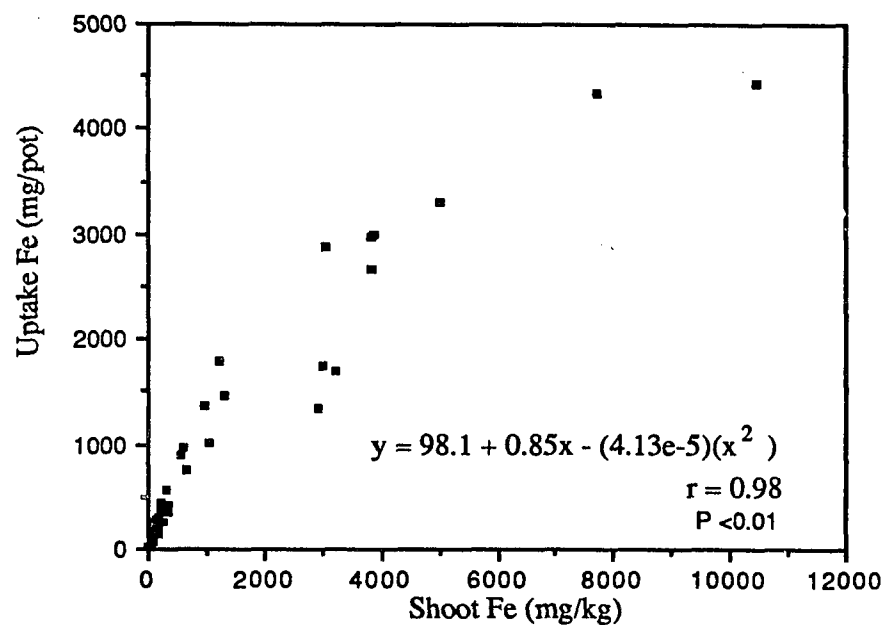


Figure 13. Relationship between Fe uptake and Fe content in shoot tissue for the IR 26.

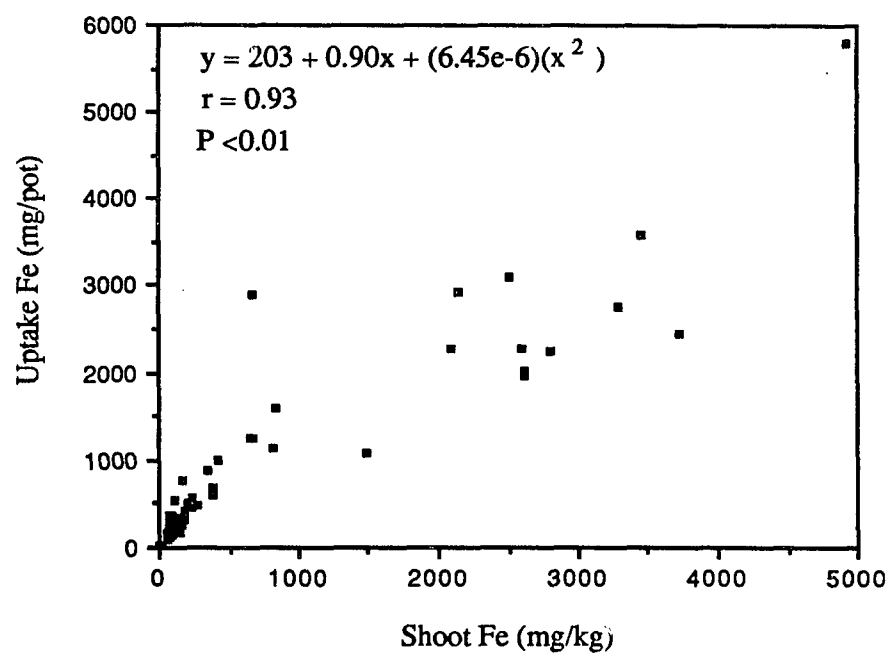


Figure 14. Relationship between Fe uptake and Fe content in shoot tissue for the IR 46.

function of  $\text{Fe}^{2+}$  activity in terms of  $\text{pFe}^{2+}$  (negative log of  $\text{Fe}^{2+}$  activity) as depicted in Figures 15 and 16. These plots include the relationship between shoot Fe and  $\text{pFe}^{2+}$  expressed as a polynomial equation describing the curvilinear relationship. Schwab and Lindsay (1983) suggested that plant uptake of Fe from low  $\text{Fe}^{2+}$  levels (below  $\text{pFe}^{2+}$  of 8.5) is probably due to absorption of organic Fe complexes or passive absorption. They found uptake of Fe at  $\text{pFe}^{2+}$  from 8 to 4 is directly related to  $\text{pFe}^{2+}$ . In this study, the results revealed that shoot Fe levels or Fe uptake was somewhat related to  $\text{pFe}^{2+}$ . At high levels,  $\text{Fe}^{2+}$  probably overwhelmed the iron excluding and iron retaining capacity of the roots resulting in excessive uptake of Fe in shoots (Tadano and Yoshida, 1978). Thus, in this study, the critical level of  $\text{Fe}^{2+}$  seemed to be at a  $\text{pFe}^{2+}$  of 3.

Total water-soluble Fe levels ( $\text{Fe}_s$ ) and the divalent charge fraction due to Fe in the soil solution ( $\text{E}'\text{-Fe}$ ) are the other two variables to be considered for their relationship with shoot Fe. Shoot Fe levels in both varieties are plotted as a function of  $\text{Fe}_s$  and  $\text{E}'\text{-Fe}$  in Figures 17, 18, 19, and 20.  $\text{WsFe}$  yielded the highest correlation coefficient with shoot Fe as compared to that of  $\text{pFe}^{2+}$  and  $\text{E}'\text{-Fe}$ . It may not be appropriate to conclude that shoot Fe related to  $\text{WsFe}$  significantly better than to other Fe variables in the soil solution. Figures 19 and 20 showed that shoot Fe was positively associated with  $\text{E}'\text{-Fe}$ . At an  $\text{E}'\text{-Fe}$  of 0.45 and below, shoot Fe nearly formed straight line relationship with  $\text{E}'\text{-Fe}$  whereas at  $\text{E}'\text{-Fe}$  of 0.45 and higher, excessive concentrations of shoot Fe were observed. Hence, the critical level of  $\text{E}'\text{-Fe}$  in this study appeared to be at an  $\text{E}'\text{-Fe}$  of 0.45. On the other hand, Moore (1987) reported that excessive Fe uptake occurred when



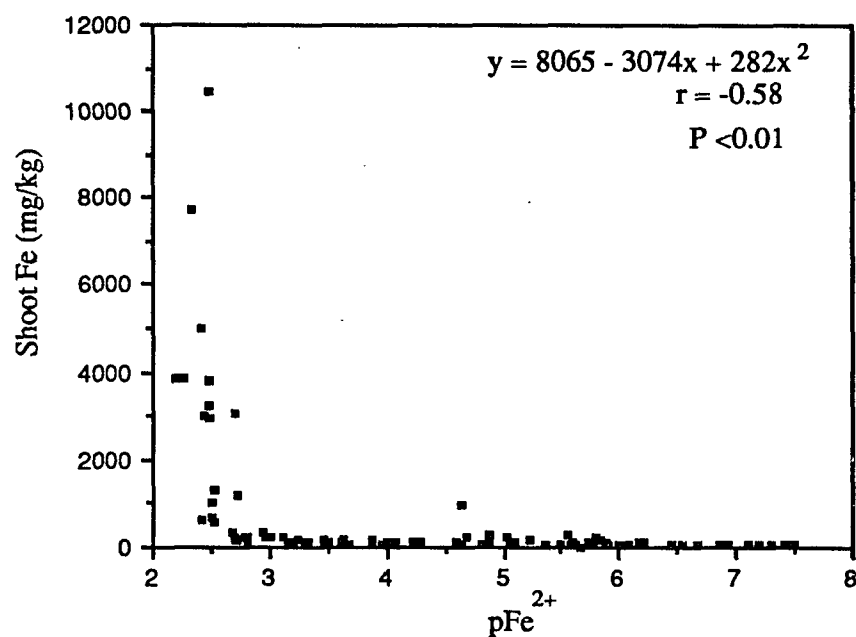


Figure 15. Relationship between Fe content in the shoot tissue and  $Fe^{2+}$  activity in soil solution for the IR 26 rice variety.

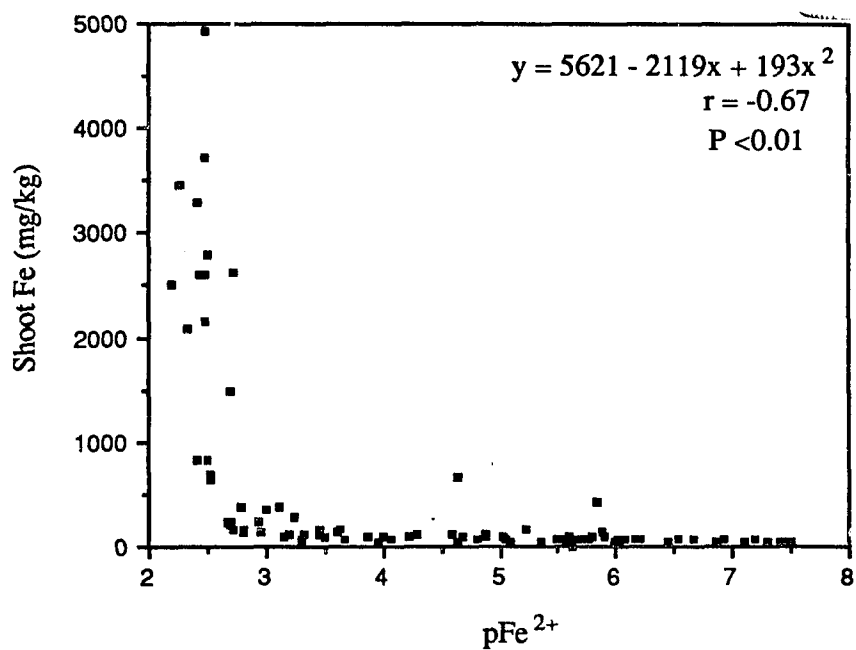


Figure 16. Relationship between Fe content in the shoot tissue and  $Fe^{2+}$  in the soil solution for the IR 46 rice variety.

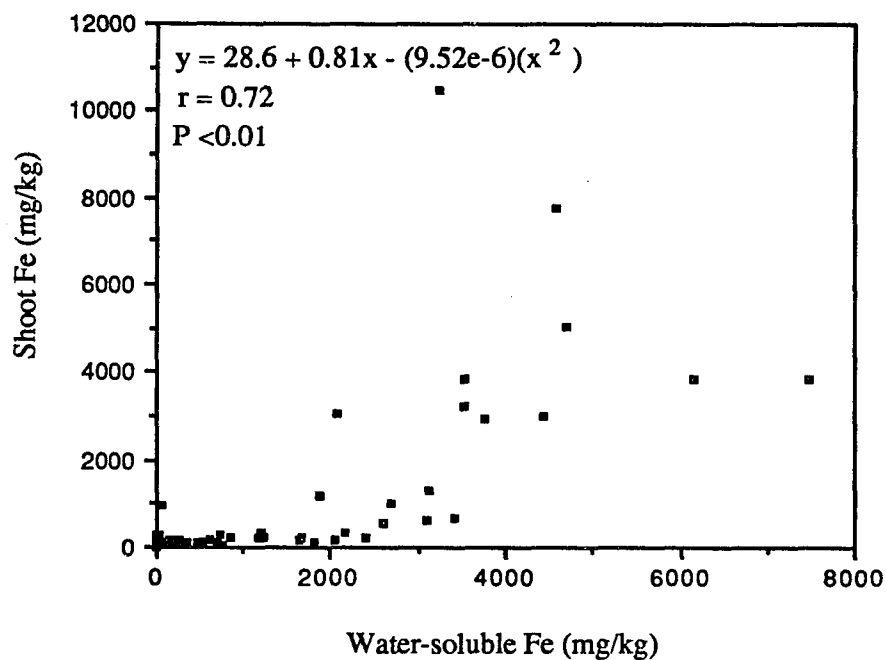


Figure 17. Relationship between Fe content in the shoot tissue and water-soluble Fe for the IR 26 rice variety.

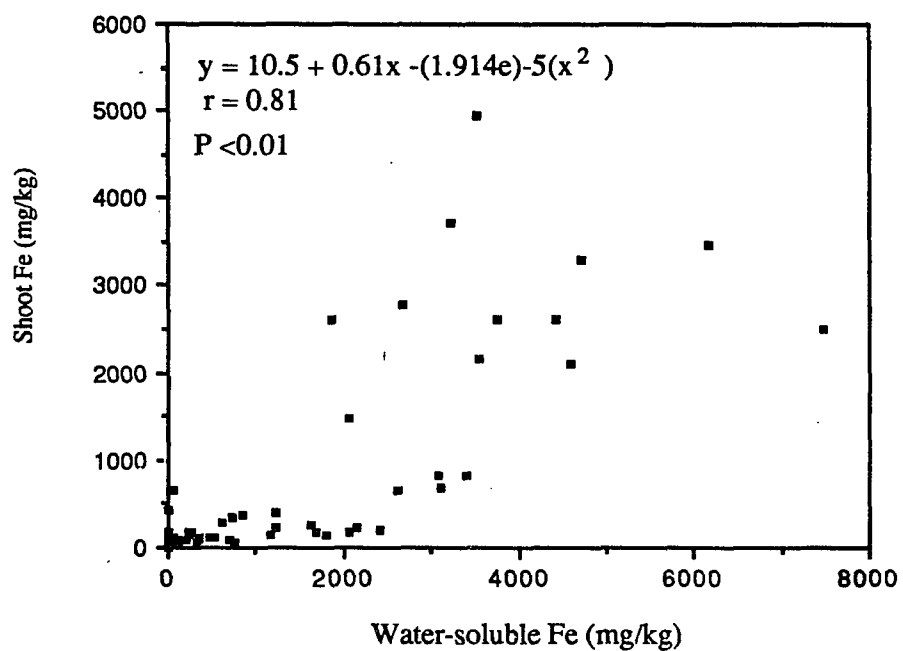


Figure 18. Relationship between Fe content in the shoot tissue and water-soluble Fe for the IR 46 rice variety.

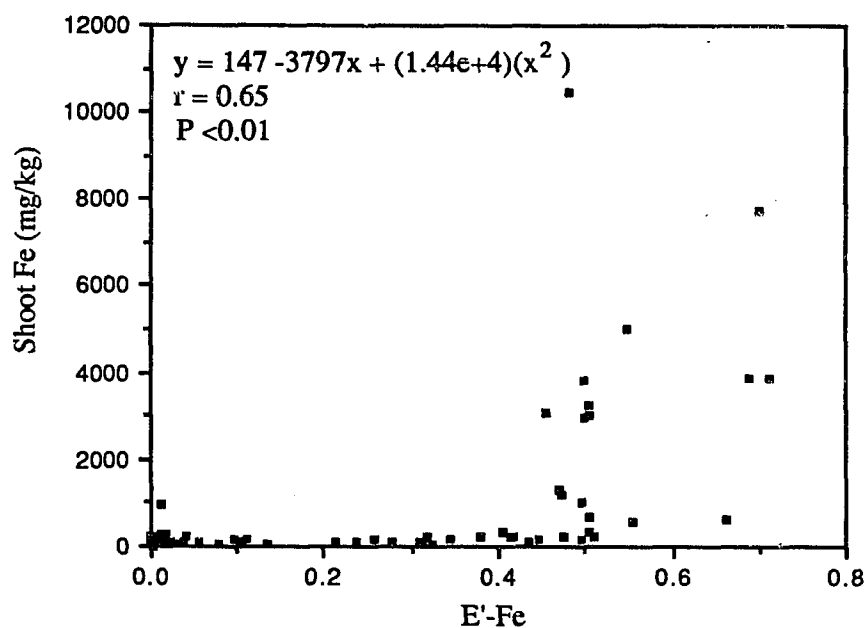


Figure 19. Relationship between Fe content in the shoot tissue and the divalent charge fraction due to Fe in the soil solution ( $E'-Fe$ ) for the IR 26 rice variety.

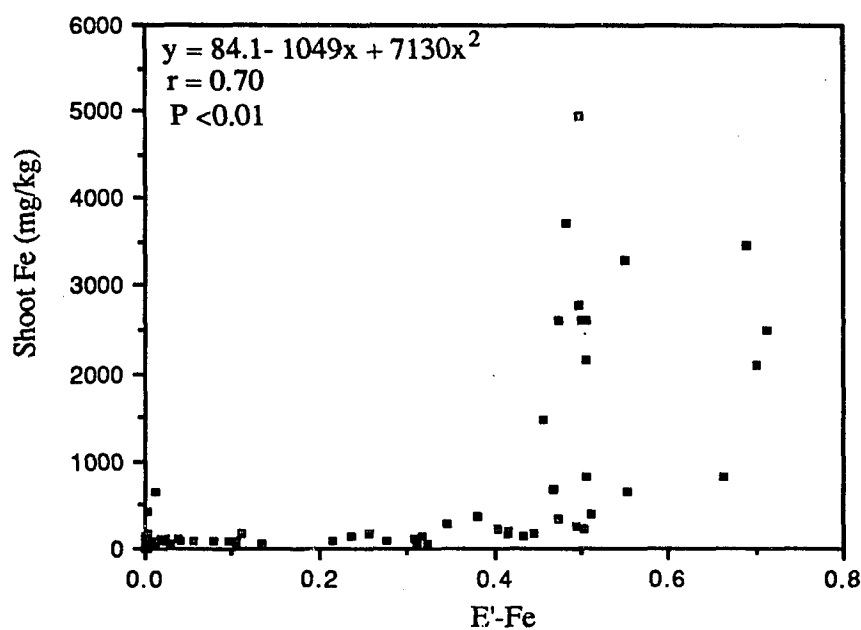


Figure 20. Relationship between Fe content in the shoot tissue and the divalent charge fraction due to Fe in the soil solution ( $E'-Fe$ ) for the IR 46 rice variety.

E'-Fe exceeds 0.75 in his study and is probably not related to the  $\text{Fe}^{2+}$  activity.

The Fe:Mn ratio in plant tissue is one of the most important plant variables affecting growth of rice. The weight gain of each variety was plotted as a function of the Fe:Mn ratio in the plant tissue as depicted in Figures 21 and 22. Weight gains by both varieties were significantly correlated with the Fe:Mn ratio in the plant tissue, and the correlation between weight gain and Fe:Mn in the IR 26 variety ( $r=-0.68$ ,  $P<0.01$ ) was somewhat higher than that in IR 46 ( $r=0-0.59$ ,  $P<0.01$ ). This may suggest that the sensitive rice variety (IR 26) tended to be more affected by the Fe:Mn ratio in the plant tissue than the tolerant variety. A wide range of weight gain data was observed (0.7 to 2.5 mg in IR 26, and 1 to 5.45 in IR 46) under low levels of the Fe:Mn ratio (0.01 to <5). At the Fe:Mn ratios of 5 or above, the weight gain of both varieties never increased greater than 50% of their highest weight gain value. It appeared in this study that an Fe:Mn ratio in the plant tissue of 5 would probably be the critical level in suppressing the growth of rice. An Fe:Mn ratio of 1.5 to 2.5 was considered as the requirement for normal plant growth Shive (1941). In this experiment, the Fe:Mn ratio ranged from 0.01 to about 26 which corresponds to the range of 0.01 to 25.8 reported by Tanaka and Navasero (1966b). Tanaka and Navasero (1966b) also found that decreases of rice growth was accompanied with increases of Fe:Mn ratio. The published critical level of Fe in the leaf tissue is  $300 \text{ mg kg}^{-1}$  at the tillering stage of rice (Yoshida, 1981). In this study it was noticed that an Fe:Mn ratio of 4.5 and higher was always associated with a concentration of Fe in the shoot tissue of over  $300 \text{ mg kg}^{-1}$ .

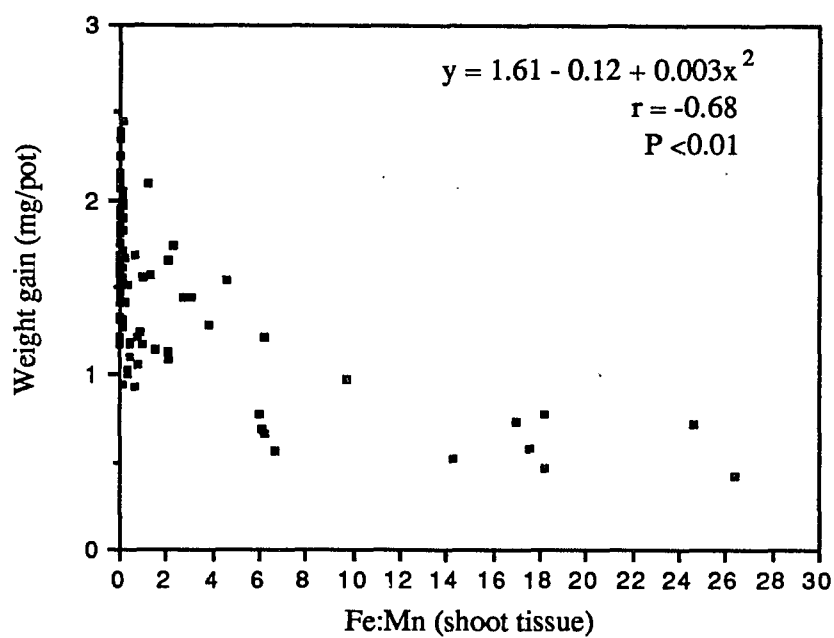


Figure 21. Relationship between weight gain and Fe:Mn ratio in the shoot tissue for the IR26 rice variety.

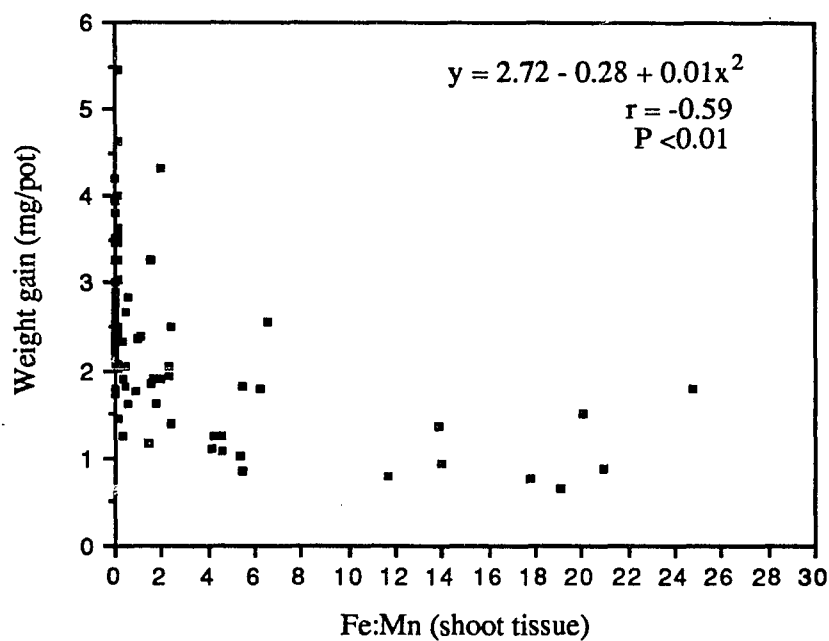


Figure 22. Relationship between weight gain and Fe:Mn ratio in the shoot tissue for the IR46 rice variety.

The relationship between the Fe:Mn ratio in plant tissue and the negative log of  $\text{Fe}^{2+}$  activity ( $\text{pFe}^{2+}$ ) and/or  $\text{pe}+\text{pH}$  are illustrated by the plots of Figures 23, 24, 25, and 26. The Fe:Mn ratio negatively correlated with  $\text{pFe}^{2+}$  and  $\text{pe}+\text{pH}$ . There was a significant correlation between  $\text{Fe}^{2+}$  activity and  $\text{pe}+\text{pH}$  with an  $r$  value of 0.87 significant at the 0.01% level. The  $\text{pe} + \text{pH}$  influenced the distribution of  $\text{Fe}^{2+}$  activity which ultimately affected growth of the rice plant. The effects of  $\text{pe} + \text{pH}$  on the transformation of Fe in the soil solution has been reported by several authors (Barnes and Back, 1964; Gotoh and Patrick, 1974; Gambrell et al., 1975; Patrick and Fontenot, 1976; Jugsujinda and Patrick, 1977; Schwab and Lindsay, 1983; Satawathananont, 1986; Moore, 1987) supporting the relationship between  $\text{pe} + \text{pH}$  and Fe found here. The relationship between the Fe:Mn ratio in the plant tissue of both varieties and  $\text{Fe}^{2+}$  activity in the soil solution yielded similar  $r$  values (Figures 23 and 24). At  $\text{pFe}^{2+}$  of 3 and lower, the Fe:Mn ratio became much greater suggesting that  $\text{Fe}^{2+}$  activity overwhelmed the iron excluding and/or immobilization capacity of the roots (Tadano and Yoshida, 1978). Van der Vorm and Van Diest (1979a) reported that high Fe to Mn levels in the plant tissue directly related to a high Fe concentration in the growth media. They observed high Fe and Mn in the plant tissue under low pH, and anaerobic conditions which is somewhat similar to the content of Mn in the shoot tissue observed in this study. Relationship between shoot Fe and negative log of  $\text{Fe}^{2+}:\text{Mn}^{2+}$  activity ratio or  $\text{p}(\text{Fe}^{2+}:\text{Mn}^{2+})$  are depicted in Figures 27 and 28. There was significant correlation between shoot Fe and  $\text{p}(\text{Fe}^{2+}:\text{Mn}^{2+})$  suggesting that uptake of Fe by the rice plant may be partially influenced by the Fe:Mn activity ratio in the soil solution. Iron and

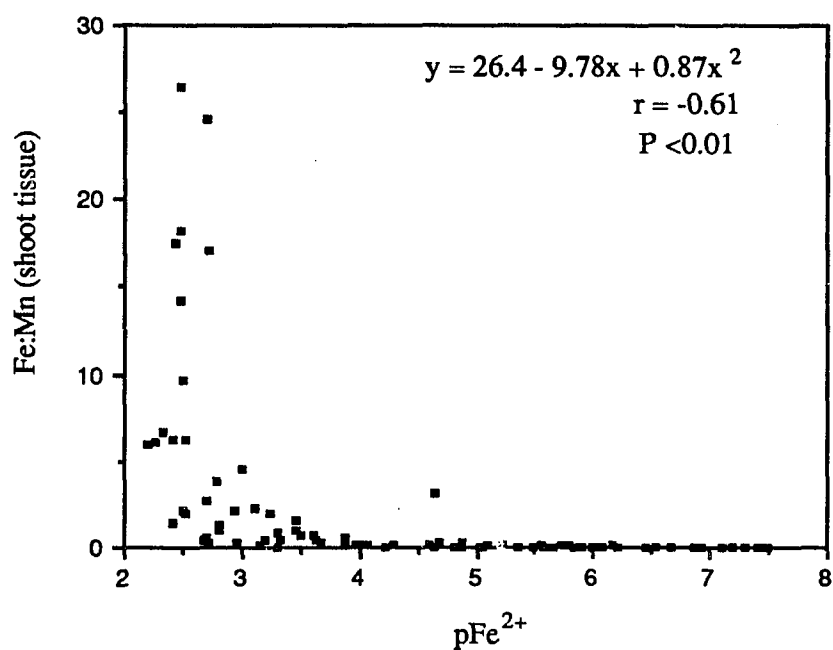


Figure 23. Relationship between Fe:Mn ratio in the plant tissue and  $Fe^{2+}$  activity in soil solution for the IR 26 rice variety.

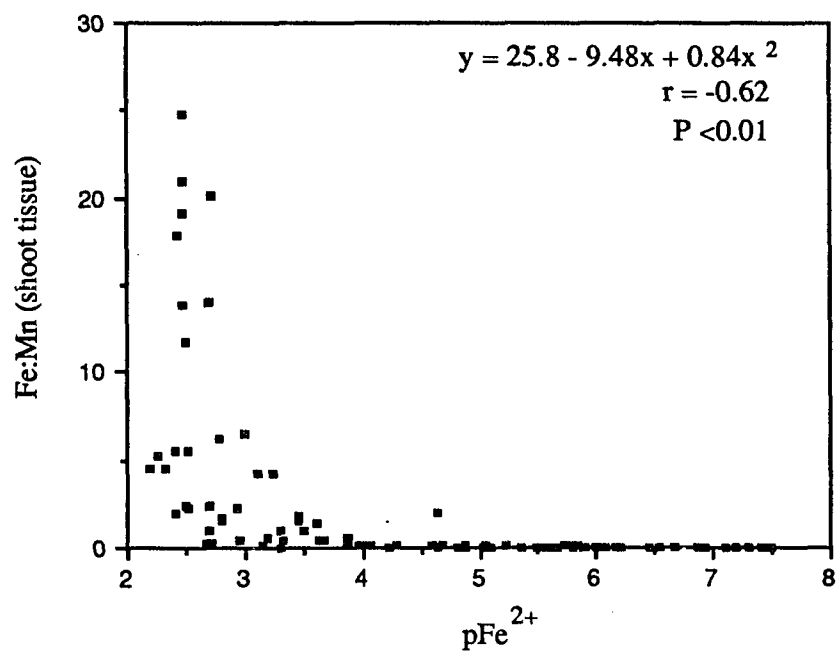


Figure 24. Relationship between Fe:Mn ratio in the plant tissue and  $Fe^{2+}$  activity in the solution for the IR 46 rice variety.

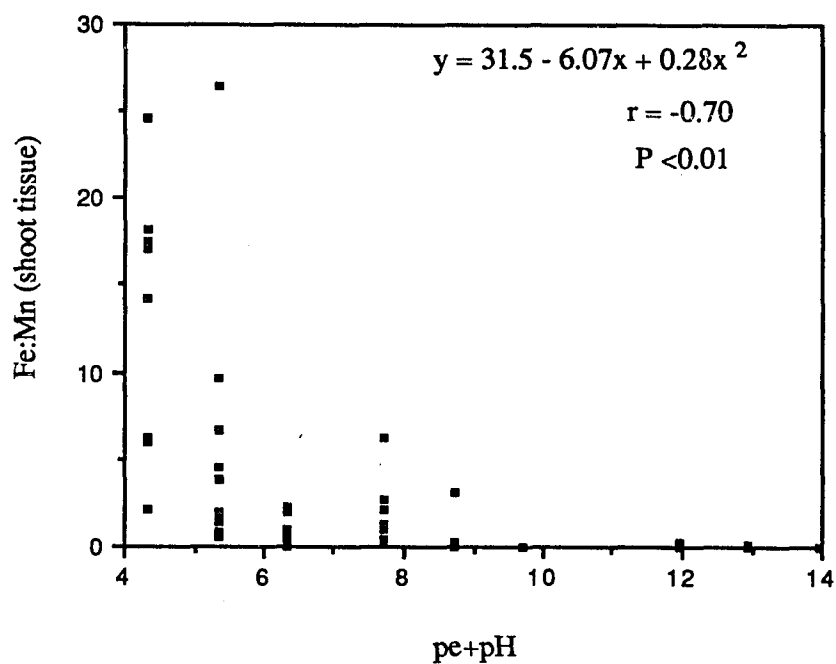


Figure 25. Relationship between Fe:Mn ratio in the shoot tissue and pe+pH for the IR 26 rice variety.

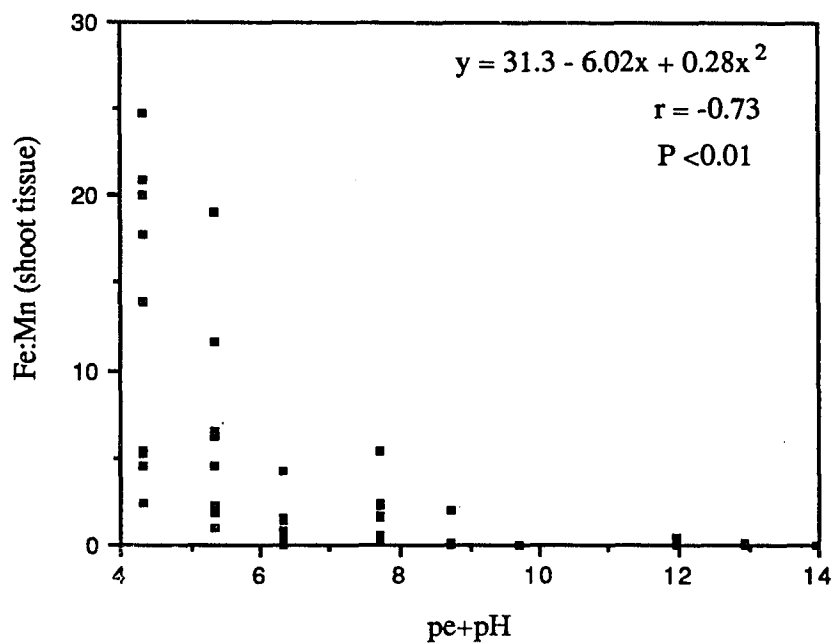


Figure 26. Relationship between Fe:Mn ratio in the plant tissue and pe+pH for the IR 46 rice variety.



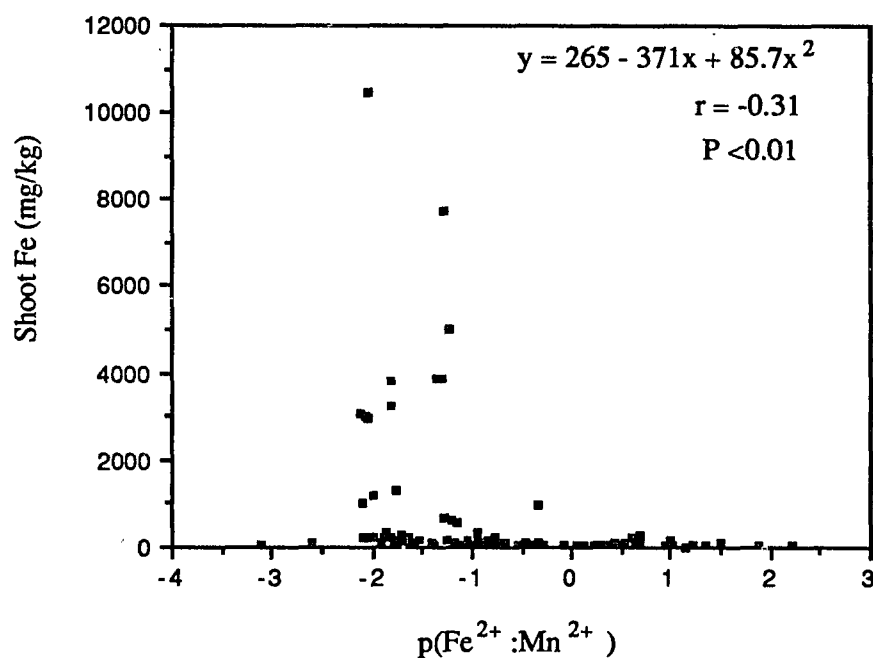


Figure 27. Relationship between Fe:Mn ratio in the shoot tissue and  $\text{Fe}^{2+}:\text{Mn}^{2+}$  activity ratio in soil solution for the IR 26 variety.

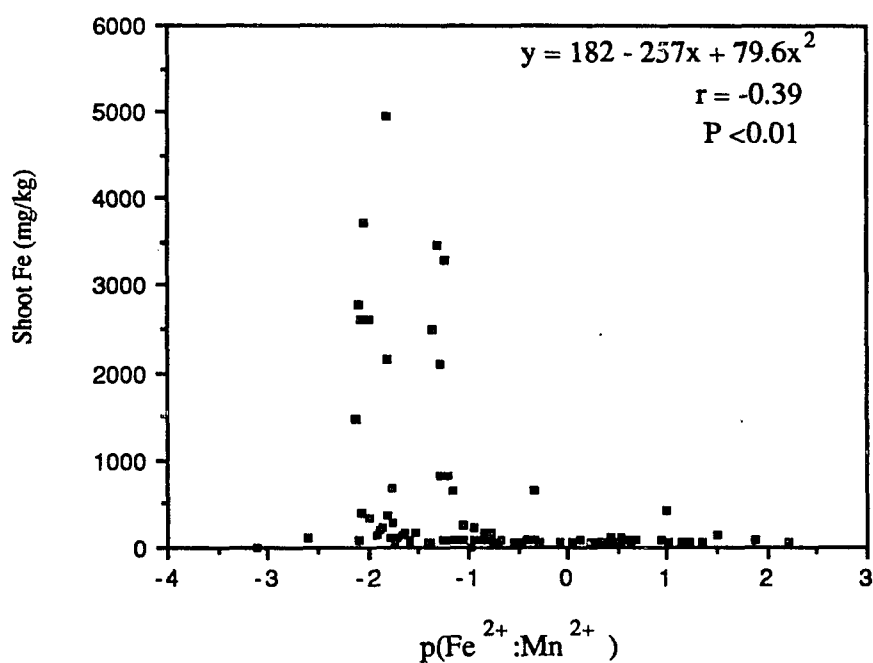


Figure 28. Relationship between Fe:Mn ratio in the shoot tissue and  $\text{Fe}^{2+}:\text{Mn}^{2+}$  activity ratio in soil solution for the IR 46 variety.

Mn interactions on rice growth has been studied by several authors (Tanaka and Navasero, 1966b; Nhung and Ponnampuruma, 1966; Ponnampuruma et al., 1973; Ponnampuruma and Soliva, 1982). These authors indicated that Mn counteracts the negative effects of excess iron physiologically.

#### Manganese availability to rice

The data indicated uptake of Mn by both rice varieties was positively related to pH and redox potential (Table 7). The pe+pH conditions ( $r=0.60$ ,  $P<0.01$ ), redox potential (Eh) levels ( $r=0.52$ ,  $P<0.01$ ), and pH ( $r=0.35$ ,  $P<0.01$ ) were positively correlated with uptake of Mn averaged over both rice varieties. Van Der Vorm and Van Diest (1979b) found that Mn uptake increased with increasing pH under aerobic conditions as was found in this study. Tanaka and Navasero (1966c) reported an increase in leaf Mn content due to increases in the pH of the culture solution. Jugsujinda and Patrick (1977) found the uptake of Mn was high at pH 5 under aerobic conditions, but then declined as soil pH was raised from 5 to 8, however, their pH range was essentially above the pH range of this study, so comparisons should not be made. Vand Der Vorm and Van Diest (1979a) reported that uptake of Mn was high under pH levels around 5-6 under anaerobic conditions of the sand media they studied. Jugsujinda and Patrick (1977) attributed high Mn uptake to high amounts of water-soluble Mn under more acid, reducing conditions which were observed by Gotoh and Patrick (1972). The reverse situation was demonstrated in this study since high Mn uptake was found in plants grown on suspensions under conditions where solution Mn levels were low. To examine this point, uptake of Mn by both varieties are plotted as a function of the negative log of  $Mn^{2+}:Fe^{2+}$  ratio or  $p(Mn^{2+}:Fe^{2+})$  in

Table 7. Mn uptake and Mn content in the shoot tissue (shoot Mn ) in the IR26 and IR46 rice varieties grown for three weeks on acid and non-acid sulfate soils under controlled redox and pH conditions.

pH-Eh	pe+pH	Uptake Mn ( mg/pot )		Shoot Mn ( mg kg <sup>-1</sup> )	
		IR26	IR46	IR26	IR46
3.5-50	4.34	252	318	338	301
3.5-250	5.34	433	628	393	299
3.5-500	6.34	1777	2900	1119	1247
4.5-50	7.72	287	323	293	208
4.5-250	8.72	3022	6295	1589	1704
4.5-500	9.72	4017	6051	2081	1994
5.5-50	11.94	441	609	374	357
5.5-250	12.94	3514	6010	2306	2326
5.5-500	13.94	4336	6541	2869	2870
LSD (0.05)		1858	1858	1047	1047

Figures 29 and 30. The high relationship was observed between Mn uptake and  $p(\text{Mn}^{2+}:\text{Fe}^{2+})$  in both IR 26 ( $r = 0.79$ ,  $P < 0.01$ ) and IR 46 ( $r = 0.78$ ,  $P < 0.01$ ) varieties. Higher levels of plant Mn were found at high  $\text{Mn}^{2+}:\text{Fe}^{2+}$  ratios, indicating that high levels of  $\text{Fe}^{2+}$  in the soil solution may exert a negative effect on the uptake of Mn. Tanaka and Navasero (1966b) found Mn uptake negatively related to Fe levels in culture solution. They noted that as Fe levels increased, Mn uptake decreased. In this study, the  $\text{Mn}^{2+}:\text{Fe}^{2+}$  activity ratios are low at low redox potentials where high solution Fe and relatively high Mn levels were supported. These high levels of Fe probably resulted in the suppression of Mn absorption by the rice plant. There was a difference between Mn concentration in the shoot tissue of the tolerant and the sensitive rice varieties.

Mn content in the shoot tissue of IR 46 ranged from as low as 57.6 to as high as 6530  $\text{mg kg}^{-1}$  with the average of 1260  $\text{mg kg}^{-1}$ . IR 26 contained shoot Mn in the range of 54.4 to 5710  $\text{mg kg}^{-1}$ . These Mn contents in shoot tissue are both above the deficiency level (20  $\text{mg kg}^{-1}$ ) at tillering stage and below the toxicity levels (7000  $\text{mg kg}^{-1}$ ) according to Yoshida (1981). Thus Mn deficiency and toxicity in these soils are unlikely in both varieties in this study.

#### CONCLUSIONS

The results showed that increases in both redox potential and pH negatively affected the levels of water-soluble and exchangeable Fe and positively affected levels of reducible Fe. Redox potential and pH had the same effect on water-soluble Mn levels as Fe. Exchangeable Mn levels were negatively related to pH, and reducible Mn levels positively

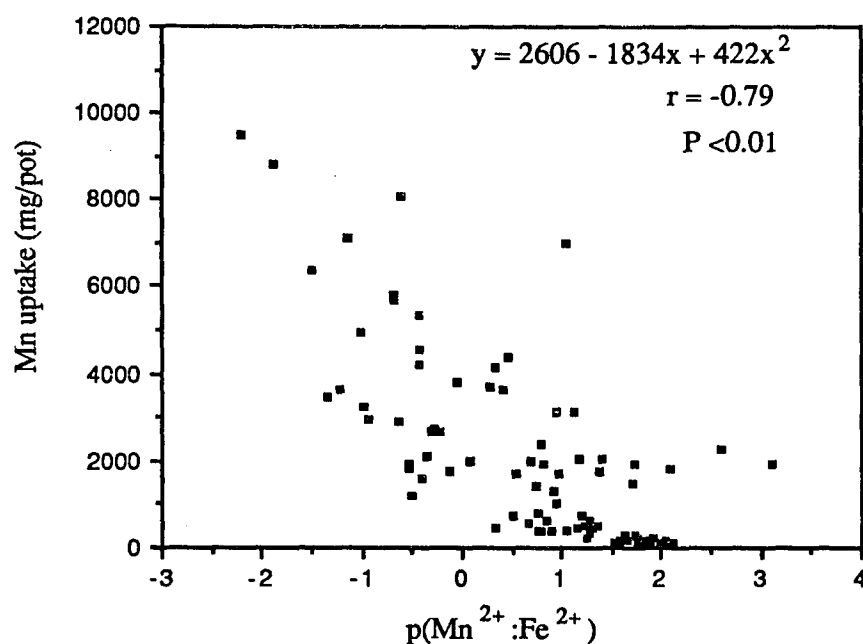


Figure 29. Relationship between Mn uptake and  $\text{Fe}^{2+}:\text{Mn}^{2+}$  activity ratio in the soil solution for the IR 26 variety.

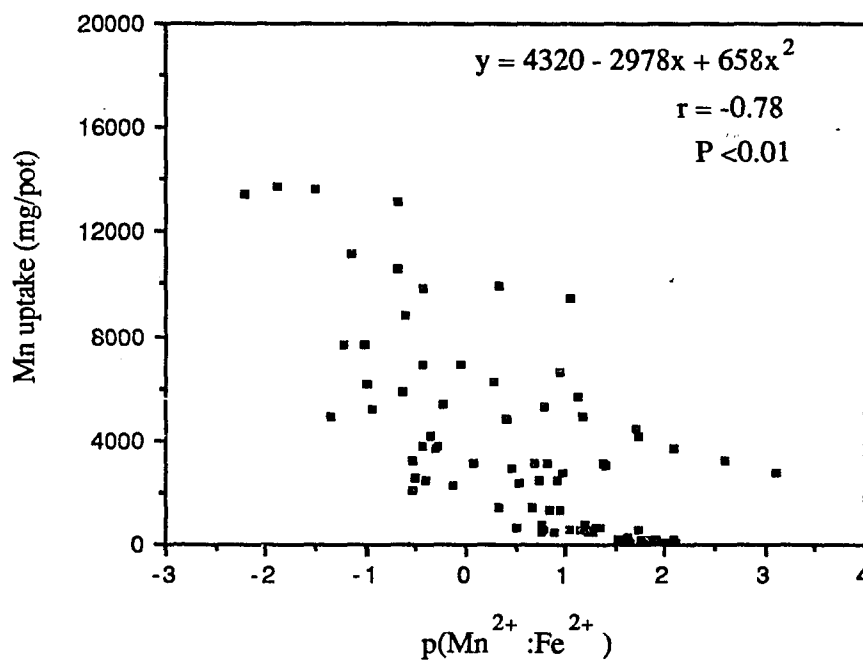


Figure 30. Relationship between Mn uptake and  $\text{Fe}^{2+}:\text{Mn}^{2+}$  activity ratio in the soil solution for the IR 46 variety.

related to pH, while Eh had less of an effect on water-soluble Mn form than it did for Fe.

Plots of  $\text{Fe}^{2+}$  activities as a function of pe+pH revealed that amorphous  $\text{Fe}(\text{OH})_3$  probably controlled solubility of  $\text{Fe}^{2+}$  at pe+pH levels of 12.95 and above while  $\text{FeOOH}$  (goethite) may influence the  $\text{Fe}^{2+}$  activity around pe+pH 11.95 and below.

Manganese activity was apparently undersaturated with respect to all of the Mn mineral species examined. The relationship between  $\text{E}'\text{-Mn}$  and  $\text{E-Mn}$  demonstrated that cation exchange reactions were probably regulating  $\text{Mn}^{2+}$  in the solution phase of these soil suspensions.

Fe uptake by rice and/or Fe content in the shoot tissue was negatively affected by increases in both redox potential and pH. The Fe uptake was strongly related to water-soluble Fe,  $\text{Fe}^{2+}$  activity, and  $\text{E}'\text{-Fe}$ . The critical level of the minimum  $\text{pFe}^{2+}$  and  $\text{E}'\text{-Fe}$  that triggers excessive uptake of Fe was probably defined at a  $\text{pFe}^{2+}$  of 3 and  $\text{E}'\text{-Fe}$  of 0.45. The average Fe content in the shoot tissue of the sensitive rice variety (IR 26) was higher than in the tolerant variety. Weight gain of both rice varieties were negatively related to Fe:Mn ratio in the shoot tissue. An Fe:Mn ratio in the shoot tissue of 4.5 and higher is probably harmful to rice growth.

Uptake of Mn and or the Mn content in shoot tissue was positively correlated with redox potential and pH. Plots of Mn uptake as a function of  $\text{Mn}^{2+}:\text{Fe}^{2+}$  activity ratio suggested that Fe may be antagonistic to uptake of Mn.

## REFERENCES

- Adams, F., and J. T. Wear. 1957. Manganese toxicity and soil acidity in relation to crinkle leaf of cotton. *Soil Sci. Soc. Am. Proc.* 21:305-308.
- Bacha, R. E., and Hossner. 1977. Characteristics of coatings formed on rice roots as affected by iron and manganese additions. *Soil Sci. Soc. Am. J.* 41:931-935.
- Barnes, I., and W. Back. 1964. Geochemistry of iron-rich ground water of Southern Maryland. *J. Geol.* 72:435-447.
- Benckiser, G., J. C. G. Ottow, S. Santiago, and I. Watanabe. 1982. Physiochemical characterization of iron-toxic soils in some Asian countries. *IRRI Res Paper Series* 85:1-11.
- Benckiser, G., S. Santiago, H. U. Neue, I. Watanabe, and J. C. G. Ottow. 1984. Effect of fertilization exudation, dehydrogenase activity, iron-reducing populations and  $Fe^{2+}$  formation in the rhizosphere of rice (*Oryza sativa* L.) in relation to iron toxicity. *Plant and Soil* 79:305-316.
- Bohn, H. L. 1970. Comparisons of measured and theoretical  $Mn^{2+}$  concentrations in soil suspensions. *Soil Sci. Soc. Am. Proc.* 34:195-197.
- Bromfield, S. M., and E. G. Williams. 1963. An estimation of the biological reduction method for estimating active iron in soils. *J. Soil Sci.* 14:346-359.
- Campbell, P. G. C., M. Bisson, R. Bangie, A. Tessner, J. Villeneuve. 1983. Speciation of aluminum in acidic freshwaters. *Anal. Chem.* 55:2246-2252.
- Chen, C. C., J. B. Dixon, and F. T. Turner. 1980. Iron coating on rice roots: morphology and models of development. *Soil Sci. Soc. Am. J.* 44:1113-1119.
- Collins, J. F., and S. W. Buol. 1970. Pattern of iron and manganese precipitation under specified Eh-pH conditions. *Soil Sci.* 110:157-162.
- DeLaune, R. D., C. N. Reddy, and W. H. Patrick, Jr. 1981. Effect of pH and redox potential on concentration of dissolved nutrients in an estuarine sediment. *J. Environ. Qual.* 10(3):276-279.
- Doyle, R. W. 1968. The origin of the ferrous ion-ferric oxide Nernst potential in environments containing dissolved ferrous ion. *Am. J. Sci.* 266:840-859.
- Gambrell, R. P., R. A. Khalid, M. G. Verloo, and W. H. Patrick, Jr. 1975. Transformations of heavy metals and plant nutrients in dredged

sediments as affected by oxidation-reduction potential and pH. Part II. Materials and methods, results and discussion. 315 p.

- Green, M. S., and J. R. Etherington. 1977. Oxidation of ferrous iron by rice (*Oryza sativa* L.) roots: a mechanism for waterlogging tolerance? J. Exp. Bot. 28:678-690.
- Gotoh, S., and W. H. Patrick, Jr. 1972. Transformation of manganese in a waterlogged soil as affected by redox potential and pH. Soil Sci. Soc. Am. Proc. 36:738-742.
- Gotoh, S., and W. H. Patrick, Jr. 1974. Transformation of waterlogged soil as influenced by redox potential and pH. Soil Sci. Soc. Am. Proc. 38:66-71.
- Howeler, R. H. 1973. Iron-induced organoging disease of rice in relation to physico-chemical changes in a flooded oxisol. Soil Sci. Soc. Am. Proc. 37:898-903.
- Ikehashi, K., and F. N. Ponnameruma. 1978. Varietal tolerance of rice for adverse soils. pp. 801-823. In F. N. Ponnameruma (ed.) Soils and rice. Int. Rice Res. Inst. Los Banos, Philippines.
- Jayawardena, S. D. G., T. Watabe, and K. Tanaka. 1977. Relation between root oxidizing power and resistant to iron toxicity in rice. Rep. Soc. Crop Sci. Breed, Kinki, Jpn. 22:38-47. Cited in Ikehashi, K., and F. N. Ponnameruma, 1978.
- Jugsujinda, A., and W. H. Patrick, Jr. 1977. Growth and nutrient uptake by rice in a flooded soil under controlled aerobic-anaerobic and pH conditions. Agron. J. 69:705-710.
- Langmuir, D., and D. O. Whittemore. 1971. Variations in the stability of precipitated ferric oxyhydroxides. In J. D. Hem (ed.) Nonequilibrium systems in natural water chemistry. Adv. Chem. Ser. 106:209-234.
- Lindsay, W. L. 1979. Chemical equilibria in soils. Wiley-Interscience, New York.
- Mandal, L. N., and R. R. Mitra. 1982. Transformation of iron and manganese in rice soils under different moisture regimes and organic matter applications. Plant and Soil 69:45-56.
- Maynard, D. E, and W. K. Fletcher. 1973. Comparison of total and partial extractable copper in anomalous and background peat samples. J. Geochem. Explor. 2:19-24.
- Mehra. O. P., and M. L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Miner. 7:317-327.



- Mendelssohn, I. A., and M. T., Postek. 1982. Elemental analysis of deposits on the roots of Spartina alterniflora Loisel. Amer. J. Bot. 69:904-912.
- Moore, P. A., Jr. 1987. Metal behavior in acid sulfate soils of Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Nhung, M.M., and F. N. Ponnampuruma. 1966. Effects of calcium carbonate, manganese dioxide, ferric hydroxide and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulfate soil. Soil Sci. 102:29-41.
- Ottow, J. C. G., G. Benckiser, and I. Watanabe. 1982. Iron toxicity of rice as a multiple nutritional stress. Trop. Agric. Res. Ser. (Japan) 15:167-179.
- Ottow, J. C. G., G. Benckiser, I. Watanabe, and S. Santiago. 1983. Multiple nutritional stress as the prerequisite for iron toxicity of wetland rice (Oryza sativa L.) Trop. Agric. (Trinidad) 60:102-106.
- Pasricha, N. S. and F. N. Ponnampuruma. 1976. Influence of salt and alkali on ionic equilibria in submerged soils. Soil Sci. Soc. Am. J. 40:374-376.
- Patrick, W. H., Jr. 1964. Extractable iron and phosphorus in a submerged soil at controlled redox potentials. Int. Congr. Soil Sci., Trans. 8th (Bucharest, Romania), IV, 605-609.
- Patrick, W. H., Jr., and R. E. Henderson. 1981a. A method for controlling redox potential in packed soil cores. Soil Sci. Soc. Am. J. 45:35-38.
- Patrick, W. H., Jr., and R. E. Henderson. 1981b. Reduction and reoxidation cycles of manganese and iron in flooded soil and in water solution. Soil Sci. Soc. Am. J. 45:855-859.
- Patrick, W. H., Jr., and F. T. Turner. 1968. Effect of redox potential on manganese transformations in waterlogged soil. Nature 220:476-478.
- Ponnampuruma, F. N. 1972. The chemistry of submerged soils. Adv. Agron. 24:29-96.
- Ponnampuruma, F. N. 1978. Electrochemical changes in submerged soils and the growth of rice. p. 421-441. In F. N. Ponnampuruma (ed.) Soils and rice. Int. Rice Res. Inst., Los Banos, Philippines.
- Ponnampuruma, F. N., T. Attanadana, and G. Beye. 1973. Amelioration of three acid sulfate soils for lowland rice. p. 391-405. In H. Dost (ed.) acid sulfate soils. Proc. Int. Symp. ILRI Pub. 18, Vol. II, Wageningen, The Netherlands.
- Ponnampuruma, F. N., R. Bradfield, and M. Peech. 1955. Physiological

- disease of rice attributable to iron toxicity. *Nature* (London) 175:265.
- Ponnamperuma, F. N., and T. A. Log, and E. M. Tianco. 1969. Redox equilibria in flooded soils: II. The manganese oxide systems. *Soil Sci.* 108:48-57.
- Ponnamperuma, F. N., and E. Martinez and T. Loy. 1966. Influence of redox potential and partial pressure of carbon dioxide on pH values and the suspension effect of flooded soils. *Soil Sci.* 101:421-431.
- Ponnamperuma, F. N., and J. L. Solivas. 1982. Field amelioration of acid sulfate soil for rice with manganese dioxide and lime p. 213-220. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils.* ILRI Pub. 31, Wageningen, The Netherlands.
- Ponnamperuma, F. N., E. M. Tianco, and T. A. Log. 1967. Redox equilibria in flooded soils: I. The iron hydroxide systems. *Soil Sci.* 103:374-382.
- Satawathonont, S. 1986. Redox, pH, and ion chemistry of acid sulfate rice soils in Thailand. Ph.D. Diss. Louisiana State Univ., Baton Rouge.
- Schwab, A. P., and W. L. Lindsay. 1983a. Effect of redox on the solubility and availability of iron. *Soil Sci. Soc. Am. J.* 47:201-205.
- Schwab, A. P., and W. L. Lindsay. 1983b. The effect of redox on the solubility and availability of manganese in a calcareous soil. *Soil Sci. Soc. Am. J.* 47:217-220.
- Sidhu, P. S., R. J. Gilkes, R. M. Cornell, A. M. Pasner, and J. P. Quirk. 1981. Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids. *Clays and Clay Miner.* 29:269-276.
- Sims, J. L., and W. H. Patrick, Jr. 1978. The distribution of micronutrient cations in soil under conditions of varying redox potential and pH. *Soil Sci. Soc. Am. J.*, Vol. 42: 258-262.
- Sposito, G. 1981. *The thermodynamics of soil solutions.* Clarendon Press, Oxford.
- Tadano, T., and S. Yoshida. 1978. Chemical Changes in submerged soils and their effect on rice growth. p. 399-420. In F.N. Ponnamperuma (ed.) *Soils and rice.* Int. Rice Res. Inst., Los Banos, Philippines.
- Takai, Y., and T. Kamura. 1966. The mechanism of reduction in waterlogged paddy soils. *Folia Microbiologica.* 11: 304-313.
- Tanaka, A., and S. A. Navasero. 1966a. Growth of the rice plant on acid sulfate soils. *Soil Sci. Plant Nutr.* 12:107-114.

- Tanaka, A., and S. A. Navasero. 1966b. Interaction between iron and manganese in the rice plant. *Soil Sci. and Plant Nutr.* 12:197-201.
- Tanaka, A., and S. A. Navasero. 1966c. Manganese content of the rice plant under water culture conditions. *Soil Sci. and Plant Nutr.* 12:67-72.
- Tanaka, A., and S. A. Navasero. 1966a. Growth of the rice plant on acid sulfate soils. *Soil Sci. Plant Nutr.* 12:107-114.
- Tanaka, A., R. Loe and S. A. Navasero. 1966. Some mechanisms involved in the development of iron toxicity symptoms in the rice plant. *Soil Sci. and Plant Nutr.* 12:158-164.
- Van Breemen, N. 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. *Agric. Res. Rep.* 848. PUDOC, Wageningen, The Netherlands.
- Van Breemen, N. 1969. The effect of ill-defined ferric oxides on redox characteristics of flooded soils. *Neth. J. Agr. Sci.* 17:256-260.
- Van Breemen, N. and F. R. Moormann. 1978. p.781-800. In F.N. Ponnampetuma (ed.) *Soils and rice*. Int. Rice Res. Inst., Los Banos, Philippines.
- Van Der Vorm, P. D. J., and A. Van Diest. 1979a. Aspects of the Fe-and Mn nutrition of rice plants. I. Iron-and manganese uptake by rice plants, grown under aerobic and anaerobic conditions. *Plant and Soil* 51:233-246.
- Van Der Vorm, P. D. J., and A. Van Diest. 1979b. Aspects of the Fe and Mn nutrition of rice plants. II. Iron and manganese uptake by rice plants, grown on aerobic water cultures. *Plant and Soil* 52:19-29.
- Virmani, S. S. 1977. Varietal tolerance of rice to iron toxicity in Liberia. *Int. Rice Res. News* 1. 2(1):4-5.
- Williams, B. G. and W. H. Patrick, Jr. 1971. Effect of Eh and pH on the dissolution of strengite. *Nature Phys. Sci.* 234:16-17.
- Yoshida, S. 1981. Fundamental of rice crop science. Int. Rice Res. Inst., Los Banos, Philippines. 269 p.

## Chapter Seven

### Aluminum Availability to Rice in Acid and Non-Acid Sulfate Soils

#### Under Controlled pH and Redox Potential Conditions

Aluminum Availability to Rice in Acid and Non-Acid Sulfate Soils Under  
Controlled pH and Redox Potential Conditions.

ABSTRACT

Aluminum availability to rice was investigated in laboratory microcosms using soil suspensions of acid sulfate (Sulfic Tropaequet) and non-acid sulfate (Typic Tropaequet) soils. Some microcosms were incubated at selected controlled redox potential conditions (500, 250, 50, and -150 mV). Others were incubated at various combinations of controlled pH and redox potential levels (3.5, 4.5, and 5.5 and redox potential levels  $\geq$  500, 250, and 50 mV respectively). Seedlings of rice varieties tolerant (IR46) and sensitive (IR26) to acid sulfate soils were planted in these soils suspensions. Three weeks after transplanting, soil solution and plant tissue samples were processed and analysed. The activity of  $Al^{3+}$  and other metals was determined by the computer program (GEOCHEM).

Results revealed that  $Al^{3+}$  activity in the soil solution was the only Al parameter negatively associated with pH in both soil types and over all of the different controlled conditions. Water-soluble Al and percent Al saturation of the CEC was negatively related to pH in both soil types under controlled pH and redox conditions, but was negatively related to pH only in acid sulfate soils under controlled redox conditions.

Aluminum uptake in both rice varieties correlated best with  $Al^{3+}$  activity in soil solution rather than with water-soluble Al or percent

Al saturation of the CEC in both soil types under controlled redox conditions.

Under controlled pH and redox conditions, only Al uptake in the IR26 rice variety grown in acid sulfate soils significantly correlated with water-soluble Al and percent Al saturation of the CEC. No statistical correlation between Al uptake and soil Al parameters for IR 46 was observed in acid and non-acid sulfate soils. Uptake of Ca, K, Mg, and Mn negatively related to  $Al^{3+}$  activity for both varieties in all soil types under controlled pH and redox conditions.

Shoot and root weight gain were significantly decreased with an increase of  $Al^{3+}$  activity in soil solution for all plants and soils under controlled pH and redox conditions. Generally, roots were more affected than shoots and the IR 26 shoots were more affected than the IR 46 shoots. No significant correlation among plant tissue and soil Al parameters was observed under controlled redox potentials where pH was not controlled.

Results indicated that the two solid phase species, jurbanite ( $Al(SO_4)(OH) \cdot 3H_2O$ ) and amorphous  $Al(OH)_3$ , probably controlled Al solubility at low and high pH conditions respectively. Aluminum may precipitate phosphate by the formation of variscite ( $AlPO_4 \cdot 2H_2O$ ) in all soil types and over all controlled conditions.

#### INTRODUCTION

Aluminum toxicity has been described as one of the several deleterious factors affecting plant growth in acid sulfate soils. Studies in several plants indicated that the symptom of Al injury appear first on the roots (Cate and Sukhai, 1964; Lafever et al., 1977) and

later on the plant tops (Tanaka and Navasero, 1966a; Reid et al., 1969; Slootmaker and Arzadun, 1969). Cutrim et al. (1981) reported that roots and stems of sensitive rice seedlings were stunted resulting in a decrease in dry weight after 21 days of rice growth in a culture solution of  $60 \text{ mg L}^{-1}$  soluble Al. Besides the negative effects on vegetative parts, Al has also been reported to interfere with uptake of several macro and microelements such as P, K, Ca, Mg, Mn, Zn, and B in many plants, including rice (Tanaka and Navasero, 1966 a; Awad et. al., 1976; Clark, 1977; Foy et. al., 1978; Fageria and Carvalho, 1982; Fageria, 1985). The mechanism of the Al-P interaction has been attributed to either the precipitation of insoluble aluminum phosphate in the soil outside the roots (Rorison, 1972; Tanaka and Navasero, 1966a), or in the roots (De Kock and Mitchell, 1957; Hackett, 1962; Tanaka and Navasero, 1966a; McCormick and Borden, 1974).

Cate and Sukhai (1964) observed the critical toxic level of Al for rice plants was as low as  $25 \text{ mg L}^{-1}$  where no nutrient cations were present in the culture media. However, Tanaka and Navasero (1966a) reported the critical level was about  $25 \text{ mg L}^{-1}$  of Al in culture solution where the rice plants received a normal supply of other nutrients. They also stated that if the plant was suffering from phosphorus deficiency, even  $15 \text{ mg L}^{-1}$  of Al would cause toxicity symptoms. Fageria and Carvalho (1982) observed the critical toxic level of Al in the tops of 21 day-old rice plants varied from 100 to  $417 \text{ mg kg}^{-1}$ , depending on the cultivars. The critical toxic level of Al has been reported to be  $300 \text{ mg kg}^{-1}$  in rice shoots at the tillering stage (Tanaka and Yoshida, 1970).

Tanaka and Navasero (1966b) reported rice plants suffer from Al toxicity under upland conditions, but not under flooded (lowland) conditions of acid sulfate soils. Jugsujinda et al. (1978) observed rice plants suffer from Al toxicity after plants had been grown in dry soil for 2 to 4 months in acid sulfate soil areas in Thailand. They noted that Al toxicity is unlikely in wetland rice because Al normally disappears soon after flooding, even on very acid soils. Under flooded conditions, the pH presumably increases to 5 and above which reduces soluble Al levels and subsequent toxicity (Tanaka and Navasero, 1966a). Lindsay et al. (1959) noted that the concentration of soluble Al in acid soils is generally less than 1 ppm at a pH above 5.5 indicating that Al decreases rapidly with increasing in pH.

Chemical form of Al have received much attention from several authors regarding their differential effects on plants. Pavan et al. (1982) reported that growth reduction of coffee seedlings correlated best with the  $Al^{3+}$  activity value rather than with percent Al saturation or total water-soluble Al. Wagatsuma and Ezoe (1985) noted that hydroxy-Al polymer ions may be more toxic to plant roots than monomer-Al ions. Alva et al. (1986) used the activity values of monomeric Al species successfully in expressing critical levels for Al toxicity over a wide range of nutrient solution composition.

Knowledge of the mechanisms controlling solubility of dissolved Al has increased through a number of published papers. Lindsay et al. (1959) noted that variscite, which probably coexists with gibbsite, controls the solubility of  $Al^{3+}$  in acid soils after the addition of phosphate. Hsu (1964) concluded that phosphate is not fixed as variscite at pH 7 in a relatively dilute phosphate solution, but is



adsorbed on amorphous  $\text{Al}(\text{OH})_3$  and iron oxides or hydroxides in soils. Lee and Pritchard (1984) found that at high pH (pH 6), the speciation of Al is controlled by the formation of solid Al phosphate and Al hydroxide. Van Breemen (1973) reported that the upper limit of dissolved Al in acid sulfate soils is regulated by a basic aluminum sulfate. Weaver and Bloom (1977) suggested that gibbsite and kaolinite may be the ultimate stable solid phases. Dixon (1977) reported the presence of microcrystalline gibbsite and kaolinite in many soils indicating that these two solid phases may regulate Al solubility. Nordstrom (1982) suggested that gibbsite and kaolinite are not stable minerals in acid sulfate waters. He stated that the likely stable solid phases could be alunogen,  $\text{Al}_2(\text{SO}_4) \cdot 17\text{H}_2\text{O}$ , alunite,  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ , jurbanite,  $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$ , and basaluminte,  $\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$ .

The objective of this study was to determine the availability of Al and its effect on growth and nutrient uptake of two rice varieties. The solid phases regulating Al solubility in acid and non-acid sulfate soils under various controlled redox potential conditions and under various combinations of controlled pH and redox potential conditions were also considered.

#### MATERIALS AND METHODS

This chapter dealt with two types of controlled physicochemical conditions of acid and non-acid sulfate soils as listed below:

- (a) controlled redox potential conditions (500, 250, 50, and -150 mV), and,

(b) controlled pH (3.5, 4.5, and 5.5) and redox potential (500, 250, and 50 mV) conditions. Materials and methods are described in detail in Chapters 4 and 5.

## RESULTS AND DISCUSSION

### Aluminum solubility

In order to determine which solid phase species controls solubility of  $\text{Al}^{3+}$  in the solution phase of the soil suspensions under both controlled pH and redox potential conditions and under controlled redox potential conditions only,  $\text{Al}^{3+}$  activity data were plotted in terms of  $\text{pAl} + 3\text{pOH}$  as a function of  $2\text{pH} + \text{pSO}_4$  as shown in Figures 1 and 2. These plots were obtained as described by Van Breemen (1973), Nordstrom (1982), and Moore (1987). Points that lie above the lines or to the right indicate undersaturation with respect to the lines of theoretical solubility of the solid phase species of Al, and points located below or to the left of the lines indicate supersaturation. Values of  $\text{pAl} + 3\text{pOH}$  distributed near and below the line of equilibrium with jurbanite ( $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$ ) and above the theoretical solubility line of basic aluminum sulfate ( $\text{AlOHSO}_4$ ) indicated that jurbanite probably controls Al solubility under a wide range of low pH values ( $\text{pH} < 5.5$ ). At pH 5.5 or above, and within the low range of sulfate activity ( $\sim 10^{-3.5}\text{M}$ ), amorphous  $\text{Al}(\text{OH})_3$  may be the solid phase regulating Al solubility. Moore (1987) reported that jurbanite regulated Al solubility at low to medium pH values (3.5 to 6.0) and amorphous  $\text{Al}(\text{OH})_3$  seemed to limit Al solubility under high pH and low sulfate activity in acid sulfate rice fields of Thailand.

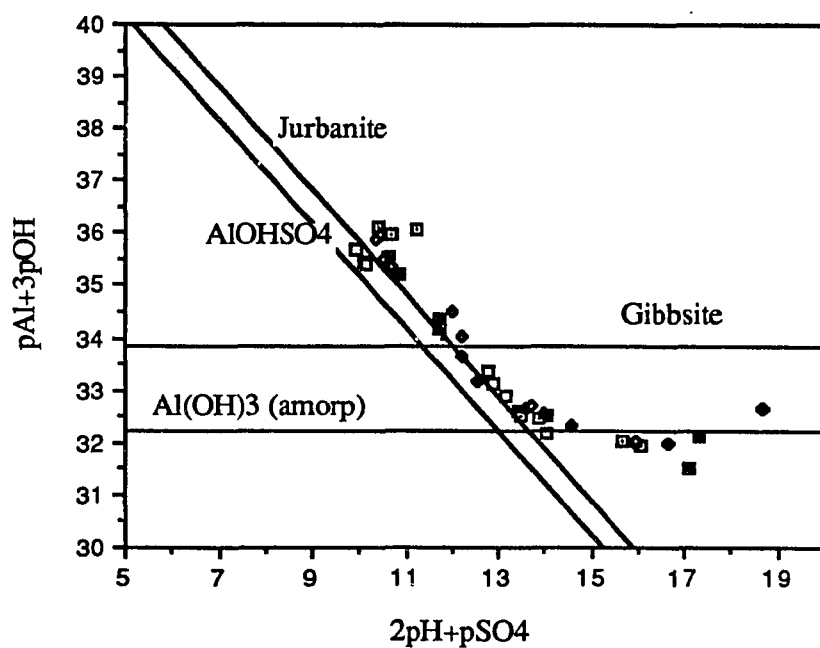


Figure 1. Relationship between  $Al^{3+}$  activity and the theoretical solubility of Al solid species in acid and non-acid sulfate soils over all controlled redox conditions.

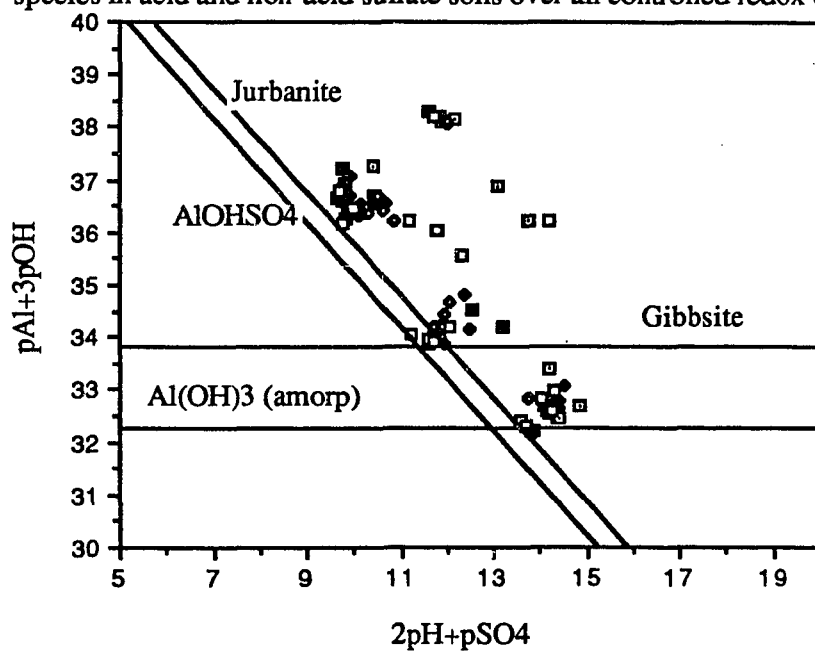


Figure 2. Relationship between  $Al^{3+}$  activity and the theoretical solubility of Al solid species in acid and non-acid sulfate soils over all controlled pH and redox potential .

Gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) did not appear to control Al solubility under controlled redox potential conditions. Under both controlled pH and redox potential conditions, some data points clustered near the stability line of gibbsite under the intermediate range of  $\text{pAl}+3\text{pOH}$  values, but these data points still indicate undersaturation with respect to gibbsite. Thus, gibbsite does not appear to regulate Al solubility in these acid and non-acid sulfate soils under both controlled pH and redox potential conditions. Misra (1974) reported a soil system where the  $\text{pAl}+3\text{pOH}$  values corresponded to that of gibbsite though the gibbsite may not have been present in the soil. Van Breemen (1976) noted that the strong dependence of  $\text{pAl}(\text{OH})_3$  on pH clearly provided evidence that aluminum oxide such as gibbsite did not influence the activity of dissolved  $\text{Al}^{3+}$ . Van Breemen (1973) reported that the upper limits of dissolved Al in acid sulfate soils and in acid mine waters were regulated by a basic aluminum sulfate with the stoichiometric composition  $\text{AlOHSO}_4$  ( $\text{pK} = 17.23 \pm 0.16$ ). Nordstrom (1982) provided information that supported a solubility control like that proposed by van Breemen (1973). Nordstrom proposed that jurbanite regulated an upper solubility limit and alunite regulated a lower solubility limit which is rarely reached because of slow nucleation and precipitation kinetics. He also stated that the mystery mineral of van Breemen which controlled dissolved aluminum in acid sulfate soils and acid mine waters corresponded well with the composition and solubility of jurbanite. The log IAP values of jurbanite have a mean value of  $-17.8(\pm 0.1)$  which is close to the value of  $-17.23(\pm 0.16)$  reported by van Breemen (1973). Results observed here suggest that the two solid phase species, jurbanite and amorphous  $\text{Al}(\text{OH})_3$ , are the stable solid phases

that control dissolved  $\text{Al}^{3+}$  in suspensions of the acid and non-acid sulfate soils examined in this study. This agrees with findings of others (Van Breemen, 1973; Nordstrom, 1982; Moore, 1987).

#### Chemistry of selected Al fractions

Under both controlled pH and redox potential conditions, total water-soluble Al was negatively related to pH. Redox potential did not significantly influence the distribution of total water-soluble Al. Regression analysis indicated that water-soluble Al increased with decreasing pH in acid sulfate soils ( $r = -0.42$ ,  $P < 0.01$ ,  $n=54$ ) and in non-acid sulfate soils ( $r = -0.67$ ,  $P < 0.01$ ,  $n=36$ ). The total water-soluble Al and pH of over all soils in this study are plotted in Figure 3. Aluminum activity and percent Al saturation of the CEC (exchangeable Al/ exchangeable (Ca+K+Mg+Fe+Mn+Al)\*100) were also negatively related to pH. The relationship between  $\text{Al}^{3+}$  activity and pH are similar in acid ( $r = -0.64$ ,  $P < 0.01$ ,  $n=54$ ) and non-acid sulfate soils ( $r = -0.59$ ,  $P < 0.01$ ,  $n=36$ ). Aluminum activity in all soils is plotted as a function of pH as shown in Figure 4. Percent Al saturation of the CEC increased with decreasing pH in acid ( $r = -0.74$ ,  $P < 0.01$ ,  $n=54$ ) and in non-acid sulfate soils ( $r = -0.66$ ,  $P < 0.01$ ,  $n=36$ ). Percent aluminum saturation of the CEC for all soils is plotted as a function of pH in Figure 5. For all soils, the water-soluble Al concentration ranged from non-detectable (in several soils) to  $56.3 \text{ mg kg}^{-1}$  (in Rangsit very acid soil). Aluminum activity ranged from  $10^{-10}$  to  $10^{-5}$  M in all soils. Percent Al saturation on the CEC ranged from 0.3 to 22 in acid sulfate soils and from 0.1 to 22 in non-acid sulfate soils.

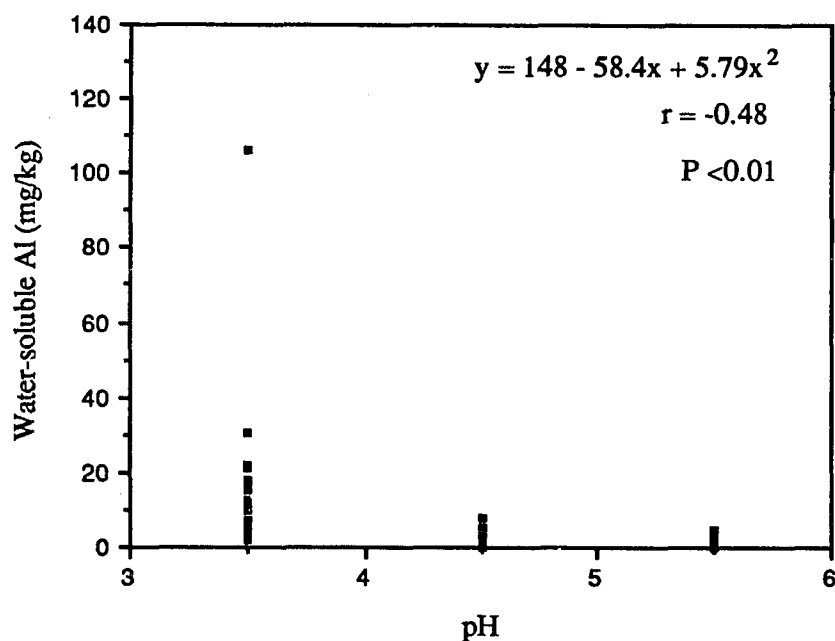


Figure 3 . Relationship between water-soluble Al and pH in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.

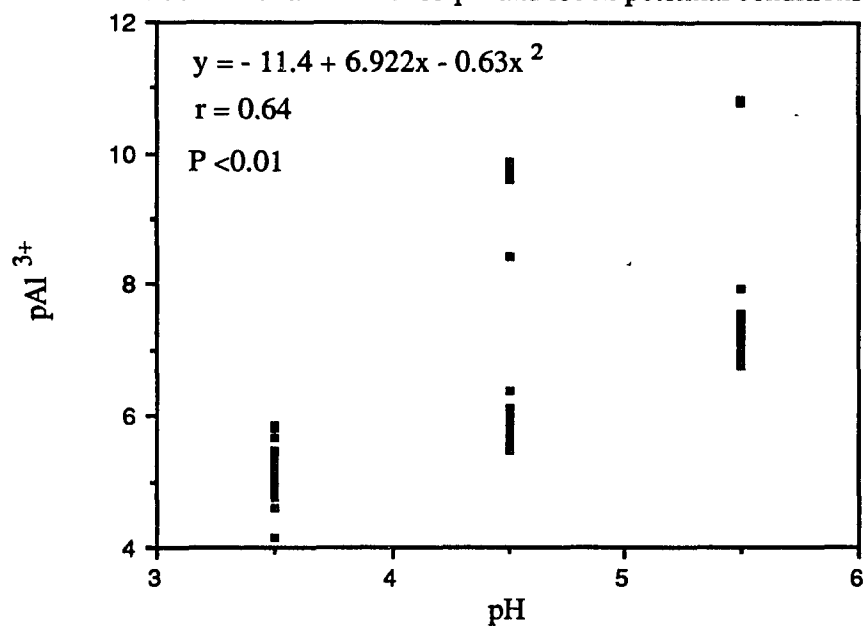


Figure 4. Relationship between  $Al^{3+}$  activity and pH in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.

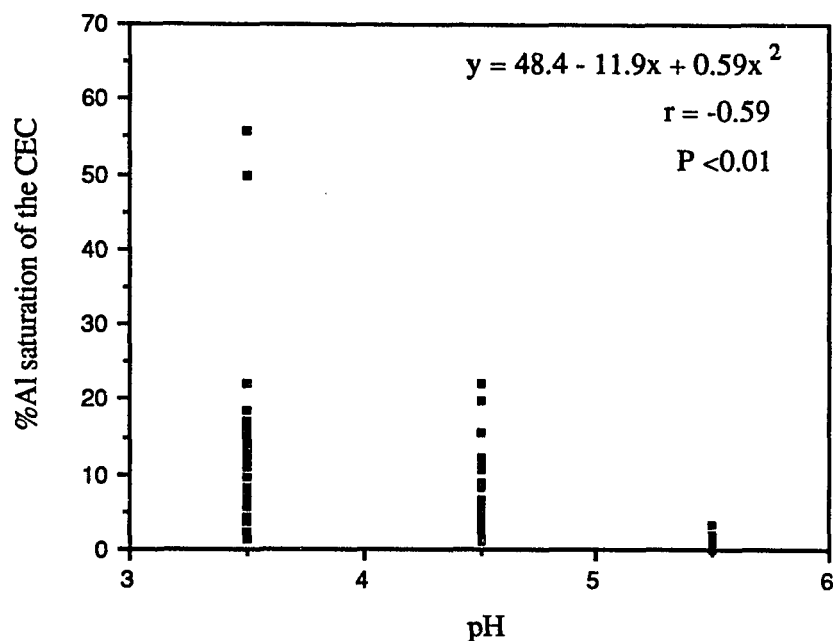


Figure 5. Relationship between percent Al saturation of the CEC and pH in acid and non-acid sulfate soils over all controlled pH and redox potential conditions.

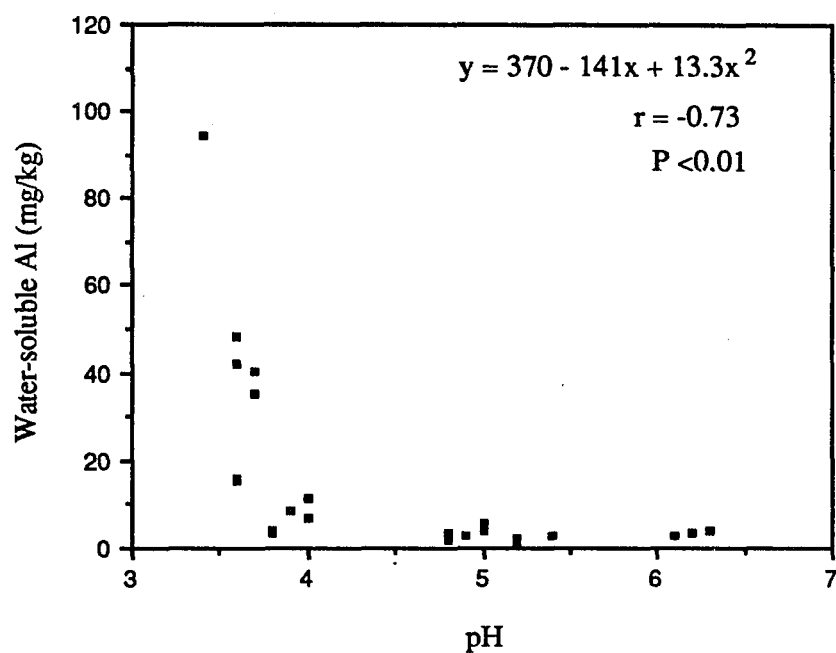


Figure 6. Relationship of water-soluble Al and pH in acid sulfate soils over all controlled redox conditions.

Under controlled redox potential only conditions, the total water-soluble Al ( $r = -0.58$ ,  $P < 0.01$ ,  $n = 24$ ), the negative log of  $\text{Al}^{3+}$  activity in the soil solution ( $r = -0.91$ ,  $P < 0.01$ ,  $n = 24$ ), and percent Al saturation of the CEC ( $r = -0.60$ ,  $P < 0.01$ ,  $n = 24$ ) were significantly correlated with pH in acid sulfate soils as illustrated in Figures 6, 7, and 8. However, in non-acid sulfate soils, only  $\text{Al}^{3+}$  activity in the soil solution was significantly correlated with pH ( $r = -0.96$ ,  $P < 0.01$ ,  $n = 16$ ). The negative log of  $\text{Al}^{3+}$  activity and pH for non-acid sulfate soils are plotted in Figure 9.

Under controlled redox potential conditions, the total water-soluble Al ranged from 1.8 to 94.6  $\text{mg kg}^{-1}$  and from 0.3 to 34.2  $\text{mg kg}^{-1}$  in acid and non-acid sulfate soils respectively. Acid sulfate soils contained  $\text{Al}^{3+}$  activities in the range of  $10^{-8.9}$  to  $10^{-3.9}$  M whereas non-acid sulfate soils had  $\text{Al}^{3+}$  activities in the range of  $10^{-13.8}$  to  $10^{-5.4}$  M. Percent Al saturation of the CEC ranged from 1.76 to 72.4 and from 0.24 to 26.6 in acid and non-acid sulfate soils respectively. It is believed that total water-soluble Al and % Al saturation of the CEC were not significantly correlated with pH in non-acid sulfate soils because of the moderately high pH ranges supporting less Al in the soil solution and on the CEC. Evans and Kamprath (1970) noted that the concentration of water-soluble Al was related to the exchangeable Al saturation. The soluble Al was quite low until the exchangeable Al exceeded 60% at which point a marked increase in soluble Al occurred. In this study, a sharp increase of water-soluble Al was observed when percent Al saturation of the CEC increased beyond 50 in acid sulfate soils. Plots of the negative log of  $\text{Al}^{3+}$  activity as a function of percent Al saturation of the CEC (Figures 10 and 11)



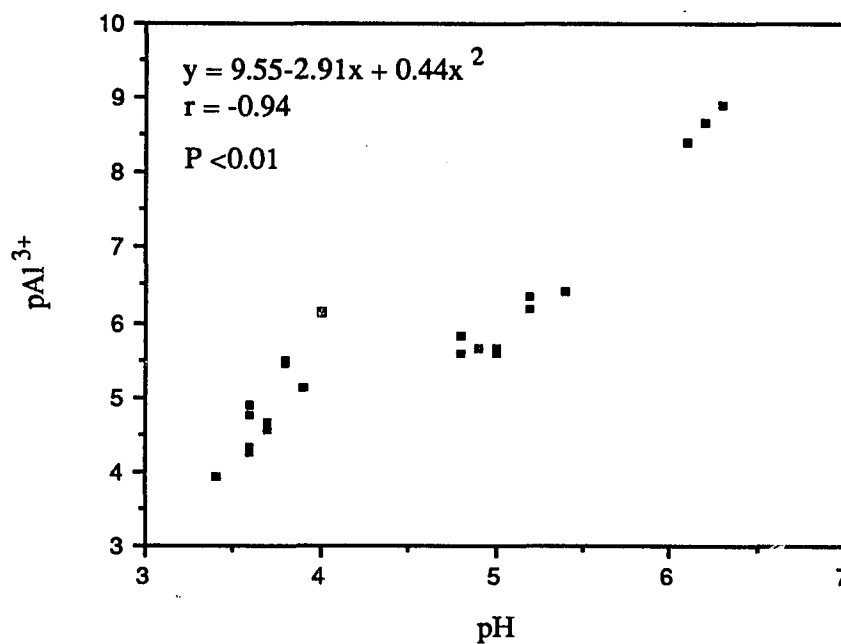


Figure 7. Relationship between the negative log of  $Al^{3+}$  activity and pH in acid sulfate soils over all controlled redox conditions.

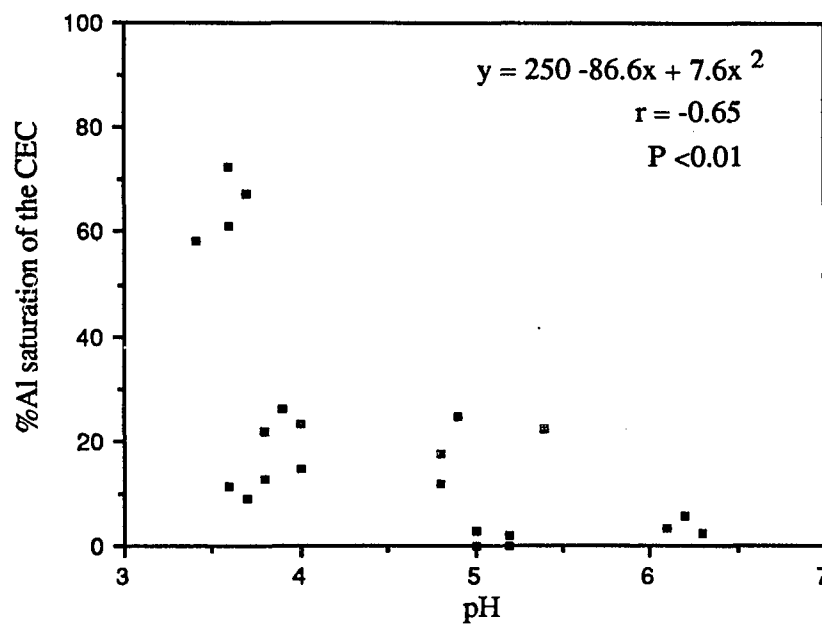


Figure 8. Relationship between percent Al saturation of the CEC and pH in acid sulfate soils over all controlled redox conditions.

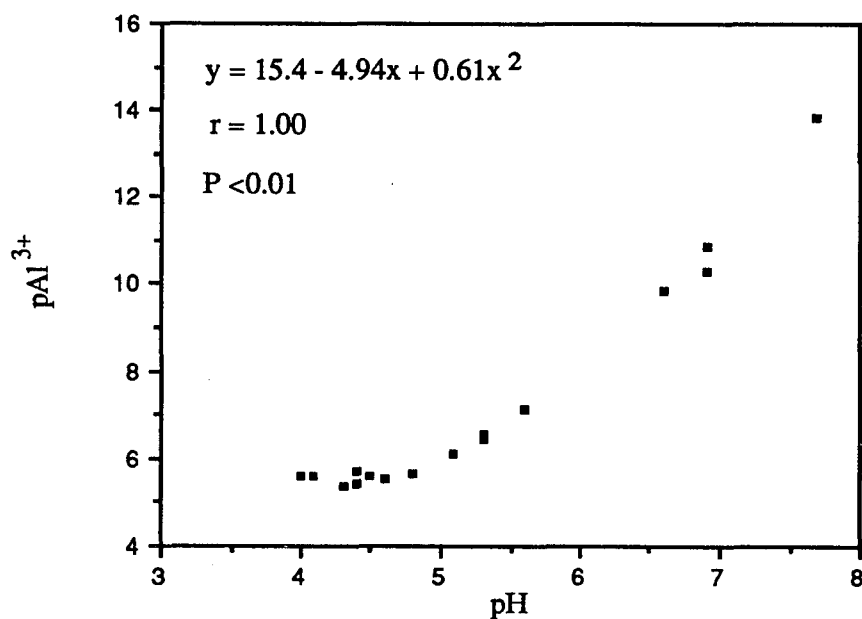


Figure 9. Relationship between the negative log of  $Al^{3+}$  activity and pH in non-acid sulfate soils overall controlled redox conditions.

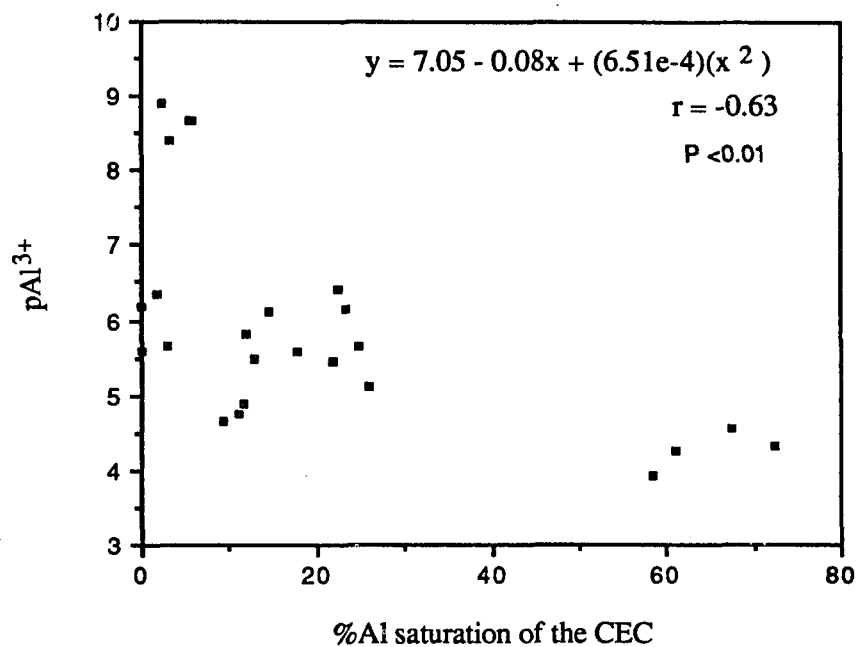


Figure 10. Relationship between the negative log of  $Al^{3+}$  activity and percent Al saturation of the CEC in acid sulfate soils over all controlled redox.

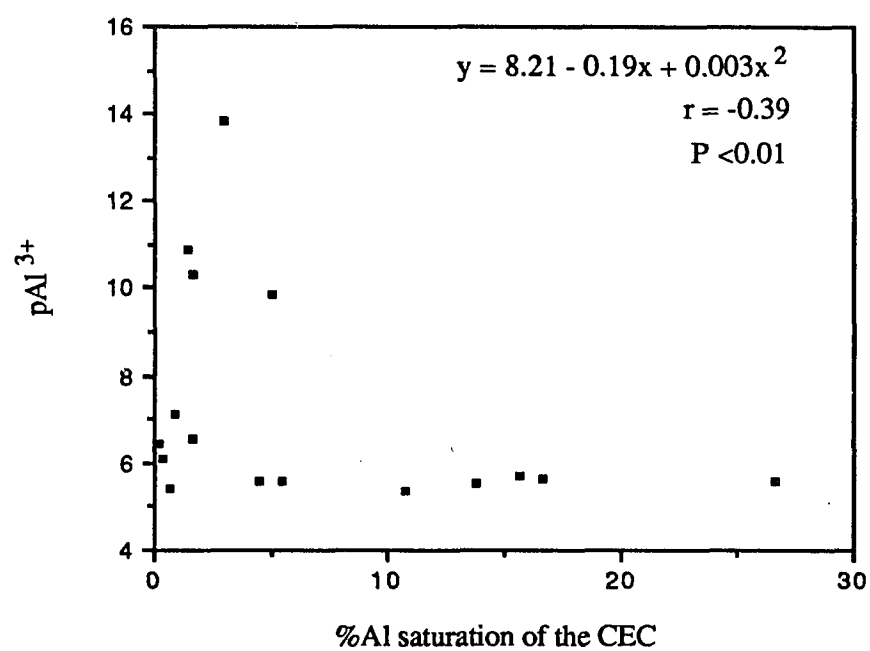


Figure 11. Relationship between  $Al^{3+}$  activity and percent Al saturation of the CEC in non-acid sulfate soils over all controlled redox conditions.

demonstrated that soluble Al positively related to percent Al saturation of the CEC, but was statistically significant only in acid sulfate soils due to the wide range of percent Al saturation of the CEC. These data suggested that  $Al^{3+}$  activity may be in near equilibrium with percent Al saturation of the CEC only in soils of low pH ranges such as in acid sulfate soils studied here. This corresponds well with the findings of Moore (1987).

Based on the experimental data, the difference between acid and non-acid sulfate soils regarding Al appears mainly as percent Al saturation of the CEC. The difference of percent Al saturation of the CEC between acid (a range of 0.18 to 22.2 with an extra high values of 49.8 and 59.9) and non-acid sulfate soils (a range of 0.13 to 22.3) under controlled pH and redox potential conditions is relatively narrower than that between acid (a range of 0.09 to 67.4) and non-acid sulfate soils (a range of 0.24 to 26.6) under only controlled redox potential conditions. This apparently was due to the unadjusted pH values of some acid sulfate soils ( a range of 3.4 to 6.3) being lower than that of non-acid sulfate soils (a range of 4.4 to 7.7) under controlled redox potential. The data for percent Al saturation of the CEC are shown in Tables 1 and 2. At a pH of 5 or above, the disappearance of a large portion of Al from both the solution and the CEC complex is thought to be due to both Al adsorption and precipitation. The relationship between water-soluble Al and percent Al saturation of the CEC was highly related in acid sulfate soils under controlled pH and redox and under controlled redox conditions only. These relationships are plotted in Figures 12 and 13. Kamprath and Fox (1971) stated that the concentration of Al in the soil solution is

Table 1. Percent Al saturation of the CEC in acid and non-acid sulfate soils under controlled pH and redox potential conditions.

pH	Eh	Non-acid		Acid sulfate soils		
		Rb	Bk	Ma	Rs	Rsa
-----% Al saturation of the CEC-----						
3.5	50	8.91*	3.05	7.30	12.15	9.34
	250	18.64	2.84	16.57	12.93	11.11
	500	16.86	5.85	14.55	15.66	52.85
4.5	50	3.97	1.75	5.14	5.70	6.12
	250	3.02	1.29	3.16	4.35	11.14
	500	9.49	2.56	11.06	10.60	21.08
5.5	50	1.71	0.41	0.69	1.18	1.65
	250	0.19	0.16	0.24	0.47	1.17
	500	0.42	0.13	0.53	0.33	0.31

\*Average of 2 replications.

Table 2. Percent Al saturation of the CEC in acid and non-acid sulfate soils under controlled redox potential conditions.

Eh(mV)	Non-acid				Acid sulfate soils					
	Rb		Bk		Ma		Rs		Rsa	
	pH	Alsat.*	pH	Alsat.	pH	Alsat.	pH	Alsat.	pH	Alsat.
-150	7.2	4.32**	6.9	1.58	6.2	2.82	6.2	5.59	5.2	23.14
50	5.4	1.36	5.2	0.27	5.2	0.12	5.2	2.49	4.8	13.81
250	4.7	15.69	4.3	4.06	4.1	17.44	3.8	23.19	3.6	70.77
500	4.5	19.32	4.5	5.16	3.7	11.97	3.6	10.51	3.5	59.38

\*Alsat.= Percent Al saturation of the CEC.

\*\*Average of 2 replications.

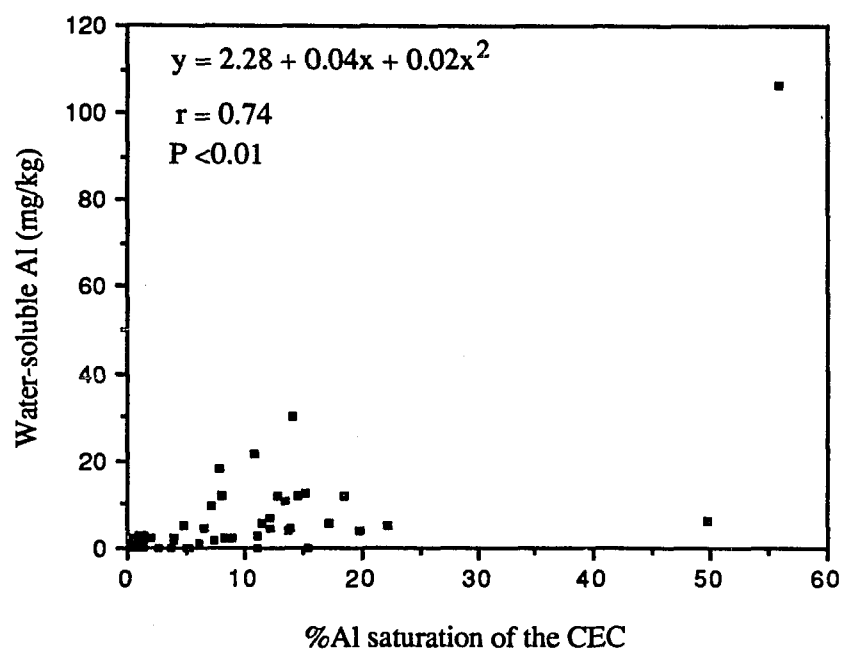


Figure 12. Relationship between water-soluble Al and percent Al saturation of the CEC in acid sulfate soils over all controlled pH and redox conditions.

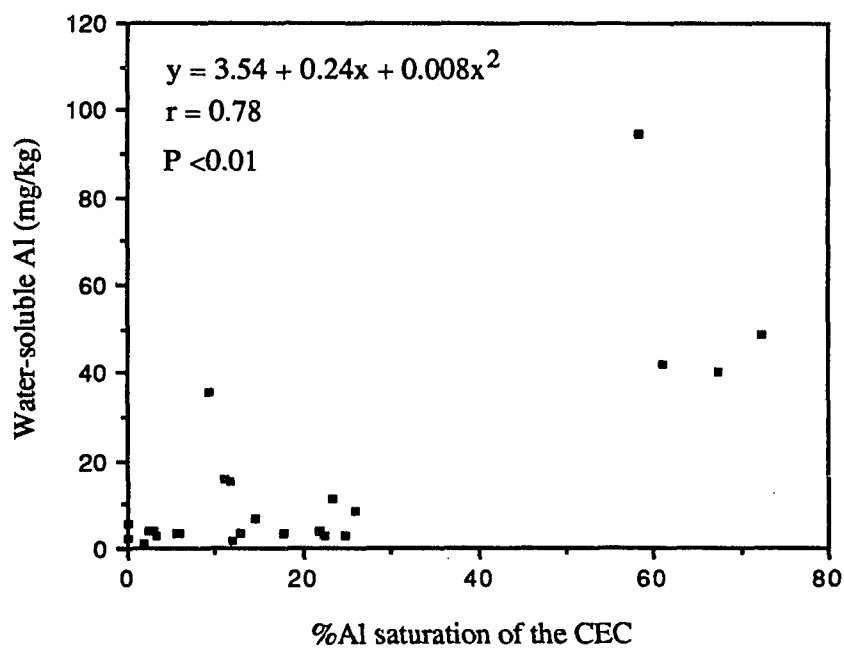


Figure 13. Relationship between water-soluble Al and percent Al saturation of the CEC in acid sulfate soils over all controlled redox conditions.

generally related to the Al saturation of effective cation exchange capacity, which agrees well with the results of this study.

#### Aluminum availability and rice growth

Uptake of Al in both rice varieties is plotted as a function of the negative log of  $\text{Al}^{3+}$  activity in the soil solution for acid and non-acid sulfate soils over all controlled redox potential conditions in Figure 14. These data indicate Al uptake correlated best with activity of  $\text{Al}^{3+}$  ( $r = 0.71$ ,  $p < 0.01$ ,  $n = 80$ ) rather than with water-soluble Al and percent Al saturation of the CEC ( $r = 0.36$ ,  $p < 0.01$ , and  $r = 0.43$ ,  $p < 0.01$ ,  $n = 80$  respectively). Al uptake is plotted as a function of Al content in the shoot tissue in Figure 15. This plot demonstrates a significant ( $r = 0.89$ ,  $p < 0.01$ ,  $n = 80$ ) curvilinear relationship between Al uptake and Al content in shoot tissue as a sharp increase in Al content in shoot tissue was observed at high level of Al uptake ( $> 300\text{mg/pot}$ ). This is thought to be due to the adverse effects of high Al uptake resulting in decreasing rice growth which in turn increased Al content in shoot tissue dramatically.

Pavan et al. (1982) reported that leaf Al of the coffee plant was significantly correlated with  $\text{Al}^{3+}$  activity in soil solution, indicating that leaf analysis may be used as a diagnostic tool for assessing Al stress. However, for the rice plant, Tanaka and Navasero (1966a) stated that the Al content in the shoot tissue cannot be easily assessed for the critical level of Al toxicity, and they suggested that Al toxicity often develops if the Al content is higher than 300 ppm. A significant correlation ( $r = 0.55$ ,  $p < 0.01$ ,  $n = 48$ ) between Al uptake and percent Al saturation of the CEC in the acid sulfate soils is demonstrated in

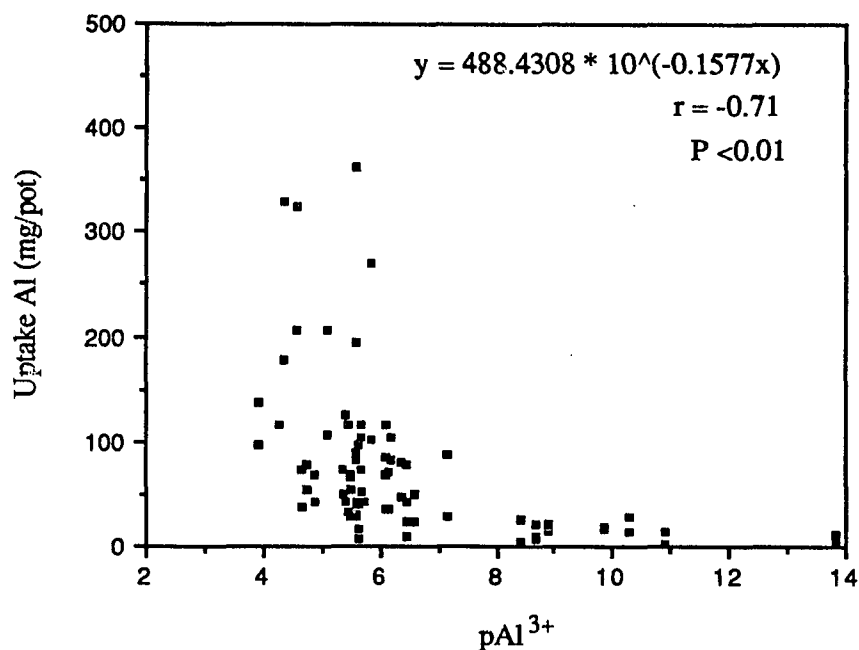


Figure 14. Relationship between Al uptake and the negative log of  $Al^{3+}$  activity for both rice varieties in all soils over all controlled redox conditions.

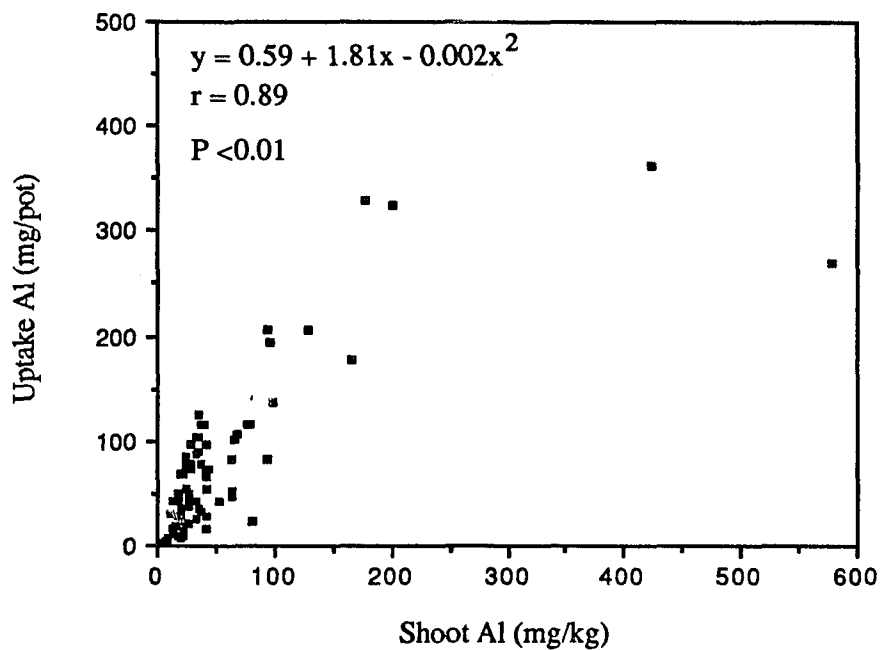


Figure 15. Relationship between Al uptake and Al content in the shoot for both rice varieties in acid and non-acid sulfate soils over all controlled redox conditions.



Figure 16. This is due to the high relationship between  $\text{Al}^{3+}$  activity in soil solution and percent Al saturation of the CEC as previously described in Figure 10. These results emphasize the importance of percent Al saturation of the CEC as an important Al parameter related to the amount of Al taken up by the rice plant.

Tanaka and Navasero (1966a) has reported that a decrease of Al uptake may be due to the precipitation of Al as aluminum phosphate on or in the roots. The point is then raised that Al may have interfered with uptake of phosphate by the rice plant in this study.

Therefore, to examine whether the formation of aluminum phosphate could occur in this work, the values of the negative log of the ion activity product of variscite ( $\text{pIAP}$  of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ) are plotted as a function of pH in Figure 17. The data show that the majority of the ion activity product values indicate supersaturation with respect to variscite. It is likely that moderately large amounts of phosphate from phosphorus fertilizer that had been applied to the soil suspension was precipitated by part of the soluble  $\text{Al}^{3+}$  forming aluminum phosphate. The above reason may be a possible explanation for the interference of phosphate uptake by Al. Precipitation of aluminum phosphate in the soil outside the roots has been reported by several workers (McLean and Gilbert, 1927; Tanaka and Navasero, 1966b; Rorison, 1972).

Under controlled pH and redox potential conditions, uptake of Al in the IR46 rice variety was not significantly correlated to any Al parameters in soil solution in all soils types. Uptake of Al by the IR 26 variety was weakly, but significantly correlated with percent Al saturation of the CEC ( $r = 0.32$ ,  $p = 0.05$ ,  $n = 90$ ) only in acid sulfate soils. Al uptake by the IR26 variety is plotted as a function of

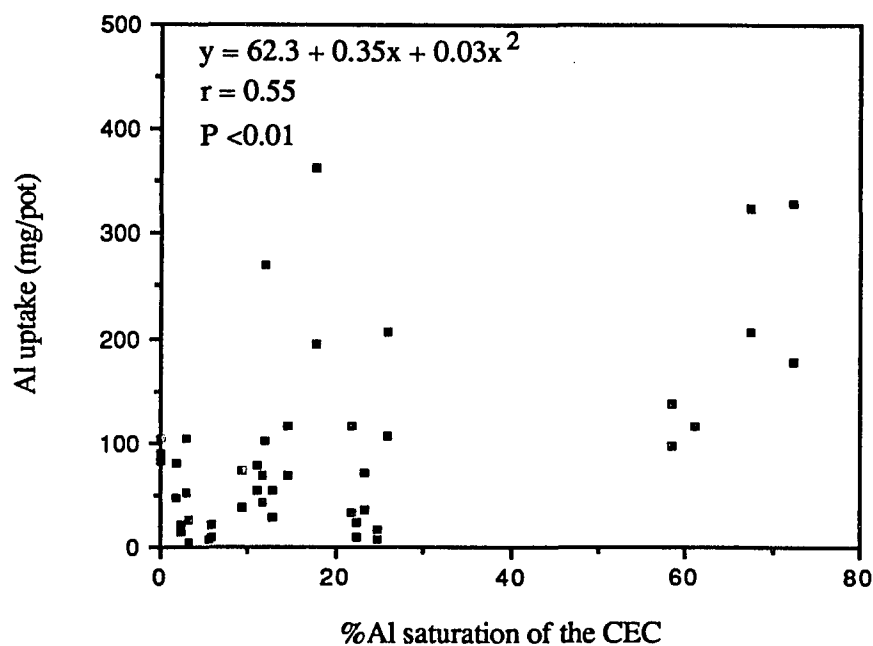


Figure 16. Relationship between Al uptake and percent Al saturation of the CEC for both rice varieties in acid sulfate soils over all controlled redox conditions.

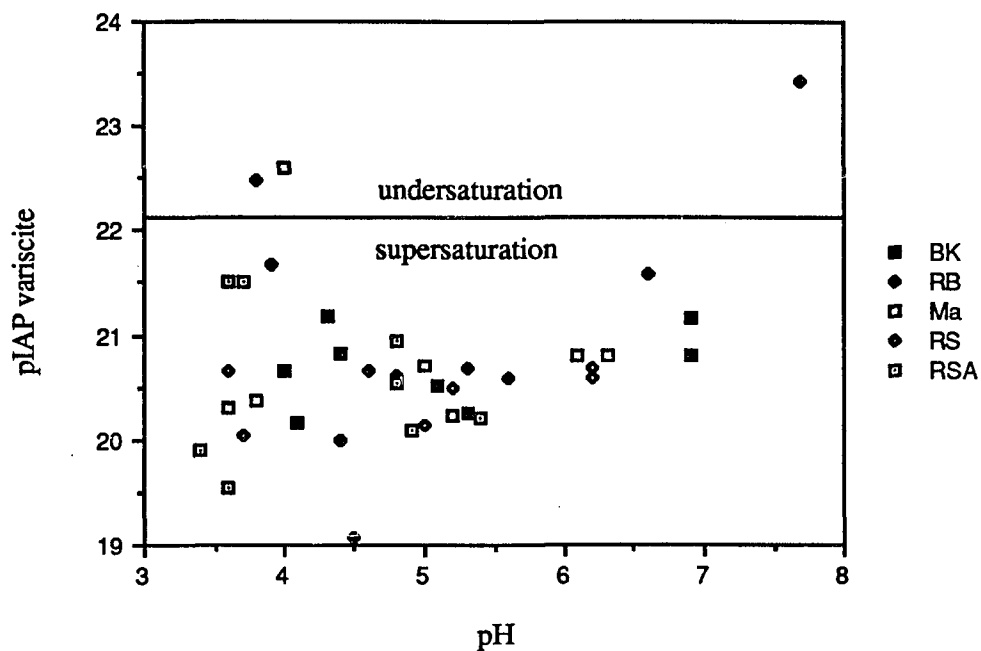


Figure 17. Relationship between the negative log of ion activity product of variscite and pH in acid and non-acid sulfate soils over all controlled redox conditions.

percent Al saturation of the CEC in Figure 18. Under controlled pH and redox conditions, shoot weight gain and root dry weight negatively related to  $\text{Al}^{3+}$  activity in soil solution. Figures 19 and 20 show that the negative effects of  $\text{Al}^{3+}$  activity on root growth ( $r = -0.38$ ,  $p < 0.01$ ,  $n = 180$ ) is higher than that on shoot growth ( $r = -0.24$ ,  $p < 0.01$ ,  $n = 180$ ) for both rice varieties and all soils. This may imply a slightly greater impact of excess Al on roots than shoots. Shoot weight gain of the sensitive variety was more affected than that of the tolerant variety as shown by their plots in Figures 21 and 22.

Under controlled pH-Eh conditions, the regression analysis revealed that uptakes of Ca, K, Mg, and Mn in both rice varieties are negatively related to  $\text{Al}^{3+}$  activity in soil solution. These relationships are demonstrated in Figures 23, 24, 25, and 26. Similar results have been reported elsewhere for Al inhibition of uptake of several macronutrients (i.e. Ca, Mg, P, and K) and micronutrients (i.e. Mn, As, Cu, and B) in the rice tops (Fageria and Carvalho, 1982; Fageria, 1985). Foy et. al. (1978) also noted that aluminum has been found to interfere with uptake of Ca, Mg, P, and K in several plants.

#### CONCLUSIONS

It is suggested from these experiments that the two solid phase species, jurbanite ( $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$ ) and amorphous  $\text{Al}(\text{OH})_3$ , control Al solubility at low and high pH conditions respectively in these soils. However, Al solubility is possibly affected by the formation of variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ) under a wide range of pH conditions in these soils under various controlled conditions.

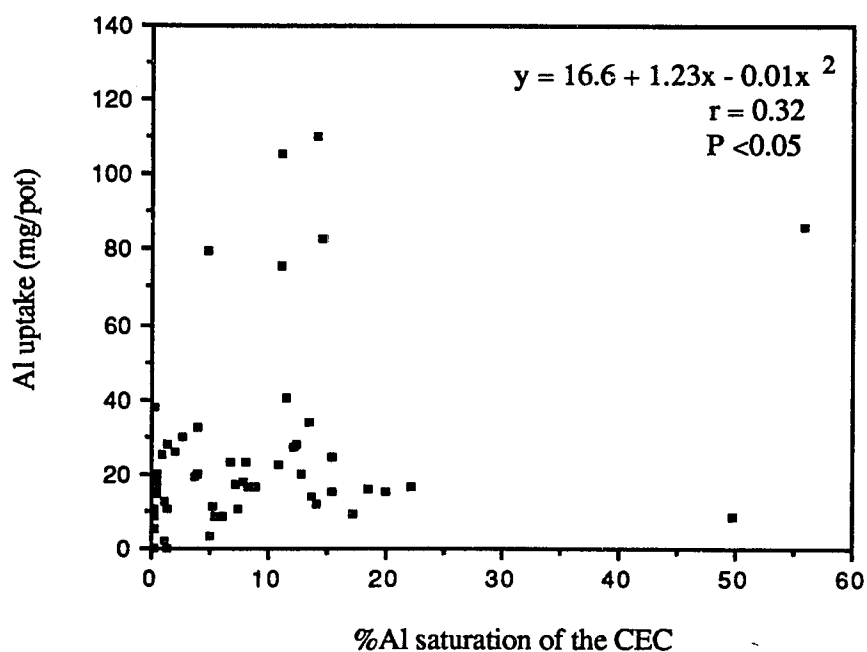


Figure 18. Relationship between Al uptake and percent Al saturation of the CEC for IR26 variety in acid sulfate soils over all controlled pH and redox potential.

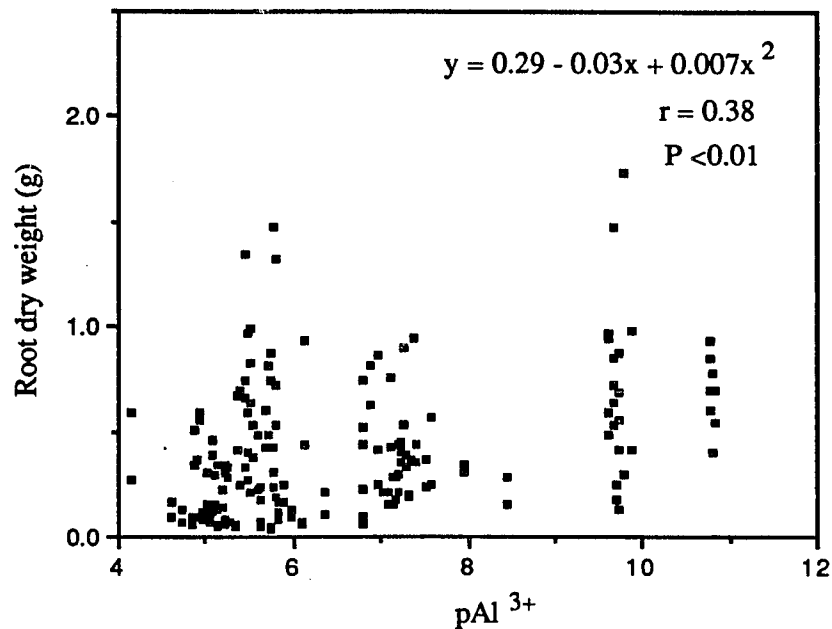


Figure 19. Relationship between root dry weight and the negative log of  $Al^{3+}$  activity for both varieties in acid and non-acid sulfate soils over all controlled pH and Eh.

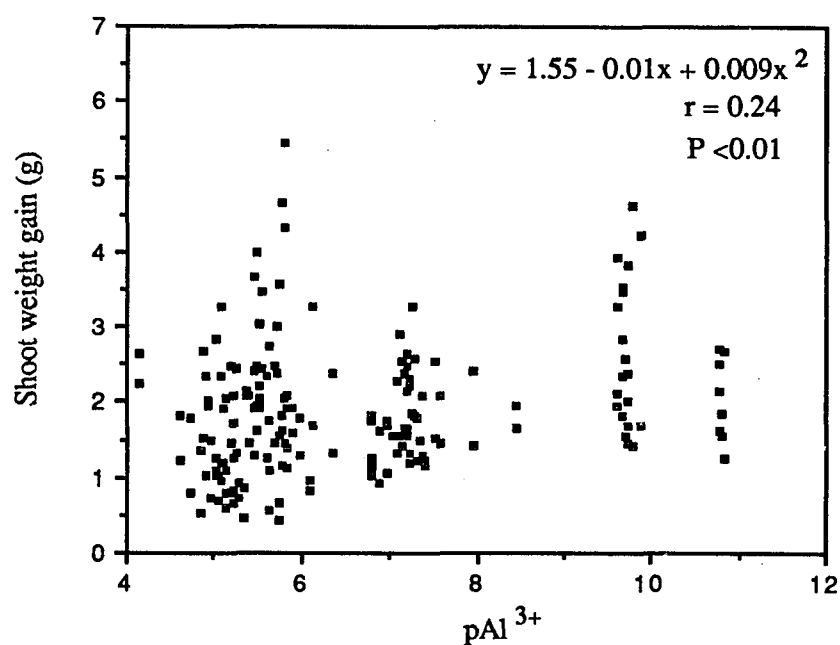


Figure 20. Relationship between shoot weight gain and the negative log of  $Al^{3+}$  activity for both varieties in acid and non-acid sulfate soils over all controlled pH and Eh.

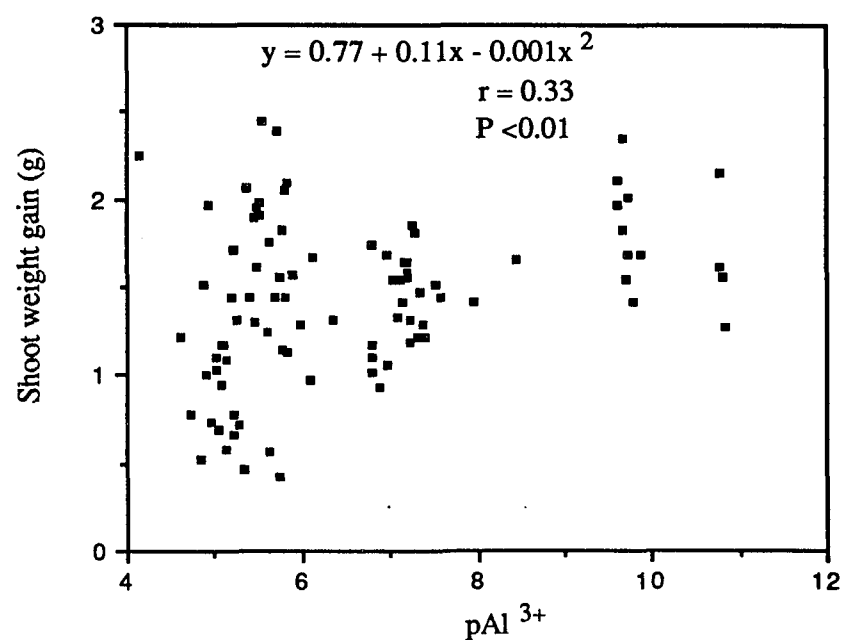


Figure 21. Relationship between shoot weight gain and the negative log of  $Al^{3+}$  activity for the IR26 variety in acid and non-acid sulfate soils over all controlled pH and Eh.

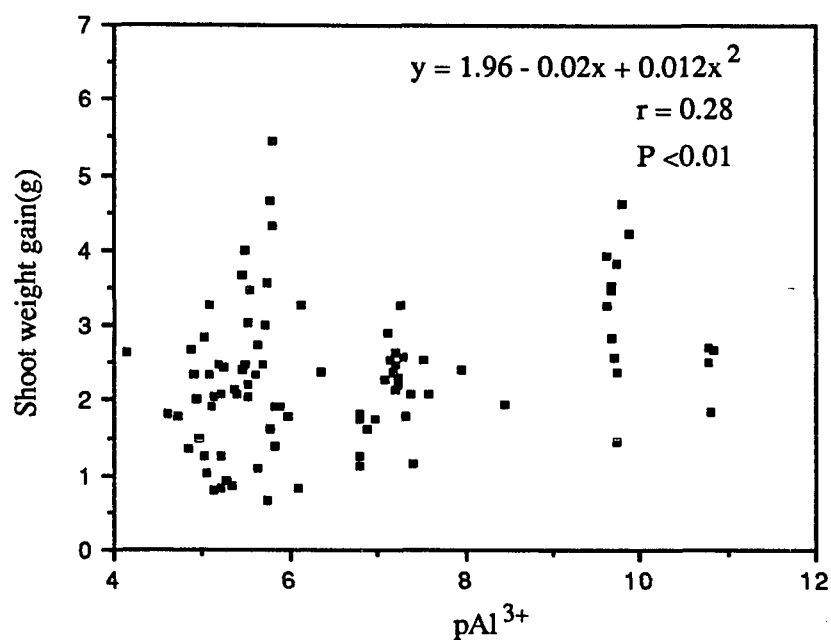


Figure 22. Relationship between shoot weight gain and the negative log of  $Al^{3+}$  activity for the IR46 variety in acid and non-acid sulfate soils over all controlled pH-Eh.

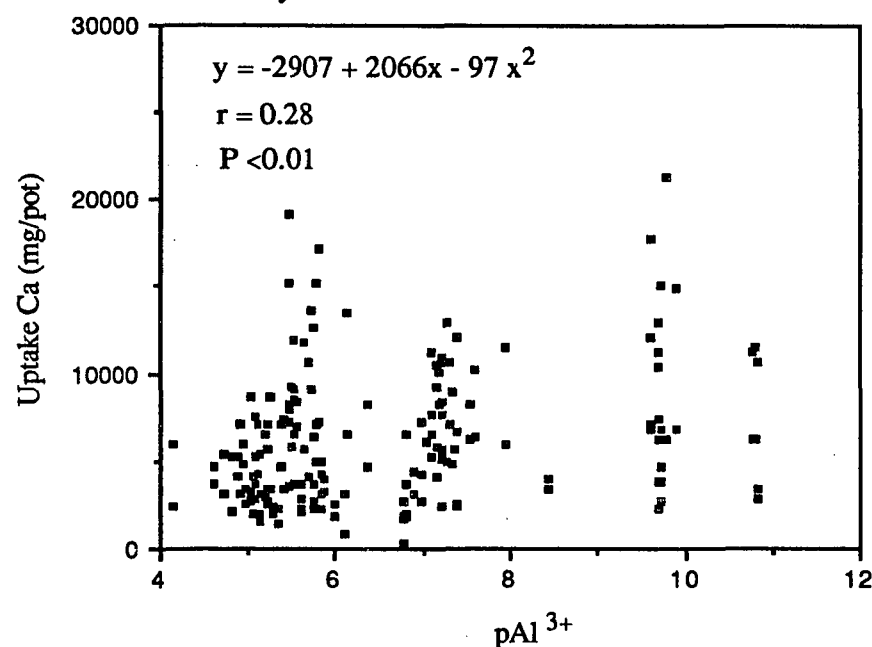


Figure 23. Relationship between Ca uptake and the negative log of  $Al^{3+}$  activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH-Eh conditions.

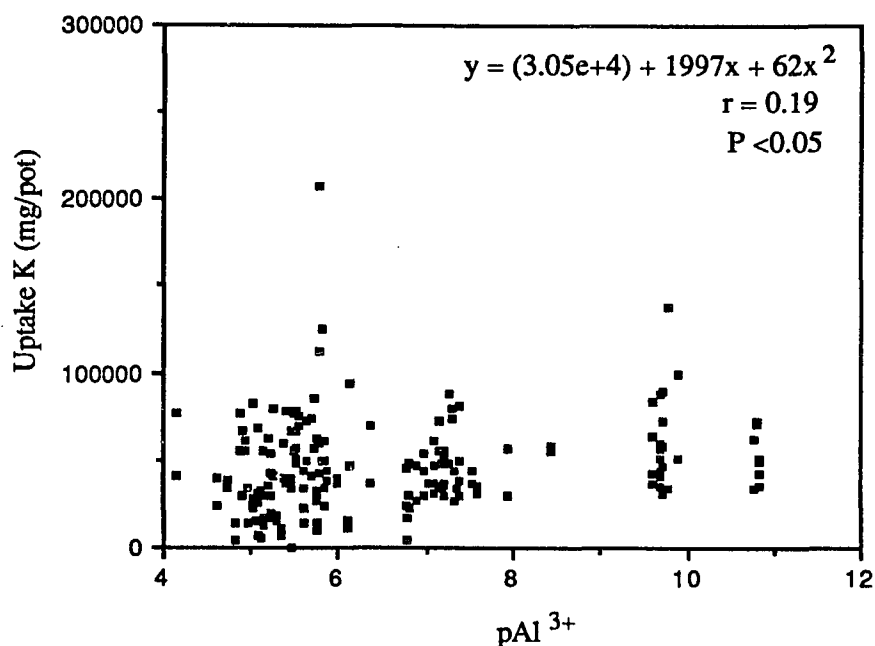


Figure 24. Relationship between K uptake and the negative log of  $Al^{3+}$  activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH-Eh conditions.

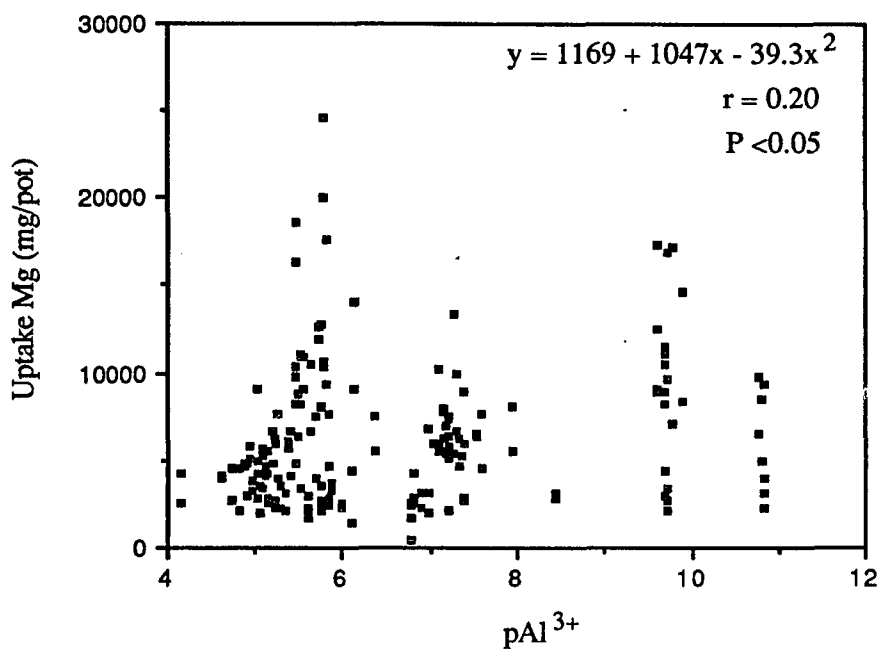


Figure 25. Relationship between Mg uptake and the negative log of  $Al^{3+}$  activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH-Eh conditions.

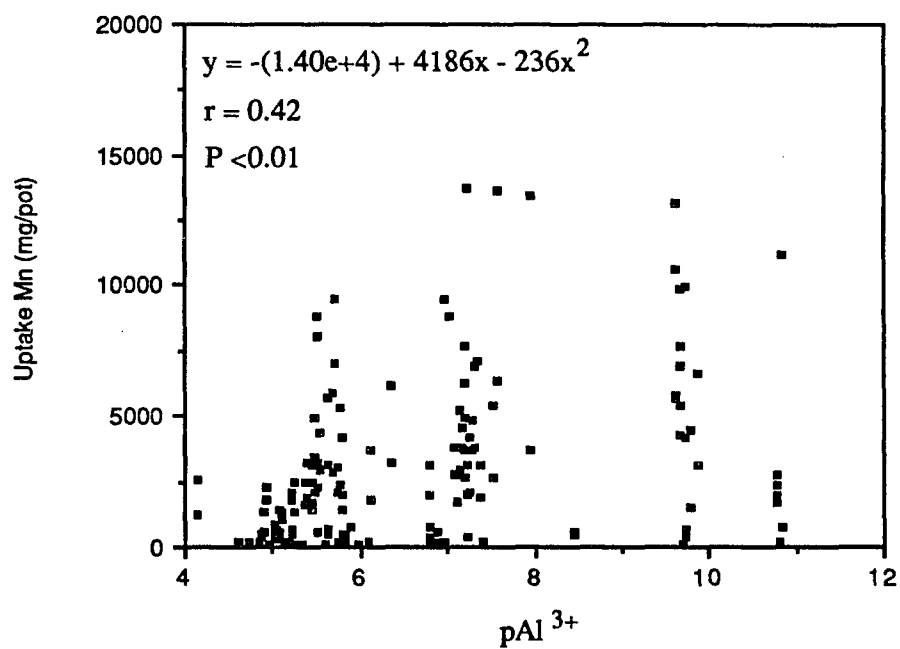


Figure 26. Relationship between Mn uptake and the negative log of Al<sup>3+</sup> activity for both rice varieties in acid and non-acid sulfate soils over all controlled pH-Eh conditions.



Under controlled pH and redox conditions, the total water-soluble Al,  $\text{Al}^{3+}$  activity, and percent Al saturation of the CEC were negatively related to pH in all soils whereas these Al parameters were negatively related to pH in only acid sulfate soils under controlled redox conditions. Aluminum activity is the only Al parameter negatively related to pH in non-acid sulfate soils under controlled redox conditions. Percent Al saturation of the CEC was strongly associated with  $\text{Al}^{3+}$  activity in soil solution.

Uptake of Al by both rice varieties correlated best with  $\text{Al}^{3+}$  activity for all soils under controlled redox conditions. Al uptake by the IR26 rice variety was significantly correlated with percent Al saturation of the CEC in only acid sulfate soils under controlled pH and redox conditions. Al uptake in IR46 was not significantly correlated with any soil Al parameters. Shoot weight gain and root dry weight of both rice varieties were negatively affected by  $\text{Al}^{3+}$  activity in all soil types. Shoot weight gain of the sensitive variety was more affected than that of the tolerant variety. It was observed that  $\text{Al}^{3+}$  activity was negatively associated with uptake of Ca, K, Mg, and Mn in both rice varieties and all soils under controlled pH and redox conditions.

#### REFERENCES

- Alva, A. K., D. K. Edwards, C. J. Asher, and F.P.C. Blamey. 1986. Effects of phosphorus/aluminum molar ratio and calcium concentration on plant response to aluminum toxicity. *Soil Sci. Soc. Am. J.* 50:133-137.
- Awad, A. S., D. G. Edwards., and P. J. Milham. 1976. Effect of pH and phosphate on soluble soil aluminum and on growth and composition of Kikuyu grass. *Plant and Soil* 45:531-542.

- Cate, R. B., Jr., and A. P. Sukhai. 1964. A study of aluminum in rice soils. *Soil Sci.* 98:85-93.
- Clark, R. B. 1977. Effect of aluminum on growth and mineral elements of Al-tolerant and Al-intolérant corn. *Plant and Soil* 47:653-662.
- Cutrim, Verediano Dos Anjos, Tan V. Nguyen, Jose Carlos Silva, and Jose Domingos Galvao. 1981. Inheritance of tolerance for aluminum toxicity in Brazilian rice *Oryza sativa* L. *International Rice Research Newsletter*, IRRI. 6(4).
- De Kock, P. C., and R. L. Mitchell. 1957. Uptake of chelated metals by plants. *Soil Sci.* 84:55-62.
- Dixon, J. B. 1977. Kaolinite and serpentine group minerals. p. 357-403. In J. B. Dixon, and S. B. Weed (ed.) *Minerals in Soil Environments*. *Soil Sci. Soc. Am.*, Madison, WI.
- Evans, C. E., and E.J. Kamprath. 1970. Lime response as related to percent Al saturation, solution Al, and organic matter content. *Soil Sci. Soc. Am. Proc.* 34:893-896.
- Fageria, N.K. 1985. Influence of aluminum in nutrient solutions on chemical composition in two rice cultivars at different growth stages. *Plant and Soil* 85:423-429.
- Fageria, N.K., and J. R. P. Carvalho. 1982. Influence of aluminum in nutrient solution on chemical composition in upland rice cultivars. *Plant and Soil* 69:31-44.
- Foy, C. D., R. L. Chaney, and M.C. White. 1978. The physiology of metal toxicity in plants. *Annu. Rev Plant Physiol.* 29:511-566.
- Hackett, C. 1962. Stimulative effects of aluminum on plant growth. *Nature* 195: 471-472.
- Hsu, Pa Ho. 1964. Adsorption of phosphate by aluminum and iron in soils. *Soil Sci. Soc. Am. Proc* 28:474-478.
- Jugsujinda, A., Y. Tadashi, and N. van Breemen. 1978. Aluminum toxicity and phosphorus deficiency in acid sulfate soils of Thailand. *International Rice Research Newsletter*, IRRI. 3(1).
- Kamprath, E. J., and C. D. Foy. 1971. Lime-fertilizer-plant interactions in acid soils. p. 105-151. In R.A. Olson (ed.) *Fertilizer technology and use* (2nd Ed.) *Soil Science Society of America*, Madison, WI.
- Lafever, H. N., L. G. Campbell, and C. D. Foy. 1977. Differential response of wheat cultivars to Al. *Agron.J.* 69:563-568.

- Lee, J., and M. W. Pritchard. 1984. Aluminum toxicity expression on nutrient uptake, growth and root morphology of Trifolium repens L. cv. 'Grasslands Huia'. Plant and Soil 82:101-116.
- Lindsay, W. L., M. Peech, and J. S. Clark. 1959. Determination of aluminum ion activity in soil extracts. Soil Sci. Soc. Am. Proc. 23:266-269.
- Lindsay, W. L., M. Peech, and J. S. Clark. 1957. Solubility criteria for the existence of variscite in soils. Soil Sci. Soc. Am. Proc. 23:357-360.
- McCormick, L. H., and F. Y. Borden. 1974. The occurrence of aluminum-phosphate precipitate in plant roots. Soil Sci. Soc. Am. Proc. 38: 931-934.
- McLean, F. T., and B. E. Gilbert. 1927. The relative aluminum tolerance of crop plants. Soil Sci. 24:163-175.
- Misra, U. K., R. W. Blanchar, and W. J. Upchurch. 1974. Aluminum content of soil extracts as a function of pH and ionic strength. Soil Sci. Soc. Am. Proc. 38:897-902.
- Moore, P. A., Jr. 1987. Metal behavior in acid sulfate soils of Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Nordstrom, D. K. 1982. The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system  $\text{Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  at 298 K. Geochim. Cosmochim. Acta 46:681-692.
- Pavan, M. A., F. T. Bingham, and P. F. Pratt. 1982. Toxicity of aluminum to coffee in Ultisols and Oxisols amended with  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{CaSO}_4\cdot\text{H}_2\text{O}$ . Soil Sci. Soc. Am. J. 46:1201-1207.
- Reid, D. A., G. D. Jones, W. H. Armiger, C. D. Foy, E. J. Koch, and T. M. Starling. 1969. Differential aluminum tolerance of winter barley varieties and selections in associated greenhouse and field experiments Agron. J. 61:218-222.
- Rorison, I. H. 1972. The effect of extreme soil acidity on the nutrient uptake and physiology of plants. p. 223-254. In H. Dost (ed.) Acid sulfate soils. Proc. Int. Symp. ILRI Pub. 18, Vol. I, Wageningen, The Netherlands.
- Slootmaker, L. A. J., and J. E. Arzadun. 1969. Selection of young barley plants for tolerance to high soil acidity in relation to some agronomic characteristics of mature plants. Euphytica 18:157-162.
- Tanaka, A., and S.A. Navasero. 1966a. Aluminum toxicity of the rice plant under water culture conditions. Soil Sci. Plant Nutr. 12:55-60.

- Tanaka, A., and S.A. Navasero. 1966b. Growth of the rice plant on acid sulfate soils. *Soil Sci. Plant Nutr.* 12:107-114.
- Tanaka, A., and S. Yoshida. 1970. Nutritional disorders of the rice plant in Asia. *Int. Rice Res. Inst. Tech. Bull.* 10.
- Van Breemen, N. 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. *Soil Sci. Soc. Am. Proc.* 37:694-697.
- Van Breemen, N. 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. *Agric. Res. Rep.* 848. PUDOC, Wageningen, Netherlands.
- Wagatsuma, T., and Y. Ezoe. 1985. Effect of pH on ionic species of aluminum in medium and on aluminum toxicity under solution culture. *Soil Sci. Plant Nutr.* 31:547-561.
- Weaver, R. M., and P. R. Bloom. 1977. Solution activities of aluminum and silicon in highly weathered soils that contain gibbsite and kaolinite. *Soil Sci. Soc. Am. J.* 41:814-817.

**Chapter Eight**  
**Summary and Conclusions**

## SUMMARY AND CONCLUSIONS

The effects of controlled pH and redox potential conditions on transformations of several nutrients of interest and their effects on growth of rice were studied in laboratory microcosms using acid sulfate (Sulfic Tropaequept) and non-acid sulfate (Typic Tropaequept) soil materials from Thailand. Some microcosms were incubated at selected controlled redox potential conditions (500, 250, 50, and -150 mV) with no pH control. Others were incubated at various combinations of controlled pH and redox potential levels (pH levels of 3.5, 4.5, and 5.5 and redox potential levels  $\geq$  500, 250, and 50 mV respectively). Rice seedlings of acid sulfate soil-tolerant and sensitive varieties (IR 46 and IR 26, respectively) were planted in these soil suspensions. Three weeks after rice transplanting, the soil solution and plant tissue samples were processed and analysed for various soil and plant properties. Metal activities in the soil solution were determined by the computer program (GEOCHEM).

The results suggested that both redox potential and pH significantly affected the transformations of various fractions of Fe and Mn in both soil types. Acidity (pH) strongly influenced the solubility of Al in acid sulfate soils. Water-soluble Fe and exchangeable Fe were inversely related to both pH and redox potential and reducible Fe was positively related. Redox potential and pH had the same effect on water-soluble Mn levels as Fe. Exchangeable Mn levels negatively related to pH and reducible Mn levels positively related to pH, while Eh had less of an effect on water-soluble Mn than it did for Fe. Water-soluble Al and percent Al saturation of the CEC negatively

related to pH in both soil types under controlled pH and redox potential conditions, but negatively related to pH in only acid sulfate soils under controlled redox potential conditions. Aluminum activity in the soil solution was the only Al parameter negatively associated with pH in both soil types and over all controlled conditions.

Fe uptake by rice was negatively affected by increases in both redox potential and pH. Iron uptake was strongly related to water-soluble Fe,  $\text{Fe}^{2+}$  activity, and  $E'\text{Fe}$ . The critical level of the minimum  $p\text{Fe}^{2+}$  and  $E'\text{-Fe}$  that triggers excessive uptake of Fe by the rice plant was probably defined at  $p\text{Fe}^{2+}$  of 3 and  $E'\text{-Fe}$  of 0.45 respectively. The average Fe content in the shoot tissue of the sensitive variety (IR 26) was greater than that of the tolerant variety (IR 46). Growth of both rice varieties was negatively related to Fe:Mn ratio in the shoot tissue. An Fe:Mn ratio in the shoot tissue of 4.5 and higher is probably harmful to rice growth.

Uptake of Mn was positively correlated with redox potential and pH. The negative relationship between Mn uptake and  $p(\text{Mn}^{2+}:\text{Fe}^{2+})$  activity ratio suggested that Fe may have antagonistic effect upon Mn uptake.

Aluminum uptake by both rice varieties correlated best with  $\text{Al}^{3+}$  activity for both soil types under controlled redox conditions. Aluminum uptake by the IR 26 variety was significantly correlated with percent Al saturation of the CEC only in acid sulfate soils under controlled pH and redox potential conditions. On the other hand, Al uptake by IR 46 was not significantly correlated with any soil parameters. Shoot and root weight gains and root dry weight of both rice varieties were negatively affected by  $\text{Al}^{3+}$  activity in both soil types. Growth of the sensitive variety was somewhat more affected than

that of the tolerant variety. It was observed that  $\text{Al}^{3+}$  activity was negatively associated with uptake of Ca, K, Mg, and Mn in both rice varieties and both soil types under controlled pH and redox potential conditions.

Experimental data illustrated that amorphous  $\text{Fe}(\text{OH})_3$  probably controlled solubility of  $\text{Fe}^{2+}$  at  $\text{pe} + \text{pH}$  around 12.95 and above and goethite ( $\text{FeOOH}$ ) may regulate the  $\text{Fe}^{2+}$  solubility at  $\text{pe} + \text{pH}$  of about 11.95 and below.

Manganese solubility was not controlled by any solid phases that could be determined. Equilibrium between  $\text{E}'\text{-Mn}$  (the divalent charge fraction in the soil solution due to Mn) and  $\text{E-Mn}$  (the divalent charge fraction on the CEC due to Mn) demonstrated that cation exchange reactions may regulate Mn solubility.

It is suggested from these experiments that the two solid phase species, jurbanite ( $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$ ) and amorphous  $\text{Al}(\text{OH})_3$ , control Al solubility at low and high pH conditions respectively. Aluminum probably precipitates P in the form of variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ).

Regression analyses by the stepwise technique and the maximum  $R^2$  improvement procedure revealed that several independent variables were significantly associated with the variation of weight gain of the two rice varieties.

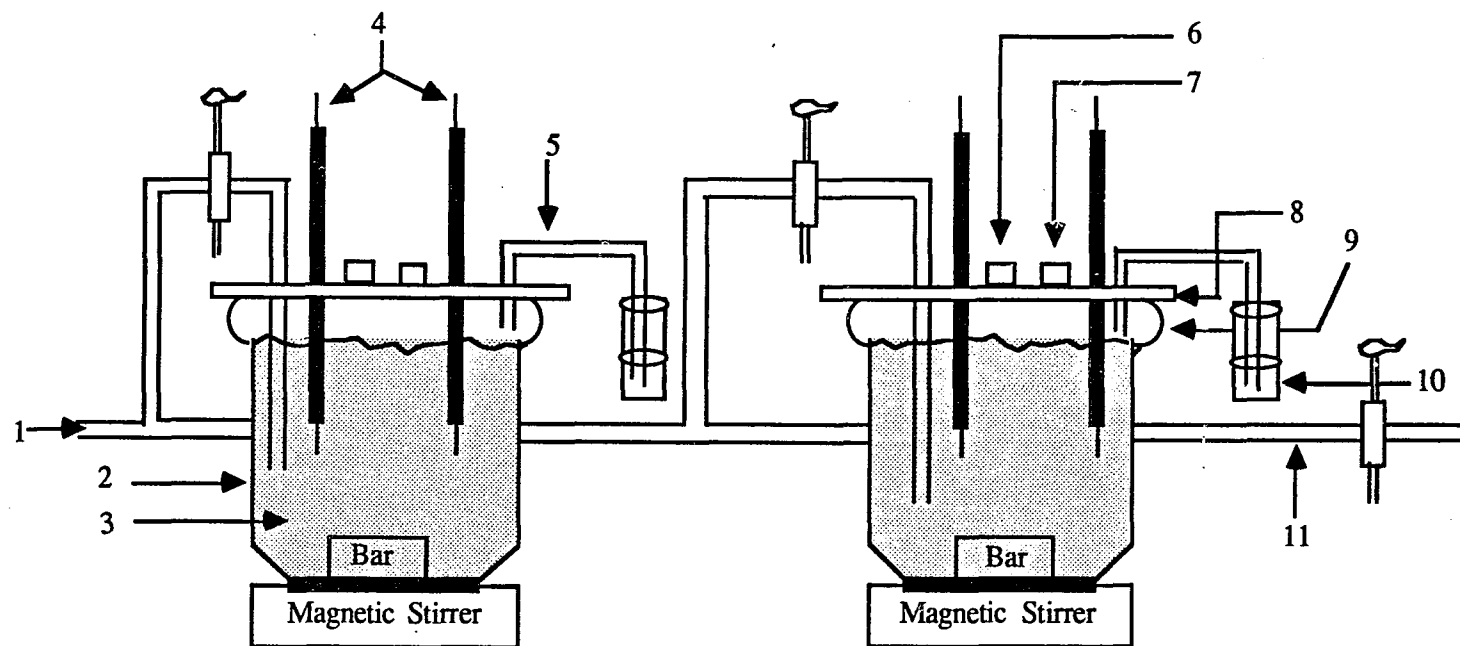
Under controlled redox potential conditions, redox ( $\text{pe} + \text{pH}$ ) was the most important variable positively associated with rice weight gain which was attributed to the combined effects of Eh and pH on transformations of Fe, Mn, Al, and Zn affecting their plant availability. The Fe:Mn ratio in shoot tissue was the most important variable negatively associated with weight gain suggesting the



antagonistic effect of the two metals on growth of rice. Growth of both varieties was generally lower in the acid sulfate soil and under low redox (a range of pe + pH from 2.82 to 4.57) in both soil types. Growth of IR 26 was more affected by the strongly reduced conditions (-150 mV) of acid sulfate soils.

Under controlled pH and redox potential conditions, the Fe:Mn ratio in shoot tissue was also the most important variable negatively associated with the rice weight gain. Activity of  $\text{Al}^{3+}$  consistently adversely affect weight gain of both rice varieties in acid sulfate soils. Growth of both rice varieties was generally lower under low pe + pH levels of both soil types.

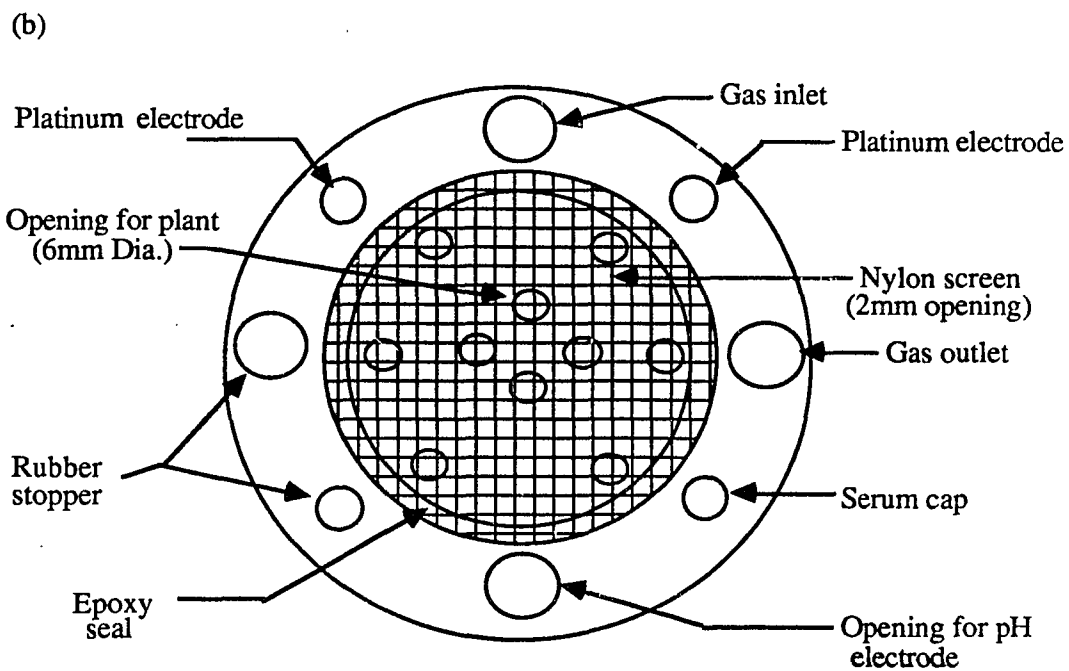
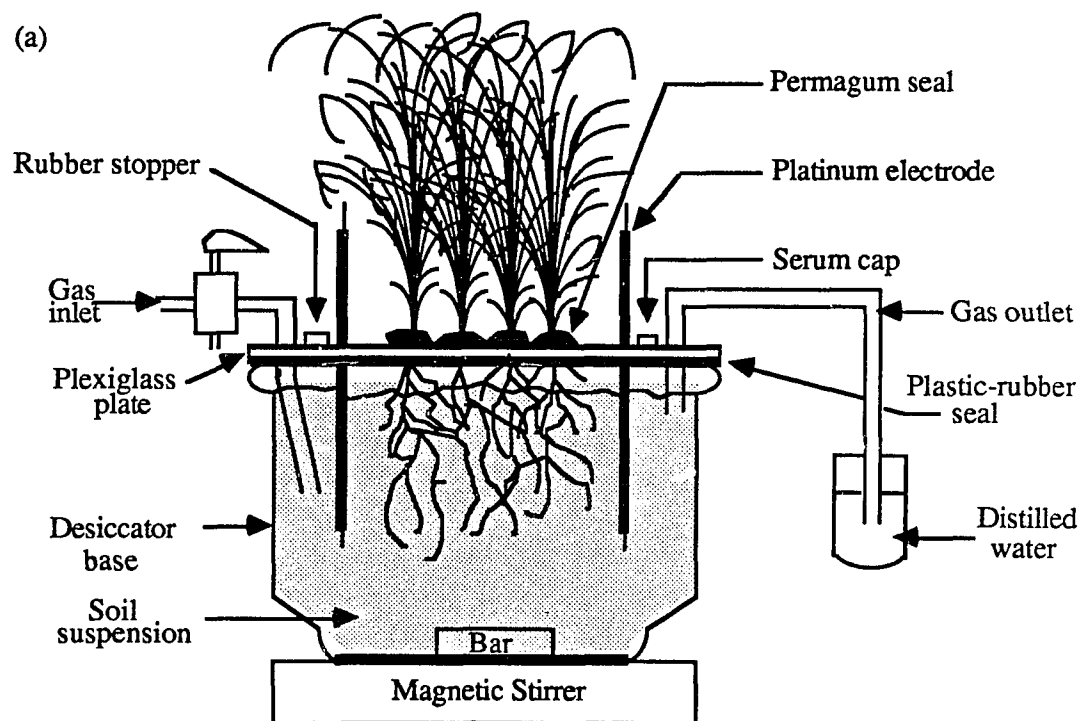
## Appendix



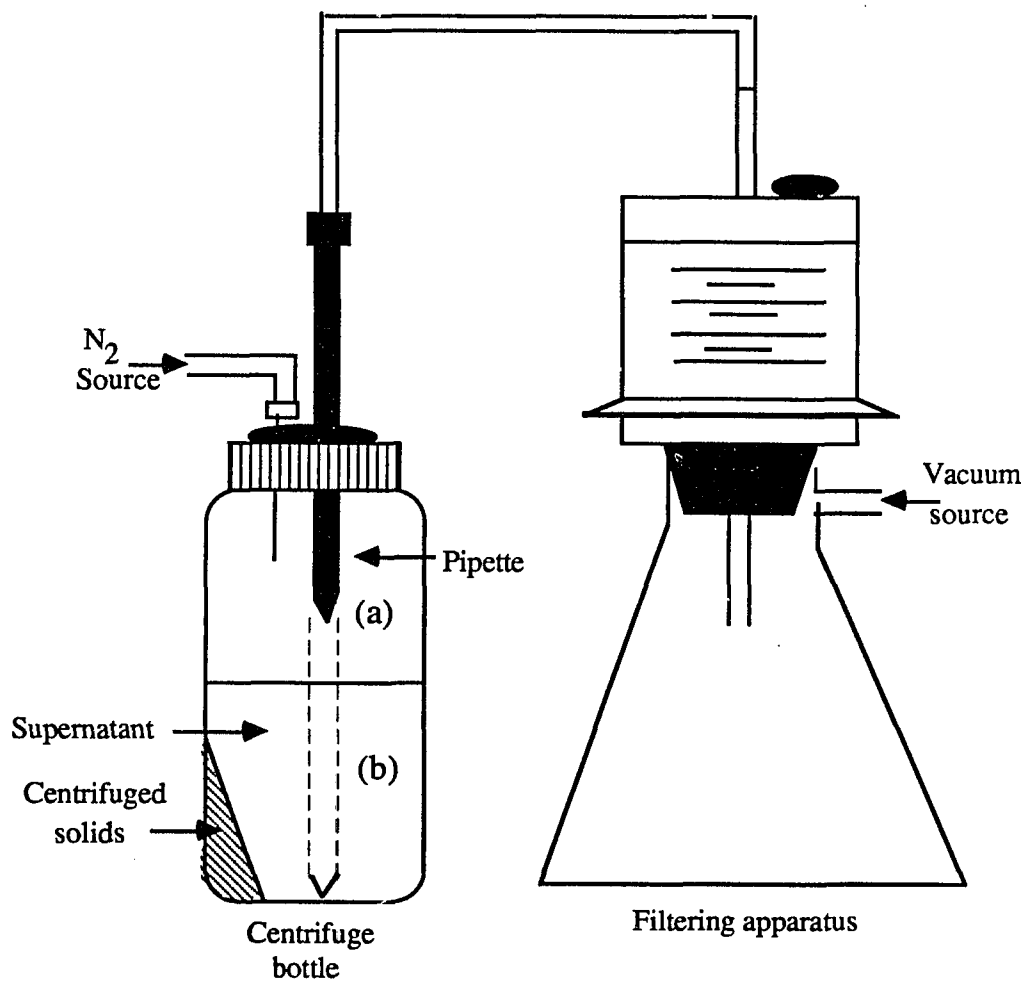
1. Gas Inlet
2. Desiccator Base
3. Soil Suspension
4. Platinum Electrodes
5. Gas Outlet
6. Rubber Stopper

7. Serum Cap
8. Plexiglass Plate
9. Plastic Rubber Seal
10. Distilled Water
11. Gas Pipe

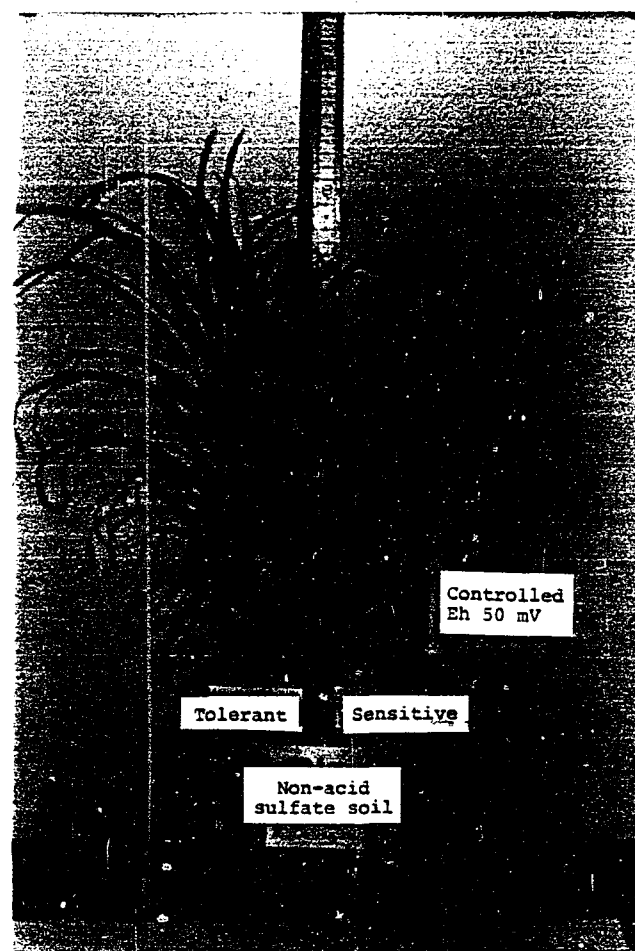
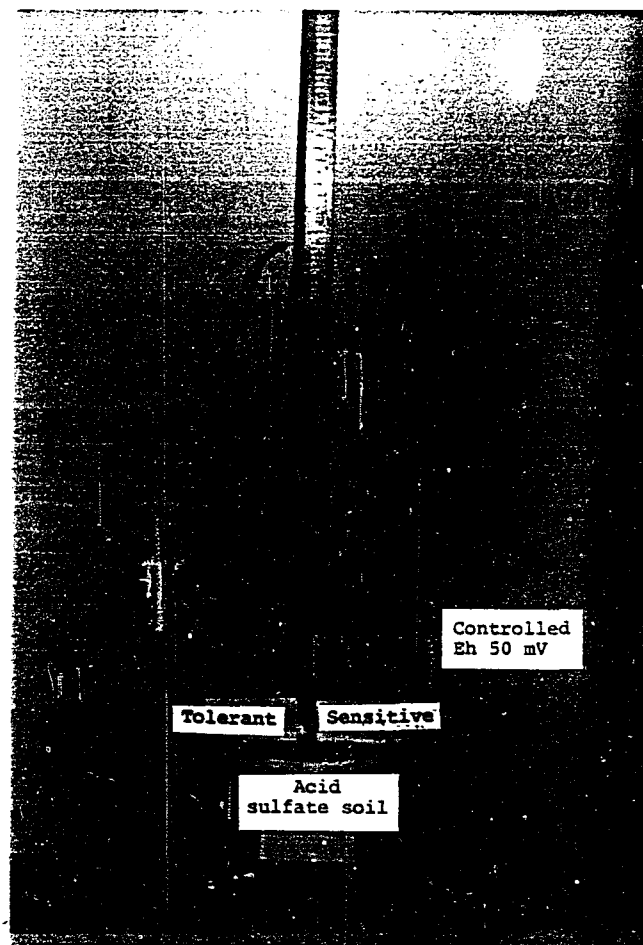
Appendix Figure A1. The apparatus for incubation of the soil suspension at controlled pH and redox potential conditions ( after Jugsujinda, 1976 ).



Appendix Figure A 2. Diagram of plant growth/soil incubation apparatus after transplanting rice (a) and a plexiglass plate (b) designed for use in supporting rice seedlings in controlled system (after Jugsujinda, 1976).



Appendix Figure A3. Apparatus for filtering supernatant solutions under a N<sub>2</sub> atmosphere;  
(a) pipette in N<sub>2</sub> purge position and  
(b) pipette in filtering position  
(after Gambrell et al., 1975).



Appendix Plate 1. Differences in growth of tolerant and sensitive rice varieties (IR46 and IR26 respectively ) grown over a 3-week period in an acid sulfate soil ( Sulfic Tropaquet , Rangsit very acid ) and a non-acid sulfate soil ( Typic Tropaquet , Ratchaburi ) under controlled redox potential conditions.

Appendix Table A1. Preparation of stock solutions for nutrient culture solution.<sup>1</sup>

Chemical Compound	Molecular Weight	Element	Atomic Weight of the Element	Preparation of Stock Soln (g/L of compd in Dist. Water)	mL of Stock Soln per L of Culture Soln <sup>2</sup>	Concentration of Element of Nutrient Soln (mg L <sup>-1</sup> )
NH <sub>4</sub> NO <sub>3</sub>	80.048	N	14.0067	22.859	5	40.00
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	137.998	P	30.9739	8.911	5	10.00
K <sub>2</sub> SO <sub>4</sub>	166.240	K	39.1020	34.012	5	40.00
CaCl <sub>2</sub> ·2H <sub>2</sub> O	147.030	Ca	40.0800	29.347	5	40.00
MgSO <sub>4</sub> ·7H <sub>2</sub> O	246.498	Mg	24.3120	81.112	5	40.00
MnCl <sub>2</sub>	125.844	Mn	54.9380	0.229 (3)		0.50
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	1235.860	Mo	95.9400	0.129 (3)		0.05
H <sub>3</sub> BO <sub>3</sub>	61.832	B	10.8100	0.229 (3)		0.20
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	287.544	Zn	65.3800	0.009 (3)	5	0.01
CuSO <sub>4</sub> ·5H <sub>2</sub> O	249.698	Cu	63.5460	0.008 (3)		0.01
FeNaEDTA	367.050	Fe	55.8470	3.943 (3)		3.00
Citric acid (monohydrate)				11.900 (3)		

<sup>1</sup> After Tanaka and Navasero (1966), Jugsujinda (1976), Yoshida et al. (1976), modified.

<sup>2</sup> Use distilled water to prepare culture solution and adjust final pH to 5.5.

(3) Dissolve chemical compound separately; then combine with 50 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. Make up to 1 liter volume with distilled water.

## REFERENCES

- Adam, F. 1974. Soil solution. p. 441-481. In E. W. Carson (ed.) The plant root and its environment. University Press of Virginia, Charlottesville.
- Allam, A. 1971. Soluble sulphides in rice fields and their in vitro effects on rice seedlings. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Allam, A. L., and J. P. Hollis. 1972. Sulfide inhibition of oxidases in rice roots. *Phytopathology* 62:634-639.
- Allam, A. L., G. Pitts, and J. P. Hollis. 1972. Sulfide determinations in submerged soils with an ion-selective electrode. *Soil Sci.* 114:456-467.
- Allison, L.E., and G.D. Scarseth. 1942. A biological reduction method for removing free iron oxides from soils and colloidal clays. *J. Am. Soc. Agron.* 34:616-623.
- Amacher, M. C. 1984. Determination of ionic activities in soil solutions and suspensions: principal limitations. *Soil Sci. Soc. Am J.* 48:519-524.
- Ando, T., S. Yoshida, and I. Nishiyama. 1983. Nature of oxidizing power of rice roots. *Plant and Soil* 72:57-71.
- Andrew, C. S., A. D. Johnson and R. L. Sandland. 1973. Effect of aluminum on the growth and chemical composition of some tropical and temperate pasture legumes. *Aust. J. Agr. Res.* 24:325-339.
- Andriesse, J. P., N. van Breemen, and W. A. Blokhuis. 1973. The influence of mud lobsters (*Thalassina anomales*) on the development of acid sulfate soils in mangrove swamps in Sarawak. p. 11-39. In H. Dost (ed.) Acid sulfate soils. *Proc. Int. Symp. ILRI Pub.* 18, vol II, Wageningen, The Netherlands.
- Aomine, S. 1962. A review of research on redox potentials of paddy soils in Japan. *Soil Sci.* 94:6-13.
- Arkley, T. H., D. N. Munns, and C. M. Johnson. 1960. Preparation of plant tissue for micronutrient analysis. Removal of dust and spray contaminants. *J. Agr. Food Chem.* 8:318-321.
- Armstrong, W. 1967. The use of polarography in the assay of oxygen diffusion from roots anaerobic media. *Physiol. Plant.* 20:540-553.
- Armstrong, W. 1969. Rhizosphere oxidation in rice: an analysis of intervarietal difference in oxygen flux from the roots. *Physiol. Plant.* 23:623-630.



- Armstrong, W. 1971. Oxygen diffusion from the roots of rice grown under non-waterlogged conditions. *Physiol. Plant.* 24:242-247.
- Armstrong, W. 1971b. Radial oxygen losses from intact rice roots as affected by distance from the apex, respiration and waterlogging. *Plant Physiol.* 25:192-197.
- Arnon, D. I. and Johnson, C. M. 1942. Influence of hydrogen ion concentration on the growth of higher plants under controlled conditions. *Plant Physiol.* 17:525-539.
- Attanandana, T. 1982. Fertility problems of acid sulfate soils of Thailand. D. Agr. Thesis, Kyoto Univ., Japan.
- Attanandana, T., and J. Chanchaoensook. 1980. Soil and plant analysis. *Dep. Soil Sci., Kasetsart Univ., Thailand.* 103 p. (in Thai).
- Attanandana, T., and S. Vacharotayan. 1982. Chemical characteristics and fertility status of acid sulfate soils of Thailand. p. 118-130. In H. Dost and N. van Breemen (ed). *Proc. Bangkok Symp. on acid sulfate soils.* ILRI Pub. 31, Wageningen, The Netherlands.
- Attanandana, T., and S. Vacharotayan. 1983. Rock phosphate utilization on acid sulphate soils of Thailand. Paper No. 12. In KU/FFTC (ed.) *Ecology and manangement of problem soils in Asia.* Kasetsart Univ., Bangkok, Thailand.
- Avadhani, P. N., H. Greenway, R. Lefroy, and L. Prior. 1978. Alcoholic fermentation and malate metabolism in rice germinating at low oxygen concentrations. *Aust. J. Plant Physiol.* 5(1):15-25.
- Awad, A. S., D. G. Edwards., and P. J. Milham. 1976. Effect of pH and phosphate on soluble soil aluminum and on growth and composition of Kikuyu grass. *Plant and soil* 45:531-542.
- Ayotade, K. A. 1977. Kinetics and reactions of hydrogen sulfide in solution of flooded rice soils. *Plant and Soil* 46:381-389.
- Baba, I. 1958. Methods of diagnosing Akiochi, iron, and sulfide toxicity in the wet zone rice field of Ceylon. *Trop. Agric.* 114:231-236.
- Bacha, R. E. and Hossner. 1977. Characteristics of coatings formed on rice roots as affected by iron and manganese addition. *Soil Sci. Soc. Am. J.* 41:931-935.
- Baham, J. 1984. Prediction of ion activities in soil solutions: Computer Equilibrium Modeling. *Soil Sci. Soc. Am. J.* 48:525-531.
- Beck, M. T. 1977. Ciritical evaluation of equilibrium constants in solution-stability constants of metal complexes. *Pure Appl. Chem* 49:129-135.

- Benckiser, G., J. C. G. Ottow, I. Watanabe, and S. Santiago. 1984a. The mechanism of excessive iron-uptake (iron toxicity) of wetland rice. *J. Plant Nutrition*. 7:177-185.
- Benckiser, G., J. C. G. Ottow, S. Santiago, and I. Watanabe. 1982. Physiochemical characterization of iron-toxic soils in some Asian countries. *IRRI Res Paper Series* 85:1-11.
- Benckiser, G., S. Santiago, H. U. Neue, I. Watanabe, and J. C. G. Ottow. 1984. Effect of fertilization exudation, dehydrogenase activity, iron-reducing populations and  $Fe^{2+}$  formation in the rhizosphere of rice (*Oryza sativa* L.) in relation to iron toxicity. *Plant and Soil* 79:305-316.
- Berner, R. A. 1964. Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure. *J. Geol.*, 72, 293-306.
- Berner, R. A. 1966. Chemical diagenesis of some modern carbonate sediments. *Am. J. Sci.* 264:1-36.
- Berner, R. A. 1970. Sedimentary pyrite formation. *Am. J. Sci.* 268:1-23.
- Berner, R. A. 1971. Principles of chemical sedimentology. McGrawHill, New York. 240 p.
- Bertani, A., I. Brambilla, and F. Menegus. 1980. Effect of anaerobiosis on rice seedlings: growth, metabolic rate, and fate of fermentation products. *J. Exp. Bot.* 31:325-331.
- Beye, G. 1971. Amelioration of two acid sulphate soils for rice. *IRRI Saturday seminar. Int. Rice Res. Inst. Los Banos, Laguna. Philippines.* p. 19.
- Black, C. A. 1965. Methods of soil analysis. *Agronomy* 9. Part 2. American Society of Agronomy, Madison, WI.
- Blackwelder, B. W., O. H. Pilkey, and J. D. Howard. 1979. Late Wisconsinan sea levels on the Southeast U.S. Atlantic shelf based on in-place shore line indicators. *Science* 204:618-520.
- Blair, A. W., and A. L. Price. 1923. Studies on the toxic properties of soils. *Soil Sci.* 15:109-129.
- Bloomfield, C. 1969. Sulfate reduction in waterlogged soils. *J. Soil Sci.* 20:207-221.
- Bloomfield, D., and J. K. Coulter. 1973. Genesis and management of acid sulfate soils. *Adv. Agron.* 25:256-326.
- Bohn, H.L. 1968. Electromotive force of inert electrodes in soil suspensions. *Soil Sci. Soc. Am. Proc.* 32:211-215.

- Bohn, H.L. 1970. Comparison of measured and theoretical Mn concentrations in soil suspensions. *Soil Sci. Soc. Am. Proc.* 34:195-197.
- Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1979. *Soil Chemistry*. Wiley, New York.
- Borthakur, H. P., and N. N. Mazumder. 1968. Effect of lime on nitrogen availability in paddy soils. *J. Indian Soil Sci. Soc.* 16:143-147.
- Bradford, K. J., and D. R. Dilley. 1978. Effects of root anaerobiosis on ethylene production, epinasty, and growth of tomato plants. *Plant Physiol.* 61:506-509.
- Bradley, D.B., and D.H. Sieling. 1953. Effect of organic anions and sugars on phosphate precipitation by iron and aluminum as influenced by pH. *Soil Sci.* 76:175-180.
- Bray, R. H., and Kurtz, L. T. 1945. Determination of total, organic and available forms of phosphorus in soils. *Soil Sci.* 59:39-45.
- Bremner, J. M. 1965. Total nitrogen. In C. A. Black (ed.) *Methods of soil analysis*. *Agronomy* 9:1149-1178.
- Brinkman, R. 1982. Social and economic aspects of the reclamation of acid sulfate soils areas. p. 21-36. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Brinkman, R. and Pons, L. J. 1973. Recognition and prediction of acid sulfate soil conditions. p. 169-203, In H. Dost (ed.) *Acid sulfate soils*. *Proc. Int. Symp. ILRI Pub.* 18, Vol. I. Wageningen, The Netherlands.
- Broadbent, F. E., and O. C. Reyes. 1971. Uptake of soil and fertilizer nitrogen by rice in some Philippine rice soils. *Soil Sci.* 112:200-205.
- Bromfield, S.M. 1960. Some factors affecting the solubility of phosphates during the microbial decomposition of plant material. *Aust. J. Agr. Res.* 11:304-316.
- Bromfield, S.M., and E. G. Williams. 1963. An estimation of the biological reduction method for estimating active iron in soils. *J. Soil Sci.* 14:346-359.
- Brown, J. C., J. E. Ambler, R. L. Chaney, and C. D. Foy. 1972. Differential responses of plant genotypes to micronutrients p. 389-418. In J. J. Mortvedt, P. M. Ciordano, and W. L. Lindsay (ed.) *Micronutrients in Agriculture*, Soil Society of America, Madison, WI.
- Buurman, P., N. van Breemen, and A. G. Jongmans. 1973. A fossil acid sulphate soil in ice-pushed Tertiary deposits near Uelsen (Kreis

- orthern, *soils.*  
*Pub.*
- Can V. L. 1987 *fate*  
*soils in* (ed.)  
*proceeding* ILRI  
*1981, 1982*
- Carson D. L. *of an*  
*land use* 828-833.
- Cate R. B., and *ce*  
*S.*
- Chamrasekarn *id*  
*formation* t. Soil  
*S. Plan.*
- Chang, S. C. *s*  
*nutrition and*  
*fertilization* rice.  
*and* Taipei.
- Chang, S. C., *s*  
*horizon*
- Chang, S. C. *nations*  
*some*
- Chao T. F., *lective*  
*autio* . Soil  
*oc.*
- Chapman H. B. *et al.*  
*( ) Meth.*
- Chapman H. B. *Aiem.*  
*The* iced  
*te soil* p.  
*1971.* mp. on  
*sulfate* s.
- Chen S. C., *s on*  
*roots* Soc.  
*44*
- Cherry E. H. *t.*  
*Gr. Soil*
- Cho Y. Y., and *growth*  
*temperatu*  
*time.*

- Nordhorn), Germany. p. 52-75. In H. Dost (ed.) Acid sulphate soils. ILRI Pub. 18, Vol. 11, Wageningen, The Netherlands.
- Can, V. L. 1981. Rock phosphate in rice production on acid sulfate soils in Vietnam. p. 187-194. In H. Dost and N. van Breemen (ed.) Proceedings of the Bangkok symposium on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Carson, C. D., and J. B. Dixon. 1983. Mineralogy and acidity of an inland acid sulfate soil of Texas. Soil Sci. Soc. Am. J. 47:828-833.
- Cate, R. B., and A. P. Sukhai. 1964. A study of aluminum in rice soils. Soil Sci. 98:85-93.
- Chandrasekaran, S., and T. Yoshida. 1973. Effect of organic acid transformations in submerged soils on growth of the rice plant. Soil Sci. Plant Nutr. 19:39-45.
- Chang, S. C. 1976. Phosphorus in submerged soils and phosphorus nutrition and fertilization of rice. p. 93-116. In The fertilization of paddy soils and fertilizer applications for rice. Food and Fertilizer Center for Asia and the Pacific Council. Taipei.
- Chang, S. C., and M. L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84:133-144.
- Chang, S. C., and M. L. Jackson. 1958. Soil phosphorus fractionations in some representative soils. J. Soil Sci. 9:109-119.
- Chao, T. T., and Liyi Zhou. 1983. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. Soil Sci. Soc. Am. J. 47: 225-232.
- Chapman, H. D. 1965. Cation exchange capacity. In C. A. Black et al. (ed.) Method of soil analysis. Agronomy 9:891-901.
- Charoenchamratchee, C., B. Tantisira, P. Chitnusun, and V. Sin-Aiem. 1982. The effects of liming and fertilizer applications of acid sulfate soils for improvement of rice production in Thailand. p. 157-171. In H. Dost and N. van Breemen (ed.) Proc Bangkok symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Chen, C. C., J. B. Dixon, and F. T. Turner. 1980. Iron coatings on rice roots: morphology and models of development. Soil Sci. Soc. Am. J. 44:113-1119.
- Chenery, E. M. 1954. Acid sulfate soils in Central Africa. Int. Congr. Soil Sci. Trans. 5th (Leopoldville) IV:195-198.
- Cho, D. Y., and F. N. Ponnamperna. 1971. Influence of soil temperature on the chemical kinetics of flooded soils and the growth of rice. Soil Sci. 112:184-1119.

- Cholitzkul, W., and E. H. Tyner. 1971. Inorganic phosphorus fractions and their relation to some lowland rice soils of Thailand. Proceedings of the international symposium soil fertility eval., New Delhi 1:7-20.
- Clark, R. B. 1977. Effect of aluminium on growth and mineral elements of Al-tolerant and Al-intolerant corn. Plant and Soil 47:653-662.
- Clark, J. S., C. A. Gobin and P. N. Sprout. 1961. Yellow mottles in some poorly drained soils of the lower Fraser Valley, British Columbia. Can. J. Soil Sci. 41:218-227.
- Clarkson, D. T. 1965. The effect of aluminium and some other trivalent metal cations on cell division in the root apices of Allium cepa. Ann. Bot. 29: 309-315.
- Clarkson, D. T. 1967. Interactions between aluminum and phosphorus on root surfaces and cell wall materials. Plant and Soil 27:347-356.
- Clarkson, D. T. 1969. Metabolic aspects of aluminium toxicity and some possible mechanisms for resistance. p. 381-397. In I.H. Rorison (ed.) Ecological Aspects of the Mineral Nutrition of Plants. Blackwell, Oxford.
- Clarkson, D. T. and Sanderson, J. 1971. Inhibition of the uptake and long distance transport of calcium by aluminium and other polyvalent cations. J. Exp. Bot. 2: 837-751.
- Cole, C. V., and M. L. Jackson. 1950. Solubility equilibrium constant of dihydroxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. Soil Sci. Soc. Am. Proc. 15:84-88.
- Collins, J.F., and S.W. Buol. 1970a. Pattern of iron and manganese precipitation under specified Eh-pH conditions. Soil Sci. 110:157-162.
- Collins, J.F., and S.W. Buol. 1970b. Effect of fluctuations in the Eh-pH environment of iron and/or manganese equilibria. Soil Sci. 110:111-118.
- Connell, W. E., and W. H. Patrick. 1968. Sulphate reduction in soil. Effects of redox potential and pH. Science 159:86-87.
- Connell, W. E., and W. H. Patrick. 1969. Reduction of sulphate to sulphide in waterlogged soil. Soil Sci. Soc. Am. Proc. 33:711-715.
- Conner, S. D. and O. H. Sears 1922. Aluminum salts and acids at varying hydrogen concentration, in relations to plant growth in water cultures. Soil Sci. 13:23-41.
- Coulter, J. K. 1973. The management of acid sulfate soils and pseudo-acid sulfate soils for agriculture and other uses. p. 255-274. In H. Dost (ed.) Acid sulfate soils. Proc. Int. Symp. ILRI Pub. 18, Vol. I. Wageningen, The Netherlands.

- Crawford, R. M. M. 1966. The control of anaerobic respiration as a determining factor in the distribution of the genus *Senecio*. *J. Ecol.* 54:403-413.
- Crawford, R. M. M., and P. D. Tyler. 1969. Organic acid metabolism in relation to flooding tolerance in roots. *J. Ecol.* 57:235-244.
- Das, D. K., and R.L. Jat. 1972. Adaptability of maize to high soil water conditions. *Agron. J.* 64:849-850.
- Das, D. K., and R. L. Jat. 1977. Influence of three soil-water regimes on root porosity and growth of four rice varieties. *Agron. J.* 69(2):197-200.
- De Gee, J. C. 1950. Preliminary oxidation potential determination in a "Sawah" profile near Bogor, Java. *Trans. Int. Congr. Soil Sci.* 1:300-303.
- De Kock, P. C., and R. L. Mitchell. 1957. Uptake of chelated metals by plants. *Soil Sci.* 84:55-62.
- Dent, D. 1986. Acid sulphate soils: a baseline for research and development. ILRI Pub. 39, Wageningen, The Netherlands.
- Dent, D. L., and R. W. Raiswell. 1982. Quantitative models to predict the rate and severity of acid sulfate development: a case study in The Gambia. p. 73-95. In H. Dost and N. van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- De, P. K. and L. N. Mandal. 1957. Physiological disease of rice. *Soil Sci.* 84:367-376.
- Dhanpat, R., and W. L., Lindsay. 1975. A thermodynamic model for predicting the formation, stability, and weathering of common soil minerals. *Soil Sci. Soc. Am. Proc.* 39:991-996.
- Driessen, P. M. and Ismangun. 1973. Pyrite containing sediments of southern Kalimantan, Indonesia: their soils, management and reclamation. p. 345-348. In H. Dost (ed.) *Acid sulfate soils*. *Proc. Int. Symp.* ILRI Pub. 18, Vol. II., Wageningen, The Netherlands.
- Engelstad, O. P., A. Jugsujinda, and S. K. Dedatta. 1974. Response by flooded rice to phosphate rocks varying to citrate solubility. *Soil Sci. Soc. Am. Proc.* 38:524-529.
- Engler, R. M., and W. H. Patrick, Jr. 1973. Solubilization of minerals by flooded soil as affected by chemical oxidants. *Soil Sci.* 95:115-114.
- Environmental Protection Agency. 1983. Method for chemical analysis of water and wastes. U. S. Environmental Protection Agency. Office of Technology Transfer. Washington, D. C. EPA-600/4-79-020.

- Evans, H., and R. B. Cate, Jr. 1962. Studies in the improvement of problem soils in British Guiana. *World Crops* 14:370-373.
- Fageria, N. K. 1985. Influence of aluminum in nutrient solutions on chemical composition in two rice cultivars at different growth stages. *Plant and Soil* 85:423-429.
- Fageria, N. K. and J. R. P. Carvalho. 1982. Influence of aluminum in nutrient solution on chemical composition in upland rice cultivars. *Plant and Soil* 69:31-44.
- Fanning, D. S. 1978. Soil morphology, genesis, classification, and geography. Dep. of Agron. Univ. of Maryland.
- FAO/UNESCO. 1979. Soil map of the world, scale 1:5,000,000. Volumes I-X, UNESCO, Paris.
- Fleming, A. L., and C. D. Foy. 1968. Root structure reflects differential aluminum tolerance in wheat varieties. *Agron. J.* 60:172-176.
- Foy, C. D. 1974. Effect of aluminum on plant growth. p. 601-642. In E. W. Carson (ed.) *The plant root and its environment* Univ. Press of Virginia, Charlottesville.
- Foy, C. D., W. H. Armiger, L. W. Briggie, and D. A. Reid. 1965. Differential aluminum tolerance of wheat and barley varieties in acid soil. *Agron. J.* 57:113-4517.
- Foy, C. D., H. N. Lafever, J. W. Schwartz, and A. L. Fleming. 1974. Aluminum tolerance of wheat cultivars related to region of origin. *Agron. J.* 66:751-758.
- Foy, C. D., R. L. Chaney, and M. C. White. 1978. The physiology of metal toxicity in plants. *Annu. Rev Plant Physiol.* 29:511-566.
- Francis, C. M., A. C. Devitt, and P. Steele. 1974. Influence of flooding on the alcohol dehydrogenase activity of roots of Trifolium subterraneum L. *Aust. J. Plant Physiol.* 1:9-13.
- Fukui, H. 1973. Environmental determinants affecting the potential productivity of rice: A case study of the Chao Praya river basin of Thailand. Ph.D. diss. Kyoto Univ., Japan.
- Furbish, W. J. 1963. Geologic implications of jarosite, pseudomorphs after pyrite. *Am. Mineral.* 48:703-706.
- Gambrell, R. P., R. A. Khalid, M. G. Verloo, and W. H. Patrick, Jr. 1975. Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Part II. Materials and methods, results and discussion.



- Garrels, R. M., and C. L. Christ. 1965. Solutions minerals and equilibria. Harper, New York.
- Goldhaber, M. B., and I. R. Kaplan. 1974. The sulfur cycle. p. 527-655. In E. D. Goldberg (ed.) The sea, Vol. 5, Marine chemistry. Wiley Interscience, New York.
- Gotoh, S., and Y. Onikura. 1971. Organic acids in flooded soil receiving added rice straw and their effect on the growth of rice. Soil Sci. Plant Nutr. 17:1-8.
- Gotoh, S., and W. H. Patrick, Jr. 1972. Transformation of manganese in a waterlogged soil as affected by redox potential and pH. Soil Sci. Soc. Am. Proc. 36:783-742.
- Gotoh, S., and W.H. Patrick, Jr. 1974. Transformation of iron in a waterlogged soil as affected by redox potential and pH. Soil Sci. Soc. Am. Proc. 38:66-71.
- Graetz, R. A., D. R. Keeney and R. B. Aspiras. 1973. Eh status of Lake sediment-water systems in relation to nitrogen transformation. Limnol. Oceanogr. 18:908.
- Green, M. S. and J. R. Etherington. 1977. Oxidation of ferrous iron by rice (*Oryza sativa* L.) roots: a mechanism for waterlogging tolerance? J. Exp. Bot. 28:678-690.
- Grime, J. P, and J. G. Hodgson. 1969. An investigation of the ecological significant of lime-chlorosis by means of large-scale comparative experiments. p. 67-99. In I.H. Rorison (ed.) Ecological aspects of the mineral nutrition of plants, Blackwell Scientific Publ., Oxford, England.
- Gunawardena, I. W. 1979. Field screening for tolerance to iron toxicity and phosphorus deficiency. Paper presented at the International Rice Research Conference, April 16-20, 1979. Los Banos, Philippines.
- Hackett, C. 1962. Stimulative effects of aluminum on plant growth. Nature 195:471-472.
- Harmsen, K., and N. van Breemen. 1975. Translocation of iron in acid sulfate soils. II. Production and diffusion of dissolved ferrous iron. Soil Sci. Soc. Am. Proc. 39:1148-1153.
- Haque, I. 1977. Iron toxicity in Sierra Leone rice. Int. Rice Res. Newl. 2(1):10.
- Hart, M. G. R., A. J. Carpenter, and J. W. O. Jeffery. 1963. Problems in reclaiming saline mangrove soils in Sierra Leone. Agron. Trop. 18:800-802.

- Harter, R. D. and E. O. McLean. 1965. The effect of moisture level and incubation time on the chemical equilibria of a Toledo clay loam soil. *Agron. J.* 57:583.
- Hartwell, B. L. and F. R. Pember. 1918. The presence of aluminum as reason for the difference in the effect of so-called acid soil on
- Hesse, P. R. 1963. Phosphorus relationships in a mangrove swamp mud with particular reference to aluminum toxicity. *Plant and Soil.* 19:205-218.
- Hollis, J. P. 1967. Toxicant diseases of rice. *Louisiana Agr. Exp. Sta. Bull* 614.
- Hook, D. D., C. L. Brown, and P. P. Kormanik. 1971. Inductive flood tolerance in swamp tupelo [*Nyssa sylvatica* var. *biflora* (Walt.) Sarg.]. *J. Exp. Bot.* 22:78-89.
- Howeler, R. H. 1973. Iron-induced organo-oxidizing disease of rice in relation to physico-chemical changes in a flooded oxisol. *Soil Sci. Soc. Am. Proc.* 37:898-903.
- Howeler, R. H., and L. E. Cadavid. 1976. Screening of rice cultivars for tolerance to Al toxicity in nutrient solutions as compared with a field screening method. *Agron. J.* 68:551-555.
- Ikehashi, H. and F. N. Ponnampereuma. 1978. Varietal tolerance of rice for adverse soils. p. 801-823. In F. N. Ponnampereuma (ed.) *Soils and Rice*. International Rice Research Institute, Los Banos, Philippines.
- Imaizumi, K., and S. Yoshida. 1958. Edaphological studies on silicon supplying power of paddy soils. *Bull. Natl. Inst. Agric. Sci. B,* 8:261-304.
- IRRI (International Rice Research Institute). 1964. Annual Report 1964. Los Banos, Philippines. 335 p.
- IRRI (International Rice Research Institute). 1954. Annual Report 1965. Los Banos, Philippines. 335 p.
- IRRI (International Rice Research Institute). 1966. Annual Report 1966. Los Banos, Philippines. 357 p.
- IRRI (International Rice Research Institute). 1967. Annual Report 1967. Los Banos, Philippines. 308 p.
- IRRI (International Rice Research Institute). 1970. Annual Report 1969. Los Banos, Philippines. 266 p.
- IRRI (International Rice Research Institute). 1971. Annual Report 1970. Los Banos, Philippines. 265 p.

- IRRI (International Rice Research Institute). 1973. Annual Report 1972. Los Banos, Philippines. 246 p.
- IRRI (International Rice Research Institute). "Research Highlights" in the International Rice Research Institute Annual Report 1973. Los Banos, Philippines.
- IRRI (International Rice Research Institute). 1979. Annual Report for 1978. Los Banos, Philippines. 478 p.
- IRRI (International Rice Research Institute). 1985. Annual Report for 1984. Los Banos, Philippines. 504 p.
- Islam, A., and M. A. Elahi. 1954. Reversion of ferric iron to ferrous iron under waterlogged conditions and its relation to available phosphorus. *J. Agr. Sci.* 45:1-2.
- Ivarson, K. C., G. J. Ross, and N. M. Miles. 1982. Microbiological transformations of iron and sulfur and their applications to acid sulfate soils and tidal marshes. p. 57-76. In J. A. Kittrick, D. S. Fanning, and L. R. Hossner (ed.) *Acid sulfate weathering*. Spec. Pub. 10. Soil Science Society of America, Madison, WI.
- Jackson, W. T. 1955. Role of adventitious roots in the recovery of shoots following the flooding of original root system. *Am. J. Bot.* 42:816-819.
- Jackson, M. L. 1958. *Soil chemical analysis*. Prentice-Hall Inc., Englewood Cliffs, New Jersey.
- Jackson, M. B., K. Gales, and D. J. Campbell. 1978. Effect of waterlogged soils conditions on the production of ethylene and on water relationships in tomato plants. *J. Exp. Bot.* 29:183-193.
- Jakobsen, P., W. H. Patrick, Jr., and B. G. Williams. 1981. Sulfide and methane formation in soils and sediments. *Soil Sci.* 132:279-287.
- Jansson, S. L. 1958. Tracer studies on nitrogen transformations in soil with special attention to mineralization-immobilization relationships. *Kungl. Lantbr. Ann.* 24:101-361.
- Jenne, E. A. 1977. Trace element sorption by sediments and soils - sites and processes. p. 425-553. In W. Chappel and K. Petersen (ed.) Vol. 2. *Symposium and molybdenum in the environment*. Marcel Dekker Inc. New York, U.S.A.
- Jensen, C. R., L. H. Stolzy, and J. Letey. 1967. Tracer studies of oxygen diffusion through roots of barley, corn and rice. *Soil Sci.* 103:23-29.
- John, C. D., and H. Greenway. 1976. Alcoholic fermentation and activity of some enzymes in rice roots under anaerobiosis. *Aust. J. Plant Physiol.* 3:325-336.

- John, C. D., V. Limpinuntana, and H. Greenway. 1974. Adaptation of rice to anaerobiosis. *Aust. J. Plant Physiol.* 1:513-520.
- Jones, J. P., and R. L. Fox. 1978. Phosphorus nutrition of plants influenced by manganese and aluminum uptake from an Oxisol. *Soil Sci.* 126(4):230-236.
- Joshi, M. M., I. K. A. Ibrahim, and J. P. Hollis. 1973. Oxygen release from rice seedlings. *Physiol. Plant* 29:269-271.
- Jugsujinda, A. 1976. Growth and nutrient uptake by rice under controlled oxidation-reduction and pH conditions in a flooded soil. Ph.D. diss., Louisiana State Univ., Baton Rouge.
- Jugsujinda, A., P. Duangpattra, S. Suwanwaong, and B. R. Jackson. 1971. Sources of rock phosphates and their residual effects on flooded rice. Paper presented at the 3rd TVA Meeting of Advisory Committee on Rice Fertilization, Muscle Shoal, Alabama, U.S.A.
- Jugsujinda, A., and S. Suwanwaong. 1972. Sources of phosphate for flooded rice. Paper presented at the 4th TVA Meeting of Advisory Committee on Rice Fertilization, Bangkok, Thailand.
- Jugsujinda, A., and S. Suwanwaong. 1973. Sources of rock phosphate for flooded rice. *Proc. 2nd Asean Soil Conf., Soil Res. Inst. Bogor, Indonesia.* 11:251-265.
- Jugsujinda, A., Y. Tadashi, and N. van Breemen. 1978. Aluminum toxicity and phosphorus deficiency in acid sulfate soils of Thailand. *International Rice Research Newsletter, IRRI.* 3(1).
- Kanareugsa, C., J. Somboondumrongkul, and J. Takahashi. 1983. Attempt at improving the productivity of acid sulfate soils. Paper No. 9. In *KU/FFTC (ed.) Ecology and management of problem soils in Asia.* Kasetsart Univ., Bangkok, Thailand.
- Kanareugsa, C., and Y. Chantrataragul. 1972. Liming effects on the growth and yield of rice in combination with various rates of nitrogen and phosphate. *Annual Research Report on Rice Fertilization Experiment for 1971.* Soil Fertility Branch, Technical Division, Rice Department, Ministry of Agriculture, Thailand.
- Kawaguchi, K., and K. Kyuma. 1969. Lowland rice soils in Thailand. *Nat. Sci. Ser. N-4.* Center for Southeast Asian Studies, Kyoto University. 270 p.
- Kawaguchi, K., and Kyuma. 1977. Paddy soils in Tropical Asia. Their nature and fertility. *Monographs of the Center of Southeast Asian Studies, Kyoto University.* 258 p.
- Kawalec, A. 1973. World distribution of acid sulphate soils. p. 292-295. In H. Dost (ed.) *Acid sulphate soils.* *Proc. Int. Symp. ILRI Pub.* 18, Vol. I., Wageningen, The Netherlands.

- Kawase, M. 1974. Role of ethylene in induction of flooding damage in sunflower. *Physiol. Plant.* 31:29-38.
- Kawase, M. 1978. Anaerobic elevation of ethylene concentration in waterlogged plants. *Amer. J. Bot.* 65:736-740.
- Kawase, M. 1981. Effect of ethylene on aerenchyma development. *Amer. J. Bot.* 68:651-658.
- Kawase, M., and R. E. Whitmoyer. 1980. Aerenchyma development in waterlogged plants. *Amer. J. Bot.* 65:736-740.
- Kerridge, P. C., M. D. Dawson, and D. P. Moore. 1971. Separation of degrees of aluminum tolerance in wheat. *Agron. J.* 63:586-591.
- Keve, W. Vander, and B. Yenmanas. 1972. Detailed reconnaissance soil survey of Southern Central Plain area. Soil survey report no. 89 LDP, Bangkok, Thailand.
- Khalid, R. A., W. H. Patrick, Jr. and F. J. Peterson. 1976. Relationships between soil phosphorus and rice yield as affected by aerobic and anaerobic soil conditions. *Proc. 16th Rice Tech. Working Group*, 103-104, Lake Charles, Louisiana.
- Khalid, R. A., W. H. Patrick, Jr. and R. D. Delaune. 1977. Phosphorus sorption characteristics of flooded soils. *Soil Sci. Soc. Am. J.* 41:305-310.
- Khasawneh, T. E. 1971. Solution ion activity and plant growth. *Soil Sci. Soc. Am. Proc.* 35:426-436.
- Kittrick, J. A. 1977. Mineral equilibria and the soils system. pp. 1-25. In J. B. Dixon and S. B. Weed (ed.) *Minerals in soil environments*. Soil Science Society of America, Madison, WI.
- Kittrick, J. A., and M. L. Jackson. 1955. Rate of phosphate reaction with soil minerals and electron microscope observation and on the reaction mechanism. *Soil Sci. Soc. Am., Proc.* 19:292-295.
- Koenig, F. F. R. 1950. A "sawah" profile near Bogor (Java). *Trans. Fourth Int. Congr. Soil Sci.* 1:297-300.
- Komes, A. 1973a. The reclamation of some problem soils in Thailand. *Soils of the ASPAC Region; Part 5. Thailand, Tech. Bull. 14.* Food and Fertilizer Technology Center, Taipei.
- Komes, A. 1973b. Reclamation and maintenance of fertility of major soils in Thailand. *Thai J. Agric. Sci.* 6:127-143.
- Kordan, H. A. 1974. The rice root in relation to oxygen supply and root growth in seedlings germinating under water. *New Phytol.* 73:695-697.

- Koyama, T., Chammek, and P. Snitwongse. 1973. Varietal difference of Thai rice in resistance to phosphorus deficiency. Tech Bull. 4. TARC, Min. Agric. For., Japan. 32 p.
- Lafever H. N., L. G. Campbell, and C. D. Foy. 1977. Differential response of wheat cultivars to Al. Agron. J. 69:563-568.
- Lance, J. C. and R. W. Pearson. 1969. Effects of low concentrations of aluminum on growth and water and nutrient uptake by cotton roots. Soc. Soil Sci. Am. Proc. 33:95-98.
- Lee, J. and M. W. Pritchard. 1984. Aluminum toxicity expression on nutrient uptake, growth and root morphology of Trifolium repens L. cv. 'Grasslando Huia'. Plant and Soil. 82:101-116.
- Lee, K. K., T. Castro, and T. Yoshida. 1977. Nitrogen fixation throughout growth and varietal differences in nitrogen fixation by the rhizosphere of rice planted in pots. Plant and Soil 48:613-619.
- Lee, K. K., and T. Yoshida. 1977. An assay technique of measurement of nitrogen activity in root zone of rice for varietal screening by the acetylene reduction method. Plant and Soil 46:126-134.
- Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley, New York.
- MacLean, A. A., and T. C. Chiasson. 1966. Differential performance of two barley varieties to varying aluminium concentrations. Can. J. Soil Sci. 46:147-153.
- MacLeod, L. B., and I. P. Jackson. 1967. Aluminum tolerance of two barley varieties in nutrient solution, peat, and soil culture. Agron. J. 59:359-363.
- Magistad, O. C. 1925. The aluminium content of the soil solution and its relation to soil reaction and plant growth. Soil Sci. 20:181-227.
- Mahapatra, I. C. 1966. Soil phosphate transformations under various soil-water conditions. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Maneewon, M., N. Thawornwong, and B. Tantisira. 1982. Study on rates of marl for rice production on acid sulfate soils in Thailand. p. 172-186. In H. Dost and N. van Breemen (ed.) Proc. Bangkok Symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Marius, C. 1982. Acid sulphate soils of the mangrove area of Senegal and Gambia. p. 103-136. In H. Dost and N. van Breemen (ed.) Proc. Bangkok Symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Marwaha, R. S., and B. O. Juliano. 1976. Aspects of nitrogen metabolism in rice seedling. Plant Physiol. 57:923-927.

- Matsuguchi, T., B. Tangcham, and S. Pakiyuth. 1970. Nitrogen-fixing microflora and its activity in paddy soil of Thailand. Proc. 1st Asean Soil Conf., Bangkok, Thailand.
- Maurya, D. M. 1978. Anatomical basis of flood resistance in rice. Indian Journal of Genetics and Plant Breeding 38(2):184-185.
- McCormick, L. H., and F. Y. Borden. 1974. The occurrence of aluminium phosphate precipitate in plant roots. Soil Sci. Soc. Am. Proc. 38:931-934.
- McKeague, J. A., and M. G. Cline. 1963. Silica in soils. Adv. Agron. 15:339-396.
- McLean, F. T., and B. E. Gilbert. 1927. The relative aluminium tolerance of crop plants. Soil Sci. 24:163-175.
- McManmon, M., and R. M. M. Crawford. 1971. A metabolic theory of flooding tolerance: the significance of enzyme distribution and behavior. New Phytol. 70:299-306.
- Mitsui, S. Dynamic Aspects of Nutrient Uptake. p. 53 In The Mineral Nutrition of the Rice Plant. John Hopkins Press, Baltimore, Md.
- Mitsui, S., S. Aso, and K. Kumazawa. 1951. Dynamic studies on the nutrient uptake by crop plants I. The nutrient uptake of rice roots as influenced by hydrogen sulfide (in Japanese, English summary). J. Sci. Soil Manure, Japan. 22:46-52.
- Miyake, K. 1916. The toxic action of soluble aluminium salts upon the growth of the rice plant. J. Biol. Chem. 25:23-38.
- Moorman, F. R. 1963. Acid sulfate soils (cat-clay) of the tropics. Soil Sci. 95: 271-275.
- Moorman, F. R. 1963. Characteristics and improvement of acid sulfate soils (Part 2). On the forms of oxidizable sulphur. J. Sci. Soil Manure, Japan. 38:117-120.
- Mortimer, C. H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29:280-329.
- Motomura, S. 1961. Dissolution of iron compounds in soils by milk vetch extract. Soil Sci. Plant Nutr. 7:54-60.
- Motomura, S. 1962. Effect of organic matters on the formation of ferrous iron in soils. Soil Sci. Plant Nutr. 8:20-29.
- Motomura, S., A. Sieryosakul, and W. Cholitkul. 1975. Liming effect on the growth and yield of rice in combination with various rates of nitrogen and phosphorus on acid sulfate soils. In International Rice Research Conference contribution 13. Los Banos, Philippines. 9p.

- Mugwira, L. M., S. M. Elgawhary, and K. I. Patel., 1976. Differential tolerance of triticale, wheat, rye and barley to aluminium in nutrient solution. *Agron. J.* 68:782-787.
- Muljadi, D., A. M. Posner, and J. P. Quirk. 1966. Mechanism of phosphate absorption by kaolinite, gibbsite, and pseudoboehmite. Part I. The isotherms and the effect of pH on adsorption. *J. Soil Sci.* 17:212-229.
- Munns, D. N. 1965. Soil acidity and growth of legume. II. Reactions of aluminium and phosphate in solution and effects of aluminium, phosphate, calcium and pH on Medicago sativa L. and Trifolium subterraneum L. in solution culture. *Aust. J. Agric. Res.* 16: 743-755.
- Nissenbaum, A., B. J. Presley and I. R. Kaplan. 1972. Early diagenesis in a reducing fjord, Saanich inlet, British Columbia-I. Chemical and Isotopic Changes in Major Components of Interstitial Water. *Geochim. Cosmochim. Acta* 36:1007.
- Nhung, M. M., and F. N. Ponnamperna. 1966. Effects of calcium carbonate, manganese dioxide, ferric hydroxide, and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulfate soil. *Soil Sci.* 102:29-41.
- Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. p. 37-56. In J. A. Kittrick, D. S. Fanning, and L. R. Hossner (ed.) *Acid sulfate weathering*. Spec. Pub. 10, Soil Science Society of America, Madison, WI.
- Okazaki, M., and H. Wada. 1976. Some aspects of pedogenic processes in paddy soils. *Pedologist* 20:139-150.
- Okuda, A., and E. Takahashi. 1965. The role of silicon. p. 123-146. In *The mineral nutrition of the rice plant*. Johns Hopkins Press, Baltimore, Maryland.
- Osborne, J.F. 1984. Soil analysis as a guide to acidity classes in mature acid sulfate soils of the Southern Central Plain of Thailand. p. 10-23. In *Proceedings of the 5th ASEAN soil conference on "Soil Science as a Tool for Rural Development."* Bangkok, Thailand.
- Osugi, S., and K. Kawaguchi. 1938. A physiological disorder associated with application of ammonium sulfate in paddy rice (In Japanese, English summary). *J. Sci. Soil Manure, Japan.* 12:453-462.
- Ota, Y. 1968. Studies on the occurrence of the physiological disease of rice called "bronzing" (In Japanese with English summary). *Bull. Natl. Inst. Agric. Sci. Nishigahara. Tokyo. Japan. Series D. No.* 18:97-100.
- Ottow, J. C. G., G. Benckiser, and I. Watanabe. 1982. Iron toxicity of rice as a multiple nutritional stress. *Trop. Agric. Res. Ser.* (Japan) 15:167-179.



- Ottow, J. C. G., G. Benckiser, I. Watanabe, and S. Santiago. 1983. Multiple nutritional stress as the prerequisite for iron toxicity of wetland rice (*Oryza sativa* L.) Trop. Agric. (Trinidad) 60:102-106.
- Ottow, J. C. G., and H. Glathe. 1971. Isolation and identification of iron reducing bacteria from gley soils. Soil Biol. Biochem. 3:43-55.
- Panabokke, C. R. 1975. Problem rice soils in Sri Lanka. Paper presented at the International Rice Research Conference, April 21-24, 1975. Los Banos, Philippines. 5 p.
- Park, N. J., Y. S. Park, K. H. Lee, and Y. S. Kim. 1972. The effect of limie and wollastonite on an acid sulfate soil. J. Korean Soc. Soil Fert. 5:25-32.
- Park, Y. D., and A. Tanaka. 1968. Studies of the rice plant on an "Akiochi" soil in Korea. Soil Sci. Plant Nutr. 14:27-34.
- Pasricha, N. S. and F. N. Ponnampuruma. 1976. Influence of salt and alkali on ionic equilibria in submerged soils. Soil Sci. Soc. Am. J. 40:374-380.
- Patrick, W. H., Jr. 1960. Nitrate reduction rates in a submerged soil as affected by redox potential. Trans. Seventh Int. Congr. Soil Sci. 2:494-500.
- Patrick, W. H., Jr. 1964. Extractable iron and phosphorus in submerged soils at controlled redox potential. Int. Congr. Soil Sci., Trans. 8th, Bucharest, Romania. IV:605-608.
- Patrick, W.H., Jr., B.G. Williams, and J.T. Moraghan. 1973. A simple system for controlling redox potential and pH in soil suspensions. Soil Sci. Soc. Am. Proc. 37:331-332.
- Patrick, W. H., Jr. and D. S. Mikkelsen. 1971. Plant nutrient behavior in flooded soils. p. 187-125. In R.C Dinaouer (ed.) Fertilizer Technology and Use. 2nd ed. Soil Science Society of America, Madison, WI.
- Patrick, W. H., Jr., D. S. Mikkelsen, and B. R. Wells. 1985. Plant nutrient behavior in flooded soil. p. 197-228. In Fertilizer Technology and Use. 3rd ed. Soil Science Society of America, Madison, WI.
- Patrick, W. H., Jr. and I. C. Mahapatra. 1968. Transformation and availability to rice of nitrogen and phosphorus in waterlogged soils. Adv. Agron. 20:323-359.
- Patrick, W. H., Jr., and K. R. Reddy. 1976. Nitrification reactions in flooded soils and water bottoms: dependence on oxygen supply and ammonium diffusion. J. Environ. Qual. 5:469-472.

- Patrick, W. H., Jr., and K. R. Reddy. 1978. Chemical changes in rice soils. p. 361-380. In F. N. Ponnamperna (ed.) Soils and Rice. International Rice Research Institute, Los Banos, Laguna, Philippines.
- Patrick, W. H., Jr., and R. A. Khalid. 1974. Phosphate release and sorption by soils and sediments effect of aerobic and anaerobic conditions. Science 186:53-55.
- Patrick, W. H., Jr. and R. D. Delaune. 1972. Characterization of the oxidized and reduced zones in flooded soils. Soil Sci. Soc. Am. Proc. 36:573.
- Patrick, W. H., Jr. and R. Wyatt. 1964. Soil nitrogen loss as result of alternate submergence and drying. Soil Sci. Soc. Am. Proc. 28:647-653.
- Patrick, W. H., Jr., S. Gotoh, and B. G. William. 1973. Strengite dissolution in flooded soils and sediments. Science 179:564-472.
- Pawluk, S., and M. Duda. 1978. Reorganization of soil materials in the genesis of an acid sulfate Luviolic soil of the Peace River region. Alberta. Can. J. Soil Sci. 58:209-220.
- Pearsall, W. H. 1938. The soil complex in relation to plant communities. I. Oxidation-reduction potentials in soils. J. Ecol. 26:180-193.
- Pearsall, W. H., and C. H. Mortimer. 1939. Oxidation-reduction potentials in soils, natural water and muds. J. Ecol. 27:483-501.
- Pearson, G. A. 1961. The salt tolerance of rice. Int. Rice Comm. Newsl. 10:1-4.
- Pearson, G. S. 1959. Factors influencing salinity of submerged soils and growth of Calora rice. Soil Sci. 87:198-206.
- Peech, M. 1965. Exchange acidity. In C. A. Black et al. (ed.) Method of soil analysis. Agronomy 9:905-926.
- Pierre, W. H., and A. D. Stuart. 1933. Soluble aluminium studies: The effects of phosphorus in reducing the detrimental effects of soil acidity on plant growth. Soil Sci. 36:211-227.
- Pitts, R. G. 1971. Exploration in the chemistry and microbiology of Louisiana rice plant-soil relationship. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Poelman, J. N. B. 1973. Soil material rich in pyrite in non-coastal areas. p. 197-207. In H. Dost (ed.) Acid sulphate soils. Proc. Int. Symp. ILRI Pub. 18, vol. II, Wageningen, The Netherlands.

- Ponnamperuma, F. N. 1955. The chemistry of submerged soils in relation to the growth and yield of rice. Ph.D. diss. Cornell Univ., Ithaca, N. Y.
- Ponnamperuma, F. N. 1958. Lime as a remedy for a physiological disease of rice associated with excess iron. *Int. Rice Comm. Newsl.* 7(1):10-13.
- Ponnamperuma, F. N. 1965. Dynamic aspects of flooded soils and the nutrition of the rice plant. p. 295-328, 461-462. In *The mineral nutrition of the rice plant*. John Hopkins Press, Baltimore, Md.
- Ponnamperuma, F. N. 1967. A theoretical study of aqueous carbonate equilibria. *Soil Sci.* 103:90-100.
- Ponnamperuma, F. N. 1972. Chemistry of submerged Soils. *Adv. Agron.* 24:29-95.
- Ponnamperuma, F. N. 1978. Electrochemical changes in submerged soils and the growth of rice. p. 421-441. In F.N. Ponnamperuma (ed.) *Soils and Rice*. International Rice Research Institute. Los Banos, Laguna, Philippines.
- Ponnamperuma, F. N., E. Martinez, and T. Loy. 1966. Influence of redox potential and partial pressure of carbon dioxide in pH values and the suspension effect of flooded soils. *Soil. Sci.* 101:421-431.
- Ponnamperuma, F. N., and J. L. Solivas. 1982a. Field amelioration of an acid sulfate soil for rice with manganese dioxide and lime. p. 213-22. In H. Dost and van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Ponnamperuma, F. N., and J. L. Solivas. 1982b. Varietal reactions of rice to iron toxicity of an acid sulfate soil. p. 213-222. In H. Dost and N. van Breemen (ed.) *Proceedings of the Bangkok symposium on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Ponnamperuma, F. N., R. Bradfield, and M. Peech. 1955. Physiological disease of rice attributable to iron toxicity. *Nature* 175:265.
- Ponnamperuma, F. N., T. A. Loy, and E. M. Tianco. 1969. Redox equilibria in flooded soils: II. The manganese oxide systems. *Soil Sci.* 108:48-57.
- Ponnamperuma, F. N., T. Attanandana, and G. Beye. 1973. Amelioration of three acid sulfate soils for lowland rice. p 391-406. In H. Dost (ed.) *Acid sulphate soils*. *Proc. Int. Symp.* ILRI Pub. 18, vol. II, Wageningen, The Netherlands.
- Pons, L. J. 1973. Outline of the genesis, characteristics, classification, and improvement of acid sulfate soils. p. 3-27. In H. Dost (ed.) *Acid sulphate soils*. *Proc. Int. Symp.* ILRI Pub. 18, Vol. I, Wageningen, The Netherlands.

- Pons, L. J., and N. van Breemen. 1982. Factors influencing the formation of potential acidity in tidal swamps. p. 37-51. In H. Dost and N. van Breemen (ed.) Proc. Bangkok Symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Pons, L. J., N. van Breemen, and P. M. Driessen. 1982. Physiography of coastal sediments and developments of potential soil acidity. p. 1-18. In J. A. Kittrick, D. S. Fanning, and L. R. Hossner (ed.) Acid sulfate weathering. Spec. Pub. 10, Soil Science Society of America, Madison, WI.
- Pons, L. J. and W. van der Kevie. 1969. Acid sulphate soils in Thailand. Soil Survey Rept., Land Dev. Dept., Bangkok, SSR-81. 69p.
- Postgate, J. R. 1959. Sulfate reduction by bacteria. Ann. Rev. Microbiol. 13:505-520.
- Presley, B. J., and I. R. Kaplan. 1968. Changes in dissolved sulfate, calcium and carbonate from interstitial water of near-shore sediments. Geochim. Cosmochim. Acta 32:1037-1048.
- Rao, D. N., and D. S. Mikkelsen. 1977. Effect of rice straw additions on production of organic acids in a flooded soil. Plant and Soil 47:303-311.
- Rasmussen, G. K. 1975. Cellulase activity, endogenous abscisic acid, and ethylene in four citrus cultivars during maturation. Plant Physiol. 56:765-767.
- Reddy, C.N., Aroon Jugsujinda, and W.H. Patrick, Jr. 1976. A system for growing plants under controlled redox potential conditions. Agron. J. 68:987-989.
- Redman, F. H., and W. H. Patrick, Jr. 1965. Effect of submergence on several biological and chemical soil properties. La. Agr. Exp. Sta. Bull. 592.
- Reid, D. A., A. L. Fleming, and C. D. Foy. 1971. A method for determining aluminium response of barley in nutrient solution in comparison to response in Al-toxic soil. Agron. J. 63:600-603.
- Reid, D. A., G. D. Jones, W. H. Armiger, C. D. Foy, E. J. Koch, and T. M. Starling. 1969. Differential aluminium tolerance of winter barley varieties and selections in associated greenhouse and field experiments Agron. J. 61:218-222.
- Rickard, D. T. 1973. Sedimentary iron sulphid formation. p. 28-62. In H. Dost (ed.) Acid sulphate soils. ILRI Pub. 18, Vol. I, Wageningen, The Netherlands.
- Rickard, D. T. 1975. Kinetics and mechanism of pyrite formation at low temperatures. Am. J. Sci. 275:636-652.

- Roberts, W. M. B., A. L. Walker, and A. S. Buchanan. 1969. The chemistry of pyrite formation in aqueous solution and its relation to the depositional environment. *Mineral. Deposita* 4: 18-29.
- Rodrigo, D. M. 1963. Redox potential with special reference to rice culture. *Trop. Agr.* 69:2-16.
- Rojanasoonthon, S. 1978. Rice soils of Thailand. p. 73-85. In F. N. Ponnampetuma (ed.) *Soils and rice*. International Rice Research Institute, Los Banos, Philippines.
- Rorison, I. H. 1965. The effect of aluminium on the uptake and incorporation of phosphate by excised Sainfoin roots. *New Phytol.* 64:23-27.
- Rorison, I. H. 1972. The effect of extreme soil acidity on the nutrient uptake and physiology of plants. p. 223-254. In H. Dost (ed.) *Acid sulfate soils*. Proc. Int. Symp. ILRI Pub. 18, Vol. I, Wageningen, The Netherlands.
- Ross, G. J., K. G. Ivarson, and N. M. Miles. 1982. Microbial Formation of Basic Ferric Sulfates in Laboratory systems and in soils. p. 77-94. In J. A. Kittrick, D. S. Fanning, and L. R. Hossner (ed.) *Acid sulfate weathering*. Spec. Pub. 10. Soil Science Society of America, Madison, WI.
- Russell, E. W. 1961. *Soil Conditions and plant growth*, Ed. 9. Longmans, Green and Co., Ltd., London. 688 p.
- Sahu, B. M. 1968. Bronzing disease of rice in Orissa as influence by soil types and manuring and its control. *J. India Soc. Soil Sci.* 16:41-54.
- Sanchez, P. A., and A. M. Briones. 1973. Phosphorus availability of some Philippine rice soils as affected by soil and water management practices. *Agron. J.* 65:226-228.
- SAS Institute. 1985. *SAS user's guide: Statistics*, Version 5th ed. SAS Institute Inc., Cary, NC, USA.
- Satawathananont, S. 1986. Redox, pH, and ion chemistry of acid sulfate rice soils in Thailand. Ph.D. diss. Louisiana State Univ., Baton Rouge.
- Savant, N. K., and R. Ellis, Jr. 1964. Changes in redox potential and phosphorus availability in submerged soil. *Soil Sci.* 98:388-394.
- Singer, P. C. and W. Stumm. 1970. Acidic mine drainage: the rate determining step. *Science* 167: 1121-1123.
- Shapiro, R. E. 1958a. Effect of flooding on availability of phosphorus and nitrogen. *Soil Sci.* 85:190.

- Shapiro, R. E. 1958b. Effect of organic matter and flooding on availability of soil and synthetic phosphates. *Soil Sci.* 85: 267-272.
- Sheikh, K. H. 1973. Effects of flooding and drainage and their alternation on the growth and uptake of nutrients by rice. *Oryza satvia* L., indica, var. IR-8. *J. Exp. Bot.* 24:64-75.
- Sholkovitz, e. 1973. Interstitial water chemistry of the Santa Barbara basin sediments. *Geochim. Cosmochim. Acta* 37:2043.
- Sloutmaker, L. A. J. 1974. Tolerance to high soil acidity in wheat related species, rye and triticale. *Euphytica* 23:505-162.
- Sloutmaker, L. A. J., and J. E. Arzadun. 1969. Selection of young barley plants for tolerance to high soil acidity in relation to some agronomic characteristics of mature plants. *Euphytica* 18:157-162.
- Soileau, J. M., P. O. Engelstad, and J. B. Martin. 1969. Cotton growth in an acid fragipan sub-soil. II. Effects of soluble calcium, magnesium and aluminium on roots and tops. *Soil Sci. Soc. Am. Proc.* 33:919-924.
- Sombatpanit, S. 1970. Acid sulfate soils: Their nature and properties. Unpublished Thesis Royal Agric. C
- Sombatpanit, S. 1975. Improvement of acid sulfate soil in Thailand. *Int. Rice Res. Conf. Contrib.* 26. 3 p.
- Sombatpanit, S., and L. Wangpaiboon. 1973. Study on the lime requirement of an aluminum-rich sulfate soil. Paper presented at Twelfth Conf. Agric. Biol. Sci. Kasetsart University, Bangkok, Thailand.
- Sparks, D.L. 1984. Ion activities: an historical and theoretical overview. *Soil Sci. Soc. Am. J.* 48:514-518.
- Sposito, G. 1981. The thermodynamics of soil solutions. Oxford University Press, London.
- Sposito, G. 1984. The future of an illusion: ion activities in soil solution. *Soil Sci. Soc. Am. J.* 48:531-536.
- Sposito, G., and S. V. Mattigod. 1977. On the chemical foundation of the sodium adsorption ratio. *Soil Sci. Soc. Am. J.* 41:323-329.
- Sposito, G., and S. V. Mattigod. 1979. GEOCHEM: A computer program for the calculation of chemical equilibria in soil solution and other natural water systems. Kearny Foundation of Soil Science, Univ. of Calif., Riverside.
- Starkey, R. L., and H. O. Halvorson. 1927. Studies on the transformation of iron in nature. Part 2. Concerning the importance of microorganisms in the solution and precipitation of iron. *Soil Sci.* 24:381-402.

- Steel, R. G. D., and J. H. Torrie. 1980. Principles and procedures of statistics. McGraw-Hill, New York.
- Stumm, W., and J. J. Morgan. 1981. Aquatic chemistry. John Wiley, New York.
- Sturgis, M. B. 1936. Changes in oxidation-reduction equivalent in soils as related to the physical properties of the soil and the growth of rice. La. Agric. Exp. Sta., Bull. No. 271.
- Suwanwaong, S. 1960. A summary report on the efficiency of nitrogenous and phosphatic fertilizers for rice in Thailand. Tech. Bull., Tech. Div., Rice Dep., Bangkok, Thailand.
- Sweeny, R. E., and I. R. Kaplan. 1973. Pyrite framboid formation: laboratory synthesis and marine sediments. Econ. Geol. 68:618-634.
- Takai, Y. 1961. The reduction of paddy soils and microbial metabolism. Technics for Agriculture 16:213-216.
- Takai, Y. and T. Kamura. 1966. The mechanism of reduction in waterlogged paddy soil. Folia Microbiol. 11:304-313.
- Takijima, Y. 1964. Studies on the mechanism of root damage of rice plants in the peat paddy fields. I. Root damage and growth inhibitory substances found in the peaty and peat soil. Soil Sci. Plant Nutr. 10:231-238.
- Tanaka, A., R. Loe, and S. A. Navasero. 1966. Some mechanisms involved in the development of iron toxicity symptoms in the rice plant. Soil Sci. Plant Nutr. 12:158-164.
- Tanaka, A., R. P. Mulleriyawa, and T. Yasu. 1968. Possibility of hydrogen sulfide induced iron toxicity of the rice plant. Soil Sci. Plant Nutr. 14:1-6.
- Tanaka, A., and S. A. Navasero. 1966a. Aluminum toxicity of the rice plant under water culture conditions. Soil Sci. Plant Nutr. 12:55-60.
- Tanaka, A., and S. A. Navasero. 1966b. Growth of the rice plant on acid sulfate soils. Soil Sci. Plant Nutr. 12:107-114.
- Tanaka, A., and S. A. Navasero. 1966c. Chlorosis of the rice plant induced by high pH of culture solution. Soil Sci. Plant Nutr. 12:213-219.
- Tanaka, A., and S. A. Navasero. 1967. Carbon dioxide and organic acids in relation to the growth of rice. Soil Sci. Plant Nutr. 13:25-30.
- Tanaka, A., and S. Yoshida. 1970. Nutritional disorders of the rice plant in Asia. Int. Rice Res. Inst., Tech. Bull. 10. 51p.

- Temple, K. L., and A. R. Colmer. 1951. The autotrophic oxidation of iron by a new bacterium: Thiobacillus ferrooxidans. J. Bacteriol. 62:605-611.
- Tian-ren, Yu. 1985. Physical chemistry of paddy soils. Science Press, Beijing and Springer-verlag, New York. 217 p.
- Thawornwong, N., and A. van Diest. 1974. Influence of high acidity and aluminium on the growth of lowland rice. Plant and Soil 41:107-114.
- Thompson, J. G. 1972. Occurrence of acid sulphate soil in Rhodesia. Rhodesian Journal of Agriculture Research 10. p. 153-157.
- Tomlinson, T. E. 1957. Changes in sulphide-containing mangrove soil on drying and their effect upon the suitability of the soil for the growth of rice. Empire J. Exp. Agr. 25:108-118.
- Toure, M. 1982. Improvement of acid sulfate soils: effects of lime, wood ash, green manure, and preflooding. p. 223-236. In H Dost and N. van Breemen (ed.) Proc. Bangkok Symp. on acid sulfate soils. ILRI Pub. 31, Wageningen, The Netherlands.
- Turner, P. D., and R. A. Bull. 1967. Diseases and disorders of the oil palm in Malaysia. Incorporated Society of Planters, Kuala Lumpur.
- Turner, F. T., and W. H. Patrick, Jr. 1968. Chemical changes in waterlogged soils as a result of oxygen depletion. Int. Congr. Soil Sci., Trans. 9th, Adelaide, Australia. IV:53-65.
- Tyler, P. D., and R. M. M. Crawford. 1970. The role of shikimic acid in waterlogged roots and rhizomes of *Iris pseudacorus* L. J. Exp. Bot. 21:677-682.
- United States Department of Agriculture. 1954. L. A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. USDA Agric. Handbook No.60, U.S. Government Printing Office, Washington, D.C.
- United States Department of agriculture. 1975. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA Agric. Handbook No. 436, U.S. Government Printing Office, Washington, D.C.
- Uwanliyom, J., and C. Charoenchamratcheep. 1983. Liming of acid sulfate paddy soils of Bangkok Plain. Paper No. 10. In KU/FFTC (ed.) Ecology and management of problem soils in Asia. Kasetsart Univ., Bangkok, Thailand.
- Valencia, I. G. 1962. The effect of flooding on the availability of phosphorus and on the growth of lowland rice. Ph.D. diss. Univ. of Wisconsin, Madison.
- Vamos, R. 1967. The role of reduction processes in soil in the formation in adventitious root in rice. Soil Fert. Abstr. 30:2438.



- van Breemen, N. 1971. Method of analysis. Laboratory information paper no. 3. Soil Survey Div., Bangkok, Thailand.
- van Breemen, N. 1973. Soil forming processes in acid sulfate soils. p. 66-130. In H. Dost (ed.) Acid sulfate soils. ILRI Pub. 18, Vol. I., Wageningen, The Netherlands.
- van Breemen, N., and L. J. Pons. 1978. Acid sulfate soils and rice. P. 739-762. In F.N. Ponnampereuma (ed.) Soils and rice. International Rice Research Institute, Los Banos, Philippines.
- van Breemen, N. 1975. Acidification and deacidification of coastal plain soils as a result of periodic flooding. Soil Sci. Soc. Am. Proc. 39:1153-1157.
- van Breemen, N. 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. Agric. Res. Rep. 848, PUDDC, Wageningen. 263 p.
- van Breemen, N. 1982. Genesis, morphology, and classification of acid sulfate soils in coastal plains. p. 95-108. In J. A. Kittrick, D. S. Fanning, and L. R. Hossner (ed.) Acid sulfate weathering Spec. Pub. 10. Soil Science Society of America, Madison, WI.
- van Breemen, N. and F. R. Moormann. 1978. Iron toxic soils. p. 781-800. In F. N. Ponnampereuma (ed.) Soils and Rice. International Rice Research Institute, Los Banos, Laguna, Philippines.
- Vangnai S., T. Attanandana, and A. Tawetekul. 1974. Sulfide formation and rice yield in Ongkarak soils (in Thai, English summary) Kasetsart J. 8:23-27.
- van Wallenburg, C. 1973. Cat-clay soils and potential cat-clays in inland polders in the western part of the Netherlands. p 264-283. In H. Dost (ed.) Acid sulfate soils. ILRI Pub. 18, Vol. I., Wageningen, The Netherlands.
- Varade, S. B., J. Letey, and L. H. Stolozy. 1970. Crop adaptation to high soil water conditions. Calif. Agric. 24:15.
- Virmani, S. S. 1978. Some results of varietal screening for tolerance to iron toxicity in Liberia. Paper presented at the International Rice Research Conference, April 17-21, 1978. Los Banos, Philippines. 9p.
- Wagner, D. P., D. S. Fanning, J. E. Foss, M. S. Patterson, and P. A. Snow. 1982. Morphological and mineralogical features related to sulfide oxidation under natural and disturbed land surfaces in Maryland. p. 109-125. In J. A. Kittrick, D. S. Fanning, and L. R. Hossner (ed.) Acid sulfate weatherings Spec. Pub. 10, American Society of Agronomy, Madison, Wis.
- Waring, S. A., and J. M. Bremner. 1964. Ammonium production in soil under waterlogged conditions as an index of nitrogen availability. Nature 201:951-952.

- Watts, J. C. D. 1969. Phosphate retention in acid sulfate pond muds from the Malacca area. *Malays. Agric. J.* 14:187-202.
- Woolhouse, H. W. 1969. Differences in the properties of the acid phosphatases of plant roots and the significance in the evolution of edaphic ecotypes. p. 357-380. In I.H. Rorison (ed.) *Ecological aspects of the mineral nutrition of plants*. Brit. Ecol. Soc. Symp. 9, Blackwell Scientific Publ., Oxford, England.
- Wright, K. E. 1937. Effects of phosphorus and lime in reducing aluminium toxicity of acid soils. *Plant Physiology* 12:173-181.
- Wright, K. E. 1943. Internal precipitation of phosphorus in relation to aluminium toxicity. *Plant Physiology* 18:708-712.
- White, R. E. 1977. Studies on mineral absorption by plants. III. The interaction of aluminium. Phosphate and pH on the growth of *Medicago sativa*. *Plant and Soil* 46:195-208.
- Xuan, Vo-Tong, Nguyen Kim Oquang and Le Quang Tri. 1982. Rice cultivation on acid sulfate soils in the Vietnamese Mekong Delta. p. 251-259. In H. Dost and van Breemen (ed.) *Proc. Bangkok Symp. on acid sulfate soils*. ILRI Pub. 31, Wageningen, The Netherlands.
- Yamada, N., and Y. Ota. 1958. Study on the respiration of crop plants (8). Effect of hydrogen sulfide and lower fatty acids on the respiration of root in rice plant. *Proc. Crop Sci. Soc. Jpn.* 27:155-160.
- Yamane, I. 1958. Metabolism in muck paddy soil. 2. Determination of gases evolved from paddy field estimation of decomposable organic matter. *Soil Plant Food* 4:25-31.
- Yamane, I. 1974. Solution pH of submerged soils. *Rep Inst. Agric. Res Tohoku Univ.* 25:1-11.
- Yamane, I. 1978. Chemical changes in submerged soils and their effect on rice growth. p. 381-397. In F.N. Ponnampurna (ed.) *Soils and Rice*. International Rice Research Insititute, Los Banos, Laguna, Philippines.
- Yamane, I. 1978. Electrochemical changes in rice soils. p. 381-397. In F.N. Ponnampurna (ed.) *Soils and Rice*. International Rice Research Insititute. Los Banos, Laguna, Philippines.
- Yamane, I., and K. Sato. 1967. Effect of temperature on the decomposition of organic substances in flooded soil. *Soil Sci. Plant Nutr.* 13:94-100.
- Yoshida, S. and T. Tadano. 1978. Adaptation of plants to submerged soils. p. 233-255. In Jung, G.A. (ed.) *Crop Tolerance to Suboptimal Land Conditions*. Spec. Pub. 32, American Society of Agronomy, Madison, WI.

- Yoshida, S. 1981. Fundamentals of rice crop science. IRRI. Los Banos, Laguna, Philippines. 269 p.
- Yoshida, S., D. A. Forno, J. H. Cock, and K. A. Gomez. 1976. Laboratory manual for physiological studies of rice. Int. Rice Res. Inst., Los Banos, Philippines. 83 p.
- Yoshida, T., and F. E. Broadbent. 1975. Movement of atmospheric nitrogen in rice plants. Soil Sci. 120:288-291
- Yoshida, T., and R. R. Ancajas. 1973. Nitrogen fixing activity in upland and flooded rice fields. Soil Sci. Soc. Am. Proc. 37:42-46.
- Yoshida, T., Y. Takai, and D. C. Del Rosario. 1975. Molecular nitrogen content in a submerged rice field. Plant and Soil 42:653-660.
- Yuan, T. L., W. K. Robertson, and J. R. Neller. 1960. Forms of newly fixed phosphorus in three acid sandy soils. Soil Sci. Soc. Am. Proc. 42:447-450.

## VITA

Jirapong Prasittikhet was born 22 June, 1947 in Uthai Thani, Thailand. He received a B.S. degree in Soil Science in 1970 from Kasetsart University, Bangkok.

He began his professional career as a research fellow in the Department of Agriculture in 1970. He received the USAID scholarship for his graduate study at the University of Arkansas, in 1975. He received an M.S. in Agronomy in 1977 and returned to his post in Thailand.

He attended Louisiana State University in January 1983 for his advanced study in Agronomy which was financially supported by the USAID project. He is presently a candidate for the doctorate of Agronomy.

His permanent address is 52/69 Soi Thawon, Sukhapiban 1 Road, Klongkoom, Bangkok, Bangkok 10240, Thailand.

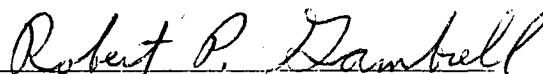
## DOCTORAL EXAMINATION AND DISSERTATION REPORT


Candidate: Jirapong Prasittikhet

Major Field: Agronomy

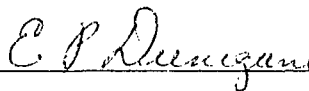
Title of Dissertation: Metal Availability and Rice Growth Under Controlled  
Redox Potential and pH Conditions in Acid Sulfate  
Soils of Thailand

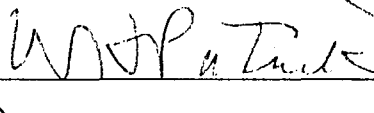
Approved:

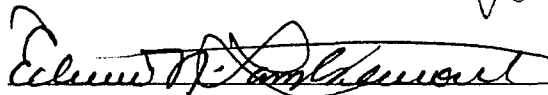
  
Major Professor and Chairman

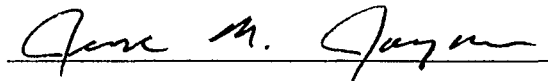
  
Dean of the Graduate School

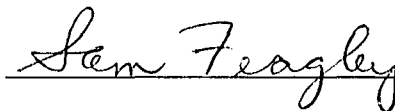
### EXAMINING COMMITTEE:











Date of Examination:

October 1, 1987