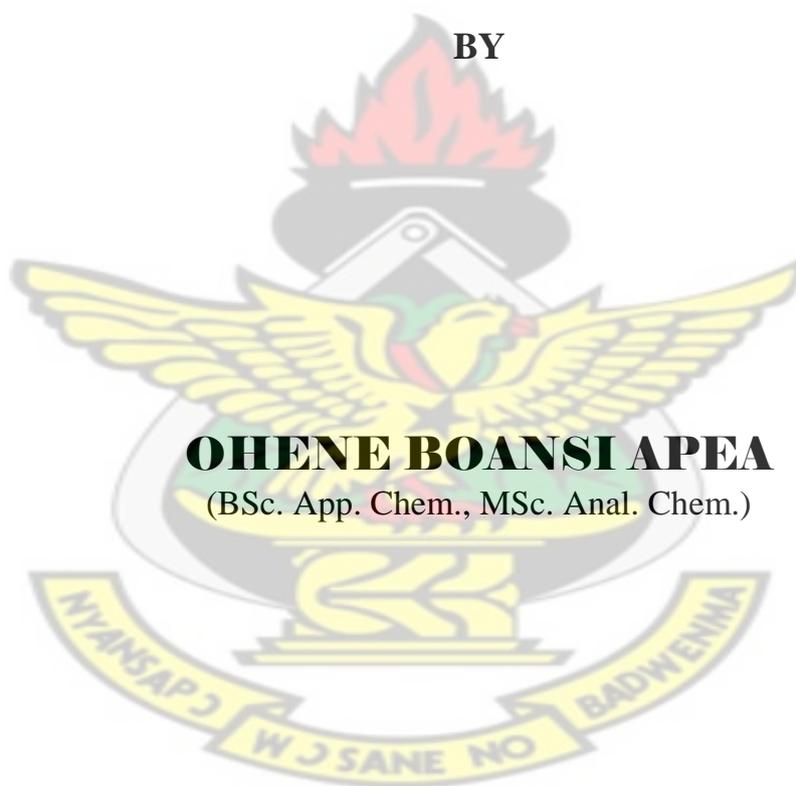


***Modeling the Role of Humic Substances in the
Distribution of Trace Metals in Selected
Ecosystems in Ghana***

KNUST

BY



OHENE BOANSI APEA

(BSc. App. Chem., MSc. Anal. Chem.)

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY,
KWAME NKURUMAH UNIVERSITY OF SCIENCE AND
TECHNOLOGY IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
FACULTY OF SCIENCE

APRIL, 2015

DEDICATION

This thesis is dedicated to my father Ohene Apea-Kubi (Prof.), mentor Professor James, H. Ephraim, my beloved wife Christiana and son Jason, and daughter Janina and also my siblings.

KNUST



CERTIFICATION

I, Ohene Boansi Apea, hereby declare that this submission is my own work towards the PhD and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of this University, except where due acknowledgement has been made in the text.

Ohene Boansi Apea
Signature Date

Certified by:
Prof. J. H. Ephraim
(Supervisor) Signature Date

Certified by:
Dr. Godfred Darko
(H. O. D) Signature Date

ABSTRACT

The complexity of semi-natural ecosystems in terms of the composition and chemical properties of the solid and solution phases has caused researchers to develop intelligent and innovative ways of modeling and using the models to describe the chemistry of metal distribution in natural environments. But a comprehensive model that adequately describes the role humic substances play in trace metal distribution in semi-natural ecosystems is absent. The colloidal properties and aggregation properties at cloud point have not been effectively correlated with its cation binding properties. In view of these the role of humic substances in trace metal distribution at the mining communities at Talensi-Nabdam District of Upper East Region of Ghana were modeled in this study. Development of the models was based on the novel idea that there is a relationship between the fraction of metal associated with humic matter, intrinsic properties of the humic matter and metal partition constant. A quantitative account of the role of humic substance in metal distribution was studied using component factor analysis approach to model the speciation and distribution phenomena of trace metals at the selected ecosystem for the study. The properties of humic substance and the interactions of trace metals were correlated and used to develop mathematical models for the description of the role of humic substance in metal partition. The conceptual and mathematical models were proved to have the potential to explain the humic-impacted-partition of trace metals when they were fitted to data obtained from field and simulation experiments. The distribution model explained 97.99% of the factors which influence trace metal distribution in the terrestrial environment out of which humic substances accounts for more than 30 % of all the factors. The speciation model also showed that humic substances account for

13.06% of the variables which determine trace metal speciation at the ecosystem studied. It was concluded that humic substances play a significant role in trace metal distribution in terrestrial environment. The mathematical models gave good correlations and R^2 values when fitted to data from simulation experiments. The models described the trace metal partition well in terms of humic acid (HA) complexation and partition. The overall impression of the models is that HA influences Cu distribution in soil solution system to an extent determined by the relative proportion of other cations which compete with the metal for both the humic acid and the soil mineral. The models also indicated that modification of the solid phase by HA introduces two major heterogeneous binding sites in the solid phase (i.e., the organic and inorganic binding sites) and that changes in the relative moles of the site types are determined by the cation binding and hydrophobic properties of HA. The models indicated that the properties of humic substance which makes it capable of influencing trace metal distribution are hydrophobicity, detergent properties and metal complexing ability.

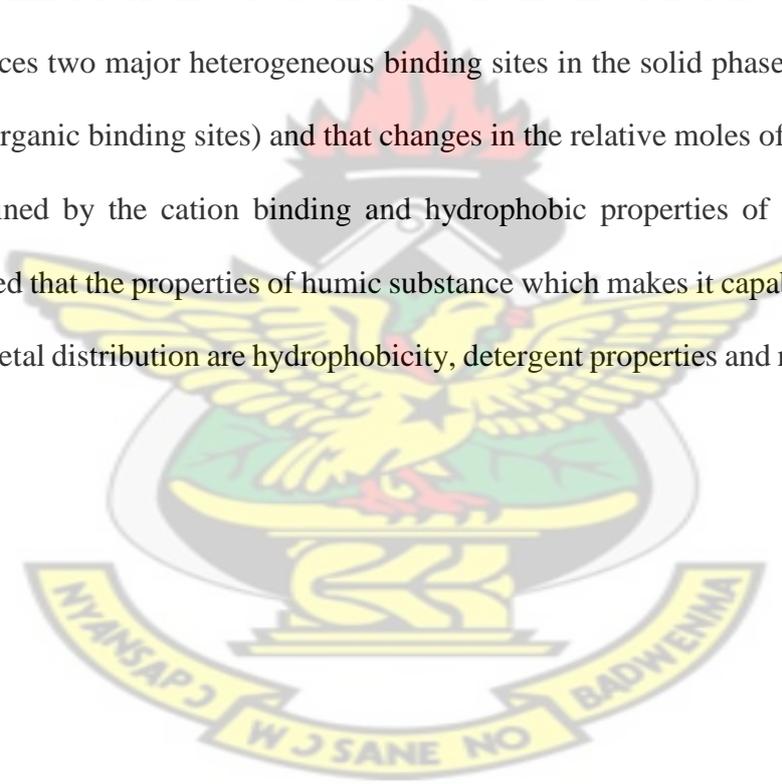


TABLE OF CONTENTS

| | |
|---|--------------|
| DEDICATION..... | III |
| CERTIFICATION..... | IV |
| ABSTRACT..... | V |
| LIST OF TABLES..... | XVI |
| LIST OF FIGURES..... | XVIII |
| ACKNOWLEDGEMENT..... | XXII |
| CHAPTER ONE | |
| 1.0 INTRODUCTION..... | 1 |
| 1.2 BACKGROUND OF THE PROJECT..... | 4 |
| 1.3 SIGNIFICANCE OF THE PROJECT..... | 5 |
| 1.4 PROBLEM STATEMENT..... | 6 |
| 1.5 GENERAL OBJECTIVES..... | 13 |
| 1.6 SPECIFIC OBJECTIVES..... | 13 |
| 1.7 SCOPE OF THE STUDY..... | 15 |
| CHAPTER TWO | |
| LITERATURE REVIEW..... | 16 |
| 2.0 DESCRIPTION OF HUMIC SUBSTANCES..... | 16 |
| 2.1 HUMIC SUBSTANCE INTERACTION AND MODELS..... | 20 |
| 2.2 METAL SORPTION..... | 24 |
| 2.3 EFFECTS OF COMPLEXING AGENTS..... | 25 |

| | | |
|---------|--|----|
| 2.4 | RELATIVE EFFECTIVENESS OF DIFFERENT SORBENTS | 27 |
| 2.5 | SURFACE COATING | 29 |
| 2.6 | SORPTION KINETICS OF TRACE ELEMENTS IN SOLIDS AND SOLID MATERIALS | 30 |
| 2.7 | DIFFERENT FORMS OF METALS IN SOIL | 32 |
| 2.8 | ASSOCIATIONS OF SOIL COLLOIDS | 35 |
| 2.9 | EVIDENCE OF METAL ORGANIC INTERACTION..... | 36 |
| 2.9.1 | <i>Density of reactive sites on metal-(oxyhydr)oxide surfaces.....</i> | 36 |
| 2.9.2 | <i>Conceptual Models of the Metal Oxide/Aqueous Solution Interface Region.....</i> | 39 |
| 2.9.2.1 | General comments on the structure and reactivity of hydrated metal oxide surfaces:..... | 39 |
| 2.9.2.2 | Acid-base reactions at metal-(oxyhydr)oxide-water interfaces: | 40 |
| 2.9.2.3 | Differences in reactivity of different metal oxide surfaces:..... | 42 |
| 2.9.2.4 | Ligand-exchange reactions: | 45 |
| 2.9.2.5 | Oxidation-reduction (redox) reactions on metal oxide surfaces: | 47 |
| 2.9.2.6 | The dynamic nature of metal-(oxyhydr)oxide surfaces— dissolution/precipitation reactions: | 48 |
| 2.9.2.6 | Effect of substitutional defects on surface reactivity: | 49 |
| 2.9.3 | <i>XAFS Spectroscopy Studies of Trace Cation Sorption</i> | 50 |
| 2.10 | EFFECTS OF COMPLEXING LIGANDS ON METAL ION | 53 |
| 2.11 | TERNARY SURFACE COMPLEXES | 54 |
| 2.12 | METAL ION-INORGANIC LIGAND COMPLEXES..... | 55 |
| 2.13 | NATURAL ORGANIC MATTER AND CATION-ORGANIC LIGAND COMPLEXES | 60 |
| 2.13.1 | <i>Natural Organic Matter (NOM) binding to mineral surfaces:</i> | 60 |

| | | |
|--------------------------|--|-----------|
| 2.13.2 | <i>Binding of aqueous cations to NOM:</i> | 62 |
| 2.13.3 | <i>Effects of adsorbed NOM on cation sorption:</i> | 64 |
| 2.13.4 | <i>Competition between NOM and mineral surfaces for cations:</i> | 68 |
| 2.14 | MODELING ION BINDING TO HUMIC SUBSTANCES: | 73 |
| 2.14.1.1 | ..Modeling Approach: Binding Sites and Complexation Reactions:..... | 77 |
| 2.14.1.2 | ..Electrostatic Effects:..... | 79 |
| 2.14.1.3 | Counterion Accumulation:..... | 84 |
| 2.14.2 | MODEL VI..... | 85 |
| 2.14.2.1 | ..Model description:..... | 85 |
| 2.14.2.2 | ..Binding sites and intrinsic equilibrium constants..... | 86 |
| 2.14.2.3 | ..Electrostatic effects:..... | 89 |
| CHAPTER THREE | | |
| 3.0 | METHODOLOGY | 93 |
| 3.1 | DESCRIPTION OF THE STUDY AREA | 93 |
| 3.1.1 | <i>Selected Ecosystems</i> | 93 |
| 3.1.2 | <i>Sampling Area</i> | 93 |
| 3.1.3 | <i>Topography and Drainage</i> | 95 |
| 3.1.4 | <i>Climate and Vegetation</i> | 95 |
| 3.2 | SAMPLING TECHNIQUE..... | 95 |
| 3.3 | SAMPLE PREPARATION..... | 96 |
| 3.4 | COLLECTION OF GIS DATA FROM THE STUDY AREA AND SELECTED ECOSYSTEMS..... | 96 |
| 3.5 | EXPERIMENTAL PROCEDURES | 97 |
| 3.5.1 | <i>Chemicals and Instruments</i> | 97 |
| 3.5.2 | <i>Nutrient Analysis</i> | 98 |

| | | |
|--------|---|-----|
| 3.6 | ACCOUNTING FOR THE AMOUNT OF HUMIC SUBSTANCES | 98 |
| 3.6.1 | <i>Determination of Organic Carbon</i> | 98 |
| 3.6.2 | <i>Preparation of Glucose Standards</i> | 99 |
| 3.7 | TOTAL TRACE METALS ANALYSIS | 100 |
| 3.7.1 | <i>Digestion of Solid Samples (DS):</i> | 100 |
| 3.7.2 | <i>Digestion of Liquid Samples (DL):</i> | 100 |
| 3.8 | HUMIC SUBSATANCE EXTRACTION, FRACTIONATION AND ISOLATION | 101 |
| 3.8.1 | <i>Extraction Fractionation and Isolation of Metal Bound Humic Substances:..</i> | 101 |
| 3.8.2 | <i>Extraction and Fractionation of Humic Substances in Soil Samples:</i> | 101 |
| 3.8.3 | <i>Isolation of Humic Substance Extracts for Interaction Experiments:</i> | 102 |
| 3.9 | DETERMINATION OF METAL AND HUMIC SPECIES IN SOIL SOLUTION SYSTEM..... | 103 |
| 3.10 | DETERMINATION OF METAL SPECIES IN THE TERRESTRIAL ENVIRONMENT | 105 |
| 3.10.1 | <i>Speciation Analysis Using Sequential Extraction Method</i> | 105 |
| 3.10.2 | <i>Digestion of extracts from speciation analysis</i> | 106 |
| 3.11 | CONTROLLED EXPERIMENTS..... | 107 |
| 3.11.1 | <i>Preparation of Soil Free of Humic Acid</i> | 107 |
| 3.11.2 | <i>Preparation of Preloaded Soil Samples</i> | 107 |
| 3.11.3 | <i>Determination of Equilibrium Time Under Humic Conditions</i> | 108 |
| 3.11.4 | <i>Determination of Equilibrium Time under Non-Humic Conditions</i> | 108 |
| 3.11.5 | <i>Determination of Equilibrium Constant at Different pH Under Humic Conditions</i> | 109 |

| | | |
|--|--|------------|
| 3.11.6 | <i>Determination of Equilibrium Constant at Different pH Under Non- Humic Conditions</i> | 111 |
| 3.11.7 | <i>Effect of Humic Acid Concentration on Metal Distribution in Soil Solution System</i> | 111 |
| 3.11.8 | <i>Effect of Background Electrolyte on the Interactions and</i> | 112 |
| 3.11.8.1 | <i>Aqueous Based Ternary System (Soil-Metal- HA):</i> | 112 |
| 3.11.8.2 | <i>Aqueous-Based Binary (Metal-Humic) System:</i> | 113 |
| 3.11.9 | <i>Effect of Temperature on Humic Acid Behaviour and Interactions</i> | 114 |
| 3.11.9.1 | <i>Aqueous Based Ternary System (Soil Metal-Humic):</i> | 114 |
| 3.11.9.2 | <i>Aqueous Based Binary System (Metal-Humic):</i> | 114 |
| DEVELOPMENT OF THE MODELS | | 115 |
| 3.13 | INTRODUCTION | 115 |
| 3.13.1 | <i>DEVELOPMENT OF THE CONCEPTUAL MODEL</i> | 117 |
| 3.13.2 | <i>DESCRIPTION OF SOLUTION PHASE CHARACTERISTICS</i> | 117 |
| 3.13.3 | <i>DESCRIPTION OF SOLID PHASE CHARACTERISTICS</i> | 119 |
| 3.13.4 | <i>MODELING ASSUMPTIONS AND CONDITIONS</i> | 122 |
| 3.13.5 | <i>HUMIC SUBSTANCE PARTITION AS A FUNCTION OF</i> | 124 |
| 3.13.5.1 | <i>Distribution in Soil-Solution System</i> | 124 |
| 3.13.5.2 | <i>Theory of humic substance partition in soil-solution system:</i> | 127 |
| 3.13.5.3 | <i>The relationship between K_{DL} and trace metal distribution in soil-solution system</i> | 129 |
| 3.13.6 | <i>MECHANISM OF ION ADSORPTION IN SOIL-SOLUTION SYSTEM</i> | 131 |
| 3.13.6.1 | <i>Ion Adsorption</i> | 131 |
| 3.13.6.2 | <i>Complexation Reactions</i> | 134 |
| 3.13.6.3 | <i>Ion Adsorption and Metal Partition</i> | 134 |

| | | |
|-------------------------------------|---|------------|
| 3.14 | DEVELOPMENT OF MATHEMATICAL MODELS | 136 |
| 3.14.1 | <i>MODELS DEVELOPED FOR LOW pH CONDITION</i> | <i>136</i> |
| 3.14.2 | <i>Determination of the relationship between ligand partition and K_{DM}.....</i> | <i>138</i> |
| 3.14.3 | <i>Determination of the effect of ligand partition on $[M]$, and Q_{ML}</i> | <i>138</i> |
| 3.15 | MODELS DEVELOPED FOR HIGH pH CONDITION..... | 140 |
| 3.15.1 | <i>Determination of the effect of ligand partition on K_{DM}.....</i> | <i>140</i> |
| 3.15.2 | <i>Determination of the relationship between the partition constant for metal- ligand complex and K_{DM}</i> | <i>141</i> |
| 3.16 | RELEVANCE OF THE MATHEMATICAL MODELS ADOPTED..... | 142 |
| 3.16.1 | <i>Effect of HS on Trace Metal Distribution</i> | <i>145</i> |
| 3.16.2 | <i>Distribution at low pH, constant temperature and pressure:</i> | <i>145</i> |
| 3.16.3 | <i>Distribution at high pH, constant temperature and pressure:</i> | <i>147</i> |
| CHAPTER FOUR..... | | 149 |
| RESULTS AND DISCUSSION | | 149 |
| 4.0 | INTRODUCTION..... | 149 |
| 5.1 | CHEMICAL CHARACTERIZATION OF THE TERRESTRIAL ENVIRONMENTS OF THE SELECTED ECOSYSTEMS IN GHANA..... | 150 |
| 4.1.1 | <i>TOPOGRAPHY AND MATERIAL TRANSPORT</i> | <i>150</i> |
| 4.1.2 | <i>CHARACTERIZATION OF THE STUDY ENVIRONMENT</i> | <i>152</i> |
| 4.1.3 | <i>SPATIAL DISTRIBUTION OF TRACE METALS AND SOIL PROPERTIES AT THE ECOSYSTEM.....</i> | <i>154</i> |
| 4.1.4 | <i>TRACE METAL DISTRIBUTION, AVAILABILITY AND TRANSPORT</i> | <i>161</i> |
| 4.2 | ENVIRONMENTAL CHARACTERISTICS AS A FUNCTION OF TRACE METAL DISTRIBUTION IN THE TERRESTRIAL ENVIRONMENT | 164 |

| | | |
|---------|--|-----|
| 4.2.1 | <i>DISTRIBUTION OF HUMIC SUBSTANCES IN SELECTED TERRESTRIAL ENVIRONMENTS</i> | 166 |
| 4.2.2 | <i>DISTRIBUTION OF METAL BOUND HUMIC SUBSTANCES</i> | 167 |
| 4.2.3 | <i>OTHER TRACE METAL SPECIES IN THE TERRESTRIAL ENVIRONMENTS</i> | 169 |
| 4.2.4 | <i>EQUILIBRIUM PARTITION OF TRACE METALS IN SELECTED TERRESTRIAL ENVIRONMENTS</i> | 170 |
| 4.2.5 | <i>Relationship between Metal Distribution and Characteristics of the Terrestrial Environment</i> | 172 |
| 4.2.5.1 | <i>Environmental Characteristics and their Effect on Metal Distribution</i> | 172 |
| 4.2.5.2 | <i>Relationship between Environmental Characteristics and Metal Distribution Constant</i> | 174 |
| 4.3 | ADSORPTION KINETICS AND INTRA-PARTICLE DIFFUSIVITIES OF Cu IN SOIL-SOLUTION SYSTEM | 177 |
| 4.3.1 | <i>The Effect of Humic Acid on the Kinetics of Trace Metal Distribution in Soil.</i> | 177 |
| 4.3.2 | <i>Distribution Constants of Metals in Soil Solution Systems under Humic and Non-humic Conditions.</i> | 178 |
| 4.3.3 | <i>Sorption Dynamics</i> | 180 |
| 4.3.4 | <i>Determination of Adsorption Rate Constants</i> | 181 |
| 4.3.5 | <i>Intra-Particle Diffusivity</i> | 184 |
| 4.3.6 | <i>Evaluation of Activation Energy</i> | 192 |
| 4.4 | EFFECT OF TEMPERATURE ON THE DYNAMICS OF METAL AND HUMIC ACID DISTRIBUTION IN TERRESTRIAL ENVIRONMENT | 193 |
| 4.4.1 | <i>Metal – Humic Interaction and Behaviour in Aqueous Solution</i> | 193 |

| | | |
|--------------------------|---|------------|
| 4.4.2 | <i>The Effect of Humic Acid on Trace Metal Distribution in Soil-Solution System at Different Temperatures</i> | 198 |
| 4.4.3 | <i>Temperature Dependence of Metal Partition Constant in Soil-Solution System</i> | 200 |
| 4.5 | EFFECT OF ELECTROLYTE BACKGROUND CONCENTRATION ON THE BEHAVIOUR OF METAL AND HUMIC ACID IN SOIL..... | 205 |
| 4.5.1 | <i>Aqueous Solution</i> | 205 |
| 5.5.2 | <i>Soil – Solution System</i> | 215 |
| 5.5.3 | <i>Modeling the Effect of Background Electrolyte</i> | 224 |
| 4.6 | THE DYNAMICS OF METAL AND HUMIC ACID INTERACTIONS IN SOIL-SOLUTION SYSTEM | 226 |
| 4.7 | RATIO OF METAL-OCCUPIED INORGANIC AND ORGANIC BINDING SITES IN THE SOLID PHASE OF SOIL-SOLUTION SYSTEM..... | 235 |
| 4.7.1 | <i>Effect of pH on the Ratio of Occupied-sites</i> | 237 |
| 5.7.2 | <i>The influence of Background Electrolyte on SR</i> | 242 |
| 4.7.3 | <i>The relationship between site ratio and metal partition</i> | 245 |
| 5.8 | SUITABILITY OF PROPOSED MODELS | 249 |
| 4:8.1 | <i>Test of Speciation Model</i> | 249 |
| 5.8.2 | <i>Test of Distribution Model</i> | 251 |
| 4.8.3 | <i>Suitability of Adopted Models</i> | 252 |
| 4.8.4 | <i>Effect of pH on Model Constants</i> | 257 |
| 4.9 | CHEMICAL IMPLICATION OF RELATIONSHIPS | 260 |
| CHAPTER FIVE..... | | 262 |
| 5.0 | CONCLUSION..... | 262 |
| 5.1 | CONCLUSIONS DRAWN ON OBJECTIVES | 262 |

6.2 NOVELTY 267

REFERENCES..... 270

APPENDIX 1 300

APPENDIX 2 301

APPENDIX 3 302

APPENDIX 4 303

APPENDIX 5 304

APPENDIX 6 305

APPENDIX 7 306

APPENDIX 8 307

APPENDIX 9 307

APPENDIX 10 308

APPENDIX 11 309

APPENDIX 12 310

APPENDIX 13 311

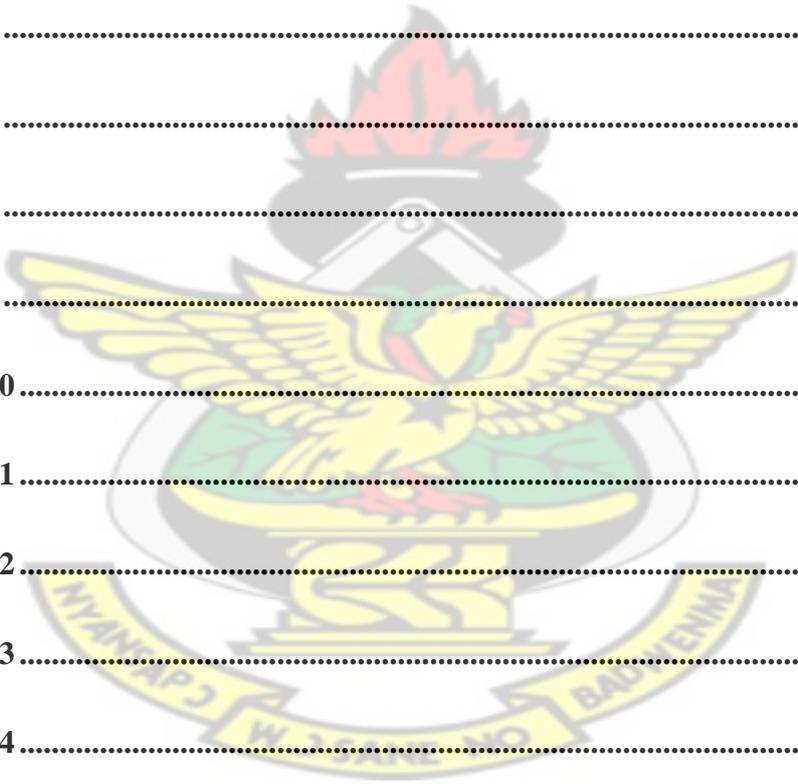
APPENDIX 14 312

APPENDIX 15 313

APPENDIX 16 321

APPENDIX 17 323

KNUST



LIST OF TABLES

| | |
|---|-----|
| Table 3.1: Mass of Cu added to soil samples..... | 107 |
| Table 3.2: Equilibrium time for metal partition in soil | 108 |
| Table 3.3: Mass of metal and humic acid components of the setup..... | 109 |
| Table 3.4 Mass of Cu in sample..... | 111 |
| Table 3.5 Composition of set up | 112 |
| Table 4.1: Concentration of Trace metals in sediment samples..... | 162 |
| Table 4.2: Variation in the concentration of metal species at the study area..... | 167 |
| Table 4.3: Proportion of metal species in the terrestrial environments..... | 170 |
| Table 4.4: Average KDM of the metals at the study area and ecosystems | 171 |
| Table 4.5: Free energy values of metal distribution at the study area and ecosystems* | 171 |
| Table 4.6: Principal characteristics of the terrestrial environment..... | 173 |
| Table 4.7: Multiple regression data for the relationship between KDM and characteristics of the terrestrial environment..... | 176 |
| Table 4.8: Pseudo second order rate law constants and statistics for metal adsorption in soil-solution system* | 182 |
| Table 4.9: Experimentally determined and predicted amount of metal adsorbed at equilibrium (mg/g)*..... | 183 |
| 4.3.5 Intra-Particle Diffusivity | 184 |
| Table 4.10: Intra-particle diffusion rate constants and activation energy for metal adsorption under non-humic conditions..... | 186 |
| Table 4.11: Intra-particle diffusion rate constants and activation energy for metal adsorption under humic conditions..... | 187 |

| | |
|--|-----|
| Table 4.12: Mass and concentration of solution species..... | 193 |
| Table 4.13: Stability constants and free energies of reactions in solution | 194 |
| Table 4.14: Mass (mg) of Metal and Humic Acid Species in Aqueous Solution | 206 |
| Table 4.15: Relationship between aggregation quotient and concentration of background electrolyte..... | 211 |
| Table 4.16: Relationship between stability constant of ML complex and concentration of background electrolyte..... | 214 |
| Table 4.17: Changes in the amount* of metal and ligand forms with Concentration Background Electrolyte in Soil-solution System..... | 216 |
| Table 4.18: Variation of aggregation quotient, stability and distribution constants with electrolyte concentration..... | 219 |
| Table 4.19: Relationship between aggregation quotient, stability and distribution constants with electrolyte concentration at pH 4.7 | 220 |
| Table 4.20: Relationship between aggregation quotient, stability and distribution constants with electrolyte concentration at pH 10 | 221 |
| Table 4.21: Changes in the amount* of metal and ligand forms with Mass of Metal-Added in Soil- solution System..... | 228 |
| Table 4.22: Variation of the Amounts of Metal-Bound Humic acid and Free Energies of Distribution and Metal Complexation with Added Metal..... | 229 |
| Table 4.23: Regression analysis of metal and humic interactions in soil-solution system | 232 |
| Table 4.24: Statistics of adopted models..... | 253 |
| Table 4.25: Statistics of Model 4 under varying conditions of background electrolyte | 256 |
| Table 4.26: Slopes of Models at the pH conditions studied..... | 257 |
| Table 4.27: Relationship between QML and KDM from field data | 260 |

LIST OF FIGURES

| | |
|--|-----|
| Figure 2.1: Model structure of fulvic acid..... | 18 |
| Figure 2.2: Model structure of humic acid | 18 |
| Figure 2.3: Chemical properties of humic substances | 19 |
| Figure 2.4: Forms of trace metals. | 33 |
| Figure 3.1: Map of Talensi-Nabdam District | 94 |
| Figure 3.2: Extraction and fractionation of metal and humic acid species from soil samples..... | 104 |
| Figure 3.3: A flow chart showing the fractionation and analysis of the components of soil – solution system | 110 |
| Figure 3.4: Extraction and fractionation of metal and humic acid species in aqueous-based binary systems | 113 |
| Figure 4.1 Illustration of the conceptual model of metal and humic acid interaction, and transfer between phases in soil-solution system | 128 |
| Figure 4.1: Map portraying topography, drainage paths and selected ecosystems at the study area | 151 |
| Figure 4.2: Maps showing the relationship between trace metal and the properties of the terrestrial environments at Accra | 158 |
| Figure 4.3: Maps showing the relationship between trace metal and the properties of the terrestrial environments at Kejetia | 159 |
| Figure 4.4: Maps showing the relationship between trace metal and the properties of the terrestrial environments at Tarkwa | 160 |
| Figure 4.5: Change in KDM with time: Change in KDM with time in soil containing HA at pHs 3.87, 4.7, 6.85 and 10. | 177 |
| Figure 4.6: Change in KDM with time: Change in KDM with time in soil free from HA at pHs 3.87, 4.7, 6.85 and 10. | 178 |
| Figure 4.7: Change in KDM with time under humic and non-humic conditions at pH 3.87. | 179 |
| Figure 4.8: Change in KDM with time under humic and non-humic conditions at pH 4.7. | 179 |

| | |
|--|-----|
| Figure 4.9: Change in KDM with time under humic and non-humic conditions at pH 6.85 | 180 |
| Figure 4.10: Change in KDM with time under humic and non-humic conditions at pH 10. | 180 |
| Figure 4.11: Linear plot representing second order rate model for metal adsorption in soil-solution system under non-humic conditions | 182 |
| Figure 4.12: Linear plot representing second order rate model for metal adsorption in soil-solution system under humic conditions | 183 |
| Figure 4.13: A plot of LDF model for metal adsorption in soil-solution system under non-humic conditions | 188 |
| Figure 4.14: A plot of LDF model for metal adsorption in soil-solution system under humic conditions | 188 |
| Figure 4.15: A plot of Weber-Morris model for metal adsorption in soil-solution system under non-humic conditions | 190 |
| Figure 4.16: A plot of Weber-Morris model for metal adsorption in soil-solution system under humic conditions | 190 |
| Figure 4.17: The variation of stability constant with temperature at pH 4.7 in aqueous solution. | 196 |
| Figure 4.18: The variation of stability constant with temperature at pH 10 in aqueous solution. | 196 |
| Figure 4.19: The variation of aggregation constant with temperature at pH 4.7 and 10 in aqueous solution. | 197 |
| Figure 4.20: The variation of aggregated (s), and un-aggregated (l) ligands with temperature at pH 4.7 and 10 in aqueous solution. | 198 |
| Figure 4.21: The variation of distribution constant with temperature at pH 4.7 and 10 in soil – solution system. | 198 |
| Figure 4.22: The variation of aggregation constant with temperature at pH 4.7 and 10 in soil - solution system. | 199 |
| Figure 4.23: Changes in Mass of un-aggregated (aq) metal bound to humic acid with concentration of background electrolyte at pH 4.7 and 10.... | 207 |
| Figure 4.24: Changes in Mass of aggregated (s) metal bound to humic acid with concentration of background electrolyte at pH 4.7 and 10..... | 207 |

| | |
|---|-----|
| Figure 4.25: Changes in Mass of aggregated (s) and un-aggregated (aq) humic acid (L) with concentration of background electrolyte at pH 4.7. | 208 |
| Figure 4.26: Changes in Mass of aggregated (s) and un-aggregated (aq) humic acid (L) with concentration of background electrolyte at pH 10..... | 208 |
| Figure 4.27: Changes in the extent of metal binding to un-aggregated humic acid (aq) with concentration of background electrolyte at pH 4.7and 10. | 209 |
| Figure 4.28: Changes in the extent of metal binding to aggregated humic acid in solution (s) with concentration of background electrolyte at pH 4.7and 10. | 209 |
| Figure 4.29: Variation of aggregation quotient with concentration of background electrolyte at pH 4.7 and 10. | 211 |
| Figure 4.30: Plot of predicted aggregation quotient with concentrated background electrolyte at pH 4.7 and 10. | 212 |
| Figure 4.31: Observed versus predicted aggregation quotient at pH 4.7. | 212 |
| Figure 4.32: Observed versus predicted aggregation quotient at pH 10. | 213 |
| Figure 4.33: Changes in free energy of aggregation with concentration of background electrolyte. | 214 |
| Figure 4.34: Mass of aggregated (s) and un-aggregated (aq) humic acid versus electrolyte concentration in soil-solution system at pH 4.7. | 216 |
| Figure 4.35: Mass of aggregated (s) and un-aggregated (aq) humic acid versus electrolyte concentration in soil-solution system at pH 10... | 217 |
| Figure 4.36: Plot of fitted model for the relationship between aggregation quotient and concentration of background electrolyte. | 222 |
| Figure 4.37: Plot of fitted model for the relationship between distribution constant for humic acid and concentration of background electrolyte. | 222 |
| Figure 4.38: Variation of Mass (mg) of metal bound to un-aggregated humic acid (aq) with metal added. | 230 |
| Figure 4.39: Variation of Mass (mg) of metal bound to aggregated humic acid (s) with metal added. | 230 |

| | |
|--|-----|
| Figure 4.40: Variation of the extent of metal bound to soil with concentration of free metal in solution. | 231 |
| Figure 4.41: Effect of pH on humic acid partition in soil-solution system. | 233 |
| Figure 4.42: Effect of pH on the aggregation of humic acid in soil-solution System. | 234 |
| Figure 4.44: Ratio of Cu-occupied sites versus mass of Cu added to the system at pH 3.72 and 10. | 238 |
| Figure 4.45.0: Site ratio vs pH at different MCu. | 239 |
| Figure 4.46: QMLx vs pH at different MCu 240 | 240 |
| Figure 4.47: SR versus QMLx: Plot A is for pH 3.72 and plot B is for pH 10. ... | 241 |
| Figure 4.48: SR versus Concentration of background electrolyte at pH 4.7 and 10 | 243 |
| Figure 4.49: QMLx versus KDL at pH 4.7 and 10. | 243 |
| Figure 4.50: SR versus KDL at pH 4.7 and 10 | 243 |
| Figure 4.51: SR versus QML at pH 4.7 and 10. | 245 |
| Figure 4.52: SR versus KDM at pH 4.7 and 10. | 246 |
| Figure 4.53: SR versus KDM at various pH values. | 247 |
| Figure 4.54: QML versus KDL at pH 3.72. | 255 |
| Figure 4.55: SR versus KDL at pH 3.72. | 255 |

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KNUST



CHAPTER ONE

1.0 INTRODUCTION

The fate of trace metals in the natural environment is of great concern, particularly near former mining sites, dumps and industrial centers. And the mobility, transport, bioavailability, bioaccumulation and total concentration of the chemical forms of the metals are dependent on a complex function of many factors (Adriano, 1992). Thus our ability to understand how the factors influence their speciation and fate in the environment is crucial to our health and ecosystem.

In addition, in order to estimate the effects and potential risks associated with the elevated elemental concentrations that result from natural weathering of mineral deposits or from mining activities, the fraction of elemental abundances and concentration of chemical forms in water, sediment, and soil that are bioavailable must be determined.

It has been observed that a significant fraction of trace metals in many natural environments are complexed to natural organic materials (NOM), usually the humic substances (HS). For example, > 90% of dissolved Cu and Zn in sea waters are usually found to be complexed with natural organic ligands. Approximately 95% of trace metals transported from land to sea by surface waters are adsorbed on mineral particles directly, or are bound to organic matter coating these particles (Khan et al. 2006). Moreover, during such transportation, sorbed species may be redistributed between the aqueous and solid phases as a result of changes in the physicochemical conditions of the water, leading to redistribution among various competitive equilibria, including the formation of soluble

complexes with inorganic ions and molecules. Therefore, scientific research projects on humic substances aimed at increasing our understanding of chemical features and processes governing trace metal distribution in an environment as a result of metal-humic interactions require models as important research tools (Hummel, 1997).

Our knowledge of the role of HS in the natural environment has surged (Tipping, 2002), consequently, there is a considerably worldwide research effort aimed at characterizing and understanding their environmental behaviour.

Table 1.1: Environmental issues involving humic substances

| <i>Issue</i> | <i>Role of humic substances</i> |
|---------------------|---|
| Carbon cycle | Major C pool, transformations, transport and accumulation |
| Heavy metals | Binding, transport, influence on bioavailability |
| Nutrient control | Binding of iron and phosphate |
| Photochemistry | Mediation of light-driven reactions |
| Weathering | Enhancement of mineral dissolution rates |
| Ecosystem buffering | Control of proton and metal ion concentrations, persistence |

Research efforts on humic substances have surged and the use of models to describe the acid-base properties and the cation binding properties of these substances have received close attention in recent times. This is because modeling of protons and metal by humic substances (HSs) is relevant to many environmental problems. And over the years, many laboratory studies have been made of the interactions, and a large body of data has accumulated. In spite of the challenges

such as binding site heterogeneity and salt dependency, chemical models are needed to encapsulate the knowledge of humic matter interactions vis-a-vis metal partition needed to allow application to “real-world” situations.

As part of the effort to address the difficulty associated with humic ion-binding modeling, Tipping and Hurley, (1992) used the work of Marinsky and colleagues as the basis of a simplified model (Humic Ion-Binding Model V; thereafter denoted Model V) which included i) site heterogeneity (discrete site with a range of affinities, together with the formation of bidentate sites), ii) electrostatic effects (including the contribution of counter-ion accumulation to binding) and iii) competition among protons and metal ions. Model V described published data sets with some success, and the parameters obtained for metal binding (intrinsic equilibrium constants) displayed encouraging parallels with analogous constants for simpler organic acids. In addition, Model V and its predecessor (Model VI) have been used to analyze field data for water and soil samples (Tipping et al 1995a). As part of WHAM (Windermere Humic Aqueous Model), Model V has been incorporated into a dynamic model used to simulate catchment chemical behavior.

A series of models were also developed by Van Riemsdijk and colleagues (Benedetti et al., 1995, 1996 a, b,; Kinniburgh et al., 1996). They characterized binding site heterogeneity by the use of continuous distribution of equilibrium constants, together with electrostatic sub-models. The most recent of these, the NICA-Donnan Model (NICA = Non Ideal Competitive Adsorption), which has been shown to fit very well the extensive data sets obtained by these workers, not only binding results covering wide range of free metal ion concentration (Benedetti et al., 1995) but also detailed competition experiments (Kinniburgh et al., 1996).

Gustafsson, (2001) also developed the Stockholm Humic Model (SHM) to describe the binding of protons and metals to humic substances.

Even though the use of surface complexation models in combination with the humic ion-binding models have been used to describe speciation in soil and water, effective description of the role of humic substances in metal partition in semi-natural ecosystem has not been modeled. Moreover, how the colloidal properties of humic substances affect metal partition under the influence of the fluctuating pH and ionic strength of aquatic and terrestrial systems has not been properly discussed. It was in line with these that this work sought to investigate and model the role of humic substances in the distribution of trace metals in the terrestrial environment of the ecosystems at the Gold-mining communities at Talensi-Nabdam District.

1.2 BACKGROUND OF THE PROJECT

The retention and mobility of many metal ions in soils and natural waters is greatly influenced by humic substances, and many metal ions are strongly bound to the humic substances (HSs). It is impossible to understand metal ion transport and bioavailability without considering their interaction with humic substances. This is as a result of the fact that observation has shown that humin and humic acids (HAs) in soil participate in the retention of metals, while fulvic acids (FAs), and to a lesser extent HAs, are involved in the transport in soils and natural waters (Clapp, et al 2001).

Humic substance (HS) models developed so far have considered mostly structure and reaction models (equilibrium models) in an attempt to explain its properties and nature of interactions with cations. However, models that describe

the mechanism and the nature of transport and distribution pattern of metals with respect to their interaction with humic substances are yet to receive much attention.

The observed properties and characteristics of humic substances as they interact with metal ions can be harnessed to explain, and predict the role HSs play in trace metal distribution in environment as well as their toxicity. Thus, the outcome of this project will increase our knowledge of the dynamics of trace metals in geomedia and bring us to terms with the indispensable role of HSs in nature with respect to environmental degradation and the toxicity of metal contaminants.

In addition, the indiscriminate disposal of industrial and domestic waste in urban centers, the increased use of agrochemicals, as well as the increase in illegal mining activities in Ghana, which call for concern will be alleviated, because, our knowledge of the dynamics of contaminants in our environment will lead to the development of more effective alternative environmental remediation techniques.

1.3 SIGNIFICANCE OF THE PROJECT

Humic substances are highly abundant organic compounds formed in soils and sediments by the decay of dead plants, microbes and animals. And the binding properties of these compounds have been noted to regulate the chemical reactivity and bioavailability of metal ions in the natural environment (Tipping, 2002). In addition, the structure and all the properties of humic substances are not fully understood. Consequently, there is a worldwide research effort aimed at characterizing and understanding their environmental behavior.

Our immediate environment is host to a vast number of chemical reactions. And environmental chemists seek to define and quantify these reactions, make analytical determinations of reactants and products, construct predictive models

and relate their findings to the functioning of ecosystems. As such a major part of the research effort is expected to take account of humic substances and mineral particulates, because these abundant, poorly defined, components have been noted to exert a powerful and ubiquitous chemical influence on the environment (Tipping, 2002).

Humic substances have found many applications ranging from environmental remediation to agriculture through to medicine (Tipping, 2002). However, over and above these practical and utilitarian matters, the greatest present interest in humic substances concerns their roles in the natural environment.

This project is hence an endeavour geared at fostering scientific advancement in the area of environmental studies vis-a-vis humic substances.

1.4 PROBLEM STATEMENT

The distribution of trace metals between mineral surfaces and natural organic matter, NOM, (in the solid phase) plays a major role in determining the trace metal content of natural waters. The sorptive interactions at the solid-water interface has been observed to have a strong influence on trace metal mobility and bioavailability in semi-natural ecosystems, and industrial settings (Stumm and Morgan, 1996; Drever, 1997; Tadanier et al. 2002; Sposito, 2004; Koretsky et al. 2009a and 2009b). The dynamics of sorptive interactions and the factors which influence the sorption processes have thus been of particular interest to scientists for years because of its importance to many environmental problems (Tipping, 1998; 2002).

In a terrestrial environment, the chemical composition of the soil-solid and the soil-solution phases, to a great extent determine the behavior and fate of trace metals. To understand the chemical processes responsible for the distribution of trace metals in soil-solution systems, and to understand the chemistry of the metal-adsorbing surfaces such as silicates, metal oxides, natural organic matter, biomass and organisms (such as Bacteria) (Tipping, 2002) scientists have adopted the use of modeling and spectroscopic methods in their studies.

Humic substances have been noted to influence the speciation of trace metals in terrestrial and aquatic environments. However, the chemistry and molecular structure are still under study. In view of the importance of the cation binding to humic matter, in natural environments there has been a long history of attempts to model cation binding to humic substances (Bufle, 1988; Riemsdijk et al., 1992; Koopal et al., 2001). This type of modeling addresses the speciation of metal ions in the natural environment. While the earlier works were quite successful in describing individual data sets, their scope in terms of pH range, competing metal ions and ionic strength was often very limited and did not match the range of conditions found in natural waters (Koopal et al., 2001). The metal binding 'constants' were mostly conditional, in the sense that they depended on the pH, ionic strength, and the presence of other metal ions. Ideally, the binding constants should be a property of the humic substance alone and should not vary with solution chemistry (Koopal et al., 2001). If binding models are to be used in general purpose chemical speciation programs then they must address these basic issues. The ability to account for proton-metal and metal-metal competition provides a challenging test for such models. In the last decade or two, models such as Model V/VI, NICA-Donnan and the SHM have attempted to address these

issues (Tipping et al., 1992, 1998; Koopal et al., 1994; Benedetti et al., 1995; Kinniburgh et al., 1996, 1999). Koopal et al. (2001) indicated that the issues are unavoidable and reflect the underlying complexity of the system. They added that, at the root of the complexity are: 1) the extreme binding site heterogeneity, 2) the variable stoichiometry of the binding reactions, and 3) the presence of electrostatic interactions. Insight into the functional group heterogeneity have been given via a number of experimental techniques, including titrations in aqueous and non-aqueous media, derivatization techniques (Ephraim et al., 1989), ^{13}C -nuclear magnetic resonance, infrared and ultraviolet spectrometry (Aiken et al., 1985). In spite of this, modeling binding by humic substances is still complicated by the heterogeneous nature of humic binding sites both for protons and metals. Furthermore, the salt dependence of proton binding to humic substances varies from sample to sample and has not been completely understood on a mechanistic level (Gustafsson, 2001). Thus in modeling these features (total amount of dissociating sites and relative acid strengths) may be presented in two ways: first some sort of continuous distribution of pKa values may be used as in the NICA-Donnan model (Benedetti et al., 1996). Second, the humic substance may be assumed to have a series of discrete-site pKa values, as in model V/VI of Tipping and Hurley (1992), and Tipping (1998). Although discrete, the individual sites used in the second approach do not physically represent present sites. Therefore, the approach to use is mainly a matter of taste. Both also produce the same number of adjustable parameters (Gustafsson, 2001).

The description of the salt dependence of proton binding to humic substance is also a subject of controversy (Gustafsson, 2001). According to Gustafsson (2001), Avena and co-workers (1999) argued that humic substances

(HS) should be described as permeable gels of spherical geometry, some humic charge is neutralized by counter ions inside the gel where part of the charge is neutralized on the exterior parts. It was claimed that the different approaches represent simplifications of this general situation. The two model approaches most frequently used are:

1. The HS viewed as impermeable spheres, and the charge is assumed to be localized on the exterior part (Tipping et al., 1992; Bartschent et al., 1992).
2. The HS are considered to form a gel phase, separate from the bulk water phase. A Donnan-type equilibrium governs the distribution of counterions between the two phases. The humic charge inside the gel is neutralized by counterions inside the gel. Such a model was originally proposed by Marinsky and co-workers, and a similar description was introduced into the NICA-Donnan model (Benedetti et al., 1996).

Although the first approach has been shown to work excellently well for individual data sets, difficulty arises when considering the differences to variations in salt dependence experienced for different HS samples. Avena et al., (1999) attributed these differences to variations in particle radii and site densities, and were able to provide reasonable fits with these adjustable parameters. Tipping and Hurley (1992), on the other hand, defined an 'electrostatic interaction factor' which could be adjusted to fit the different data sets. The first approach is not necessarily good. To obtain salt dependence in the second approach, a potential gradient from the gel phase to the bulk solution is calculated. Apart from these two model approaches, there are other factors that may be considered for the correct description of the salt dependence (Gustafsson, 2001). For instance, the occurrence of counterion condensation if

the site density exceeds a certain value implies that this effect is probably not significant for HS.

Trace metal distribution and speciation in natural environments is also influenced by the nature and composition of soil/sediment minerals, and particulate matter in solution phase. Therefore, mechanistically oriented models should ideally account for the structural characteristics of the mineral-water interphase like type of binding sites, the electrostatic profile near the surface, and the location of the adsorbed metal ions in it (van Riemsdijk et al., 1998; Brown et al., 1999). In this respect, therefore, in evaluation of the potential bioavailability of trace metals in natural environment, researchers use mechanistic surface complexation models. Tadanier and Eick (2002) indicated that the models are widely used to estimate the distribution of oxyanions and metals between sorbed and solution phases as well as their ionic speciation within these phases. The underlying physics and chemistry of adsorption phenomena are described in these models using equilibrium adsorption reactions which place adsorbed ions in specific electrostatic planes within an electrical double layer (EDL) adjacent to the mineral surface (Tadanier and Eick, 2002), the constant capacitance, diffuse double-layer (DDL), basic stern, and triple layer models have been extensively applied to describe surface adsorption on mineral surfaces (Westall and Hohl, 1980; Hayes et al., 1991; Tadanier and Eick, 2002). These models, according to Tadanier and Eick (2002), require several user specified adjustable fitting parameters including capacitance of the EDL and types of reactive surface sites and their densities, and rely on an arbitrarily defined amphoteric description of ionizable surface functional groups. These shortcomings have recently been addressed through

the development of the charge distribution multisite complexation (CD-MUSIC) model (Tadanier and Eick, 2002). In spite of these innovations in modeling, the practical limitation is that there are differences in the reactivity of clean and water-exposed surfaces (Goldberg et al., 2001).

It is evident that the complexity of the semi-natural ecosystems in terms of the composition and chemical properties of the solid and solution phase components has caused researchers to develop intelligent and innovative ways of using models to describe the chemistry of metal distribution in natural environments. But a proper description and modeling of the role humic substances play in trace metal distribution has not been closely studied. Its intrinsic properties have not been effectively correlated with its cation binding properties. Even though its properties have been closely studied, how those properties influence the behavior of other species such as trace metals have not been effectively described in relation to the metal distribution.

The intrinsic properties of HS are responsible for their functions in natural environments (Dubal et al., 2004). Thus studies into the relationship between humic matter properties and reactivity, and how the relationship affects the partition of other species such as trace metals are crucial to our understanding of the behavior of humic substances and how it affects our health.

With respect to model application to field studies, the need for optimization of the density of binding sites also indicate that a more comprehensive account of the natural organic matter (NOM) is required (Dubal et al. 2004). Studies involving the applications of humic ion-interaction models are not limited to the simulation of measured values in a natural system but also concern comparisons between models, and the discrepancy is often balanced by

changing the value of the metal-binding constant, using empirical relations registered in the model database, and the use of 'active' humic substances (Tipping et al. 1995a, 1995b; Christensen et al. 1998; Christensen and Christensen, 1999; Christensen and Christensen, 2000; Loft and Tipping, 2000; Benedetti et al. 2002; Dubal et al. 2004). The poor match between data from well-constrained conditions of humic-metal interactions and those from the field which have resulted in model calibration are important chemical factors which have to do with the complexity of the systems, particularly the nature of NOM and mineral makeup of the soil/sediment phase of the systems. So far only a single study by van Hees et al. (2001), reported by Dubal et al. (2004), has considered the effectiveness of some small organic molecules (i.e. biochemical compounds) versus HS in natural waters. In addition, no specific effort has also been made to consider effects due to microbial substrates and metabolites that readily interact with the soil chemistry, either at the acid-base and metal complexation levels (sugars, amino acids, LMWOAs under anaerobic conditions), or at the redox level (use of various terminal electron acceptors such as nitrate, sulfate, iron or manganese) (Dubal et al. 2004). Moreover, the range of macromolecules exhibiting a ratio of hydrophobic versus hydrophilic bonds lower than humic acid and fulvic acids, the ability of the organic molecules to be biodegraded by soil microorganisms (which has effect on its metal binding capacity on a short time-scale and also on longer one by slowly modifying the structure of the humic matter) in relation to biokinetic mechanisms (Dubal et al. 2004) have not been taken into account in modeling studies. Therefore, legitimization of hypothesis to overcome uncertainties regarding the actual NOM speciation and binding properties, as

well as the choice of a well-defined calibration strategy to fit measured data as proposed by Dubal et al. (2004) are essential in our quest to effectively describe the geochemical and biogeochemical processes that influence our health and fragile ecosystem with the aid of models.

In view of the challenges and the neglected areas in the research on metal speciation and the modeling of humic ion-binding in natural system, this study seeks to consider modeling the role of humic substances in trace metal distribution in semi-natural ecosystems in terms of the intrinsic properties of humic substances.

1.5 GENERAL OBJECTIVES

In order to model the role of humic substances in trace metal distribution in the selected ecosystems in Ghana, the research endeavour focused on a set of objectives. The general objectives were:

- To develop a conceptual model for the description of the role of humic substances in the distribution of selected trace metals in the terrestrial environment of the selected ecosystems for the study.
- To develop mathematical models based on the theoretical framework to enable description of the role of humic substances in trace metal distribution in the terrestrial environment of the selected ecosystems.
- To test the suitability of the mathematical models to describe the role of humic acid in the distribution of trace metals in soil-solution systems.

1.6 SPECIFIC OBJECTIVES

The specific objectives of the research are as follows:

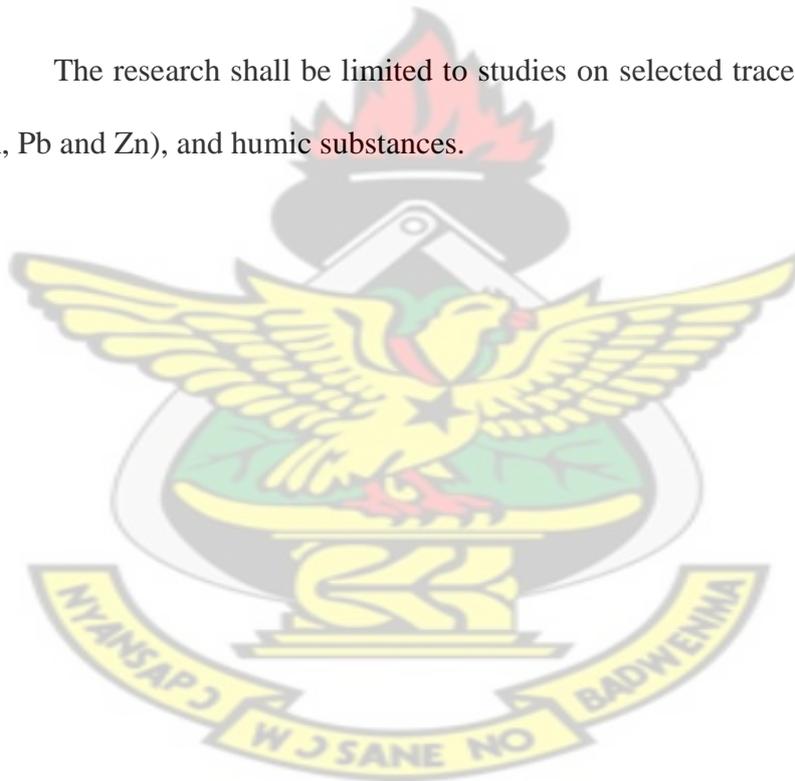
- Perform chemical characterization of the mining-impacted terrestrial environments of the selected ecosystems.
- Determine the relationship between environmental characteristics and trace metal distribution in the terrestrial environments of the selected ecosystems.
- Apply statistical modeling to determine the magnitude and impact of the factors which control trace metal partition in the terrestrial environments of the selected ecosystems.
- Determine the relationship between metal partition constant and the principal characteristics of the terrestrial environments of the selected ecosystem.
- Develop a conceptual model that describes how trace metal partition is influenced by humic matter.
- Develop mathematical models to describe the role of humic substance on trace metal partition.
- Test the applicability of the mathematical models using data from controlled experiments.
- Use the mathematical models to explain the effect of pH and background electrolyte on trace metal partition in soil-solution system.

1.7 SCOPE OF THE STUDY

The research will be limited to investigations leading to the development of a mathematical model for the distribution of trace metals in soil. The investigations shall include studies on:

1. Determination of the factors which influence trace metal partition in terrestrial environment.
2. Determination of the factors which influence humic matter and trace metal partition in soil-solution system.

The research shall be limited to studies on selected trace metals (Cd, Cu, Mn, Pb and Zn), and humic substances.



CHAPTER TWO

LITERATURE REVIEW

2.0 DESCRIPTION OF HUMIC SUBSTANCES

Definition and occurrence: HS may be defined as naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in colour, of high molecular weight and refractory. They are also described as complex, acidic organic molecules formed by the decomposition of plant, animal and microbial material (Tipping, 2000). HSs are abundant and persistent in the biosphere and immediate subsurface, and are present in particulate and dissolved forms in soil, waters and sediments,

The humic substances found in soils, oceans, and deep lakes are generally autochthonous, while those in streams and shallow lakes are more often allochthonous. Flowing surface and ground water are responsible for their distribution throughout the hydro- and lithosphere. They are formed through aerobic and anaerobic decomposition of (mostly) plant detritus, as well as secondary microbial synthesis. Differences in origin, age, and genesis lead to a high degree of chemical and morphological complexity that makes the compounds difficult to characterize (Ghabour, 1999).

Structure and Properties: The structure of HSs is strongly related to the biological components from which they are formed. The greatest difference among these biological components is between those of marine and terrestrial environments. Terrestrial HAs which are generally derived from lignin are more aromatic than marine humic acids while marine HSs

have more protein and carbohydrate residues, which are the main components of marine algae. The low molecular weight humics are more prevalent in sediments and in river and sea water, while heavier ones predominate soils (Von Wandruszka, 2000).

Humic substances (HS) are the product of decomposition chemistry and not the ordered chemistry of biological products. Thus, no chemical, labeled “humic substances” exist (Hummel, 1997). HS are composed of complicated organic mixtures which are linked together in a random manner, resulting in extraordinarily complex material. The special properties of HS result from this extreme heterogeneity, and their high chemical reactivity (Mikkelsen, 2005). They generally have a high aromatic content, estimated (from ^{13}C NMR spectra) to range from 20 to 60% of the carbon present. Heteroatomic functionalities include phenols and other alcohols, ketones/quinones, aldehydes, carboxylic acids, amino- and nitro-groups, and sulfur containing entities such as mercaptans, sulphates, and sulphonates (Von Wandruszka, 2000). The abundance of carboxyl groups and weakly acidic phenolic groups in HSs contribute to their complexation and ion-exchange properties. They have also been observed to exhibit both hydrophobic and hydrophilic characteristics and can bind to soil mineral surfaces (Mikkelsen, 2005).

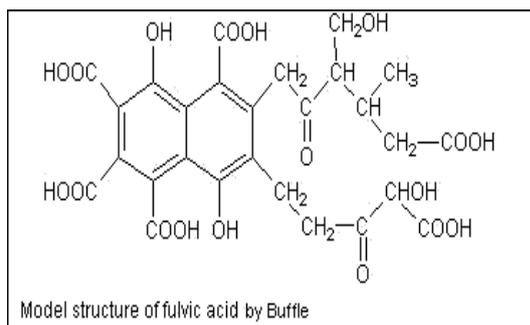


Figure 2.1: Model structure of fulvic acid

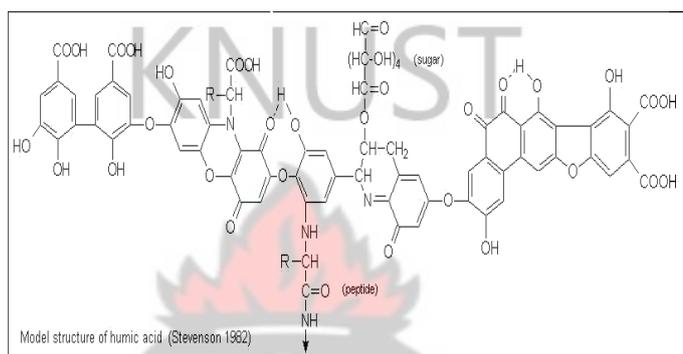


Figure 2.2: Model structure of humic acid

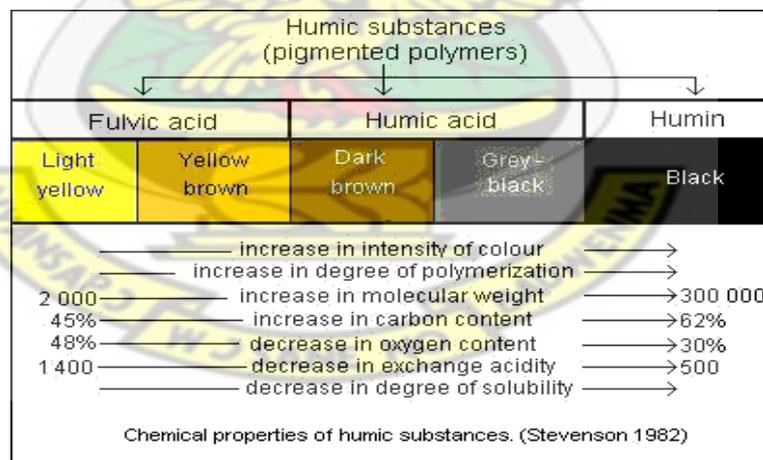
Classification: The diversity among HSs makes their classification difficult (Wandruszka, 2000). Traditionally, HSs have been considered to comprise fractions distinguished by their solubility and adsorption properties (Tipping, 2002). It is, therefore, customary to divide them into (three) operationally defined classes, broadly based on their solubility characteristics. They include,

- Humic acid (HA): these are the acid component of HSs which are soluble in bases but insoluble (precipitates) in acids;
- Fulvic acids (FA): These are the acid component of HSs which are soluble in both bases and acids;
- Humin: The components of HSs which are not readily soluble in acids on bases.

Humin may consist of HA in strong association with humic matter, highly condensed insoluble humic matter, fungal melanine, and parafinic substances. Broadly, HAs and humin occur mostly in soils and sediments as part of the solid phase, while FAs are more mobile and account for a major part of the dissolved organic matter (DOM) in natural waters (Tipping, 2002; Wandruszka, 2000).

Other classification schemes emphasize the origin of HSs (soil, aquatic, sediment) rather than pure (operational) classifications based upon procedures applied for fractionating this complex mixture of natural substances (Kördel, 1997; Hummel, 1997).

These classes (fractions of HS) differ in colour, C- and N-content from FAs beyond HAs to humins, the solubility in water as well as acid and reductive properties decrease while their molecular size increase. The postulated relationships are as shown below



(Source: Kördel, 1997)

Figure 2.3: Chemical properties of humic substances

2.1 HUMIC SUBSTANCE INTERACTION AND MODELS

In the search for insight into the chemical behaviour, properties, and structures of humic substances as well as their role and importance in life, the use of integrated approach involving a combination of experiments and modeling studies have become another commonly used tool in the hands of research chemists. Humic substance models have provided a wealth of information about humic substances, their interactions and activities in an environment. Thus in a research of this kind the use of models is a necessity that requires an understanding of existing HS models, and metal-mineral-HS interactions.

Metal interaction in the environment: The presence of and transport of trace metals and radionuclides lead to metal-ion contamination of natural and semi-natural ecosystems (sediments, soils, and water) and constitute a potential source of health risk for plants, humans and other organisms. Whatever their source, trace metals may interact with other components present in the natural system, such as dissolved low-molar-mass organic or inorganic ligands, high-molar-mass particle organic or inorganic materials and living organisms. These interactions have consequences for metal transport, bioavailability, and risk assessment (Merdy et al, 2006).

Evaluation of the nature of the relationship between metals and biological populations is dependent on our knowledge of the fate and distribution pattern of metals in a given environment.

Insight into the dynamics of trace metals in natural systems can be gained by combining experiments and modeling studies, but this approach

is feasible only when the metal interactions with the different components can be described adequately (Merdy et al, 2006).

Metal-particle interaction: Complexation reactions of metal ions with low-molar-mass components are well understood. But high-molar-mass particles with metal ions is rather diverse because they may exist alone or associate together. Therefore, the behaviour of mineral oxides and organic matter must be clearly distinguished in models (Merdy et al. 2006). Metal-particle interactions have two main aspects: 1) The ions bind to the sites on the mineral surface, the functional groups of the NOM (particle) or both. 2) Electrostatic effects occur because the charge of the ions affects the NOM particles, or both.

The site binding can be described with affinity or stability constants provided that lateral interactions (except for electrostatic interactions) between the sites can be neglected. Site competitions as well as electrostatic interaction affect metal-ion binding and the competition between different metal ions. Modeling metal-particle interactions therefore requires binding modes with two interdependent parts, 1) a site-binding model and an 2) electrostatic model. The commonly used electrostatic models include an electric double layer (EDL) model for impenetrable surfaces and a Donnan model for particles that are penetrable for ions (Tippings, 2002).

Metal-NOM Interactions: The interaction models for metals and NOM, and specifically for the dissolved fraction, are different from the mineral models because of the strong heterogeneity and the complex diverse structure of HSs. The diversity of existing models is related to the

extent to which the solution conditions (pH, ionic strength, and different metals present) are taken into account (Merdy et al. 2006).

Humic substances are complex mixtures of different molecules with well known chemical heterogeneity of the HA and FA, the variable charge/potential of the molecules, competition among a wide range of ions and a variable stoichiometry of the various binding reactions. Yet all these complexity requires a balanced simplification in order to arrive at models that are feasible in practice. A model description of a specific HS is therefore at best describing the average particle behavior no matter how well the HS is defined (Van Reimsdijk et al. 2006). Depending on the precise nature of the HS, its reactivity may deviate from that of other humics. However, in general, a fairly close similarity is observed for HAs and FAs and so a “generic” behaviour can be defined for them along with certain variability. This variability can be seen from the variation in the behavior of individual FAs and HAs and the resulting spread in model parameter values. The use of “generic” model constants for ‘unknown’ humics is based on the assumption that the HA and FA in question behave with these generic properties, or at least reasonably close to them. Reality may deviate significantly from this assumption but the range of variability is roughly known and so could be propagated through the calculations. Acquiring datasets for the full calibration of individual HSs is a major task and so the additional uncertainty associated with the use of generic model constants has to be balanced against effort involved in undertaking such a set of calibrations (Van Reimsdijk, et al. 2006).

Ternary interactions: Humic particles also bind strongly to metal oxide and hydroxide particles. Such associations may occur as complex colloids in surface waters and soil solutions (Allard et al, 2004) and certainly do so in the solid phase of soils and sediments (Van Reimsdijk et al. 2006).

The binding of metal ions into HA or FA when bound to a mineral particle may be quite different from the binding to the humics when it is not associated with such a particle (Christl et al. 2001; Weng et al. 2004; Saito et al. 2005). Similarly metal ions bound directly to the mineral surface sites are affected by the presence of adsorbed humics. It is well established that ion binding to oxides is quite dependent on the electrostatic potential profile in the vicinity of the surface and that this potential will be strongly affected by the presence of adsorbed humics (Saito et al. 2004). Therefore metal ion binding to oxides will be similarly strongly affected. Metal ion binding to the oxide and, in turn, this will affect the adsorption of the humics (Van Reimsdijk et al. 2006).

In the natural environment, metal oxide, hydroxide, and even carbonate minerals, not only provide important reactive surfaces for cations, but also for anions such as sulphate, phosphate, and arsenate, etc. The binding of anions to oxide and hydroxide surfaces will also be affected by the presence of adsorbed HSs. Therefore humics not only influence the binding of anions through their effect on the potential near the competition site but also cations.

Modeling these ternary interactions requires not the combination of two types of models (ion binding model for oxide surfaces and an ion binding

model for the humics), but also a model for the binding of the humics to the oxide surface (Van Reimsdijk et al. 2006).

A review of humic substance models: Basically there are two types of HS models namely, structural and binding models, but attention will be paid to the latter. There have been many attempts to model mathematically the reactions of cations with HSs. The models developed to date, nearly all of which have been equilibrium models, can be classified as parameterized and predictive. Parameterized models predominate with only a few attempts at a predictive approach (Tipping, 2002).

It has been observed that when correctly chosen stoichiometry is incorporated into an equilibrium model, it leads to agreement with observations. HSs are much less amenable to such an analysis because stoichiometries are difficult to determine in these poorly characterized heterogeneous systems, and clear-cut choices among possible reaction schemes are not easily made (Tippings, 2002). Therefore, for a researcher trying to understand the properties of these compounds, a model provides a way of trying the state of knowledge, and a means by which experiments can be designed.

2.2 METAL SORPTION

The distribution (sorption or retention) of trace metals between inorganic mineral (clay minerals, metals oxides and oxyhydroxides) and organic humic substances (humic acid, and fulvic acid) is one of the most important geochemical processes controlling the fate, transport and bioavailability of metals in soil environment.

2.3 EFFECTS OF COMPLEXING AGENTS

Organic and inorganic complexing agents may either hinder or promote the sorption of metal cations, depending, respectively on whether the metal complexes, which they form, remain in solution or are themselves sorbed by the mineral, and on whether sorbed complexes are bound more strongly or less so than the free cations. But some complexing agents have no effect (or no net effect) on metal sorption, at least under certain conditions (e.g. within a given pH range). The effects of complexing are complicated as they depend on specific properties of the complexing agents, metals and sorbents, and on various environmental factors such as the pH and ionic strength of the aqueous phase. Therefore, each case has to be examined individually (Parker, 1998).

Anionic complexing agents, including organic acids and cations, often prevent or reverse the association of metal cations with negatively charged sorbents such as clay minerals by forming stable cations. Their effect is two-fold: they compete with the minerals for the cations and the complexes remain separated from the minerals by electrostatic repulsion. Alternatively, the complexes themselves may be sorbed, although their affinity for the mineral surface is not necessarily the same as that of the free metal cations. Thus, complexing agents may increase the proportion of the metal taken up from solution if the complex is subject to sorption, as with positively charged complexes sorbed by clay.

Interactions of humic matter with metals and colloidal minerals are complex. And the effects of humic matter on the sorption of metals by mineral particles may depend on environmental parameters such as pH,

rich in weakly acidic -COOH and phenolic n-OH groups, humic matter usually bears a net negative charge and comprises some of the most effective, abundant and wide-spread natural complexing agents. Fulvic acids may interfere with the sorption of metals by clay. Probably, owing to their high solubility in water (resulting in solubilization of the metals that they bind), and their negative charge (resulting in electrostatic repulsion by clay). Nevertheless, both fulvic and humic acids, along with their chelated metals, are commonly bound to clay minerals and oxides, although the higher molecular weight humic fractions may be sorbed preferentially in at least some cases (Marsi, 1992). Humic matter is bonded to minerals by bridging mechanisms where by ligands of the humic matter are coordinated to polyvalent metal cations at the mineral surface, and by H- bonding and Van der Waal's forces. The interactions between complexing agents, minerals colloids, and metals are modified by environmental variables, such as pH, which affect surface charges of colloids, protonation and deprotonation of acidic ligands, metals speciation, the strength and mechanisms of binding by ligands and sorption sites and so on. pH also plays an important part in the behaviour of complexing agents. Thus, because humic matter complexes metals, mainly by means of acidic ligands whose H^+ ions are split off when the metals are bound, the stability of the complexes is higher under alkaline than under acidic conditions. But in acidic pH range humic complexes are more efficiently sorbed by clay and oxides, probably because, the negative charges of the humic matter are largely neutralized by protonation of acidic functional groups.

Accordingly, variations in environmental factors and specific properties of the reactions may well account for apparent paradoxes, as in the opposing effects of fulvic acids. Additional complications exist because complexing agents like mineral colloids bind metals preferentially. For instance, Cl^- adsorbs $\text{Hg}(\text{II})$ more effectively than $\text{Cu}(\text{II})$ from minerals because it forms more stable dissolved anionic complexes with $\text{Hg}(\text{II})$, and the relative affinities of heavy metals for humic matter may depend on any one of several metal properties, including electronegativity and ionization potentials, or may conform to the Irving-Williams series of complex stabilities. In any event, the relative affinities of humic matter and other complexing agents for metals are variable and are not necessarily the same as those of mineral colloids, which in turn differ among themselves in that regard. Therefore, the metal preferences of composite colloids such as clay-humic complexes may be difficult to predict and interpret.

2.4 RELATIVE EFFECTIVENESS OF DIFFERENT SORBENTS

Fe and Mn oxides are the most important binding agents for heavy metals in soil and aquatic environments, (Parker, 1998). A body of evidence accumulated by different scientists have established that Fe, Mn, Al oxides, and usually organic matter too have higher sorption capacities for heavy metals and metalloids than clay minerals do. This important generalization has been strikingly illustrated by comparing the Zn sorption capacities of amorphous Fe and Al oxides, $\delta\text{-MnO}_2$, bentonite (ie. Montmorillonite) and humic acid in CaCO_3 - buffered medium (Parker 1998). The results show that the cation exchange capacity varied in the

order, humic acid >>bentonite> oxides, whereas the sorption capacity for Zn varied in the order, oxides> humic acid>> bentonite.

There are indications too that sorption capacity tends to correlate positively with strength of binding (Xing et al, 1995), although this is not necessarily true. In short, freshly precipitated oxides, and to a lesser extent humic matter, are much more effective scavengers of heavy metals than even the most efficient sorbents among clay minerals, indicating that specific sorption and other complexation processes are the dominant binding mechanisms. However, clay particles play important roles as carriers of associated oxides and humic matter.

Although oxides as a whole are the most effective sorbents of heavy metals, they differ appreciably among themselves in their sorption capacities (Pickering, 1990; Parker, 1998), and in their tendency to release sorbed metals. They also show marked preferences for particular metals, such generalization, however is to be viewed with caution, as the sorption capacity of an oxide is a function of crystalline particle size, and specific surface as well as elemental composition. It has been observed repeatedly that the sorption capacity of any oxide is critically dependant on whether the oxide is “amorphous” or crystalline. Owing to their high specific surface, freshly precipitated amorphous oxide gels invariably have much higher sorption capacities than the well-crystallized phases that eventually form from these gels during ageing, (Surift and Mcloren, 1991). Indeed crystallization may be accompanied by release of sorbed or coprecipitated metals, presumably because they cannot be filled into the crystal structure.

Differences in the sorption capacities of Mn, Fe, and Al oxides vary with physicochemical conditions. Manceau et al. (1992) repeated that below a critical pH the percentage of dissolved Pb(II) sorbed by Mn, Fe and Al oxides varied in the order: Mn >> Fe > Al, implying that the properties of the Mn oxide were most conducive to the surface complexing of Pb²⁺ ions. In contrast, the three oxides were equally efficient sorbents at higher pH values, suggesting indiscriminate deposition of complex hydrolysates on any available surface. Coatings of organic matter, phosphate, and other impurities may also be important because, besides masking the surfaces to which they are sorbed, they affect the physical properties of oxides. Organic matter may either block the precipitation of Fe oxide or promote it, and organic compounds (e.g. certain carboxylic acids) may retard the crystallisation of Fe oxide gels and clay minerals and affect their crystal structures, preserving unstable configurations indefinitely. Thus organic substances, besides binding metals directly, may influence the metal-binding capability of an oxide or clay mineral.

2.5 SURFACE COATING

In their native state, clay particles along with silt and sand grains are commonly coated to a greater or a lesser extent with Fe and Mn oxides (Parker, 1998). Oxides may be deposited on the surfaces of other oxides as well. For instance, a layer of MnOOH could be precipitated on top of an FeOOH deposit following an increase in the ambient dissolved O₂ level.

In addition, clay and oxide minerals, including oxide films on clays, may be created with humic substance. (Marsi, 1992). Because oxides and humic matter are efficient scavengers of heavy metals and have

much higher sorption capacities for these metals than clay minerals do, it is probable that the apparent sorption of heavy metals by clay, and other phenomena involving the surfaces of clay crystals are partially, if not principally due to these coatings. But effects of coatings are variable and complex (Parker, 1998). Humic acid coatings or Fe oxide may either enhance trace element sorption or decrease it.

In summary, coatings and other impurities on mineral surfaces are virtually ubiquitous, and they may radically alter the surface properties of the particles; consequently, the importance of their effects on the adsorption and desorption of trace metals by these particles can scarcely be over emphasized. Surface coatings promote sorption if they are more effective sorbents than the particles on which they were deposited, but they may hinder sorption by blocking sorption sites on these particles (or possibly by promoting aggregation of mineral particles). Whether a surface deposit has the one effect or the other may depend on a combination of circumstances, and both effects could occur simultaneously, thus the net result may be hard to predict.

Although natural oxide and organic coatings on soil minerals are widely regarded as important and are frequently mentioned in literature, their roles have seldom been assessed or even considered in research on interactions between trace metals and soil minerals.

2.6 SORPTION KINETICS OF TRACE ELEMENTS IN SOLIDS AND SOLID MATERIALS

Many studies have appeared in the literature on various aspects of metal sorption. Results from these studies have been used to develop

government regulations, devise clean up strategies, and develop models that predict the fate of trace elements in the environment. However, in conducting these studies researchers often overlook two important aspects:

- 1) The length of time soils are exposed to a contaminant (residence time) in the laboratory is relatively short compared with the much longer residence times that exist in field contaminated soils, and
- 2) The kinetics of metal sorption and desorption are often slow. These oversights lead to improper evaluation of contaminant behaviour in the environment, resulting in regulations that may be improper, and models and remediation strategies that may be unsuccessful.

Many studies rely on an equilibrium approach to predict the retention of trace metals on natural materials and subsequent migration through the vadose zone. Researchers often focus on determining parameters such as distribution coefficients, and the maximum amount of sorption possible. These studies are often based on the metal solid interaction over a short period (24 hours or less) because it is assumed that the reaction has reached completion. However, field soils are seldom, if ever, at equilibrium. Often laboratory studies are also far from equilibrium, and slow sorption may change the distribution between solid and solution over a period of time (Smith and Comans, 1996; Sparks, 1998). This is primarily due to slow metal sorption and desorption kinetics. The failure to account for the slow kinetics results in either, under predictions of the amount of trace metals retained by soils and minerals, or over prediction of trace metal availability in the environment.

Most soils are heterogeneous media that contain a host of different minerals, solids and organic materials. Thus, the interaction of trace elements with soils is a heterogeneous process. Due to the heterogeneity of soil, these processes can occur simultaneously. A measured sorption or desorption rate often reflects a combination of all of the sorption mechanisms.

However, it is possible that one mechanism may dominate at a particular time in the sorption reaction and the measured rate is primarily an expression of that reaction rate. For example, outer-sphere complexation which can precede surface precipitation. The significance of this continuum in sorption is that, while many sorption and desorption reactions may appear to have reached equilibrium, in fact the reaction can be continuous, and the slow process will not be measured if the experimentalist studies a short reaction time. In such cases, important secondary processes, which are slower than the primary process, may be completely overlooked. Thus predictions on the fate of the trace metal may be inaccurate.

2.7 DIFFERENT FORMS OF METALS IN SOIL

The different forms of a metal are important in considering their distribution in soil under different conditions with respect to the effect of their relative distribution on the environment and organisms. The USEPA adopted this concept in formulating regulations for biosolids (with limits based on total concentrations of a metal but took into account, through field research studies, how much was actually available to a plant). The forms

shown in the figure 2.4 below result from six different chemical processes within the soil.

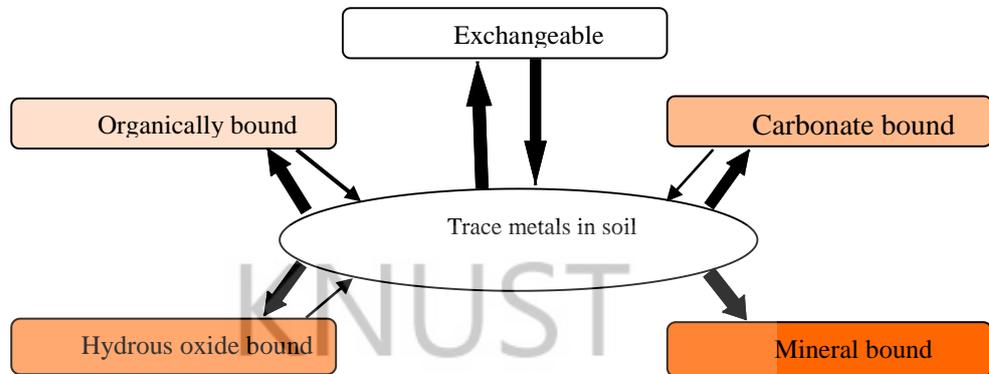


Figure 2.4: Forms of trace metals, based on their interaction with the different phases of the soil. As the forms change they move in the direction indicated by thicker arrows. The darker the rectangle, the less available are the trace metals.

In Soil Solution: Water in soil naturally contains salts. Most metals in solution form positive ions. The soil solution generally provides plants with all of their nutrients.

Exchangeable: Most soil particle surfaces are negatively charged (called anions), especially clay particles and organic matter. These negative charges attract positive charges and hold them somewhat like magnets. Such places in the soil are called exchange sites. Since most metals are positively charged, they are attracted and held at these exchange sites. There is a relationship between the number of cations on exchange sites and the number in solution; when those in solution are exhausted, others replace them from the exchange sites. And when more cations are added to the soil solution, many migrate onto exchange sites. These two forms are by far the most active biologically, and any metal must be in one of

these two forms before a plant can take it up. The other forms require alteration before a plant can assimilate them. If the metal is bound in an organic form, that organic matter must decompose. If it is bound in a chemical compound, the soil chemistry must change – often dramatically – before the metal becomes soluble.

Organically bound: When plants and soil fauna take up metals, they generally are incorporated into organic substances. However, metals can also be attracted to or surrounded by organic substances in the soil solution (chelation). In organic form, they are unavailable for interaction until the organic substances decompose. Some of these organic materials decompose quickly, temporarily releasing metals back into the soil solution; others decompose very slowly (up to hundreds of years for humus).

Combined with carbonates: In soils with neutral or higher pH (alkaline soils), large amounts of calcium may be presents as calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) or calcium carbonate (CaCO_3 , lime). Other metals (including trace elements) can take the place of calcium and form solids (precipitate). If precipitates do form, they usually contain more than one trace metal and often form mixed crystals that include combinations of major elements, typically calcium or iron. Simple solids can become available when soil becomes acidic (pH decreases), but the more mixed and crystalline the solids are, the less likely are they to solubilize.

Adsorbed by hydrous oxides: Elements like iron (Fe), manganese (Mn), and aluminum (Al) combine with oxygen (oxidize) to form solids, often coating soil surfaces. One example is rust; iron oxides give some

soils a reddish color. Metals may form solids with these other elements (coprecipitation) or become wrapped in the coatings (are adsorbed). When this happens, the metals are in stable forms that resist change.

Bound inside of minerals: Clay particles made of layers of silicon with oxygen or aluminum with oxygen form slowly but continually. As these clays form, metal ions can take the place of the silicon or aluminum (isomorphous substitution). Such mineral-bound metals are essentially unavailable (at least for hundreds of thousands of years).

All these forms can and do change, given enough time. However, as the size of the arrows in the figure 2.4 above increase, the tendency is for available forms to become less available with time. In other words when an organic substance containing a metal decomposes, that metal is temporarily released into the solution (becomes available). At that time, other changes may take place. The metal may be reincorporated into new organic matter or be bound by one of the other mechanisms. A change in the soil's environmental factors can also change the forms of metals. As soil becomes acidic (pH drops below 5), some oxides dissolve and the available portion of metals may increase. Also as pH drops and soil becomes acidic, aluminum, iron, and manganese become more soluble. Some plants are acid loving (e.g., azaleas, blueberries), but most tolerate acid soils and grow poorly in them.

2.8 ASSOCIATIONS OF SOIL COLLOIDS

Natural soil colloids are organo-mineral associations of various soil constituents, which are the main contributors to sorption and transport processes affecting contaminants in soil and aquatic environments.

Because interactions between soil constituents can significantly alter the amount and nature of the surface exposed by soil colloids for contaminant sorption, predictions of the extent of sorption based on the sum of the sorption capacities of the individual soil constituents may result in serious deviation from the reality. Consequently, sorption predictions from soil composition would be greatly improved with a better understanding of how interactions between individual soil constituents affect the sorption behavior of naturally occurring soil colloids (Cornejo et al. 2003).

2.9 EVIDENCE OF METAL ORGANIC INTERACTION IN SEMI-NATURAL ECOSYSTEMS

2.9.1 Density of reactive sites on metal-(oxyhydr)oxide surfaces.

The density of surface sites capable of participating in acid-base, ligand exchange, or electron-transfer (redox) reactions with ions in solution is an additional factor that should be considered in discussions of sorption processes (see, e.g., Yates, 1975; Yates and Healy, 1975; Furlong et al., 1981; James and Parks, 1982; Davis and Kent, 1990, Koretsky et al. 1998). Estimates of surface site densities for various metal -(oxyhydr)oxides and (alumino)silicates have been made using a variety of very different strategies. James and Parks (1982) summarized published values obtained by several methods for several metal-(oxyhydr)oxides. For goethite, for example, they list values ranging from 5.4 sites/nm² from NaOH titration, to 16.4 sites/nm² from tritium exchange, to 16.8 sites/nm² based on consideration of the surface crystal structure. Site density estimates based on a consideration of the atomic arrangements of the most common goethite surfaces [(110) and (021): Cornell et al., 1974] are 4.4 sites/nm²

(proton acceptor sites) and 6.7 sites/nm² (proton donor sites), which were derived by assuming that the surfaces in contact with aqueous solutions are simple terminations of the bulk crystal structure (i.e., no reconstruction) (Sposito, 1984). Using molecular statics calculations, Rustad et al. (1996) predicted a site density of between 15 and 16 reactive sites/nm² for goethite crystals dominated by (110) and (021) crystal faces, which is consistent with the tritium exchange results reported by Yates and Healy (1975) and the estimates of site densities based on surface crystal structure. A recent estimate of the density of "protonatable" sites on lepidocrocite (γ -FeOOH), based on proton release during base titration from pH 3.4 to 7.3 (the latter value being the pH_{PZNPC} of lepidocrocite, Zhang et al., 1992), is 0.88 sites/nm² (Manceau et al., 2000b). In addition, recent estimates of the reactive site densities on hematite, based on analyses of structural sites on different hematite faces, are 9 to 16 sites/nm² (Barron and Torrent, 1996) and 4.5 to 27.3 sites/nm² (Koretsky et al., 1998). Other estimates of reactive site densities have come from the maximum extent to which a solute adsorbs onto a sorbent.

The ranges of surface site densities, such as those reported above for Fe(III)-(oxyhydr)oxides, are due to a number of factors, including different experimental or theoretical methods and different solid preparation, each of which may produce different site populations or are sensitive to different types of sites (e.g., those with different acidities). Thus, site density measurements should be used as approximations only and verified by independent methods if possible.

An important question related to the issue of surface site density is to what extent the density of available reactive surface sites limits the sorption capacity or number of aqueous metal ions that can be sorbed on a solid surface. It is clear that mineral surfaces in contact with aqueous solutions are likely to contain more than a single type of binding site (see e.g., Knozinger and Ratnasamy, 1978; Benjamin and Leckie, 1980; Benjamin and Bloom, 1981; Schindler et al. 1987; Hiemstra and Van Riemsdijk, 1996; Bargar et al. 1997d; Eng et al. 2000; Trainor et al. 2002). Several possible reasons for different types of surface sites include the following: (1) structural differences in exposed crystal faces lead to differences in oxygen coordination of the solid's cation(s) on different surfaces, hence differences in site acidity and anion bonding (see, e.g., Knozinger and Ratnasamy, 1978; Sposito, 1984); (2) some crystal structures result in more than one type of site on a single crystal face (e.g., the hydrated α - Al_2O_3 (1-102) surface, Trainor et al., 2002); and (3) structural defects of various types on surfaces offer small concentrations (perhaps 5-10%) of particularly reactive sites (see, e.g., Liu et al. 1998a). Perhaps this last idea underlies the assumption of a small population of strongly sorbing sites on metal-(oxyhydr)oxides. Such a population of defect sites on metal-(oxyhydr) oxide surfaces could explain the commonly observed rapid initial uptake of metal ions on these sorbents from aqueous solutions.

In addition to these structural arguments, thermodynamic considerations indicate that anions should adsorb at lower activity onto more energetic sites, and onto less energetic sites when the anion activity

or other contributions to the free energy of adsorption provide a larger drive. As available sites fill, there are at least two options for further adsorption reactions: (1) adsorption may continue until all available surface sites are occupied, then stop; or (2) existing sorbed material may provide additional adsorption sites, so that sorption continues onto both pre-adsorbed adion complexes and the free surface. In either case, when the surface is entirely covered, some other process, such as precipitation, possibly nucleated by pre-adsorbed material, must take over if uptake is to continue.

It should be clear from this discussion that more experimental and theoretical studies are required to understand the structural nature, number, energetics, and differences in reactivity of different reactive sites on mineral surfaces, particularly defect sites. Spectroscopic studies, coupled with atomic resolution AFM or STM (where possible), surface-sensitive infrared spectroscopy, second harmonic generation, and high-resolution x-ray photoemission studies, on mineral surfaces in contact with aqueous solutions are needed to provide some of this information.

2.9.2 Conceptual Models of the Metal Oxide/Aqueous Solution Interface Region

2.9.2.1 General comments on the structure and reactivity of hydrated metal oxide surfaces:

Although there has been a great deal of work on the geometric and electronic structures of clean metal oxide surfaces (see, e.g., Henrich and Cox, 1994; Gibson and LaFemina, 1996; Henrich, 1996; Brown et al., 1999a), very little is known by

direct observation about the geometric and electronic structures of hydrated metal oxide or (alumino) silicate surfaces in air or in contact with bulk water, which are the relevant surfaces in aquatic environments (Brown, 2001). Even in air, metal-(oxyhydr) oxide surfaces are likely to have multiple monolayers of sorbed water. For example, α - Al_2O_3 surfaces have been shown by thermo-gravimetric analysis to have the equivalent of one monolayer of water at a relative humidity (RH) of approximately 35% and the equivalent of more than 20 monolayers at 95% RH (Yan et al., 1987). In the case of high-surface-area silica, Miyata (1968) found the equivalent of 26 monolayers of water at a RH of 98%, and Pashley and Kitchener (1979) found the equivalent of 50 monolayers of water on quartz at 100% RH. When exposed to liquid water, many metal oxide surfaces become hydrated or hydroxylated over time. The outermost surfaces of aluminum oxides such as α - Al_2O_3 , for example, hydroxylate rapidly (within a matter of minutes) (Liu et al., 1998d) followed by hydroxylation of more extensive regions, resulting in conversion of the surface region of aluminum oxides into boehmite (α - AlOOH) and bayerite (γ - $\text{Al}(\text{OH})_3$) (Dyer et al., 1993; Lee and Condrate, 1995; Laiti et al., 1998; Wijnja and Schulthess, 1999; Eng et al., 2000), and, given sufficient time, to gibbsite (α - $\text{Al}(\text{OH})_3$), the thermodynamically stable hydrated alumina phase (Hemingway and Sposito, 1996). Thus the surfaces of aluminum oxides used in aqueous sorption experiments are not likely to have the same structures or compositions as the anhydrous starting material.

2.9.2.2 Acid-base reactions at metal-(oxyhydr)oxide-water interfaces:

It is generally accepted that oxygens on metal-(oxyhydr)oxide surfaces in contact with liquid water or water vapor are bonded to protons, with doubly protonated surface oxygens present at acidic pHs and singly or non-protonated surface

oxygen atoms present at basic pHs (Schindler et al., 1976b; Schindler, 1981). Thus metal oxide surfaces can undergo acid-base reactions and behave amphoterically as a function of pH. As early as 1929 in the metallurgical literature, Gaudin (1929) observed that "It appears established ... that H^+ and OH^- ions react with the mineral surfaces ... and that they have much to do with the adherence of [selectively adsorbing surfactants]". Later, Gaudin and Rizo-Patron (1942) suggested that mineral surfaces react with water to produce hydroxide functional groups; thus for SiO_2 , the $Si^{\delta+}$ and $O^{\delta-}$ exposed at the surface by fracture would hydrolyze water, producing presumably ionizable $-SiOH$ groups. These ideas grew rapidly, and later, for example, Kurbatov et al. (1951) suggested an adsorption mechanism involving cation exchange of Co^{2+} with the protons in surface functional groups. In addition, years of work that suggested similar models of surface hydroxylation, site ionization, and adsorption of cations and anions by exchange with hydrogen and hydroxide ions dissociated from surface sites—all by inference from froth flotation reagent behavior have been summarized.

More direct information on the protonation of surface oxygen atoms on quartz and other metal oxides have been provided by surface-sensitive infrared spectroscopy studies. Among the earliest were those by Peri and Hannan (1960) and Peri (1966), which established the presence of $SiOH$ and $AlOH$ sites on the surfaces of Al_2O_3 and SiO_2 gels. Using attenuated total reflection (ATR) IR spectroscopy, Fripiat et al. (1965) and Anderson and Parks (1968) used IR spectroscopy, coupled with measurements of surface electrical conductivity, to argue that the hydroxide functional groups or sites (generically, MOH) on alumina and silica gels and clays ionize by deprotonation in humid gaseous atmospheres, as forecast by Gaudin and Rizo-Patron (1942) for quartz surfaces immersed in water. Changes in pH observed

upon immersion of high surface area oxides in water after corrections for changes caused by dissolution suggest protonation of MOH (in acidic solutions) and deprotonation (in alkaline solutions), leading to observable, pH-dependent surface charge and potential (see, e.g., summary in Parks, 1990). On high-surface-area "catalytic" aluminas, Knozinger and Ratnasamy (1978) found evidence for five different types of surface OH groups using IR spectroscopy.

The results of many other surface-sensitive spectroscopic studies of the interaction of water with a number of metal oxide surfaces are summarized by Thiel and Madey (1987), Noguera (1996), and Henderson (2002). Some of these studies report temperature programmed desorption (TPD) measurements of molecular water or hydroxyl release from "clean" metal oxide surfaces in ultra-high vacuum environments (e.g., Stirniman et al., 1996; Gunster et al., 2000).

In parallel with these low-temperature TPD studies, there have been a number of room-temperature O 1s core-level and O 2p-valence band photoemission studies of the interaction of water vapor with UHV-cleaned single crystal metal oxide surfaces using synchrotron radiation [e.g., MgO (Liu et al., 1998a; 1998b), CaO (Liu et al., 1998c), α -Al₂O₃ (Liu et al., 1998d), α -Fe₂O₃ (Liu et al., 1998d), Fe₃O₄ (Kendelewicz et al., 2000b), and MnO (Kendelewicz et al., 1999)]. What is clearly demonstrated by these and other similar studies is that most freshly exposed metal oxide surfaces react rapidly with liquid water or water vapor in the atmosphere and become fully hydroxylated.

2.9.2.3 Differences in reactivity of different metal oxide surfaces:

Macroscopic uptake measurements have shown that some metal-(oxyhydr)oxides and (alumino) silicates are more reactive than others for particular anions. For example, the alkaline earth cations show different affinities on hydrous

iron oxides versus hydrous aluminum oxides, with the order of uptake being, $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$ on RFO and $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ on HAO (Kinniburgh and Jackson, 1981). This reversal of affinities is thought to be due to the differences in the structure of water at the interfaces, presumably caused by differences in dielectric constants of the two solids (Berube and DeBruyn, 1968a).

A straightforward example of the differences in reactivity of different sorbents for a single sorbing cation comes from a macroscopic uptake study by Kohler et al. (1992), who found the following order of affinities of different sorbents for Np(V) (with approximate pH_{ads} values given in parentheses and the adsorption edge data normalized to equimolar surface sites): goethite (5.5) > hematite (6.0) > gibbsite (6.8) > kaolinite (8.2) > albite (10.3) > quartz (12). The pH_{PZC} of these sorbents is as follows: goethite (7.5-8.3), hematite (8.5), gibbsite (10.0), kaolinite (3.5-5.4), albite (2.6), and quartz (2-3) (values from Sverjensky, 1994, except for goethite [from Hingston et al., 1972] and kaolinite [from Parks, 1967 and Schroth and Sposito, 1997]). Thus goethite, hematite, and gibbsite sorb Np(V) well below their pH_{PZC} values, where their surfaces are positively charged, suggesting that Np(V) forms relatively strong chemical bonds with surface functional groups on these three sorbents. In contrast, sorption of Np(V) on the other phases occurs well above their pH_{PZC} , suggesting that the bonds between Np(V) and surface functional groups on these sorbents are not as strong or that the adsorption free energy must include a repulsive term (James and Healy, 1972b). This example shows that quartz, in particular, has relatively non-reactive surfaces, as is also indicated by its slow weathering rates in most natural environments. This relatively low reactivity can be understood qualitatively by considering bond valence constraints, as discussed later.

Among the common mineral sorbents, manganese and iron oxides play a prominent role in sorbing first-row transition metal ions and heavy metal ions from natural waters (Usui, 1979; Li, 1982; Stumm and Morgan, 1981).

Takematsu (1979) and Li et al. (1984) determined the relative affinities of divalent cations in seawater for goethite, vernadite, and aluminosilicate phases (clays) and found that vernadite has the highest K_d and that pelagic clay minerals have the lowest. The higher affinity of many cations for vernadite and goethite versus clay minerals is attributed to the smaller intrinsic acidity constants of vernadite and goethite relative to clay minerals (for the reaction $-X-OH = -X-O^- + H^+$) and to the higher dielectric constants of vernadite (0.32) (Murray, 1975) and goethite vs. clay minerals (4.5 to 8) (Keller, 1966), resulting in a smaller $\Delta G_{\text{solvation}}$ for Mn and Fe oxides than for clay minerals (Takematsu, 1979; Li et al., 1984).

To provide more fundamental understanding of the differences in reactivity of metal oxides surfaces, it is instructive to consider the differences in reactivity of clean versus water-exposed metal oxide surfaces, which are significant. Most clean metal oxide surfaces (e.g., fresh fracture surfaces or those under ultra-high vacuum conditions) are much more reactive than hydrated surfaces (i.e., those in contact with a humid atmosphere or bulk water) because of the presence of a larger number of coordinatively unsaturated surface atoms in the former case. For example, on the clean MgO(100) surface, there should be 5-coordinated Mg and O ions on terraces, 4-coordinated Mg and O atoms along edges, and 3-coordinated Mg and O atoms at corners. A number of theoretical studies have predicted that corner and edge sites are significantly more reactive than terrace sites, which are not predicted to cause water to dissociatively chemisorb (e.g., Scamehorn et al., 1994; Langel and Parrinello, 1994). This difference is attributed to the greater degree of

undercoordination of edge and corner sites on clean MgO(100). However, more recent theoretical work on the reactivity of water on clean MgO(100) (e.g., Giordano et al., 1998, 2000; Johnson et al., 1999; Odelius, 1999) has predicted that water does indeed dissociatively chemisorb on MgO(100) terrace sites, in agreement with experimental studies (see Liu et al., 1998b; Brown et al., 1999b). Recent theoretical studies of the interaction of water with the α -Al₂O₃ (0001) surface (Hass et al., 1998; Wang et al., 2000) also predict that water should dissociatively chemisorb, in agreement with experimental work (e.g., Liu et al., 1998d).

A recent study by Goldberg et al. (2001) examined changes in reactivity of amorphous Al-oxides to aqueous borate, arsenite, arsenate, and molybdate ions as a function of differences in preparation method, which produced significant initial differences in surface areas of the dry powders. They found, however, that upon reaction of these different powders with aqueous solutions, the initially high surface areas decreased and the initially low surface areas increased to a surface area of 32.4 ± 2.8 m²/g. Based on these results, they concluded that initial surface area is not a good indicator of reactivity of synthetic amorphous Al-oxides.

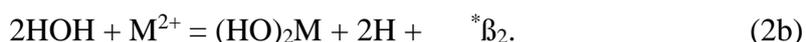
2.9.2.4 Ligand-exchange reactions:

The reaction of metal-(oxyhydr)oxide and (alumino)silicate surfaces with aqueous cations, resulting in inner-sphere surface complexes, is widely believed to involve ligand exchange in which M-O bonds of the hydrated ion break and M ions bond directly to surface oxygens, with a release of protons (Kurbatov et al., 1951; Schindler, 1981; Schindler and Stumm, 1987) (see sample reactions (1a) and (1b)).

Sorption of adion M onto site XOH:



and hydrolysis:



One reason for invoking this type of reaction mechanism is that between one and two or more protons are released on average for each divalent cation sorbed on Al and Fe(III)-oxide surfaces (Hohl and Stumm, 1976; Davis and Leckie, 1978a; Benjamin and Leckie, 1981a; Kinniburgh and Jackson, 1981). In contrast, when adions form weakly bound outer-sphere surface complexes, it is assumed that they remain fully hydrated and are attracted to the surface through simple electrostatic attraction or through H-bonding. In this case, one might expect minimal proton release on an electrostatic basis. Kinniburgh and Jackson (1981) cite several references attesting to proton yields below 1.2 per cation for sorption of alkaline earth cations.

One problem in estimating the number of protons released during such ligand-exchange reactions is that one cannot be certain where the protons originate. In addition to proton release during the ligand exchange reaction [reaction (1a)], it is also possible for protons to be released during hydrolysis reactions near the interface [reaction (2a)] or even in the bulk solution. At present, there is no straightforward way to distinguish between these two possibilities, which makes interpretation of proton release data from macroscopic uptake measurements difficult.

Casey and co-workers have pointed out that the rates and mechanisms of ligand exchange reactions of solution complexes are useful guides to the rates and

mechanisms of similar reactions on metal-(oxyhydr) oxide surfaces (Casey and Westrich, 1992; Casey, 1995). For example, a recent ^{17}O NMR study of oxygen exchange on different structural sites of the Al_{13} polyoxocation $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$, which is claimed to be similar to structural units on aluminum hydroxide surfaces, showed a large difference ($\approx 10^7$) in the labilities of two structurally similar bridging oxygens. This suggests that surface reactivity is very sensitive to molecular structure (Phillips et al., 2000).

2.9.2.5 Oxidation-reduction (redox) reactions on metal oxide surfaces:

In addition to ligand exchange and acid-base type reactions discussed above, the surfaces of metal-(oxyhydr)oxide containing redox-sensitive cations such as Fe(II) or Mn(IV) may undergo redox reactions, some of which involve photo-redox processes (e.g., Waite, 1990). Such reactions can fundamentally change the structure and reactivity of mineral surfaces (e.g., White, 1990; Scherer et al., 1999; White and Peterson, 1999). Redox reactions result in electron transfer from an electron donor atom or molecule to an electron acceptor atom or molecule. An example is the reduction of Cr(VI) to Cr(III) on magnetite surfaces, which involves the transfer of an electron from three Fe(II) ions at or near the surface to Cr(VI), resulting in the production of three Fe(III) (e.g., Peterson et al., 1997) (see section entitled " CrO_4^{2-} sorption reactions"). Similar mechanisms have been proposed for Cr(VI) reduction on Fe(II)-bearing micas (e.g., Ilton et al., 2000), and for selenate (CrO_4^{2-}) reduction to Se(0) on green rust surfaces (e.g., Myneni et al., 1997). Chromium(III) can also be oxidized to Cr(VI) on MnO_2 surfaces (e.g., Fendorf and Zazoski, 1991). Such reactions, under abiotic conditions, can result in the formation of a "passivating" layer that can dramatically reduce the probability of electron transfer and effectively stop the redox reaction. Such is the case for Cr(VI)

reduction on magnetite surfaces, which quickly become passivated by a 15-30 Å thick layer of (Fe(III),Cr(III))OOH (Peterson et al., 1997b; Kendelewicz et al., 2000a; Brown et al., 2001).

*2.9.2.6 The dynamic nature of metal-(oxyhydr)oxide surfaces—
dissolution/reprecipitation reactions:*

Metal-(oxyhydr)oxide and (alumino)silicate surfaces are rarely static when in contact with aqueous solutions, organic matter, or microbial biofilms. In these situations, minerals often undergo dissolution reactions, which may be promoted by organic ligands (e.g., Furrer and Stumm, 1986; Stone and Morgan, 1987; Stumm and Furrer, 1987; Maurice et al., 1995; Ludwig et al. 1996) and microorganisms (e.g., Hersman et al. 1995; Urrutia et al. 1998, 1999; Zachara et al. 1998; Dong et al. 2000; Fredrickson et al. 2000, 2001; Hersman, 2000; Maurice et al. 2000; Hersman et al. 2001; Kukkadapu et al. 2001; Liu et al., 2001a, 2001b; Maurice et al. 2001a, 2001b). Many metal-(oxyhydr)oxides and (alumino)silicates show enhanced dissolution in aqueous solutions at low and high pH, with minimum solubility at near neutral pH values (e.g., α -Al₂O₃). The mechanism of dissolution reactions of simple metal oxides has been related to the number of protonation and deprotonation steps leading to the detachment of the hydrated metal ion rather than to the number of protons needed to form feasible activated metal complexes, and the rates are found to be similar to water ligand exchange of dissolved metal complexes (Casey and Ludwig, 1996). Surprisingly, there is not as much difference as expected in the dissolution rates of rutile crystals that have different types and numbers of defects (Casey et al., 1988), suggesting that bulk dislocation density is not a useful measure of potential sites for etch pit growth on rutile crystal surfaces.

There is also the possibility of dissolution/precipitation reactions, involving the incorporation of ions dissolved from the surface plus other ions in solution into a new phase that may or may not be associated with the surface. For example, Thompson et al. (1999b, 2000) found evidence for the formation of a Co(II)-Al-hydroxalcalite-like phase closely associated spatially with the surfaces of kaolinite particles that form when kaolinite is reacted with $\text{Co}(\text{NO}_3)_2$ solutions unsaturated with respect to known Co-(oxyhydr)oxide solids.

Bacteria may also promote precipitation reactions (referred to as biomineralization) that can sequester metal ions from solution. For example, bacterial degradation of urea promotes calcium carbonate precipitation in some aquifer systems. Warren et al. (2001) found that such precipitates can incorporate up to 95% of the Sr^{2+} added to solution at the 1 mM level within 24 hours, resulting in the formation of a solid solution with calcite and vaterite, whereas the incorporation of UO_2^{2+} was not as effective, with only 30% uptake. Cu^{2+} sequestration by this mechanism was found to be poor because of toxic effects on the bacteria.

2.9.2.6 Effect of substitutional defects on surface reactivity:

Another important factor affecting surface reactivity is substitutional defects in metal-(oxyhydr)oxides. For example, it is well documented that small quantities of Al(III) substituted for Fe(III) in goethite alters its dissolution rate (Schwertmann, 1984, 1991; Schwertmann and Cornell, 1991; Schulze and Schwertmann, 1984, 1987; Cornell and Schwertmann, 1996). In addition, Ainsworth et al. (1989) have shown that Al-substituted goethite is a less effective sorbent for aqueous chromate than Al free goethite, with the pH_{ads} for Al-goethite shifted to lower pH values at all chromate concentrations considered (6×10^{-6} M

to 5×10^{-4} M). Ainsworth et al. (1985) found a similar effect for phosphate adsorption on Al-substituted versus Al-free goethites. Because most minerals contain substitutional impurities, some at concentrations higher than a few mole percent, it is important to understand the impact of such substitutions on surface reactivity and other related variables such as surface area, crystal morphology, aging time, and degree of crystallinity of the sorbent (e.g., Martinez and McBride, 1988a, 1988b, 1999, 2000, 2001; Ainsworth et al., 1994). For example, several studies have shown that Al-substituted hematites adsorb phosphate oxoanions preferentially on non-basal faces (Barrón et al., 1988; Colombo et al., 1994). Additional studies of these types are clearly needed to provide a better understanding of the effects of substitutional impurities on mineral surface reactivity.

2.9.3 XAFS Spectroscopy Studies of Trace Cation Sorption

Reaction Products

Divalent copper is present in aqueous solutions at low concentrations (< 0.1 M) dominantly as the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex at lower pH values, dominantly as dimeric $\text{Cu}_2(\text{H}_2\text{O})_4(\text{OH})_2^{2+}$ complexes at intermediate pH values, and as a variety of mononuclear hydrolysis products at higher pH values (Baes and Mesmer, 1986). Because of its d^9 electronic configuration, its first coordination shell of six oxygen ligands is typically tetragonally distorted due to the Jahn-Teller effect, resulting in four equatorial oxygens at ≈ 1.98 Å and two axial oxygens at ≈ 2.34 Å in solution (Magini, 1982). These two axial oxygens are difficult to characterize using XAFS spectroscopy (Filiponi et al., 1994; Cheah et al., 1998).

There have been a number of macroscopic uptake and spectroscopic studies of Cu^{2+} sorption onto metal-(hydr)oxides and silicates, including $\alpha\text{-SiO}_2$ (Vuceta, 1976; Benjamin and Leckie, 1980), amorphous silica (Schindler et al., 1976a;

Bourg and Schindler, 1978; Bourg et al., 1979; Bassetti et al. 1979; von Zelewsky and Bemtgen, 1982; Motschi, 1984; Park et al. 1993, Xia et al. 1997c, 1998; Cheah et al. 1998, 1999, 2000); γ -Al₂O₃ (Elliot and Huang, 1979; Ottaviani and Martini, 1980; Benjamin and Leckie, 1980; Martini et al. 1980, Motschi, 1984; Harsh et al. 1984; Cheah et al. 1997, 1998, 2000), amorphous and crystalline Al-hydroxides (McBride, 1978a; McBride et al. 1984; Micera et al. 1987; Weesner and Bleam, 1997; Karthikeyan et al. 1999), goethite (Padmanabham, 1983, Bochatay et al. 1997; Robertson and Leckie, 1998); manganese oxide (Fu et al, 1991); anatase (Cheah et al. 2000), micas (Farquhar et al., 1996, 1997), perthitic feldspar (Farquhar et al., 1997), and clay minerals (Clark and McBride, 1984; Morton et al., 2001). The spectroscopic studies in this group suggest that Cu(II), (1) forms dominantly inner-sphere complexes on these surfaces, except for the permanently charged sites of montmorillonite, where Cu(II) forms outer-sphere complexes, (2) forms dominantly mononuclear monodentate and bidentate complexes at sufficiently low Cu(II) surface coverages and dimers and hydroxo-bridged clusters or precipitates at high Cu(II) surface coverages, and (3) bonds more strongly to Al-hydroxide and oxide phases than to SiO₂.

The XAFS study of Cheah et al. (2000) of Cu(II) sorption products on amorphous silica, γ -Al₂O₃, and TiO₂ (anatase) at pH 6.0 to 6.5, [Cu]_T = 0.09 to 1.6 mM, Cu sorption density = 0.60 to 0.98 $\mu\text{mol}/\text{m}^2$, and I = 0.1 M (NaNO₃) showed that hydroxo-bridged Cu(II) polymers or Cu(II)-containing precipitates (most likely Cu(OH)₂) formed on these surfaces [$d(\text{Cu-Cu}) \approx 2.95 \text{ \AA}$], with larger cluster sizes on amorphous silica than on γ -Al₂O₃ or anatase at similar sorption densities. However, at very low Cu(II) sorption densities (0.007 and 0.05 $\mu\text{mol}/\text{m}^2$), Cu(II) was found to form dominantly inner-sphere, monodentate or bidentate complexes

on the γ -Al₂O₃ surface [$d(\text{Cu-Al}) \approx 2.8\text{\AA}$], sharing corners and/or edges with Al(O,OH)₆ octahedra, and dominantly innersphere monodentate (corner-sharing) complexes on amorphous silica [$d(\text{Cu-Si}) = 2.98 - 3.05 \text{ \AA}$] (Cheah et al., 1998). The effect of aging time on Cu (II) sorption products on these same low coverage amorphous silica and γ -Al₂O₃ sorption samples was also studied by Cheah et al. (1998). The ratio of dimeric to monomeric Cu(II) surface complexes was found to increase significantly with contact time (up to 90 h) between the sorbent and the Cu²⁺-containing solution, suggesting an increase in cluster size with aging. Similar results were obtained in EPR, XAFS, and magnetic susceptibility studies of Cu(II) sorption products on aluminum hydroxide (McBride, 1982), gibbsite (McBride et al., 1984), boehmite (Weesner and Bleam, 1997; Xia et al., 1998), silica (Xia et al., 1997c, 1998), and mica (Farquhar et al., 1996, 1997). The XAFS study of Cu(II) sorption on montmorillonite by Morton et al. (2001) was carried out at two different ionic strengths, so that Cu(II) sorption on the permanently charged sites (Na concentrations of 0.02 mol/L and pH <7) and on edge sites (Na concentration of 0.1 mol/L) could be distinguished. The Cu(II) sorbed at permanent charge sites was outer-sphere and could be desorbed by decreasing pH. At edge sites, both hydroxo-bridged Cu(II) monomers and dimers were detected. The Cu(II) on these sites was found to be irreversibly adsorbed at Cu(II) coverages <20 $\mu\text{moles/g}$ clay at pH 4.2 and at coverages >50 $\mu\text{moles/g}$ clay at pH 6.8. The irreversibility of the higher coverage samples was attributed, in part, to the formation of dimer surface complexes.

2.10 EFFECTS OF COMPLEXING LIGANDS ON METAL ION SORPTION ON METAL OXIDES

Seawater and freshwater contain a number of inorganic and organic ligands that can form complexes with the divalent metal cations discussed above. In seawater, for example, the most important inorganic ligands are Cl^- , SO_4^{2-} , CO_3^{2-} , and OH^- , with free-ion concentrations of 0.56 M, 1.16×10^{-2} M, 8.29×10^{-5} M, and 9.35×10^{-7} M, respectively (Dyrssen and Wedborg, 1974). In Mississippi River water, the dominant inorganic ligands are HCO_3^- , SO_4^{2-} , and Cl^- , with concentrations of 1.85×10^{-3} M, 5.5×10^{-4} M, and 6.8×10^{-4} M, respectively (Hem, 1985). The dominant types of metal-inorganic ligand solution complexes for 58 metal ions in model seawater (pH 8.2) and freshwaters (pH 6 and 9) were predicted by Turner et al. (1981) using equilibrium speciation calculations. Similarly, the dominant types of metal-inorganic and metal-organic ligand solution complexes of many of the same metal ions in freshwater (pH 7) and seawater (pH 8.2) were predicted by Stumm and Morgan (1981). The results of these calculations for Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} are summarized by Benjamin and Honeyman (1992) and are reported in Table 6. In addition, Murray (1992) summarized the calculations of Stumm and Morgan (1981) on the relative abundances of metal ion-organic ligand solution complexes formed by Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} and six organic ligands containing common functional groups in seawater.

The results can be summarized as follows: (1) carbonate and sulfate ions are the most important inorganic ligands (other than water molecules and hydroxide ions) complexing Co^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} in freshwater at pH 6 and 9; (2) chloride is the most important inorganic ligand complexing Cd^{2+} and Hg^{2+} in freshwater at pH 6; (3) chloride ion is the dominant inorganic ligand complexing Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} ,

and Pb^{2+} in seawater, other than hydroxide ions (in the absence of organic ligands); and (4) organic ligands, when included, are the dominant complexing agents of Cu^{2+} in both freshwater and seawater.

The question posed here is what effect, if any, do these ligands have on metal ion sorption on mineral surfaces in contact with freshwater or seawater. Many investigators have studied this question using macroscopic methods, with results and interpretations which show that the presence of complexing ligands may inhibit or enhance cation sorption on particle surfaces in several ways. Inhibition may result from (1) formation of non-adsorbing metalligand solution complexes (MacNaughton and James, 1974; Theis and West, 1986; Barow and Cox, 1992; Music and Ristic, 1992; Gunneriusson and Sjoberg, 1993); and/or competitive adsorption, or blockage of reactive surface sites by the anionic ligand (MacNaughton and James, 1974; Vuceta, 1976; Vuceta and Morgan, 1978; Benjamin and Leckie, 1982; Theis and West, 1986), enhancing the positive charge on a metal oxide surface below its pH_{pzc} by specific adsorption of an anionic ligand, which should reduce electrostatic repulsion of the cation by the surface (Diaz-Barrentos et al., 1990; Yao and Millero, 1996); (2) formation of metal-ligand ternary surface complexes (Bollard et al., 1977; Schindler and Stumm, 1987; Schindler, 1990; Lamy et al., 1991); and/or (3) formation of multinuclear oligomers or surface precipitates (Bollard et al. 1977; Benjamin and Bloom, 1981; Corey, 1981; Farley et al. 1985; Hawke et al. 1989; Brown, 1990; Chisholm-Brause et al. 1991; Fendorf et al. 1992b; Lutzenkirchen and Behra, 1996).

2.11 TERNARY SURFACE COMPLEXES

Cations normally sorb weakly or not at all at low pH and strongly at high pH. Anions show the opposite pH dependence, sorbing weakly at high pH and strongly at low pH. In the presence of complexing ligands, L, sorption of a cation, M, may be

inhibited at all pH values, or inhibited when $\text{pH} > \text{pH}_{\text{ads}}$ and enhanced when $\text{pH} < \text{pH}_{\text{ads}}$ (Davis and Leckie, 1978b). In cases where M is present predominantly as M-L complexes, and still sorbs when $\text{pH} > \text{pH}_{\text{ads}}$, sorption can be labeled "cation-like" (Benjamin and Leckie, 1981c), and it is thought that the complex binds to the surface through M, forming a ternary complex referred to as a Type A ternary surface complex (Schindler and Stumm, 1987). When sorption is enhanced while $\text{pH} < \text{pH}_{\text{ads}}$, sorption may exhibit "anion-like" pH dependence, and it is thought that the complex binds to the surface through the ligand, forming a complex referred to as Type B by Schindler and Stumm (1987). Ligands that tend to form Type B complexes are likely to be multiply charged or multifunctional (Davis and Leckie, 1978b). This phenomenon is well known in electrochemistry as anion-induced adsorption (Gulens, 1979). Surface-sensitive spectroscopy offers the opportunity to test these hypotheses by looking for direct metal-to-surface (M-S) bonding in cation-like sorption; to determine whether or not the ligand modifies the M-S bond distance, hence bond energy (is inhibition caused by competition alone or is the M-S bond weakened as well?); and to verify the absence of M-S bonding in anion-like sorption.

2.12 METAL ION-INORGANIC LIGAND COMPLEXES

The effects of inorganic complexants such as Cl^- , CO_3^{2-} , SO_4^{2-} , and $\text{S}_2\text{O}_3^{2-}$ on metal-ion sorption at metal-(oxyhydr)oxide-aqueous solution interfaces can be significant, as shown by the results of macroscopic uptake studies (see Table 8). These effects have been discussed in general terms by a number of authors (e.g., Kinjo and Pratt, 1971; Stumm and Brauner, 1975; Davis and Leckie, 1978b, 1980; Vuceta and Morgan, 1978; Benjamin and Leckie, 1981c, 1982; Stumm and Morgan, 1981, 1996; Honeyman, 1984; and Benjamin and Honeyman, 1992). In addition to these macroscopic uptake studies, there have been about a dozen in situ XAFS studies of

these types of ternary systems. Several representative examples of these macroscopic uptake and XAFS studies of the interaction of metal-inorganic ligand complexes with mineral surfaces are discussed below, with an emphasis on Pb(II) and Hg(II). In order to understand the potential interactions of metal ions with inorganic ligands near the mineral- solution interface, we must first consider how such ligands accumulate in the EDL. The common inorganic ligands chloride, carbonate, sulfate, as well as less common ones (e.g., thiosulfate, phosphate, nitrate, and perchlorate) in natural waters accumulate in the diffuse layer at mineral-solution interfaces at pH values below the pH_{PZC} of the solid, where the ligand-free solid surface is positively charged. These ligands can specifically sorb to many minerals through either covalent or hydrogen bonding with the surface resulting in either innersphere complexes or specifically bound outersphere complexes. Therefore, they should reduce the positive charge on sorbent surfaces at $pH < pH_{PZC}$. This reduction in positive charge should enhance the sorption of aqueous cations at the solid-solution interface. There is also the possibility that these specifically bound ligands will form ternary complexes (Type A or Type B) with metal cations; however, spectroscopic data are needed to confirm or refute this possibility on a case by case basis. In contrast, those ligands that act as "indifferent" electrolytes, such as nitrate and perchlorate, do not form direct bonds with the sorbent surface, and thus are non-specifically sorbed through weak electrostatic forces and do not significantly alter surface charge. Therefore, "indifferent" ions should not have much impact on trace cation sorption on mineral surfaces. There is evidence from macroscopic uptake measurements that sulfate and carbonate ligands may indeed enhance sorption of divalent metal ions in model sorption systems. For example, Ostergren et al. (2000b) found that the presence of sulfate at the goethite-solution interface increased the uptake of Pb(II) by a factor of 30% (at pH 5, $[Pb]_T = 0.3 \text{ mM}$

and $[\text{SO}_4^{2-}]_T = 0.63 \text{ mM}$, 5 g/L goethite; surface area (goethite) = $95 \text{ m}^2/\text{g}$, $\Gamma_{\text{sulfate}} = 1.0 \text{ } \mu\text{mol}/\text{m}^2$, $\Gamma_{\text{pb(II)}} = 0.5 \text{ } \mu\text{mol}/\text{m}^2$) relative to the sulfate-free system. At this pH value, sulfate should form dominantly inner- sphere complexes at A-type (singly coordinated) oxo groups on the goethite surface, based on ATR-FTIR measurements (Peak et al., 1999; Ostergren et al., 2000b) and consideration of bond valence arguments for the bulk-terminated goethite surface, as discussed earlier. The addition of carbonate to the Pb(II)-goethite-water system (at pH 5, $[\text{Pb}]_T = 0.045 \text{ mM}$, $\text{PCO}_2 = 1 \text{ atm.}$, 1g/L goethite; surface area (goethite) = $90 \text{ m}^2/\text{g}$, $\Gamma_{\text{pb(II)}} = 0.4 \text{ } \mu\text{mol}/\text{m}^2$) enhances Pb(II) uptake on goethite by a factor of 18% (Ostergren et al., 2000a). In this pH range, carbonate has been shown to lower the electrophoretic mobility and decrease the pH_{PZC} of Al- and Fe-oxides (Su and Suarez, 1997). These data, coupled with ATR-FTIR spectroscopy measurements, suggest that carbonate forms inner-sphere monodentate complexes on these oxides (Su and Suarez, 1997). Coupled XAFS and ATR-FTIR spectroscopic results (Ostergren et al., 2000a, 2000b) show that when Pb(II) (at sorption densities of $0.4 \text{ to } 4 \text{ } \mu\text{mol}/\text{m}^2$) sorbs on goethite powders in the presence of aqueous solutions (pH 5-7; 0.1 M NaNO_3 or 0.1 M NaHClO_4) containing sulfate ($\Gamma_{\text{sulfate}} = 0.5 \text{ to } 1.5 \text{ } \mu\text{mol}/\text{m}^2$) or carbonate ($\text{PCO}_2 = 1 \text{ atm}$) oxoanions, dominantly Type-A ternary surface complexes are formed in which the complex is bonded to the goethite surface through Pb(II) ions. In contrast to the above studies, van Geen et al. (1994) used macroscopic uptake measurements of Cr(VI) on goethite to show that CO_2 (at $[\text{CO}_2] = 0.4 \times 10^{-4} \text{ to } 0.6 \times 10^{-4} \text{ M}$ and pH 3 to 8) significantly inhibits Cr(VI) adsorption and suggested that mineral oxide surface sites that control solid/solute partitioning of metal ions in natural systems may be largely bound to adsorbed carbonate species.

Phosphate also enhances the sorption of Pb(II) on goethite and boehmite surfaces, although the mechanisms are thought to be different (Weesner and Bleam, 1998). Using a combination of electrophoretic mobility and XAFS spectroscopy measurements, these authors found that the presence of phosphate on both surfaces leads to the formation of lead phosphate surface phases that may be highly dispersed.

Chloride may also enhance Pb(II) sorption on goethite, relative to the same concentration of nitrate ion, under certain conditions [pH 4-6.5; 0.1 M NaCl], by forming ternary surface complexes (Barrow et al., 1981; Gunneriusson et al., 1994; Bargar et al., 1998). However, under other conditions, chloride may not affect (0.5 M NaCl; Balistrieri and Murray, 1982b) or may inhibit (1.0 M NaCl; Rose and Bianchi-Mosquera, 1993) Pb(II) sorption by forming non-adsorbing solution complexes with Pb(II). For example, Bargar et al. (1997c) examined the effect of 0.1 M Cl⁻ on Pb(II) sorption on goethite and γ -Al₂O₃ at pH 5-7, Pb(II) sorption densities of 1.2 to 5 $\mu\text{mol}/\text{m}^2$, and [Pb]_T of 0.24 to 4.53 mM. At pH 7, the presence of Cl⁻ had no discernable effect on the Pb(II)/goethite or Pb(II)/ γ -Al₂O₃ XAFS spectra; this was interpreted as indicating no Cl⁻ ligand effect on Pb(II) sorption on these sorbents. However, at pH \leq 6, the EXAFS spectra of Pb(II)/goethite were consistent with the presence of Pb(II)-chloro ternary surface complexes, attached to the goethite surface through both Pb-O_{surface} and Pb-Cl-Fe_{surface} bonds (B-type ternary complex), indicating that both Pb(II) and Cl bond to the goethite surface in an inner-sphere fashion. Pb-Cl-Al surface ternary complexes were not observed on γ -Al₂O₃ surfaces.

The effect of chloride ions on the uptake of Hg(II) by hydrous ferric oxides (HFO) as a function of pH is well illustrated by the study of Avotins (1975), who found that the pH_{ads} was shifted from ≈ 6.7 to ≈ 10.5 as [Cl⁻] was increased from 10⁻³ M to 1 M (all at constant total Hg concentration of 3.4 \times 10⁻⁵ M). The observed inhibition of

Hg(II) sorption on HFO with increasing $[Cl^-]$ is presumably related to the formation of $HgCl_x$ or $Hg(Cl,OH)_x$ solution complexes, which replace $Hg(OH)_x$ complexes on the HFO surface.

Hg(II) sorption to quartz (MacNaughton and James, 1974), goethite (Gunneriusson and Sjöberg, 1993), and γ -alumina (Bargar et al., 1997c) is also strongly inhibited as the concentration of chloride in these sorption systems increases, based on macroscopic measurements. Nonetheless, a careful modeling study suggests that a ternary $FeOHHgCl$ surface complex dominates sorption of Hg(II) on goethite at some combinations of pH and chloride concentration (Gunneriusson and Sjöberg, 1993). EXAFS spectroscopic analysis of the Hg(II)-chloride-goethite system indicates the presence of both Cl and Fe second neighbors around Hg(II) with increasing chloride concentrations, as initially proposed by Bargar et al. (1997c), which is consistent with the formation of $FeOHClHg$ ternary surface complexes bonded in an inner-sphere fashion to the goethite surface, as is also suggested by thermodynamic constraints (Gunneriusson and Sjöberg, 1993).

In contrast to the effects of chloride, sulfate ligands appear to mildly enhance Hg(II) sorption to goethite and γ -alumina under the conditions of the macroscopic uptake measurements by Kim et al. (2001). The slight increase in Hg(II) sorption with increasing concentration of sulfate observed in the macroscopic uptake measurements implies some association between Hg(II) and sulfate at the goethite surface. However, this effect was too small to be easily detected with EXAFS spectroscopy in the experimental study of Kim et al. (2000).

A final example of the effect of inorganic ligands on metal ion uptake on oxides comes from the XAFS study of Collins et al. (1999a) on Cd(II) sorption on goethite in the presence of sulfate or phosphate. On the "pristine" goethite (110) surface, Cd(II)

was found to form inner-sphere, bidentate, double corner-sharing complexes. Both sulfate and phosphate were found to enhance the uptake of Cd(II) on goethite, but no spectroscopic evidence for ternary sorption complexes with these ligands was found, suggesting that the ligands may sorb to surface sites other than those occupied by Cd(II) (Colins et al., 1999a).

2.13 NATURAL ORGANIC MATTER AND CATION-ORGANIC LIGAND COMPLEXES

2.13.1 *Natural Organic Matter (NOM) binding to mineral surfaces:*

NOM is thought to bind to mineral surfaces through the interaction of weak acidic functional groups (e.g., phenolic groups) on the NOM with relatively basic surface hydroxyls on mineral surfaces (Kummert and Stumm, 1980; Davis, 1982). Surfaces of minerals such as quartz, which have relatively acidic surface hydroxyls, do not bind NOM as strongly as the surfaces of minerals with basic surface hydroxyls, such as gibbsite. Thus the extent of coverage of a mineral surface by NOM may not be extensive in all cases, and is not well known in natural systems in general. Enhanced binding of NOM or simpler organic ligands to iron and aluminum oxide surfaces also occurs when the ligands have carboxylic or phenolic groups in ortho positions (e.g., salicylate, phthalate, or EDTA) relative to ligands with single functional groups or groups in meta or para positions (e.g., phenol, benzoic acid) (Davis and Leckie, 1978b; Rubio and Matijevic, 1979; Kummert and Stumm, 1980). For example, organic ligands with two adjacent phenolic groups (e.g., catechol, protocatechuic acid) show strong adsorption to metal- (oxyhydr)oxide surfaces. These results strongly suggest that the stereochemistry of functional groups on organic ligands plays a major role in the adsorption of NOM on mineral surfaces (Davis, 1984). Another factor that affects the

adsorption of NOM on mineral surfaces is the presence of aqueous inorganic ligands such as sulfate and phosphate that can compete with NOM for adsorption sites, thus reducing the uptake of NOM on these surfaces (e.g., Tipping, 1981; Ali and Dzombak, 1996b).

When NOM coats a mineral surface, the properties of the surface may change significantly (e.g., acquiring an overall negative charge at $\text{pH} < \text{pH}_{\text{pzc}}$, which should change the characteristics of the EDL and the electrostatic attraction of the surface for aqueous cations. There have even been suggestions that some, perhaps many, particles suspended in natural aqueous systems may be negatively charged due to adsorbed organic material (Neihof and Loeb, 1972; Hunter and Liss, 1979; Hunter 1980; Davis and Gloor, 1981; Tipping, 1981; Tipping and Cooke, 1982; Davis, 1984). More recent model system work by Au et al. (1999) led to the conclusion that "an adsorbed layer of NOM with a negative electrical potential is formed at the interface of NOM-coated particles regardless of the solution condition studied and probably of the properties of the particles." However, these suggestions have not been sufficiently tested in natural systems to be validated, and evidence presented later on the form of organic matter associated with continental shelf sediments (Ransom et al., 1997) appears to contradict them.

What is not known in any of these studies, however, is how changes in the macromolecular structure of NOM as a function of pH and ionic strength affect its binding to particle surfaces or how changes in solution conditions affect the stability of NOM on particle surfaces. Also not known is how the binding of NOM to particle surfaces affects its macromolecular structure. A recent synchrotron x-ray microscopy study of fluvial fulvic acid as a function of pH, ionic strength, and solution composition, with spatial resolution of about 50 nm, (Myneni et al., 1999) showed

major changes in macromolecular structure as a function of these variables, including significant disaggregation of the humic substance with increasing pH. These changes likely reflect changes in protonation, deprotonation, and metal complexation of the NOM functional groups, and are almost certain to affect the binding of humic substances to mineral surfaces and of cations to functional groups in humic substances.

2.13.2 Binding of aqueous cations to NOM:

The binding of aqueous cations on NOM not associated with mineral surfaces is thought to occur primarily at carboxylic and phenolic-type hydroxyl groups via the same types of ligand exchange mechanisms that occur during sorption of aqueous cations on hydroxylated mineral surfaces (e.g., Schnitzer and Skinner, 1965; Goodman and Cheshire, 1973, 1975, 1976; Cheshire et al., 1977; McBride, 1978b; Saar and Weber, 1980; Murray and Linder, 1984; Sposito, 1986; Frimmel, 1988; Robertson and Leckie, 1999). In addition, thiol groups are thought to be good binding sites for first-row transition metal ions such as Cu(II) and heavy metals such as Hg(II) (Buffle, 1988; Xia et al., 1999). Several models for the binding of cations by humic substances have been developed which use a Donnan-type expression for electrostatic interactions (Marinsky et al., 1980, 1995; Tipping and Hurley, 1992; Benedetti et al., 1995, 1996). The model developed by Tipping and Hurley, for example, assumes eight proton-dissociating groups in humic materials, each distinguished by an intrinsic pK value. Values of pK predicted from this model for the binding of divalent metal cations to humic material decrease in the order: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} \approx \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. Using a variant of this model (the Nonideal Competitive Adsorption Isotherm-Donnan Model; Benedetti et al., 1995), Benedetti et al. (1996) showed that in soil solutions, 50% of the Cd^{2+} and 99.99% of the Cu^{2+} is bound to dissolved organic matter.

In addition to macroscopic uptake studies of heavy metals by NOM, which generally show strong complexation of metals like Cu(II) and Pb(II) but weak complexation of Cd(II) (e.g., Saar and Weber, 1980; Tipping and Hurley, 1992), several EXAFS spectroscopy studies have examined the binding of Pb(II) and first-row transition metal cations to NOM (Xia et al., 1997a, 1997b). These studies have shown that Co(II) and Ni(II) are coordinated by six oxygens, with one to two 2nd-neighbor C atoms, indicating the formation of inner-sphere complexes with aquatic fulvic acid (FA), humic acid (HA), and Chelex-extracted soil humic substances (HS) at pH 4. Cu(II) in FA, HA, and HS was found to occur in a tetragonally distorted octahedral environment (due to the Jahn-Teller effect), with four equatorial oxygens at ≈ 1.94 Å and two axial oxygens at ≈ 1.98 Å and 4-5 second-neighbor C atoms at ≈ 3.05 - 3.16 Å, also indicating inner-sphere complexation at pH 4 (Xia et al., 1997b). Zn(II) is bonded to six oxygens [$d(\text{Zn-O}) \approx 2.10$ Å] in both FA and HA, but to two thiols [$d(\text{Zn-S}) = 2.33$ Å] and four oxygens [$d(\text{Zn-O}) = 2.13$ Å] and two 2nd-neighbor C atoms [$d(\text{Zn-C}) = 3.29$ Å] in HS at pH 4. Pb(II) is coordinated by four oxygens at $d(\text{Pb-O})$ distances of 2.30 to 2.44 Å depending on pH, which ranged from 4 to 6, and to two 2nd-neighbor C atoms [$d(\text{Pb-C}) = 3.25$ Å], indicating inner-sphere complexation of Pb(II) by HS (Xia et al., 1997a). Because the above XAFS studies were carried out on freeze-dried samples, it is possible that inner-sphere complexation was induced by the freeze-drying process. However, Xia et al. (1997a) pointed out that the EXAFS results for Cu(II) and Pb(II), which suggest the presence of water molecules in the 1st-shell coordination sphere of the cations, argue against alteration of the metal complexes upon freeze drying.

Sarret et al. (1997) have also used EXAFS spectroscopy to determine the nature of Zn(II) complexation by humic substances. They found that at low Zn concentrations

(300 to 5000 mg/Kg), Zn(II) forms inner-sphere octahedral and tetrahedral complexes, depending on the type of humic substance. At intermediate Zn concentrations (32 g/Kg), Zn(II) occurs in octahedral coordination and a number of different Zn sites is observed. At high Zn concentrations (500g/kg), most Zn was found to form outer-sphere complexes.

In another EXAFS study, Xia et al. (1999) found that Hg(II) is bonded to one carboxylic (or phenolic) oxygen [$d(\text{Hg-O}) = 2.02 \text{ \AA}$] and one reduced sulfur functional group [$d(\text{Hg-S}) = 2.38 \text{ \AA}$] in soil humic acid. Based on comparison of model EXAFS calculations with experimental EXAFS spectra, Xia et al. (1999) also suggested a 2nd coordination shell of one carbon atom [$d(\text{Hg-C}) = 2.78 \text{ \AA}$] and one disulfide/ disulfane S [$d(\text{Hg-S}) = 2.93 \text{ \AA}$] around Hg(II), indicating inner-sphere complexation. In light of the significantly larger number of oxygen versus reduced S ligands in soil humic acid, Xia et al. (1999) argued that Hg(II) should not be expected to have more than one 1st-shell reduced sulfur ligand. They also argue that the presence of two reduced sulfur atoms in the 1st and 2nd coordination shells of Hg(II) provides strong evidence that Hg(II) prefers to bond to reduced S functional groups in soil humic acid.

2.13.3 Effects of adsorbed NOM on cation sorption:

Organic ligands such as short chain amines, carboxylic acids, amino acids, and phenols can enhance sorption of metal ions on metal oxides by forming ternary surface complexes bound to one or more surface sites through either the metal ion or the ligand. There is also abundant evidence of metal-ion-enhanced sorption of organic solutes. For example, the adsorption of ionic alkyl surfactants (e.g., the common detergents and conditioners Nadodecyl (or "lauryl") sulfonates and amines) on oxides and silicates depends heavily on pH and ionic strength, apparently because the pH-dependent surface charge of the solid contributes to the adsorption bond through

electrostatic attraction. When the sign of the surface charge is the same as that of the surfactant anion, adsorption can be enhanced by addition of a bivalent inorganic ion of opposite charge—even such weakly sorbing cations as Ca^{2+} . The cation is thought to act as a bridge between a surface site and the organic anion (Healy and Fuerstenau, 1972; Parks, 1975). Hard water, i.e., the presence of Ca^{2+} or Mg^{2+} , enhances sorption and coagulation of humic materials (Sholkovitz and Copland, 1981; Tipping, 1981; Davis, 1982), thus reducing their mobility and altering their role in contaminant control. Calcium or Mg^{2+} ion enhancement of sorption of the carboxylic acids common in crude petroleum, or of anionic surfactants used in surfactant flooding (Gogarty, 1983a, 1983b) could conceivably interfere with petroleum recovery operations. Again, the role of cations in metal ion-enhancing sorption of organic solutes has been inferred, but apparently not explored directly.

There have been a significant number of experimental studies of the effects of simple organic ligands on cation sorption on model metal-(oxyhydr) oxide surfaces, including both macroscopic uptake measurements and spectroscopic characterization of the reaction products. There have also been macroscopic uptake studies of the effects of organic matter on metal ion sorption in more complex systems, including: the interaction of Cd(II) with organic matter in soils (Almas et al., 2000); Cu(II) with soil humic acid (Robertson and Leckie, 1999); Hg(II) with soil organic matter (Yin et al., 1996; Xia et al., 1999); Pb(II) with soil organic matter and soil particles (Strawn and Sparks, 2000); and Zn(II) with organic matter in soils (Almas et al., 2000) and with humic material (Sarret et al., 1997). The following discussion of selected results from these studies illustrates some of the effects that NOM may have on metal ion sorption processes.

Cu(II) is known to sorb strongly to organic functional groups (e.g., to nitrogen of porphyrin groups in humic acid; Goodman and Cheshire, 1973), and, according to the equilibrium speciation modeling, its speciation in both freshwater (pH 7) and seawater (pH 8.2) is dominated by Cu(II)-organic ligand complexes. Based on the useful analogy between the stability of solution complexes and sorption complexes of cations and cation-ligand pairs (e.g., Kummert and Stumm, 1980), perhaps it is not surprising that NOM sorbed on mineral surfaces is a strong sorbent for Cu(II) as well. One of the first systematic studies of the effect of NOM on Cu(II) sorption on a metal oxide was that of Davis (1984), who examined the effect of NOM (extracted from the surface sediment of Lake Urnersee, Switzerland) on the sorption of Cu(II) and Cd(II) on γ -Al₂O₃ (Alon) over the pH range 4 to 8. Davis found that Cu(II) is more strongly complexed by the functional groups of the adsorbed NOM than by the NOM-free alumina surface and that the apparent stability constant for the Cu(II)-sorbed organic matter complex is approximately equal to the stability constant for the aqueous Cu(II)-organic complex. In contrast, the adsorption of Cd(II) is essentially unaffected by the presence of organic matter adsorbed on the alumina surface, suggesting weak complex formation of Cd(II) with the organic ligands (Davis, 1984).

A recent EXAFS spectroscopy study by Alcacio et al. (2001) of the sorption of Cu(II) on goethite in the presence of humic material illustrates the molecular-scale information that can be obtained from this approach. At adsorbed humic acid concentrations of <88 g/kg goethite, they found evidence of Cu(II)-2nd-neighbor Fe pair correlations in the EXAFS spectra [$d(\text{Cu-Fe}) = 3.17$ to 3.20 \AA], indicating the formation of Type A ternary surface complexes. In contrast, at adsorbed humic acid concentrations between 216 and 236 g/kg goethite, they found no evidence of Cu(II)-

Fe(III) pair correlations in the EXAFS spectra, which they interpreted as indicating Type B ternary surface complexes.

As discussed earlier, the primary functional groups in NOM that bind cations are carboxyl and hydroxyl groups, as well as amino groups. A number of cation sorption studies in the presence of organic matter have used simple organic ligands containing these functional groups as surrogates for more complex NOM. For example, Davis and Leckie (1978b) studied the effect of several simplified organic ligands (picolinic acid, 2,3-pyrazinedicarboxylic acid (2,3-PDCA), glutamic acid) on Cu(II) sorption on amorphous iron oxide as a function of pH. They found under the conditions of their experiments that glutamic acid significantly enhanced Cu(II) sorption and that 2,3-PDCA had a small enhancing effect relative to the Cu(II)-amorphous iron oxide system without organic ligands. However, Cu(II) sorption on amorphous iron oxide was found to be inhibited by picolinic acid. Based on these results, as well as the adsorption behavior of the organic ligands on amorphous iron oxide in the absence of Cu(II), Davis and Leckie (1978b) concluded that when the major functional groups of the organic ligand bond to the mineral surface, the ligand will have a minor effect on cation adsorption. Picolinic acid, salicylic acid, and protocatechuic acid fall into this category. They also concluded that when the adsorbed organic ligand has strongly complexing functional groups oriented outward toward the aqueous solution (e.g., glutamic acid, 2,3-PDCA, ethylenediamine), cation sorption can be significantly enhanced. At the time of this pioneering study by Davis and Leckie (1978b), there had been no XAFS spectroscopic studies on similar systems, so no quantitative molecular-scale information was available on the bonding of metalligand complexes to mineral surfaces. More recently, XAFS methods, coupled with ATR-FTIR methods, have provided this type of information.

Glutamic acid is an appropriate simplified surrogate for NOM because it contains two carboxyl and one amino group. These groups strongly complex transition metal cations such as Cu(II). Fitts et al. (1999) conducted a combined EXAFS, ATR-FTIR, and macroscopic uptake study of the effect of glutamic acid on the adsorption of Cu(II) on γ -Al₂O₃ (Degussa Aluminum Oxide C) over the pH range 4 to 9 and ionic strengths ranging from 0.001 to 0.5 M (NaNO₃ background electrolyte). Two types of Cu(II)-glutamate-alumina interactions were observed. At acidic pH values, glutamate forms a bridge between Cu(II) and the alumina surface (Type B ternary complex), with Cu(II) bonded to two amino acid headgroups (⁺H₃NCHR⁻COO⁻) and the side-chain carboxylate groups attracted to the alumina surface through long-range electrostatic forces. This 1:2 Cu:glutamate outer-sphere ternary complex results in enhanced uptake of Cu(II) relative to the glutamate-free system. Under basic pH conditions, EXAFS analysis provides evidence for inner-sphere bonding of Cu(II) to the alumina surface (Type A ternary complex), and FTIR spectra indicate that Cu(II) is bonded to one glutamate molecule, resulting in a 1:1 Cu:glutamate molecule. These Cu(II)-glutamate surface complexes on alumina differ significantly from Cu(II)-glutamate solution complexes in the absence of alumina under similar solution conditions, where Cu(H₂O)₆²⁺ predominates at pH 4 to 6 and where Cu(glutamate)₂²⁻ predominates at pH > 7.

2.13.4 Competition between NOM and mineral surfaces for cations:

The examples discussed above show that: (1) cations can bind strongly to functional groups in humic materials, particularly carboxyl, phenol, and thiol groups; (2) NOM can bind to mineral surfaces through the same types of functional groups; (3) NOM adsorption can be inhibited by inorganic ligands such as sulfate and phosphate which compete for the same types of surface sites; and (4) organic ligands

can enhance cation sorption on mineral surfaces through the formation of Type A or Type B ternary complexes, or can inhibit cation adsorption in some cases [e.g., Cu(II)-bipyridine complexes on γ -Al₂O₃ (Bourg et al., 1979); Cu(II)-picolinic acid-amorphous iron oxide (Davis and Leckie, 1978b); Cu(II)-glycine-gibbsite (McBride, 1985a)]. One possible reason for enhanced adsorption of cations by organic ligands relative to organic-free mineral surfaces is the greater degree of stereochemical "flexibility" (chelating effect) of the organic molecules, which can lead to more stable bonding of the cation to organic ligands. Cu(II) and Hg(II), in particular, benefit from this chelating effect because their first coordination spheres are typically highly distorted, with two long [Cu(II)] or short [Hg(II)] axial bonds, and four or more significantly shorter [Cu(II)] or longer [Hg(II)] equatorial bonds. Pb(II), which exhibits a range of distorted coordination environments in solids (see, e.g., Bargar et al., 1997a), may also benefit from this chelating effect. Another factor that must be considered in such comparisons is the possibility that there may be more dissolved organic matter than mineral particles in a natural water column, and that the organic matter may have a higher density of reactive functional groups than the surfaces of most metal-(oxyhydr)oxides or (alumino)silicates. In most cases, however, there is little or no quantitative information about these differences between organic ligands and mineral surfaces.

Several macroscopic uptake and surface complexation modeling studies (e.g., Mantoura et al., 1978; Balistrieri et al., 1981; Davis, 1984) have led to the suggestion that the adsorption properties of particles are controlled by organic coatings on particles. This suggestion is based on the postulate that most particles in seawater are coated by films of organic matter (Niehof and Loeb, 1974; Loeb and Niehof, 1977; Hunter and Liss, 1979).

The study by Balistrieri et al. (1981) builds on the "organic film" postulate, and derives a scavenging model for trace metals in the deep ocean as these metals interact with sinking marine particles. These authors concluded that the equilibrium constants describing the interaction of trace metals with marine particles are more like those of organic compounds than those of model metal oxides, and therefore, that the particles are coated by organics. These conclusions are based on a number of assumptions, including the following: (1) that the sorption of trace metal ions on marine particles can be adequately described by two reactions—one involving the adsorption of the free metal ion, and one involving the adsorption of the first hydrolysis complex of the trace metal ion; (2) that the solution complexation constants and hydrolysis constants of trace metal ions in seawater are the same as those in model solutions from which the constants were derived; (3) that an adsorbed organic compound behaves in the same manner (interpreted here to mean that it binds cations in the same manner) as a free organic molecule in solution; (4) that the density of reactive surface sites on marine particles is the same as on various model oxides used in laboratory sorption studies (0.1 to 10 moles/kg); (5) that the intrinsic binding constants for surface sites on model metal oxide particles are the same as those that would apply to uncoated marine particles under the surface charge conditions that would exist in natural seawater at pH 7.8 (the average pH of the deep ocean); (6) that the density of reactive functional groups in dissolved organic matter in seawater, as well as that of model organic compounds, is equivalent to the highest values derived from model metal oxides used in laboratory sorption studies (10 moles/kg); and (7) that no dissolved metal-organic complexes are present in seawater.

The "organic film" or "monolayer" hypothesis has been challenged by Ransom et al. (1997), who used transmission electron microscopy to examine the forms of

organic matter in continental margin sediments. This study found that the organic matter in these sediments is "primarily patchy in distribution and occurs as discrete, discontinuous blebs and micro-blebs of differentiated and undifferentiated protoplasm, bacterial cells, and associated mucopolysaccharide networks, and localized smears generally associated with clay minerals and domain junctions in clay-rich flocs, not as thin uniform grain coatings or as in-fillings of nicks or etch pits on sediment grains with high degrees of surface roughness" (Ransom et al., 1997).

Although quite different in terms of solid-to-solution ratios and other variables such as ionic strength relative to aquatic systems, soils provide another system in which the relative importance of metal oxide versus organics in the uptake of trace metals can be assessed. For example, Martinez and McBride (1999) studied the uptake of Cu(II), Zn(II), Cd(II), and Pb(II) in aged ferrihydrite (HFO)- organic matter (ORG) systems and found that: (1) Cd(II) and Zn(II) solubility followed the order HFO = HFO+ORG > ORG; (2) Cu(II) was most soluble in the aged ORG systems and least soluble in the aged HFO system; and (3) Pb(II) was most soluble in the ORG system. In a somewhat more complex system, Almas et al. (2000) found that the addition of organic matter to soils containing Zn(II) and Cd(II) resulted in increased solubility of both ions, due to the formation of aqueous organo-metallic complexes. In another study of the mobility and extractability of Cu(II), Ni(II), Zn(II), and Cd(II) in several soils, one of which was rich in organics, Tyler and McBride (1982) found that the order of mobility was $\text{Cu(II)} \ll \text{Zn(II)} \leq \text{Ni(II)} \leq \text{Cd(II)}$, and that these ions were less extractable from an organic soil than from acid soils (both limed and unlimed). They interpreted these results as indicating partially irreversible binding of the metal ions to the organic matter.

The effect of soil organic matter (SOM) on the sorption and desorption of Pb(II) was studied by Strawn and Sparks (2000) at pH 5.5 and $I = 0.05$ M in two soils differing dramatically in organic matter content. The correlations between SOM in the soils and the % Pb desorbed suggest that SOM is significant in the slow desorption reactions of Pb. Pb L_{III}-EXAFS analysis of the soil treated to remove SOM showed O and Si backscatterers around Pb(II), whereas O and C backscatterers were present around Pb(II) in the untreated soil samples. These results suggest that Pb(II) sorbs dominantly to SOM in the untreated soils and to silicate particles in the treated soils. As in the case of natural organic matter in continental-margin sediments discussed earlier, it appears that the organic matter in acid soils is present in low-surface-area configurations, such as organo-clay aggregates, rather than as dispersed coatings on mineral grains (Mayer and Xing, 2001).

Results of experiments like the ones for the soil systems described above are highly dependent on organic:solid ratio, the types of organics present, the relative density of surface functional groups on both the organics and the solids, as well as other factors. So caution must be used in interpreting these results and in generalizing the findings to other systems, particularly to aquatic systems such as those discussed earlier. However, the results from soil systems do show some parallels with those from aquatic systems, in particular the tendency of ions like Cu(II) and Hg(II) to be strongly complexed by organic matter, the relatively weak binding of Cd(II) by organic matter, and the importance of hydrous manganese and iron oxides as sinks for trace metals.

There have been some suggestions (e.g., Davis and Leckie, 1978b; Davis, 1984) that the presence of organic coatings on mineral surfaces can block reactive surface sites and thus inhibit the sorption of cations. This suggestion has been difficult to evaluate until recently because of the lack of appropriate spectroscopic probes.

However, this suggestion does not appear to be true in the few cases studied using X-ray standing wave measurements (Templeton et al., 2001). Other indications that organic coatings on solids do not fundamentally change the reactivity of solid surfaces for water and organic molecules come from XPS studies of the effects of "adventitious" carbon on the reactivity of surfaces (Barr and Seal, 1995) and high level molecular dynamics modeling studies, which show that organic sorbates can diffuse rapidly to an alumina surface through a relatively thick organic film (Sainte Claire et al., 1997).

2.14 MODELING ION BINDING TO HUMIC SUBSTANCES:

DESCRIPTION OF SELECTED MODELS

The modeling of protons and metal by humic substances (HSs) is relevant to many environmental problems. Over the years, many laboratory studies have been made of the interactions, and a large body of data has accumulated. Chemical models needed to encapsulate this knowledge are needed to allow application to "real-world" situations (Tipping, 1997).

The modeling of humic-ion binding has been a subject of interest for many years and a number of formulations have been published. In early work with soil humic acid, Tipping, (1997) reported that, the competition for binding between metal ions and protons, and estimated metal binding from displacements of pH titration curves has been recognized. He added that the study was extended by taking account of electrostatic effects associated with the build-up of coulombic charge. Other works e.g. Bresnahan et al., (1978), favoured the use of conditional stability constants, valid for single pH and ionic strength, to describe metal-humic interactions. Development of statistical approaches to characterizing humic binding sites for protons and metal ions has been used, but this did not extend to a coupled model in which proton-metal competition could be accounted for. Marinsky and coworkers (Marinsky and Ephraim,

1986; Ephraim et al., 1986; Ephraim and Marinsky, 1986) showed that the observed decrease in apparent binding strength with site occupation could be due to both site heterogeneity, i.e. variability in non-specific coulombic attraction as increasing cation binding decreases the net humic charge (negative).

Tipping and Hurley, (1992) used the work of Marinsky and colleagues as the basis of a simplified model (Humic Ion-Binding Model V; thereafter denoted Model V) which included: i) site heterogeneity (discrete site with a range of affinities, together with the formation of bidentate sites), ii) electrostatic effects (including the contribution of counter-ion accumulation to binding) and iii) competition among protons and metal ions. Model V described published data sets with some success, and the parameters obtained for metal binding (intrinsic equilibrium constants) displayed encouraging parallels with analogous constants for simpler organic acids. An advantage of the Model V was its ability to use small data sets to estimate the intrinsic equilibrium constants, thereby allowing comparison of results from studies of different fulvic acids, under different conditions, and by different techniques. Overall, application of the model showed that there is considerable consistency among available data sets for ion-binding by HS. The model has been applied to a range of metals, including the alkaline earths, aluminium, transition metals, lanthanides and actinides (Tipping and Hurley, 1992; Tipping et al., 1995b). Model V and its predecessor (Model VI) have been used to analyze field data for waters (Tipping et al. 1991) and soils (Tipping et al. 1995a). As part of WHAM (Windermere Humic Aqueous Model), Model V has been incorporated into a dynamic model used to simulate catchment chemical behavior (Tipping, 1996).

A series of models developed by Van Riemsdijk and colleagues (Benedetti et al., 1995a, b, 1996; Kinniburgh et al. 1996), have characterized binding site

heterogeneity by the use of continuous distribution of equilibrium constants, together with electrostatic sub-models. The most recent of these, the NICA-Donnan Model (NICA = Non Ideal Competitive Adsorption), which has been shown to fit very well the extensive data sets obtained by these workers, not only binding results covering wide range of free metal ion concentration (Benedetti et al., 1995a) but also detailed competition experiments (Kinniburgh et al. 1996).

Modeling the acid–base behavior and metal complexation of humic substances (HS) is complicated by the heterogeneous nature of humic binding sites, both for protons and metals. Furthermore, the salt dependence of proton binding to HS varies from sample to sample and has not been completely understood on a mechanistic level (Gustafsson et al., 2001). As for the acid–base properties of HS, it is widely recognized that several different sites, with different acid strengths, are important. The most dominant site types are carboxylic acid-type groups at $\text{pH} < 7$, and phenolic-acid-type groups at higher pH (Ephraim et al. 1986; Tipping and Hurley, 1992; Gustafsson et al. 2001). As a result, the pH dependence of proton binding shows a smooth curve, with progressively increasing dissociation over a very wide pH range. Furthermore, the proton binding properties vary between different samples, both in the total amount of dissociating sites and in their relative acid strengths (Gustafsson et al. 2001). In a model, these features can be represented in two different ways. First, some sort of continuous distribution of pK_a values may be used, as in the NICA–Donnan model. Second, the HS may be assumed to have a series of discrete-site pK_a values, as in Model V/VI of Tipping and Hurley (1992, 1998). Although discrete, the individual sites used in the latter approach do not physically represent present sites. Therefore, the choice of approach is mainly a matter of taste, and both approach also produce about the same number of adjustable parameters (Gustafsson et al. 2001).

The description of the salt dependence of proton binding to HS has been subject to controversy. Avena et al. (1999) argued that HS should be described as permeable gels of spherical geometry. Some humic charge is neutralized by counterions inside the gel, whereas part of the charge is neutralized on the exterior parts. It was claimed that different model approaches represent simplifications of this general situation. The two model approaches often used are (Gustafsson et al. 2001). (i) The HS are viewed as impermeable spheres, and the charge is assumed to be localized on the exterior part (Tipping and Hurley, 1992; Bartschat et al. 1992). To solve for the electrostatic contribution to cation binding, Bartschat et al. (1992) used the Diffuse Layer Model as the interface model, whereas Tipping and Hurley (Tipping and Hurley, 1992) used an empirical charge–potential relationship. Although this approach has been shown to work excellently for individual data sets, difficulties arise when considering the differences in salt dependence experienced for different HS samples. Avena *et al.* (1999) attributed these differences to variations in particle radii and site densities and were able to provide reasonable fits with these adjustable parameters. Tipping and Hurley (1992), on the other hand, defined an “electrostatic interaction factor” which could be adjusted to fit the different data sets. (ii) The HS are considered to form a gel phase, separate from the bulk water phase. A Donnan-type equilibrium governs the distribution of counterions between the two phases. The humic charge inside the gel is neutralized by counterions inside the gel. Such a model was originally proposed by Marinsky et al. (1982), and a similar description was introduced into the NICA–Donnan model (1996). To obtain the salt dependence, a potential gradient from the gel phase to the bulk solution is calculated. This is done in different ways in the two models. To account for HS-specific differences in salt dependence in the NICA–Donnan model, the gel volume was used as an adjustable parameter. Although very

good fits were obtained in a wide variety of data sets (Maline et al. 2001), Avena *et al.* (1999) remarked that the gel volumes used in the NICA-Donnan model were unrealistically high (Gustafsson et al. 2001).

Apart from these two model approaches, there are other factors that may be considered for the correct description of the salt dependence (Gustafsson et al. 2001). For example, counterion condensation may occur if the site density exceeds a certain value. However, results obtained implies that this effect is probably not significant for HS. The SHM (Stockholm Humic Model) descends mainly from the impermeable sphere approach and Tipping's discrete-site pKa formalism. The SHM, employs the Basic Stern Model (BSM) as the interface model and it includes new, largely empirical, equations to account for the extra screening of charge occurring inside the gel volume. In the sections below shows the concepts the SHM and Model VI were built on.

2.14.1 **Stockholm Humic Model**

2.14.1.1 *Modeling Approach: Binding Sites and Complexation Reactions:*

The SHM employs a discrete-site approach to describe the pH dependence of HS dissociation. The method used is almost exactly identical to the one described by Tipping and Hurley (1992, 1998). Here a summary of the details is given. The HS dissociation reaction can be written as



where R represents the humic molecule and K_i is an intrinsic dissociation constant, defined in the following. There are eight RH sites of different acid strengths and so there are eight K_i values. It is again important to stress that these eight sites do not describe physically present discrete sites; rather they should be regarded as mathematical constructs enabling the description of the proton binding of HS having

a range of unknown acid–base equilibria (Gustafsson et al., 2001). The four strongest acid sites (numbers 1–4) are referred to as type A sites, whereas sites 5–8 are type B sites. The strongest acid sites probably represent mainly carboxylic acid groups, whereas the type B sites are thought to represent weaker acids such as phenolic acids. Four constants ($\log K_A$; $\log K_B$; $1pK_A$ and $1pK_B$) are needed to define the eight $\log K_i$ values, according to

$$i = 1-4 : \log K_i = \log K_A - [(2i-5)/6]\Delta pK_A \quad \dots\dots\dots (2)$$

$$i = 5-8 : \log K_i = \log K_B - [(2i-13)/6]\Delta pK_B \quad \dots\dots\dots (3)$$

The total amount of proton-dissociating sites, n (mol g⁻¹), is the sum of all type A and B sites. Within each site group (A or B) all sites are present in equal amounts; however, the partitioning between type A and B groups may vary, depending on the nature of the humic sample (Gustafsson et al., 2001). It has been assumed that for fulvic acids, the total amount of type B sites is 30% of the amount of type A sites; whereas for humic acids, the amount of type B sites is 50% of that of the type A sites.

In the SHM, cations may form both monodentate and bidentate complexes. Metal binding is assumed to involve one or two proton binding sites (monodentate or bidentate coordination). Monodentate complexes are assumed to form only with type A sites according to Eq. [2] (i.e., the carboxylic acid groups). Bidentate complexes are assumed to be either dicarboxylic- (involving two type A sites) or salicylic-acid-like (involving one type A site and one type B site). The total number of possible site combinations is 26 (10 dicarboxylic and 16 salicylic-acid-like), but in order to speed up computations only 6 different representative combinations were used, 2 dicarboxylic and 4 salicylic-acid-like (Gustafsson et al., 2001). At this stage, no evaluation has been made of whether this reduction of bidentate reactions led to any significant difference in model fits. The combinations used were the same as those

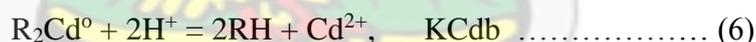
used by Tipping (1998) except that he also used 2 additional site combinations, each involving two type B sites. The inclusion of such combinations in the SHM is possible, but tests indicated poorer fits for metal binding data (Gustafsson et al., 2001). As an example, the reaction for the stability of monodentate Cd complexes is written as



Again the K_{Cdm} constant is an intrinsic constant, which includes electrostatic correction terms. In the SHM, it is assumed that all proton sites have identical K_{Cdm} values, in accordance with Model V (Tipping and Hurley, 1992). However, to account for heterogeneity of site affinity for metal complexation, the parameter ΔLK_2 is introduced:

$$\log K_{Cdm,x} = \log K_{Cdm} + x * \Delta LK_2, \quad x = 0, 1, 2, 3. \quad \dots\dots\dots (5)$$

This allows each site to be subdivided into a maximum of four sub-sites with differing affinity for metal–humic complexation. Gustafsson et al., (2001) set x to 0 for 90.1% of the sites, 1 for 9%, and 2 for 0.9%, but these settings can be changed. For bidentate Cd complexes, the corresponding equations are written as



$$\log K_{Cdb,x} = \log K_{Cdb} + 2x * \Delta LK_2. \quad x = 0, 1, 2, 3 \quad \dots\dots\dots (7)$$

In this case, K_{Cdb} includes not only electrostatic correction terms but also a correction term for bidentate complexes (Hiemstra et al., 1996). As has been discussed by Tipping (1998), the ΔLK_2 value is an empirical parameter that expresses heterogeneous metal binding caused by the presence of a small number of high affinity metal complexation sites on HS (e.g., amino and thiol groups).

2.14.1.2 Electrostatic Effects:

In the SHM, the bulk of the HS are considered to form gels. These are primarily treated as impermeable spheres and the electrostatic interactions on the surfaces are

modeled using BSM (Rietra et al., 1999). However, depending on their configuration and size, some humic molecules may have certain groups outside the gel that behave like normal monomeric molecules (Ephraim et al., 1986, 1995). Electrostatic interactions within this part of the HS are considered to be negligible. In the BSM, the possibility to handle fractional charges and a routine for calculating concentrations of ions of the diffuse layers from the counterion charge density were included (Gustafsson et al., 2001). The charge–potential relationship of the surface (*o*) plane is given by

$$\sigma_o = C(\psi_o - \psi_d), \dots\dots\dots (8)$$

where σ_o is the surface charge density in the *o*-plane ($C\ m^{-2}$), C is the Stern layer capacitance (Fm^{-2}), ψ_o is the surface potential (V), and ψ_d is the potential in the *d*-plane (i.e., the head end of the diffuse layer). The Stern layer capacitance for the gel-like humic surfaces is not known. In this study a value of $2\ F\ m^{-2}$ was used, which was found to provide reasonable fits to the data. In the absence of complex-forming metals, one would expect (ideally) σ_o to be related to the concentration of dissociated functional groups through

$$\sigma_o = [R](F/A_s * S), \dots\dots\dots (9)$$

where F is the Faraday constant, A_s is the specific surface area ($m^2\ g^{-1}$), and S is the solid HS concentration ($g\ L^{-1}$). To estimate A_s , the site density N_s needs to be known. From the assumed spherical geometry and the humic radii (Table 1), N_s was estimated to $1.2\ sites\ nm^{-2}$ for both humic and fulvic acids. In the *d*-plane, the charge–potential relationship is given by the difference between the diffuse-layer charge and the *o*-plane charge. For the former, the Poisson–Boltzmann equation results in the well-known Gouy–Chapman equation in the case of a flat plane. For the assumed spherical geometry of the humic gel surfaces, an exact analytical solution is not known

(Gustafsson et al., 2001) . An approximation (Ohshima et al., 1982) has been used in this instance, resulting in the charge– potential relationship

$$\sigma_d = A \cdot \sqrt{8000RTc\epsilon_o D} \cdot \sinh\left(\frac{F\psi_d}{2RT}\right) - \sigma_o, \quad \dots\dots\dots (10)$$

$$A = \sqrt{1 + \left(\frac{2}{\kappa \cdot r \cdot \cosh^2\left(\frac{F\psi_d}{4RT}\right)}\right) + \left(\frac{8 \cdot \ln \cosh\left(\frac{F\psi_d}{4RT}\right)}{(\kappa \cdot r)^2 \sinh\left(\frac{F\psi_d}{4RT}\right)}\right)} \quad \dots\dots\dots (11)$$

where σ_d is the surface charge density in the d -plane ($C\ m^{-2}$), c is the concentration of a 1:1 background electrolyte, ϵ_o is the permittivity of vacuum, D is the dielectric constant of water, R and T have their usual meanings, r is the radius of the HS, while κ is the Debye–Hückel parameter, which is defined as

$$\kappa = \left(\frac{2F^2 c \cdot 1000}{D\epsilon_o RT}\right)^{0.5} \quad \dots\dots\dots (12)$$

For all fulvic acid samples, a radius of 0.75 nm was assumed, whereas for humic acid the radius was set to 1.8 nm. These radii are close to the ones used by Tipping (1998) (0.8 and 1.72 nm, respectively). The specific surface area and site density were then calculated from the assumed spherical geometry. In the absence of complex-forming metals, the d -plane is empty, and consequently $\sigma_d = 0$.

Protons are assumed to bind to the o -plane exclusively, and therefore only the electrostatic term $\exp(-F\psi_o / RT)$ is needed to correct the intrinsic K_i constant. For complexed cations, the CD-MUSIC approach has been used (Hiemstra et al., 1996), which allows the adsorbed ion to bind to both o - and d -planes. This is caused by the fact that the complexed cation in a mono- or bidentate complex is still coordinated to water molecules residing in the d -plane. Therefore, part of the charge of the cation is attributed to the d -plane. The CD value describes the fraction of the cation valence that is attributed to the o -plane, and in this study a CD value of 0.25 has been assumed for monodentate complexes, whereas a value of 0.6 or 0.62 has been used for bidentate complexes (Gustafsson et al., 2001). Although no rigorous optimization was made,

preliminary studies indicated that the model performance was rather insensitive to the CD value (Gustafsson et al., 2001). The “gel fraction” parameter, g_f , determines the exact value of the stoichiometry of the electrostatic correction terms ($0 \leq g_f \leq 1$). This reflects the fact that in the SHM, the electrostatic interactions are confined to the part of the HS that is aggregated in gel-like structures (Gustafsson et al., 2001). It was found that this application of the BSM alone was unable to correctly describe the salt dependence of proton binding; too low salt dependence was observed. This probably reflects the extra screening of charge inside the gel volume (Gustafsson et al., 2001). To improve the description, the “ion pair” concept (Hiemstra et al., 1996; Rietra et al., 1999) was initially explored. According to this concept, some counterions contribute to extra charge screening by entering the d -plane. In the SHM, such an ion pair reaction for NaC might be written as



However, this description failed to describe some of the proton titration data sets investigated, particularly at high ionic strength when the model predicted the ion pairs to completely dominate the surface speciation, in obvious conflict with the data (Gustafsson et al., 2001). This suggests that the assignment of a separate species R^-Na^+ is fundamentally incorrect, at least in the case of HS gel structures (Gustafsson et al., 2001). For the SHM model purposes, it was found that a much more promising reaction involved the total charge of the HS present in the gel as the dummy component X^- (for systems without sorbed metals the total concentration of X^- was calculated as $g_f \times [R^-]$). Therefore, the surface speciation of the humic surface R is not affected, regardless of the concentration of screening counterions (Gustafsson et al., 2001). Hence the following type of reaction could be defined:



This reaction included an electrostatic correction term using the assumption that the counterions in the gel screened the surface charge in the o-plane. For a C value of $2F^{-2}$, a K_C value of $10^{0.8}$ was found to provide a reasonable fit to proton titration data. The K_C value was assumed to be the same for all monovalent cations (Gustafsson et al., 2001). For cations with a charge higher than 1, the constant was modified according to the Gaines–Thomas formalism to reflect the preference of these ions for exchange positions in the gel. Although the actual surface speciation was not affected by the screening counterions, this model description caused a reduction of σ_o (Gustafsson et al., 2001). The resulting σ_o used in the calculations was therefore not identical to the “real” σ_o as implied by Eq. [9], but may be interpreted as an “effective” surface charge density. At this point, it is interesting to note that although empirical in nature, this way of accounting for charge screening in the HS gel structure results in mathematical expressions that are similar to the ones used by Benedetti et al., (1996). This can be realized when relating the concentration of screening H^+ ions in the gel to the solution H^+ activity. For a HS sample with $g_f = 1$,

$$[XH^+] = \frac{[X^-]\{H^+\} \exp\left(-\frac{F\psi_o}{RT}\right)}{K_C} \dots\dots\dots (15)$$

where { } and [] denote activities and concentrations, respectively. This equation can be compared to the Donnan-type equilibrium used in the gel models,

$$\langle H^+ \rangle = [H^+] \exp\left(-\frac{F\psi_g}{RT}\right), \dots\dots\dots (16)$$

where $\langle H^+ \rangle$ is the concentration of screening H^+ ions in the gel phase, $[H^+]$ is the concentration in the water phase, and ψ_g is the Donnan potential. If the gel volume is much smaller than the volume of the bulk solution, Eq. [16] can be rewritten as

$$[XH^o] = [H^+] \exp\left(-\frac{F\psi_g}{RT}\right) \cdot \frac{v_G}{v_B}, \dots\dots\dots (17)$$

where v_G and v_B are the gel volume and bulk solution volume, respectively. By comparing Eq. [17] to Eq. [15], it can be seen that if ψ_g is assumed to be proportional to ψ_o (as is implied by the Marinsky model), v_G has to be dependent on the particle surface charge if the models are mathematically equivalent. If on the other hand, v_G does not change with pH (5), ψ_g has to vary less with pH than ψ_o . These requirements seem to be in good agreement with previous model applications using the gel models (Gustafsson et al., 2001).

2.14.1.3 Counterion Accumulation:

If the gel-like HS is assumed to be in a separate phase, then counterions are bound to the HS to ensure charge neutrality. The NICA–Donnan model and Model V/VI rely on this assumption (Tipping and Hurley, 1992; Benedetti et al., 1996). It is also possible to use this assumption in the SHM. As a result, two populations of counterions are used in the model; these might be described as screening and nonscreening counterions. Surprisingly few studies have addressed the issue of whether gel-like HS structures in dissolved HS behave as a separate phase or not. Some studies (Van den Hoop et al., 1990) indicate that at least some of the counterions maintain their aqueous activity, a result which seems to be inconsistent with the assumptions made in the NICA–Donnan model and Model V/VI.

The SHM calculation as explained does not consider counterion accumulation in addition to those bound to component X⁻. This means that the remaining counterions were treated as fully dissolved ions. Results obtained by assuming charge neutrality in a separate gel phase does not differ greatly for the data sets of Gustafsson et al., 2001, implying that the treatment of counterions was not of major importance. However, in HS-rich soil solutions at low ionic strength, the issue of counterion activities may become critical for successful modeling (Gustafsson et al., 2000, 2001).

The model fits for proton binding showed that the SHM is at least as successful as Model V/VI in explaining the pH and salt dependences of proton binding. Concerning the metal binding data, it appears that the SHM is capable of correctly capturing metal binding data in monocomponent systems of constant ionic strength, at widely different pH and equilibrium concentrations. Competitive interactions were also reasonably well described, at least for the Ca–Cd system (Gustafsson, 2001). This evidence suggests that the model assumptions made concerning the predominance of mono- and bidentate complexes are largely correct. The model performance as reported by Gustafsson, (2001) is less convincing concerning the proton exchange stoichiometries and the ionic strength dependence of metal complexation. However, according to Gustafsson, (2001), some fixed model parameters (such as the combination of bidentate sites, and the CD values) have not been optimized. Also, an uncertain assumption is that all proton sites have the same proton–metal exchange constant according to Eqs. [4] and [6]. To modify this description, an extra parameter may be introduced, as in Model VI (6) (Gustafsson, 2001). Clearly, there is considerable room for improvement to the model.

2.14.2 Model VI

2.14.2.1 Model description:

Model VI pictures humic substances as rigid spheres of uniform size, with ion-binding groups positioned on the surface (Tipping, 1997). Thus, from the outset, the possible influences of variations in molecular conformation on binding properties are neglected, as is the possibility, proposed by Bartschat et al., (1992), that binding site heterogeneity may be generated by differences in electrostatic properties among molecules of different size. Tipping, (1997) found that in applying Model V to proton-and metal-binding data there were distinct differences

between fulvic and humic acids, but that there was no consistent dependence on the sources of the two materials (soil, water etc.). The same approach is adopted in the development of Model VI with the aim of obtaining “universal” description for each type of humic material (Tipping, 1997).

2.14.2.2 *Binding sites and intrinsic equilibrium constants:*

In Model VI, proton dissociation is represented by postulating 8 groups of different acid strengths. The dissociation reaction can be written generally as;



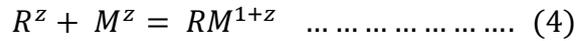
Where R represents the humic molecule, and Z is the net charge. The reactions are characterized by intrinsic equilibrium constants, which refer to proton dissociation under conditions where there is no electrostatic influence on the reaction. The negative logarithms of the equilibrium constants are denoted by pK₁ – pK₈. The 4 most strongly-acid groups (groups 1-4) are referred to as type A groups, and consist mainly of carboxylic acid groups, while the remaining 4 groups (type B) represent weaker acids, such as phenolic acids (Tipping, 1997). The 8 pK₁ values are expressed in terms of four constants (pK_A, pK_B, ΔpK_A and ΔpK_B) as follows;

$$\text{For } i = 1-4 : \log K_i = \log K_A - [(2i-5)/ 6]\Delta pK_A \dots \dots \dots (2)$$

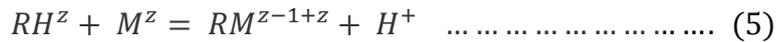
$$\text{For } i = 5-8 : \log K_i = \log K_B - [(2i-13)/ 6]\Delta pK_B \dots \dots \dots (3)$$

Each type A group is assigned an abundance of n_A/4 mol/g humic matter, and each typeB group an abundance of n_A/8 mol/g. thus, within a type, each group is present in equal amounts, and there are half as many type B groups as type A groups. The imposed regularity of the groups facilitates the formulation of multidentate binding sites of metals, as described below.

Metal ions, and their first hydrolysis products, compete with each other, and with protons, for the type A and type B groups. Most simply, monodentate binding takes place according to the general reaction (Tipping, 1997);



In Model V, the monodentate binding of a metal was expressed by the metal proton exchange;



Described by the equilibrium constant K_{MHA} for each type A site, and by K_{MHB} for each type B site. Thus, the logarithm of the equilibrium constant for the reaction described by equation (4), for a type A site, was written;

$$\log K(i) = \log pK_A + \frac{(2i-5)}{6} \Delta pK_A - pK_{MHA} \dots \dots \dots (6)$$

Since pK_A , ΔpK_A and pK_{MHA} are constants, the strength of binding of a metal to the different type A sites exactly parallels that for protons, and the same is the case for the type B sites. In Model VI, this parallelism is relaxed (Tipping, 1997), the equilibrium constants being expressed for type A sites by;

$$\text{For } K(i) = \log K_{MA} + \frac{(2i-5)}{6} \Delta K_1 \dots \dots \dots (7)$$

and for type B sites by;

$$\text{for } K(i) = \log K_{MB} + \frac{(2i-13)}{6} \Delta K_1 \dots \dots \dots (8)$$

where ΔK_1 is a constant that is estimated from data fitting. If sufficiently precise and extensive data are available, a value for ΔK_1 for each site type can be estimated (Tipping, 1997).

Model V allows metals to bind at bidentate sites, created by pairing the proton sites. The equilibrium constant for a bidentate site composed of monodentate sites I and j is given by combining values for the monodentate sites (Tipping, 1997);

$$\log K(i, j) = \log K(i) + \log K(j). \quad \dots\dots\dots (9)$$

In Model VI, a more elaborate scheme is employed, which generates a wider range of metal binding strengths. Both bidentate and tridentate sites are permitted and their ranges of binding strength are increased by additional terms (Tipping, 1997). Thus, for bidentate sites (*i, j*);

$$\log K(i, j) = \log K(i) + \log K(j) + x \cdot \Delta LK_2 \quad \dots\dots\dots (10)$$

While for tridentate sites (*i, j, k*);

$$\log K(i, j, k) = \log K(i) + \log K(j) + \log K(k) + y \cdot \Delta LK_2 \quad \dots\dots (11)$$

The values of *x* and *y* are chosen to make possible a range of binding strengths, characterized by a single parameter, and extending over three decades. Thus, for bidentate sites the value of *x* is set to 0 for 90.1% of the sites, 1 for 9% and 2 for 0.9%. for a tridentate site, *y* is set to 0, 1.5 and 3, again for 90.1%, 9% and 0.9% respectively. Greater ranges of binding strength could be achieved by including smaller proportions of sites with *x* > 2 and *y* > 3. The adjustment term ΔLK_2 can be determined by data fitting if the data set covers a sufficient range. In principle, each metal has a characteristic ΔLK_2 (Tipping, 1997).

Thus, the main difference between Models V and VI is that the latter can take more account of binding site heterogeneity, by allowing tridentate sites and by having the two adjustable parameters ΔLK_1 and ΔLK_2 to improve the description of the distributions of binding strengths (Tipping, 1997).

In both Models V and VI, the fraction of proton sites that contribute to the bidentate or tridentate sites is determined geometrically, by assuming the proton sites to be randomly positioned on the surface of spherical molecules of radius 0.8 nm (FA) or 1.72 nm (HA). Pairs of groups are considered to form bidentate sites, or triples to form tridentate sites, if they are less than or equal to 0.45 nm apart. The fraction of

sites forming bidentate sites is denoted by f_{prB} and that for tridentates is f_{prT} . For FA, $f_{prB} = 0.42$, $f_{prT} = 0.03$, while for HA, the corresponding values are 0.50 and 0.065. The bidentate and tridentate sites are fixed entities; with respect to metal binding, they are unable to revert to monodentate behavior under any circumstances (Tipping, 1997).

In Model VI, if all combinations of proton sites are allowed, 36 different bidentate sites and 120 different tridentate sites can form. The abundances of these sites depend on their composition, in terms of type A and type B sites, the latter being present at half the total abundance of the former (Tipping, 1997). For example, tridentate sites comprising 3 type A proton sites are 8 times more abundant than those comprising 3 type B sites. To avoid over-complication, and to speed computations, a sub-set of sites is used in the model, while maintaining the relative proportions of the contributing proton sites (Tipping, 1997). To do this, Tipping, (1997) allowed bidentate or tridentate sites to consist only of different proton sites, and representative combinations are adopted. This leads to 72 different sites, because of the heterogeneity terms (equations 10 and 11). With the addition of 8 monodentate sites, there are 80 different sites in all. For HA the commonest has an abundance of ca. 4×10^{-4} mol/g, the rarest (tridentate sites consisting of 3 type B proton sites) ca 9×10^{-9} mol/g. The second figure corresponds approximately to 1 site per 7500 molecules for HA of molecular weight 15000; for FA of molecular weight 150, the corresponding figure is 1 in 10^5 .

2.14.2.3 *Electrostatic effects:*

All the above reactions are described with intrinsic equilibrium constants, which apply to the (usually) hypothetical case where the reactants are uncharged. In nearly all cases however, the reactions do involve charged species, and therefore electrostatic interactions must be taken into account (Tipping, 1997). In Models V and VI, this is

done with a correction term, the form of which is based on the Dubye-Hukel and Gouy-Chapman theories (Tipping, 1997). For proton dissociation, this leads to an expression for the humic charge-dependent equilibrium quotient $K_H(\mathbf{Z})$;

$$RH^z = R^{z-1} + H^+; \quad K_H(Z) = \frac{[R^{z-1}]a_{H^+}}{RH^z} = K_H \exp(2wZ). \quad \dots (12)$$

Here, Z is the net humic charge (eq/g), K_H is the intrinsic dissociation constant, square brackets indicate concentrations, a is activity, and w is the ionic strength-dependent electrostatic interaction factor, which is given by the empirical expression

$$w = P \cdot \log_{10} I \quad \dots \dots \dots (13)$$

Where P is a constant and I is ionic strength. The equation implies that w is zero at $I = 1$ M; the model is unlikely to find application at ionic strengths higher than this. For the binding of a metal ion to a monodentate site, the charge-dependent equilibrium quotient $K_M(Z)$ applies;

$$\begin{aligned} R^z + M^z &= RM^{z+z}; \quad K_H(Z) = \frac{[RM^{z-1}]}{[R^z]a_M} \\ &= K_M \exp(-2wzZ). \quad \dots (14) \end{aligned}$$

Where K_M is the intrinsic association constant for the metal ion.

The net humic charge Z is an average value, obtained experimentally from considerations of charge-balance. If the molecules were homogeneous with respect to size and ionizing groups, there would be a distribution of charges at any given instant, but in a dynamic equilibrium this would not be fixed with respect to individual molecules (Tipping, 1997). In the model, size homogeneity is assumed, but there must be heterogeneity of binding sites, because there are so many different types. Thus, there must be a distribution of charges, even when averaged over time at equilibrium. Therefore the use of the average value of Z to calculate the electrostatic effect on

binding implies the approximation that humic molecule bears this average charge (Tipping, 1997).

The electrostatic correction term mentioned above takes account of the existence of the electrical double layer at the molecular surface. It relates the activity of free ion in bulk solution to its effective activity at the point of interaction with the specific ion-binding group at the surface, this being greater or smaller depending upon whether the ion in question is electrostatically attracted or repelled (Tipping, 1997). The counterion excess and coion deficit associated with the electrical double layer also contribute to the overall binding of ions by the humic molecules. In the Guoy-Chapman/Dubye-Huckel theory, the distributions of counter- and co-ions in the vicinity of the surface are given by the Boltzmann factors, the use of which leads to the expressions for the electrostatic correction term for specific binding (equations 13 and 14). In Models V and VI, the distributions of counter- and co-ions are not calculated with the Boltzmann equation, which requires integration over distance, together with truncation of the diffuse layer at some (arbitrary) distance from the surface. Instead, the diffuse layer/bulk solution system is approximated by a simple Donnan model, in which coions are assumed to be completely absent (Tipping, 1997). This requires the definition of a volume V_D , adjacent to the surface within which the accumulation takes place. The annular thickness of this region is approximated by the reciprocal of ionic strength-dependent Dubye-Huckel parameter k , leading to the following expression;

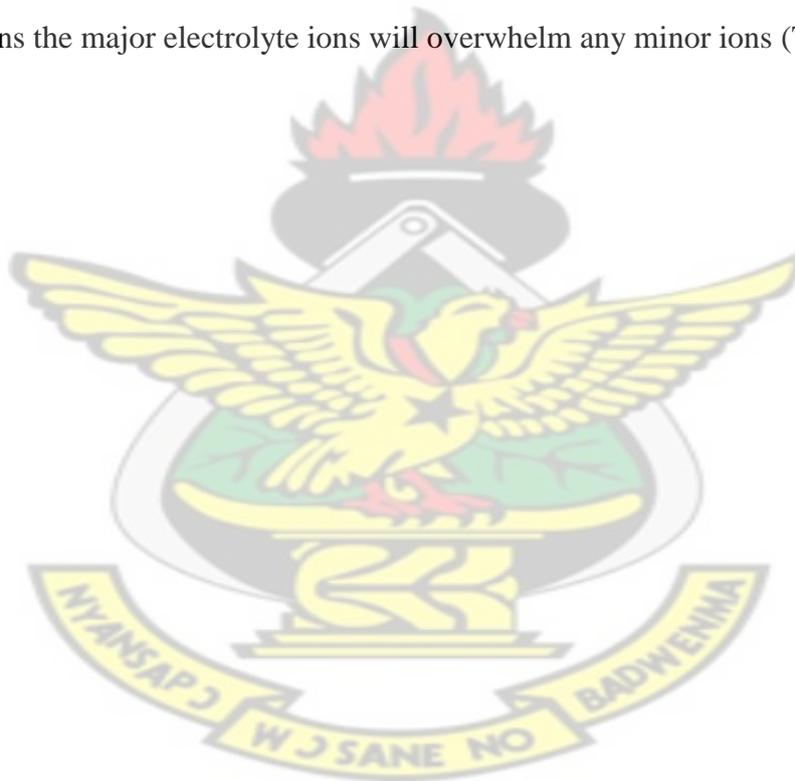
$$V_D = \frac{10^3 N}{M} \frac{4\pi}{3} \left[\left(r + \frac{1}{k} \right)^3 - r^3 \right] \quad \dots \dots \dots (15)$$

Where N is Avogadro's number, M is molecular weight, and r is molecular radius.

Within the volume V_D , there must be sufficient accumulated counterions to balance the surface charge. The ratios of concentrations of ions in the Donnan volume to those in the bulk solution are given by;

$$\frac{c_D(i)}{c_S(i)} = K_{sel}(i) \cdot R^{Z_{mod}(i)} \dots \dots \dots (16)$$

Where $Z_{mod}(i)$ is the modulus of the charge on species i , R is the ratio required for the sum of counterion charges to balance the humic charge Z , and $K_{sel}(i)$ is an adjustable selectivity coefficient. The accumulation of counterions as a binding mechanism is most significant at low ionic strength, and in high ionic strength solutions the major electrolyte ions will overwhelm any minor ions (Tipping, 1997).



CHAPTER THREE

3.0 METHODOLOGY

3.1 DESCRIPTION OF THE STUDY AREA

3.1.1 Selected Ecosystems

The ecosystems selected for the studies are the mining communities called Accra, Kejetia and Tarkwa all in the Talensi-Nabdam District of the Upper East Region of Ghana (figure 3.1).

3.1.2 Sampling Area

The Talensi-Nabdam District is one of the newly created districts, carved out from the Bolgatanga District Assembly. It is located in the Upper East Region and has its capital at Tongo. It is bordered to the North by the Bolgatanga District, South by the West and East Mamprusi Districts (both in the Northern Region), Kassena-Nankana District to the West and the Bawku West District to the East. The district lies between latitude $10^{\circ}15'$ and $10^{\circ}60'$ North of the equator and longitude $0^{\circ}31'$ and $10^{\circ}.5'$ and west of the Greenwich Meridian. It has a total land area of 912km^2 (Bisnab, 2009).

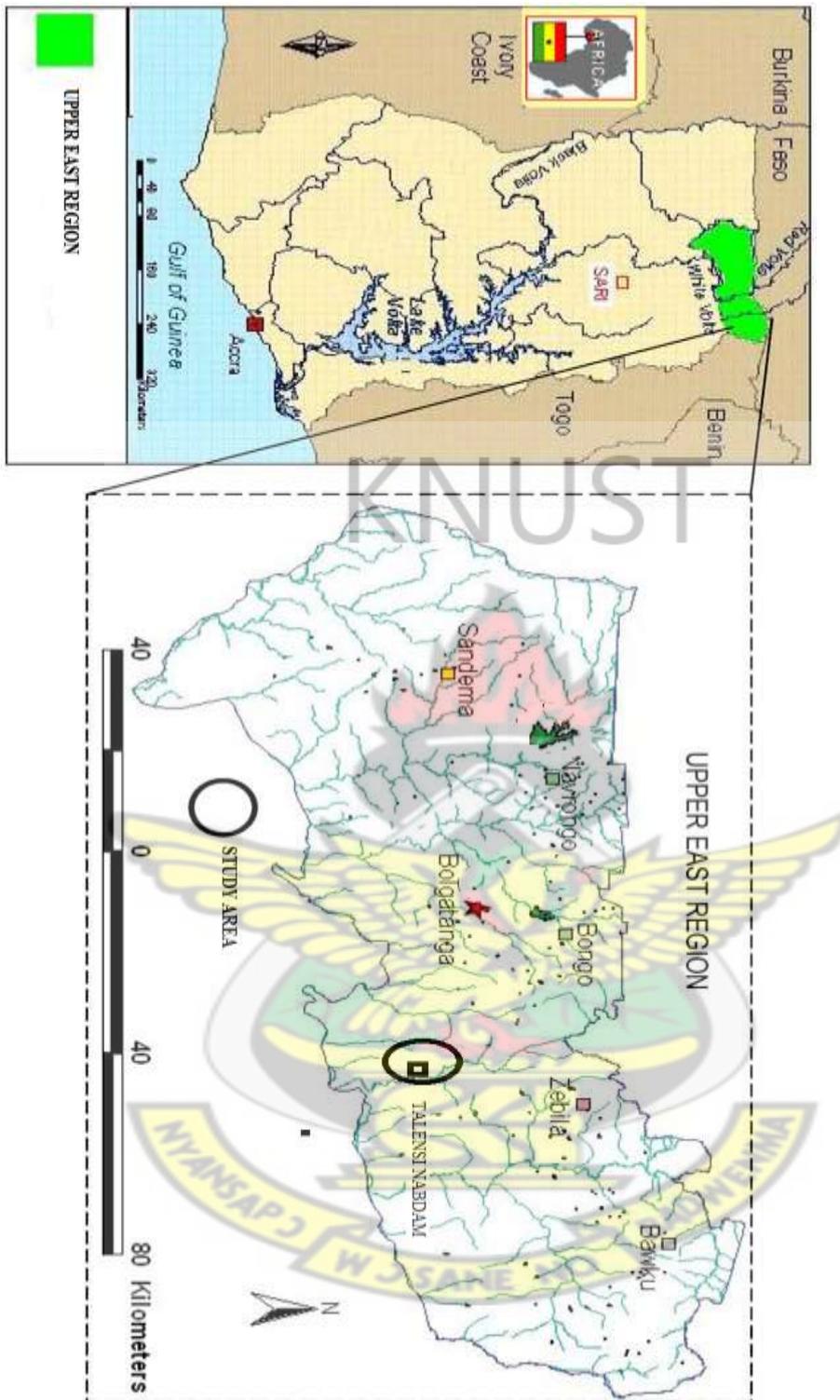


Figure 3.1: Map of Talensi-Nabdam District

3.1.3 Topography and Drainage

The topography of the district is dominated by relatively undulating lowlands with gentle slopes ranging from 1% to 5% gradient with some isolated rocks, out crops, some upland and slopes at the Tongo and Nangodi areas. It falls within the Birimian, Tarkwaian and Voltarian rocks of Ghana. There are evidence of the presence of minerals especially gold. The district is drained mainly by the Red and White Volta and their tributaries (Bisnab, 2009).

3.1.4 Climate and Vegetation

The climate is classified as tropical, and has two distinct seasons, a wet rainy season, which is erratic, and runs from May to October, and a long dry season that stretches from October to April with hardly any rains. The mean rainfall ranges between 88mm-110mm but with an annual rainfall of 950mm. The area experiences a maximum temperature of 45°C degrees Celsius in March and April and minimum of 12°C degrees in December (Bisnab, 2009).

The vegetation is Guinea savannah Woodland consisting of short widely spread deciduous trees and a ground flora of grass, which get burnt by fire or dried by the sun during the long dry season. The most common economic trees are the sheanuts, dawadawa, baobab and acacia (Bisnab, 2009).

3.2 SAMPLING TECHNIQUE

Soil samples were taken from within and around the mining communities. Information such as farmlands, mine sites (active), high lands, and low lands, fresh tailings site, etc., were noted at each sampling location and point to enable effective discussion of the data in terms of observed activity and topography of the land.

The community was divided into five sampling locations and ten sampling points per location. At the sampling points, the surface litter were removed and a ‘V’

shaped cut to a depth of 30 cm was made in the sampling point using spade. Thick slices of soil from top to bottom of exposed face of the 'V' shaped cut were collected and place in a clean container. The samples were mixed thoroughly and foreign materials like roots, stones, pebbles and gravels were removed from the bulk sample. The bulk sample was reduced to one kilogram by quartering sample size reduction method, and collected in a clean labelled polythene bag (with information like name of the community, location number, point number, and date of collection). The sampling procedure was repeated at all locations and sampling points.

3.3 SAMPLE PREPARATION

Solid samples (soil, and sediment) were air dried in a dust free environment. The aggregates were broken down ground and sieved using a sieve with 2mm mesh size. The sieved dried samples were stored in polyethylene containers for analysis.

3.4 COLLECTION OF GIS DATA FROM THE STUDY AREA AND SELECTED ECOSYSTEMS

The way points were recorded using GPS (accurate to 3m) and analyzed with the aid of MapInfo geographical information system software. Waypoints were taken from:

- ✓ All sampling points (soil, sediment, and water);
- ✓ All activity areas (mine pits, gold extraction sites, farms etc).

The data was used to discuss the interrelationship between physical mining activity on ground, at the selected ecosystem, the land form (elevation), concentration of metal forms in the terrestrial environments of the ecosystems, the characteristics of the terrestrial environments, and the densities of mobile and readily available forms of the metal.

Surface (Grids) and contour maps were used to explain the spatial distribution of materials. Maps of contours super-imposed on grids were also used to discuss the inter-relationship between variables.

3.5 EXPERIMENTAL PROCEDURES

3.5.1 Chemicals and Instruments

Below are the chemicals and instruments used for the laboratory experiments. Unless otherwise stated all chemicals were of analytical grade. Detailed information about the chemicals and instruments are in appendix 16.

| CHEMICALS* | | INSTRUMENTS | |
|------------|--------------------------------|-------------|-------------------------------------|
| 1 | Acetic acid | 1 | UV-Visible spectrophotometer |
| 2 | Ammonium acetate | 2 | Atomic absorption spectrophotometer |
| 3 | Barium chloride | 3 | Centrifuge |
| 4 | Copper sulphate | 4 | Mechanical shaker |
| 5 | D-Glucose | 5 | Oven |
| 6 | Hydrochloric acid | 6 | Thermostatic water bath |
| 7 | Hydrofluoric acid | 7 | Hot plate |
| 8 | Hydrogen peroxide | 8 | pH meter |
| 9 | Hydroxylamine hydrochloride | 9 | Thermometer |
| 10 | Nitric acid | | |
| 11 | Perchloric acid | | |
| 12 | Potassium hydroxide | | |
| 13 | Potassium permanganate | | |

- 14 Sodium acetate
- 15 Sodium hydroxide
- 16 Sulfuric acid

3.5.2 Nutrient Analysis

The soil nutrient analysis was conducted at Soil Research Institute of the Center for Scientific and Industrial Research, Kumasi. The methods were adopted from manual of Selected Methods for Soil and Plant Analysis by the International Institute of Tropical Agriculture, Nigeria (1979). The procedures were followed to determine the soil pH, soil particle sizes (structure, using hydrometer method), organic carbon, organic matter, exchangeable acidity, exchangeable cations, available phosphorus and potassium (using Bray's method).

3.6 ACCOUNTING FOR THE AMOUNT OF HUMIC SUBSTANCES

Modified Walkley-Black method described by Forster (1995) for rapid determination of organic carbon and organic matter in soil was adopted to account for the amount of humic substances in field and simulation experiment.

3.6.1 Determination of Organic Carbon

Solid soil samples: To a known mass of solid samples (sediment, soil solid phases, soil 0.5g, and glucose-standard, etc.) were added 10ml of 0.167M $K_2Cr_2O_7$ solution followed by the immediate addition of 20ml concentrated H_2SO_4 . The mixture was allowed to cool and 50ml of $BaCl_2$ solution (4g/l) was added and the mixture was swirled to mix thoroughly, and allowed to stand for 1 hour. Then 10ml of distilled water was added and the mixture was allowed to stand overnight. The mixture was

centrifuged at 2500 rpm for 15 min., the supernatant was decanted and its volume noted. The absorbance reading of the supernatants and blanks were read at 580nm using uv-spectrophotometer. The concentration of organic carbon and organic matter in the samples were calculated using calibration plots of standards prepared under the same conditions.

Liquid Samples: To the liquid samples (soil solution phase, and humic substance extracts) were added 10ml 0.167M $K_2Cr_2O_7$ solution followed by the addition of 20ml concentrated H_2SO_4 . The mixture was allowed to cool and 50ml of $BaCl_2$ solution (4g/L) was added and the mixture was swirled to mix thoroughly, and allowed to stand for 1 hour. Then 10ml of distilled H_2O was added to each of the solutions and then allowed to stand overnight. Each solution was centrifuged at 2500 rpm for 15 min., the supernatant was decanted and its volume noted. The absorbance of the supernatants and blanks were read at 580nm using uv-spectrophotometer. The concentration of organic carbon and organic matter in the samples were calculated using calibration plots of glucose standards (Section 3.6.2) prepared under the same conditions.

3.6.2 Preparation of Glucose Standards

A stock solution of glucose standard (5000 mgC/L) was prepared by dissolving 13.76g of D-glucose in 200ml distilled water, swirled until complete dissolution and then diluted to 1.0L in a volumetric flask.

Standards for Solid Samples: Amounts of 0.5, 1.0, 1.5, 2.0, and 2.5ml of the glucose standard were measured into separate beakers and dried at 100°C in an oven. This gave dry masses of glucose containing 2.5, 5.0, 7.5, 10, and 12.5mgC respectively. The absorbance readings of the standards were then determined using the method for organic carbon determination in solids as outline in Section 3.7.1

Standards for Liquid Samples: From the glucose stock solution containing 5mg C/ml, were measured 1, 2, 3, 4 and 5ml aliquot and their respective absorbance readings were then determined using the method for organic carbon determination in liquids as outlined in Section 3.6.1

3.7 TOTAL TRACE METALS ANALYSIS

3.7.1 Digestion of Solid Samples (DS):

A known mass of the solid sample (sediment, soil solid phases, soil, etc.) was moistened with 0.5 ml distilled water, 1.0 ml HClO₄ and 4.0 ml HNO₃ were then added. The mixture was then heated to near dryness using medium heat on a hot plate. The digestion was repeated for sediment samples. To the dry and cool sample were added 1ml conc. HNO₃ and heated again for 5 minutes, followed by the addition of 20 ml distilled water, swirling for 5 min., and filtration into 100 ml measuring cylinder. The filter paper was washed well with 6ml of dilute HNO₃ acid (5ml of 68% HNO₃ in 100ml distilled water). The filtrate was then diluted to 100 ml, bottled and kept for trace metal analysis.

3.7.2 Digestion of Liquid Samples (DL):

To 5ml of the sample solution (soil solution phase, water, and humic substance extracts), was added 2ml concentrated HNO₃. The mixture was then evaporated to near dryness on a hot plate and allowed to cool. To the cooled mass was added 2ml of concentrated HCl followed by the addition of 1ml concentrated HNO₃. The contents of the vessel were then evaporated to dryness. A drop of concentrated HCl was added and diluted to 50ml and filtered. The filtrate obtained was then diluted to 100ml with distilled water after a thorough washing of the residue with distilled water (all

washings were added to the filtrate). A blank was prepared following the same procedure.

3.8 HUMIC SUBSATANCE EXTRACTION, FRACTIONATION AND ISOLATION

3.8.1 Extraction Fractionation and Isolation of Metal Bound Humic Substances:

To a known mass of sample was added 0.5M NaOH to obtain a soil (solid phase) to extractant ratio of 1:10 (w/v) followed by continuous shaking for 1.0 hr. The suspension was centrifuged at 4000 rpm for 15 min and the supernatant separated by decantation. The supernatant was acidified with 6M HCl with constant stirring to pH 1.0 and the suspension was allowed to stand for 12hrs. The suspension was centrifuged at 2500 rpm for 15min., followed by decantation to separate the humic acid (precipitate) from the fulvic acid (supernatant). The humic acid was digested using digestion procedure DS (section 3.7.1), and the resulting solution was analyzed for its trace metals content using AAS. The fulvic acid fraction was also digested with digestion procedure DL (section 3.7.2) and analyzed with AAS for trace metals. The concentrations were used to compute the masses of metals bound to humic acid and fulvic acid. The analysis was carried out for all soil samples.

3.8.2 Extraction and Fractionation of Humic Substances in Soil Samples:

Determination of the amount in mgC of humic substances in the soil samples was carried out by extraction from 10g of the soil sample with 0.5M NaOH extractant. The soil to extractant ratio was 1:10 (w/v). The mixture of soil and extractant was agitated continuously for 2hrs, and the suspension was centrifuged at 4000rpm for 15min then decanted. The supernatant was acidified and allowed to stand for 12hrs.

The suspension was then centrifuged again at 2500rpm for 15min. to separate the humic acid (precipitate) from the fulvic acid (supernatant). The humic acid was re-dissolved in 0.5M NaOH. The total organic carbon content of the fulvic and dissolved humic acid solution were determined and used to account for the mass of humic and fulvic acids in the soil samples.

3.8.3 Isolation of Humic Substance Extracts for Interaction Experiments:

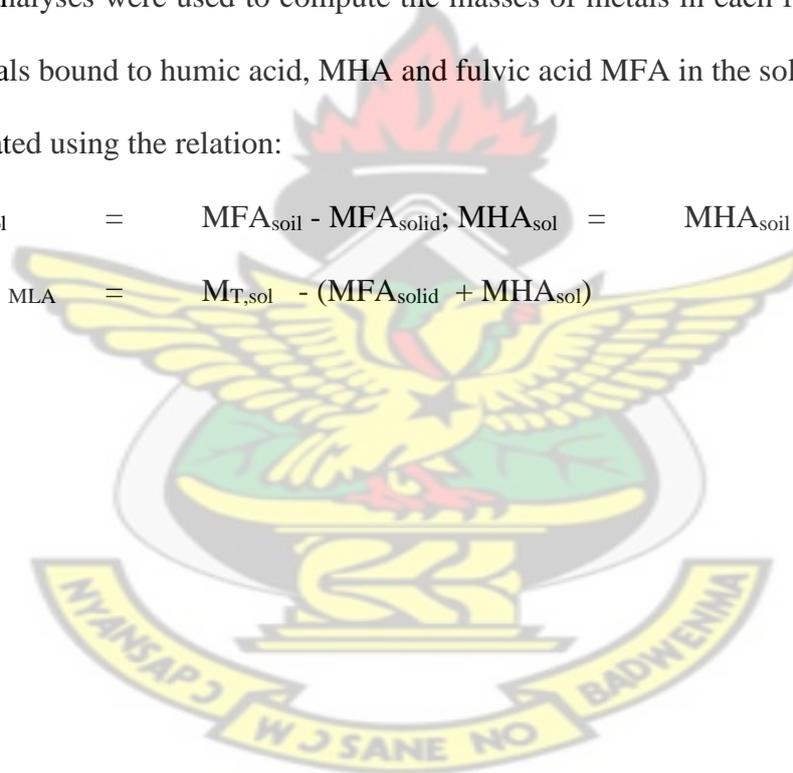
To 100g of soil sample was added 1000ml 0.1M HCl (to remove all possible labile materials and to improve the yield of the alkali-soluble materials), the suspension obtained was shaken for 1.0 hr., and then centrifuged at 2500 rpm for 10min. The supernatant was discarded after decantation. To the residue was added 1.0M NaOH to obtain a solid to extractant ratio of 1:10 w/v., and sealed to avoid air entry during the extraction process (the reason for the exclusion of air is the possibility of structural change in the presence of O₂). The vessel (polypropylene) was shaken for 12 hrs, centrifuged at 4000 rpm for 15 min., and decanted. The supernatant was filtered to remove light-weight or floating materials. The filtrate was then acidified immediately to pH 2.0 with concentrated HCl to precipitate the humic acid. The humic acid and fulvic acid fractions were then separated by centrifugation at 2500 rpm for 15 min.

To the humic acid fraction was added 50ml 0.1M KOH and then centrifuged. The supernatant obtained was acidified with 10ml 6M HCl to pH 1.0 followed by centrifugation. To the precipitate obtained after decantation was added 50ml 0.3M HF. The mixture was then centrifuged followed by decantation. The residue (precipitate) obtained was dialyzed against water (distilled) and then dried at 40 °C in oven. The dry mass was powdered and kept for experiments.

3.9 DETERMINATION OF METAL AND HUMIC SPECIES IN SOIL SOLUTION SYSTEM.

The determination of the amounts of metal species in the phases of soil solution system was carried out in three steps viz: involving the separation of system phases, extraction and fractionation, and quantification of species. The soil solution system was set up by adding 50ml of distilled water to 10g each of the soil samples (30). The resulting mixture was allowed to stand for 24hours. After which the setups were analyzed as expressed in figure 3.2. The concentrations of the fractions obtained after AAS analyses were used to compute the masses of metals in each form. The masses of metals bound to humic acid, MHA and fulvic acid MFA in the solution phase were calculated using the relation:

$$MFA_{sol} = MFA_{soil} - MFA_{solid}; MHA_{sol} = MHA_{soil} - MHA_{solid}; M_{M+, MLA} = M_{T,sol} - (MFA_{solid} + MHA_{sol})$$



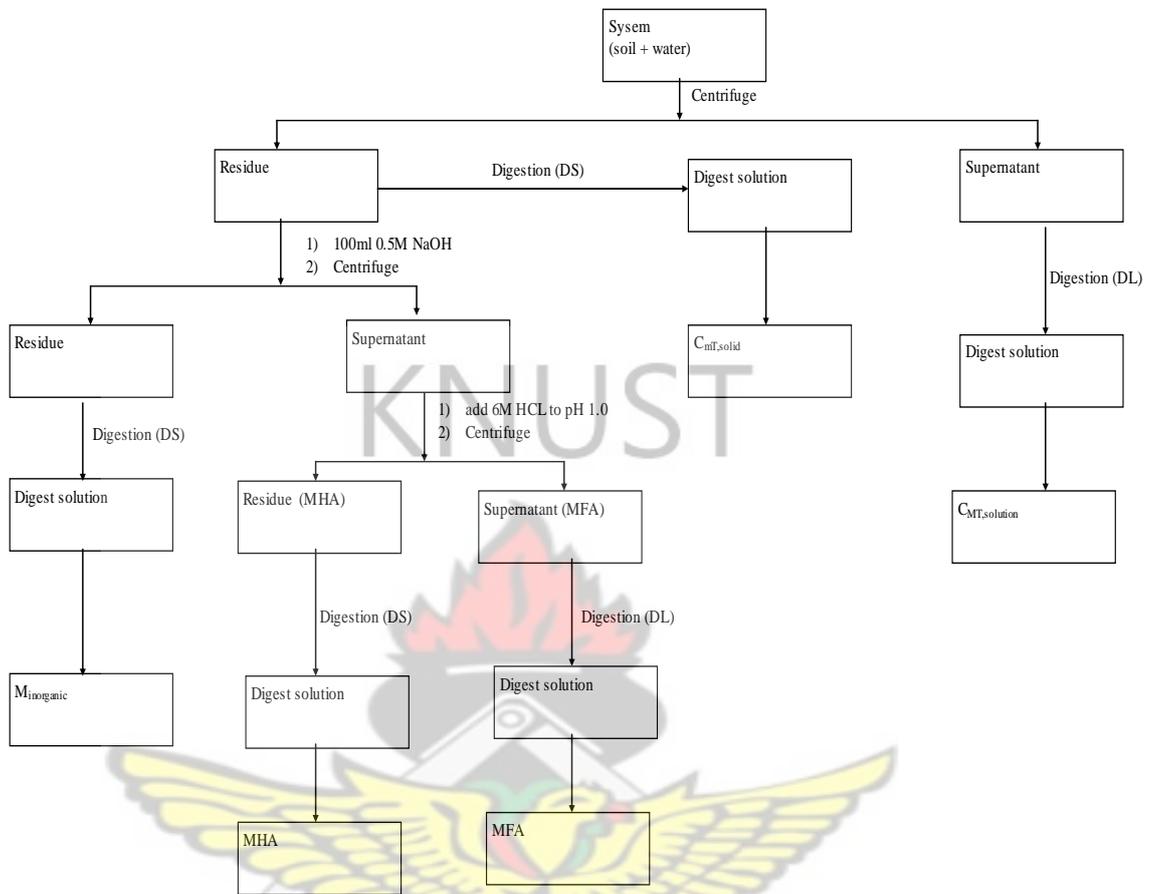


Figure 3.2: Extraction and fractionation of metal and humic acid species from soil samples

3.10 DETERMINATION OF METAL SPECIES IN THE TERRESTRIAL ENVIRONMENT

3.10.1 Speciation Analysis Using Sequential Extraction Method

One gram of each soil sample was weighed and transferred into 250mL beakers and the metal forms were extracted and analyzed as explained below.

Water soluble: The samples were extracted with 15 ml distilled water for 2.0 hrs (using equal volume of the water as blank and the concentration determined using the equation, $M_{\text{sample}} = M_{\text{extract}} - M_{\text{blank}}$.) with continuous shaking. The extract was separated from the solid residue by centrifugation at 4000 rpm for 20 min. The supernatant was decanted, into polyethylene bottles and kept at 26 °C until analysis. The residue was washed by adding 20 ml distilled water, shaken for 25 min. and centrifuging at 3000 rpm. The supernatant was decanted and discarded, taking care not to discard any of the solid residues.

Exchangeable: The residues from water-soluble fractions were extracted with 15mL of 1.0M NH₄OAc at a pH of 7.0 for 1 hr with continuous shaking. The extract was separated and stored as in the first step. The residue was washed as in the previous step and the supernatant was decanted and discarded.

Carbonate bound: The residues from exchangeable fractions were extracted with 8.0mL of 1.0 M NaOAc (adjusted to pH 5.0 with HOAc) for 5hr after swirling for 2.0 min. The extract was separated and stored as in the first step. The residue was also washed as in the first step, and the supernatant was decanted and discarded.

Fe-Mn Oxides-bound: The residues from carbonate fractions were extracted with 15ml 0.04M hydroxylamine hydrochloride in 25% (v/v) HOAc (pH of 2.0) at 96 °C with occasional agitation for 6.0hrs. The extract was separated and stored as in the first

step. The residue was also washed as in the first step, and the supernatant was decanted and discarded.

Organic-bound: The residues from Fe-Mn oxide fractions were extracted with 3mL of 0.02M HNO₃ and 5mL of 30% H₂O₂ (adjusted to pH 2.0 with HNO₃). The mixture was heated to 85°C for 2hrs, with occasional agitation. A second 3.0mL aliquot of 30% H₂O₂ (adjusted to pH 2.0 with HNO₃) was added and the mixture heated again to 85°C for 3hrs with intermittent agitation. After cooling, 5mL of 3.2M NH₄OAc in 20% (v/v) HNO₃ was added and the samples were diluted to 10mL with distilled water and agitated continuously for 30min. The extract was separated and stored as in the first step. The residue was also washed as in the first step, and the supernatant was decanted and discarded.

Residual: The residues from organic fractions were digested with aqua regia as described below. The mixture was filtered and the filtrates were diluted to 100 ml and stored in a polypropylene bottle until analysis.

Blanks were measured in parallel for each set of analyses using the extraction reagents described above. The metal concentrations of the supernatants from each step were analyzed by AAS after digestion with aqua regia as described in section 3.10.2.

3.10.2 Digestion of extracts from speciation analysis

The extracts and residue from speciation analysis were digested by adding 10ml of a mixture of concentrated HCl and HNO₃ in a screw top bottle. The preparation was heated on a steam bath for one hour, cooled and filtered after adding three drops of concentrated HCl. The filtrates were diluted to 100ml with distilled water, bottled and analyzed with AAS.

3.11 CONTROLLED EXPERIMENTS

3.11.1 Preparation of Soil Free of Humic Acid

Soil sample which does not contain humic acid was prepared by adding 500ml of 1M NaOH to 100g soil sample. The mixture was kept on a mechanical shaker to agitate for 12hrs. The mixture was then filtered. The residue, 1, obtained was kept. The filtrate was centrifuged and the residue, 2 obtained was added to the former. The mass of combined residue was dried at 105 °C in an oven. The dry mass of residue was ground to pass through 2mm sieve. The sieved sample free from humic acid was labeled 'soil devoid of humic acid', and kept for use in simulation experiments.

3.11.2 Preparation of Preloaded Soil Samples

Preloading of the soil samples was carried out by adding to 10g soil sample, the volume of metal solutions equivalent to the mass of the metal required. Distilled water was added to the mixture to obtain soil to solution ratio of 1:2, followed by continuous shaking and intermittent stirring every one hour. The mixture was then dried in the oven at 103 °C. The dry mass was crushed and ground to pass through 2mm sieve, labeled 'preloaded raw soil' and kept for use in simulation experiments.

The loading experiment was repeated for soil devoid of humic acid and labeled, 'preloaded soil devoid of humic acid'. The masses of metal added to 10g of preloaded soils are as presented in table 3.1.

Table 3.1: Mass of Cu added to soil samples

| Metal | Mass of metal added to 10g of soil (mg) | | | | |
|-------|---|-----|-----|-----|-----|
| Cu | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 |

3.11.3 Determination of Equilibrium Time Under Humic Conditions

To 10g of the preloaded raw soil containing 1.2mg Cu was added 30ml of distilled water and 0.02g of humic acid. To the mixture was added 20ml of buffer pH 3.72 to obtain a solid/solution ratio of 1:5. Ten replicate sets were prepared and each set was allowed to stand for periods indicated in table 3.2 below.

Table 3.2: Equilibrium time for metal partition in soil

| | | | | | | | | | | |
|------------|-----|---|-----|---|---|---|---|----|----|----|
| Set No | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Time (hrs) | 0.5 | 1 | 1.5 | 2 | 4 | 6 | 8 | 10 | 17 | 24 |

The mixtures were then centrifuged at 3000rpm followed by decantation to separate phases. The residue was digested with digestion procedure, DS (section 3.7.1). The supernatants were also digested using digestion procedure DL (section 3.7.2). The digest solutions were then analyzed for Cu. The experiment was repeated for pH 4.7, 6.85 and 10 independently.

3.11.4 Determination of Equilibrium Time under Non-Humic Conditions

To 10g of the preloaded soil devoid of humic acid containing 1.2mg Cu was added 30ml of distilled water and 0.02g of humic acid. To the mixture was added 20ml of buffer pH 3.72 to obtain a solid/solution ratio of 1:5. Ten replicate sets were prepared and each set was allowed to stand for periods as indicated in table 3.3. The mixtures were then centrifuged at 3000rpm followed by decantation to separate phases. The residue was digested with digestion procedure. DS (section 3.7.1). The supernatants were also digested using digestion procedure DL (section 3.7.2). The digest solutions were then analyzed for Cu. The experiment was repeated independently, for pH 4.7, 6.85 and 10.

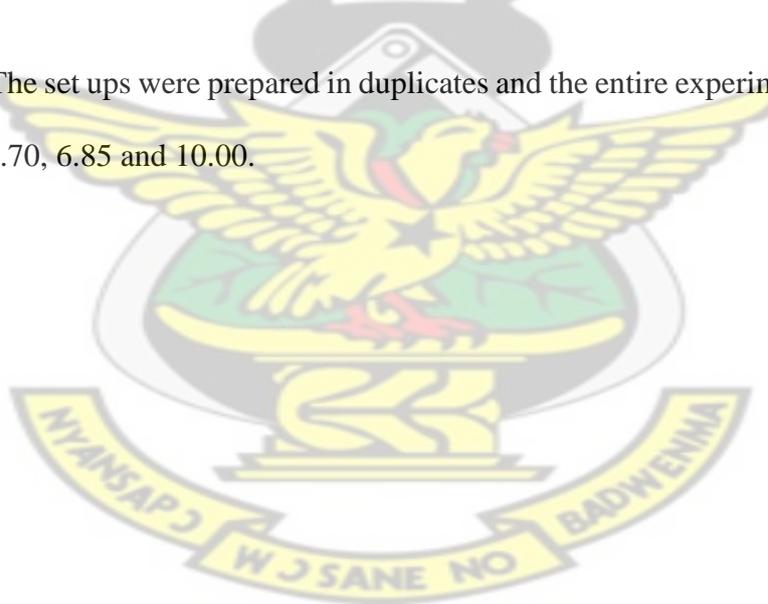
3.11.5 Determination of Equilibrium Constant at Different pH Under Humic Conditions

To 10g of preloaded soil samples A, B, C, D, and E containing varying masses of added Cu as shown in table 3.3. In different vessels were add 0.02g of humic acid. This was followed by the addition of 20ml distilled water and 30ml of pH 3.72 buffer solution to all mixtures. The mixtures were then agitated gently for 24 hours, after which they were subjected to fractionation and analysis using the procedure outlined in fig 3.3.

Table 3.3: Mass of metal and humic acid components of the setup

| Element | Preloaded sample | | | | |
|---------|------------------|------|------|------|------|
| | A | B | C | D | E |
| Cu (mg) | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 |
| HA(g) | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |

The set ups were prepared in duplicates and the entire experiment was repeated for pH 4.70, 6.85 and 10.00.



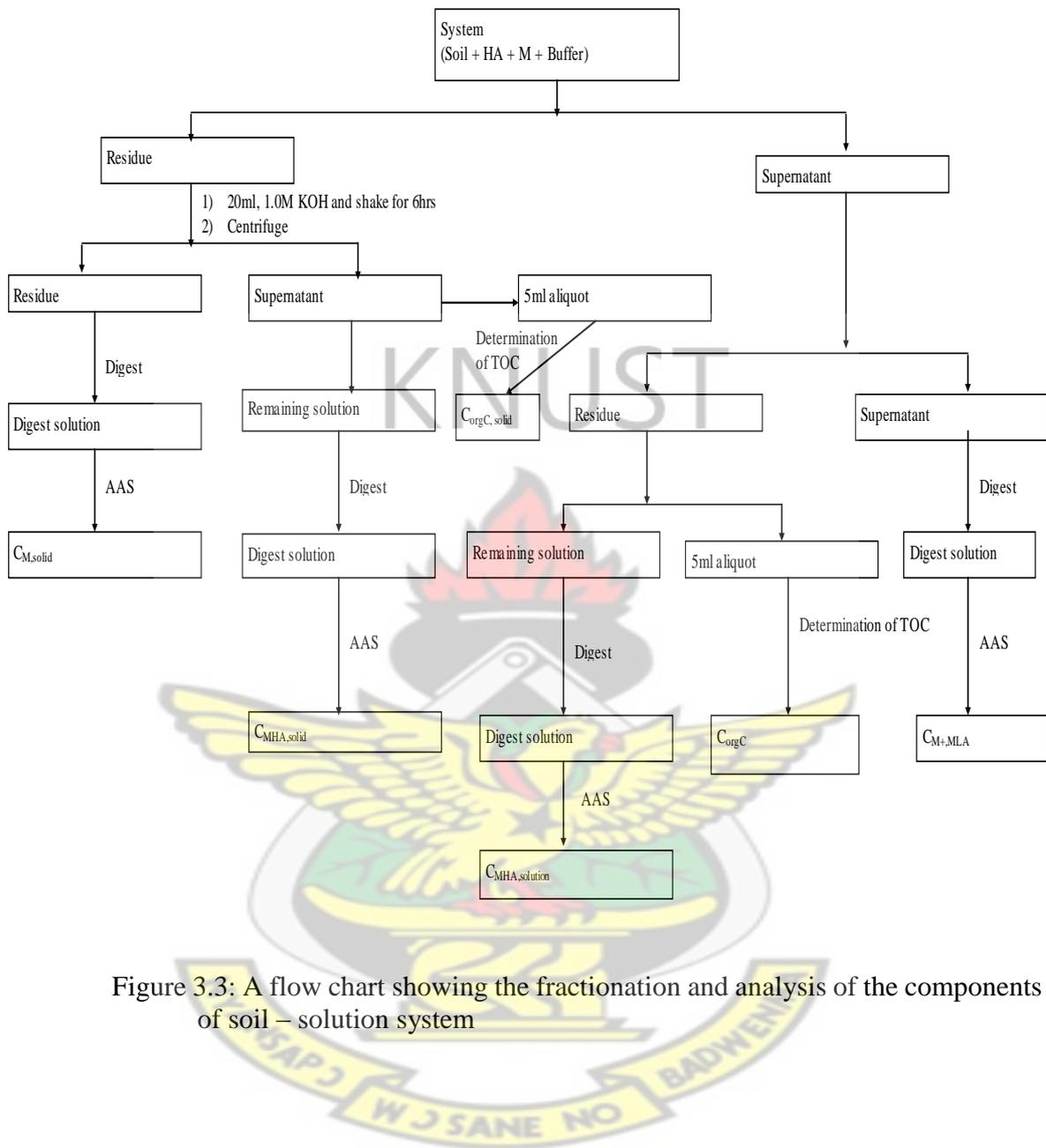


Figure 3.3: A flow chart showing the fractionation and analysis of the components of soil – solution system

3.11.6 Determination of Equilibrium Constant at Different pH Under Non-Humic Conditions

To 10g of preloaded soil samples A, B, C, D, and E containing varying masses of added Cu (table 3.4) but devoid of humic acid in separate vessels were added 20ml of distilled water and 30ml of pH 3.72 buffer solution. The mixtures obtained were agitated gently for 24 hours. The contents of the vessels were centrifuged at 3000rpm for 15 minute followed by decantation to separate the solid (residue) and liquid (supernatant) phases. The solid and liquid phases were subsequently, digested with digestion procedures DS and DL respectively. The digest solutions obtained were analyzed for Cu using AAS. The mixtures were prepared and analyzed in duplicates. The experiment was also repeated at pH 4.7, 6.85 and 10.0. The data generated were used to discuss the partition of metals between the solid and solution phases of soil solution system under non-humic condition.

Table 3.4 Mass of Cu in sample

| Element | Composition of Preloaded sample | | | | |
|---------|---------------------------------|-----|-----|-----|-----|
| | A | B | C | D | E |
| Cu (mg) | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 |

3.11.7 Effect of Humic Acid Concentration on Metal Distribution in Soil Solution System.

To 10g of preloaded soil sample containing the same masses of added Cu (1.2mg) in vessels A, B, C, D and E were added varying masses of humic acid as shown in the table 3.5.

Table 3.5 Composition of set up

| Element | Component of vessel. | | | | |
|---------------------|----------------------|------|-----|------|-----|
| | A | B | C | D | E |
| Mass of samples (g) | 10 | 10 | 10 | 10 | 10 |
| HA (g) | 0.02 | 0.04 | 0.0 | 0.08 | 0.1 |

Exactly 20ml of distilled water and 30ml of pH 3.72 buffer solution were added to the mixture in each vessel. The setup was prepared in duplicates. The contents of the vessels were agitated gently for 24 hours and analyzed by following the steps outlined in fig 3.3. The experiment was repeated for pH 4.7, 6.85 and 10.0.

3.11.8 Effect of Background Electrolyte on the Interactions and Distributions of Metals and Humic Acid in Aqueous Based Systems.

3.11.8.1 Aqueous Based Ternary System (Soil-Metal- HA):

An amount of 0.02g of humic acid were measured into five vessels A, B, C, D and E. To each vessel was added 10g of preloaded soil sample containing equal masses of added Cu (1.2g). Exactly 5ml of KCl solutions with concentrations 0.01 0.05, 0.1, 0.5 and 1.0M were added to the contents of vessel A, B, C, D and E respectively. This was followed by the addition of 5ml of distilled water and 35ml of pH 4.7 buffer solution each to the content of all the vessels.

The mixtures were agitated for 24 hours and subjected to fractionation and analysis by following the steps outlined in fig 3.2. The experiment was repeated for pH 10.0

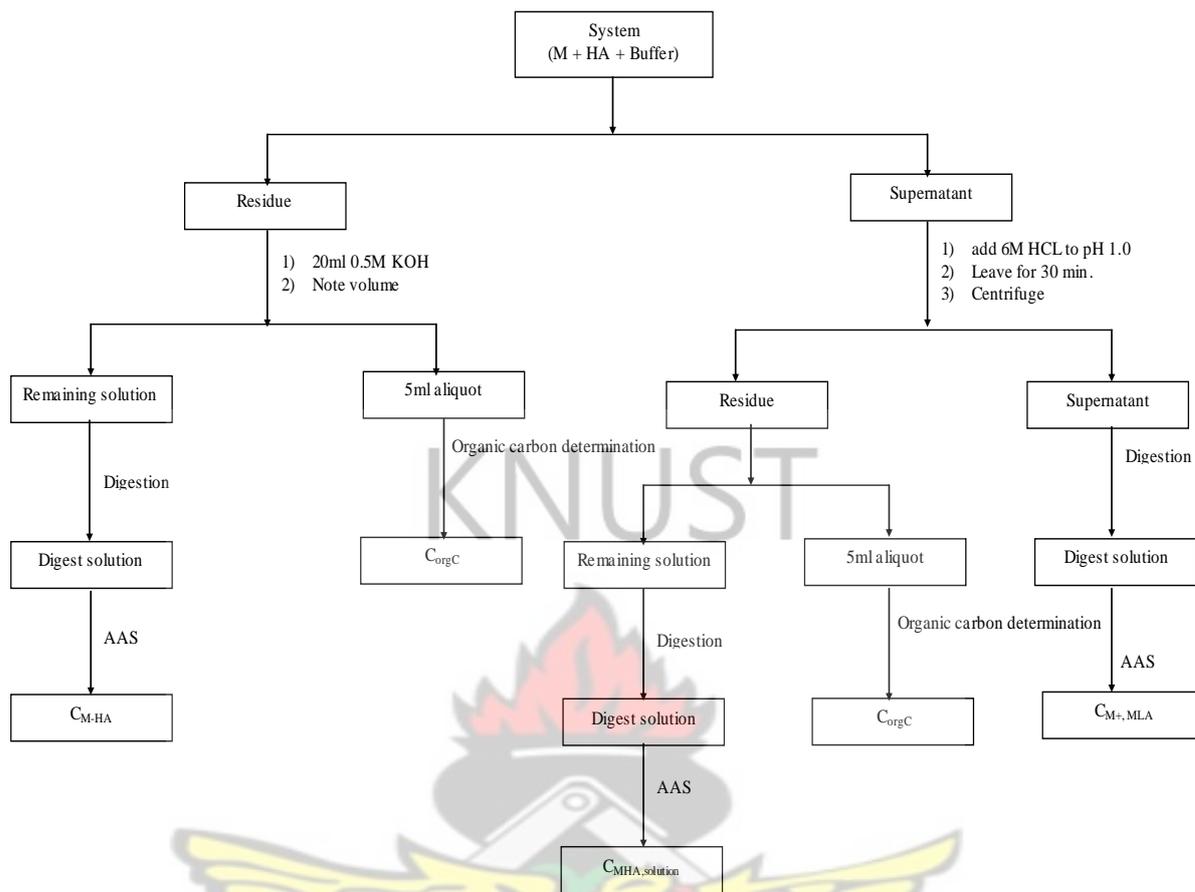


Figure 3.4: Extraction and fractionation of metal and humic acid species in aqueous-based binary systems

3.11.8.2 Aqueous-Based Binary (Metal-Humic) System:

Exactly 0.02g of humic acid were measured into five beakers A, B, C, D, and E, followed by the transfer of 5ml of 240ppm Cu solution. This was followed by the addition of 5ml KCl solutions with concentrations 0.01, 0.05, 0.1, 0.5 and 1.0m for beakers A, B, C, D and E respectively. To the resulting solution in each vessel were added 5ml distilled water and 35ml of pH 4.7 buffer solution.

The solutions were allowed to stand for 24 hours after which they were subjected to fractionation and analysis by following the steps outlined in fig 3.4. The experiment was repeated for pH 10. Preparations were made in duplicates.

The data obtained was used for discussing the effect of background electrolyte on the behavior of humic acid in aqueous based systems.

3.11.9 Effect of Temperature on Humic Acid Behaviour and Interactions

3.11.9.1 Aqueous Based Ternary System (Soil Metal-Humic):

An amount of 0.02g of humic acid were measured into five vessels A, B, C, D and E. To each vessel was added 10g of preloaded soil samples containing equal mass of added Cu (1.2mg). To the mixtures was added 10ml of distilled water. The mixtures were agitated for 24 hours at 25, 30, 35, 40 and 45°C for vessels A, B, C, D and E respectively. Fractionation and analysis of the mixtures were carried out by following the steps outlined in fig 3.3. The experiment was repeated for pH 10.

3.12.9.2 Aqueous Based Binary System (Metal-Humic):

To 0.02g of humic acid in five beakers A, B, C, D and E were added 5ml of 240ppm Cu solution. This was followed by the addition of 5ml distilled water and 35ml of pH 4.7 buffer solution. The resulting solutions in vessels A, B, C, D and E were kept at temperatures 25, 30, 35 40 and 45°C respectively.

The contents of the vessels were then analyzed by following the procedure outlined in fig 3.4. The experiment was repeated for pH 10.0

DEVELOPMENT OF THE MODELS

3.13 INTRODUCTION

The presence of trace metals and their transportation in an environment lead to contamination of natural ecosystems. And the contamination constitutes a potential source of health risk for plants, humans and other organisms. This is because irrespective of the source of the trace metals, they interact with other components (such as inorganic, organic materials and living organisms) present in the environment, and the interaction of the metals determine how toxic they become, how they are transported in an environment, and how they enter into the food chain and end-up on our dining tables.

Human activities such as farming, industry, mining, and waste disposal end up introducing potentially harmful trace metals into our environment. This ultimately results in a situation where Governments have to spend a lot of money on environmental remediation each year to ensure good health and safe environment. Unfortunately, the presence of the metals is sometimes detected only when people begin to fall sick or die. A lot of money which otherwise could have been used to provide essential services are often spent on combating the effect of the trace metal contaminant.

It has been observed that retention and mobility of many metal ions in soils and natural waters is greatly influenced by humic substances. Therefore, since metal ions bind strongly to humic substances, it is impossible to understand the metal ion transport and bioavailability without considering their interaction with humic substances (Clapp, et al 2001).

Humic substance (HS) models developed so far have considered mostly structure and reaction models in an attempt to explain its properties and nature of

interactions with metals and organic compounds (such as xenobiotics). However, models that describe the mechanism and the nature of transport and distribution pattern of metals with respect to their interaction with humic substances are yet to receive much attention.

Humic acids can be dissolved in aqueous media, accumulate at interfaces, can form self-assemblages, solubilize organic compounds, exist in different colloidal states depending on the solution conditions, can undergo clouding under certain solution conditions, and be adsorbed at mineral surfaces (Tombacz et al. 1999; Tipping, 2002). Some of these properties influence the distribution of humic acid between the phases of soil-solution systems. Changes in the relative proportion of humic acids at system phases bring about a redistribution of associated trace metals in the system. However, several authors have considered only the presence and or adsorption of humic substances in the studies of metal partition in soil-solution system (Petrovic et al. 1999).

The properties and characteristics of humic substances as they interact with metal ions can be harnessed to model the role HSs play in trace metal distribution in terrestrial environment. The outcome of which will increase our knowledge of the dynamics of trace metals under humic conditions in geomeia, and to bring us to terms with the indispensable role of HSs in nature.

In addition, man's ability to effectively evaluate the nature of the relationship between metals and biological populations is dependent on his knowledge of the fate and distribution pattern of metals in a given environment. This project has therefore been designed to provide insight into the dynamics of trace metals in natural systems.

Therefore, as part of the research process, this chapter seeks to explain the theoretical considerations underlying the development of the models in this study to

explain the role of humic substances in trace metal distribution in terrestrial environment.

3.13.1 DEVELOPMENT OF THE CONCEPTUAL MODEL

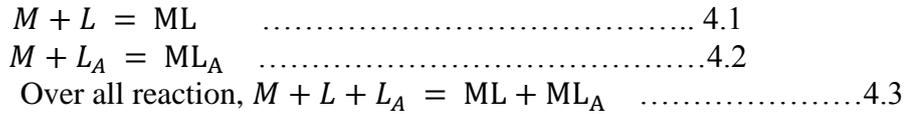
In this study it was acknowledged that conceptual framework is a prerequisite to mathematical modeling. There was thus the need to clearly describe the conceived picture of the idealized system, and the system must be an approximation of the actual system to enable the mathematical models to be applicable to both systems.

The semi-natural ecosystem (soil) under study is considered to be an open system made up of two major phases, soil-solid and soil-solution (pore water) phases. Metals can move from one phase to another under conditions determined by the pH and ionic strength of the solution phase, as well as the temperature and humidity of the surroundings. Trace metals associate with negatively charged surfaces or ions in both phases and humic substances are considered a significant component of the system and can interact with ions in the solution phase as well as the solid phase minerals. The nature and interactive properties of the solid phase, properties of the solution phase, humic substances and the prevailing conditions of the surroundings of the system are considered as factors capable of influencing metal speciation and partition in the system.

3.13.2 DESCRIPTION OF SOLUTION PHASE CHARACTERISTICS

The solution phase of the system is considered to be aqueous based and contain free metal ions, M , free organic ligands, L , free inorganic ligands, L_A , organic complex, ML , and inorganic complex, ML_A . The solution phase also contains a fixed amount of other metal ions which do not significantly influence the interaction of the trace metal of interest. If it is assumed that there is no association between L and L_A . Then trace

metal interactions in the solution phase under equilibrium conditions may be expressed as follows:



Solution phase aggregates and precipitates (both organic and inorganic) are assumed to eventually settle and form part of the solid phase at equilibrium. And trace metal interaction is not influenced by co-precipitation or encapsulation in growing aggregates, etc. Considering the reactions in the solution phase, the stability constants in this phase may be given as,

$$\begin{aligned}
 K_{ML} &= \frac{[ML]}{[M][L]} && \dots\dots\dots 4.4 \\
 K_{MLA} &= \frac{[ML_A]}{[M][L_A]} && \dots\dots\dots 4.5
 \end{aligned}$$

Effect of pH: At low pH, oxyhydroxides dissolve to form cationic species (Al^{3+} , $AlOH^{2+}$, $Al(OH)_2^+$ etc.). Therefore, at low pH, cation-trace metal competition for the ligands is expected to occur. Thus, the free metal ion concentration, $[M]$, will be affected depending on the relative affinities of the cations for the ligands.

If it is assumed that mineral dissolution takes place too slowly to introduce cationic species and in addition, if no significant hydrolysis of minerals occurs, then the concentration of anionic species will be negligible at low pH. Therefore, at low pH, the dominant metal interactions will be, $M + L = ML$, as written in equation (1), and the total concentration of organic ligands, T_L , may be expressed as,

$$T_L = [ML] + [L] \dots\dots\dots 4.6$$

At high pH, oxyhydroxide solids dissolve to form anions leading to increase in L_A .

Therefore, it is considered that, $M + L = ML$, and $M + L_A = ML_A$ reactions will

be observed in the solution. The total concentration of trace metal in the soil solution, T_M , may be expressed as

$$T_M = [M] + [ML_A] + [ML] \dots\dots\dots 4.7$$

At high pH, L is intrinsically hydrophilic thus it will transfer binding sites from the solid phase to the solution phase. The extent of metal binding to L, v_{ML} , in the solution phase may be expressed as,

$$v_{ML} = \frac{[ML]}{T_L} \dots\dots\dots 4.8$$

Since $T_L = [ML] + [L]$ (equation, 4.6) at all pH, v_{ML} is dependent on the property of L that determines its concentration in solution phase at any given pH. However, v_{ML_A} , according to the assumption is expected to decrease with pH.

$$v_{ML_A} = \frac{[ML_A]}{T_{L_A}} \dots\dots\dots 4.9$$

This is because, at low pH, T_{L_A} is assumed to be zero.

3.13.3 DESCRIPTION OF SOLID PHASE CHARACTERISTICS

Sorptive interactions at solid-water interface strongly influence trace metal distribution in semi-natural ecosystems. Metals, oxyanions and humic substance adsorption on soil mineral surfaces are controlled by a complex array of geochemical factors including pH, ionic composition and strength of embathing solution, chemical functionality and crystallography of mineral surfaces involved (Tadanier, 2002; Tipping, 2002).

In this study, the solid phase is considered as an oxide surface which can interact with protons, metal cations, inorganic anions, and humic substances. Moreover, the solid phase is capable of developing surfaces with exposed hydroxyl groups when in contact with water, and can bind and release ions in a manner that can be represented by, $SOH + H^+ = SOH_2^+$, $SOH = SO^- + H^+$ (Where

S = solid surface). The solid surface can also interact with metal cations, inorganic anions and organic ligands, *L*. The solid surface – organic ligand interactions may be represented as,



And the total concentration of *L* and *M* adsorbed are ([*SL*] + [*M(SL)*]) and ([*MS*] + [*M(SL)*]) respectively. The occurrence of the interactions and concentrations of the sorbates are determined by the geochemical factors (such as pH), and the properties of both the sorbent and the sorbates.

It was assumed that interactions occur at separate binding sites on the oxide surface, and the total number of binding sites is equivalent to the moles of sorbates adsorbed. And the numbers of insoluble colloidal precipitates or aggregates that settle on the surface are considered as having negligible effect on the partitioning of species, particularly trace metals, between the system phases.

Therefore, at low pH the total concentration of metal adsorbed by the solid surface, T_{MS} , is the sum of *MS*, *M(SL)* and $ML_{(s)}$ (where $ML_{(s)}$ is the concentration of all forms of metals that have settled on the solid phase as precipitate or trapped during humic matter aggregation). At high pH, metals adsorbed directly on the solid phase (*MS*), $ML_{(s)}$ and *M(SL)* will sum up to give the total metal concentration in the solid phase, T_{MS} . This is because the organic ligand, *L* (humic substance), being hydrophilic at this pH will be in solution, however metal-associated non-specifically adsorbed organic ligands and metal induced aggregates are considered to be capable of occurring at high pH and consequently increase metal-associated ligand forms in the solid phase.

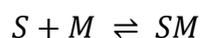
In addition, the total organic ligand concentration in the solid phase, T_{SL} , at low pH will be the sum of SL, M(SL), and $ML_{(s)}$. At high pH, $T_{SL} = SL + M(SL) + ML_{(s)}$, due to ternary complex formation and precipitation of ligand aggregates ($L_{(s)}$). The extent of metal bound to the solid phase, v_M , at all pH may be expressed as,

$$v_M = \frac{T_{MS}}{M_S} = \frac{[MS] + [M(SL)] + [ML_{(s)}]}{M_S} \dots\dots\dots 4.13$$

Where M_S = mass of solid surface.

The fate of trace metals in the soil environment are directly related to their speciation and partitioning between soil-solid and soil solution. The presence of trace metals in the solid phase is a result of precipitation and adsorption to components of the soil, processes that are highly pH dependent. Varying contents of organic matter and metal oxides may result in varying capacity for metal sorption onto soils (Tipping, 2000). The interaction of trace metal ions with natural soil particles is complex, involving multiple mechanisms. Including the soil components is necessary to develop an understanding of the effect of humic matter on the relative strength of metal adsorption to the soil, especially the effect of humic matter on metal distribution in the soil system.

Thus, in the model development the solid surface, S, is also considered as a material with different adsorbing sites. Consisting of heterogeneous surface with the following class of adsorbing sites, Oxide (ox), Organic matter (OM), Carbonate (CO_3), Clay(c), for trace metals. If the binding sites are identical for each class, and are non-interacting, then at equilibrium, the reaction below may be written for all binding sites.



$$K_{S-M} = \frac{[SM]}{[S][M]}$$

$$[SM]_{tot} = [M_{OM}] + [M_{Ox}] + [M_{CO_3}] + [M_c]$$

And the metal distribution may also be expressed as proposed by Allen et al. 1996,

$$K_{DM} = \frac{[SM]_{tot}}{[M]} = \sum_{sites} K_{Si-M}[S]$$

Where K_{Si-M} is the conditional stability constant for the reaction of the metal with the i th class of sorption sites; and $[SM]_{tot}$ is the total concentration of metal adsorbed per unit mass of surface.

Using this relationship and the Hill equation (Koopal et al, 2001) below, the relationship between the distribution of trace metal and humic matter partition may be properly explained in terms of the chemistry of the processes.

$$v_M = \frac{(K_i[M]_i)^{n_i}}{1 + (K_i[M]_i)^{n_i}}$$

Where v_M is the fraction of the reference sites occupied by a trace metal i , K_i the intrinsic affinity of the metal i for the reference sites, and $[M]_i$ the concentration of the metal in solution. n_i is the stoichiometry (cooperativity) of the binding reaction. That is each i th site becomes occupied with n_i molecules of the metal.

However in order to effectively explain the processes well, the idealized system is also considered to experience solid phase modification by the humic matter. The modification introduces two major binding sites (organic and inorganic sites). Thus changes in the site ratio and the factors responsible may be utilized to describe how humic substances influence trace metal partition.

3.13.4 MODELING ASSUMPTIONS AND CONDITIONS

Many reactions are far from equilibrium in the natural environment. In addition, reactions in solution can be fast enough, such that under some conditions, equilibrium is achieved sufficiently rapidly that the reaction is essentially

instantaneous (Tipping, 2002). However, the assumption of equilibrium allows a researcher to draw on enormous amount of available equilibrium data determined for well defined reactions under controlled conditions, to calculate the extents of the different reactions. The following assumptions have therefore been made to enable a better description of the effect of humic substance on metal partition in soil – solution system.

- The role of humic substances in trace metal distribution may be modeled by relating partition constants, stability constant (M-HS), extent of metal binding to humic matter, changes in net humic charge, and adsorption of L and M to soil solid.
- The humic matter is a multisite adsorption surface, and individual sites do not interact with each other.
- Mineral dissolution does not change the mass of solid phase significantly at high pH.
- Mineral dissolution takes place too slowly for the dissolution reaction itself to be significant at low pH and control solution concentration,
- The semi-natural ecosystem under study is made up of two distinct phases, the solid phase (soil) and the solution phase.
- The interactions/binding processes of species in the system reach equilibrium rapidly within the time frame of the experiment (24hrs).
- All reactions in the binary system are at equilibrium at specified geochemical conditions of temperature, pressure and pH.
- There is no association between organic and inorganic ligands in solution.
- Colloidal particles of metal-ligand associations, and individual ligands, form part of the solution phase.

- HS Aggregates and precipitates are assumed to eventually settle and form part of the solid phase.
- Trace metal interaction is not influenced by co-precipitation or encapsulation in growing aggregates, etc.
- No significant hydrolysis of minerals occurs at low pH.

3.13.5 HUMIC SUBSTANCE PARTITION AS A FUNCTION OF TRACE METAL DISTRIBUTION

3.13.5.1 *Distribution in Soil-Solution System*

According to the accepted principles of colloid science, systems are considered to exhibit colloidal properties when the dimensions of the dissolved or dispersed components are in the range of 1 to 1000nm (Tombacz et al 1999). Depending on the chemical composition of dissolved or dispersed components and on the molecular interactions with the solvent molecules, a given type of colloidal system can generally be formed. For example;

- A macromolecular solution results if polymer is dissolved in an appropriate solvent or
- A micellar solution is formed when a surface active solute concentrations are above a critical value (critical micelle concentration, CMC) or
- Dispersions result in which solid particles or immiscible liquid droplets are dispersed.

According to Tombacz et al (1999), colloidal character (i.e. specific properties and changes of colloidal state) can be expected for aqueous humic systems because of the size ranges that they display in either the dissolved or dispersed (precipitated) state. They stated that, various solution condition dependent intra- and intermolecular

interactions can be supposed in aqueous systems of humic substances, and because of their random formation, any uniform behavior of the polydisperse product cannot be expected and only trends of properties can be predicted.

Hydrophobic moieties such as long alkyl side-chains from fatty acid residues provide amphiphilic character in humic molecules, therefore analogue properties similar to those of surface active agents can be expected (Tombacz et al 1999). The formation of self-assembled systems due to hydrophobic interactions can also be expected, as for example in the formation of oriented bilayers in membrane-like structures when humic matter form coatings on mineral surfaces in soils or as micellar solutions that can solubilize otherwise water-insoluble organic compounds (Tombacz et al 1999).

The dissociation of the carboxylic and hydroxyl groups on humic substances in aqueous media leads to the spontaneous formation of an electric double layer (EDL). Therefore, the electrostatic interactions they undergo are responsible for the conformational changes of humic macroions as well as the colloidal stability of humic solutions and in the aggregation of the individual humic macroions (Tombacz et al 1999; Tipping, 2002).

At high pH and low ionic strength the functional groups are fully ionized and the chemically linked charges endeavour to situate themselves as far apart as possible. However, expansion of the aromatic network is limited by the chemical cross-linkages. Therefore, the extent of expansion and compression of cross-linked humic nanospheres is much smaller than for linear polyelectrolytes. The expanded or collapsed net works are totally or partially penetrable by water molecules, and the formation of water impenetrable units can be supposed after precipitation of humic materials. The macroscopic aggregation of humic acid particles (referred to as precipitation,

coagulation, flocculation or phase separation) is mainly determined by the screened electric field developed from the dissociation of acidic groups bound chemically to the cross-linked polymeric network of humic molecules. Like any other aqueous colloidal dispersion, the colloidal stability of an aqueous humic acid solution prior to the onset of macroscopic phase separation is controlled chemically and electrostatically (Tombacz et al 1999).

The inherent polydispersity in the size distribution of humic samples and the spontaneous changes in their conformational and aggregation states that take place under even slightly changing solution conditions are the reasons for the differences in their average molecular weight.

In a nutshell it can be stated that polyelectrolyte-, surfactant-, and charged nanoparticle-like colloidal behavior have been predicted and observed for aqueous systems of humic acids. Moreover, in an aqueous medium the main external factors that influence the colloidal state of humic acids are pH, ionic strength, the presence of di- or multivalent metal ions, cationic organic compounds, organic liquids and solid particles.

If an assumption is made based on the statement made by Tombacz et al (1999) that the building blocks of humic nanospheres are amphiphilic units containing hydrophilic groups linked chemically to an aromatic and/or aliphatic hydrophobic part then these amphiphilic units will associate to form loose aggregates (similar to their macromolecular coils or micelles of liophilic colloids). The loose polar nanospheres (mainly negatively charged groups) will be hydrophilic. So they will be penetrated fully by water. In dilute solutions at appropriate pH, the alkali salts of humic acids are considered to be real colloidal solutions, showing the properties of both cross-linked polyelectrolyte and surfactant solutions. Characteristic colloidal processes of dissolved

humic acids are therefore conformational changes, adsorption at different interfaces, and self-assembly in solution and at solid interfaces. In addition, it is assumed that changes in solution conditions such as a decrease in pH or addition of multivalent metal ions or organic cations will induce the formation of compact humic aggregates. Neutralization or screening of the charges will not facilitate the penetration of water into the molecule and so compact, hydrophobic nanospheres will be formed.

Changes in the colloidal state of humic substances are responsible for the transition of the humic matter from dissolved to disperse state. Consequently, the partition of humic substances between the solid and solution phases of soil-solution system is a function of its colloidal state under defined solution conditions.

3.13.5.2 Theory of humic substance partition in soil-solution system:

During phase separation, metals associated with (or bonded to) humic substances move from solution phase to solid phase. The transfer of metal-bound humic substance to the solid phase affects the relative proportion of the metal in the phases of the soil system.

Colloidal processes involving humic substances are spontaneous and the colloidal state of humic substances changes continuously in environmental systems. Adsorption on mineral surfaces, dissolution and precipitation of humic materials under changing conditions are common in semi-natural ecosystems (e.g., terrestrial and aquatic environments). Since the induced precipitation and coagulation of humic substances are reversible, the relative proportion of metal bound humic substances in the system phases will be dependent on the pH, concentration of neutral salt(s) and the relative concentration of the trace metal in the solution phase.

Since trace metals associate with organic matter especially the humic substances in terrestrial environment, their distribution is discussed in terms of the

distribution constants by considering the fraction of the total metal bound to humic matter. Using figure 4.1, where L and ML species are present in the solid phase as:

- Compact aggregates (ag): formed as a result of i) the formation of hydrophobic units (by charge screening or neutralization), ii) metal induced aggregation, and iii) conformational changes.
- Adsorbed species (a): these are species adsorbed unto the solid phase material by electrostatic attraction.

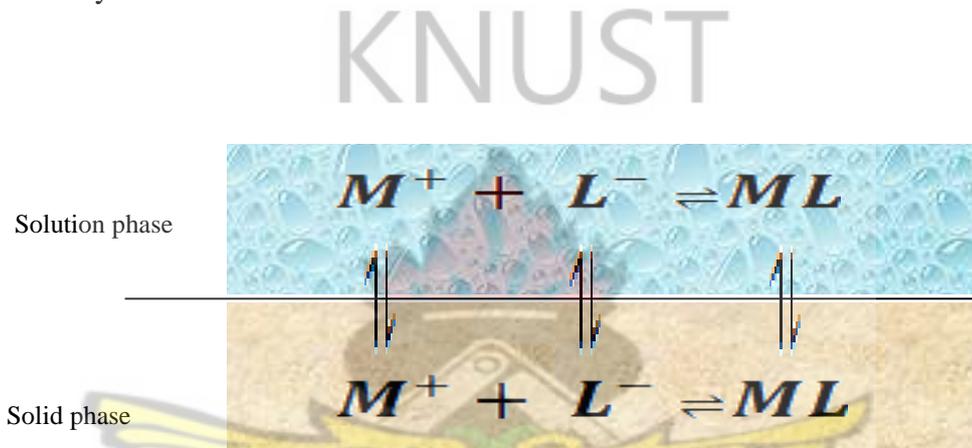


Figure 4.1 Illustration of the conceptual model of metal and humic acid interaction, and transfer between phases in soil-solution system

L and ML will occur as adsorbed (L_a , ML_a) and aggregate (L_{ag} , ML_{ag}) forms in the solid phase. If the partition of L is analyzed separately in terms of aggregation and adsorption, then the partition constant due to aggregation ($Q_{ag,L}$) and adsorption ($Q_{a,L}$) may be expressed as:

$$Q_{a,L} = \frac{\sum(L_a + ML_a)/M_s}{[L]} = \frac{L_{adsorbed}/M_s}{[L]} \dots \dots \dots 4.14$$

Where $a \Rightarrow$ adsorbed specie on solid phase; $L_{adsorbed}$ = sum of the masses of all forms of the ligand, L, soluble and insoluble adsorbed unto the soil minerals in the solid phase of the soil-solution system; M_s = mass of the solid phase; $[L]$ = ligand concentration in solution.

$$Q_{ag,L} = \frac{\sum(L_{ag} + ML_{ag})/M_s}{[L]} = \frac{L_{aggregate}/M_s}{[L]} \dots \dots \dots 4.15$$

Where $ag \Rightarrow$ macroscopic aggregates of the ligand which has separated from solution to the solid phase; $L_{aggregate}$ = sum of the masses of all forms of the ligand (L) which has separated from solution to the solid phase of the soil-solution system.

From equation 4.14 and 4.15, $[L]$ may be written as,

$$[L] = \frac{L_{aggregate}/M_s}{Q_{ag,L}} = \frac{L_{adsorbed}/M_s}{Q_{a,L}}$$

If the overall partition constant (K_{DL}) for the ligand is expressed as:

$$K_{DL} = \frac{(L_{aggregate} + L_{adsorbed})/M_s}{[L]}$$

and

$$K_{DL} = \frac{(L_{aggregate}/M_s) + (L_{adsorbed}/M_s)}{[L]}$$

$$\Rightarrow K_{DL} = \frac{Q_{ag,L}[L] + Q_{a,L}[L]}{[L]}$$

Therefore,

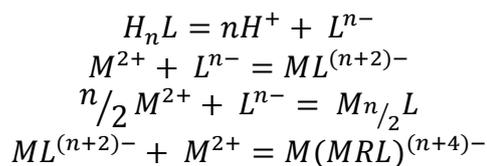
$$K_{DL} = Q_{ag,L} + Q_{a,L} \dots \dots \dots 4.16$$

Hence the partition constant for humic substance is a sum of the partition constants due to aggregation and solid phase adsorption of the humic substance (i.e., the ligand). Consequently, it may be concluded that the distribution of humic substances between the phases of soil-solution system is controlled by the adsorption and colloidal properties of the humic matter.

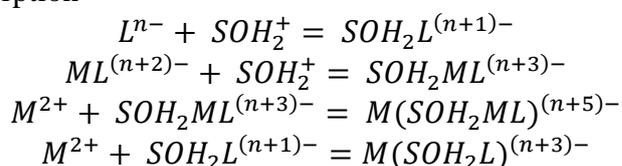
3.13.5.3 The relationship between K_{DL} and trace metal distribution in soil-solution system

The following hypothetical relationships are conceived for a poly-functional material such as humic substance which exhibit poly-electrolyte properties.

Complexation



Adsorption



Where M = trace metal; L = humic substance; SOH = solid phase

The reactions indicate that all forms of humic matter may have trace metal associated with them, so if the metals are transported alongside the humic matter, then the partition constant for the ligand would include those forms of the ligand which have trace metal bound to them as expressed below.

$$Q_{a,L} = Q_{a,ML} + Q_{a,SL}$$

$$Q_{ag,L} = Q_{ag,ML} + Q_{ag,SL}$$

Where $Q_{a,ML}$ and $Q_{ag,ML}$ = partition constants for all forms of metal bound ligand adsorbed and as aggregate respectively; $Q_{a,SL}$ and $Q_{ag,SL}$ = partition constants for all forms of non metal bound ligand adsorbed and as aggregate respectively.

As such the overall partition constant for the ligand is,

$$K_{DL} = Q_{a,ML} + Q_{ag,ML} + Q_{a,SL} + Q_{ag,SL}$$

If $Q_{a,ML} + Q_{ag,ML} = K_{D,ML}$ and $Q_{a,SL} + Q_{ag,SL} = K_{D,SL}$

Then,

$$K_{DL} = K_{D,ML} + K_{D,SL} = Q_{ag,L} + Q_{a,L}$$

Where $K_{D,ML}$ = partition constant for ligands associated with trace metal; $K_{D,SL}$ = partition constant for ligands which are not associated with trace metals.

Thus, if the distribution constant for trace metal is expressed as:

$$K_{DM} = \frac{(MS + MSL)/M_s}{([M^+] + [ML_{inorganic}] + [M_{ML}])}$$

Where MS = mass of trace metal bound to the solid phase; M_{MSL} = mass of all forms of metal bound ligand; M^+ = free metal in solution; $L_{inorganic}$ = inorganic ligand; M_{ML} = all forms of metal bound ligand in solution.

And

$$K_{DM} = \frac{(MS + MSL)/M_s}{[M^+] + [ML_{inorganic}]} + \frac{MS/M_s}{[M_{ML}]} + \frac{M_{MSL}/M_s}{[M_{ML}]}$$

If $\frac{M_{MSL}/M_s}{[M_{ML}]} = Q_{ML}$, then,

$$K_{DM} = \frac{(MS + MSL)/M_s}{[M^+] + [ML_{inorganic}]} + \frac{MS/M_s}{[M_{ML}]} + Q_{ML}$$

But the magnitude of Q_{ML} is dependent on $K_{D,ML}$, consequently K_{DM} is a function of the distribution of humic matter in soil system at specified solution conditions.

When K_{DM} and $K_{D,ML}$ are expressed in terms of moles of binding sites then,

$$K_{DM} = \frac{(MS + MSL)/M_s}{[M^+] + [ML_{inorganic}]} + \frac{MS/M_s}{[M_{ML}]} + K_{D,ML} \dots \dots \dots 4.17$$

$$\text{Or } K_{DM} = \frac{(MS+MSL)/M_s}{[M^+]+[ML_{inorganic}]+[M_{ML}]} + K_{D,ML}$$

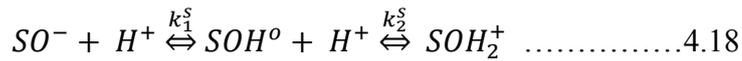
and it can be stated more succinctly that trace metal distribution is in part a function of the surface adsorption and aggregation properties of humic substances present in the system. And this conclusion is better explained with the aid of ion adsorption mechanisms as discussed below.

3.13.6 MECHANISM OF ION ADSORPTION IN SOIL-SOLUTION SYSTEM

3.13.6.1 Ion Adsorption

The soil-solution system is pictured as having a solid phase (composed of a mixture of oxide and hydroxide minerals) with heterogeneous binding sites (capable of forming mono, bi, and tridentate complexes). Therefore, the solid phase is expected to exhibit binding site heterogeneity and also have the ability to be modified by humic substance, L (adsorbed $[L_a]$, adsorbed aggregate $[L_{ag, a}]$ and reactive-aggregate $[L_{ag, asso}]$ forms).

The solid phase is also seen as capable of exhibiting surface ionization reactions noted for the amphoteric behavior of oxide and hydroxide minerals (Dzombak and Morel, 1990; Hiemstra et al., 1989a, 1999; Sposito, 1989; Stumm, 1992a; Westall, 1980; Zelazny et al., 1996). The protonation of the amphoteric ligands of the solid phase can be described in two step reaction process as depicted below with two association constants.



$$k_1^s = \frac{[SOH^o]}{[SO^-][H^+]} \dots\dots\dots 4.19$$

$$k_2^s = \frac{[SOH_2^+]}{[SOH^o][H^+]} \dots\dots\dots 4.20$$

Where k^s = surface association constant; S = bulk mineral cation;

The overall surface association constant expression, $K^s = k_1^s k_2^s [H^+]$, indicates that the overall surface charge of the solid phase is dependent on the extent of surface protonation/deprotonation and other coordinated ions. The solid phase is therefore a surface which has the capacity to exhibit positive charge at low pH, and negative charge at high pH values based upon the protonation of the surface functional groups.

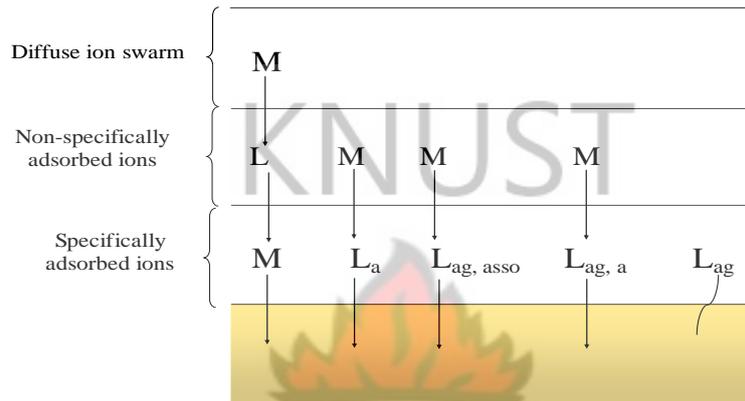
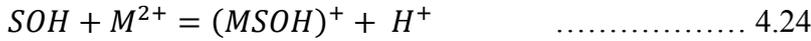
Ion adsorption in the conceptualized soil-solution system can therefore be separated into two: specific (inner-sphere) and non-specific (outer-sphere) adsorption (figures 4.2-3). The non-specific adsorption refers to ions (solvated) that form weakly bound complex with specific surface groups. The weakly bound complexes are considered to interact with surface functional groups to form outer-sphere complexes (figures 4.2-3), and can be presented as follows,



These are considered to be due to hydrogen, electrostatic, and van der Waals bonding (Sposito, 1989; Stumm, 1992b; Zelazny et al., 1996). In addition, the remaining surface charge is balanced in a delocalized sense by ions located in the diffuse ion swarm (figures 4.2-3).

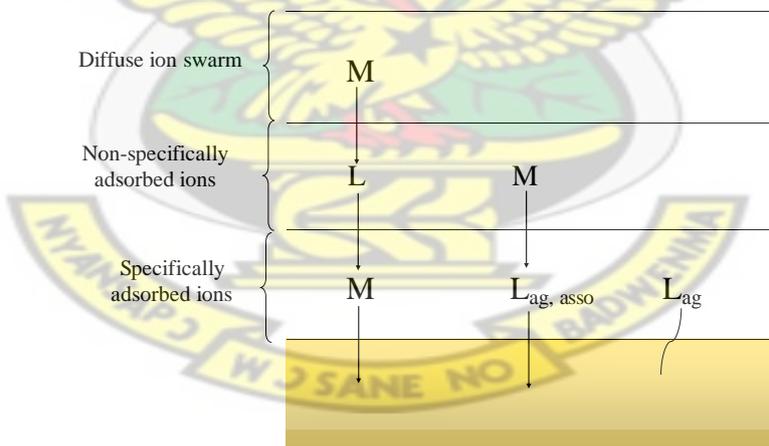
Specific adsorption in this case refers to solution ions that form a complex with a specific surface functional group (s) and the complexes formed are referred to as inner-sphere complexes. During the formation of cation inner-sphere complexes, the

surface hydroxyl groups act as charge donors and increase the overall electron density of the coordinated metal and alter many of its chemical properties (toxicity etc.).



L is the ligand; M is the metal of interest; L_a is adsorbed ligand; L_{ag, a} is adsorbed ligand aggregate; L_{ag, asso} is ligand aggregate which is not chemically associated with the mineral surface.

Figure 4.2: Illustration of idealized mechanism of ion adsorption at low pH

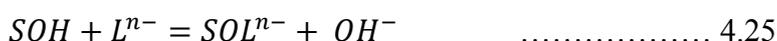


L is the ligand; M is the metal of interest; L_{ag, asso} is ligand aggregate which is chemically associated with the mineral surface; L_{ag} is ligand aggregate which is not chemically associated with the mineral surface.

Figure 4.3: Illustration of idealized mechanism of ion adsorption at high pH

During the formation of anion inner-sphere complexes (eg. L⁻, and inorganic ligands such as CrO₄²⁻, AsO₃³⁻), mineral cations act as Lewis

acids exchanging the electrons of the surface OH group(s) with those of the adsorbate (a ligand exchange reaction process).



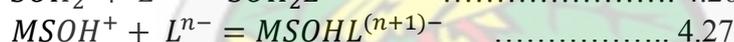
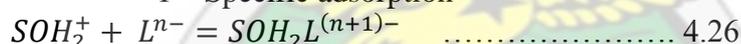
In addition, monodentate (mononuclear), bidentate (mono and binuclear) and multidentate (mono, bi and trinuclear) species can be formed at the solid phase mineral surface. The formation of inner sphere complexes on the surface of the solid phase mineral is therefore strongly dependent on pH.

3.13.6.2 *Complexation Reactions*

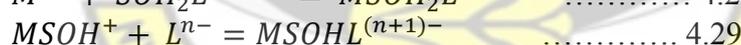
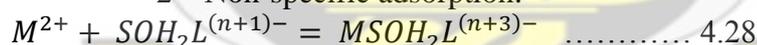
Complexation reactions at low and high pH conditions expected for the conceptual model of ion adsorption mechanism (figures 4.2-3) are enumerated below. The reactions involve interaction between the humic substance (L), and a divalent trace metal. The different forms in which the humic substance occurs in the solid phase are considered in the reactions.

Low pH condition

1- Specific adsorption

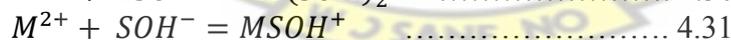
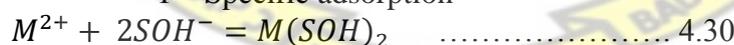


2- Non-specific adsorption:

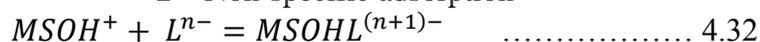


High pH condition

1- Specific adsorption



2- Non-specific adsorption



3.13.6.3 *Ion Adsorption and Metal Partition*

Metal bound to humic substance (L) in the solid phase can be considered to be specifically bound if the L acts as a new surface which is not affected by its association with the solid phase mineral. In this case therefore, the metal partition constant (K_{DM})

may be defined to include all forms of metal in the modified solid phase (i.e. in terms of binding sites). Thus, there will be two categories of metal forms, metal-bound-inorganic sites and metal-bound-organic site forms. Since these forms are available at all pH, the partition constant may be expressed generally as,

$$K_{DM} = \frac{1}{T_M} \sum (V_{M,inorganic} + V_{M,organic}) \dots\dots\dots 4.33$$

Where T_M = total metal concentration in the solution phase; $V_{M, inorganic}$ = extent of metal binding to the solid phase inorganic sites; $V_{M, organic}$ = extent of metal bound to organic sites in the solid phase.

But if it is assumed that for the conceptualized system, $T_M = [M] + [ML]$ at low pH and $T_M = [M] + [ML_A] + [ML]$ at high pH. Where L_A is inorganic ligand in solution phase, then, at low pH, equation 4.33 becomes,

$$K_{DM} = \frac{1}{[M] + [ML]} \sum (V_{M,inorganic} + V_{M,organic})$$

Rearranging and dividing through by $[ML_{(s)}]$ gives,

$$\frac{1}{Q_{ML}} = \frac{[ML]}{[ML_{(s)}]} = \frac{\sum (V_{M,inorganic} + V_{M,organic})}{[ML_{(s)}]} \left(\frac{1}{K_{DM}} \right) - \frac{[M]}{[ML_{(s)}]} \dots\dots 4.34$$

Similarly, at high pH,

$$K_{DM} = \frac{1}{[M](1 + K_{ML_A}[L_A]) + [ML]} \sum (V_{M,inorganic} + V_{M,organic})$$

And $\gamma = (1 + K_{ML_A}[L_A])$,

$$\therefore K_{DM} = \frac{1}{[M]\gamma + [ML]} \sum (V_{M,inorganic} + V_{M,organic})$$

Hence rearranging and dividing through by $[ML_{(s)}]$ gives,

$$\frac{1}{Q_{ML}} = \frac{[ML]}{[ML_{(s)}]} = \frac{\sum (V_{M,inorganic} + V_{M,organic})}{[ML_{(s)}]} \left(\frac{1}{K_{DM}} \right) - \frac{[M]\gamma}{[ML_{(s)}]} \dots\dots 4.35$$

The derivations show that at all pH, $\frac{1}{Q_{ML}} \propto \frac{1}{K_{DM}}$. This shows that at all pH the extents of metal complexation in both phases of the soil solution system have effect on the partition of the trace metal in the system. Therefore, the ability of humic substance to occur in both phases of the soil-solution system simultaneously is responsible for its effect on the partition of trace metals.

Humic substances, therefore, may be considered with respect to the theory discussed as capable of using their aggregation and cation binding properties to control a fraction of trace metals in soil-solution system. The role it plays in determining metal partition is hence tagged to their intrinsic properties that promote their partition within the system and the ability to form a complex with the trace metal and determines their mobility. A measure of their effect on trace metal partition may be assessed using double reciprocal models.

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3.14 DEVELOPMENT OF MATHEMATICAL MODELS

3.14.1 MODELS DEVELOPED FOR LOW pH CONDITION

Effect of free ligand concentration on K_{DM} : For a binary system at equilibrium under constant temperature, and pressure at low pH,

$$K_{DL} = \frac{(T_{SL})/M_S}{T_L} \dots\dots\dots 4.36$$

Where K_{DL} is the partition constant for organic ligand (L); M_S is the mass of solid phase; T_{SL} is the total concentration of adsorbed organic ligand on the solid phase; T_L is the total concentration of organic ligand in solution.

$$\text{Let } v_L = \frac{T_{SL}}{M_S} \dots\dots\dots$$

From equation (4.6), $T_L = [ML] + [L]$

$$\text{So, } K_{DL} = \frac{v_L}{[ML] + [L]} \dots\dots\dots 4.37$$

Now, the distribution constant, K_{DM} , of trace metal, M, is written as,

$$K_{DM} = \frac{(T_{MS})/M_S}{T_M} \dots\dots\dots 4.38$$

But, $v_M = \frac{T_{MS}}{M_S}$, and $T_M = [M] + [ML]$

$$\therefore K_{DM} = \frac{v_M}{[M] + [ML]} \dots\dots\dots 4.39$$

Since $K_{ML}[M][L] = [ML]$ $\dots\dots\dots 4.40$

$$K_{DM} = \frac{v_M}{[M] + K_{ML}[M][L]} \dots\dots\dots 4.41$$

And $K_{DM} = \frac{v_M}{[M](1 + K_{ML}[L])}$ $\dots\dots\dots 4.42$

Let the strength of metal ion adsorption to the solid phase, K_{pm}^* , be

$$K_{pm}^* = \frac{v_M}{[M]} \dots\dots\dots 4.43$$

Therefore, substituting K_{pm}^* in equation 4.42 gives,

$$K_{DM} = \frac{K_{pm}^*}{(1 + K_{ML}[L])} \dots\dots\dots 4.44$$

From equation (4.40), (4.44) becomes,

$$K_{DM} = \frac{K_{pm}^*}{1 + \left(\frac{[ML]}{[M]}\right)} \dots\dots\dots 4.45$$

$$\therefore \left(\frac{[ML]}{[M]}\right) = \frac{K_{pm}^*}{K_{DM}} - 1 \dots\dots\dots 4.46$$

$$\text{or } [ML] = \frac{[M]K_{pm}^*}{K_{DM}} - [M] \dots\dots\dots 4.47$$

$$\text{And } K_{ML}[L] = K_{pm}^* \left(\frac{1}{K_{DM}}\right) - 1 \dots\dots\dots 4.48$$

$$\text{or } 1/[L] = \frac{1}{\left(\left(\frac{K_{pm}^*}{K_{ML}}\right)\frac{1}{K_{DM}} - K_{ML}^{-1}\right)} \dots\dots\dots 4.49$$

$$\text{but, } \left(\frac{K_{pm}^*}{K_{ML}}\right) = A,$$

$$\text{Therefore, } 1/[L] = \left(\frac{1}{A}\right) K_{DM} - K_{ML} \dots\dots\dots 4.50$$

$K_{DM} = K_{pm}^*$, when $L \approx 0$ and when the soil organic ligands do not interact with metal ions or, when the organic ligands are cationic. Under these conditions, $K_{DM} = K_{pm}^* = K_D^0$, where K_D^0 is the distribution constant for the metal in the absence of L.

From equation 4.47, ML increases with decrease in K_{DM} . But ML may increase with increase in K_{DM} when ML in the solid phase increases with increase in the aggregation of L and vice versa. Aggregation (hydrophobicity) decreases with pH, as such the relationship in equation 4.47 may have a positive or negative gradient depending on the conditions and processes which control the distribution of ML and L in the system. Therefore, it is better to relate K_{DM} with aggregation and distribution constants for L.

Hence dividing through equation 4.47 by $[ML_{(s)}]$ gives,

$$\frac{[ML]}{[ML_{(s)}]} = \frac{[M]K_{pm}^*}{[ML_{(s)}]K_{DM}} - \frac{[M]}{[ML_{(s)}]} = \frac{1}{Q_{ML}} \dots\dots\dots 4.51$$

Multiplying through equation 4.49 and 4.50 by $L_{(s)}$ gives,

$$L_{(s)} / [L_{(aq)}] = \left(\frac{L_{(s)}K_{ML}}{K_{pm}^*}\right) K_{DM} - K_{ML}L_{(s)} = Q_L \dots\dots\dots 4.52$$

$$\text{Or } \frac{L_{(s)}}{[L_{(aq)}]} = \left(\frac{L_{(s)}}{A}\right) K_{DM} - K_{ML}L_{(s)} = Q_L \dots \dots \dots 4.53$$

For $L_{(s)}$ expressed in mass per gram of solid surface Q_L may be replaced by K_{DL} as shown below,

$$\frac{L_{(s)}}{[L_{(aq)}]} = \left(\frac{L_{(s)}}{A}\right) K_{DM} - K_{ML}L_{(s)} = K_{DL} \dots \dots \dots 4.54$$

3.14.2 Determination of the relationship between ligand partition and K_{DM}

Relating equation (4.38) and (4.41) give,

$$K_{DL} = \frac{v_L}{[L] + K_{ML}[M][L]} \dots \dots \dots 4.55$$

$$\text{And } K_{DL} = \frac{v_L}{[L](1 + K_{ML}[M])} \dots \dots \dots 4.56$$

Rearranging equation (4.56) gives,

$$K_{ML}[L] = \frac{v_L}{[M]K_{DL}} - \frac{[L]}{[M]} = \frac{[ML]}{[M]} \dots \dots \dots 4.57$$

Equating equations (4.48) and (4.57) gives,

$$K_{pm}^* \left(\frac{1}{K_{DM}}\right) - 1 = \frac{v_L}{[M]K_{DL}} - \frac{[L]}{[M]} \dots \dots \dots 4.58$$

Rearrangement gives,

$$K_{pm}^* \left(\frac{1}{K_{DM}}\right) = \frac{v_L}{[M]K_{DL}} + \left(1 - \frac{[L]}{[M]}\right)$$

$$\text{And } \left(\frac{1}{K_{DM}}\right) = \left(\frac{v_L}{[M]K_{pm}^*}\right) 1/K_{DL} + \left(\frac{(1 - [L]/[M])}{K_{pm}^*}\right) \dots \dots \dots 4.59$$

Expansion of K_{pm}^* and rearrangement of equation (4.55) gives,

$$\left(\frac{1}{K_{DM}}\right) = \left(\frac{v_L}{v_M}\right) 1/K_{DL} + \left(\frac{1}{K_{pm}^*} - \frac{[L]}{v_M}\right) \dots \dots \dots 4.60$$

3.14.3 Determination of the effect of ligand partition on $[M]$, and Q_{ML}

Rearrangement of equation 4.55 gives,

$$K_{ML}[M][L] = \frac{v_L}{K_{DL}} - [L] \dots \dots \dots 4.61$$

$$\text{But, } K_{ML}[M][L] = [ML]$$

$$\therefore [ML] = \frac{v_L}{K_{DL}} - [L] \dots \dots \dots 4.62$$

The formation of metal-ligand complex may not always lead to the transfer of the ligand to the solid phase. As such the relationship in equation 4.62 may not be valid under all circumstances. This is because metal induced aggregation is not the only means by which organic ligand may be transferred to the solid phase. Thus, it is better

to relate the ligand partition constant with a variable which relates well with the transfer process. Using variables such as the ratio [ML] to [M], and [ML] to [ML_(s)] will give a better correlation over a wide range of conditions. Therefore, at constant pH and ionic strength, equation 4.62 may be re-modified as follows.

Dividing through equation (4.62) by [M] gives,

$$\frac{[ML]}{[M]} = \left(\frac{\nu_L}{[M]}\right) \frac{1}{K_{DL}} - \frac{[L]}{[M]} \quad \dots\dots\dots 4.63$$

And with ML_(s) the relationship becomes,

$$\frac{[ML]}{[ML_{(s)}]} = \left(\frac{\nu_L}{[ML_{(s)}]}\right) \frac{1}{K_{DL}} - \frac{[L]}{[ML_{(s)}]}$$

But $\frac{[ML]}{[ML_{(s)}]} = \frac{1}{Q_{ML}}$ thus,

$$\frac{1}{Q_{ML}} = \left(\frac{\nu_L}{[ML_{(s)}]}\right) \frac{1}{K_{DL}} - \frac{[L]}{[ML_{(s)}]} \quad \dots\dots\dots 4.64$$

Also dividing through equation (4.37) by K_{ML}[L] gives,

$$[M] = \frac{\nu_L}{K_{DL}K_{ML}[L]} - K_{ML}^{-1} \quad \dots\dots\dots 4.65$$

But, $\frac{\nu_L}{[L]} = K_{PL}^*$

$$\therefore [M] = \frac{K_{PL}^*}{K_{DL}K_{ML}} - K_{ML}^{-1} \quad \dots\dots\dots 4.66$$

Now if $\frac{K_{PL}^*}{K_{ML}} = \alpha$, then equation 4.66 becomes,

$$[M] = \alpha \frac{1}{K_{DL}} - K_{ML}^{-1} \quad \dots\dots\dots 4.67$$

The inverse relationship between [M] and K_{DL} may not always be as the equation (4.67) suggests. This is because, H⁺ and other competing metals (and electrolyte-cation) can also influence the aggregation or transfer of L to the solid phase. Another reason is that apart from metal induced aggregation, other transfer processes such as conformational changes (due to ionic strength and temperature) and ligand adsorption onto the solid phase may be responsible for the ligand transfer. As such a rather more specific relationship which takes into account the fraction of ligand transfer due to the metal of interest must be introduced.

Therefore, at constant temperature, pH and ionic strength, the ratio of metal-ligand complex formed, to the free metal concentration, β, can be related to the ligand

partition constant by equation 4.63, since $\frac{[ML]}{[M]} = [ML]$ formed per unit $[M]$ and represented by β , then,

$$\beta = \left(\frac{v_L}{[ML]}\right) \frac{1}{K_{DL}} - \frac{[L]}{[M]} \dots\dots\dots 4.68$$

However, at constant temperature and pH when the ionic strength varies, the electrolyte-cation will exert a significant influence on the partition of organic ligand in the system. Thus, a change in the ratio of free metal to electrolyte-cation ($[M]/[E^+]$) will result in a corresponding change in the partition constant for the organic ligand when the concentration of proton (since pH is constant) and other competing metals are constant. In this regard equation 4.67 may be rewritten by introducing the concentration of electrolyte-cation $[E^+]$ as shown below.

$$\frac{[M]}{[E^+]} = \left(\frac{\alpha}{[E^+]}\right) \frac{1}{K_{DL}} - ([E^+]K_{ML})^{-1} \dots\dots\dots 4.69$$

Equations 4.63, 4.64, 4.68 and 4.69, will be applicable at both high and low pH conditions.

3.15 MODELS DEVELOPED FOR HIGH pH CONDITION

3.15.1 Determination of the effect of ligand partition on K_{DM}

For a binary system at equilibrium under constant temperature, pressure and high pH condition,

$$K_{DM} = \frac{(T_{MS})/M_S}{T_M} \dots\dots\dots 4.70$$

But, $v_M = \frac{T_{MS}}{M_S}$, and $T_M = [M] + [ML_A] + [ML]$

$$\therefore K_{DM} = \frac{v_M}{[M] + [ML_A] + [ML]} \dots\dots\dots 4.71$$

From the expression for stability constants, $K_{ML}[M][L] = [ML]$, and $K_{ML_A}[M][L_A] = [ML_A]$. Equation 4.71 may be rewritten as,

$$K_{DM} = \frac{v_M}{[M] + K_{ML_A}[M][L_A] + K_{ML}[M][L]} \dots\dots\dots 4.72$$

$$\text{and, } K_{DM} = \frac{v_M}{[M](1 + K_{ML_A}[L_A] + K_{ML}[L])} \dots\dots\dots 4.73$$

$[L_A]$ does not change when the system's bulk density and pH are constant.

Therefore, $\gamma = (1 + K_{ML_A}[L_A]) = \text{constant}$, at defined geochemical conditions of temperature, solid solution ratio and pH, as such equation 4.73 may be rewritten as,

$$K_{DM} = \frac{v_M}{[M](\gamma + K_{ML}[L])} \dots\dots\dots 4.74$$

But, $K_{pm}^* = \frac{v_M}{[M]}$

$\therefore K_{DM} = \frac{K_{pm}^*}{(\gamma + K_{ML}[L])}$, and

$$K_{ML}[L] = K_{pm}^* \left(\frac{1}{K_{DM}} \right) - \gamma \dots\dots\dots 4.75$$

$$1/[L] = \left(\frac{K_{ML}K_{DM}}{K_{pm}^*} \right) - \frac{K_{ML}}{\gamma} \dots\dots\dots 4.76$$

If $A = \frac{K_{pm}^*}{K_{ML}}$, then $1/[L] = \left(\frac{K_{DM}}{A} \right) - \frac{K_{ML}}{\gamma}$

In this case also when $L \approx 0$, the distribution constant will be expressed as,

$$K_{DM} = \frac{v_M}{[M](1 + K_{ML_A}[L_A])} = \frac{K_{pm}^*}{\gamma} \dots\dots\dots 4.77$$

$\therefore K_{DM} = \frac{1}{\gamma} K_D^0 \dots\dots\dots 4.78$

When the aggregation and the distribution constants of the ligand are introduced, equation 4.76 become,

$$K_{DL} = Q_L = \frac{L_{(s)}}{[L]} = \left(\frac{L_{(s)}K_{ML}K_{DM}}{K_{pm}^*} \right) - \frac{K_{ML}L_{(s)}}{\gamma} \dots\dots\dots 4.79$$

3.15.2 Determination of the relationship between the partition constant for metal-ligand complex and K_{DM}

From equation 4.71, $K_{DM} = \frac{v_M}{[M] + K_{ML_A}[M][L_A] + [ML]}$

$$K_{DM} = \frac{v_M}{[M](1 + K_{ML_A}[L_A]) + [ML]}$$

$$= \frac{v_M}{[M]\gamma + [ML]}$$

$\therefore [ML] = \frac{v_M}{K_{DM}} - [M]\gamma$

$\Rightarrow [ML] = v_M \frac{1}{K_{DM}} - [M]\gamma \dots\dots\dots 80$

Dividing through by $[M]$ gives,

$$\frac{[ML]}{[M]} = \left(\frac{v_M}{[M]} \right) \frac{1}{K_{DM}} - \gamma \dots\dots\dots 4.81$$

But, $\frac{v_M}{[M]} = K_{pm}^*$

$$\frac{[ML]}{[M]} = K_{pm}^* \left(\frac{1}{K_{DM}} \right) - \gamma \dots\dots\dots 4.82$$

Dividing equation 4.80 through by $[ML_{(s)}]$ gives,

$$\frac{[ML]}{[ML_{(s)}]} = \left(\frac{v_M}{[ML_{(s)}]} \right) \frac{1}{K_{DM}} - \gamma [M] / [ML_{(s)}] \dots\dots\dots 4.83$$

Therefore, $\frac{1}{Q_{ML}} = \left(\frac{v_M}{[ML_{(s)}]} \right) \frac{1}{K_{DM}} - \gamma [M] / [ML_{(s)}] \dots\dots\dots 4.84$

3.16 RELEVANCE OF THE MATHEMATICAL MODELS ADOPTED

To prove that humic substance is a factor in trace metal distribution, mathematical relations which can be utilized to show that in a soil-solution system, trace metal partition is influenced by the ability of humic substance to partition itself between the phases of the system and form a complex compound with the metal in both phases. The effect of humic matter on trace metal partition, can be explained in terms of the factors which control the adsorption, complexation and aggregation properties of the humic matter. Trace metal partition is influenced by the ability of humic acid to modify the surface of the solid phase of the system; competitive adsorption on the humic substance influence metal partition in the system, are required. In view of these, the models adopted are outlined below, and in each case the letters 'g' and 'C' are used to reduce the complexity of the models, and to indicate the slope and intercept respectively.

Model 1, $1/Q_{ml} = g(1/K_{DM}) - C$, referred to as Ligand Complex Partition Effect Model (LCPEM) is applicable at all pH. LCPEM may be utilized to explain how the occurrence of metal-ligand complex in either phase of a soil-solution system affects the metal partition constant (K_{DM}). The model can be used to explain how modification of the surface of the solid phase mineral by humic substance contributes to changes in the metal partition constant at different conditions of pH and ionic strength.

The slope of the model at low pH is given as, $g = V_m/[ML_{(s)}]$. It measures the ratio of total metal-occupied sorption sites in the solid phase to the total metal-occupied sites on the ligand in the solid phase (as aggregates or as adsorbed ligands). The slope (considered as occupied-site ratio) will be sensitive to changes in pH and

ionic strength, as well as the nature of the solid phase (mineral composition). Thus, the value of the occupied-site ratio may be used to characterize soil types with defined solution characteristics. In addition, variations in solution pH and ionic strength (or conductivity) with occupied-site ratio may be used to discuss the behavior of the system with respect to metal partition.

The slope at high conditions of pH is given as, $g = V_M/[ML_{(s)}]$, and it accounts for the extent of metal binding with the amount of the metal-ligand complex formed in the solid phase under defined conditions of the system. Change in the extent of metal binding with complexation (the slope) is a unique property of the solid phase at any given conditions of the system (pH and Ionic strength) and may be used to discuss changes in metal partition by humic substance as in the case of the slope at low pH. The slopes may be used to explain how the relationship between humic substance and solid phase minerals influences the interaction of trace metals in the solid phase.

It must be noted that at all pH, the slopes of the model can effectively explain 'occupied-site ratio' (The site ratio in this case is the ratio of organic and inorganic occupied binding sites in the solid phase). It is applicable in discussing solid phase modification by humic matter.

Model 2, $Q_L = gK_{DM} - C$, referred to as Ligand-Exchange Effect Model (LEEM), relates the humic substance partition with metal partition. It may be used to indicate whether hydrophobic character of humic substance in response to changes in cation concentrations has effect of the partition of the metal of interest. LEEM is applicable at all pH and its slope, $g = L_{(s)}K_{ML}/K_{pm}^*$, accounts for the relationship between the stability of the metal-ligand complex in the solution phase with the strength of the metal-binding to the solid phase under defined system conditions. The model can be used to find out whether the strength of the relationship between humic

substance and the solid phase has a corresponding effect on metal partition. The slope may also be used to determine the effect of metal complexation with humic matter on the binding of the metal in the solid phase. LEEM may be effective for discussing systems with low ionic strength and negligible metal-metal competition for humic substance.

Model 3, $K_{DL} = gK_{DM} - C$, referred to as Ligand Partition Effect Model (LPEM) may be used to discuss the effect of humic substance adsorption on metal partition. The model is applicable at all pH and the slope, $g = V_L K_{ML} / K_{pm}^*$, may be used as in LEEM (model 2).

Model 4, $[ML]/[M] = g(1/K_{DL}) - C$, referred to as Complex Depletion and Ligand Aggregation Model (CDLAM). This model is applicable at all pH and may be used to explain the relationship between the metal-ligand complex formed in solution per unit free metal ion and ligand aggregation. The model may be used to study how pH and ionic strength affect the behavior of humic substance during complexation, and its consequent effect on metal partition. At low pH, the slope ($g = V_L/[M]$) accounts for changes in the extent of ligand adsorption (availability) in the solid phase per unit free metal. The slope is sensitive to pH and ionic strength. But at high pH the slope ($g = V_M/[M]$) accounts for the strength of metal binding to the solid phase and will be sensitive to pH and ionic strength. This implies that at low pH the slope (which invariably connotes the amount of metal-occupied organic binding sites in the solid phase per unit concentration of ligand complex in solution) is a function of humic matter phase separation properties, while at high pH the slope is a function of both the properties of the solid phase minerals and the humic matter.

Model 5, $\frac{[M]}{[E^+]} = \left(\frac{\alpha}{[E^+]}\right) \frac{1}{K_{DL}} - ([E^+]K_{ML})^{-1}$, which is referred to as Competitive Adsorption and Ligand Partition Model (CALPM), can be employed to

discuss how metal aquo ion and electrolyte-cation influence the adsorption of humic substance onto solid phase minerals at different conditions of pH. The slope may be used to interpret the effect of the strength of humic substance adsorption on the stability of metal-ligand complex under conditions of varying background electrolyte at constant pH. The model can throw light on how the stability of metal-ligand complex, electrolyte-cation and metal aquo ion relates with the partition of humic substances in soil-solution system at defined pH.

Model 6, $\frac{1}{Q_{ML}} = g \frac{1}{K_{DL}} - C$, referred to as Complex Exchange and Ligand

Partition Model (CELPM) may be used to study the relationship between metal-ligand complexation and ligand aggregation in soil solution system. The model relates changes in the extent of metal binding to humic matter in solid and solution phases with the partition of the humic matter between the system phases. The slope, $\left(\frac{v_L}{[ML(s)]}\right)$, may be used to determine the effect of pH and ionic strength on the relationship between the extent of humic substance binding to the solid phase and the moles of binding site occupied by trace metal on the adsorbed humic substance.

3.16.1 Effect of HS on Trace Metal Distribution

The role of humic substance in trace metal distribution in a terrestrial environment was modeled by taking into account, the properties and behaviour of humic substances in a binary system, and interpreting these in light of their effect on the distribution of trace metals between the major phases of the solid-solution system in the environment.

3.16.2 Distribution at low pH, constant temperature and pressure:

The role of humic substance may be explained by analyzing the nature of the relationship between the fraction of metal-ligand complex in solution, $[ML]$, and the

partition constant of organic ligand, K_{DL} , at various pH, bulk density (solid-solution ratio), and $[L]$. It is understood that the solid phase of systems from different terrestrial environments vary, as such the strength of trace metal adsorption, K_{pm}^* , will vary from one soil sample to another (Tipping, 2002).

The effect of $[L]$ on K_{DM} at any given pH may be explained using model 2 at various low pH conditions. All humic acids are practically in the solid phase below pH 2. As a result, fulvic acid will be the major organic ligand which influences metal distribution.

$$\left(\frac{[ML]}{[M]}\right) = \frac{K_{pm}^*}{K_{DM}} - 1$$

$$K_{ML}[L] = K_{pm}^* \left(\frac{1}{K_{DM}}\right) - 1$$

The partition of humic substance in natural environment influences metal distribution in a terrestrial environment. The effect of L partition (K_{DL}) on K_{DM} may be explained using Model 3. The model indicates that K_{DM} may reach a critical value (at high pH) where L has no effect on trace metal distribution. This is because, L will remain in solution and influence metal forms in solution. However, an exception must be made of metals which cause the humates to aggregate and subsequently precipitate (i.e., pseudomicellation), as well as temperature and concentration of background electrolyte.

According to Tipping (2002), K_{DL} may be described by incorporating the net humic charge as shown below.

$$K_{DL} = \frac{v_L}{T_L} = \exp\{\beta(Z_i: -|Z|)\}$$

Where $|Z|$ is the magnitude of net charge on L (assumed over the specific binding sites), $|Z_i|$ is the magnitude of a 'characteristic' charge (regarded as a measure of hydrophobicity), and β is a scaling constant.

A combination of Model 3 and Tipping's equation above is expressed as,

$$\left(\frac{1}{K_{DM}}\right) = \left(\frac{v_L}{v_M}\right) 1 / (\exp\{\beta(Z_i: |-|Z|)\}) + \left(\frac{1}{K_{pm}^*} - \frac{[L]}{v_M}\right) \dots \dots \dots 4.85$$

He explained that the greater the net charge, the less is the tendency of the humic matter (L in this case) to be absorbed by the soil. The extent of partitioning was assumed to depend upon the competition between hydrophobicity, which favours absorption, and the solvation of charged groups, which promotes water solubility.

In this work it has been considered that the role of humic substance in trace metal distribution in a terrestrial environment can be (partly) explained in terms of the hydrophobic and hydrophilic character of humic matter.

3.16.3 Distribution at high pH, constant temperature and pressure:

At high pH solution phase composition changes thereby increasing the number and types of binding sites in the phase due to the dissolution of oxhydroxides from the solid phase. Since inorganic ligands, L_A , cannot increase beyond a critical value (since its concentration is dependent on extent of solid phase dissolution at a defined pH), it may be deduced from Models 1 -4 that, K_{DM} will be influenced by the amount of free L and M ions in the solution phase. And the effect of L on K_{DM} may be interpreted in terms of the intrinsic properties of humic substances which determine the extent of ML and not the net charge or hydrophobicity.

$$K_{ML}[L] = K_{pm}^* \left(\frac{1}{K_{DM}}\right) - \gamma$$

$$1/[L] = \left(\frac{K_{ML}K_{DM}}{K_{pm}^*}\right) - \frac{K_{ML}}{\gamma}$$

The constant, γ , accounts for the presence of inorganic ligands in solution. When $\gamma = 1$ (at $L_A = 0$) it implies that no solid phase dissolution or introduction of inorganic ligands into the solution phase occurred, and the only binding sites in the solution phase are organic ligands (Model 3). And this is possible at low pH as shown below.

$$1/[L] = \left(\frac{1}{A}\right) K_{DM} - K_{ML}$$

The differences in solubility between FA and HA (necessarily based on chemical differences) greatly influence metal distribution in geomeia (Tipping, 2002; Reddy et al, 2005). The changes in the hydrophobic and hydrophilic character of humic substances allow them to influence metal distribution, by transferring binding sites from solid phase to solution at high pH and vice versa. While FA remains soluble at all pH (natural) in soil. HA precipitates at low pH (≤ 2) (Von Wandruszka, 2000; Tipping, 2002).

Observation has shown that HA solutions flocculate when ionic strength is raised. That is, aggregation of humic polymers proceeds in a continuous fashion to form precipitates as salt concentration is increased (as shown by Model 5). Lowering the pH of aqueous HA solutions has an effect similar to adding metal salts all through in a less pronounced manner (Von Wandruszka, 2000). Thus high metal ion concentration to some extent may reduce metal solubility, mobility and toxicity. Therefore, changes in K_{DM} will vary with the concentration of humic substances in solution at various pH.

In the natural environment, metal oxide, hydroxide, and even carbonate minerals, provide important reactive surfaces for metals. In the investigation of the role of humic substances in K_{DM} , there is the need to consider surface adsorption models which consider all surface adsorption sites. This approach can be discussed using the relationship below. This is a combination of Model 1 and Allen et al., (1996) expression for K_{DM} (section 4.3).

$$\frac{1}{Q_{ML}} = \left(\frac{v_M}{[ML_{(s)}]}\right) \frac{1}{\sum_{sites} K_{Si-M}[S]} - \left(\gamma[M]/[ML_{(s)}]\right) \dots \dots \dots 4.86$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 INTRODUCTION

In this chapter the outcome of both field and laboratory experiments are discussed. The discussion focuses on the chemical properties and characteristics of the semi-natural ecosystems of the study area in relation to the physical mining activity as well as the major environmental characteristics of the ecosystems, to determine the factors which influence the spatial distribution of trace metals at the study area. Attempt is also made to explain the extent and nature of the relationship between the major environmental characteristics and trace metal partition. The discussion also focused on trace metal distribution phenomena (using a ternary system containing Cu and characterized soil sample (Appendix 2) from the study area) by explaining with the aid of the data obtained, the effect of temperature and background electrolyte concentration, on Cu partition in soil-solution system. The kinetics and mechanism of Cu distribution is also discussed. In addition, the inter-relationship between the system-variables was discussed in relation to the models developed in chapter 4. The concept of binding-site heterogeneity proposed by Ephraim (1986) has been adopted to explain how humic substances influence Cu partition in ternary system. The validity and applicability of the mathematical and conceptual Models are also discussed.

5.1 CHEMICAL CHARACTERIZATION OF THE TERRESTRIAL ENVIRONMENTS OF THE SELECTED ECOSYSTEMS IN GHANA

This section focuses on the patterns of spatial distribution of tracemetals at three gold mining communities (at Talensi-Nabdam District) in relation to soil properties and industrial activities at the study area, to determine whether land modification by anthropogenic activity directly or indirectly affect the distribution of trace metals in the ecosystem and beyond.

4.1.1 TOPOGRAPHY AND MATERIAL TRANSPORT

Analysis of the GIS data from the mining area at Talensi-Nabdam District gave the recent surface characteristic (elevation) for the study area (3.5sqmi) as shown in figure 5.1. The three dimension surface map clearly shows that Accra is on a higher plane than Kejetia, and Tarkwa is in a low land between Accra and Kejetia. Survey studies revealed that Tarkwa is well drained and full of gullies created by erosion. The directions of water course on the map (Figure 5.1) show that materials are carried into the White Volta from the three communities during the wet season (from June to September), as indicated by the block arrows and clearly explained by the three dimension surface map.

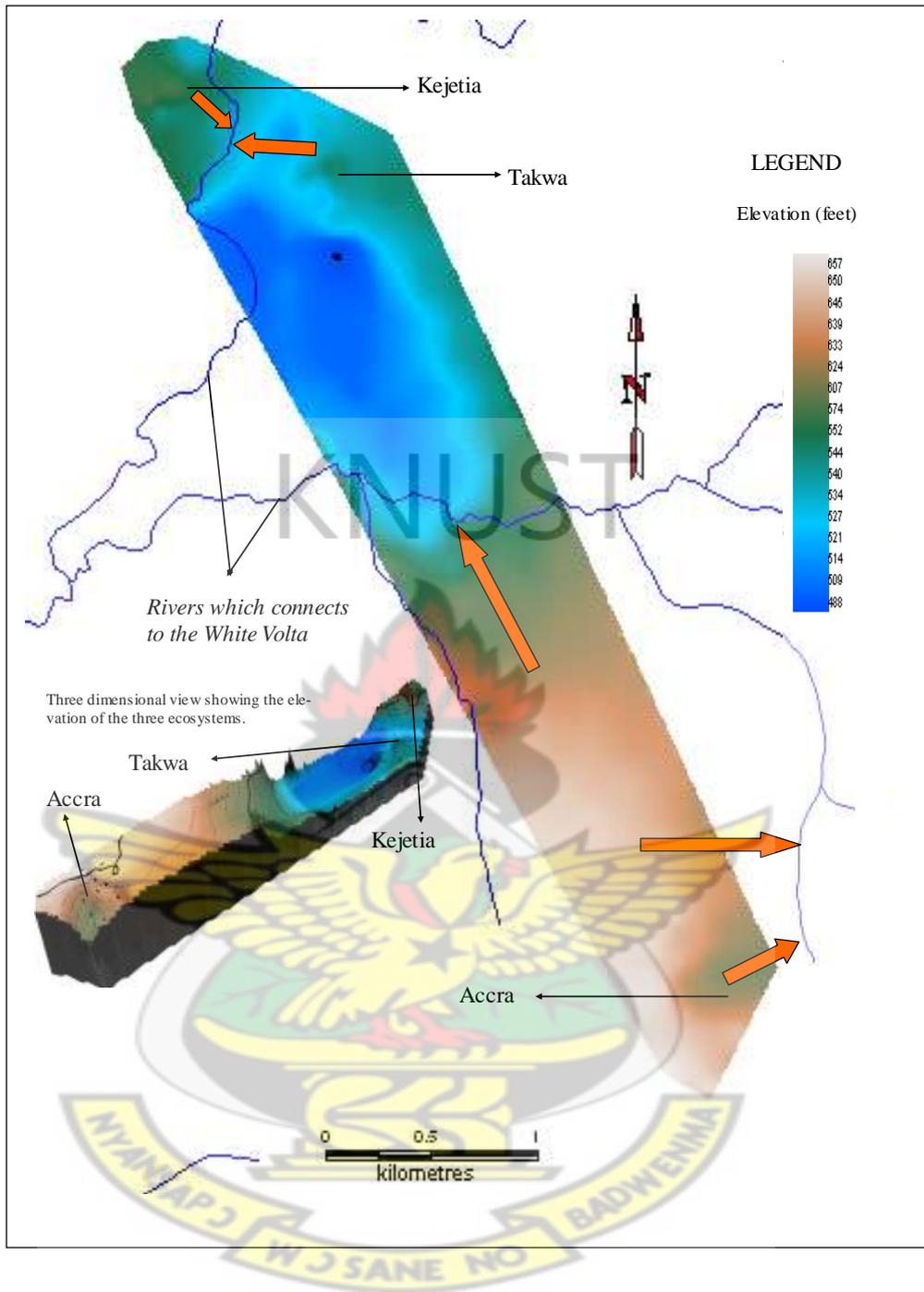


Figure 4.1: Map portraying topography, drainage paths and selected ecosystems at the study area

This indicates that trace metals which are in the mobile form will be easily transported from the mining communities to the White Volta. However, it is worth noting that gold extraction is also carried out at the banks of the river and this is likely to result in a contribution to the concentration of trace metals in the water body over

time, depending on the chemical properties of the minerals which make up the tailings and waste earth materials from dug outs.

The three ecosystems are characterized by small pits created by surface mining all around the communities. Extraction of the gold is carried out on large and small scale basis within the communities. Tailings are also dumped near extraction sites.

4.1.2 CHARACTERIZATION OF THE STUDY ENVIRONMENT

Chemical Composition and Properties of the Soil at the Study Area: The data obtained from nutrient analysis indicated that, the soil at the study area is silt loam (Appendix 3) with a pH of 5.81. The organic matter concentration is 1.8% (SEM = 0.085) and it was observed that it varied from one community to another in the order, Accra > Kejetia > Tarkwa. In addition, the organic matter varied linearly with pH.

The exchangeable acidity was observed to be 0.2 meq/100g (SEM = 0.017) at the study area. The effective cation exchange and base saturation were also observed to be 11.51 meq/100g (SEM = 1.106) and 97.74% (SEM = 0.317) respectively. The high base saturation close to 100% is characteristic of arid region soils (Lajos, 2008). And this value is preferred for most plants, but not essential for tree fruit production. It also indicates that there is a high availability of nutrient cations such as Ca, Mg, K and Na to plants. In addition, the base saturation (97.74%) suggests that the cation exchange capacity of the soil is occupied by hydrogen and/or aluminum ions. About 20-70% of ion exchange capacity of many soils is caused by colloidal humic substances. Therefore, humic substances may influence the cation exchange capacity of the soil.

Cations are not held equally tight by soil colloids and the relative concentrations of the cations in soil solution provide information about their degree of adsorption. In neutral to moderately alkaline soils, Ca^+ and Mg^{2+} dominate, and Na^+

exists in low quantities in well drained soils. In this study the average pH was found to be 5.8, and the concentrations of exchangeable cations were observed to vary in the order $\text{Ca} > \text{Mg} > \text{Na}$ (Appendix 3). The same trend was observed in all the three communities at the study area (Appendix 4).

It has been reported that effective cation exchange capacity (ECEC) and base saturation (BS) increase with increase in pH of soil (Lajos, 2008). This was also observed in all the communities at the study area as shown in (Appendix 4). It was observed that the effective cation exchange capacity and organic matter concentrations vary from community to community in the order, Accra > Kejetia > Tarkwa. Mechanical analysis of the soil samples from all the communities revealed that the concentrations of silt, sand and clay vary in the order silt > sand > clay. In addition, the soil texture at the study area and all the communities is silt loam.

The average nitrogen concentration, 0.125% (SEM = 0.004), in the soil at the study area being greater than 0.105% is an indication that the soil is fertile in terms of nitrogen supply. It was also found to vary in concentration from community to community in the same order as organic matter, ECEC and BS (Accra > Kejetia > Tarkwa). The concentration of available phosphorus, P, also varies in the same order as BS, but the concentration of available potassium, K, is in the order Kejetia > Tarkwa > Accra (Appendix 4). The available P and K are within acceptable range and thus suggest that the soil is fertile in terms of available P and K, and the high concentration of available K is perhaps because of contribution from bush burning which is a common activity in Northern Ghana.

The nutrient analysis suggests that the soils at the study area are fertile-in terms of the parameters estimated-for agricultural purposes. It was apparently evident from the results discussed above that, soil fertility increases in the order, Accra > Kejetia >

Tarkwa. This is perhaps so because, mining activity in Accra is low compared to the other two communities. Moreover, whereas mining activity at Tarkwa has declined over the years, and presently less active than Kejetia, the level of environmental disturbance is less at Kejetia than Tarkwa. And mining activity became high only in recent times at Kejetia. The topography of the communities also plays a very important role, because some of the communities are more affected by erosion and drainage than others (Appendix 3).

The soil has a high cation exchange capacity of 11.51 cmol+/kg, thus, there is need for assessment of the relative proportion and distribution of trace metals in the soil to enable a proper assessment of the impact of the mining activity on the distribution and availability of trace metals that are of nutritional value or potentially harmful to organisms. The analysis revealed that the elements Cu, Cd, Mn, Pb, and Zn were present in the soil with average concentrations, 12.34 (SEM = 2.026), 4.97 (SEM = 0.577), 138.31 (SEM = 21.515), 101.12 (SEM = 24.17), and 34.99 (SEM = 6.574) ppm respectively (Appendix 3) at the study area. It was also observed that the trace metal concentrations in the soil at all communities varied in the order Mn > Pb > Zn > Cu > Cd (Appendix 4). Mn and Pb have concentrations greater than 80 ppm in all the communities whereas Cd, Cu and Zn have concentrations ranging between 4-55 ppm (Appendix 3).

4.1.3 SPATIAL DISTRIBUTION OF TRACE METALS AND SOIL PROPERTIES AT THE ECOSYSTEM

Spatial Analysis of the Properties of the Terrestrial Environments: At Accra the effective cation exchange capacity (ECEC) and pH of the terrestrial environment are high around the community and low within the community (Appendix 5). The two properties have high values at the terrestrial environment of the old

settlement site at Accra. It must be noted that the old settlement site has its terrestrial environment highly mixed with underground earth materials which have characteristically high ECEC. The organic matter is also observed to have high values at abandoned extraction sites and farm lands.

At Kejetia the pH and ECEC decrease towards the center of the community (Appendix 4) while the organic matter has high values at low mining activity areas and farm lands. At Tarkwa a similar pattern is observed for the spatial distribution of pH and ECEC (Appendix 7). The organic matter was also noted to be high at farmland and low activity sites.

Relationship between Metals and the Properties of the Terrestrial Environment: Peijnenburg, (1997) reported that, the most important soil characteristics which influence metal partitioning are the adsorption phases (clay, organic matter, and oxyhydroxides), the amount of available sorption sites (related to the cation exchange capacity), pH, and competitive sorbed ions (such as Ca, Na, K etc.). It has been noted in this study that, field-base distribution constants for Co, Cu, Ni, Pb, and Zn can be analyzed by relating them with the observed principal characteristics of the terrestrial environment. Therefore, in order to understand how the characteristics of the terrestrial environment in this study influence metal distribution, metal contours superimposed on surface maps of the soil characteristics (pH, organic matter, and effective cation exchange) were used.

Analysis of the maps revealed that the degree of overlap between metals and pH (Figure 4.2) at Accra was quite high for Cu and Pb. The overlap was comparatively low for Cd, Mn and Zn. The organic matter gave a high degree of overlap for Zn, while Cd, Cu Mn and Pb indicate partial overlaps (Figure 4.2). The ECEC on the other hand overlaps well with Cd and Pb, while Zn indicates a partial overlap. Cu and Mn were

noted to have little or no overlap with ECEC (Figure 4.2). The observations imply that there is some measure of relationship between the characteristics of the environment and the concentration of metals at Accra.

At Kejetia the pH does not overlap with the metal contours (Figure 4.3). With the exception of Cu, organic matter indicates some measure of association with Cd, Mn, Pb and Zn. In addition, Cu is the only metal which overlaps (partially) with ECEC (Figure 4.3). Thus, with the exception of organic matter, pH and ECEC do not influence the spatial distribution of metals at Kejetia.

At Tarkwa the analysis of the spatial distribution of the metals with respect to the characteristics of the terrestrial environment revealed that, with the exception of Cd and Pb, the degree of overlap of the other elements with pH is (very) low (Figure 4.4). The influence of organic matter on the spatial distribution of metals is observed to be high for Pb and low for Cd, Cu, Mn and Zn (figure 4.4). The ECEC influence Cd and Pb greatly (Figure 4.4), and the degree of overlap observed for Cu and Mn indicate that the influence of ECEC on Cu and Mn is not much, and it has virtually no influence on Cu and Zn distribution.

It may be inferred from the observations that the inconsistent metal-characteristic relationship from ecosystem to ecosystem is possibly because the chemical properties of the metals in relation to the chemical characteristic of the terrestrial environment cease to be a function of the spatial distribution of the metals by virtue of the sporadic human activity. It may be stated that the spatial distribution of trace metals in the terrestrial environments of the ecosystems are not influenced by chemical reaction, but rather the activities of man (such as unorganized and uncoordinated mining activities) and natural events (e.g. erosion).

In addition, the observed relationship between pH organic matter and ECEC of the individual mining communities appear to suggest a reflection of the chemical effect of the characteristics on trace metal distribution within the terrestrial environment.

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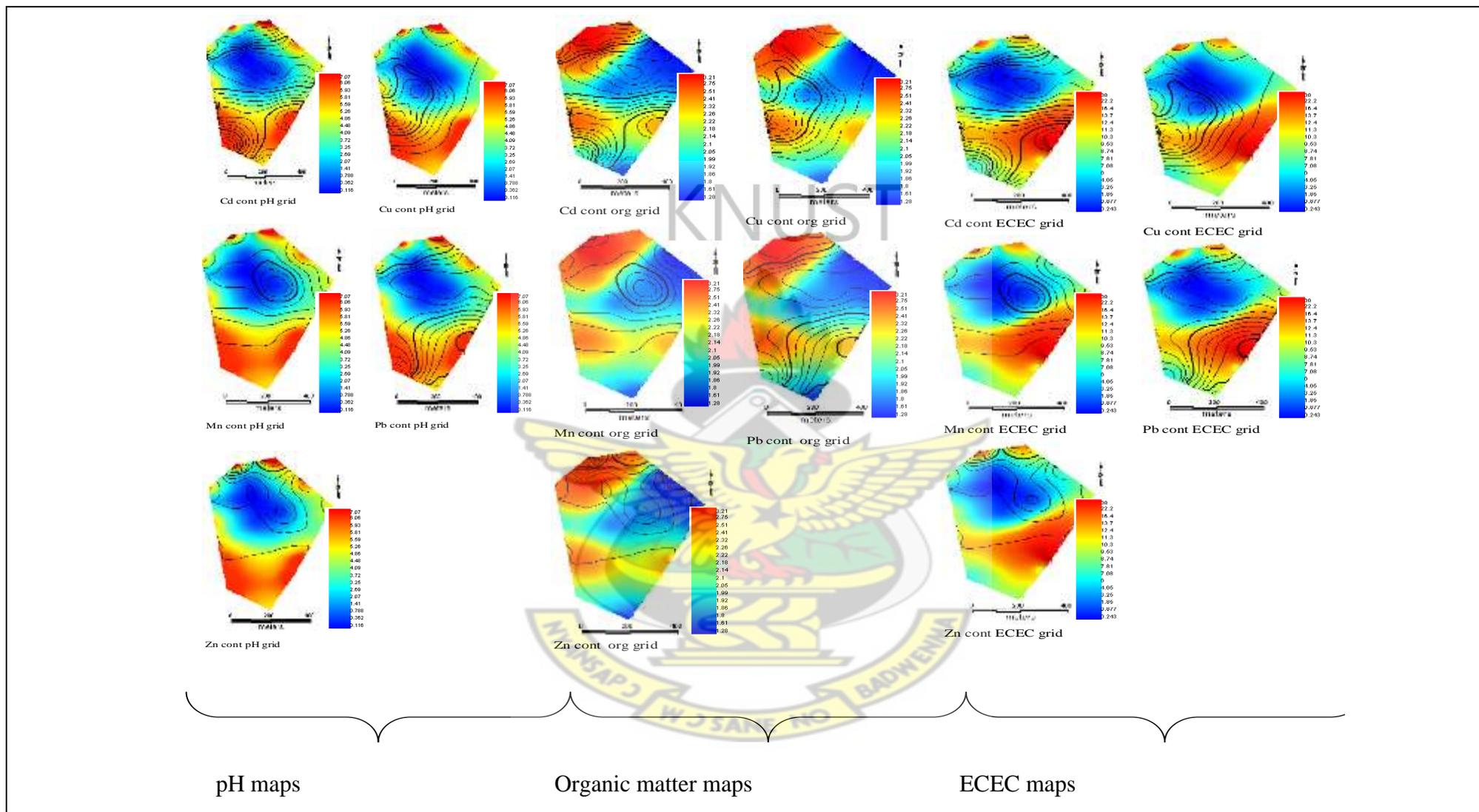


Figure 4.2: Maps showing the relationship between trace metal and the properties (pH, Organic matter ad ECEC) of the terrestrial environments at Accra (the colour bar is a legend to indicate the magnitude of parameters in terms of the colors)

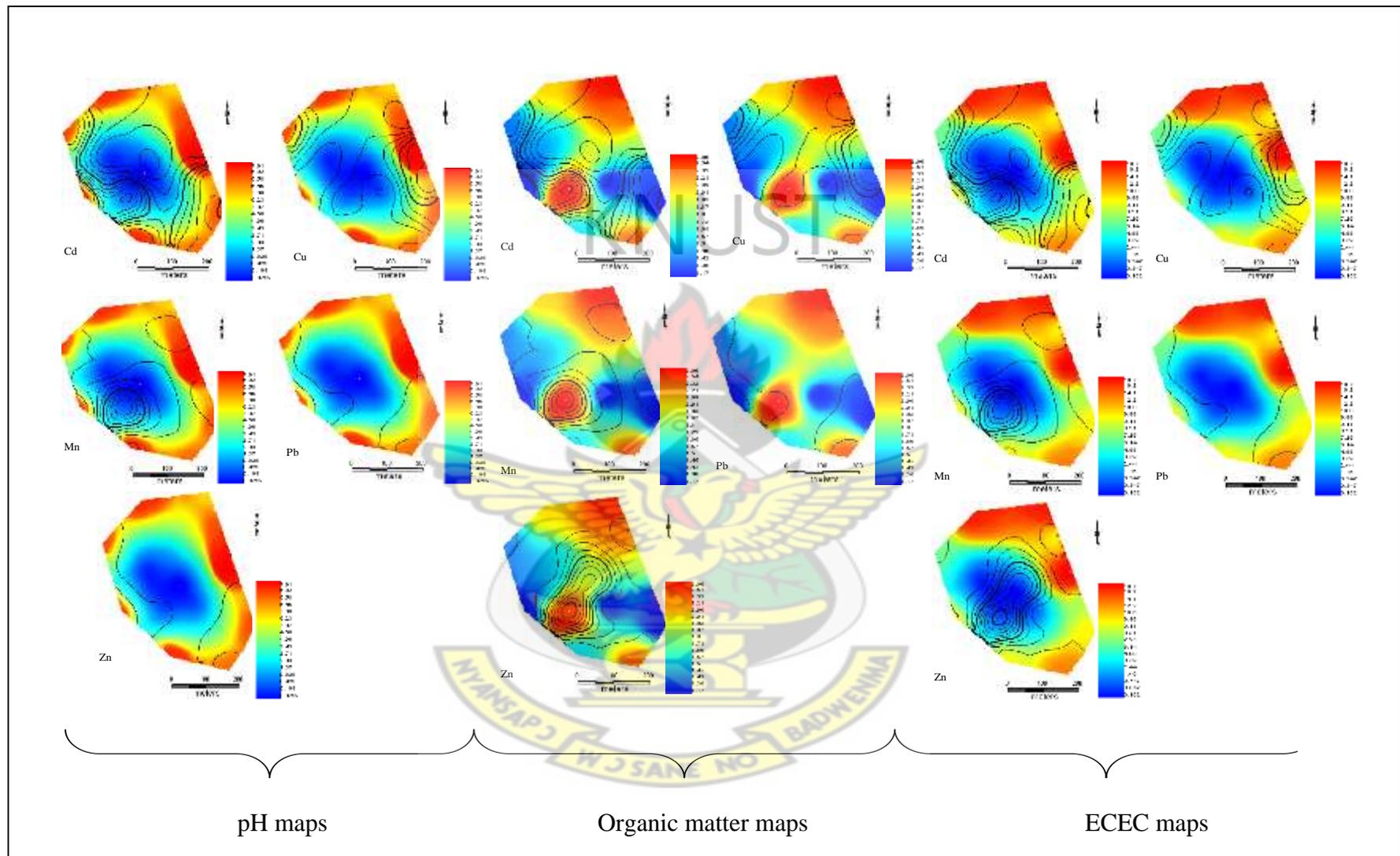


Figure 4.3: Maps showing the relationship between trace metal and the properties (pH, Organic matter and ECEC) of the terrestrial environments at Kejetia (the colour bar is a legend to indicate the magnitude of parameters in terms of the colors)

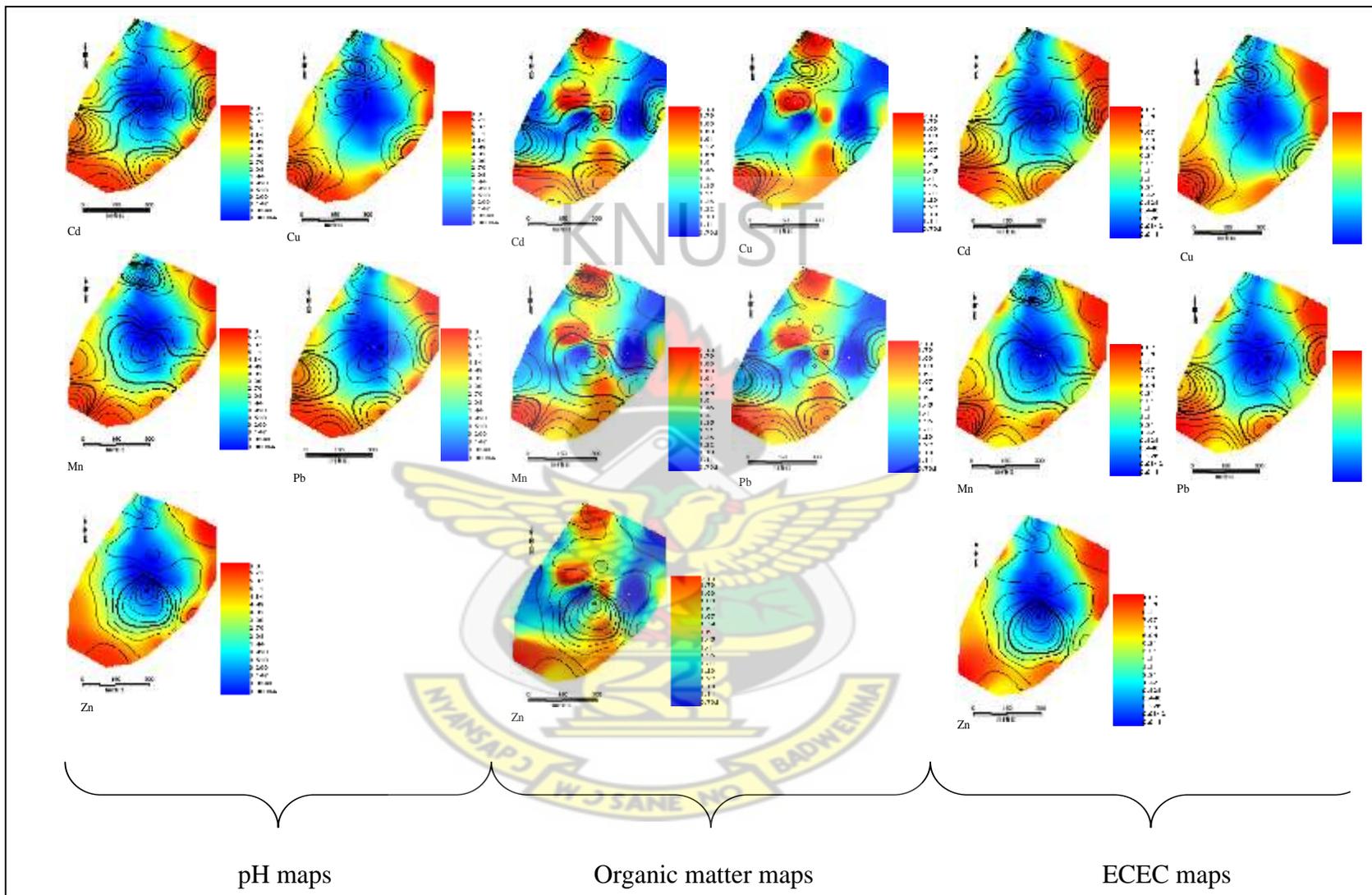


Figure 4.4: Maps showing the relationship between trace metal and the properties (pH, Organic matter ad ECEC) of the terrestrial environments at Tarkwa (the colour bar is a legend to indicate the magnitude of parameters in terms of the colors)

4.1.4 TRACE METAL DISTRIBUTION, AVAILABILITY AND TRANSPORT

Speciation: Trace metals have been known to interact chemically with humic substances (Tipping, 2002). Humic substances have the propensity to influence the distribution of trace metals in soil, thus in order to better understand the potential effect of mining activity on changes in the availability, speciation and distribution of trace metals, chemical analysis of the metal species and their fractions in the soil becomes imperative.

Chemical analysis of the soil at the study area revealed that there are more metals bound to humic substances (Co, 79.86%; Cu, 85.19%; Ni, 89.12%; Pb, 95.66%; Zn, 81.61%) than inorganic binding sites, S_{in} (Co, 20.13%; Cu, 14.81%; Ni, 10.88%; Pb, 4.34%; Zn, 18.39%) in the soil (Appendix 8). It was also observed that there are more metal bound humic substances in the solution phase (81.16%) than the solid phase of the soil (18.84%). The high proportion of metal bound humic substance in the solution phase is because they are hydrophilic at the pH of the soil (Accra, 6.04; Kejetia, 5.92; Tarkwa, 5.48) as confirmed by the distribution of humic substances in the soil system, which indicates that there are more humic matter in the solution phase (Accra, 78.38%; Kejetia, 85.26%; Tarkwa, 81.16%) than in the solid phase (Accra, 21.62%; Kejetia, 14.74%; Tarkwa, 19.83%) of the soil. The data in appendix 10 also indicate that apart from humic matter, inorganic ligands in the solution phase also form a complex compound with a significant proportion of the total metal in the solution phase (Co, 47.17%; Cu, 37.13%; Ni, 27.55%; Pb, 39.44%; Zn, 45.76%). There are also more metal bound humic acid than metal bound fulvic acid in both phases of the soil system (Appendix 8).

Distribution: The distribution constant for the trace metals (Cu, 0.0073; Co, 0.0019; Ni, 0.0005; Pb, 0.0009; Zn, 0.0030) indicate that there are more metals in the solution phase than the solid phase. These observations presuppose that there are more available and mobile forms (as indicated by the distribution constants) of the trace metals

in the terrestrial environment, as such the characteristics of the environment and the solubility of the metals suggest a potential increase in trace metal concentration in underground and surface waters over time.

Transport: Metals are continuously added to freshwater systems because of the erosion caused by rainwater. The erosion in the drainage areas of river systems typically in order of 5cm/1000 years and the rivers of the world each year transports approximately 24 billion tons of materials to the oceans (Andersen, 2007). Human activities such as plowing, forest destruction, etc., are estimated to have increased the amount of material transported by the rivers by a factor of 2-3 (Andersen, 2007) within those years during the transportation of trace metals, the available forms of the metals which succeed in entering into biota impact on human health in diverse ways, as such scientific investigations geared at understanding their transportation from land to water bodies, surface or underground is imperative and in this study, the network of water bodies at the study area becomes active during the raining season. In addition, the water bodies flow into a river (referred to as V-river in this document) which empties into the White Volta (figure 4.1). Analysis of sediment samples collected from the beds of the water bodies presents the information in table 4.1.

Table 4.1: Concentration (ppm) of Trace metals in sediment samples

| Element | Accra river | | Tarkwa river | | Kejetia river | | V-river | |
|---------|-------------|------|--------------|------|---------------|------|---------|------|
| | Mean | SEM* | Mean | SEM | Mean | SEM | Mean | SEM |
| Cd | 5.25 | 0.09 | 9.00 | 0.26 | 5.91 | 0.09 | 1.98 | 0.11 |
| Cu | 12.02 | 0.32 | 14.80 | 0.21 | 15.14 | 0.12 | 16.98 | 0.10 |
| Pb | 109.66 | 0.19 | 111.44 | 0.20 | 69.46 | 0.17 | 40.38 | 0.17 |
| Mn | 38.60 | 0.26 | 114.18 | 0.10 | 237.56 | 0.16 | 69.36 | 0.22 |
| Zn | 11.34 | 0.20 | 21.00 | 0.12 | 32.72 | 0.09 | 5.78 | 0.07 |

NB: * SEM is standard error of the mean; See figure 5.1 for the location of V-river.

According to Andersen (2007) most trace metals in river systems are transported in a particulate form (by suspended particles with diameter less than 100µm) especially for metals that form part of the mineral structure of the inorganic particles (Fe, Al). However, in fresh waters which receive trace metals from drainage areas with most of the metals in the dissolved form, it is expected that the concentration of metal accumulated in the river beds will be low. However this is subject to changes in the characteristics of the river (such as pH, hardness, etc.). Such changes will have varying effects on the concentrations of trace metals in terms of their adsorption by surfaces like humic substances (McCarthy, 2001) and clay etc. Consequently, sediments will have concentrations of the trace metals not totally reflecting their composition in the drainage. In this research, a partial reflection of the order of metal distribution (Mn>Pb>Zn>Cu>Cd) in the soil at the mining communities is observed in the sediments (where Mn and Pb have comparatively high concentrations, and Cd has the least concentration). This is considered to be as a result of the nature of human activities at the communities. The disparity in the concentration of trace metals in the sediments from different water bodies at the study area is because of the topography of the communities (which promotes material transport from land to the rivers by erosion), and the mining activity (gold extraction at the bank of the rivers from disposed tailings, surface rocks and powdered wastes) which takes place in and around the water bodies located at the mining communities.

It has been noted that the metal contents and chemical composition of freshwater in different river systems vary strongly with the geological characteristics of the drainage areas (Andersen, 2007). It was also observed in this study that the drainage in this case transports materials from the modified top soil to the water bodies thereby influencing the water system. In essence the mining activity has a great impact on the chemistry of the water bodies. The resultant effect of this change on human health will not be limited to the

immediate towns, it will resonate to all those who rely directly or indirectly on the White Volta. Hence the sporadic and unorganized mining activity which is not supervised has the propensity to influence human health.

In conclusion, material distribution at the study area is greatly influenced by the haphazard mining activity. The soil is fertile and has high available metals. The mining (gold) area is well drained and thus has the potential to transport mobile metals to the White Volta. The topography of the area makes it easy for the mobile forms of the trace metals and other phytotoxic metals associated with illegal mining to be transported to the White Volta.

4.2 ENVIRONMENTAL CHARACTERISTICS AS A FUNCTION OF TRACE METAL DISTRIBUTION IN THE TERRESTRIAL ENVIRONMENT

The prediction of the effects of pollutants on a terrestrial environment requires assessment of their interaction with soils (López-Sánchez et al. 2003). Therefore, understanding the chemistry of heavy metals in their interaction with other soil components such as clay minerals, humic substances and soil solution, or to assess their mobility and retention as well as their availability to plants requires a proper interpretation of their interaction models (Peijnenburg et al. 1997; Merdy et al. 2006).

Bioavailability and toxicity of trace metals in soil may be expressed in terms of pore-water concentrations (Peijnenburg et al. 1997). It is of great practical interest and importance to have a quantitative understanding of the distribution of trace metals between the soil phases. Mathematical model may be exploited to assess trace metal interaction and distribution in soil (Peijnenburg et al. 1997; Cornejo et al., 2003; Boruvka et al. 2004; Rimmer et al. 2004; Merdy et al. 2006).

Trace metals exist in the soil in immobile and mobile forms. The mobile forms occur with the exchange processes in the soil and with the changing composition, pH, etc. of soil. Determination of the mobile forms of trace metals is important for understanding their migration patterns in terrestrial environments and their uptake by plants (Rimmer et al. 2004).

Several soil properties influence metal adsorption, desorption and equilibrium between solid and solution phases. These factors include soil pH, clay content, organic matter cation exchange capacity (CEC) and iron/aluminum oxides (McBride et al., 1997; Cornejo et al. 2003). These factors vary from one terrestrial environment to another and they have significant effect on soil-solution partitioning which exerts a major control on the bioavailability, transport and retention of heavy metals in soil (Tipping et al. 2003). A quantitative description of their effect on trace metal distribution in a perturbed terrestrial environment will provide insight into the chemistry of trace metal distribution in a mining-impacted terrestrial environment such as Talensi-Nabdam District in Ghana. Several approaches have been identified to explain how such factors control metal partition. The use of empirical relationship derived by multiple regression analysis which relates metal partition constants with soil characteristics, and the use of mechanistic models that describe the interactions more comprehensively have been reported as being capable of providing good description of trace metal chemistry in soil (McBride et al. 1997; Peijnenburg et al. 1997; Tippings et al. 2003).

Accounts of the interrelationship between principal factors that influence trace metal distribution in terrestrial environment and determination of their relative effect on metal partition are discussed in the following sections.

4.2.1 DISTRIBUTION OF HUMIC SUBSTANCES IN SELECTED TERRESTRIAL ENVIRONMENTS

The data obtained from humic substance fractionation and isolation from the soil samples obtained from the terrestrial environment at the selected ecosystems revealed that humic acid and fulvic acid are present in the soil at varying concentrations (Appendix 9). The concentrations vary from ecosystem to ecosystem in the order Tarkwa (3.708 mgC/g) > Accra (3.707 mgC/g) > Kejetia (2.909 mgC/g). Moreover, the minimum and maximum values are in the range of 1.2950-5.8490 and 1.02-1.7384 mg/g for humic and fulvic acid respectively over the entire study area (Appendix 9). The proportion of humic acid (51.85% w/w) in the terrestrial environment at the entire study area is observed to be higher than the proportion of fulvic acid (48.15% w/w). A similar observation was made at the ecosystems, Accra and Tarkwa (Appendix 10), however the proportion of fulvic acid (54.09% w/w) was more than the proportion of humic acid (45.91% w/w) at Kejetia.

Humic acid and fulvic acid were also observed to partition themselves between the major phases-soil and solution- of the terrestrial environment. The mean values of humic acid are 0.937, 0.394, and 0.666 mg/g in the solid phase, and fulvic acid values are 0.5749, 0.5388, and 0.6387 mg/g at Accra, Kejetia and Tarkwa respectively. In addition, the mean values of humic acid are 2.7692, 2.5137, and 3.0427 mg/g in the solution phase and fulvic acid values are 2.7158, 2.8886, and 2.2295 mg/g at Accra, Kejetia and Tarkwa respectively (Appendix 9). It was noted that the proportions of humic acid and fulvic acid in the solid phase are lower than the solution phase of the terrestrial environment at all the selected ecosystems. This indicates that more than three parts of the humic substance remain in the solution phase. The pH of the soil at Accra, Kejetia and Tarkwa are 6.02, 5.92 and

5.48 respectively, and at these pH values humic substances are hydrophilic as such the occurrence of high humic substance concentration (81%) in the solution phase of the terrestrial environment at the study area is as a result of the intrinsic property of the humic substances.

The data (Appendix 10) also reveals that with the exception of Kejetia, humic acid is higher (48.15%) than fulvic acid (51.85%) in each of the major phases of the terrestrial environments at the selected ecosystems.

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4.2.2 DISTRIBUTION OF METAL BOUND HUMIC SUBSTANCES

IN SELECTED TERRESTRIAL ENVIRONMENTS

The masses of five trace metals (Cu, Co, Ni, Pb, and Zn) bound to humic substances in the terrestrial environments of the selected ecosystems were studied. The magnitudes of trace metal humates and fulvates do not vary in the same pattern among the terrestrial environments at the ecosystems studied (Appendix 11). However, the average concentrations of metal species in the terrestrial environment, and its phases, for the study area gave the order outlined in table 4.2.

Table 4.2: Variation in the concentration of metal species at the study area

| | Species* | Order |
|-------------------------|----------|------------------------|
| Terrestrial Environment | M_{HA} | Cu > Ni > Zn > Pb > Co |
| | M_{FA} | Ni > Pb > Co > Zn > Cu |
| Soil phase | M_{HA} | Cu > Ni > Zn > Co > Pb |
| | M_{FA} | Ni > Cu > Pb > Zn > Co |
| Solution phase | M_{HA} | Ni > Pb > Cu > Co > Zn |
| | M_{FA} | Ni > Pb > Co > Zn > Cu |
| | M_{LA} | Ni > Pb > Co > Zn > Cu |

NB: * M_{HA} = metal-bound humic acid; M_{FA} = metal-bound fulvic acid; M_{LA} = metal bound to inorganic ligands in solution.

The data also revealed that the concentrations of metal bound humic acids are generally higher than the concentrations of metal bound fulvic acids in the

terrestrial environments and their phases at Accra, Kejetia and Tarkwa (Appendix 12). It was equally noted (Appendix 13) that with the exception of Ni and Pb which had more metal bound fulvic acid (Ni = 51.19%w/w; Pb = 35.4%w/w), than the inorganic bound forms (Ni = 10.88%w/w; pb = 4.34%w/w) the terrestrial environments at the ecosystems are characterized by comparatively high proportion of Cu, Co and Zn bound humic acid (Cu = 76.59%w/w; Co = 59.99%w/w; Zn = 71.10% w/w) and inorganic mineral (Cu = 14.81%w/w; Co = 20.13%w/w; Zn = 18.39% w/w) or ligands (Cu = 37.13%w/w; Co = 47.17%w/w; Zn = 45.76% w/w) than the fulvate forms (Cu = 8.60% w/w; Co = 19.87% w/w; Zn = 10.51% w/w). The data also indicate that with the exception of Ni with more than half of its total form in the terrestrial environment at the study area being fulvate (Ni = 51.19%w/w), more than half of the other trace metals exist in association with humic acids (Cu = 76.59%w/w; Co = 59.99%w/w; Pb = 60.26%w/w; Zn = 71.10%w/w) than any other form. That is to say that Cu, Co, Pb and Zn speciation, mobility and bioavailability are subject to changes in humic acid concentration in the terrestrial environments at the study area.

It may also be noted (Appendix 12) that concentrations of the trace metals are higher in the solution phase than the solid phase of the terrestrial environments. This may be because the humic substances (Appendix 10) are mostly in the solution phase. According to Tipping (2002), humic substances transfer binding sites from solid to solution phase at high pH, thus the comparatively high concentration of metals in the solution phase of the terrestrial environment is mainly due to the hydrophobicity of humic substances at the pH of the soil. It may be added that the high concentration of mobile forms of the trace metals in the terrestrial environment may be considered to be significantly due to their relationship with humic substances in the environment.

4.2.3 OTHER TRACE METAL SPECIES IN THE TERRESTRIAL ENVIRONMENTS

Other species of trace metals were also determined, and it was observed that ionic forms (M_{water}), exchangeable forms (M_{ex}), carbonate bound forms (M_{carb}), oxide bound forms (M_{ox}), organic bound forms (M_{org}), and mineral bound forms (M_{mineral}) of the metals occur in the terrestrial environments. A significant proportion of the metals exist in the form of M_{carb} , M_{ox} , M_{org} , and M_{mineral} . The metal form with least abundance in the terrestrial environment is M_{water} . The occurrence of oxide bound and organic bound forms are quiet significant in most cases. Except for Co and Zn were the carbonate forms are appreciably higher than their organic forms in most cases.

The occurrence of high proportion of organic, carbonate and oxide bound forms of the trace metals suggest that under favourable conditions such as pH, the available and mobile forms of the metals will increase. Humic substances which occur in high concentration in the environments will significantly influence the relative proportion of the trace metals in the solid and solution phases of the terrestrial environment. Since the ionic and exchangeable forms of the trace metals are low, the availability and mobility of the metals are bound to be dependent on the characteristics of the terrestrial environment such as pH and available sorption sites at defined environmental conditions.

Table 4.3: Proportion of metal species in the terrestrial environments

| Ecosystem | Metal | Species (%) | | | | | |
|-----------|-------|--------------------|-----------------|-------------------|--------------------|------------------|----------------------|
| | | M _{water} | M _{ex} | M _{carb} | M _{oxide} | M _{org} | M _{mineral} |
| Accra | Cu | 0.40 | 0.66 | 3.96 | 3.30 | 14.81 | 76.89 |
| | Co | 1.07 | 17.22 | 29.44 | 15.19 | 2.91 | 34.17 |
| | Ni | 0.13 | 0.91 | 0.59 | 56.78 | 30.33 | 11.26 |
| | Pb | 4.63 | 16.12 | 10.10 | 29.16 | 15.46 | 24.52 |
| | Zn | 1.03 | 2.72 | 18.41 | 40.66 | 8.00 | 29.18 |
| Kejetia | Cu | 0.42 | 0.51 | 11.01 | 24.40 | 24.07 | 39.59 |
| | Co | 0.71 | 2.18 | 22.61 | 40.63 | 4.52 | 29.33 |
| | Ni | 0.19 | 15.67 | 1.03 | 32.36 | 45.04 | 5.72 |
| | Pb | 4.50 | 8.68 | 2.77 | 53.82 | 16.18 | 14.06 |
| | Zn | 1.55 | 5.64 | 18.98 | 46.87 | 5.32 | 21.63 |
| Tarkwa | Cu | 0.05 | 0.08 | 94.10 | 0.78 | 3.22 | 1.76 |
| | Co | 1.21 | 21.00 | 45.98 | 6.61 | 21.65 | 3.57 |
| | Ni | 0.35 | 1.02 | 2.15 | 86.21 | 9.28 | 1.00 |
| | Pb | 7.32 | 14.25 | 6.58 | 24.25 | 21.01 | 26.59 |
| | Zn | 0.93 | 10.36 | 14.49 | 54.57 | 9.49 | 10.17 |

4.2.4 EQUILIBRIUM PARTITION OF TRACE METALS IN SELECTED TERRESTRIAL ENVIRONMENTS

The average values of the distribution constant (K_{DM}) for trace metal distribution between the major phases of the terrestrial environment are as presented in table 4.4 for the entire study area and the three selected ecosystems. The data suggests that $K_{DM} \ll 1.0$ for all the metals studied. This indicates that there are more metals in the solution phase of the environment than the solid phase. This accounts for the reason why the amounts of metals in the mobile phase are more than the immobile phase, and also the comparatively high total available metals in the environments.

Table 4.4: Average K_{DM} of the metals at the study area and ecosystems

| Element | Mean K_{DM} | | | |
|---------|---------------|----------|----------|------------|
| | Accra | Kejetia | Tarkwa | Study area |
| Cu | 0.007143 | 0.011574 | 0.003065 | 0.007261 |
| Co | 0.003307 | 0.000885 | 0.001414 | 0.001868 |
| Ni | 0.000528 | 0.000607 | 0.000448 | 0.000528 |
| Pb | 0.000324 | 0.001740 | 0.000681 | 0.000915 |
| Zn | 0.002644 | 0.004621 | 0.001766 | 0.003010 |

NB: * Study area = Entire geographical area covering the three mining communities (Kejetia, Tarkwa and Accra)

The K_{DM} are generally high at Kejetia for Cu (0.011574), Ni (0.000607), Pb (0.00174) and Zn (0.004621) than the other ecosystems. The highest value of K_{DM} for Co occurs at Accra (0.003307) and has the least value at Kejetia (0.000885). The distribution constants for the metals at the study area vary in the order Cu > Zn > Co > Pb > Ni.

The average values of the free energies for trace metal distribution between the major phases of the terrestrial environments were computed (table 4.5) and the general observation is that the $\Delta G > 1.0$, implying that the transfer of metals from the solid phase to the solution phase of the terrestrial environment is more thermodynamically feasible and spontaneous than the transfer to the solid phase from solution.

Table 4.5: Free energy values of metal distribution at the study area and ecosystems*

| Element | Mean Free energy (J/mol.K) | | | |
|---------|----------------------------|-----------|-----------|------------|
| | Accra | Kejetia | Tarkwa | Study area |
| Cu | 15603.304 | 15614.424 | 15969.302 | 15729.010 |
| Co | 17096.562 | 20033.028 | 18553.646 | 18561.079 |
| Ni | 21637.528 | 21396.302 | 22319.990 | 21784.607 |
| Pb | 23704.123 | 20463.189 | 23068.256 | 22411.856 |
| Zn | 16032.447 | 15180.817 | 17359.801 | 16191.022 |

NB: * The free energy values were obtained for interactions at 35 °C; Study area = Entire geographical area covering the three mining communities (Kejetia, Tarkwa and Accra)

The average free energies for the metals range in order of magnitude from 15729.01-22411.856 J/mol.K. In addition, the relative ease (in terms of the magnitude of their free energies) with which metals are transported to the solution phase is in the order $\text{Cu} > \text{Zn} > \text{Co} > \text{Ni} > \text{Pb}$ at the terrestrial environments of all the ecosystems. This trend suggests the relative ease with which the metals will become available in solution and consequently their mobility.

4.2.5 Relationship between Metal Distribution and Characteristics of the Terrestrial Environment

4.2.5.1 Environmental Characteristics and their Effect on Metal Distribution

In order to determine the relative effect of the characteristics of the terrestrial environment on trace metal distribution, principal component analysis procedure was used. The solid and liquid phase characteristics such as available sites on oxide and humic substance surfaces, pH of solution phase, available inorganic ligand sites in solution, amount of free metal ions, total organic matter and total available sorption sites in amounts related to the cation exchange capacity of the solid phase were used to determine the principal characteristics of the terrestrial environment which control the distribution of the individual metals between the major phases of the environment.

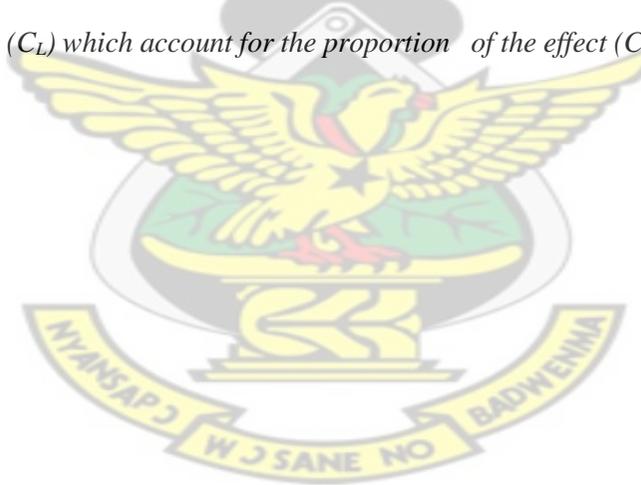
Using the selection criteria: eigenvalue >1 and correlation coefficient >0.6 , the data in table 4.6 were obtained. The information indicated that the major characteristics of the terrestrial environment responsible for changes in metal distribution are:

- i. pH of the solution phase, C_{pH} .
- ii. Total amount of available sorption sites, $C_{available\ sites}$.
- iii. Specific binding sites by oxide minerals, C_{ox} .
- iv. Specific binding site by humic substances, C_{HS} .

Table 4.6: Principal characteristics of the terrestrial environment

| Metal | Component model* | Cumulative effect of principal characteristics | Cumulative effect due to other (minor) characteristics |
|-------|--|--|--|
| Co | $K_{dm} = 0.3122C_{pH} + 0.2502C_{available\ site} + 0.1564C_{ox}$ | 71.88 | 28.12 |
| Cu | $K_{dm} = 0.2771C_{pH} + 0.2141C_{ox} + 0.1598C_{HS}$ | 65.10 | 34.90 |
| Ni | $K_{dm} = 0.3315C_{pH} + 0.1985C_{ox} + 0.1773C_{HS}$ | 70.73 | 29.27 |
| Pb | $K_{dm} = 0.3899C_{pH} + 0.2003C_{available\ site}$ | 59.02 | 40.98 |
| Zn | $K_{dm} = 0.5176C_{pH} + 0.1797C_{available\ site}$ | 69.73 | 30.27 |

NB: * The coefficients are component loadings (C_L) which account for the proportion of the effect ($C_{effect} = 100 \times CL$) due to a characteristic; Models were obtained at 95-99% confidence level.



The table 4.6 indicates that pH is the characteristic which has a common effect on the distribution of all the metals studied in the environment. The trace metals, Co, Cu, and Ni are all influenced by C_{ox} and this accounts for 15.64, 21.41 and 19.85% (computed from the component loadings) respectively, of the total effect of the characteristics of the environment on their distribution. Copper and nickel distributions are also specifically influenced by the available humic matter sites with 15.98 and 17.73% of the total effect respectively. While Co, Pb and Zn are indiscriminately influenced by all sorption sites and this accounts for 25.02, 20.03 and 17.97% respectively of the total effect due to characteristics of the terrestrial environment. It must be noted that the total available sites are contributions from soil minerals and organic matter content of the soil which undoubtedly implies site contribution by humic matter.

It may thus be inferred from the analysis that the pH of the solution phase, available sorption sites in the environment, and the available sorption sites on oxide and humic matter surface for specific metals have 71.88, 65.10, 70.73, 59.02, and 69.73% cumulative effect on Co, Cu, Ni, Pb and Zn distributions respectively. The cumulative effect of minor characteristics (which are considered to include salinity, temperature, ionic strength etc.) account for about 40.98% or less of the total effect of the characteristics of the environment on the distribution of the metals.

4.2.5.2 Relationship between Environmental Characteristics and Metal Distribution

Constant

Analyzing K_{DM} as a function of the characteristics of the terrestrial environment requires relating K_{DM} with the most important characteristics of the environment. According to Peijnenburg et al (1997), the most important soil characteristics which influence metal distribution are the adsorption phases (clay, organic matter, and

oxyhydroxides), the amount of available sorption sites (related to the cation exchange capacity), pH, and competitive sorbed ions (such as Ca, Na, K etc.). This is in agreement with the outcome of the principal component analysis which revealed that pH and available sorption sites are the principal characteristics of the terrestrial environment that influence metal distribution.

Field-based distribution constants for Co, Cu, Ni, Pb, and Zn were analyzed by relating them with the observed principal characteristics of the terrestrial environment. They include pH, total organic matter (TOM), effective cation exchange capacity (ECEC), extent of metal binding to humic matter in solution (V_{MHS}), and concentration of metal unbound to humic matter in solution ($C_{M+,MLA}$). Multiple regression analysis was used to analyze K_{DM} as a function of the environmental characteristics. The regression equations and statistics are as presented in table 4.7.

The P-values are less than 0.01 as such there is a statistically significant relationship between the variables at 90% confidence level or higher (table 4.7). R^2 values of the equations are in the range of 67.438- 92.613%, this indicates that the equations as fitted explain most of the variability in the distribution of the metals between the phases of the environment (table 4.7). The standard error of the estimate (SEE) which shows the standard deviation of the residuals suggests that the values can be used to construct prediction limits for new observations.

Table 4.7: Multiple regression data for the relationship between K_{DM} and characteristics of the terrestrial environment

| Element | Regression equation* | Statistics ¹ | | | | |
|---------|--|-------------------------|------|-------|---------|--------|
| | | R ² (%) | SEE | MAE | P-value | CL (%) |
| Co | $\text{Log}(K_{DM}) = -a - b \cdot \text{log}(V_{MHS}) - c \cdot \text{log}(ECEC)$ | 84.684 | 0.73 | 0.363 | 0.060 | 90.000 |
| Cu | $\text{Log}(K_{DM}) = -a - b \cdot \text{log}(V_{MHS}) - c \cdot \text{log}(ECEC)$ | 92.613 | 0.32 | 0.176 | 0.020 | 95.000 |
| Ni | $\text{Log}(K_{DM}) = -a - b \cdot \text{log}(V_{MHS})$ | 67.438 | 0.91 | 0.547 | 0.045 | 95.000 |
| Pb | $\text{Log}(K_{DM}) = -a + b \cdot \text{log}(TOM)$ | 80.491 | 0.40 | 0.248 | 0.015 | 95.000 |
| Zn | $\text{Log}(K_{DM}) = -a - b \cdot \text{log}(V_{MHS})$ | 71.353 | 0.51 | 0.379 | 0.034 | 95.000 |

NB: * a , b , and c are constants; ¹ SEE = standard error of the estimate, MAE = mean absolute error, CL = confidence level

The regression equations show that the distribution constants of Co and Cu are functions of V_{MHS} and ECEC (table 4.7). The distribution constants of Ni and Zn are influenced only by V_{MHS} , while K_{DM} for Pb is a function of total organic matter, and directly so for the mass of humic substances (table 4.7).

The R^2 values of the regression equations (table 4.7) indicate that 84.64%, 92.61%, 67.44%, 80.49%, and 71.35% of the variability in the distribution of Co, Cu, Ni, Pb, and Zn respectively in the terrestrial environment can be explained using the regression equations. In essence the observation implies that trace metal distribution in terrestrial environment is influenced by humic substances, available sorption sites on mineral surfaces, and solution pH.

The high proportion (81%) of the total amount of humic substances in the terrestrial environment found in the solution phase contributes to the occurrence of high metal concentration in the phase. The principal characteristics of the terrestrial environment have more effect on the distribution of the trace metals than the minor characteristics. Therefore the trace metals exist in high concentration in the mobile forms than the immobile forms. Thus the tendency for the elevation of the concentration of trace metals in underground and surface waters at the study area is

expected. The principal characteristics of the terrestrial environment are functions of trace metal distribution in the environments.

4.3 ADSORPTION KINETICS AND INTRA-PARTICLE DIFFUSIVITIES OF Cu IN SOIL-SOLUTION SYSTEM

4.3.1 The Effect of Humic Acid on the Kinetics of Trace Metal Distribution in Soil.

Analysis of the kinetic data indicates that, alternating adsorption and desorption processes occur in the system at all pHs and the alternating processes reach a climax where the rates of both processes are at equal- equilibrium state. It was observed that the strength of metal adsorption to the solid phase V_m , varies inversely with the solution concentration of the metal, C_m . Mineral dissolution, electrostatic forces and ionization among others may be responsible for changes in the values of V_m and C_m .

A similar observation was made in humic acid free system. As such the physicochemical processes responsible for metal exchange between the solid and solution phases of the soil system, exist at all pH, and is not influenced by humic acids.

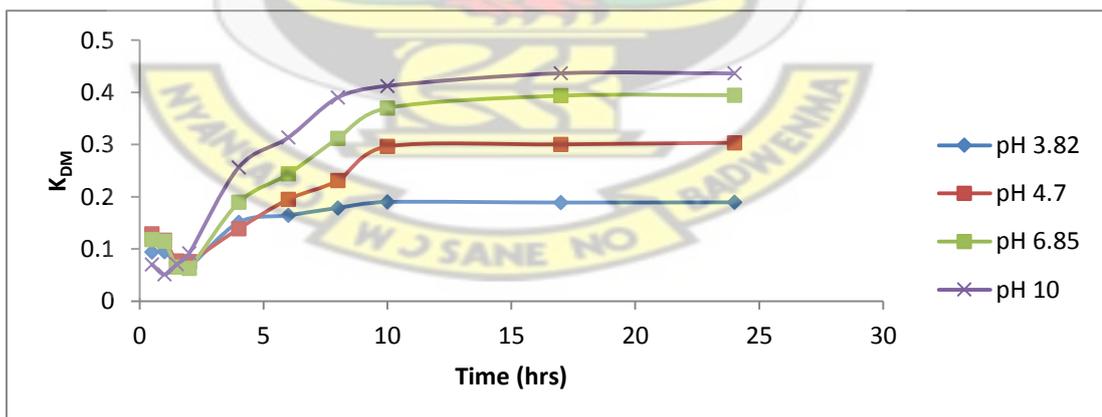


Figure 4.5: Change in K_{DM} with time: Change in K_{DM} with time in soil containing HA at pHs 3.87, 4.7, 6.85 and 10.

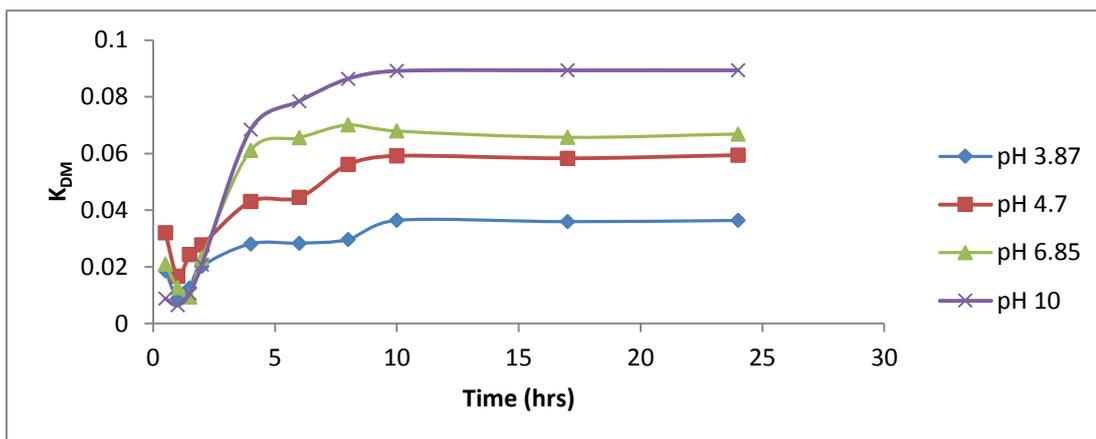


Figure 4.6: Change in K_{DM} with time: Change in K_{DM} with time in soil free from HA at pHs 3.87, 4.7, 6.85 and 10.

Equilibrium is reached after 10 hours under both humic and non-humic conditions (figure 4.5-4.6). The plots show that initial rise in solution concentration (C_m) from 0-0.5 hrs occurs at all pH and under both conditions. This indicates that materials (ions) are initially transferred from the solid phase to the solution phase (desorption, dissolution or mineralization process) before metal exchange between the two phases is initiated at 1.5 hrs. The amount of metal released into the solution phase varies with pH. From figures 4.5-4.6 it may be observed that K_{DM} values are higher in humic conditions than non-humic conditions. At equilibrium, K_{DM} values vary with pH in the order $10 > 6.85 > 4.7 > 3.87$ under both humic and non-humic conditions.

4.3.2 Distribution Constants of Metals in Soil Solution Systems under Humic and Non-humic Conditions.

Although humic acid does not appear to significantly influence, the attainment of equilibrium, it affects greatly the value of the equilibrium constant at all pH conditions (figure 4.7-10). Relatively higher values of equilibrium constant are observed in humic conditions than non-humic conditions at all reaction times as depicted in figure 4.7 (and Appendix 14). This is because it has strong affinity for

cations, and will influence their relative proportions in the system phases as the humic acid concentration changes in the phases. The results also indicate that, humic acid transfer metal from solution to the solid phase. Consequently, higher amounts of metal will be in the solid phase under humic conditions than non humic conditions. In addition, more metals will leave the solution phase under humic conditions than non-humic conditions.

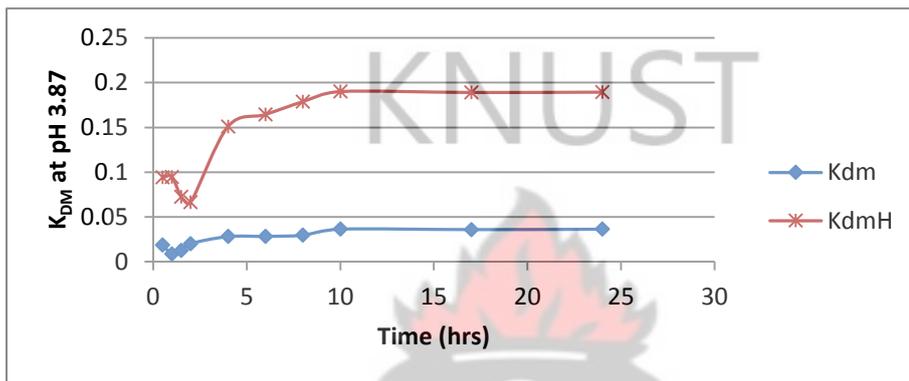


Figure 4.7: Change in K_{DM} with time under humic and non-humic conditions at pH 3.87.

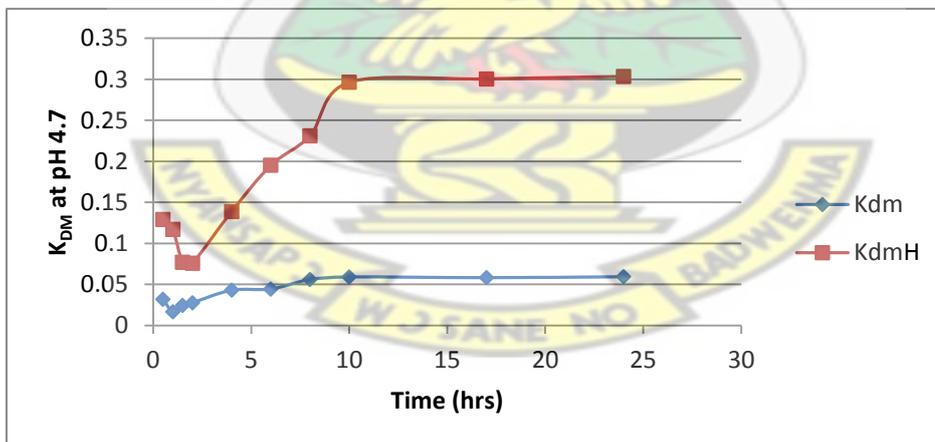


Figure 4.8: Change in K_{DM} with time under humic and non-humic conditions at pH 4.7.

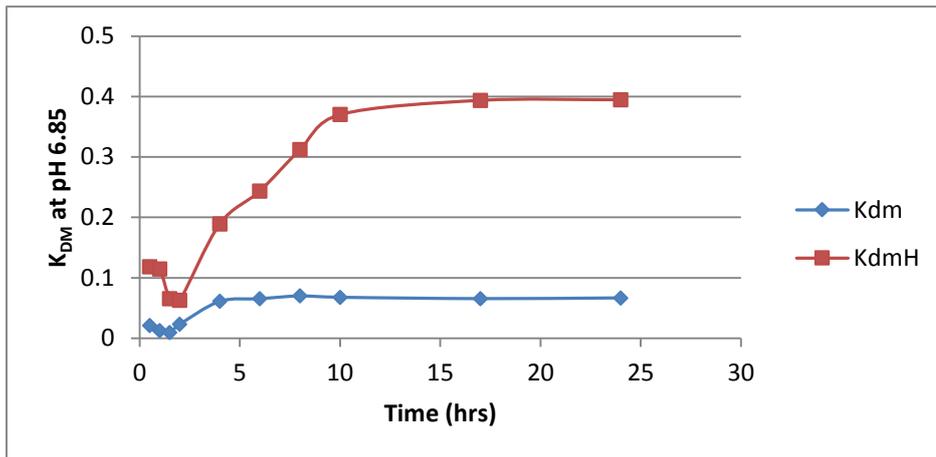


Figure 4.9: Change in K_{DM} with time under humic and non-humic conditions at pH 6.85

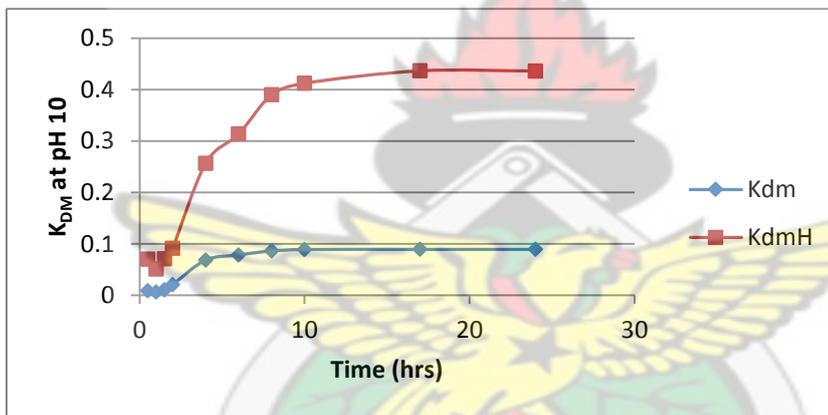


Figure 4.10: Change in K_{DM} with time under humic and non-humic conditions at pH 10.

4.3.3 Sorption Dynamics

The dynamics of metal distribution in soil-solution systems may be described by studying the sorption dynamics in the system. The kinetics of metal adsorption on soil under humic and non-humic conditions at various pH (3.72, 4.7, 6.85, and 10) were analyzed by using kinetic models as discussed below. The applicability of the models was analyzed from their plots and conformity between experimental data and the model predicted values expressed by the R^2 statistic. Relatively high values of R^2 were

considered as indicating applicability of any given model to effectively describe the kinetics of the adsorption process.

4.3.4 Determination of Adsorption Rate Constants

The kinetic parameters that describe metal adsorption on soil mineral according to zero, pseudo 1st, pseudo 2nd order, modified Freundlich equation (MFE) and Elovich equation were determined to find out the kinetic model which best describes the metal partition process. All the models were obtained at 90-99% confidence levels.

Zero order rate equation as expressed by Wahba et al. (2007) did not give good fit to the data for metal adsorption under humic and non-humic conditions. The R^2 values for pseudo-first order rate equation (expressed by Ibrahim et al. 2006) were generally low, but high for adsorption at pH 3.72 under non-humic conditions. This indicates that pseudo-first order equation can only be used to adequately describe metal adsorption at low pH under non-humic conditions. Ibrahim et al. (2006) reported that if the pseudo-first order equation cannot be fitted to experimental results, then they differ in two important aspects: 1) $k_1(V_e - V_t)$ does not represent the number of available adsorption sites (Where, V_e and V_t are the amounts of metal adsorbed (mg/g) at equilibrium and at any time t , respectively and k_1 is the pseudo-first order rate constant, min^{-1}) and, 2) $\log V_e$ is not equal to the intercept of the plot of $\log(V_e - V_t)$ against t . They explained that this is due to a boundary layer or external resistance controlling at the beginning of the adsorption.

The sorption data was also analyzed using pseudo-second order rate equation and the R^2 values obtained after fitting a second order equation to the data indicated that pseudo-second order kinetic equation may be used to adequately describe metal adsorption (Table 4.8). A plot of $\frac{t}{V_t}$ vs. t (figure 4.11-4.12) yielded a good straight line with $R^2 > 99\%$ for metal adsorption under both conditions at all pH.

Table 4.8: Pseudo second order rate law constants and statistics for metal adsorption in soil-solution system*

| Condition | Statistic/ Constant s | pH | | | |
|-----------|-----------------------------|------------|------------|------------|------------|
| | | 3.72 | 4.7 | 6.85 | 10 |
| Non-humic | k_2 | 8.7911E-02 | 5.6612E-02 | 4.3090E-02 | 2.7161E-02 |
| | h_0 | 3.1319E-03 | 2.2785E-03 | 2.1232E-03 | 2.1072E-03 |
| | R^2 | 9.9692E+01 | 9.9238E+01 | 9.9092E+01 | 9.9031E+01 |
| | Corr | 9.9846E-01 | 9.9618E-01 | 9.9545E-01 | 9.9514E-01 |
| | SE | 1.4537E+02 | 2.1552E+02 | 2.1280E+02 | 1.7523E+02 |
| | P-value | 0.0000E+00 | 0.0000E+00 | 0.0000E+00 | 0.0000E+00 |
| Humic | k_2 | 8.8922E-02 | 7.6025E-02 | 7.8822E-02 | 4.9727E-02 |
| | h_0 | 2.9928E-03 | 3.3300E-03 | 4.0430E-03 | 3.3068E-03 |
| | R^2 | 9.9735E+01 | 9.9303E+01 | 9.9309E+01 | 9.9090E+01 |
| | Corr | 9.9868E-01 | 9.9651E-01 | 9.9654E-01 | 9.9544E-01 |
| | SE | 1.3855E+02 | 1.9747E+02 | 1.8171E+02 | 1.8335E+02 |
| | P-value | 0.0000E+00 | 0.0000E+00 | 0.0000E+00 | 0.0000E+00 |

NB: * Corr = correlation coefficient; SE = standard error of estimate

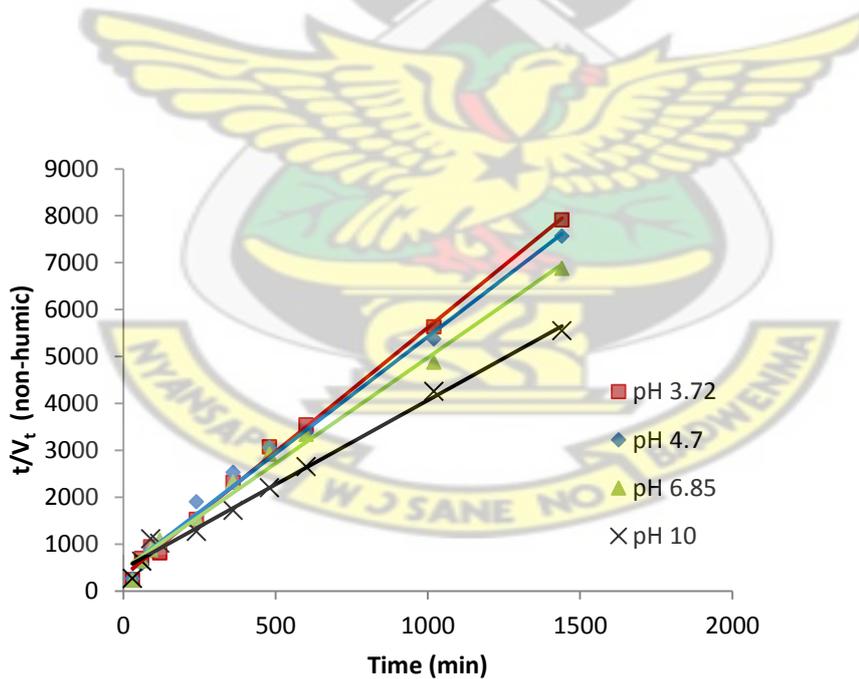


Figure 4.11: Linear plot representing second order rate model for metal adsorption in soil-solution system under non-humic conditions

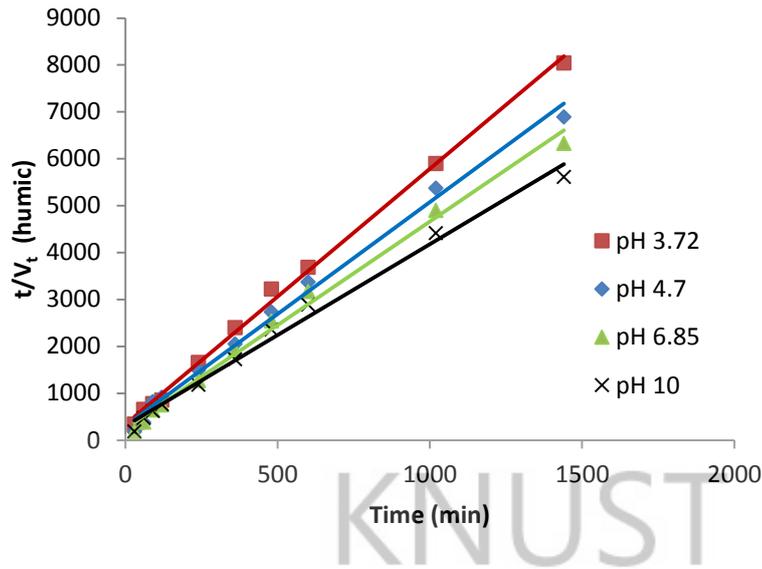


Figure 4.12: Linear plot representing second order rate model for metal adsorption in soil-solution system under humic conditions

The applicability of the model to describe the kinetic process is seen in the closeness with which it could predict the amount of metal adsorbed at equilibrium at 99% confidence level as shown in table 4.9.

Table 4.9: Experimentally determined and predicted amount of metal adsorbed at equilibrium (mg/g)*

| Condition | pH 3.72 | | pH 4.7 | | pH 6.85 | | pH 10 | |
|-----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | $V_{e, \text{expt}}$ | $V_{e, \text{pred}}$ |
| Non-humic | 0.182 | 0.188 | 0.190 | 0.201 | 0.209 | 0.222 | 0.259 | 0.279 |
| Humic | 0.179 | 0.183 | 0.209 | 0.209 | 0.227 | 0.226 | 0.257 | 0.258 |

NB: * *expt* = experimentally determined; *pred* = predicted

The initial adsorption rate, h_0 , of the metal decreases with pH under non-humic conditions (table 4.8). This indicates that initial adsorption of the metal is faster at low pH than at high pH as indicated by k_2 , and the implication of h_0 is that the amount of metal adsorbed per gram of the soil increases with pH and the rate decreases because of the increase in external mass transfer resistance. An opposite behavior is noted for

metal adsorption under humic conditions (table 4.8; Appendix 14), this indicates that the presence of humic acid in the soil-solution system decreases the amount of metal adsorbed by the soil at higher pH. This is because humic acids' hydrophilicity increases with pH and under these conditions of pH humic acid essentially transfers binding sites from solid phase to solution phase (Tipping, 2002).

The modified Freundlich equation, MFE, gave relatively low R^2 values, indicating that they cannot describe the adsorption appropriately under the humic and non-humic conditions (table 4.7) at all pH. Analysis of the data indicates that pseudo-second order kinetic rate equation is more appropriate for use in describing the kinetics of metal adsorption in the soil-solution system under humic and non-humic conditions at all pH (table 4.7 and 8), except adsorption at pH 3.2 under non-humic conditions (table 4.8) where pseudo-first order kinetic equation is more adequate.

4.3.5 Intra-Particle Diffusivity

The adsorption kinetics which describes the metal adsorption rate is an important characteristic in evaluating the efficiency of metal adsorption. In a system free from organic ligands such as humic acids, the transport of metal from solution to the adsorbent (soil) is considered to occur in several steps. These may include the following (Igwe et al. 2008):

- i) Diffusion of the metal solute from the solution to the film surrounding the particle (Bulk diffusion),
- ii) Diffusion from the film to the particle surface (external mass transfer resistance, EMTR),
- iii) Diffusion from the particle surface to the internal sites (pore diffusion, surface diffusion or internal mass transfer resistance), and

iv) Uptake which can involve several mechanisms such as physic-chemical sorption, ion exchange, precipitation or complexation (Weber and Digiano, 1996; Igwe et al. 2007; Igwe et al, 2008).

According to Igwe et al. (2008) the rate of attainment of equilibrium for the adsorption of metal on a sorbent, may thus be either film diffusion controlled or particle diffusion controlled. However, the transport mechanism is expected to change when organic complexing ligand like humic acid which has the ability to interact with the soil adsorbent and coat its surface. The strong affinity of humic acid for metal ions, its hydrophobicity and aggregation properties are expected to contribute to changes in the distribution phenomena, transport and adsorption mechanisms of metals in soil-solution system. In order to effectively describe the kinetics of metal adsorption under humic and non-humic conditions, intra-particle diffusion models were employed.

The diameter of the adsorbate relative to the porosity of the adsorbent indicates the extent to which the sorption kinetics follows the linear driving force, LDF, mass transfer kinetic model. When the rate-limiting step is pore diffusion, then there is a barrier at the pore entrance (Horsfall and Vicente, 2007). Thus the degree to which the LDF model fits the data will give an indication or otherwise of the porosity of the soil adsorbent and how humic acid affects the porosity of the adsorbent. The LDF plots for metal adsorption to the soil phase under humic and non humic conditions are shown in the figures below. The data shows that the metal adsorption into the matrix of the soil is film-diffusion controlled rate-limiting mechanism under both humic and non-humic conditions tables 4.10 and 4.11.

Table 4.10: Intra-particle diffusion rate constants and activation energy for metal adsorption under non-humic conditions

| Model | Statistic/ constants | pH : non-humic condition | | | |
|----------------------|-------------------------|--------------------------|----------|----------|----------|
| | | 3.72 | 4.7 | 6.85 | 10 |
| LDF | k_p | 0.00693 | 0.00746 | 0.00679 | 0.00557 |
| | R^2 | 86.98470 | 90.45530 | 90.87070 | 79.03770 |
| | Corr | -0.93266 | -0.95108 | -0.95326 | -0.08890 |
| | SE | 1.32176 | 1.19536 | 1.06218 | 1.41495 |
| | P-value | 0.00010 | 0.00000 | 0.00000 | 0.00060 |
| W-M | k' | 0.00260 | 0.00306 | 0.00360 | 0.00568 |
| | X_{id} | 0.09724 | 0.08610 | 0.08475 | 0.06984 |
| | R^2 | 69.88130 | 92.06510 | 86.59550 | 84.33200 |
| | Corr | 0.83595 | 0.95951 | 0.93057 | 0.91833 |
| | SE | 0.01947 | 0.01023 | 0.01614 | 0.02792 |
| | P-value | 0.00260 | 0.00000 | 0.00010 | 0.00020 |
| Activation energy | E_a (kJ/mol.K) | -8.6778 | -8.3603 | -7.8338 | -6.6524 |

NB: * Corr = correlation coefficient; SE = standard error of estimate

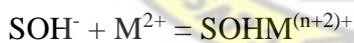
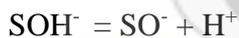
A careful examination of the data (table 4.10) for non-humic conditions suggests that metal adsorption at pH 4.7 and 6.85 is more linear with $R^2 > 90\%$, and a comparatively higher overall rate, k_{LDF} . The observation implies the occurrence of pore diffusion controlled rate-limiting mechanism or the occurrence of internal mass transfer resistance (IMTR). This observation seems to suggest that the adsorption process goes through different mass transfer resistance phases as the soil surface change in response to the changes in pH. In respect of this the following phases are considered:

Table 4.11: Intra-particle diffusion rate constants and activation energy for metal adsorption under humic conditions

| Model | Statistic/ Constants | pH : Humic condition | | | |
|-------------------|-------------------------|----------------------|----------|----------|----------|
| | | 3.72 | 4.7 | 6.85 | 10 |
| LDF | k_p | 0.00643 | 0.00600 | 0.00607 | 0.00633 |
| | R^2 | 77.71960 | 67.16240 | 67.77260 | 68.98470 |
| | Corr | -0.88159 | -0.81953 | -0.08232 | -0.83057 |
| | SE | 1.69959 | 2.07097 | 2.06419 | 2.09458 |
| | P-value | 0.00070 | 0.00370 | 0.00340 | 0.00290 |
| W-M | k' | 0.00268 | 0.00203 | 0.00221 | 0.00357 |
| | X_{id} | 0.08982 | 0.12793 | 0.14069 | 0.12381 |
| | R^2 | 82.27310 | 59.65310 | 82.86730 | 86.80310 |
| | Corr | 0.90705 | 0.77235 | 0.91032 | 0.93168 |
| | SE | 0.01419 | 0.01907 | 0.01146 | 0.01587 |
| | P-value | 0.00030 | 0.00880 | 0.00030 | 0.00010 |
| Activation energy | E_a (kJ/mol.K) | -8.8257 | -8.1402 | -7.7293 | -7.0536 |

NB: * Corr = correlation coefficient; SE = standard error of estimate

- a) Film diffusion stage at low pH: At this pH, the developed positively charged surface (as illustrated below) forms a charged repulsive layer capable of reducing the adsorption rate by preventing greater access to the relatively few negatively charged sites.



- b) Pore diffusion stage at intermediate pH: At these pH conditions, the positively charged repulsive layer is at a minimum, creating a relatively higher negatively charged adsorption sites which cause the mass transport of metal ions to be controlled internally at the particle surface. Hence the high rate of adsorption.
- c) Film diffusion stage at high pH: At high pH positively charged sites are negligible compared to the total number of negative sites and this creates an external film which

slows down the metal ions, and hence the observation of film diffusion controlled rate-limiting mechanism of metal adsorption.

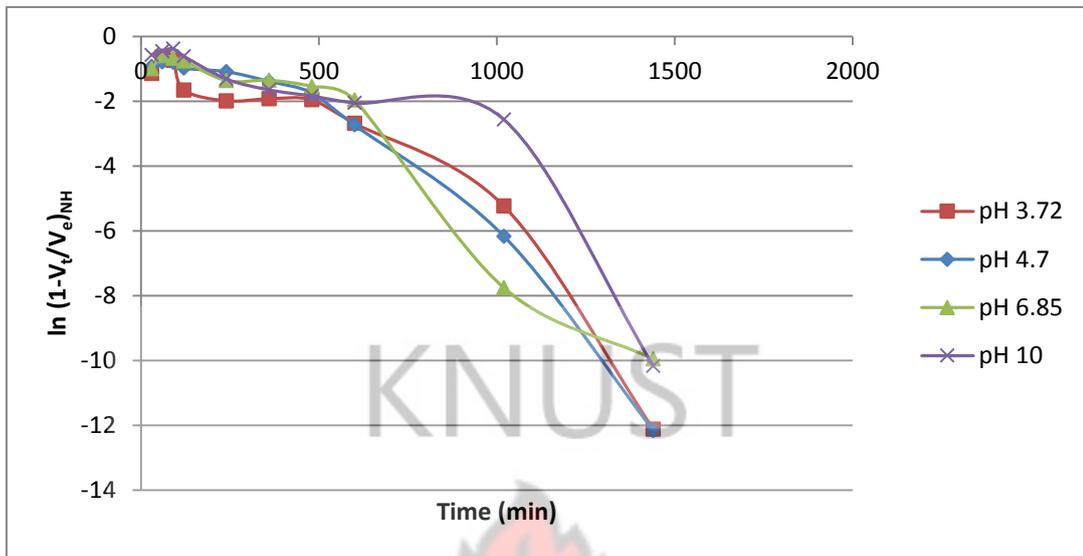


Figure 4.13: A plot of LDF model for metal adsorption in soil-solution system under non-humic conditions

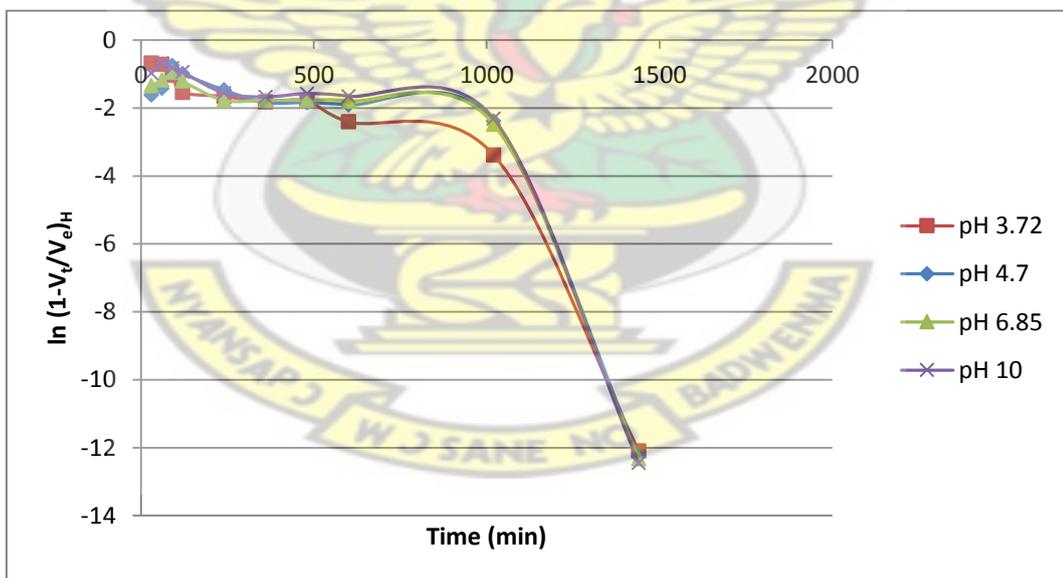


Figure 4.14: A plot of LDF model for metal adsorption in soil-solution system under humic conditions

The plot of LDF model for metal adsorption under humic conditions (figure 4.14) on the other hand did not give a straight line, which shows that metal adsorption follows film diffusion controlled rate-limiting mechanism at all pH. This is considered to be the additional negative charge sites introduced to the soil surface by humic acid due to surface attachment, complexation and aggregation. This may be illustrated as, $\text{SOH}_2^+ + \text{L}^{n-} = \text{SOH}_2\text{L}^{(n+1)-}$, $\text{SOH}_2\text{L}^{(n+1)-} + \text{M}^{2+} = \text{MSOH}_2\text{L}^{(n+3)-}$, $\text{SOH}^- + \text{M}^{2+} = \text{MSOH}^+$, $\text{MSOH}^+ + \text{L}^{n-} = \text{MSOHL}^{(n+1)-}$, $\text{ML}_{(\text{aq})} = \text{ML}_{(\text{s})}$, $\text{HL}_{(\text{aq})}^+ = \text{HL}_{(\text{s})}^+$.

The possibility of intra-particle diffusion was also explored by Weber-Morris model (W-M) equation by Igwe et al. (2007), and according to Horsfall and Vicente (2007), if the plot of V_t vs $t^{0.5}$ gives a straight line, the adsorption is controlled by surface diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process. The figures 4.15 and 4.16 below show the plots exhibited by the data. The multi linearity of the plots (figures 4.15 and 4.16) indicates the adsorption process goes through three steps (S1, S2, and S3) to reach equilibrium (figures 4.15 and 4.16).

Under non-humic conditions (figure 4.15), S1 represents the instantaneous adsorption stage characterized by film diffusion. The second stage, S2, is the gradual adsorption stage where intra-particle diffusion is rate-limiting and S3 is the final equilibrium stage where intra-particle diffusion starts to slow down.

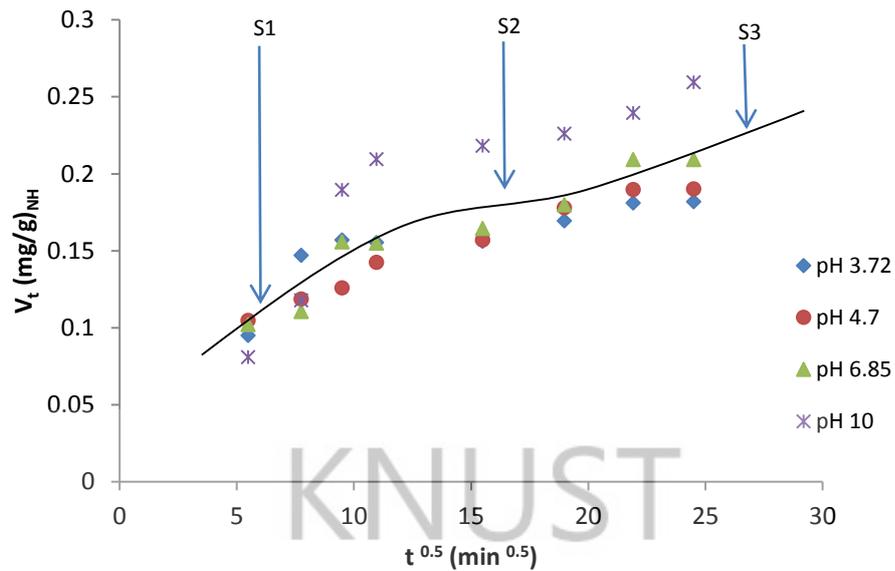


Figure 4.15: A plot of Weber-Morris model for metal adsorption in soil-solution system under non-humic conditions

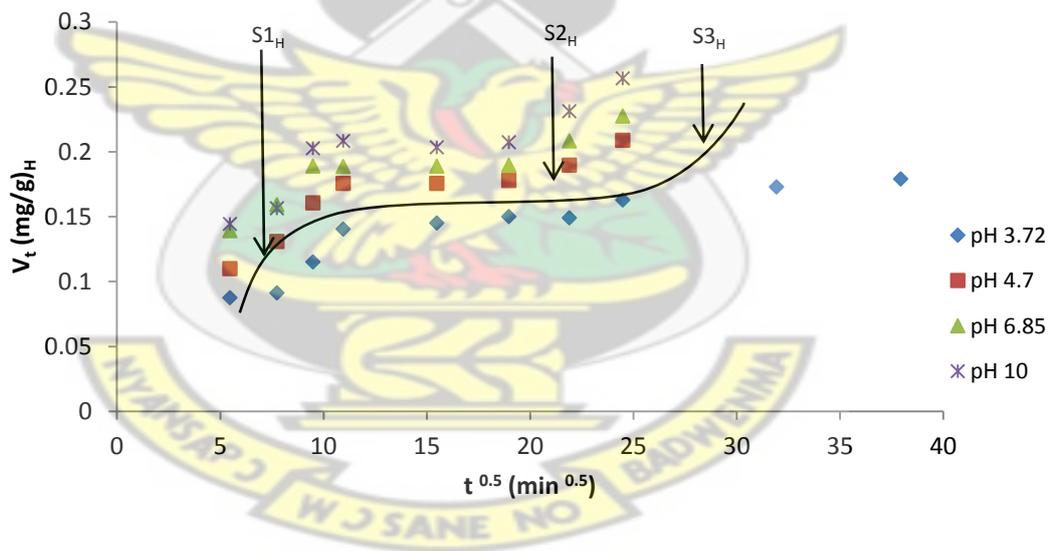


Figure 4.16: A plot of Weber-Morris model for metal adsorption in soil-solution system under humic conditions

Under humic conditions the three stages may be explained differently. The second order rate constants (table 4.13 and 4.14) indicate that the rate of metal adsorption increases at all pH under humic conditions. In addition the initial adsorption

rate, h_o , increases in the presence of humic acid, except at pH 3.72. This implies that the presence of humic acid in the system promotes the removal of the metal from solution. The boundary layer diffusion effect (thickness), X_{id} , reduces when humic acid is introduced into the soil-solution system indicating a corresponding reduction in adsorption capacities of the soil surface (table 4.10 and 4.11). The reductions in adsorption capacities thus suggest that the soil mineral surfaces have either been modified or coated by humic acid. Thus, the increased adsorption observed may be as a result of the humic acid transporting metal to the solid phase as a complex, or by means of metal adsorption to the humic acid coated sites on the mineral surface. The transportation of metal to the solid phase by the humic acid, and complexation within the soil matrix by humic acid (which coats the mineral surface) appear to compensate for the reduction in adsorption capacity of the soil mineral. In this light therefore, the stages depicted in figure 4.16 may be explained as follows:

- 1) The first stage, $S1_H$, is seen as the instantaneous adsorption or external surface adsorption stage (figure 4.16) where metal sorption occurs at both organic coated and inorganic sorption sites in the solid phase, and also as a result of metal-humic complex in the solid phase as an aggregate (due to hydrophobicity or coagulated pseudomicelles), or as part of adsorbed humic acid.
- 2) The second stage, $S2_H$, is the gradual adsorption stage where internal mass transfer resistance is experienced by the metal as a result of slow migration of metals to more deeply hidden destinations in the solid phase and within adsorbed or aggregated humic acids in the solid phase, to form inner sphere complex (section 3.13.6). This stage is more prolonged under humic conditions than non-humic conditions. This is considered to be due to modification of the solid phase by the humic acid, which provides more binding sites for the metal and yet introduce

stearic hindrance to metal binding with inner sites and perhaps as a result of electrostatic repulsion by positively charged sites in the solid phase.

- 3) The third stage, S_{3H}, is the equilibrium stage where metal sorption slows down.

The kinetic data hence revealed that, at all the pH studied, metal adsorption in soil-solution system under both humic and non-humic conditions follow second order rate law. In addition, the overall transport mechanism of adsorbate to the adsorbent surface is a combination of film, pore and surface diffusions with the rate limiting step being film diffusion controlled under all conditions of pH studied.

4.3.6 Evaluation of Activation Energy

The adsorption rate constant, k_2 , was used to evaluate the activation energy, using an Arrhenius form of equation expressed by Horsfall Jnr and Vicente (2007), as:

$$k_2 = h_o \exp\left(-\frac{E_a}{RT}\right)$$

Where k_2 is the second order adsorption equilibrium constant (mg/g.min.), h_o is the initial rate constant for second order, E_a is activation energy, R is the gas constant (8.314 J/K mol) and T is the absolute temperature (K).

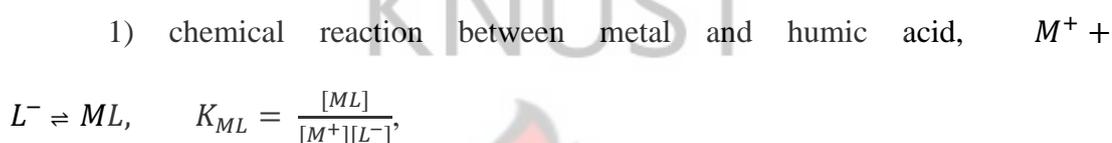
The linear form of the Arrhenius-like expression (below) was applied to the data.

$$\ln k_2 = \ln h_o - \frac{E_a}{RT}$$

The values of E_a computed for metal adsorption under humic and non-humic conditions are negative (table 4.10, indicating that the adsorption process is exothermic and does not require external application of heat. The data in table 4.11 shows that the amount of heat librated is higher when humic acid is present in the system.

4.4 EFFECT OF TEMPERATURE ON THE DYNAMICS OF METAL AND HUMIC ACID DISTRIBUTION IN TERRESTRIAL ENVIRONMENT

In order to understand the dynamics of trace metal and humic acid distributions at different temperatures the following interactions and processes were studied at temperatures 25, 30, 35, 40, and 45 °C independently at pH 4.7 and 10.



The amounts of interacting species, stability constants of products and the free energies of the events were accounted for.

4.4.1 Metal – Humic Interaction and Behaviour in Aqueous Solution

The outcome of the investigation indicated that after 24hrs the concentration of free metal ions in solution were more than metal bound ligands at all pH and temperature (table 4.12).

Table 4.12: Mass and concentration of solution species

| pH | T (K) | Mass (mg) | | Concentration | |
|-----|--------|----------------|--------|---------------------------------------|--|
| | | M ⁺ | ML | C _{m+} (mg.L ⁻¹) | C _{ML} (mg.mgC ⁻¹ .L ⁻¹) |
| 4.7 | 298.15 | 1.2423 | 0.1943 | 21.8333 | 0.3075 |
| | 303.15 | 1.1083 | 0.1467 | 20.0333 | 0.2459 |
| | 308.15 | 0.9839 | 0.1806 | 17.4630 | 0.2334 |
| | 313.15 | 0.9010 | 0.2311 | 27.9125 | 1.5194 |
| | 318.15 | 1.6509 | 0.1929 | 72.9000 | 1.6487 |
| 10 | 298.15 | 0.7664 | 0.3132 | 9.4417 | 1.7846 |
| | 303.15 | 0.4042 | 0.3367 | 1.4362 | 1.8369 |

| | | | | | |
|--|--------|--------|--------|---------|--------|
| | 308.15 | 1.5671 | 0.4502 | 25.9744 | 1.5909 |
| | 313.15 | 1.4339 | 0.3036 | 45.2120 | 1.4034 |
| | 318.15 | 1.1564 | 0.2794 | 43.8500 | 1.9428 |

The values of the stability constants for the formation of ML and aggregation of humic acid, (HL), show that there were more reactants than products at equilibrium (table 4.13). The free energies (table 4.13) indicate that the formation of ML and aggregation of HL are endergonic, and the products are thermodynamically unstable under the conditions of the study.

Table 4.13: Stability constants and free energies of reactions in solution

| pH | T (K) | Stability constants | | | Free Energies | | |
|-----|--------|---------------------|--------|---------|-----------------|-----------------|---------------------|
| | | K_{ML} | Q_L | Q_M | ΔG_{QL} | ΔG_{QM} | $\Delta G_{K_{ML}}$ |
| 4.7 | 298.15 | 8.41E-05 | 0.6364 | 1.4338 | 1119.89 | -892.75 | 23251.07 |
| | 303.15 | 8.33E-05 | 0.7586 | 2.6938 | 695.96 | -2496.50 | 23662.86 |
| | 308.15 | 3.85E-05 | 0.0534 | 32.7286 | 7501.52 | -8932.95 | 26029.89 |
| | 313.15 | 0.000346 | 0.6774 | 1.3834 | 1013.56 | -844.58 | 20740.62 |
| | 318.15 | 0.000128 | 0.6552 | 0.9375 | 1118.04 | 170.63 | 23699.98 |
| 10 | 298.15 | 0.003722 | 0.5000 | 4.1654 | 1717.43 | -3535.22 | 13859.01 |
| | 303.15 | 0.021445 | 0.3913 | 11.5503 | 2363.78 | -6163.99 | 9679.74 |
| | 308.15 | 0.000432 | 0.0800 | 71.3674 | 6468.06 | -10929.38 | 19838.16 |
| | 313.15 | 0.000108 | 0.2034 | 13.0244 | 4144.73 | -6680.02 | 23770.94 |
| | 318.15 | 0.000155 | 0.2553 | 6.2915 | 3609.72 | -4862.87 | 23198.68 |

The aggregation of metal bound humic acids on the other hand gives rise to more products than un-aggregated metal bound humic acids at equilibrium (table 4.13). The free energy also indicates that aggregation of ML is exergonic, and the aggregate is more thermodynamically stable than the un-aggregated species (table 4.13). The observation was noted at pHs 4.7 and 10, and at all the temperatures the reactions were carried out. Tipping, (2002) observed that, At $pH < 3$ humic acids are noted to undergo virtually complete aggregation followed by precipitation. Hence in this study, at pH 4.7 and 10 it is expected that there will be more humic acid in solution at conditions of low salinity. Von Wandruzka

and Engebretson (2001) have also reported that, the addition of metals to a solution of humic acid makes them aggregate.

The effect of temperature on the extent of metal binding to humic acid differs at pH 4.7 and 10. At pH 4.7, the stability constant has a minimum at 35 °C and a maximum value at 40 °C (figure 4.12). This indicates that more ML is produced at 35 than 40 °C. A different behavior is observed at pH 10, where a sharp reduction in the stability constant is observed from 25 – 40 °C. It was noted that the reaction is endergonic and ML is thermodynamically unstable (table 4.13). The stability of ML is influenced by temperature. At pH 4.7 the ML is more stable at 40 °C than 35 °C. This implies that even though [ML] varies, temperature does not change the free energy of the reaction. It may be concluded that since the rates of the reverse and forward reactions in the formation of ML are not affected by temperature at equilibrium, then it affects the concentration of the humic acid anion available for binding, by changing the conformation of the humic acid in the presence of high metal concentration, hence the occurrence a pseudomicellar aggregation at cloud point. The system will only adjust itself to annul the change imposed on it by a reduction in the concentration of the humic acid anion available for binding (Le Chatlier's principle). But ultimately, pseudomicellar aggregations will alter the order of the reaction. Von Wandruszka (2000) also reported that HA aggregation caused by cations, occurs when the solutions are heated. Clouding is a phenomenon familiar from surface chemistry: nonionic surfactants, especially those with polyoxyethylene (POE) hydrophilic moieties, display an inverse temperature–solubility relationship. Von Wandruszka (2000), also made a similar observation with HA solutions that were partially neutralized by the addition of metal ions. When heated, they too, underwent clouding, forming a black colloidal precipitate that eventually coagulated. Clouding therefore interferes in the binding of metals to humic acids in a way that does seem to affect the kinetics of the reaction.

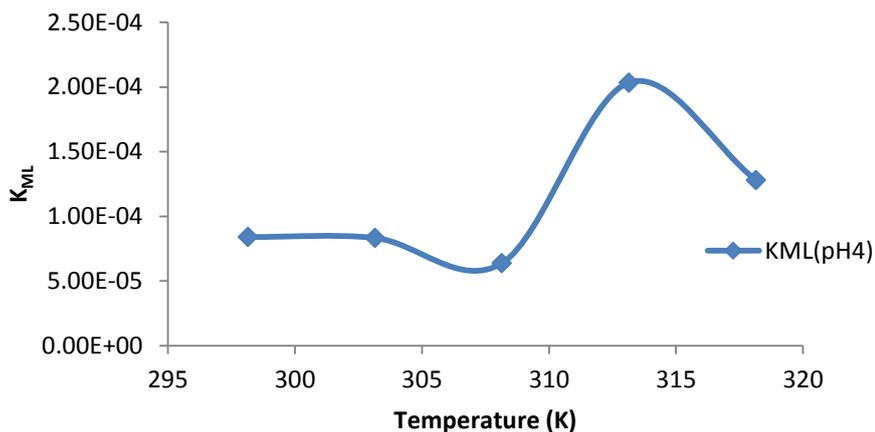
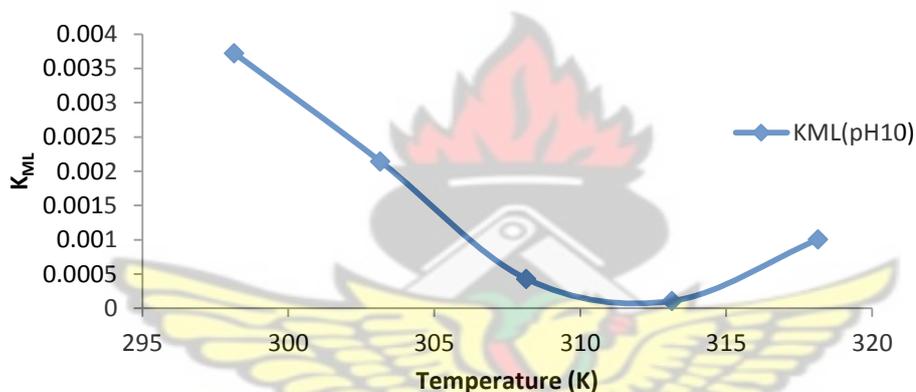


Figure 4.17: The variation of stability constant with temperature at pH 4.7 in aqueous



solution.

Figure 4.18: The variation of stability constant with temperature at pH 10 in aqueous solution.

The result also revealed that at pH 4.7 humic acid aggregation peaks at 30 and 40°C, and has a minimum at 35 °C (figure 4.19). At pH 10, aggregation of humic acid decreases from 25 °C to a minimum at 35 °C and then increases up to 45 °C (figure 4.19). Thus the minimum aggregation occurs at the same temperature, 35 °C, for both conditions of pH (figures 4.19 and 4.20).

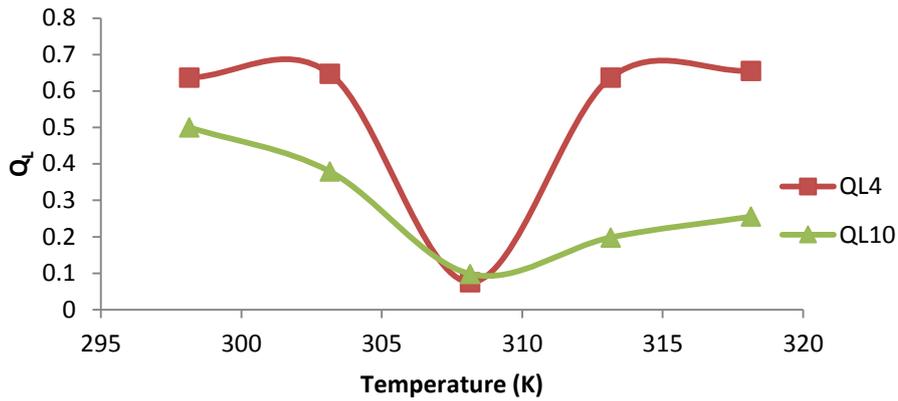
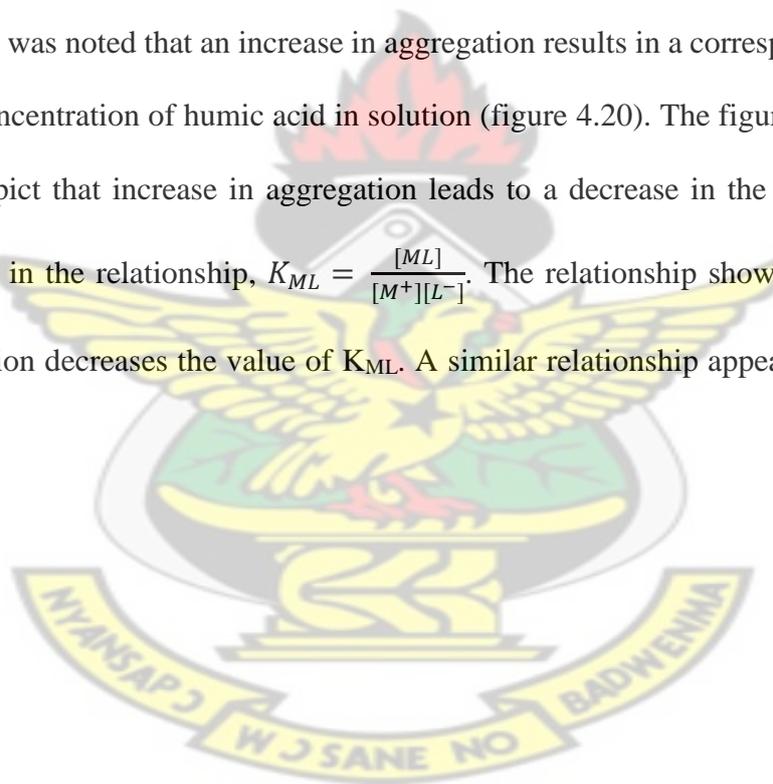


Figure 4.19: The variation of aggregation constant with temperature at pH 4.7 and 10 in aqueous solution.

It was noted that an increase in aggregation results in a corresponding decrease in the concentration of humic acid in solution (figure 4.20). The figures (figures 4.17-4.20) depict that increase in aggregation leads to a decrease in the value of K_{ML} as expected in the relationship, $K_{ML} = \frac{[ML]}{[M^+][L^-]}$. The relationship shows that, at pH 4.7 aggregation decreases the value of K_{ML} . A similar relationship appears to exist at pH 10.



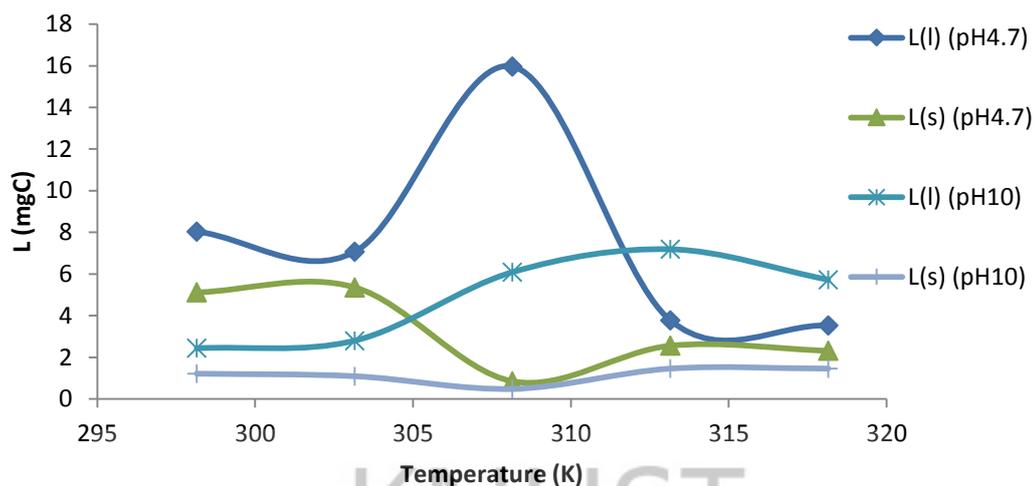


Figure 4.20: The variation of aggregated (s), and un-aggregated (l) ligands with temperature at pH 4.7 and 10 in aqueous solution.

4.4.2 The Effect of Humic Acid on Trace Metal Distribution in Soil-Solution System at Different Temperatures

The effect of humic acid on trace metal distribution was studied under different conditions of temperature. Observations revealed that the distribution constant for the metal has a maximum at 25 °C at pH 4.7 and 10. Minimum values were noted at 30 °C and 35 °C for pH 4.7 and 10 respectively as shown in figure 4.21.

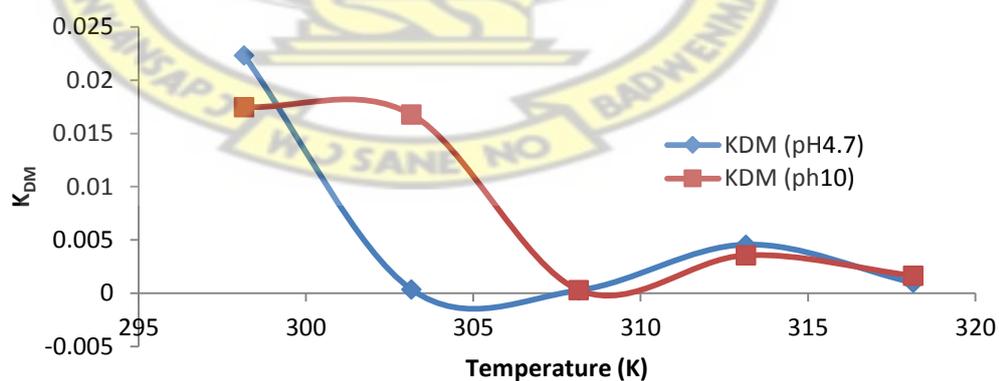


Figure 4.21: The variation of distribution constant with temperature at pH 4.7 and 10 in soil – solution system.

The plot (figure 4.21) indicates that metal concentration in the solution phase increases rapidly from 25 – 35 °C at pH 4.7 and 25 – 30 °C at pH 10. The rapid increase was observed to be followed by a gradual decrease in solution concentration of Cu.

Aggregation of humic acid in the soil - solution system has minimum values at 30 – 40 °C under both conditions of pH. Maximum values were noted to occur at 25 and 45 °C for pH 4.7 and 10 respectively. Fairly similar behavior was observed for the humic acid in aqueous solution containing metal and humic acid (figure 4.19) at both conditions of pH. This supposes that the aggregation characteristic of humic acid is virtually the same at any given temperature in both aqueous solution and soil – solution systems.

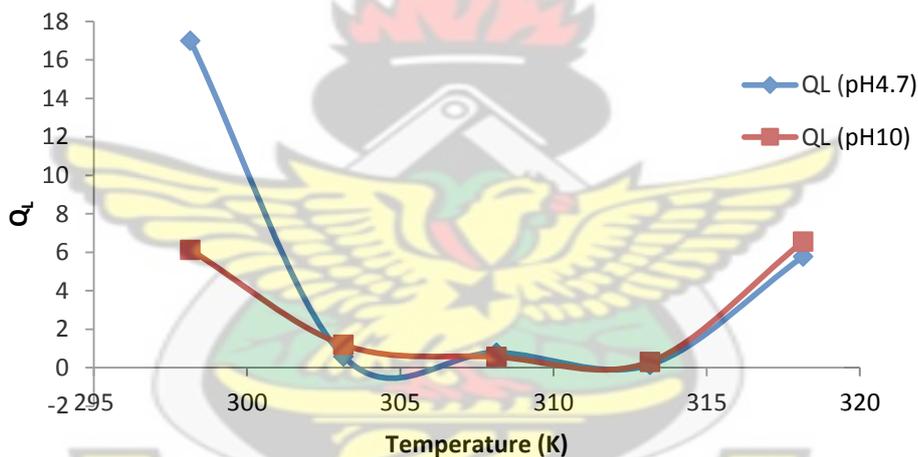


Figure 4.22: The variation of aggregation constant with temperature at pH 4.7 and 10 in soil - solution system.

The response of the stability constant, K_{ML} , for the formation of ML in aqueous solution to temperature changes was compared with the response of distribution constant, K_{DM} , and aggregation constant, QL , to temperature change. The outcome revealed that the temperatures at which K_{DM} is high are the temperatures at which K_{ML} is low (figures 4.17, 18, and 21). This implies that metal distribution changes with the amount of ML in the system. The interrelationship between variables does not break

down at all temperatures. Thus temperature has no effect on the chemical interaction of the species and as such it influences only the relative amounts of interacting species.

The deductions show that the response of K_{ML} to changes in temperature is the same in aqueous solution and soil – solution systems. Accordingly, these deductions presuppose that the free energies of the reaction between metal and humic acid in the two systems will have the same sign at all temperatures.

Relating the humic acid aggregation and metal distribution constants obtained from soil – solution system, divulged that humic acid aggregation constant increases with increase in metal distribution constant. Highest values of the two constants occur at 25 °C, and minimum values at 30 – 40 °C for both pH conditions. The apparent relationship exists because of the formation of pseudomicellar aggregation and ligand adsorption. When humic acid aggregates leave the solution phase they essentially transfer metals to the solid phase, and ultimately increase the distribution constant, K_{DM} .

It was observed that the aggregation constant, Q_L , varies inversely with K_{ML} . Reduction in Q_L leads to an increase in $[L^-]$, consequently K_{ML} will decrease. This relationship indicates that a decrease in Q_L must result in a corresponding decrease in $[ML]$, but it is not necessarily so. An increase in ML is also an expected outcome, because the formation of ML is also dependent on important factors such as pH, concentration of inorganic anions, adsorption capacity of mineral adsorbent, and concentration of free metal ions, etc.

4.4.3 Temperature Dependence of Metal Partition Constant in Soil-Solution System

The extent of trace metal partition in terrestrial environments (soil-solution system) is dependent on the prevailing geochemical conditions and the physicochemical

properties of the embathing solution. Partition constants for trace metals are thus identified in this study as a function of a number of chemical and physical processes which are determined by the nature of the system and prevailing geochemical conditions. Thus, in modeling the role humic substances play in trace metal partition in terrestrial environment, it is expedient to understand how metal partition is influenced by varying conditions of temperature. In this section the thermodynamics of metal complexation, partition, and phase separation of humic acid are discussed.

$$\text{pH 4.7: } \ln(K_{ML}) = 1.44114 - 3271.14(1/T)$$

Correlation Coefficient = 0.600184; R-squared = 36.022 percent; Standard Error of Est. = 0.41955; P-value = 0.284; Confidence level = 90%; $\Delta S = 11.98167 \text{ J/K.mol}$; $\Delta H = 27196.25796 \text{ J/K.mol}$

$$\text{pH 10: } \ln(K_{ML}) = -42.2033 + 10810.1(1/T)$$

Correlation Coefficient = 0.646167; R-squared = 41.7532 percent; Standard Error of Est. = 1.22878; P-value = 0.2358; Confidence level = 90%; $\Delta S = -350.8782 \text{ J/K.mol}$; $\Delta H = -89874.34 \text{ J/K.mol}$

$$\text{pH 4.7: } \ln(K_{DM}) = -39.7333 + 10269.3(1/T)$$

Correlation Coefficient = 0.518758; R-squared = 26.911 percent; Standard Error of Est. = 1.62876; P-value = 0.3705; Confidence level = 90%; $\Delta S = -330.3426562 \text{ J/K.mol}$; $\Delta H = -85378.9602 \text{ J/K.mol}$

$$\text{pH 10: } \ln(K_{DM}) = -44.4502 + 12016.6(1/T)$$

Correlation Coefficient = 0.74992; R-squared = 56.238 percent; Standard Error of Est. = 1.02016; P-value = 0.1444; Confidence level = 90%; $\Delta S = -369.5589628 \text{ J/K.mol}$; $\Delta H = -99906.0124 \text{ J/K.mol}$

$$\text{pH 4.7: } \ln(Q_L)_{\text{aqueous}} = -1.70948 + 251.129(1/T)$$

Correlation Coefficient = 0.0183598; R-squared = 0.0337081 percent; Standard Error of Est. = 1.31616; P-value = 0.9766; Confidence level = 90%; $\Delta S = -14.21261672 \text{ J/K.mol}$; $\Delta H = -2087.886506 \text{ J/K.mol}$

$$\text{pH 10: } \ln(Q_L)_{\text{aqueous}} = -13.9775 + 3875.6(1/T)$$

Correlation Coefficient = 0.513155; R-squared = 26.3328 percent; Standard Error of Est. = 0.623851; P-value = 0.3760; Confidence level = 90%; $\Delta S = -116.208935 \text{ J/K.mol}$; $\Delta H = -32221.7384 \text{ J/K.mol}$

$$\text{pH 4.7: } \ln(Q_L)_{\text{soil}} = -22.3074 + 6991.1(1/T)$$

Correlation Coefficient = 0.309972; R-squared = 9.60827 percent; Standard Error of Est. = 2.06368; P-value = 0.6117; Confidence level = 90%; $\Delta S = -185.4637236 \text{ J/K.mol}$; $\Delta H = -58124.0054 \text{ J/K.mol}$

$$\text{pH 10: } \ln(Q_L)_{\text{soil}} = -8.20541 + 2655.91(1/T)$$

Correlation Coefficient = 0.158905; R-squared = 2.52508 percent; Standard Error of Est. = 1.58809; P-value = 0.7985; Confidence level = 90%; $\Delta S = -68.21977874 \text{ J/K.mol}$; $\Delta H = -22081.23574 \text{ J/K.mol}$

NB: *Vant Hoff equation* $\left(\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}\right)$ was used to obtain the expressions above for the equilibrium partition and stability constants for humic acid partition and binding with Cu at pH 4.7 and 10.

The temperature dependence of metal partition was assessed by fitting the data into the Van't Hoff equation (see equations above). The outcome of the analysis indicates that the relationship between temperature (T) and the equilibrium constant, K_{ML} , for the formation of metal-humic complex; metal partition constant (K_{DM}); and humic acid aggregation constant for aqueous system, $(Q_L)_{\text{aqueous}}$, and soil-solution system, $(Q_L)_{\text{soil}}$, ranged from moderately strong to relatively weak relationship (as shown by the statistics of the Vant Hoff equations above).

The R^2 values suggest that at pH 4.7 and 10, temperature accounts for less than 60% of the factors responsible for changes in the values of the constants. Thus, as suggested in sections 4.4.1 and 4.4.2, not all the processes which influence metal partition are temperature dependent. The data also revealed that, humic acid partition constant in both systems, and metal partition constant in soil-solution system are all exothermic processes (as shown by the Vant Hoff equations above). This presupposes that while phase separation of humic acid as result of 'clouding' is temperature dependent, the subsequent transfer of the aggregates to the solid phase is not. The deduction implies that the physical and chemical processes responsible for the transfer of humic acid to the solid phase are not temperature controlled. This is probably one of the reasons for the reduction of K_{DM} with temperature (as observed in section 4.4.2). The collapse of outer-sphere complexes on the solid phase, and increased stability of colloidal suspensions after clouding, and the slow rate of transfer of metal bound humic aggregates are the possible reasons why increasing temperature reduces K_{DM} . The entropy values (see Vant Hoff equations above) also indicates that metal and humic acid transfer are not entropy driven, and the free energies as indicated from the

thermodynamic data of the Vant Hoff equations above shows that transfer to solution phase is more favourable than transfer to solid phase (that is for metal complex formation, metal and humic acid transfer within the system). The activation energy is negative at all the pH studied (section 4.3.6) for metal partition, and negative for humic acid partition (from the data above).

The data indicates that both metal and humic acid partitions in soil-solution system are exothermic, with negative entropy and activation energy values, hence the partition processes (with respect to metal and humic acid transfer to the solid phase) do not require external application of heat. In addition, observation made in this study indicates that, phase separation at cloud point is only a precursor to humic acid aggregation, precipitation and subsequent transfer to the solid phase (hence the weak relationship noted between Q_L and temperature at pH 4.7 and 10). Field studies (section 4.2.4) also revealed that the transfer of metal to the soil-solid phase is a spontaneous process. However, it must be noted that while the transfer of metal is not strictly temperature dependent, the availability of metal forms for transport is based on electrostatic and complexation processes (as indicated in sections 3.13.5 and 3.13.6), and the latter is temperature dependent at pH 4.7. As shown by the Vant Hoff equations above, K_{ML} is a function of temperature at pH 4.7, endothermic ($\Delta H = 27196.25796 \text{ J/K.mol}$), has positive entropy ($\Delta S = 11.98167 \text{ J/K.mol}$), and positive activation energy at all the temperatures studied (25, 30, 35, 40, and 45 °C). Hence the availability of metal-humic acid complex in the system is temperature dependent at low pH. However, at high pH (10) complexation is exothermic ($\Delta H = -89874.34 \text{ J/K.mol}$), not entropy driven ($\Delta S = -350.8782 \text{ J/K.mol}$), and has negative activation energy at all the temperatures studied, consequently complexation is a spontaneous process at high pH. The deductions therefore, suggest that the availability of metal forms for transport is

in-part temperature dependent if the total sum of metal forms to be transported includes humic-bound forms. In this respect therefore, it may be stated that the heat needed for metal complex formation at low pH is obtained from the exothermic processes in the system, since the metal and humic acid partition are, overall, exothermic processes. The partition of metal in soil-solution system is therefore synergistic. It is clearly evident that the inferences made in sections 4.4.1 and 4.4.2 are true, and that temperature does not influence the rate of metal partition but influences greatly the relative amounts of interacting species as a consequence of conformational change of the humic matter in the presence of metals at cloud point.

The moderately strong relationship (statistically) between K_{DM} and temperature is as a result of the dependence of metal partition on complexation, and the transfer of metal-bound humic acids to the solid phase. In addition, the ease with which humic acid separates from solution at all pH due to different conditions such as low pH, cloud point (temperature), high background electrolyte concentration, adsorption, and high metal concentration etc., enables it to control a fraction of the total trace metal in either phase of the soil-solution system. These account for the reason why K_{DM} is strongly related to Q_{DL} , Q_L and Q_{ML} as revealed during the modeling (in chapter 3.0) and proved in section 4.8. It can therefore, be stated that, the dependence of metal partition on temperature is purely a function of the temperature dependent processes (complexation and aggregation) that promote the availability of metal forms which have the potential to be transferred to the solid phase.

4.5 EFFECT OF ELECTROLYTE BACKGROUND CONCENTRATION ON THE BEHAVIOUR OF METAL AND HUMIC ACID IN SOIL

In order to understand the effect and implications of background electrolyte concentration on metals and humic acid behaviour and interactions. Binary and ternary systems were studied at pH 4.7 and 10 independently at electrolyte (KCl) concentration of 0.001, 0.005, 0.01, 0.05, and 0.1 mol/L. The composition of the systems are:

- 1) **Binary:** Aqueous solution (containing Cu and humic acid) and,
- 2) **Ternary:** Soil - solution system (a mixture of soil and water containing metal and humic acid).

4.5.1 Aqueous Solution

The data from the studies on metal-ligand interactions and ligand aggregation characteristics in aqueous solution shows that there was more M^+ at equilibrium than metal bound humic acid ($ML_{(aq)}$ and $ML_{(s)}$) at all pH. However, $[M^+]$ was higher at pH 4.7 than pH 10 which is an indication that metal binding increased with pH. As a result $[ML]$ is higher at pH 10 than pH 4.7. The data also revealed the occurrence of more un-aggregated humic acid, ($L_{(aq)}$), than the amount of aggregated humic acid, ($L_{(s)}$), at pH 4.7 and 10.

Table 4.14: Mass (mg) of Metal and Humic Acid Species in Aqueous Solution

| pH | Electrolyte (mol/L) | $M_{L(s)}$ | $M_{L(aq)}$ | M^+ | $L_{(aq)}$ | $L_{(s)}$ |
|-----|---------------------|------------|-------------|-------|------------|-----------|
| 4.7 | 0.001 | 0.090 | 0.084 | 1.553 | 4.875 | 0.244 |
| | 0.005 | 0.079 | 0.086 | 1.462 | 4.266 | 0.853 |
| | 0.01 | 0.108 | 0.078 | 1.293 | 4.022 | 1.219 |
| | 0.05 | 0.035 | 0.076 | 1.302 | 3.656 | 1.462 |
| | 0.1 | 0.031 | 0.073 | 1.446 | 3.169 | 2.437 |
| 10 | 0.001 | 0.122 | 0.096 | 1.025 | 10.603 | 2.194 |
| | 0.005 | 0.180 | 0.089 | 1.035 | 9.262 | 3.900 |
| | 0.01 | 0.222 | 0.089 | 1.081 | 8.775 | 6.337 |
| | 0.05 | 0.193 | 0.084 | 1.161 | 8.531 | 7.312 |
| | 0.1 | 0.185 | 0.083 | 1.252 | 8.166 | 7.800 |

The mass of metal bound to un-aggregated humic acid ($M_{L(aq)}$) decreases with increasing concentration of background electrolyte at pH 4.7 and 10. This indicates that metal binding to humic acids decreases with increase in electrolyte concentration. The observation presupposes that the concentration of background electrolyte has effect on the stability of ML species. The mass of humic acid in solution, $L_{(aq)}$, was noted to decrease with increasing concentration of background electrolyte, the mass of humic acid aggregates, $L_{(s)}$, on the other hand increase with electrolyte concentration as shown in table 4.14. This suggests that humic acid depletes from solution as a result of aggregation.

It was observed that, metal humic binding increases sharply at low electrolyte concentration. The sudden increase in the mass of metal bound to aggregated humic acid (figure 4.25-26), $M_{L(s)}$, results in a corresponding drop in the mass of metal bound to un-aggregated humic as shown below (figure 4.23).

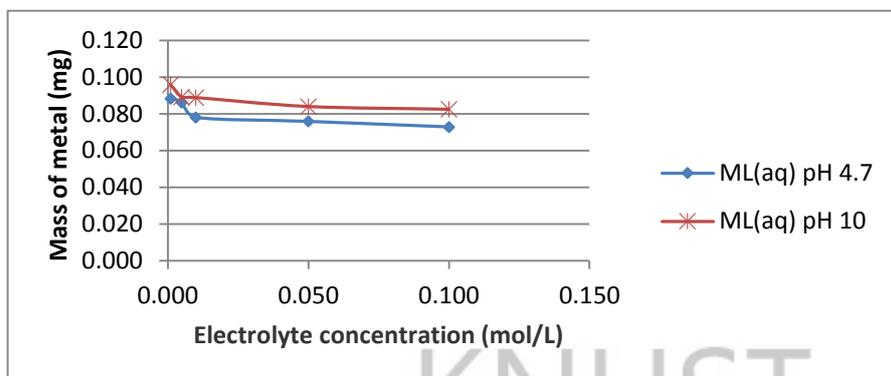


Figure 4.23: Changes in Mass of un-aggregated (aq) metal bound to humic acid with concentration of background electrolyte at pH 4.7 and 10

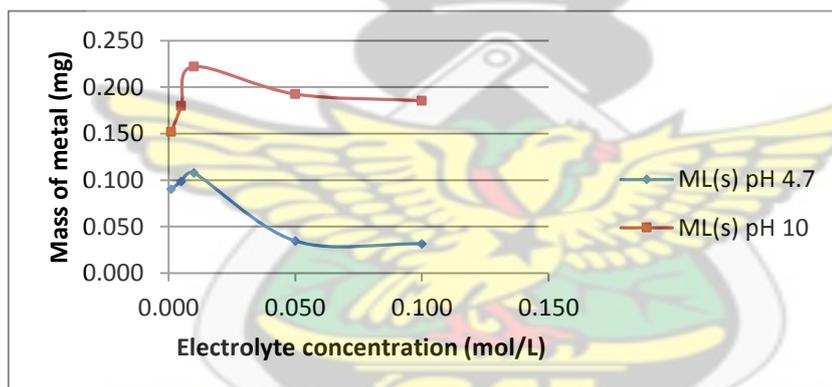


Figure 4.24: Changes in Mass of aggregated (s) metal bound to humic acid with concentration of background electrolyte at pH 4.7 and 10

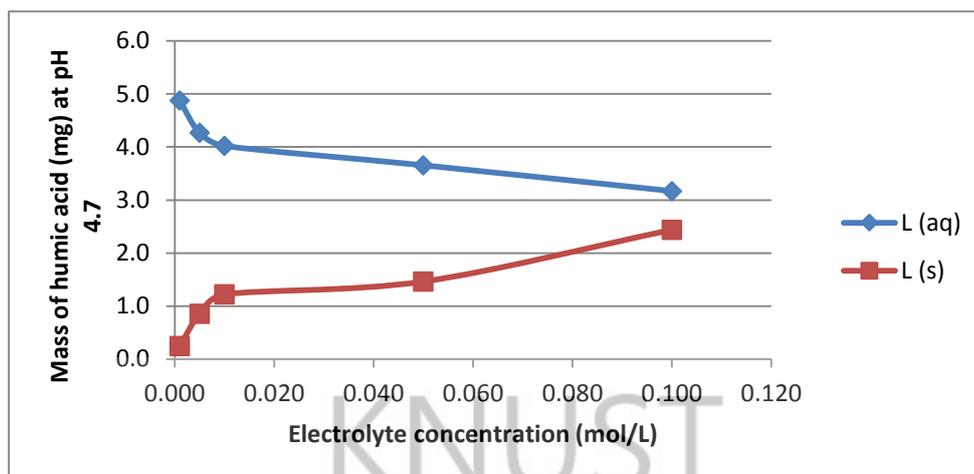


Figure 4.25: Changes in Mass of aggregated (s) and un-aggregated (aq) humic acid (L) with concentration of background electrolyte at pH 4.7

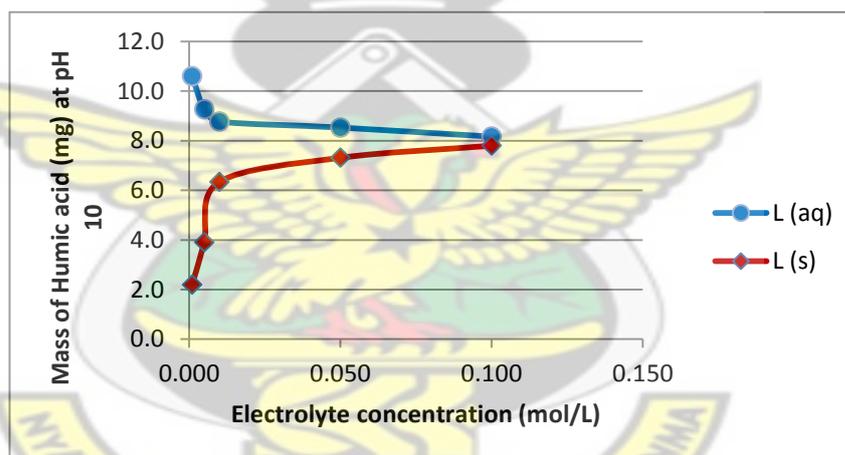


Figure 4.26: Changes in Mass of aggregated (s) and un-aggregated (aq) humic acid (L) with concentration of background electrolyte at pH 10

The behavior of the humic matter as shown in figures 4.24 and 4.26 where a sudden reduction in aqueous humic acid results in a corresponding rise in the aggregated form tend to suggest that it is the conversion of humic acid from soluble to insoluble form which accounts for the change in the amount of metal bound to it. This behavior was observed at both pH (4.7 and 10).

Figures 4.23 and 4.24 also indicate that more metal bind to the humic acid at pH 10 than pH 4.7. This supports the fact that metal binding increases with pH (Tipping 2002).

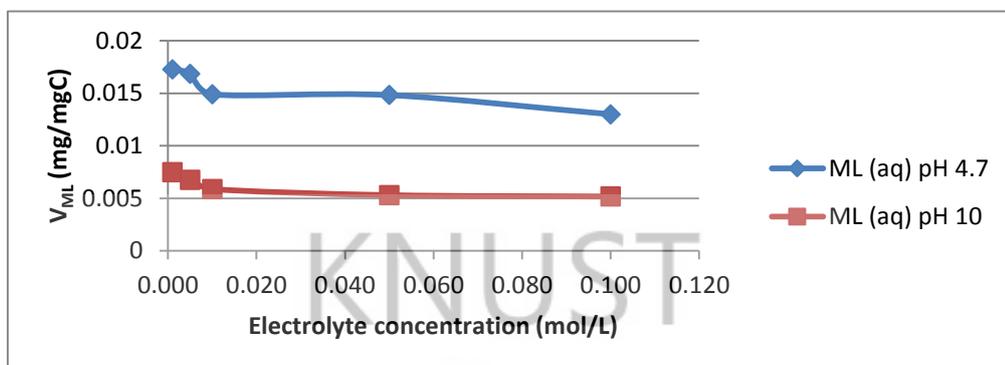


Fig 4.27: Changes in the extent of metal binding to un-aggregated humic acid (aq) with concentration of background electrolyte at pH 4.7 and 10

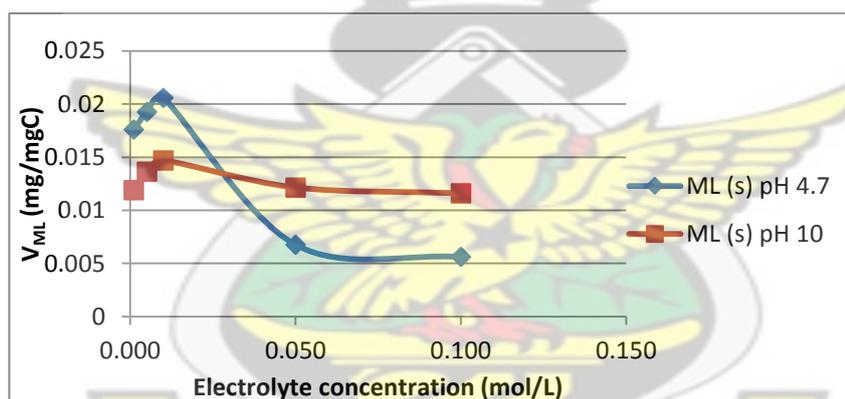


Fig 4.28: Changes in the extent of metal binding to aggregated humic acid in solution (s) with concentration of background electrolyte at pH 4.7 and 10

The plot of the extent of metal binding to humic acid ML against the concentration of background electrolyte indicates that beyond 0.01 mol/L electrolyte concentration, the amount of aqueous ML decreases with electrolyte concentration at both low and high pH (4.7 and 10). The characteristic rise in ML at low electrolyte concentration in both plots show that the metal – humic complex is stable at low electrolyte concentration (0.001-0.01), the instability of the complex occurs at

electrolyte concentration > 0.01 , and it is independent of pH. The observations support the inference that metal humic acid complexation decreases with salinity, and instability of the complex reaches a critical value at 0.01 mol/L of electrolyte concentration in this illustration.

It was also noted that even though the amount of humic acid aggregated increases with electrolyte concentration (fig 4.25-4.26), the amount of metal bound to the aggregated humic acid decreases with electrolyte concentration (fig 4.27) at both pH. The sharp drop in $ML_{(s)}$ at pH 4.7 from $0.01 - 0.05 \text{ mol/L}$ of background electrolyte below pH 10 line shows that more than one factor is responsible for humic acid aggregation, the metal of interest and protons. At pH 4.7 when the salinity is increased, aggregation of the humic acid will be expected to proceed in a more spontaneous manner because the total number of cations (M^+ and H^+) will apparently double or increase by a fraction greater than 1.0 and cause increased neutralization of the humic acid. This will result in a situation whereby even though binding increases with pH (figs 4.23 and 4.24), the amount of metal bound to humic acid will apparently appear to be low at high pH (10) than low pH (4.7) because of cation-cation competition for humic acid (figs 4.27 and 4.28).

The aggregation quotient, $Q_L = L_{(s)} / L_{(aq)}$, which is a measure of the extent of aggregation is observed to increase with the concentration of background electrolyte. The aggregation increases rapidly at low electrolyte concentration ($0.001-0.01 \text{ mol/L}$) and proceed gently at electrolyte concentration > 0.01 at pH 4.7 and 10 (fig 4.29).

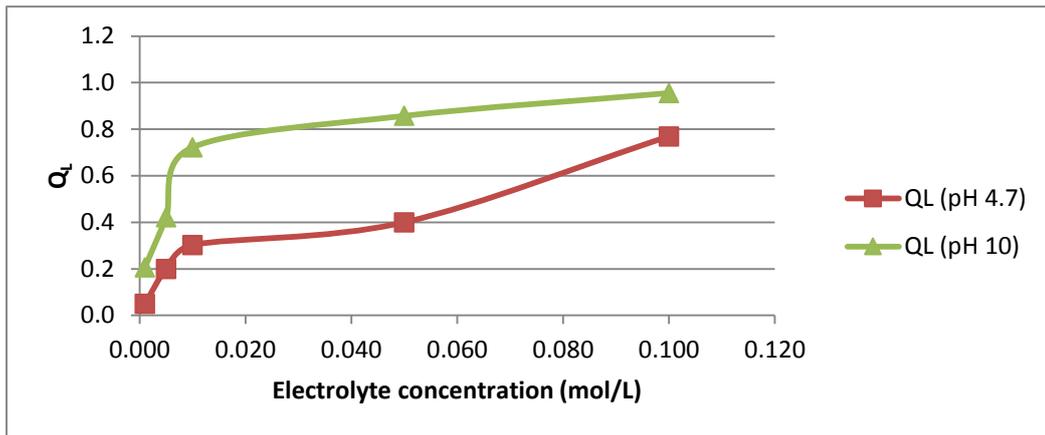


Fig 4.29: Variation of aggregation quotient with concentration of background electrolyte at pH 4.7 and 10

Regression analysis of the data gave P-value < 0.01 indicating that there is a statistically significant relationship between aggregation quotient and electrolyte concentration at 99% confidence level or higher as shown below (table 4.15).

Table 4.15: Relationship between aggregation quotient and concentration of background electrolyte

| | |
|----------------|--|
| <i>pH 4.7:</i> | $\frac{1}{Q_L} = \frac{0.0184499}{[\text{Electrolyte}]} + 1.51233$ |
| | Correlation Coefficient = 0.998767; R-squared = 99.7536 percent; Standard Error of Est. = 0.441916; P-value = 0.0001; Confidence level = 99% |
| <i>pH 10:</i> | $\frac{1}{Q_L} = \frac{0.00374048}{[\text{Electrolyte}]} + 1.16633$ |
| | Correlation Coefficient = 0.986337; R-squared = 97.256 percent; Standard Error of Est. = 0.301076; P-value = 0.0019; Confidence level = 99% |

Where [Electrolyte] = concentration of background electrolyte (mol/L).

The R-Squared statistic indicates that the model as fitted explains 99.7536% of the variability in Q_L after transforming to a reciprocal scale to linearize the model. The

model also shows that aggregation is a function of salinity at constant temperature and pH.

The correlation coefficients indicate a relatively strong relationship between the variables, as the model was used to predict the aggregation quotient at the two pH. The outcome shows the same characteristic as the experimental value (fig 4.29). The observed and predicted Q_L values were not significantly different from each other (fig 4.31 and 4.32) at both pH.

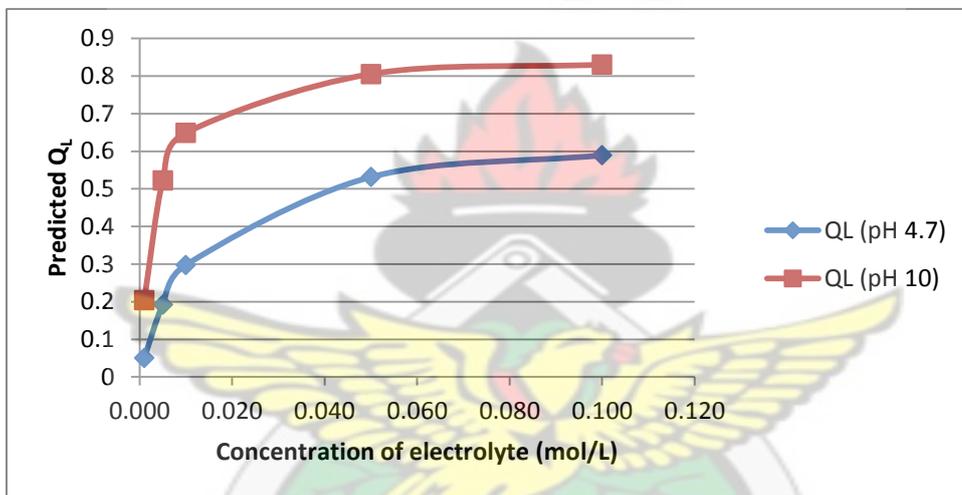


Fig 4.30: Plot of predicted aggregation quotient with concentrated background electrolyte at pH 4.7 and 10

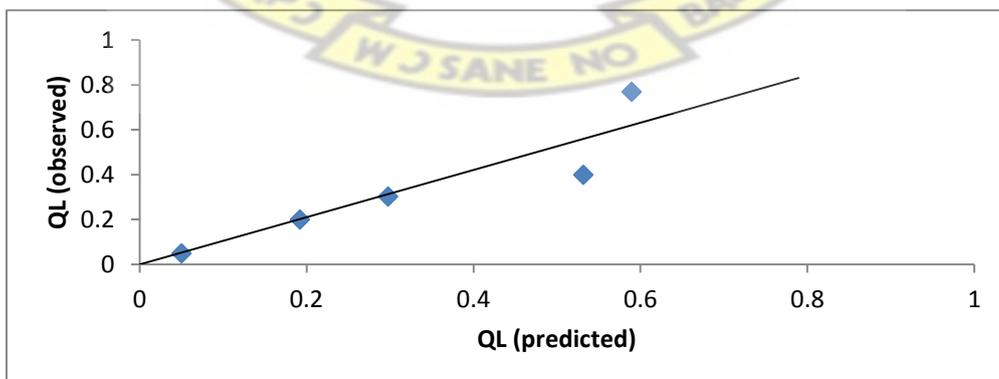


Fig 4.31: Observed versus predicted aggregation quotient at pH 4.7

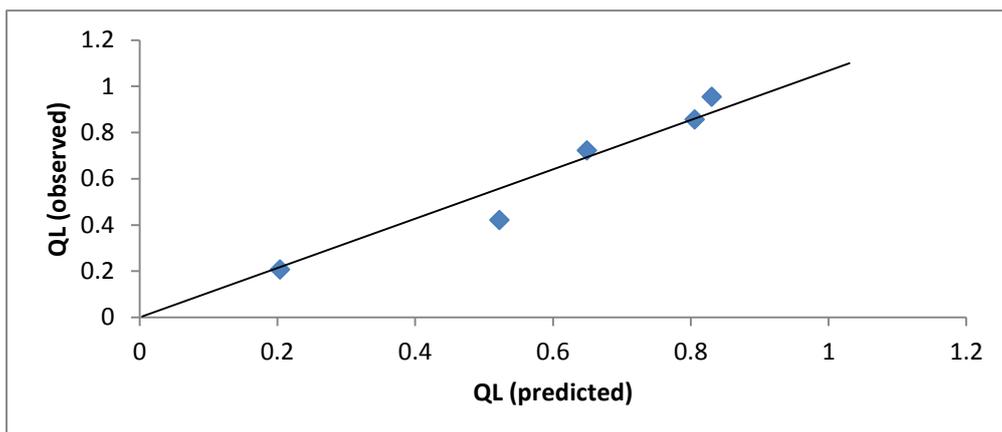


Fig 4.32: Observed versus predicted aggregation quotient at pH 10

The free energy of the aggregation process at both pH revealed that the thermodynamic stability of humic acid aggregates increases with electrolyte concentration (fig 4.33). The rapid aggregation process at low electrolyte concentration is as a result of a rapid increase in the entropy of the system due to coulombic effects. According to Wandruzska and Engebretson (2001), when salts are added to humic acids, the initial interactions between the cations and negatively charged groups on humic acid are purely coulombic in nature. They added that, “outer sphere” complexes form relatively quickly and are responsible for the initial contraction of the humic acid chains, and the establishment of enhanced pseudomicellar domains. The complexes formed are not thermodynamically stable and slowly change as the metal finds its optimal location within the humic structure, as a consequence the domains gradually disintegrate. This suggests that the link observed (fig 4.29) is due to the formation of pseudomicellar domains.

Conformational change leading to aggregation at constant temperature and pH was observed to be endergonic thermodynamic process (figure 4.33). The free energies also suggest that the aggregated form will predominate in the system at electrolyte concentrations $\gg 0.1\text{mol/L}$ (figure 4.33).

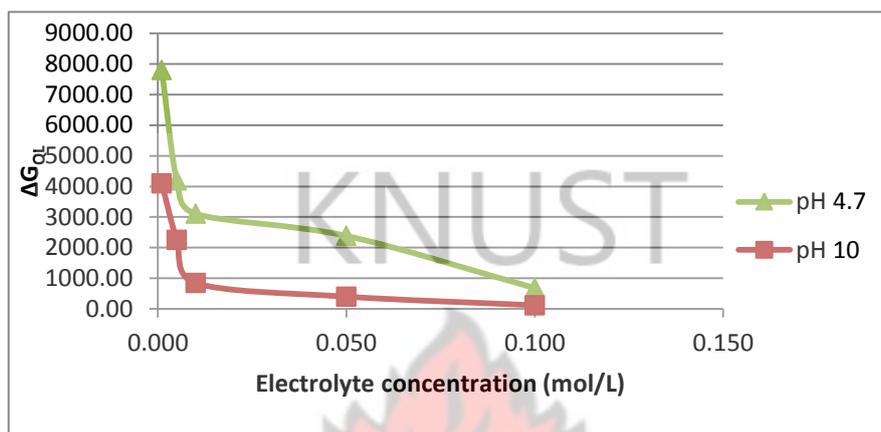


Fig 4.33: Changes in free energy of aggregation with concentration of background electrolyte

Regression analysis of the experimental data shows that the stability constant for the formation of metal humic complex varies inversely as the concentration of background electrolyte as shown in table 4.16. A moderately strong relationship exists between the variables at 90% confidence level ($P\text{-value} \geq 0.1$). The relationship is statistically significant at 90% confidence level and can explain a significant proportion of the variability ($R^2 > 55\%$) which control the stability of ML complex in aqueous solution containing the species.

Table 4.16: Relationship between stability constant of ML complex and concentration of background electrolyte

pH 4.7:

$$\frac{1}{K_{ML}} = 116119.0 * [\text{Electrolyte}] + 93956.5$$

Correlation Coefficient = 0.74738; R-squared = 55.8688 percent; Standard Error of Est. = 5026.9; P-value = 0.1465; Confidence level = 90%

pH 10:
$$\frac{1}{K_{ML}} = 706614.0 * [\text{Electrolyte}] + 220804.0$$

Correlation Coefficient = 0.84587; R-squared = 715496 percent; Standard Error of Est. = 21699.2; P-value = 0.0709; Confidence level = 90%

Where [Electrolyte] = concentration of background electrolyte.

5.5.2 Soil – Solution System

The effect of electrolyte concentration on trace metal speciation and distribution under humic conditions in soil was also investigated. The data generated revealed that the mass of metal bound to humic acid in the aqueous phase ($M_{L(aq)}$) and the mass of humic acid in the aqueous phase ($MassL_{(aq)}$) decrease with increase in the concentration of background electrolyte at both conditions of pH (4.7 & 10). The free metal ion (M^+) on the other hand, increased with increase in the concentration of the electrolyte as shown in the table 4.17. The mass of metal adsorbed to the solid phase adsorbent (MS) decreased with increasing concentration of the electrolyte whereas the mass of humic acid in the solid phase ($MassL_{(s)}$) increased with increase in electrolyte concentration at both pH. The mass of metal bound to the humic acid in the solid phase ($M_{L(s)}$) decreased with increasing concentration of the electrolyte at pH 4.7 and increased with increasing concentration of the electrolyte at pH 10 (table 4.17).

Table 4.17: Changes in the amount* of metal and ligand forms with Concentration Background Electrolyte in Soil-solution System

| pH | Electrolyte (mol/L) | $M_{L(aq)}$ | $M_{L(aq)}$ | M^+ | MassL(aq) | MassL(s) | $M_{L(s)}$ | $M_{L(s)}$ | MS |
|-----|---------------------|-------------|-------------|---------|-----------|----------|------------|------------|------|
| 4.7 | 0.00100 | 0.07380 | 0.00893 | 0.01230 | 5.34906 | 2.91767 | 0.00119 | 0.00981 | 0.58 |
| | 0.00500 | 0.06800 | 0.00857 | 0.02110 | 4.70069 | 3.23375 | 0.00077 | 0.00610 | 0.51 |
| | 0.01000 | 0.06550 | 0.00831 | 0.03210 | 4.37650 | 3.50120 | 0.00042 | 0.00330 | 0.41 |
| | 0.05000 | 0.05980 | 0.00820 | 0.03910 | 3.56604 | 3.72813 | 0.00034 | 0.00250 | 0.47 |
| | 0.10000 | 0.04780 | 0.00638 | 0.03956 | 3.24185 | 4.25493 | 0.00029 | 0.00220 | 0.24 |
| 10 | 0.00100 | 0.07430 | 0.00881 | 0.03660 | 5.99743 | 2.43139 | 0.00038 | 0.00320 | 0.51 |
| | 0.00500 | 0.05830 | 0.00668 | 0.03590 | 5.83533 | 2.89335 | 0.00047 | 0.00410 | 0.25 |
| | 0.01000 | 0.05010 | 0.00594 | 0.03850 | 5.34906 | 3.07976 | 0.00070 | 0.00590 | 0.20 |
| | 0.05000 | 0.04680 | 0.00533 | 0.04050 | 4.70069 | 4.08473 | 0.00073 | 0.00640 | 0.18 |
| | 0.10000 | 0.03990 | 0.00436 | 0.04250 | 4.21441 | 4.93572 | 0.00111 | 0.01020 | 0.11 |

NB: *The units of MassL(aq), MassL(s), are in mgC; $M_{L(aq)}$, $M_{L(s)}$, and MS are in mg/10g soil; $M_{L(aq)}$, and $M_{L(s)}$, are in mg/mgC

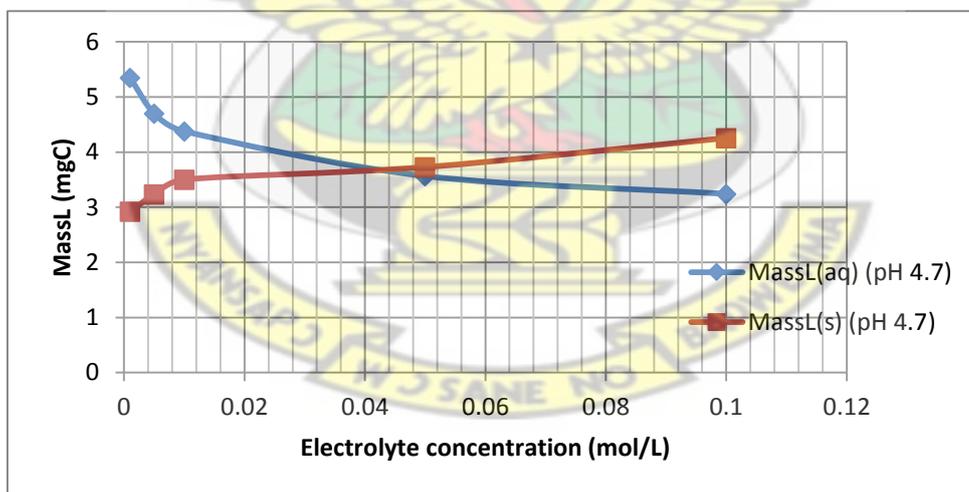


Fig 4.34: Mass of aggregated (s) and un-aggregated (aq) humic acid versus electrolyte concentration in soil-solution system at pH 4.7

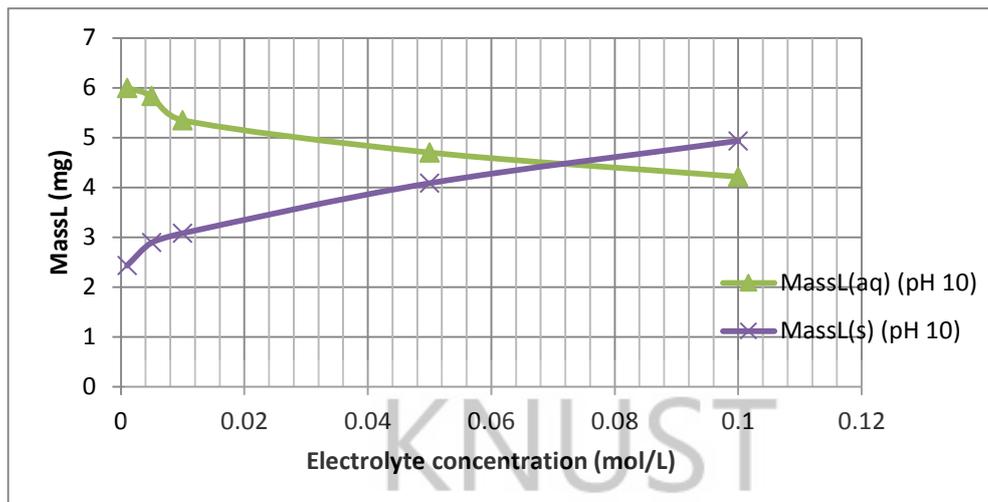


Fig 4.35: Mass of aggregated (s) and un-aggregated (aq) humic acid versus electrolyte concentration in soil-solution system at pH 10

The figures 4.34 and 4.35 show that the characteristic rise in aggregation of humic acid as a result of the formation of pseudomicellar domains, followed by a gradual increase as observed in aqueous solution (figures 4.34 and 4.35) also occur in soil – solution system. In addition, the effect appears to be more pronounced at low pH than high pH, probably because of the apparent reduction of free metal concentration at high pH (due to surface adsorption by the soil). Wandruzska and Engebretson (2001) stated that at low salt concentration, humic acids are not swamped by metal ions and such interactions are not conducive for the formation of enhanced pseudomicelles. In addition, the amounts of humic acid in the solid and solution phases were equal at pH 4.7 and 10 at background electrolyte concentrations 0.0415 and 0.066 mol/L respectively (figure 4.34 and 4.35). This suggests that increasing background electrolyte implies pushing the humic acid aggregation process through stages of thermodynamically non-spontaneous phase ($\Delta G > 0$) to an equilibrium phase ($\Delta G = 0$) and finally to a spontaneous aggregation stage ($\Delta G < 0$). The critical electrolyte

concentration where aggregation reaches equilibrium is lower at pH 4.7 (0.041 mol/L) than pH 10 (0.67 mol/L) probably because the humic acid and soil surface are more negatively charged at pH 10 than at pH 4.7, as such more electrolyte ions are required at higher pH. The concentration of added electrolyte at which aggregation reaches equilibrium is expected to be lower for soil - solution systems than aqueous systems (compare figures 4.23, 4.24, 4.34 and 4.35) at both pH. This is because in soil - solution systems desorption of metals from the solid phase increases the concentration of the solution phase, therefore the ionic strength of the solution phase of a soil - solution system will be higher than aqueous systems when the same amount of electrolyte is added to the systems. On this basis, low added electrolyte concentrations will be required to bring aggregation process to equilibrium faster in soil – solution system than in aqueous system.

It was observed under all pH conditions that the metal distribution constant (K_{dm}) and the stability constant for M-L complex were noted to decrease with increase in electrolyte concentration. The distribution constant (K_{dL}) for humic acid transfer to the solid phase, and the aggregation constant on the other hand, increased with increasing electrolyte concentration (table 4.18).

Table 4.18: Variation of aggregation quotient, stability and distribution constants with electrolyte concentration

| pH | Electrolyte (mol/L) | K_{ML} | K _{dm} | K _{dL} | Q_L |
|-----|---------------------|----------|-----------------|-----------------|----------|
| 4.7 | 0.001000 | 0.000188 | 0.024045 | 0.001909 | 0.545455 |
| | 0.005000 | 0.000115 | 0.020478 | 0.002408 | 0.687931 |
| | 0.010000 | 0.000076 | 0.015026 | 0.002800 | 0.800000 |
| | 0.050000 | 0.000075 | 0.016973 | 0.003659 | 1.045455 |
| | 0.100000 | 0.000064 | 0.009936 | 0.004594 | 1.312500 |
| 10 | 0.001000 | 0.000054 | 0.016974 | 0.001459 | 0.405405 |
| | 0.005000 | 0.000042 | 0.009504 | 0.001735 | 0.495833 |
| | 0.010000 | 0.000037 | 0.008262 | 0.001958 | 0.575758 |
| | 0.050000 | 0.000039 | 0.007682 | 0.003041 | 0.868966 |
| | 0.100000 | 0.000040 | 0.005535 | 0.004216 | 1.171154 |

The results of fitting the data to curvilinear models show that K_{DM} and K_{ML} are strongly related to the concentration of background electrolyte at all the pH studied. The models also indicated that the relationship, shown below (Table 4.19), can explain over 90% of the variability in the data. The models indicate that metal complexation and distribution reduce with increase in background electrolyte concentration.

The statistical analysis also indicated that the distribution (K_{DL}) and aggregation (Q_L) constants for humic acid, as shown below (Table 4.19 and 4.20), were strongly related with the electrolyte concentration. However, the models obtained after fitting the data to curvilinear models revealed that increasing the concentration of the background electrolyte doubles the aggregation (Q_L) and the amount of humic acid in the solid phase (and hence K_{DL}) of the soil – solution system at both pH. That is the magnitude of aggregation and distribution constants for humic acid vary with the square root of electrolyte concentration as shown below (Table 4.19) at both pH conditions studied.

Table 4.19: Relationship between aggregation quotient, stability and distribution constants with electrolyte concentration at pH 4.7

| |
|--|
| $K_{ML} = 1.19414E - 7 \left(\frac{1}{C_{\text{electrolyte}}} \right) + 0.0000719468$ <p>Correlation Coefficient = 0.97391; R-squared = 94.85 percent; Standard Error of Est. = 0.000134094; P-value = 0.0050; Confidence level = 99%</p> |
| $Q_L = 2.55904 \left(\sqrt{C_{\text{electrolyte}}} \right) + 0.49842$ <p>Correlation Coefficient = 0.994621; R-squared = 98.9271 percent; Standard Error of Est. = 0.0363581; P-value = 0.0005; Confidence level = 99%</p> |
| $K_{dL} = 0.00895665 \left(\sqrt{C_{\text{electrolyte}}} \right) + 0.00174447$ <p>Correlation Coefficient = 0.994621; R-squared = 98.9271 percent; Standard Error of Est. = 0.000127253; P-value = 0.0005; Confidence level = 99%</p> |
| $K_{dm} = 0.00000834164 \left(\frac{1}{C_{\text{electrolyte}}} \right) + 0.0161714$ <p>Correlation Coefficient = 0.886784; R-squared = 78.6386 percent; Standard Error of Est. = 0.00209516; P-value = 0.0449; Confidence level = 95%</p> |
| $K_{dm} = 6.191 * ML_{(s)} + 0.0200252 * MS + 0.0051426$ <p>R-squared = 99.6023 percent; Standard Error of Est. = 0.000350138; Mean absolute error = 0.000188262; P-value = 0.004; Confidence level = 99%</p> |

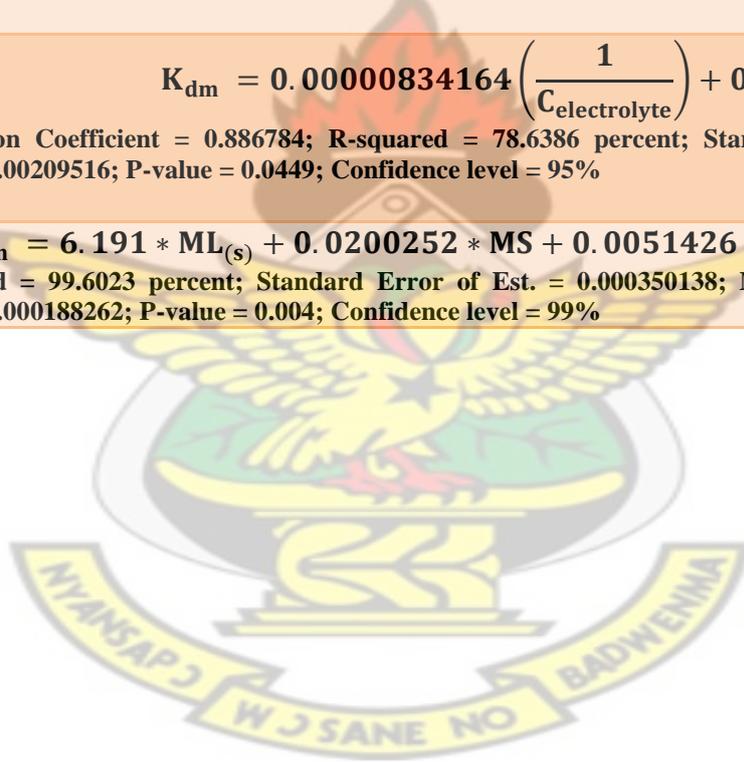


Table 4.20: Relationship between aggregation quotient, stability and distribution constants with electrolyte concentration at pH 10

$$K_{ML} = 1.60312E - 8 \left(\frac{1}{C_{\text{electrolyte}}} \right) + 0.0000381291$$

Correlation Coefficient = 0.977837; R-squared = 95.6166 percent; Standard Error of Est. = 0.00; P-value = 0.00

$$Q_L = 2.65157 \left(\sqrt{C_{\text{electrolyte}}} \right) + 0.309842$$

Correlation Coefficient = 0.997713; R-squared = 99.5431 percent; Standard Error of Est. = 0.0245077; P-value = 0.0001; Confidence level = 99%

$$K_{dL} = 0.00959755 \left(\sqrt{C_{\text{electrolyte}}} \right) + 0.0010574$$

Correlation Coefficient = 0.99471; R-squared = 98.9448 percent; Standard Error of Est. = 0.000135218; P-value = 0.0005; Confidence level = 99%

$$K_{dm} = 0.0000102675 \left(\frac{1}{C_{\text{electrolyte}}} \right) + 0.00686036$$

Correlation Coefficient = 0.980631; R-squared = 96.1638 percent; Standard Error of Est. = 0.000988276; P-value = 0.0032; Confidence level = 99%

$$K_{dm} = 77727.2 * K_{ML} + 11.2463 * Q_L - 3203.74 * K_{dL} - 414.623 * K_{dms} - 1.81553$$

R-squared = 100 percent; Standard Error of Est. = 0.00; Mean absolute error = 0.00; P-value = 0.0



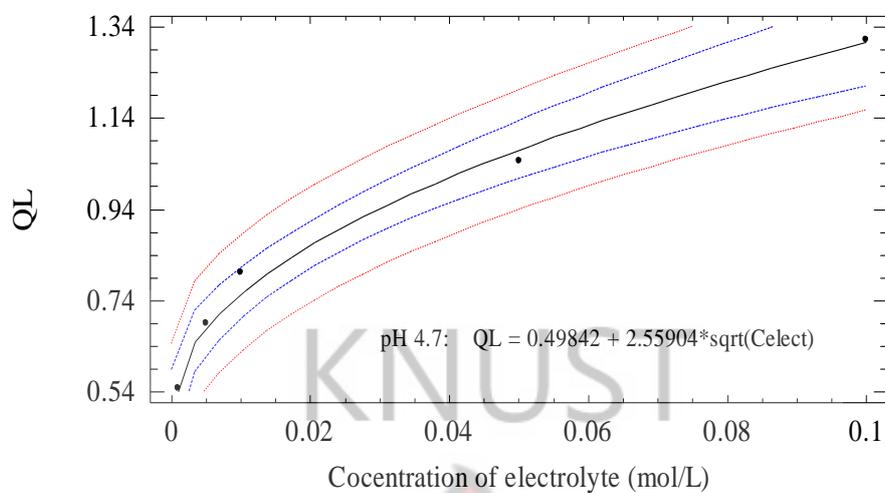


Fig 4.36: Plot of fitted model for the relationship between aggregation quotient and concentration of background electrolyte

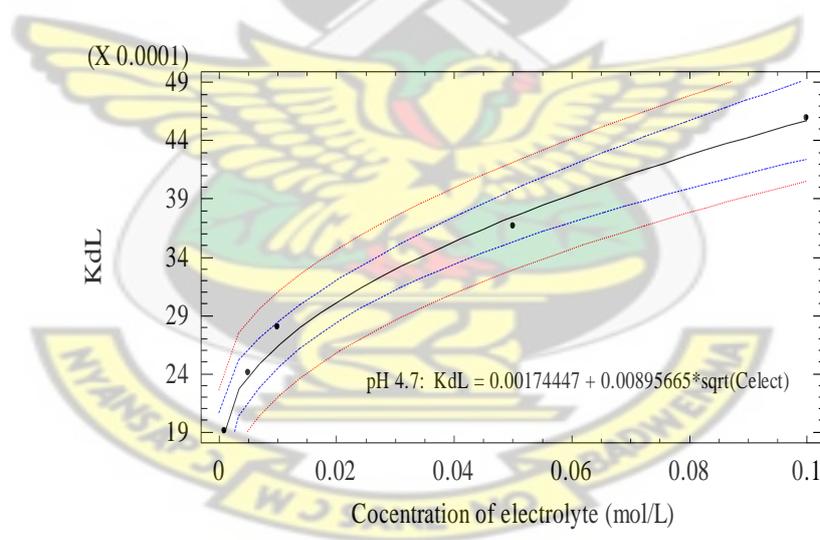


Fig 4.37: Plot of fitted model for the relationship between distribution constant for humic acid and concentration of background electrolyte

Plots of the fitted models above also show the presence of the characteristic sharp rise in aggregation and reduction in M-L Complexation at low electrolyte concentrations at all pH.

The results of multiple regression analysis below depict that the distribution of trace metal in the soil – solution system is controlled by the K_{ML} and K_{dL} at pH 4.7. At pH 10 the distribution of trace metal in the soil – solution system is controlled by the K_{ML} , K_{dL} , and Q_L . The observation implies that trace metal distribution under increasing concentration of electrolyte may be effectively explained in terms of ligand adsorption to mineral surface, ligand aggregation and metal – humic complexation. Whereas complexation effect on metal distribution occurs at all pH, it may be deduced from the models that at pH 4.7 ligand adsorption other than aggregation is mainly the characteristic of humic acid which influences metal distribution. At pH 10 both ligand adsorption and aggregation are responsible for changes in metal distribution.

pH 4.7: $K_{dm} = 6.191 * ML_{(s)} + 0.0200252 * MS + 0.0051426 \dots\dots\dots 4.1$

R-squared = 99.6023 percent; Standard Error of Est. = 0.000350138; Mean absolute error = 0.000188262; P-value = 0.004; Confidence level = 99%

$$K_{dm} = 77727.2 * K_{ML} + 11.2463 * Q_L - 3203.74 * K_{dL} - 414.623 * K_{dms} - 1.81553 \dots\dots\dots 4.2$$

R-squared = 100 percent; Standard Error of Est. = 0.00; Mean absolute error = 0.00; P-value = 0.0

The data which also indicate that the extent of metal adsorbed to sorption sites in the soil decrease with increase in the concentration of free metal ions in solution (C_{M+}) (table 4), suggests that adsorption to mineral surface is influenced by competition for the adsorption sites by the electrolyte cation (K^+). A similar observation was made by Petruzzelli and Pezzarossa (2003) in a research on the influence of ionic strength on heavy metal sorption processes by soil. Petruzzelli and Pezzarossa (2003) concluded that increase in ionic strength (by the addition of $CaCl_2$), decrease the sorption of Cd and Cu, due to the competition of Ca ions for the sorption sites in the soils. They added

that influence of ionic strength was related to the mechanisms of heavy metal sorption by the soil.

It may be stated that the effect of background electrolyte concentration on trace metal distribution in soil is as a result of its ability to induce ligand aggregation, reduce metal – ligand complexation, and initiate competition of electrolyte cation (K^+) with the metal of interest for sorption sites in the soil. The hydrophobicity/aggregation and metal complexing properties of humic acid are considered as what allows it to significantly affect the distribution constant of metal in soil solution system under various conditions of ionic strength.

5.5.3 Modeling the Effect of Background Electrolyte

In order to affirm the remarks about the effect of background electrolyte on trace metal distribution in soil, statistical component factor analysis for data reduction was used to determine the processes which are affected by electrolyte concentration. The models (equations 4.3 and 4.4) were obtained using the selection criteria, eigenvalues > 0.7 and correlation coefficient > 0.8 (appendix: ionic strength factor analysis). The models show that electrolyte concentration accounts for 90.5% of the variables which influence metal distribution in soil – solution system at pH 4.7, and at pH 10 it accounts for 99.79% of the variables. The models also show that only one factor, $f_{metal\ adsorption}$, may be used to explain the effect of electrolyte concentration at pH 4.7, and at pH 10 two factors are required, $f_{aggregation}$ and $f_{metal\ adsorption}$. The metal adsorption factor, $f_{metal\ adsorption}$, implies metal ligand binding and metal sorption by soil, while aggregation factor, $f_{aggregation}$, implies metal induced pseudomicellar aggregation.

$$\text{Electrolyte effect}_{(pH\ 4.7)} = 0.9050 f_{\text{metal adsorption}} \dots\dots 4.3$$

$$\text{Electrolyte effect}_{(pH\ 10)} = 0.8495 f_{\text{aggregation}} + 0.1483 f_{\text{metal adsorption}} \dots\dots 4.4$$

The increase in free metal ion (M^+) is as a result of competition at the soil surface, because metal adsorption decreases with increase in electrolyte concentration, in addition, metal - ligand complexation decreases with electrolyte concentration (Tables 4.17-19). These processes promote the formation of hydrophobic forms of the humic acid. Therefore at pH 4.7 electrolyte concentrations directly influence metal binding to humic acid, and the reduction of the extent of metal adsorption at mineral surface, as shown by model 4.3. The implication of the factor model is that increasing electrolyte concentration decreases metal distribution in soil – solution system by reducing metal adsorption and decreasing metal ligand complexation. Therefore the only means by which metal will be transferred to the solid phase is through complexation and the formation of hydrophobic forms of humic acid. The rotated factor pattern confirms this fact by indicating that $f_{\text{metal adsorption}} = 0.84ML$ (where 0.84 is a measure of the strength of the relationship between the variables) which implies that the factor is characterized by complexation. Thus pseudomicellar aggregates are not major forms by which humic acid transfers metal to the solid phase at low pH (4.7 in this case). Thus, adsorption of Cu to the solid phase directly or through ternary complex formation, is likely to be the major means by which Cu is transferred to the solid phase.

At pH 10 on the other hand metal adsorption factors account for only 14.83% of the processes influenced by electrolyte concentration, and aggregation factor accounts for 84.95%. Humic acids are hydrophilic at high pH (Tipping, 2002) and because it is highly deprotonated at pH 10 it is expected that more metal will bind to the ligand, but the presence of other anions such as OH^- and Cl^- from the electrolyte

and the presence of K^+ will initiate competition in the system. Metal competition for the ligand and anion competition for the metal will ultimately reduce the average mass of metal bound to humic acid to be lower at high pH than low pH (Table 4.17). Electrostatic interaction in the system solution leads to aggregation of humic acid, which is the reason why aggregation is the major process affected by electrolyte concentration. The aggregates formed at pH 10 will transfer associated metals from solution phase to the solid phase, therefore at high pH increase in electrolyte concentration influences metal distribution mainly by inducing humic acid aggregation, and influencing metal adsorption within the system.

4.6 THE DYNAMICS OF METAL AND HUMIC ACID INTERACTIONS IN SOIL-SOLUTION SYSTEM

Dynamics of Metal and Humic Acid Interactions: An experiment where the concentration of trace metal in a soil - solution system containing the 0.02g of humic acid was varied at constant temperature (40 °C), and bulk density (solid solution ratio of 1:5) was conducted to investigate the effect of metal - humic acid interactions on the distribution of the metal in the system. The data obtained in table 4.21 indicated that the amount of free metal concentration in solution (M^+), metal adsorbed on soil absorption sites (M_S), metal bound to humic acid in soil phase ($M_{HA(s)}$) and the mass of humic acid in the soil phase ($L_{(s)}$) increased with increase in the mass of metal added to the system. The mass of metal bound to humic acid in solution ($M_{HA(aq)}$) and the mass of free humic acid in solution ($L_{(aq)}$) decreased with increase in M_{added} . These trends were observed at pH 3.72 – 10 (table 4.21).

It was observed that the mass of metal bound per unit mass of humic acid in the solution phase ($ML_{(aq)}$) decreases with increase in M_{added} , but the mass of metal bound

per unit mass of humic acid in the solid phase ($ML_{(s)}$) increased with increase in M_{added} (table 4.22). Even though the mass of metal bound per unit mass of humic acid in the solution phase decreased giving the impression that metal-humic complexation declined upon increasing metal concentration in the system, the extent of metal binding to humic acid in the system illustrates that complexation actually increase when the concentration of metal in the system is increased. The apparent reduction in complexation in the solution phase proves that humic acid was transferred to the solid phase, hence the increase in $ML_{(s)}$ with concentration of metal in the system. The inference suggests that increasing metal concentration in the system promotes hydrophobicity of the humic acid, and consequently increased aggregation ($L_{(s)}$).



Table 4.21: Changes in the amount* of metal and ligand forms with Mass of Metal-Added in Soil-solution System

| pH | Mass of species (mg) | | | | | | |
|------|----------------------|---------|----------------|--------------------|---------------------|-------------------|------------------|
| | M _{added} | MS | M ⁺ | M _{HA(s)} | M _{HA(aq)} | L _(aq) | L _(s) |
| 3.72 | 0.4 | 0.08430 | 0.00890 | 0.18900 | 0.00160 | 9.36625 | 60.74208 |
| | 0.8 | 0.16330 | 0.02470 | 0.27600 | 0.00150 | 9.38882 | 76.41509 |
| | 1.2 | 0.59620 | 0.03070 | 0.42620 | 0.00140 | 6.45482 | 81.38756 |
| | 1.6 | 0.70830 | 0.06530 | 0.70280 | 0.00080 | 2.46457 | 82.09443 |
| | 2 | 0.84480 | 0.06810 | 0.68220 | 0.00030 | 1.69270 | 84.07488 |
| | 0 | | | | | | |
| 4.7 | 0.4 | 0.16550 | 0.00810 | 0.17150 | 0.00210 | 5.98538 | 41.49815 |
| | 0.8 | 0.35420 | 0.01170 | 0.28360 | 0.00180 | 5.51593 | 48.99341 |
| | 1.2 | 0.44790 | 0.01650 | 0.65700 | 0.00140 | 5.16385 | 55.20899 |
| | 1.6 | 0.57080 | 0.01490 | 0.80520 | 0.00090 | 4.34233 | 68.18859 |
| | 2 | 0.80780 | 0.02990 | 0.87910 | 0.00050 | 2.58193 | 80.53444 |
| | 0 | | | | | | |
| 6.85 | 0.4 | 0.18070 | 0.01900 | 0.13350 | 0.00510 | 8.77494 | 26.50763 |
| | 0.8 | 0.31120 | 0.01300 | 0.38700 | 0.00420 | 7.74578 | 33.82008 |
| | 1.2 | 0.75370 | 0.01880 | 0.50290 | 0.00320 | 7.27634 | 28.26036 |
| | 1.6 | 0.73341 | 0.02240 | 0.86230 | 0.00240 | 6.43225 | 41.68096 |
| | 2 | 0.74650 | 0.02970 | 0.99820 | 0.00180 | 5.63329 | 49.46736 |
| | 0 | | | | | | |
| 10 | 0.4 | 0.16180 | 0.01500 | 0.11890 | 0.00770 | 7.74578 | 43.16783 |
| | 0.8 | 0.26620 | 0.00870 | 0.42890 | 0.00520 | 6.54509 | 64.16674 |
| | 1.2 | 0.40980 | 0.02410 | 0.88830 | 0.00410 | 4.62219 | 71.15013 |
| | 1.6 | 0.56770 | 0.02570 | 1.09040 | 0.00280 | 3.61109 | 85.99440 |
| | 2 | 0.61800 | 0.03430 | 1.30670 | 0.00250 | 3.05137 | 84.82441 |
| | 0 | | | | | | |

NB: *The units of MassL(aq), MassL(s), are in mgC; M_{L(aq)}, M_{L(s)}, and MS are in mg/10g soil; ML_(aq), and ML_(s), are in mg/mgC

Table 4.22: Variation of the Amounts of Metal-Bound Humic acid and Free Energies of Distribution and Metal Complexation with Added Metal

| pH | M _{added} | ML _(aq) | ML _(s) | V _{ML(sys)} | ?G _{Kdm} | ?G _{QL} | ?G _{KML(sys)} |
|------|--------------------|--------------------|-------------------|----------------------|-------------------|------------------|------------------------|
| 3.72 | 0.4 | 2.282E-05 | 2.696E-03 | 1.045E-05 | 6161.610 | -4865.326 | 17559.365 |
| | 0.8 | 1.748E-05 | 3.217E-03 | 1.653E-05 | 6557.414 | -5456.436 | 19021.561 |
| | 1.2 | 1.594E-05 | 4.852E-03 | 3.620E-05 | 4887.613 | -6595.617 | 17548.262 |
| | 1.6 | 9.461E-06 | 8.311E-03 | 1.486E-04 | 6155.281 | -9123.781 | 15837.973 |
| | 2 | 3.498E-06 | 7.954E-03 | 2.115E-04 | 5980.386 | -10163.537 | 15027.204 |
| 4.7 | 0.4 | 4.423E-05 | 3.612E-03 | 2.321E-05 | 5400.220 | -5039.185 | 734.479 |
| | 0.8 | 3.302E-05 | 5.203E-03 | 4.556E-05 | 3861.514 | -5683.849 | 544.236 |
| | 1.2 | 2.319E-05 | 1.088E-02 | 1.014E-04 | 3165.688 | -6166.337 | -642.321 |
| | 1.6 | 1.241E-05 | 1.110E-02 | 1.229E-04 | 2269.884 | -7166.775 | -1407.940 |
| | 2 | 6.016E-06 | 1.058E-02 | 1.844E-04 | 3610.817 | -8952.787 | -820.853 |
| 6.85 | 0.4 | 1.445E-04 | 3.784E-03 | 1.701E-05 | 7820.171 | -2877.084 | 3761.961 |
| | 0.8 | 1.010E-04 | 9.311E-03 | 5.832E-05 | 4256.406 | -3835.756 | 175.854 |
| | 1.2 | 9.005E-05 | 1.415E-02 | 9.395E-05 | 3367.603 | -3531.077 | -104.797 |
| | 1.6 | 4.988E-05 | 1.792E-02 | 1.285E-04 | 3168.391 | -4863.236 | -575.208 |
| | 2 | 3.267E-05 | 1.812E-02 | 1.514E-04 | 3502.476 | -5654.114 | -211.675 |
| 10 | 0.4 | 1.512E-04 | 2.335E-03 | 1.220E-05 | 7957.831 | -4470.858 | 4012.213 |
| | 0.8 | 7.354E-05 | 6.065E-03 | 4.408E-05 | 3768.403 | -5940.774 | -195.725 |
| | 1.2 | 5.411E-05 | 1.172E-02 | 1.096E-04 | 4215.449 | -7114.876 | -144.920 |
| | 1.6 | 3.125E-05 | 1.217E-02 | 1.554E-04 | 3430.475 | -8250.452 | -711.855 |
| | 2 | 2.845E-05 | 1.487E-02 | 2.197E-04 | 3764.823 | -8653.101 | -918.915 |

NB: *The unit(s) of M_{added} is in mg; ML_(aq), and ML_(s), are in mg/mgC; ΔG is in J/mol

The data revealed that the mass of metal bound humic acid in the solid and solution phases increase with increase in pH. The extent of metal bound to the solid phase (V_m) was also noted to increase with pH (figures 4.21-23). As a result it may be inferred from the observations and deductions that, aggregation of humic acid significantly influence the value of V_m. Metal distribution between the phases of the system is therefore a function of humic acid aggregation.

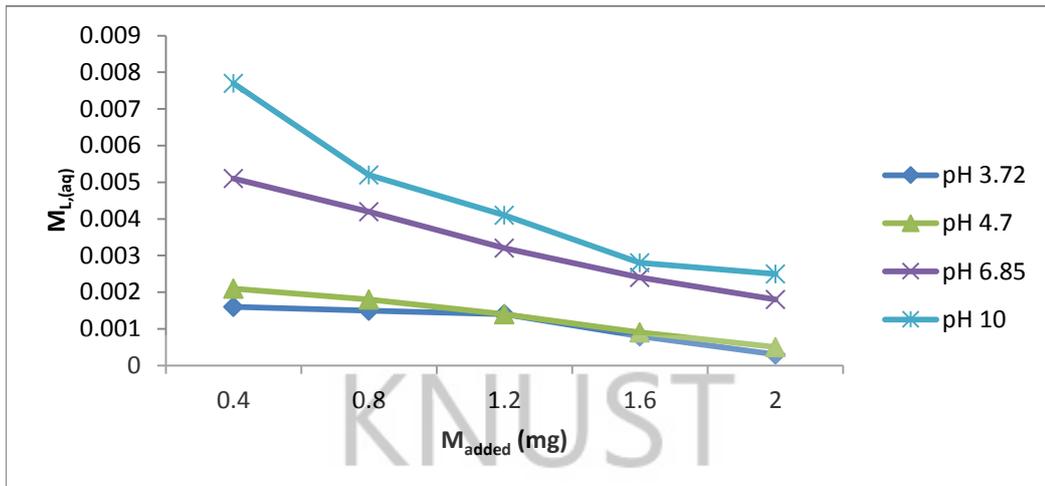


Figure 4.38: Variation of Mass (mg) of metal bound to un-aggregated humic acid (aq) with metal added

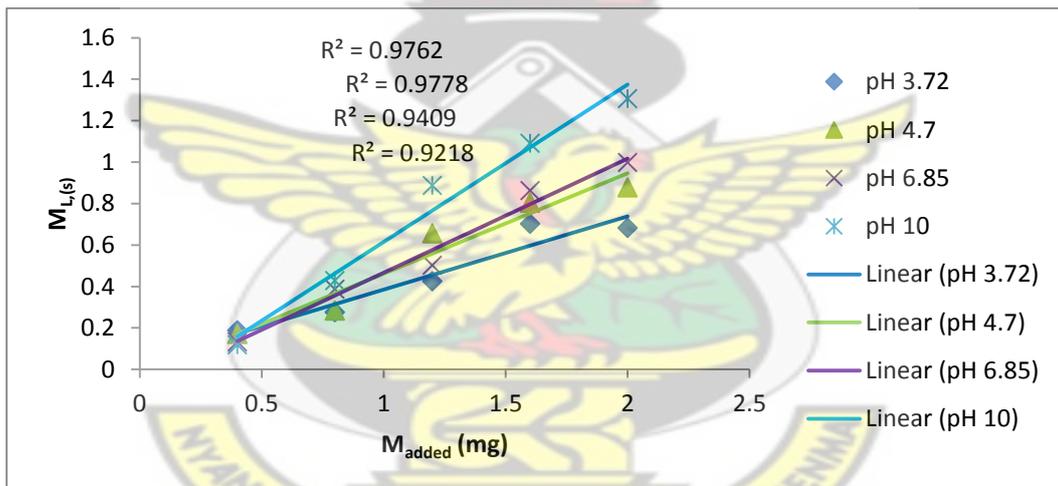


Figure 4.39: Variation of Mass (mg) of metal bound to aggregated humic acid (s) with metal added

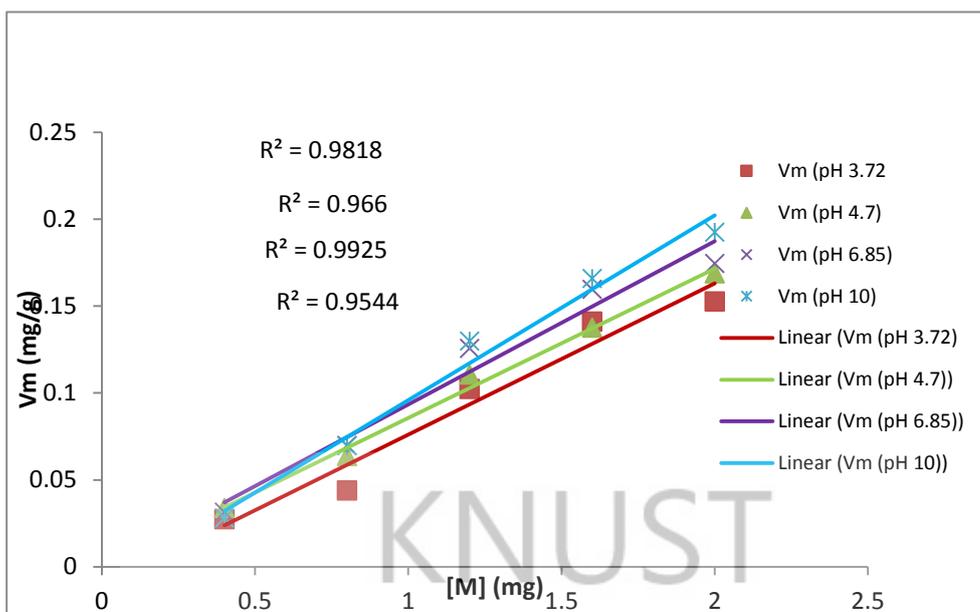


Figure 4.40: Variation of the extent of metal bound to soil with concentration of free metal in solution

Interactive Processes in Soil-Solution System: Data from regression analysis in table 4.23 obtained at 90% confidence level and higher, revealed that a strong inverse relationship exists between the concentration of ML complex in the solution phase and free metal (M^+) concentration in solution at all pH. The aggregation quotient on the other hand exhibits strong direct (linear) relationship with free metal concentration at all pH. This indicates that ML complexes are transferred to the solid phase from solution in the form of aggregates. The relationship between ML and the extent of metal binding to the solid phase, V_m , supports this inference by exhibiting a strong to moderately strong inverse relationship from pH 3.72-10.

Table 4.23: Regression analysis of metal and humic interactions in soil-solution system

| Variables | Relationship | Statistic | pH | | | |
|----------------------------|------------------------|----------------|----------|----------|-----------|----------|
| | | | 3.72 | 4.7 | 6.85 | 10 |
| $K_{dL} \propto M^+$ | $y = ax + b$ | Corr | 0.9476 | 0.9649 | 0.7860 | 0.8626 |
| | | R ² | 89.8023% | 93.1050% | 61.7840% | 74.4118% |
| $K_{dL} \propto K_{DM}$ | $y = ax + b$ | Corr | 0.703199 | 0.8405 | 0.8885 | 0.9458 |
| | | R ² | 49.4489% | 70.6395% | 78.9463% | 89.4620% |
| $K_{DM} \propto Q_L$ | $y = ax + b$ | Corr | 0.4299 | 0.7241 | 0.7619 | 0.9036 |
| | | R ² | 18.4797% | 52.4256% | 58.0607% | 81.6429% |
| $C_L \propto K_{DM}$ | $y = a\frac{1}{x} + b$ | Corr | 0.7034 | 0.7514 | 0.9454 | 0.8710 |
| | | R ² | 49.4834% | 56.4538% | 98.3860% | 75.8660% |
| $V_m \propto M^+$ | $y = ax + b$ | Corr | 0.9459 | 0.8809 | 0.7295 | 0.8872 |
| | | R ² | 89.4835% | 77.5934% | 53.2159% | 78.7172% |
| $C_L \propto V_m$ | $y = a\frac{1}{x} + b$ | Corr | 0.9474 | 0.9172 | 0.9776 | 0.9640 |
| | | R ² | 98.7510% | 84.1298% | 95.5764% | 92.9345% |
| $V_m \propto ML$ | $y = a\frac{1}{x} + b$ | Corr | 0.7422 | 0.8801 | 0.8681 | 0.9727 |
| | | R ² | 55.09% | 77.4658% | 75.3621% | 94.6220% |
| $ML_{(aq)} \propto M^+$ | $y = a\frac{1}{x} + b$ | Corr | 0.8888 | 0.9364 | 0.8886 | 0.8485 |
| | | R ² | 79.0000% | 87.6905% | 78.9537% | 71.9909% |
| $K_{dL} \propto M_{added}$ | $y = ax + b$ | Corr | 0.5789 | 0.9389 | 0.9601 | 0.9394 |
| | | R ² | 33.5171% | 88.1554% | 92.1700% | 88.2391% |
| $K_{DM} \propto V_{ms}$ | $y = ax + b$ | Corr | 0.3583 | 0.9254 | 0.9346 | 0.8993 |
| | | R ² | 12.8409% | 85.6274% | 87.3497% | 80.8793% |
| $V_{ms} \propto C_m$ | $y = ax^b$ | Corr | 0.9170 | 0.7929 | 0.0563 | 0.4804 |
| | | R ² | 84.0959% | 62.8631% | 0.317133% | 23.0794% |
| $V_{ms} \propto M^+$ | $y = ax + b$ | Corr | 0.8991 | 0.9379 | 0.6133 | 0.8807 |
| | | R ² | 80.8377% | 87.9637% | 37.6183% | 77.5714% |
| $K_{DM} \propto ML$ | $y = a\frac{1}{x} + b$ | Corr | 0.7645 | 0.7928 | 0.8044 | 0.9381 |
| | | R ² | 58.4483% | 96.8580% | 64.7061% | 87.9996% |
| $Q_L \propto M^+$ | $y = ax + b$ | Corr | 0.9469 | 0.9621 | 0.8288 | 0.8905 |
| | | R ² | 89.6567% | 92.5689% | 68.6911% | 79.2966% |
| $V_m \propto C_m$ | $y = ax^b$ | Corr | 0.9480 | 0.7622 | 0.0449 | 0.4070 |
| | | R ² | 89.8758% | 58.0999% | 0.2018% | 16.5660% |

NB: α = proportional; Corr = correlation coefficient; a and b = constants

In addition, a strong direct relationship between humic acid distribution constant, K_{dL} , and free metal concentration in solution at all pH (table 4.23) supports the deduction that, increasing metal concentration leads to the transfer of humic acid to the solid phase as aggregates. However, it must be noted that at low pH the solid phase is positive (Petrovic, 1999; Tipping, 2002) and humic acid adsorption is expected to occur. Thus, humic acid distribution may be considered to be characterized by

adsorption and aggregation processes. And because the two processes are dependent on factors such as pH, ionic strength, and temperature predicting the distribution of humic acid across pH will be difficult. But at constant temperature and pH it is expected that K_{dL} and Q_L will increase with increase in free metal concentration as confirmed from the strong direct relationship between free metal concentration and K_{dL} as well as Q_L (table 4.23).

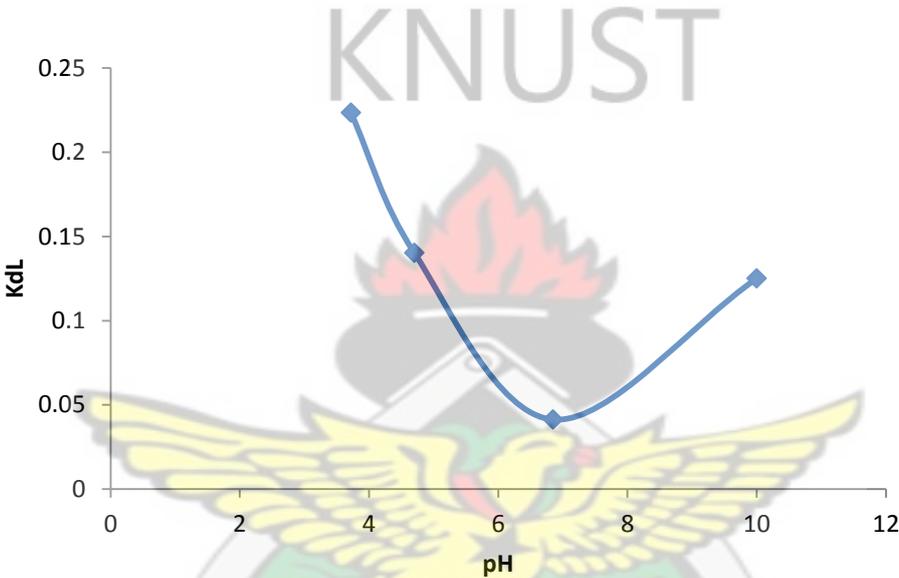


Figure 4.41: Effect of pH on humic acid partition in soil-solution system

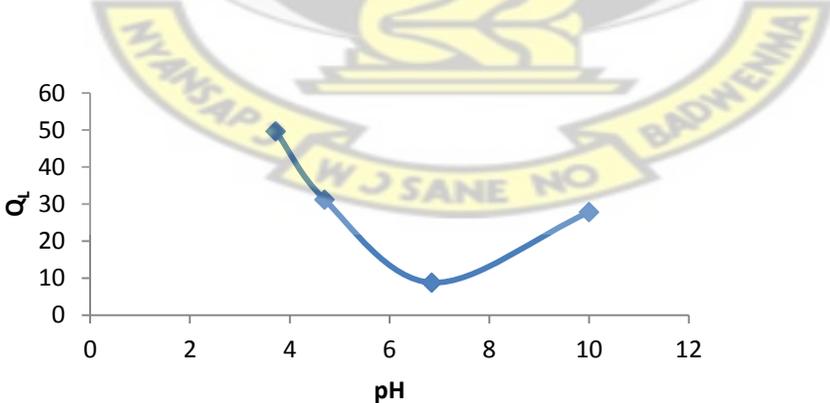


Figure 4.42: Effect of pH on the aggregation of humic acid in soil-solution system

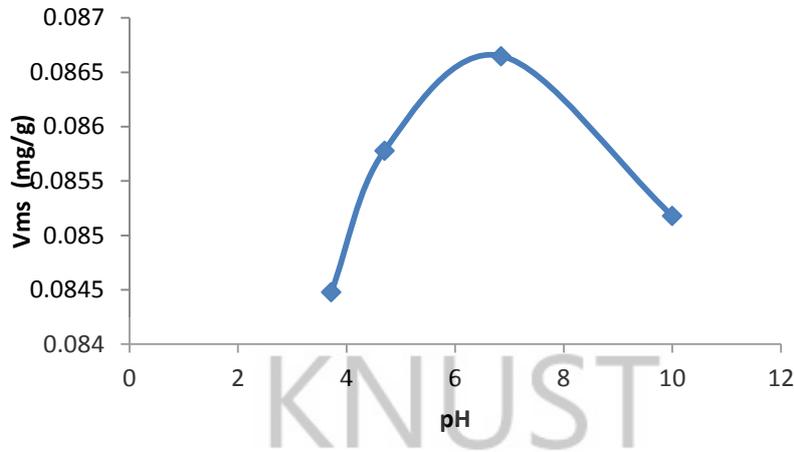
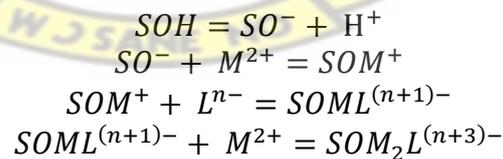


Figure 4.43: Effect of pH on the extent of metal bound to soil sorption sites

When pH is varied at constant temperature and ionic strength, humic acid distribution is expected to decrease with pH. But the soil composition in the system may change the expected outcome. In figure 4.41 and 4.43 K_{dL} and Q_L go through a minimum where humic acid concentration in solution (C_L) is at its peak, and V_L is minimum. This is considered as the point or pH at which humic acid distribution is no longer controlled by adsorption at the mineral surface. The increase in Q_L and K_{dL} at pH 10 may also be as a result of a net positive charge at the mineral surface caused by metal ions bound to the surface as illustrated below (Petrovic, 1999; tipping, 2002).



Thus, Q_L and K_{dL} are functions of humic acid adsorption and hydrophobicity at $pH < 6.85$, and a function of aggregation due to pseudomicellation and weak adsorption processes as illustrated above at $pH > 6.85$ in this system. This suggests that at all pH when $[M^+]$ is appreciably high, K_{DM} will be influenced by K_{dL} .

A strong direct relationship was noted between the extent of metal bound to inorganic sorption sites in the solid phase, V_{ms} , and free metal concentration at all pH (table 4.23). However, V_{ms} increases with increase in pH (figure 5.43). But its relationship with K_{DM} , although strong at pH 4.7-10, is weak at pH 3.72. This is as a result of the fact that metal adsorption at pH 3.72 is weak, because of positive charge developed by mineral surfaces at low pH a condition which favours adsorption of negatively charged species such as humic acids by the soil surface.

These deductions imply that K_{DM} is affected by the net adsorption properties of the soil mineral and, the behavior and binding properties of humic acids in the system. This is supported by the strong relationship between K_{DM} and K_{dL} ; K_{dm} and Q_L ; K_{dm} and ML ; K_{dm} and V_{ms} ; K_{dm} and C_L ; V_m and ML as explained by the Models 1-6 (section 3).

4.7 RATIO OF METAL-OCCUPIED INORGANIC AND ORGANIC BINDING SITES IN THE SOLID PHASE OF SOIL-SOLUTION SYSTEM

Modification of the solid phase of soil-solution system has been noted to occur at all pH as observed from the kinetic studies (section 4.3.3), and interaction studies (section 4.6). The presence of organic binding sites created by the humic acid introduces the idea of competitive adsorption and site 'deprivation' in the solid phase.

Research indicates that when the sign of the solid phase is the same as the adion (e.g. ligand adsorption onto soil at high pH), adsorption can be enhanced by the addition of a bivalent inorganic ion of opposite charge- even such weakly sorbing cations as Ca^{2+} (Parks et al., 2001). The cation is thought to act as a bridge between a surface site and the organic adion (Healy and Fruerstenau, 1972; Parks, 1975). For instance, in the study

of the effect of NOM on Cu (II) sorption Davis (1984) examined the sorption of Cu (II) and Cd (II) on γ -Al₂O₃ (Alon) over the pH range of 4-8, and found that Cu (II) is more strongly complexed by the functional groups of the adsorbed NOM than by the NOM-free alumina surface (as proposed in section 3.15) and that the apparent stability constant for the Cu (II)-sorbed organic matter complex is approximately equal to the stability constant for the aqueous Cu (II)- organic complex. In contrast, Cd (II) is not affected by the presence of organic matter adsorbed on the alumina surface. Thus, the formation of Type A and Type B ternary complexes has been reported and used to discuss NOM-enhanced adsorption of cations (Davis and Leckie, 1978b; Bourg et al., 1979; McBride, 1985a; Parks, 2001). According to Parks (2001) a possible reason for enhanced adsorption of cations by organic ligands is the greater degree of stereochemical “flexibility” (chelating effect) of the organic molecules, which can lead to more stable bonding of the cation to organic ligands (Cu (II) and Hg (II) are known to benefit from this chelating effect).

The competition between NOM and mineral surfaces for cations is therefore a noted phenomenon. But the discussion has not yet highlighted the effect of the competition phenomenon in relation to metal partition in soil-solution system containing humic substance under the influence of pH and background electrolyte. This section therefore, seeks to address this gap in knowledge.

Parks (2001) stated that “organic film” or “monolayer” hypothesis has been challenged by Ransom et al., (1997), who used transmission electron microscopy to examine the forms of organic matter in continental margin sediments. The study found that the organic matter in these sediments is primarily patchy in distribution and occurs as discrete, discontinuous blebs and micro-blebs of differentiated and undifferentiated organic coatings, and not as thin uniform grain coatings or as in-fillings of nicks or etch

pits on sediment grains with high degree of surface roughness. Mayer, (1999) found that marine aluminosilicate sediments have generally less than 15% of their surfaces coated by organic matter and that most minerals in the sediments have largely naked surfaces.

In this study it is assumed that humic substance may exist in the solid phase as 1) adsorbed ligands: bound to discrete sites on solid phase mineral surface through Type A and Type B ternary complex formation, and 2) un-adsorbed ligands: not bound to the solid phase minerals. In addition, the presence of the bound ligands reduce the number of binding sites on the soil mineral by a magnitude equivalent to the number of ligand sites utilized for the interaction. The free inorganic binding sites can bind to free metal ions while the free sites on the mineral-bound ligands can also form complexes with the free metal ions. On this basis, the ratio of occupied heterogeneous sites is expressed as,

$$SR = \frac{S_{in}}{S_{or}} \dots\dots\dots 5.5$$

Where SR = ratio of occupied-sites; S_{in} = moles of metal-occupied inorganic sites; S_{or} = moles of metal-occupied organic sites.

4.7.1 Effect of pH on the Ratio of Occupied-sites

The influence of added metal at various pH: When the total concentration of metal in soil-solution was varied by adding known amounts of Cu at pH 3.72 and 10, it was noted that at pH 3.72 SR-added-Cu relationship obey a double reciprocal linear model (figure 4.44) as shown below.

$$SR = \frac{1}{(0.105199 + 1.38231/M_{Cu})} \dots\dots\dots 4.6$$

$R^2 = 94.3542\%$; $Corr = 0.971361$; $SEE = 0.316629$; $CL = 99\%$; $P\text{-value} = 0.0058$
 Where M_{Cu} = mass of Cu

SR increases with increase in the amount of added Cu. This suggests that increasing the amount of Cu in the system leads to an increase in SR. Thus the change results in populating Cu on the inorganic binding sites than the organic sites. Probably

the apparent reduction in the moles of Cu-occupied organic sites is due to variation in the relative concentration of Cu and proton in both phases. If more Cu neutralizes the solid phase than protons then the solution phase will have high concentration of protons. In this case the presence of HA in the solid phase as aggregates will only transfer specifically bound Cu along with it, and the adsorbed HA on both proton and Cu neutralized sites on the mineral surface is likely to undergo competitive adsorption by H^+ and Cu^{2+} , however, since proton concentration in the system is constant (constant pH), increasing concentration of Cu will increase the probability of Cu adsorption onto adsorbed ligand than protons, consequently, there is the likely occurrence of more ML species in the solid phase than HL.

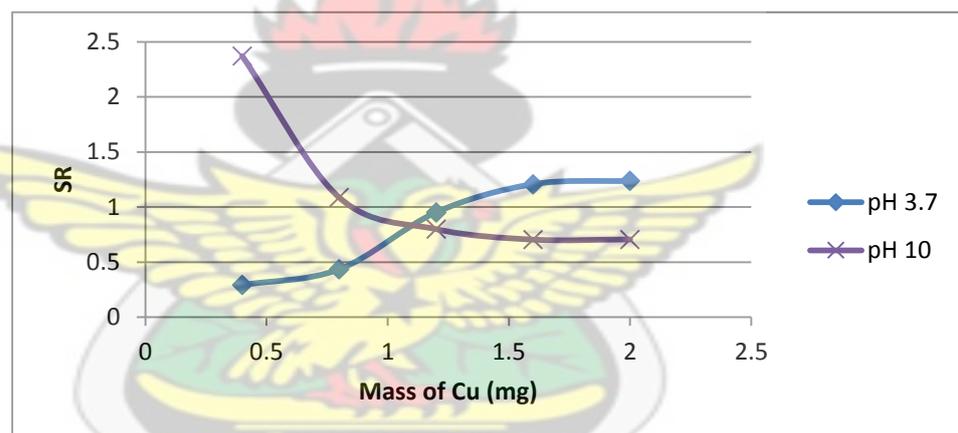


Figure 4.44: Ratio of Cu-occupied sites versus mass of Cu added to the system at pH 3.72 and 10

At pH 10 a decrease in SR with increase in added Cu is observed (figure 4.44). Organic sites are preferred to the inorganic sites. Due to reduced Cu^{2+}/H^+ competition at pH 10 metal induced aggregation is most likely the major mode of Cu transfer to the solid phase. The combination of metal bonded to both adsorbed and

$$SR = \exp(-0.713766 + 0.629188/M_{Cu}) \dots\dots\dots 4.7$$

$$R^2 = 99.5359\%; \text{Corr} = 0.997677; \text{SEE} = 0.040232; \text{CL} = 99\%; \text{P-value} = 0.0001$$

Where M_{Cu} = mass of Cu

aggregated humic acid ligands considerably increase the moles of Cu-occupied organic sites in the solid phase than the inorganic sites.

The influence of pH at high and low metal concentrations:

Changes in pH was investigated at low added metal value of 0.4 and 0.8mg, and high added metal values of 1.6 and 2.mg. changing the pH at low metal values resulted in an increase in SR with pH (figure 4.45) and the relationship may be described using the equation 5.8 for both low metal values.

$$SR = 3.79558 - 12.9925/M_{Cu} \dots\dots\dots 4.8$$

$R^2 = 97.8241\%$; $Corr = -0.989061$; $SEE = 0.176028$; $CL = 95\%$; $P\text{-value} = 0.0109$

Where M_{Cu} = mass of Cu

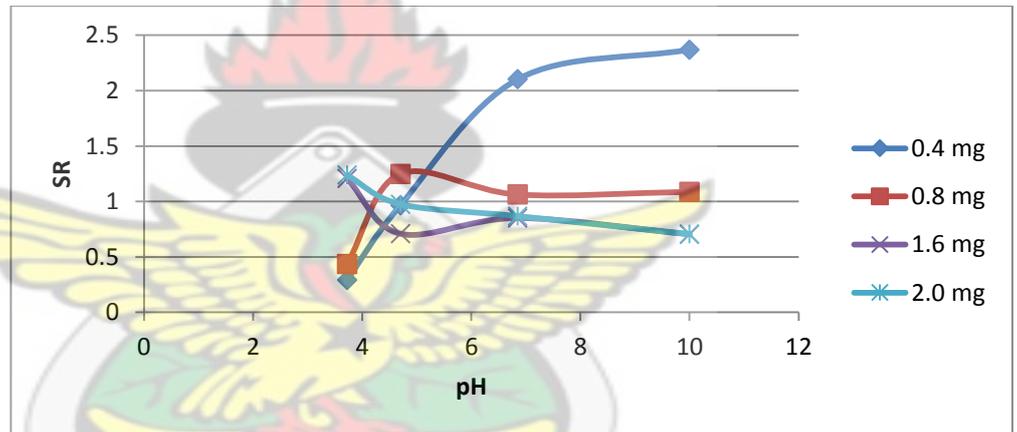


Figure 4.45.0: Site ratio vs pH at different M_{Cu}

Increasing pH at high added-metal values resulted in a reduction in SR. this implies that organic sites are populated more than inorganic sites. The reduced binding of Cu to inorganic sites probably indicates a difference in the relative affinity of Cu for the two site types.

However, the effect of pH on the Cu-complex exchange quotient (Q_{MLx}) indicates that at all Cu-added values, more ML species are formed in solution than in the solid phase as pH increases as shown in the plot below (figure 4.46).

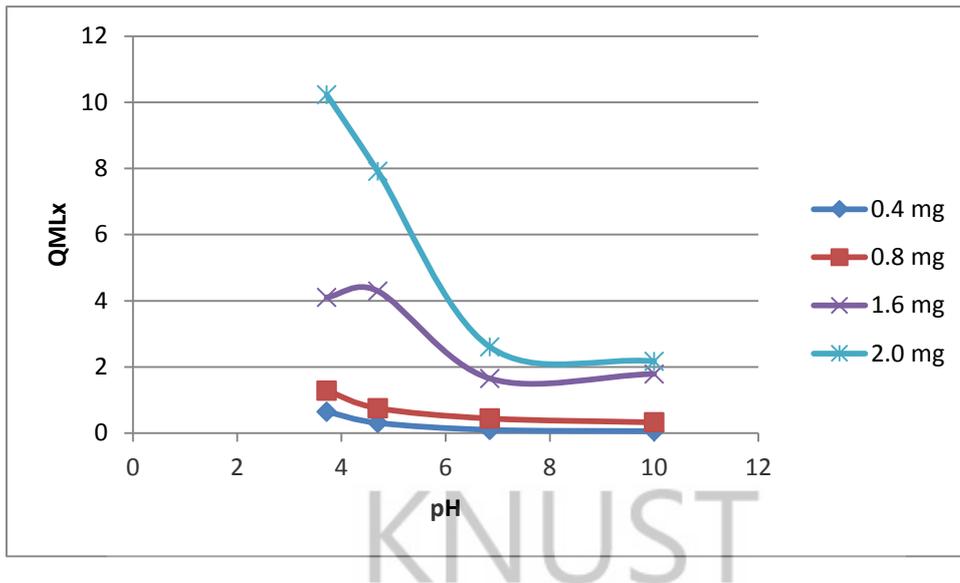
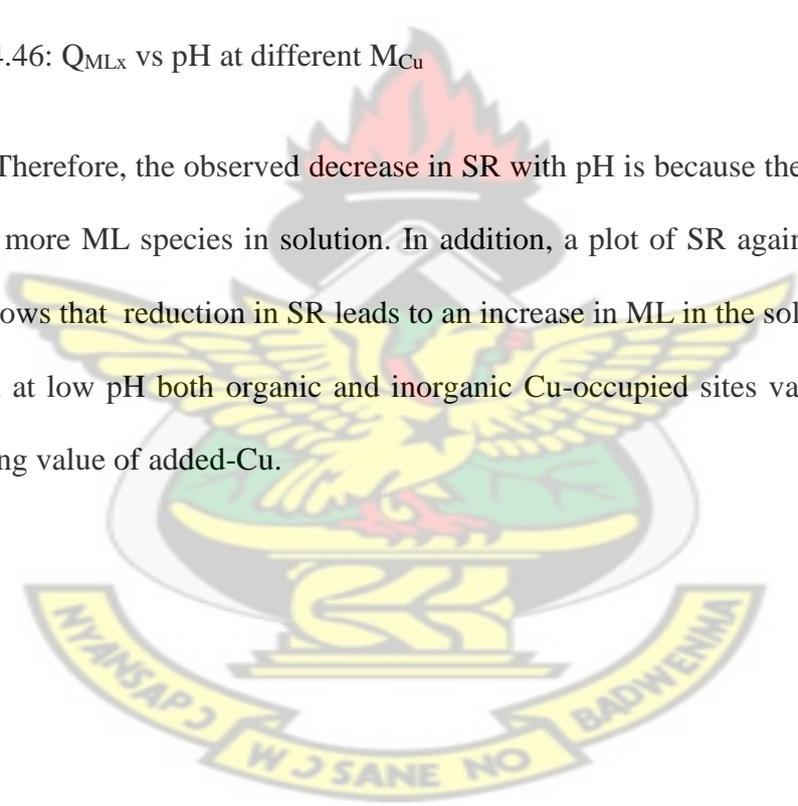
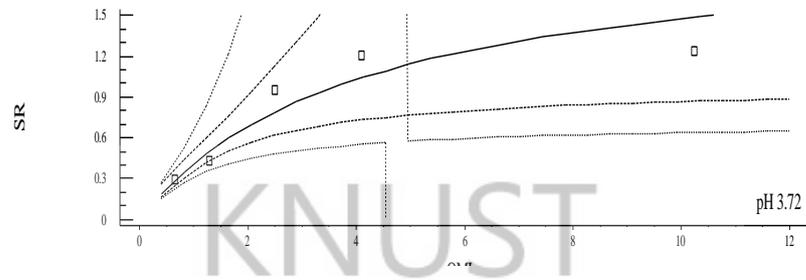


Figure 4.46: Q_{MLx} vs pH at different M_{Cu}

Therefore, the observed decrease in SR with pH is because the added Cu goes to form more ML species in solution. In addition, a plot of SR against Q_{MLx} (figure 4.47) shows that reduction in SR leads to an increase in ML in the solid phase at high pH, and at low pH both organic and inorganic Cu-occupied sites vary linearly with increasing value of added-Cu.



Plot A



Plot B

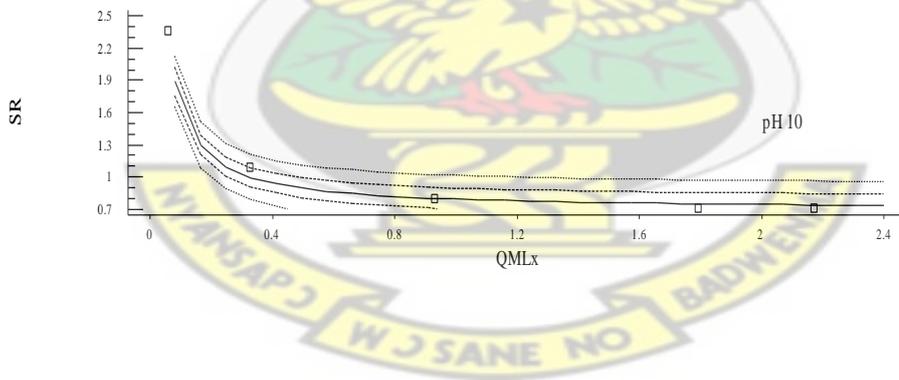


Figure 4.47: SR versus Q_{MLx} : Plot A is for pH 3.72 and plot B is for pH 10 (dotted lines indicate prediction and confidence limits at 95%)

Therefore, Cu adsorption onto organic sites varies linearly with adsorption onto inorganic sites at low pH (3.72), and an inverse relationship occurs at high pH (10). Meanwhile, the amount of added-Cu increase with increase in the moles of Cu-occupied inorganic sites at pH 3.72, and an increase with increase in the moles of Cu-occupied organic sites at pH 10 (figure 4.44).

Thus, Cu-ligand relationship is a major factor in the partition of the metal. The metal modifies the hydrophobic character of the ligand at high pH (10), and promotes its adsorption and hydrophobic character at low pH (3.72) by inducing aggregation and providing adsorption site for the ligand in the solid phase. In addition, changes in pH at constant system composition merely varies $[H^+]/[M^{2+}]$ ratio and favours the population of one site over the other. At high metal concentration, pH favours the population of organic sites, and favours inorganic sites at low metal concentration.

5.7.2 The influence of Background Electrolyte on SR

At pH 4.7 SR increases with increase in the concentration of background electrolyte, while at pH 10 SR reduces with background electrolyte (figure 4.48). In sections 4.47 and 4.48 it was stated that background electrolyte essentially transfers ligand to the solid phase thus ligand partition increases with the concentration of background electrolyte. However, at pH 4.7 the effect of background electrolyte on metal complexation and consequently on SR is different probably because Cu-L complexation is reduced due to the competitive H^+ and electrolyte-cations. Thus the increased transfer of ligand to the solid by the background electrolyte at low pH occurs simultaneously with a reduction in Cu-occupied organic sites (figure 4.49). Under these conditions it appears Cu^{2+} is not the preferred cation for the neutralization of the organic sites. This implies that most of the proton and electrolyte-cation are preferred for the neutralization of the organic sites.

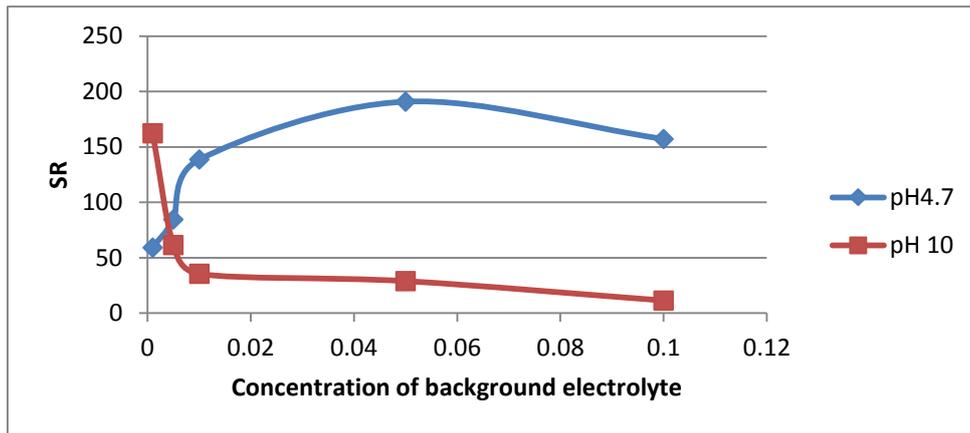


Figure 4.48: SR versus Concentration of background electrolyte at pH 4.7 and 10

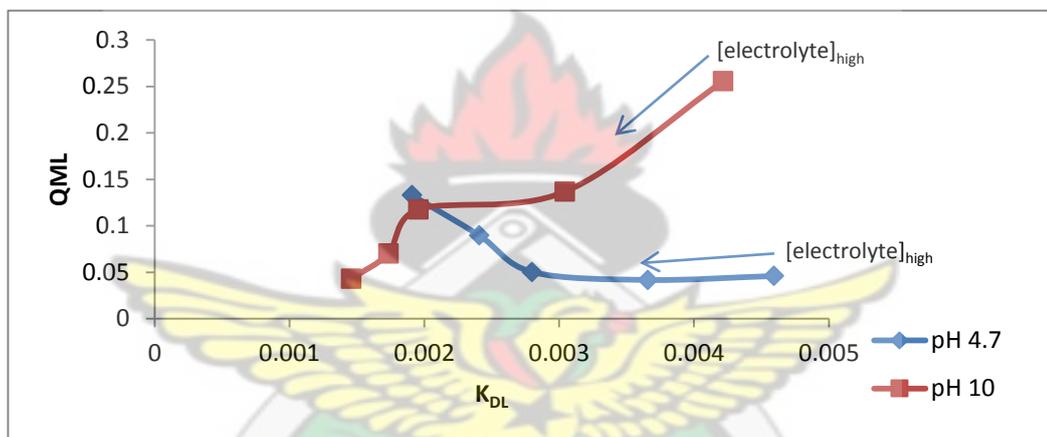


Figure 4.49: QML_x versus K_{DL} at pH 4.7 and 10 (arrows indicate direction of decreasing concentration of electrolyte)

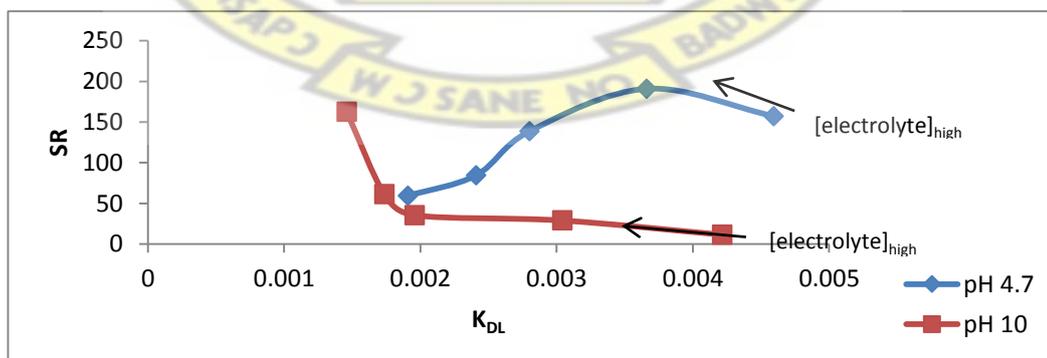


Figure 4.50: SR versus K_{DL} at pH 4.7 and 10 (arrows indicate direction of decreasing concentration of electrolyte)

At pH 10 on the other hand, the organic sites are apparently the preferred binding sites for the metal while the proton and electrolyte-cations neutralize the solid phase inorganic sites (figure 4.48-4.50).

Figure 4.49 indicates that at pH 4.7 ligand partition constant (K_{DL}) increases with a decrease in the amount of Cu-L complex in the solid phase as the concentration of background electrolyte is raised but at pH 10 ligand partition increases with increase in the solid phase metal complex as the concentration of background electrolyte is raised. Therefore since ligand partition does not necessarily promote the formation of M-L complex in the solid phase at all pH, the ligand partition constant would not correlate well with metal partition constant (K_{DM}).

Even though at any given pH Q_{ML} reduces with increasing concentration of background electrolyte, changes in SR with Q_{ML} (figure 4.51) suggests that as the concentration of background electrolyte increases at pH 4.7, SR increases with a decrease in Q_{ML} . At pH 10 on the other hand, increase in the concentration of background electrolyte results in a decrease of SR with Q_{ML} . Thus as with pH, the concentration of background electrolyte has the ability to selectively determine the favoured binding site for Cu in the solid phase

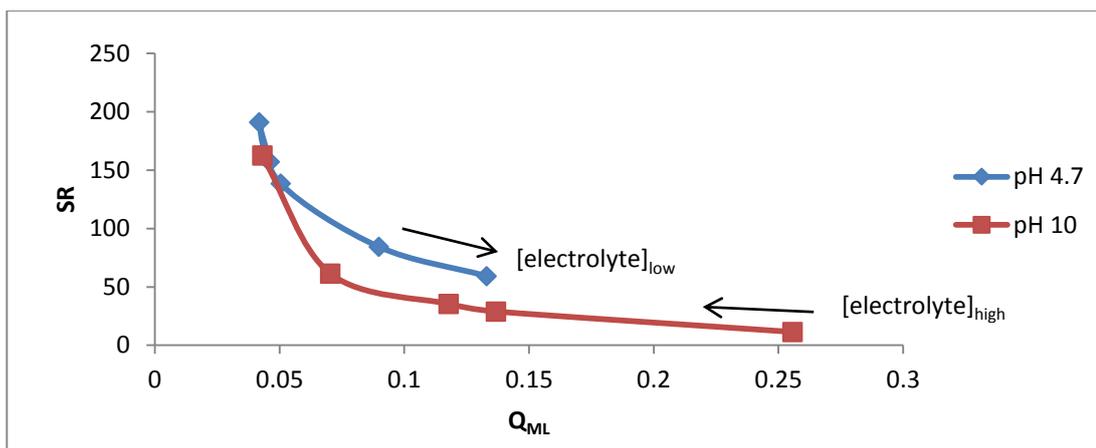


Figure 4.51: SR versus Q_{ML} at pH 4.7 and 10 (arrows indicate direction of decreasing concentration of electrolyte)

4.7.3 The relationship between site ratio and metal partition

Effect of background electrolyte: The relationship between SR and K_{DM} can be addressed under the conditions of varying concentration of background electrolyte to determine the type of site which promotes metal partition.

As the concentration of background electrolyte decreases, SR decreases with K_{DM} at pH 4.7 (figure 4.52). And under the same conditions, SR increases with increase in K_{DM} at pH 10. The relationship suggests that at low pH (4.7) the moles of Cu-occupied organic sites increase with decreasing concentration of background electrolyte, and decrease with decreasing concentration of background electrolyte at high pH (10).

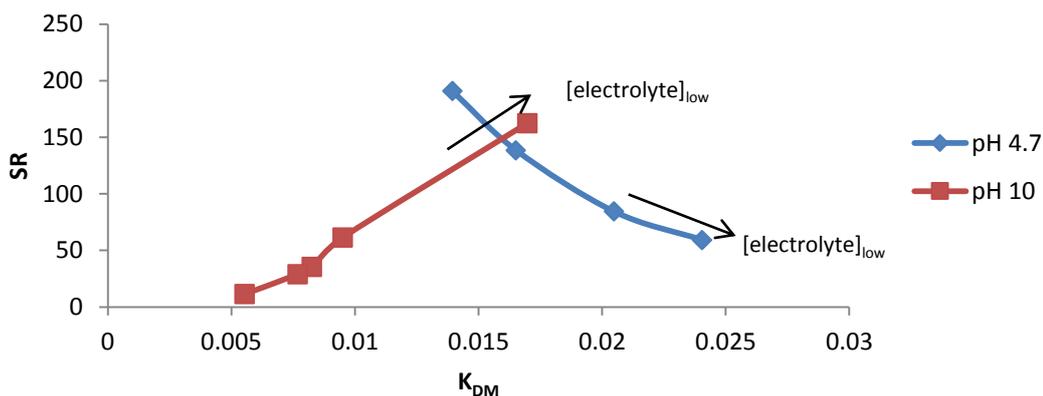


Figure 4.52: SR versus K_{DM} at pH 4.7 and 10 (arrows indicate direction of decreasing concentration of electrolyte)

At all pH, K_{DM} increases with decreasing concentration of background electrolyte. The experiment revealed from figure 4.52 that at pH 4.7 Cu-occupied organic sites are largely responsible for increase in the value of K_{DM} . But at pH 10, Cu-occupied inorganic sites increase the numerical value of K_{DM} .

Effect of pH: The effect of pH was investigated by relating SR, pH and K_{DM} . From the figure (4.53) it was noted that the partition constant for Cu increases with pH and simultaneously decreases with SR. The figures show that population of inorganic sites in the solid phase increase as pH reduces. However, organic binding sites are more populated than inorganic sites at all pH conditions studied. This observation is in agreement with the conclusion drawn by Davis, (1984) for Cu (II) sorption on γ - Al_2O_3 at pH range 4-8, that Cu (II) is more strongly complexed by functional groups of adsorbed NOM than by the NOM-free alumina surface with the same apparent stability constant as in solution. Parks et al., (2001) attributed the possible reason to the greater degree of 'flexibility' (chelating effect) of the NOM which can lead to more stable bonding of Cu to NOM. In addition, Cu benefits from this effect because its first coordination sphere is typically highly distorted with two long axial bonds and four or

more significantly shorter equatorial bonds. Another factor considered is the possibility of the occurrence of more adsorbed NOM on the mineral surface and the NOM may have a higher density of available reactive sites than the surface of the solid phase mineral oxide. In this study the ratio of Cu-occupied binding sites gave values which indicate that site ratio (SR) is dependent on pH and background electrolyte. It was noted that at all concentrations of the background electrolyte SR was characterized with values greater than 1.0 which indicates that there were more Cu-occupied inorganic sites than organic sites. Moreover, it was observed that at any given pH the SR varies with the amount of Cu added to the system. The conclusion drawn is that for the system under study in this research is that, the density of each site type (i.e organic and inorganic binding sites in the solid phase or ligand-bound and ligand free sites in the solid phase) varies with the relative concentration of protons, electrolyte-cations (E^+) and Cu ions in the system and the variation is governed by factors which control ligand transfer to the solid phase. Thus SR is a constant which is be defined by the ionic composition of the soil-solution system.

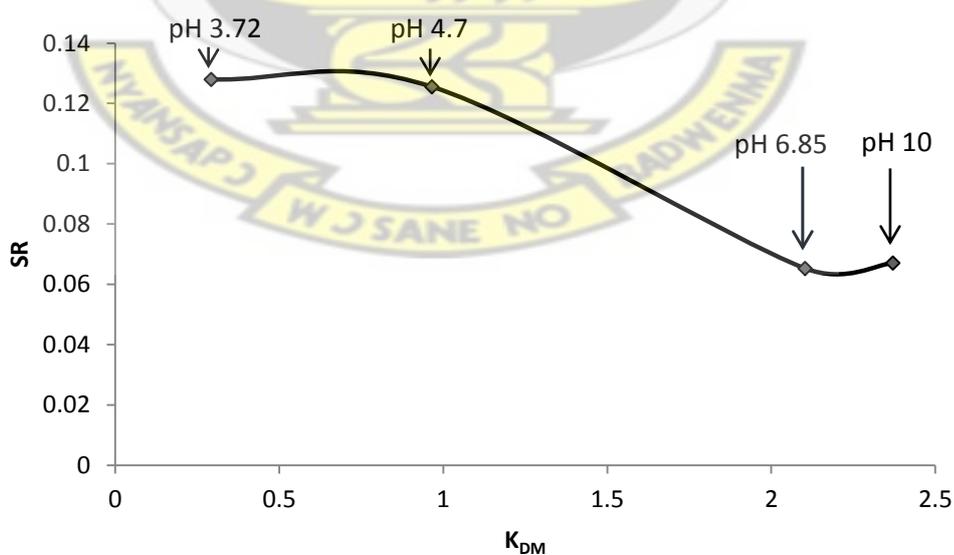


Figure 4.53: SR versus K_{DM} at various pH values

pH appears to have the same effect on K_{DM} as background electrolyte at low pH. This is because pH is invariably $[H^+]$, and the higher the pH the lower the concentration of H^+ . In essence, it implies that K_{DM} generally increases with decreasing $[H^+]$. But as to what site type has more Cu is partly dependent on the concentration of the Cu and the relative affinity of Cu for the site types at the defined pH. In this study it was observed that Cu-occupied organic sites increase as pH increased, suggesting that Cu has greater affinity for the organic sites than inorganic sites (ligand-free sites in the solid phase) as noted by Davis (1984)

Electrostatic interaction theory supports the observed relationship between pH and K_{DM} , in the sense that at low $[H^+]$ (i.e. high pH) the ligand and mineral surfaces are negatively charged and electrostatic repulsion between the ligand and the mineral surface will limit the amount of ligand in the solid phase, as observed in the decrease of Q_{ML} with pH. These observations suppose that increase in the amount of Cu in the solid phase by HA is not by adsorbed ligand but possibly by other mechanisms such as phase separation of HA due to its colloidal properties (as proposed in section 4.6.1).

Therefore, under varying conditions of background electrolyte and pH, the role of humic acid (the ligand) in, metal partition is the provision of alternate binding sites for metal adsorption in the solid phase and routes for the population of Cu in the solid phase.

5.8 SUITABILITY OF PROPOSED MODELS

Simulation experiments were carried out to generate the data required to test the models. The chemical characteristics and composition of the soil sample used for the simulation experiments are presented in appendix 14. Testing the suitability of the models was initiated in the following order:

1. Test of conceptual model: This was carried out by determining the factors which affect metal speciation in a terrestrial environment.
2. Test of distribution model: This was carried out by accounting for the factors which affect trace metal distribution in a terrestrial environment.
3. Application of mathematical models to explain the role of humic substance in trace metal distribution in soil using data from simulated experiments.

Component factor analysis was used for the factor tests with the aid of SAS Stat Studio 3.1 software. STATGRAPHICS plus 3.0 software was used to test the reliability and applicability of the models.

4:8.1 Test of Speciation Model

Factor analysis for data reduction was used and the selection criteria adopted are eigenvalues ≥ 1 and correlation coefficient > 0.8 . The result of the component factor analysis shows that three factors may be used for explaining trace metal speciation in a terrestrial environment. Climatic conditions promoting weathering ($f_{climate}$), chemical characteristics of the soil solution (f_{sol}) and humic matter (f_{HS}) are the factors observed to affect trace metal speciation in the terrestrial environment. The relative effects of the factors on trace metal speciation are as shown in the model below.

$$Speciation = 0.5639 f_{climate} + 0.2482 f_{sol} + 0.1306 f_{HS} \dots \dots \dots 4.9$$

The model explains 94.27% ($R^2= 0.9427$) of the variability in the data as such it may be used to make forecasts regarding changes in the extent of trace metal speciation in the selected ecosystem. It was also observed that the effect of each factor on particular metal species can be monitored using the relations below.

$$M_{\text{water}} = 0.86626f_{\text{climate}} + 0.03699 f_{\text{sol}} - 0.26729 f_{\text{HS}} \quad \dots\dots\dots 4.10$$

$$M_{\text{exchangeable}} = -0.05043f_{\text{climate}} + 0.99638 f_{\text{sol}} + 0.04738 f_{\text{HS}} \quad \dots\dots\dots 4.11$$

$$M_{\text{carbonate}} = 0.97122f_{\text{climate}} + 0.02067 f_{\text{sol}} - 0.08150 f_{\text{HS}} \quad \dots\dots\dots 4.13$$

$$M_{\text{oxide}} = -0.03589f_{\text{climate}} + 0.99623 f_{\text{sol}} + 0.05676 f_{\text{HS}} \quad \dots\dots\dots 4.14$$

$$M_{\text{organic}} = 0.97704f_{\text{climate}} - 0.07724 f_{\text{sol}} - 0.10058 f_{\text{HS}} \quad \dots\dots\dots 4.15$$

$$M_{\text{Si}} = 0.92976f_{\text{climate}} - 0.14396 f_{\text{sol}} - 0.18975 f_{\text{HS}} \quad \dots\dots\dots 4.16$$

$$M_{\text{HS}} = -0.19142f_{\text{climate}} + 0.07893 f_{\text{sol}} + 0.95628 f_{\text{HS}} \quad \dots\dots\dots 4.17$$

The models indicate that f_{HS} contributes positively to the formation of $M_{\text{exchangeable}}$, and M_{oxide} . This implies that humic substances provide exchangeable surface for metals and also provide adsorption sites for the metal on the oxide, possibly by coating the mineral oxide surface. Humic substances interact with free metal ions in solution to form a soluble or insoluble metal-ligand complex, ML, thereby reducing the concentration of M_{water} as indicated by equation (4.10). It may be observed from equations 4.15 and 4.18, that the silicate mineral is not coated with humic substance and that the release of metal from the mineral matrix or the formation of M_{organic} , $M_{\text{carbonate}}$ and M_{Si} depends solely on climatic conditions and perhaps other biotic factors. Equations 4.11, and 4.13 reveal that chemical characteristics (e.g., pH, ionic strength, conductivity, etc.) of the solution phase in a terrestrial environment, plays a major role in the formation of $M_{\text{exchangeable}}$ and M_{oxide} .

5.8.2 Test of Distribution Model

Using component factor analysis with the factor selection criteria eigenvalue ≥ 1 and correlation coefficient > 0.8 , three factors may be considered when explaining trace metal distribution in the terrestrial environment. The model below (Equation 4.17), indicates that solution phase properties, $f_{SOLprop}$ (such as ionic strength, pH, conductivity, etc), properties of humic substances, f_{HSprop} (such as hydrophobicity, and detergent properties), and solid phase characteristics, $f_{SOLIDxtic}$ (such as surface charge density and dissolution properties of the minerals) are the factors which control trace metal distribution in a terrestrial environment. The model as fitted can explain 91.15% ($R^2 = 0.9115$) of the variability within the data, as such the model may be used to make forecasts.

$$K_{DM} = 0.5065 f_{SOLprop} + 0.2344 f_{HSprop} + 0.1705 f_{SOLIDxtic} \dots \dots 5.17$$

When the factor selection criteria is taken as eigenvalue ≥ 0.5 and correlation coefficient > 0.8 it introduces another factor, f_{HScptx} , (Equation 4.18) which has been of particular importance in explaining cation binding to humic substances. The factor (f_{HScptx}) as explained by Ephraim et al., (1986) and Ephraim and Marinsky, (1986) describes how binding site heterogeneity, electrostatic ('polyelectrolytic') effects, and competition among cations influence cation – humic interactions.

$$K_{DM} = 0.5065 f_{SOLprop} + 0.2344 f_{HSprop} + 0.1705 f_{SOLIDxtic} \\ + 0.0684 f_{HScptx} \dots \dots 4.18$$

The model (Equation 5H.10) as fitted explains 97.99% of the factors which influence trace metal distribution in a terrestrial environment. The solution phase properties ($f_{SOLprop}$), account for 50.65% of the factors which influence trace metal distribution in a terrestrial environment. In addition, properties of humic substances, f_{HSprop} , account for 23.44%, solid phase characteristics, $f_{SOLIDxtic}$, 17.05%, and cation binding to humic substances, f_{HSplx} , 6.84%.

It may be concluded that humic substances play a significant role in trace metal distribution in a terrestrial environment. Furthermore, trace metal distribution should be discussed in terms of:

- ionic strength, pH, and conductivity of the solution phase,
- hydrophobicity, and detergent properties of humic substances,
- surface charge density and dissolution properties of the minerals,
- and heterogeneity, electrostatic ('polyelectrolytic') effects, and competition among cations during cation – humic interactions.

4.8.3 Suitability of Adopted Models

The validity and applicability of the adopted models were tested by fitting the models to data obtained from simulated experiments with Cu. The validity of the models was assessed by using the regression data from the variables. The statistical and chemical analyses of the validity of the individual models were considered under two conditions- varying pH and concentration of background electrolyte. The models were developed under the assumed conditions of constant temperature, pH and ionic strength while metal and ligand concentrations were considered as capable of varying. Thus, the chosen ideal scenario for comparative study of the validity of the models based on the conceptual model is, increasing metal concentration in a stable

environment where humic substance concentration is constant but can vary its composition in the phases of the terrestrial environment at constant temperature, pH and ionic strength.

The results obtained after fitting the data from simulation studies to describe the relationship between the variables in the models are as presented in table 4.24.

Table 4.24: Statistics of adopted models

| Model | Statistics* | pH | | | |
|--|----------------|----------------|----------------|----------------|----------------|
| | | 3.72 | 4.7 | 6.85 | 10 |
| Model 1 $\frac{1}{Q_{ML}} \propto \frac{1}{K_{DM}}$ | Cor | 0.8621 | 0.9948 | 0.9936 | 0.9979 |
| | R ² | 74.3204 | 98.9682 | 98.7290 | 99.5852 |
| | SE | 2.2543 | 0.0152 | 0.0527 | 0.0529 |
| | P-Value | 0.0602 | 0.0004 | 0.0006 | 0.0001 |
| | CL | 90 | 99 | 99 | 99 |
| Model 2 $Q_L \propto K_{DM}$ | Cor | 0.69988 | 0.724058 | 0.761976 | 0.903564 |
| | R ² | 48.9829 | 52.4256 | 58.0607 | 81.6429 |
| | SE | 0.02381 | 1.68684 | 5.43605 | 3.75927 |
| | P-Value | 0.1882 | 0.1666 | 0.1343 | 0.0354 |
| | CL | 90 | 90 | 90 | 95 |
| Model 3 $K_{DL} \propto K_{DM}$ | Cor | 0.7032 | 0.840473 | 0.828517 | 0.945843 |
| | R ² | 49.4489 | 70.6395 | 78.9463 | 89.462 |
| | SE | 0.0237 | 1.32516 | 12.7817 | 6.01444 |
| | P-Value | 0.1852 | 0.0746 | 0.0439 | 0.015 |
| | CL | 90 | 90 | 95 | 95 |
| Model 4 $\beta \propto \frac{1}{K_{DL}}$ | Cor | 0.9726 | 0.9670 | 0.8942 | 0.9985 |
| | R ² | 94.5866 | 93.5156 | 79.9521 | 99.7077 |
| | SE | 0.0003 | 0.1621 | 0.3849 | 0.0632 |
| | P-Value | 0.0054 | 0.0071 | 0.0407 | 0.0001 |
| | CL | 99 | 99 | 95 | 99 |
| Model 5 $\left(\frac{[M]}{[E^+]}\right) \propto \frac{1}{K_{DL}}$ | Cor | | 0.9378 | | 0.7856 |
| | R ² | | 87.9490 | | 61.7168 |
| | SE | | 55.1477 | | 301.812 |
| | P-Value | | 0.0184 | | 0.1153 |
| | CL | | 95 | | 90 |
| Model 6 $\frac{1}{Q_{ML}} \propto \frac{1}{K_{DL}}$ | Cor | 0.9888 | 0.9548 | 0.9309 | 0.9782 |
| | R ² | 97.7755 | 91.1603 | 86.655 | 95.6836 |
| | SE | 0.0992 | 0.4436 | 1.7089 | 1.7087 |
| | P-Value | 0.0014 | 0.0115 | 0.0216 | 0.0039 |
| | CL | 99 | 95 | 95 | 99 |

NB: * *Corr* = correlation coefficient; *SE* = standard error of estimate; *CL* = confidence level

Table 4.24 shows the output of fitting the models to the data obtained from the simulation studies to describe the role of humic acid in Cu distribution between the solid and solution phases of soil-solution system.

The p-values in the results (table 4.24) indicate that, there is a statistically significant relationship between the variables at a confidence level ranging from 90-99%. The R^2 values also show that the Models as fitted explain a significant proportion of the variability in the dependent variables. And correlation coefficients generally indicate the existence of a relatively strong relationship between the variables. In addition, standard error of the estimates shows that the value of the standard deviation of the residuals can be used to construct prediction limits for new observations.

The statistical analysis indicates that the Models are applicable at all the pH values studied and the relative applicability of any given model across pH varies with the R^2 values. The results indicate that Models 1, 4 and 6 gave higher R^2 and correlation coefficient values than the other models. Moreover, the R^2 values being less than 100% implies that other variables are also involved in the observed behavior of the system by the models. However, the models explain the observed phenomenon to a larger extent than the other variables.

The results indicate that the Model 1 explains a significant proportion of variability in the data at pH values greater than 3.72 and this suggests that the relatively high concentration of protons at this pH play a significant role by interfering in the complexation of metal to the ligand since metal partition at low pH is basically controlled by inorganic sites in the solid phase (figure 4.53). The plot below (figure 4.54) shows that Q_{MLx} increases with increase in K_{DL} but the position of the trend line (and the gradient) suggests that increasing the amount of Cu added to the system changes the amount of metal complexed in the solid phase by only 0.0211. Moreover,

in spite of the strong relationship between the two variables, K_{DL} increases with SR at pH 3.72. Thus K_{DL} does not necessarily lead to the population of Cu at the organic binding site in the solid phase. The possible explanation could be that protons interfere in metal retention in the solid phase by humic acid or that the chemical environment favours the population of Cu at the inorganic sites.

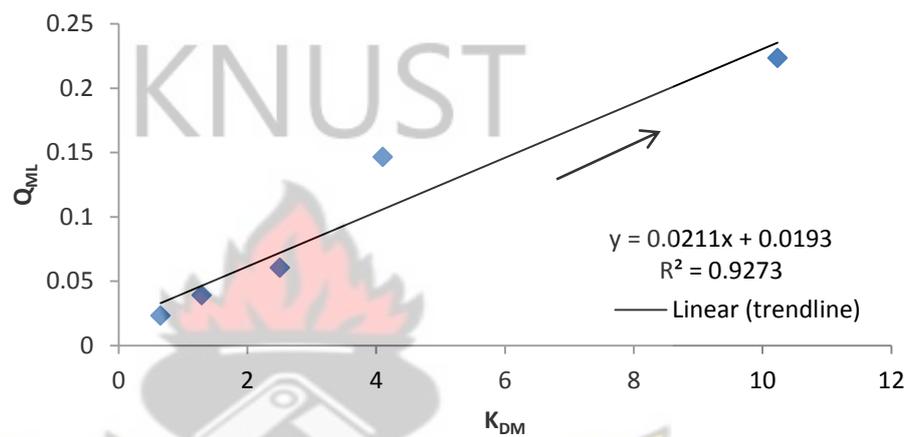


Figure 4.54: Q_{ML} versus K_{DL} at pH 3.72 (arrow show direction of increasing [Cu])

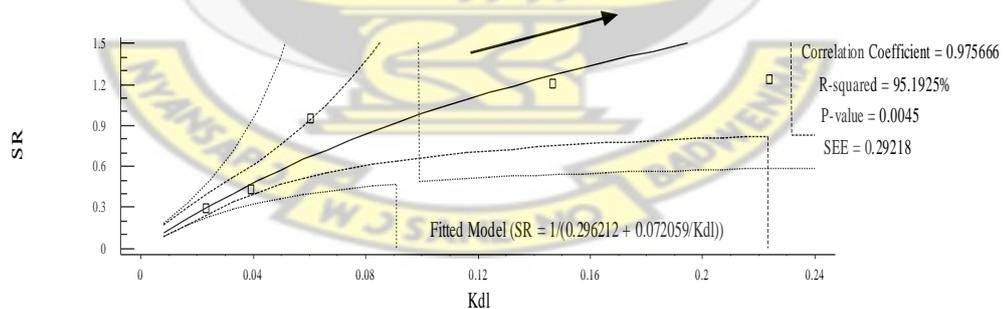


Figure 4.55: SR versus K_{DL} at pH 3.72 (arrow shows direction of increasing [Cu]; dotted lines indicate prediction and confidence limits)

The model was tested under conditions of changing background electrolyte concentration, and it was observed that the Model is able to describe the relationship between the variables when the concentration of background electrolyte changes at pH 4.7 as shown by the regression equation below.

$$Q_{ML} = 1/(-13.305 + 0.535087/K_{DM}) \dots\dots\dots 4.19$$

Corr = 0.8703; R² = 75.7336%; SEE = 4.0449; P-value = 0.0550; CL = 90

However, at pH 10 a negative gradient is observed from the regression equation for Model 1 as shown below (equation 4.20). The negative sign indicates that background electrolyte has an opposite effect on the two variables. Q_{ML} increases with ionic strength and K_{DM} has high values at low concentrations of the electrolyte. Thus the sign (equation 4.20) indicates that data to which the model is fitted were obtained under conditions of changing concentration of background electrolyte.

$$Q_{ML} = 1/(30.8952 - 0.163292/K_{DM}) \dots\dots\dots 4.20$$

Corr = -0.9490; R² = 90.0658%; SEE = 2.7529; P-value = 0.0137; CL = 95

While Model 6 fits data at all conditions of pH it also gives a negative gradient at high pH (10) under conditions of varying background electrolyte. Models 4 and 5, on the other hand, fit at all conditions of pH and background electrolyte.

Table 4.25: Statistics of Model 4 under varying conditions of background electrolyte

| Model | Statistics* | pH | |
|---------|----------------|----------------|----------------|
| | | 4.7 | 10 |
| Model 4 | Cor | 0.9498 | 0.9621 |
| | R ² | 90.2184 | 92.5546 |
| | SE | 0.0823 | 0.0167 |
| | P-Value | 0.0134 | 0.0088 |
| | CL | 95 | 99 |

The Models indicate that the role of humic acid in the distribution of Cu in soil-solution system is based on its intrinsic properties which enable it to provide alternative

binding sites in the solid phase and also transport the metal directly to the solid phase as part of its adsorbed and aggregated forms. These can be effectively described with the models.

4.8.4 Effect of pH on Model Constants

The slopes (g values) of the models (Table 4.26) can be used to discuss metal distribution in humic conditions (section 4.16). The slopes obtained for this study were regressed with pH and it was noted that the slopes for Model 1 varied linearly (positively) with pH. And the slope (Model 1) which determines binding site heterogeneity in the solid phase is a characteristic property of the phase at any given pH. The linear relationship (equation 4.21) suggests that large increments in Q_{ML} are required for increase in K_{DM} as pH rises. And that Cu-ligand complex (CuL) in the solid phase contributes significantly to K_{DM} at high pH. While at low pH, CuL in

Table 4.26: Slopes of Models at the pH conditions studied.

| pH | Model 1 | Model 2 | Model 3 | Model 4 | Model 6 |
|-------|----------|-----------|----------|-------------|----------|
| 3.72 | 0.019866 | 22.745800 | 2.274580 | 6.42269E-05 | 0.036482 |
| 4.70 | 0.055533 | 2.921780 | 0.292178 | 0.045656 | 0.105661 |
| 6.85 | 0.077777 | 0.858159 | 0.085816 | 0.027599 | 0.156327 |
| 10.00 | 0.145496 | 4.195730 | 0.419573 | 0.063037 | 0.434211 |

The solution phase contributes significantly to K_{DM} . This implies that humic acid contributes more to changes in Cu distribution at low pH through the formation of aggregates, and at high pH through the formation of ternary complexes/adsorption (surface reactions). It may thus be concluded that at any given ionic strength and temperature, the role of humic acid in Cu distribution is dependent on the major mechanism which promotes its association with/retention in the solid phase at a defined pH. In addition, the formation of solution complexes contributes more to Cu transfer to the solid phase by humic acid at low pH than at high pH.

$$g = -0.0439586 + 0.0187774 * pH \dots\dots\dots 4.21$$

Corr = 0.9872; R² = 97.4641%; SEE = 0.0103; P-value = 0.0128; CL = 95

The relationship between the slope for Models 2 and 3 (equation 4.22) on the other hand indicate that the exchange of humic acid between the phases of the soil-solution system (g for Model 2), and the partition constant for humic acid (g for Model 3) varies inversely with pH.

$$g = -10.9772 + 102.575/pH \dots\dots\dots 5.22$$

Corr = -0.7505; R² = 56.3278%; SEE = 0.8205; P-value = 0.2495; CL = 90

The relationship indicates that the occurrence of HA in the solid phase reduces as pH increases. This is because pH has the ability to modify the surface charges of HA and the solid phase minerals, and it has been observed that the two materials become more negatively charged as pH rises (Parks, 2001; Tippings, 2002), they repel each other. However, HA is observed in the solid phase at all pH and this indicates that more than one mechanism is involved in their transfer to the solid phase. Models 2 and 3 (Table 4.24) indicate that the influence of HA on metal transfer to the solid phase is stronger at higher pH values. This connotes that, as in the system under study, when protons (H⁺) and electrolyte-cations (E⁺) are low, the metal determines its own mode of transportation to the solid phase by HA. Probably cation enhanced sorption and coagulation of HA as proposed in section 4.8.5 and reported by Davis, (1984) for pH range 4-8, are responsible for metal transfer by HA to the solid phase. Model 6 shows that the relationship between the amount of Cu-ligand complex (CuL) in the solid phase and the amount HA in the phase are strong at all pH. But the presence of competing cations such as E⁺ at high pH (Model 6; section 4.6), increases ligand transfer (K_{DL}) at the expense of complexation.

Analysis of Model 4 indicates that its slope varies linearly with pH (equation 4.23). The observation suggests that concentration of the free metal ion $[Cu^{2+}]$ decreases with pH. That is increasing pH increases metal complexation with HA and reduces $[Cu^{2+}]$ and HA partition. This relationship also indicates that at low pH Cu is possibly transferred to the solid phase through Type B ternary complex formation (anion-induced adsorption) and aggregation of HA.

$$g = \exp(1.60895 - 35.0888/pH) \dots\dots\dots 4.23$$

Corr = -0.7957; R² = 63.3164%; SEE = 2.4263; P-value = 0.2043; CL = 90

In addition, the occurrence of HA in the solid phase at high pH is partly dependent on the extent to which CuL complex is formed in solution. Therefore, while ligand transfer or partition is crucial for trace metal partition, the relationship between Q_L or Q_{ML} and K_{DM} is mainly hinged to CuL complexation.

Model 6 indicated that there is a strong relationship between complexation and ligand partition at all pH. And the relationship is dependent on factors which control the complexation and adsorption of HA. The slope of Model 6 which relates with the extent of HA adsorption and moles of Cu-occupied organic sites in the solid phase, varies linearly with the square of pH. That is pH change only brings about a fractional change in the slope. Thus the sensitivity to changes in pH is significant in Model 1 than Model 6.

$$g = (-0.0470873 + 0.0695978 * pH)^2 \dots\dots\dots 4.24$$

Corr = 0.9837; R² = 96.7826%; SEE = 0.0432; P-value = 0.0162; CL = 95

The effect of pH on the slope also indicates that, the moles of Cu-occupied organic sites in the solid phase reduces with the amount of HA in the solid phase. The strong relationship between HA and Cu distribution as indicated by Model 1 demonstrates that the relative amount of metal-ligand complex can be utilized as indicators for

determining the relative distribution of trace metals in terrestrial environment as shown below (Table 4.27). From the data it is evident that K_{DM} varies with Q_{ML} .

Table 4.27: Relationship between Q_{ML} and K_{DM} from field data

| | Accra | | Kejetia | | Tarkwa | |
|-------------|----------|----------|----------|----------|----------|----------|
| Trace metal | Q_{ml} | K_{DM} | Q_{ml} | K_{DM} | Q_{ml} | K_{DM} |
| Cu | 0.328552 | 0.007143 | 0.215330 | 0.011574 | 0.320394 | 0.003065 |
| Co | 0.161917 | 0.003307 | 0.065606 | 0.000885 | 0.107901 | 0.001414 |
| Ni | 0.040154 | 0.000528 | 0.042031 | 0.000607 | 0.048015 | 0.000448 |
| Pb | 0.016209 | 0.000324 | 0.018765 | 0.001740 | 0.012590 | 0.000681 |
| Zn | 0.363603 | 0.002644 | 0.277698 | 0.004621 | 0.260039 | 0.001766 |

4.9 CHEMICAL IMPLICATION OF RELATIONSHIPS

The results of the fitted models to the data indicate that the models give good fits. The ability of models to give good fit is because of two different properties of humic substances, hydrophobicity and detergent properties. These properties are responsible for changes in the values of K_{DL} , Q_L and Q_{ML} across pH.

Hydrophobicity, heterogeneity and electrostatic effects may be used to discuss the role of humic substance in trace metal distribution and indicate that, hydrophobicity causes the relative proportion of humic substance between the system phases to vary with pH. In addition, this change transfers binding sites to and from solution to the solid phase. Moreover, ML complex may aggregate, form precipitate and transfer to the solid phase. This behavior ultimately affects metal distribution as indicated by the Models.

The heterogeneity and polyelectrolytic effects of humic matter have direct effect on cation binding to humic matter, therefore, the relative ease with which MHS are formed, and the property of the MHS complex, contribute to changes in the relative proportion of ML in the system phases. In addition, the observation that at high pH

humic substances are intrinsically hydrophilic, suggests that hydrophobicity is not the major property of humic substances responsible for the change in humic matter partition at high pH, thus other mechanisms (as proposed in section 4) occur to promote the ability of humic substance to influence a fraction of the proportion of Cu in the solid phase.

Mineral dissolution is high at high pH, this indicates that ionic strength of the solution phase will rise at constant bulk density. Moreover, aggregation of humic polymers proceeds in a continuous fashion to form precipitates as ionic strength increase (Von Wandruszka, 2000). This implies that concentration of ML in the solution phase will vary with ionic strength and cause a change in humic matter partition (K_{DL}). Consequently K_{DM} will vary with K_{DL} (as indicated by Models 2 and 3).

Precipitation of humic matter will not have effect on K_{DM} if electrostatic effect and site affinity do not promote cation binding to humic matter. Thus, the intrinsic properties of humic substances which promote the formation of ML significantly influence metal distribution by increasing the amount of ML available for distribution.

The deductions and observations indicate that the properties of HA which promote its partition and interaction with Cu accords it the unique ability to influence metal partition in soil-solution system. The role of humic substances in metal partition in soil solution system is by providing alternative binding sites at the individual phases of the system, and also by providing alternative route for the exchange of metal between the phases of the system.

CHAPTER FIVE

5.0 CONCLUSION

The role of humic substances in trace metal partition in mining-impacted terrestrial environment was modeled with specific objectives of providing a good account of humic-impacted partition of trace metals in terrestrial environment. The conclusions drawn from the outcome of the research on the basis of the objectives, and philosophical statements are as enumerated below.

5.1 CONCLUSIONS DRAWN ON OBJECTIVES

To develop a conceptual model for the description of the role of humic substances in the distribution of selected trace metals in the terrestrial environment of the selected ecosystems for the study: The outcome of the field and controlled experiments proved that the conceptual model indeed describes the role of humic substance in trace metal distribution. It was observed that humic substance accounts for more than a quarter (30.28%) of the factors which control trace metal distribution in the terrestrial environments studied. In addition, field data revealed that, climatic conditions promoting weathering (f_{climate}), chemical characteristics of the soil solution (f_{sol}) and humic matter (f_{HS}) are the factors observed to affect trace metal speciation in the terrestrial environment. The relative effects of the factors on trace metal speciation are 56.39%, 24.82% and 13.05% respectively. The model indicates that f_{HS} contributes positively to the formation $M_{\text{exchangeable}}$ and M_{oxide} .

Solution phase properties (f_{SOLprop}), properties of humic substances (f_{HSprop}), solid phase characteristics ($f_{\text{SOLIDxtic}}$) and complexation factor (f_{HScplx}), are the

factors which control trace metal distribution in a terrestrial environment with, 50.65, 23.44, 17.05 and 6.84% relative effects respectively.

The data indicates that, humic substances play a significant role in trace metal distribution in terrestrial environment. And trace metal distribution should be discussed in terms of, ionic strength, pH, and conductivity of the solution phase; hydrophobicity, and detergent properties of humic substances; surface charge density and dissolution properties of the minerals; and heterogeneity, electrostatic ('polyelectrolytic') effects, and competition among cations during cation – humic interactions.

As conceptualized, the study revealed at 99% confidence level that a strong linear relationship exists between humic acid and trace metal partition constants. It is thus concluded that trace metal partition is a function of humic matter partition, and the partition of humic acid is dependent on its adsorption, cation binding and phase separation properties.

To develop mathematical models based on the theoretical framework to enable description of the role of humic substances in trace metal distribution in the terrestrial environment of the selected ecosystems: Mathematical models for the description of the role of humic substance in the distribution of trace metals in soil-solution system were successfully developed. Six linear equations were adopted for use in describing metal partition in terms of humic matter partition. The Models were applicable at all pH, and they gave appreciably high correlations at >90% confident level.

Model 1, $1/Q_{ml} = g(1/K_{DM}) - C$, referred to as Ligand Complex Partition Effect Model (LCPEM) is applicable at all pH. LCPEM explains how the occurrence of metal-ligand complex in either phase of a soil-solution system affects the metal partition. The model can be used to explain how modification of the surface of the solid phase mineral

by humic substance contributes to changes in the metal partition constant at different conditions of pH and ionic strength. Its slope at low pH ($g = V_m/[ML_{(s)}]$), measures the ratio of total metal-occupied sorption sites in the solid phase to the total metal-occupied sites on the ligand in the solid phase (as aggregates or as adsorbed ligands). The slope (considered as occupied-site ratio) is sensitive to changes in pH and ionic strength, as well as the nature of the solid phase (mineral composition). Thus, the value of the occupied-site ratio can be used to characterize soil types with defined solution characteristics.

At high conditions of pH the slope ($g = V_M/[ML_{(s)}]$), accounts for the extent of metal binding with the amount of the metal-ligand complex formed in the solid phase under defined conditions of the system. Change in the extent of metal binding with complexation (the slope) is a unique property of the solid phase at any given conditions of the system (pH and Ionic strength) and may be used to discuss changes in metal partition by humic substance as in the case of the slope at low pH.

The model, therefore, is effective in discussing how the relationship between humic substance and solid phase minerals influences the interaction and partition of trace metals in soil-solution system.

Model 2, $Q_L = gK_{DM} - C$, referred to as Ligand-Exchange Effect Model (LEEM), relates the humic substance partition with metal partition. It indicates whether hydrophobic character of humic substance in response to changes in cation concentrations has effect on the partition of the metal of interest. The slope, $g = L_{(s)}K_{ML}/K_{pm}^*$, accounts for the relationship between the stability of the metal-ligand complex in the solution phase with the strength of the metal-binding to the solid phase under defined system conditions. The model can be used to find out whether the strength of the relationship between humic substance and the solid phase has a

corresponding effect on metal partition. The slope may also be used to determine the effect of metal complexation with humic matter on the binding of the metal in the solid phase. LEEM is effective for discussing systems with low ionic strength and negligible metal-metal competition for humic substance.

Model 3, $K_{DL} = gK_{DM} - C$, referred to as Ligand Partition Effect Model (LPEM) can be used to discuss the effect of humic substance adsorption on metal partition. In addition, Model 4 ($[ML]/[M] = g(1/K_{DL}) - C$) which is referred to as Complex Depletion and Ligand Aggregation Model (CDLAM), has the ability to explain the relationship between the metal-ligand complex formed in solution per unit free metal ion and ligand aggregation. The model is applicable for the study of how pH and ionic strength affect the behavior of humic substance during complexation, and its consequent effect on metal partition. At low pH, the slope ($g = V_L/[M]$) accounts for changes in the extent of ligand adsorption (availability) in the solid phase per unit free metal. The slope is sensitive to pH and ionic strength. But at high pH the slope ($g = V_M/[M]$) accounts for the strength of metal binding to the solid phase. The data revealed that the slope varies linearly with pH and changes in pH lead to exponential increase in the slope and consequently the transfer of humic acid to the solid phase due to complexation. It is concluded from the data analyzed that at low pH the slope is a function of humic matter phase separation properties only, while at high pH the slope is a function of both the properties of the solid phase minerals and the humic matter.

In addition, Model 5, $\frac{[M]}{[E^+]} = \left(\frac{\alpha}{[E^+]}\right) \frac{1}{K_{DL}} - ([E^+]K_{ML})^{-1}$, which is referred to as Competitive Adsorption and Ligand Partition Model (CALPM), can be employed to discuss how metal aquo ion and electrolyte-cation influence the adsorption of humic substance onto solid phase minerals at different conditions of pH. The slope gives information on the effect of the strength of humic substance adsorption on the stability

of metal-ligand complex under conditions of varying background electrolyte at constant pH. The model can throw light on how the stability of metal-ligand complex, electrolyte-cation and metal aquo ion relates with the partition of humic substances in soil-solution system at defined pH.

Additionally, Model 6, $\frac{1}{Q_{ML}} = g \frac{1}{K_{DL}} - C$, referred to as Complex Exchange and Ligand Partition Model (CELP) explains the relationship between metal-ligand complexation and ligand aggregation in soil solution system. The model relates changes in the extent of metal binding to humic matter in solid and solution phases with the partition of the humic matter between the system phases. The slope, $\left(\frac{v_L}{[ML(s)]}\right)$, determines the effect of pH and ionic strength on the relationship between the extent of humic substance binding to the solid phase and the moles of binding site occupied by trace metal on the adsorbed humic substance. The results of the controlled experiments indicated that the slope is more sensitive to changes in ionic strength than pH. The pH must double to indicate a significant change in the slope.

To test the suitability of the mathematical models to describe the role of humic acid in the distribution of trace metals in soil-solution systems: The models were successful in characterizing the partition of Cu in soil-solution system containing humic acid. The models indicated that humic acid modifies the solid phase and introduces two major binding site types (organic and inorganic) their proportion of which vary according to the pH and ionic strength of the embathing solution.

The models also indicated that humic acid contributes more to changes in Cu distribution at low pH through the formation of aggregates, and at high pH through the formation of ternary complexes/adsorption (surface reactions). It is concluded that at any given ionic strength and temperature, the role of humic acid in Cu distribution is

dependent on the major mechanism which promotes its association with/retention in the solid phase at a defined pH.

In addition, more than one mechanism is involved in metal transfer to the solid phase. Models 2 and 3 indicate that the influence of HA on metal transfer to the solid phase is stronger at higher pH values. Moreover, when protons (H^+) and electrolyte-cations (E^+) are low the metal determines its own mode of transportation to the solid phase by HA.

Furthermore, Model 6 specifies that the relationship between the amount of Cu-ligand complex in the solid phase and the amount HA in the phase are strong at all pH. But the presence of competing cations such as E^+ at high pH, increases ligand transfer (K_{DL}) at the expense of complexation. Model 4 showed that while ligand transfer or partition is crucial for trace metal partition, the relationship between ligand aggregates/complexes and K_{DM} is mainly hinged on CuL complexation.

Consequently, the models are effective tools for the description of metal partition in terrestrial environments.

6.2 NOVELTY

Development of the models was based on the novel idea that there is a relationship between the fraction of metal associated with humic matter, its intrinsic properties which enable it to undergo phase separation, and metal partition constant. In addition, an understanding of the intricate relationship between the behavior of humic substance (as a consequence of its adsorption, colloidal and complexation properties) and the interactions of trace metals can be used to develop mathematical models to describe the role of humic substance in the partition of the metals in soil-solution system. The models established that, 1) the density of each site type (i.e organic and

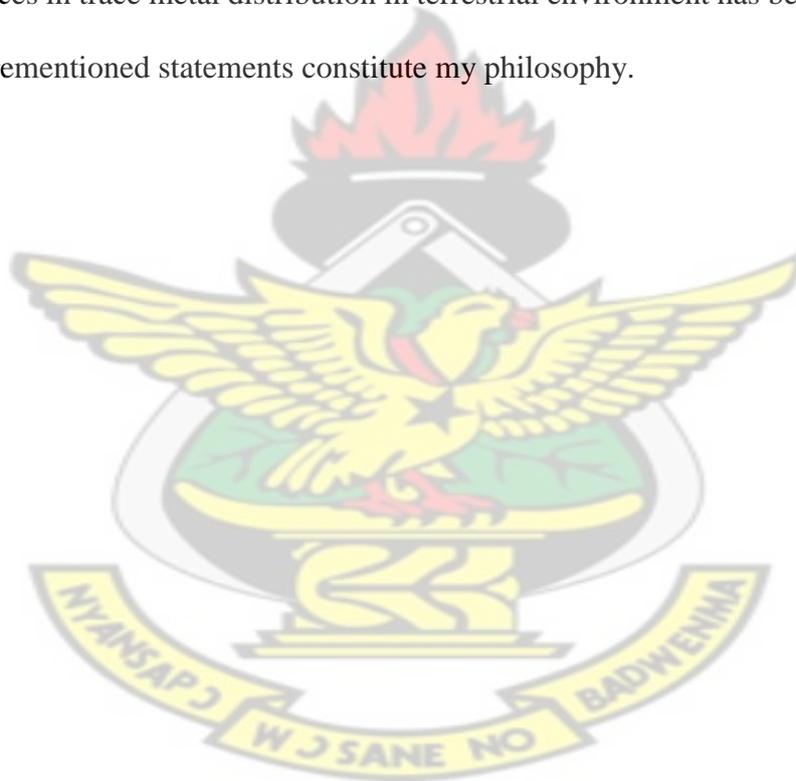
inorganic binding sites in the solid phase or ligand-bound and ligand free sites in the solid phase) varies with the relative concentration of protons, electrolyte-cations (E^+) and Cu ions in the system and the variation is governed by factors which control ligand transfer to the solid phase. 2) The binding site ratio is a constant which is defined by the ionic composition of the soil-solution system. 3) At constant ionic strength, metal partition constant (K_{DM}) is a function of metal-ligand complex exchange quotient (Q_{ML}) and the relationship can be expressed mathematically using a double reciprocal linear equation. 4) At constant ionic strength, K_{DM} varies linearly with changes in the relative proportion of humic matter in the phases of soil-solution system. 5) Humic acid partition constant (K_{DL}) has a strong direct linear relationship Q_{ML} at constant ionic strength. 6) At constant pH the ratio of free metal ion concentration to electrolyte cation concentration has a strong inverse linear relationship with K_{DL} . 7) At constant ionic strength, β a quotient which defines the ratio of metal-ligand complex concentration to free metal ion concentration in solution varies inversely with K_{DL} .

In soil-solution system, humic acid increases the initial adsorption rate of metals, but reduces the adsorption efficiency of the soil (adsorbent) while compensating for the reduction in efficiency by introducing more metal into the solid phase by the formation of metal-ligand complex directly in the solid phase, and transfer of metal-associated aggregates to the solid phase. More than one mechanism is involved in the transfer of metal to the solid phase by humic substances, and this causes the observed overall increase in metal adsorption by the solid phase.

Finally, the properties of humic substance which promote its partition and interaction with metals accord it the unique ability to influence metal partition in soil-solution system. And a good account of humic-impacted partition of trace metals can only be given when the humic matter exists in both phases of the system in proportions

determined by the prevailing factors which control the adsorption, colloidal, and cation binding properties of the humic matter. Consequently, the role humic substances play in trace metal partition is the provision of additional binding sites for the metal in both phases of soil-solution system in proportions determined by the physicochemical properties of the solution phase. In addition, it provides alternative route for the exchange of metal between the phases of the system.

The presentation in this thesis has come to show how the role of humic substances in trace metal distribution in terrestrial environment has been modeled, and the aforementioned statements constitute my philosophy.



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APPENDIX 1

Summary of Parameters used in Model Development

| <i>Parameter</i> | <i>Description</i> | <i>How found</i> |
|------------------|--|-------------------------------|
| K_{DL} | Partition constant for organic ligand | Fitted from experimental data |
| K_{DM} | Distribution constant for trace metal | Fitted from experimental data |
| v_M | Strength of metal adsorption to solid phase | Fitted from experimental data |
| v_{ML} | Strength of metal adsorption to organic ligand in solution phase | Fitted from experimental data |
| v_{MA} | Strength of metal adsorption to inorganic ligand in solution phase | Fitted from experimental data |
| v_L | Strength of organic ligand adsorption to solid phase | Fitted from experimental data |
| M | Trace metal | Fitted from experimental data |
| MS | Metal bound to solid surface | Analysis |
| M_S | Mass of solid surface (soil) | Analysis |
| L | Free organic ligand in solution phase | Calculated |
| L_A | Free inorganic ligand in solution phase | Calculated |
| ML | Metal bound organic ligand in solution phase | Calculated |
| $M + ML_A$ | Sum of free metal ion and metal bound inorganic ligand in solution phase | Analysis |
| ML_A | Metal bound inorganic ligand in solution phase | Fitted from experimental data |
| $ML_{(s)}$ | Aggregates and precipitates that form part of solid phase | Fitted from experimental data |
| S | Solid phase surface | |
| K_{ML} | Stability constant for metal bound organic ligand species (ML) | Fitted from experimental data |
| K_{MA} | Stability constant for metal bound inorganic ligand species (ML_A) | Fitted from experimental data |
| K_{PL}^* | Strength of free organic ligand adsorption to solid phase | Fitted from experimental data |
| K_{PM}^* | Strength of free metal ion adsorption to solid phase | Fitted from experimental data |
| A | Constant indicating the ratio of strength of free metal ion adsorption to solid phase, to the Stability constant for metal bound organic ligand (K_{PM}^*/K_{ML}) | Fitted from experimental data |
| Q_L | Exchange quotient (or aggregation constant) | Fitted from experimental data |
| Q_{ML} | Exchange quotient for ML complex | Fitted from experimental data |

APPENDIX 2

Properties and composition of soil sample used for the simulation experiment

| Property* | Estimated value | Major Oxides (%) | | Minor Elements (ppm) | | | |
|-------------------------------|-----------------|--------------------------------|---------------|----------------------|--------|----|------|
| | | | | | | | |
| pH (1:1) water | 5.71 | Na ₂ O | 0.85 | V | 620.00 | I | 4.40 |
| Org Carbon (%) | 0.86 | MgO | 1.55 | Cr | 170.00 | Cs | 6.90 |
| Total N % | 0.13 | Al ₂ O ₃ | 11.05 | Co | 192.00 | Ba | 52.1 |
| Org Matter % | 1.17 | SiO ₂ | 68.22 | Ni | 41.80 | La | 15.0 |
| Exchangeable Ca ⁺⁺ | 6.41 | P ₂ O ₅ | 0.27 | Cu | 19.40 | Ce | 20.0 |
| Exchangeable Mg ⁺⁺ | 2.67 | SO ₃ | 0.07 | Zn | 34.40 | Hf | 15.0 |
| Exchangeable K ⁺ | 0.30 | Cl | 0.00 | Ga | 3.10 | Ta | 14.0 |
| Exchangeable Na ⁺ | 0.23 | K ₂ O | 0.02 | As | 3.30 | Pb | 8.80 |
| T.E.B | 9.60 | CaO | 0.01 | Rb | 4.50 | Bi | 3.60 |
| E.A (Al+H) | 0.20 | TiO ₂ | 0.05 | Sr | 3.80 | Th | 10.0 |
| ECEC (cmol+/kg) | 9.80 | MnO | 0.10 | Y | 1.50 | | |
| Base saturation (%) | 98.06 | Fe ₂ O ₃ | 8.53 | Zr | 23.20 | | |
| Available P (ppm) | 4.17 | L.O.I | 10.05 | Nb | 6.10 | | |
| Available K (ppm) | 107.13 | TOTAL | 100.76 | Mo | 8.00 | | |
| | | | | Sb | 1.90 | | |

NB: * T.E.B = total exchangeable base; E.A = exchangeable acidity; ECEC = Effective cation exchange capacity; Unit of exchangeable cations = (cmol+/kg); L.O.I = loss on ignition

APPENDIX 3

Soil Composition and Properties at Study Area*

| Composition | Mean | SEM | SD | Variance | Skewness |
|--|---------|--------|---------|-----------|----------|
| pH (1:1) water | 5.807 | 0.119 | 0.671 | 0.451 | 1.107 |
| Org Carbon (%) | 1.010 | 0.047 | 0.345 | 0.119 | 0.591 |
| Total N % | 0.125 | 0.004 | 0.024 | 0.001 | 0.443 |
| Org Matter % | 1.800 | 0.085 | 0.618 | 0.382 | 0.634 |
| Exchangeable cations (cmol+/kg) Ca | 7.947 | 1.015 | 5.739 | 32.938 | 3.457 |
| Exchangeable cations (cmol+/kg) Mg | 2.818 | 0.260 | 1.470 | 2.161 | 1.553 |
| Exchangeable cations (cmol+/kg) K | 0.324 | 0.018 | 0.101 | 0.010 | 0.986 |
| Exchangeable cations (cmol+/kg) Na | 0.229 | 0.048 | 0.271 | 0.074 | 4.386 |
| T.E.B | 11.308 | 1.113 | 6.297 | 39.652 | 2.724 |
| Exch A (Al+H) | 0.200 | 0.017 | 0.098 | 0.010 | 0.678 |
| ECEC (cmol+/kg) | 11.508 | 1.106 | 6.254 | 39.118 | 2.751 |
| Base saturation (%) | 97.749 | 0.317 | 1.794 | 3.220 | -1.997 |
| Available Bray P (ppm) | 3.849 | 0.295 | 1.641 | 2.693 | 0.606 |
| Available Bray K (ppm) | 95.152 | 4.426 | 25.035 | 626.775 | 0.502 |
| Sand (%) | 35.509 | 3.455 | 13.821 | 191.027 | -0.711 |
| Silt (%) | 56.392 | 2.674 | 10.695 | 114.378 | 0.715 |
| Clay (%) | 8.099 | 1.067 | 4.269 | 18.224 | 0.955 |
| Zn (ppm) | 34.996 | 6.574 | 47.860 | 2290.601 | 2.990 |
| Cu (ppm) | 12.342 | 2.026 | 14.751 | 217.584 | 1.372 |
| Cd (ppm) | 4.970 | 0.577 | 4.198 | 17.623 | 0.552 |
| Pb (ppm) | 101.125 | 11.002 | 80.096 | 6415.391 | 0.978 |
| Mn (ppm) | 138.311 | 21.515 | 156.634 | 24534.140 | 3.801 |

NB: * SEM = standard error of mean; SD = standard deviation

APPENDIX 4

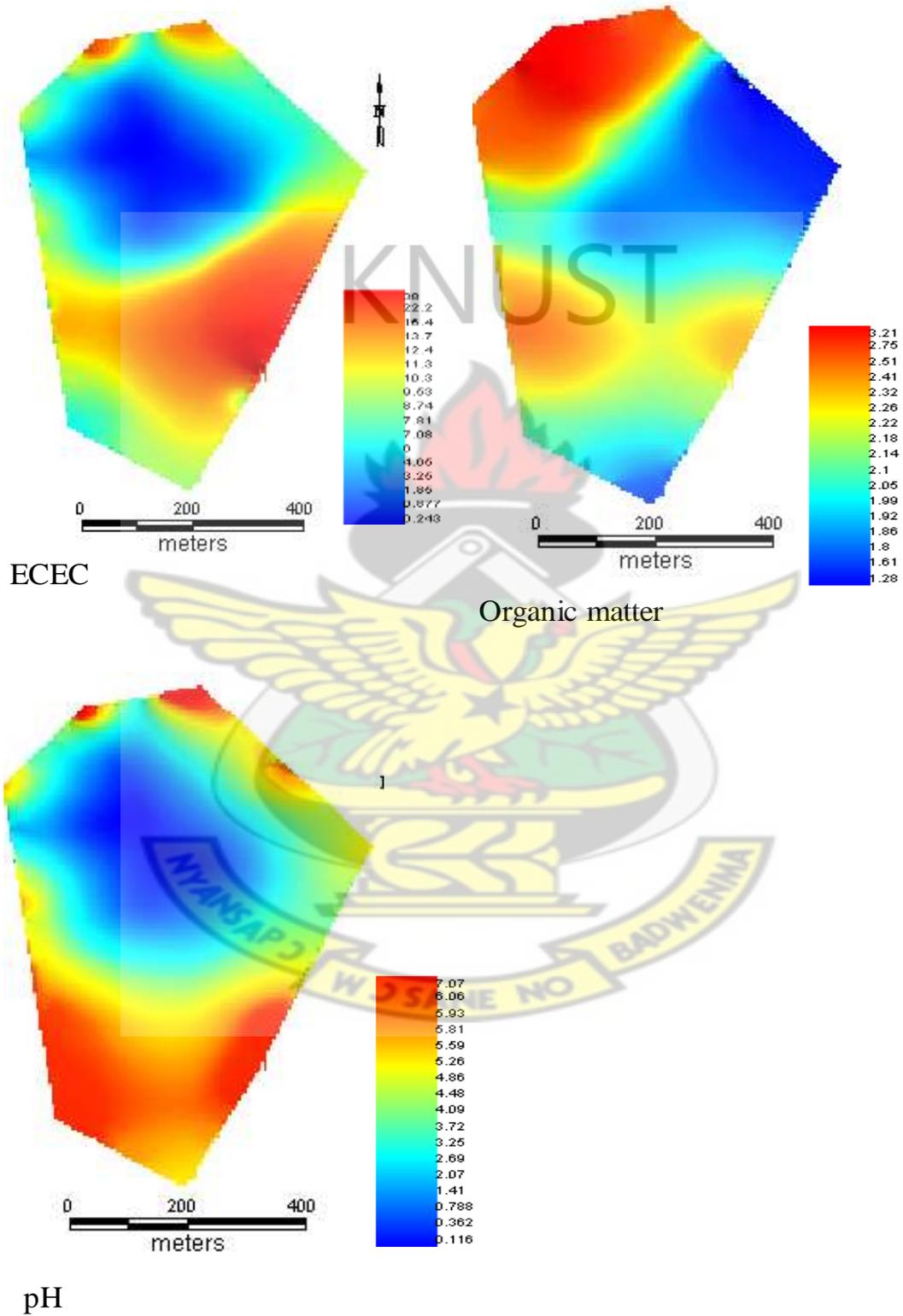
Average Values of Soil Composition and Properties at the Mining Communities*

| Parameter | Accra | Kejetia | Tarkwa |
|----------------------------|---------------|---------------|---------------|
| pH (1:1) water | 6.04(0.18) | 5.92(0.24) | 5.48(0.17) |
| Org Carbon (%) | 1.21(0.07) | 1.08(0.10) | 0.81(0.05) |
| Total N % | 0.14(0.01) | 0.13(0.01) | 0.11(0.01) |
| Org Matter % | 2.21(0.14) | 1.83(0.17) | 1.48(0.09) |
| Exchangeable Ca (cmol+/kg) | 9.47(2.56) | 8.66(1.33) | 5.78(0.74) |
| Exchangeable Mg (cmol+/kg) | 3.22(0.56) | 2.70(0.41) | 2.52(0.37) |
| Exchangeable K (cmol+/kg) | 0.32(0.03) | 0.38(0.03) | 0.27(0.02) |
| Exchangeable Na (cmol+/kg) | 0.13(0.01) | 0.26(0.05) | 0.29(0.13) |
| T.E.B (cmol+/kg) | 13.15(2.69) | 12.01(1.47) | 8.84(1.09) |
| Exch A (Al+H) (cmol+/kg) | 0.15(0.03) | 0.19(0.02) | 0.26(0.03) |
| ECEC (cmol+/kg) | 13.30(2.68) | 12.19(1.46) | 9.10(1.07) |
| Base saturation (%) | 98.47(0.32) | 98.27(0.27) | 96.55(0.73) |
| Available Bray P (ppm) | 4.38(0.58) | 4.00(0.45) | 3.23(0.48) |
| Available Bray K (ppm) | 84.00(9.71) | 109.64(5.49) | 93.13(5.08) |
| Sand (%) | 35.22(3.81) | 37.48(8.35) | 33.42(4.68) |
| Silt (%) | 57.10(2.71) | 54.40(6.26) | 58.07(4.20) |
| Clay (%) | 7.68(1.311) | 8.12(2.26) | 8.50(2.05) |
| Zn (ppm) | 54.39(18.11) | 27.92(8.82) | 25.72(5.77) |
| Cu (ppm) | 12.54(3.72) | 12.85(3.34) | 11.85(3.50) |
| Cd (ppm) | 6.14(1.22) | 5.13(1.07) | 4.01(0.77) |
| Pb (ppm) | 121.46(24.17) | 97.27(18.35) | 88.96(15.61) |
| Mn (ppm) | 133.67(30.65) | 195.00(62.99) | 103.04(17.48) |

*NB: * numbers in brackets are standard error of mean (SEM).*

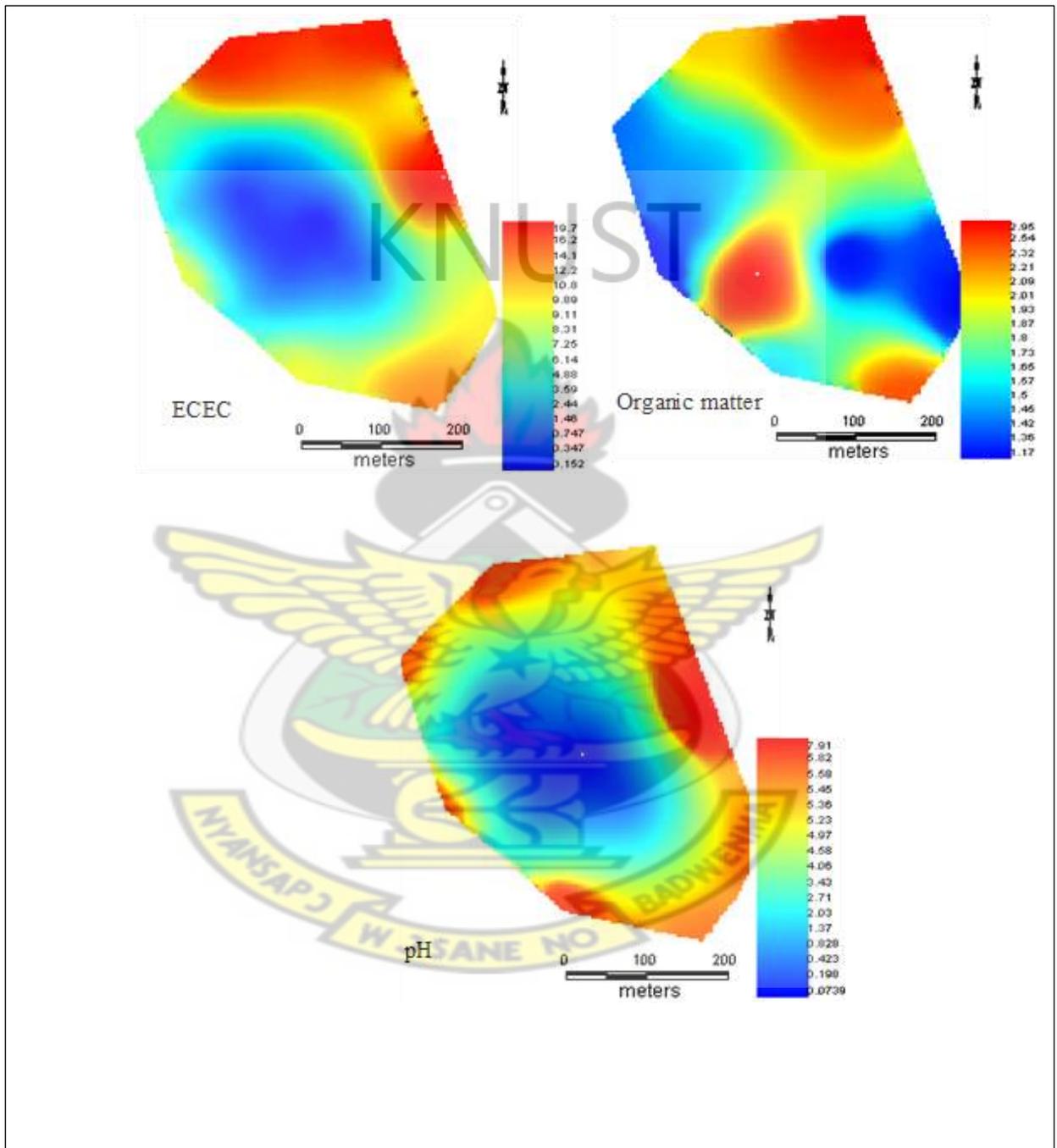
APPENDIX 5

Surface map of the properties of the terrestrial environment at Accra



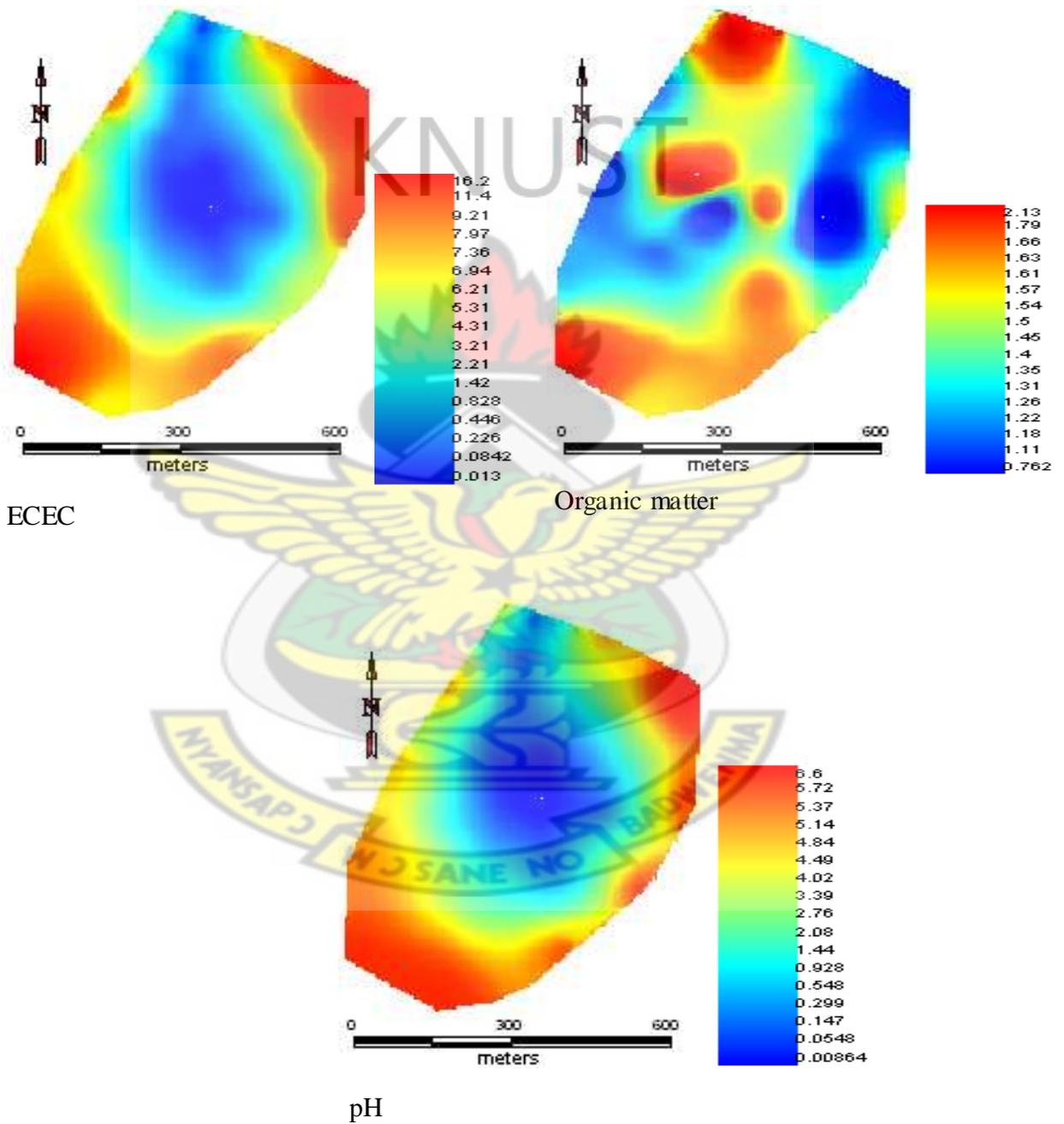
APPENDIX 6

Surface map of the properties of the terrestrial environment at Kejetia



APPENDIX 7

Surface map of the properties of the terrestrial environment at Tarkwa



APPENDIX 8

Proportion of trace metal fractions in soil at the study area

| Element | % M fraction in Soil | | | % M fraction in Solid phase | | | % M fraction in Solution | | |
|---------|----------------------|-------|-----------------|-----------------------------|-------|-----------------|--------------------------|-------|-------------------|
| | HA | FA | S _{in} | HA | FA | S _{in} | HA | FA | Sol _{in} |
| Co | 59.99 | 19.87 | 20.13 | 37.27 | 13.65 | 49.08 | 43.63 | 9.20 | 47.17 |
| Cu | 76.59 | 8.60 | 14.81 | 41.51 | 8.20 | 50.29 | 59.63 | 3.24 | 37.13 |
| Ni | 37.93 | 51.19 | 10.88 | 54.62 | 18.93 | 26.45 | 23.32 | 49.13 | 27.55 |
| Pb | 60.26 | 35.40 | 4.34 | 29.87 | 9.76 | 60.38 | 41.26 | 19.31 | 39.44 |
| Zn | 71.10 | 10.51 | 18.39 | 47.72 | 4.65 | 47.63 | 48.20 | 6.04 | 45.76 |

APPENDIX 9

Average Concentration of Humic Substance fractions in the Terrestrial Environments*

| Humic substance fractions | Accra | | Kejetia | | Tarkwa | | Entire study area | |
|---------------------------|-------|-------|---------|-------|--------|-------|-------------------|-------|
| | Mean | SEM | Mean | SEM | Mean | SEM | Mean | SEM |
| Soil HA (mgC/g) | 3.707 | 0.370 | 2.909 | 0.252 | 3.708 | 0.440 | 3.441 | 0.214 |
| Soil FA (mgC/g) | 3.291 | 0.560 | 3.427 | 0.421 | 2.869 | 0.407 | 3.196 | 0.264 |
| Solid HA (mgC/g) | 0.937 | 0.123 | 0.394 | 0.077 | 0.666 | 0.050 | 0.666 | 0.064 |
| Solid FA (mgC/g) | 0.575 | 0.067 | 0.539 | 0.062 | 0.639 | 0.081 | 0.584 | 0.040 |
| Solution HA (mgC) | 2.769 | 0.399 | 2.514 | 0.260 | 3.043 | 0.433 | 2.775 | 0.211 |
| Solution FA (mgC) | 2.716 | 0.537 | 2.889 | 0.444 | 2.230 | 0.348 | 2.611 | 0.256 |
| Soil-HS (mgC/g) | 6.998 | 0.668 | 6.336 | 0.401 | 6.576 | 0.609 | 6.637 | 0.322 |
| Solid-HS (mgC/g) | 1.513 | 0.158 | 0.934 | 0.086 | 1.304 | 0.110 | 1.250 | 0.081 |
| Solution-HS (mgC/g) | 5.485 | 0.626 | 5.402 | 0.423 | 5.273 | 0.531 | 5.387 | 0.297 |
| Total in system (mgC/g) | 6.998 | 0.668 | 6.336 | 0.401 | 6.576 | 0.609 | 6.637 | 0.322 |

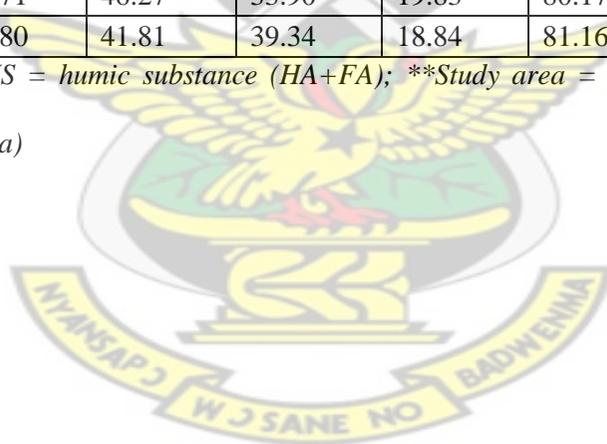
*NB: * SEM = Standard error of the mean; NB: *HA = humic acid; FA = fulvic acid; HS = humic substance (HA+FA)*

APPENDIX 10

Proportion of Humic Substance in the Terrestrial Environment at the Selected Ecosystems*

| Ecosystem | % HS fraction within soil | | % proportion of HS fraction at each phase relative to the total in the system | | | | % proportion of HS between phases | | % Proportion of HS fraction within phases | | | |
|---------------------|---------------------------|-----------|---|-----------|-----------|-----------|-----------------------------------|--------------------|---|-----------|-----------|-----------|
| | | | Solid | | Solution | | | | Solid | | Solution | |
| | <i>HA</i> | <i>FA</i> | <i>HA</i> | <i>FA</i> | <i>HA</i> | <i>FA</i> | <i>HS Solid</i> | <i>HS Solution</i> | <i>HA</i> | <i>FA</i> | <i>HA</i> | <i>FA</i> |
| <i>Accra</i> | 52.98 | 47.02 | 13.41 | 8.22 | 39.5 | 38.8 | 21.6 | 78.38 | 62.00 | 38.00 | 50.49 | 49.51 |
| <i>Kejetia</i> | 45.91 | 54.09 | 6.24 | 8.50 | 39.67 | 45.59 | 14.74 | 85.26 | 42.31 | 57.69 | 46.53 | 53.47 |
| <i>Tarkwa</i> | 56.38 | 43.62 | 10.11 | 9.71 | 46.27 | 33.90 | 19.83 | 80.17 | 51.01 | 48.99 | 57.71 | 42.29 |
| <i>Study Area**</i> | 51.85 | 48.15 | 10.04 | 8.80 | 41.81 | 39.34 | 18.84 | 81.16 | 53.28 | 46.72 | 51.52 | 48.48 |

NB: **HA* = humic acid; *FA* = fulvic acid; *HS* = humic substance (*HA*+*FA*); ***Study area* = Entire geographical area covering the three mining communities (*Kejetia*, *Tarkwa* and *Accra*)



APPENDIX 11

Concentration of metal species in the terrestrial environment of the study area

| | | Concentration (ug/g) of metal species | | | | |
|--------------------------------|-------------------------|---------------------------------------|-----------|-----------|-----------|-----------|
| | | <i>Cu</i> | <i>Co</i> | <i>Ni</i> | <i>Pb</i> | <i>Zn</i> |
| Terrestrial Environment | <i>M_{HA}</i> | 53.725 | 40.797 | 49.492 | 43.990 | 44.432 |
| | <i>M_{FA}</i> | 4.074 | 8.059 | 88.359 | 18.742 | 4.891 |
| | <i>M_T</i> | 67.359 | 56.608 | 147.319 | 65.042 | 62.819 |
| Soil phase | <i>M_{HA}</i> | 11.412 | 3.916 | 4.678 | 1.029 | 9.980 |
| | <i>M_{FA}</i> | 1.778 | 0.916 | 1.138 | 0.164 | 0.917 |
| | <i>M_T</i> | 38.713 | 9.987 | 7.896 | 5.363 | 26.083 |
| Solution phase | <i>M_{HA}</i> | 42.314 | 36.881 | 42.739 | 42.961 | 34.451 |
| | <i>M_{FA}</i> | 2.296 | 7.143 | 22.864 | 18.579 | 3.973 |
| | <i>M_{LA}</i> | 26.350 | 39.478 | 44.699 | 41.100 | 32.763 |
| | <i>M_{HS,T}</i> | 44.609 | 44.024 | 90.675 | 61.540 | 38.425 |
| | <i>M_T</i> | 70.959 | 83.502 | 135.373 | 102.640 | 71.188 |

NB: * *M_{HA}* = metal-bound humic acid; *M_{FA}* = metal-bound fulvic acid; *M_T* = total metal; *M_{LA}* = metal bound to inorganic ligands in solution; *M_{HS,T}* = total metal bound to humic substance.

APPENDIX 12

Concentration of metal species in the terrestrial environment of the selected ecosystems

| | Cu (ug/g) | | | Co (ug/g) | | | Ni (ug/g) | | | Pb (ug/g) | | | Zn (ug/g) | | | |
|-----------------------|-------------------------|----------------|--------------|--------------|----------------|--------------|--------------|----------------|--------------|--------------|----------------|--------------|--------------|----------------|---------------|--------|
| | <i>Accra</i> | <i>Kejetia</i> | <i>Takwa</i> | <i>Accra</i> | <i>Kejetia</i> | <i>Takwa</i> | <i>Accra</i> | <i>Kejetia</i> | <i>Takwa</i> | <i>Accra</i> | <i>Kejetia</i> | <i>Takwa</i> | <i>Accra</i> | <i>Kejetia</i> | <i>Tarkwa</i> | |
| Environment | <i>M_{HA}</i> | 71.848 | 42.264 | 43.100 | 37.272 | 35.406 | 42.295 | 54.886 | 40.656 | 46.387 | 47.351 | 39.872 | 37.649 | 50.124 | 37.170 | 38.947 |
| | <i>M_{FA}</i> | 4.565 | 3.638 | 3.908 | 10.427 | 6.175 | 8.017 | 96.135 | 103.535 | 73.878 | 26.125 | 9.423 | 22.188 | 5.240 | 5.546 | 4.009 |
| | <i>M_T</i> | 87.033 | 55.922 | 52.289 | 58.359 | 48.612 | 56.312 | 164.931 | 154.191 | 125.365 | 77.297 | 51.284 | 60.847 | 82.564 | 52.176 | 47.797 |
| Soil phase | <i>M_{HA}</i> | 17.556 | 5.928 | 9.683 | 5.562 | 1.816 | 3.971 | 4.347 | 4.714 | 4.650 | 1.038 | 0.649 | 0.712 | 13.469 | 8.544 | 8.137 |
| | <i>M_{FA}</i> | 1.341 | 2.205 | 1.724 | 1.085 | 0.744 | 0.929 | 1.483 | 1.102 | 0.860 | 0.134 | 0.259 | 0.032 | 1.294 | 0.740 | 0.728 |
| | <i>M_T</i> | 31.367 | 29.833 | 51.546 | 12.867 | 6.870 | 9.650 | 9.140 | 7.257 | 6.510 | 2.772 | 8.218 | 4.064 | 36.704 | 29.053 | 13.526 |
| Solution phase | <i>M_{HA}</i> | 54.292 | 36.336 | 33.418 | 31.710 | 33.590 | 38.324 | 50.539 | 35.942 | 41.737 | 46.314 | 39.223 | 36.936 | 36.655 | 28.626 | 30.810 |
| | <i>M_{FA}</i> | 3.224 | 1.434 | 2.185 | 9.342 | 5.431 | 7.088 | 94.652 | 102.432 | 73.018 | 25.991 | 9.164 | 22.157 | 3.947 | 4.806 | 3.281 |
| | <i>M_{LA}</i> | 52.442 | 24.656 | -1.442 | 36.150 | 36.310 | 39.574 | 61.139 | 44.502 | 45.837 | 48.534 | 33.902 | 34.626 | 41.913 | 18.316 | 30.989 |
| | <i>M_{HS,T}</i> | 57.516 | 37.769 | 35.602 | 41.052 | 39.021 | 45.412 | 145.191 | 138.374 | 114.755 | 72.304 | 48.387 | 59.093 | 40.602 | 33.432 | 34.092 |
| | <i>M_T</i> | 109.958 | 62.425 | 34.160 | 77.202 | 75.331 | 84.986 | 206.330 | 182.876 | 160.593 | 120.838 | 82.289 | 93.720 | 82.515 | 51.749 | 65.081 |

*NB: * M_{HA} = metal-bound humic acid; M_{FA} = metal-bound fulvic acid; M_T = total metal; M_{LA} = metal bound to inorganic ligands in solution; M_{HS,T} = total metal bound to humic substance.*

APPENDIX 13

Proportion of trace metal species in the terrestrial environments of the ecosystems

| | | % M-HS in Soil | | | % M-HS in Solid phase | | | % M-HS in Solution phase | | |
|----|------------|-----------------|-----------------|--------------------|-----------------------|-----------------|--------------------|--------------------------|-----------------|-----------------|
| | | M _{HA} | M _{FA} | M _{inorg} | M _{HA} | M _{FA} | M _{inorg} | M _{HA} | M _{FA} | M _{LA} |
| Cu | Study area | 76.59 | 8.60 | 14.81 | 41.51 | 8.20 | 50.29 | 59.63 | 3.24 | 37.13 |
| | Accra | 75.76 | 6.77 | 17.48 | 54.63 | 4.31 | 41.05 | 53.47 | 5.27 | 41.27 |
| | Kejetia | 70.84 | 9.28 | 19.88 | 24.20 | 11.37 | 64.43 | 50.84 | 5.05 | 44.10 |
| | Takwa | 83.16 | 9.75 | 7.08 | 45.70 | 8.92 | 45.38 | 48.49 | 4.78 | 46.73 |
| Co | Study area | 59.99 | 19.87 | 20.13 | 37.27 | 13.65 | 49.08 | 43.63 | 9.20 | 47.17 |
| | Accra | 49.57 | 24.66 | 25.77 | 40.59 | 9.36 | 50.04 | 31.92 | 25.71 | 42.37 |
| | Kejetia | 66.85 | 13.63 | 19.51 | 33.72 | 19.05 | 47.23 | 42.03 | 8.35 | 49.62 |
| | Takwa | 63.56 | 21.31 | 15.12 | 37.50 | 12.53 | 49.97 | 41.83 | 17.54 | 40.63 |
| Ni | Study area | 37.93 | 51.19 | 10.88 | 54.62 | 18.93 | 26.45 | 23.32 | 49.13 | 27.55 |
| | Accra | 35.07 | 52.32 | 12.62 | 45.76 | 21.57 | 32.67 | 21.18 | 48.22 | 30.60 |
| | Kejetia | 30.68 | 55.57 | 13.75 | 60.29 | 18.87 | 20.83 | 18.79 | 50.11 | 31.09 |
| | Takwa | 48.05 | 45.68 | 6.27 | 57.81 | 16.34 | 25.86 | 28.95 | 37.70 | 33.34 |
| Pb | Study area | 60.26 | 35.40 | 4.34 | 29.87 | 9.76 | 60.38 | 41.26 | 19.31 | 39.44 |
| | Accra | 53.53 | 39.75 | 6.72 | 41.47 | 14.49 | 44.04 | 32.86 | 31.62 | 35.52 |
| | Kejetia | 75.26 | 19.84 | 4.90 | 14.85 | 11.19 | 73.96 | 56.56 | 16.40 | 27.04 |
| | Takwa | 52.00 | 46.60 | 1.40 | 33.27 | 3.59 | 63.13 | 34.40 | 42.98 | 22.62 |
| Zn | Study area | 71.10 | 10.51 | 18.39 | 47.72 | 4.65 | 47.63 | 48.20 | 6.04 | 45.76 |
| | Accra | 63.42 | 8.31 | 28.27 | 44.67 | 4.54 | 50.79 | 43.23 | 7.71 | 49.06 |
| | Kejetia | 71.48 | 12.99 | 15.53 | 39.96 | 3.58 | 56.46 | 60.14 | 19.25 | 20.61 |
| | Takwa | 78.40 | 10.24 | 11.36 | 58.51 | 5.84 | 35.64 | 45.21 | 8.93 | 45.86 |

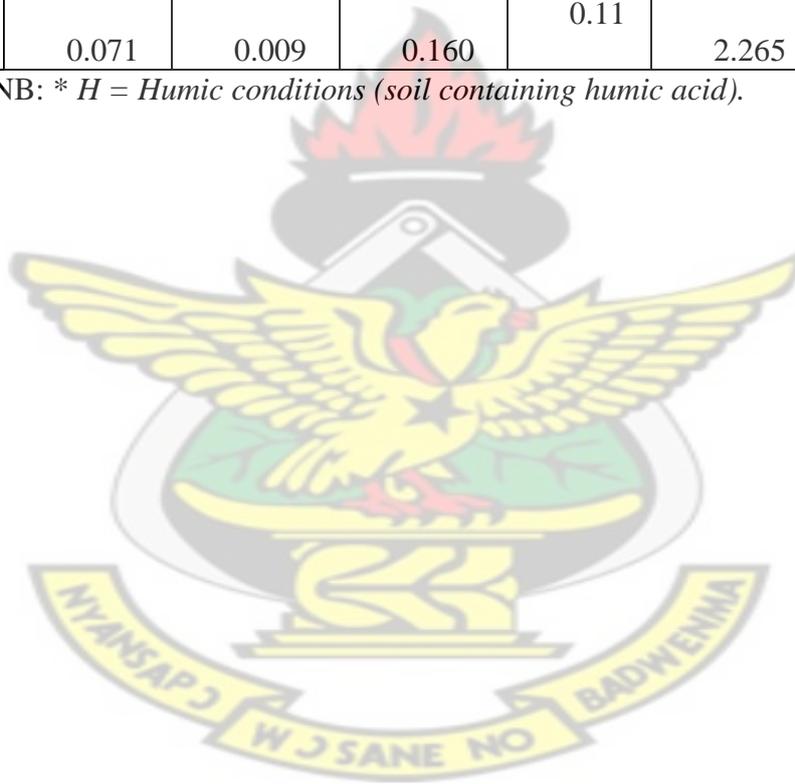
NB: * NB: *HA = humic acid; FA = fulvic acid; HS = humic substance (HA+FA); M-HS = metal-bound humic substance; M_{HA} = metal-bound humic acid; M_{FA} = metal-bound fulvic acid; M_{LA} = metal bound to inorganic ligands in solution; **Study area = Entire geographical area covering the three mining communities (Kejetia, Tarkwa and Accra)

APPENDIX 14

Trace metal partition constant obtained under humic and non-humic conditions

| pH | Partition constant | | Solid Phase (mg/g) | | Solution Phase (mg/L) | |
|-------|--------------------|----------|--------------------|-------|-----------------------|--------|
| | K_{dmH}^* | K_{dm} | V_{mH} | V_m | C_{mH} | C_m |
| 3.870 | 0.094 | 0.019 | 0.088 | 0.12 | 0.929 | 6.633 |
| 4.700 | 0.129 | 0.032 | 0.167 | 0.11 | 1.295 | 3.597 |
| 6.850 | 0.118 | 0.021 | 0.168 | 0.13 | 1.423 | 6.256 |
| 10.00 | 0.071 | 0.009 | 0.160 | 0.11 | 2.265 | 12.709 |

NB: * H = Humic conditions (soil containing humic acid).



APPENDIX 15

SOFTWARE SCREEN SHOTS

MANUAL ENTRY OF DATA

Ternary Phase values form

KNUST

The screenshot displays the 'NIFTY TMDM SOIL SYSTEM' application window. The menu bar includes 'File', 'Data Entry', 'Import Data', 'Report', and 'Help'. The active window is titled 'Ternary System Parameters' and contains the following fields and controls:

- Data Description:** A dropdown menu.
- Date:** A date selector showing '20/11/2012'.
- pH:** A text input field.
- Ionic Strength:** A text input field.
- Temperature:** A text input field.
- Bulk Density:** A text input field.

Below the input fields are four buttons: 'Save', 'Cancel', 'Delete', and 'Exit'. At the bottom of the window is a table with the following columns:

| ID | DataDescription | PH | IonicStrength | Temperature | BulkDensity | DataDate |
|----|-----------------|----|---------------|-------------|-------------|----------|
|----|-----------------|----|---------------|-------------|-------------|----------|

Solution phase

NIFTY TMDM SOIL SYSTEM

File Data Entry Import Data Report Help

Solution Phase Parameters

Data Description 20/11/2012

Conc Organic Ligand [L]

Conc Inorganic Ligands

Conc Metal-Bound Organic Ligand [ML]

Con Ligand That has complex with Metal [L_m]

Con Inorganic Ligand That has complex with Metal [L_{am}]

Conc Metal-Bond Inorganic Ligands

Conc Metal ion [M^{n+}]

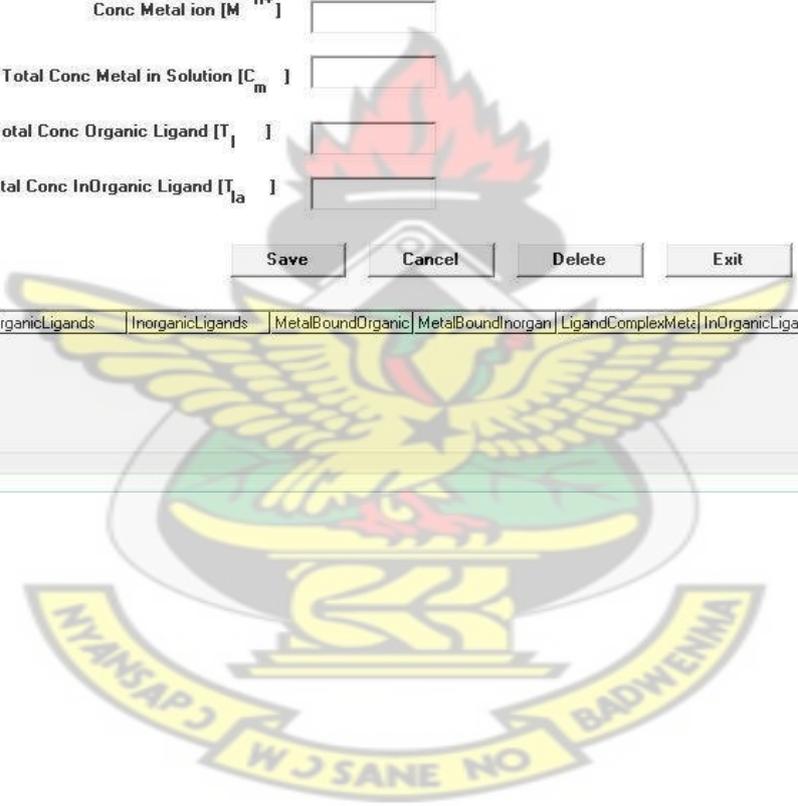
Total Conc Metal in Solution [C_m]

Total Conc Organic Ligand [T_l]

Total Conc InOrganic Ligand [T_{la}]

Save Cancel Delete Exit

| ID | OrganicLigands | InorganicLigands | MetalBoundOrganic | MetalBoundInorgan | LigandComplexMeta | InOrganicLigandCor | TotalOrganic | Tot |
|----|----------------|------------------|-------------------|-------------------|-------------------|--------------------|--------------|-----|
| | | | | | | | | |



Solid Phase

NIFTY TMDM SOIL SYSTEM

File Data Entry Import Data Report Help

Solid Phase Parameters

Data Description 20/11/2012

Conc Metal Bound to Oxide Sorption Sites

Conc Metal Bound to Carbonate Sorption Sites

Conc Metal Bound to Organic Sorption Sites

Con Ligand That has complex with Metal [L_m]

Con Inorganic Ligand That has complex with Metal [L_{am}]

Conc Metal Bound to Clay Sorption Sites

Conc Metal Bound to adsorbed organic matter

Conc Metal Bound to organic matter aggregates in soil matrix

Total Conc Metal Bound to all soil sorption sites

Mass of Solid Phase [M_s]

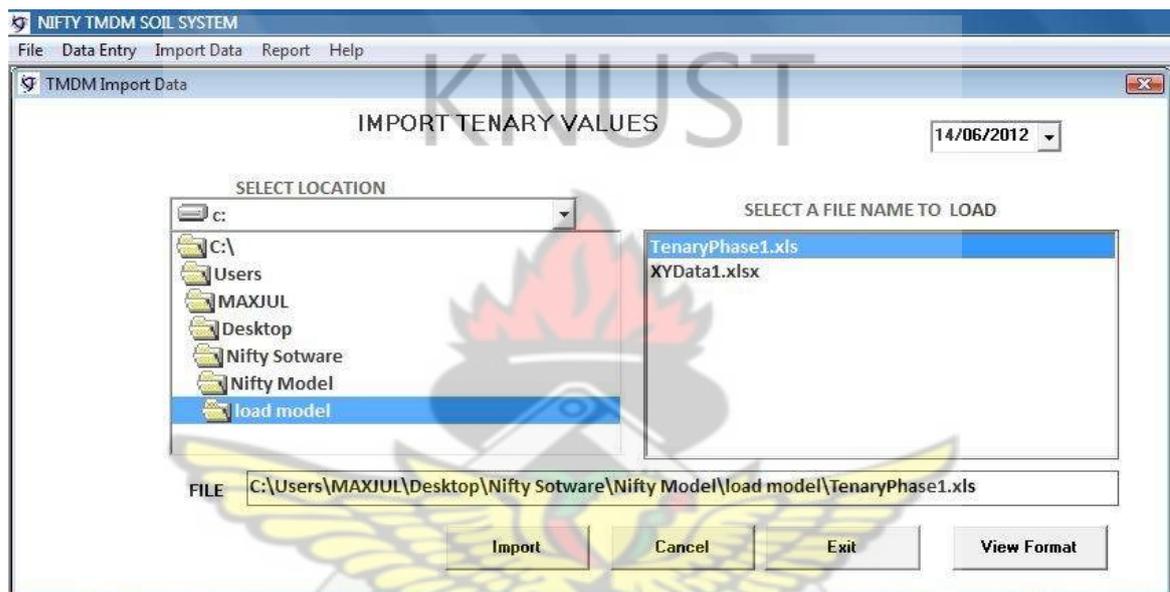
Total Conc Organic Ligand [T_l]

Save Cancel Delete Exit

| ID | OxideSorption | CarbonateSorption | OrganicSorption | ClaySorption | AdsorbedOrganicM: | LigandComplexMet: | InOrganic |
|----|---------------|-------------------|-----------------|--------------|-------------------|-------------------|-----------|
| | | | | | | | |

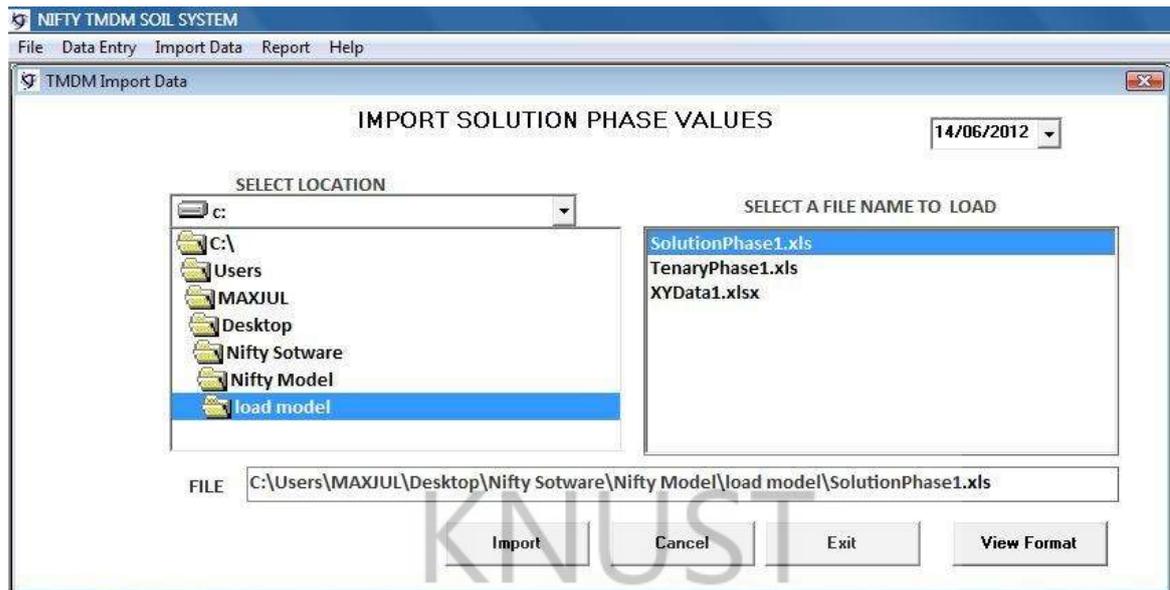
IMPORTING DATA FROM A FILE

Tenary Phase

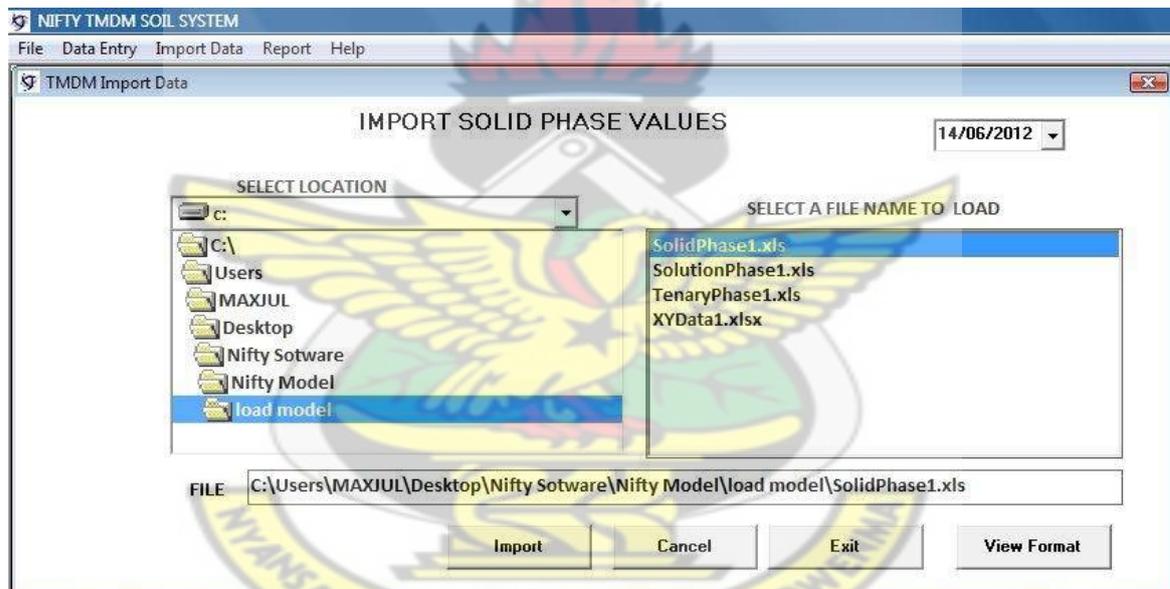


Solution Phase

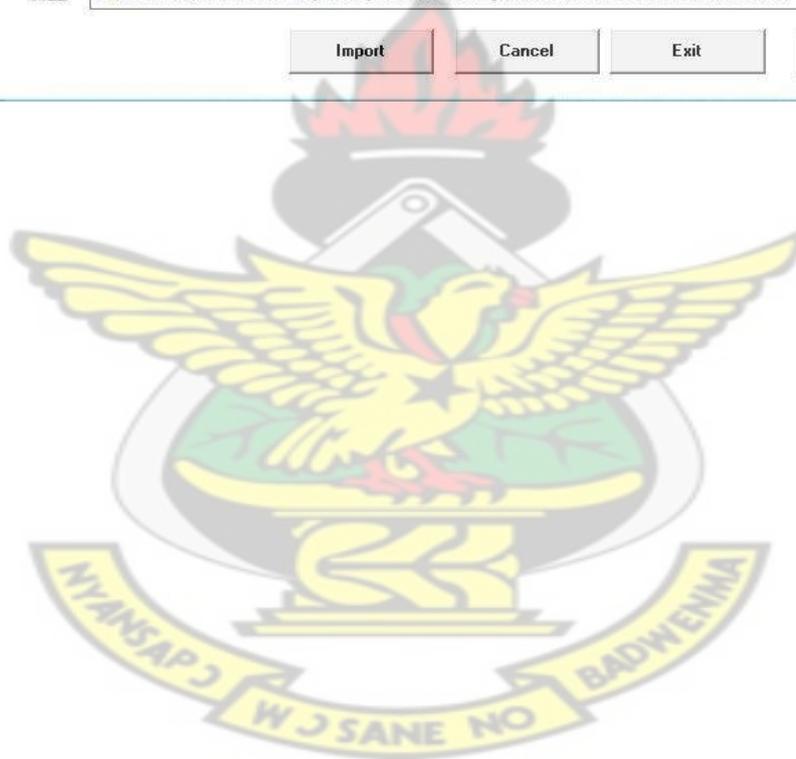
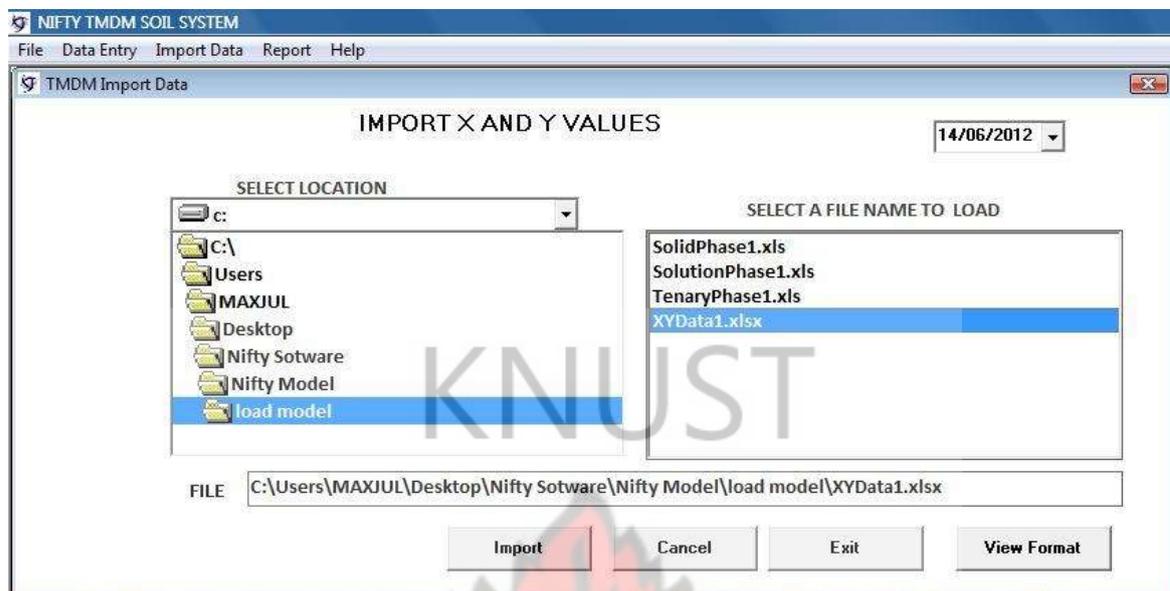




Solid Phase



X and Y Values



PREPARING REPORT

By Models

NIFTY TMDM SOIL SYSTEM
File Data Entry Import Data Report Help

Models

SELECT MODEL(S)

All Models

Model 1: Ligand Complex Partition Effect Model (LCPEM) $1/Q_{ml} = g(1/KDM) - C$

Model 2: Ligand-Exchange Effect Model (LEEM) $QL = gKDM - C$

Model 3: Ligand Partition Effect Model 1 (LPEM) $KDL = gKDM - C$

Model 4: Complex Depletion and Ligand Aggregation Model (CDLAM) $1/B = g(1/KDL) - C$

Model 5: Complex depletion and metal partition model (CDMP) $1/B = g(1/KDM) - C$

Model 6: Competitive Adsorption and Ligand Partition Model (CALPM) $G = g(1)/K_{DL} - C$

Model 7: Complex Exchange and Ligand Partition Model (CELPM) $1/Q_{ML} = g 1/K_{DL} - C$

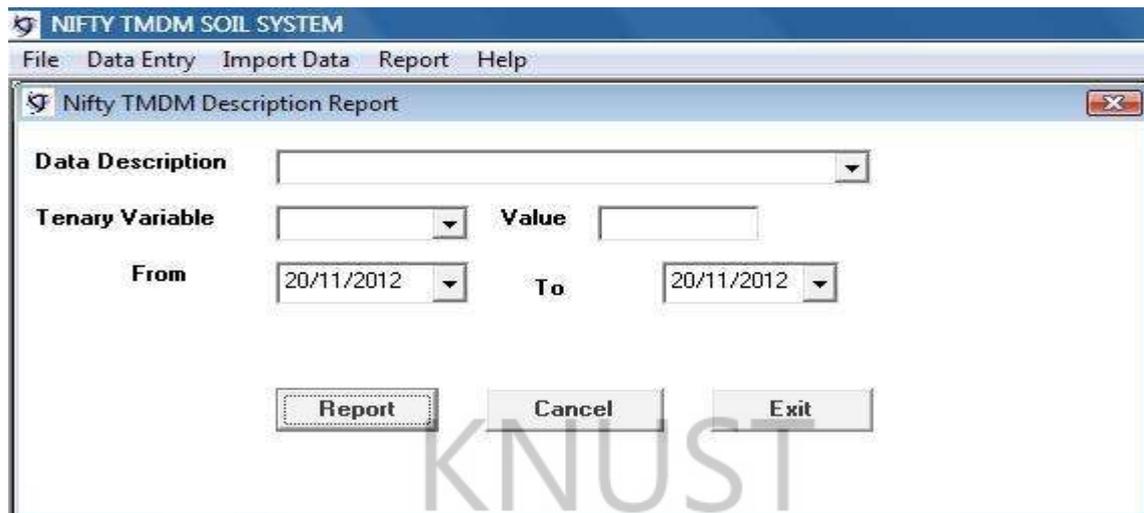
Data Description:

From: To:

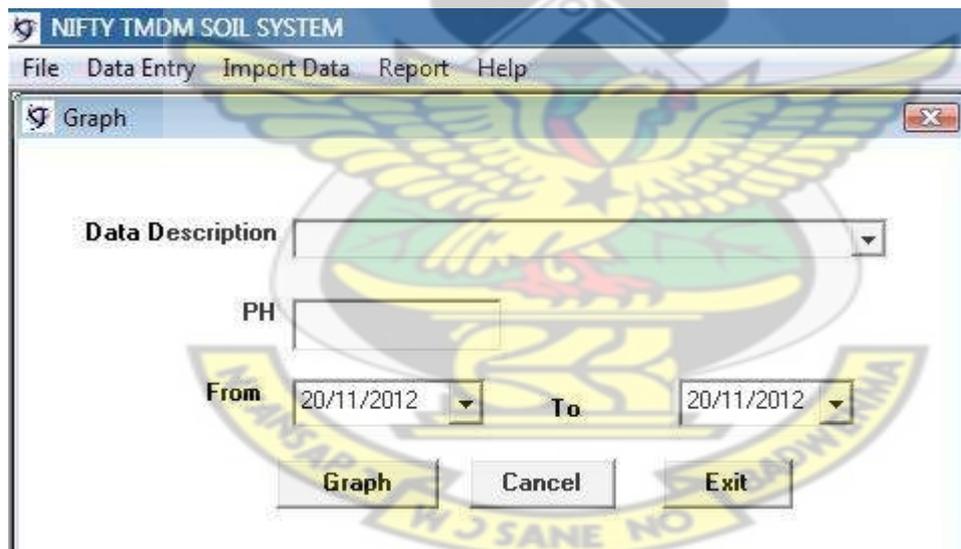
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APPENDIX 16

List of Chemicals and Instruments

List of Chemicals

| S/No | Item | Assay (%) | Molecular weight (g/mol) | Specific gravity | Manufacturer | Country |
|------|---|-----------|--------------------------|------------------|---------------|---------|
| 1 | Acetic Acid (CH ₃ COOH) | 99.8 | 60.05 | 1.05 | BDH PROLABO | England |
| 2 | Hydrochloric Acid (HCl) | 36.8 | 36.4 | 1.19 | BDH PROLABO | England |
| 3 | Nitric Acid (HNO ₃) | 68.5 | 63.01 | 63.01 | BDH PROLABO | England |
| 4 | Sulfuric Acid (H ₂ SO ₄) | 96.2 | 98.08 | 1.84 | BDH PROLABO | England |
| 5 | Ammonium Acetate: (CH ₃ COONH ₄) | 97 | 77.08 | N/A | PANREAC | Spain |
| 6 | Barium Chloride 2-hydrate (BaCl ₂ .H ₂ O) | 100 | 244.28 | N/A | PANREAC | Spain |
| 7 | Copper Sulphate 5-hydrate (CuSO ₄ .5H ₂ O) | 99.5 | 249.68 | N/A | PANREAC | Spain |
| 8 | Sodium Acetate (CH ₃ COONa) | 99 | 82.03 | N/A | PANREAC | Spain |
| 9 | Potassium Hydroxide (KOH) | 85 | 56.11 | N/A | PANREAC | Spain |
| 10 | Sodium Hydroxide (NaOH) | 99 | 40 | N/A | BDH PROLABO | England |
| 11 | Potassium Permanganate (KMnO ₄) | 99 | 158.03 | N/A | BDH PROLABO | England |
| 12 | 12. Potassium dichromate (K ₂ Cr ₂ O ₇) | 99 | 294.18 | N/A | BDH PROLABO | England |
| 13 | D-Glucose (C ₆ H ₁₂ O ₆) | 99 | 180.16 | N/A | PANREAC | Spain |
| 14 | Hydroxylamine hydrochloride (H ₂ NOH.HCl) | 99 | 69.49 | N/A | SIGMA-ALDRICH | USA |
| 15 | Perchloric acid (HClO ₄) | 70 | 100.46 | 1.7 | BDH PROLABO | England |
| 16 | Hydrofluoric acid (HF) | 50 | 20.01 | 1.2 | SIGMA-ALDRICH | USA |
| 17 | Hydrogen peroxide (H ₂ O ₂) | 30 | 34.01 | 1.13 | PANREAC | Spain |

List of Instruments

| S/no. | Instrument | Brand/model | Manufacturer | Country |
|-------|--------------------|--|---------------------------|-----------|
| 1 | Spectrophotometer | Jenway 6405 UV/Vis Spectrophotometer | Barloworld scientific Ltd | England |
| 2 | Water bath | Heizbad HB digit | Heidolph | Germany |
| 3 | AAS | Varian 240 FS | Varian company | Australia |
| 4 | Centrifuge | Selecta Centro 8 | JP selecta S.A | Spain |
| 5 | pH meter | Crison basic 20 | Crison Instruments S.A | Spain |
| 6 | Conductivity meter | Crison Basic 30 | Crison instrument S.A | Spain |
| 7 | Thermometr | Hanna HI 935005 K-thermocouple thermometr | Hanna Instruments | Spain |
| 8 | Shaker | HS 260 control | Ika-werk GMBH & CO.KG | Germany |
| 9 | Hot plate | Selecta Combiplac | JP selecta S.A | Spain |
| 10 | Oven | Selecta | JP selecta S.A | Spain |

APPENDIX 17

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PUBLISHED PAPERS FROM THESIS

