Modeling of Glyphosate and Metal-Glyphosate Speciation in Solution and at Solution-Mineral Interfaces

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Akademisk avhandling

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Abstract
Glyphosate (N-(phosphonomethyl)glycine, PMG, H₃L) is a widely used organophosphorous herbicide. It interacts with metal ions and mineral surfaces, which may affect its mobility, degradation and bioavailability in the environment. However, these interactions are far from fully understood. This thesis is a summary of five papers discussing the complexation of PMG with metal ions in aqueous solution and the adsorption of PMG and/or Cd(II) on different mineral surfaces.

The complexation of PMG with the metals Cd(II) or Al(III) in aqueous solution was investigated with macroscopic and molecular scale techniques. Potentiometric titration data were combined with EXAFS, ATR-FTIR and NMR spectroscopic data to generate solution equilibrium models. In the PMG-Cd(II) system, only mononuclear complexes were formed, while both mono and binuclear complexes were observed in the PMG-Al(III) system.

EXAFS, ATR-FTIR, and XPS measurements showed that PMG adsorbs to the surfaces of goethite (α-FeOOH), aged γ-alumina (γ-Al₂O₃) and manganite (γ-MnOOH) through one oxygen of its phosphonate group to singly-coordinated surface sites. Surface complexation models consistent with these spectroscopic results were fit to adsorption data using the pK reaction formalism. Electrostatic effects were accounted using either the Extended Constant Capacitance Model (ECCM) or the Basic Stern Model (BSM), and the charge of the surface complexes was distributed over the different planes. The formation of the surface complexes was described according to the following reactions:

\[ {\text{MeOH}}^{0.5-} + {\text{H}_3}\text{L} \leftrightarrow {\text{MeHL}}^{1.5-} + {\text{H}_2}\text{O} + \text{H}^+ \]  
\[ \beta^{\text{MeHL}^{1.5-}} \]

\[ {\text{MeOH}}^{0.5-} + {\text{H}_3}\text{L} \leftrightarrow {\text{MeL}}^{2.5-} + {\text{H}_2}\text{O} + 2\text{H}^+ \]  
\[ \beta^{\text{MeL}^{2.5-}} \]

The coadsorption of PMG and Cd(II) on the surfaces of goethite and manganite results in the formation of ternary mineral-PMG-Cd(II) surface complexes, as suggested from EXAFS results. Previous EXAFS measurements have also established the coordination geometries for the binary goethite-Cd(II) and manganite-Cd(II) surface complexes. In addition to the surface reactions in the binary mineral-Cd(II) and mineral-PMG systems, a single ternary complex with the stoichiometry \( {\text{MeLCd(OH)}}^{1.5-} \) was sufficient to explain coadsorption data:

\[ {\text{MeOH}}^{0.5-} + {\text{H}_3}\text{L} + \text{Cd}^{2+} \leftrightarrow {\text{MeLCd(OH)}}^{1.5-} + 3\text{H}^+ \]  
\[ \beta^{\text{MeLCd(OH)}^{1.5-}} \]

It was concluded that the affinity of PMG for the three mineral systems decreases within the series: goethite > aged γ-Al₂O₃ > manganite. The formation of the ternary surface complex is more significant on goethite surfaces than on manganite surfaces.

Keywords
herbicide, glyphosate, goethite, aged γ-alumina, bayerite, manganite, cadmium(II), aluminium(III), potentiometric titration, adsorption, surface complexation model, speciation
Modeling of Glyphosate and Metal-Glyphosate Speciation in Solution and at Solution-Mineral Interfaces

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Department of Chemistry
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It was concluded that the affinity of PMG for the three mineral systems decreases within the series: goethite > aged γ-Al$_2$O$_3$ > manganese. The formation of the ternary surface complex is more significant on goethite surfaces than on manganese surfaces.

Keywords: herbicide, glyphosate, goethite, aged γ-alumina, bayerite, manganite, cadmium(II), aluminium(III), potentiometric titration, adsorption, surface complexation model, speciation


80 pages and 5 papers
The River Speaks

Down from the mountains of eternal snow
The streams come tumbling, joining as they flow
   To send a river winding toward the sea.
   I listen, and the river speaks to me.

   It tells of meadows on a thirsty plain;
   Of gardens blooming where there is no rain;
   Of mighty cities built upon its banks;
   Of living things that owe the river thanks.

   The waters speak to me, and hurry on,
   Eager to come and eager to be gone.
   Almost it seems as if the river knew
   How many things there are for it to do.

   Sometimes it pauses, to lay up a store
   of liquid wealth in lake and reservoir,
   Then leaps a dam and hastens on again,
   Turning a wheel to light the homes of men.

   The river speaks, and deserts cease to be;
   Wide fields grow green, and ships go down to the sea,
   I hear the water singing as it goes:
   "Let life go on, because the river flows."

(Gene Lindberg)
Modeling of Glyphosate and Metal-Glyphosate Speciation in Solution and at Solution-Mineral Interfaces

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This thesis contains a summary and a discussion of the following papers, referred to in the text by their numbers I-V.

I. Thermodynamic and Spectroscopic Studies of Cadmium(II) – N- (phosphonomethyl)glycine (PMG) Complexes
   Madeleine Ramstedt, Caroline Norgren, Julia Sheals, Dan Boström, Staffan Sjöberg, Per Persson
   Inorganica Chimica Acta, 357, 1185-1192, 2004

II. Co-adsorption of Cadmium(II) and Glyphosate at the Water-Manganite (γ-MnOOH) Interface
   Madeleine Ramstedt, Caroline Norgren, Andrei Shchukarev, Staffan Sjöberg, Per Persson

III. Adsorption of Glyphosate (PMG) on Goethite (α-FeOOH): Surface Complexation Modeling combining Spectroscopic and Adsorption Data
    Caroline M. Jonsson, Per Persson, Staffan Sjöberg, John S. Loring
    Submitted to Environmental Science and Technology

IV. Glyphosate Complexation to Aluminium(III) in Solution and to the Surface of Aged γ-Al₂O₃. Chemical Speciation Models Combining Spectroscopic and Macroscopic Data.
    Caroline M. Jonsson, Julia Jönsson, Ingegärd Andersson, Per Persson, Staffan Sjöberg, John S. Loring
    Manuscript

V. Surface Complexation Modeling of Cadmium(II) and Glyphosate Adsorption at the Surface of Manganite (γ-MnOOH) and Goethite (α-FeOOH)
   Caroline M. Jonsson, Staffan Sjöberg
   Manuscript

Publication of interest but not included in the thesis:

- Chemical Speciation of N – (phosphonomethyl)glycine, PMG, in Solution and at Mineral Interfaces
  Madeleine Ramstedt, Caroline Norgren, Julia Sheals, Andrei Shchukarev, Staffan Sjöberg; Surface and Interface Analysis, 36, 1074-1077, 2004

Please note: In July 2006 the author changed her surname from Norgren to Jonsson.
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ABBREVIATIONS

Al(III)   Aluminium(III)
ATR-FTIR  Attenuated Total Reflectance - Fourier Transform Infrared
BSM      Basic Stern Model
C        Capacitance
CCM      Constant Capacitance Model
Cd(II)   Cadmium(II)
CD       Charge Distribution
Cu(II)   Copper(II)
dl      Diffuse Layer
ECCM     Extended Constant Capacitance Model
EDL      Electrostatic Double Layer
EXAFS    Extended X-ray Absorption Fine Structure
Fe(III)  Iron(III)
H$_3$L   Protonated Ligand (here: Glyphosate)
Mn(III)  Manganese(III)
MUSIC    Multisite Complexation
NMR      Nuclear Magnetic Resonance
PMG      N-(phosphonomethyl)glycine, Glyphosate
Q        Charge at a Specific Surface Plane
SCM      Surface Complexation Model
TPM      Three Plane Model
XPS      X-ray Photoelectron Spectroscopy
XRD      X-ray Powder Diffraction
α-FeOOH  Goethite (Iron(III) hydroxide)
β-Al(OH)$_3$  Bayerite (Aluminium(III) hydroxide)
γ-Al$_2$O$_3$ gamma-Alumina (Aluminium(III) oxide)
γ-MnOOH  Manganite (Manganese(III) hydroxide)
$\beta$   Formation Constant, or Surface Plane in BSM and ECCM
$\Psi$    Surface Potential
$\sigma$  Surface Charge Density, or Standard Deviation
POPULÄRVETENSKAPLIG SAMMANFATTNING


Glyfosat reagerar med andra ämnen och kan därmed bli mer stabilt och skyddat från nedbrytning. Tungmetaller som finns i jordar och vattendrag bildar starka kemiska föreningar med glyfosat. Dessutom adsorberas* glyfosat i hög grad till ytan av mineralpartiklar. Ett ämne som befinner sig i vattenlösning är ofta mer biotillgängligt och mer kapabelt till att spridas, medan möjligheten till fastläggning i jordar och sediment ökar då ämnet adsorberats till en mineralpartikel. I sjöar, hav och vattendrag kan partiklar transporterats, och därmed ta med sig adsorberade ämnen långa sträckor. I naturliga jordar och vattendrag finns stora mängder av mineralpartiklar innehållande järn, aluminium och mangan och dessa kan påverka både tungmetallers och glyfosats öde i naturen.

I denna avhandling studeras de reaktioner som sker mellan glyfosat och metallerna kadmium och aluminium i en vattenlösning. Dessutom studeras adsorption av glyfosat på tre olika mineralytor; götit (ett järnmineral), åldrad gamma-alumina (ett aluminiummineral) och manganit (ett manganmineral). Slutligen har glyfosat och kadmium adsorberats
samtidigt till några av mineralerna för att möjliggöra en jämförelse av de olika kemiska systemen.


* herbicid ~ växtbekämpningsmedel
* mobilitet ~ rörlighet, spridning
* biotillgänglighet ~ ett mått på hur mycket av ämnet som kan tas upp av en organism
* adsorbera ~ fastna på ytan av någonting
* spektroskopi ~ samlingsnamn för analysmetoder där olika typer av spektrum studeras
1. INTRODUCTION

Glyphosate, or N-phosphonomethylglycine (PMG), is one of the most widely used herbicides in the world today. It has been on the market since 1974 and constitutes the active substance of several commercially available products, e.g. Roundup®, Rodeo®, Accord®, and Touchdown®. These glyphosate containing herbicides are used not only in agriculture but also in forests, along highways, and in private gardens. The herbicide is taken up by the leaves, and no plants are known to be naturally resistant to the action of glyphosate. It functions by inhibiting an enzyme in the biosynthesis of aromatic amino acids; a pathway present in plants but not in animals (1,2).

The persistence of glyphosate in the environment depends partly on the microbial activity of the soil, since the degradation of the molecule is mainly determined by microbial processes. On the other hand, the inactivation of glyphosate in soils occurs mainly through adsorption onto mineral surfaces. However, as a consequence of frequent usage, glyphosate has been introduced to many different compartments of the environment, and there have been a number of incidents where glyphosate and its primary metabolite, aminomethylphosphonic acid (AMPA), have been found in surface and ground waters. The mobility and leaching of glyphosate may increase, for example due to high rainfall events shortly after application (3). Glyphosate adsorbs mainly through the phosphonate moiety of the molecule (4) and as a consequence, phosphate can be expected to compete with glyphosate for binding sites on the minerals. This has been confirmed and the competition may also result in a higher mobility of glyphosate in phosphate rich soils (5,6).

That glyphosate forms complexes with metal ions in solution has been reported by several authors (7-9). Metal ions also influence the adsorption of glyphosate onto mineral surfaces, either directly through ternary complex formation or indirectly by making the surface more positively charged and more prone to anion adsorption. The adsorption normally decreases the toxicity of the herbicide to plants, and the surface interactions can
also affect the susceptibility of glyphosate to degradation, although recently published results showed that glyphosate is still microbially degradable when adsorbed to the iron hydroxide, goethite (α-FeOOH) (10). A number of studies, including the work within this thesis, show that glyphosate adsorbs strongly to the surfaces of iron-, aluminium- and manganese (hydr)oxide minerals (3,4). These minerals are abundant in soils and sediments and are therefore of high importance when discussing the fate of glyphosate (11).

To help predict the fate of glyphosate in nature, it is important to understand its speciation (chemical forms) in solution and at the mineral-water interface. Speciation is important when discussing the degradation, bioavailability and toxicity of glyphosate. Solution equilibrium and surface complexation models represent an encompassing approach to the speciation of glyphosate because they take into account pH and total concentrations of ligands, metals, and surface sites. To find the most realistic model, it is essential to understand at a molecular level how glyphosate interacts with metals in solution and adsorbs to mineral surfaces. Hence, chemical equilibrium models should be based not only on macroscopic studies (e.g. potentiometry and adsorption experiments) but also on structural characterizations and quantitative results from spectroscopic methods. The use of complementary techniques gives an extended understanding of glyphosate-metal and mineral interactions. By predicting speciation, solution equilibrium and surface complexation models help us come one step closer to a more complete understanding of the impact of glyphosate on the environment.

1.1 Aim of the Thesis

The objective of this thesis was to study the complexation of glyphosate with the metal ions Cd(II) and Al(III) in aqueous solution, as well as the (co)adsorption of glyphosate and Cd(II) on the surfaces of goethite (α-FeOOH), aged γ-alumina (γ-Al₂O₃) and manganite (γ-MnOOH). Data were collected using potentiometric titrations, batch
adsorption experiments, and spectroscopic methods, and then compiled into surface complexation models. In order to generate a surface complexation model for a ternary mineral-PMG-metal system, it is crucial to define the subsystems (Figure 1). Hence, the protonation reactions of soluble species, PMG-metal complexation reactions in solution, the acid-base properties of the mineral surface, as well as the binary mineral-PMG and mineral-metal systems must be well understood in terms of formation constants and other model parameters. The speciation in the above mentioned chemical systems will be presented and discussed.

\[ \equiv \text{MeOH}^{0.5-} \quad \equiv \text{Me}^{2+/3+} \]

Figure 1. Schematic figure illustrating the interactions between subsystems. The notations $\equiv \text{MeOH}^{0.5-}$ and $\text{Me}^{2+/3+}$ represent a general mineral surface site and a di- or trivalent metal ion, respectively.

2. (HYDR)OXIDE MINERALS

(Hydr)oxide minerals containing iron, aluminium and manganese are ubiquitous in the environment. They occur in soils and sediments and are abundant in waters of rivers, lakes and oceans. At their surfaces, they interact with both metals and organic and inorganic ligands, and affect the transportation and possibly the degradation of these substances. Through the adsorption of ligands and metals, the charge of the mineral surface is affected, which in turn can influence the aggregation and transport of the particles.

The characteristics and properties of a (hydr)oxide mineral surface are determined by the structure of the underlying crystal. Different minerals have different types of surface
functional groups depending on the cleavage planes within the crystal structure. The surface groups are different from the atoms within the crystal structure by being unsaturated and therefore more reactive. The reactive sites are considered the surface oxygens, and these are distinguished by their coordination number to underlying metal atoms in the bulk (12-15). When surface oxygens come into contact with water they react to form hydroxyl (OH) or terminal water sites at the surface.

Due to the charge of the formed surface site, another water molecule will adsorb to it, which consequently results in a multilayer of water molecules that do not behave exactly as the water molecules in solution, but are affected by the surface. In addition, ions and molecules (generally denoted ligands) in solution can be adsorbed to the surface and thereby form surface complexes. Ligands can be associated with the surface in different ways. An outer-sphere complex is formed when one or more water molecules are present between the ligand and the surface metal, and this type of complex is mainly stabilized by electrostatic attractions. On the other hand, when a direct chemical bond is formed between the ligand and the surface metal, then the complex is called inner-sphere. Inner-sphere complexes are classified according to the number of surface sites that the ligand is bound to. If the ligand is coordinated to only one surface site, the complex is considered mononuclear. Ligands can be bound in either a monodentate or a bidentate fashion in mononuclear complexes. When two surface sites are involved, the surface complex is considered binuclear, and the ligand is usually bound in a bidentate-bridging configuration. Ligands that coordinate in a bidentate fashion may lead to more stable complexes due to the chelate effect.

In this thesis, goethite (α-FeOOH), aged γ-alumina (γ-Al₂O₃) (with a bayerite-like surface in aqueous suspension after aging), and manganite (γ-MnOOH) were chosen as model, well characterized, crystalline minerals that are representative of naturally occurring (hydr)oxides. Some details of these minerals are presented below.
2.1 Goethite (α-FeOOH)

The goethite used in Papers III and V was synthesized according to the method described by Hiemstra et al. (13). Briefly, KOH was added to a solution of Fe(NO$_3$)$_3$×9H$_2$O, and the formed precipitates were aged for 100 h at 60 ºC and then dialyzed for two weeks to remove dissolved potassium nitrate and excess potassium hydroxide. The goethite structure was confirmed by X-ray powder diffraction (XRD) and electron microscopy, and a specific surface area of 85 m$^2$/g was determined using the BET N$_2$ adsorption method (16).

Goethite particles were found to be well crystallized needles (17). The dominating crystal plane {110} accounts for more than 90% of the surface area (18), while the other 10% from the terminations of the particles can be approximated by the {001} plane. The {110} plane exhibits singly- (≡FeOH$^{0.5-}$), doubly- (≡Fe$_2$OH) and triply-coordinated (≡Fe$_3$O$^{0.5-}$) sites, displayed along rows, while the {001} plane exhibits only singly- and doubly-coordinated oxygens (Figure 2) (17). Predictions of the reactivity of the different types of surface functional groups (14) suggest the singly coordinated (≡FeOH$^{0.5-}$) and one type of the triply coordinated (≡Fe$_3$O$^{0.5-}$) sites to be responsible for the acid-base properties of the goethite surface in the pH range 1-11. Based on crystallographic data, the total concentrations of singly- and triply-coordinated sites are 3.64 and 2.73 sites/nm$^2$, respectively (19), which corresponds to a total concentration of proton active sites of 10.6 μmol/m$^2$. 
2.2 Aged γ-Alumina (γ-Al₂O₃)

When γ-alumina (γ-Al₂O₃) is suspended in water, the surface of the particles transform into a bayerite (β-Al(OH)₃) structure (20,21). The aged γ-Al₂O₃ used in Paper IV was synthesized by suspending γ-Al₂O₃ (99.995% purity) in water for at least one month to produce a bayerite-like surface with a BET surface area (16) of 131 m²/g. XRD measurements (22) performed on particles of aged γ-Al₂O₃ showed not only the powder diffraction characteristics for γ-Al₂O₃ but also signs of bayerite. Thus some characteristics of pure bayerite (23) were assumed to be applicable for the surface of aged γ-Al₂O₃ used in the adsorption experiments in Paper IV.

Bayerite is a dimorph of gibbsite and has a monoclinic crystal structure with sheets containing ring systems of octahedrally coordinated aluminium ions that are organized along the {001} direction (Figure 3). Hydrogen bonds keep the sheets together, which suggests that {001} cleavage planes should be abundant. Bayerite is well developed in the z direction and thus has a high proportion of {100} and {110} edges. These edges display both singly- (≡AlOH₀.₅⁻) and doubly-coordinated (≡Al₂OH) surface oxygens, although only
the singly-coordinated sites are considered to be proton active. The density of these singly-coordinated sites calculated from the crystallographic structure of synthetic bayerite is 8.35 sites/nm$^2$ (23). This corresponds to a total concentration of proton active sites of 13.9 $\mu$mol/m$^2$.

![Figure 3. The crystal structure of bayerite. Sheets are kept together by hydrogen bonds.](image)

### 2.3 Manganite (γ-MnOOH)

The manganite used in Papers II and V was synthesized according to Giovanoli & Leuenberger (24) by mixing NH$_3$, MnSO$_4$ and H$_2$O$_2$. The mixture was heated to 95 °C under stirring for 6 h, and the solid formed was washed, dried, ground, and stored as a powder. The manganite structure was confirmed by XRD and the BET surface area (16) was determined to be 41 m$^2$/g.

The manganite crystals were needle shaped (25) and the crystal structure consists of Jahn-Teller elongated Mn(III)-O$_6$ octahedra that are arranged in a rutile-type structure (Figure 4) (25). The {010} plane has been shown to be predominant and constitutes a plane of cleavage. The singly coordinated surface sites (=MnOH$_{0.5}^-$) are expected to be the most reactive sites (25). Their crystallographic site density is 7.9 sites/nm$^2$, which corresponds to a total concentration of proton active sites of 13.1 $\mu$mol/m$^2$. 

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Figure 4. The crystal structure of manganite, modified from Ramstedt et al. (25), showing the position of the {010} plane as dotted lines. Hydrogens of the surface sites are omitted for clarity.

3. SURFACE COMPLEXATION MODELING

Surface complexation models (SCM) can be used to describe the equilibrium reactions that take place at the interface between a mineral surface and the solution. There are different types of SCMs, and which one to apply depends not only on the properties of the surface, metal(s), and ligand(s), but also on what type of data that is available for the chemical system. Surface complexation theory treats adsorption of ions according to thermodynamic concepts of complexation in solution, and electrostatic effects at the surface-solution interface are addressed by theories that describe the electrostatic double layer (EDL). In addition, surface-site heterogeneity can be taken into account if several different types of surface sites are reactive.

3.1 Properties of the Mineral Surface

The surface sites on (hydr)oxide minerals are referred to as oxygens, and these oxygens are distinguished by the number of metal ions within the crystal substructure to which they are coordinated. Thus, surface oxygens that are coordinated to one, two or three
metals are called singly-, doubly- or triply-coordinated surface sites, respectively. The charge of these surface sites is determined by the coordination mode of the metal in the crystal structure, according to the Multisite Complexation (MUSIC) model developed by Hiemstra and based on Pauling’s bond valence theory (12,13,26). Assuming the charge is distributed symmetrically over surrounding bonds (27) a formal bond valence (v) can be defined as:

\[ v = \frac{z}{CN} \]  

where z is the valency of the metal and CN is the coordination number. In all (hydr)oxides in this thesis, the metal is trivalent (Me(III)) and octahedrally coordinated to six oxygen atoms. This means that each oxygen atom will neutralize the charge of the metal by one sixth, resulting in a formal charge of +0.5 at each bond. Thus, the charge of a singly-coordinated surface site would be either +0.5 or -0.5, depending on the protonation state, according to:

\[ \equiv \text{MeOH}_2^{0.5^+} \rightleftharpoons \equiv \text{MeOH}^{0.5^-} + H^+ \quad \text{pK}_a \]  

This concept is known as the 1pK model, since one reaction can describe the protonation/deprotonation of the surface. The same approach can be used for the triply-coordinated surface sites (\( \equiv \text{Me}_3\text{OH}^{0.5^+} \) and \( \equiv \text{Me}_3\text{O}^{0.5^-} \), respectively), while the doubly-coordinated surface sites (\( \equiv \text{Me}_2\text{OH} \)) would be neutral and thus require two reactions with corresponding pK\(_a\) values to describe their protonation/deprotonation. A significant reduction in adjustable parameters is obtained with the 1pK approach, since this pK\(_a\) value can be experimentally obtained from potentiometric titration data as the pH\(_{\text{pzc}}\) (\( \text{pzc} = \) point of zero net proton condition). The pH\(_{\text{pzc}}\) is the pH where the net charge of the
particle surface is zero, i.e. the total positive charge is equal to the total negative charge. This pH value often coincides with the pH_{iep} (iep = isoelectric point), which is the pH at which the particles have zero mobility in an applied electric field (28).

### 3.2 Surface Complexation Models

All surface complexation models are based on some fundamental concepts, defined by Dzombak and Morel (29):

- Adsorption takes place at specific surface sites to form surface complexes, in a similar manner as complexation reactions in solution.
- Adsorption reactions can be described quantitatively by mass law equations.
- Surface charge is a result from the surface complex formation.
- The effect of surface charge on surface complexation can be taken into account by applying charge dependent formation constants.

Due to electrostatic effects that develop at the solid-solution interface when protons or other ligands are adsorbed, oppositely charged ions from the ionic medium in solution will adsorb as well, resulting in electroneutrality at the surface. The electrostatic double layer (EDL) that is created at the surface can be described using several standard electrostatic models and a brief presentation of the models used in this thesis is given below. The electrostatic model is manifested as a correction to an equilibrium constant of a surface reaction, analogous to an activity coefficient correction for reactions in solution. Accordingly, an apparent formation constant (β_{app}) for a surface complex is the product of an intrinsic constant (β_{int}) and the appropriate electrostatic corrections:

\[
β_{app} = β_{int} \sum_{i=1}^{N} e^{(-Δz_i \Psi i / FRT)}
\]  \[3\]
In Equation [3], \( N \) is the number of planes at which charges are assumed to be located, and this is model dependent. \( \Delta z_i \) is the difference in charge between the formed and reacting surface species at the \( i^{th} \)-plane, and \( \Psi_i \) is the potential at this plane.

### 3.2.1 Constant Capacitance Model (CCM)

The Constant Capacitance Model (CCM) can be seen as the analogue to the constant ionic medium approach in aqueous solution. The mineral-water interface is described as a compact layer that acts as a parallel plate capacitor (Figure 5). According to the CCM, surface complexes are of inner-sphere type, i.e. ligands are coordinated directly at the surface plane (0-plane). The counter ions that neutralize the surface charge are placed at a second plane at a distance from the surface. In the inner part of the EDL (between the two planes) the capacitance is constant but the potential is assumed to drop extensively and the contribution of counter ions outside the compact layer can be completely neglected. Consequently, the parameters are restricted to a certain constant high ionic strength. The surface potential \( (\Psi_0) \) is related to the surface charge \( (\sigma_0; \text{C/m}^2) \) and the specific capacitance \( (C; \text{C/V·m}^2) \), according to:

\[
\Psi_0 = \frac{\sigma_0}{C}
\]  

[4]
3.2.2 Extended Constant Capacitance Model (ECCM)

The CCM can be converted into the Extended Constant Capacitance Model (ECCM) (31). Two planes of specific adsorption are included in this model (Figure 6). Inner-sphere complexes are adsorbed at the surface plane, outer-sphere complexes at the β-plane, while counter ions from the electrolyte are treated in the same way as in the CCM. Thus, the constants are only valid for a specific ionic medium, and the effects caused by counter-ions are embedded in the constants (31). The ECCM can be seen as two constant capacitance layers with the total capacitance of the interface given by:

\[
\frac{1}{C_{tot}} = \frac{1}{C_1} + \frac{1}{C_2}
\]  

[5]
where $C_1$ corresponds to the inner layer (between the surface plane and the $\beta$-plane) and $C_2$ corresponds to the outer layer (between the $\beta$-plane and the bulk solution). The potentials and the charges at the surface plane and the $\beta$-plane are related according to Equations [6] and [7].

$$\Psi_\beta = \frac{\sigma_0 + \sigma_\beta}{C_2} \quad [6]$$

$$\Psi_0 - \Psi_\beta = \frac{\sigma_0}{C_1} \quad [7]$$

Figure 6. Schematic representation of the surface-solution interface according to the Extended Constant Capacitance Model (ECCM). The potential ($\Psi$) as a function of distance from the surface ($x$). Modified from reference (30).

### 3.2.3 Basic Stern Model (BSM)

The Basic Stern Model (BSM) is the simplest model that accounts for ionic-strength dependence in the equilibrium constants of surface reactions. It is able to cover a broad range of ionic strengths and describes electrolyte specific behavior by introducing ion-pair
formation between the ions of the electrolyte and the oppositely charged surface functional
groups. In order to describe the electrostatic double layer, an inner compact layer is
combined with a diffuse layer (Figure 7). In the diffuse layer, values of the surface potential
decrease to zero with distance from the surface. The surface charge is related to the surface
potential, according to the Gouy-Chapman theory (11) of the electrostatic double layer.
Charges of surface complexes may be placed either at the surface plane (0-plane) or at the
plane that separates the inner layer from the diffuse layer (β-plane). Electroneutrality of the
interface is defined by:

\[ \sigma_0 + \sigma_\beta + \sigma_{\text{dl}} = 0 \]  \[8\]

where \( \sigma_0 \), \( \sigma_\beta \) and \( \sigma_{\text{dl}} \) are the charge densities at the 0-plane, the β-plane, and in the diffuse
layer, respectively. Also, the values of \( \Psi_0 \) and \( \Psi_\beta \) are calculated according to:

\[ \Psi_0 - \Psi_\beta = \frac{\sigma_0}{C_{\text{Stern}}} \]  \[9\]

where \( C_{\text{Stern}} \) is the capacitance of the charge-free Stern layer, located between the 0-plane
and the β-plane.
Figure 7. Schematic representation of the surface-solution interface according to the Basic Stern Model (BSM). The potential ($\Psi$) as a function of distance from the surface ($x$). Modified from reference (32).

Within the work of this thesis, the above mentioned electrostatic models have been used depending on the properties of the mineral surfaces involved. In Papers III, IV and V the Basic Stern Model was used to describe the adsorption of PMG on aged $\gamma$-Al$_2$O$_3$, as well as both PMG and Cd(II) on the surface of goethite. The BSM is appropriate since the protonation and adsorption reactions that take place at the surfaces of both these minerals show a significant dependence on ionic strength. However, the properties of manganite in aqueous suspension are different than those of goethite and aged $\gamma$-Al$_2$O$_3$. The ECCM was used in Paper V to describe the adsorption of PMG and Cd(II) on manganite since no ionic strength dependence has been observed in the protonation of its surface (25).

3.2.4 Charge Distribution (CD)

The Charge Distribution (CD) concept is a combination of the classical Gouy-Chapman treatment of the diffuse double layer (11) and the distribution of charge in a solid
crystal as introduced by Pauling in 1929 (26). In this concept, adsorbed ligands are not treated as point charges, but instead their charge is distributed in the interfacial region, which is a more realistic approach with bulky ligands having several functional groups such as the PMG molecule investigated in this thesis. The CD concept is used in combination with the ECCM and BSM electrostatic models. A fraction \((f)\) of the charge of a surface complex is assumed to be located at the 0-plane while the other fraction \((1-f)\) is assumed at the \(\beta\)-plane. The actual charges that are placed in the 0-plane and the \(\beta\)-plane are denoted \(Q_0\) and \(Q_\beta\), respectively. Hence, the sum of \(Q_0\) and \(Q_\beta\) equals the total charge of the surface complex. Often, the values of the charge distribution coefficients \((f\) and \((1-f)\)) are assumed using Pauling’s bond valence theory (26), but in this work the possibility that these coefficients can be treated as fitting parameters is investigated. Here, the charge distribution is optimized upon by treating \(Q_0\) as an unknown parameter.

### 3.3 Calculations and Data Treatment

Activity coefficients \((\gamma_i)\) were calculated according to the Davies equation (11), where \(I\) is the ionic strength and \(z_i\) is the charge of species \(i\):

\[
\log_{10} \gamma_i = -0.509 z_i^2 \cdot \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)
\]

Z-curves and distribution diagrams were calculated using WinSGW, a program package for equilibrium calculations based on the SOLGASWATER algorithm (33).

LAKE (34), a nonlinear least-squares computer program capable of treating multistep method data simultaneously, was used to model the complexation of PMG and metal ions in aqueous solution. The sum of the squares of the deviations \((U)\) between calculated and experimental values are minimized, according to:
\[ U = \sum_{i=1}^{N} w_i \left( A_{i,\text{calc}} - A_{i,\text{meas}} \right)^2 \tag{11} \]

where \( A_i \) is the total concentrations of the components, free species concentrations, NMR chemical shifts, NMR integral values, or a combinations of these. The weighting factor, \( w_i \), is used to properly adjust the contributions to \( U \) by the different data types.

MAGPIE (35) is a computer program that was used to model the potentiometric and adsorption data for all the solution-mineral systems investigated in this thesis. In this software, the sum of the squares of the deviations (\( U \)) between calculated and experimental data are minimized using a nonlinear least-squares approach (36), and calculated values are evaluated using the SOLGASWATER algorithm by Eriksson (33). A residual sum of squares is calculated for both total proton concentration (\( U^{\text{TotH}} \)) and adsorption (\( U^{\text{Ads}} \)) data, and the total residual sum of squares (\( U \)) is:

\[ U = U^{\text{TotH}} + w \cdot U^{\text{Ads}} \tag{12} \]

The weighting factor (\( w \)) in Equation [12] is not based on experimental errors of the observations, but set to a value so that the data from different techniques span the same range of numerical values to avoid bias in the optimization. This method for determining the weighting factor is model independent and assumes that the two data types have approximately the same relative error.

Total proton concentrations were analyzed by minimizing the following sum of the squares of the deviations:

\[ U^{\text{TotH}} = \sum_{i=1}^{N} \left( H_{i,\text{calc}}^{\text{TotH}} - H_{i,\text{meas}}^{\text{TotH}} \right)^2 \tag{13} \]
where $H_{i,\text{Calc}}^{\text{Tot}}$ and $H_{i,\text{Meas}}^{\text{Tot}}$ are the calculated and measured total proton concentrations, respectively, for the $i^{\text{th}}$ data point and $N$ is the overall number of data points. Similarly, adsorption data were treated according to:

$$U_{\text{Ads}} = \sum_{i=1}^{N} \left( C_{i,\text{Calc}}^{\text{Ads}} - C_{i,\text{Meas}}^{\text{Ads}} \right)^2$$  \[14\]

where $C_{i,\text{Calc}}^{\text{Ads}}$ and $C_{i,\text{Meas}}^{\text{Ads}}$ are the calculated and measured concentrations of PMG adsorbed on the different mineral surfaces. Values of $H_{i,\text{Calc}}^{\text{Tot}}$ and $C_{i,\text{Calc}}^{\text{Ads}}$ were calculated from the obtained surface complexation models.

4. TECHNIQUES

4.1 Potentiometric Titrations

In this work potentiometric titrations were used for two purposes. First, the complexation of PMG with $H^+$ and the metal ions Cd(II) and Al(III), respectively, was studied in aqueous solution in order to determine the stoichiometries and formation constants of the formed complexes (Papers I and IV). Second, the (de)protonation reactions of the surface of aged $\gamma$-Al$_2$O$_3$ were studied with this technique in Paper IV.

The potentiometric titrations were performed with an automatic system (37). In order to avoid contamination from CO$_2$(g) from the air (since this may affect the proton balance of the system), an inert atmosphere was established in the closed titration vessel by using continuous flow of Ar(g) or N$_2$(g). The titrations were performed in a thermostated room and the titration vessel was immersed in an oil bath in order to maintain a constant temperature of 25.0 ± 0.1 °C. The titration equipment was composed of two electrodes: a
glass electrode and an Ag/AgCl reference electrode. The free proton concentration in the solution or suspension was determined by measuring the voltage of the cell:

- Ag, AgCl(s) | ionic medium || equilibrium solution/suspension | glass electrode +

The obtained values of proton concentration were recalculated into proton activity \((\text{pH} = -\log_{10}\{\text{H}^+\})\), using the Davies equation (Equation [10]).

In Paper I and IV (PMG-Cd(II) and PMG-Al(III) complexation in solution), stable potentials ±0.1 mV were usually reached within 15-60 minutes after each addition of acid or base. Tests for reversibility were performed and the equilibria were found to be completely reversible. In Paper IV (protonation reactions of aged \(\gamma\)-Al\(_2\)O\(_3\)), drifting potentials within ±0.5 mV were reached 5-15 hours after each addition of coulometrically generated OH\(^-\) ions or acid, and the equilibria were found to be reversible.

In this thesis, the results from the potentiometric titrations are often visualized as Z-curves, where Z is defined as:

\[
Z = \frac{H - [H^+] + [OH^-]}{[X]_{\text{TOT}}} \tag{[15]}
\]

and \([X]_{\text{TOT}}\) is the total concentration of a component.

### 4.2 Batch Adsorption Experiments

The adsorption of PMG in absence or presence of metal ions at the different mineral surfaces was studied in a series of batch experiments. These experiments were performed at 25 °C in a constant ionic medium of 0.1 M Na(Cl). PMG, and in some cases Cd(II), was added to the mineral suspensions. Aliquots of the suspensions were added to individual batch-sample tubes, and then the pH was adjusted in each sample by adding known
amounts of standardized acid or base. All samples were purged with Ar(g) or N\textsubscript{2}(g) to eliminate CO\textsubscript{2} from the air. The samples were placed on a rotating sample holder to avoid sedimentation of the particles and were equilibrated for at least a week. After equilibrium was reached, \(-\log_{10}[\text{H}^+]\) was measured in each tube using a combination glass electrode that was calibrated in solutions of known H\textsuperscript{+} concentrations. The obtained proton concentrations were recalculated into proton activity (pH = \(-\log_{10}\{\text{H}^+\}\)), using the Davies equation (Equation [10]). The samples were centrifuged in order to separate the solid phase from the solution. The concentrations of PMG and/or Cd(II) in the supernatant were analyzed, and the quantities adsorbed at the surface were calculated as the difference between the total concentrations and the concentrations in the supernatant. Two different techniques were used to measure the concentration of PMG in solution. In Papers II, III and a part of Paper V, a fraction of the PMG molecules in the stock solution was labeled with \textsuperscript{14}C, and the activity in the supernatant was measured with an automatic scintillation counter (Beckman LS6500). In Paper IV and a part of paper V, the PMG concentration was analyzed with Ion Chromatography (IC), by using an ion-exchange instrument from Metrohm Ltd. For a more detailed description of the IC apparatus, see Paper IV. Atomic absorption spectroscopy (AAS) was used to analyze Cd(II) concentrations, as well as any Fe(aq) and Mn(aq) that may have been present due to dissolution of the minerals goethite and manganite.

4.3 Spectroscopic Measurements

Results from previous spectroscopic measurements were used as a basis for the surface complexation modeling in this work. Each technique has its own advantages and limitations, and the combination of different methods have been employed for a better understanding of the systems investigated. The techniques used were ATR-FTIR and EXAFS spectroscopies, XPS, and NMR spectroscopy. Hence, the principles for these methods will be presented shortly below.
4.3.1 ATR-FTIR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy (38) is used to measure the energy changes related to the vibrations of the atoms in a molecule. Different molecular vibrations absorb at different wavelengths of the infrared spectrum, and each functional group of a molecule has a unique vibrational frequency. The analysis can be used to identify the functional groups of a sample. It also gives information about how the structure of these functional groups changes as a consequence of variations in chemical environment. When analyzing samples that are too thick or that absorb the infrared light too strongly for standard transmittance measurements, an attenuated total reflectance (ATR) cell can be used. In ATR, a sample is placed in contact with an infrared transparent crystal of relatively high reflective index. The infrared beam is totally internally reflected at the interface between this crystal and the sample, but the light still penetrates a few micrometers into the sample. This penetration depth provides a suitable pathlength for measuring the spectra of solids or liquids. The ATR-FTIR technique was used to study the different functional groups of the PMG molecule and its interactions with metal ions and mineral surface sites. This information can be used to determine the structure and sometimes the stoichiometries of the surface complexes formed in the different systems.

4.3.2 EXAFS Spectroscopy

Extended X-ray absorption fine structure (EXAFS) spectroscopy (39) is used to study the local surroundings of a specific element and can be applied to crystals, amorphous solids, liquids, solutions and gases. A monochromatic X-ray beam is directed at the sample and interacts with the electrons bound in the atoms of that sample. As the X-ray photon energy is increased above the binding energy of a core level electron, the radiation is absorbed, and this can be seen as an absorption edge. On the high photon energy side of the absorption edge a series of oscillations is observed, and these oscillations give information about the elemental identity and the number of the neighboring atoms.
Information about the distance to the surrounding atoms can also be obtained. EXAFS spectroscopy was used here to study the interactions of PMG with metal ions. The technique gives structural information about PMG-metal complexes that form in aqueous solution and at mineral surfaces.

4.3.3 XPS

X-ray photoelectron spectroscopy (XPS) (40) is a chemical analysis tool used to study the surface of a sample. The elemental composition of the surface is probed by bombarding the sample with high energy X-rays. These X-rays cause ejection of inner level electrons from the atoms in the sample, and the kinetic energies of the emitted electrons are measured. The binding energy of the electrons is characteristic of each element, and is also influenced by the chemical surroundings and oxidation state of the atom. Hence, XPS can provide information not only about the surface composition, but also about chemical bonding of the surface components. In this work XPS was used mainly to study the (de)protonation of the amine group of surface complexes formed when PMG was adsorbed at the mineral surfaces.

4.3.4 NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is based upon the quantum mechanical magnetic properties of the nucleus of an atom (41,42). All nuclei possess intrinsic angular momentum, or spin, arising from the neutrons and protons within the atom. Nuclei of certain isotopes, with an even number of protons and an odd number of neutrons, or vice versa, possess half-integer nuclear spins and are thus NMR active. The NMR signal comes from the excitement of the nuclei from one energy level to another. This separation of energy levels occurs only when the nucleus is placed in a magnetic field and is in the radio-frequency range of the electromagnetic spectrum. A specific radio-frequency pulse is applied, causing excitation from the lower to the higher energy level. When the pulse is switched off, the subsequent relaxation of the nucleus back to the
equilibrium state is detected by a coil. This information is analyzed and presented in terms of intensity versus chemical shift (\( \delta \)). The obtained chemical shift is nucleus specific and depends largely upon the electric environment around the nucleus. The NMR technique can provide quantitative as well as qualitative equilibrium data, kinetic data, and detailed structural information about the element studied. Within the work of this thesis \(^{31}\text{P}\)- and \(^{27}\text{Al}\)-NMR spectroscopies were used to study the complexation of PMG and Al(III) in solution.

5. COMPLEXATION AND COORDINATION CHEMISTRY OF PMG

5.1 Chemical Speciation of PMG in Solution

PMG has a low solubility in water (1.2% at 25 °C), which is probably due to the strong intermolecular hydrogen bonding within the crystal lattice. However, significant amounts of PMG have been found in natural waters and it is essential to explore and identify the speciation of the herbicide in order to understand the processes that occur in the environment. This section describes the properties of PMG in solution and its interactions with dissolved metal ions.

5.1.1 Acid-base Properties of PMG

PMG has the empirical formula C\(_3\)H\(_8\)NO\(_5\)P and a relative molecular mass of 169.1 g/mol. In solution, the molecule has a zwitterionic structure (H\(_3\)L), as illustrated in Figure 8, and it can easily react with protons or form complexes with metal ions (and mineral surfaces) through the three functional groups; the phosphonate, the amine and the carboxylate group.
Figure 8. Structural formula of PMG (H₃L). \( \text{pK}_{a1} = 2.22; \text{pK}_{a2} = 5.44; \text{pK}_{a3} = 10.13 \) (in 0.1 M Na(Cl)) (43).

Throughout this thesis PMG will often be referred to as \( L^{3-} \) as the fully deprotonated ligand. The order in which the functional groups become protonated starts with the amine group (\( \text{HL}^2^- \)), followed by one of the oxygens on the phosphonate group (\( \text{H}_2\text{L}^- \)) and finally the carboxylate group (\( \text{H}_3\text{L} \)). The protonation of the second oxygen of the phosphonate group (\( \text{H}_4\text{L}^+ \)) occurs outside the normal pH range and is therefore not considered here. The deprotonation constants of PMG determined in Paper IV at different ionic strengths are shown in Table 1.

**Table 1. Deprotonation Constants of PMG in Na(Cl) Ionic Medium (T=25 °C)**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( I = 0.1 \text{ M} )</th>
<th>( I = 0.6 \text{ M} )</th>
<th>( I = 0 \text{ M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{L} \Rightarrow \text{H}_2\text{L}^- + \text{H}^+ )</td>
<td>-2.25 ± 0.006</td>
<td>-2.17 ± 0.01</td>
<td>-2.44</td>
</tr>
<tr>
<td>( \text{H}_3\text{L} \Rightarrow \text{HL}^{2-} + 2\text{H}^+ )</td>
<td>-7.70 ± 0.01</td>
<td>-7.39 ± 0.01</td>
<td>-8.33</td>
</tr>
<tr>
<td>( \text{H}_3\text{L} \Rightarrow L^{3-} + 3\text{H}^+ )</td>
<td>-17.61 ± 0.03</td>
<td>-17.35 ± 0.05</td>
<td>-19.14</td>
</tr>
</tbody>
</table>

\( ^a \) Errors are reported as ± 3\( \sigma \).

\( ^b \) Constants determined in Paper IV.

\( ^c \) Calculated at zero ionic strength using the Davies equation from the values at \( I = 0.1 \text{ M Na(Cl)} \).

Figure 9 shows the distribution of PMG in 0.1 M Na(Cl) as a function of pH, calculated with the constants in Table 1, using the computer program WinSGW.
Figure 9. Speciation of PMG in aqueous solution (I = 0.1 M Na(Cl)). $F_{\text{PMG}}$ is the fraction of PMG found in respective solution species. $[\text{PMG}]_{\text{tot}} = 5$ mM. Equilibrium constants according to Table 1.

5.1.2 Hydrolysis of Metal Ions

Metal ions in aqueous solution act as Lewis acids (11). This means that they have an empty orbital available for the acceptance of a pair of electrons, which leads to the formation of a hydration shell around the metal ion. Many metal ions coordinate six water molecules per metal ion. The acidity of the water molecules in the hydration shell differs depending on the size and charge of the central metal ion. As a result of the positive charge of the metal ion, repulsion of protons of water molecules in the hydration shell occurs stepwise. Generally, for a trivalent metal ion ($\text{Me}^{3+}$) these deprotonation steps can be described as:

\[
\text{Me(}H_2\text{O})_6^{3+} \rightleftharpoons \text{Me}(H_2\text{O})_5\text{OH}^{2+} + \text{H}^+ \rightleftharpoons \text{Me}(H_2\text{O})_4(\text{OH})^{+}_2 + 2\text{H}^+ \rightleftharpoons ... \quad [16]
\]

The metal ions studied in this thesis were Cd(II) and Al(III). The stability constants of the formed hydrolysis species of these metals were taken from the literature (44,45) and were used in the different calculations concerning metal-PMG complexation, in solution and at the mineral surfaces.
5.1.3 PMG – Metal Complexation

PMG has been described as the ideal herbicide because it seems to be degraded in soils within a few days to the non-toxic products carbon dioxide, phosphate and ammonia. However, it is not fully clear what role metal complexation plays in this process. Due to the three donor groups (-CO$_2^-$, -PO$_3^{2-}$ and -NH) of the PMG molecule (Figure 8), it forms stable complexes with several metal ions, e.g. Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Fe$^{3+}$, Al$^{3+}$ and La$^{3+}$ (7). The fact that this strong complexation occurs may have an influence on the rate of degradation and thereby the bioavailability and toxicity of both PMG and heavy metals. In order to study the complexation reactions with PMG and metal ions in aqueous solution, Cd(II) and Al(III) were used in this work as model substances (Paper I and IV, respectively).

5.1.3.1 PMG – Cd(II)

Cd(II) is a non-essential heavy metal that is often present as a contaminant in the environment, particularly in agricultural soils, as is PMG. Few data for this system have been presented in the literature. Motekaitis et al. (7), as well as Kobylecka et al. (46) reported provisional values of formation constants for some PMG-Cd(II) complexes in solution. However, due to the disagreement of those results, the need for another investigation of this system was imminent.

The complexation of PMG and Cd(II) in 0.1 M Na(Cl) at 25 °C was studied with potentiometric titrations in Paper I, and the data are visualized as Z-curves in Figure 10.
Figure 10 shows that the PMG-Cd(II) complexation becomes significant at pH > 5. In this pH range the average amount of protons taken up (or released) per PMG molecule, as implied by $Z$, depends on the $[\text{PMG}]_{\text{tot}}:[\text{Cd(II)}]_{\text{tot}}$ ratio. The calculations confirmed that mainly three complexes can explain the data in Figure 10, and these complexes have the compositions CdHL, CdL$^-$, and CdL$_2$$^4^-$. There was no indication of the formation of polynuclear complexes, but small effects due to the formation of a mixed CdL(OH)$^{2-}$ complex were found at pH ≥ 9. The formation constants of the four PMG-Cd(II) complexes were determined using the computer program LAKE and the result from the calculation is shown in Table 2.
Table 2. Results of the Equilibrium Analysis of PMG-Cd(II) Complexation in Solution (T=25 °C), Using the Computer Program LAKE

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log_{10} \beta (\pm 3\sigma)^a )</th>
<th>( \log_{10} \beta (I=0)^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_3\text{L} + \text{Cd}^{2+} \rightleftharpoons \text{CdHL} + 2\text{H}^+ )</td>
<td>(-5.69 \pm 0.06)</td>
<td>(-5.58)</td>
</tr>
<tr>
<td>( \text{H}_3\text{L} + \text{Cd}^{2+} \rightleftharpoons \text{CdL}^- + 3\text{H}^+ )</td>
<td>(-11.16 \pm 0.02)</td>
<td>(-11.16)</td>
</tr>
<tr>
<td>( 2\text{H}_3\text{L} + \text{Cd}^{2+} \rightleftharpoons \text{CdL}_2^{4-} + 6\text{H}^+ )</td>
<td>(-25.02 \pm 0.06)</td>
<td>(-27.04)</td>
</tr>
<tr>
<td>( \text{H}_3\text{L} + \text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdL(OH)}^{2-} + 4\text{H}^+ )</td>
<td>(-21.1 \pm 0.1)</td>
<td>(-21.55)</td>
</tr>
</tbody>
</table>

\(^a\) Constants for the deprotonation of \( \text{H}_3\text{L} \) were taken from Table 1, while the hydrolysis constants of \( \text{Cd}^{2+} \) in solution were taken from reference (44).

\(^b\) Constants determined in 0.1 M Na(Cl), (Paper I).

\(^c\) Calculated at zero ionic strength using the Davies equation from the values at \( I = 0.1 \) M Na(Cl).

The constants in Table 2 were used to calculate theoretical Z-curves which can be seen as solid lines in Figure 10. The fit to the experimental data is very good and the speciation of PMG in solution, in the presence of Cd(II) as a function of pH, can be seen in Figure 11.

![Figure 11. Speciation of PMG in solution in the presence of cadmium(II), calculated according to the parameters in Table 2. \( I = 0.1 \) M Na(Cl). \( F_{PMG} \) is the fraction of PMG found in respective solution species. \( [PMG]_{tot} = 4 \) mM; \( [\text{Cd(II)}]_{tot} = 2 \) mM.](image-url)
Further, measurements with FTIR and EXAFS spectroscopies were performed on solutions containing CdL$^-$ and CdL$_2^{4+}$, in order to investigate the structures of these complexes (Paper I). The EXAFS spectroscopic results of the CdL$^-$ complex suggested a structure where all three donor groups of PMG are involved to form two five-membered chelate rings, as shown in Figure 12.

![Figure 12](image)

Figure 12. Molecular structure of CdL$^-$, identified in EXAFS analysis. The phosphonate and carboxylate chelate rings are illustrated in the figure. Hydrogens are omitted for clarity.

The structure of CdL$_2^{4+}$ was also found to consist of five-membered chelate rings, but with two PMG molecules per Cd(II). The structures of both complexes were similar to those found for the corresponding PMG-Cu(II) complexes (47) except for the lack of Jahn-Teller distortion in the PMG-Cd(II) complexes.

5.1.3.2 PMG – Al(III)

Aluminium is the most abundant metal in the earth’s crust, which means that it is present in practically all natural waters. Currently, there is only one study in the literature (48) that considers PMG-Al(III) complexation in solution. This study was performed in 0.1 M Na(NO)$_3$ at 25 °C, and the following soluble species were suggested: AlHL$^+$, AlL$^-$, AlHL$_2^{2-}$ and AlL$_3^{3-}$. To further investigate the PMG-Al(III) system and explore the possibility of polynuclear complex formation, both potentiometric titrations and $^{27}$Al- and
$^{31}\text{P}$-NMR spectroscopic measurements were performed in 0.6 M Na(Cl) in Paper IV. Some of the potentiometric titration data are visualized as Z-curves in Figure 13.

![Z-curves figure](image)

Figure 13. $Z_{H,L}$ as a function of pH for the ternary $H^+\text{-PMG-Al(III)}$ system. (I = 0.6 M Na(Cl)). Full curves are calculated using constants given in Table 3. The different symbols denote the following [Al(III)]$_{tot}$: [PMG]$_{tot}$ ratios (in mM): (♦) 0:5; (●) 5:20; (▲) 5:5.

Figure 13 shows that complexation between Al(III) and PMG starts under relatively acidic conditions (pH $\approx$ 1.5) and results in the release of protons. Samples for $^{27}\text{Al}$- and $^{31}\text{P}$-NMR spectroscopic measurements were taken from several of the different potentiometric titrations to assure precise values of total concentrations of Al(III), PMG and protons, as well as pH of the solutions. These $^{27}\text{Al}$- and $^{31}\text{P}$-NMR spectra are shown in Figure 14.

In the spectra in Figure 14, sharp signals are obtained for the free (uncomplexed) Al(III) and PMG species. In addition, the $^{27}\text{Al}$-NMR spectra (Figure 14, top) contain only three additional peaks. The peak labeled 1 appears in very acidic solutions, and peak numbers 2 and 3 grow in intensity with increasing pH and higher PMG to Al(III) ratio. In contrast, a great number of additional peaks appear in the $^{31}\text{P}$-NMR spectra (Figure 14, bottom), which are probably due to the formation of different isomers with the same stoichiometry. No change in the chemical shift values with pH was observed, indicating that there is no deprotonation of the phosphonate group.
Figure 14. NMR spectra of solutions with [Al(III)]_{Tot}:[PMG]_{Tot} ratio (in mM) of: 20:20 (samples s1-s7), and 5:20 (samples s8-s16). Top figure) $^{27}$Al-NMR spectra, where chemical shift values are referenced to Al(H$_2$O)$_6^{3+}$ (0 ppm). Bottom figure) $^{31}$P-NMR spectra, where chemical shift values are referenced to 85% H$_3$PO$_4$ (0 ppm).
To summarize the results from NMR spectroscopic measurements, it was concluded that different isomers with the same stoichiometry are likely to form and there was no indication of deprotonation of the phosphonate group. Further, the maximum average number of PMG molecules coordinated to Al(III) under pH 5 is approximately 1.7, indicating that the predominating Al(III) complexes contain a maximum of two coordinating PMG ligands. This information was used as a basis for the equilibrium analysis to determine the nuclearities, the degree of protonation, and the formation constants of the different complexes formed. Both mononuclear and polynuclear complexes were needed to explain the data in Figure 13 and the final model, determined using the computer program LAKE, is reported in Table 3.

Table 3. Reactions and Formation Constants in the H⁺-PMG-Al(III) System (T = 25 °C, I = 0.6 M Na(Cl))

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Log₁₀ β (±3σ)²¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺ + H₃L ⇌ AlH₂L⁺² + H⁺</td>
<td>0.4 ± 0.03</td>
</tr>
<tr>
<td>Al³⁺ + 2H₃L ⇌ AlH₃L₂⁺ + 3H⁺</td>
<td>-1.7 ± 0.05</td>
</tr>
<tr>
<td>Al³⁺ + 2H₃L ⇌ AlH₂L²⁺ + 4H⁺</td>
<td>-5.8 ± 0.4</td>
</tr>
<tr>
<td>Al³⁺ + 2H₃L ⇌ AlHL₂⁻ + 5H⁺</td>
<td>-10.1 ± 0.3</td>
</tr>
<tr>
<td>2Al³⁺ + 2H₃L ⇌ Al₂H₂L₂⁺² + 4H⁺</td>
<td>-1.8 ± 0.3</td>
</tr>
<tr>
<td>2Al³⁺ + 2H₃L ⇌ Al₂HL₂⁺² + 5H⁺</td>
<td>-4.3 ± 0.2</td>
</tr>
</tbody>
</table>

²¹ Constants determined in Paper IV.

The model presented in Table 3 was used to calculate the distribution of Al(III) at two ratios of [Al(III)]ₜₒₜ and [PMG]ₜₒₜ (Figure 15).
Figure 15. Distribution diagrams for the ternary H⁺-PMG-Al(III) system in 0.6 M Na(Cl), calculated using the equilibrium constants in Table 3. [Al(III)]_{Tot}:[PMG]_{Tot} ratios are (in mM): a) 20:20, and b) 5:20. F_{Al(III)} is the fraction of the total concentration of Al(III) found in respective solution species. Dotted lines represent calculations extrapolated above the pH values of the experimental data.

The good agreement between the calculated and experimental data is demonstrated in Figure 13. Nonetheless, it is important to emphasize that the speciation of the PMG-Al(III) system is much more complicated than portrayed in Table 3 due to the formation of different isomers of the complexes. Interpretation of the stability constants of the different species suggests that they contain five-membered chelate rings, and the strong complexation between Al(III) and PMG implies that the solubility of Al(III)-containing minerals will increase in the presence of PMG, which is illustrated for aged γ-Al₂O₃ in section 5.2.2.2.
5.2 Chemical Speciation of PMG at Solution-Mineral Interfaces

Within the work of this thesis (Paper III, IV and V) a number of studies have been performed in order to investigate the chemical processes that take place at the water-mineral interface when PMG and PMG-metal complexes are adsorbed to the mineral surfaces of goethite, aged $\gamma$-Al$_2$O$_3$, and manganite. The development of a detailed surface complexation model requires a stepwise determination of the subsystems involved. Apart from knowing the chemical processes that occur for soluble species in solution, the protonation reactions of the pure mineral surface need to be investigated and described separately. Additionally, the parameters describing the adsorption of PMG and PMG-metal complexes are included in order to obtain a more complete surface complexation model. The chemical systems that include mineral surfaces are described below.

5.2.1 Adsorption of Protons

5.2.1.1 Goethite – $H^+$

The basic charging behavior of goethite particles was thoroughly investigated by Boily et al. (17). The surface sites $\equiv$FeOH$^{0.5-}$ and $\equiv$Fe$_3$O$_4^{0.5-}$ (Figure 2) were suggested to be responsible for the protonation reactions at the surface. The acid-base properties in 0.1 M Na(Cl) and 0.1 M Na(NO$_3$) have been determined by Lützenkirchen (19), using the 1pK BSM. The protonation reactions and corresponding formation constants, as well as the charges of the surface complexes ($Q_0$ and $Q_\beta$), are shown in Table 4.
5.2.1.2 Aged γ-Al₂O₃ – H⁺

The (de)protonation of the aged γ-Al₂O₃ surface in 0.1 M Na(Cl) was investigated by potentiometric titrations in Paper IV. A selection of potentiometric data points is shown in Figure 16, where Z is defined as the average number of H⁺ bound or released per surface site (≡AlOH⁰.⁵⁰⁻).

![Figure 16](image)

**Figure 16.** Experimental potentiometric data of aged γ-Al₂O₃ in 0.1 M Na(Cl), visualized as a Z(pH) curve. The solid line was calculated using constants in Table 4.

The surface properties were modeled using the 1pK BSM and the following protonation and ion-pairing reactions were considered at the aged γ-Al₂O₃ surface:

\[
\equiv\text{AlOH}^{0.5-} + H^+ \rightleftharpoons \equiv\text{AlOH}_2^{0.5+} \quad \text{Log}_{10} \beta^{\equiv\text{AlOH}_2^{0.5+}} \quad [17]
\]

\[
\equiv\text{AlOH}^{0.5-} + \text{Na}^+ \rightleftharpoons \equiv\text{AlOH}^{0.5-}\text{Na}^+ \quad \text{Log}_{10} \beta^{\equiv\text{AlOH}^{0.5-}\text{Na}^+} \quad [18]
\]

\[
\equiv\text{AlOH}_2^{0.5+} + \text{Cl}^- \rightleftharpoons \equiv\text{AlOH}_2^{0.5-}\text{Cl}^- \quad \text{Log}_{10} \beta^{\equiv\text{AlOH}_2^{0.5-}\text{Cl}^-} \quad [19]
\]
The value of $\log_{10} \beta = \text{AlOH}_{2}^{0.5+}$ was set at 8.2, as indicated by the pH_{pzc} for aged $\gamma$-Al$_2$O$_3$ in 0.1 M Na(Cl) ionic medium. This value also coincides with the results of Laiti et al. (20). The values of $\log_{10} \beta = \text{AlOH}^{0.5+-Na}^+$ and $\log_{10} \beta = \text{AlOH}_{2}^{0.5+-Cl^-}$ were assumed to be +0.1, as previously suggested by Hiemstra et al. (23) for synthetic bayerite. The only unknown parameter was the capacitance of the Stern layer, $C_{\text{Stern}}$. Hence, this value was optimized in MAGPIE using the potentiometric titration data in Figure 16, assuming Equations [17-19]. The capacitance value was determined to be $1.28 \pm 0.01 \text{ F/m}^2$ (Table 4) and the fit to the experimental data is shown as the solid line in Figure 16.

5.2.1.3 Manganite – $H^+$

The manganite surface properties were investigated in 0.1 M Na(Cl) by Ramstedt et al. (25). The acid-base properties were modeled with the 1pK CCM, including a surface complex between Na$^+$ and the negatively charged surface site due to specific Na$^+$ interactions with the surface at higher pH. The reactions and corresponding formation constants are shown in Table 4.
Table 4. Acid-base Properties of Goethite, Aged \( \gamma \)-Al\(_2\)O\(_3\) and Manganite (T = 25 °C, I = 0 M)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log_{10} \beta^a )</th>
<th>( Q_0 )</th>
<th>( Q_\beta )</th>
<th>SCM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protonation of Goethite Surface</strong>(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{FeOH}^{0.5-} + H^+ \rightleftharpoons \equiv \text{FeOH}_2^{0.5+} )</td>
<td>9.4</td>
<td>+0.5</td>
<td>—</td>
<td>BSM</td>
</tr>
<tr>
<td>( \equiv \text{FeOH}^{0.5-} + Na^+ \rightleftharpoons \equiv \text{FeOH}^{0.5-} \text{Na}^+ )</td>
<td>-0.69</td>
<td>-0.5</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{FeOH}^{0.5-} + H^+ + NO_3^- \rightleftharpoons \equiv \text{FeOH}_2^{0.5+} \text{NO}_3^- )</td>
<td>8.51</td>
<td>+0.5</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{FeOH}^{0.5-} + H^+ + Cl^- \rightleftharpoons \equiv \text{FeOH}_2^{0.5+} \text{Cl}^- )</td>
<td>9.08</td>
<td>+0.5</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{Fe}_2\text{O}^{0.5-} + \text{H}^+ \rightleftharpoons \equiv \text{Fe}_2\text{OH}^{0.5+} )</td>
<td>9.4</td>
<td>+0.5</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{Fe}_2\text{O}^{0.5-} + \text{Na}^+ \rightleftharpoons \equiv \text{Fe}_2\text{OH}^{0.5-} \text{Na}^+ )</td>
<td>-0.69</td>
<td>-0.5</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{Fe}_2\text{O}^{0.5-} + H^+ + NO_3^- \rightleftharpoons \equiv \text{Fe}_2\text{OH}^{0.5-} \text{NO}_3^- )</td>
<td>8.51</td>
<td>+0.5</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{Fe}_2\text{O}^{0.5-} + H^+ + Cl^- \rightleftharpoons \equiv \text{Fe}_2\text{OH}^{0.5-} \text{Cl}^- )</td>
<td>9.08</td>
<td>+0.5</td>
<td>-1</td>
<td></td>
</tr>
</tbody>
</table>

\( C_{\text{Stern}} = 0.94 \text{ F/m}^2; \) BET surface area = 85 m\(^2\)/g

Surface site density: singly = 3.64 sites/nm\(^2\), triply = 2.73 sites/nm\(^2\)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log_{10} \beta^c )</th>
<th>( Q_0 )</th>
<th>( Q_\beta )</th>
<th>SCM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protonation of Aged ( \gamma )-Al(_2)O(_3) Surface</strong>(^d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{AlOH}^{0.5-} + H^+ \rightleftharpoons \equiv \text{AlOH}_2^{0.5+} )</td>
<td>8.31</td>
<td>+0.5</td>
<td>—</td>
<td>BSM</td>
</tr>
<tr>
<td>( \equiv \text{AlOH}^{0.5-} + Na^+ \rightleftharpoons \equiv \text{AlOH}^{0.5-} \text{Na}^+ )</td>
<td>0.21</td>
<td>-0.5</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{AlOH}^{0.5-} + H^+ + Cl^- \rightleftharpoons \equiv \text{AlOH}_2^{0.5-} \text{Cl}^- )</td>
<td>8.52</td>
<td>+0.5</td>
<td>-1</td>
<td></td>
</tr>
</tbody>
</table>

\( C_{\text{Stern}} = 1.28 \pm 0.01 \text{ F/m}^2; \) BET surface area = 131 m\(^2\)/g

Surface site density: singly = 8.35 sites/nm\(^2\)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log_{10} \beta^d )</th>
<th>( Q_0 )</th>
<th>( Q_\beta )</th>
<th>SCM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protonation of Manganite Surface</strong>(^d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \equiv \text{MnOH}^{0.5-} + H^+ \rightleftharpoons \equiv \text{MnOH}_2^{0.5+} )</td>
<td>8.2</td>
<td>+0.5</td>
<td>—</td>
<td>CCM</td>
</tr>
<tr>
<td>( \equiv \text{MnOH}^{0.5-} + \text{Na}^+ \rightleftharpoons \equiv \text{MnOHNa}^{0.5+} )</td>
<td>-1.44</td>
<td>+0.5</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

\( C = 0.39 \text{ F/m}^2; \) BET surface area = 41 m\(^2\)/g

Surface site density: singly = 7.9 sites/nm\(^2\)

---

\( ^a \) Constants for surface complexes are intrinsic.

\( ^b \) Reference (19).

\( ^c \) Capacitance determined in Paper IV; Error is reported as \( \pm 1\sigma \). Formation constants according to reference (23).

\( ^d \) Reference (25).
5.2.2 Adsorption of PMG

Generally, PMG adsorbs strongly to mineral surfaces, which may decrease its mobility and efficiency as a herbicide. It adsorbs through the phosphonate moiety of the molecule, and the surface complexation models obtained for the adsorption of PMG on goethite, aged γ-Al₂O₃ and manganite, respectively, are discussed below.

5.2.2.1 Goethite – PMG

The adsorption of PMG to the surface of goethite in 0.1 M Na(NO₃) was described in terms of a surface complexation model in Paper III. The total proton concentration and the adsorption data from batch adsorption experiments (4) are shown in Figure 17. It is clear from Figure 17 that PMG adsorbs strongly to the goethite surface. In the pH interval 3 to 5, the adsorption is close to 100% for all total concentrations of PMG, except for the two highest concentrations, where some ligand was detected in solution. The data indicate that the surface is nearly saturated below pH 5 with about 2.7 μmol/m² of PMG adsorbed. Generally, the amount of PMG adsorbed decreases with increasing pH (above pH 5), which can be explained by the fact that the surface becomes less positively charged due to the deprotonation of surface sites. The unfavorable electrostatic conditions for a negatively charged PMG to adsorb to the negatively charge goethite surface is the probable explanation for the observation of only about 0.5 μmol/m² of PMG adsorbed at or above the pH_{pzpc} of goethite (9.3 in 0.1 M Na(NO₃) ionic medium). However, the fact that PMG is still adsorbed at these high pH values demonstrates the strong covalent bond between the phosphonate group of PMG and the goethite surface.
Figure 17. (a) Total proton concentrations and (b) adsorbed PMG concentrations on goethite, versus pH from batch adsorption experiments in 0.1 M Na(NO$_3$)$_3$. Solid lines are calculated using the model in Table 5. The legend in (a) gives [PMG]$_{tot}$ (in $\mu$mol/m$^2$) for each batch series, and this legend also applies to the adsorption data in (b). Note that total proton concentrations were not correctly monitored in all batch series; hence, these data were excluded from (a).
Previous measurements (4) with XPS and FTIR spectroscopy showed that mainly two PMG-goethite surface complexes are formed in the pH range 3-9.5. They are inner-sphere complexes and are coordinated to the surface Fe(III) in a monodentate fashion through one of the phosphonate oxygens. The two complexes differ in protonation state, since it was concluded from XPS measurements that the amine group gets deprotonated at higher pH. Neither the phosphonate nor the carboxylate groups are protonated throughout the pH range studied. The formed surface complexes were assumed to have the stoichiometries $\equiv$FeHL$^{1.5-}$ and $\equiv$FeL$^{2.5-}$, and their proposed structures are shown in Figure 18. The infrared spectra indicated that within the $\equiv$FeHL$^{1.5-}$ complex there is intramolecular hydrogen bonding between the protons of the amine group and both the phosphonate and carboxylate groups. These hydrogen bonds are illustrated as dotted lines in Figure 18.

![Figure 18. Proposed stoichiometries and structures of PMG-goethite surface complexes based on previous results from infrared spectroscopic and XPS measurements.](image)

The strategy was to model the PMG adsorption with the 1pK BSM using the data in Figure 17. Apart from the reactions describing (de)protonation of PMG in solution (Table 1) and the protonation of the goethite surface in 0.1 M Na(NO$_3$) medium (Table 4), Equations [20]
and [21] below were assumed to describe the formation of \( \equiv \text{FeHL}^{1.5-} \) and \( \equiv \text{FeL}^{2.5-} \), respectively.

\[
\begin{align*}
\equiv \text{FeOH}^{0.5-} + \text{H}_3\text{L} &\rightleftharpoons \equiv \text{FeHL}^{1.5-} + \text{H}^+ + \text{H}_2\text{O} & \beta^{\text{FeHL}^{1.5-}} \quad [20] \\
\equiv \text{FeOH}^{0.5-} + \text{H}_3\text{L} &\rightleftharpoons \equiv \text{FeL}^{2.5-} + 2\text{H}^+ + \text{H}_2\text{O} & \beta^{\text{FeL}^{2.5-}} \quad [21]
\end{align*}
\]

where \( \beta \) is the intrinsic formation constant.

The calculation involved an optimization of the formation constants (\( \beta^{\text{FeHL}^{1.5-}} \) and \( \beta^{\text{FeL}^{2.5-}} \)) and \( Q_0 \) values (\( Q_0^{\text{FeHL}^{1.5-}} \) and \( Q_0^{\text{FeL}^{2.5-}} \)) for the two surface species. A small correction in the initial total proton concentration resulted in a fit to species distribution of the two complexes in excellent agreement with FTIR spectroscopic data. The final results for the formation constants and \( Q_0 \) values are reported in Table 5. The excellent agreement between the calculated and the experimental data is shown in Figure 17.

**Table 5. Proposed Surface Complexation Model (T = 25 °C, I = 0 M) for the Adsorption of PMG onto Goethite**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log_{10} \beta^c )</th>
<th>( Q_0^c )</th>
<th>( Q_0^\beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \equiv \text{FeOH}^{0.5-} + \text{H}_3\text{L} =\equiv \text{FeHL}^{1.5-} + \text{H}_2\text{O} + \text{H}^+ )</td>
<td>4.70 ± 0.08</td>
<td>-0.18 ± 0.02</td>
<td>-1.32</td>
</tr>
<tr>
<td>( \equiv \text{FeOH}^{0.5-} + \text{H}_3\text{L} =\equiv \text{FeL}^{2.5-} + 2\text{H}^+ + \text{H}_2\text{O} )</td>
<td>-3.9 ± 0.1</td>
<td>-0.7 ± 0.1</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

\( ^a \) Determined from adsorption data in 0.1 M Na(\( \text{NO}_3 \)). The BSM was used to account for electrostatic effects.

\( ^b \) The capacitance of the Stern layer is 0.94 F/m\(^2\). Errors are reported as ± 1σ.

\( ^c \) Constants for surface complexes are intrinsic.

\( \Delta z_0^{\text{FeHL}^{1.5-}} = 0.32, \Delta z_\beta^{\text{FeHL}^{1.5-}} = -1.32, \Delta z_0^{\text{FeL}^{2.5-}} = -0.2, \) and \( \Delta z_\beta^{\text{FeL}^{2.5-}} = -1.8. \)

The possibility to vary the charge distribution for the goethite-PMG surface complexes has been very valuable. The results show that the charge in the 0-plane (\( Q_0 \)) of \( \equiv \text{FeHL}^{1.5-} \) is less negative than the corresponding charge of \( \equiv \text{FeL}^{2.5-} \). The difference may be explained by the intramolecular hydrogen bonding within the protonated surface complex. This hydrogen bonding probably relocates negative charge from the 0-plane and toward the outer \( \beta \)-plane.
When the amine group is deprotonated at higher pH, this hydrogen bond is lost. Consequently, the charges at the 0- and β-planes become more negative in \( \equiv \text{FeL}^{2,5-} \). It can also be noted that the extra negative charge given by the deprotonation of the amine group seems to be evenly distributed between the 0-plane and β-plane (-0.5 each).

The distribution of PMG as a function of pH, and at total concentrations of 0.8 and 2.3 \( \mu \text{mol/m}^2 \) has been calculated according to the model in Table 5. As can be seen in Figure 19 for both total PMG concentrations, \( \equiv \text{FeHL}^{1,5-} \) is the dominant surface complex below pH 5. Depending on the total concentration of PMG, \( \equiv \text{FeL}^{2,5-} \) starts to form between pH 4 and 6. At pH \( \geq 8 \) or 9, depending on surface coverage, \( \equiv \text{FeL}^{2,5-} \) is the dominating surface complex, but it still coexists with \( \equiv \text{FeHL}^{1,5-} \) at the highest pH. This speciation is in excellent agreement with the infrared spectroscopic results (4). Infrared spectra collected at a total PMG concentration of 2.3 \( \mu \text{mol/m}^2 \) and covering the range 4.2 < pH < 8.5 show that \( \equiv \text{FeHL}^{1,5-} \) is the dominant surface complex until at least pH 5.7. The \( \equiv \text{FeL}^{2,5-} \) complex is clearly detected at pH 6.0, but a mixture of the protonated and unprotonated forms exists at pH 8.5. Infrared spectroscopic data at a total PMG concentration of 0.8 \( \mu \text{mol/m}^2 \) also show that the \( \equiv \text{FeL}^{2,5-} \) is detected at pH 6.0. Furthermore, the spectra indicate that the ratio of the concentrations of \( \equiv \text{FeL}^{2,5-} \) and \( \equiv \text{FeHL}^{1,5-} \) is larger at a total PMG concentration of 0.8 \( \mu \text{mol/m}^2 \) compared to the concentration of 2.3 \( \mu \text{mol/m}^2 \) at pH 6, which is also predicted by the surface complexation model obtained here.
Figure 19. Distribution of PMG in solution and at the surface of goethite calculated according to the parameters in Table 5, assuming a 10 g/L suspension, a specific surface area of 85 m$^2$/g, and a 0.1 M Na(NO$_3$) ionic medium. $F_{\text{PMG}}$ is the fraction of total concentration of PMG found in respective species.

5.2.2.2 Aged $\gamma$-Al$_2$O$_3$ – PMG

To estimate the influence of the strong complexation of PMG-Al(III) in solution (Section 5.1.3.2) on the dissolution of aged $\gamma$-Al$_2$O$_3$, some theoretical calculations were performed with WinSGW in Paper IV. These calculations were based on the reactions in Table 1, Table 3, as well as the hydrolysis constants for Al(III) in solution (45). The result of these calculations is shown in Figure 20, where the theoretical solubility of aged $\gamma$-Al$_2$O$_3$ in the presence of PMG was plotted. The solid line represents the solubility of aged $\gamma$-Al$_2$O$_3$
(Log \( S_{\text{Al}} \)) depending on \( \text{pH} \) in the absence of PMG, while the dotted lines denote the solubility at various total concentrations of PMG. Figure 20 shows that the solubility of \( \gamma\text{-Al}_2\text{O}_3 \) is affected by PMG and that the solubility increases with increasing total concentration of PMG under neutral to acidic conditions. This information was carefully considered when planning the adsorption experiments in Paper IV. The total concentrations of PMG, as well as the \( \text{pH} \) range, were chosen so that the solubility of the mineral was not significantly (Log \( S_{\text{Al}} \leq 10^{-5} \) M) affected by PMG.

![Figure 20. Theoretical dissolution of aged \( \gamma\text{-Al}_2\text{O}_3 \) in the absence and presence of PMG. (\( \text{T} = 25 \degree \text{C}, \text{I} = 0.6 \text{ M Na(Cl)} \)).](image)

The adsorption of PMG on the surface of aged \( \gamma\text{-Al}_2\text{O}_3 \) was investigated in 0.1 M Na(Cl), and Figure 21 shows the total proton concentration and adsorption data from these batch experiments. According to Figure 21b, as much as 2.0 \( \mu \text{mol/m}^2 \) PMG can be accommodated at the surface at the lowest \( \text{pH} \) of the experiments (\( \text{pH} 5.5 \)). This value corresponds to about 15% of the singly-coordinated surface sites. With increasing \( \text{pH} \), the adsorption of PMG decreases due to the unfavorable electrostatic conditions for a negatively charged PMG to adsorb to a negatively charged surface. Despite this, a significant amount of PMG is still bound to the aged \( \gamma\text{-Al}_2\text{O}_3 \) surface above its \( \text{pH}_{\text{pzc}} \) of
8.2 (in 0.1 M Na(Cl) ionic medium), which may reflect strong covalent bonding between the phosphonate group and surface Al(III).

![Graph showing $Z_{H,L}$ versus pH and adsorbed PMG concentrations on aged $\gamma$-Al$_2$O$_3$ versus pH, from batch adsorption experiments in 0.1 M Na(Cl). Solid lines are calculated using Model #1 in Table 6. The legend in (a) gives [PMG]$_{tot}$ (in $\mu$mol/m$^2$) for each batch series, and this legend also applies to the adsorption data in (b). Note that total proton concentrations were not correctly monitored in all batch series; hence, these data were excluded from (a).]
In Paper IV, characterizations of formed surface complexes in the aged $\gamma$-Al$_2$O$_3$-PMG system were performed using ATR-FTIR spectroscopy and XPS. The infrared spectra (Figure 22) suggest that two surface complexes are formed, which are bound to the surface in a monodentate fashion through one of the phosphonate oxygens. The two complexes differ by the protonation state of the amine group, which was also confirmed with XPS results. The formation of a possible (doubly-protonated) third surface complex at low pH could not be completely excluded from the interpretation of the infrared spectra. However, this complex is probably only a minor species above pH 5.5, which is the lowest pH value in the experiments. Hence, the possibility of such a complex was neglected in the surface complexation modeling.

Figure 22. ATR-FTIR spectra of PMG adsorbed on the surface of aged $\gamma$-Al$_2$O$_3$ (I = 0.1 M NaCl). [PMG]$_{tot}$ = 2.5 $\mu$mol/m$^2$. The spectra of L$^{3-}$(aq) and HL$^{2-}$(aq) are shown for comparison.
Based on the spectroscopic information, the stoichiometries $\equiv\text{AlHL}^{1.5-}$ and $\equiv\text{AlL}^{2.5-}$ were proposed for the surface complexes, and the adsorption of PMG on the aged $\gamma$-$\text{Al}_2\text{O}_3$ surface can be described by:

$$\equiv\text{AlOH}^{0.5-} + \text{H}_3\text{L} \rightleftharpoons \equiv\text{AlHL}^{1.5-} + \text{H}_2\text{O} + \text{H}^+ \quad \beta^{\equiv\text{AlHL}^{1.5-}} \quad [22]$$

$$\equiv\text{AlOH}^{0.5-} + \text{H}_3\text{L} \rightleftharpoons \equiv\text{AlL}^{2.5-} + \text{H}_2\text{O} + 2\text{H}^+ \quad \beta^{\equiv\text{AlL}^{2.5-}} \quad [23]$$

where $\beta$ is the intrinsic formation constant. To explain the adsorption of PMG to the surface of aged $\gamma$-$\text{Al}_2\text{O}_3$, the data in Figure 21 were modeled using the 1pK BSM to account for electrostatic effects. Apart from the reactions relating the protonation of PMG in solution (Table 1) and the protonation of the aged $\gamma$-$\text{Al}_2\text{O}_3$ surface (Table 4), Equations [22] and [23] were assumed to describe the formation of $\equiv\text{AlHL}^{1.5-}$ and $\equiv\text{AlL}^{2.5-}$, respectively. As a first attempt, the formation constants for these complexes, as well as their charges at the 0-plane, $Q_0^{\equiv\text{AlHL}^{1.5-}}$ and $Q_0^{\equiv\text{AlL}^{2.5-}}$, were optimized simultaneously in MAGPIE. The numerical results from the calculation are presented as Model #1 in Table 6 and the fit to the experimental data is visualized in Figure 21.

Distribution diagrams based on Model #1 are shown in Figure 23 at total PMG concentrations of 0.7 and 2.5 μmol/m². The infrared data in Figure 22 were collected of samples at a total PMG concentration of 2.5 μmol/m², and the corresponding distribution diagram (Figure 23, bottom) shows good semi-quantitative agreement with these spectra. The wavenumber position of the $\nu_{\text{C-O}}$ peak is indicative of the protonation of the amine group. In the spectra at both pH 4.9 and pH 6.9, the absorbance maximum for this band is at about 1600 cm⁻¹, which is evidence that $\equiv\text{AlHL}^{1.5-}$ is the prevalent surface complex at these pH values. In good agreement with these spectral data, the distribution diagram also shows that the $\equiv\text{AlHL}^{1.5-}$ complex dominates the surface at these pH values. A shoulder at about 1570 cm⁻¹ due to the $\equiv\text{AlL}^{2.5-}$ surface complex is observed in the spectrum at pH 8.3, and
the model also predicts that the concentration of the $\equiv AlL_{2.5}^-$ surface complex has increased significantly by this pH value. At pH 9.0, the absorbance maximum of the $\nu_{\text{C-O}}$ peak is at about 1580 cm$^{-1}$ and there is a shoulder at 1600 cm$^{-1}$, which implies that a mixture of $\equiv AlHL_{1.5}^-$ and $\equiv AlL_{2.5}^-$ exists at the surface. Similarly, the distribution diagram shows that an equal mixture of the two complexes is present at the surface at pH 9.

Figure 23. Distribution of PMG in solution and at the surface of aged $\gamma$-Al$_2$O$_3$ calculated according to the parameters in Table 6 (Model #1) and assuming a 10 g/L suspension, a specific surface area of 131 m$^2$/g, and a 0.1 M Na(Cl) ionic medium. $F_{PMG}$ is the fraction of the total concentration of PMG found in respective species.
Model #1 in Table 6 predicts the experimental adsorption data reasonably well, although there are deviations above pH 8.5. Also, the speciation agrees very well with the spectroscopic evidence. However, there may be reasons to question the obtained charge distribution. The 0-plane in the BSM is usually considered to be located at the plane of the surface (27), and assuming the 0-plane is located at the same position as the surface oxygens, Pauling’s bond valence theory (26) estimates $Q_0$ values of -0.25 for each surface complex. According to Model #1, $Q_0$ for the $≡\text{AlL}^{2.5-}$ surface complex is $0.1 \pm 0.4$, and this value could be reasonable considering its error. However, $Q_0$ for the $≡\text{AIHL}^{1.5-}$ complex is positive $0.22 \pm 0.05$, which is less reasonable assuming that the 0-plane is located at the surface. This positive value suggests that the 0-plane is placed further away from the surface, hence closer to the protonated amine group of the PMG molecule. A possibility to achieve more realistic values of $Q_0$ might be to use a more advanced electrostatic model, with three planes to distribute the charge of the bulky ligand, instead of two planes in the BSM. However, a disadvantage of a more advanced model is that it introduces additional unknown parameters.

As a second step in the modeling procedure, the possibility of assigning charge distributions to the $≡\text{AlHL}^{1.5-}$ and $≡\text{AlL}^{2.5-}$ surface complexes to those distributions determined previously for corresponding PMG-goethite surface complexes (Paper III) was tested. The data in Figure 21 were modeled again, although this time the values of $Q_0^{\equiv\text{AlHL}^{1.5-}}$ and $Q_0^{\equiv\text{AlL}^{2.5-}}$ were fixed to -0.18 and -0.7, respectively. The two unknown formation constants of the surface complexes were optimized simultaneously and the result is reported in Table 6, designated as Model #2. The fits to the total proton concentration and adsorption data using Model #2 (not shown here), turned out practically as good as the fits using Model #1. However, that Model #2 fails to semi-quantitatively agree with the infrared spectroscopic results is clear from the distribution diagrams shown in Figure 24. The diagram for a total PMG concentration of 2.5 μmol/m$^2$ (Figure 24, bottom) shows that
the $\equiv \text{AlL}^{2.5-}$ surface complex is significant over the entire pH range from 5 to 9.5, which is clearly not supported by the spectra in Figure 22. For example, Model #2 predicts that at pH 8.3 and at a total ligand concentration of 2.5 $\mu$mol/m$^2$, the $\equiv \text{AlL}^{2.5-}$ complex almost completely dominates at the surface. However, the infrared spectrum at this pH shows that the $\equiv \text{AlL}^{2.5-}$ is present only as a minor complex, and $\equiv \text{AlHL}^{1.5-}$ is the predominate surface species.

Figure 24. Distribution of PMG in solution and at the surface of aged $\gamma$-Al$_2$O$_3$ calculated according to the parameters in Table 6 (Model #2) and assuming a 10 g/L suspension, a specific surface area of 131 m$^2$/g, and a 0.1 M Na(Cl) ionic medium. $F_{\text{PMG}}$ is the fraction of the total concentration of PMG found in respective species.
The poor semi-quantitative agreement with the infrared spectroscopic results implies that the assumption that the charge distributions for the PMG-surface complexes in the PMG-aged $\gamma$-$\text{Al}_2\text{O}_3$ system can not be approximated by using the corresponding charge distributions in the PMG-goethite system. Therefore, Model #1 is suggested to be the appropriate surface complexation model to describe the adsorption of PMG to the surface of aged $\gamma$-$\text{Al}_2\text{O}_3$.

### Table 6. Proposed Surface Complexation Model ($T = 25^\circ\text{C}$, $I = 0\text{ M}$) for the Aged $\gamma$-$\text{Al}_2\text{O}_3$-PMG-Cd(II) System$^a$

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\log_{10} \beta^b$</th>
<th>$Q_0$</th>
<th>$Q_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorption of PMG onto Aged $\gamma$-$\text{Al}_2\text{O}_3$ (Model #1)$^c$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv \text{AlOH}<em>{0.5^-} + H_3L \rightleftharpoons \equiv \text{AlHL}</em>{1.5^-} + H_2O + H^+$</td>
<td>4.1 ± 0.1</td>
<td>0.22 ± 0.05</td>
<td>-1.72</td>
</tr>
<tr>
<td>$\equiv \text{AlOH}<em>{0.5^-} + H_3L \rightleftharpoons \equiv \text{AlL}</em>{2.5^-} + H_2O + 2H^+$</td>
<td>-4.2 ± 0.2</td>
<td>0.1 ± 0.4</td>
<td>-2.6</td>
</tr>
<tr>
<td><strong>Adsorption of PMG onto Aged $\gamma$-$\text{Al}_2\text{O}_3$ (Model #2)$^d$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv \text{AlOH}<em>{0.5^-} + H_3L \rightleftharpoons \equiv \text{AlHL}</em>{1.5^-} + H_2O + H^+$</td>
<td>3.1 ± 0.1</td>
<td>-0.18</td>
<td>-1.32</td>
</tr>
<tr>
<td>$\equiv \text{AlOH}<em>{0.5^-} + H_3L \rightleftharpoons \equiv \text{AlL}</em>{2.5^-} + H_2O + 2H^+$</td>
<td>-3.60 ± 0.05</td>
<td>-0.7</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

$^a$ The BSM was used to account for electrostatic effects. The capacitance of the Stern layer is 1.28 F/m$^2$ (Table 4). Errors are reported as ± 1σ.

$^b$ Constants for surface complexes are intrinsic.

$^c$ $\Delta z^\equiv_{\text{AlHL}_{1.5^-}} = 0.72$, $\Delta z^\equiv_{\text{AlHL}_{1.5^-}} = -1.72$, $\Delta z^\equiv_{\text{AlL}_{2.5^-}} = 0.6$, and $\Delta z^\equiv_{\text{AlL}_{2.5^-}} = -2.6$. Errors are one standard deviation.

$^d$ Q values assumed to be identical those determined for corresponding PMG-goethite complexes (Table 5). $\Delta z^\equiv_{\text{AlHL}_{1.5^-}} = 0.32$, $\Delta z^\equiv_{\text{AlHL}_{1.5^-}} = -1.32$, $\Delta z^\equiv_{\text{AlL}_{2.5^-}} = -0.2$, and $\Delta z^\equiv_{\text{AlL}_{2.5^-}} = -1.8$. 

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5.2.2.3 Manganite – PMG

The adsorption of PMG to the surface of manganite in 0.1 M Na(Cl) was investigated in Papers II and V. The data in Figure 25 show that PMG adsorbs significantly to the surface of manganite in the pH range 6 to 10. The adsorption decreases with increasing pH, and this trend was also observed for the adsorption of PMG to goethite and aged $\gamma$-Al$_2$O$_3$ (see above).

![Figure 25. Adsorbed PMG concentrations as a function of pH from batch adsorption experiments in 0.1 M Na(Cl). The solid lines are fits to the data based on the surface complexation model in Table 7.](image)

The spectroscopic measurements in Paper II suggest that two major surface complexes are formed when PMG adsorbs to manganite. Both are inner-sphere complexes and are coordinated in a monodentate fashion to a singly-coordinated site of the manganite surface. The complexes differ in protonation state, since the amine group of PMG gets deprotonated as pH increases. Accordingly, these complexes are assumed to have the stoichiometries $\equiv$MnHL$^{1.5-}$ and $\equiv$MnL$^{2.5-}$, and to form according to Equations [24] and [25].
\[ \equiv \text{MnOH}^{0.5-} + H_3L \rightleftharpoons \equiv \text{MnHL}^{1.5-} + H_2O + H^+ \quad \beta^{\text{MnHL}^{1.5-}} \quad [24] \]
\[ \equiv \text{MnOH}^{0.5-} + H_3L \rightleftharpoons \equiv \text{MnL}^{2.5-} + H_2O + 2H^+ \quad \beta^{\text{MnL}^{2.5-}} \quad [25] \]

The modeling strategy in Paper V was to assume Equations [24] and [25], as well as the reactions for the (de)protonation of the manganite surface (Table 4), and the (de)protonation of PMG in aqueous solution (Table 1). The ECCM was used, and the charge distribution of the manganite-PMG complexes was assumed to be similar to the charge distribution obtained for the goethite-PMG system. Hence, the \( Q_0 \) and \( Q_\beta \) values for \( \equiv \text{MnHL}^{1.5-} \) and \( \equiv \text{MnL}^{2.5-} \) were fixed to the values determined for \( \equiv \text{FeHL}^{1.5-} \) and \( \equiv \text{FeL}^{2.5-} \), respectively, in Paper III.

The ECCM requires two capacitance values according to Equation [5]. The capacitance value from the CCM-based model of the surface of manganite determined previously by Ramstedt et al. (25) was used as the total capacitance (\( C_{tot} \)), while \( C_1 \) was co-varied with the formation constants \( \beta^{\text{MnHL}^{1.5-}} \) and \( \beta^{\text{MnL}^{2.5-}} \) in Paper V. The optimized values are reported in Table 7, and the fit to the experimental adsorption data can be seen in Figure 25, where the calculated PMG adsorption is shown by the solid lines.

**Table 7. Proposed Surface Complexation Model (T = 25 °C, I = 0 M) for the Adsorption of PMG onto Manganite**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log_{10} \beta^b )</th>
<th>( Q_0^c )</th>
<th>( Q_\beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \equiv \text{MnOH}^{0.5-} + H_3L \rightleftharpoons \equiv \text{MnHL}^{1.5-} + H_2O + H^+ )</td>
<td>2.62 ± 0.22</td>
<td>-0.18</td>
<td>-1.32</td>
</tr>
<tr>
<td>( \equiv \text{MnOH}^{0.5-} + H_3L \rightleftharpoons \equiv \text{MnL}^{2.5-} + H_2O + 2H^+ )</td>
<td>-4.06 ± 0.18</td>
<td>-0.7</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

\( a \) Determined from adsorption data in 0.1 M Na(Cl). The ECCM was used to account for electrostatic effects. Errors are reported as \( \pm 1\sigma \).

\( b \) Constants for surface complexes are intrinsic.

\( c \) Q values assumed to be similar to the corresponding goethite-PMG system (Table 5).

\( d \) Capacitance values optimized in Paper V. \( C_{tot} = 0.39 \text{ F/m}^2 \) (25).
The parameters in Table 7 were used to calculate the distribution of PMG in solution and at the surface of manganite at two different total concentrations of PMG as a function of pH (Figure 26). The speciation of PMG is dependent on surface coverage, and the unprotonated surface species (=MnL\textsuperscript{2.5}−) appears to be the predominant surface complex over the entire pH range studied. The speciation seen in Figure 26 is in good agreement with the spectroscopic evidence in Paper II, which suggested that the concentration of the unprotonated surface complex is more or less constant with pH.

Figure 26. Distribution of PMG in solution and at the surface of manganite, calculated according to parameters in Table 7. I = 0.1 M Na(Cl). F\textsubscript{PMG} is the fraction of PMG found in respective species. [PMG]\textsubscript{tot} is a) 2.44 μmol/m\textsuperscript{2}, and b) 9.76 μmol/m\textsuperscript{2}.
5.2.3 Adsorption of PMG, Metal Ions and Metal – PMG Complexes

When PMG is adsorbed to the surface through the phosphonate moiety of the molecule, the amine and carboxylate groups can interact with metal ions in solution. This behavior results in the formation of ternary complexes at the surface. These ternary surface complexes can generally be categorized into Type A and Type B complexes, which is illustrated in Figure 27. In Type A complexes, the metal ion acts as a bridge between the surface and the ligand, while in Type B complexes the ligand acts as a bridge between the surface and the metal.

![Figure 27. Position of the adsorbed ligand (L\textsuperscript{n-}) and metal ion (Me\textsuperscript{n+}) in ternary surface complexes. a) Type A complex; b) Type B complex.](image)

Previous spectroscopic studies (Paper II) of the manganite-PMG-Cd(II) system, identified a ternary surface complex with a Type B structure. This system was further investigated in terms of surface complexation models in Paper V. The goethite-PMG-Cd(II) system was also modeled in Paper V, although this system has not yet been investigated spectroscopically. However, ternary complexes were identified using EXAFS in the goethite-PMG-Cu(II) system (43). Thus, it was speculated that a ternary complex is also present in the goethite-PMG-Cd(II) system. This complex was assumed to have a similar stoichiometry as the corresponding ternary complex in the manganite-PMG-Cd(II) system.
In the surface complexation models obtained for these ternary systems, the formation of binary manganite-Cd(II) and goethite-Cd(II) surface complexes was also considered.

5.2.3.1 Manganite – PMG – Cd(II)

The adsorption of PMG and Cd(II) in the presence of each other on the surface of manganite was investigated in 0.1 M Na(Cl) in Paper V. The adsorption data from these batch experiments are shown in Figure 28 and 29, where also the binary manganite-PMG and manganite-Cd(II) adsorption data have been added for comparison. The adsorption of PMG (Figure 28) is increased in the presence of Cd(II), within the whole pH range studied, probably due to electrostatic effects and/or the formation of a ternary surface complex.

Figure 28. PMG adsorption, in absence and presence of Cd(II) on manganite as a function of pH, from batch adsorption experiments in 0.1 M Na(Cl). The solid lines are fits to the data based on surface complexation models in Table 7 and 8. The different symbols denote the following [PMG]_{tot}:[Cd(II)]_{tot} ratios (in μmol/m²): (Δ) 1.22:0; (♦) 2.44:0; ( ) 9.76:0; (▲) 4.82:4.76.

A similar trend can be seen for Cd(II) at low pH (Figure 29), where electrostatics and/or the formation of a ternary surface complex result in an increased adsorption of Cd(II) below pH 8.2 (pH_{iep} of manganite). Above pH_{iep}, the manganite surface becomes
more negatively charged and the formation of the negatively charged ternary surface complex decreases, mainly due to extensive Cd(II)-PMG complexation in solution.

Figure 29. Cd(II) adsorption, in absence and presence of PMG on manganite as a function of pH, from batch adsorption experiments in 0.1 M Na(Cl). The solid lines are fits to the data based on surface complexation models in Table 8. The different symbols denote the following [PMG]tot:[Cd(II)]tot ratios (in μmol/m²): (♦) 0:7.3; (■) 4.82:4.76.

Before the ternary manganite-PMG-Cd(II) system was addressed, the formation of a binary manganite-Cd(II) surface complex was investigated. Previous EXAFS spectroscopic characterizations (49) of such a complex showed that Cd(II) adsorbs inner-spherically with a mononuclear bidentate geometry. The adsorption of Cd(II) to manganite was modeled using the CCM, including the hydrolysis constants of Cd(II) in aqueous solution (44), as well as the reactions describing the protonation of the manganite surface (Table 4). The formation reaction of the binary manganite-Cd(II) complex was assumed to be:

$$\equiv \text{MnOH}^{0.5-} + \text{Cd}^{2+} + n\text{H}_2\text{O} \rightleftharpoons \equiv \text{MnOHCd(OH)}_n^{(n+0.5)-} + n\text{H}^+ \beta^n\text{MnOHCd(OH)}_n^{(n+0.5)-}$$ \[26\]
The charge of this surface complex was positioned at the surface plane (0-plane) of the CCM, and the formation constant of the complex was the only unknown parameter optimized in the model. The best fit to the experimental data was obtained from a complex with \( n=2 \). However, the fit was not satisfactory above \( pH \) 8. By including the solubility product for \( \text{Cd(OH)}_2(s) \) (50) in the calculations, thus assuming the possible formation of a surface precipitate of Cd-hydroxide, the fit was improved satisfactorily. The obtained \( \log_{10}\beta \) value for the formation of the \( \equiv\text{MnOHCd(OH)}_2^{0.5-} \) complex is shown in Table 8, and the resulting fit to the experimental data can be seen in Figure 29.

Further, in the presence of both PMG and Cd(II), a ternary monodentate surface complex displaying a Type B structure is formed, according to the spectroscopic evidence in Paper II. This complex was assigned the stoichiometry \( \equiv\text{MnLCd(OH)}_n^{(n+0.5)-} \) and the adsorption can be attributed to the following reaction:

\[
\equiv\text{MnOH}^{0.5-} + \text{H}_3\text{L} + \text{Cd}^{2+} \rightleftharpoons \equiv\text{MnLCd(OH)}_n^{(n+0.5)-} + (n+2)\text{H}^+ + \beta^{\equiv\text{MnLCd(OH)}_n^{(n+0.5)-}} \tag{27}
\]

In the calculations, the appropriate reactions in solution, the reactions for the binary manganite-PMG system (Table 7), as well as Equations [26] and [27] were used, and the 1pK ECCM was employed to correct for electrostatic effects. The calculation involved the determination of \( n \) in Equation [27], \( \beta^{\equiv\text{MnLCd(OH)}_n^{(n+0.5)-}} \), and the charge of the complex at the surface plane (\( Q_0^{\equiv\text{MnLCd(OH)}_n^{(n+0.5)-}} \)). Different values of \( n \) were tested to find the minimum in the residual sum of squares. The best fit to experimental data was obtained with \( n=1 \), which confirms the stoichiometry \( \equiv\text{MnLCd(OH)}^{1.5-} \). The result of the optimization is presented in Table 8.
Table 8. Proposed Surface Complexation Model (T = 25 °C, I = 0 M) for the Manganite-PMG-Cd(II) System\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reactions\textsuperscript{b}</th>
<th>$\log_{10} \beta$\textsuperscript{c}</th>
<th>$Q_0$</th>
<th>$Q_\beta$</th>
<th>SCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption of Cd(II) on Manganite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv$MnOH$_{0.5-}^+$ + Cd$^{2+}$ + 2H$_2$O $\rightleftharpoons$ MnOHCd(OH)$_2^{0.5-}$ + 2H$^+$</td>
<td>-13.58 ± 0.17</td>
<td>-0.5</td>
<td></td>
<td>CCM</td>
</tr>
<tr>
<td>Co-adsorption of PMG and Cd(II) on Manganite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv$MnOH$_{0.5-}^+$ + H$<em>3$L + Cd$^{2+}$ $\rightleftharpoons$ MnLCd(OH)$</em>{1.5-}$ + 3H$^+$</td>
<td>-7.18 ± 0.09</td>
<td>-0.56 ± 0.07</td>
<td>-0.94</td>
<td>ECCM</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Determined from adsorption data in 0.1 M Na(Cl). The CCM and the ECCM were used to account for electrostatic effects at the mineral surface. Errors are reported as ± 1$\sigma$. The overall capacitance ($C_{\text{tot}}$) in CCM is 0.39 F/m$^2$ (Table 4). In ECCM, $C_1$ = 0.43 F/m$^2$; $C_2$ = 3.64 F/m$^2$ C (Table 7).

\textsuperscript{b} Reactions for Manganite-H$^+$ in Table 4. Reactions for Manganite-PMG in Table 7. Reactions for aqueous PMG-Cd(II) complexes in Table 2.

\textsuperscript{c} Constants for surface complexes are intrinsic.

The new model was used to calculate distributions diagrams to visualize the speciation at total PMG and Cd(II) concentrations of 4.8 $\mu$mol/m$^2$ (Figure 30). The distribution of PMG (Figure 30a) shows that $\equiv$MnLCd(OH)$_{1.5-}$ is the predominant PMG containing surface species throughout the entire pH interval studied, while the binary $\equiv$MnHL$_{1.5-}$ and $\equiv$MnL$_{2.5-}$ complexes exist only to a small extent at low pH. It is interesting to note that the fraction of PMG that is bound in the ternary $\equiv$MnLCd(OH)$_{1.5-}$ species decreases with increasing pH due to the strong complexation between PMG and Cd(II) in solution. This may also be an effect of the decrease in surface charge when the surface sites are deprotonated at higher pH. The distribution of Cd(II) in Figure 30b indicates that $\equiv$MnLCd(OH)$_{1.5-}$ is the predominant Cd(II) containing surface species between pH 6 and 9. The binary $\equiv$MnOHCd(OH)$_2^{0.5-}$ surface species starts to form at pH 7, and the fraction of Cd(II) accounted by this surface complex increases with increasing pH. It is evident from Figure 30 that complexation of PMG with Cd(II) in solution effectively competes with Cd(II) and PMG adsorption at the manganite surface.
Figure 30. Distribution of a) PMG, and b) Cd(II), in presence of each other, in solution and at the surface of manganite, calculated according to the parameters in Table 8. I = 0.1 M Na(Cl). $F_{\text{PMG}}$ and $F_{\text{Cd(II)}}$ is the fraction of total concentrations of PMG and Cd(II), respectively, found in respective species. $[\text{PMG}]_{\text{tot}} = [\text{Cd(II)}]_{\text{tot}} = 4.8 \, \mu\text{mol/m}^2$.

Figure 31 shows possible structures of the surface complexes formed in the ternary manganite-PMG-Cd(II) system, as suggested from EXAFS spectroscopic results. This figure is not to scale and should only be used as a tool for a further understanding of the molecular structures of the surface complexes.
5.2.3.2 Goethite – PMG – Cd(II)

The second ternary system studied in Paper V was the co-adsorption of PMG and Cd(II) on the surface of goethite. Figures 32 and 33 show the adsorption data in this ternary system. It is clear from Figure 32 that PMG adsorbs strongly in the presence of Cd(II) throughout the entire pH range studied. The adsorption curves are relatively flat compared to the adsorption trend in the binary goethite-PMG system (Figure 17). This may be due to formation of ternary surface complexes and/or the fact that Cd(II) adsorbs directly to the surface and thereby increases the surface charge, which facilitates the adsorption of negatively charged PMG. Interestingly, the same saturation coverage (2.5 μmol/m$^2$) below
pH 5) was observed in both the binary goethite-PMG- and ternary goethite-PMG-Cd(II) systems.

![PMG adsorption diagram](image)

Figure 32. PMG adsorption, in presence of Cd(II), on goethite as a function of pH, from batch adsorption experiments in 0.1 M Na(Cl). The solid lines are fits to the data based on surface complexation model in Table 9. The different symbols denote the following [PMG]_tot/[Cd(II)]_tot ratios (in μmol/m²): (♦) 1.22:1.22; (●) 1.53:1.53; (▲) 2.43:2.43; (■) 3.06:1.53; (■) 3.06:3.06.

The adsorption of Cd(II) in the presence of PMG (Figure 33) increases with increasing pH, and the adsorption is favored by the deprotonation of surface sites at higher pH. The data suggest that saturation of the surface was achieved at about 2.6 μmol/m² of adsorbed Cd(II).
Figure 33. Cd(II) adsorption, in presence of PMG, on goethite as a function of pH, from batch adsorption experiments in 0.1 M Na(Cl). The solid lines are fits to the data based on surface complexation model in Table 9. The different symbols denote the following [PMG]$_{tot}$/[Cd(II)]$_{tot}$ ratios (in μmol/m$^2$): (♦) 1.22:1.22; ( ) 1.53:1.53; (▲) 3.06:1.53; (●) 2.43:2.43; (■) 3.06:3.06.

Previous spectroscopic characterizations of binary goethite-Cd(II) surface complexes (51) confirmed that Cd(II) binds to goethite as inner-sphere binuclear bridging surface complexes. This system has been modeled by Boily et al. (51), using the Three Plane Model (TPM) (27), applying a charge distribution to the binary surface complex that corresponds to a Q$_0$ value of -0.33. The following reaction was considered:

$$2\equiv\text{FeOH}^{0.5-} + \text{Cd}^{2+} = (\equiv\text{FeOH})_2\text{Cd}^+$$

The strategy in Paper V was to apply the BSM, but the charge distribution of (≡FeOH)$_2$Cd$^+$ was assumed to be similar to that distribution determined in the TPM. Hence the value of Q$_0$ was fixed to -0.33. The formation constant for the (≡FeOH)$_2$Cd$^+$ complex was corrected according to Venema et al. (52):
\[ \beta_{0,2,1}(2 \equiv \text{FeOH}^{0.5-} + \text{Cd}^{2+} = (\equiv \text{FeOH})_2\text{Cd}^+) = \beta_{0,2,1,\text{(gt)}} \times [\equiv \text{Fe(OH)}]_{1(1,0)\text{tot}} \]  \[29\]

where \([\equiv \text{Fe(OH)}]_{1(1,0)\text{tot}}\) is the total concentration of singly coordinated sites and \(\beta_{0,2,1,\text{(gt)}}\) is the solid concentration-dependent constant obtained from the ratio of products and reactants. This correction coefficient \((\beta_{0,2,1,\text{(gt)}})\) was introduced in the mass reaction equations as a dummy component in MAGPIE and WinSGW.

A surface complexation model was previously determined for the binary goethite-PMG system in 0.1 M Na(NO\(_3\)) ionic medium (Table 5). The two surface complexes formed in this system have the stoichiometries \(\equiv \text{FeHL}^{1.5-}\) and \(\equiv \text{FeL}^{2.5-}\). However, since data used to study the ternary goethite-PMG-Cd(II) system were collected in 0.1 M Na(Cl) rather than 0.1 M Na(NO\(_3\)), the formation constants of \(\equiv \text{FeHL}^{1.5-}\) and \(\equiv \text{FeL}^{2.5-}\) were reoptimized in the modeling of the ternary system. However, the charge distributions (\(Q_0\) values) of the binary surfaces complexes were assumed to be the same as obtained in 0.1 M Na(NO\(_3\)).

There is no spectroscopic information available in the literature, regarding the structure of a ternary goethite-PMG-Cd(II) complex. Consequently, this complex was assumed to have a similar structure as the ternary manganite-PMG-Cd(II) surface complex, i.e. a Type B structure, according to the following reaction:

\[ \equiv \text{FeOH}^{0.5-} + \text{H}_3\text{L} + \text{Cd}^{2+} = \equiv \text{FeLCd(OH)}_n^{(n+0.5)-} + (n+2)\text{H}^+ \]

The 1pK BSM was used to model the co-adsorption of PMG and Cd(II) on goethite, assuming Equations [28-30], the reactions for the soluble species included in this system, as well as the reactions for the protonation of the goethite surface in 0.1 M Na(Cl) ionic medium (Table 4). Apart from the determination of \(n\) for the ternary complex in Equation [30], the calculation involved a determination of the intrinsic formation constant for this
complex, $\beta^{=FeLcd(OH)_{1.5^-}}$, as well as its charge at the 0-plane $Q_0^{=FeLcd(OH)_{1.5^-}}$. Further, the formation constants of the binary goethite-PMG complexes, $\beta^{=FeHL_{1.5^-}}$ and $\beta^{=FeL_{2.5^-}}$, respectively, as well as the binary goethite-Cd(II) complex, $\beta^{(FeOH)_{2}Cd^{+}}$, were optimized. In the calculation, two series of adsorption data from the binary goethite-PMG system (in 0.1 M Na(Cl) ionic medium) were also included to further constrain the determination of the formation constants of these complexes. The five unknowns were varied simultaneously in MAGPIE, and a value of $n=1$ gave the best fit to the adsorption data:

$$\equiv FeOH^{0.5^-} + H_3L + Cd^{2+} \rightleftharpoons \equiv FeLcd(OH)^{1.5^-} + 3H^+ \quad \beta^{=FeLcd(OH)^{1.5^-}} \quad [31]$$

The numerical values from the optimization are reported in Table 9 and the fit to the experimental data is shown as solid lines in Figures 32 and 33. The charge distribution of the $\equiv FeLcd(OH)^{1.5^-}$ complex ($Q_0 = -0.77 \pm 0.05$) turned out to be similar to the corresponding value in the manganite system ($Q_0 = -0.6 \pm 0.1$).
Table 9. Proposed Surface Complexation Model (T = 25 °C, I = 0 M) for the Goethite-PMG-Cd(II) System

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Log₁₀ β</th>
<th>Q₀</th>
<th>Qβ</th>
<th>SCM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorption of Cd(II) on Goethite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2≡FeOH⁰.⁵⁻ + Cd²⁺ ⇌ (≡FeOH)₂Cd⁺</td>
<td>7.32 ± 0.06</td>
<td>-0.33</td>
<td>1.33</td>
<td>BSM</td>
</tr>
<tr>
<td><strong>Adsorption of PMG on Goethite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡FeOH⁰.⁵⁻ + H₃L ⇌ ≡FeHL₁.⁵⁻ + H₂O + H⁺</td>
<td>4.21 ± 0.03</td>
<td>-0.18</td>
<td>-1.32</td>
<td>BSM</td>
</tr>
<tr>
<td>≡FeOH⁰.⁵⁻ + H₃L ⇌ ≡FeL₂.⁵⁻ + H₂O + 2H⁺</td>
<td>-3.54 ± 0.09</td>
<td>-0.7</td>
<td>-1.8</td>
<td></td>
</tr>
<tr>
<td><strong>Co-adsorption of PMG and Cd(II) on Goethite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡FeOH⁰.⁵⁻ + H₃L + Cd²⁺ ⇌ ≡FeLCd(OH)₁.⁵⁻ + 3H⁺</td>
<td>-6.41 ± 0.08</td>
<td>-0.77 ± 0.05</td>
<td>-0.73</td>
<td>BSM</td>
</tr>
</tbody>
</table>

**a** Determined from adsorption data in 0.1 M Na(Cl). The BSM was used to account for electrostatic effects at the mineral surface. The capacitance of the Stern layer (C_Stern) is 0.94 F/m². Errors are reported as ± 1σ.

**b** Reactions for Goethite-H⁺ in Table 4. Reactions for aqueous PMG-Cd(II) complexes in Table 2.

**c** Constants for surface complexes are intrinsic.

**d** The values of Q₀ and Qβ were fixed according to reference (51).

**e** The values of Q₀ and Qβ were fixed to corresponding values determined in 0.1 M Na(NO₃) (Table 5).

Figure 34 shows distribution diagrams for the ternary goethite-PMG-Cd(II) system where the total concentrations of both PMG and Cd(II) are 1.53 μmol/m². These diagrams were calculated according to the model in Table 9 and cover the pH range of the experimental data. The distribution of PMG (Figure 34a) suggests that ≡FeHL₁.⁵⁻ is exclusively the dominating PMG containing surface species between pH 3 and 6. This complex gets deprotonated as pH increases, thus forming ≡FeL₂.⁵⁻ beginning at pH 4. On the other hand, at pH 6 and above, the binary goethite-PMG complexes are suppressed due to the formation of the ternary ≡FeLCd(OH)₁.⁵⁻ complex. When comparing Figure 30 and Figure 34, it is obvious that the complexation of PMG-Cd(II) in solution is not as significant in the goethite-PMG-Cd(II) system as in the corresponding manganite-PMG-Cd(II) system. Figure 34b shows the distribution of Cd(II) in the presence of PMG. Almost no Cd(II) is adsorbed to the surface at low pH, which is a typical behavior of positively charged metal ions. At pH 4 and above, significant amounts of the binary (≡FeOH)₂Cd⁺
complex starts to form. However, at pH > 7 approximately 30% of the adsorbed Cd(II) exists in the form of the ternary $\equiv$FeLCd(OH)$_{1.5}^-$ complex.

Figure 34. Distribution of a) PMG, and b) Cd(II), in presence of each other, in solution and at the surface of goethite, calculated according to the parameters in Table 9. $F_{\text{PMG}}$ and $F_{\text{Cd(II)}}$ are the fractions of PMG and Cd(II), respectively, found in respective species. Total concentrations of each of PMG and Cd(II), are 1.53 $\mu$mol/m$^2$.

Interestingly, it was found that identical proton stoichiometries and similar charge distributions provided the best explanation to experimental data in both the manganite-PMG-Cd(II)- and goethite-PMG-Cd(II) systems. A simple model assuming the formation of a single ternary complex was found to explain the experimental data in both systems.
6. CONCLUSIONS

Complexation in different glyphosate systems has been studied in solution and at the mineral surfaces of goethite, aged $\gamma$-Al$_2$O$_3$ and manganite. Metal complexation in solution was interpreted in the presence of the divalent Cd$^{2+}$ and trivalent Al$^{3+}$ ions. The speciation schemes for these two metal ions are very different and reflect their solution/coordination chemistry. Complexation between Cd(II) and H$_3$L starts in slightly acidic (pH 5) solutions and the predominating complexes are CdHL, CdL$^-$, and CdL$_2^{4-}$. CdL$^-$, and CdL$_2^{4-}$ contain the fully deprotonated ligand (L$^3-$). According to EXAFS and ATR-FTIR spectroscopic results (Paper 1), these two complexes contain two five-membered chelate rings, which causes a stabilization of the complexes. This is also reflected in the step-wise stability constants Log$_{10}$K$_1$(Cd$^{2+}$ + L$^3$ = CdL$^-$) = 7.98 and Log$_{10}$K$_2$(CdL$^-$ + L$^3$ = CdL$_2^{4-}$) = 3.26. A comparison can be done with the corresponding values for glycine, which are 4.22, 3.57 and 2.0 (CdL$^3-$). These values indicate an extra stabilization caused by the phosphonate group in glyphosate. The stability of the protonated complex CdHL (Log$_{10}$K(Cd$^{2+}$ + HL$^2$ = CdHL) = 2.75) is close to the stability of the CdHPO$_4^{2-}$ complex, which has a Log$_{10}$K = 2.91 (53). This indicates that the proton in CdHL is located at the phosphonate group, which was also corroborated from ATR-FTIR spectroscopic data in Paper 1, as well as the pK$_a$ value for CdHL being 5.58, which is close to pK$_a$(H$_2$L) = 5.89. It can also be noted that a mixed hydroxo complex CdL(OH)$_2^{2-}$ forms in slightly alkaline solutions (pK$_a$(CdL$^-$) = 10.39) and this is a complex with a similar composition as the ternary goethite and manganite surface complexes.

Speciation and equilibria in the glyphosate-Al(III) system are more complicated than in the glyphosate-Cd(II) system. Complexation starts in acidic solutions (pH 1.5) and the pH range was limited (pH $\leq$ 5) by precipitation reactions. The different species turned out to be mixed protonated complexes. As outlined in Paper IV, the stability of the different complexes indicates the presence of chelate effects. Furthermore, the formation of
binuclear complexes is extensive, and the presence of yet unknown isomers puts additional complexity to this system. However, thanks to qualitative and quantitative $^{27}$Al- and $^{31}$P-NMR studies, speciation and equilibria (except for possible isomers) could be determined. Measurements are in progress to refine the speciation schemes involving isomers.

The adsorption of PMG to mineral surfaces is related to several different parameters; i) the chemical composition of the mineral, ii) the concentration of reactive surface sites, iii) the solid concentration and the surface area, iv) the available pH range accessible for adsorption and the chemical composition of the bulk solution, and v) the characteristics of the electrostatic double layer. This means that ranking different minerals in terms of affinity for a given ligand or metal ion/metal complexes cannot be done by simply comparing intrinsic surface stability constants. To give a qualitative and quantitative picture of the adsorption of PMG, Cd(II) and PMG-Cd(II) complexes on the minerals some calculations have been performed. In an attempt to normalize the different systems, the reactive surface site concentration of the three mineral systems was set equal. Figure 35 shows the adsorption of PMG, in the absence of Cd(II), to the surface of goethite, aged $\gamma$-Al$_2$O$_3$ and manganite, respectively. It is clear that the affinity of PMG for the different mineral systems decreases within the series: goethite $>$ aged $\gamma$-Al$_2$O$_3$ $>$ manganite.

![Figure 35. Adsorption of PMG on the mineral surface of goethite (▲), aged $\gamma$-Al$_2$O$_3$ (♦), and manganite (■). [MeOH$^{H^+}$]$_{tot}$ = 11 mM; [PMG]$_{tot}$ = 2 mM.](image-url)
The adsorption of Cd(II), in the absence of PMG, on manganite and goethite was plotted in Figure 36. The difference in the shape of the adsorption curves for the two minerals is related to the difference in composition and stability between the binuclear bridging goethite-Cd(II) complex \((\equiv\text{FeOH})_2\text{Cd}^+\) and the binary mononuclear edge-sharing manganite-Cd(II) complex \(\equiv\text{MnOHCd(OH)}^{0.5-}\). The goethite-Cd(II) complex is positively charged and starts to form already at about pH 4. On the other hand, the manganite-Cd(II) surface complex is a mixed (hydr)oxy complex with a negative charge and starts to form at around pH 8. Obviously, Cd\(^{2+}\) coordinated in the edge sharing mode is more easily hydrolyzed at the surface of manganite.

The co-adsorption of PMG and Cd(II) on the surface of manganite and goethite, respectively, results in the formation of a ternary complex, with a Type B structure \((\equiv\text{MeOH}^{0.5-})_{\text{tot}} \cong 2.6 \text{ mM}; [\text{Cd(II)}]_{\text{tot}} = 1 \text{ mM}.)\) The same stoichiometry of this ternary complex was found for both systems and Figure 37 shows the concentration of the complexes formed on manganite and goethite, as a function of pH. Clearly, the ternary complex is formed to a higher extent at
The surface of goethite than on manganite. It can thus be concluded that the formation of the ternary complex \( =\text{MeLCdOH}^{1.5} \) is more significant on goethite surfaces than on manganite surfaces.

![Graph showing concentration vs pH](image)

Figure 37. Concentration (in mM) of ternary surface complexes formed on goethite (▲), and manganite (■). \([=\text{MeOH}^{0.5}]_{\text{tot}} = 2.6 \text{ mM}; [\text{PMG}]_{\text{tot}} = [\text{Cd(II)}]_{\text{tot}} = 2 \text{ mM.}\)

The different systems studied in the present thesis posed a challenging modeling problem; they involved a number of coupled surface reactions, significant complexation in solution, and were constrained by different spectroscopic data. Still, it is surprising how rather simplistic models seem to fit (though not always perfect) to the experimental data. Unfortunately, at present there is no experimental technique for measuring the distribution of charge within the electrostatic double layer. This means that determination of the localization of charge within the different planes at mineral surfaces has to wait for the development of new techniques and theories within the field of surface science.
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