



Cadmium and lead removal with direct filtration
by Thomas Paul Engleson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering
Montana State University
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Abstract:

Few studies have investigated trace metal removals with water treatment unit operations and processes. Nowhere in the literature has the author found a reference to trace metal removal with a direct filtration water treatment scheme. To provide this basic information, a direct filtration pilot plant was used to collect cadmium and lead removal data.

The major variables investigated were coagulant dosage and pH. In addition, the effects of coagulant type, polymer, alkalinity and humic materials on cadmium removal efficiencies were studied.

The direct filtration pilot plant was modeled to incorporate many of the design features of operational direct filtration plants. Forty-four pilot plant runs were conducted to collect samples for the following measurements: pH, turbidity, headloss changes and metal concentration. Metal samples were analyzed on a custom built atomic absorption spectrophotometer developed at Montana State University.

Cadmium and lead removals obtained with direct filtration were not significantly different from removals reported in the literature for conventional coagulation water treatment.

Cadmium removal was strongly pH dependent, removals increasing with higher pH. The cadmium MCL was only met above pH 9.

Interestingly, it was discovered that hardness in the experimental water resulted in very low turbidity levels at alkaline pH, outside the thermodynamic boundaries of aluminum. As a result of this phenomenon, it was possible to define, in terms of coagulant dosage and pH, an operating region where both turbidity and cadmium MCLs were met concurrently.

Lead removals were independent of pH and were generally high. The lead MCL was met for all pH and coagulant dosages investigated. Therefore, MCLs for both turbidity and lead were met concurrently whenever the turbidity MCL was satisfied.

Bench-scale tests were conducted to identify the predominant removal mechanism(s) for cadmium and lead. The evidence suggests that a combination of processes may be responsible for the removals obtained within the pilot plant.

Using the operational guidelines delineated in this study, direct filtration is capable of supplying an effluent water that meets turbidity and trace metal MCLs concurrently.

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A thesis submitted in partial fulfillment
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of

Master of Science

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Civil Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

August 1984

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of a thesis submitted by

Thomas Paul Engleson

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ABSTRACT

Few studies have investigated trace metal removals with water treatment unit operations and processes. Nowhere in the literature has the author found a reference to trace metal removal with a direct filtration water treatment scheme. To provide this basic information, a direct filtration pilot plant was used to collect cadmium and lead removal data.

The major variables investigated were coagulant dosage and pH. In addition, the effects of coagulant type, polymer, alkalinity and humic materials on cadmium removal efficiencies were studied.

The direct filtration pilot plant was modeled to incorporate many of the design features of operational direct filtration plants. Forty-four pilot plant runs were conducted to collect samples for the following measurements: pH, turbidity, headloss changes and metal concentration. Metal samples were analyzed on a custom built atomic absorption spectrophotometer developed at Montana State University.

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Interestingly, it was discovered that hardness in the experimental water resulted in very low turbidity levels at alkaline pH, outside the thermodynamic boundaries of aluminum. As a result of this phenomenon, it was possible to define, in terms of coagulant dosage and pH, an operating region where both turbidity and cadmium MCLs were met concurrently.

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Bench-scale tests were conducted to identify the predominant removal mechanism(s) for cadmium and lead. The evidence suggests that a combination of processes may be responsible for the removals obtained within the pilot plant.

Using the operational guidelines delineated in this study, direct filtration is capable of supplying an effluent water that meets turbidity and trace metal MCLs concurrently.

CHAPTER 1

INTRODUCTION

With the advent of sophisticated techniques and methods for the analysis of trace metals came a better understanding of the health dangers imposed by these substances. One avenue through which people are exposed to metal contaminants is drinking water. Concern over this exposure resulted in the Environmental Protection Agency (EPA) establishing maximum contamination levels (MCL) for ten trace inorganics. Central to this study are the metals lead and cadmium with their respective MCLs of 0.05 and 0.01 mg/L.

The sources and health effects of lead and cadmium are well documented in the literature [2,6,7,9,11] and will not be repeated here. Let it suffice to say that man's industrial and manufacturing activities significantly concentrate these elements. Durum [1] observed that the special difficulty with trace metals is their persistence. This persistence allows metals to be transported for considerable distances oftentimes ending up in surface and underground waters.

Studies of trace metal removal from drinking water are rare. The studies found in the literature evaluate trace metal removal by conventional coagulation and lime softening processes. Nowhere in the literature has the author found a reference to trace metal removal with a direct filtration water treatment scheme. This study investigated trace metal removal with a direct filtration water treatment pilot plant.

Direct filtration has received considerable attention in the past decade. Direct filtration refers to a treatment scheme wherein filtration is not preceded by sedimentation. For many waters, this treatment scheme is an economical alternative to more conventional coagulation treatment.

More information is needed to better categorize those waters that can best be treated by direct filtration. The Direct Filtration subcommittee of the American Water Works Association Filtration Committee published a report [22] in 1980 which included research recommendations. One area of research that was specifically mentioned was the investigation of removal efficiencies for heavy metals and other trace inorganics with direct filtration.

This study was divided into three parts:

1. Pilot plant operation and sampling
2. Trace metal analysis
3. Data evaluation

The pilot plant was designed to incorporate many of the design features of operational, direct filtration plants. Forty-four pilot plant runs were conducted to collect samples for the following measurements: pH, turbidity, headloss, and metal concentration.

The metal samples were analyzed on a Varian AA-5 atomic absorption spectrophotometer with a Woodriff Constant Temperature Furnace. The furnace was developed at Montana State University and has an analytical capability better than many commercially available spectrophotometers.

Results obtained were evaluated with the understanding that metal removal, where required, is only one facet of the water treatment picture. For direct filtration to provide an acceptable effluent water, adequate turbidity removal and metal removal must be accomplished simultaneously. It is hoped that this study will provide information useful in meeting this goal.

CHAPTER 2

THE PROBLEM

The extent to which cadmium and lead enter surface and underground waters is of importance to this study. It is also important to consider the potential magnitude of the problem based upon what is known of natural water chemistry.

Distribution of Lead and Cadmium

Both scattered and intensive surveys [1,11] show that the elements cadmium and lead are widely distributed in low concentrations in the nation's waters. A few of the survey results are included in Table 1.

Table 1. Intensive Survey Results for Lead and Cadmium in Surface and Ground Waters [1,11].

Date	Investigator	No. Samples	Detection Frequency	Ave. Conc.* mg/L	Max Conc. mg/L	Comments
Lead						
1970	Durum et al.	727	63%	0.002	0.890	filtered samples mostly river
1962- 1967	Kopp & Kroner	1577	19.3%	0.023	0.14	lakes and rivers
1970	Dutt & McCreary	677	—	—	0.518	ground waters
Cadium						
1970	Durum et al.	727	46%	0.002	0.130	filtered samples mostly river
1962- 1967	Kopp & Kroner	1577	2.5%	0.01	0.12	lakes and rivers

*Detectable.

The maximum concentrations encountered are well in excess of established MCLs. To assess the potential extent of trace metal contamination, it is necessary to be familiar with the water quality parameters affecting the distribution of trace metals in natural waters. The pertinent parameters are listed in Table 2 [3,5].

Table 2. Parameters Affecting the Distribution of Trace Metals in Natural Waters [3,5].

-
1. pH
 2. Concentration and type of trace metal
 3. Concentration and type of complexing agents
 - a. inorganic
 - b. organic
 4. Types of suspended materials (adsorbents) and their surface areas
 5. Oxidation-reduction potential
 6. Temperature
-

These parameters will control the total soluble metal concentration as well as the fraction transported in insoluble form. For a water incorporating only the more generally applicable parameters from Table 2, it is possible to calculate dissolved metal concentrations using published thermodynamic data. Solubility modeling has been used by many others [3,6,7, 17,30,39] and will be explained in greater detail in Chapter 5.

Lead

Hem and Durum [6] have calculated soluble lead concentrations from solubility diagrams. Calculations indicate that above pH 8.0, the solubility of lead is below 0.01 mg/L regardless of the total soluble inorganic carbon concentration (C_T). Near pH 6.5, however, the solubility of lead could surpass 0.30 mg/L for a water having a low C_T . This concentration is six times the MCL. It is important to note that other complexed species could significantly increase the solubility of lead. In addition, particulate lead and lead adsorbed onto surfaces could greatly increase the gross lead concentration in a water. Based on these calculations and survey findings, lead appears to be a significant threat to water quality.

Cadmium

Similar calculations for cadmium also demonstrate a potential for contamination [7]. For a low C_T , the solubility does not get much below 1.0 mg/L even at pH 10. Another significant discovery is found in Table 1. The survey conducted by Kopp and Kroner detected cadmium in only 40 out of 1577 samples, however, the average concentration of these 40 samples was very close to the MCL. A clear threat to water quality exists.

Research Considerations

Five major considerations led to the decision to investigate trace metal removal with a direct filtration pilot plant.

1. The above discussion demonstrates that the potential for metal contamination exists. A more regional concern is that some towns in Montana have trouble meeting the MCLs for lead and cadmium [9].
2. Direct-filtration has become an attractive alternative to more conventional coagulation treatment due to savings in capital, operation, and maintenance costs [28]. Several direct filtration plants are operating in Montana and are well suited to the relatively low turbidity, color-free water in this region.
3. As mentioned in the introduction, no references were found in the literature that dealt with trace metal removal with direct filtration. This basic information could prove useful in determining the feasibility of this treatment option for a water containing lead and/or cadmium.
4. Research at Montana State University [15] showed that for coagulant dosages suitable for direct filtration, usually less than 20 mg/L, the best turbidity removals occurred within a narrow pH range, pH 6.5 to 7.0. This finding together with theoretical solubility calculations, created doubt as to the feasibility of meeting the MCLs for both metal and turbidity concurrently.

5. The physical differences between a conventional coagulation treatment scheme and a direct filtration treatment scheme could be significant with regard to metal removal. The long detention times in the flocculator and sedimentation basin might prove significant from a kinetics standpoint.

CHAPTER 3

OBJECTIVES

The overall objective of this study is to add to the body of knowledge about direct filtration and thereby better define the capacity for a direct filtration treatment plant to provide a water meeting all of the drinking water standards. The specific objectives were:

1. To evaluate the removal efficiencies for lead and cadmium within a direct filtration pilot plant.
2. To establish operational guidelines that will result in an effluent water that meets both the MCL for turbidity and metal concentration.
3. To identify the predominant removal mechanism(s).
4. To compare results obtained with data found in the literature for conventional treatment schemes.

CHAPTER 4

TRACE METAL REMOVAL IN WATER TREATMENT
—AN OVERVIEW

The mechanisms of trace metal removal in conventional water treatment may be either one or a combination of several processes—precipitation, coprecipitation and adsorption. The purpose of this chapter is to introduce some of the common water treatment operations and processes and their associated mechanism(s) for metal removal.

Definitions

In this study the following definitions apply [5]:

Precipitation

Precipitation refers to the addition of a chemical in sufficient quantity that it causes the solubility of the dissolved species in question to be exceeded.

Coprecipitation

Coprecipitation refers to the inclusion in a precipitate of substances that are normally soluble under the conditions of the precipitation. The mechanism of coprecipitation can be (1) surface adsorption in which the coprecipitating species are adsorbed at the surface of the precipitate, or (2) occlusion in which the coprecipitate is mechanically trapped, or otherwise incorporated, in the rapidly forming precipitate. Coprecipitation is a special case of adsorption.

Adsorption

Adsorption refers to the accumulation of substances at a surface or interface.

Coagulation

Coagulation involves the aggregation of colloidal particles due to destabilization and flocculation. Aggregation produces larger particles that can be removed by sedimentation and/or filtration.

Conventional Coagulation Water Treatment

Rarely have water treatment plants been designed with the removal of specific trace metals in mind; however, the operations and processes employed in conventional water treatment do demonstrate some capacity for trace metal removal [4,5,10,11].

The common water treatment operations and processes which show promise of providing some removal of trace metals from drinking water are found in Table 3 [4]. Trace metals are transferred from the liquid (soluble) phase to the solid (insoluble) phase by the mechanisms of precipitation, coprecipitation and adsorption. Trace metals transferred to the solid phase, as well as the trace metal fraction already in the insoluble fraction, are removed by coagulation followed by sedimentation and/or filtration.

Direct Filtration Water Treatment

Some of the same mechanisms of trace metal removal are possible with direct filtration as with conventional water treatment.

Coagulation followed by filtration should effectively remove trace metals associated with the insoluble fraction. The lower coagulant dosages utilized in direct filtration might diminish the importance of coprecipitation as a mechanism for removal.

Precipitation as a result of pH control is possible with direct filtration. It is generally believed that the low solubility limits of the insoluble metal hydroxide and metal carbonate controls cadmium and lead solubility [6,7,10,26,27].

Table 3. Metal Removal With Conventional Water Treatment [4].

Treatment Process	Intended Purpose	Potential Mechanism(s) for Trace Metal Removal
1. Coagulation followed by sedimentation and filtration a. aluminum sulfate b. iron salts c. coagulant aids. (clays, silica, polymers)	Turbidity and color removal	<i>Coprecipitation</i> with amorphous, hydrous aluminum and ferric oxides. <i>Adsorption</i> on clays or sediments. Removal of above by coagulation, sedimentation and filtration
2. Precipitation a. lime (CaO) and soda (Na ₂ CO ₃) b. sodium hydroxide (NaOH)	Hardness removal and pH control	<i>Precipitation</i> as oxides, carbonates, sulfides, or phosphates. Possible <i>coprecipitation</i> with CaCO ₃ and Mg(OH) ₂
3. Adsorption a. activated carbon	Taste and odor removal	<i>Adsorption</i> on activated carbon, removal of metallo-organic complexes.
4. Oxidation a. chlorine (Cl ₂) b. potassium permanganate (KMnO ₄) c. ozone (O ₃)	Iron and manganese removal	Oxidation to more insoluble forms that <i>precipitate</i> out. Oxidation of complexing organics that interfere with other coagulation and precipitation reactions.

For a water requiring softening, direct filtration will not be the preferred treatment option due to the large sludge volume generated. However, the solubility of CaCO₃ (s) is sufficiently low that some hardness removal is possible, and, coprecipitation of trace metal may occur [24].

Adsorption onto activated carbon is also quite possible with direct filtration since granular activated carbon can be used in the filters.

If oxidation for iron and manganese removal is required, direct filtration may be used. Oxidation, followed directly by filtration, has been used successfully to treat these waters.

In summary, the removal mechanisms of precipitation, coprecipitation and adsorption are possible within a direct filtration scheme and some level of trace metal removal is anticipated.

CHAPTER 5

PREVIOUS RELATED STUDIES

The previous works related to this study deal with the chemistry of aqueous metals, specifically, the processes mentioned in Chapter 4 which transfer the trace metal from the liquid phase to various solid phases. Data from the literature will be presented in accordance with these potential solubility controlling processes—precipitation, coprecipitation and adsorption.

Trace Metal Distribution

The distribution of the trace metal in a given water is essential for any subsequent discussion of metal removal. The removal processes are directly affected by the chemical form of the metal in solution. Singer [5] lists the more common forms of trace metals in Table 4.

Table 4. Distribution of Trace Metals in Natural Waters [5].

-
- A. Soluble
 - 1. Free metal ion
 - 2. Simple hydroxo complexes
 - 3. Other soluble complexes
 - a. Organo complexes
 - b. Inorganic complexes
 - B. Insoluble
 - 1. Hydrous metal oxides
 - 2. Adsorbed metals on suspended particles
 - 3. Macromolecular organometal complexes
-

Models

The many constituents of a water are in competition for the available metals and several models are used to handle the simultaneous equilibria that this implies. The more sophisticated models are computer programs such as REDEQL 2 [3], ADSORP [30], and MINEQL [50] which can calculate the relative contribution to metal solubility for several species and can take into account adsorption phenomenon as well. These and other models referenced in this study are equilibrium models using thermodynamic data to predict solubilities.

The use of an equilibrium approach in describing the distribution of trace metal necessitates that precautions be taken in interpreting model results. Weber and Posselt [58] discuss model validity in some detail. They emphasize that the most important limiting factor in many applications of thermodynamic solubility relationships is the slow attainment of equilibrium. Others have observed this as well [17,29,40,46]. Slow reaction kinetics can be especially problematic when applying model results to water treatment processes with their relatively short detention times [11,17].

Parameters Controlling Metal Solubility

The chemical composition of surface waters vary widely with location. Quite commonly anionic species such as hydroxide (OH^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) are present in sufficient concentration to form complexes with metal ions.

For certain waters, organic ligands are significant and included in the equilibrium model. Humic acids (HA) and fulvic acids (FA) are widely distributed in soils and sediments and form complexes with trace metals upon entering surface waters [41,42,43].

Numerous solids can be suspended in a water and can provide ample surface area for adsorption to occur. These suspended surfaces can include metal oxides, clays/silts and

particulate organic materials. Solids that become part of the bottom sediments continue to play an important role in controlling the distribution of trace metals via adsorption/desorption reactions [19,26,39].

To discuss all the potential interactions is not possible. The remainder of this section will deal with interactions considered important to this study.

Inorganic Ligands. Table 5 lists stability constants for metal-inorganic ligand complexes for cadmium and lead. Stability constants are adjusted for the experimental conditions of ionic strength (I) = 0.003M and temperature (T) = 20°C using the Guntelberg Equation and the van't Hoff-Arrhenius Equation, respectively. These equations are commonly used and explained elsewhere [26].

Table 5. Inorganic Complex Formation Equilibria for Cadmium and Lead.

Complex Reaction	Stability Constant, K*	Reference
$\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{CdOH}^+$	$10^{3.81}$	[39]
$\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2^0$	$10^{7.72}$	[39]
$\text{Cd}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_3^-$	$10^{8.94}$	[27]
$\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4^0$	$10^{2.40}$	[39]
$\text{Cd}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CdCO}_3^0$	$10^{3.97}$	[29]
$\text{Cd}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CdHCO}_3^+$	$10^{2.3}$	[39]
$\text{Pb}^{2+} + \text{OH}^- \rightleftharpoons \text{PbOH}^+$	$10^{5.98}$	[30]
$\text{Pb}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_2^0$	$10^{10.32}$	[30]
$\text{Pb}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_3^-$	$10^{13.39}$	[30]
$\text{Pb}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_4^{2-}$	$10^{16.27}$	[30]
$\text{Pb}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{PbCO}_3^0$	$10^{5.00}$	[26]
$\text{Pb}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4^0$	$10^{2.70}$	[26]
$\text{Pb}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{PbHCO}_3^+$	$10^{2.80}$	[30]

*For T = 20°C, I = 0.003M.

Organic Ligands. The Bozeman tap water used in this study was an unpolluted surface water with a measured total organic carbon (TOC) content ranging from 1 to 5 mg/L

[44]. The lower limit corresponding to periods of low runoff (turbidity ≤ 1 NTU). Reportedly, the organo-metallic complexes increase metal solubility, interfere with adsorption, prevent agglomeration, and interfere with removal by filtration [4]. Fristoe and Nelson [46] determined conditional constants for cadmium-organic ligand complexes. In principle, the difference in the amount of metal adsorbed onto a cationic resin in the presence and absence of an organic ligand is used to calculate the stability constant for the complex. The conditional stability constants are calculated from Equation (1) and are presented in Table 6.

$$\beta_L = \frac{[M_L]}{[M_{T-L}] \{L\}} \quad (1)$$

where,

β_L = conditional stability constant, L/mg

$[M_L]$ = concentration of metal-organic ligand complex, moles/L

$[M_{T-L}]$ = concentration of total soluble metal minus $[M_L]$, moles/L

$\{L\}$ = organic ligand concentration, mg/L TOC.

Table 6. Conditional Stability Constants for Cadmium-Organic Ligand Complexes [46].

pH	5.0	6.0	6.5	7.0	8.0	9.0
β_L , L/mg (20°C)	0.05	0.18	0.19	0.21	0.05	0.0

Humic Materials. Naturally occurring polyelectrolytes referred to by such names as humic and fulvic acids are widely distributed in soils and sediments where they form water-soluble and water-insoluble complexes with metal ions [41]. A few studies have characterized these natural complexing ligands and conditional complexation stability constants with various metals have been evaluated. Table 7 lists some conditional stability constants for humic-metal complexes.

Table 7. Conditional Stability Constants for Humic-Metal Complexes for pH 7.5.

Metal	$\log \beta_{11}^*$	$\log \beta_{21}^*$	Reference
Pb (II)	6.0	13.2	[41]
Pb (II)	4.7**	—	[30]
Cd (II)	6.0	11.2	[41]
Cd (II)	6.3	11.7	[43]

**From empirical equation $\log \beta_{11}^* = 0.625 \times \text{pH}$.

where,

$$\beta_{11}^* = \frac{\beta_{11}}{\{H\}^x} = \frac{[MHA]}{[M^{2+}][H_x HA]} \quad (2)$$

$$\beta_{21}^* = \frac{\beta_{21}}{\{H\}^y} = \frac{[M_2 HA]}{[M^{2+}]^2 [H_y HA]} \quad (3)$$

and, [MHA] and [M₂ HA] represent metal-humic complexes.

Due to the color causing properties of humic materials, some researchers have developed empirical equations relating the extent of complexation by humic materials to the light absorbing properties of the water. Gardiner [29] developed the following equation for cadmium:

$$\log \frac{[\text{Cd complex}]}{[\text{Cd}^{2+}]} = 0.64 \log A_{400} + 0.20 \text{ pH} - 1.14 \quad (4)$$

where, A₄₀₀ is the absorbance of the filtered solution at a wavelength of 400 nm.

Suspended Solids. Many researchers have treated adsorption surfaces analogous to soluble ligands. Conditional adsorption constants (K_{ads}) have been calculated for various homogeneous and mixed suspensions [3,39,46]. The following equation can be used:

$$K_{\text{ads}} = \frac{MS}{M_T S_T} \quad (\text{L/g}) \quad (5)$$

where, MS = total concentration of metal-solid complexes (mol/L); M_T = total soluble concentration of metal, free and complexed (mol/L); and S_T = total concentration of solid

phase (g/L). The conditional adsorption constant, K_{ads} , is specific for a particular set of chemical and physical characteristics that compose the solid-solution system. In other words, Equation (5) treats implicitly all complex formation equilibria that control constituent species concentrations of MS and M_T .

The experimental data needed to calculate, K_{ads} , and the procedures used are included in References [39] and [46].

Adsorption equilibria data will be presented in a later section.

Generalized Metal Speciation and Distribution Model

Equation (6) has been used to determine the fraction of total metal incorporated in a specific metal-ligand or metal-surface complex [46].

$$\alpha(j)_n = \frac{\beta(j)_n [L(j)]^n}{1 + \sum_j \sum_i \beta(j)_i [L(j)]^i + \sum_m K_{ads} S_m [\alpha_m]^{-1}} \quad (6)$$

where, $\alpha(j)_n$ = species fraction of metal-ligand complex $ML(j)_n$, or metal surface complex, $ML(j)_n S$ (dimensionless); j = ligand-type identifier; i = ligand number; n = stoichiometry of metal-ligand complex; $\beta(j)$ = stability constant for metal ligand complex of type j ; $[L(j)]$ = concentration of complexing ligand of type j (mol/L); S_m = concentration of adsorbing solid of type m (g/L); and $\alpha_m = [M]/[M_T]$ = free metal ion fraction of soluble species.

Using Equation (6), or a modification thereof, it is possible to plot soluble species concentration versus pH. This is done in Figures 1 and 2 for the experimental water used in this study. The procedures and assumptions required in making these diagrams will be discussed in Chapter 7, Speciation and Distribution Model.

Precipitation

Both cadmium and lead combine with various anions in solution to form insoluble compounds. These reactions transferring metal from the liquid phase to the solid phase and

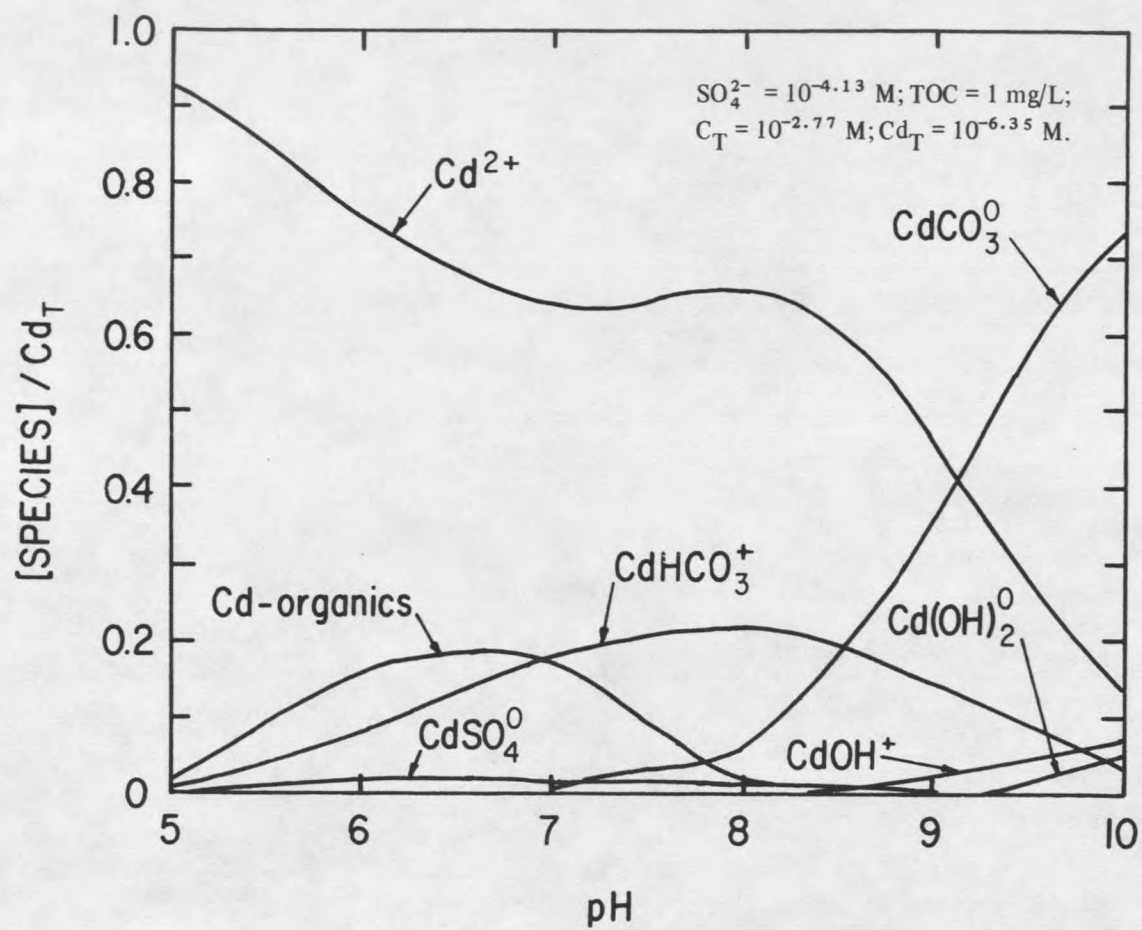


Figure 1. Speciation model for cadmium.

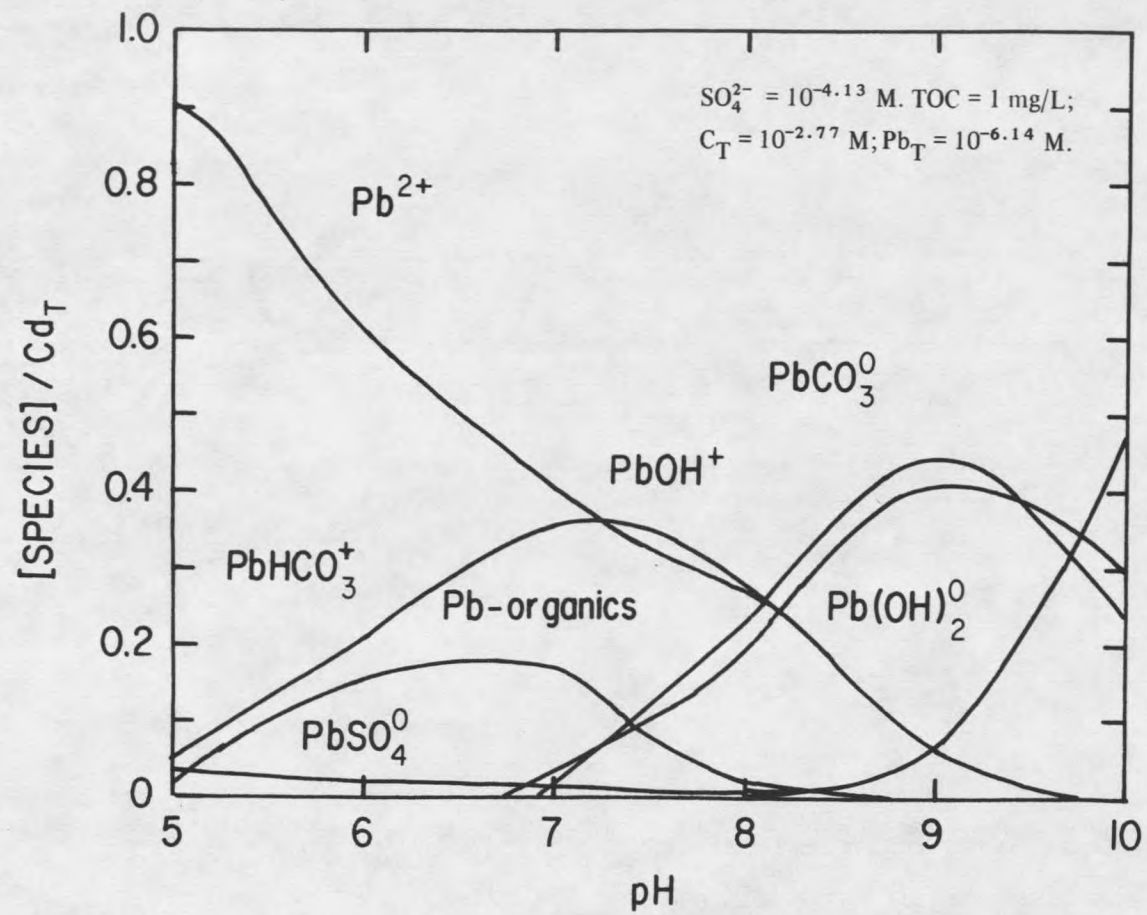


Figure 2. Speciation model for lead.

back to the liquid phase (dissolution) often regulate the concentrations of dissolved metal species. Table 8 lists the more common mineral sources for cadmium and lead along with their solubility products (K_{sp}). Hem's [6,7] calculations indicate that the insoluble compounds of sulfur will not control solubility for pH, total sulfur concentration and redox potential commonly found in oxic waters. In addition, the stability field of the basic carbonate, $Pb_3(CO_3)_2(OH)_2(s)$, occurs over so short a pH range that its contribution can also be omitted without introducing a significant error [6].

Metal-H₂O System

The simplest model used to interpret observed concentrations of trace metal in naturally occurring waters incorporates the metal and the components of pure water—hydrogen ions and hydroxide ions.

Table 8. Mineral Sources of Cadmium and Lead.

Mineral Source	Solubility Product	K_{sp}^*	Reference
$CdCO_3(s)$	$K_{sp} = [Cd^{2+}][CO_3^{2-}]$; $10^{-10.77}$, $10^{-11.66}$	[19],[7, 26]
$Cd(OH)_2(s)$	$K_{sp} = [Cd^{2+}][OH^-]^2$; $10^{-13.36}$, $10^{-14.05}$	[17],[7]
$CdS(s)$	$K_{sp} = [Cd^{2+}][S^{2-}]$; $10^{-27.0}$	[24]
$PbCO_3(s)$	$K_{sp} = [Pb^{2+}][CO_3^{2-}]$; $10^{-13.54}$, $10^{-13.96}$	[17],[6]
$Pb(OH)_2(s)$	$K_{sp} = [Pb^{2+}][OH^-]^2$; $10^{-14.85}$, $10^{-19.29}$	[17],[6]
$PbS(s)$	$K_{sp} = [Pb^{2+}][S^{2-}]$; $10^{-27.5}$	[24]
$PbSO_4(s)$	$K_{sp} = [Pb^{2+}][SO_4^{2-}]$; $10^{-7.8}$	[26]
$Pb_3(CO_3)_2(OH)_2(s)$	$K_{sp} = [Pb^{2+}]^3 [CO_3^{2-}]^2 [OH^-]^2$; $10^{-18.8}$	[17]

*Hydroxides and carbonates adjusted to T = 20°C and I = 0.003M.

Both lead and cadmium salts show varying degrees of acidity when dissolved in water. This observation is explained by the reaction of the metal ion with the solvent water, referred to as hydrolysis. Hydrolysis reactions can be described by either dissociation or complexation reactions and oftentimes occurs in a stepwise manner [26,27]. The general

hydrolysis reactions given below are for a divalent metal and represent the exchange of OH^- for an H_2O molecule from the inner coordinate sphere.



K_1 through K_4 are the stepwise formation constants.

A mass balance for the soluble metal species in the metal- H_2O system is written:

$$M_{T_s} = [\text{M}^{2+}] + [\text{MOH}^+] + [\text{M}(\text{OH})_2^0] + [\text{M}(\text{OH})_3^-] + [\text{M}(\text{OH})_4^{2-}] \quad (11)$$

where, M_{T_s} equals the total soluble metal concentration. Substituting the formation constants in Equations (7) through (10) into Equation (11) results in the following equation:

$$M_{T_s} = [\text{M}^{2+}](1 + \beta_1 [\text{OH}^-] + \beta_2 [\text{OH}^-]^2 + \beta_3 [\text{OH}^-]^3 + \beta_4 [\text{OH}^-]^4) \quad (12)$$

where, $\beta_1 = K_1$; $\beta_2 = K_1 \cdot K_2$; $\beta_3 = K_1 \cdot K_2 \cdot K_3$; $\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$.

In the divalent metal- H_2O system the maximum solubility is controlled by the insoluble hydroxide species with the stoichiometry $\text{M}(\text{OH})_2 (s)$. The corresponding solubility product is found in Table 8. The free-metal concentration can be calculated from Equation (13) below.

$$[\text{M}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} \quad (13)$$

Substituting this value into Equation (12) gives the following expression for solubility, S:

$$S = \frac{K_{sp}}{[\text{OH}^-]^2} (1 + \beta_1 [\text{OH}^-] + \beta_2 [\text{OH}^-]^2 + \beta_3 [\text{OH}^-]^3 + \beta_4 [\text{OH}^-]^4) \quad (14)$$

Solving Equation (14) for various pH results in theoretical hydroxide solubility curves as shown in Figures 3 and 4. The hydrogen ion and hydroxide ion concentrations are related as follows for $T = 20^\circ\text{C}$, $I = 0.003\text{M}$:

$$[\text{H}^+][\text{OH}^-] = K_w \approx 10^{-14.12} \quad (15)$$

In equation form, pH and hydrogen ion concentration are related by the following expression:

$$\text{pH} = -\log [\text{H}^+] \quad (16)$$

It is convenient to plot these hydroxide solubility curves using equations relating the metal hydroxide solid species in equilibrium with the various soluble species. These equations are presented below and can be derived using Equations (7) through (10), (13) and (15).

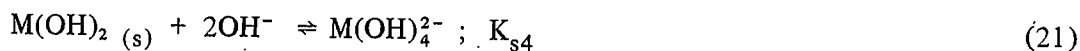
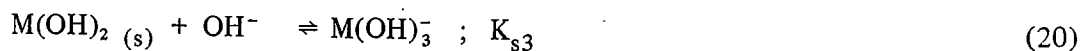
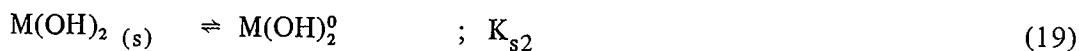
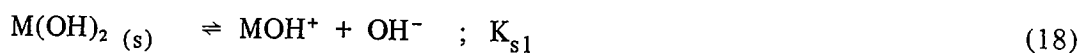
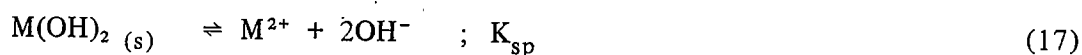


Table 9 lists the hydroxide solubility constants from the various references used in this study. The theoretical hydroxide solubility curves plotted in Figures 3 and 4 give some indication of the variance in thermodynamic data found in the literature.

Metal-H₂O-Carbonate System

Most waters contain appreciable quantities of dissolved carbon species resulting from heterogeneous equilibria with atmospheric carbon dioxide and carbon containing minerals. It is generally believed that together with the insoluble metal hydroxide, insoluble metal carbonate, $\text{MCO}_3 \text{ (s)}$, oftentimes regulates the metal concentration found in natural waters [6,7,11,26]. Modeling a metal-H₂O-carbonate system is complicated by the diprotic nature of carbonic acid as well as equilibria between the two solid phases and the several soluble species.

Modeling water treatment processes with a closed carbonate system, constant C_T , is usually justified [17]. The pertinent equilibria for carbonic acid in aqueous solution are given below for $T = 20^\circ\text{C}$ and $I = 0.003\text{M}$.

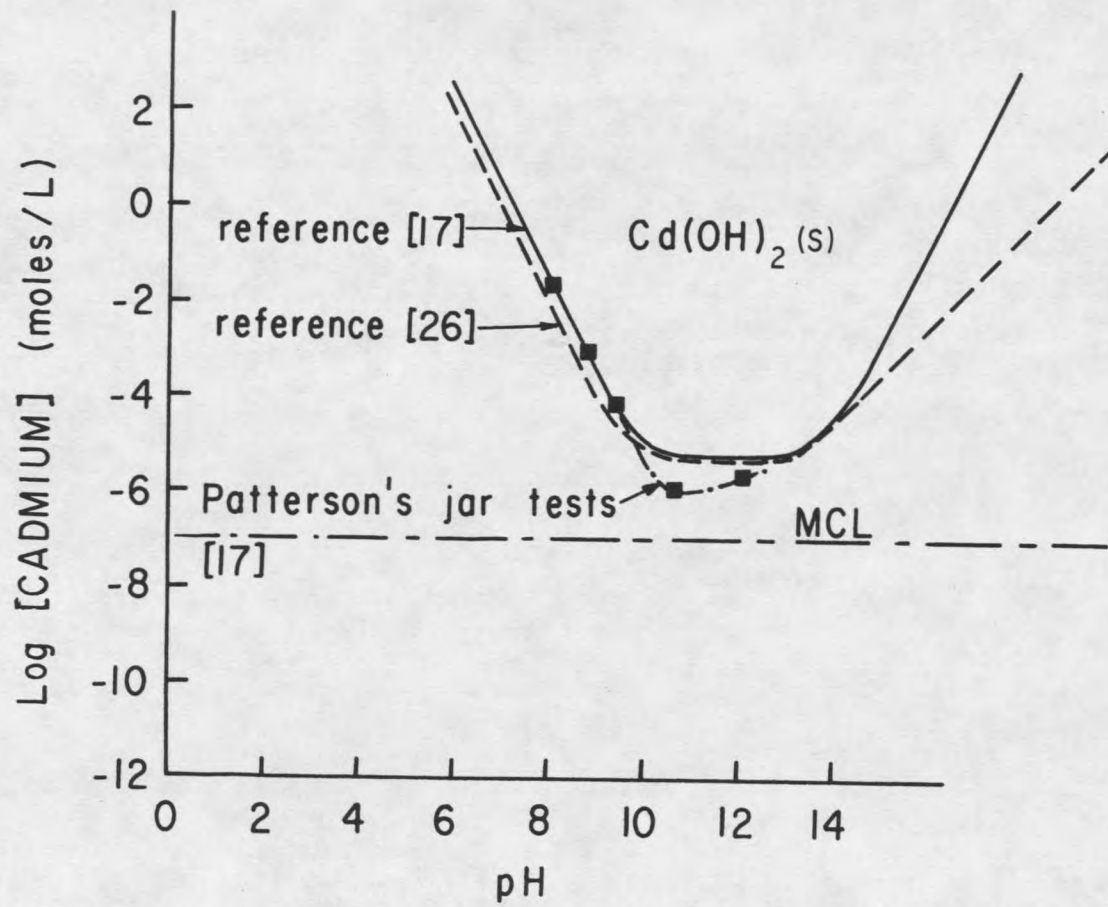


Figure 3. Cadmium hydroxide solubility diagram.

