INVESTIGATION OF LEAD HYDROLYTIC POLYMERIZATION AND INTERACTIONS WITH ORGANIC LIGANDS IN THE SOIL/SEDIMENT-WATER ENVIRONMENT

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Dissertation Prepared for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS

December 2002

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Sanmanee, Natdhera, Investigation of lead hydrolytic polymerization and interactions with organic ligands in the soil/sediment-water environment. Doctor of Philosophy (Environmental Science), December 2002, 186 pp., 29 tables, 43 illustrations, references, 64 titles.

The objective of this research was to investigate lead speciation in the soil/sediment-water environment and to better understand how the species affect lead mobility under different environmental conditions. The research involved both field soil and sediment samples as well as standard lead solutions. Field samples were fully characterized and extracted by aqueous and organic solvents. The results were compared and evaluated with the metal speciation model, MINTEQA2. Hydrolytic polymerization and organic complexation studies were conducted with standard lead solutions under controlled experimental conditions.

Results of the field samples showed that pH, dissolved cations, ionic strength, dissolved organic matter, and nature of the soil/sediment matrix play major roles in the distribution and mobility of lead (Pb) from contaminated sites. In the aqueous equilibration experiment, the magnitude of Pb^{2+} solubilization was in the order of pH4>pH7>pH9. The results were in good agreement with MINTEQA2 predictions. An important finding of the research is the detection of Pb polymerization species under controlled experimental conditions. At pH 5.22, Pb polymeric species were formed at rate of 0.03 per day. The role of Pb complexation with organic matter was evaluated in both field and standard samples. Different methodologies showed three types of organically bound Pb. A very small fraction of Pb, in the ppb range, was extractable from the

contaminated soil by polar organic solvents. Sequential extractions show that 16.6±1.4 % of the Pb is organically complexed. Complexation of Pb with fulvic acid provided new information on the extent of Pb association with soluble organic matter.

The overall results of this research have provided new and useful information regarding Pb speciation in environmental samples. The results, in several instances, have provided verification of MINTEQA2 model's prediction. They also revealed areas of disagreement between the models prediction and the experimental results. A positive note regarding the experimental work done in the research is the verification of the mass balance in all the repeated experiments.

ACKNOWLEDGMENTS

I wish to express my deepest gratitude to my Major Professor, Dr. Farida Y. Saleh, for her support, guidance, and patience throughout this work. My gratitude also extends to the other members of my committee: Dr. Kenneth L. Dickson, Dr. Samuel F. Atkinson, Dr. Paul F. Hudak, and Dr. Thomas W. LaPoint, each of whom helped me over different hurdles.

I would like to thank the Royal Thai government who granted me the scholarship to pursue a doctoral degree in Environmental Science at the University of North Texas from 1997 to 2002. Also, for the support to finish this work, I want to thank University of North Texas for the Graduate School Scholarship during the 2000-2001 academic year and Charles E. & Joann Bond Scholarship for the 2002-2003 academic year.

Thanks to my friends and other professors who gave their precious time to help me on laboratory works including Dr. James Kennedy, Dr. Reid Ferring, Johnny Byers, Ahmed Kadry, Margaret Forbes, Elizabeth Roberts, David Garrett, Jessica White, Stacy Wright, and Jason Condor. Finally, I would like to thank my husband, Sirichai Sanmanee, for his invaluable support and patience.

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INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

General Statements

Lead is one of the most persistent pollutants in the environment. In human history, it seems probable that the use of primitive furnaces to extract lead from its ores was the first such smelting practice recognized by humans. Early uses of lead were for building materials, pigments for glazing ceramics, and pipes for transporting water. Others in Europe were for decorative fixtures, roofs, pipes, and window in castles and cathedrals.[1,2]

During 1900s, uses of lead were primarily for ammunition, brass, burial vault liners, ceramic glazes, leaded glass and crystal, paints or other protective coatings, water lines and pipes, cable covering, caulking lead, and solders.[2-4] Uses for lead continued to increase with the growth in population and the national economy.[2] Even though there was a significant shift in lead end-use-patterns by the mid-1980s due to the elimination of the use of lead in gasoline, paints, solders, and water systems, demands for lead for industrial applications including lead-acid storage batteries are rising.[5]

Lead discharged into the environment is toxic to most living organisms.[1,4,6,7] Once it enters their bodies, the bodies never decompose lead into another more easily tolerated substances.[6] Excess lead in a human body can cause serious damage to the brain, kidneys, nervous system, and red blood cells. Usually, children are more

susceptible to lead in the lower level than adults.[4,8] Because its toxicity is persistent, once lead has been dispersed and redeposited into the environment, it will remain to poison future generations unless it is controlled or removed.[3,4,9] Under the new standards of United States Environmental Protection Agency (USEPA), the action level for lead in drinking water is 15 parts per billion (ppb) or μg/L. There are more than 40 million U.S. residents estimated by USEPA using water that contain lead in excess of the drinking water standard.[10]

The toxicity of lead has been widely recognized not to relate merely by the total concentration.[11-19] For this reason, lead bioavailability and its formation have come to attention. One of the important factors that affect lead bioavailability is the formation of polymeric species, some of which may be soluble.[20,21] Another one is partitioning of lead between dissolved and sorbed on solid phases especially on organic material.[11,15,16] Both critically influence metal transport, reactivity, and bioavailability. In different locations, the predominance of specific processes will vary depending on types of binding surfaces, physical and chemical factors, and their relative abundance in the environment.[13-15,17,18]

Since the hydrolysis and polymeric species of lead had been rarely mentioned due to the limitations of analytical methods and study of organically bound lead had not been clearly clarified, the investigation of lead polymeric and organically bound species was conducted in this research under controlled experiments. This is in order to help in better understanding fate and behavior of lead including some major factors controlling lead speciation. Soil collected in polluted and non-polluted areas were studied including standard soil. A new speciation scheme was developed and evaluated. It involved

investigations of distribution and speciation of lead in the samples under different extraction methods by aqueous and organic solvents, as well as, by the conventional sequential extraction method. The aqueous extraction was done under three different pH levels and the organic extraction was done by using organic solvents of increasing polarity. Major cations, anions, and ligands were analyzed in the target samples and in different fractions. Results from all extraction schemes were put in a lead distribution diagram. The diagram was evaluated and compared to results of the MINTEQA2—a computer prediction model of USEPA.

Objectives

1. To develop a comprehensive scheme to evaluate the speciation of lead compounds under different environmental and experimental conditions.

2. To investigate lead polymeric species and to evaluate their effects on lead mobility.

3. To investigate lead-organic complexation and understand how organic materials affect lead mobility.

Research Hypotheses

1. In field soil and sediment samples, lead solubilization is primarily dependent on pH, ionic strength, soluble organic matter, and the nature of the soild samples.

2. Organic solvent extraction of field samples gives a direct measure of the organically bound lead.

3. Lead hydrolytic polymerization species may be contribute to lead mobility in the environment.

4. Lead complexation with dissolved organic matter affects the mobility and transport of lead in the environment.

1.2 Literature Review

Lead Use in Human History

Lead, symbol Pb from the latin *plumbum*, is one of the most persistent pollutants in the environment. Lead has been used throughout much of human history. The prehistoric metal apparently was used for glazing pottery by the early Egyptians as far back as 7000-5000 BC.[1,2]

Elemental lead is very corrosion-resistant, dense, ductile, and malleable. Because of its properties, early uses of lead as a construction material in early time included building materials, pigments for glazing ceramics, and pipes for transporting water. The castles and cathedrals of Europe also contain considerable quantities of lead in decorative fixtures, roofs, pipes, and windows.[2]

Prior to the early 1900s, uses of lead in the United States were primarily for ammunition, brass, burial vault liners, ceramic glazes, leaded glass and crystal, paints or other protective coatings, and water lines and pipes.[2-4] Technological developments during World War I resulted in the addition of bearing metals, cable covering, caulking lead, and solders to the list of lead uses.[2]

During the 1920s the development of tetraethyl lead (TEL) considerably improved the burning characteristics of gasoline in internal combustion engines. This resulted in the design of highly efficient engines capable of giving high power and economy.[2]

With the growth in production of public and private motorized vehicles and the associated use of starting-lighting-ignition (SLI) lead-acid storage batteries and terne metal for gas tanks after World War I, demand for lead increased[1,2,5,22] Uses for lead continued to increase with the growth in population and the national economy. The use of lead for radiation shielding in medical analysis and video display equipment and as an additive in gasoline, have contributed the increase of demand for the element. In 1974 on a world basis, lead used for batteries and gasoline additives accounted for over 50% of the world wide lead consumption.[2]

By the mid-1980s, there was a significant shift in lead end-use patterns. Much of the shift was a result of the United States lead consumers compliance with environmental regulations that significantly reduced or eliminated the use of lead in gasoline, paints, solders, and water systems.[2]

More recently, as the use of lead in some products has continued to decline, the demand for lead in SLI-type batteries is rising including the demand from industries for certain applications, such as motive sources of power for industrial forklifts, airport ground equipment, mining equipment, and a variety of non-road utility vehicles, as well as stationary sources of power in uninterruptible electric power systems for hospitals, computer and telecommunications networks, and load-leveling equipment for electric utility companies. The world consumption of lead in 2000 was over 6 million tons and 86% of the total world consumption belonged to western world as illustrated in Table 1.1.

Table 1.1 Lead consumption[5]

	Annual Totals (Thousand tones)			
	1997	1998	1999	2000
Europe	1,968	1,951	1,998	2,071
Africa	121	132	128	126
America	2,100	2,194	2,247	2,256
Asia	1,771	1,673	1,810	1,943
Oceania	70	64	64	50
World Total	6,030	6,014	6,247	6,446
Of Which Western World	5,254	5,234	5,436	5,572

*From International Lead and Zinc Study Group. http://www.ilzsg.org/statistics.asp?pg=lead, Accessed 5/9/2001. (Used with permission).

The major consumption of lead is for lead-acid storage batteries. Average end use patterns from international study by International Lead and Zinc Study Group over the last five years are illustrated in Figure 1.1.[5]

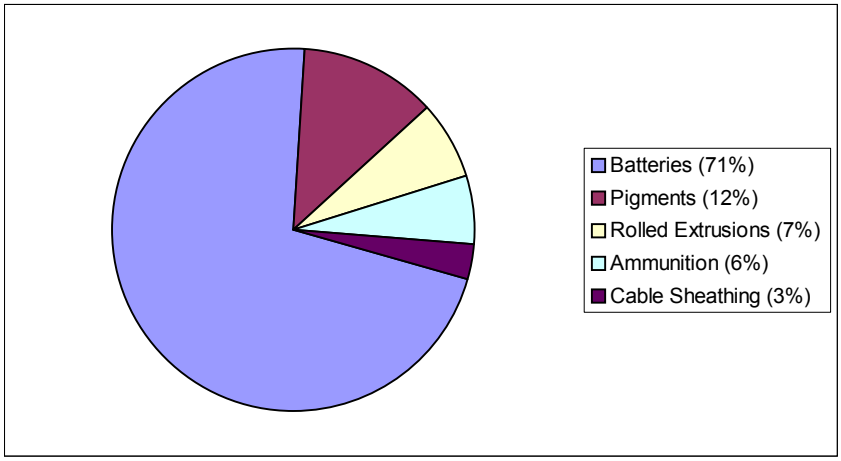


Figure 1.1 Estimating end uses of lead by International Lead and Zinc Study Group[5] during 1996-2000, http://www.ilzsg.org/statistics.asp?pg=eco, Accessed 5/9/2001. (Used with permission).

Geochemistry of Lead

Lead is the most abundant of natural heavy elements and it occurs in nature as four stable isotopes in varying relative amounts: ^{204}Pb (1.2 to 1.6 percent in almost all samples), ^{206}Pb (20 to 28%), ^{207}Pb (20 to 23%), and ^{208}Pb (50 to 54%).[23]
In addition, four short lived radioactive isotopes: ^{210}Pb, ^{211}Pb, ^{212}Pb, and ^{214}Pb occur in nature as decay products of uranium and thorium.[1,23,24]

Lead exists in three oxidation states, 0, +2, and +4,[1,25] but ionic form (Pb^{2+}) is the most abundant.[1,23] Lead can be oxidized to Pb^{4+} under strong oxidizing conditions, such as in hot arid areas,[1] and few simple compounds of Pb^{4+} other than PbO_2 are stable.[23]

According to soft and hard acids and bases (HSAB) concept, Pb^{2+} prefers soft bases such as S^{2-}.[26] Most of lead insoluble forms is sulfide ore—galena (PbS).[1,23,26] Divalent lead is also commonly found as the selenide and telluride, as well as in a large number of sulfo-salts where it acts as the cation. In moderately oxidizing environments, lead is involved in the formation of a large number of minerals, such as lead oxides, sulfates, arsentats, phosphates, and carbonates.[1] Most of these are very rare, and only three are found in sufficient abundance to form mineable deposit: galena (PbS), cerussite ($PbCO_3$), and anglesite ($PbSO_4$).[1,23,25] During weathering, galena is slowly oxidized by atmospheric oxygen to either the sulfate (angelesite) or the carbonate (cerussite), as indicated by the following equations:

$$PbS + 2O_2 \rightarrow PbSO_4 \quad (1.1)$$

$$PbS + CO_2 + H_2O + 2O_2 \rightarrow PbCO_3 + H_2SO_4 \quad (1.2)$$

Cerussite usually is formed at a pH above 6 and anglesite at a pH below 6.[27]

Because of its ionic radius (between 1.18 and 1.32 Å), Pb^{2+} can replace potassium (1.33 Å), strontium (1.12-1.27 Å), barium (1.34-1.43 Å), calcium (0.99-1.06 Å), and sodium (0.95-1.0 Å) in mineral lattices. Among the silicate minerals, potassium feldspars of pegmatites are notable accumulators of lead; micas usually contain less lead than the potassium feldspars.[1] The lead content in rock-forming minerals is shown in Appendix 1.2. Lead ore is commonly present together with ores of copper, zinc, silver, arsenic, and antimony in complex vein deposits, but lead ore also may occur in a variety of igneous, metamorphic, and sedimentary rocks.[25] The high concentrations of lead in iron and manganese oxides reflect the fact that these compounds have a very strong affinity for lead.[1]

The accepted average value for the lead content of the earth's crust is 15 mg/kg.[23,28] The highest concentrations of lead occur in the upper horizon of the soil with small additions, leached down to the subsoil. Parent material influences native lead content and soils in suspected ore areas have levels up to 45,000 mg/kg.[23]

Lead content of young residual soils is strongly influenced by the parent rock from which they are derived. However, in mature soils developed on deeply weathered parent material, other factors may affect and obscure this relationship. These factors include oxidation and reduction reactions, organically complexation by organic materials, sorption by clay, adsorption of lead by hydroxides of iron and manganese, local solution and transportation by organic acids, and cycling by vegetation. In general, lead is more mobile in acid soils than in alkaline soils, tending to be leached out of the former and to form residual concentrations in the latter.[28]

Physical and Chemical Properties of Metallic Lead

Lead, like most metals, is soft when very pure. Its inherent luster is usually masked by a dull surface coating of its oxide.[29] It crystallizes in the face-centered cubic system with a minimum interatomic distance of 3.492 Å. Important physical attributes of metallic lead include high density, softness, flexibility and malleability, low melting point, weld ability and low elastic limit. These properties, as well as its high lubricity, low electrical conductivity, high corrosion resistance and high coefficient of expansion determine its widespread industrial applications.[1] The physical and chemical properties of lead are shown in Table 1.2.

Table 1.2 Some properties of lead[30]

Characteristics	Lead properties
Atomic number	82
Atomic weight (g)	207.19
Electronic structure	$[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$
Melting point (˚C)	327.5
Boiling point (˚C)	1,740
Ionization enthalpies (kJ mol^{-1})	
1^{st}, 2^{nd},3^{rd}, 4^{th}	715.3, 1450, 3080, 4082
Electronegativity	1.8
Covalent radius (Å)	1.44
Ionic radius of Pb^{2+}, Pb^{4+} (Å)	1.21, 0.775

Data source: Cotton F, Wilkinson, G. Advanced Inorganic Chemistry, 4^{th} ed.: J. Wiley; 1980. p. 589-616

Chemistry of Lead in the Aqueous Environment

Lead is classified as a B-type metal cation, also referred as soft acid. B-type metal cations have a more readily deformable electron sheath (high polarizability) than A-type metals and are characterzed as "soft sphere" cations.[31] Table 1.3 shows the classification of metal ions in solutions.

B-type metal ions coordinate preferentially with bases containing I, S, or N as donor atoms. [31] "Thus metal ions in this class may bind ammonia more strongly than water, CN^- in preference to OH^-, and form more stable I^- or Cl^- complexes than F^- complexes. These metal cations, as well as transition-metal cations, form insoluble sulfides and soluble complexes with S^{2-} and HS^-."[31] (p.285)

Regarding the sharing of an electron pair between the central atom and the ligand (covalent bond), the tendency toward complex formation increases with the capability of the cation to take up electrons (increasing ionization potential of the metal) and with decreasing electronegativity of the ligand (increasing tendency of the ligand to donate electrons). In the series F, O, N, Cl, Br, I, S, the electronegativity decreases from left to right, whereas the stability of complexes with B-type cations increases.[31]

"For transition metal cations, a reasonably well-established rule on the sequence of complex stability, the Irving-Williams order, is valid." [31] (p.285) According to this rule, the stability of complexes increases in the series $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Pb^{2+}$ for almost every ligand.[26] For classification schemes of electron donors, a simple attempt at classifying "hard" and "soft" bases reveal that "hard" and "soft" are not absolute, but gradually varying qualities. The so-called HSAB rules indicate the

Table 1.3 Classification of Metal Ions.[31]

A-Type Metal Cations	Transition-Metal Cations	B-Type Metal Cations
Electron configuration of inert gas; low polarizability; "hard spheres"; (H^+), Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	One to nine outer shell electrons; not spherically symmetric: V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}	Electron number corresponds to Ni^0, Pd^0, and Pt^0 (10 or 12 outer shell electrons); low electronegativity; high polarizability; "soft spheres": Cu^+, Ag^+, Au^+, Tl^+, Ga^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}
According to Pearson's (1963) Hard and Soft Acids		
Hard Acids	Borderline	Soft Acids
All A-type metal cations plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, UO^{2+}, VO^{2+}	All bivalent transition-metal cations plus Zn^{2+}, Pb^{2+}, Bi^{3+}, SO_2, NO^+, $B(CH_3)_3$	All B-type metal cations minus Zn^{2+}, Pb^{2+}, Bi^{3+}
Also species such as BF_3, BCl_3, SO_3, RSO_2^+, RPO_2^+, CO_2, RCO^+, R_3C^+		All metal atoms, bulk metals I_2, Br_2, ICN, I^+, Br^+
Preference for ligand atom:		
N >> P		P >> N
O >> S		S >> O
F >> Cl		I >> F
Qualitative generalizations on stability sequence:		
Cations: Stability ∝ (charge/radius)	Cations: Irving–Williams order: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$	
Ligands: $F > O > N = Cl > Br > I > S$		Ligands: $S > I > Br > Cl = N > O > F$
$OH^- > RO^- > RCO_2^-$		
$CO_3^{2-} >> NO_3^-$		
$PO_4^{3-} >> SO_4^{2-} >> ClO_4^-$		

*From Stumm, W, Morgan, JJ. Aquatic Chemistry, 3rd edition: Copyright © 1996 by J. Wiley & Sons, Inc; Table 6.3 p. 284, (This material is used by permission of J. Wiley & Sons, Inc).

preference of hard acids to associate or react readily with hard bases and soft acid with soft bases.[31]

By taking into account bonding due to both covalent and ionic interactions, the covalent index, X_m^2 can be plotted versus an ionic index, Z^2/r (X_m = metal ion electronegativity, Z = charge of metal, r = ionic radius of metal) to differentiate between type A, borderline, and type B metals (showed in Figure 1.2). The covalent index is a reflection of the ability of the metal to accept electrons from a donor ligand. The ionic index measures the possibility of ionic bond formation. So, more highly charged species tend to be found on the right-hand side of the diagram. These are also the species that tend to act as Bronsted acids.[32]

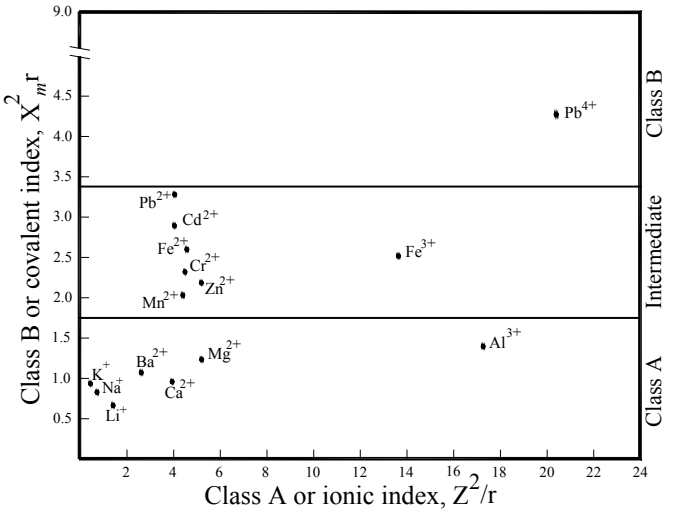


Figure 1.2 Classification of some metals of environmental importance. Stability of complexes increases with increasing ionic and/or covalent index.[31,32] Adapted from Nieboer, E. and Richardson, D.H. The Replacement of the Nondescriptive Term Heavy Metals by a Biologically and Chemically Significant Classification of Metal Ions, *Environ. Pollut. Ser,* 1980. B 1, 3-26

The tendency for formation of complexes with ligands other than water is generally in the order type B metals > borderline metals > type A metals. The type B metals also form more stable complexes with oxygen-donating compounds than do borderline and type A metals.[31,32]

Assuming that lead is present within the typical 'normal' concentration range in water and the water contains carbonate, sulfate, and chloride at levels approximately equal to that found in average river water, the principal inorganic aqueous species of lead at pH4, 7, and 9 are shown in Table 1.4.[32]

Table 1.4 Principal aqueous species of lead.[32]

	pH = 4		pH =7		pH = 10	
	Oxidizing environment	Reducing environment	Oxidizing environment	Reducing environment	Oxidizing environment	Reducing environment
Lead	Pb^{2+}	Pb^{2+}	Pb^{2+}	Pb^{2+}	$Pb(OH)_2$	$Pb(OH)_2$
	$PbSO_4^0$		$PbOH^+$	$PbOH^+$	$PbCO_3$	$PbCO_3$
			$PbHCO_3^+$	$PbHCO_3^+$	$Pb(CO_3)_2^{2-}$	$Pb(CO_3)_2^{2-}$
			$PbCl^+$(sw)	$PbCl^+$(sw)		
			$PbSO_4^0$(sw)			

Note: sw = seawater, pH ~ 8, Coordinated water molecules are not included in the formula.
Data source: Vanloon, GW, Duffy, SJ. Environmental Chemistry: A Global Perspective: Oxford University Press, Inc.; 2000. Table 1.4 p. 266

Stability constant of dissolved lead species and their thermodynamic data is shown in Table 1.5. Speciation of Pb(II) under freshwater conditions calculated by Stumm and Morgan [31] is shown in Figure 1.3.

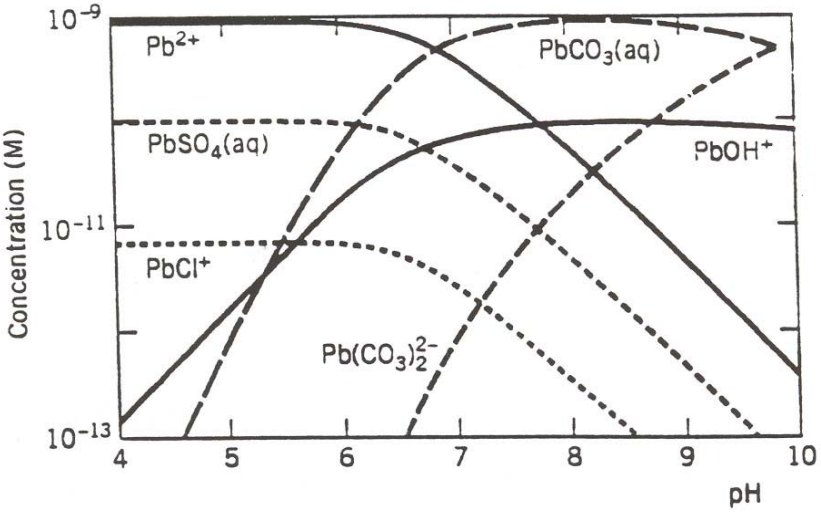


Figure 1.3 Speciation of Pb(II) (10^{-9} M) under freshwater conditions ($C_T = 2 \times 10^{-3}$ M). (Points are calculated.) For species and equilibrium constants see Appendix 1.3 [31] (From Stumm, W, Morgan, JJ. Aquatic Chemistry, 3rd edition: Copyright © 1996 by J. Wiley & Sons, Inc; Figure 6.15 p. 296, (This material is used by permission of J. Wiley & Sons, Inc).

Fate and Transport of Lead

Lead like other trace metals can be transported into different environmental compartments. The cycling of the trace metals involves a common set of biogeochemical processes, which are illustrated schematically in Figure 1.4.

Processes that remove metals to solid phases are particularly important in mitigating the effects of contaminant metals introduced into aquatic ecosystems.[33] For example, the amount of lead leached from a soil sample, spiked with 1.840 mg/kg of water-soluble lead, decreased with increasing amounts of peat loading.[11]

Table 1.5 Stability constant of dissolved lead species and their thermodynamic data.

Species	Stability constant (log K)	ΔG^0_f kJ	(kcal)	References
Pb^{2+}		-24.4	(-5.8)	Generally accepted
$PbOH^+$	7.83	-226.4	(-54.1)	(a)
$Pb(OH)_2^0$	10.8	-400.8	(-95.8)	(a and d)
$Pb(OH)_3^-$	13.9	-575.7	(-137.6)	(a and d)
$Pb_3(OH)_4^{2+}$	32.7	-888.7	(-212.4)	(b and c)
$Pb_4(OH)_4^{4+}$	36.7	-936.4	(-223.8)	(b and c)
$Pb_6(OH)_8^{4+}$	69.4	-1802.5	(-430.8)	(b and c)
Pb^{4+}	pE^0 28.6	-302.5	(-72.3)	(a)
PbF^+	2.0			(d)
PbF_2^0	3.4			(d)
$PbCl^+$	1.6	-164.8	(-39.4)	(a and d)
$PbCl_2^0$	1.8	-297.1	(-71.0)	(a and d)
$PbCl_3^-$	1.7	-408.4	(-97.6)	(a and d)
$PbCl_4^{2-}$	1.4	-557.3	(-133.2)	(a and d)
$PbClO_3^+$	-0.32	-25.9	(-6.2)	(a)
$Pb(ClO_3)_2^0$	-0.61	-27.6	(-6.6)	(a)
$PbBr^+$	1.8			(a and d)
$PbBr_2^0$	2.6			(d)
$PbBr_3^-$	3.0			(d)
PbI^+	2.0	-64.4	(-15.4)	(a)
PbI_2	3.15	-109.2	(-26.1)	(a)
PbI_3^-	3.92	-132.2	(-31.6)	(a)
PbI_4^{2-}	4.47	-204.6	(-48.9)	(a)
$PbSO_4^0$	2.8	-784.5	(-187.5)	(a and d)
$Pb(NO_3)^+$	1.07	-141.8	(-33.9)	(a)
$Pb(P_2O_7)^{2-}$	11.2	-2007.5	(-479.8)	(a)
$PbHPO_4^0$	15.5			(d)
$Pb(HPO_4)_2^{2-}$	2.37	-2216.3	(-529.7)	(a)
$PbH_2PO_4^+$	21.1			(d)
$PbCO_3^0$	6.4	-588.7	(-140.7)	(a)
$Pb(CO_3)_2^{2-}$	9.8	-1136.0	(-271.5)	(a)
$PbCSN^+$	0.89	63.2	(15.1)	(a)
$Pb(CSN)_2^0$	1.15	154.4	(36.9)	(a)

(a) Summarized by Nriagu,1978[1]

(b) Olin, 1960[34]

(c) Olin, 1960[20]

(d) Summarized by Morel and Janet, 1993[35]

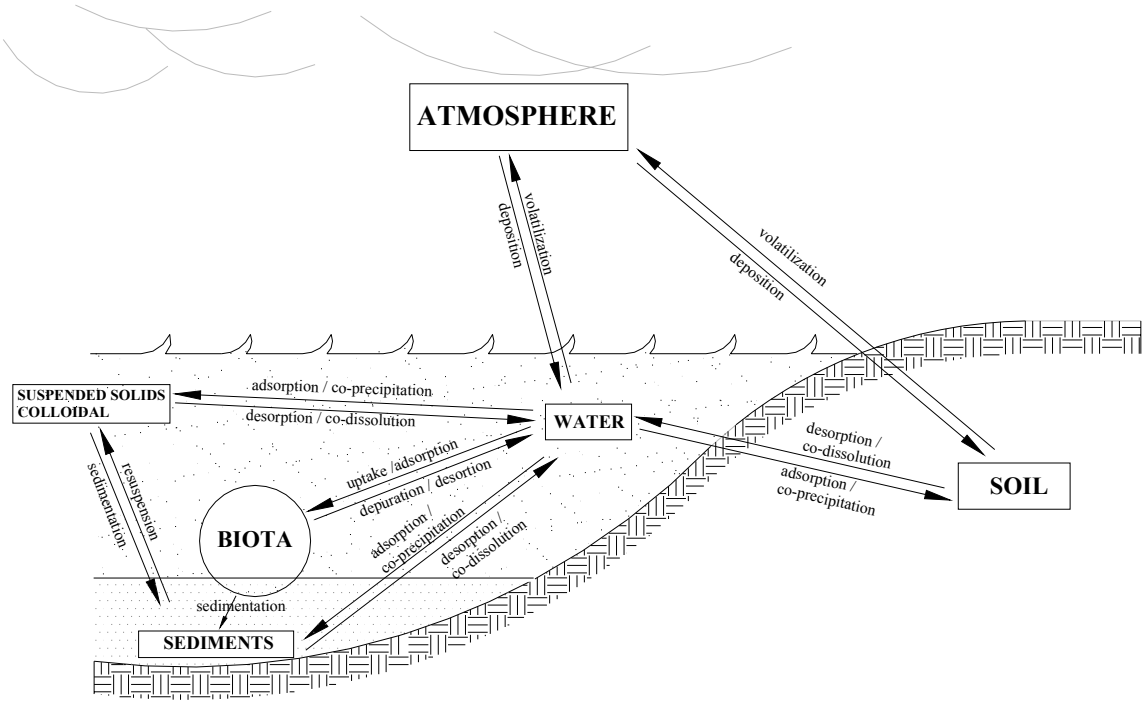
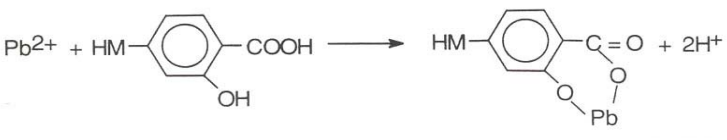


Figure 1.4 Schematic diagram of processes controlling the biogeochemical cycling of metals in aquatic environment

Lead sorbs on surface soils or suspended solids that are rich with organic matter such as humic material.[32] An example of lead binding with a functional group of organic materials given by Vanloon and Kraemer[32] is in the reaction below:



(1.3)

Because the tendency for formation of complexes with ligands other than water is generally in the order type B metals > borderline metals > type A metals as described in

the previous section, Pb(II)— a type B metal has large stability constants. Complexation in these cases involves covalent bonding and bidentate chelates are likely important.[32] Other examples of humic material functional groups are shown in Figure 1.5.

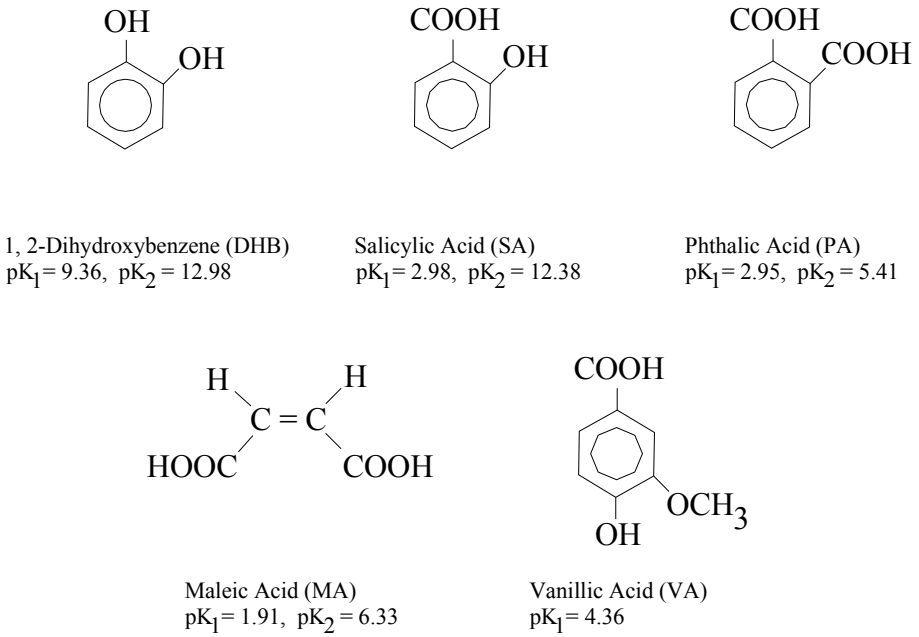


Figure 1.5 Examples of humic material functional groups available from complexation reaction.[32,35,60]

Nevertheless, toxic organic compounds can be broken down into nontoxic constituents; barring transmutation, the potential toxicity of metals can never be completely eliminated.[33] The partitioning of metals between dissolved and sorbed on solid phases critically influences metal transport, reactivity, and bioavailability. It is widely recognized, however, that metal bioavailability and toxicity are not determined merely by the total, dissolved metal concentrations. The distribution of the metal among various inorganic and organic metal species governs bioavailability, which is related to

the free metal concentration or activity. In different locations, the predominance of specific process will vary. For instance, in comparison of lead adsorbed on six soils, lead was found mostly in exchangeable and oxide bound fractions. The study showed that the heavy metal adsorption and speciation reaction did not reach equilibrium within a day in soils dominated by layer-silicates and poorly crystalline oxide minerals. The 'equilibrium' adsorption data from conventional adsorption experiments should be, therefore, of limited value in predicting the fate of heavy metals incorporated into soils having such clay mineral composition. The experimental result also showed that the heavy metal retaining capacity of soils could not simply be related to the total iron oxide content of soils.[13]

Lead is commonly regarded as being geochemically immobile.[1] It may be derived from natural or anthropogenic sources. The low concentration of lead in surface waters is evidence that lead is not readily solubilized during chemical weathering.[1,31] The sorption equilibrium for lead is approached quite rapidly. Organic matter was determined to be the primary immobilization agent for ionic lead. Fixation by interaction with clay minerals or by surface adsorption processes appeared to be of less consequence.[13,23]

Sorption of Lead on Soil and Organic Matters

Sorption to soils and sediments is of great importance to the health and well being of humans because sorption is a primary line of defense between disposal sites and pathways to man. Intentional of inadvertent anthropogenic inputs of metals to environment increase the concentration of metals in surface soils and waters. The sorption of these metals by soils and sediments is the most important and immediate

means whereby their concentrations in waters are reduced before contact and uptake by fish and other aquatic food sources. Sorption also reduces the concentration of these metals before they reach municipal water supplies and groundwater and before contact with livestock or agricultural products via irrigation water.

Because there are many factors that control sorption of metals on soils, such as pH, redox potential, organic matters, and types of binding surfaces,[11-19,36] sorption on soils and sediments may vary from location to location, and from one condition to another condition. Virtually, no predictive capability currently exists to anticipate the adsorption of metals from soil solutions and natural waters without incurring large uncertainties. Most of them come from lack of interpretative ability and capability to predict adsorption quantitatively stems from an inadequate basic understanding of the factors affecting sorption, particularly the nature of principal sorbing substrates, specific sorption sites, and the mechanisms of sorption. Thus, recent interest in this area is encouraging, and a review of the factors affecting metal sorption is timely.[37]

"Lead that exists in soils in an ion exchangeable form or is bound to carbonates is potentially more hazardous than lead which is bound to iron and manganese oxides or to organic matter."[15] (p.5152) The amount of lead leached from a soil sample, spiked with 1.840 mg/kg of water-soluble lead, decreased with increasing amounts of peat loading.[11] Good correlation between the solubilities of lead and dissolved organic carbon in contaminated Boreal Forest Soil showed that organic colloids/particles were of great importance in transporting lead from surface soil to mineral soil. Released lead from surface layer is reimmobilized in mineral soil mainly through the adsorption of ionic Pb^{2+}

or organic lead colloids. Increasing liming (increasing pH) does not always decrease the solubility and bioavailability of lead if it enhances the higher formation of dissolved organic lead complexes.[15] Sorption isotherms of lead in weathered porous material indicated that at any given pH, lead adsorbed more strongly in the surface soil compared to the subsurface soil material.[16] Batch experiments indicated that lead sorption was more affected by soil organic matter and hydroxy-interlayered vermiculite present in surface soil than by iron oxides present in subsurface soil material.[16]

Since the organic materials such as humic and fulvic acids have many functional groups, determining their stability complexation constants with metals are difficult especially when the competitive effects among cations, including protons, and the influence of ionic strength need to take into account. Thus, it usually results in a relatively broad distribution of complex stability constants, K.[38-42] The logarithmic (log) K of lead-humic complexation by Susetyo, et al. published in 1991 using fluorescence titrations was 5.2 and the value was used in the MINTEQA2 version 4.02, a computer software of USEPA, in calculation lead Gaussian distribution. [40,43] Christensen, et al. published in 1999 cited that the model and its default database gave the best estimates of Cu and Pb complexation for both leachate-polluted ground water samples.[42] Another study using an ion-selective electrode found the approximate log K of lead with Suwanee humic acid equal to 4.92 ± 0.36. The log K of Pb-Fulvic acid (FA) by Weber and Saar when the Pb:FA equal to 1:1 at the 2×10^{-4} M FA was 4.69.[38] They also found that Pb^{2+} removal from solution increased when Pb^{2+}-FA began to precipitate, implying mechanisms of Pb^{2+} removal other than complexation.[38]

Lead sorption in clays usually increases with increasing pH, decreasing solid/solution ratio, and decreasing ionic strength. In the study of lead retention in smectite, at the same concentration of lead—2mM, increasing ionic strength from 10 mM to 50 mM decreases lead sorption about half at the pH below the lead hydrolysis point. This indicates that the mechanism of lead sorption in the low pH range was primarily ion exchange.[17] In this study, MINTEQA2 simulation of lead speciation at different pH shows that only aqueous Pb^{2+} and $PbNO_3^+$ exist at pH below 5.2. In the range of pH 5.3 to 5.6, a small percentage of aqueous $PbCO_3$ and $PbHCO_3^+$ are predicted to be present, and at pH above 5.6, aqueous $PbOH^+$ is predicted to be formed.[17]

Adsorption mechanisms of lead on montmorillonite by conducting equilibrium and X-ray absorption structure (XAS) spectroscopy studies indicated that lead could be adsorbing via two mechanisms, depending on ionic strength.[14] At low ionic strength (I=0.006 M) lead adsorption is pH-independent: 97% of the available lead is removed from solution at pH 4.42 and 100% at pH 8.0, respectively. XAS results reveal that at pH 4.48-6.4 the local atomic structure (LAS) surrounding the adsorbed lead is similar to the LAS surrounding aqueous Pb^{2+}, confirming that the adsorption mechanism is outer-sphere complexation. At higher ionic strength (I=0.1 M) lead adsorption is pH-dependent, suggesting inner-sphere complexation as the adsorption mechanism: 43% of the available lead is removed from the solution at pH 4.11 and 98.9% at pH 7.83. XAS results show that the LAS surrounding the adsorbed lead atom is similar to the LAS surrounding reference compounds in which lead is forming covalent bonds ($Pb_4(OH)_4^{4+}$ (aq) and a sample of γ-Al_2O_3 with lead adsorbed via inner-sphere complexation). These similarities

indicate that lead is forming inner-sphere complexes on the montmorillonite at this ionic strength and pH.[14] In studying the competitive sorption of copper and lead on the hematite (at the oxide-water interface), at very low pH, copper and lead were predominantly adsorbed as outer-sphere surface complex ($SO\text{-}Me^{+}$). At slightly acidic to high pH, the inner-sphere surface species of both metals ($SOMe^{+}$) dominated the calculated adsorbed amounts.[36] With increasing site density, ΔpK of the stability constants for protonation reactions increased and metal surface complexes decreased steadily.[36]

In summary, lead adsorbed more on soil that contains higher organic content such as surface soils.[15,16] Sorption of lead is also pH and ionic strength dependent.[14,36] At low ionic strength, outer-sphere complexations seem to control the adsorption of lead and take all of the soluble lead from water, but at higher ionic strength, inner-sphere complexations are dominate and leave the considerable soluble lead at lower pH range.[14,36] Increasing the pH does not always increase the iron-oxide bound complex of lead if it enhances the organic dissolved lead species. In considering the surface oxide site density varied from 2 to 20 sites/nm^2, the experimental data and model calculations exhibit no surface saturation on hematite in the pH range from 3 to 11.[36]

Hydrolysis and Polymeric Species of Lead

Hydrolysis, in inorganic chemistry, refers specifically to introduction of HOH or OH into a molecule or ion resulting in converting to new ionic species or to precipitates—oxides, hydroxides, or basic salts. “In all solution environments, the bare metal ions are in continuous search of a partner. All metal cations in water are hydrated;

that is, they form aquo complexes."[31] (p.258) This is not surprising since most metal atoms form strong bonds to oxygen, and the OH^- ligand is always present in water at concentrations which can be varied over an unusually wide range (>1 to < 10^{-14} *m*). A general formation reaction for a soluble hydrolysis product might be written as

$$XM^{z+} + yOH^- \rightleftharpoons M_x(OH)_y^{(xz-y)+} \qquad (1.4)$$

Because of the number and diversity of the hydroxide complexes which can be formed in solution, the resulting chemical behavior of a given metal in a given valence can be a complicated function of pH and concentration and if the identity and stability of the hydrolysis products are not known. This is because the hydroxide complexes formed are often polynuclear, which means they contain more than one metal ion. This can result in the formation of a far greater variety of species than would be the case if only mononuclear species were formed during the hydrolysis of a cation. The diversity of possible species and the number which can appear more or less simultaneously greatly complicate the problem of identifying them and determining their stability. Even today, hydrolytic polymerization of most metal ions in aquatic systems is still not quite understood. Other limitations include the lack of fast and reliable analytical methods and the precipitation of insoluble hydro-oxo and hydroxy-oxo-metal phases which may not be stable. Because of these difficulties, it is perhaps not surprising that, although cation contamination has been studied for a century, only few occasional cases have mentioned about hydrolysis products.

Hydrolysis reactions usually are catalyzed by acids and bases, but also occur with water more slowly without benefit of catalysts. The general kinetic expression for hydrolysis of many neutral chemicals (RX) in water can be expressed as

$$d[RX\}/dt = k_h[RX] = (k_A[H^+] + k'_N[H_2O] + k_B[OH^-])[RX] \quad (1.5)$$

where k_A, k_B, and k'_N are process rate constant for the acid-, base-catalyzed, and neutral (water) processes, respectively. The concentration of water is usually constant and is always much greater than that of the chemical RX; therefore $k'_N[H_2O]$ is constant, k_N. The pseudo first-order rate constant (K) is the observed rate constant for hydrolysis at a specific pH and temperature

$$K = k_A[H^+] + k_N + k_B[OH^-] \quad (1.6)$$

At constant pH, $[H^+]$ and $[OH^-]$ are constant, and Equation 1.6 may be rewritten as

$$d[RX]/dt = K[RX] \quad (1.7)$$

$$\ln(C_0/C_t) = Kt \quad (1.8)$$

Equation 1.6 shows that hydrolysis reactions are pH dependent. At high or low pH, the first or last term is usually dominant, whereas k_N is often most important near pH 7. From K, the half-life of the hydrolysis reaction is

$$t_{1/2} = \ln 2/K \quad (1.9)$$

In addition to H^+, OH^-, and H_2O, other chemical species in surface waters may act as acids or bases to promote hydrolysis, in the presence of general acid or base Z, the first-order rate expression for loss of chemical has an additional term for Z.

$$K = k_A[H^+] + k_N + k_B[OH^-] + k_z[Z] \quad (1.10)$$

Where k_z and [Z] are the rate constant and concentration for Z. "The most important effect of general acid or base catalysis is found in laboratory experiments that use buffers such as phosphate to control pH. Buffer anions may catalyze hydrolysis, leading to erroneously high values for rate constants." [44] (p.103) To avoid or reduce the problem, low concentrations of buffers—millimolar rage, should be applied. Anionic species in natural waters can cause general base catalysis as well, but these effects are usually minimal. [44]

Because lead exits in aqueous solution almost entirely as Pb (II) species,[1] Pb (II) forms a number of hydroxide complexes. Lead monomeric species are $PbOH^+$, $Pb(OH)_2^0$, and $Pb(OH)_3^-$ and lead polymeric species are Pb_2OH^{3+}, $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$.[1,21,45,46] Their proposed structures of polynuclear lead hydroxy complexes are shown in the Figure 1.6.

Figure 1.6 Proposed structures of polynuclear lead hydroxy complexes[1,21] (From Nriagu, JO. The Biogeochemistry of Lead in the Environment Part A: Elsevier/North-Holland Biomedical Press; 1978. Figure 8.1, p.226, (Used with permission).)

Stability constants of a metal (M) with a ligand (L) can be obtained from the reaction,

$$ML_{n-1} + L = ML_n \quad (1.11)$$

$$K_n = \frac{\{ML\}}{\{(ML_{n-1})\}\{L\}}$$

and stability constants of a metal (M) with a protonated ligand (HL) can be obtained from the reaction,

$$ML_{n-1} + HL = ML_n + H^+ \quad (1.12)$$

$$^*K_n = \frac{\{ML\}\{H^+\}}{\{(ML_{n-1})\}\{HL\}}$$

Cumulative reactions are written as

$$mM + nL = M_mL_n \quad (1.13)$$

$$\beta_{nm} = \frac{\{M_mL_n\}}{\{M\}^m\{L\}^n}$$

For protonated ligands $^*\beta_{nm}$ is used. K_1 and $^*K_1$ values for $PbOH^+$ are shown in Table 1.6.

Table 1.6 K_1 and $^*K_1$ values for $PbOH^+$ [1]

Log K_1	Log $^*K_1$	Comments
7.52	-6.49	Uncertain ionic strength (I)
7.82	-6.18	Corrected to I = 0
6.9	-7.1	In 1 M KNO_3
	-7.9	In 3 M $NaClO_4$
	-7.8	In 0.3 M $NaClO_4$
	-7.93	In 2 M $NaClO_4$
	-8.84	In 2 M $NaClO_4$

*From Nriagu, JO. The Biogeochemistry of Lead in the Environment Part A: Elsevier/North-Holland Biomedical Press; 1978. Table 8.1, p.224, (Used with permission).

Obviously ionic strength and medium interaction have contributed to the disparities. Lead is known to form a variety of simple and mixed nitrate complexes of moderate stability, and thus those measurements made in concentrated nitrate solutions are likely to include these species.[1] Perchlorate solutions are preferred since they generally give no medium interactions.[20,34,45,46] Examples of possible reactions cited by Olin[34] and Olin and Carell[45] in 3 M $NaClO_4$ are;

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \qquad \beta_{1,1} = 10^{-7.9} \qquad (1.14)$$

$$2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+ \qquad \beta_{1,2} = 10^{-6.4} \qquad (1.15)$$

$$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+ \qquad \beta_{4,3} = 10^{-22.87} \qquad (1.16)$$

$$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+ \qquad \beta_{4,4} = 10^{-19.25} \qquad (1.17)$$

$$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+ \qquad \beta_{8,6} = 10^{-42.1} \qquad (1.18)$$

Other hydrolysis constants are summarized by Baes and Mesmer[21] in Table 1.7.

Distribution of hydrolysis product at ionic strength 1 *m* and 25 °C at three different total lead concentrations is shown in Figure 1.7. Distribution of lead hydroxy species in terms of pH and $\{Pb(II)_{tot}\}$ is shown in Figure 1.8.

In Figure 1.8, the overwhelming dominance of $PbOH^+$ at moderate pH values and lead activities is obvious. $Pb(OH)_3^-$ dominates above pH 10.95, and the polynuclear species above log $\{Pb(II)_{tot}\} = -3$. However, in the system that contains carbonates, lead prefers to form complex with carbonates than hydroxides as shown in Figure 1.5 and 1.9. Therefore, lead hydrolytic polymeric species could be found only if the carbonate species in the water are eliminated.

Table 1.7 Stability constants of hydrolysis products[21]

Medium	Temp (° C)	$PbOH^+$	Pb_2OH^{3+}	$Pb_4(OH)_4^{4+}$	$Pb_6(OH)_8^{4+}$	$Pb_3(OH)_4^{2+}$	$Pb(OH)_2$	$Pb(OH)_3^-$	Reference
1.5 *M* $Mg(ClO_4)_2$	25		-6.49	-18.90					(a)
1.5 *M* $Ba(ClO_4)_2$	25		-6.30	-19.16					(a)
3 *M* NaCl	25						-20.33	-32.21	(a)
3 *M* $NaClO_4$	25		-6.30	-19.19					(a)
3 *M* $NaClO_4$	25						-17.5	-29.00	(a)
0.3 *M* $NaClO_4$	25						-17.2	-27.99	(a)
3 *M* $NaClO_4$	25	-7.9		-19.25	-42.14	-22.87			(b)
0.3 *M* $NaClO_4$	25	-7.8		-19.90	-42.66	-23.35			(c)
0.6 *M* $Ba(NO_3)_2$	20	-8.7		-18.75					(a)
0.06 *M* $Ba(NO_3)_2$	20	-8.4		-18.05					(a)
2 *M* $NaClO_4$	25	-7.9		-19.35					(a)
2 *M* $NaNO_3$	25	-8.8	-7.11	-21.72					(a)

(a) Summarized by Baes and Mesmer[21] (b) Olin and Carell[45] (c) Olin[34]

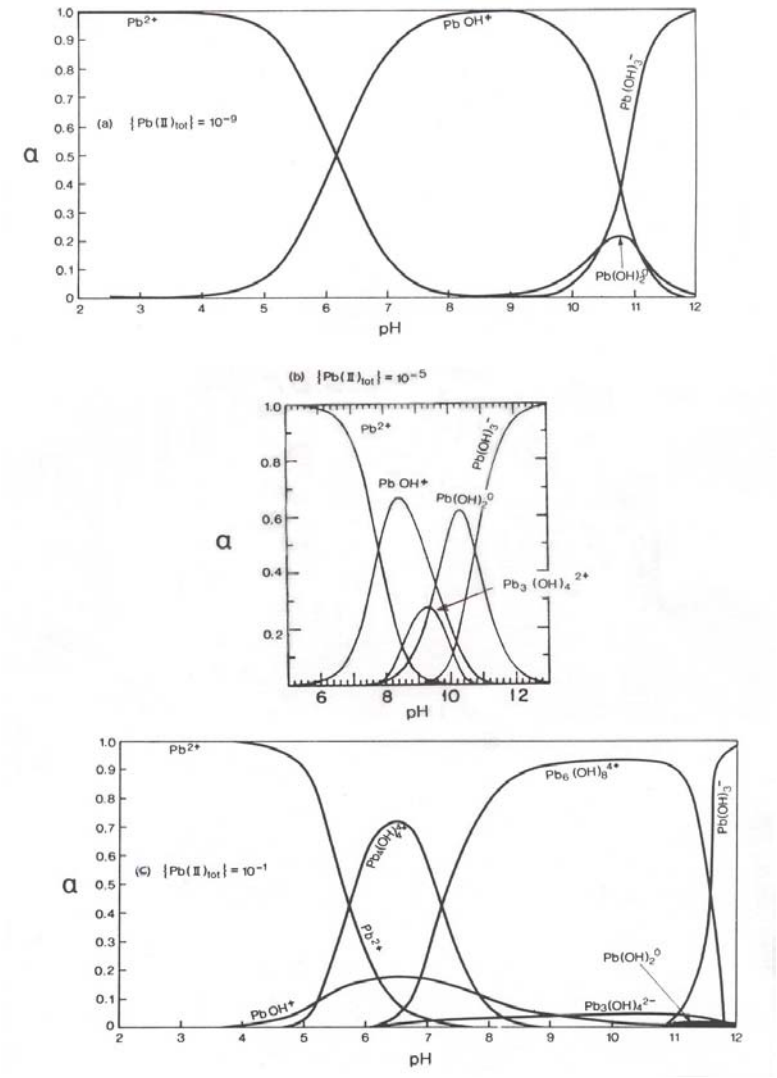


Figure 1.7 Distribution of lead hydroxy species in terms of pH and α (the fraction of total dissolved lead that the species makes up)[1,21] (a) $\{Pb(II)_{tot}\} = 10^{-9}$, (b) 10^{-5}, and (c) 10^{-1} (a and c from Nriagu, JO. The Biogeochemistry of Lead in the Environment Part A: Elsevier/North-Holland Biomedical Press; 1978. Table 8.2, p.227 (Used with permission) and b from Baes, C, Mesmer, R. The Hydrolysis of Cations: Copyright © 1976 by J. Wiley and Sons, Inc. Figure15.9 p. 364. This material is used with permission by J.Wiley and Sons, Inc.

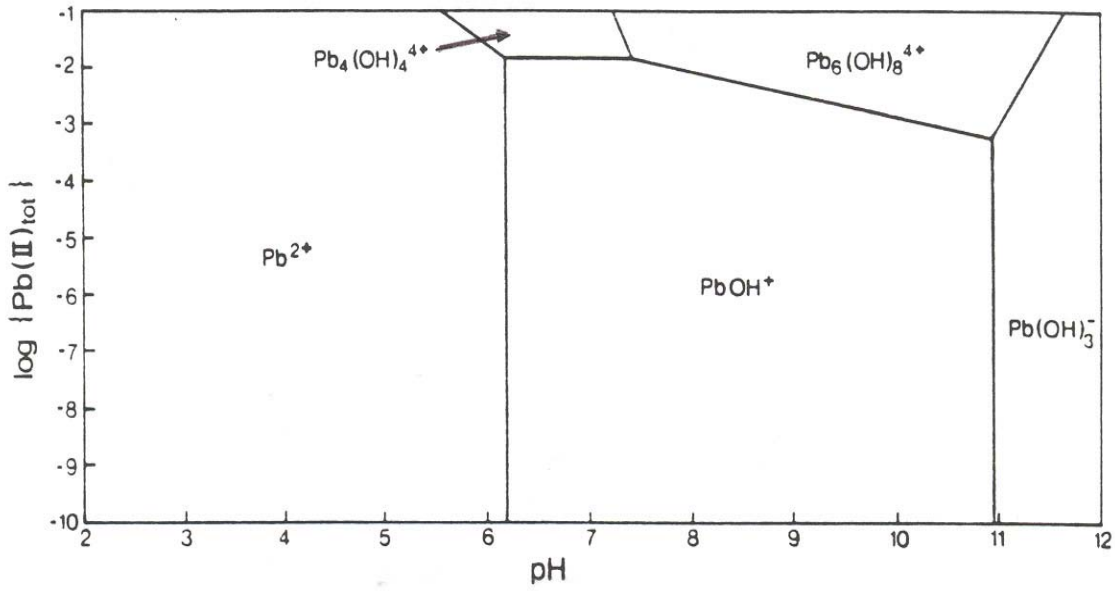


Figure 1.8 Distribution of lead hydroxy species in terms of pH and $\{Pb(II)_{tot}\}$. The lines are equal activity boundaries.[1] (From Nriagu, JO. The Biogeochemistry of Lead in the Environment Part A: Elsevier/North-Holland Biomedical Press; 1978. Table 8.3, p.228, (Used with permission).)

Toxicity of Lead

Lead is toxic to humans and animals when it is ingested especially ionic lead (Pb^{2+}). The body mistakes Pb^{2+} for Ca^{2+}. The Pb^{2+} then attaches to and disrupts enzymes essential to the functioning of the brain and other cells. Because it is an element, the body never decomposes Pb^{2+} into another more easily tolerated substance.[6]

Although adults are susceptible to the toxic effects of lead, children are at higher risk. Most of the lead that is absorbed into a child's brain remains there all his life time. A

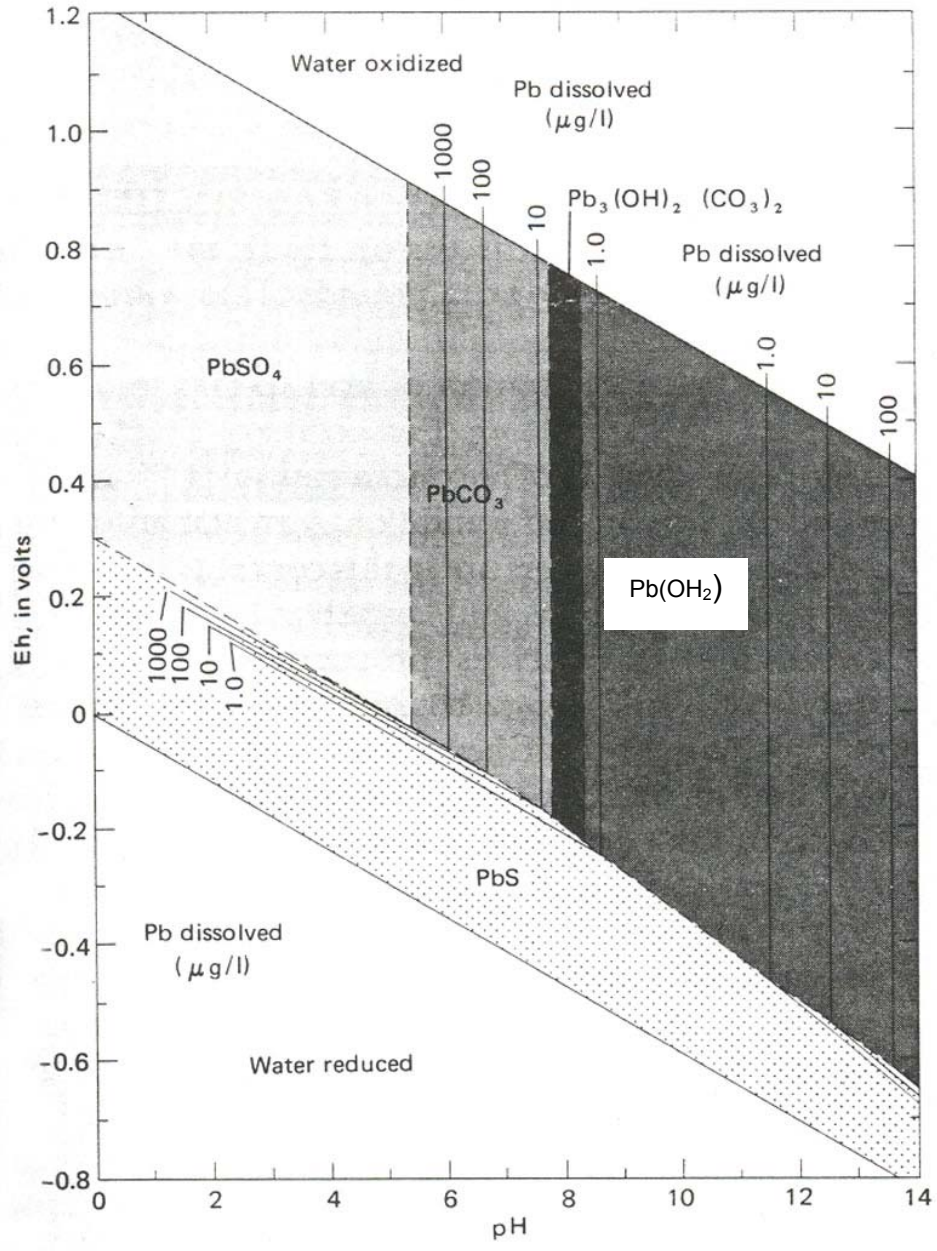


Figure 1.9 Fields of stability for solids and solubility of lead in system Pb + CO_2 + S + H_2O at 25 °C and 1 atm. Pressure, ionic strength (I) 0.005.[47]

(From Hem, JD. Inorganic Chemistry of Lead in Water, Lovering TG. editor, Lead in the Environment: U.S. Government Printing Office; 1976. Figure 1 p. 6)

child's mental and physical development can be irreversibly stunted by lead.[4,6] In the United States, the National Center for Environmental Health estimates that about 4.4% of children aged 1 to 5 have high level of lead in their bodies.[8] Excess lead in the human body can cause serious damage to the brain, kidneys, nervous system and red blood cells. At very high levels of lead exposure, lead poisoning can cause mental retardation, coma, convulsions, and even death. More commonly, children are poisoned through chronic, low-level exposure which can cause reduced IQ and attention span, hyperactivity, impaired growth, reading and learning disabilities, hearing loss, insomnia, and a range of other health, intellectual, and behavioral effects.[4,8]

Lead is also a systemic poison and can induce deleterious effects in living organisms. For example, as an electropositive metal, lead has a high affinity for the sulfhydryl (SH) group. Enzymes that depend on the SH group as the active site are therefore, inhibited by lead. In this case, lead reacts with the SH group on the enzyme molecule to form mercaptide, leading to inactivation of the enzyme.[7] The following reaction depicts such a relationship:

$$2RSH + Pb^{2+} \rightarrow R\text{-}S\text{-}Pb\text{-}S\text{-}R + 2H^{+} \qquad 1.14$$

Examples of the sulfhydryl-dependent enzymes include adenyl cyclase and amino transferases. Adenyl cyclase catalyzes the conversion of ATP to cyclic AMP needed in brain neurotransmission. Aminotransferases are involved in transamination and thus important in amino acid metabolism. Divalent lead (Pb^{2+}) is similar in many aspects to calcium (Ca^{2+}) and may exert a competition action in body processes such as mitochondrial respiration and neurological functions. Lead can interact with nucleic

acids, leading to either decreased to increased protein synthesis. Lead can impair the formation of red blood cells. The mechanism involved in the impairment is that lead inhibits both δ-aminolevulinic acid dehydratase and ferrochelatase. These two key enzymes are involved in heme biosynthesis.[7]

Lead is very toxic. Once lead has been dispersed and redeposited in the environment, it will remain to poison living generations of children unless it is controlled or removed.[3,4,9] Under the new standards of United States Environmental Protection Agency (USEPA), lead is considered a hazard if there are greater than 400 mg/kg of lead in bare soil in children's play areas or 1200 mg/kg average for bare soil in the rest of the yard.[48] The standard for drinking water currently is 15 part per billion (ppb) or μg/L.[10] EPA estimates that more than 40 million U.S. residents use water that contain lead in excess of the standard for drinking water.[10]

Plants exposed to high levels of lead from ambient air and soils can accumulate the metal and manifest toxicity. The toxicity and presence of other trace metals vary greatly among plant species. Based on *in vitro* studies, toxicity sequence have been determined for several species. Lead can decrease cell division at very low concentrations and inhibits the electron transport in corn mitochondria.[7] As summarized by Landis and Yu (published in 1999), Barley plants were shown to be more sensitive to lead than to chromium, cadmium, nickel, or zinc, and exposure to relatively high levels of lead was shown to inhibit seed germination. The effect of lead on germination, however, was found to be less severe compared to several other metals such as cadmium, arsenic, and

mercury. Following plant uptake, lead moves into the food chain and thus can affect animals and humans.[7]

In the aquatic environment, metal bioavailability is influenced by physical, chemical, and biological factors. "Physical factors include temperature, phase association (solid, liquid, or gas), physical adsorption, sequestration by occlusion within a solid phase, or depositional regime as dictated by water movement. Chemical factors include those influencing speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility, and phase transitions such as those associated with precipitation, coprecipitation, or chemical adsorption. Both organic and inorganic species contribute to these phenomena. A myriad of biological factors can also modify bioavailability including trophic interactions, biochemical or physiological adaptation, microhabitat utilization, animal size and age, and particular species characteristics. Physical and chemical factors can also interact with these biological factors. For example, temperature, pH, or Cl^- can modify gill function and, consequently, uptake of dissolved metals." [49] (p.39)

A major class of chemicals that affects bioavailability is the ligand. Ligand influence may be direct, such as sequestering the metal by complexation, or indirect, such as influencing gill function.[49] As mentioned in the section 1.4, class B metals have a particularly high affinity of the binding sites containing N/S donor ligands.[31] Therefore, organisms containing N/S binding sites such as surface and subsurface proteins will be bound.[50] The toxicity of metals on organisms is generally in the order type B metals > borderline metals > type A metals.[31]

"The aquo ion is thought to be the most available species, although other complexes may also be taken up. Consequently, the effect of ligands on metal bioavailability is often deemed a direct result of dissolved ligand competition with binding sites on the gill or gut surface for the free metal ion."[49] (p.44) Ligands possessing O atoms would have high affinities for class A metals and tendencies for ionic bond formation, e.g., carboxyl or phenolic groups, and those possessing N or S, e.g., amino or sulfhydryl groups would have high affinities for class B metals.

From the study of metal bioaccumulation in cultured phytoplankton by Fisher published in 1986), the volume concentration factor (VCF = amount of metal per unit cell volume/amount per unit seawater volume) was measured for phytoplankton exposed to metals ranging from weakly complexed to hydrolysis-dominated.[51] Figure 1.10 shows a clear correlation between these VCF values and the log of the solubility products for the corresponding metal hydroxides. There is a gradual increase in VCF with a plateau occurring for hydrolysis dominated metals. In Figure 2.10a, class B metals show stronger complex than class A metals. Plots of metals that have intermediate tendencies for hydrolysis, i.e., $11 < \log -K_{so}$ MOH < 23 in Figure 1.10d against either Z^2/r of $\Delta\beta$ showed no marked improvement in prediction metal VCF, suggesting that neither characteristic alone dominated the correlation. However, nonparametric analyses of Fisher's data suggest that both were significantly correlated ($\alpha = 0.05$) with the VCF.[49,51]

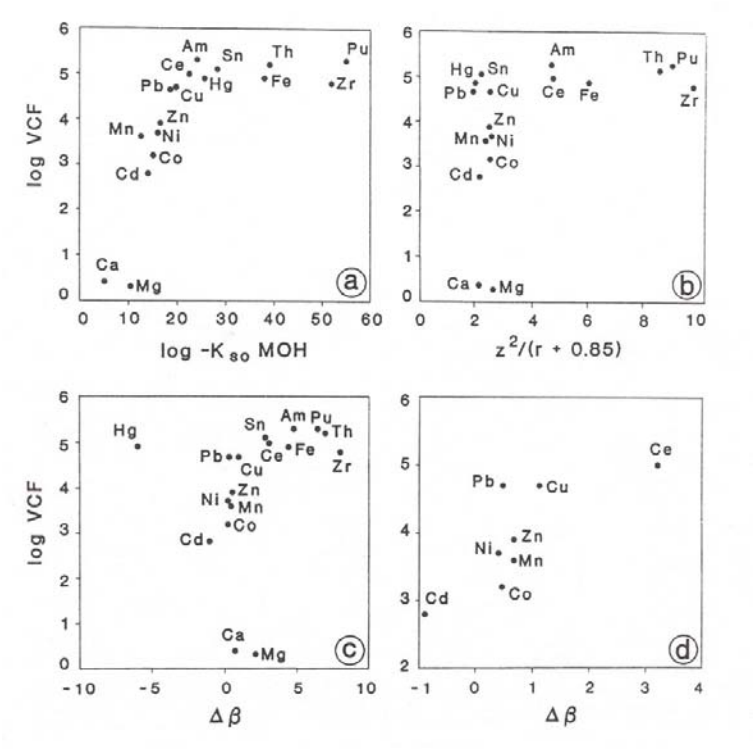


Figure 1.10 Phytoplankton bioaccumulation of metals based on metal-ligand complexation trends. a) relating the volume concentration factor (VCF) to the log of the solubility products for the pertinent metal hydroxides. [51 cited in 49] b) and c) show the less obvious effects of Z^2/r and $\Delta\beta$ on the VCF. For metals intermediate between hydrolysis-dominated and weakly complexed metals ($11 < \log -K_{so}$ MOH <23) (in d)), $\Delta\beta$ has a clear influence, but the $\log\text{-}K_{so}$ MOH still fits best. [49] (From Newman MC, Jagoe CH. Ligands and the Bioavailability of Metals in Aquatic Environments. Hemelink JL, Landrum PF, Bergman HL, Benson WH, editors. Bioavailability: Physical, Chemical, and Biological Interactions: Lewis Publishers & CRC Press Inc.; 1994. p. 45, (Used with permission).)

CHAPTER 2

EXPERIMENTAL SECTION

As shown in the previous chapter, studies on metals transport mobility and bioavailability have been limited by the lack of a comprehensive scheme to evaluate the organically bound metal species and the contribution of metal hydroxy complexes to the overall soluble metal fraction. The overall objective of this research is to develop such scheme utilizing field soil samples, standard sediment and standard Pb solutions.

In this research, two schemes and one computer model were used to study the distribution and behavior of lead species. One involved investigations of distribution and speciation of lead in contaminated soils and sediment samples under different extraction methods by aqueous and organic solvents. The second scheme involved a hydrolytic polymerization and organic complexation experiments using standard lead (Pb) solutions. Figure 2.1 shows the experimental outline. Homogenized soils were extracted with aqueous buffers at three pH levels. The organic extraction scheme involved the extraction of the solid samples with organic solvents of increasing polarity. Major cations, anions, and ligands were analyzed in the target samples.

Soils samples were fully characterized in terms of the major cations, anions, cation exchange capacity (CEC), and total organic carbon content. Table 2.1 shows the methodology and instrument used for measurement of different parameters. For the soil samples, aliquots of samples were subjected to aqueous buffer extraction at three pH

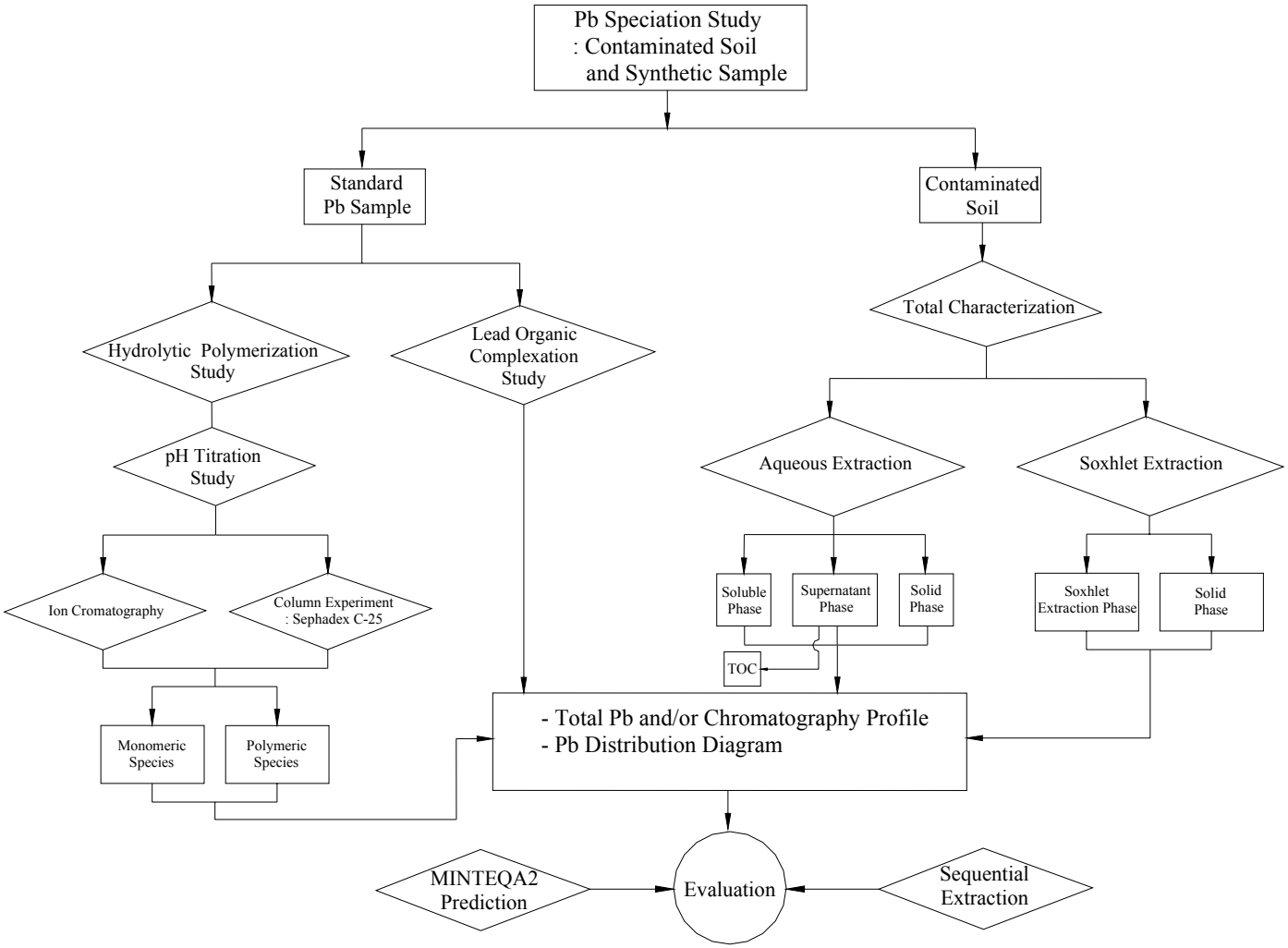


Figure 2.1 Experimental outline

levels and Soxhlet organic solvent extraction using solvents of increasing polarity. Results from both extraction schemes were put in a lead distribution diagram. The diagram was evaluated and compared to results of the MINTEQA2 prediction model (a computer software of United States Environmental Protection Agency (USEPA)), and the conventional sequential extraction scheme.

In the second scheme, the hydrolytic polymerization study involved the use of ion and column chromatography to separate and verify the formation of Pb polymeric species. The organic complexation study involved the complexation with aquatic fulvic acid at three molar ratios.

2.1 Material and Reagents

Field Soil and Sediment Samples

Three types of soil samples were used in this study. Two were from sites near an automotive battery factory and one was a standard river sediment number 1645 purchased from U.S. Department of Commerce National Bureau of Standards, Washington, D.C. 20234. The Dallas soil samples were collected by Stacy Wright, an environmental specialist of the City of Farmer Branch. One of the samples is referred to as reference soil and the second is referred to as contaminated soil. The reference soil was obtained from a non-polluted area nearby as shown in Figure 2.2. The contaminated soil was obtained at the front of GNB Technologies Automotive Battery Factory, 1880 Valley View Lane, Farmers Branch, TX 75234-8905 as shown in Figures 2.2, 2.3, and 2.4. Both samples were surface soil samples collected on April 6, 2000 and were air dried under room temperature. Dried samples were homogenized and filtered by passing through 68 μm

nylon sieve. The homogenized sieved samples were used throughout the experiment. Standard sediment sample was used as received.

Table 2.1 Methodologies and instruments

Parameters or Experiments	Methodologies	Instruments
Soil Characterization		
Cations	Acid Digestion	AAS
Anions	Chromatographic Methods	IC
	Dry Weight/Acid Digestion	
	Ascorbic Colorimetric Method	Spectrophotometer
Cation Exchange Capacity	Compulsive Exchange Method	pH & conductivity meters
Hydrolysis and Polymeric Species		
Cation Exchange Chromatography	Chromatographic Method	IC
	Acid Digestion	AAS
Column Experiment	Acid Digestion	AAS
Aqueous Extraction	Acid Digestion	AAS
	Chromatographic Methods	HPLC
Total Organic Carbon (TOC)	Combustion-Infrared Method	TOCA
Soxhlet or Organic Extraction	Acid Digestion	AAS
	Chromatographic Methods	HPLC
Kudernal-Danish Preconcentration	Acid Digestion	AAS
	Chromatographic Methods	HPLC
Lead-Organic Complexation	Chromatographic Method	HPLC
Sequential Extraction	Series of Chemical Extraction	AAS

Note: AAS = Atomic Absorption Spectrophotometer
IC = Ion Chromatography
TOCA = Total Organic Carbon Analyzer
GC = Gas Chromatography
HPLC = High Performance Liquid Chromatography

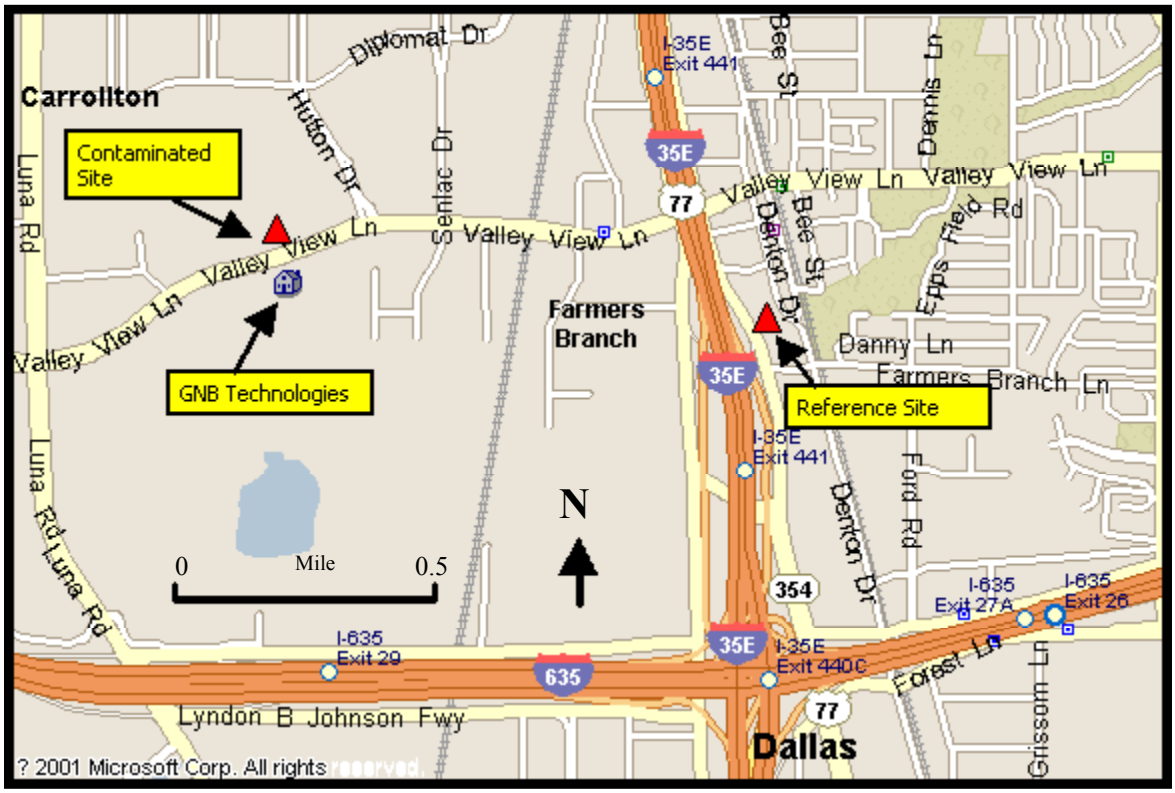


Figure 2.2 Locations of the reference soil obtained from nearby I-35 and the contaminated soil in front of GNB Technologies, a lead acid storage battery factory located at Farmer Branch, Texas 75234-8905

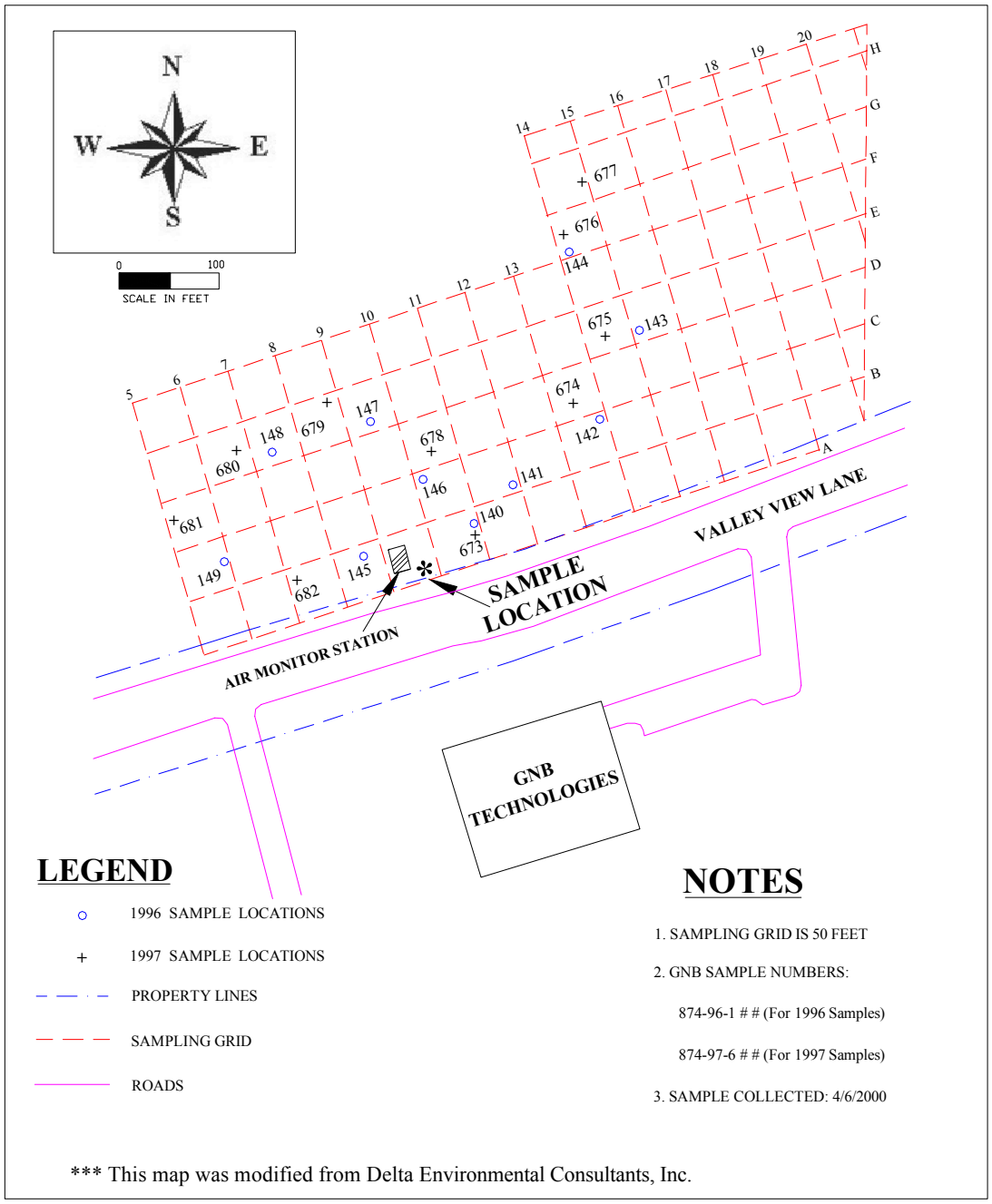


Figure 2.3 Lead contaminated soil sample location collected on April 6, 2000 and other sampling sites in 1996 and 1997. The data of previous study are in Appendix 2.1.

a) Lead contaminated soil sample on April 6, 2000

b) Closer look of contaminated soil sample site on April 6, 2000

Figure 2.4 Lead contaminated soil location in front of GNB Technologies Automotive Battery Factory, 1880 Valley View Lane, Farmers Branch, TX 75234-8905, April 6, 2000. (Photo taken by Stacy Wright)

Reagents

All reagents and chemicals used are listed in Table 2.2. The sources of manufacture and Chemical Abstracts Service (CAS) number are included for each.

Table 2.2 Names of reagents and their CAS number including their company names

Reagents	CAS No.	Company
Cations		
Aluminum standard reference solution		
- solute aluminum chloride	7784-13-6	Fisher Scientific
- dilute hydrochloric acid	7647-01-0	Fisher Scientific
- water	7732-18-5	Fisher Scientific
Iron standard reference solution		
- solute ferric nitrate	7782-61-8	Fisher Scientific
- nitric acid 2%	7697-37-2	Fisher Scientific
- water	7732-18-5	Fisher Scientific
$PbNO_3$	10099-74-8	Sigma
MnO_2	1313-13-9	Fisher Scientific
$CaCO_3$	471-34-1	Fisher Scientific
Magnesium standard powder	No. CAS No.	Mallinckrodt
NaCl	7647-14-5	EM Science
KCl	7447-40-7	Fisher Scientific
CaCl	7647-01-0	J.T. Baker
$La(NO_3)_3 \cdot 6H_2O$	10277-43-7	J.T. Baker
Anions		
Na_2SO_4	7757-82-6	Fisher Scientific
KNO_3	7757-79-1	Baker
CH_3COOH	64-19-7	EM Science
KH_2SO_4	7778-77-0	Fisher Scientific
Phenolphthalein indicator	77-09-8	Eastman

Table 2.2 (Continued)

Reagents	CAS No.	Company
NaOH pellets	1310-73-2	VWR
Percholric acid	7601-90-3	Baker
H_2SO_4	7664-93-9	EM Science
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	12054-85-2	Sigma
$K(SbO)\cdot C_4H_4O_6\cdot 1/2\ H_2O$	28300-74-5	Sigma
Ascorbic acid	50-81-7	Sigma
D-gluconic acid, sodium	527-07-1	Aldrich
Boric acid	10043-35-3	Fisher Scientific
$Na_2B_4O_7\cdot 10\ H_2O$	1303-96-4	Fisher Scientific
Total organic carbon (TOC)		
$C_8H_5KO_4$	877-24-7	Fisher Scientific
H_2PO_4	7664-93-9	Fisher Scientific
Cation exchange capacity (CEC)		
$BaCl_2\cdot 2H_2O$	10326-27-9	EM Science
Ammonium Chloride	12125-02-9	Baker
$MgSO_4\cdot 7H_2O$	10034-99-8	Fisher
Aqueous		
$NaC_2H_3O_2\cdot 3H_2O$	6131-90-4	Fisher Scientific
$Na_2HPO_4\cdot 7H_2O$	7782-85-6	Mathesen Coleman & Bell Manufacturing Chemists
O-Phosphoric acid	7664-38-2	Fisher Scientific
Soxhlet extraction by organic solvents		
Hexane	110-54-3	Fisher Scientific
Acetonitril	75-05-8	Fisher Scientific

Table 2.2 (Continued)

Reagents	CAS No.	Company
Chloride	75-05-2	Fisher Scientific
Methanol	67-56-1	Fisher Scientific
Nitric acid	7697-37-2	Fisher Scientific
Lead nitrate	10099-74-8	Fisher Scientific
Sequential extraction		
$MgCl_2 \cdot 6\ H_2O$	7791-18-6	Fisher Scientific
$NH_2OH \cdot HCl$	5470-11-1	AVOCADO Research Chemicals Ltd.
H_2O_2	7722-84-1	Fisher Scientific
Ammonium acetate	631-61-8	Fisher Scientific
Sodium perchlorate	7601-89-0	Sigma and Aldrich
Perchloric acid	7601-90-3	J.T. Baker
Pyridine	110-86-1	Sigma and Aldrich
Potassium oxalate	6487-48-5	Fisher Scientific
Fulvic acid	No CAS no.	International Humic Substances Society (IHSS)

Stock Lead Solutions

Lead stock solutions were prepared differently depending on the types of experiments. For hydrolytic polymerization study, 1000 mg/L lead was prepared with carbonate free water that was acidified with $HClO_4$ till its pH was less than 2 (~1.87). For the other experiments, lead stock solution was prepared with Milli-Q® water (obtained

from Milli-Q® water purification system, Millipore Corporation) that was acidified with HNO_3 till its pH less than 2.

2.2 Instrumentation

High Performance Liquid Chromatography (HPLC) System

Hewlett Packard (HP) 1090 LC system was equipped with an ultraviolet-visible (UV-Vis) photodiode array (PDA) detector, DR-5 ternary solvent delivery pump, HP 85 B Computer, and HP 7470 plotter. Two columns were used. One was HP ODS Hypersil C18 column, 5 μm, 200 mm length × 2.1 mm i.d. and the other one was Nova-Pak® C18, 3.9 × 300 mm, 60 Å. 4 μm column obtained from Millipore Corporation.

Ion Chromatography (IC) System

HPLC Water 501 solvent delivery system with single pump connected with either Water IC-Pak anion exchange column serial no. T00321A 01, size 4.6 × 150 mm or cation exchange column IonPac CS5A 4 mm P/N 46100 Dionex Chromatography. Millipore Waters conductivity detector model 430 was used and connected with Water 740 Data Module. Both were obtained form Millipore Corporation.

Atomic Absorption Spectrophotometer (AAS) System

1. A Perkin Elmer Model 2380 atomic absorption spectrophotometer was equipped with an Impact Bead nebulizer and either a graphite furnace (GFAAS) or an air/acetylene flam source. All of the data results were shown on a digital screen.

2. Varian SpectrAA-600 with Zeeman background correction was connected with GTA-100 and graphite furnace. A Pentium III 120 mHz was used to control the program and store data. The data then was printed through HP4000 printer.

Total Organic Carbon (TOC) Analyzer with Infrared Detector

Thermo Environmental Instruments Inc., ThermoGlas™ Analytical Instruments 1200 TOC Analyzer.

Electron Microscope

JEOL Technics Ltd instrument, JSTM- 300 Scanning Microscope

Spectrophotometer

Beckman DU-64 Spectrophotometer

pH Meter

Orion Research Digital Ion Analyzer model 501, equipped with an Orion pH Ross electrode model 8103. Calibration of the pH meter was accomplished using analytical reagent grade pH buffers from the Ricca Chemical Co., of Arlington, Texas. Two point calibrations were used throughout the research.

Analytical Balance

Analytical balance XA-200 DS with 5 digits-accuracy was obtained from Fisher Scientific.

Drying Oven

1. A low temperature oven, 103-105 °C was obtained from Lab-Line Instruments, Inc.

2. A high temperature oven, up to 1,200 °C, Type 600 Furnace was obtained from Thermolyne.

2.3 Methods

Characterization of Soil

1. Soil Type

Soil samples were passed through a sieve, pore size 2 mm to separate gravel. Forty grams of soil were analyzed to determine sand, silt, and clay by sedimentation method according to the Methods of Soil Analysis.[52] The ratio of each fraction would designated the type of the soils.[53] [54] Generally clay particle is less than 0.002 mm. Silt particle is less than 0.02 mm, and sand is bigger than 0.02 mm. The analysis was performed by Johnny Byers, a teaching assistant and master candidate student in Applied Geography Department at University of North Texas.

2. Soil Color

Air dried soils were compared with Munsell chart color.[55]

3. Moisture Content

Air dried soils were heated at 103-105 °C for 24 hours and quantified dried weight according to Standard Methods[56] for measuring total solid. The remaining weight represented the total solid and the lost weight was quantified as the moisture content. Three replicates were made and reheated and weighted until weight change was less than 4% of the previous weight.

4. pH

Soil sample of 0.5 g was equilibrated in 10 mL. water till there was no change of pH (approximate 5-6 days).

5. Cation exchange capacity (CEC)

Compulsive exchange method according to Methods of Soil Analysis Part 3 Chemical Methods[57] was applied to all soils. The soils were initially saturated with barium ion (Ba^{2+}) and then brought to an ionic strength similar to that of the original soil solution. The Ba^{2+} was then exchanged by magnesium ion (Mg^{2+}) by addition of $MgSO_4$, which precipitated $BaSO_{4(s)}$. After readjustment of the ionic strength to value comparable to that of the soil solution, the quantity of Mg^{2+} adsorbed (=CEC) was estimated as the loss of Mg^{2+} from the $MgSO_4$ solution added.

6. Volatile and fixed organic carbon

Dried soils from above the method (103-105 °C) were ignited according to Standard Methods[56] to a constant weight at 500 ± 50 °C. The remaining solids represented the fixed total solids while the weight lost on combustion represented the volatile solids.

7. Cations: Aluminum (Al), Calcium (Ca), Iron (Fe), Potasium (P), Lead (Pb), Magnesium (Mg), Manganese (Mn), and Sodium (Na)

All cations were analyzed by the leaching technique which involved heating 1 g soil with 30 mL 10% HNO_3 on a hotplate for 15 minutes. Total Digestion Method according to Standard Method[56] was also applied to the analysis of lead in order to compare the results with the leaching technique. All samples were filtered with 0.45 μm

pore size of Nuclepore polycarbonate membrane filter obtained from Whatman. Filtrates were analyzed by flame AAS and only Al was done by Perkin Elmer GFAAS. Electron microscope technique was also applied to air dried soil to determine mineral content. Analysis was performed by David Garett, an Electron Microscope technician at University of North Texas.

7. Anions: Sulphate (SO_4^{2-}), Nitrate (NO_3^-), Chloride (Cl^-), Bicarbonate (HCO_3^-), Carbonate (CO_3^{2-}), and Phosphate (PO_4^{3-})

Soluble sulphate, nitrate, chloride, and bicarbonate were analyzed by ion chromatography. Soluble anions were leached from soil samples by equilibrating 3 g of soil with 60 mL Milli-Q® water for 5 days before they were injected into IC 501 system. The IC experimental conditions are shown in Table 2.4.

Total phosphate was analyzed by digestion with perchloric and nitric acid according to Methods of Soil Analysis Part 3 Chemical Methods.[58] The digested samples were analyzed for the total amount of phosphate by the ascorbic acid colorimetric method according to Standard Methods with a spectrophotometer.[56]

8. Silicon Dioxide (SiO_2)

Silicon dioxide was defined by measuring dry weight of soil residue after excessive digestion with perchloric and nitric acids till pale yellow sand-like residue was apparent.

<u>Aqueous Extraction: at pH 4, 7, and 9</u>

One gram soil was equilibrated with 100 mL. of each buffer and shaken for 7 days in an Erlenmayer flask closed with parafilm. The slurry was then centrifuged at 3,000

rpm for 40 minutes. The aqueous liquid was divided into two parts. The one that was filtered was called soluble fraction and the other one that was not filtered was called supernatant.

The supernatant of 30 mL total volume was acidified with 3.3 mL HNO_3 and heated for 15 minutes. Then, it was filtered with Nuclepore polycarbonate membrane filter pore size 0.45 μm. The filtrate was analyzed for total lead. The soil residue was divided into two portions. One portion was digested with 30 mL of 10% HNO_3 for 15 minutes and the second was used to measure the moisture content. Moisture content of the soil residue was determined by drying known weight at 103 °C 24 hours, reheated and weighted until weight change was less than 4% of the previous weight.

Digested supernatant and digested residue were analyzed for lead by Flam AAS and the filtrates were analyzed by Varian GFAAS. The Varian conditions are shown in Table 2.5. Only filtered or soluble fraction of pH 4 experiment was analyzed for four major metals namely Mg, Ca, Al, and Fe. Filtered fractions of pH4 and 7 were also analyzed by HPLC using gradient program I as shown in Table 2.3. The supernatants obtained from aqueous extraction at pH 4, 7, and 9 were also analyzed for total organic carbons by injecting 200 μL into TOC analyzer.

Soxhlet Extraction and Kudernal-Danish Experiments

Ten grams of soil were put into a thimble which was inserted into a Soxhlet apparatus as shown in Figure 2.5. The method is based on repeated extraction of the soil sample by condensed organic solvent. Once the level of the solvent in the thimble had reached the siphon valve, it would flow down into the round flask below and be reheated

to condense again. This represented a complete cycle. A series of organic solvents of increasing polarity, which included of hexane, acetonitrile, methylene chloride, and methanol, were applied to the soil sample and extracted for 360 cycles each.

After completing the extraction cycles, all organic solvents were adjusted to 80 mL and divided into two parts. One was stored for further analysis by HPLC according to the experimental conditions in Table 2.3. The experimental conditions were modified from the studies of Saleh and Ong (published in 1989)[59] and Saleh and Liao (published in 1994).[60]

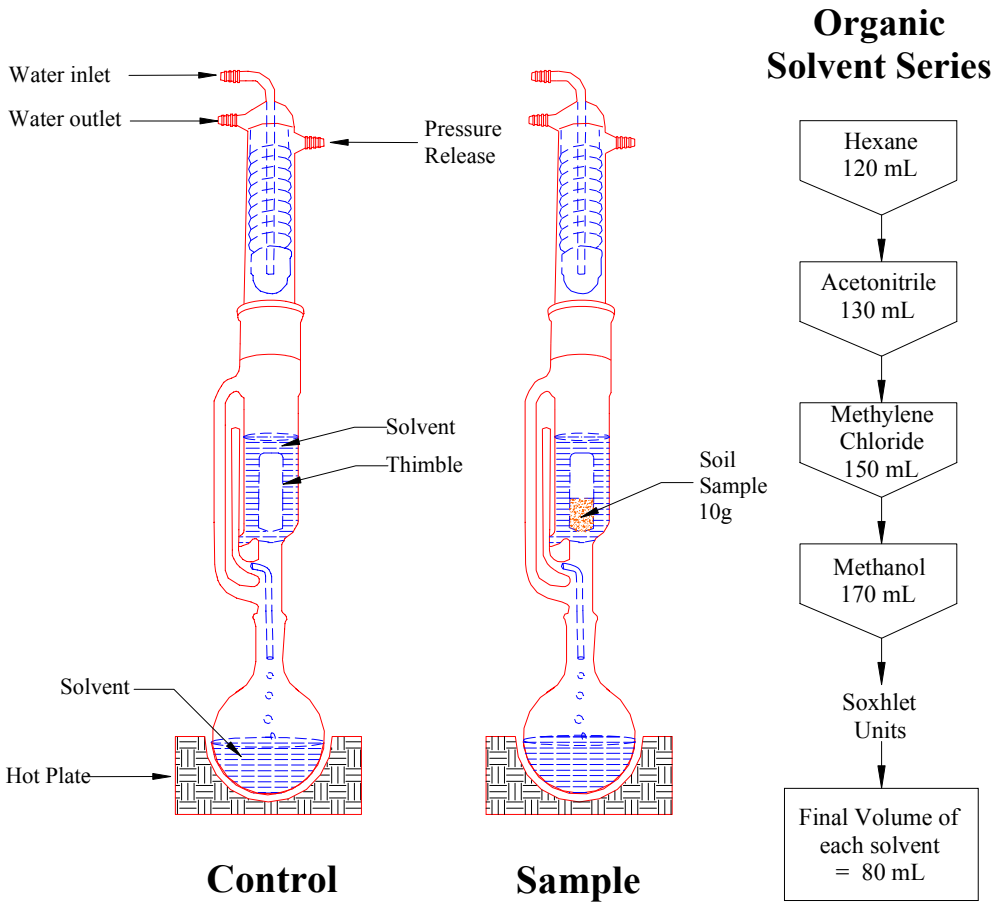


Figure 2.5 Soxhlet apparatus

The other half of solvents was preconcentrated with Kudernal-Danish apparatus as shown in the Figure 2.6. The purpose of this method was to concentrate the volume of extracted organic solvents with minimum loss of organic solvents. The heating temperature was controlled at 100 °C by using water bath. The final volume was brought down to 10 or 15 mL. This fraction was further analyzed by Varian GFAAS. The conditions are in Table 2.5.

Sequential Extraction

A series of sequential extraction was applied to 2 g soil in order to separate lead in different fractions as shown in Figure 2.7. The extraction procedures were basically from Tessier, et al. (published in 1979),[61] but was slightly modified according to Morrow, et al (published in 1996)[62] and Wada, et al. (published in 1999).[13] The following steps were followed.

1. Water exchangeable fraction was extracted from the soil by shaking for 1 hour with 16 mL of 1 M $MgCl_2$. Then, it was centrifuged at 3,500 rpm for 30 mins. The liquid was withdrawn and acidified with HNO_3 to pH lower than 2 and was later analyzed by AAS. The residue was washed with 16 mL Milli-Q® water, centrifuged and transferred to the next step. The washing solution was discarded.

2. Oxide bound fraction was extracted from the residue of step 1 by refluxing for 6 hours at 96±2 °C with 40 mL of 0.04 M $NH_2OH{\bullet}HCl$ in 25 (v/v)% acetic acid. Then, it was centrifuged and washed with Milli-Q® water the same as in step 1.

3. Organically complexed fraction was extracted from the residue from step 2 by adding 10 mL of 30% H_2O_2 and 6 mL of 0.02 M HNO_3 adjusted to pH 2 with HNO_3, and

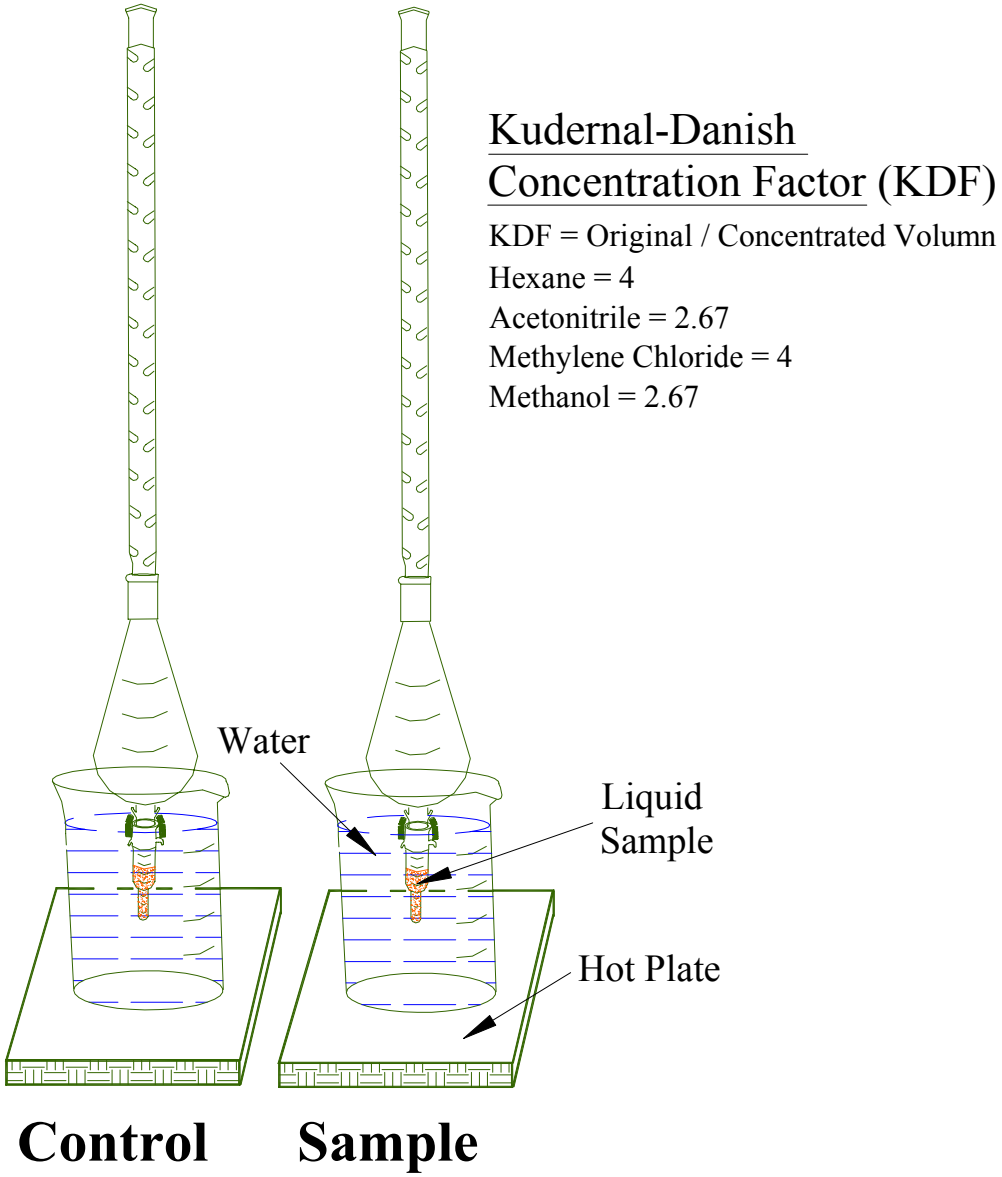


Figure 2.6 Kudernal-Danish apparatus

Sequential Extraction Diagram

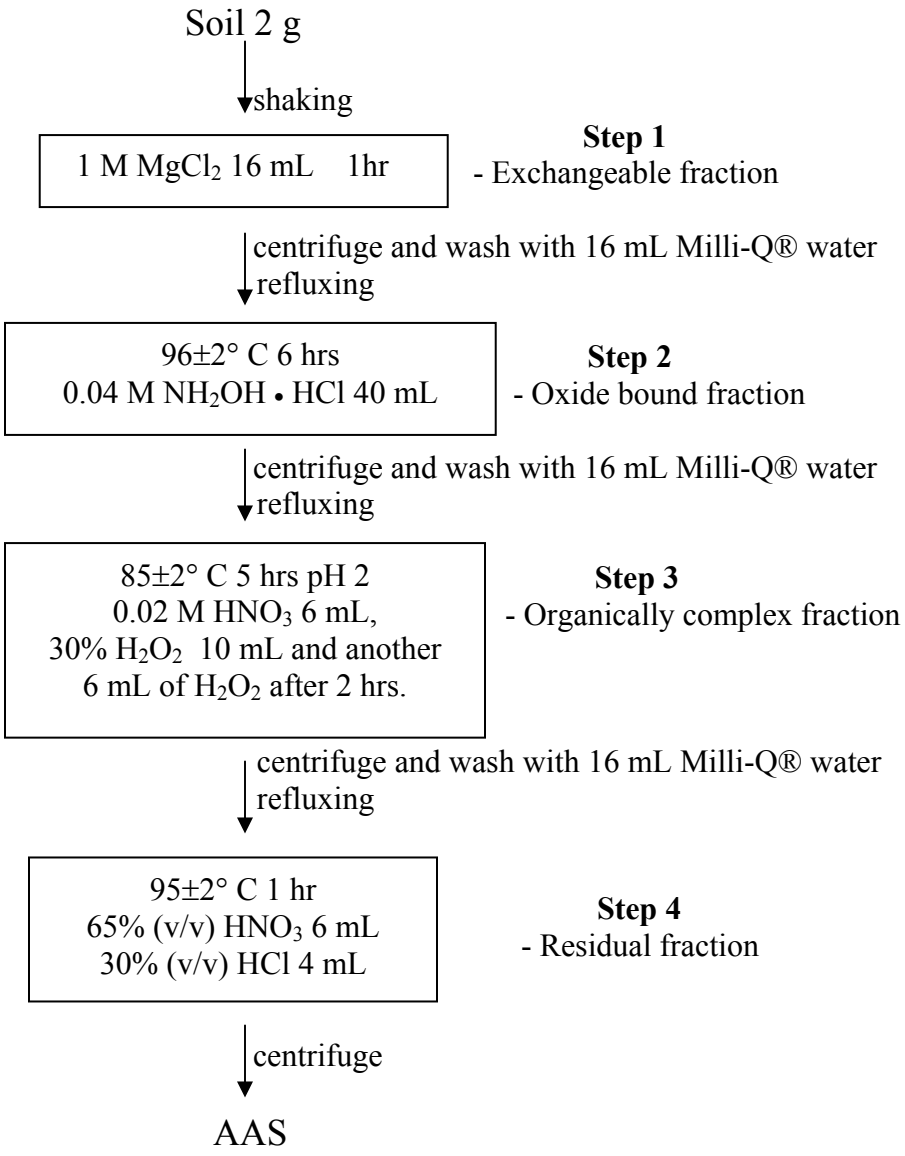


Figure 2.7 Sequential extraction diagram to determine lead speciation from soils

the mixture was heated to 85±2 °C for 2 hours with occasional agitation. A second 3 mL aliquot of 30%H_2O_2 (adjusted to pH 2 with HNO_3) was added and the sample was heated again to 85±2 °C for 3 hours with intermittent agitation. After cooling, 10 mL of 3.2 M Ammonium acetate in 20 (v/v)% HNO_3 were added and the sample was diluted to 30 mL and agitated continuously for 30 minutes. The addition of Ammonium acetate was designed to prevent adsorption of the extracted metals onto the oxidized soil or sediment. Finally, the fraction was centrifuged and washed with Milli-Q® water the same as mentioned in step 1.

4. The Residual fraction was extracted from the residue of step 3 by refluxing at 95±2 °C for 1 hour with 6 mL of 65 (v/v)% HNO_3 and 4 mL of 30 (v/v)% HCl. Then, it was centrifuged and separated the aqueous fraction to further analyze by AAS.

Hydrolytic Polymerization Study

Three methodologies were applied for study of lead hydrolytic polymerization species. All experiments were done under stream of nitrogen to prevent the formation of insoluble $PbCO_3$. The first methodology was a pH titration study. The second and third involved IC and column chromatography (CC). The pH titration study was done by titrating lead to form hydroxide and polymeric species. NaOH was used as a titrant. The titration continued till lead started to form a polymer and eventually precipitate. The results of the pH titration study allowed the proper selection of the pH of the eluents in the IC and CC experiments.

In the ion chromatography experiment, 250 ml of standard lead 10 mg/L was prepared from Pb stock solution. The selected range of pH for polymeric species was 4.7-

7.2 and the pH for monomeric species was 4. Criteria used to select the pHs were based on the literature as shown in Figure 1.7 and my preliminary study of polymeric species. The literature showed that no polymeric species would be formed at pH 4 or less. This pH was selected to compare monomeric lead with polymeric species at pH 5.5 where the preliminary study indicated that polymeric species would be formed. All medium and mobile phase in this experiment were 10 mM $NaClO_4$ adjusted to the desirable pHs with $HClO_4$ or NaOH. All samples were run through HPLC Water 501 using cation exchange column and conductivity detector. IC conditions are shown in Table 2.4.

The Sephadex column chromatography experiment was modified from studies of Cr(III) by Mabamalu.[63] Sephadex C-25 1.3 g was dissolved in 50 mL Milli-Q® water and packed into a column diameter 1 cm as shown in Figure 2.8. The resin was equilibrated with 10 ml 1M $NaClO_4$ and 0.01 M $HClO_4$ (E_1) before an aliquot of 5 mL sample of 5 mg/L lead adjusted pH to 5.2 (E_0) was applied. Then, series of eluents of increasing ionic strength were used. Five eluents were used as shown in Figure 2.8. One milliliter of the next eluent was always used to elute the previous eluent into the container and combined as a previous fraction. Milli-Q® water was applied thereafter before a mixture of strong base of saturated $K_2C_2O_4$ and NaOH was added as a final eluent (E_5). Two moles of $NaClO_4$ and 0.02 M $HClO_4$ (E_2) and 4M $NaClO_4$ and 0.04 M $HClO_4$ (E_3) were analyzed by Flame AAS. E_0, E_1, 6M $NaClO_4$ and 0.06 M $HClO_4$ (E_4), Mlli-Q® water, and E_5 were analyzed by Varian GFAAS. The conditions are shown in Table 2.5.

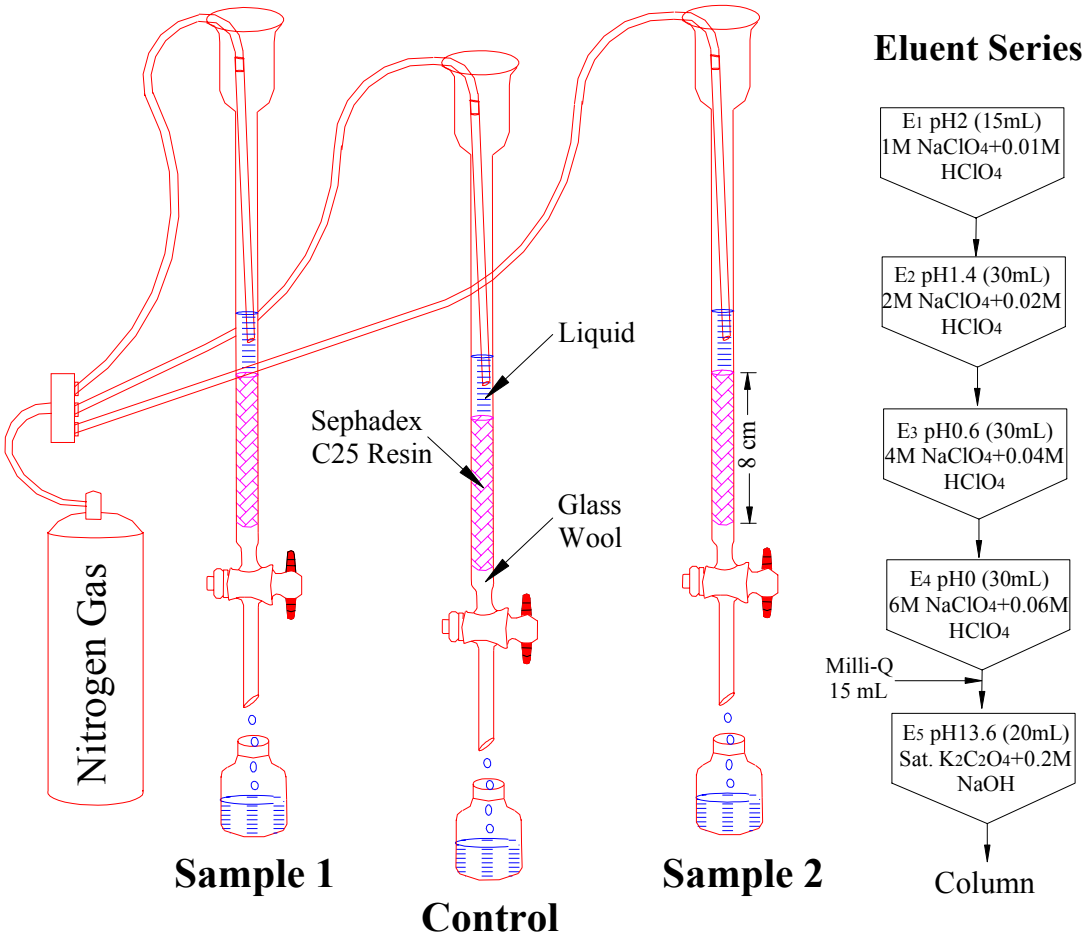


Figure 2.8 Column experiment with Sephadex C25 resin, flow = 1.1-1.2 mL/min

Lead-Organic Complexation Study

The design of this experiment is based on earlier studies by Saleh and Ong (published in 1989)[59] and Saleh and Liao (published in 1994).[60] In this experiment fulvic acid (FA) was mixed with Pb in 0.01 M phosphate buffer. The molar ratios of Pb: FA were 0:0, 0:1, 1:1, 1:2, and 1:3, respectively. The formula weight of FA was considered equal to 1,000 g. One thousand milligrams per liter of FA was prepared by weighting 0.1

g of FA dissolving with Milli-Q® water into 100 mL volumetric flask. Ten milliliters of 1000 mg/L of standard Pb was adjusted with Milli-Q® water to make a standard Pb 200 mg/L in 50 mL volumetric flask. Phosphate buffer concentrate (0.4 M, pH 7) was prepared by dissolving 12.7 g of monopotassium hydrogen phosphate (MW. 136.1) and 32.15 g of di-sodium hydrogen phosphate heptahydrate (MW 268.1) into 500 ml Milli-Q® water. 0.1 M of buffer solution was made by four-fold dilutions of phosphate buffer concentrate (0.4 M, pH 7).

The 0.02%, 200 mg/L, or 2×10^{-4} M FA was prepared by adding 2 mL of 1000 mg/L FA into 10 mL volumetric flask. One milliliter of 0.1 M buffer was added to make the concentration of 0.01 M buffer. Later, 41.4 mg/L or 2×10^{-4} M was added by adding 2.1 mL from 200 mg/L Pb solution. The higher ratios of FA were prepared by adding more FA volumes two and three folds, respectively giving FA concentrations of 4×10^{-4} M and 6×10^{-4} M. The mixtures after adjusting the volumes were set for 3 days in the refrigerator at 10 °C for equilibration. They were allowed to achieve the room temperature and filtered by 0.45 μm nylon filter prior to inject into the HPLC. Selected wavelengths were 254, 260, and 280 nm, respectively. The mobile phase consisted of acetonitrile and Milli-Q® water acidified with acetic acid to pH = 2.9. The gradient elution program II in Table 2.3 was used.

In this study, a preparative experiment involved the collection of several fractions from the HPLC of all the samples. Six fractions representing the entire elution time of 25 minutes were collected. The volumes of each fraction were adjusted to 10 mL before

Table 2.3 HPLC-experimental conditions

Gradient program	Mobile phase	pH at 25 °C	Gradient time	% A	% B	Column type	Samples
I	A: H_2O + 0.01 % AcH	4.0	$t_{0\ min}$	99	1	Hypersil ODS C18, 5 μm,	Soxhlet solvent extractants
	B: CH_3CN		$t_{2\ min}$	70	30	200 mm length × 2.1 mm	of contaminated soil and
			$t_{16\text{-}20\ mins}$	15	85	i.d.; flow = 0.3 mL/min	soluble fractions of pH4 and 7
II	A: H_2O + 0.45 % AcH	2.9	$t_{0\ min}$	80	20	Novapak® C18, 4 μm, 300	Pb-FA complexation
	B: CH_3CN		$t_{2\ min}$	70	30	mm length × 3.9 mm i.d.;	Experiment
			$t_{4\ min}$	50	50	flow = 0.4 mL/min	
			$t_{5\ min}$	40	60		
			$t_{6\ min}$	20	80		
			$t_{7\ min}$	18	82		
			$t_{8\text{-}13\ mins}$	16	84		
			$t_{15\ min}$	15	85		
			$t_{20\text{-}25\ mins}$	99	1		

analyzed by Perkin Elmer GFAAS. Each sample was injected directly into the GFAAS three times each. The GFAAS condition was shown in Table 2.5. The series of standard was made from Pb stock solution 1000 mg/L and adjusted the volume with 1% HNO_3.

Table 2.4 Ion chromatography column characteristics and operating conditions

Ion Chromatography	Anions	Pb
Characteristics		
Type	Waters IC-PAK A HC	IonPac CS5A
Guard column	Waters Guard PAK	IonPac CG5A
Functionality	Polymethacrylate/quaternary ammonium	Sulfonic alkanol quaternary ammonia
Particale size (μm)	10	9
Exchange capacity (μeq/mL)	30 ± 3	20-40
Operating conditions		
Mobile phase	Borate/gluconate	Sodium perchlorate
Flow rate (mL/min)	2.0	1.0
Back pressure (psi)	1100	1100
Sample injection size (μL)	200	1000
Detector sensitivity (μS)	50	500
Integrator parameters		
Attenuation	8	32
Minimum peak area integrated	0.0	0.0
Minimum peak height integrated	4.0	10
Minimum peak width integrated	0.1	0.1
Chart speed (cm/min)	2	1

Table 2.5 GFAAS conditions for Varian and Perkin Elmer atomic absorption spectrophotometers

Experiment	Type of GFAAS	Step	Temp (°C)	Time (seconds)	Flow Conditions (L/min)	Matrix Modification	Standard Preparation	Sample Dilution Factor
Aqueous Extraction	Varian							
Dissolved pH4	Program I	1	85	5	3	Phosphoric acid	In 1% HNO_3	None
		2	95	40	3	5 μL co-injection		
		3	120	10	3			
		4	400	5	3			
		5	400	1	3			
		6	400	2	0			
		7*	2100	1	0			
		8*	2100	2	0			
Dissolved pH7 and 9	Program I					None	In 1% HNO_3	None
Soxhlet Extraction								
Hexane	Program II	1	55	60	3	Same as I	Same as I	None
		2-8	Same as I					
Acetonitrile	Program III	1	65	60	3	Same as I	Same as I	None
		2-8	Same as I					
Methylene Chloride	Program IV	1	35	60	3	Same as I	Same as I	None
		2-8	Same as I					
Methanol	Program V	1	55	60	3	Same as I	Same as I	None
		2-8	Same as I					

Table 2.5 (Continued)

Experiment	Type of GFAAS	Step	Temp (°C)	Time (seconds)	Flow Conditions (L/min)	Matrix Modification	Standard Preparation	Sample Dilution Factor
Hydrolytic	Varian							
Polymerization Study	Program VI	1	85	5	3	5 μl of phosphoric	In 1% HNO_3	E_0 = 12.5
For E_0, E_1, E_4, Milli-		2	95	40	3	acid 1000 μL/L	Quality control was	E_1 = 12.5
Q® water, and E_5		3	120	10	3	co-injection	done by checking	E_4 = 40
		4	500	5	3		with standard	Milli-Q®
		5	500	1	3		addition technique.	water = 40
		6	500	2	0			E_5 = 16.7
		7*	2100	1	0			
		8*	2100	2	0			
				Ramp/Hold				Fraction
Lead-Organic	Perkin	1	130	10/40	0.15	None		I = 6.25
Complexation Study	Elmer	2	500	10/90	0.15			II = 16.7
		3*	2300	2/10	0		In 1% HNO_3	III = 166.7
		4	30	5/10	0.15			IV = 12.5
								V = 6.25
								VI = 2.5

* Atomization step, λ = 283.3 nm

2.4 Computer Model

Lead species were compared with theoretical model, MINTEQA2 version 4.02 which was available from the USEPA.[43] Principally, the model is appropriate for calculation the equilibrium composition of dilute solutions containing trace metals in laboratory or natural aqueous systems. It can be used to calculate the mass distribution among the dissolved, adsorbed, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressure. A comprehensive database is adequate for solving a broad range of problems without need for additional user-supplied equilibrium constants. The thermodynamic database includes 30 organic components and over 500 species. Accessory databases are provided for modeling the adsorption of various metals to an iron-oxide surface and for modeling the complexation or metals with dissolved natural organic matter by using Gaussian distribution model. The primary user-supplied input data for the model are the total dissolved concentrations of system components (e.g., Ca^{2+}, Mg^{2+}, Pb^{2+}, SO_4^{2-}, Cl^-, etc.). The input data into the model in this research was in the form of total concentration. The setting condition always allowed solid to precipitate. The definitions of components and species, and model predictions are in Appendix 3.1.

2.5 Calculation

Hydrolytic Polymerization Study

Rate of the reaction was considered first order reaction. Its kinetic formation constant (K) was calculated from the equation below.

$$C = C_0 e^{-kt} \tag{2.1}$$

C = the concentration of Pb at time t,

C_0 = the concentration of Pb at t = 0

Its half life ($t_{1/2}$) was;

$$t_{1/2} = \frac{0.693}{k} \tag{2.2}$$

Lead-Organic Complexation Study

Conditional stability constant based on ligand complexation constant (K) with i bonding sites was calculated from the equations below.

$$K = \frac{\sum [PbL_{i(bond)}]}{[Pb_{(free)}]\sum [L_{i(free)}]} \tag{2.3}$$

$$K = \frac{Pb_T - [Pb]}{[Pb](L_T - Pb_T + [Pb])} \tag{2.4}$$

L_T = Total stoichiometric concentrations of ligand

Pb_T = Total stoichiometric concentrations of Pb

An average 1:1 metal-to-ligand stoichiometry was assumed for the mixtures of binding sites.

CHAPTER 3

RESULTS AND DISCUSSION

The results of the research are organized into three major sections. The first section presents the results of the field soil and standard sediment experiments. The second section presents the results of the hydrolytic polymerization experiments. The third section presents the results of the lead-organic complexation experiment.

3.1 Field Soil and Standard Sediment Experiments

Soil Geographical Data, Chemical and Physical Characterizations

Soils samples collected from the automotive battery factory that were designated reference and contaminated soils were fully characterized for their chemical and physical properties. The purchased sediment soil was not fully characterized because it had been changed out of its original texture already. So, only some parameters would be discussed for this sediment.

The two sample soils showed their different origins as indicated in a soil survey of Dallas County as shown in Table 3.1.[64] The survey indicated that contaminated site was Silawa fine sandy loam (as shown in Figure 3.2) with brown color which was similar to the color of analyzed contaminated soil as shown in Table 3.2 and Figure 3.3. However, the reference site was a Wilson-Urban land complex with dark grayish brown clay loam. This was different from the reference soil collected for the study which was slightly greenish yellow. The collected contaminated soil also contains a lot of gravel around

Table 3.1 Soil descriptions of sample and reference sites obtained from soil survey of Dallas County, Texas[64]

Site	Soil name	Area	Depth (inches)	Color	Type	Permeability	Landuse	Class
Contaminated Site	Silawa fine sandy loam 1 to 3 percent slopes	10-50 acres	0-10	Brown fine sandy loam	Neutral	Moderate	Pasture and cropland	Sandy loam range site
			10-19	Yellowish red sandy clay loam	Slightly acid			
			19-34	Reddish yellow sandy clay loam	Medium acid			
			34-44	Reddish yellow fine sandy loam	Strongly acid			
			44-80	Reddish yellow loamy fine sand	Medium acid			
Reference Site	Wilson-Urban land complex, 0 to 2 percent slopes 60% Wilson 30% Urban 10% Other	15 to a few hundred acres	0-5	Dark grayish brown clay loam	Middle alkaline	Very slow	Wilson soil has medium potential for urban uses	Was not assigned
			5-42	dark gray clay	Neutral			
			42-56	Very dark gray and olive brown	Neutral			
			56-64	Light to olive brown clay	Moderately alkaline			

Data source: Coffee DR, Hill RH, Ressel DD. Soil Survey of Dallas County, Texas United States Department of Agriculture Soil Conservation Service in Cooperation with Texas Agricultural Experiment Station; 1980. pp. 65-69.

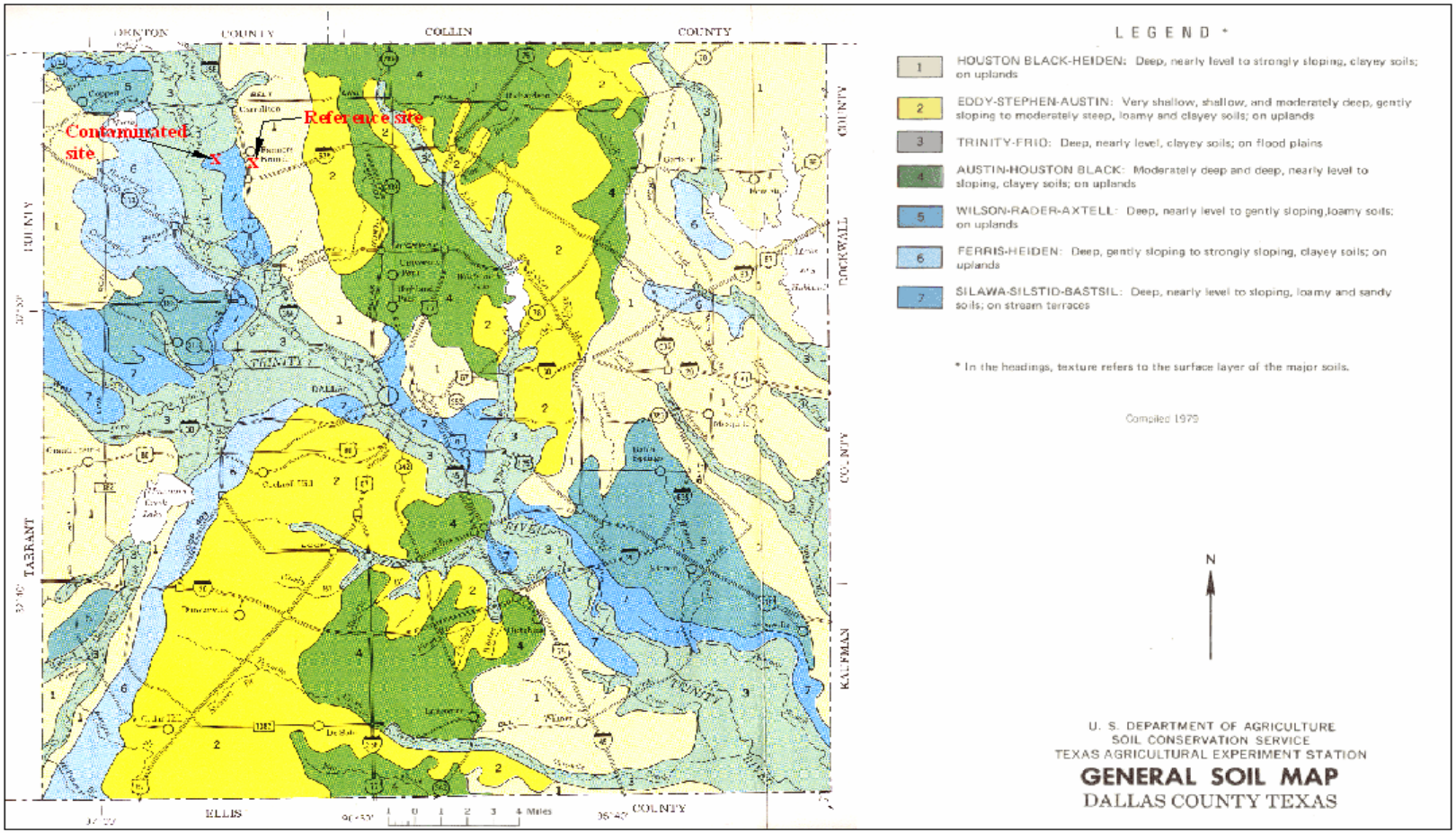


Figure 3.1 Soil map of Dallas County, Texas[64] (*Modified from: Coffee DR, Hill RH, Ressel DD. Soil Survey of Dallas County, Texas United States Department of Agriculture Soil Conservation Service in Cooperation with Texas Agricultural Experiment Station; 1980. p. 154.

Table 3.2 Other physical and chemical properties

Properties	Reference Soil	Contaminated Soil	Standard Sediment
Type of Soil	sandy loam	sandy loam	NM
Gravel (%)*	0.3	15.4	NM
Sand (%)*	60.04	67.96	NM
Silt (%)*	36.26	30.44	NM
Clay (%)*	3.7	1.6	NM
Color (Hue/Value/Chroma)	5Y/4/4	YR10/4/4	NM
Moisture Content (%)± SD	11.38 ± 0.25	5.94 ± 0.76	NM
(CV%)	(2.2%)	(12.8%)	
pH at 22 °C ± SD	7.83±0.01	8.15±0.04	8.15±0.02
(CV%)	(0.1%)	(0.5%)	(0.2%)
Cation Exchange Capacity (m M/kg)**	140	66.2	0
Volatile Solid (%)± SD (CV%)	5.68±0.26 (4.6%)	2.63±0.1 (3.8%)	9.15 ± 0.2 (2.2%)
Fixed Solid (%)± SD (CV%)	94.32±0.26 (0.3%)	97.37±0.1(0.1%)	90.85 ±0.2(0.2%)

* = Single measurement from original soils 300 g, ** single measurement from 30 g soils, SD = Standard deviation, No. of replication (n) = 3, CV = Coefficient of variation, NM = Not measured

15.4% of its weight and the reference soil contains only 0.3%. The ratios of sand, silt, and clay of both soils indicate that they both are sandy loam as shown in Figure 3.2. The slightly difference of the collected soils' properties from the survey data might be because of the weathering and changing of the surface soils from anthropogenic and natural sources.

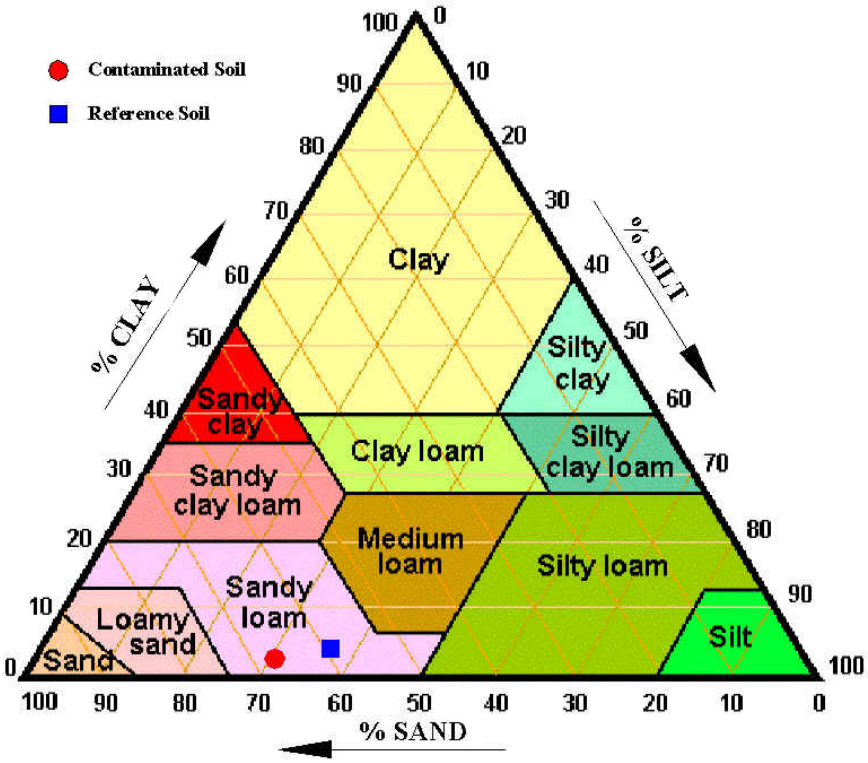


Figure 3.2 Soil diagram

Both subsurface soils and their permeability were also significantly different. Even though the surface soil was neutral at the contaminated site, the soils underneath were more acidic. It implies that the cations leached from the surface soils could penetrate downward to the groundwater faster when it was compared to the reference soil where the subsurface soils were neutral and alkaline. The permeability of contaminated soil was moderate and the reference soil was very slow. This would increase the movement of the metal cations to further distance in the contaminated region than in the reference region.

The reference soil contains more moisture content around 11.38% and the contaminated soil contains 5.94% as illustrated in Table 3.2. The pHs of reference, contaminated soils, and standard sediment after equilibrating in water for 3 days at 22 °C are 7.8, 8.1, and 8.2 and their cation exchange capacities are 140, 66.2, and 0 m M/kg, respectively. Volatile solid (VS) is the highest in standard sediment, 9.15%. In the reference and contaminated soils, VSs are 5.68 and 2.63 %, respectively. On the contrary, fixed solid (FSs) is the highest in contaminated soil, 97.37%. They are 94.32 and 90.58% in reference soil and standard sediment.

Major cations and anions in both soils were analyzed. The results are shown in Tables 3.3, 3.4, and Figure 3.3. The most abundant elements found in the two soils are aluminum, calcium and iron. The order of the concentrations of the three elements in reference soil is Calcium (Ca) > Ion (Fe) > Aluminum (Al) and for the contaminated soil is Fe>Ca>Al. Total lead concentration in the reference, contaminated soil, and standard sediments are 18.5, 100.4, and 618 mg/kg, respectively based on dry weight.

Silicon dioxide (SiO_2) was found to be major component in both soils. They were 7.496×10^5 mg/kg and 7.094×10^5 mg/kg in the reference and contaminated soils, respectively. The other two major anions are carbonate and phosphate. The carbonate was found to be 2.1×10^4 mg/kg and 3.3×10^4 mg/kg, respectively. For the phosphate, it was 2.2×10^3 mg/kg in reference soil and 1.8×10^3 mg/kg in contaminated soil. Other soluble anions are sulphate, nitrate and bicarbonate. There was no soluble chloride present in the water after equilibrated both soils for 3 days.

Table 3.3 Major cations and anions

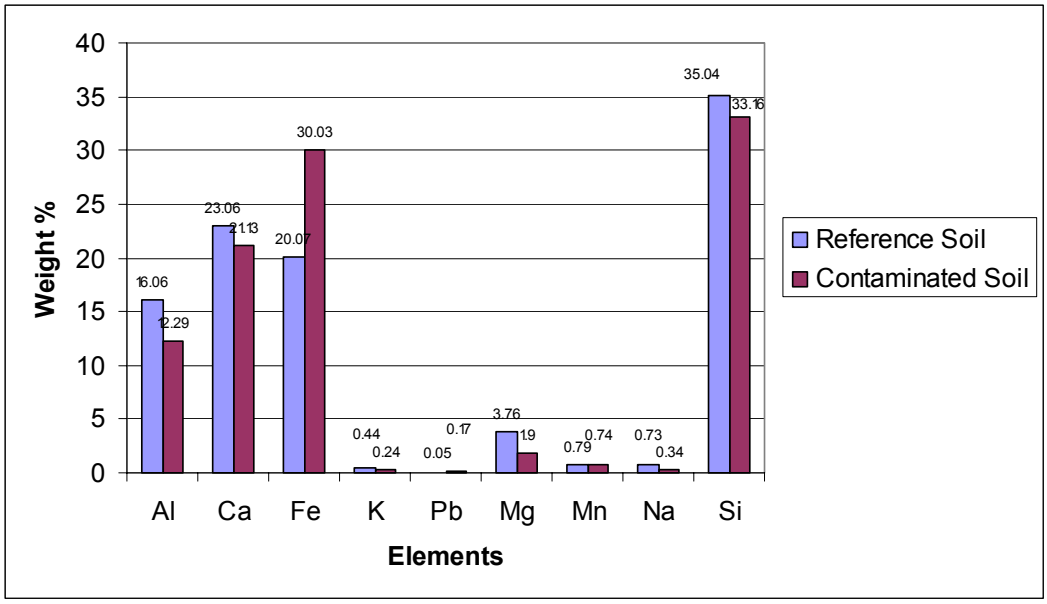
Major Ions	Reference Soil mg/kg (±SD) (CV%)	Contaminated Soil mg/kg (±SD) (CV%)
Major Cations		
Aluminum (Al^{3+})	6,360 ± 120 (1.9%)	7,252 ± 271 (3.7%)
Calcium (Ca^{2+})	9,133 ± 115 (1.3%)	12,466 ± 407 (3.3%)
Iron (Fe^{2+})	7,951 ± 315 (4.0%)	17,713 ± 266 (1.5%)
Potassium (K^{+})	174.5 ± 0 (0%)	144 ± 0 (0%)
Lead (Pb^{2+})	18.5 ± 0.9 (4.9%)	100.4 ± 1.4 (1.4%)
Magnesium (Mg^{2+})	1,490 ± 50 (3.4%)	1,120 ± 39 (3.5%)
Manganese (Mn^{2+})	314.3 ± 4.6 (1.5%)	438.2 ± 5.7 (1.3%)
Sodium (Na^{+})	289.3 ± 65.8 (22.7%)	198.1 ± 24.2 (12.2%)
Major Anions		
Soluble Sulfate (SO_4^{2-})	64.3 ± 3.8 (5.9%)	816.7 ± 5.8 (0.7%)
Soluble Nitrate (NO_3^{-})	0.68 ± 0.038 (5.6%)	0.34 ± 0.007 (2.1%)
Soluble Chloride (Cl^{-})	0 ± 0 (0%)	0 ± 0 (0%)
Soluble Bicarbonate (HCO_3^{-})	2.88 ± 0.3 (10.4%)	2.11 ± 0.1 (4.7%)
Total Carbonate (CO_3^{2-})	20,800 ± 300 (1.4%)	33,000 ± 0 (0%)
Total Phosphate (PO_4^{3-})	2,200.6 ± 43.5 (2.0%)	1,849.8 ± 40.8 (2.2%)
Silicon Dioxide (SiO_2)	7.496×10^5 ± 2,000 (0.3%)	7.094×10^5 ± 1,000 (0.1%)

SD = Standard deviation, No. of replicate (n)= 3 or 4, CV = Coefficient of variation

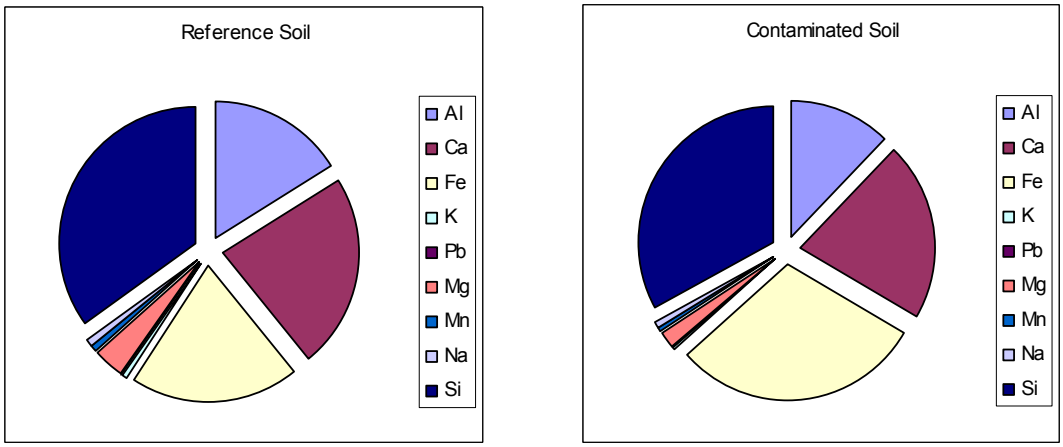
Table 3.4 Percent of major elements in soil samples by total acid digestions

Major Elements	Reference Soil (%)	Contaminated Soil (%)
Aluminum (Al)	16.06	12.29
Calcium (Ca)	23.06	21.13
Iron (Fe)	20.07	30.03
Potassium (K)	0.44	0.24
Lead (Pb)	0.05	0.17
Magnesium (Mg)	3.76	1.9
Manganese (Mn)	0.79	0.74
Sodium (Na)	0.73	0.34
Silicon (Si)	35.04	33.16

The percentages of all measured elements are shown in Table 3.4 and Figure 3.3. Silicon (Si) was found to be the most abundant in the two soils accounting for 35.04% in the reference soil and 33.16% in the contaminated soil. Fe accounted for 20.07% in and 30.03% in both soils, respectively. That explained the more brown color in the contaminated soil than in the reference soil because of the red color of iron oxide. Lead (Pb) was found at 0.17% in the contaminated soil and 0.05% in the reference soil. Other elements that were analyzed included Al, Ca, potassium (K), magnesium (Mg), manganese (Mn) , and sodium (Na). The order of the elements in reference soil was Si>Ca>Fe>Al>Mg>Mn>Na>K>Pb and the order in contaminated soil was Si>Fe>Ca>Al>Mg>Mn>Na>K>Pb.



a) Comparison of major elements in the reference and contaminated soils by total acid digestions



b) Pie chart of major elements in the reference and contaminated soils

Figure 3.3 Comparison of major elements in the reference and contaminated soils by total acid digestions (Al = Aluminum, Ca = Calcium, Fe = Iron, K = Potassium, Pb = Lead, Mg = Magnesium, Mn = Manganese, Na = Sodium, Si = Silicon)

All cations and anions can be presented in terms of millieqivalent per liter (meq/L) as shown in Table 3.5. The order of cations in the reference soil was Al>Ca>Fe>Mg>Na>Mn>K>Pb and the order in the contaminated soil was Al>Fe>Ca>Mg>Mn>Na>K>Pb. The charges made the orders different from the orders of their concentrations. The sum of cations in the reference soil was 1.597 and 2.184 meq/L in contaminated soil. The sum of anions was 0.717 and 1.14 meq/L, respectively. The highest concentrations of anions in both soil was CO_3^{2-}. It attributed more than 96% of the total milliequivalents of anions.

Electron microscope technique was used to roughly estimate the mineral contents of the soils. Most minerals found by this method are similar to those measured by the wet technique. The results are shown in Table 3.6 and Figure 3.4. The order of magnitude for concentrations in the reference soil was Si>Al>Fe>K>Ca>Cu>Titanium (Ti) and for the contaminated soil was Si>Fe>Al>Ca>K>Ti>Sulfur (S). Comparison of the two methods indicates that the major four abundance elements found are Si, Fe, Ca, and Al in both soils.

In summary, both reference and contaminated soils were sandy loam with a slightly different in the compositions. The higher Fe concentration in contaminated soil made the reddish color appearance. It contained more gravels than the reference soil. The lead concentration in the reference soil, coming from natural deposition and non-point source, was a little higher than the average lead in the earth's crust which was 15 mg/kg [1,28]while the concentration in the contaminated soil was 5.4 times higher than in the reference. Furthermore, the contaminated soil had lower CEC than the reference soil.

Table 3.5 Major cations and anions in terms of milliequivalent calculated from data in Table 3.3

Ions	Reference Soil (milliequivalent/L)	Contaminated Soil (milliequivalent/L)
Major Cations		
Al^{3+}	7.07×10^{-1}	8.06×10^{-1}
Ca^{2+}	4.57×10^{-1}	6.23×10^{-1}
Fe^{2+}	2.85×10^{-1}	6.34×10^{-1}
K^{+}	4.46×10^{-3}	3.68×10^{-3}
Pb^{2+}	1.79×10^{-4}	9.7×10^{-4}
Mg^{2+}	1.22×10^{-1}	9.18×10^{-2}
Mn^{2+}	1.14×10^{-2}	1.59×10^{-2}
Na^{+}	1.26×10^{-2}	8.61×10^{-3}
Sum of Cations	1.597	2.184
Major Anions		
SO_4^{2-}	1.34×10^{-3}	1.71×10^{-2}
NO_3^{-}	1.1×10^{-5}	5.48×10^{-6}
Cl^{-}	0	0
HCO_3^{-}	4.72×10^{-5}	3.46×10^{-5}
CO_3^{2-}	6.93×10^{-1}	1.1
PO_4^{3-}	2.26×10^{-2}	1.99×10^{-2}
Sum of Anions	0.717	1.14

Table 3.6 Characterization of soil by Electron Microscopy technique

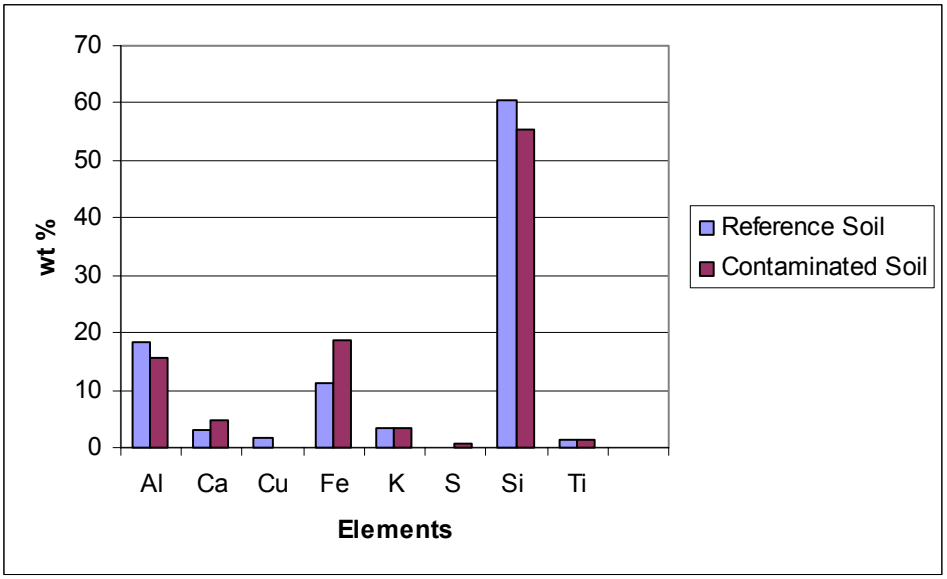
Ions	Reference Soil (%)	Contaminated Soil (%)
Aluminum (Al)	18.45	15.56
Calcium (Ca)	3.19	4.77
Copper (Cu)	1.71	0
Iron (Fe)	11.37	18.77
Potassium (K)	3.47	3.36
Sulfur (S)	0	0.84
Silicon (Si)	60.42	55.36
Titanium (Ti)	1.4	1.35

* Data based on average of two replicates

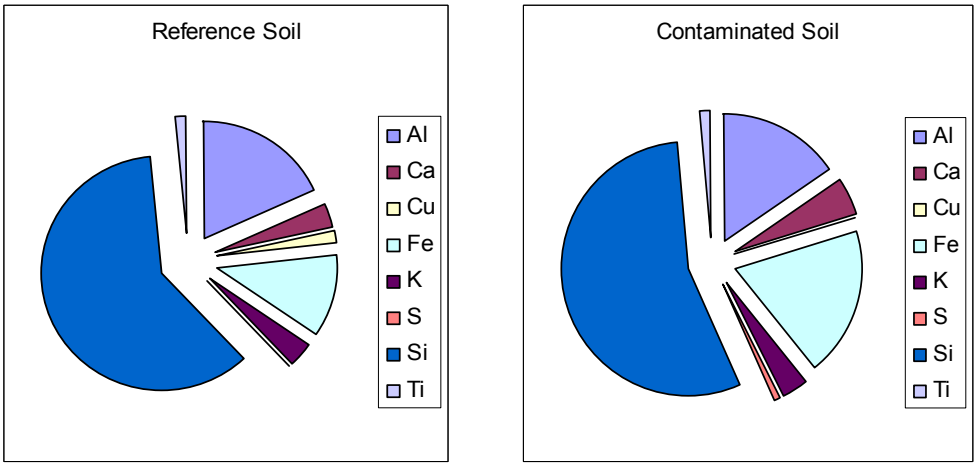
Together with its geographical properties—higher permeability and acidity in the underneath regions, the lead in contaminated soil was expected to be leached and move to further distance than of the reference soil in which it was less permeability, neutral and alkaline in the subsurface areas.

Aqueous Equlibration Experiments at pH 4, 7 and 9

The objectives of these experiments were to evaluate the release of lead and other ions solubilization under environmentally relevant pH conditions. Samples were equilibrated for seven days in a closed system as described on pages 51-52. Samples were analyzed for dissolved, supernatant, and residual lead concentrations. Results are present in Table 3.7. To verify the mass balance results were compared to the total lead content in



a) Comparison of major elements in the reference and contaminated soils by Electron Spectroscopy technique



b) Pie chart of major elements in the reference and contaminated soils

Figure 3.4 Comparison of major elements in the reference and contaminated soils by Electron Spectroscopy technique (Si = Silicon, Al = Aluminum, Fe = Iron, K = Potassium, Ca = Calcium, Cu = Cupper, Ti = Titanium, and S = Sulfur)

Table 3.7 Comparison of released lead at three different pHs: pH 4, 7, and 9

pH	Dissolved (mg/kg) ± SD (CV%)	Supernatant (mg/kg) ± SD (CV%)	Residue (mg/kg) ± SD (CV%)	% Recovery*
pH 4				
Reference Soil**	1.3±0.09 (6.9%)	1.7±0.3 (17.6%)	18.6±2.2 (11.8%)	109.9
Contaminated Soil**	25.2±2.2 (8.7%)	25.8±3.3 (12.8%)	70.1±8.1 (11.6%)	95.5
Standard Sediment	105.1±2.6 (2.5%)	109.1±3.8 (3.5%)	561.1±37 (6.6%)	108.4
pH 7				
Reference Soil	0.06±0.015 (25%)	3.3±0.28 (8.5%)	16.8±0.9 (5.4%)	108.4
Contaminated Soil	0.06±0.04 (66.7%)	7.7±0.29 (3.8%)	94.5±4.3 (4.6%)	101.8
Standard Sediment	ND*	NM	652.7±7.3 (1.1%)	105.8
pH 9				
Reference Soil	ND	1.1±0.18 (16.4%)	23.05±1.5 (6.5%)	130.54
Contaminated Soil	ND	3.7±0.32 (8.6%)	106.47±4.6 (4.3%)	109.7
Standard Sediment	ND*	NM	633.67±5.6 (0.9%)	102.5

*% Recovery = {(Supernatant + Residue)/total lead}100

SD = Standard deviation, No. of replicate (n) = 3; ** n = 4, CV = Coefficient of variation

ND = Lower than detection limit (1 μg/L), ND* = Lower than detection limit (1 mg/L)

NM = Not measured

the original samples.

Only dissolved fraction at pH 4 gave a significant release of lead. This supported the idea of substitution in which abundance H^+ could replace metal ions and resulted in Pb^{2+} release. The amounts of released Pb in the dissolved fractions of reference, contaminated soils, and standard sediment at pH 4 were 1.3, 25.2, and 105.1 mg/kg, respectively. This accounted for 7, 26.4, and 18.7% of their initial Pb contents. The supernatant fractions contained slightly higher of Pb than the dissolved fractions. The percent of Pb in the supernatant fractions were 9.1, 27, and 19.4%, respectively. The results indicate that almost all of Pb in the supernatant fractions is dissolved.

The dissolved fractions at pH7 and 9 of the reference and contaminated soil are very small compared to their supernatant factions. At pH 7, the percentages of dissolved Pb are 0.4 and 0.06% while the supernatant fractions are 19.6 and 8.1%, respectively. At pH 9, the dissolved fractions of both soils are lower than 1 μg/L. However, the percentages of Pb in the supernatant fractions are 4.8 and 3.5%, respectively. This indicates that the higher pH results in the lower release of Pb in both the dissolved and supernatant fractions. Moreover, the higher pH also contributed Pb in the supernatant fraction rather than in the dissolved fraction. This indicates the Pb is associated with colloidal or particulate matters or involved in formation of a bigger species.

MINTEQA2 model (a computer software from United States Environmental Protection Agency (USEPA)) was used to predict the distributions of Pb species in the contaminated soil and the results are shown in the Table 3.8. At pH 4 the model predicts that 30% of Pb would be ionic lead (Pb^{2+}). The model prediction is very close to my

Table 3.8 Lead speciations distribution among dissolved and adsorbed species at three different pHs by MINTEQA2

pH	Species	Fraction Associated (%)
4	Pb^{2+}	30.0
	PbDOM	10.2
	Pb[Acetate]	51.5
	$Pb[Acetate]_2$	7.9
7	Pb^{2+}	3.6
	PbDOM	87.6
	$PbCO_{3\ (aq)}$	4.7
	$PbHCO^{3+}$	3.7
9	PbDOM	4.3
	$PbOH^{+}$	6.8
	$Pb(OH)_{2\ (aq)}$	1.4
	$Pb(CO_3)_2^{2-}$	41.6
	$PbCO_3$ (aq)	45

Note: MINTEQA2's calculations are in Appendices 3.2, DOM = Dissolved Organic Matters

experiment, 27%. Other fractions that MINTEQA2 predicted are PbDOM, Pb[Acetate], and $Pb[Acetate]_2$. These species might not be in the soluble forms as the fractions found in my experiment shown that they were in the residue. The full MINTEQA2 calculations of pH4 are shown in Appendix 3.2.

At pH 7, MINTEQA2 predicts only 3.6% of Pb would be Pb^{2+} while in my aqueous experiment the results shows 7.7% in the supernatant fraction. It should be noted

that the dissolved fraction contributed only to 0.06% which means that most fraction was not ionic lead. MINTEQA2 also indicated that 3.7% would be $PbHCO_3^+$. Both Pb^{2+} and $PbHCO_3^+$ containing ionic charges that might associate with colloid species and that would make a total of 7.3% which is close to the experimental results. The other two fractions that MINTEQA2 predicted are PbDOM and $PbCO_3$ which equaled to 87.6% and 4.7% respectively. These two species are more likely to occur as a residue as they add up to 92.3% which is close to the experimental result of 94.5%. The full MINTEQA2 calculations of pH 7 are shown in Appendix 3.2.

At pH 9 as shown in Table 3.8, MINTEQA2 predicts that all Pb species would be bound and no ionic lead would be present. These support the data from the aqueous experiment where no lead is detected over 1 μg/L in the dissolved fraction. However, the contribution of lead in supernatant around 3.7% might come from some adsorbed species associated with colloidal particles. Nevertheless, the residue still yield 106.47% of lead indicating the majority of the species was bound species the same as calculation by MINTEQA2. The full MINTEQA2 calculations of pH 9 are shown in Appendix 3.2.

The other four majors metals leached in dissolved fractions at pH4 are shown in Table 3.9. Figures 3.5 and 3.6 shows comparison between the concentrations and the solubilized ion at pH 4. For the reference soil, Mg, Al, and Fe are 18.7, 1.4, and 0% of their total concentration, respectively. For the contaminated soil, they are 33.1, 4.4, and 12.2%, respectively. On the contrary, the concentrations of Ca in both soils were increased to be 120% in reference soil and 125% in contaminated soil. This is due to the interaction of the acetate buffer and carbonate in the soil resulting in the release of

Table 3.9 Comparison of other major four metals released (dissolved forms) after equilibrated in pH 4 with their total concentrations.

Type of soils	Calcium (mg/kg) ± SD (CV%)	Magnesium (mg/kg) ± SD (CV%)	Aluminum (mg/kg) ± SD (CV%)	Iron (mg/kg) ± SD (CV%)
Reference Soil				
Total Digestion	9,133.3±115.5	1,490±3.4	6,360±120	7,951±314.6
	(1.3%)	(0.2%)	(1.9%)	(4.0%)
pH 4**	10,950±0	278.1±13	95.6±6.8	ND
	(0%)	(4.7%)	(7.1%)	-
Contaminated Soil				
Total Digestion	12,465.8±12.5	1,119.5±39.1	7,252±271.4	17,713±265.6
	(0.1%)	(3.5%)	(3.7%)	(1.5%)
pH 4**	15,562.5±0	370.3±3.1	320±1.8	2,168.8±32.7
	(0%)	(0.8%)	(0.6%)	(1.5%)
Standard Sediment				
Total Digestion	NM	NM	NM	NM
pH 4	32,583.3±2,796	6,100±151.6	842.7±20.3	5,110±70.6
	(8.6%)	(2.5%)	(2.4%)	(1.4%)

NM = not measured, ND = Lower than detection limit (0.5 mg/L)

SD = Standard deviation, No. of replicate (n) = 3; ** n = 4, CV = Coefficient of variation

calcium ion (Ca^{2+}) in solution.

In summary, at the pH 4 where H^+ is dominant, Pb^{2+} can be leached from the soil as shown in the experimental data and in the calculation by the MINTEQA2. The pH 7 shows lower released amount of Pb^{2+} while the pH 9 is the least. Other four major cations also released at pH 4. Since equilibrating at pH 4 was just leaching ions, other cations were expected to be less than their total concentrations. This was true in the case of Mg,

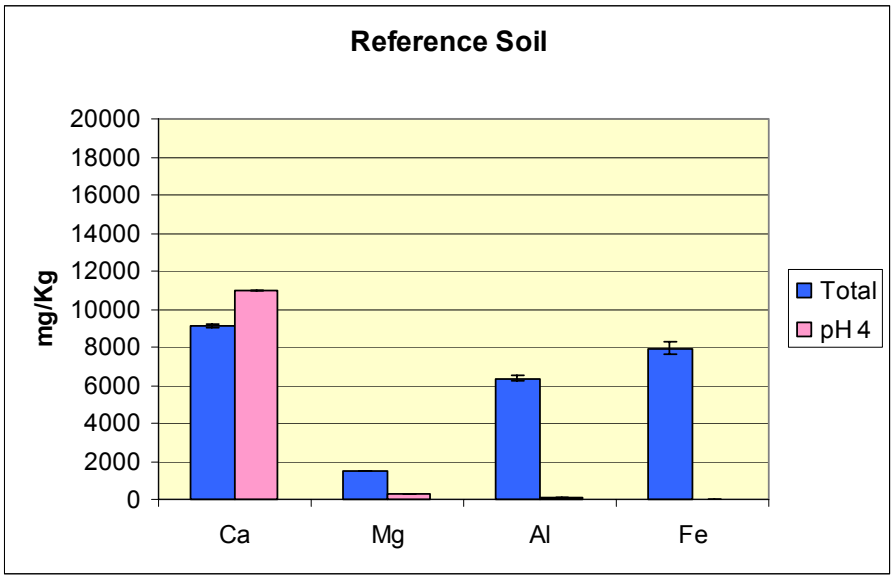


Figure 3.5 The comparison of concentrations of calcium (Ca), magnesium (Mg), aluminum (Al), and Iron (Fe) from the reference soil in dissolved fraction at pH4 and from total digestion with standard deviations

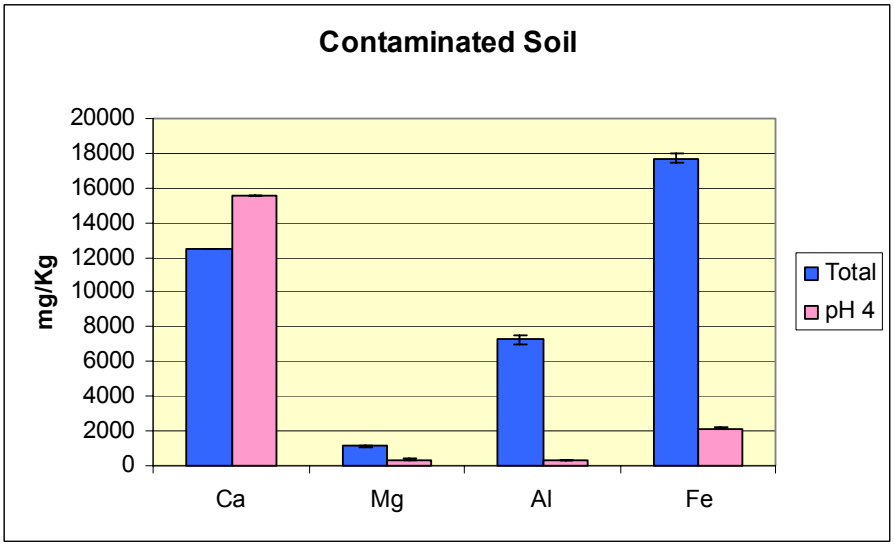


Figure 3.6 The comparison of concentrations of calcium (Ca), magnesium (Mg), aluminum (Al), and Iron (Fe) from the contaminated soil in dissolved fraction at pH4 and from total digestion with standard deviations

Al, and Fe. Calcium concentration was close to its total concentration due to solubilization of $CaCO_3$ at pH 4 caused by acetic acid. The MINTEQA2 version 4.02 seemed to predict lead species quite well among three tested pHs. The equilibrium constants of these species were close to the experiment values. Thus, MINTEQA2 has given good agreement with my experimental results.

MINTEQA2 Input Parameters

In evaluating the validity of MINTEQA2 selection of the proper input parameters is crucial. As seen from the previous discussion, there was good agreement between the experimental results and the model's prediction. However, when the model is applied to environments conditions, it is hard for the users to measure all parameters of the solids and aqueous samples. Using different parameter model's predictions for the contaminated soil and standard sediment were used and were compared to the experimental results as shown in Table 3.10. The table gives an idea for the users to select needed parameters. For the contaminated soil, equilibrated with acetate buffer at pH4, ionic strength 0.407 and DOM 50.6 mg/L was used.

The model was applied with three scenarios. In the first scenario, input parameters included all parameters and Pb_{Total} and precipitation was allowed for all solids. In the second scenario, input parameter included soluble cations including Pb(II) and in the third scenario, only soluble Pb(II) was used. No precipitation was allowed in the second or third scenarios. Results in Table 3.10 shows that first and second scenarios are close and in good agreement with the experimental results.

Table 3.10 Comparison of lead species distributions from different MINTEQA2 inputs with experimental result at pH 4 and ionic strength 0.407

MINTEQA2 Input	Pb^{2+} (%)	PbDOM (%)	Pb[Acetate] (%)	$Pb[Acetate]_2$ (%)
Contaminated soil				
(Same ionic strength, pH, DOM, and buffer)				
Pb_{Total} & All parameters*	30.0	10.2	51.5	7.9
Pb(II) & 4 soluble major cations**	29.9	11.3	51.0	7.8
Pb(II) **	19.2	5.0	43.0	32.8
Experimental result	27	NM	NM	NM
Standard sediment				
(Same Pb(II), 4 soluble major cations, ionic strength,				
pH, and buffer, but vary DOM)				
DOM = 91.5 mg/L** (10% of VS)	30.4	10.5	51.4	7.8
DOM = 176 mg/L** (19.2% of VS)	27.3	19.4	46.2	7.0
DOM = 915 mg/L** (100% of VS)	11.0	67.4	18.7	2.8
Experimental result	17	NM	NM	NM

*Precipitation is allowed for all solids. ** Precipitation is not allowed. NM = not measured.
MINTEQA2's inputs and Pb distributions are in Appendix 3.3.

The standard sediment was not fully characterized as the soil samples. Arbitrary values were used for DOM based on the percentage of volatile solids (VS) as levels of DOM were chosen as 10%, 19.2%, and 100% of the experimental VS. As shown in Table 3.10, Pb^{2+} distribution depends on the amount of DOM as well as the major soluble cations. It is also noted that concentrations of the soluble cations in the standard sediment are much higher than in the soil samples (as shown in Table 3.9). The exercise shows that users should characterize aqueous samples in terms of pH, ionic strength, major soluble

cations and DOM in order to make reasonable prediction of Pb distribution using MINTEQA2.

In summary, the MINTEQA2 model is useful to save the cost of analysis in which many samplings are needed. In this experiment, with the fixed matrix conditions, the needed parameters are the four major soluble cations and the DOM for Pb species prediction. Nevertheless, the laboratory experiment is still needed to obtain the accurate result whether there is any more needed factor when the model is applied form different locations to locations or different conditions to conditions.

HPLC Characterization of pH 4 and 7 Aqueous Extracts

The aqueous extracts were analyzed by reversed phase high performance liquid chromatography (RP-HPLC) from Hewlett Packard as described on page 52 using gradient program I in Table 2.3. Figures 3.7 and 3.8 show chromatograms of the contaminated soil extract at pH 4 and 7, respectively. No significant difference between the control and the sample can be detected. The weak signal may be attributed to the dissolved organic matters in the sample. The MINTEQA2 model in Table 3.7 predicts 10.2% PbDOM. This amount would account for 5 mg/L while the detection limit of this method was 15 mg/L. Furthermore, since any injection that was made into RP-HPLC was filtered through 45 μm filter paper, dissolved organic matter (DOM) that was expected to be found with this method might not be able to pass through the filter. Supernatant fractions were all analyzed for total organic carbon (TOC) as described in page 52. The results are shown in Table 3.11. The data of TOC at pH 4 are questionable due to the interference of acetate buffer.

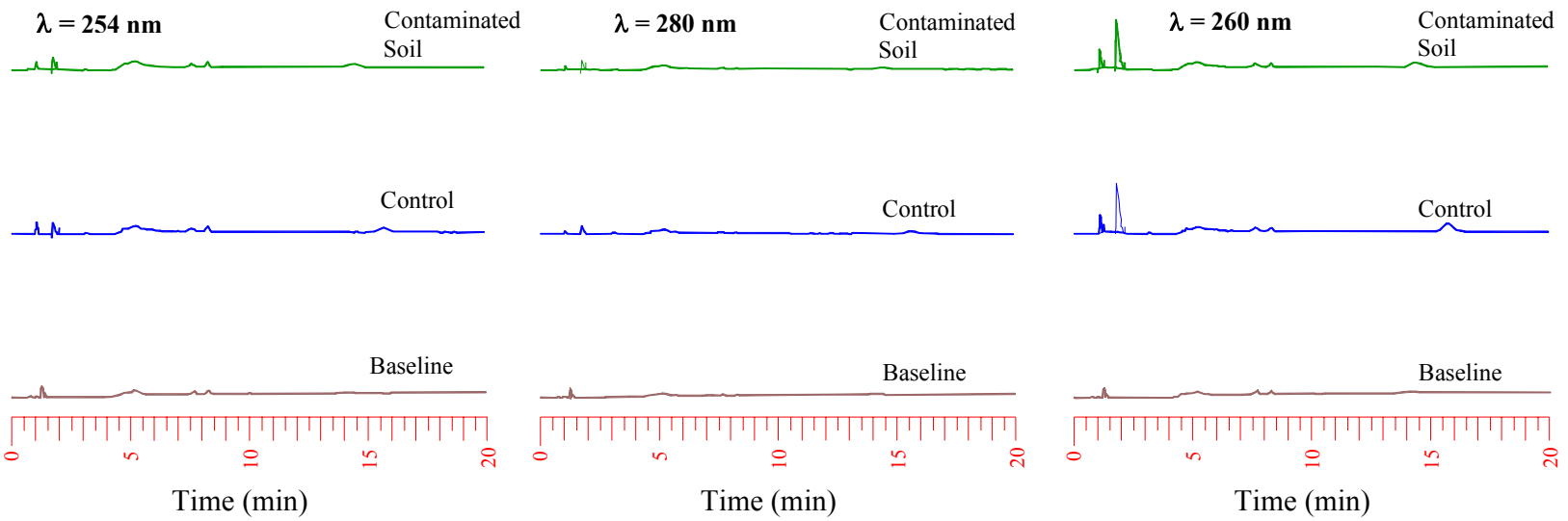


Figure 3.7 Ultraviolet (UV) chromatograms of pH 4 dissolved fractions of contaminated soil, sample loop 20 μL, λ = 254, 280, and 260 nm. Condition I in Table 2.3

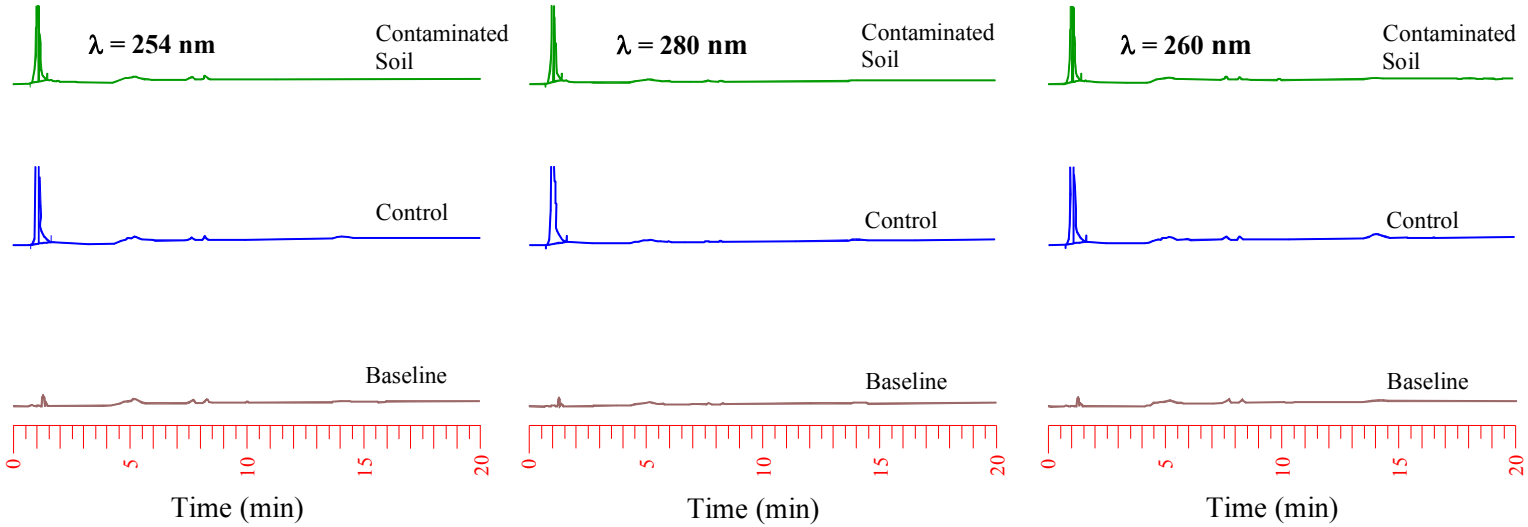


Figure 3.8 UV chromatograms of pH 7 dissolved fractions of contaminated soil, sample loop 20 μL, λ = 254, 280, and 260 nm. Condition I in Table 2.3.

Table 3.11 The amounts of total organic carbon (TOC) in supernatant fractions

Supernatant at Different pH	Reference Soil (mg/kg) ± SD (CV%)	Contaminated Soil (mg/kg) ± SD (CV%)
pH 4	57.5±35.9 (62.4%)	50.6±7.8 (15.4%)
pH 7	41.9±1.4 (3.3%)	18.5±1.6 (8.6%)
pH 9	32.09±5 (15.6%)	18.4±3.2 (17.4%)

SD = Standard deviation, No. of replicate (n) = 3, CV = Coefficient of variation

Another attempt was made on pH 7 extract of contaminated soil by adjusting the pH to 4 and 2 in order to enhance the signal of DOM and PbDOM. This is because the MINTEQA2 predicts that 87.6 % of lead is bound into dissolved organic matter (as shown in Table 3.8). However, as shown in the Figures 3.9 and 3.10, there is no improvement in the ultraviolet (UV) signals in both figures. This might be because of adjustment of these pHs diluting the DOM since its original pH of supernatant was a little above the detection limit, 18.5 mg/L, compared with fulvic acid, 15 mg/L. As mentioned earlier, filtering supernatant before injection into the RP-HPLC might also filter some DOM and PbDOM too. As a result, DOM and PbDOM could not be detected from aqueous experiment directly.

In summary, leaching of PbDOM from the aqueous experiment at pH 4 and 7 showed no different signal from the control. This might be because of the low concentrations of the samples and their matrix problems. Matrix modification by adjusting to lower pH could not improve the signal. This might be because the dilution factor made the sample out of range; otherwise, the form of PbDOM might not be able to

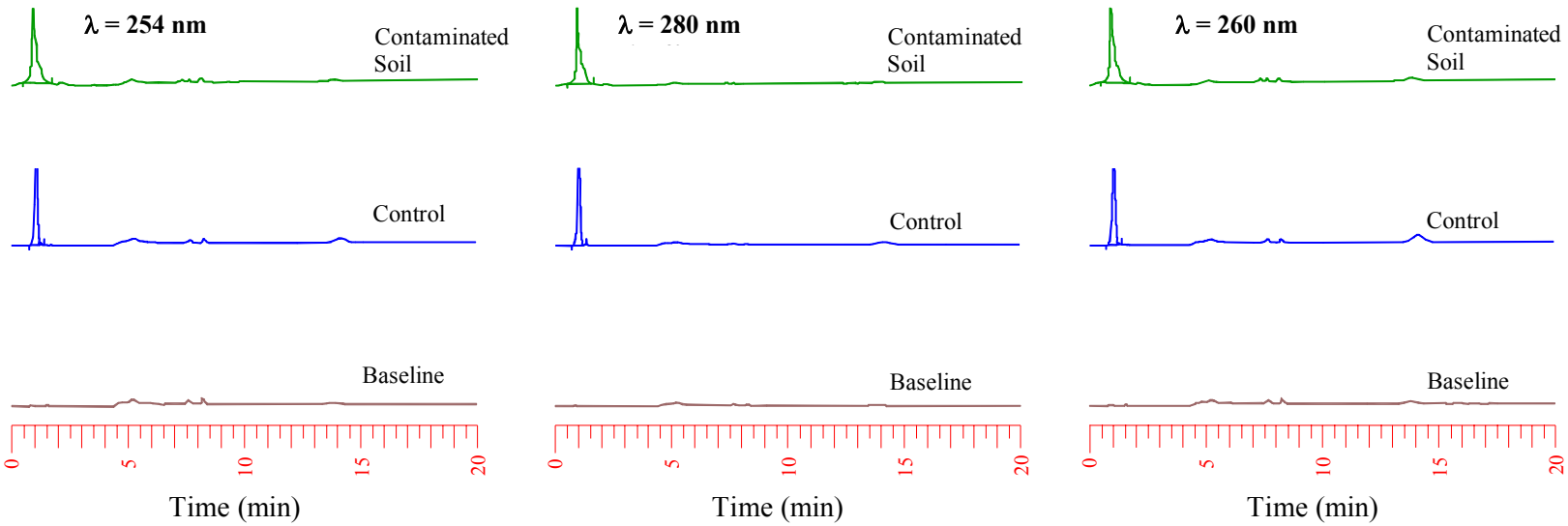


Figure 3.9 UV chromatograms of pH 7 dissolved fractions of contaminated soil that was acidified to pH4, sample loop 20 μL, λ = 254, 280, and 260 nm. Gradient program I in Table 2.3.

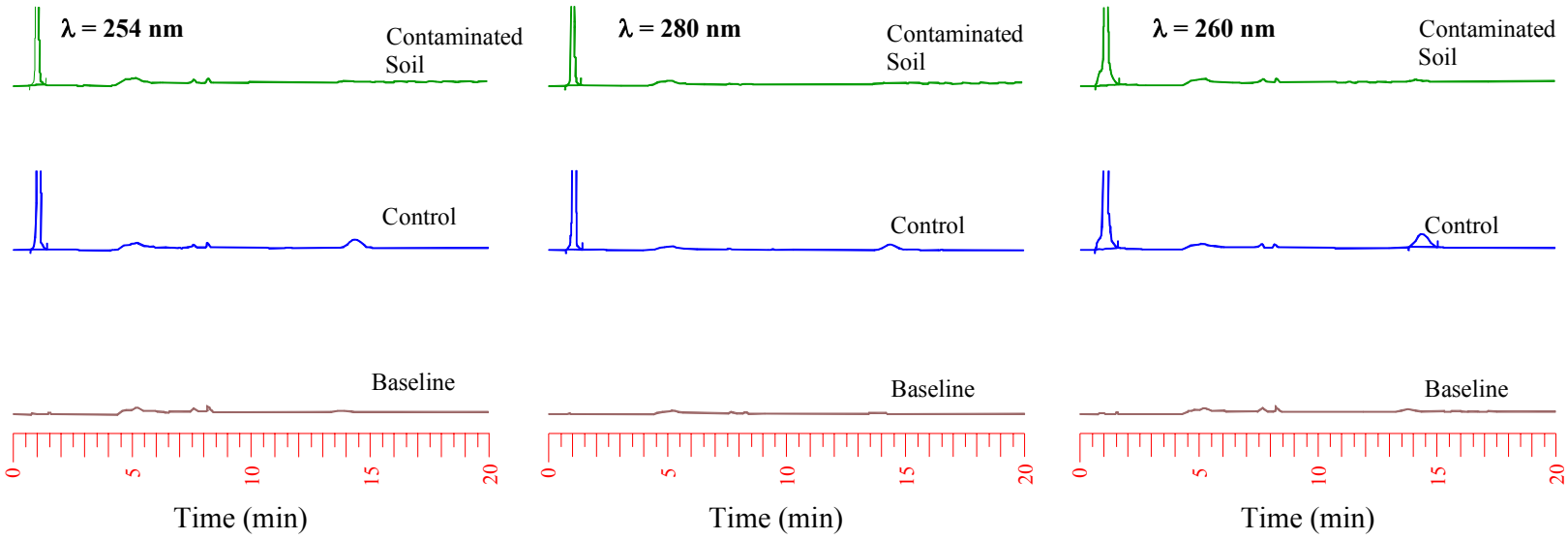


Figure 3.10 UV chromatograms of pH 7 dissolved fractions of contaminated soil that was acidified to pH 2, sample loop 20 μL, λ = 254, 280, and 260 nm. Gradient program I in Table 2.3.

penetrate through the filter as the MINTEQA2 predicted that the amount of PbDOM corresponded to the fraction in the residue rather than in the dissolved fraction as discussed in the previous section.

Soxhlet Extraction and Kudernal-Danish Experiments

The objective of these experiments was to extract the organically bound Pb from the contaminated soil sample using a series of organic solvents of increasing polarity. The experiment was performed as described on page 52-54 and as shown in the Figures 2.5-2.6. Extracts of each solvent phase were analyzed by RP-HPLC and by graphite furnace atomic absorption spectroscopy (GFAAS) from Varian. In the GFAAS analysis, the drying steps of each extraction solvent were changed from the default database to be around 85% of its boiling point and drying times were extended to 60 seconds. Table 3.12 shows the Pb concentrations in the organic solvent extracts. Trace amounts of Pb

Table 3.12 Lead concentrations in each extracted Soxhlet solvent after preconcentrated with Kudernal-Danish technique

Fractions ordered by polarity	Lead concentration (mg/kg) ± SD (CV%)
Hexane	ND
Methylene chloride	ND
Acetonitrile	$4.34 \times 10^{-3} \pm 0.77 \times 10^{-3}$ (17.7%)
Methanol	$42.63 \times 10^{-3} \pm 2.33 \times 10^{-3}$ (5.5%)
Extracted soil residue	102.5
Sum	102.55
Total	100.4
Recovery (%)*	102.1

ND = Lower than detection limit, 1 μg/L; SD = Standard deviation, No. of replication (n) = 3, CV = Coefficient of variation, *Recovery (%) = (Sum/Total) × 100

were detected only in the acetonitrile and the methanol extracts at concentrations of 4.34 $\times 10^{-3}$ and 42.63 $\times 10^{-3}$ mg/kg, respectively. The table also shows that most of the Pb is still associated with the soil residue. The sum of the organically bound Pb represents only 0.05% of the total Pb in the contaminated soil sample. The
solvent Soxhlet extracts were also analyzed by RP-HPLC. Figures 3.11-3.14 shows the UV chromatograms.

The chromatograms show no difference of the UV absorption of the control and contaminated soil samples. Even though lead was detected in the acetonitrile and methanol extracts as shown in Table 3.12, the concentrations were in the ppb range which was very small. Thus, any absorption that might occur would not be noticed on the chromatograms.

In summary, the Soxhlet extraction and Kudernal-Danish experiments shed some light on the nature of the organically bound Pb in the contaminated soil sample. The results indicate that none of the organically bound Pb is completely non-polar. The amount of Pb extracted in the methanol is almost ten times higher than that extracted with acetonitrile. This indicates that Pb-organic complex is more of a polar nature. The RP-HPLC chromatograms provided fingerprints of the extracts but no distinction could be made between the control and the sample.

Sequential Extraction Experiment

The objective of this experiment was to apply the conventional chemical extraction method to the soils and sediment samples and to compare the results with the.

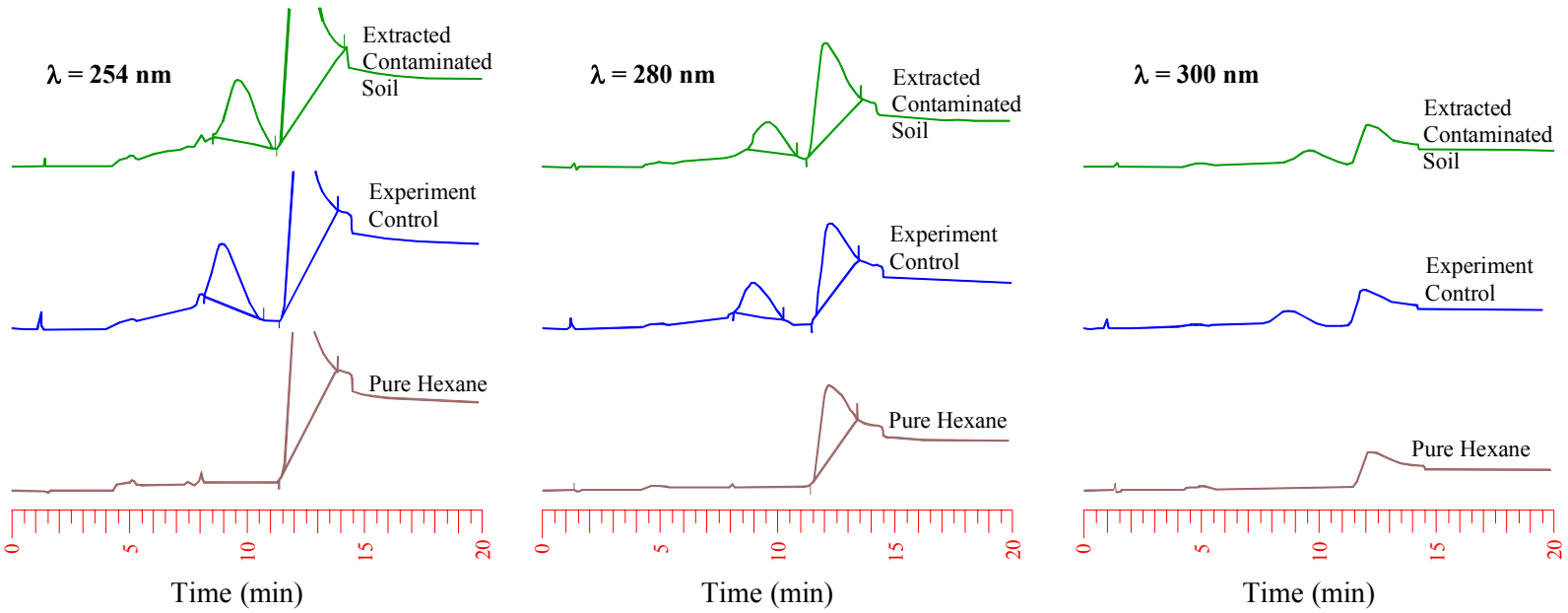


Figure 3.11 UV chromatograms of dissolved fractions of Soxhlet extracted hexane, sample loop 20 μL, λ = 254, 280, and 260 nm. Gradient program I in Table 2.3.

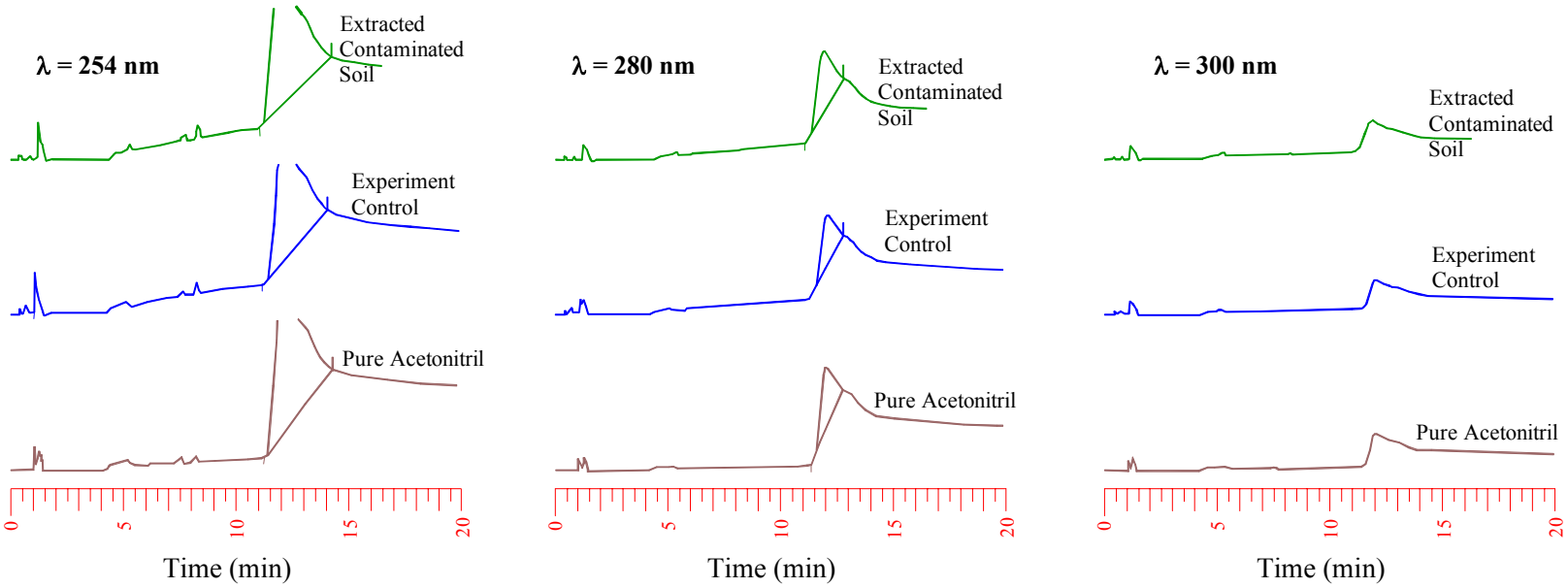


Figure 3.12 UV chromatograms of dissolved fractions of Soxhlet extracted acetonitrile, sample loop 20 μL, λ = 254, 280, and 300 nm. Gradient program I in Table 2.3.

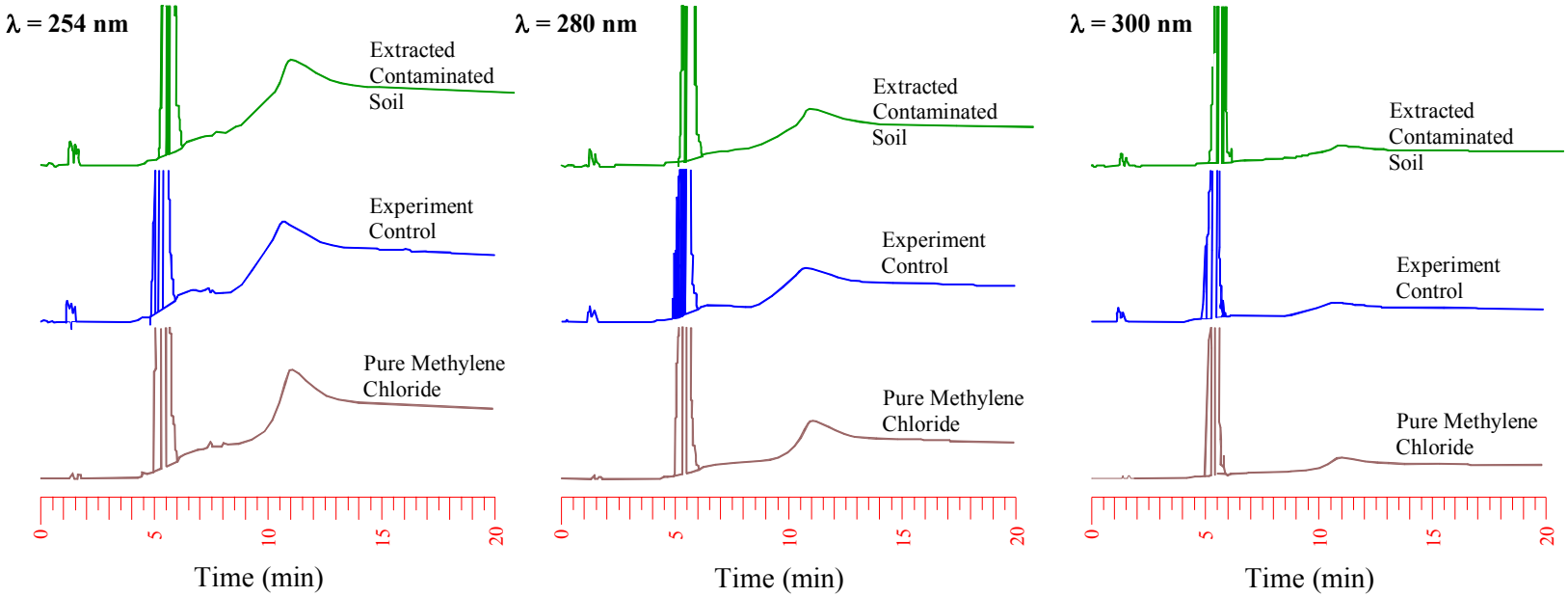


Figure 3.13 UV chromatograms of dissolved fractions of Soxhlet extracted methylene chloride, sample loop 20 μL, λ = 254, 280, and 300 nm. Gradient program I in Table 2.3.

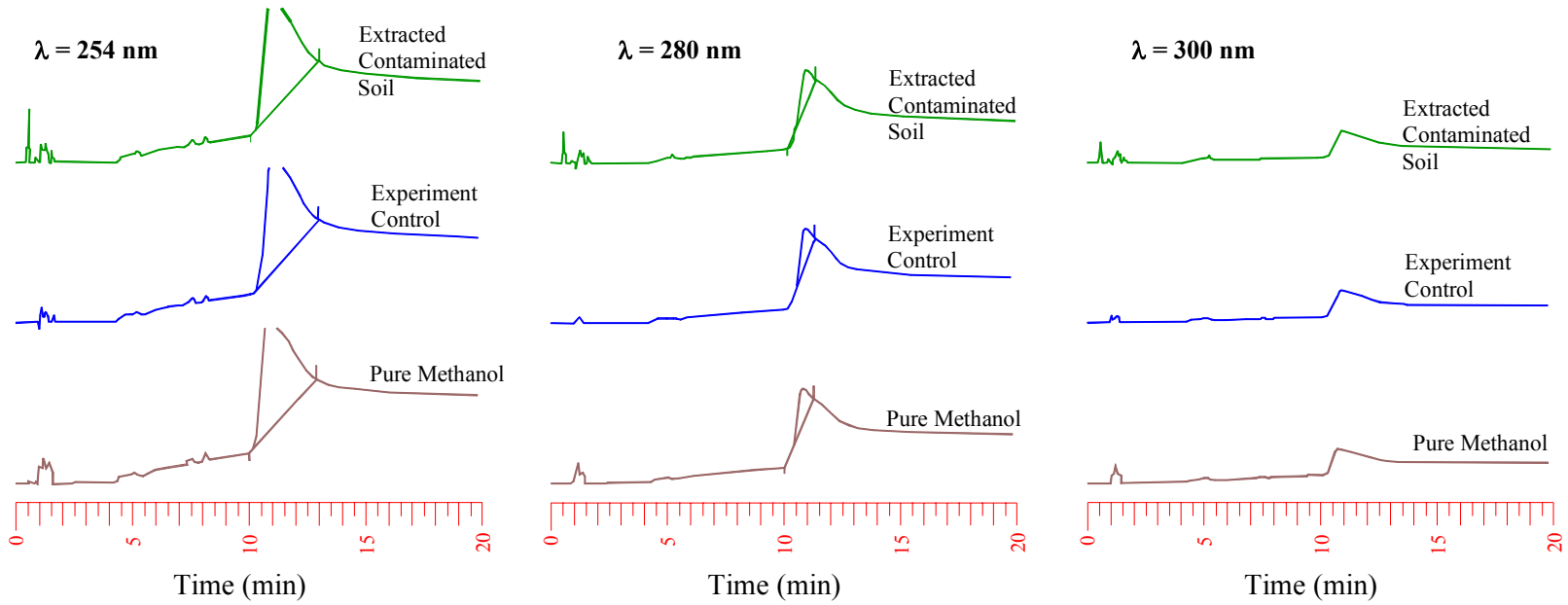


Figure 3.14 UV chromatograms of dissolved fractions of Soxhlet extracted methanol, sample loop 20 μL, λ = 254, 280, and 300 nm. Gradient program I in Table 2.3.

Table 3.13 Lead concentrations in four different fractions by sequential chemical extraction

Fractions	Reference Soil (mg/kg) ± SD (CV%)	Contaminated Soil (mg/kg) ± SD (CV%)	Standard Sediment (mg/kg) ± SD (CV%)
Exchangeable	0	0	0
Oxide Bound	9.2±0.7 (7.6%)	67.8±2.0 (2.9%)	560.9±8.9 (1.6%)
Organically Complexed	0	16.3±1.4 (8.6%)	0
Residual	9.2±0.7 (7.6%)	13.8±1.3 (9.4%)	50.3±5.2 (10.3%)
Sum	18.39	97.9	608.8
Total	18.5	100.4	618.17
% Recovery*	99	97.5	98.4

*% Recovery = Sum ÷ Total Lead, SD = Standard deviation, No. of replicate (n) = 3, CV = Coefficient of variation

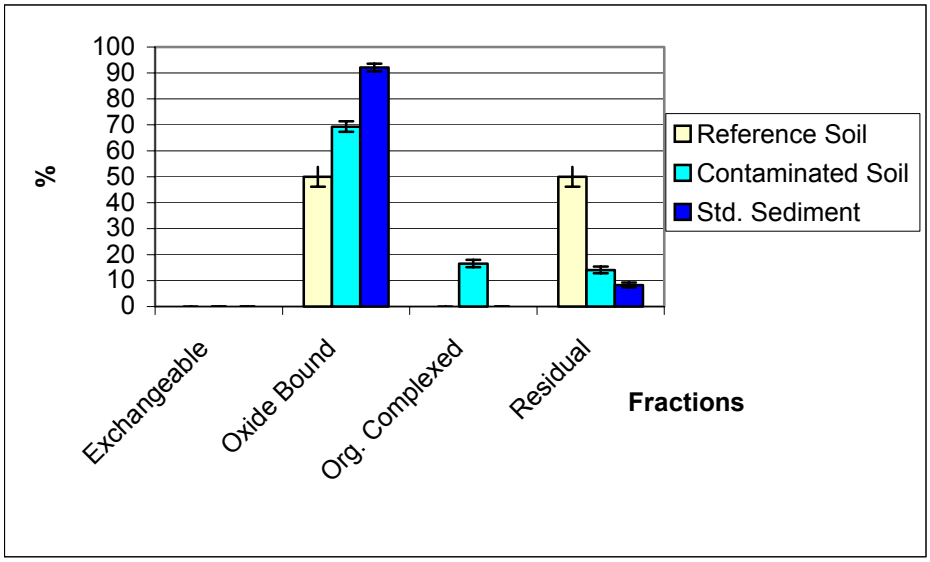


Figure 3.15 Lead concentrations in four different fractions with standard deviations by sequential chemical extraction

other methods used to investigate the field samples. The results are shown in Table 3.13 and Figure 3.15

Most of the Pb was found in the oxide bound fractions. They accounted for 50, 69.3, and 92.1% in the reference, contaminated soils, and standard sediment, respectively. The residual fractions accounted for 50, 14.1, and 8.3%, respectively. Only in contaminated soil, lead was found in the organic complex fraction, 16.6%.

It should be noted that lead organic complexed concentration seemed to be much higher than measured by Soxhlet extraction in which the concentrations were in ppb level. This indicated the varieties of organic functional groups on soil that might not be extractable with the organic solvents. The oxide bound fractions also related to their properties. Since both reference and contaminated soils were sandy loam, oxide and hydroxide of Fe and Al might play an important role in this fraction, especially contaminated soil which contained more Fe as indicated by its more reddish color. The residual fractions of all three samples are usually of less concern since they would not be leached to become toxic into the environment. So, these fractions usually attribute as an inherent mineral in soils. In the reference soil where the lead came from its ore origin and non-point source, this fraction accounted for 50% while in contaminated soil where it was contaminated from the battery factory, the lead in this fraction was only 14.1%. Thus, there would be more available lead that could be leached from soil into the environment in the contaminated soil than in the reference soil.

In summary, even though sequential extraction could not determine how much of lead would be leached into the environment directly, it could give an idea of the potential

of lead that could become available. As known that the toxicity of lead would depend on the environmental condition, change of pH, ionic strength, and other chemicals or species would affect on the mobility of lead. Examples are shown in the aqueous extraction experiment where the amount of dissolved Pb^{2+} at each pH was changed accordingly. However, the sequential extraction was still useful in giving the information of how much lead in the certain fractions that could be leached into the environment and what action that might be effect directly and indirectly to the fractions.

3.2 Hydrolytic Polymerization Study

The study of lead hydrolytic polymerization species involved three types of experiments. The first one involved pH titration curve to establish the pH range for polymeric species formation. The second and third experiments involved the use of ion and column chromatography to isolate the polymeric species. All polymerization experiments were performed under nitrogen to eliminate formation of lead carbonate.

As shown in the literature review, Pb^{2+} can form a number of hydroxide complexes which are monomeric and polymeric species.[1,20,21,34,45,46] The pH titration was performed by titrating solutions with and without Pb with certain concentration of base as described on pages 57-59. Figure 3.16 shows the titration of Pb 10 mg/L in 10 mM $NaClO_4$ medium with 0.011 M NaOH. The blank curve shows the titration of 10 mM $NaClO_4$, at pH 4, without Pb. The titration curves indicate that OH^- groups in the sample were utilized to form hydroxyl species with Pb as the amount of NaOH in the sample line was higher than of the blank at the same pH. The range of pH between 4.7 and 7.2 showed uptake OH^- without precipitation. As a result, a pH range between 5 and 7.2 was

chosen to study the hydrolysis of lead in the subsequent chromatography experiments. For monomeric study, pH4 was used.

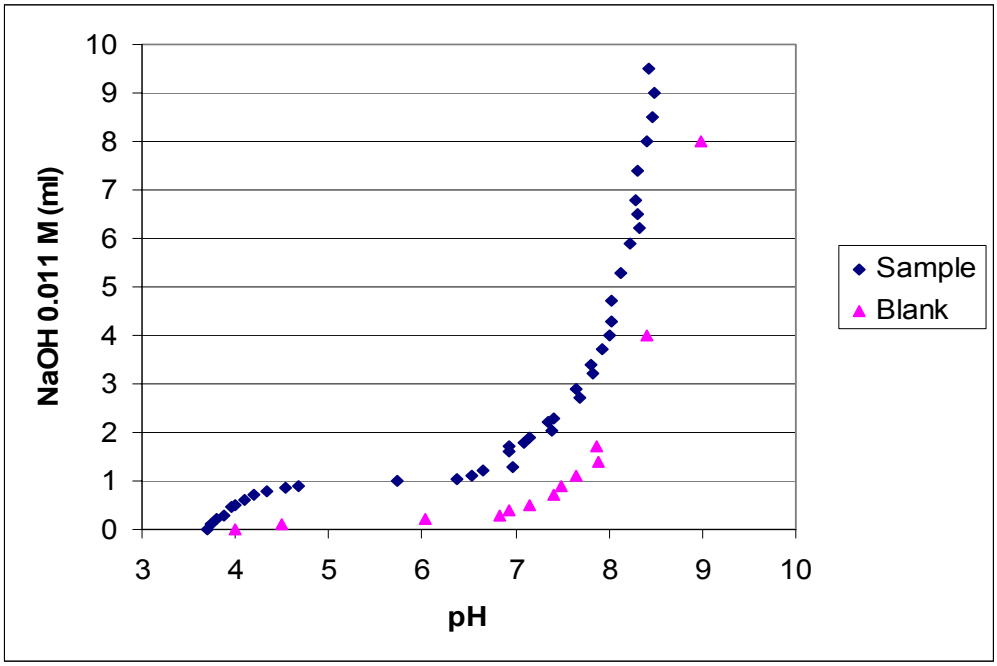


Figure 3.16 Titration curves of 10 mg/L Pb in 10 mM $NaClO_4/HClO_4$ and blank with 0.011 M NaOH

Ion Chromatography (IC) Study

The objective of the IC experiment was to detect and isolate Pb polymeric species using IC. Hydrolytic polymerization of chromium—Cr(III) had been successfully separated by IC in our research laboratory.[63] The studies indicated that products of hydrolytic polymerization of Cr(III) after fractionation on Sephadex column using eluents of increasing ionic strength could be detected by IC with UV detector. The IC separation of the monomers and low oligomers was achieved with a low mixed resin column using

eluent consisting of 2M $NaCLO_4$/0.02M $HClO_4$ at pH 4.5. In the aged sample, the dimeric and trimeric Cr(III) species were detected in the second fraction of the aged sample at k′ of 1.09 and 1.70, respectively. The third fraction also contained trimeric species with k′ of 1.79. The overall Cr(III) recovery from all Sephadex fractions was 100.76%.

In this experiment, the same strategy was applied. The sephadex column with increasing ionic strength eluents was used as illustrated in the Figure 2.8. The low mixed resin column was also used with the lower ionic strength at 10 mM $NaClO_4$ at pH 4 for the monomer and at pH 5.5 for the polymer. Because Pb monomeric and polymeric species did not absorb any UV region, conductivity detector was used instead of the UV detector. Because of the nature of the conductivity detector, a strong ionic strength solution could not be used as a mobile phase.

In the study of monomeric species, as reviewed from the literature (Figure 1.7) and as illustrated in the preliminary study in Figure 3.16, at pH below 4 only monomeric species could exist without further hydrolysis. In this IC experiment at pH 4, only monomeric Pb species are predominant as shown in the Figure 3.17. The figure shows no significant change of an area of monomeric peaks at retention time (t_r) 11 mins after 3 days.

At pH 5.22, IC chromatograms indicated progressive appearance of peak at t_r 12.951 minutes with increased signals on day 7, as shown in Figure 3.18. It was also noted that the sample pH increased from 5.12 on day 3 to 9.11 on day 7 and was associated with some precipitation of white murky flakes in the solution.

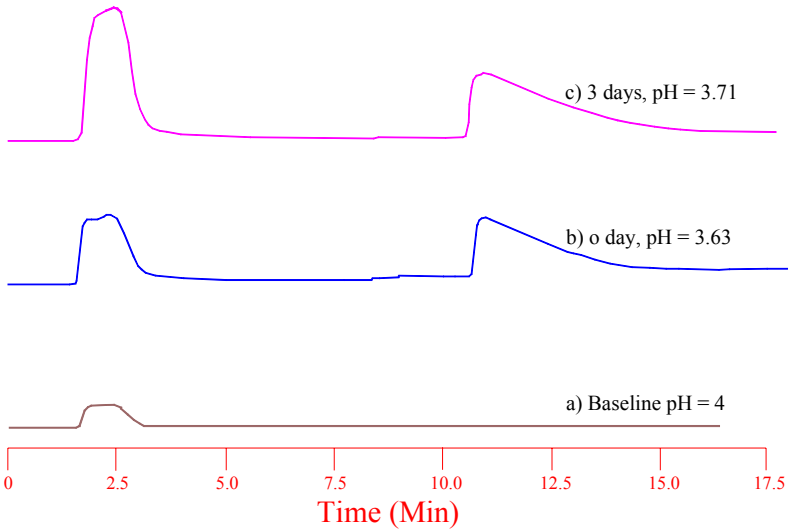


Figure 3.17 Lead monomeric species at pH 4 during 3 days, mobile phase = 10 mM $NaClO_4$ pH 4, IC-condition as shown in Table 2.4.

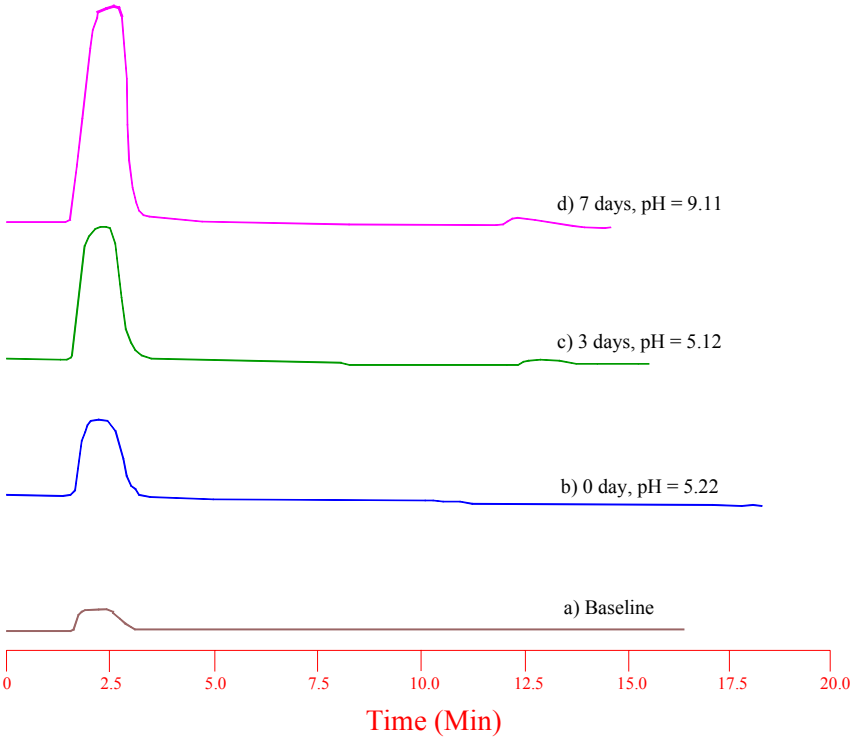


Figure 3.18 Lead polymeric species at pH 5.22 during 7 days, mobile phase = 10 mM $NaClO_4$ pH 5.5, IC-condition as shown in Table 2.4.

In order to gain more signal for the polymeric species, the experiment was repeated but the sample pH was raised to 7.22 while the mobile phase pH was remained the same, 5.5. As shown in the Figure 3.19, an increased signal was apparent at t_r between 9 and 11 minutes. The sample pH decreased from 7.22 at 2.5 minutes to 5.87 after 1,442.5 minutes indicating utilizing consumption of OH^- via hydrolysis.

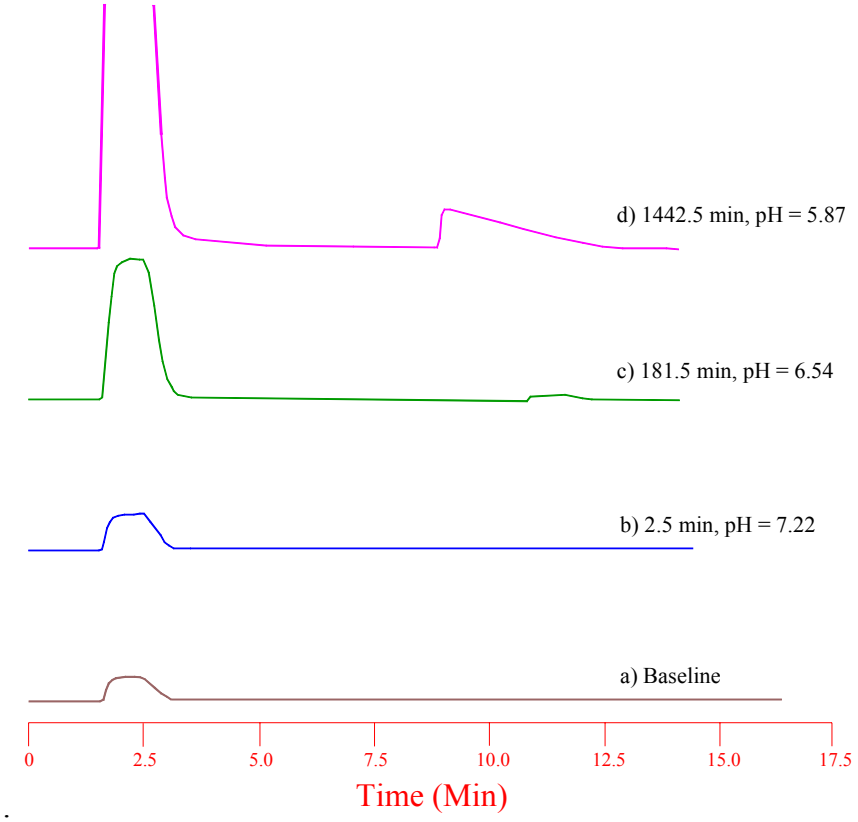


Figure 3.19 Lead polymeric species at pH 7.22 over 24 hours, mobile phase = 10 mM $NaClO_4$ pH 5.5, IC-condition as shown in Table 2.4

To confirm that the peak found in Figure 3.19 was not monomeric species, a fresh sample at pH ~ 4 was prepared. Both aged sample from Figure 3.19 and its mobile phase were acidified with $HClO_4$ to pH ~ 4 where the monomeric species had been found previously (Figure 3.17). The result shown in Figure 3.20 indicated that lead polymeric species did exist. Aged sample that was acidified to pH 3.68 had two peaks. The first peak occurred at t_r around 9 minutes similar to the fresh sample at pH 3.44 which showed monomeric species at the same t_r. The other peak indicates formation of polymeric species at longer t_r.

In summary, the IC experiments confirmed the formation of Pb polymeric species. However, the quality of the chromatograms and the peak resolution were

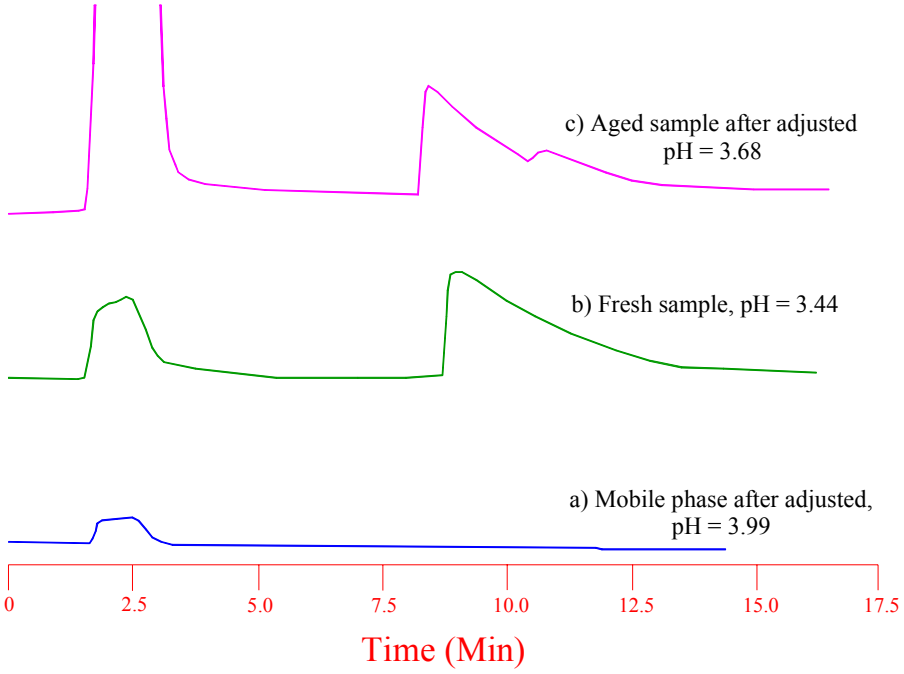


Figure 3.20 Lead mono- and polymeric species, mobile phase = 10 mM $NaClO_4$ pH 5.5 acidified to 3.99, IC-condition as shown in Table 2.4

unsatisfactory. Several factors contributed to this situation. First, the conductivity detector was used to detect Pb species which contributed to the weak signal. In case of the Cr(III) study, UV detector was used which had more enhanced signal at wave length 436 nm.[63] Second, due to the high atomic weight of Pb, conductivity signals showed broad peaks. Additional difficulties were encountered due to irreversible sorption of Pb on the IC column and inability to obtain satisfactory mass balance in the preparative experiments. Due to these problems, the IC experiment was discontinued at this point.

Sephadex Column Experiment

The objective of Sephadex column chromatograph was to separate the polymeric fractions and to establish a mass balance of all the Pb species. The experiment was performed as described in pages 57-59 and in Figure 2.8, the medium was Milli-Q® water (obtained from Milli-Q® water purification system, Millipore Corporation) free of carbon dioxide and the pH was adjusted to 5.22 by using 0.2 M pyridine giving the ionic strength of solution (I) = 0.004. The major eluting solution compositions were still $NaClO_4/HClO_4$ with a series of stronger concentrations. The last eluent was saturated $K_2C_2O_4$ with NaOH. The concentrations in each fraction were shown in the Table 3.14 and Figure 3.21.

As shown in the Table 3.14 and Figure 3.21, two major fractions were separated throughout the experiment. The largest fraction was eluted by a mixture of 2M $NaClO_4$ and 0.02 M $HClO_4$ (E_2) accounted for 83.55% at day 0. Later, it gradually decreased to 74.85% at day 14. While lead fraction in E_2 was decreasing, lead fraction in 4M $NaClO_4$ and 0.04 M $HClO_4$ (E_3) was increasing. Over 14 days, lead in E_3 fraction was increased

Table 3.14 Lead concentration (%) after eluted through Sephadex columns, ionic strength (I) 0.004

Fractions	Day 0 ± SD (CV%)	Day 2 ± SD (CV%)	Day 14 ± SD (CV%)
First 5 ml of 5 ppm Pb (E_0)	ND	ND	ND
1M $NaClO_4$ + 0.01M $HCLO_4$ (E_1)	ND	ND	ND
2M $NaClO_4$ + 0.02M $HCLO_4$ (E_2)	83.55 ± 4.6 (5.5%)	80.15 ± 3.3 (4.1%)	74.85 ± 0.5 (0.7%)
4M $NaClO_4$ + 0.04M $HCLO_4$ (E_3)	16.45 ± 4.6 (28%)	19.83 ± 3.3 (16.6%)	25.1 ± 0.6 (2.4%)
6M $NaClO_4$ + 0.06M $HCLO_4$ (E_4)	ND	ND	ND
Milli-Q	ND	ND	ND
Saturated $K_2C_2O_4$ + 0.2 M NaOH (E_5)	ND	0.25 ± 0.04 (16%)	ND
Average Recovery (%)	98.5	97.7	103.3
pH of Sample	5.22	4.2	4.05

SD = Standard deviation, No. of replicate (n) = 2 ; ND = less than detection limit 1 μg/L, CV = Coefficient of variation

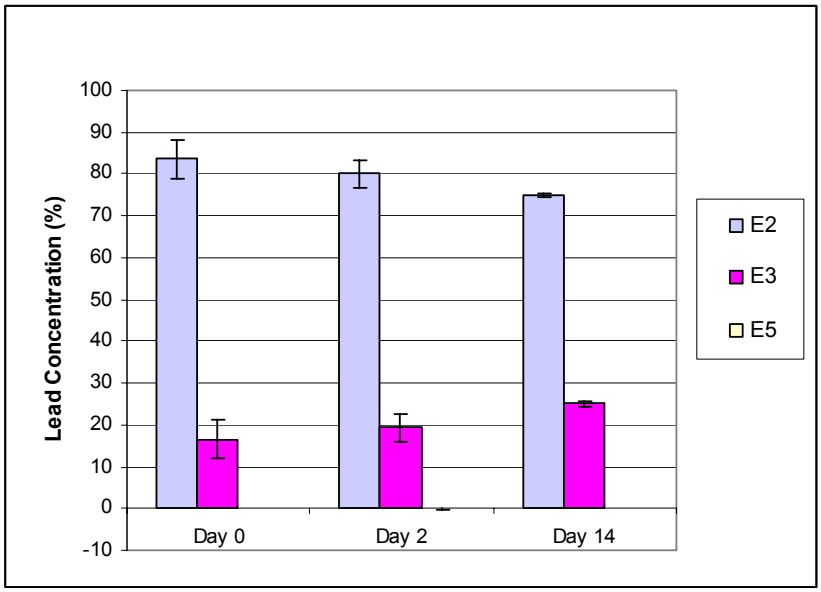


Figure 3.21 Percent lead concentrations in Sephadex fractions with standard deviations, E_2 = 2 M $NaClO_4$ + 0.02M $HCLO_4$, E_3 = 4M $NaClO_4$ + 0.04M $HCLO_4$, and E_5 = Saturated $K_2C_2O_4$ + 0.2 M NaOH

from 16.45 to 25.1% accounting for 52.6% of the initial concentration.

In column chromatography, the first eluted fraction is usually a smaller molecule which is Pb^{2+} and the latter fraction is the bigger molecules which are polymeric or other bigger ionic molecules such as $PbOH^{+}$ and $Pb(OH)_3^{-}$. The first eluted fraction in the experiment was E_2. This faction decreased while the latter fraction which was E_3 increased indicating the change of Pb^{2+} to be other forms.

The results of the Sephadex experiment show recovery of all Pb species ranging from 98.5 at day 0, to 97.7 on day 2 and 103 on day 14. The data show gradual increases of E_3, respectively. Lead polymeric species with first order kinetic constant (K) of 0.03 per day (day^{-1}) and half life of 23 days

As shown in Figures 1.7, trimeric and tetrameric lead polyhydroxy species $(Pb_3(OH)_4)^{2-}$ and $Pb_4(OH_4)^{4-}$ may be formed at Pb(II) total concentration of 10^{-5} M to 10^{-1} M. At total Pb (II) concentration of 10^{-5}, Pb trimeric species may contribute to up to 28% of the total Pb (II) concentration at pH range between 7.5 and 11. At total Pb (II) concentration of 10^{-1} M, tetrameric Pb hydroxyl species may contribute up to 72% of the total Pb (II) concentration at pH range between 4.7 and 8.8. Trimeric Pb hydroxyl species may contribute up to 4 percent of the total Pb concentration at pH range between 6.4 and 12.

Data from this experiment were used in MINTEQA2 (as illustrated in Appendix 3.4). The model predicts that 99.6% of lead would be soluble (Pb^{2+}) and its final pH would be 5.243. This contradicts to the experimental results where the pH moved downward to 4.25 and 4.05 eventually, indicating OH^{-} loss to form polymeric species.

The disagreement between the model and the experiment may be due to the lack of an appropriate kinetic polymeric database species.

In summary, lead hydrolysis could appear at pH 5.22. Once it was forming, the reaction took OH^- from water yielding lower pH. In this experiment, the longer experimenting time the lower pH of sample would be. There was no further investigation for how far of the pH would reduce or in the other words, there was no determination of the end point of polymeric species in this experiment. Further investigation of the kinetics and equilibrium of Pb hydroxyl species is highly recommended to evaluate their role in the fate and distribution of Pb species, especially under reduced conditions that may prevail in hazardous waste sites.

3.3 Lead-Organic Complexation Study

The objective of this experiment was to study Pb complexation with fulvic acid (FA) to gain more understanding of the role of metals organics complexation in aquatic systems. The approach used in this experiment was to utilize purified FA and standard Pb solution to calculate Pb-FA conditional stability constant and to compare the results with published values and MINTEQA2 predictions. The experiment was conducted as described on page 59-62. Samples were analyzed by RP-HPLC using gradient program II as shown in Table 2.3. Figures 3.22 to 3.24 show UV chromatograms of the samples at three wave lengths, 254, 260 and 280 nm. Table 3.15 shows the total areas of the chromatograms at the three wave lengths. Chromatograms of uncomplexed FA (Pb:FA =

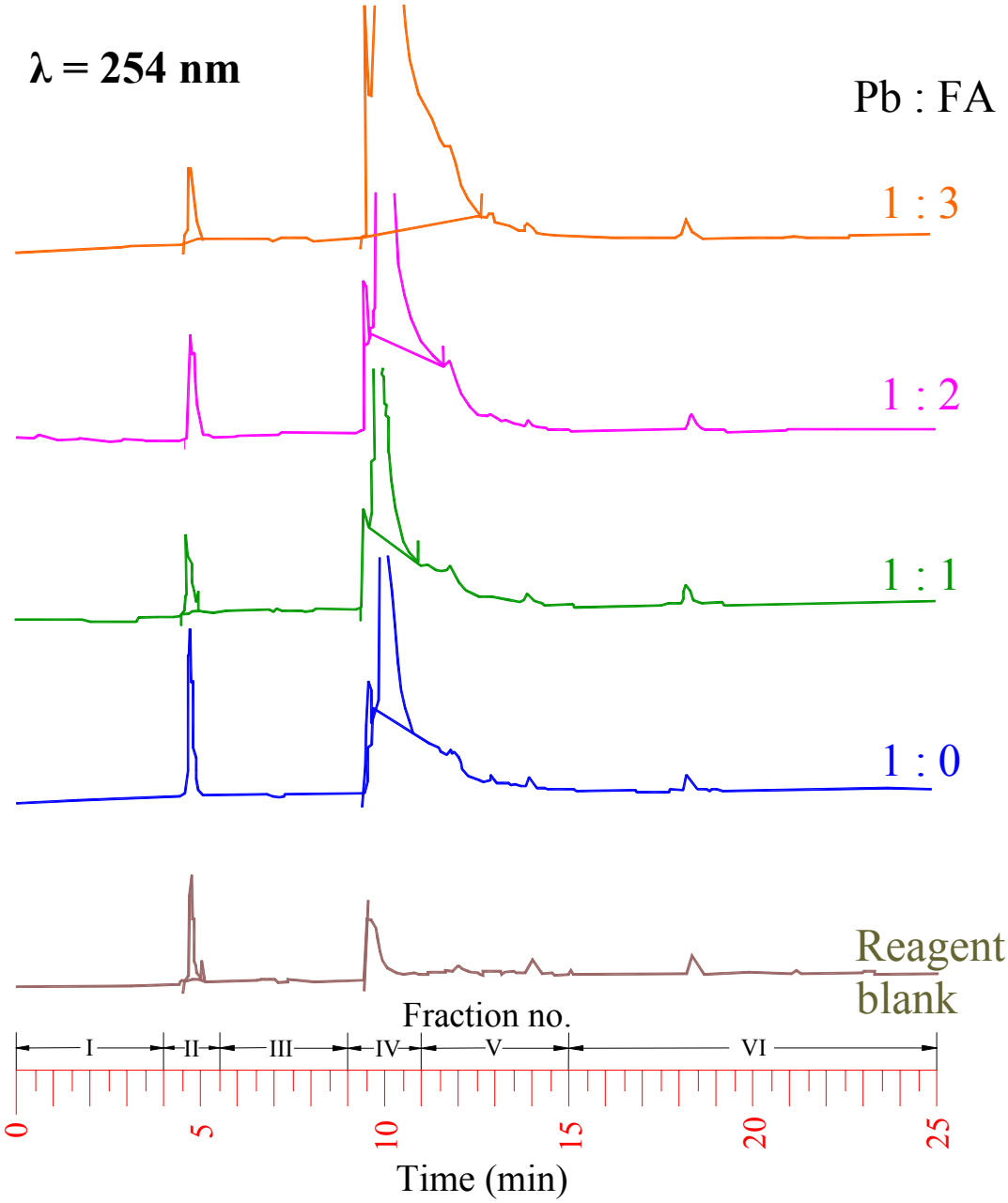


Figure 3.22 UV chromatograms of lead (Pb):fulvic acid (FA), ratio 1 = 2×10^{-4} M, sample loop = 20 μL, λ = 254 nm, Novapak® C18, gradient elution condition II as shown in Table 2.3

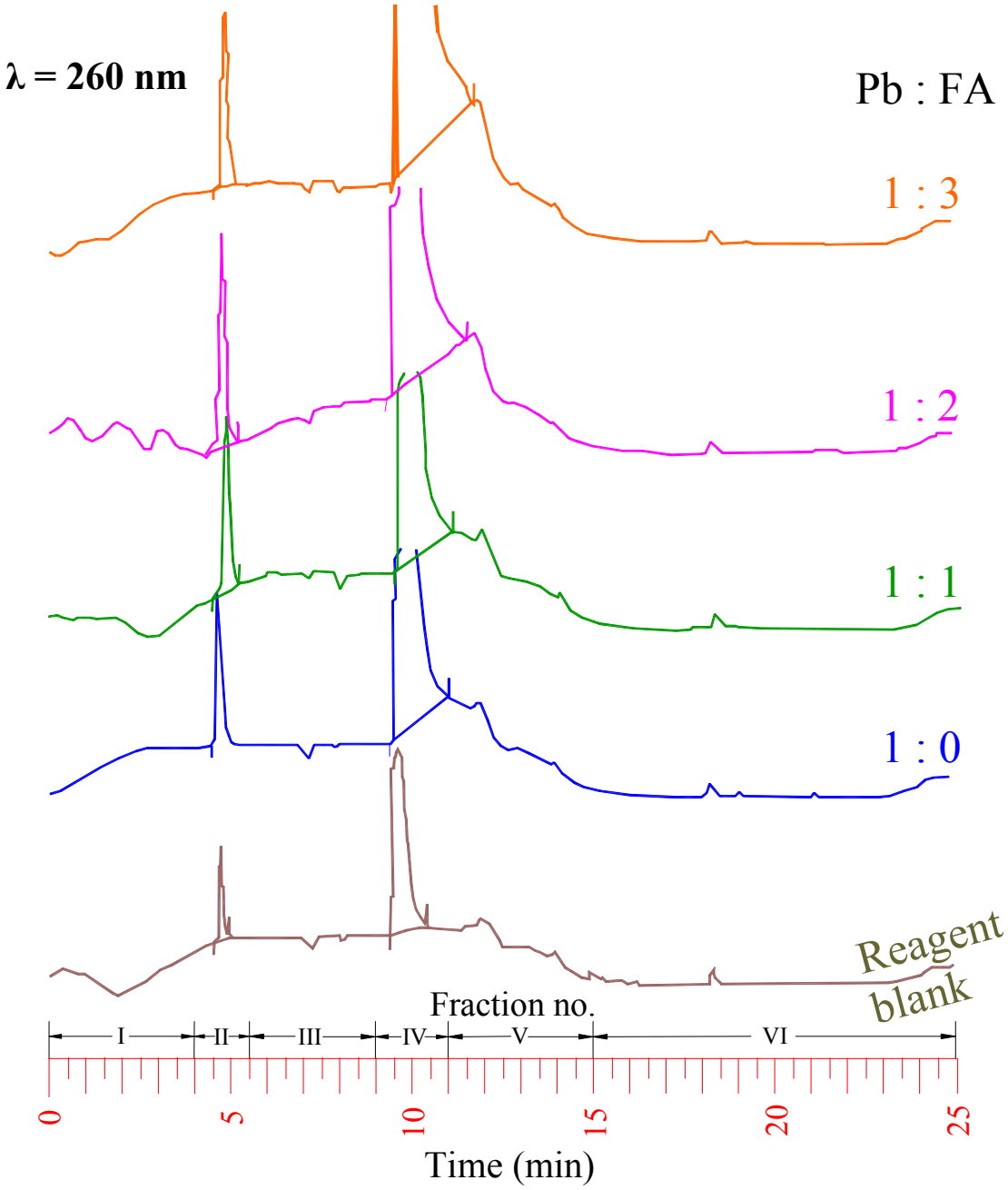


Figure 3.23 UV chromatograms of lead (Pb):fulvic acid (FA), ratio 1 = 2×10^{-4} M, sample loop = 20 μL, λ = 260 nm, Novapak® C18, gradient elution condition II as shown in Table 2.3.

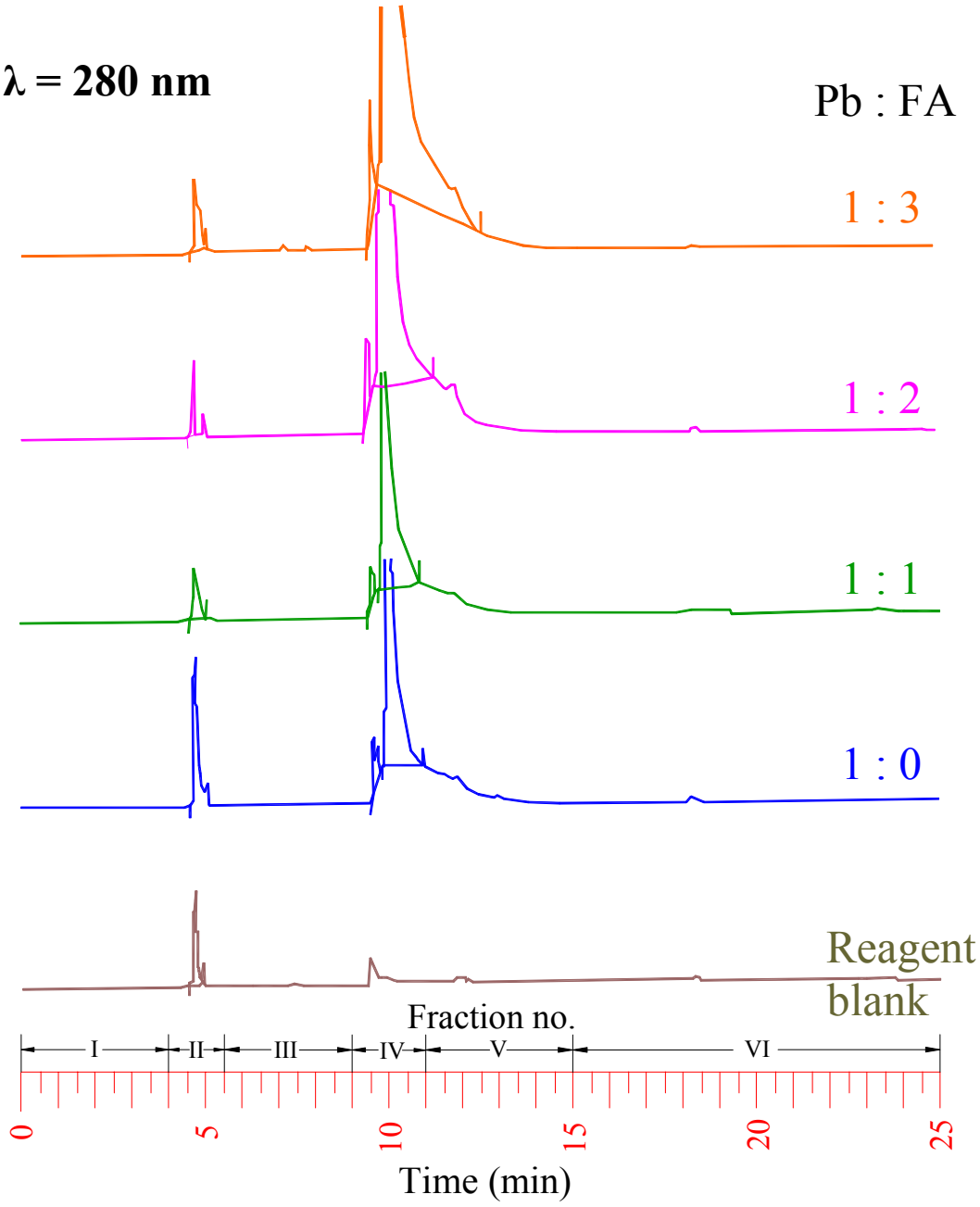


Figure 3.24 UV chromatograms of lead (Pb):fulvic acid (FA), ratio 1 = 2×10^{-4} M, sample loop = 20 μL, λ = 280 nm, Novapak® C18, gradient elution condition II as shown in Table 2.3.

Table 3.15 Total areas of UV chromatograms of Pb:FA

Pb:FA	Total Area at λ 254 nm ± SD (CV%)	Total Area at λ 260 nm ± SD (CV%)	Total Area at λ 280 nm ± SD (CV%)	Ratio of Area at 280/254
0:1*	2,276.8 ± 451.3 (19.8%)	1,925.8 ± 400.2 (20.8%)	4,397.5 ± 445.6 (10.1%)	1.93
1:1*	2,337.0 ± 262.2 (11.2%)	1,901.3 ± 177.9 (9.4%)	5,012.0 ± 287.3 (5.7%)	2.14
1:2	6,299.0 ± 333.7 (5.3%)	4,699.0 ± 243.6 (5.2%)	8,933.5 ± 576.2 (6.4%)	1.41
1:3	13,902.3 ± 3,670.0 (26.4%)	8,094.5 ± 1,333.4 (16.5%)	13,090.8 ±1,371.5 (10.5%)	0.94

* There is no significantly difference between total areas of Pb:FA = 0:1 and 1:1.
The statistic is shown in Appendix 3.5, SD = Standard deviation, No. of replicate (n) =3 and 4, CV = Coefficient of variation

0:1) shows the resolution of at least seven absorption peaks. The peaks between t_r 4 and 5.5 minutes represent the hydrophilic components of FA. The peaks between t_r 9 and 11 minutes represent the hydrophobic components of FA. Total UV absorption areas at wave lengths 254 and 260 nm are comparable (2,276 and 1,925). Total UV absorption at λ 280 nm is almost double of these values 4,397.5. The ratio of UV absorption areas at λ280/λ254 is taken as indication of sample degree of aromaticity or double bond conjugation. Chromatograms of uncomplexed FA are comparable to earlier characterization of FA by the same technique in our laboratory Saleh and Liao.[60] Chromatograms of 1:1 Pb-FA did not show notable difference from the uncomplexed FA, as confirmed by statistical analysis of the total absorption areas in Appendix 3.5. The λ280/λ254 area ratio is 2.14 indicating the same level of aromaticity or conjugation as

the uncomplexed FA. Results are not surprising since earlier RP-HPLC chromatograms of pH4 and 7 did not reveal new features.

Examination of chromatograms of 1:2 and 1:3 Pb:FA shows the resolution of the same number of peaks but with stronger absorption intensities. The ratio of area at λ280/λ254 are 1.42 and 0.94 for the 1:2 and 1:3 Pb:FA, respectively. The decreases indicate that FA-Pb molar ratio affects notable changes in the overall structure of FA, resulting in less aromaticity or conjugation.

From the preparative complexation experiment described on pages 59-62, fractions were analyzed for Pb by Perkin-Elmer GFAAS as shown in Table 2.5. Results are shown in Table 3.16 and Figure 3.25. Conditional stability constants were calculated for fractions II and III-IV. The table shows good recoveries of the total amount of Pb in each sample. The first fraction which corresponds to the void volume represents Pb^{2+} species. The second fraction could be attributed to the first binding site in FA molecule. The conditional stability constant for this site are 3.36, 3.04, and 2.75, for the 1:1, 1:2, and 1:3 Pb:FA, respectively. Fractions III and IV were combined and the stability constant for the combined site are 4.31, 3.95, and 3.71, for the 1:1, 1:2, and 1:3 Pb:FA, respectively. Several Pb-FA models are reported in the literature with binding sites ranging from two to seven.[38-42] Table 3.16 shows comparison between the amount of Pb in each fraction.

As shown in Table 3.17, MINTEQA2 predicts that 62.7% is PbDOM. This value is very close to the experimental data of 61.2% for the combined fractions of Pb:FA 1:1.

Table 3.16 Lead concentrations in each fraction and their stability constant (K), Pb = lead and FA = fulvic acid

Fraction No. Time (mins)	I 0 – 4 μg ± SD (CV%)	II 4 – 5.5 μg ± SD (CV%)	III 5.5 – 9 μg ± SD (CV%)	IV 9 – 11 μg ± SD (CV%)	V 11 - 15	VI 15 – 25	Total (μg)	Recovery (%)
Pb:FA								
0:1	0	0	0	0	0	0	0	-
1:1	0.09 ± 0.01 (11.1%)	0.17 ± 0.04 (23.5%)	0.34 ± 0.03 (8.8%)	0.07 ± 0.01 (14.3%)	0	0	0.67	91.27
(% of 1:1)	13.45	25.37	50.75	10.45	(0)	(0)	(100)	
Log K		⟵ 3.36 ⟶	⟵———	4.31 ———⟶				
1:2	0.03 ± 0.02 (66.7%)	0.22 ± 0.04 (18.2%)	0.47 ± 0.05(10.6%)	0.09 ± 0.02 (22.2%)	0	0	0.8	104.55
(% of 1:2)	3.75	27.5	58.75	11.25	(0)	(0)	(100)	
Log K		⟵ 3.04 ⟶	⟵———	3.95 ———⟶				
1:3	0.05 ±0.03 (60.0%)	0.16 ± 0.03 (18.8%)	0.39 ± 0.06(15.4%)	0.08 ± 0.03 (37.5%)	0	0	0.67	87.38
(% of 1:3)	7.46	23.88	58.21	11.94	(0)	(0)	(100)	
Log K		⟵ 2.75 ⟶	⟵———	3.71 ———⟶				

* The concentration among Pb:FA equal to 1:1, 1:2. and 1:3 at between 9 to 11 mins are not significantly different. The statistic is shown in Appendix 3.5. SD = Standard deviation, No. of replicate (n) = 3 and 4, CV = Coefficient of variation, Detection limit = 1μg/L

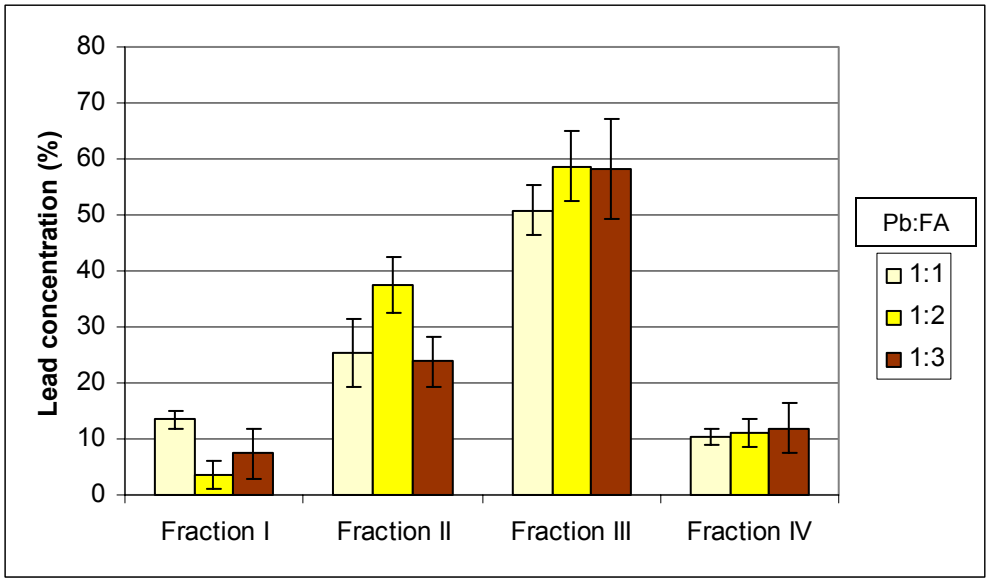


Figure 3.25 Percent of lead in each fraction with its standard deviation; Fraction I = fraction collected between 0-4 minutes, Fraction II = 4-5.5 minutes, Fraction III = 5.5-9 minutes, and Fraction IV = 9-11 minutes, respectively

Table 3.17 Percent distribution of lead in each fraction predicted by MINTEQA2

Pb:DOM	Pb^{2+}(%)	PbDOM (%)	Log K
1:1	37.3	62.7	5.255
1:2	18.9	81.1	5.268
1:3	10.9	89.1	5.277

Note: FA concentration was input as DOM. Charge on DOM species were calculated based on speciation. MINTEQA2's calculations are in Appendix 3.6

Even though MINTEQA2 used different value of log K, 5.255 into the model, the results are still close. At higher Pb:FA molar ratios of 1:2 and 1:3, MINTEQA2 predicted 81.1%. and 89.1% PbDOM, respectively. The experimental results in Table 3.14 show less percentages possibly due to difference in the logarithmic stability constant (log K) values.

Published data of log K on Pb-FA[38] and Pb-humic acid (HA)[39] are 4.69 and 4.92. The calculated log K in this study, 4.31 is in good agreement with the values. The lower log K for Pb-FA than Pb-HA is not surprising. It is generally known that FA has simpler structure than HA.

In summary, the Pb-FA complexation study provided new information an the extent of Pb association with organic matter. The results of the 1:1 Pb-FA are in good agreement with MINTEQA2 prediction and with published stability constant data. Additional research is needed to identify the nature and number of binding sites in DOM and the extent of their contribution to the overall fate and transport of Pb in the aquatic environment.

3.4 Conclusions and Recommendations

The objective of this research was to develop a comprehensive scheme to evaluate the speciation of lead compounds under different environmental and experimental conditions. The research focused on lead hydrolytic polymerization and interactions with organic ligands to better understand how the species affect lead mobility under different environmental conditions. The research involved both field soil and sediment samples as well as standard lead solutions. In this research, two schemes were developed. One was the investigation of distribution and speciation of lead under different extraction

methods—aqueous and organic solvent extractions. The other was hydrolytic polymerization and organic complexation experiments using standard lead solutions. The results were compared and evaluated with the MINTEQA2 model. The following conclusions and recommendations are based on the results and observations attained in the research, within the experimental parameters previously described:

1. According to the geographical data of the soil samples and their properties, lead in the contaminated soil would be more mobile than in the reference soil. Other factors that aggravate the mobility, such as the change of pH and ionic strength would result in increased mobility and transport of lead from on location to another. In the aqueous equilibration experiment, the magnitude of the Pb^{2+} solubilization is in the order of pH 4> pH 7> pH 9 and the results are in agreement with MINTEQA2 predictions.

2. MINTEQA2 was executed with different input parameters to establish the minimum required data. Results show that users should characterize aqueous samples in terms of pH, ionic strength, major soluble cations, and DOM in order to make good model's predictions.

3. In the Soxhlet extraction and Kudernal-Danish preconcentration study, the amount of lead extracted in the methanol was 42.63×10^{-3} mg/kg and was almost ten times higher than that extracted with acetonitrile. This indicates that lead-organic complex is more of a polar nature. Other less polar solvents did not extract any measurable amounts of lead. The organically extracted lead was in the part per billion range.

4. Sequential extraction experiment could not determine how much of lead would be leached into the environment directly but gave the relevant background information on the bound lead in different fractions. The organically complexed lead by this method was much higher than measured by the Soxhlet extraction. This indicates presence of insoluble organic matter that might not be extractable with the organic solvents. The higher content of lead in the oxide bound fractions of the contaminated soil than of the reference soil relates to their properties in which the contaminated soil contains three times more iron.

5. In the hydrolytic polymerization study, the pH titration established the pH range for polymeric species formation. The IC experiments confirmed the formation lead polymeric species and the Sephadex experiment established the kinetics of polymerization and predicted an excellent mass balance of all lead species. The overall results of these experiments indicate that lead polymeric species can be formed at pH greater than 5.22 and may contribute up to 52.6% of the initial total lead concentration. Lead polymerization rate constant at pH 5.22 was 0.03 per day and its $t_{1/2}$ was 23 days. Due to lack of an appropriate kinetic polymeric species data base in MINTEQA2, the model did not predict polymeric species. The detection of soluble lead polymerization species is an important finding of this research. Further research is recommended to establish the structures, equilibrium, and kinetic constants for their formations either by inventing a new detector that is compatible with ion chromatography or by utilizing a new methodology to investigate metal ions polymeric species. It is also recommended to

modify MINTEQA2 to account for the formation of metals polymeric species such as Pb(II) and Cr(III).

6. Pb-FA complexation experiment provided new information on the extent of lead association with organic matter. Mass balances of lead in different fractions were excellent. Calculated lead conditional stability constants were in good agreement with MINTEQA2 model data base and with published data. At 1:1 Pb-FA molar ratio, 61.2% of lead was bound to FA, and MINTEQA2 predicted 62.7% PbDOM at the same molar ratio. At higher Pb-FA molar ratios the experimental result were lower than model prediction possibly due to differences between the experimental and the model's stability constants at the higher molar ratio. Further research is recommended in order to better understand the nature and number of binding sites in DOM and their contribution to the over all fate and transport of lead in the aquatic environment. As new analytical tools are developed, our understanding of the structure and interactions of natural organic ligands are likely to improve.

In summary, this research has provided new information on the distribution and mobility of different lead species in the soil/sediment-water environment. New methodologies for evaluation of organically bound lead species and lead polyhydroxy species have been developed. Furthermore, the results in several instances have provided verification of MINTEQA2 model's prediction. The results also revealed areas of disagreement between the models prediction and the experimental data. A final positive note regarding the experimental work done in the research is the verification of the mass

balance in all the repeated experiments which is an approach that is highly recommended in environmental research.

APPENDIX 1

APPENDIX 1.1

DEFINITIONS OF TERMS

DEFINITIONS OF TERMS

"Sorption is used as a general term, encompassing both adsorption and absorption. Precipitation reactions are specifically excluded from the definition of sorption."[37] (p.84)

"*Adsorption* is used to describe that portion of metal binding to particle surfaces, which is readily reversible. It is a portion of the mass sorbed that is appropriately described by the surface complexation model of adsorption. A definition of reversibility should specify the time frames over which both adsorption and desorption occurs. Additional research is needed."[37] (p.84)

"*Absorption* is used herein to describe that portion of sorption that possesses a significant time dependency. It is presumed that the rate of absorption is limited by one or more diffusion barriers. The time dependency may result from diffusion into pores whose size may require the sorbing ions to diffuse through an electric field to reach the interior of aggregates. Solid state diffusion into the structure of the solid is also propable."[37] (p.85)

Ligands are anions or molecules which form coordination compounds with metals. Ligands occupying one, two, three, etc., positions are referred to as unidentate, bidentate, tridentate, etc. Complex formation with multidentate ligands is called chelation, and the complexes are called *chelates.* If there is more that one meta atom (central atom) in a complex, it is called multi- or polynuclear complexes.[31]

Ions pairs are ions of opposite charge that approach within a critical distance effectively form an ion pair and are no longer electrostatically effective (outer-sphere complexes).[31] "The metal ion or the ligand or both retain the coordinated water when the complex compound is formed; that is, the metal ion and the base are separated by one or more water molecules."[31] (p. 255)

Complexes refer to most stable entities that result from the formation of largely covalent bonds between a metal ion and an electron-donating ligand—the interacting ligand is immediately adjacent to the metal cation—are called complexes (inner-sphere complexes).[31] (p.255)

APPENDIX 1.2

LEAD CONTENT IN ROCK-FORMING MATERIALS

Table A1.2 Summary of published analyses of lead content of igneous and metamorphic rocks.[28]

Rock type	No. of analyses	Lead content (ppm)		
		Range	Arithmetic average	Median
Granitic rocks	536	0-200	25.0	18
Granodiorite, adamellite	317	0-80	22.0	16
Diorite, quartz diorite	122	0-76	14.0	11
Alkalic rocks	153	0-500	22.0	16
Ultramafic rocks	34	0-37	2.0	…
Rhyolite, obsidian	273	0-200	21.0	18
Latite, quartz latite	49	0-50	25.0	21
Dacite, rhyodacite	121	0-300	12.0	11
Andesite	203	0-150	12.0	8
Basalt, gabbro, diabase	372	0-100	7.5	4
Trachyte, phonolite	33	0-60	18.0	16
Gneiss	274	0-80	20.0	12
Schist	81	0-100	15.0	15
Amphibolite	51	0-50	11.0	9

… = no data

*From Fleischer M. Lead in Igneous and Metamorphic Rocks and in Their Rock-Forming Minerals. Lovering TG, editor. Lead in the Environment: United States Prining Office; 1976. Table 8, p. 27

APPENDIX 1.3

SPECIES AND EQUILIBRIUM CONSTANTS

UNDER FRESHWATER CONDITIONS

Table A1.3 Pb(II) Speciation in Fresh Water.[31]

Components		Pb^{2+}	CO_3^{2-}	SO_4^{2-}	Cl^-	H^+	log K ($I = 5 \times 10^{-3}$, 25°C)
Species	Pb^{2+}	1	0	0	0	0	0
	$PbOH^+$	1	0	0	0	−1	−7.77
	$Pb(OH)_2$	1	0	0	0	−2	−17.17
	$Pb(OH)_3^-$	1	0	0	0	−3	−28.1
	$PbCO_3(aq)$	1	1	0	0	0	6.2
	$Pb(CO_3)_2^{2-}$	1	2	0	0	0	9.4
	$PbSO_4$	1	0	1	0	0	2.54
	$PbCl$	1	0	0	1	0	1.47
	$PbCl_2$	1	0	0	2	0	1.60
	$PbCl_3$	1	0	0	3	0	1.44
	$PbCl_4$	1	0	0	4	0	1.40
	HCO_3^-	0	1	0	0	1	10.20
	$H_2CO_3^*$	0	1	0	0	2	16.51
	CO_3^{2-}	0	1	0	0	0	0
	SO_4^{2-}	0	0	1	0	0	0
	Cl^-	0	0	0	1	0	0
	TOTX	10^{-9}	2×10^{-3}	3×10^{-4}	2.5×10^{-4}	pH given	

*From Stumm, Warner and Morgan, James J. 1996 *Aquatic Chemistry*, 3rd edition, Copyright © 1996 by J. Wiley & Sons, Inc; Tableau 6.4a p. 294, (This material is used by permission of J. Wiley & Sons, Inc).

APPENDIX 2

APPENDIX 2.1

PREVIOUS STUDIES OF LEAD CONTAMINATIONS AT GNB SITES

BY DELTA ENVIRONMENTAL CONSULTANTS, INC

Table A2.1 Previous studies of lead contamination at GNB sites by Delta Environmental Consultants, Inc

Year	Sample I.D.	Total Lead (mg/kg)
1996	874-96-140	65
	874-96-141	80
	874-96-142	29
	874-96-143	33
	874-96-144	35
	874-96-145	182
	874-96-146	27
	874-96-147	50
	874-96-148	10
	874-96-149	13
	874-96-150	<0.01
1997	874-97-673	67
	874-97-674	178
	874-97-675	39
	874-97-676	95
	874-97-677	73
	874-97-678	30
	874-97-679	153
	874-97-680	17
	874-97-681	80
	874-97-682	29
	874-97-683	<0.010

APPENDIX 3

APPENDIX 3.1

MINTEQA2'S DEFINITIONS

COMPONENTS AND SPECIES DEFINITIONS

Type I Components as Species in Solution

These are the components themselves defined as actual chemical species. As mentioned above, in the general case, a component need not be an actual chemical species. The set of available components in MINTEQA2 happens to include components that are all bona fide chemical species (excepting the electrostatic components). Thus, all (non-electrostatic) components in a MINTEQA2 problem will also be defined as Type I species.

Type II Other Species in Solution or Adsorbed

These are all dissolved species other than those that are Type I. These may be complexes or free ions, for example, Cr^{3+} (the component for Cr^{3+} is $Cr(OH)_2^+$). In so far as components may be thought of as reactants, Type II species may be considered aqueous and adsorption reaction products.

Type III Species with Fixed Activity

Generally, these are either species that are present at fixed equilibrium activity or are mock species that define a fixed equilibrium activity relationship between two real species. Examples of a Type III species are any solids that are explicitly constrained to be present at equilibrium (not subject to complete dissolution; an infinite solid), any components whose activities are explicitly constrained to a given equilibrium value (e.g. fixed pH or pe), any gases whose partial pressures are explicitly constrained to a given equilibrium pressure, or any mock species whose equilibrium activity is explicitly

constrained to an equilibrium value (such as a redox couple that fixes the equilibrium activity ratio of two components that form a redox pair.)

Type IV Finite Solids

These are solid phases that are presumed present initially or precipitate from the solution. In the latter case, the appropriate components are depleted in the aqueous phase to "create" the precipitated solids. With MINTEQA2, it is also possible to specify one or more precipitated solids as present initially at some given amount (per liter basis). For those Type IV solids that are specified as present initially, the entire amount may dissolve if equilibrium demands it and the concentrations of the appropriate components will then be supplemented in the aqueous phase.

Type V Possible (Undersaturated) Solids

These are solid phases that are defined in MINTEQA2; however, they are not oversaturated, do not oversaturated, do not physically exist, and thus have no direct impact on the equilibrium problem. When the solution becomes oversaturated with respect to a particular possible solid, and if that solid is more oversaturated than any other possible solid composed of the same components, MINTEQA2 will precipitate that solid depleting the aqueous phase concentrations of the appropriate components. The newly precipitated solid is then re-assigned as a Type IV species. If any Type IV solid dissolves completely so that its entire mass is shifted to the aqueors phase, that solid is reassigned as Type V. Note that in PRODEFA2 and in the listing of input data that MINTEQA2 includes in its output file, Type V solids are referred to as POSSIBLE solids. In the

listing of equilibrated results however, Type V species are referred to as UNDERSATURATED solids.

APPENDIX 3.2

MINTEQA2'S OUTPUTS OF pH 4, 7, AND 9

MINTEQA2'S OUTPUT OF pH 4

Part 1 and Part 4

PART 1 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 17-SEP-2002 TIME: 16: 1:49

Lead Equlibrating with Acetate Buffer at pH4 (with DOC) of contaminated soil
File name pH4_(3)
Component file (COMP.DBS): comp.dbs COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00 09/30/1999

Temperature (Celsius): 25.00
Units of concentration: mg/L
Ionic strength: 0.407 molal; FIXED
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed for all solids in the thermodynamic database and
the print option for solids is set to: 1
Maximum iterations: 500 and use convergence assist measure
The method used to compute activity coefficients is: Davies equation
Intermediate output file

---

330 0.000E+00 -4.00 y
30 7.252E+01 -1.57 y
150 1.247E+02 -1.51 y
281 1.771E+02 -1.50 y
410 1.440E+00 -3.43 y
600 1.004E+00 -4.31 y
460 1.120E+01 -2.34 y
470 4.380E+00 -3.10 y
500 1.386E+03 -1.22 y
770 7.405E+03 -0.11 y
732 8.170E+00 -3.07 y
140 3.300E+02 -1.26 y
580 1.849E+01 -2.71 y
992 3.558E+03 -1.22
144 0.000E+00 -6.00

H2O has been inserted as a COMPONENT
3 1
330 4.0000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.000E-04	-4.000	0.000E+00
30	Al+3	2.692E-02	-1.570	7.252E+01
150	Ca+2	3.090E-02	-1.510	1.247E+02
281	Fe+3	3.162E-02	-1.500	1.771E+02
410	K+1	3.715E-04	-3.430	1.440E+00
600	Pb+2	4.898E-05	-4.310	1.004E+00
460	Mg+2	4.571E-03	-2.340	1.120E+01
470	Mn+2	7.943E-04	-3.100	4.380E+00
500	Na+1	6.026E-02	-1.220	1.386E+03
770	H4SiO4	7.762E-01	-0.110	7.405E+03
732	SO4-2	8.511E-04	-3.070	8.170E+00
140	CO3-2	5.495E-02	-1.260	3.300E+02
580	PO4-3	1.950E-03	-2.710	1.849E+01
992	Acetate	6.026E-02	-1.220	3.558E+03
144	DOM1	1.000E-06	-6.000	0.000E+00
2	H2O	1.000E+00	0.000	0.000E+00

*** SPECIAL PARAMETERS for Dissolved Organic Matter:

Percent Organic Carbon:	50.00
DOC (mg/L):	50.60
Molecular Weight (g):	1000.00

Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:

Total Acidity (umol/mgC):	1.00
Total site concentration (mol/L):	5.060E-05

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 8.635E-02 Sum of ANIONS = 7.311E-02

PERCENT DIFFERENCE = 8.301E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:

Al+3	Log activity guess: -2.61
Fe+3	Log activity guess: -5.91
Mn+2	Log activity guess: -4.09
H4SiO4	Log activity guess: -1.11
SO4-2	Log activity guess: -4.07
CO3-2	Log activity guess: -10.94
PO4-3	Log activity guess: -15.28

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

DOM1
- 40.1 Percent bound in species # 144 DOM1
- 9.5 Percent bound in species #1443300 H DOM
- 39.2 Percent bound in species #1440300 Al DOM
- 10.1 Percent bound in species #1441500 Ca DOM

Acetate
- 20.7 Percent bound in species # 992 Acetate
- 78.6 Percent bound in species #3309921 H[Acetate]

Ca+2
- 94.5 Percent bound in species # 150 Ca+2
- 5.1 Percent bound in species #1509920 Ca[Acetate]

CO3-2
- 99.3 Percent bound in species #3301401 H2CO3 (aq)

K+1
- 99.6 Percent bound in species # 410 K+1

SO4-2
- 85.1 Percent bound in species # 732 SO4-2
- 1.9 Percent bound in species # 307320 AlSO4+
- 4.3 Percent bound in species #1507320 CaSO4 (aq)
- 7.9 Percent bound in species #5007320 NaSO4-

Mg+2
- 93.5 Percent bound in species # 460 Mg+2

6.2 Percent bound in species #4609920 Mg[Acetate]

PO4-3

96.5 Percent bound in species #3305801 H2PO4-

1.8 Percent bound in species #1505802 CaH2PO4+

Na+1

99.6 Percent bound in species # 500 Na+1

Pb+2

30.0 Percent bound in species # 600 Pb+2

10.2 Percent bound in species #1446000 Pb DOM

51.5 Percent bound in species #6009921 Pb[Acetate]

7.9 Percent bound in species #6009922 Pb[Acetate]2

H2O

94.1 Percent bound in species # 303300 AlOH+2

5.8 Percent bound in species # 303301 Al(OH)2+

H+1

18.6 Percent bound in species #3301401 H2CO3 (aq)

80.7 Percent bound in species #3309921 H[Acetate]

H4SiO4

100.0 Percent bound in species # 770 H4SiO4

Fe+3

6.6 Percent bound in species #1442810 Fe DOM

1.8 Percent bound in species #2813300 FeOH+2

27.4 Percent bound in species #2813301 Fe(OH)2+

4.9 Percent bound in species #2815800 FeHPO4+

2.7 Percent bound in species #2819920 Fe[Acetate]

34.5 Percent bound in species #2819921 Fe[Acetate]2

21.8 Percent bound in species #2819922 Fe[Acetate]3

Mn+2

91.6 Percent bound in species # 470 Mn+2

8.3 Percent bound in species #4709920 Mn[Acetate]

Al+3

84.0 Percent bound in species # 30 Al+3

13.1 Percent bound in species #1440300 Al DOM

1.7 Percent bound in species # 303300 AlOH+2

1.1 Percent bound in species # 307320 AlSO4+

MINTEQA2'S OUTPUT OF pH 7

Part 1 and Part 4

```
_____________________________________ PART 1 of OUTPUT FILE _____________________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS: 17-SEP-2002  TIME: 23: 0: 4


Lead Equlibrating with Phosphate Buffer at pH7 (with DOC)  of contaminated soil
File name pH7_(6)
Component file (COMP.DBS):          comp.dbs    COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF):    thermo.unf  THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS):   gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF):            type6.unf   TYPE6 V4.00 09/30/1999

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: mg/L
 Ionic strength:  0.368 molal; FIXED
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 Maximum iterations: 500 and use convergence assist measure
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
   330  0.000E+00   -7.00 y
    30  7.252E+01   -1.57 y
   150  1.247E+02   -1.51 y
   281  1.771E+02   -1.50 y
   410  1.440E+00   -3.43 y
   600  1.004E+00   -4.31 y
   460  1.120E+01   -2.34 y
   470  4.380E+00   -3.10 y
   500  2.060E+03   -1.05 y
   770  7.405E+03   -0.11 y
   732  8.170E+00   -3.07 y
   140  3.300E+02   -1.26 y
   580  8.521E+03   -1.05 y
   144  0.000E+00   -6.00

 H2O has been inserted as a COMPONENT
 3   1
   330     7.0000     0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS
```

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.000E-07	-7.000	0.000E+00
30	Al+3	2.692E-02	-1.570	7.252E+01
150	Ca+2	3.090E-02	-1.510	1.247E+02
281	Fe+3	3.162E-02	-1.500	1.771E+02
410	K+1	3.715E-04	-3.430	1.440E+00
600	Pb+2	4.898E-05	-4.310	1.004E+00
460	Mg+2	4.571E-03	-2.340	1.120E+01
470	Mn+2	7.943E-04	-3.100	4.380E+00
500	Na+1	8.913E-02	-1.050	2.060E+03
770	H4SiO4	7.762E-01	-0.110	7.405E+03
732	SO4-2	8.511E-04	-3.070	8.170E+00
140	CO3-2	5.495E-02	-1.260	3.300E+02
580	PO4-3	8.913E-02	-1.050	8.521E+03
144	DOM1	1.000E-06	-6.000	0.000E+00
2	H2O	1.000E+00	0.000	0.000E+00

*** SPECIAL PARAMETERS for Dissolved Organic Matter:
Percent Organic Carbon: 50.00
DOC (mg/l): 18.50
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:
Total Acidity (umol/mgC): 1.00
Total site concentration (mol/l): 1.850E-05

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 1.167E-01 Sum of ANIONS = 2.857E-01

PERCENT DIFFERENCE = 4.200E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
Al+3 Log activity guess: -7.92
Fe+3 Log activity guess: -11.94
Mn+2 Log activity guess: -4.09
H4SiO4 Log activity guess: -1.11
SO4-2 Log activity guess: -4.06
CO3-2 Log activity guess: -5.67
PO4-3 Log activity guess: -6.83

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

DOM1
87.6 Percent bound in species # 144 DOM1

1.2 Percent bound in species #1443300 H DOM

2.8 Percent bound in species #1441500 Ca DOM

8.4 Percent bound in species #1444600 Mg DOM

SO4-2
89.1 Percent bound in species # 732 SO4-2

10.7 Percent bound in species #5007320 NaSO4-

Mg+2
27.4 Percent bound in species # 460 Mg+2

10.9 Percent bound in species #4605801 MgH2PO4+

60.9 Percent bound in species #4605802 MgHPO4 (aq)

CO3-2
85.1 Percent bound in species #3301400 HCO3-

12.8 Percent bound in species #3301401 H2CO3 (aq)

1.8 Percent bound in species #5001401 NaHCO3 (aq)

K+1
90.7 Percent bound in species # 410 K+1

9.3 Percent bound in species #4105800 KHPO4-

Na+1
86.2 Percent bound in species # 500 Na+1

13.7 Percent bound in species #5005800 NaHPO4-

PO4-3

53.1 Percent bound in species #3305800 HPO4-2

32.6 Percent bound in species #3305801 H2PO4-

14.0 Percent bound in species #5005800 NaHPO4-

H2O

93.4 Percent bound in species #3300020 OH-

5.7 Percent bound in species # 303302 Al(OH)4-

H+1

38.0 Percent bound in species #3305800 HPO4-2

46.7 Percent bound in species #3305801 H2PO4-

10.0 Percent bound in species #5005800 NaHPO4-

3.8 Percent bound in species #3301400 HCO3-

1.2 Percent bound in species #3301401 H2CO3 (aq)

Fe+3

89.5 Percent bound in species #2813301 Fe(OH)2+

6.5 Percent bound in species #2813302 Fe(OH)3 (aq)

4.0 Percent bound in species #2815800 FeHPO4+

H4SiO4

99.8 Percent bound in species # 770 H4SiO4

Mn+2

97.3 Percent bound in species # 470 Mn+2

2.6 Percent bound in species #4701400 MnHCO3+

Pb+2

3.6 Percent bound in species # 600 Pb+2

87.6 Percent bound in species #1446000 Pb DOM

4.7 Percent bound in species #6001401 PbCO3 (aq)

3.7 Percent bound in species #6001402 PbHCO3+

Ca+2

33.3 Percent bound in species # 150 Ca+2

4.0 Percent bound in species #1441500 Ca DOM

53.8 Percent bound in species #1505800 CaHPO4 (aq)

2.1 Percent bound in species #1505801 CaPO4-

6.2 Percent bound in species #1505802 CaH2PO4+

Al+3

3.6 Percent bound in species # 303301 Al(OH)2+

4.9 Percent bound in species # 303303 Al(OH)3 (aq)

91.3 Percent bound in species # 303302 Al(OH)4-

MINTEQA2'S OUTPUT OF pH 9

Part 1 and Part 4

```
_____________________________________ PART 1 of OUTPUT FILE _____________________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS: 17-SEP-2002  TIME: 23:45:34


Lead equilibrated with Borate Buffer at pH9 (with DOC)  of contaminated soil
File name pH9_(1)
Component file (COMP.DBS):          comp.dbs    COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF):    thermo.unf  THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS):   gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF):            type6.unf   TYPE6 V4.00 09/30/1999

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: mg/L
 Ionic strength:  0.711 molal; FIXED
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 Maximum iterations: 500 and use convergence assist measure
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
   330  0.000E+00   -9.00 y
    30  7.252E+01   -1.57 y
   150  1.247E+02   -1.51 y
   281  1.771E+02   -1.50 y
   410  1.440E+00   -3.43 y
   600  1.004E+00   -4.31 y
   460  1.120E+01   -2.34 y
   470  4.380E+00   -3.10 y
   500  3.574E+03   -0.81 y
   770  7.405E+03   -0.11 y
   732  8.170E+00   -3.07 y
   140  3.300E+02   -1.26 y
   580  1.849E+01   -2.71 y
   144  0.000E+00   -6.00
    90  3.109E+04   -0.30

 H2O has been inserted as a COMPONENT
  3   1
   330     9.0000     0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS
```

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.000E-09	-9.000	0.000E+00
30	Al+3	2.692E-02	-1.570	7.252E+01
150	Ca+2	3.090E-02	-1.510	1.247E+02
281	Fe+3	3.162E-02	-1.500	1.771E+02
410	K+1	3.715E-04	-3.430	1.440E+00
600	Pb+2	4.898E-05	-4.310	1.004E+00
460	Mg+2	4.571E-03	-2.340	1.120E+01
470	Mn+2	7.943E-04	-3.100	4.380E+00
500	Na+1	1.549E-01	-0.810	3.574E+03
770	H4SiO4	7.762E-01	-0.110	7.405E+03
732	SO4-2	8.511E-04	-3.070	8.170E+00
140	CO3-2	5.495E-02	-1.260	3.300E+02
580	PO4-3	1.950E-03	-2.710	1.849E+01
144	DOM1	1.000E-06	-6.000	0.000E+00
90	H3BO3	5.012E-01	-0.300	3.109E+04
2	H2O	1.000E+00	0.000	0.000E+00

*** SPECIAL PARAMETERS for Dissolved Organic Matter:

Percent Organic Carbon: 50.00
DOC (mg/L): 18.40
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:

Total Acidity (umol/mgC): 1.00
Total site concentration (mol/L): 1.840E-05

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 1.885E-01 Sum of ANIONS = 1.233E-02

PERCENT DIFFERENCE = 8.772E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:

Al+3 Log activity guess: -15.86
Fe+3 Log activity guess: -17.23
Mn+2 Log activity guess: -4.09
H4SiO4 Log activity guess: -1.14
SO4-2 Log activity guess: -4.05
CO3-2 Log activity guess: -3.59
PO4-3 Log activity guess: -7.07

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

H3BO3
18.8 Percent bound in species # 90 H3BO3

2.0 Percent bound in species #5000901 NaH2BO3 (aq)

16.9 Percent bound in species #3300900 H2BO3-

3.4 Percent bound in species #3300901 H5(BO3)2-

58.9 Percent bound in species #3300902 H8(BO3)3-

Na+1
93.4 Percent bound in species # 500 Na+1

6.4 Percent bound in species #5000901 NaH2BO3 (aq)

SO4-2
79.2 Percent bound in species # 732 SO4-2

20.5 Percent bound in species #5007320 NaSO4-

DOM1
76.5 Percent bound in species # 144 DOM1

22.0 Percent bound in species #1441500 Ca DOM

1.5 Percent bound in species #1444600 Mg DOM

K+1
100.0 Percent bound in species # 410 K+1

CO3-2
8.8 Percent bound in species # 140 CO3-2

79.7 Percent bound in species #3301400 HCO3-

7.9 Percent bound in species #5001400 NaCO3-

3.2 Percent bound in species #5001401 NaHCO3 (aq)

H2O

93.8 Percent bound in species #3300020 OH-

5.6 Percent bound in species # 303302 Al(OH)4-

H+1

4.9 Percent bound in species #5000901 NaH2BO3 (aq)

42.5 Percent bound in species #3300900 H2BO3-

4.3 Percent bound in species #3300901 H5(BO3)2-

49.4 Percent bound in species #3300902 H8(BO3)3-

H4SiO4

84.3 Percent bound in species # 770 H4SiO4

15.6 Percent bound in species #3307700 H3SiO4-

Fe+3

5.7 Percent bound in species #2813301 Fe(OH)2+

38.5 Percent bound in species #2813302 Fe(OH)3 (aq)

55.9 Percent bound in species #2813303 Fe(OH)4-

PO4-3

62.4 Percent bound in species #3305800 HPO4-2

1.2 Percent bound in species #1505801 CaPO4-

35.3 Percent bound in species #5005800 NaHPO4-

Mn+2

97.4 Percent bound in species # 470 Mn+2

1.0 Percent bound in species #4703300 MnOH+

1.5 Percent bound in species #4701400 MnHCO3+

Al+3

99.9 Percent bound in species # 303302 Al(OH)4-

Ca+2

36.8 Percent bound in species # 150 Ca+2

60.4 Percent bound in species #1500901 CaH2BO3+

1.2 Percent bound in species #1441500 Ca DOM

1.2 Percent bound in species #1501401 CaCO3 (aq)

Pb+2

4.3 Percent bound in species #1446000 Pb DOM

6.8 Percent bound in species #6003300 PbOH+

1.4 Percent bound in species #6003301 Pb(OH)2 (aq)

41.6 Percent bound in species #6001400 Pb(CO3)2-2

45.0 Percent bound in species #6001401 PbCO3 (aq)

Mg+2

49.4 Percent bound in species # 460 Mg+2

1.1 Percent bound in species #4601400 MgCO3 (aq)

48.8 Percent bound in species #4600901 MgH2BO3+

APPENDIX 3.3

MINTEQA2'S INPUT PARAMETERS

Pb (II) & 4 SOLUBLE MAJOR CATIONS

Part 1 and Part 4 (Only Pb (II))

PART 1 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 1-OCT-2002 TIME: 16:22: 4

Soluble cations at pH4 (equilibrated with acetate buffer) of contaminated soil
File name so_(1)
Component file (COMP.DBS): comp.dbs COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00 09/30/1999

Temperature (Celsius): 25.00
Units of concentration: mg/L
Ionic strength: 0.407 molal; FIXED
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed only for those solids specified as ALLOWED
in the input file (if any).
Maximum iterations: 200
The method used to compute activity coefficients is: Davies equation
Intermediate output file

---

330 0.000E+00 -4.00 y
600 2.520E-01 -5.91 y
150 1.556E+02 -2.56 y
460 3.703E+00 -3.94 y
30 3.200E+00 -4.45 y
992 3.558E+03 -1.22 y
500 1.386E+03 -1.22 y
144 0.000E+00 -6.00
280 2.169E+01 -3.41

H2O has been inserted as a COMPONENT
3 1
330 4.0000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.000E-04	-4.000	0.000E+00
600	Pb+2	1.230E-06	-5.910	2.520E-01
150	Ca+2	2.754E-03	-2.560	1.556E+02
460	Mg+2	1.148E-04	-3.940	3.703E+00
30	Al+3	3.548E-05	-4.450	3.200E+00

992	Acetate	6.026E-02	-1.220	3.558E+03
500	Na+1	6.026E-02	-1.220	1.386E+03
144	DOM1	1.000E-06	-6.000	0.000E+00
280	Fe+2	3.890E-04	-3.410	2.169E+01
2	H2O	1.000E+00	0.000	0.000E+00

*** SPECIAL PARAMETERS for Dissolved Organic Matter:
Percent Organic Carbon: 50.00
DOC (mg/L): 50.60
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:
Total Acidity (umol/mgC): 1.00
Total site concentration (mol/L): 5.060E-05

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 6.985E-02 Sum of ANIONS = 6.071E-02

PERCENT DIFFERENCE = 7.000E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
Al+3 Log activity guess: -3.97
Fe+2 Log activity guess: -3.41

PART 4 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 1-OCT-2002 TIME: 16:22: 4

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2

29.9 Percent bound in species # 600 Pb+2

11.3 Percent bound in species #1446000 Pb DOM

51.0 Percent bound in species #6009921 Pb[Acetate]

7.8 Percent bound in species #6009922 Pb[Acetate]2

Pb (II)

Part 1 and Part 4 (Only Pb (II))

```
_____________________________________ PART 1 of OUTPUT FILE _____________________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS:  1-OCT-2002  TIME: 17:36:27


Soluble cations at pH4 (equilibrated with acetate buffer) no 4 ions of contaminate soil
File name so_(111)
Component file (COMP.DBS):          comp.dbs    COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF):    thermo.unf  THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS):   gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF):            type6.unf   TYPE6 V4.00 09/30/1999

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: mg/L
 Ionic strength:  0.407 molal; FIXED
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 Maximum iterations: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
   330  0.000E+00   -4.00 y
   600  2.520E-01   -5.91 y
   992  3.558E+03   -1.22 y
   500  1.386E+03   -1.22 y
   144  0.000E+00   -6.00 y

 H2O has been inserted as a COMPONENT
  3   1
   330     4.0000     0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

  ID       Name       ACTIVITY GUESS    log GUESS   ANAL TOTAL
   330  H+1              1.000E-04        -4.000   0.000E+00
   600  Pb+2             1.230E-06        -5.910   2.520E-01
   992  Acetate          6.026E-02         -1.220   3.558E+03
   500  Na+1             6.026E-02        -1.220   1.386E+03
   144  DOM1               1.000E-06        -6.000   0.000E+00
     2  H2O              1.000E+00         0.000   0.000E+00

--------------------------------------------------------------------------------
```

*** SPECIAL PARAMETERS for Dissolved Organic Matter:
Percent Organic Carbon: 50.00
DOC (mg/L): 50.60
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:
Total Acidity (umol/mgC): 1.00
Total site concentration (mol/L): 5.060E-05

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 6.059E-02 Sum of ANIONS = 6.070E-02

PERCENT DIFFERENCE = 9.120E-02 (ANIONS - CATIONS)/(ANIONS + CATIONS)

PART 4 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 1-OCT-2002 TIME: 17:36:27

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2

19.2 Percent bound in species # 600 Pb+2

5.0 Percent bound in species #6009922 Pb[Acetate]2

43.0 Percent bound in species #1446000 Pb DOM

32.8 Percent bound in species #6009921 Pb[Acetate]

DOM = 10% OF VS

Part 1 and Part 4 (Only Pb (II))

```
_____________________________________ PART 1 of OUTPUT FILE _____________________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS:  1-OCT-2002  TIME: 15:47:58


Soluble cations at pH4 (equilibrated with acetate buffer) of standard sediment
File name so_(22)
Component file (COMP.DBS):          comp.dbs    COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF):    thermo.unf  THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS):   gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF):            type6.unf   TYPE6 V4.00 09/30/1999

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: mg/L
 Ionic strength:  0.407 molal; FIXED
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 Maximum iterations: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
   330  0.000E+00   -4.00 y
   600  1.051E+00   -5.91 y
   150  3.258E+02   -2.56 y
   460  6.100E+01   -3.94 y
    30  8.427E+00   -4.45 y
   992  3.558E+03   -1.22 y
   500  1.386E+03   -1.22 y
   144  0.000E+00   -6.00
   280  5.110E+01   -3.04

 H2O has been inserted as a COMPONENT
 3   1
   330     4.0000     0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

  ID       Name       ACTIVITY GUESS    log GUESS   ANAL TOTAL
   330  H+1              1.000E-04        -4.000   0.000E+00
   600  Pb+2             1.230E-06        -5.910   1.051E+00
   150  Ca+2             2.754E-03        -2.560   3.258E+02
   460  Mg+2              1.148E-04        -3.940   6.100E+01
```

```
 30  Al+3            3.548E-05      -4.450   8.427E+00
992  Acetate         6.026E-02      -1.220   3.558E+03
500  Na+1            6.026E-02      -1.220   1.386E+03
144  DOM1            1.000E-06      -6.000   0.000E+00
280  Fe+2            9.120E-04      -3.040   5.110E+01
  2  H2O             1.000E+00       0.000   0.000E+00

--------------------------------------------------------------------------------
 *** SPECIAL PARAMETERS for Dissolved Organic Matter:
    Percent Organic Carbon:                  50.00
    DOC (mg/L):                              91.50
    Molecular Weight (g):                  1000.00
    Charge on DOM species are calculated based on speciation

  ** DOC COMPONENT 144:
    Total Acidity (umol/mgC):                1.00
    Total site concentration (mol/L):        9.150E-05

    The ratio Cs/Cn is:                      0.50

--------------------------------------------------------------------------------


    Charge Balance: UNSPECIATED

     Sum of CATIONS=  8.480E-02 Sum of ANIONS =  6.084E-02

     PERCENT DIFFERENCE =  1.645E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

          ---------------------------------------------------
          IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
             Al+3       Log activity guess:   -3.55
             Fe+2       Log activity guess:   -3.04

          ---------------------------------------------------


_____________________________________ PART 4 of OUTPUT FILE _____________________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS:  1-OCT-2002  TIME: 15:47:59

           PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
          TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2
       30.4     Percent bound in species #    600   Pb+2

       10.5     Percent bound in species #1446000   Pb DOM

       51.4     Percent bound in species #6009921   Pb[Acetate]

        7.8     Percent bound in species #6009922   Pb[Acetate]2
```

DOM = 19.2% OF VS

Part 1 and Part 4 (Only Pb (II))

PART 1 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 2-OCT-2002 TIME: 14:21:54

Soluble cations at pH4 (equilibrated with acetate buffer)
File name so_std176
Component file (COMP.DBS): comp.dbs COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00 09/30/1999

Temperature (Celsius): 25.00
Units of concentration: mg/L
Ionic strength: 0.407 molal; FIXED
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed only for those solids specified as ALLOWED
in the input file (if any).
Maximum iterations: 200
The method used to compute activity coefficients is: Davies equation
Intermediate output file

---

330 0.000E+00 -4.00 y
600 1.051E+00 -5.91 y
150 3.258E+02 -2.56 y
460 6.100E+01 -3.94 y
30 8.427E+00 -4.45 y
992 3.558E+03 -1.22 y
500 1.386E+03 -1.22 y
144 0.000E+00 -6.00
280 5.110E+01 -3.04

H2O has been inserted as a COMPONENT
3 1
330 4.0000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.000E-04	-4.000	0.000E+00
600	Pb+2	1.230E-06	-5.910	1.051E+00
150	Ca+2	2.754E-03	-2.560	3.258E+02
460	Mg+2	1.148E-04	-3.940	6.100E+01
30	Al+3	3.548E-05	-4.450	8.427E+00
992	Acetate	6.026E-02	-1.220	3.558E+03

```
  500  Na+1            6.026E-02      -1.220   1.386E+03
  144  DOM1            1.000E-06      -6.000   0.000E+00
  280  Fe+2            9.120E-04      -3.040   5.110E+01
    2  H2O             1.000E+00       0.000   0.000E+00

--------------------------------------------------------------------------------
 *** SPECIAL PARAMETERS for Dissolved Organic Matter:
    Percent Organic Carbon:                  50.00
    DOC (mg/L):                             176.00
    Molecular Weight (g):                  1000.00
    Charge on DOM species are calculated based on speciation

  ** DOC COMPONENT 144:
    Total Acidity (umol/mgC):                1.00
    Total site concentration (mol/L):        1.760E-04

    The ratio Cs/Cn is:                      0.50

--------------------------------------------------------------------------------


    Charge Balance: UNSPECIATED

     Sum of CATIONS=  8.480E-02 Sum of ANIONS =  6.108E-02

     PERCENT DIFFERENCE =  1.626E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

          ---------------------------------------------------
          IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
             Al+3       Log activity guess:   -3.55
             Fe+2       Log activity guess:   -3.04

          ---------------------------------------------------
```


PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2

27.3 Percent bound in species # 600 Pb+2

19.4 Percent bound in species #1446000 Pb DOM

46.2 Percent bound in species #6009921 Pb[Acetate]

7.0 Percent bound in species #6009922 Pb[Acetate]2

DOM = 100% OF VS

Part 1 and Part 4 (Only Pb (II))

_____ PART 1 of OUTPUT FILE _____

MINTEQA2 v4.02 DATE OF CALCULATIONS: 2-OCT-2002 TIME: 14: 8:24

Soluble cations at pH4 (equilibrated with acetate buffer) of standard sediement
File name so_(222)
Component file (COMP.DBS): comp.dbs COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00 09/30/1999

Temperature (Celsius): 25.00
Units of concentration: mg/L
Ionic strength: 0.407 molal; FIXED
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed only for those solids specified as ALLOWED
in the input file (if any).
Maximum iterations: 200
The method used to compute activity coefficients is: Davies equation
Intermediate output file

---

330 0.000E+00 -4.00 y
600 1.051E+00 -5.91 y
150 3.258E+02 -2.56 y
460 6.100E+01 -3.94 y
30 8.427E+00 -4.45 y
992 3.558E+03 -1.22 y
500 1.386E+03 -1.22 y
144 0.000E+00 -6.00
280 5.110E+01 -3.04

H2O has been inserted as a COMPONENT
3 1
330 4.0000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.000E-04	-4.000	0.000E+00
600	Pb+2	1.230E-06	-5.910	1.051E+00
150	Ca+2	2.754E-03	-2.560	3.258E+02
460	Mg+2	1.148E-04	-3.940	6.100E+01
30	Al+3	3.548E-05	-4.450	8.427E+00
992	Acetate	6.026E-02	-1.220	3.558E+03

```
  500  Na+1          6.026E-02     -1.220   1.386E+03
  144  DOM1          1.000E-06     -6.000   0.000E+00
  280  Fe+2          9.120E-04     -3.040   5.110E+01
    2  H2O           1.000E+00      0.000   0.000E+00

--------------------------------------------------------------------------------
 *** SPECIAL PARAMETERS for Dissolved Organic Matter:
    Percent Organic Carbon:                50.00
    DOC (mg/L):                           915.00
    Molecular Weight (g):                1000.00
    Charge on DOM species are calculated based on speciation

  ** DOC COMPONENT 144:
    Total Acidity (umol/mgC):              1.00
    Total site concentration (mol/L):      9.150E-04

    The ratio Cs/Cn is:                    0.50

--------------------------------------------------------------------------------


    Charge Balance: UNSPECIATED

     Sum of CATIONS=  8.480E-02 Sum of ANIONS =  6.315E-02

     PERCENT DIFFERENCE =  1.463E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

          ----------------------------------------------------
          IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
             Al+3       Log activity guess:   -3.55
             Fe+2       Log activity guess:   -3.04

          ----------------------------------------------------
```


PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2

11.0 Percent bound in species # 600 Pb+2

67.4 Percent bound in species #1446000 Pb DOM

18.7 Percent bound in species #6009921 Pb[Acetate]

2.8 Percent bound in species #6009922 Pb[Acetate]2

APPENDIX 3.4

Pb DISTRIBUTION BY MINTEQA2

AT pH 5.22

Pb DISTRIBUTION AT pH 5.22

Part 1-6

```
_____________________________________ PART 1 of OUTPUT FILE _____________________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS: 17-SEP-2002  TIME:  7:44:44


Lead Perchlorate pH 5.22
File name Pb_(1)
Component file (COMP.DBS):          comp.dbs    COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF):    thermo.unf  THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS):   gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF):            type6.unf   TYPE6 V4.00 09/30/1999

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength:  0.004 molal; FIXED
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 Maximum iterations: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
   330  6.026E-06   -5.22 y
   600  2.410E-05   -4.62 y
   492  2.410E-05   -4.62 y

 H2O has been inserted as a COMPONENT

INPUT DATA BEFORE TYPE MODIFICATIONS

  ID       Name      ACTIVITY GUESS    log GUESS   ANAL TOTAL
   330  H+1             6.026E-06       -5.220   6.026E-06
   600  Pb+2            2.399E-05       -4.620   2.410E-05
   492  NO3-1           2.399E-05       -4.620   2.410E-05
     2  H2O             1.000E+00        0.000   0.000E+00


    Charge Balance: UNSPECIATED

     Sum of CATIONS=  5.423E-05 Sum of ANIONS =  2.410E-05

     PERCENT DIFFERENCE =  3.846E+01  (ANIONS - CATIONS)/(ANIONS + CATIONS)
```

PART 2 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 17-SEP-2002 TIME: 7:44:45

CONSTRAINTS ON COMPONENT ACTIVITIES

As specified, this chemical system is OPEN with respect to the following components:

H2O

Activities of the following components are constrained by the species shown:

COMPONENT	SPECIES	TYPE
H2O	H2O	3

PART 3 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 17-SEP-2002 TIME: 7:44:45

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL mol/L	DIFF FXN	LOG ACTVTY	RESIDUAL
0	NO3-1	2.410E-05	-1.032E-07	-4.62000	1.007E-07
1	NO3-1	2.410E-05	1.710E-06	-4.61814	1.708E-06
2	H+1	6.026E-06	1.315E-09	-5.24332	7.035E-10

ID No	Name	Total Conc(M)	Conc (M)	log Activity	Diff fxn
330	H+1	6.026E-06	6.115E-06	-5.24341	-4.833E-15
600	Pb+2	2.410E-05	2.401E-05	-4.73877	4.749E-15
492	NO3-1	2.410E-05	2.409E-05	-4.64788	-1.870E-18
2	H2O	0.000E+00	-8.852E-08	0.00000	0.000E+00

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID No	Name	Conc (M)	log Act	Charge	Act Coef	New logK
330	H+1	6.115E-06	-5.24341	1.00	0.93374	0.030
600	Pb+2	2.401E-05	-4.73877	2.00	0.76015	0.119
492	NO3-1	2.409E-05	-4.64788	-1.00	0.93374	0.030

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID No	Name	Conc (M)	log Act	Charge	Act Coef	New logK
6004921	Pb(NO3)2 (aq)	2.318E-13	-12.63452	0.00	1.00092	1.400
3300020	OH-	1.889E-09	-8.75359	-1.00	0.93374	-13.967
6003300	PbOH+	8.658E-08	-7.09235	1.00	0.93374	-7.567
6003301	Pb(OH)2 (aq)	4.505E-12	-11.34594	0.00	1.00092	-17.094
6003302	Pb(OH)3-	8.516E-18	-17.09953	-1.00	0.93374	-28.061
6003303	Pb2OH+3	4.334E-11	-10.63112	3.00	0.53954	-6.129
6003304	Pb3(OH)4+2	9.738E-18	-17.13065	2.00	0.76015	-23.769
6003305	Pb(OH)4-2	4.518E-24	-23.46412	-2.00	0.76015	-39.580
6003306	Pb4(OH)4+4	3.214E-18	-17.96941	4.00	0.33389	-19.512
6004920	PbNO3+	6.503E-09	-8.21664	1.00	0.93374	1.200

Type III - SPECIES WITH FIXED ACTIVITY

ID No	Name	Conc (M)	New logK	Enthalpy
2	H2O	-8.852E-08	0.000	0.000

Type V - UNDERSATURATED SOLIDS (not present at equilibrium)

ID No	Name	Conc (M)	New logK	Enthalpy
2060000	MASSICOT	7.146E-08	-12.894	66.848
2060001	LITHARGE	1.133E-07	-12.694	65.501
2060002	PbO:0.3H2O	5.862E-08	-12.980	0.000
2060004	Pb(OH)2	3.963E-03	-8.150	58.534
2060005	Pb2O(OH)2	2.033E-15	-26.188	0.000

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

H+1

101.5 Percent bound in species # 330 H+1

Pb+2

99.6 Percent bound in species # 600 Pb+2

NO3-1

100.0 Percent bound in species # 492 NO3-1

H2O

2.1 Percent bound in species #3300020 OH-

97.8 Percent bound in species #6003300 PbOH+

PART 5 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 17-SEP-2002 TIME: 7:44:45

---------- EQUILIBRATED MASS DISTRIBUTION ----------

IDX	Name	DISSOLVED		SORBED		PRECIPITATED	
		mol/L	percent	mol/L	percent	mol/L	percent
330	H+1	6.026E-06	100.0	0.000E+00	0.0	0.000E+00	0.0
600	Pb+2	2.410E-05	100.0	0.000E+00	0.0	0.000E+00	0.0
492	NO3-1	2.410E-05	100.0	0.000E+00	0.0	0.000E+00	0.0
2	H2O	8.852E-08	100.0	0.000E+00	0.0	0.000E+00	0.0

Charge Balance: SPECIATED

Sum of CATIONS = 5.422E-05 Sum of ANIONS 2.410E-05

PERCENT DIFFERENCE = 3.847E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 4.000E-03

EQUILIBRIUM pH = 5.243

DATE ID NUMBER: 20020917
TIME ID NUMBER: 7444578

PART 6 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 17-SEP-2002 TIME: 7:44:45

Saturation indices and stoichiometry of all minerals

ID No	Name	SI	Composition by stoich. of components
2060000	MASSICOT	-7.146	[1.000]600 [1.000] 2 [-2.000]330
2060001	LITHARGE	-6.946	[1.000]600 [1.000] 2 [-2.000]330
2060002	PbO:0.3H2O	-7.232	[-2.000]330 [1.000]600 [1.330] 2
2060004	Pb(OH)2	-2.402	[-2.000]330 [1.000]600 [2.000] 2
2060005	Pb2O(OH)2	-14.692	[2.000]600 [3.000] 2 [-4.000]330

APPENDIX 3.5

STATISTIC CALCULATION BY SAS PROGRAM

FOR Pb:FA

STATISTIC CALCULATION

BY SAS

Statistics used to compare between two means for the areas of with (Pb:FA 1:1) and without lead (Pb:FA 0:1) were Independent T-Test for parametric distribution data and Mann Whitney U Test or Wilcoxon Two-Sample Test for non-parametric distribution data. From the distributions of the data as shown in Table A3.5.1, at wavelength 254 and 260 nm non-parametric tests were applied while at wavelength 280 nm, a parametric test was applied.

For comparing between three means of the concentrations lead of organically bound fraction at between 9 to 11 minutes as data was shown in Table A3.5.2, since one was parametric and the other two data were non-parametric distributions both parametric (One-Way Parametric ANOVA) and non-parametric (Kruskal-Wallis One-Way Multisample Test) were run to compare the results.

Conclusion of statistic tests

1. There is no significant difference between total areas at 254 nm of Pb:FA = 0:1 and 1:1, Mann Whitney U Test, P = 0.5959, $\alpha = 0.05$.

2. There is no significant difference between total areas at 260 nm of Pb:FA = 0:1 and 1:1, Mann Whitney U Test, P = 0.3074, $\alpha = 0.05$.

3. There is no significant difference between total areas at 280 nm of Pb:FA = 0:1 and 1:1, Independent T Test, P = 0.6689, $\alpha = 0.05$.

4. There are no significant differences among Pb:FA 1:1, 1:2, and 1:3 at between 9 to 11 minutes both by One-Way Parametric ANOVA, $P = 0.6205$, $\alpha = 0.05$ and Kruskal-Wallis One-Way Multisample Test, $P = 0.2963$, $\alpha = 0.05$.

Table A3.5.1 Total areas of fulvic acid with and without lead and when the ligand was incresed

Pb:FA 0:1	Total area at 254 nm*	Total area at 260 nm**	Total area at 280 nm***
R1	1,971	1,669	4,068
R2	1,972	1,635	4,057
R3	2,112	1,787	4,317
R4	3,052	2,612	5,148
Mean	2,276.8	1,925.8	4,397.5
SD	451.3	400.2	445.6

Pb:FA 1:1	Total area at 254 nm*	Total area at 260 nm**	Total area at 280 nm***
R1	1,989	1,661	4,630
R2	2,400	1,957	5,083
R3	2,622	2,086	5,323
Mean	2,337.0	1,901.3	5,012.0
SD	262.2	177.9	287.3

Pb:FA 1:2	Total area at 254 nm	Total area at 260 nm	Total area at 280 nm
R1	5,788	4,464	8,081
R2	6,717	5,098	9,618
R3	6,294	4,548	8,774
R4	6,397	4,686	9,261
Mean	6,299.0	4,699.0	8,933.5
SD	333.7	243.6	576.2

Pb:FA 1:3	Total area at 254 nm	Total area at 260 nm	Total area at 280 nm
R1	7,949	6,010	10,787
R2	16,466	8,780	13,707
R3	13,848	7,982	13,480
R4	17,346	9,606	14,389
Mean	13,902.3	8,094.5	13,090.8
SD	3,670.0	1,333.4	1,371.5

* There is no significant difference between total areas at 254 nm of Pb:FA = 0:1 and 1:1, Mann Whitney U Test, P=0.5959, α=0.05.

**There is no significant difference between total areas at 260 nm of Pb:FA = 0:1 and 1:1, Mann Whitney U Test, P=0.3074, α =0.05.

***There is no significant difference between total areas at 280 nm of Pb:FA = 0:1 and 1:1, Independent T Test, P=0.6689, α=0.05.

Table A3.5.2 Lead concentrations in each fraction of organically bound lead study; Pb = lead and FA = fulvic acid

Pb:FA	Time						
0:1	0-4	4-5.5	5.5-9	9-11	11-15	15-25	Total (ug)
R1	0	0	0	0	0	0	0
R2	0	0	0	0	0	0	0
R3	0.005	0.002	0.004	0.003	0	0	0.01
Average	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SD	0.00	0.00	0.00	0.00	0.00	0.00	0.01

Pb:FA	Time							Recovery
1:1	0-4	4-5.5	5.5-9	9-11*	11-15	15-25	Total (ug)	%
R1	0.081	0.174	0.347	0.065	0	0	0.667	90.6
R2	0.11	0.132	0.36	0.074	0	0	0.676	91.8
R3	0.09	0.21	0.299	0.074	0	0	0.673	91.4
Average	0.09	0.17	0.34	0.07	0.00	0.00	0.67	91.27
SD	0.01	0.04	0.03	0.01	0.00	0.00	0.00	0.61

Total injection = 0.736 ug

Pb:FA	Time							Recovery
1:2	0-4	4-5.5	5.5-9	9-11*	11-15	15-25	Total (ug)	%
R1	0.041	0.26	0.48	0.097	0	0	0.878	114.3
R2	0.05	0.24	0.41	0.12	0	0	0.78	101.6
R3	0.024	0.174	0.491	0.065	0	0	0.754	98
R4	0	0.207	0.518	0.076	0	0	0.801	104.3
Average	0.03	0.22	0.47	0.09	0.00	0.00	0.80	104.55
SD	0.02	0.04	0.05	0.02	0.00	0.00	0.05	6.99

Total injection = 0.768 ug

Pb:FA	Time							Recovery
1:3	0-4	4-5.5	5.5-9	9-11*	11-15	15-25	Total (ug)	%
R1	0.058	0.149	0.36	0.057	0	0	0.624	81.3
R2	0.0495	0.172	0.347	0.061	0	0	0.63	82
R3	0	0.194	0.36	0.127	0	0	0.681	88.7
R4	0.083	0.127	0.482	0.057	0	0	0.749	97.5
Average	0.05	0.16	0.39	0.08	0.00	0.00	0.67	87.38
SD	0.03	0.03	0.06	0.03	0.00	0.00	0.06	7.53

Total injection = 0.768 *u*g

* The concentrations among Pb:FA equal to 1:1, 1:2, and 1:3 at 9 to 11 mins are not significantly different (Kruskal-Wallis one-way multisample test, P=0.2963, $\alpha = 0.05$).

APPENDIX 3.6

MINTEQA2'S OUTPUTS OF Pb:FA

Pb:FA = 1:1

Part 1 and Part 4

PART 1 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 23-SEP-2002 TIME: 10: 1:23

Pb:FA = 1:1
File name org_(111) add buffer
Component file (COMP.DBS): comp.dbs COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00 09/30/1999

Temperature (Celsius): 25.00
Units of concentration: MOLAL
Ionic strength: 0.029 molal; FIXED
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed only for those solids specified as ALLOWED
in the input file (if any).
Maximum iterations: 200
The method used to compute activity coefficients is: Davies equation
Intermediate output file

---

330 0.000E+00 -3.80 y
600 1.780E-04 -3.75 y
144 0.000E+00 -6.00 y
410 4.700E-03 -2.33
500 3.000E-03 -2.52 y
580 1.070E-02 -1.97 y

H2O has been inserted as a COMPONENT
3 1
330 3.8000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	1.585E-04	-3.800	0.000E+00
600	Pb+2	1.778E-04	-3.750	1.780E-04
144	DOM1	1.000E-06	-6.000	0.000E+00
410	K+1	4.677E-03	-2.330	4.700E-03
500	Na+1	3.020E-03	-2.520	3.000E-03
580	PO4-3	1.072E-02	-1.970	1.070E-02
2	H2O	1.000E+00	0.000	0.000E+00

*** SPECIAL PARAMETERS for Dissolved Organic Matter:
Percent Organic Carbon: 50.00
DOC (mg/L): 200.00
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:
Total Acidity (umol/mgC): 1.00
Total site concentration (mol/L): 2.000E-04

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 8.056E-03 Sum of ANIONS = 3.266E-02

PERCENT DIFFERENCE = 6.043E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
PO4-3 Log activity guess: -13.94

_____

_____ PART 4 of OUTPUT FILE _____

MINTEQA2 v4.02 DATE OF CALCULATIONS: 23-SEP-2002 TIME: 10: 1:24

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2

37.3 Percent bound in species # 600 Pb+2

62.7 Percent bound in species #1446000 Pb DOM

DOM1

33.7 Percent bound in species # 144 DOM1

10.5 Percent bound in species #1443300 H DOM

55.8 Percent bound in species #1446000 Pb DOM

Pb:FA = 1:2

Part 1 and Part 4

PART 1 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 23-SEP-2002 TIME: 10: 6:32

Pb:FA = 1:1
File name org_(222) add buffer
Component file (COMP.DBS): comp.dbs COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00 09/30/1999

Temperature (Celsius): 25.00
Units of concentration: MOLAL
Ionic strength: 0.029 molal; FIXED
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed only for those solids specified as ALLOWED
in the input file (if any).
Maximum iterations: 200
The method used to compute activity coefficients is: Davies equation
Intermediate output file

---

330 0.000E+00 -3.48 y
600 1.850E-04 -3.73 y
144 0.000E+00 -6.00 y
410 4.700E-03 -2.33
580 1.070E-02 -1.97 y
500 3.000E-03 -2.52 y

H2O has been inserted as a COMPONENT
3 1
330 3.4800 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	3.311E-04	-3.480	0.000E+00
600	Pb+2	1.862E-04	-3.730	1.850E-04
144	DOM1	1.000E-06	-6.000	0.000E+00
410	K+1	4.677E-03	-2.330	4.700E-03
580	PO4-3	1.072E-02	-1.970	1.070E-02
500	Na+1	3.020E-03	-2.520	3.000E-03
2	H2O	1.000E+00	0.000	0.000E+00

*** SPECIAL PARAMETERS for Dissolved Organic Matter:
Percent Organic Carbon: 50.00
DOC (mg/L): 400.00
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:
Total Acidity (umol/mgC): 1.00
Total site concentration (mol/L): 4.000E-04

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 8.070E-03 Sum of ANIONS = 3.322E-02

PERCENT DIFFERENCE = 6.091E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
PO4-3 Log activity guess: -14.58

_____ PART 4 of OUTPUT FILE _____
MINTEQA2 v4.02 DATE OF CALCULATIONS: 23-SEP-2002 TIME: 10: 6:34

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2
18.9 Percent bound in species # 600 Pb+2

81.1 Percent bound in species #1446000 Pb DOM

DOM1
35.4 Percent bound in species # 144 DOM1

27.0 Percent bound in species #1443300 H DOM

37.5 Percent bound in species #1446000 Pb DOM

Pb:FA = 1:3

Part 1 and Part 4

```
_____________________________________________________________________________
_____________________________ PART 1 of OUTPUT FILE _____________________________
 MINTEQA2  v4.02   DATE OF CALCULATIONS: 23-SEP-2002  TIME: 10:18:51


Pb:FA = 1:3
File name org_(333) add buffer
Component file (COMP.DBS):          comp.dbs    COMP v4.00 09/30/1999
Thermodynamic file (THERMO.UNF):    thermo.unf  THERMO V4.00 09/30/1999
Gaussian DOM file (GAUSSIAN.DBS):   gaussian.dbsGAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF):            type6.unf   TYPE6 V4.00 09/30/1999

-------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength:  0.029 molal; FIXED
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 Maximum iterations: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

-------------------------------------------------------------------------------
   330  0.000E+00   -3.46 y
   600  1.850E-04   -3.73 y
   144  0.000E+00   -6.00 y
   410  4.700E-03   -2.33
   500  3.000E-03   -2.52 y
   580  1.070E-02   -1.97 y

 H2O has been inserted as a COMPONENT
  3   1
   330     3.4600     0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

   ID       Name       ACTIVITY GUESS    log GUESS   ANAL TOTAL
   330  H+1              3.467E-04        -3.460   0.000E+00
   600  Pb+2             1.862E-04        -3.730   1.850E-04
   144  DOM1               1.000E-06        -6.000   0.000E+00
   410  K+1              4.677E-03        -2.330   4.700E-03
   500  Na+1             3.020E-03        -2.520   3.000E-03
   580  PO4-3            1.072E-02        -1.970   1.070E-02
     2  H2O              1.000E+00         0.000   0.000E+00
```

*** SPECIAL PARAMETERS for Dissolved Organic Matter:
Percent Organic Carbon: 50.00
DOC (mg/L): 600.00
Molecular Weight (g): 1000.00
Charge on DOM species are calculated based on speciation

** DOC COMPONENT 144:
Total Acidity (umol/mgC): 1.00
Total site concentration (mol/L): 6.000E-04

The ratio Cs/Cn is: 0.50

Charge Balance: UNSPECIATED

Sum of CATIONS= 8.070E-03 Sum of ANIONS = 3.378E-02

PERCENT DIFFERENCE = 6.143E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
PO4-3 Log activity guess: -14.62

PART 4 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: 23-SEP-2002 TIME: 10:18:52

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

Pb+2

10.9 Percent bound in species # 600 Pb+2

89.1 Percent bound in species #1446000 Pb DOM

DOM1

37.4 Percent bound in species # 144 DOM1

35.1 Percent bound in species #1443300 H DOM

27.5 Percent bound in species #1446000 Pb DOM

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