SIGNIFICANCE OF pH AND pCl IN
HEAVY METAL ION REACTIONS AND
MERCURY(II) ADSORPTION BY SOIL MATERIALS

by

Hermann Carl Heinrich Hahne

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree
DOCTOR OF PHILOSOPHY
in
Agronomy

APPROVED:

Chairman. Dr. W. Kroontje

Dr. T. B. Hutcheson, Jr.

Dr. C. I. Rich

Dr. J. P. Wightman

Mr. J. A. Lutz

June 1973

Blacksburg, Virginia

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his major professor Dr. Wybe Kroontje for his guidance and encouragement throughout the past years and for the confidence he places in his students. He wishes to acknowledge Dr. Kroontje for his outgoing nature and determination which gave the author the privileged opportunity to pursue his education at this university.

Appreciation is extended to Dr. C. I. Rich, Dr. T. B. Hutcheson, Dr. J. P. Wightman and Mr. J. A. Lutz for serving on the graduate committee and their willingness to discuss matters pertaining to this investigation. A special word of thanks to Dr. Rich for the time he spent to create interest beyond the field of this investigation.

The advantage of receiving an assistantship from the university through arrangements initiated by Dr. W. Kroontje and Dr. T. B. Hutcheson, Head of the Department of Agronomy, is gratefully appreciated.

The author wishes to express his indebtedness to the Department of Agricultural Technical Services, Pretoria, Republic of South Africa, who granted the author leave of absence under unprecedented conditions. He further wishes to express his sincere appreciation to Dr. M. C. F. duPlessis, Director, Soils Research Institute, Pretoria; Messrs. J. F. Peens and H. G. Snyman, Director and Assistant Director, Tobacco Research Institute, Rustenburg, Republic of South Africa for their continuous interest and encouragement during the tenure of the graduate program.

The writer wishes to thank Dr. T. R. Terrill and Dr. G. R. Buss for their willingness to aid in solving problems encountered during the development of computer programs. He thanks Ms. Peggy Epperly for typing the manuscript and Phyllis Hypes for assisting with some of the analytical work.

A special word of thanks is given to his mother and he is grateful to his late father whose continuous encouragement and support have been of invaluable assistance throughout his educational career.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

LIST OF TABLES

LIST OF TABLES (Cont.)

LIST OF FIGURES

LIST OF FIGURES (Cont.)

Page

LIST OF FIGURES (Cont.)

INTRODUCTION

In the past five years research on heavy metals with respect to environmental quality has gained increasing momentum. Although much emphasis is placed on pollution due to man's activities, factors controlling the natural occurence and distribution of heavy metals have received equal interest. The increase in rate of sewage and industrial waste disposal as well as mining activities compound the problem of heavy metal pollution.

Although inorganic complexes have been studied extensively and are utilized in the analytical field, their subtle and rather important impact on heavy metal reactions are not always taken into account. Frequently, distributions and reactions of heavy metal ions are considered in terms of organic complexes and precipitation due to higher pH conditions or in relation to precipitating anions. Since heavy metals display toxicity at low concentrations, the solubility product approach is inadequate in assessing the status of heavy metal ions in solution. Determinations of ionic adsorption phenomena on colloidal surfaces are often based on the valency of ions which may lead to erroneous interpretations if formation of inorganic complexes is omitted. Furthermore, the competition between inorganic and organic ligands can be of significant magnitude under environmental conditions.

In the present investigation the effect of chloride and hydroxyl ions on the behavior of Hg(II), Cd(II), Zn(II) and Pb(II) in solutions were compared and related to environmental as well as experimental aspects. Chloride and hydroxyl ions were chosen since both occur at significant levels in natural waters and soil solutions.

The present investigations were performed under the following objectives:

1. To compare by computational means the degree of complexation Hg(II), Zn(II), Cd(II), and Pb(II) undergo with chloride and hydroxyl ions.
2. To assess the degree of competition between chloride and hydroxyl ions for the heavy metal ions with greater emphasis on the Hg(II)-complexes.
3. To evaluate the significance of chloride and hydroxy complexes of heavy metals with regard to solubilities of sparingly soluble salts at chloride ion concentration and pH levels encountered in natural waters and soil solutions.
4. To determine Hg(II) adsorption on clays at different Hg(II) and chloride ion concentrations with emphasis on the Hg(II) species distributions in the equilibrium solution.
5. To derive an itterative procedure for the prediction of potentiometric titrations of Hg(II)-chloride complexes at any Hg(II) and chloride ion concentrations.
6. To evaluate the potentiometric titration procedure as a means to determine the effectiveness of chlorides in competing with organic functional groups for Hg(II).

LITERATURE REVIEW

Since comprehensive reviews on heavy metals in the environment are available, the purpose of this review is to present more specific aspects pertaining to the studies undertaken. The behavior and concentration levels of Hg(II) will receive greater attention because its reactions in the environment are more complex and it was the element of main interest in these investigations.

Recent reviews by Lagerwerff (1967, 1972) present a comprehensive view of the significance of zinc, and lead, mercury and cadmium as pollutants in the environment. Mercury has also been extensively reviewed by D'Itri (1972). The importance of these elements is evident from the very low allowable concentrations in drinking water. The threshhold levels for Hg, Cd and Pb is 5, 10 and 50 μg/l, respectively (Lagerwerff, 1972).

Forms of Hg in Soils and Waters

Although the present studies deal with Hg(II), the mercuric ion, however, is not the only form in which Hg exists in soils and waters. Mercury unlike zinc, cadmium and lead is more sensitive to redox conditions. The three main oxidation states encountered are Hg^0, Hg_2^{2+} and Hg^{2+} of which the latter two are normally referred to as Hg(I) and Hg(II). Hem (1970) presents E_h - pH diagrams showing fields of stability for solid, liquid and aqueous mercury species. In assessing the advantages and disadvantages of these models Hem (1970) cautions against departures from such theoretical considerations in natural systems. The reason for limitations of the diagrams is that formation of organic complexes, the dismutation of $Hg_2^{2+} \rightleftarrows Hg^0 + Hg^{++}$ and the fact that HgS formation requires Hg(II) under reducing conditions were not included when the diagrams were prepared. The dismutation phenomenon of Hg_2^{2+} has also been reported by Glasstone (1946) and was used by Gilmour and Miller (1973) to explain data obtained from trials where Caloclor (60% Hg_2Cl_2 - 30% $HgCl_2$) were added to soils and turf.

Jernelöv (1969) quotes the redox relationship for the Hg^0 - Hg^{++} couple derived by Werner (1967) and concludes that at 2ppm Hg^{++} a redox potential of only 80 mV is required to promote oxidation of Hg^0 to Hg^{++} when the formation constant for the organo-mercuric complex is in the order of 10^{21}. Similar effects can be expected in the presence of high chloride concentrations since complexation of Hg(II) with Cl^- will affect the redox couple. Hutchinson (1957) reports that the redox potential of oxygenated water at or near natural pH values are in the range of 520 mV which, when compared to the diagrams by Hem (1970) for aqueous species, would favor Hg(II) formation.

The complexity of the reactions of mercury in nature is well illustrated by the geochemical cycle for mercury as well as the cycle of mercury interconversions presented by Jonasson and Boyle (1971). The importance of microbial activity is evident from the findings on methylation of Hg (Jensen and Jernelöv, 1969; Wood, Rosen, and Kennedy, 1968; Landner, 1971) and the decomposition of organic mercurial compounds by mercury resistant bacteria (Furukawa, Suzuki and Tonomura, 1969; Kimura and Miller, 1964).

Effect of pH and pCl on Heavy Metal Ions

Solution phenomena:

Hydrolysis, or alternatively hydroxy complexes, as well as other inorganic and organic complexes of heavy metal ions are discussed extensively in the field of analytical chemistry (Kolthoff, Sandell *et al*., 1969; Laitinen, 1960; Ringbom, 1963). The degree of complexation between heavy metal ions and organic ligands depends markedly on pH and the ionic composition of the supporting electrolyte (Ringbom, 1963; Norvell, 1972). Inorganic complexes have been well illustrated by Stumm and Morgan (1970) and Butler (1964) for both saturated and unsaturated systems. The latter author includes discussions on chloride complexes of Hg(II) and Cd(II) and hydroxy complexes of Hg(II).

Adsorption phenomena:

Hydrolysis of metal-ion complexes significantly change the adsorption characteristics of metal ions on charged colloidal materials (Stumm *et al*., 1962; Matijevic, Abramson, Schulz and Kerker, 1960; Matijevic, Abramson, Ottewill, Schulz and Kerker, 1961; Matijevic, Mathai, Ottewill and Kerker, 1961). The increase in adsorption affinity seems to be more pronounced for polynuclear polyhydroxy species. This enhancement of adsorption is likely due to the presence of a larger number of coordinated hydroxyl groups per complex ion (Stumm and O'Meila, 1968) resulting in stronger bonding at the colloid surface. Another reason for the observed differences is that the hydrated ion is present at lower pH values and, therefore, experiences greater competition by hydrogen ions for the exchange sites (Matijevic, Abramson et al., 1961).

Ion exchange equilibria of mono- and divalent cations have often been studied using the relationship derived by Gapon (1933) or its modified form (Lagerwerff and Bolt, 1959; Bower, 1959). Recently similar studies were employed with Cd(II) (Lagerwerff and Brower, 1972) and Pb(II) (Lagerwerff et al., 1973). However, unlike Na^+, K^+, Ca^{++}, and Mg^{++}, hydrolysis and chloride complexation of heavy metal ions will determine whether exchange relationships like the Gapon equation can be utilized to describe exchange phenomena. Feick, Horne, and Yeaple (1972) desorbed significant amounts of Hg(II) from freshwater sediments high in organic matter by adding NaCl and $CaCl_2$ at rates of 35 and 165 g/l, respectively.

Chloride Concentrations in Waters and Soil Solutions

The chloride ion may be regarded as a universal component of all natural waters displaying seasonal and locational variations. The chloride content of rainwater in the U.S.A. varies from >2 ppm in the East to <0.5 ppm in the West. The seasonal variation for southeast Virginia and North Carolina is in the order of 0.2 to 1 ppm (Durum, 1971).

Chloride concentrations of groundwater are highly variable. Data listed by Durum (1971) and Allison (1964) give concentration ranges of 3-40 and 17-1200 ppm, respectively. A significant factor to consider is the effect of deicing salts on chloride content of groundwater. Effect of deicing salts on natural waters have been reviewed by Hanes, Zelazny and Blaser (1970). The degree of groundwater pollution by deicing salts was remarkable in New Hampshire where affected wells contained 3500-3800 ppm chloride as compared to less than 10 ppm in the non-contaminated wells. Huling and Hollochner (1972) estimate that at least 35 percent of salt applied in winter infiltrates and eventually reaches the groundwater.

Chloride concentrations of surface waters vary markedly between localities and display seasonal fluctuations to a significant degree. Chloride concentrations at specific localities of eight rivers in the U.S.A. were in the range between a low value of 3 ppm in the Delaware river and a high value of 730 ppm in the Colorado river near the Grand Canyon. A seasonal variation of 650 ppm was observed at the latter locality (Durum, 1971). Rhoades and Bernstein (1971) show that the chloride concentration of the Rio Grande river increased with distance downstream, the difference over 456 miles being 5-630 ppm. Bubeck, Diment, Deck, Baldwin and Lipton (1971) found that deicing salts increased the chloride concentration in the Irondequoit Bay at least five fold over the last two decades with seasonal variations ranging between 100-400 ppm. They also report that during winter ten small streams and storm sewers discharging into the bay had chloride concentrations ranging from 700 to 4000 ppm. The average chloride concentrations of rivers of the world is 0.22 meq. per liter (7.8 ppm) (Rhoades *et al.*, 1971).

Chloride concentrations in soil solutions depend highly on soil type and climatic conditions. Rhoades *et al.* (1971) list soils with a chloride concentration range of 0.7-2956 meq. per liter (24-105,000 ppm). The data by Reitemeier and Richards (1944) is more complete for different soils under arid conditions with extreme chloride values of 72,000 ppm. Therefore, chloride concentrations of some soil solutions exceed levels encountered in oceans, i.e., 20,000 ppm (Klein, 1959). by an appreciable amount.

Mercury Content of Waters and Sediments

Analytical data on mercury contents of various waters have been compiled by Jonasson *et al.* (1971), Wershaw (1970), and Fleischer (1970). The general concentration ranges are as follows: Rainwater, 0.05-0.48 ppb with an average of 0.2 ppb; normal groundwaters, 0.01-0.10 ppb and groundwaters near polymetallic sulphide deposits, 1-1000 ppb; normal stream, river and lake waters, 0.01-0.1 ppb with mean of 0.03 ppb; streams and rivers near mercury deposits, 0.5-100 ppb; ocean and seas, 0.03-5.0 ppb with a mean of 0.2 ppb.

Soils contain about 20-150 ppb; near mercury deposits 200-1800 (mean 480) ppb in the A horizon and 150-600 ppb in subsequent horizons (Jonasson *et al.*, 1971). More detailed information on Hg content of soils is given by Fleischer (1970).

Mercury contents of sediments from streams and rivers, lakes and oceans are 10-700, 10-700, and <10-2000 ppb, respectively (Jonasson et al., 1971). Voege (1971) records 1-50 ppm Hg in a substantial number of sediment samples taken from areas which may have been contaminated by chlor-alkali and paper and pulp industries. The highest value of 1700 ppm Hg was obtained from the St. Clair river where the corresponding concentration in the water was 0.5 ppm Hg. Cranston and Buckley (1972) made a Hg survey in the LaHave river and estuary. The Hg concentration of the water varied between 0.036-0.380 ppb, the suspended particulate matter contained 3.59-34.4 ppm Hg, and the range in Hg concentrations for bottom sediments was 0.09-1.06 ppm.

Among the massive data available on mercury content of geological deposits, coal deposits are probably of prime importance since they are comparatively high in mercury and are utilized continuously. The concentration ranges for fossil fuels given by Jonasson et al. (1971) are: coal, 10-8500 ppb; coal in mercuferous basins (e.g., Donets and Donbas basin, USSR), 20-300,000 ppb; petroleum, 1900-21,000 ppb; natural gas (Cymric field, California), saturated with mercury vapor; Bitumins, solid hydrocarbons, and asphalts, 2,000-900,000 ppb (some such as idrialite go up to percentages of Hg). Joensuu (1971) presents data on 36 American coals which show a concentration range of 0.7-33 ppm, the samples with the highest value being from Clay, West Virginia, and Richland, Montana.

Mercury Adsorption on Clays

Limited information is available on the exchange properties of Hg(II) on sedimentary material. Ginzburg (1960) reports that preferential uptake of cations by montmorillonite follows the series Pb>Cu>Ca>Ba>Mg>Hg, and that the capacity of heavy metals to replace Ca on kaolinite is in the order Pb>Cu>Hg. Krauskopf (1956) concludes from his experiments that 96 percent of added Hg(II) was sorbed onto montmorillonite from simulated seawater at pH 7.7-8.2. Newton and Ellis (1972)[1] found that Hg(II) adsorption by bentonite was proportional to Hg(II) concentrations at low Hg(II) levels, but at the same time the percent of added Hg(II) adsorbed fell rapidly at Hg(II) concentrations above 0.2 ppm. They also report that at the 0.2 ppm Hg(II) level and pH 4.6-4.9 bentonite adsorbed 50 percent of added Hg(II) in 0.01 M $Ca(NO_3)_2$, whereas in 0.01 M $CaCl_2$ only 8.4 percent was adsorbed. At higher pH levels maximum adsorption occurred in the chloride rather than in the nitrate system.

Gilmour and Keeney (1971)[2] equilibrated river sediments with mercuric chloride and methyl mercuric chloride at a wide sediment to water ratio. In the ppb range, both mercuric forms were removed from

---

[1] Newton, D. W. and R. Ellis. 1972. Mercury adsorption by clay minerals. Agronomy Abstracts, 1972 Annual Meetings, American Society of Agronomy. Oct. 29-Nov. 2, 1972. p. 88.

[2] Gilmour, J. T. and D. R. Keeney. 1971. Sorption of mercury by river sediments. Agronomy Abstracts, 1971 Annual Meetings, American Society of Agronomy. Aug. 15-20, 1971. p. 145.

solution and nearly quantitatively sorbed, and after resuspension desorption was negligible. At ppm levels a smaller percentage of added mercury sorbed, rate of sorption was less, and relative magnitude of desorption increased when resuspended.

Potentiometric Titrations

Potentiometric titrations have frequently been used to study interactions between organic complexing agents and metal ions (Beckwith, 1955, 1959; Martin and Reeve, 1958; Khanna and Stevenson, 1962; Schnitzer and Skinner, 1963; Khan, 1969). In most cases titrations were performed at constant ionic strength with 0.1 M KCl commonly having been employed as the supporting electrolyte (Khan, 1969; Khanna *et al.*, 1962; Schnitzer *et al.*, 1963). The influence of ionic strength on metal-ion complex formations with fulvic acid has been demonstrated by Schnitzer and Hansen (1970).

Salt effects on the ionization of polyelectrolytes have been well established (Gregor and Frederick, 1957; Michaeli and Katchalsky, 1957; Gregor, Luttinger and Loebl, 1955). In general, an increase in the concentration of the supporting electrolyte promotes ionization. Kagawa and Gregor (1957) also demonstrate that a decrease in the size of the counterion increases ionization. The behavior of polyelectrolytes as opposed to monomeric acids is complicated by the electrostatic charge accumulation on the polymer as neutralization advances which results in the carboxylic acid groups becoming weaker in acidity (Gamble, 1970; Gregor *et al.*, 1955).

While reviewing potentiometric titrations it was noticed that there seems to be a lack of information on the nature of titrations where inorganic complexes, other than hydroxy complexes, participate during the course of titrations on organo-metal-ion complexes.

METHODS AND MATERIALS

Derivations of Formulas

Extensive derivations on metal ligand (organic and inorganic) reactions are given by Laitinen (1960), Kolthoff et al. (1969), and Ringbom (1963). For this reason, only the basic equations used are outlined, omitting the individual steps of their derivations.

In all calculations performed, concentrations were used excluding effects of ionic strength and activity coefficients. This approach was chosen since the effects were studied over a wide concentration range and hence, exclusion of excessive detail is desirable. Furthermore, many of the relationships reported are independent of exact stoichiometric concentrations, whereas known stoichiometry is a prerequisite for determinations of ionic strengths and subsequent activities. The use of activity coefficients has to be exercised with proper discretion (Babcock and Marion, 1972). These authors also clearly demonstrate that in systems where ion-pairing is predominant, stoichiometric concentrations require first correction for ion-pairing before activities can be applied in the calculations.

Values of the cumulative formation constants and solubility products used in the present calculations were obtained from Sillen and Martell (1964) and are listed in Table 1.

Table 1. Formation constants and solubility products used in calculations.*

	Formation constants				Solubility products	
System	Log β_1	Log β_2	Log β_3	Log β_4	Precipitate	Log Ksp
Zn-Cl	0.43	0.61	0.53	0.20	$Zn_3(PO_4)_2$	-32.04
Cd-Cl	1.32	2.22	2.31	1.86	ZnS	-25.15
Hg-Cl	6.74	13.22	14.07	15.07	$Zn(OH)_2$	-15.50
Pb-Cl	0.88	1.49	1.09	0.94	$Cd_3PO_4)_2$	-32.60
Zn-OH	4.40	12.89	15.86	15.95	CdS	-27.92
Cd-OH	4.30	7.70	10.30	12.00	$Cd(OH)_2$	-13.55
Hg-OH	11.86	22.13	---	---	$Pb_3(PO_4)_2$	-42.10
Pb-OH	7.82	10.88	13.94	16.30	PbS	-28.15
					$Pb(OH)_2$	-19.52
					HgS	-53.50
					$Hg(OH)_2$	-25.40

	Log β_1	Log β_{12}	Log β_{13}
PO_4-H	12.325	19.532	21.693
S-H	14.920	21.960	---

*Adapted from Sillen and Martell (1964).

Ionic and molecular species distributions:

The successive equilibria formed when a metal ion M^{++} reacts with an anion A^- to form j number of complexes may be represented by

$$M^{++} + jA^- \rightleftarrows MA_j^{2-j} , \qquad [1]$$

where j designates the j^{th} complex.

The cumulative formation constants for the j^{th} complex are given by

$$\beta_j = \frac{[MA_j^{2-j}]}{[M^{++}][A^-]^j} , \qquad [2]$$

where $[A^-]$ is the concentration of the unbound anion, in this study the unbound $[Cl^-]$ and $[OH^-]$.

In order to determine the fractions of the different species present at a certain $[A^-]$ concentration in terms of the total concentration of M(II) present in solution, it is necessary to define the latter. When j number of complexes are formed, the total metal-ion (bound plus unbound) concentration in solution is defined as

$$C_M = [M^{++}] + \sum_{j=1}^{j} [MA_j^{2-j}] . \qquad [3]$$

By substituting equation [2] into equation [3] and dividing by $[M^{++}]$, equation [3] resolves into

$$\frac{C_M}{[M^{++}]} = 1 + \sum_{j=1}^{j} \beta_j [A^-]^j , \qquad [4]$$

therefore, the fraction of the non-complexed metal-ion M^{++} (i.e., M^{++}/C_M) is given by

$$fr_{M^{++}} = \frac{1}{1 + \sum_{j=1}^{j} \beta_j [A^-]^j} \quad . \qquad [5]$$

The remaining fractions of the various M(II) complexes are obtainable from the expression

$$fr_{MA_j^{2-j}} = \beta_j [A^-]^j . fr_{M^{++}} \quad . \qquad [6]$$

For the present purpose a maximum of four equilibria (i.e., j=4) was considered since Cl⁻ and OH⁻ form four main complexes with the metal ions discussed, an exception being the Hg-OH system in which only two main hydroxy species are encountered. The results obtained for the hydroxy complexes are given in Figures 1-4 (pp. 33-36) and those for the chloride complexes in Figures 5-8 (pp. 42-45).

Relationships [1] through [6] may be extended for multiple systems where i number of anions complex with the metal ion simultaneously, each anion forming j number of complexes. In such multiple systems, equation [4] is extended to

$$\frac{C_M}{[M^{++}]} = 1 + \sum_{i=1}^{i} \sum_{j=1}^{j} \beta_{ij} [A_i^-]^j \quad , \qquad [7]$$

and the required fractions are determined by

$$fr_{M^{++}} = \frac{1}{1 + \sum_{i=1}^{i} \sum_{j=1}^{j} \beta_{ij} [A_i^-]^j} \qquad [8]$$

and

$$fr_{MA_{ij}^{2-j}} = \beta_{ij} [A_i^-]^j \ . \ fr_{M^{++}} \quad , \qquad [9]$$

respectively.

Relationships [8] and [9] were used to compute the simultaneous chloride and hydroxy species distributions given in Figures 9-18 (pp. 51-58, 64, and 65).

Effect of hydrolysis and chloride complexation on solubilities:

Cation and anion hydrolysis of sparingly soluble compounds is an important factor in determining solubilities from solubility products and numerous examples can be obtained in almost any analytical chemistry reference book. However, these effects are often omitted; a recent example is the determination on the solubility of $Pb(OH)_2$ reported by Lagerwerff et al. (1973). Since the effect of hydrolysis may be substantial, its importance cannot be overemphasized, while the same is true for any other complexes when present in solution.

Calculations on metal-ion hydrolysis can be performed by two alternative ways; first, the hydrated metal-ion is considered as a Brönsted acid, and secondly as the formation of complexes where the hydroxyl ions are considered as substituting ligands. The latter procedure was applied, since it entails computations similar to those described in the previous section. For the metal-ion chloride complexes the same procedure is followed. In the case of anion hydrolysis, the same principle applies when the hydrogen ion is used as the substituting ligand.

The solubility product of sparingly soluble compounds M_mX_n is defined as

$$K_{sp} = (mS)^m (nS)^n \qquad [10]$$

where S is the molar solubility, and mS and nS are the concentrations of the cation M^{n+} and anion X^{m-}, respectively. The precipitating anions are designated as X^{m-} to differentiate them from the complexing anion A^- used in the previous section.

The molar solubility of the precipitate, omitting hydrolysis or the effect of chloride complexation, is according to equation [10]

$$S = \left[\frac{K_{sp}}{m^m.n^n}\right]^{1/(m+n)} \qquad [11]$$

When M^{++} undergoes hydrolysis and/or complexation with chloride ions or any other anions, it follows from equations [4] and [5] or [7] and [8] that the amount of M^{++} in solution is

$$[M^{n+}] = fr_{M^{n+}}.C_M \qquad [12]$$

Similarly, the concentration of the precipitating anion X^{m-} when undergoing hydrolysis becomes

$$[X^{m-}] = fr_{X^{m-}}.C_X \, , \qquad [13]$$

where C_X is the total soluble amount of the precipitating anion in solution.

By substituting [12] and [13] into [11], the conditional molar solubility of the sparingly soluble compound is given by

$$S' = \left[\frac{K_{sp}}{(m^m.n^n)(fr^m_{M^{n+}}.fr^n_{X^{m-}})}\right]^{1/(m+n)} = \left[\frac{K'_{sp}}{m^m.n^n}\right]^{1/(m+n)} \qquad [14]$$

where K'_{sp} denotes the conditional solubility product. Results on conditional solubilities are given in Tables 2 and 4 (pp. 38 and 48).

Intrinsic solubilities of heavy metal hydroxides:

Solubility products, or for that matter conditional solubility products, are not always sufficient in predicting solubilities of sparingly soluble compounds. The reason is that solubility products are based on the ionic product and do not account for the solubility of compounds in its undissociated form which is referred to as the intrinsic solubility (Laitinen, 1960). The intrinsic solubility becomes important when formation of complexes takes place with the precipitating anion, of which the heavy metal hydroxides are an example. The $M(OH)_2$ species is the form with limited solubility in the M-OH sequence of complexes of Zn(II), Cd(II), Pb(II), and Hg(II).

The intrinsic solubility is normally defined as

$$S^\circ = [M(OH)_2]_{solution} = [M(OH)_2^\circ] \ . \qquad [15]$$

Using equation [2] the concentration of $M(OH)_2^\circ$ can be expressed as

$$[M(OH)_2^\circ] = \beta_2 K_{sp} = S^\circ \ . \qquad [16]$$

The intrinsic solubilities calculated by relationship [16] are listed in Table 3 (p. 41).

Prediction of potentiometric titrations of complexes:

The course of a titration in which heavy metal complexes are involved may be described with the aid of the "anion addition" or "mean anion (ligand) number" concept developed by Bjerrum (1941). In the following section the basic formulas are included for a single component system which in turn is extended to a multiple component system and finally developed to an itterative procedure for predicting potentiometric titrations. The predicted values may be compared with experimental potentiometric titration curves, which is a test of whether the chosen constants are suitable for any particular system used. Furthermore, the theoretically devised relationships may aid considerably in interpreting experimental titrations; however, such interpretations have to be exercised with caution, as shown in the discussion on potentiometric titrations. In all cases the assumption is made that only mononuclear complexes are involved.

Single component system:

The single component system describes the situation where only one complexing anion is present, and therefore, disregards any competition effects between complexes.

When an anion A^- complexes with a metal-ion M^{++} to form j number of complexes, then the total anion concentration C_A in solution is given by

$$C_A = [A^-] + \sum_{j=1}^{j} j[MA_j^{2-j}] \, . \qquad [17]$$

The average number of anions complexed per metal-ion ($\bar{n}$) is obtained by

$$\bar{n} = \frac{C_A-[A^-]}{C_M} \, , \qquad [18]$$

where C_M is defined by equation [3].

Since $[A^-]$ is the measured entity during the course of the potentiometric titration, the necessity arises to express $\bar{n}$ in terms of $[A^-]$. This is achieved by substituting equations [3] and [17] into equation [18] which results in

$$\bar{n} = \frac{\sum_{j=1}^{j} j[MA_j^{2-j}]}{[M^{++}] + \sum_{j=1}^{j} [MA_j^{2-j}]} , \qquad [19]$$

which in turn with the aid of equation [2] and subsequent division of numerator and denominator by common factor $[M^{++}]$ resolves to

$$\bar{n} = \frac{\sum_{j=1}^{j} j\beta_j[A^-]^j}{1 + \sum_{j=1}^{j} \beta_j[A^-]^j} . \qquad [20]$$

Equation [20] was used to determine $\bar{n}_{OH}$ and $\bar{n}_{Cl}$ distributions given in Figures 19 and 20 (pp. 80 and 81).

Multiple component system:

The single component system, although it indicates the behavior of each type of complex and furnishes the opportunity to test the validity of certain chosen sets of constants (i.e., β values), has the great disadvantage of being limited to ranges where no competition between the complexes takes place.

Since Hg(II) complexes at very low chloride and hydroxyl ion concentrations, the application of the single component system becomes rather remote except for titrations in the presence of only hydroxyl or chloride ions. In the latter case a chloride selective ion electrode with higher sensitivity than the ones presently available as well as acidic conditions below pH 1 are required. Therefore, for Hg(II) titrations the multiple component system becomes a necessity which is in essence only an extension of the derivations involved in the single component system.

In a multi-component system where the metal-ion complexes with i number of anions and each anion forms j number of complexes, the average anion number for the i^{th} anion ($\bar{n}_i$) is obtained by following a similar procedure outlined by equations [17] through [20] which gives

$$\bar{n}_i = \frac{\sum\limits_{j=1}^{j} j\beta_{ij}[A_i^-]^j}{1 + \sum\limits_{i=1}^{i} \sum\limits_{j=1}^{j} \beta_{ij}[A_i^-]^j} . \qquad [21]$$

Equation [21] was employed to compile $\bar{n}_{OH}$ and $\bar{n}_{Cl}$ values represented by the solid lines in Figure 21 (p. 84).

The above-mentioned relationships are all expressed in terms of unbound anion concentrations which require that $[A_i^-]$ is known or measurable and remains constant during the course of the potentiometric titration. The latter condition will hold if $C_A >> C_M$.

Itteration procedure for potentiometric titration predictions:

In the present study titrations were performed at Hg(II) and chloride concentration ranges where the unbound chloride ion concentration did not maintain constancy during the course of the titration. Therefore, in order to predict the expected course of the titration, an itteration procedure was developed which is based on equations [18] and [21].

Since the titrations were carried out by measuring the pH during the course of the titration, the itteration procedure was carried out with $[OH^-]$ as known variable and $[Cl^-]$ as the unknown variable. To demonstrate the itteration procedure more explicitly, the general terms in equation [21] are separated into more specific terms with respect to Cl^- and OH^-.

Equation [18] can be rearranged as follows

$$C_{Cl} = \bar{n}_{Cl}C_M + [Cl^-] \ , \qquad [22]$$

which by using equation [21] becomes

$$C_{Cl} = \frac{\sum_{j=1}^{4} j\beta_{Cj}[Cl^-]^j}{1 + \sum_{j=1}^{4} \beta_{Cj}[Cl^-]^j + \sum_{j=1}^{2} \beta_{Oj}[OH^-]^j} \cdot C_M + [Cl^-] \ , \qquad [23]$$

where β_{Cj} and β_{Oj} represent the j^{th} cumulative formation constant for the j^{th} chloride and hydroxy complex of Hg(II), respectively.

Relationship [23] when expressed in terms of $[Cl^-]$ becomes a fifth order polynomial which can only be solved by substituting values on a trial basis, hence making itteration a necessity.

For a particular known total Hg(II) concentration (C_M) and known total chloride concentration (C_{Cl}) the itterative solution for $[Cl^-]$ proceeds by starting, for example, at pH 2 (pOH = 12) and increasing the $[Cl^-]$ in steps of $10^{0.05}$ M from an initial $[Cl^-]$ of 10^{-10} M until the right-hand side of equation [23] equals C_{Cl}; at this point $\bar{n}_{Cl}$ and $\bar{n}_{OH}$ are calculated by equation [21] and recorded. The pH is then increased by 0.1 pH unit and the same process is repeated. This procedure is repeated until $\bar{n}_{OH}$ reaches its maximum value of 2.0, a condition reached at the end of the titration involving base addition. The results for systems containing 100 ppm Hg(II) and 10^{-3} M and

10^{-4} M [Cl^-] are given by the broken lines marked $\bar{n}'_{Cl}$, $\bar{n}'_{OH}$, and $\bar{n}''_{Cl}$, $\bar{n}''_{OH}$, respectively, in Figure 21 (p. 84).

Adsorption of Hg(II) on Clays

Preparation of clay samples:

Clay minerals used in the equilibrium studies were obtained from Ward's Natural Science Establishment, Inc. and are designated as follows: montmorillonite #25, John C. Lane Tract, Upton, Wyoming (Cat. No. 48W0230); kaolinite #3, Birch Pit, Macon, Georgia (Cat. No. 45W0230); illite #36, Morris, Illinois (Cat. No. 48W1536); and vermiculite ("Zonolite"), Libby, Montana.

The <2μ clay fraction size was extracted by the method of Jackson (1956). A sufficient amount of each clay was Ca saturated using 1N $CaCl_2$. Excess salt was removed by washing with deionized water (centrifuge method) until the silver nitrate test for chlorides in the supernatant solution was negative. The montmorillonite, illite, kaolinite, and vermiculite were then diluted to suspensions containing approximately 50, 120, 220, and 50 mg clay per 10 ml, respectively. For the adsorption study at low Hg(II) concentrations only montmorillonite, vermiculite, and kaolinite were used with suspension concentrations of approximately 50, 50, and 200 mg per 5 ml, respectively.

Equilibrations at higher Hg(II) concentrations:

Ten-ml aliquots of well shaken suspension were pipetted into 50 ml pre-weighed glass centrifuge tubes and 10 ml of $HgCl_2$ solution was added. The concentration range of the $HgCl_2$ solutions was 2.5×10^{-4}

to 0.01 M which gave the range of $HgCl_2$ added in μmoles given in Table 5 (p. 68). After equilibrating the suspensions for 12 hours on a horizontal shaker, they were centrifuged and the supernatant solutions were decanted into 50 ml polyethylene storage bottles fitted with airtight caps. Extractions for exchangeable Ca and Hg(II) were performed by adding 20 ml 0.1 M $BaCl_2$ to the clay in the centrifuge tube, shaking for two hours, centrifuging, and collecting the supernatant solution in 100 ml volumetric flasks. This step was repeated four times after which the solutions were made up to volume with 0.1 M $BaCl_2$. All treatments were duplicated.

Determinations of Ca and Hg were performed with a Perkin-Elmer Model 303 atomic absorption spectrophotometer. A recorder with recorder read-out unit was employed for the Hg determinations, which were also performed by using the flame. In all cases standard solutions were prepared in 0.1 M $BaCl_2$.

Cation exchange capacity (CEC) determinations were obtained from samples where no $HgCl_2$, only 10 ml deionized water, was added to the 10-ml suspensions.

Chloride ion concentrations in the equilibrium solution were obtained by measurements using a combination selective ion electrode for chlorides and NaCl standards. Since the ionic strength was very low (10^{-3} - 10^{-4} M) and standards were expressed in terms of concentrations, no conversion from activities to concentrations was regarded as necessary. pH determinations on the equilibrium solutions were taken as the pH values prevailing in the clay suspensions at equilibrium.

Results pertaining to this investigation are given in Tables 5 and 6 (pp. 68 and 69), which represent means of two replications.

Equilibrations at low Hg(II) concentrations:

In this investigation montmorillonite, vermiculite, and kaolinite were used. Five-ml aliquots of well-shaken suspension were pipetted into 15 ml pre-weighed tapered glass centrifuge tubes and 5 ml $HgCl_2$ solutions containing either approximately 10^{-3} M or 0.45 M NaCl were added. The Hg(II) concentrations were selected in such a way to give 0.1, 0.5, 2.5, and 5.0 ppm Hg(II) in the final suspension volumes. The suspensions were equilibrated on a horizontal shaker for 24 hours, then centrifuged, and the supernatant solutions were transferred to 25 ml polyethylene storage bottles fitted with air-tight caps.

The difference method was chosen to determine the amount of Hg(II) adsorbed to limit chances of contamination, since very small amounts of Hg(II) were involved. Determinations of Hg(II) were, therefore, performed on the original Hg(II) solutions as well as the equilibrium solution and the difference, after correction for dilution of the original solutions, was taken as the amount of Hg(II) adsorbed.

All Hg(II) determinations were performed by the flameless atomic absorption technique as described by the operation Manual 303-3119 supplied by Perkin-Elmer. The required accessories and kit described in this manual were used in conjunction with the Model 303 atomic absorption unit. Instead of using the recorder, the digital read-out unit was employed. This procedure was followed since the recorder displayed such instability that the determinations of Hg(II) at the sensitivity of the flameless technique were not possible. On the digital read-out unit the concentration mode was employed which made expansion possible. However, even with the digital read-out unit, fluctuations were hazardous throughout the sequence of determinations and, therefore, duplicates exhibited an undesirable degree of variation which necessitated statistical analysis. For each 4 to 8 samples a set of standards was run, calibrating the span on the read-out with each run.

The statistical analyses were performed by employing the SAS program for randomized complete block design using the replications and interactions containing the replication component as pooled error term (Barr and Goodnight, 1971).

The pH and pCl values were determined on the equilibrium solutions and represent the same as described in the previous section.

Results pertaining to this investigation are given in Tables 7, 8, 9 (pp. 72, 73, and 75), 14 and 15 (Appendix).

Potentiometric Titrations

Sample preparation:

Potentiometric titrations were performed on different Hg(II)-chloride solutions, peat soil sample, and a weak acid cation exchange resin. The peat soil sample (referred to as OM) was obtained from the coastal plain of North Carolina, where the soil was sampled at a depth of 5-10 cm. The resin is a methacrylic acid type (Rexyn 102 [H]) containing carboxylic active groups with total exchange capacity of 12.06 meq per gram dry weight.

The resin was dried at 50C, crushed with a pestle and mortar to a particle size passing through a 60 mesh screen (250 microns). The peat was sieved through the same screen without prior drying. The <250µ fractions were kept in air-tight containers. The <250µ peat fraction had a moisture content of 28.6 percent, and percentage organic matter was 13 percent (by combustion method).

Titrations:

The titrations were performed with the instrumentation described by Dewan and Rich (1970). In all titrations a total volume of 500 ml was used. The volume increase due to base addition amounted to 3-5 percent at the end of the titration and was regarded negligible, so that the recorded patterns were used directly. Prior to initiation of the titration all solutions and suspensions were acidified to about pH 2.5-2.8 by using a few drops of 10 M HNO_3. Nitric acid was used throughout the titrations because $Hg(II)-NO_3$ complexes are very weak compared to the chloride and hydroxy complexes of Hg(II), the logarithmic values of β_1 and β_2 being in the order of 0.11 and 0.01, respectively, which discounts any interferences by nitrates at the concentrations employed. Nitrogen gas was allowed to bubble through the stirred solution for at least 10 minutes before the titration was started. This time lag was enough to stabilize the pH of the acidified solution or suspension. Passage of nitrogen through the solution or suspension was maintained throughout the duration of the titration to preclude any CO_2 interferences.

The Hg(II) stock solution was prepared by dissolving 5.3988 g HgO in 15 ml 10 M HNO_3 in a 500 ml volumetric flask and making the solution up to volume with deionized water which gave a concentration of 0.05 g Hg(II) per 5 ml. In each Hg(II) titration 5 ml of the Hg(II) stock solution was used which gave a final concentration of 100 ppm Hg(II).

At first 100 ppm Hg(II) was titrated in the presence of 0, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} M total chloride concentrations. The chloride was in the form of $BaCl_2$, and the base additions were made with 0.1 N $Ba(OH)_2$ at the rate of 0.15 ml per minute. Blank titrations without Hg(II) addition were performed for each chloride concentration. All titrations were terminated above pH 11.

The results of these titrations are shown collectively in Figure 22 (p. 85) in which some of the blanks have been omitted since they closely resemble the reported ones.

The peat and resin were titrated with and without 100 ppm Hg(II) in the same way as described above but at a rate of 0.375 ml per minute. Amount of peat and resin used in the titrations was 1.5 and 0.2 g per 500 ml, respectively. The same total chloride concentrations were employed. Titrations on blanks and 100 ppm Hg(II) at the various chloride treatments were repeated for this rate of titration to facilitate quantitative measurements.

The titration curves are given in Figures 23-27 (pp. 91-95) where R and OM represent resin and peat, respectively.

Quantitative estimations:

The quantitative determinations for the titrations on the Hg(II) solutions at the various chloride concentrations were obtained from the pH curves at the lower rate of base addition. The amount of base required to titrate the Hg(II) or Hg(II)-chloride complexes was obtained by subtracting the titration value of the blank from that of the Hg(II) titration curve at increments of 0.5 pH units starting at pH 3 up to pH 11. pH 3 was taken as arbitrary reference point. The values are given as meq base added in Table 10 (p. 87).

The same reference point (pH 3) and increments of 0.5 pH units to pH 11 was used to obtain the titration values for Hg(II) in the presence of resin and peat. However, to obtain the Δ meq values the following subtractions were made: first the titration value for the blank was subtracted from the titration values of Hg(II), resin or peat and Hg(II) in the presence of resin or peat, and subsequently subtracting the resultant of the individual titrations of Hg(II) and resin or peat from the resultant of the titration of Hg(II) in the presence of resin or peat. This procedure was followed for each set at each total chloride concentration. The Δ meq values are given in Tables 11 and 12 (pp. 96 and 97).

RESULTS AND DISCUSSION

Effect of pH and pCl on Zn(II), Cd(II), Hg(II), and Pb(II)

The effects of pH and chloride ion concentration on Zn(II), Cd(II), Hg(II), and Pb(II) are first presented independently from one another. This approach was taken to evaluate the significance of each parameter and to compare the behavior of the different heavy metal ions more effectively. In this section calculations on known chemical principles have been included to illustrate and compare their significance and implications which are often omitted or overlooked. A recent example of such omission is evident in a determination on the solubility of $Pb(OH)_2$ by Lagerwerff et al. (1973) where activity coefficients were used but the hydrolysis of Pb^{++} to $PbOH^+$ was apparently ignored. The latter, as shown later, is of greater magnitude than the adjustment to activities.

Hydrolysis of metal ions:

The heavy metals Zn, Cd, Hg, and Pb belong to the group of oxyphilic and sulfophilic elements. The metal ions of these elements distinguish themselves from the alkali and alkaline earth ions in solution by undergoing hydrolysis at lower pH values and by displaying multiple hydrolysis at pH values encountered in the environment. Furthermore, within the group of heavy metal ions marked differences in behavior are observed which will also differentiate their reactions as pollutants in the environment. To illustrate this phenomenon, reference is made to Zn(II)-, Cd(II)-, Hg(II)-, and Pb(II)-OH systems presented in Figures 1, 2, 3, and 4, respectively. Although Zn, Hg, and Cd belong to the same group of elements in the periodic classification, they display different properties. Hg^{++} hydrolyzes in the pH range 2 to 6, the final species at pH 6 is $Hg(OH)_2$. The monohydroxy species $HgOH^+$ predominates between pH 2.2 and 3.8 (Fig. 3). Zn(II) and Cd(II) are present as the divalent ion at pH 6 and are completely soluble in the absence of precipitating anions such as phosphate and sulfide (Figures 1 and 2). Little $ZnOH^+$ forms, whereas $CdOH^+$ starts forming at pH 7-7.5 and peaks at pH 8.2-9. Formation of $Cd(OH)_2$ begins at pH 9 and peaks at pH 11. Both Zn(II) and Cd(II) form soluble $M(OH)_3^-$ and $M(OH)_4^=$ complexes at more alkaline conditions, but these species are formed at pH values higher than those normally encountered in the environment. The Pb(II)-hydroxy species (Fig. 4) indicate that $Pb(OH)_2$ formation is important above pH 9, while $PbOH^+$ is predominant between pH 6 and 10.

The relevance of the various hydroxy species distributions becomes evident in predicting degree of solubility of the different heavy metal ions which is closely related to the potential hazard when discharged into the environment. Since reactions in aqueous media represent a large proportion of those reactions occurring in the environment, knowledge of metal ion species distributions as a result of hydrolysis becomes of great importance in explaining mechanisms and planning experiments. At pH 6-7 the distribution of Hg(II) will be determined by the

Fig. 1. Distribution of Zn(II)-hydroxy species at various pH levels in a single component system.

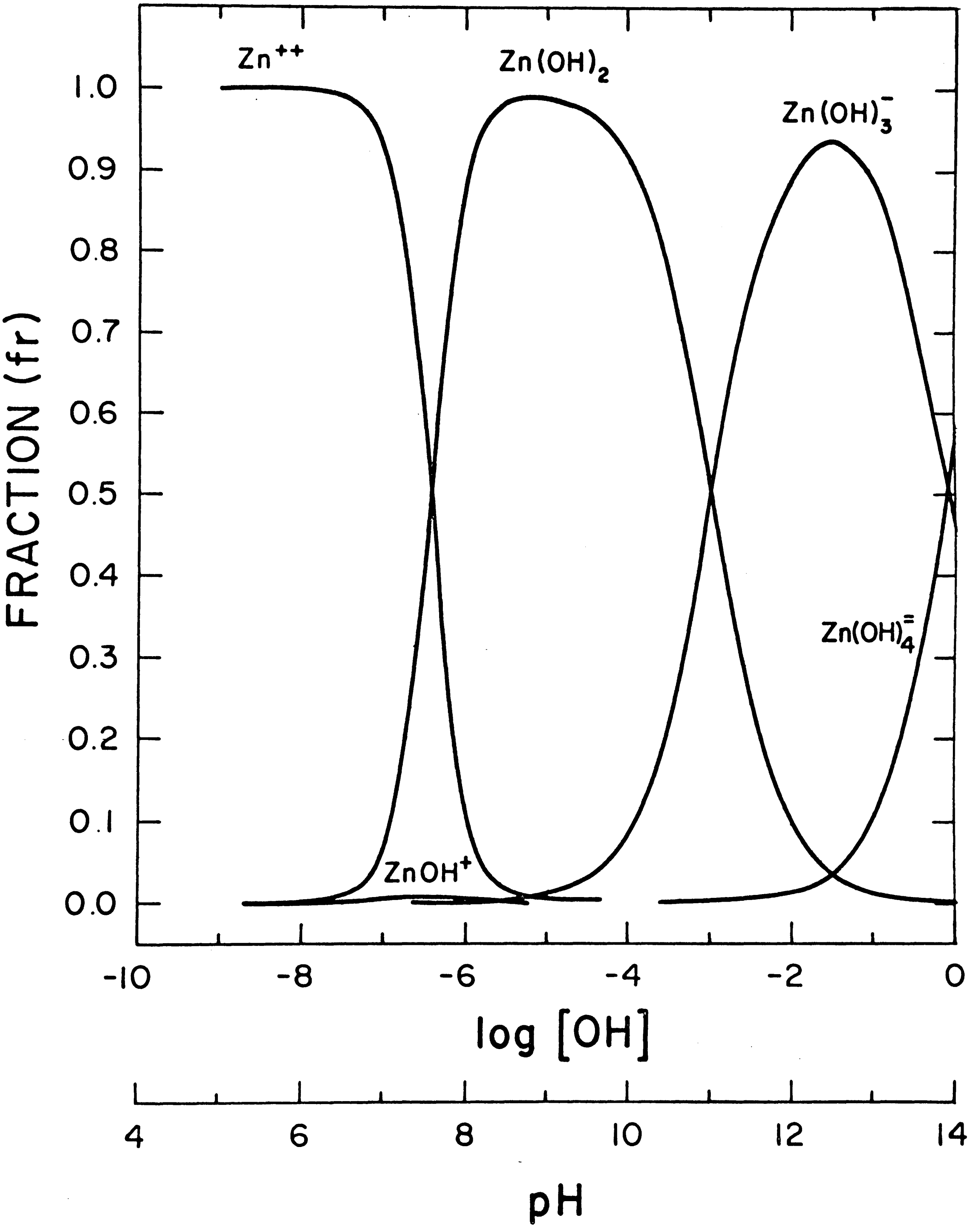

FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Zn^{++}
$Zn(OH)_2$
$Zn(OH)_3^-$
$Zn(OH)_4^=$
$ZnOH^+$
-10
-8
-6
-4
-2
0
log [OH]
4
6
8
10
12
14
pH

Fig. 2. Distribution of Cd(II)-hydroxy species at various pH levels in a single component system.

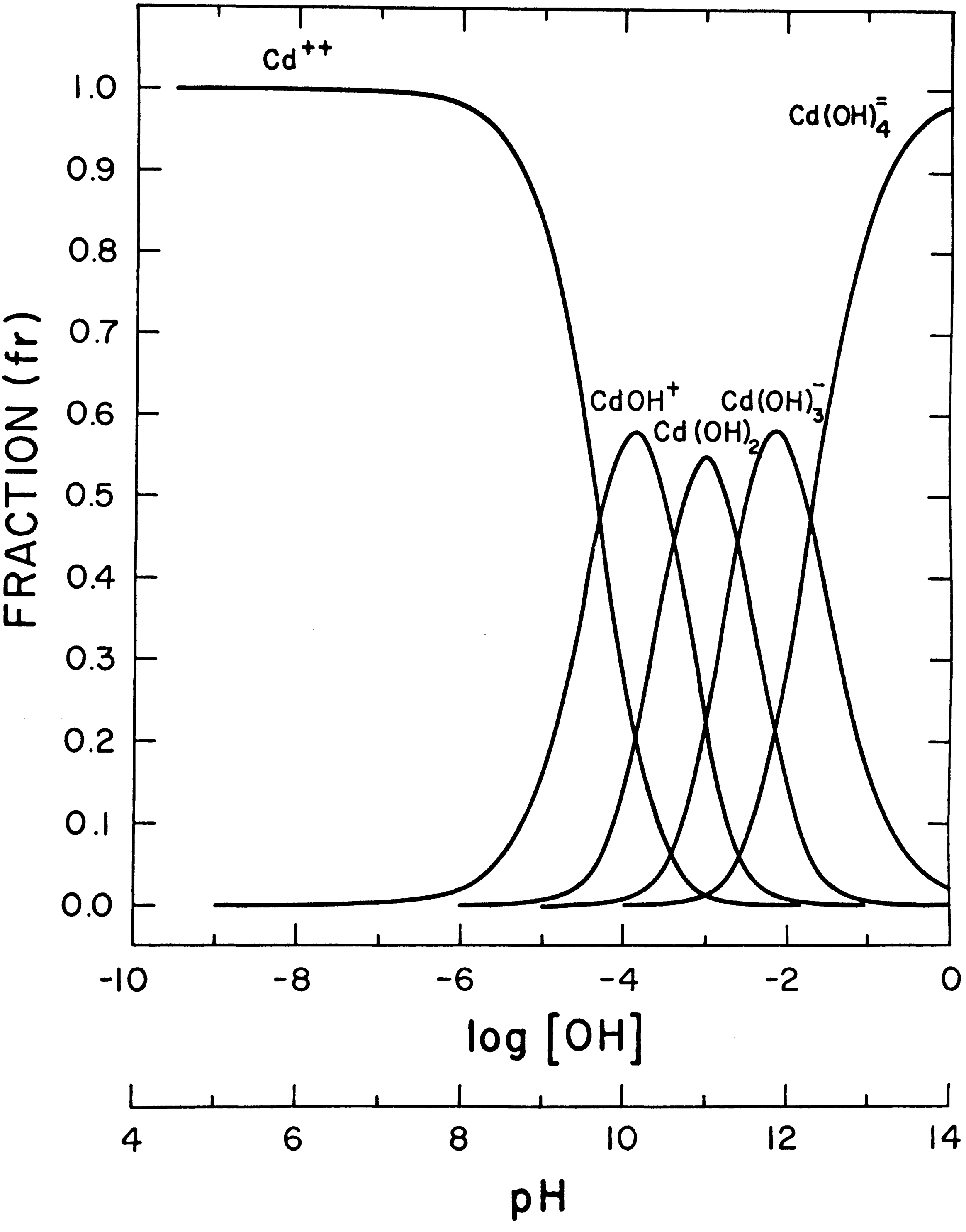

Cd++
Cd(OH)4=
CdOH+
Cd(OH)2
Cd(OH)3-
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-10
-8
-6
-4
-2
0
log [OH]
4
6
8
10
12
14
pH

Fig. 3. Distribution of Hg(II)-hydroxy species at various pH levels in a single component system.

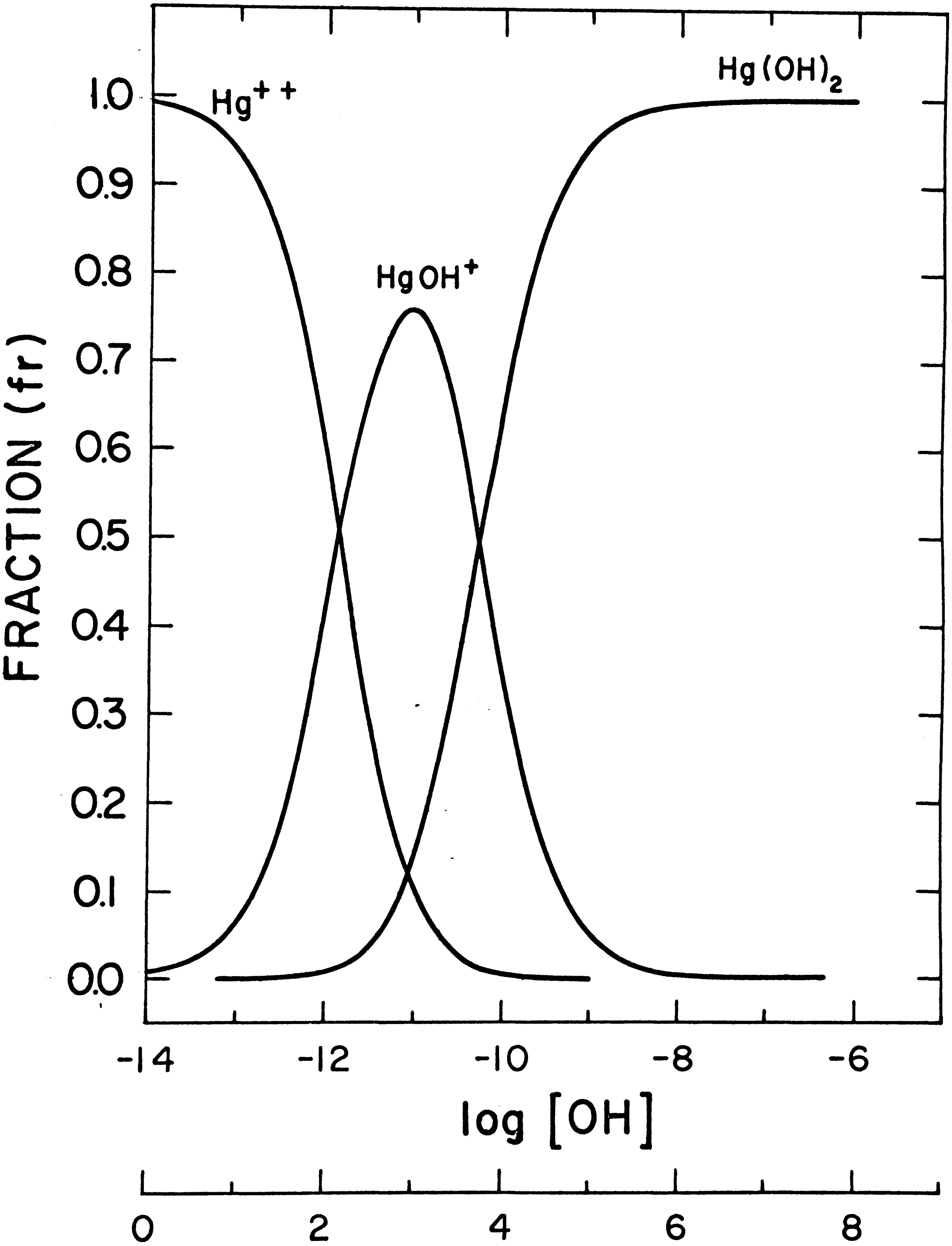
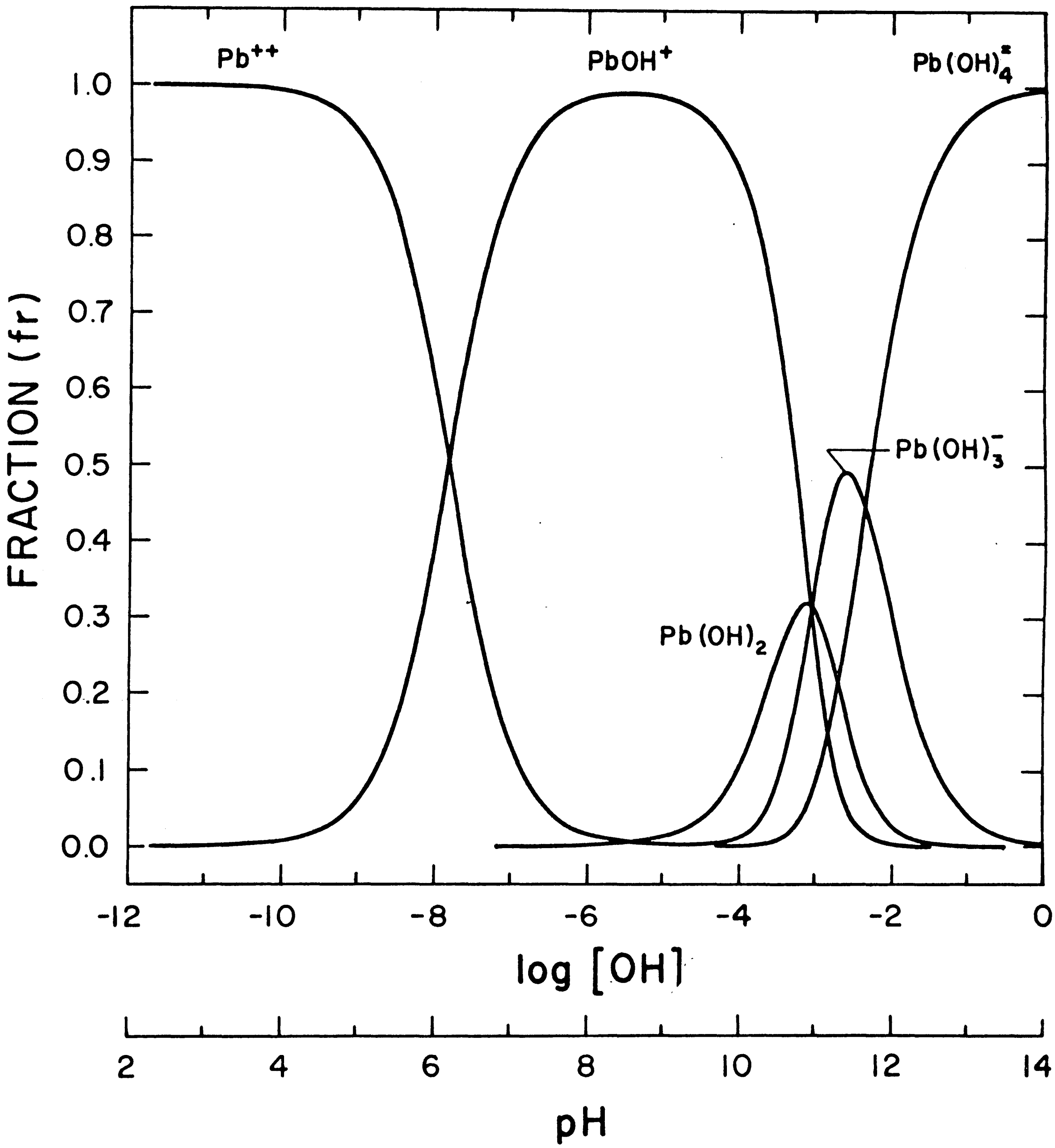

Hg^{++}
Hg(OH)$_2$
HgOH$^+$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-14
-12
-10
-8
-6
log [OH]
0
2
4
6
8
pH

Fig. 4. Distribution of Pb(II)-hydroxy species at various pH levels in a single component system.


Pb^{++}
PbOH^{+}
Pb(OH)$_4^{=}$
Pb(OH)$_3^{-}$
Pb(OH)$_2$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-12
-10
-8
-6
-4
-2
0
log [OH]
2
4
6
8
10
12
14
pH

solubility of $Hg(OH)_2$, whereas Zn(II) and Cd(II) will be present in the divalent ionic form. Assuming that no other precipitation reactions occur, all Zn^{++} and Cd^{++} are available for adsorption on suspended mineral colloids and complexation with organic matter, and may move in these forms. Hg(II) would move predominantly as $Hg(OH)_2$ which may be in soluble or precipitate form, depending on the total Hg(II) concentration. In the case of Pb(II), the divalent Pb^{++} and monovalent $PbOH^+$ occur at pH 6-7, the latter being predominant in solution. In the present appraoch only monomeric complexes were considered although the presence of multinuclear complexes has been established (Stumm et al., 1970). The degree to which multinuclear complexes form, however, is still a matter of conjecture and few definite constants for their formations are available. One reason for the uncertainty on multinuclear complexes probably is that their formations are dependent on the metal ion concentration in solution. The metal ion concentration dependency of the fractional distribution of multinuclear complexes can be shown, by performing derivations similar to those applicable to monomeric complexes.

Effect of hydrolysis on solubilities:

Hydrolysis of the ions forming sparingly soluble precipitates such as the phosphates and sulfides becomes important in determining the solubilities of such precipitates (Table 2). Anion hydrolysis is more pronounced at lower pH values, whereas the reverse is true for the cations. The data (Table 2) show hydrolysis effects only at three selected pH values which were chosen merely to demonstrate the

Table 2. Effect of cation and anion hydrolysis on the conditional solubility and solubility product at three pH values.

Precipitate	pH					
	4.0		6.0		8.0	
	*S'/S	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)
Cation and anion hydrolysis						
ZnS	$9.554\text{x}10^6$	13.96	$9.981\text{x}10^4$	10.00	$9.010\text{x}10^3$	7.90
PbS	$9.586\text{x}10^6$	13.96	$1.286\text{x}10^5$	10.22	$2.489\text{x}10^4$	8.79
CdS	$9.554\text{x}10^6$	13.96	$9.977\text{x}10^4$	10.00	$3.068\text{x}10^3$	6.97
HgS	$1.378\text{x}10^8$	16.28	$1.162\text{x}10^8$	16.13	$3.529\text{x}10^8$	17.10
$Zn_3(PO_4)_2$	$4.125\text{x}10^4$	23.08	$1.056\text{x}10^3$	15.12	$2.101\text{x}10^2$	11.61
$Pb_3(PO_4)_2$	$4.141\text{x}10^4$	23.09	$1.430\text{x}10^3$	15.78	$7.115\text{x}10^2$	14.26
$Cd_3(PO_4)_2$	$4.125\text{x}10^4$	23.08	$1.055\text{x}10^3$	15.12	$5.769\text{x}10^1$	8.81
Anion hydrolysis						
MS**	$9.554\text{x}10^6$	13.96	$9.976\text{x}10^4$	10.00	$3.038\text{x}10^3$	6.97
$M_3(PO_4)_2$	$4.125\text{x}10^4$	23.08	$1.055\text{x}10^3$	15.12	5.701x10	8.78

*S' = conditional solubility derived from conditional solubility product K'sp.
S = solubility derived from solubility product Ksp.

**M stands for Zn^{++}, Cd^{++}, Hg^{++}, and Pb^{++}.

magnitudes involved. The distributions in Figures 1-4 will give indications at which pH such effects have to be considered for Zn(II), Cd(II), Hg(II), and Pb(II). Anion hydrolysis for phosphates and sulfides is important at all pH values normally encountered in natural waters. The effects of cation hydrolysis on solubility can be obtained by dividing the values of cation and anion hydrolysis (Table 2) by the corresponding values listed under anion hydrolysis. As expected from the distributions (Figures 1-4), there is no marked cation hydrolysis effect on the solubility for Zn(II) and Cd(II) precipitates except for Zn(II) at pH 8. Pb(II) hydrolysis is important at and above pH 6. The largest hydrolysis effects on increase in solubility are encountered with Hg(II). The magnitudes of the ratios of S'/S and K'_{sp}/K_{sp} show explicitly that the hydrolysis effect if prevalent overrides activity effects by a great margin. These results also show that if hydrolysis, or for that matter ion-paring, occurs and is omitted, any ionic strength determinations based on stoichiometric concentrations will be incorrect.

Intrinsic solubilities of heavy metal hydroxides:

The complexing of the heavy metal ions with hydroxyl ions necessitates considerations with respect to the solubilities of the metal-ion hydroxides. This is especially important for $Hg(OH)_2$ and $Zn(OH)_2$ which form at pH values 2 to 6 and 7 to 12, respectively (Figures 1 and 3). When the respective solubilities are calculated from the solubility products of the corresponding hydroxides, only 0.861 ppm Zn^{++} and 0.039 ppm Hg^{++} would be accounted for as soluble. However, calculations on the intrinsic solubilities of these hydroxides show that up to 160 ppm Zn(II) can exist as soluble $Zn(OH)_2^o$ and that up to 107 ppm Hg(II) can exist as soluble $Hg(OH)_2^o$ (Table 3). Precipitation will take place only when the metal ion concentration exceeds the intrinsic solubility. The intrinsic solubilities of $Cd(OH)_2$ and $Pb(OH)_2$ are much lower, the values being 0.158 and $474x10^{-6}$ ppm Cd(II) and Pb(II), respectively.

Since, under natural conditions, the concentration of these heavy metal ions is commonly in the ppm range the intrinsic solubilities of the metal hydroxides become markedly important, especially for Zn(II) and Hg(II). Therefore, depending on the total metal ion concentrations, the hydroxides may even promote mobilization of these heavy metals since they reduce the charge of the cation and the complexing ability with organic matter and increase the solubility of sparingly soluble salts.

Chloride complexes of metal ions:

Chlorides, like hydroxyl and hydrogen ions, occur in all natural soil and water and may be regarded as one of the most mobile and persistent complexing agents with regard to heavy metals. Chlorides may also be regarded as being more selective than many organic complexing agents in that they do not complex strongly with Al^{3+}, Ca^{2+}, and Mg^{2+}. The chloride ion concentration determines the degree of complexation and also differentiates heavy metals markedly pending their affinity for such complex formations. This is illustrated by comparing Figures 5, 6, 7, and 8 giving the respective Zn(II)-, Cd(II)-, Hg(II)-, and Pb(II)-chloride complexes at different chloride ion concentrations.

Table 3. Solubilities and intrinsic solubilities of Zn, Cd, Hg, and Pb hydroxides.

Component	Solubility (S)		Intrinsic solubility (S°)	
	moles/l	ppm	moles/l	ppm
$Zn(OH)_2$	4.292x10^{-6}	861x10^{-3}	2.454x10^{-3}	160
$Cd(OH)_2$	1.917x10^{-5}	384x10^{-2}	1.412x10^{-6}	158x10^{-3}
$Hg(OH)_2$	1.961x10^{-7}	393x10^{-4}	5.370x10^{-4}	107
$Pb(OH)_2$	2.151x10^{-9}	431x10^{-6}	2.291x10^{-9}	474x10^{-6}

Fig. 5. Distribution of Zn(II)-chloride species at various pH levels in a single component system.

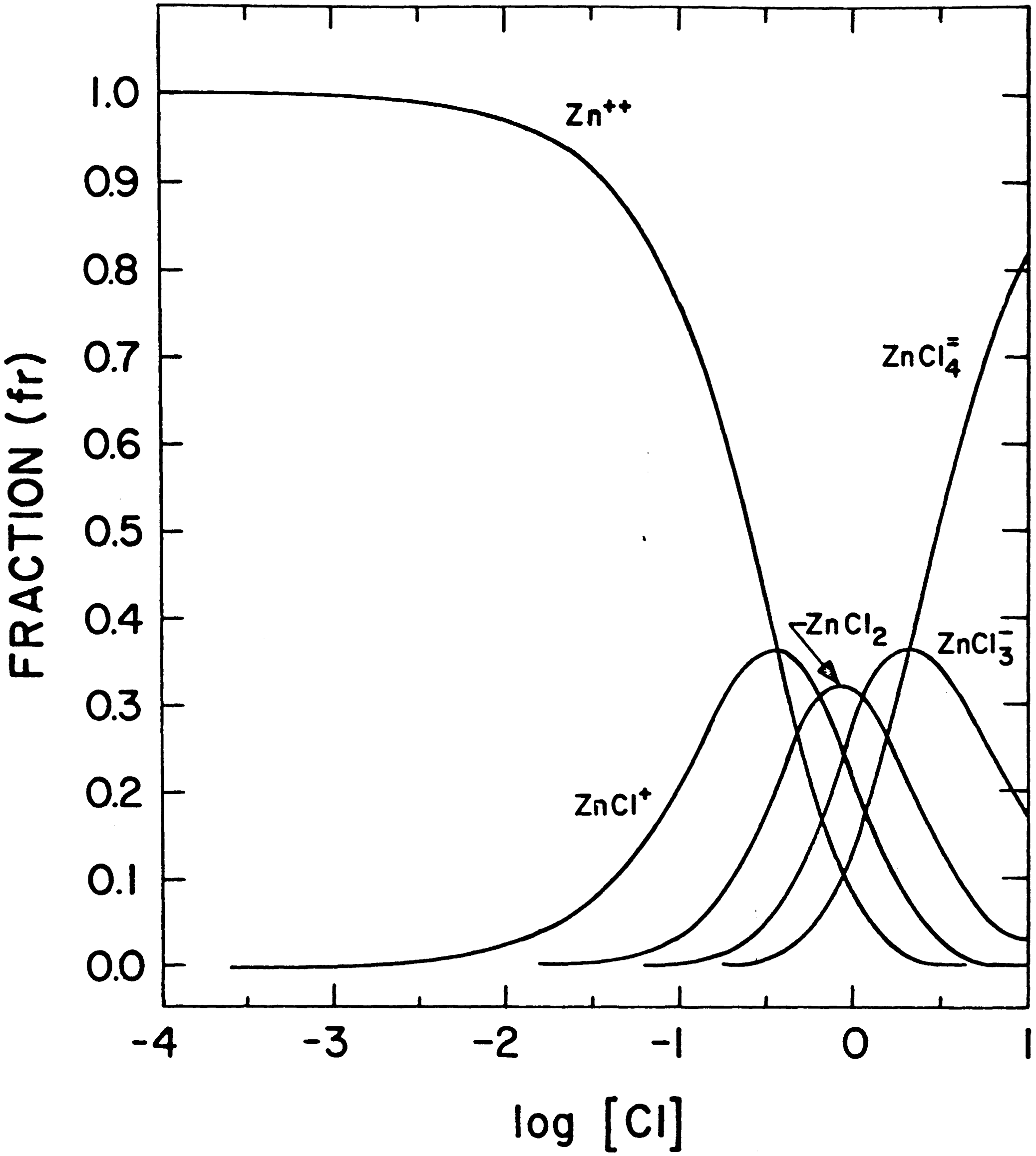

FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-4
-3
-2
-1
0
1
log [Cl]
Zn++
ZnCl+
ZnCl2
ZnCl3-
ZnCl4=

Fig. 6. Distribution of Cd(II)-chloride species at various chloride ion concentrations in a single component system.

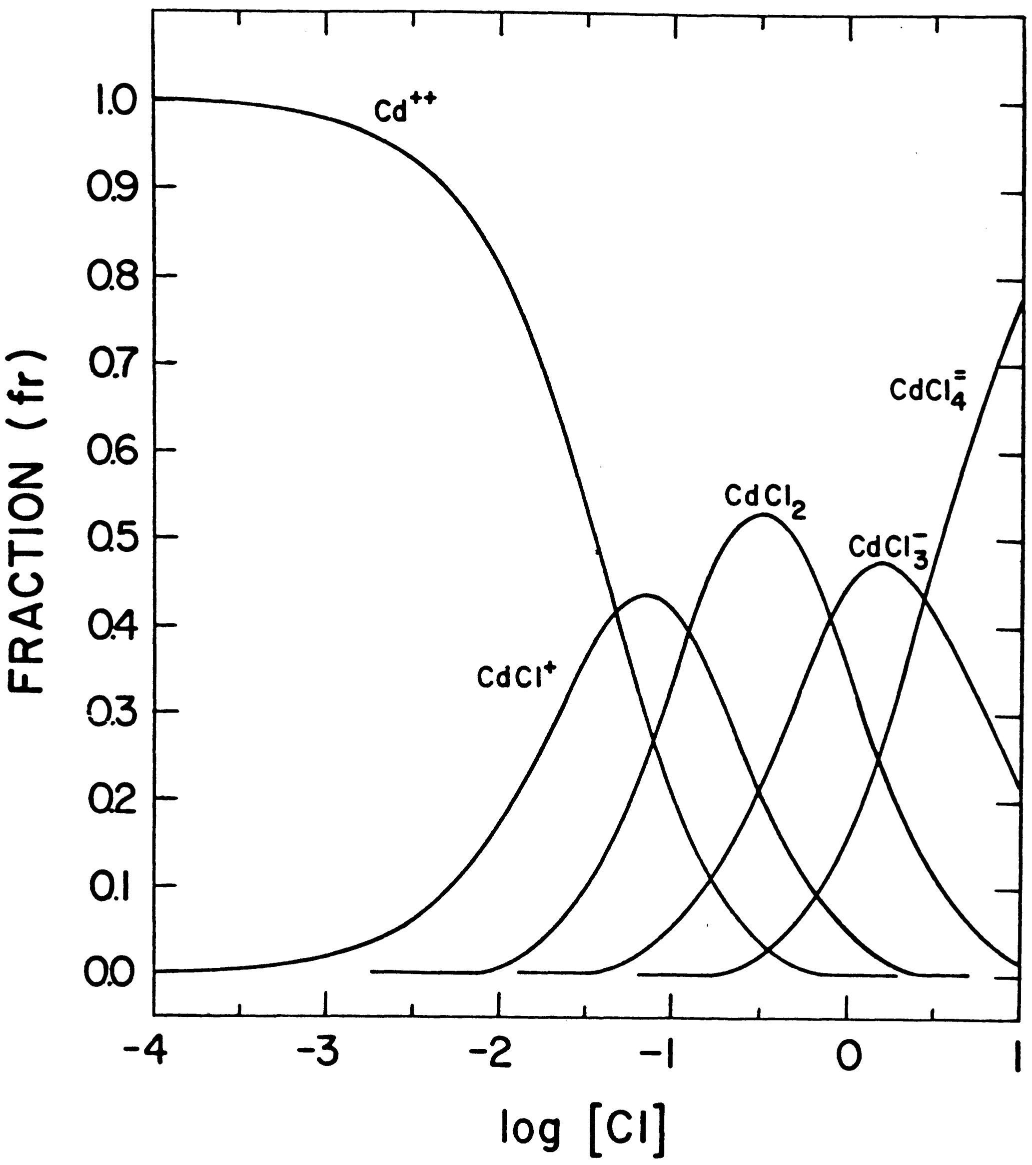

FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Cd⁺⁺
CdCl⁺
CdCl₂
CdCl₃⁻
CdCl₄⁼
-4
-3
-2
-1
0
1
log [Cl]

Fig. 7. Distribution of Hg(II)-chloride species at various chloride ion concentrations in a single component system.

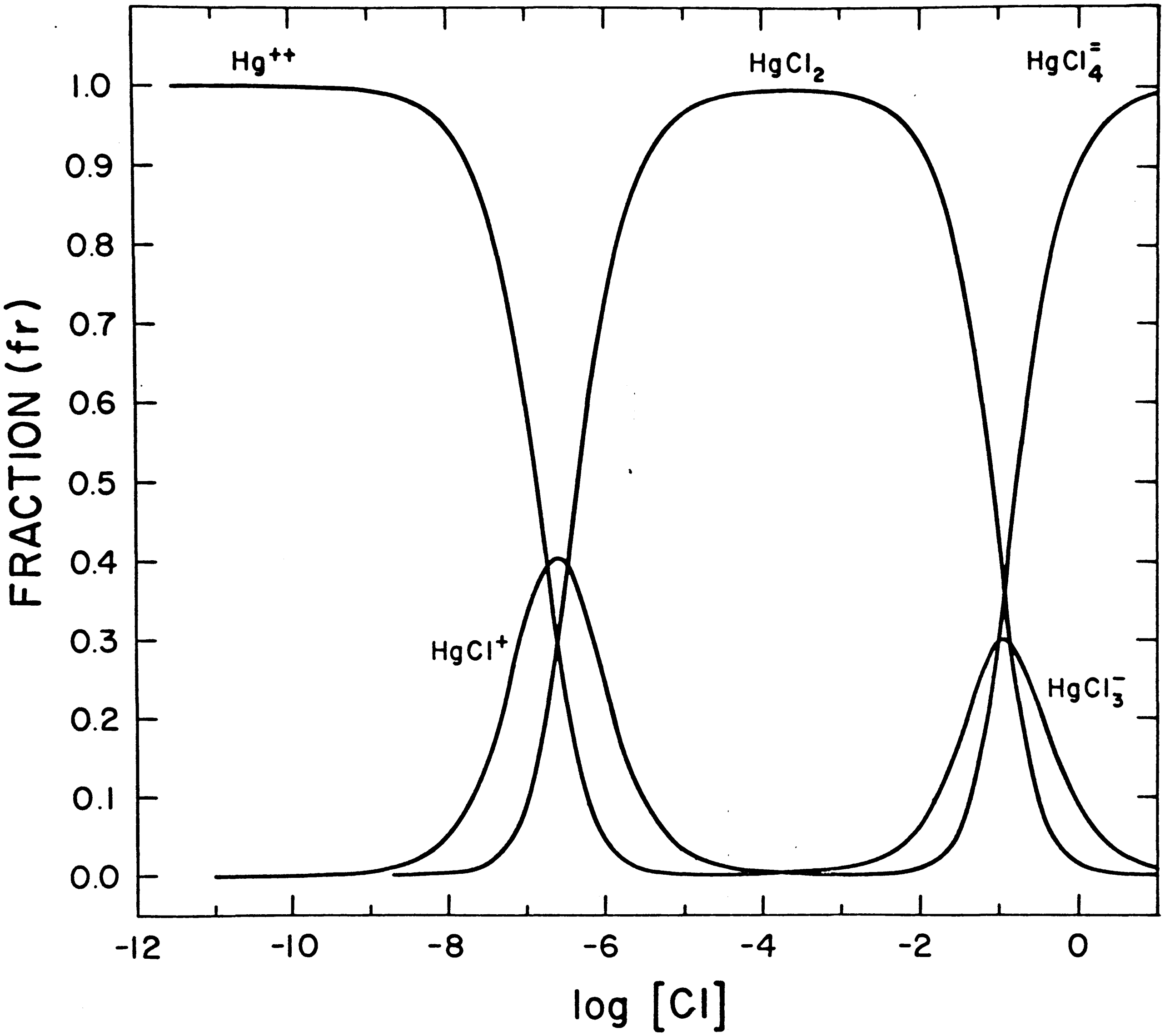
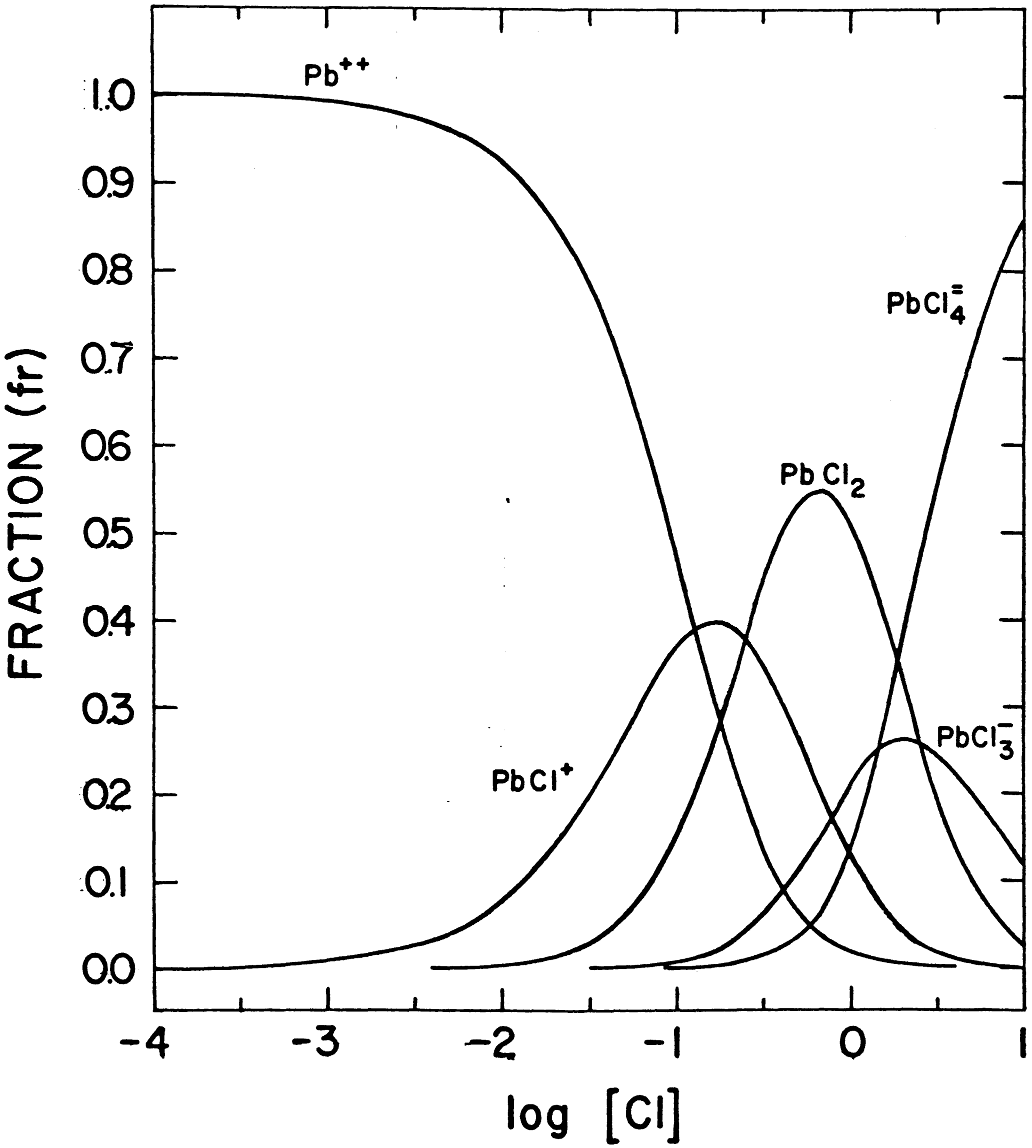

Hg^{++}
HgCl$_2$
HgCl$_4^{=}$
HgCl$^+$
HgCl$_3^-$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-12
-10
-8
-6
-4
-2
0
log [Cl]

Fig. 8. Distribution of Pb(II)-chloride species at various chloride ion concentrations in a single component system.


Pb^{++}
PbCl$_4^=$
PbCl$_2$
PbCl$_3^-$
PbCl$^+$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
−4
−3
−2
−1
0
1
log [Cl]

The Hg(II)-Cl system (Figure 7) again displays odd characteristics in that complex formation of all different species takes place at much lower chloride ion concentrations than is the case with Zn(II), Cd(II), and Pb(II). Formation of $ZnCl^+$ begins at a chloride ion concentration of 10^{-2} M (350 ppm) and peaks at $10^{-0.5}$ M (≃10,000 ppm), the formation of $ZnCl_3^-$ and $ZnCl_4^=$ becomes important only above 1M (35,500 ppm) chloride ion concentration (Fig. 5). Formation of $CdCl^+$ begins at 10^{-3} M (≃35 ppm) and peaks at $10^{-1.2}$ M (≃2,200 ppm) chloride ion concentration. $CdCl_2$ species peaks at $10^{-0.5}$ M (≃10,000 ppm) with $CdCl_3^-$ and $CdCl_4^=$ being predominant above 1M (≃35,500 ppm). The various Hg(II) complexes $HgCl^+$, $HgCl_2$, and $HgCl_3^-$ peak at chloride ion concentrations of 10^{-7} M (≃0.0035 ppm), 10^{-4} M (≃3.5 ppm), and 10^{-1} M (≃3,550 ppm), respectively. At chloride ion concentrations above 3,550 ppm $HgCl_4^=$ is predominant (Figure 7). The Pb(II)-Cl system (Figure 8) closely resembles that for Cd(II)-Cl with respect to species formations at corresponding chloride ion concentrations.

In saline and saline-sodic soils where the chloride concentrations of the soil solution range from about 1,200 to 2,900 meq. per liter (42,600-103,000 ppm) (Rhoades et al., 1971), the uncharged dichloride and the negatively charged trichloro and tetrachloro species become important for all four elements. These soils usually have pH values ranging from 8 to 9 and competition between hydroxy and chloride complexes becomes important.

Effect of chloride complexation on solubilities:

Chloride, like hydroxyl ions, when complexing with heavy metal ions will increase solubilities of sparingly soluble compounds of such heavy metal ions. The effect of chloride complexation on solubilities was calculated for three chloride ion concentrations (Table 4) and as can be expected from the distributions (Figures 5-8), this effect was most prominant in the case of Hg(II). Since measurements of chloride ion concentrations by means of chloride selective ion electrode are not always common practice, it must be emphasized that the values (Table 4) are expressed in terms of chloride ion concentrations and not total chloride concentrations. The same applies to the distributions of chloride complexes presented in Figures 5-8. If the concentration of the total metal ion (bound and unbound) and the total chloride concentrations are measured, then in the absence of hydrolysis the itterative procedure with the aid of equations [20] and [22] can be used to determine the chloride ion concentration. When at the same time hydroxy complexes exist, equations [22] and [23] should be used in the itteration. When the total metal ion concentration is very low compared to the total chloride concentration, the total chloride concentration could be used without producing a great error.

Chloride complexation with Zn(II), Cd(II), and Pb(II) affects the solubilities of the corresponding sparingly soluble salts above a chloride ion concentration of 0.01 M (350 ppm). Solubilities of Hg(II) containing precipitates are markedly increased at 10^{-4} M (3.5 ppm)

Table 4. Effect of chloride concentration on the conditional solubility and solubility product.

Precipitate	Chloride concentration					
	0.0001M		0.01M		1.00M	
	*S'/S	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)
$Zn_3(PO_4)_2$	1.000	0.00	1.016	0.04	4.604	3.32
ZnS	1.000	0.00	1.014	0.01	3.569	1.11
$Zn(OH)_2$	1.000	0.00	1.009	0.01	2.336	1.11
$Cd_3(PO_4)_2$	1.001	0.01	1.130	0.27	39.83	8.00
CdS	1.001	0.00	1.107	0.09	21.55	2.67
$Cd(OH)_2$	1.001	0.00	1.070	0.09	7.745	2.67
$Pb_3(PO_4)_2$	1.000	0.00	1.047	0.10	11.72	5.35
PbS	1.000	0.00	1.039	0.03	7.779	1.78
$Pb(OH)_2$	1.000	0.00	1.026	0.03	3.926	1.78
HgS	4.082x10^{2}	5.22	4.423x10^{4}	9.25	3.619x10^{7}	15.12
$Hg(OH)_2$	5.503x10	5.22	1.214x10^{3}	9.25	1.094x10^{5}	15.12

*S' = solubility derived from conditional solubility product K'sp.
S = solubility derived from solubility product Ksp.

chloride ion concentration where the increase of the solubility of HgS is 408 fold.

Although the complexation effects on solubilities have been shown independently for chloride and hydroxy complexes in order to emphasize the magnitude of each effect, situations will often arise where both chloride complexation and hydrolysis take place. In such cases the same procedure is followed, but instead of calculating $fr_{M^{++}}$ values according to equation [5], relationship [8] is used.

Effect of pH and pCl on Competition between Complexes

Chloride and hydroxyl ions will always be in competition for the metal ion and so will organic complexing agents as well as precipitating anions. Organo-metal-ion complexes may be in soluble or colloidal forms in waters and sediments. Chlorides are highly mobile and persistent, unlike NTA which is biodegradable (Warren and Malec, 1972) and, therefore, chlorides could be a more important factor in the distribution of some heavy metal ions than has been considered to date. This applies especially to the movement of Hg(II). The foregoing considerations substantiate the possibility that the increase in the use of deicing salts on roads may increase distribution of these metal ions or at least channel them to certain localities.

An evaluation on the degree of competition between the chloride and hydroxy complexes is required to assess the effectiveness of chlorides in mobilizing the heavy metal ions. Since Hg(II) hydrolyzes and complexes with chlorides over the widest pH and chloride ion concentration range, competition between the chloride and hydroxy complexes of Hg(II) is presented in greater detail in the following section.

Competition between chloride and hydroxy complexea of Hg(II):

The mercuric ion, as shown in Figures 3 and 7, complexes strongly with hydroxide and chloride ions which subsequently influences the mobility of Hg(II). Increasing the hydroxide ion concentration ultimately results in the formation of soluble $Hg(OH)_2^{\circ}$. Precipitation of $Hg(OH)_2$ occurs only if the concentration of Hg(II) as $Hg(OH)_2$ exceeds 107 ppm, the intrinsic solubility of $Hg(OH)_2$ being 5.37×10^{-4} M (Table 4). Chloride ions enhance formation of Hg(II)-chloride complexes which will always be in competition with the Hg(II)-hydroxy complexes as shown by the distributions in Figures 9 through 16. Both complexing mechanisms will promote mobilization of Hg(II). The degree of mobility of the various complexes will depend on the type of charge of the complex and the surrounding colloidal material. The effectiveness of the hydroxy complexes to promote Hg(II) mobilization is more restricted due to the lower intrinsic solubility of $Hg(OH)_2$ as compared to the high solubility of $HgCl_2$ which, according to Jenne (1970), is 69 g per liter at 25C.

At pH 2 (Fig. 9) and at pCl values greater than 9 ($<3.5 \times 10^{-5}$ ppm), 67.5 and 41.8 percent of the Hg(II) in solution will be in the form of Hg^{++} and $HgOH^{+}$, respectively. When the pCl value decreases to 6.5 (0.011 ppm) $HgCl^{+}$ and $HgCl_2^{\circ}$, each represents 33.4 percent of the total Hg(II) in solution and the fractions of free Hg^{++} and $HgOH^{+}$ are reduced

Fig. 9. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 2 in a two-component system.

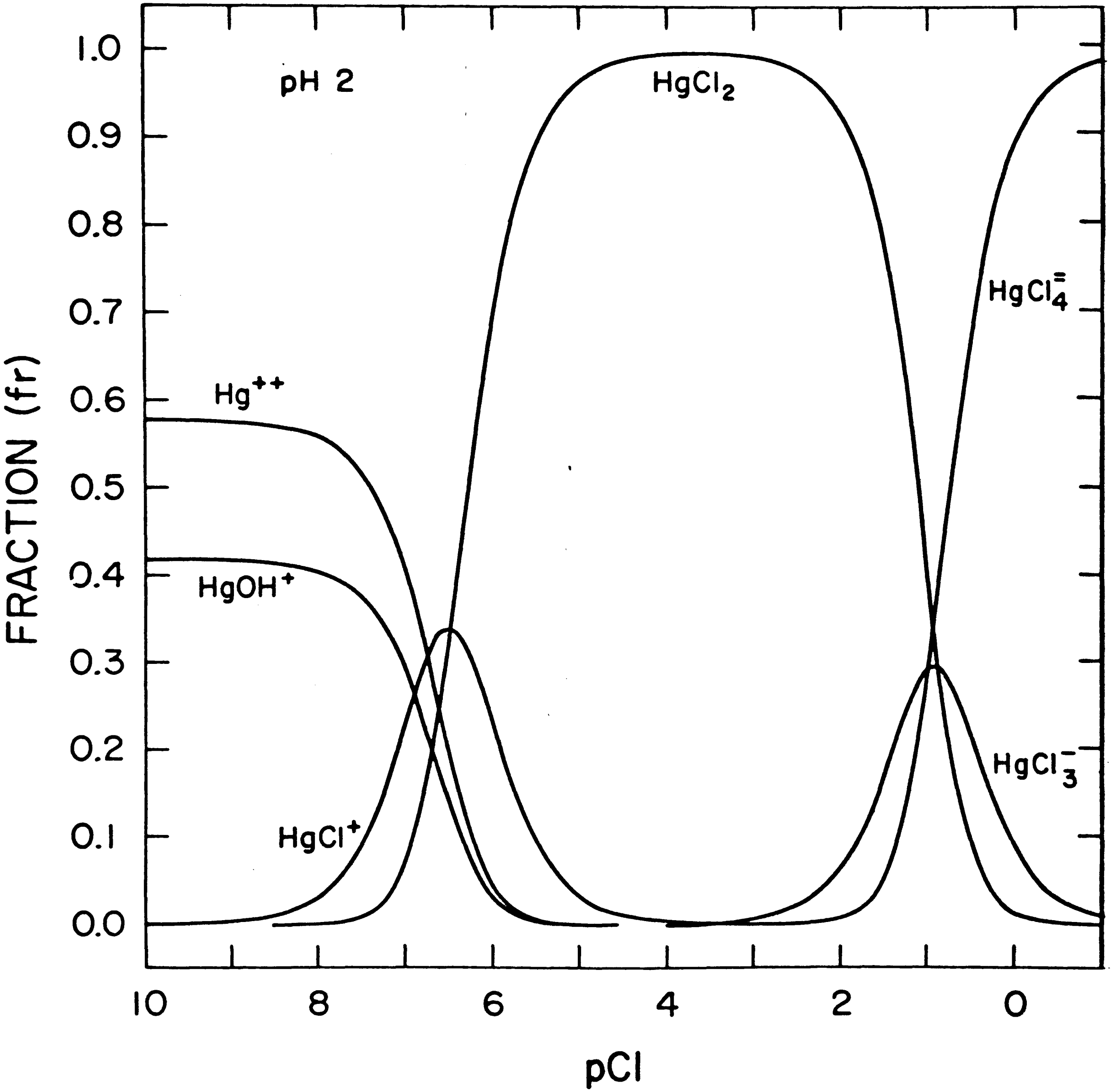

pH 2
HgCl$_2$
HgCl$_4^=$
Hg^{++}
HgOH$^+$
HgCl$^+$
HgCl$_3^-$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
10
8
6
4
2
0
pCl

Fig. 10. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 3 in a two-component system.

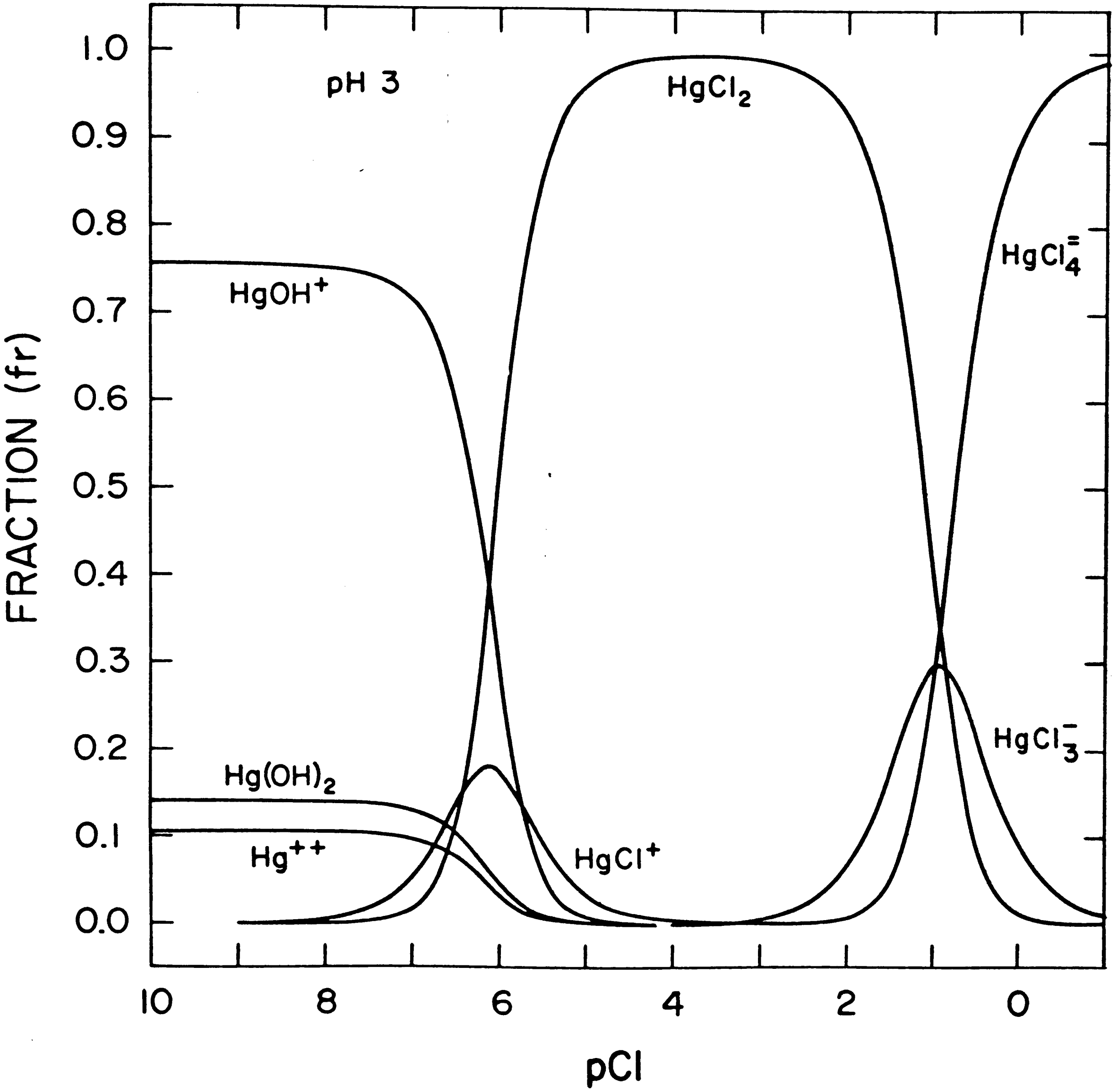

pH 3
$HgCl_2$
$HgCl_4^{=}$
$HgOH^+$
$HgCl_3^-$
$Hg(OH)_2$
Hg^{++}
$HgCl^+$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
10
8
6
4
2
0
pCl

Fig. 11. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 4 in a two-component system.

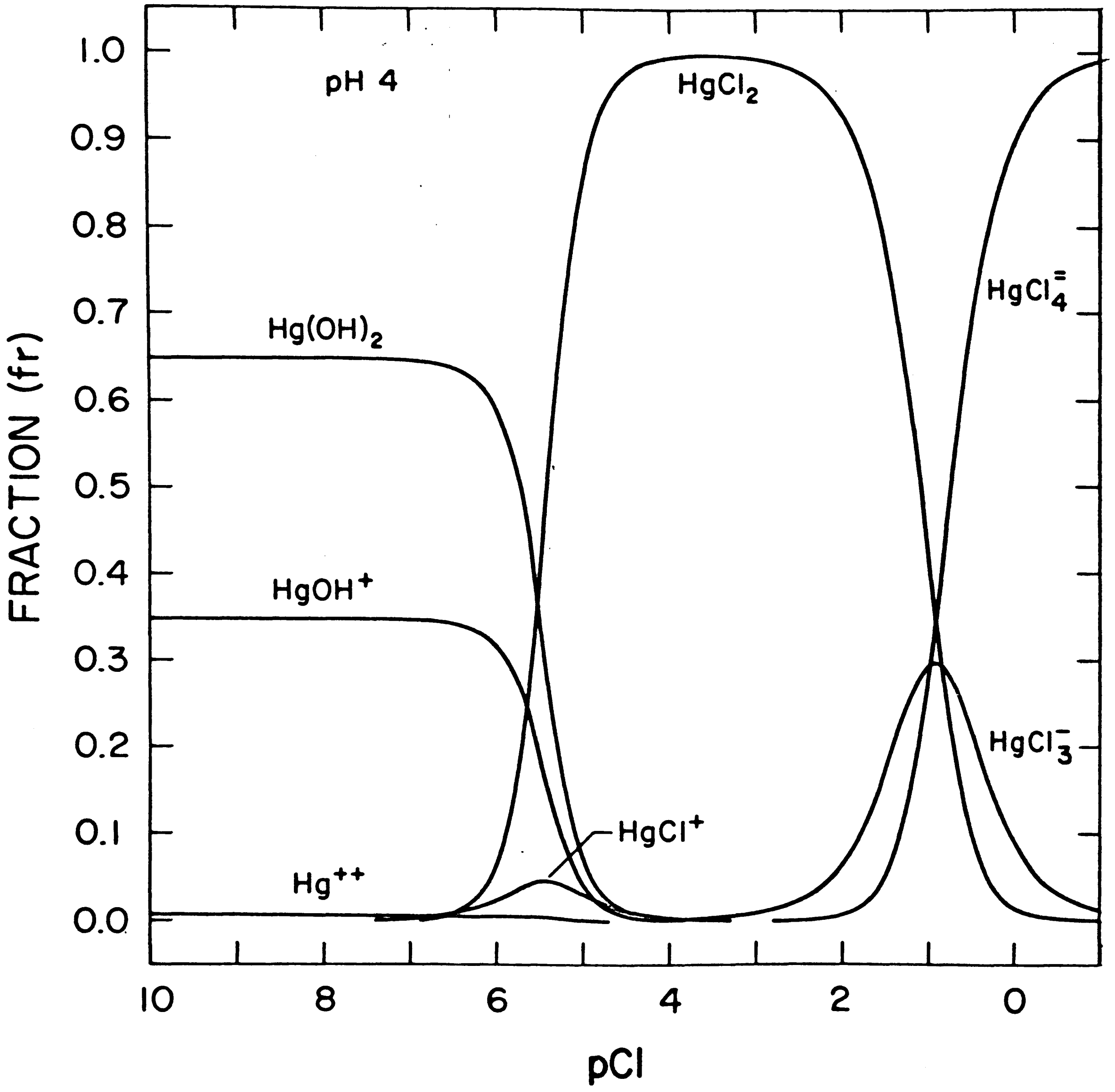

pH 4
HgCl$_2$
Hg(OH)$_2$
HgOH$^+$
HgCl$_4^=$
HgCl$_3^-$
HgCl$^+$
Hg^{++}
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
10
8
6
4
2
0
pCl

Fig. 12. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 5 in a two-component system.

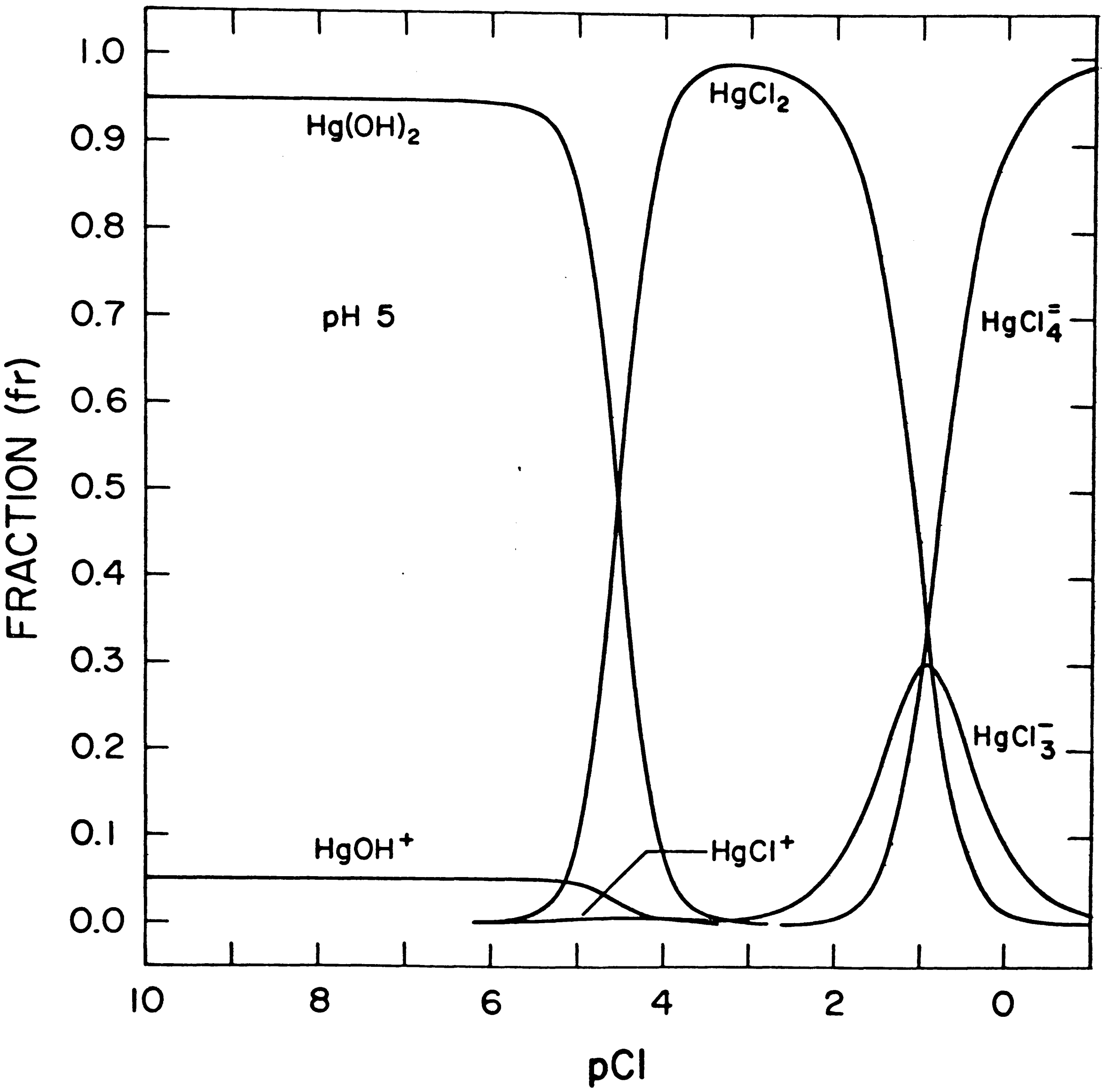
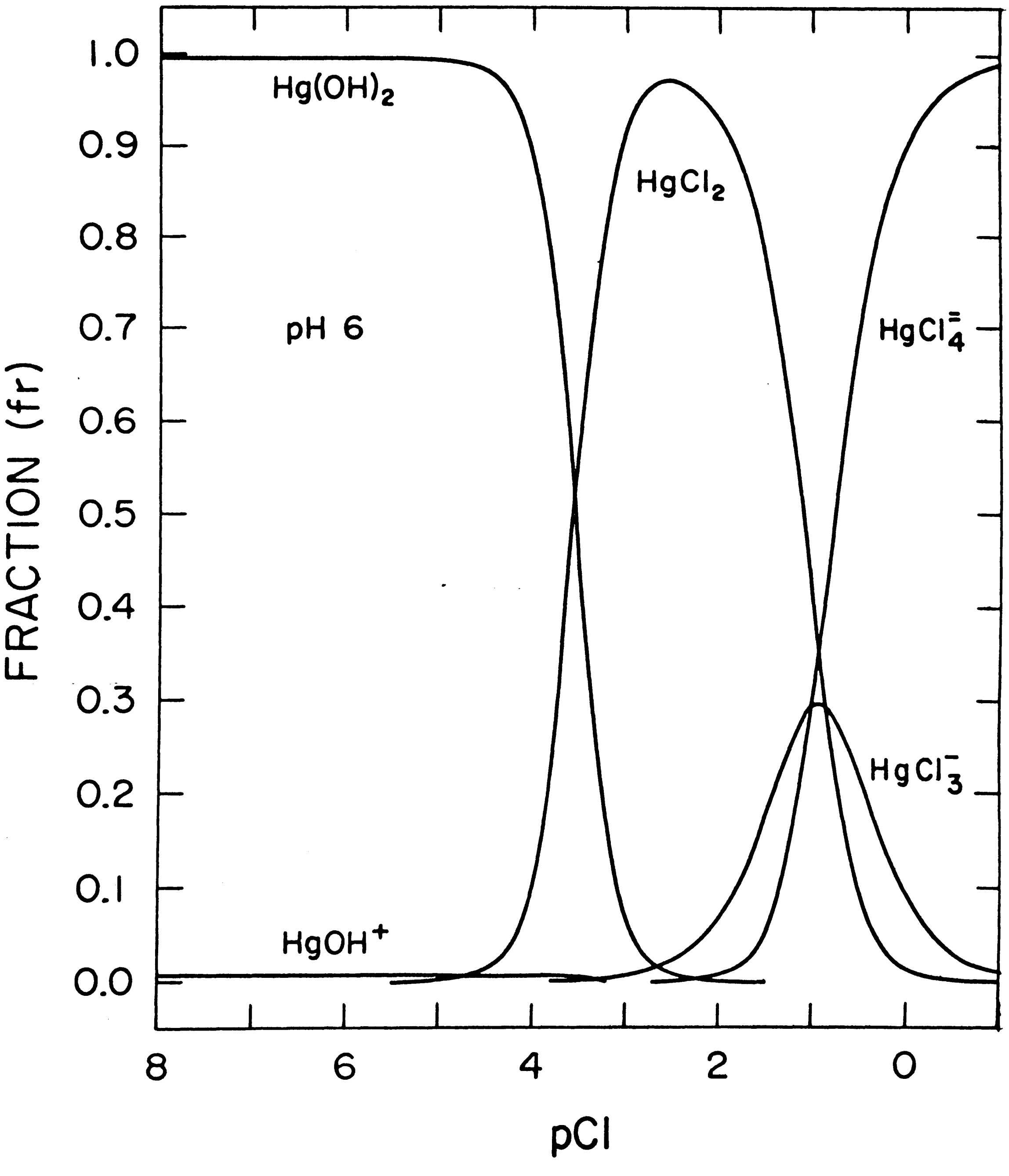

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FRACTION (fr)
10
8
6
4
2
0
pCl
$Hg(OH)_2$
$HgCl_2$
pH 5
$HgCl_4^=$
$HgCl_3^-$
$HgOH^+$
$HgCl^+$

Fig. 13. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 6 in a two-component system.



FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8
6
4
2
0
pCl
pH 6
$Hg(OH)_2$
$HgCl_2$
$HgCl_4^=$
$HgCl_3^-$
$HgOH^+$

Fig. 14. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 7 in a two-component system.

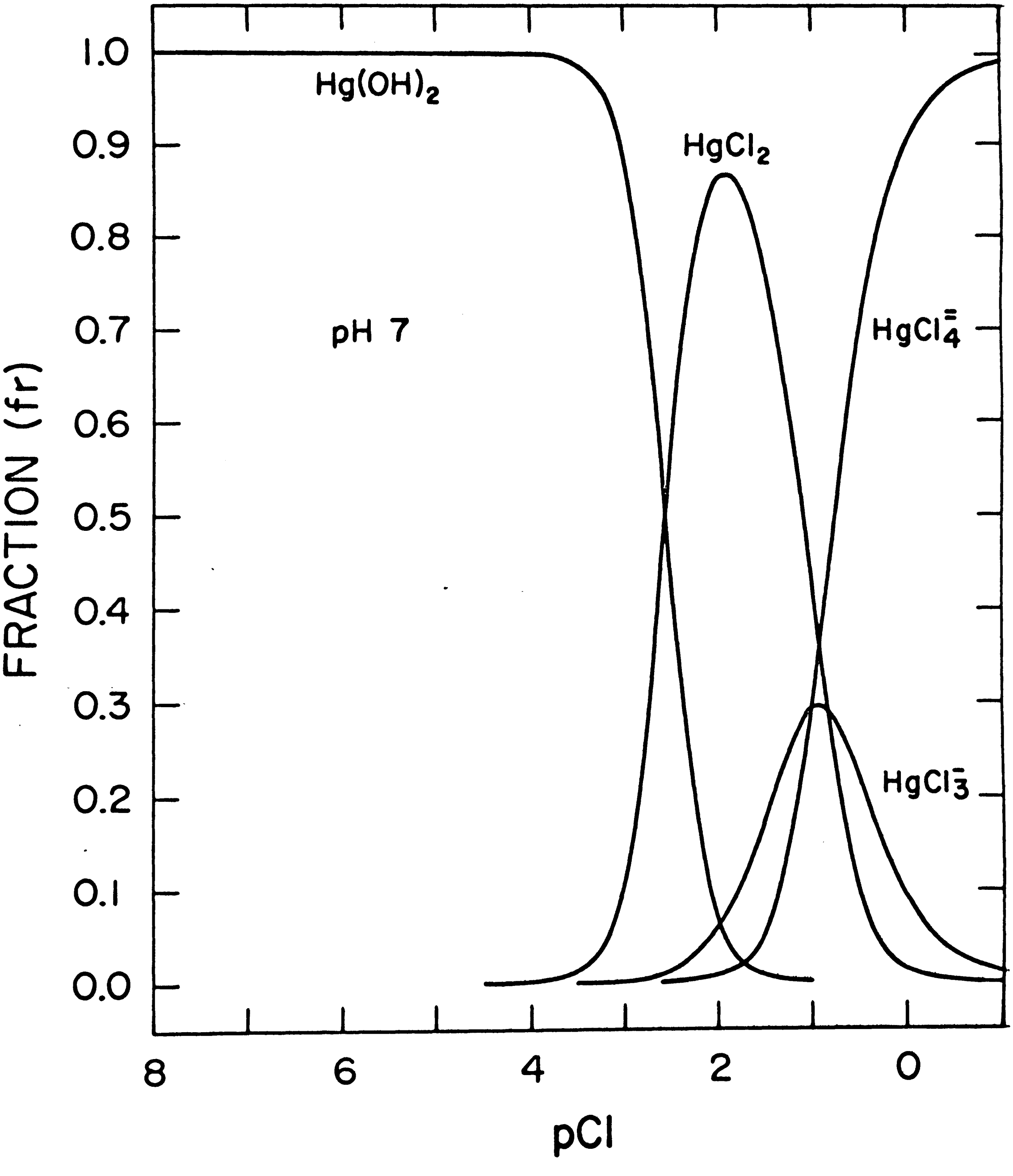

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FRACTION (fr)
8
6
4
2
0
pCl
$Hg(OH)_2$
$HgCl_2$
pH 7
$HgCl_4^=$
$HgCl_3^-$

Fig. 15. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 8 in a two-component system.

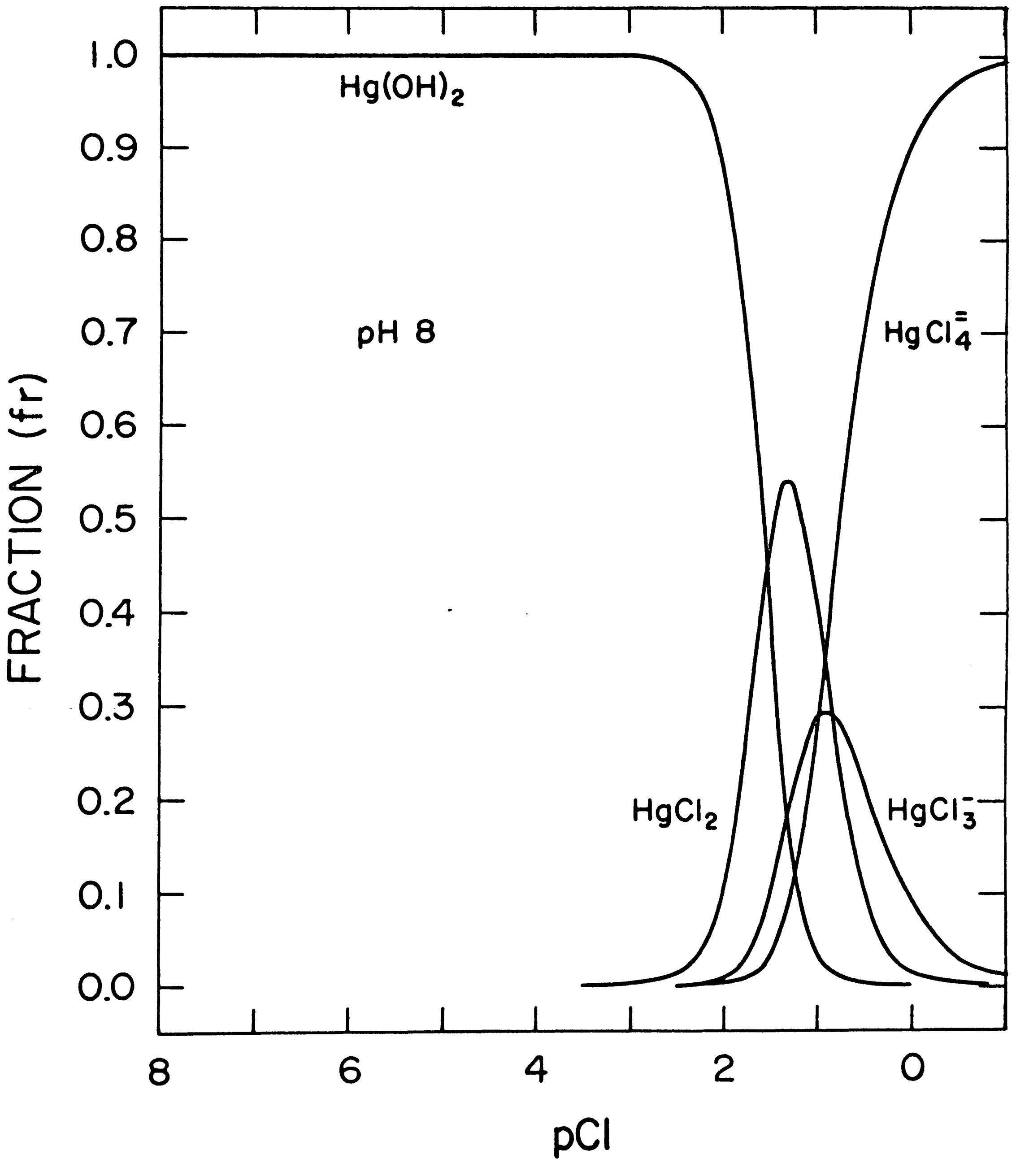
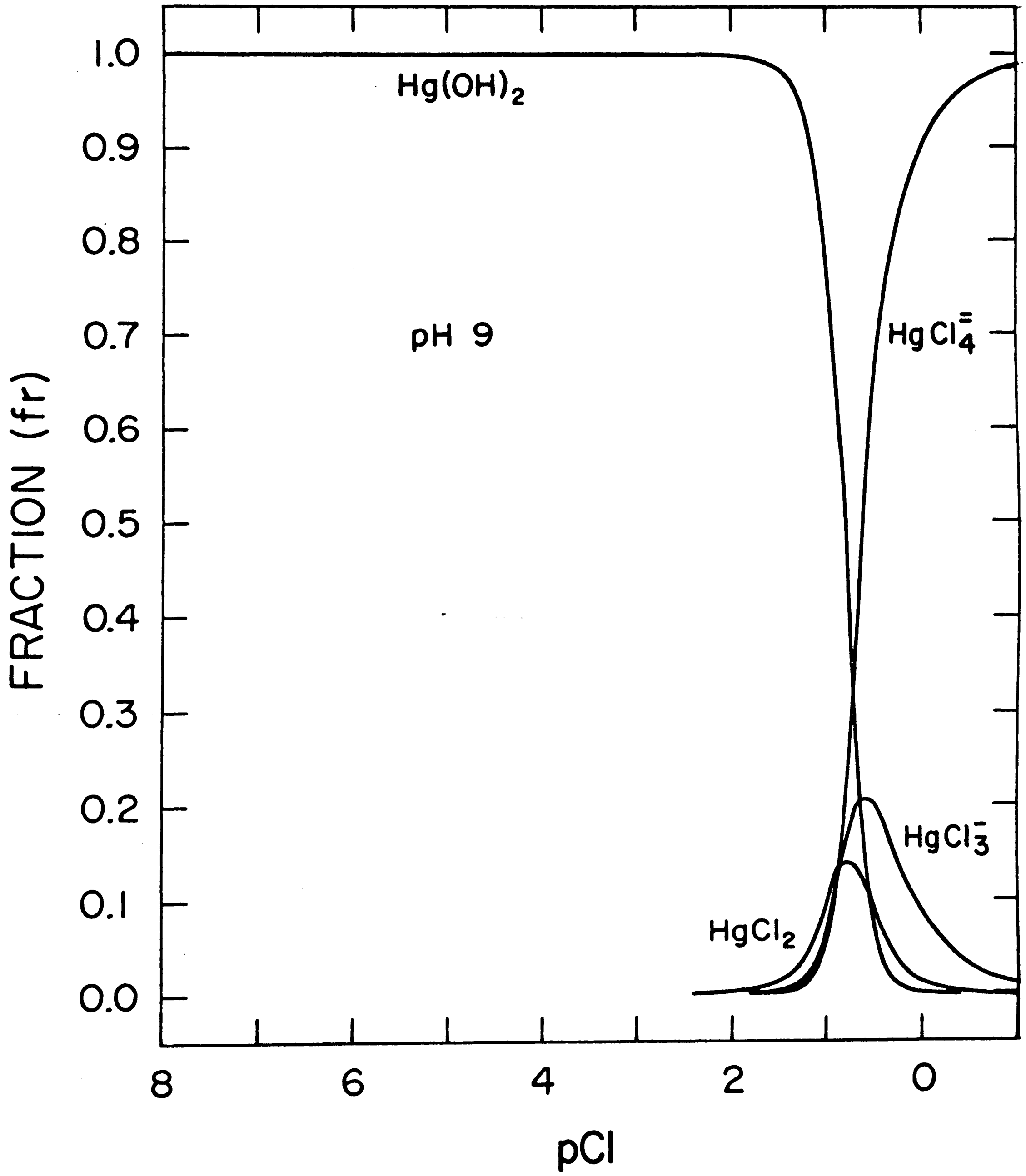

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FRACTION (fr)
$Hg(OH)_2$
pH 8
$HgCl_4^{=}$
$HgCl_2$
$HgCl_3^{-}$
8
6
4
2
0
pCl

Fig. 16. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Hg(II) at pH 9 in a two-component system.


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FRACTION (fr)
$Hg(OH)_2$
pH 9
$HgCl_4^=$
$HgCl_3^-$
$HgCl_2$
8
6
4
2
0
pCl

to 19.2 and 11 percent, respectively. In solutions with pH 3 and pCl values greater than 8 ($<3.5\times10^{-4}$ ppm), the total soluble Hg(II) will have a species distribution consisting of 10.5 percent Hg^{++}, 75.5 percent $HgOH^{+}$, and 14 percent $Hg(OH)_2^{\circ}$. With pCl values less than 5 (>0.35 ppm) all Hg(II) will be present in soluble chloride complexes (Fig. 10). $Hg(OH)_2$ is the predominant species at pH 4 and 5 when the respective pCl values are greater than 5.6 (<0.089 ppm) and 4.6 (<0.89 ppm), respectively (Figures 11 and 12). The total Hg(II) concentration in the solution will be reduced by precipitation of $Hg(OH)_2$ if the concentration of $Hg(OH)_2^{\circ}$ exceeds 5.37×10^{-4} M. Precipitation of $Hg(OH)_2$, however, should not affect the proportionality between the soluble components at measured unbound anion concentrations since the distributions are determined independent of the total Hg(II) concentrations (see equations [8] and [9]). At pH 5 the $HgOH^{+}$ fraction attains only 5 percent of the total Hg(II) present and $HgCl^{+}$ almost disappears, the maximum value being less than one percent. Precipitation of $Hg(OH)_2$, according to results presented in Figures 11 and 12, would not take place at pH 4 and 5 with pCl values less than 4 (>3.54 ppm) and 3.3 (>17.7 ppm), respectively.

The pH range 2 to 5 is important when dealing with acid mine drainages. Smith and Shumate (1971) report pH values of acid mine drainages ranging from 2.2 to 6.2, of which the majority of the samples had pH values between 2.5 and 3.5. Oliff (1963) measured pH values in the range of 2.6 to 5.2 in mineral waters from coal mines. The chloride concentrations of these samples were between 4 and 35 ppm (≃pCl 3.95-

3.0), which at low Hg(II) concentrations are high enough to mobilize more than 95 percent of the soluble inorganic Hg(II) in the form of $HgCl_2^o$ at pH 5 (Figure 12). Cairns _et al_. (1971) recorded a drop in pH from 6.4 to below 3.7 in the Indian Creek, Pennsylvania, caused by the entrance of acid mine drainage. They also report that low pH values found in most mine discharges increase the solubility of heavy metals which in turn may contribute to the high stress imposed on the aquatic environment.

The distributions given in Figures 9, 10, 11, and 12, in conjunction with the above discussion, suggest that pCl values are as important as the frequently used pH parameter in determining the solubility and mobility of Hg(II). This applies especially to systems with lower pH values. The calculations substantiate this by showing that at pH values up to 4 a chloride ion concentration of only 1.1 ppm (≃pCl 4.5) is sufficient to convert nearly all Hg(II) to $HgCl_2^o$. The result is that precipitation of $Hg(OH)_2$ and adsorption of Hg^{++} and $HgOH^+$ on inorganic sediment particles is prevented, although at low Hg(II) concentrations the sorption of molecular species on sediment particles should not be overlooked.

In the pH range 6 to 9 the $HgCl_2^o$ species decreases with increase in pH (Figures 13, 14, 15, and 16) and the next major "precipitation barrier" becomes $HgCl_4^=$ (Figure 16). The range of chloride ion concentrations where fractional to complete mobilization of Hg(II) in the form of chloride complexes will occur at pH 6, 7, 8, and 9 are respectively: pCl 5 to 2 (0.35-354 ppm), pCl 4 to 1 (3.54-3540 ppm), pCl 2.8 to 0.5 (56-11,213 ppm), and pCl 2 to 0.1 (354-28,166 ppm).

The pH range from 6 to 9 is applicable to aquatic systems of estuaries, lakes, rivers, and near-neutral to alkaline soil solutions. Abbot and Dawson (1971) state that pH levels in well-mixed estuaries are between 7.5 and 8.1, and the chloride concentration in sea-water is about 20,000 ppm (Klein, 1959), which are conditions that favor $HgCl_3^-$ and $HgCl_4^=$ formation. The data reported by Cranston et al. (1972) show a decrease in Hg content in the solution phase and bottom sediment of the LaHave estuary with increase in total salinity towards the sea. Unfortunately, the chloride concentrations at the various sampling stations were not listed. When the relationship between salinity and chlorinity cited by Harvey (1955) is considered in conjunction with the effect of the pH-pCl interaction on the Hg(II) distribution, pCl values possibly would have added another important dimension to the understanding of these findings. The same may apply to the report by White, Hinkle, and Barnes (1970) which states that thermal and mineral waters with higher salinity tend to have higher mercury contents. The pH and pCl conditions in rivers vary widely (Rhoades et al., 1971; Oliff, 1963), and inorganic distributions of Hg(II) will be affected accordingly.

Similarly the variation in pH and chloride content of soil solutions of different soils (Reitemeier et al., 1944) when related to the calculated distributions shown in Figures 9 through 16 indicates that some will favor formation of hydroxide complexes and others the formation of various chloride complexes. Although a detailed discussion on soil solutions would be too lengthy and add little to the basic concept, a few implications warrant attention. In acid soils where pH values of less than 4 may prevail in the soil solution, only 2 ppm Cl^- allows for most of the Hg(II) to be in the form of $HgCl_2^o$. Presence of hydrous Fe and Al oxides in soils displays positive charges at pH values below 5, which would favor adsorption of $HgCl_3^-$ and $HgCl_4^=$ resulting in immobilization of Hg(II). This would require a chloride ion concentration greater than 350 ppm ($pCl < 2$) and would probably take place only in areas contaminated by chlorides. A relevant example are those areas where deicing salts are used on highways. Hanes *et al*. (1970) summarized findings on water contamination with chlorides due to roadside runoff and state that there is a potential danger of salt contamination to nearby wells, ponds, and even streams with small water flow. It remains to be seen whether such detrimental salt effects are not paralleled by mercury hazards in some areas.

Very little is known to date on the movement of Hg(II) through soils. Andersson (1967), collecting leachate from a pot trial with added $HgCl_2$, found that the Hg content of the leachate increased to a maximum and then decreased to zero. This variation was attributed to temperature effects on biological activity. Unfortunately, no values for pH and chloride contents of the soil and water used in the trial are given. However, when the above-derived Hg(II) complexes are considered, a chromatographic flow of Hg(II)-chloride complexes cannot be excluded. This would have been even more likely if distilled water was used since residual amounts of Hg remained in the vicinity of application.

Competition between heavy metal hydroxy and chloride complexes at pH 8.5:

Since saline soil solutions and waters may contain chloride concentrations where the competition of hydroxy and chloride complexes of Zn(II), Cd(II), and Pb(II) in addition to Hg(II) complexes may be important, an illustrative comparison is appropriate. However, to exclude too much repetition, chloride and hydroxy complexes have been computed simultaneously only at pH 8.5, varying the chloride concentrations. This should cover the number of chloride concentration ranges in saline soil solutions quoted by Reitemeier et al. (1944) and is close to seawater conditions. The species distributions where chloride and hydroxyl ions are considered simultaneously at pH 8.5 are given in Figures 17 and 18.

When the chloride concentration range for saline-sodic soil solutions (Reitemeier et al., 1944) is considered, it is evident from Figure 17 that at pH 8.5 the $Hg(OH)_2^{\circ}$ species is non-existent and becomes important only at chloride concentrations less than 5,000 ppm ($\simeq 10^{-0.8}$ M). Above 5,000 ppm Cl^- $HgCl_3^-$ and $HgCl_4^=$ are the major species at this pH. On the other hand, $Zn(OH)_2^{\circ}$ predominates over the Zn(II)-chloride complexes at chloride concentrations less than $10^{0.4}$ M ($\simeq$89,000 ppm) and at higher chloride concentrations $ZnCl_4^=$ becomes the major species. In the case of Cd(II) and Pb(II) (Figure 18) $PbOH^+$ is the only major hydroxy species at pH 8.5 in the chloride concentration range 10^{-2} - $10^{0.2}$ M (350-56,200 ppm). Above 89,000 ppm Cl^- ($10^{0.4}$ M) $CdCl_3^-$, $CdCl_4^=$, $PbCl_3^-$, and $PbCl_4^=$ are the main complexes at this pH.

Fig. 17. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Zn(II) and Hg(II) at pH 8.5 in a two-component system.

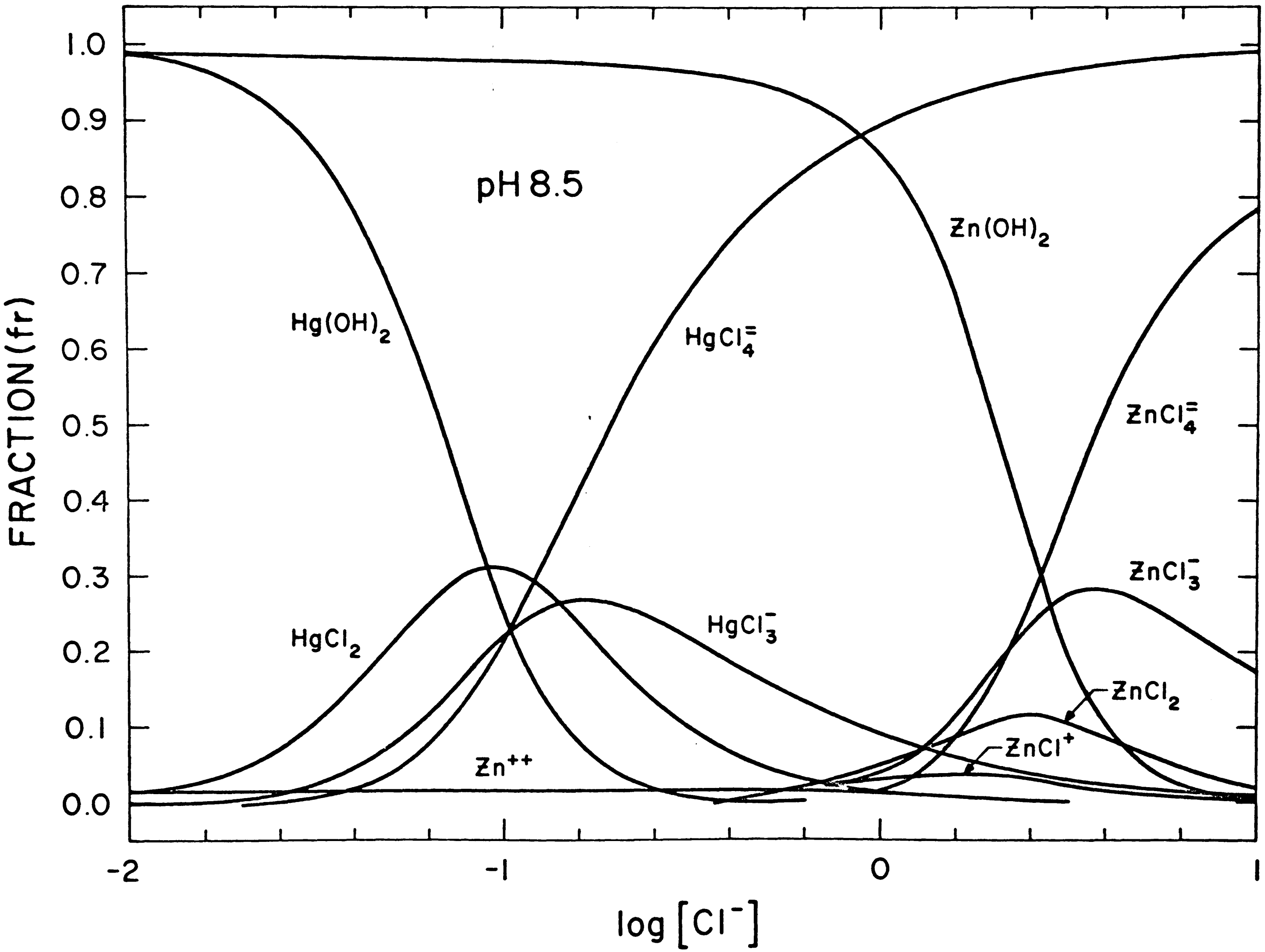
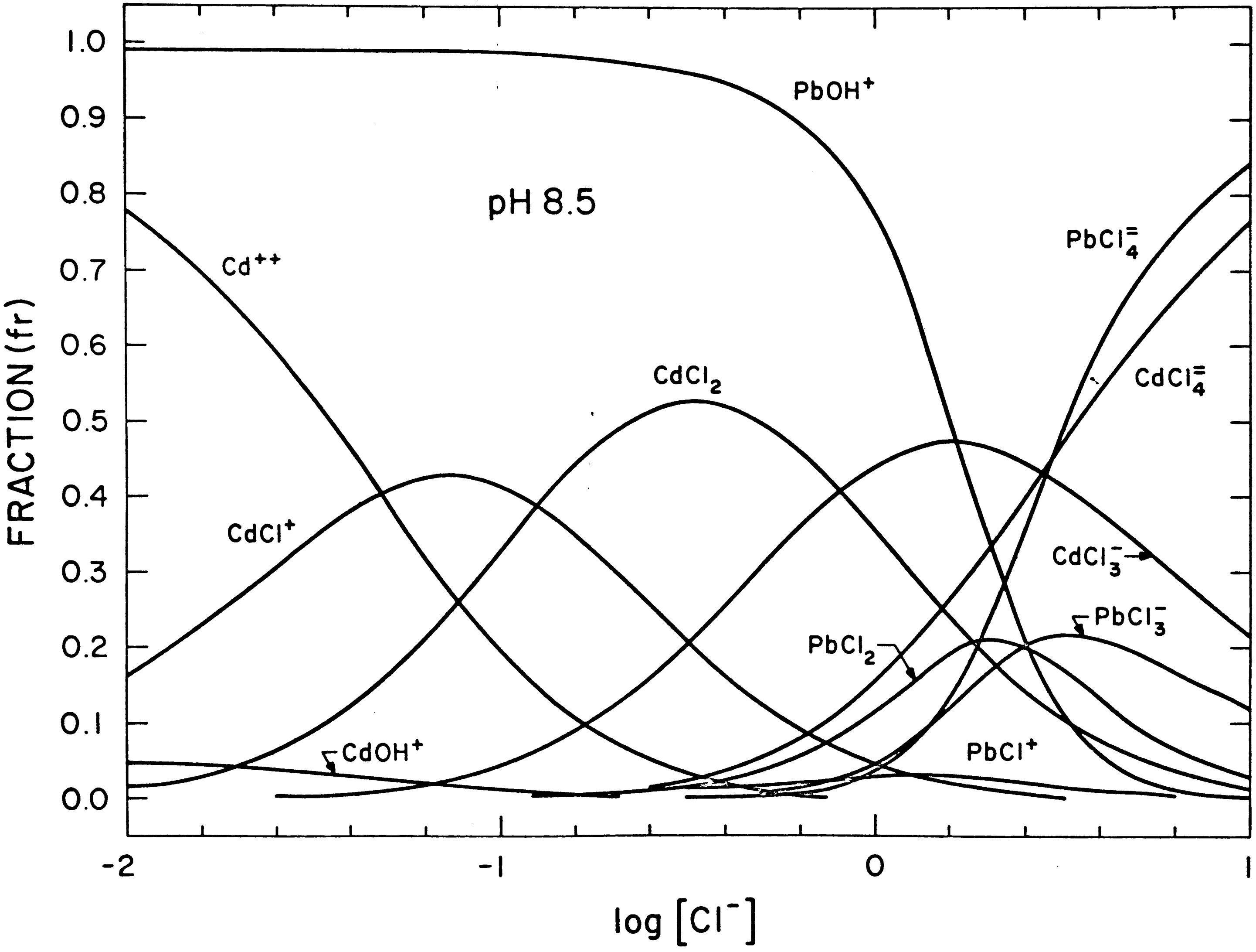

pH 8.5
FRACTION (fr)
log [Cl⁻]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-2
-1
0
1
Hg(OH)₂
HgCl₄⁼
Zn(OH)₂
ZnCl₄⁼
ZnCl₃⁻
HgCl₂
HgCl₃⁻
ZnCl₂
ZnCl⁺
Zn⁺⁺

Fig. 18. Effect of chloride ion concentration on the distribution of the hydroxy and chloride complexes of Cd(II) and Pb(II) at pH 8.5 in a two-component system.


pH 8.5
PbOH$^+$
Cd^{++}
CdCl$^+$
CdCl$_2$
PbCl$_4^=$
CdCl$_4^=$
CdCl$_3^-$
PbCl$_3^-$
PbCl$_2$
PbCl$^+$
CdOH$^+$
FRACTION (fr)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-2
-1
0
1
log [Cl$^-$]

Seawater contains about 20,000 ppm Cl^- ($\simeq 10^{-0.25}$ M) and the pH value lies between 8.1 and 8.2. Although this pH is slightly lower than pH 8.5, it becomes evident from Figures 17 and 18, without calculating exact values, that $Zn(OH)_2$ and $PbOH^+$ predominate over the chloride complexes of these metal ions. In the case of Cd(II) and Hg(II) the chloride complexes override the hydroxy complexes, the main species being $CdCl_2$, $CdCl_3^-$, $HgCl_3^-$, and $HgCl_4^=$ are expected.

Numerous more examples could be cited, but this would contribute little additional information to the basic considerations. In conclusion it must be mentioned that all the distributions are strictly limited to chloride concentration and pH conditions. As will be shown later in the section on potentiometric titrations, introduction of other ligands may appreciably modify such distributions. However, the distributions are valuable for assessing the degree to which chlorides and pH affect these heavy metal ions.

Adsorption of Hg(II) on Clays

The investigations on Hg(II) adsorption on clays were performed to evaluate firstly, whether Hg(II) adsorption takes place and, secondly, how the results relate to the behavior of Hg(II) in solution with respect to pH and pCl conditions. The initial investigation was carried out at a concentration range of 0 to 100 μmoles Hg(II) per 20 ml. In the second investigation a lower concentration range of 1-5 μg Hg(II) per 10 ml was employed accompanied by two chloride concentrations.

Adsorption study at high Hg(II) concentrations:

The investigation in which montmorillonite, illite, kaolinite, and vermiculite were equilibrated with $HgCl_2$ solutions (0-100 µmoles Hg(II) per 20 ml) showed that little, if any, adsorption occurred (Table 5). The determination of Ca^{++} was performed to facilitate check values for the adsorption of Hg^{++} or its positively charged complex ions. An increase in electrostatic adsorption of Hg^{++}, $HgOH^+$, or $HgCl^+$ would have resulted in a decrease in the amount of adsorbed Ca^{++}. The Ca^{++} and Hg(II) values (Table 5) show no treatment effects. The variation between duplicates of each treatment were of the same order as the variation between the treatments. Allowing for experimental errors, the results show that electrostatic adsorption of Hg(II) can be discounted under these experimental conditions. This is contrary to the findings reported by Krauskopf (1956), who worked at low Hg(II) concentrations and higher pH and pCl conditions by using simulated sea water. The discord in findings indicates that results should not be extrapolated beyond experimental conditions.

An explanation for the results in Table 5 was sought by relating the pH and pCl conditions of the equilibrium solutions to the distributions of Hg(II) hydroxy and chloride complexes. When the pH and pCl values (Table 6) are related to the distributions of chloride and hydroxy complexes (Figures 10, 11, and 12), it may be concluded that Hg(II) in the solution phase existed primarily in the form of $HgCl_2^{o}$. Precipitation of Hg(II) was excluded since the pH and pCl values of the equilibrium solutions when related to the distributions did not

Table 5. Effect of applied $HgCl_2$ on the Ca^{++} and Hg(II) distribution on clays.

$HgCl_2$ added	Montmorillonite		Illite		Kaolinite		Vermiculite	
	Ca^{++}	Hg(II)	Ca^{++}	Hg(II)	Ca^{++}	Hg(II)	Ca^{++}	Hg(II)
μmoles per 20 ml				meq/100g				
0.0*	96.4	0.0	25.5	0.0	7.0	0.0	113.7	0.0
2.5	97.6	4.3	24.2	1.7	6.3	0.5	109.2	0.9
10.0	97.2	3.2	24.6	1.1	6.6	1.7	111.9	4.0
20.0	98.0	4.6	24.2	1.4	6.3	0.7	108.8	3.5
40.0	95.4	3.1	24.4	1.9	6.6	0.8	110.2	1.1
60.0	97.2	---	24.2	1.5	6.6	0.1	104.6	1.3
80.0	95.7	0.7	23.8	1.6	6.2	0.3	106.7	1.1
100.0	94.9	-5.8	24.6	0.8	6.3	-0.3	106.0	-0.8

*Ca values represent CEC values for corresponding clays.

Table 6. pH and pCl values of equilibrium solutions of clay suspensions at different $HgCl_2$ treatments.

$HgCl_2$ added	Montmorillonite		Illite		Kaolinite		Vermiculite	
	pH	pCl	pH	pCl	pH	pCl	pH	pCl
µmoles per 20 ml								
0.0	4.80	3.52	4.45	3.64	4.80	4.16	4.45	3.74
2.5	4.28	3.47	4.55	3.42	4.48	4.14	4.65	3.72
10.0	3.78	3.46	4.90	3.57	4.60	4.18	4.35	3.72
20.0	3.68	3.60	4.55	3.66	4.08	4.46	4.50	3.82
40.0	3.78	3.77	4.10	3.96	4.65	--	4.30	3.66
60.0	3.75	3.77	4.00	3.49	4.08	3.43	4.45	3.90
80.0	3.90	3.72	4.35	3.58	4.08	3.72	--	--
100.0	3.90	3.77	4.75	3.92	3.75	3.92	4.50	3.83
$[Cl^-]$ range, ppm		6-13		4-13		1-13		4-8

account for a high enough fraction of $Hg(OH)_2^o$, which would have exceeded the intrinsic solubility of $Hg(OH)_2$ (Table 3) at any Hg(II) concentration used. Hence, the amount of Hg(II) shown as adsorbed to the clays (Table 5) is attributed to the experimental error which can be expected from the sensitivity limit of Hg(II) determinations by the normal atomic absorption technique. Improvement in sensitivity may be attained by using the "flameless" atomic absorption technique, although at the higher Hg(II) concentrations, excessive dilutions would have reduced much of its advantage.

The calculated distributions of Hg(II) complexes are useful for locating possible precipitation since the 0.1 M $BaCl_2$ extraction would extract all precipitated and non-precipitated (adsorbed) Hg(II) in the form of $HgCl_2^o$, $HgCl_3^-$, and $HgCl_4^=$. The distributions of Hg(II) complexes have been employed with confidence since results of potentiometric titrations, discussed in the forthcoming section, showed that the selected formation constants are in good agreement with experimental results. Extraction solutions such as $Ba(NO_3)_2$ or $Ba(CH_3COO)_2$ were not used to preclude precipitation of Hg(II) due to possible dilution effects on the chloride concentration; however, retrospectively such precipitation was found to be remote under these experimental conditions.

The above-mentioned results show that the composition of the solution phase is of prime importance when dealing with adsorption of Hg(II). This nullifies the advantage of any attempt to rank Hg(II) in preferential adsorption series with other cations. At best such attempt could be denounced as misleading in determining the behavior of Hg(II) in the vicinity of charged colloidal particles. Similarly, one may question the practice of using the Gapon relationship indiscriminately without considering hydrolysis or any other ion-pairing effect of the cation under study. A recent evaluation of Pb(II) adsorption by soils (Lagerwerff _et_ _al_., 1973), for example, does not show whether the $PbOH^+$ ion was considered, although Pb(II) concentrations were expressed as meq/g and meq/l in the Gapon equation.

Adsorption study at low Hg(II) concentrations:

The results obtained in this investigation are presented in μmoles Hg(II) adsorbed per 100 g clay (Table 7) and percentage of added Hg(II) adsorbed (Table 8). Since great variability was encountered within replications in the actual Hg(II) determinations, largely due to instrumental instability, statistical analyses were performed. Results of the analysis of variance and significant interactions are given in Tables 14 and 15 in the Appendix. The statistical analysis was regarded as a necessity, not only to show treatment effects, but also to emphasize that the experimental error involved was unfortunately large so that the actual values given in Tables 7, 8, and 15 should be regarded more as showing tendencies rather than precision data. Although the determination by the flameless atomic absorption technique has a sensitivity in the ppb range, precision and expecially reproducibility is highly dependent on the stability of the instrument. Current surges seemed to have been the main problem which probably did not only affect the electronic stability of the instrument but also the pump circulating the vapor in the system.

Table 7. Amount of Hg(II) adsorbed to clays at 0.001 and 0.5 M chloride concentrations.*

[Cl$^-$]	Hg(II) concentrations (ppm)**			
	0.1	0.5	2.5	5.0
moles/l	µmoles Hg(II)/100g			
		Montmorillonite***		
0.001	4.2	39.5	137.3	234.4
0.440	-2.5	- 4.1	22.3	1.4
		Vermiculite***		
0.001	5.9	44.6	181.0	298.1
0.440	-4.6	13.2	- 36.7	- 24.0
		Kaolinite***		
0.001	0.9	5.9	42.7	70.8
0.440	-0.5	-2.9	-13.4	-22.0

*Values represent means of two replications
(-) sign indicates negative adsorption (repulsion)

**ppm x 10 = µg/10 ml

***Weight of clay per 10 ml suspension:

Montmorillonite	53 mg
Vermiculite	47 mg
Kaolinite	182 mg

LSD's: (0.01) = 56; (0.05) = 41; (0.10) = 29

Table 8. Amount of Hg(II) sorbed by clays expressed as percentage of added Hg(II).*

[Cl$^-$]	Hg(II) concentration (ppm)**			
	0.1	0.5	2.5	5.0
moles/l	Hg(II) adsorbed (% of added)			
	Montmorillonite (53 mg)			
0.001	45.0	84.4	58.3	49.8
0.440	-27.0	- 8.7	9.5	0.3
	Vermiculite (47 mg)			
0.001	55.5	83.5	67.7	55.8
0.440	-42.7	24.7	-15.7	- 4.5
	Kaolinite (182 mg)			
0.001	32.7	43.5	62.5	51.8
0.440	-19.5	-21.5	-19.6	-15.1

*Values represent means of two replications
(-) sign indicates negative adsorption (repulsion)

**ppm x 10 = µg/10 ml

LSD's: (0.01) = 30; (0.05) = 22; (0.10) = 18

The adsorption of Hg(II) (Table 7) increased with increase in Hg(II) concentration at the lower chloride concentration on all three clays. In the case of montmorillonite and vermiculite the increase between 0.5, 2.5, and 5.0 ppm Hg(II) treatments was significant at $P = 0.01$ and highest adsorption was recorded for vermiculite. Kaolinite, as expected, gave the lowest amounts adsorbed even though the weight of kaolinite used was three to four times the amount of montmorillonite or vermiculite employed.

The lower amount of adsorption in the presence of kaolinite (Table 7) cannot be assigned only to the difference in properties of the clays but may also be a direct result of the types of the Hg(II) complexes present in the equilibrium solution. Although, at the onset of the investigation, it was the aim to have all the Hg(II) existing in the form of $HgCl_2^o$ at the lower chloride concentration, results on pH and pCl values in the equilibrium solution (Table 9) showed that this was not the case. The pH and pCl values for the equilibrium solutions of montmorillonite and vermiculite when related to Hg(II) chloride and hydroxy species distributions (Figure 14) indicate that approximately 75 percent of the Hg(II) existed in the form of $Hg(OH)_2^o$. Approximate species distributions for the kaolinite equilibrium solutions can be obtained by relating the corresponding pH and pCl values to the distributions in Figure 13, which indicates that over 90 percent of the Hg(II) in the equilibrium solution existed as $HgCl_2^o$.

Although little information is available on the behavior of neutral molecules such as $Hg(OH)_2^o$ and $HgCl_2^o$ in the presence of

Table 9. pH and pCl values of equilibrium solution of montmorillonite, vermiculite, and kaolinite suspensions at 0.001 and 0.44 M chloride concentrations.

Approximate $[Cl^-]$		Hg(II) concentrations (ppm)*			
		0.1	0.5	2.5	5.0
moles/l					
		Montmorillonite**			
0.001	pH	6.8	6.8	6.7	6.7
	pCl	2.77	2.79	2.79	2.79
0.440	pH	6.2	6.1	6.2	6.3
	pCl	0.36	0.36	0.36	0.36
		Vermiculite**			
0.001	pH	6.8	6.9	6.9	7.0
	pCl	2.81	2.81	2.81	2.84
0.440	pH	6.3	6.2	6.2	6.4
	pCl	0.36	0.36	0.36	0.36
		Kaolinite**			
0.001	pH	5.8	6.4	5.8	5.7
	pCl	2.94	2.90	2.93	2.95
0.440	pH	5.8	5.5	5.2	5.5
	pCl	0.36	0.36	0.36	0.36

*ppm x 10 = µg/10 ml

**Weight of clays per 10 ml suspension:

Montmorillonite	53 mg
Vermiculite	47 mg
Kaolinite	182 mg

negatively charged clays, it seems plausable to expect that $Hg(OH)_2^{\circ}$ aided by hydrogen bonding would be adsorbed with greater tenacity. Matijevic, Mathai et al. (1961) and Metijevic, Abramson et al.(1960, 1961) have shown in coagulation studies with AgI sols that the hydrolyzed ions of Al(III) and Th(IV) are more strongly adsorbed to the colloidal AgI than the hydrated Al^{3+} and Th^{4+}. Although the hydrolyzed Al(III) and Th(IV) are still ionic displaying a charge and will receive less competition from H^+ ions as compared to their hydrated counterparts at a lower pH, the results by Matijevic and his co-workers strongly suggest that hydroxyl groups of neutral molecular species may display adsorption affinities (chemisorption) of a significant magnitude.

When the chloride concentration was raised to 0.44 M, adsorption of Hg(II) decreased markedly (Table 7). The predominance of negative values suggests that negative adsorption occurred in most cases. The distributions (Figure 13) and pH and pCl values (Table 9) show that at these chloride concentrations the Hg(II) existed predominantly as $HgCl_4^{=}$. The positive values obtained at 0.5 ppm Hg(II) level in the presence of vermiculite and 2.5 and 5.0 ppm Hg(II) level in the presence of montmorillonite appear odd, and no explanation other than experimental error can be forwarded at this stage. The LSD values (Table 7) show little significance in differences between values obtained at the different Hg(II) concentration levels at the higher chloride concentration.

The data (Table 8) express amounts of Hg(II) adsorbed per weight of clay used as percentage of the amount of Hg(II) added at the various treatments. In the presence of montmorillonite and vermiculite (approx. 50 mg clay per 10 ml) the maximum percentage of 84 percent of added Hg(II) adsorbed was attained at the low chloride concentration at 0.5 ppm Hg(II) level. Newton and Ellis (1972)[1] report that Hg(II) adsorption of bentonite was proportional to Hg(II) concentrations at low Hg(II) levels, but at the same time the percent of added Hg(II) fell rapidly at Hg concentrations above 0.2 ppm. They also found that at 0.2 ppm Hg(II) concentration and pH 4.6-4.9 bentonite adsorbed 50 percent of added Hg(II) in 0.01 M $Ca(NO_3)_2$, whereas in 0.01 M $CaCl_2$ only 8.4 percent was adsorbed. Under higher pH conditions maximum adsorption occurred in the chloride rather than in the nitrate systems. The latter observation by Newton _et al_. (1972) is rather unexpected. In the present study the highest percentage of added Hg(II) adsorbed by kaolinite was attained at 2.5 ppm Hg(II) concentration; however, it should be noted that for kaolinite 182 mg was used, which is about 3.6 times more clay than the amounts of montmorillonite and vermiculite.

As mentioned before, in the case of the kaolinite, Hg(II) in the equilibrium solution existed predominantly as $HgCl_2^{\circ}$. However, it is not certain whether the same proportion of $HgCl_2^{\circ}$ exists at the surface of the colloids since chlorides will undergo negative adsorption which means that the solution in the vicinity of the interface will have a lower chloride concentration than the equilibrium solution. Hanes (1970) determined negative adsorption of chlorides in the presence of

---

[1] _Ibid_.

kaolinite using 5 x 10^{-3} M NaCl. At pH 6 the negative adsorption was about 0.25 meq per 100 g kaolinite. Since the pH and pCl values of the kaolinite equilibrium solutions are in the region where a slight increase in pCl values would increase the $Hg(OH)_2^{o}$ fraction markedly in the vicinity of the surface (Table 9 and Figure 13), the adsorption of Hg(II) may have actually been in the form of $Hg(OH)_2^{o}$.

The hydroxy species are more likely to be stable in the vicinity of negatively charged colloids. A possible explanation is that the deficit of hydroxyl ions near the surface as compared to the outer solution may be less than other anions. This argument is based on the condition that the ionic product of water (K_w) is a constant. If the condition of K_w constancy holds, then one would expect that the distribution of H^+ and OH^- ions is similar in the inner and outer solutions in the vicinity of charged colloidal surfaces. The ionic product constancy of water may, therefore, be regarded as a buffer mechanism against pH differences between the inner and outer solution. When the Gouy-Chapman model is used ions are only considered as point charges and no equilibria conditions such as ionic product of water are considered. Based on this model pH values in the inner solution would be substantially lower than in the outer solution.

The values for percent of Hg(II) added, adsorbed or repelled at the high chloride concentration were most consistent in the case of kaolinite (Table 8). In the presence of montmorillonite and vermiculite there was a tendency of lower percentage of added Hg(II) being repelled at the higher Hg(II) concentrations. In none of the treatments at the high chloride concentration was a percentage value of added Hg(II) close to that which Krauskopf (1956) reported for montmorillonite attained, in spite of the fact that in both cases $HgCl_4^=$ was the predominant species.

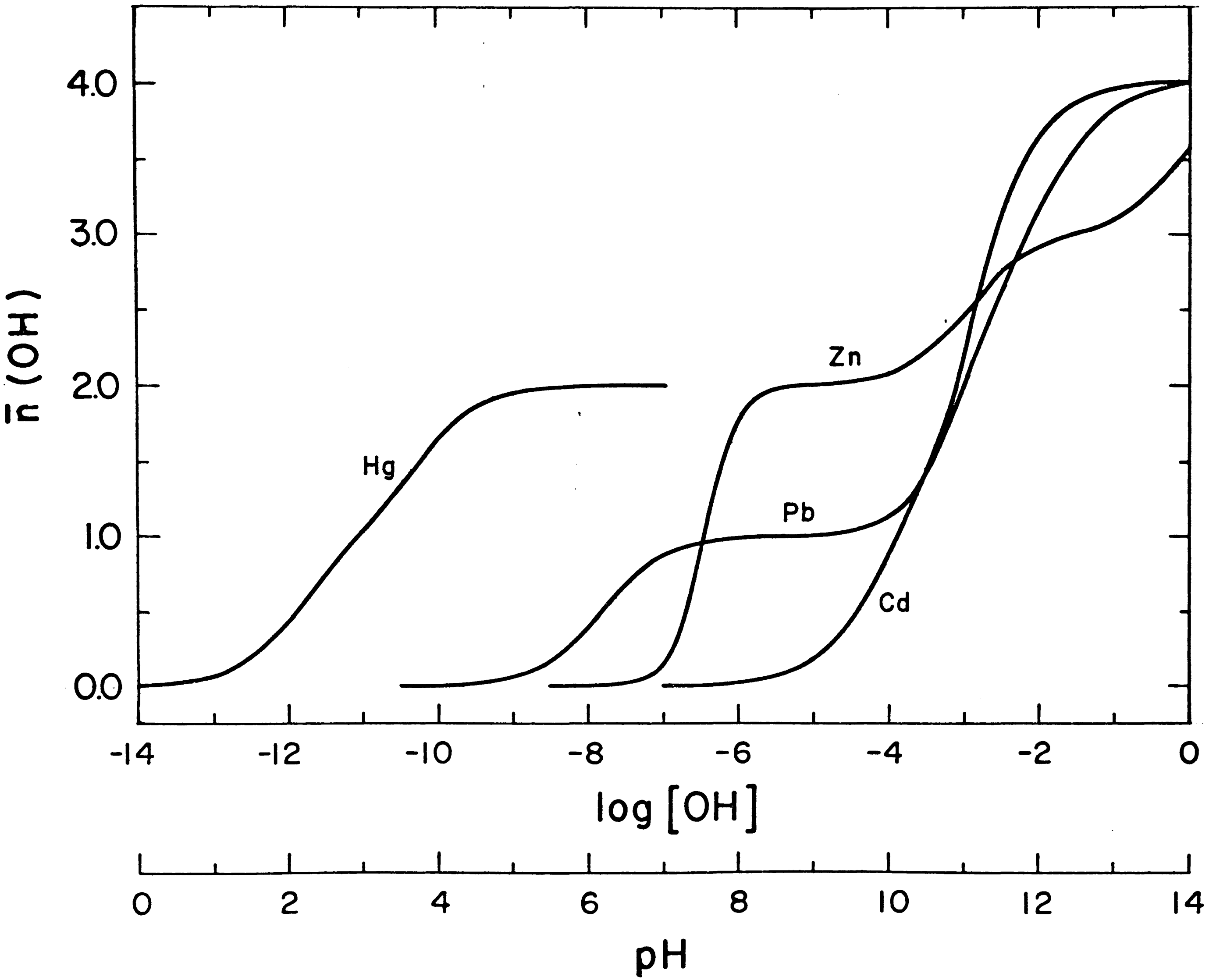
The presented data suggests that since adsorption of molecular species does take place, experimental conditions such as weight of clay per volume and concentrations of Hg(II) equilibrated may greatly affect the results and should always be reported in conjunction with measured pH and pCl values of the particular equilibrations. Without such information the terms of μmole per 100 g or percentage adsorbed are of little value. The data also reveals that adsorption of molecular species is very important when heavy metal ions are considered at low concentrations, which was not evident from the data of the previous experiment. However, the difference in adsorption between $Hg(OH)_2$ and $HgCl_2$ species needs to be studied more closely with well controlled conditions pertaining to the species distributions in solution.

Potentiometric Titrations

Prediction of titrations:

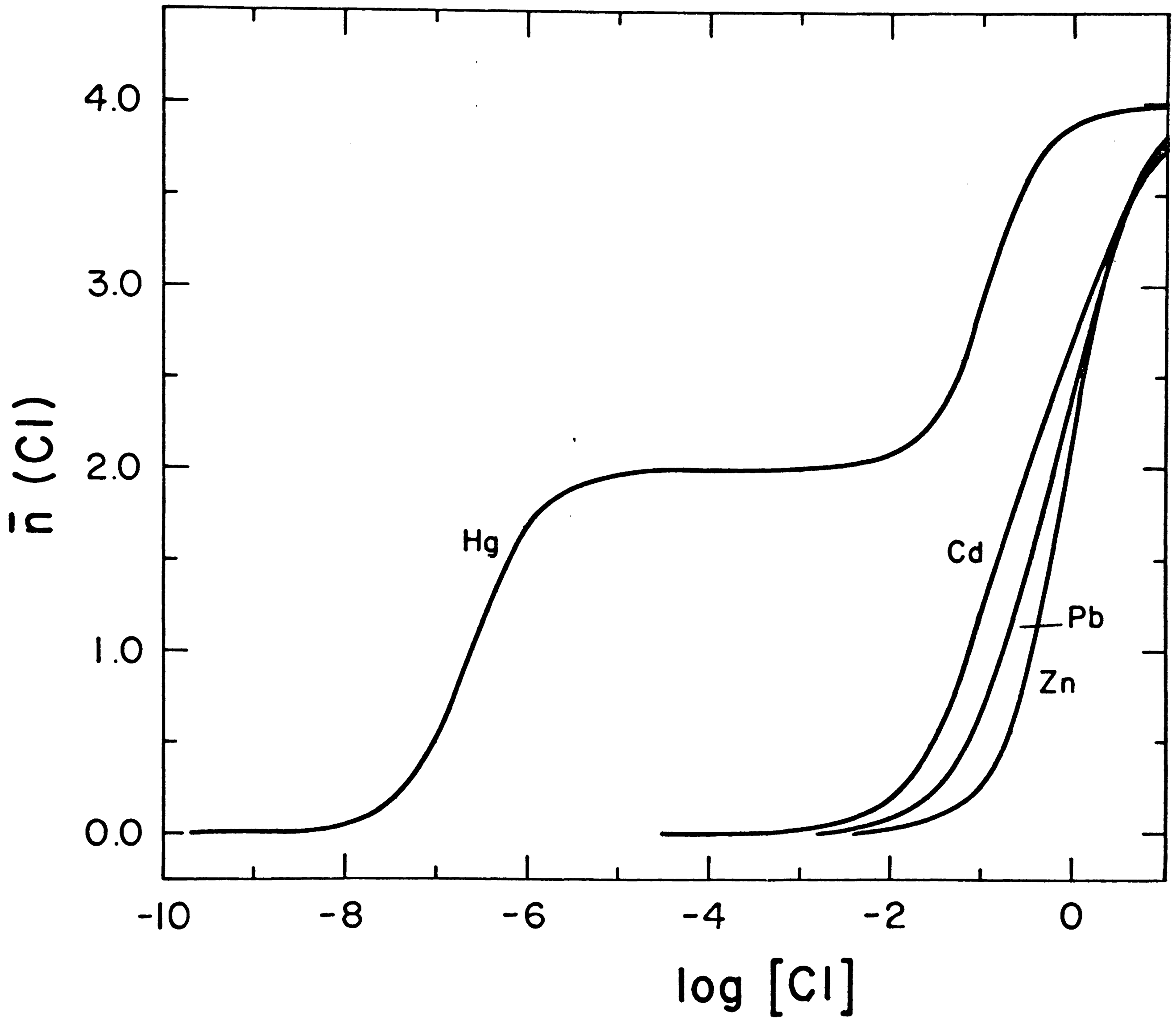
The predictions of potentiometric titrations, as mentioned before, are based on the "anion or ligand addition" concept. This means that the course of the titration is indicated by the change in $\bar{n}_{OH}$ and $\bar{n}_{Cl}$. The $\bar{n}_{OH}$ and $\bar{n}_{Cl}$ distributions for Zn(II), Cd(II), Hg(II), and Pb(II) are given in Figures 19 and 20. These values are based on equation [20] representing the single component system in which the formation of

Fig. 19. Mean anion number ($\bar{n}_{OH}$) of the single component systems for the hydroxy complexes of Zn(II), Cd(II), Hg(II), and Pb(II) at various pH levels.



4.0
3.0
2.0
1.0
0.0
$\bar{n}$ (OH)
Hg
Zn
Pb
Cd
-14
-12
-10
-8
-6
-4
-2
0
log [OH]
0
2
4
6
8
10
12
14
pH

Fig. 20. Mean anion number ($\bar{n}_{Cl}$) of the single component systems for the chloride complexes of Zn(II), Cd(II), Hg(II), and Pb(II) at various chloride ion concentrations.



4.0
3.0
2.0
1.0
0.0
$\bar{n}$ (Cl)
Hg
Cd
Pb
Zn
-10
-8
-6
-4
-2
0
log [Cl]

hydroxide or chloride complexes are considered separately from one another. The $\overline{n}_{Cl}$ values show that in the case of Zn(II), Cd(II), and Pb(II) chlorides would affect base addition titrations, in which pH measurements are taken during the course of the titration, only if the chloride ion concentration exceeds 10^{-2} M (350 ppm). The $\overline{n}_{Cl}$ and $\overline{n}_{OH}$ values also indicate that the chloride selective ion electrode, which has a lower detection limit of $1\text{-}5\times10^{-5}$ M chloride ion concentration, would be suitable to use for the study of chloride complexes of Zn(II), Cd(II), and Pb(II) below pH 6. The $\overline{n}_{Cl}$ and $\overline{n}_{OH}$ values of Hg(II), on the other hand, show clearly that potentiometric titrations of Hg(II) using the pH electrodes will be affected by chlorides at and above a chloride ion concentration of 10^{-8} M. Alternatively, the formation of the first chloride complexes may escape the sensitivity of the chloride selective ion electrode. This shows that the single component approach has a very limited application for potentiometric titrations on Hg(II) and hence, the necessity for the multiple component system as outlined by equation [21].

The distribution of $\overline{n}_{OH}$ and $\overline{n}_{Cl}$ (Figures 19 and 20) show that the hydroxy complexes of Cd(II) and chloride complexes of Cd(II), Pb(II) and Zn(II) are not well separated which is due to the smaller degree of separation of the various formation constants. This phenomenon is analagous to the pK_a values of diprotic weak acids. If the pK_a values of a diprotic acid are in close proximity the endpoints are less well separated which may obscure the detection of the two endpoints when a titration is performed.

The results of the calculations using equation [21], where $\bar{n}_{OH}$ and $\bar{n}_{Cl}$ for Hg(II) were considered simultaneously at 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} M chloride ion concentration are given by the solid line distributions in Figure 21. At a chloride ion concentration of 10^{-4} M and pH 2 $\bar{n}_{Cl} = 2$ and $\bar{n}_{OH} = 0$. With addition of base the titration of $HgCl_2^o$ complex would be expected to commence at about pH 4.4, which is the pH value where $\bar{n}_{Cl}$ decreases and $\bar{n}_{OH}$ increases. Termination of the titration would be expected at pH 7-7.2. Similarly, at chloride ion concentrations of 10^{-3}, 10^{-2}, and 10^{-1} M initiation of the titrations of Hg(II)-chloride complexes would be expected at pH 5.4, 6.4, and 7.5, respectively. The predicted pH values where the respective titrations should terminate are 8.2, 9.2, and 9.8. All the previously mentioned predictions are based on the assumption that the chloride ion concentration remains constant throughout the course of the titration. This condition is met if the total metal-ion concentration is very low compared to the chloride ion concentration, which means that any slight change in chloride ion concentration has to be below the detection limit of the titration. A second condition is that the breakdown of the Hg(II) chloride complexes and the formation of hydroxy complexes is instantaneous or at least rapid enough to preclude overtitration at any point.

Titration of Hg(II) solutions:

The results obtained from the titrations of 100 ppm Hg(II) (0.498 meq/500 ml) at total chloride concentrations of 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} M are given in Figure 22. Not all the blanks were included, since they fell within close proximity of the given ones. The titration

Fig. 21. Simultaneous mean anion numbers $\bar{n}_{OH}$ and $\bar{n}_{Cl}$ of the two-component system for chloride and hydroxy complexes of Hg(II) at various pH and chloride ion concentration levels.

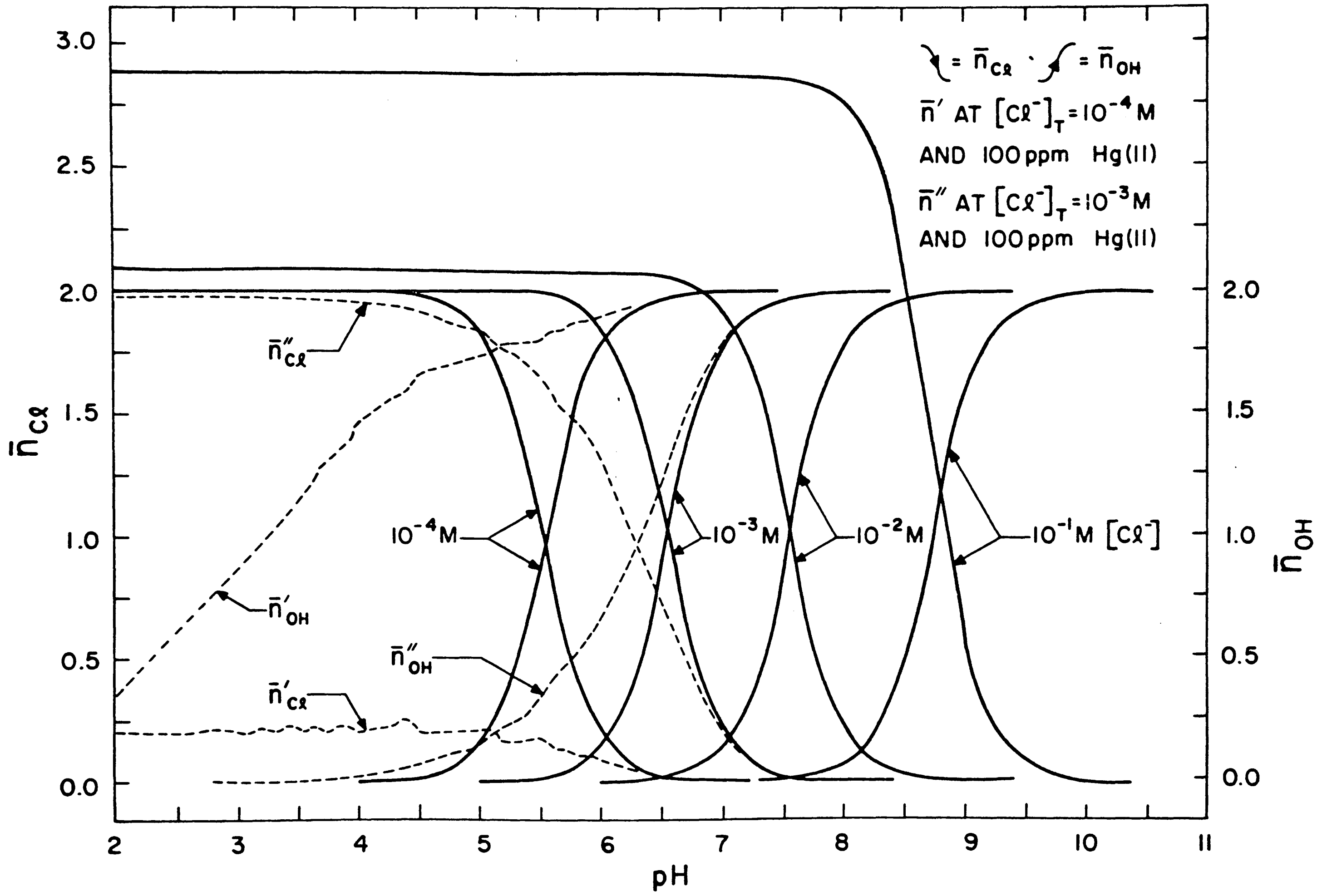
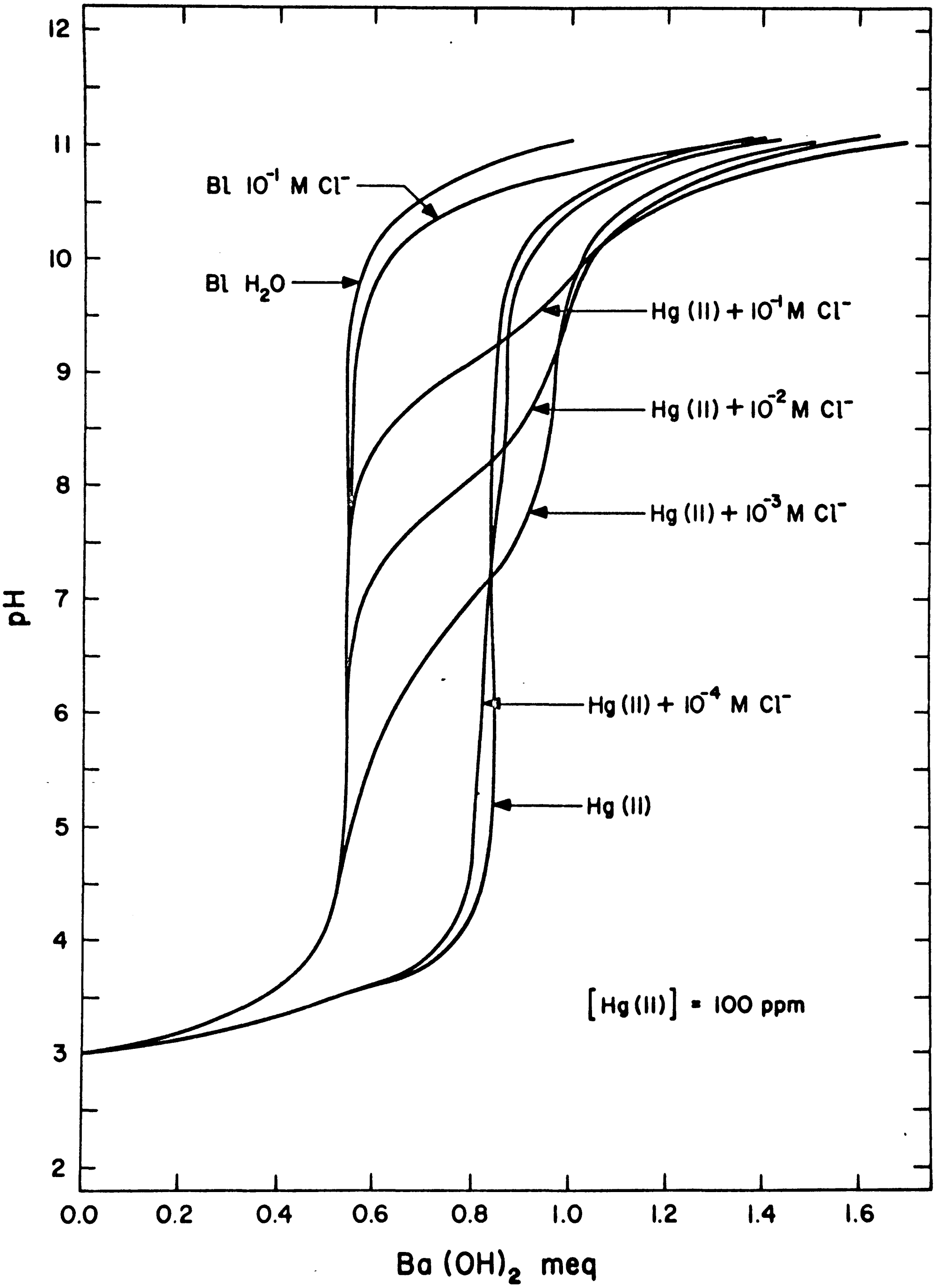

= $\bar{n}_{Cl}$, = $\bar{n}_{OH}$
$\bar{n}'$ AT $[Cl^-]_T = 10^{-4}$ M
AND 100 ppm Hg(II)
$\bar{n}''$ AT $[Cl^-]_T = 10^{-3}$ M
AND 100 ppm Hg(II)
$\bar{n}''_{Cl}$
$\bar{n}'_{OH}$
$\bar{n}''_{OH}$
$\bar{n}'_{Cl}$
10^{-4}M
10^{-3}M
10^{-2}M
10^{-1}M $[Cl^-]$
$\bar{n}_{Cl}$
$\bar{n}_{OH}$
pH
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2
3
4
5
6
7
8
9
10
11

Fig. 22. Potentiometric titrations of Hg(II) solutions with 0.1 N $Ba(OH)_2$ at total chloride concentrations of 0, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} M. (Hg(II) concentration = 0.498 meq/500 ml = 100 ppm)



pH
Ba (OH)$_2$ meq
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
2
3
4
5
6
7
8
9
10
11
12
Bl 10^{-1} M Cl$^-$
Bl H$_2$O
Hg (II) + 10^{-1} M Cl$^-$
Hg (II) + 10^{-2} M Cl$^-$
Hg (II) + 10^{-3} M Cl$^-$
Hg (II) + 10^{-4} M Cl$^-$
Hg (II)
[Hg (II)] = 100 ppm

curves of the various Hg(II)-chloride complexes were aligned to the given blank titrations to demonstrate the starting points of the titrations on the various chloride complexes. All curves are in alignment with observed pH values. The quantitative attributes are given in Table 10.

The pH values at which the titrations terminated at total chloride concentrations of 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} M are in accord with the predicted ones. The respective experimental pH values were 7.3, 8.4, 9.3, and 9.7 (Figure 22). At the termination of each titration the total chloride concentration equals the chloride ion concentration.

The pH values at which titrations of Hg(II)-chloride complexes initiated represented the predicted values only at 10^{-2} and 10^{-1}M total chloride concentration, the corresponding values being pH 6.4 and 7.4. At 10^{-4} M total chloride concentration the titration curve did not show any evidence where the titration of the Hg(II)-chloride complex was initiated. At 10^{-3} M total chloride concentration the beginning of the titration of the Hg(II)-chloride was at a lower pH, between pH 3.4 and 4.4 (Figure 22). The pH range 3.4-4.4 is given since the actual location is dependent on the graphical alignment where a shift of 0.05 inches on the chart can account for the difference. At the higher chloride concentrations this problem was less severe, since the values could always be checked by extrapolating the straight line pH increase just prior to the beginning of the titration of the complexes. The pH value where the curve deviates from the extrapolated line is the required value.

Table 10. Amount of base added during course of potentiometric titrations of 100 ppm Hg(II) at various total chloride concentrations.*

pH	Total chloride concentration, moles/l				
	0	10^{-4}	10^{-3}	10^{-2}	10^{-1}
	Base added, meq				
3.0**	0.000	0.000	0.000	0.000	0.000
3.5	0.163	0.158	0.012	0.025	0.035
4.0	0.299	0.254	0.032	0.040	0.047
4.5	0.319	0.296	0.040	0.042	0.049
5.0	0.321	0.304	0.054	0.044	0.049
5.5	0.321	0.304	0.084	0.040	0.049
6.0	0.321	0.311	0.133	0.047	0.049
6.5	0.321	0.321	0.205	0.054	0.052
7.0	0.323	0.333	0.296	0.077	0.052
7.5	0.323	0.343	0.380	0.141	0.054
8.0	0.323	0.351	0.430	0.274	0.069
8.5	0.323	0.351	0.449	0.393	0.121
9.0	0.323	0.353	0.454	0.449	0.254
9.5	0.323	0.356	0.459	0.474	0.398
10.0	0.328	0.356	0.457	0.477	0.454
10.5	0.331	0.353	0.457	0.469	0.452
11.0	0.309	0.356	0.464	0.479	0.402

*Rate of base addition was 0.015 meq per minute.
100 ppm Hg(II) = 0.498 meq Hg(II)

**pH 3 was taken as the reference point.

The reason for the discrepancy between the predicted and experimental findings is that at total chloride concentrations of 10^{-3} and 10^{-4} M the ratio of the total Hg(II) concentration to the total chloride concentration was too high. Therefore, prior to the initiation of the titration, Hg(II) complexation with chlorides lowered the chloride ion concentration markedly, subsequently causing continuous change in chloride ion concentration as the titration proceeded with base addition. The itterative prediction procedure with the aid of equations [22] and [23] made an accurate prediction possible, and in addition the chloride ion concentrations during the course of the titration could be determined at these low total chloride concentrations. At a total chloride concentration of 10^{-4} M, the broken lines marked $\bar{n}'_{Cl}$ and $\bar{n}'_{OH}$ in Figure 21 show that with 100 ppm Hg(II) in the system the Hg(II)-chloride complexes are titrated already below pH 2. Therefore, in the pH range of the present titrations no starting point for Hg(II)-chloride complex dissolution could be detected. The chloride ion concentrations at pH 2, 3, 4, 5, 6, and 7 were $10^{-7.2}$, $10^{-6.7}$, $10^{-5.9}$, $10^{-5.0}$, $10^{-4.2}$, and 10^{-4}M, respectively. The prediction of the titration of 100 ppm Hg(II) in the presence of 10^{-3} M total chloride concentration is given by the broken lines marked $\bar{n}''_{Cl}$ and $\bar{n}''_{OH}$ in Figure 21. From these values the first sign of chloride complexes being titrated can be expected around pH 4. The chloride ion concentrations during the course of this titration were $10^{-4.5}$, $10^{-4.0}$, $10^{-3.4}$, $10^{-3.0}$ M at pH 4, 5, 6, and 7, respectively. With the aid of equations [8] and [9] the exact fractions of Hg(II) complexes could be determined at all pH values whether or not the itterative procedure had to be used; however, these are not reported and would merely be a repetition of the foregoing sections.

The quantitative results in terms of meq base added are listed in Table 10 where pH 3 was taken as reference point and subsequently the base addition at pH 3 is zero. These results were obtained by substracting the amount of base added during the titration of the blanks from the amount of base added during the titration of Hg(II) at the indicated total chloride concentrations.

The data in Table 10 show that at all total chloride concentrations the maximum values for added base are obtained at pH values in the vicinity where the titration of Hg(II) or Hg(II)-chloride complexes terminates. Since 0.498 meq Hg(II) was added, it is evident that the titrations are quantitative at total chloride concentrations of 10^{-3}, 10^{-2}, and 10^{-1} M at this total Hg(II) concentration and pH range. The discrepancy of 0.04 meq can be accredited to experimental error, since at this rate of titration (4 inches per 1 meq) 0.1 inches on the chart represents 0.025 meq. Such small values are most likely beyond the accuracy limit of the titration. In the absence of chlorides and at 10^{-4} M total chloride concentration the titration did not account for all Hg(II) in solution. This can be expected since in these two cases Hg(II) was titrated at pH values below 3 (see Figures 21 and 22).

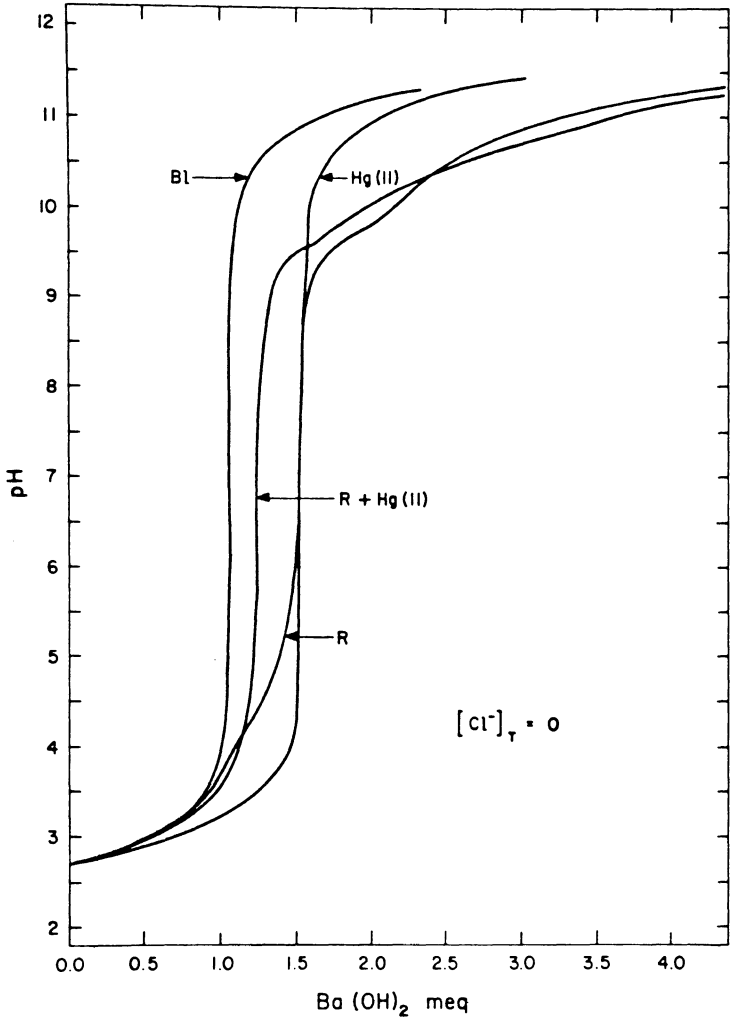
Titrations of Hg(II) in presence of resin and peat:

Once the nature of Hg(II) chloride and hydroxy complexes is established, interpretations of Hg(II) in presence of organic functional groups would appear to be relatively straight-forward, especially on a qualitative basis. However, as will be shown in the following discussion, several interacting factors during the course of the titration may lead to erroneous conclusions and make quantitative estimations completely obscure.

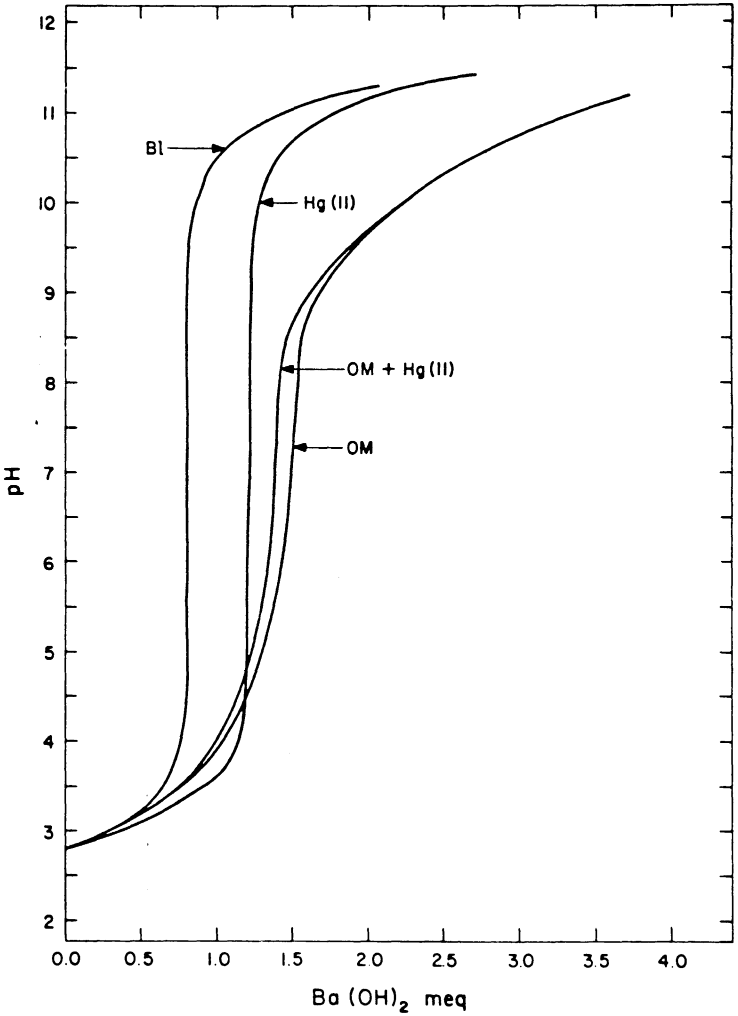
The results pertaining to Hg(II) titrations in the presence of resin and peat (referred to as OM) at different total chloride concentrations are given in Figure 23-27. These titrations were performed to establish the effectiveness of chloride and hydroxy ions to compete with organic matter for Hg(II). The resin was used to facilitate uniform material with carboxylic weak acid groups which represent a large proportion of the functional groups present in organic matter. At this point, however, it must be mentioned that according to Gamble, Schnitzer, and Hoffman (1970) carboxylic groups in the ortho position to phenolic groups give rise to bonding with metal-ions in which both the phenolic and carboxylic groups are involved.

The titrations of Hg(II) in the presence of resin and peat show marked similarities (see Figures 23-27). From these titrations it appears that the amount of Hg(II) complexed by the resin and peat was highest where no chlorides were added and decreased markedly as the total chloride concentration was increased to 10^{-3} M. To obtain a better perspective of the quantitative aspect, differences in base addition (Δ meq) were determined for the titrations in the presence of resin and peat and are listed in Tables 11 and 12. The manner in which the Δ meq values were obtained is described in the section dealing with methods and materials.

Fig. 23. Potentiometric titrations of resin, peat, and Hg(II) alone, and resin and peat in the presence of Hg(II) with no chloride addition. (R = resin, OM = peat, Bl = blank)

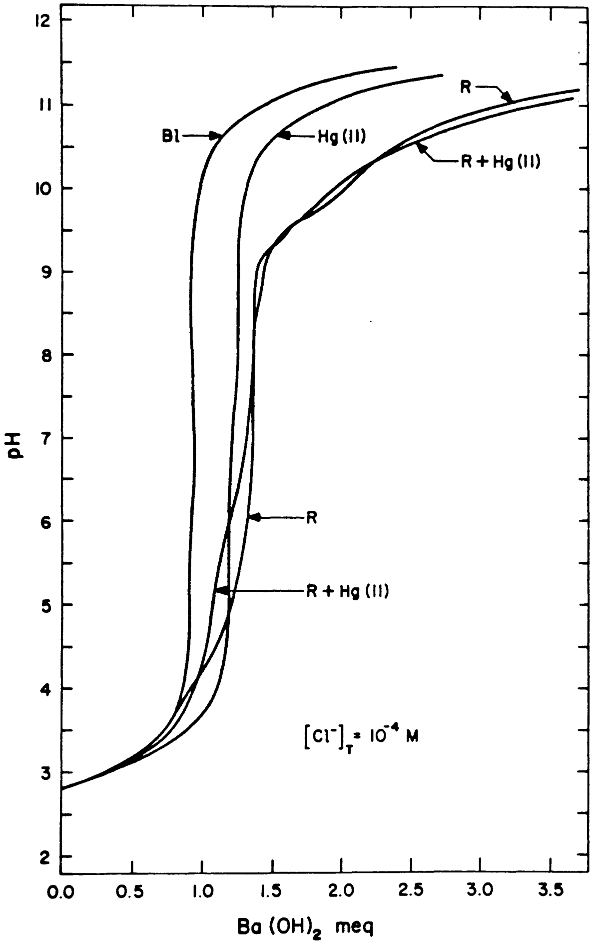


pH
Ba (OH)$_2$ meq
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
2
3
4
5
6
7
8
9
10
11
12
Bl
Hg (II)
R + Hg (II)
R
$[Cl^-]_T = 0$

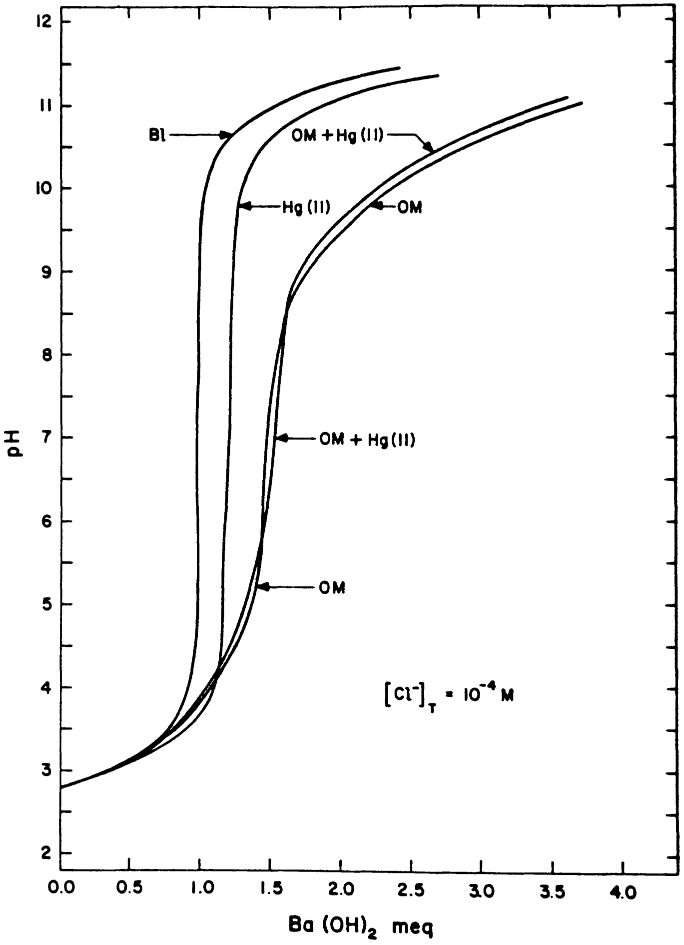


pH
Ba (OH)$_2$ meq
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
2
3
4
5
6
7
8
9
10
11
12
Bl
Hg (II)
OM + Hg (II)
OM

Fig. 24. Potentiometric titrations of resin, peat, and Hg(II) alone, and resin and peat in the presence of Hg(II) at 10^{-4} M total chloride concentration. (R = resin, OM = peat, Bl = blank)

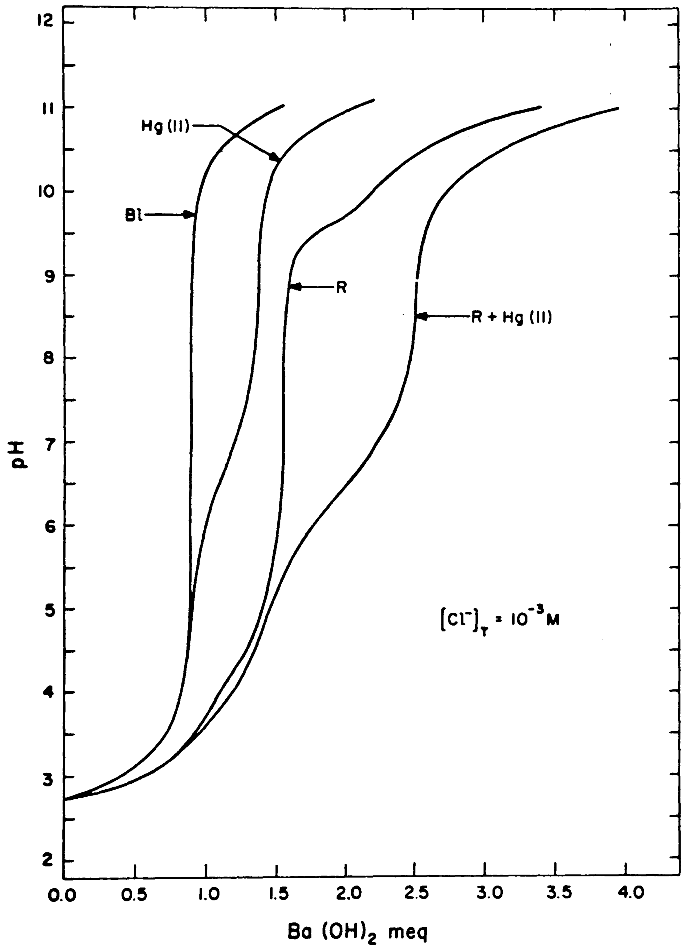


pH
12
11
10
9
8
7
6
5
4
3
2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
$Ba(OH)_2$ meq
Bl
Hg (II)
R
R + Hg (II)
R
R + Hg (II)
$[Cl^-]_T = 10^{-4}$ M

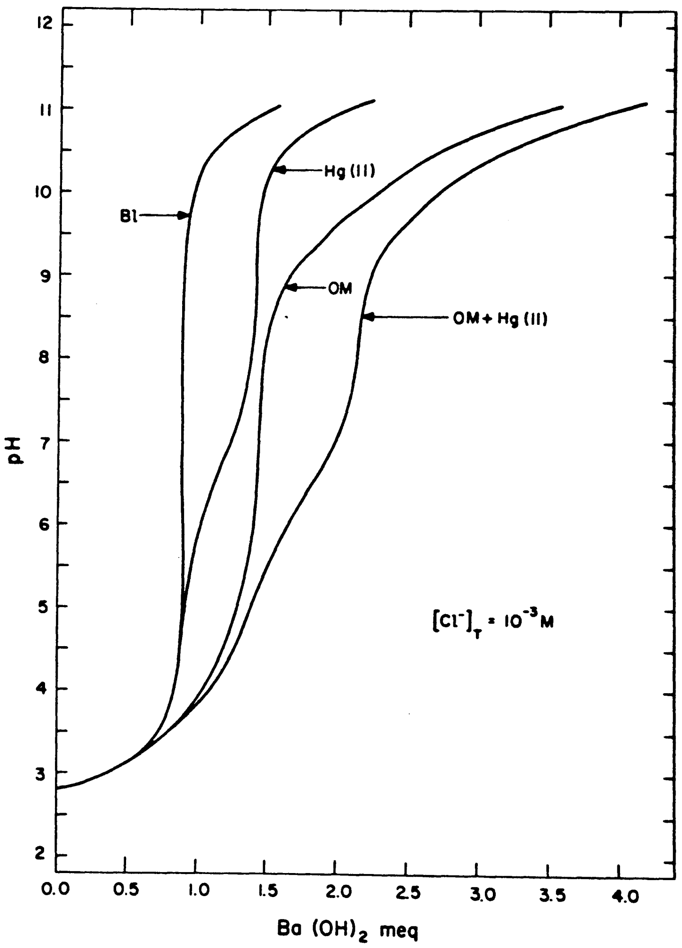


pH
12
11
10
9
8
7
6
5
4
3
2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
$Ba(OH)_2$ meq
Bl
OM + Hg (II)
Hg (II)
OM
OM + Hg (II)
OM
$[Cl^-]_T = 10^{-4}$ M

Fig. 25. Potentiometric titrations of resin, peat, and Hg(II) alone, and resin and peat in the presence of Hg(II) at 10^{-3} M total chloride concentration. (R = resin, OM = peat, Bl = blank)

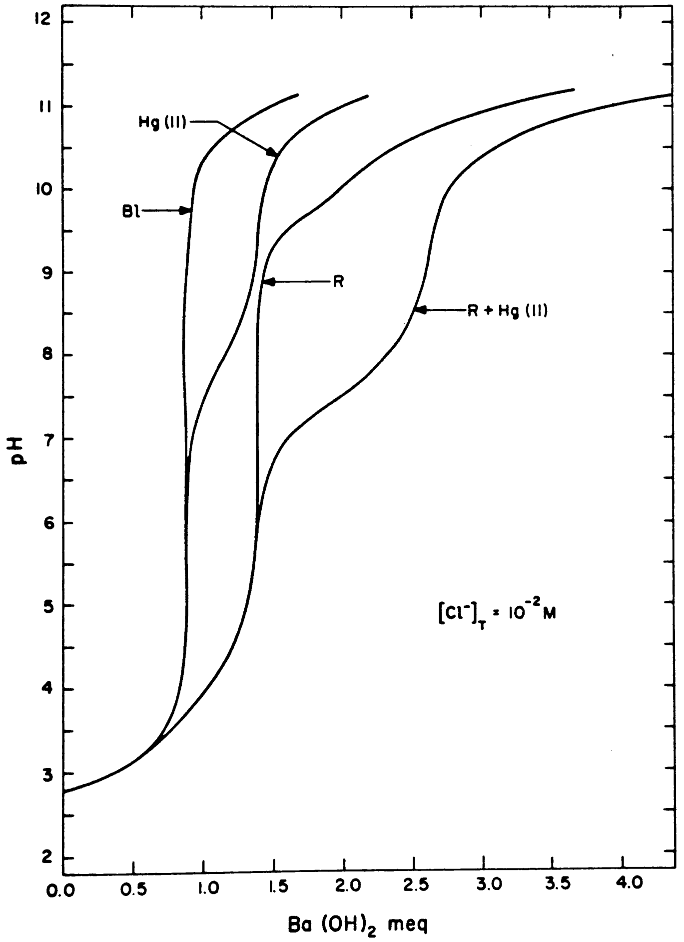


pH
12
11
10
9
8
7
6
5
4
3
2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ba (OH)$_2$ meq
Hg (II)
Bl
R
R + Hg (II)
$[Cl^-]_T = 10^{-3}M$



pH
12
11
10
9
8
7
6
5
4
3
2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ba (OH)$_2$ meq
Bl
Hg (II)
OM
OM + Hg (II)
$[Cl^-]_T = 10^{-3}M$

Fig. 26. Potentiometric titrations of resin, peat, and Hg(II) alone, and resin and peat in the presence of Hg(II) at 10^{-2} M total chloride concentration. (R = resin, OM = peat, Bl = blank)


pH
12
11
10
9
8
7
6
5
4
3
2
Hg (II)
Bl
R
R + Hg (II)
[Cl⁻]$_T$ = 10^{-2} M
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ba (OH)$_2$ meq

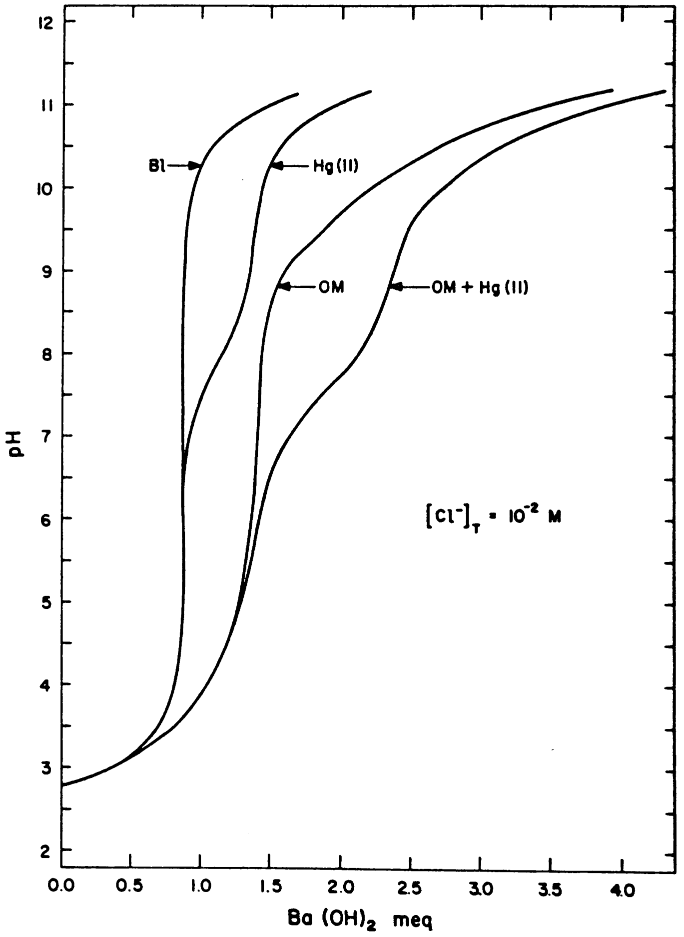
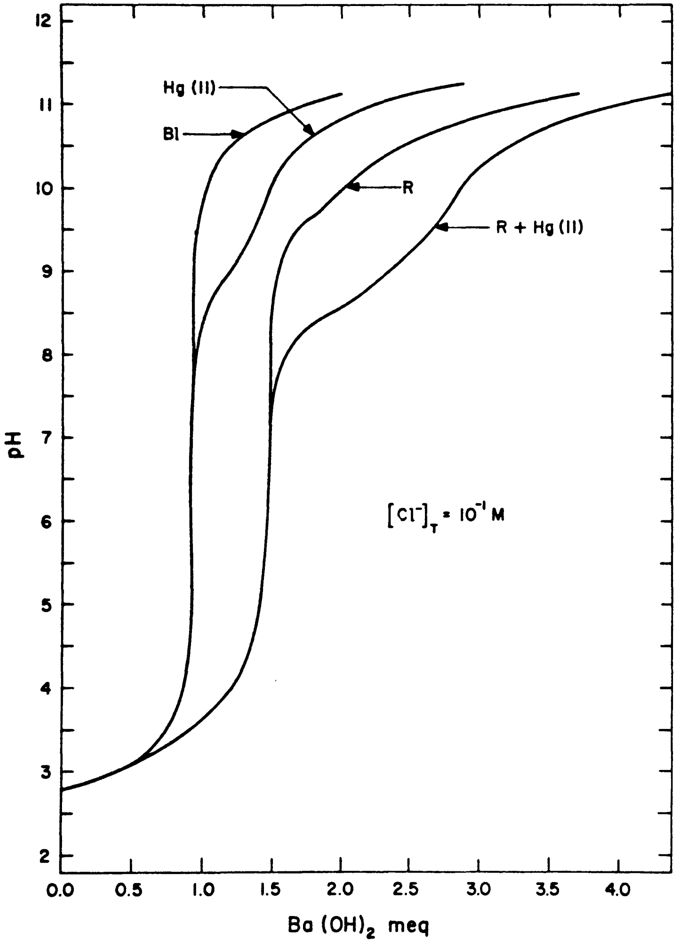

pH
12
11
10
9
8
7
6
5
4
3
2
Bl
Hg (II)
OM
OM + Hg (II)
[Cl⁻]$_T$ = 10^{-2} M
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ba (OH)$_2$ meq

Fig. 27. Potentiometric titrations of resin, peat, and Hg(II) alone, and resin and peat in the presence of Hg(II) at 10^{-1} M total chloride concentration. (R = resin, OM = peat, Bl = blank)


Hg (II)
Bl
R
R + Hg (II)
[Cl⁻]T = 10⁻¹ M
pH
2
3
4
5
6
7
8
9
10
11
12
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ba (OH)2 meq

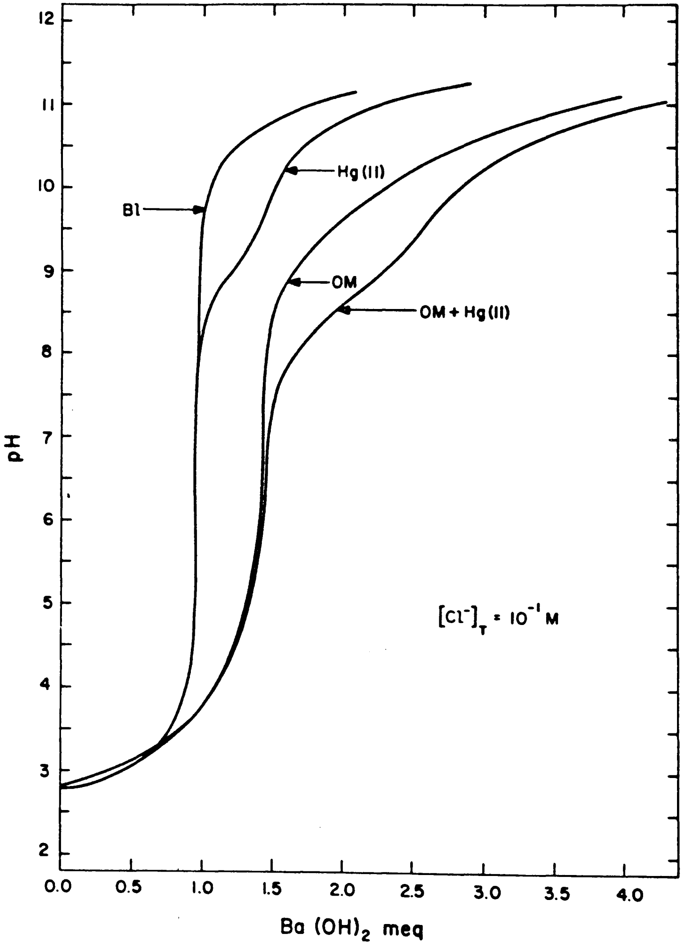

Bl
Hg (II)
OM
OM + Hg (II)
[Cl⁻]T = 10⁻¹ M
pH
2
3
4
5
6
7
8
9
10
11
12
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ba (OH)2 meq

Table 11. Difference in base added (Δ meq) between titration of resin with 100 ppm Hg(II) and the sum of the separate titrations on 100 ppm Hg(II) and resin.*

pH	Total chloride concentration, moles/l				
	0	10^{-4}	10^{-3}	10^{-2}	10^{-1}
			Δ meq		
3.0**	0.000	0.000	0.000	0.000	0.000
3.5	-0.181	-0.106	0.000	-0.013	0.019
4.0	-0.356	-0.175	0.038	-0.031	0.025
4.5	-0.469	-0.262	0.050	-0.031	0.000
5.0	-0.550	-0.331	0.025	-0.038	0.012
5.5	-0.600	-0.331	0.031	-0.056	0.025
6.0	-0.650	-0.319	0.119	-0.050	0.019
6.5	-0.656	-0.294	0.250	-0.012	0.025
7.0	-0.663	-0.269	0.400	0.119	0.031
7.5	-0.669	-0.263	0.400	0.406	0.050
8.0	-0.662	-0.256	0.419	0.575	0.119
8.5	-0.656	-0.244	0.438	0.644	0.356
9.0	-0.619	-0.224	0.413	0.619	0.575
9.5	-0.606	-0.237	0.300	0.506	0.569
10.0	-0.575	-0.344	0.025	0.200	0.388
10.5	-0.256	-0.250	0.000	0.100	0.263
11.0	0.037	-0.131	0.063	0.144	0.181

*Titration rate was 0.0375 meq per minute
100 ppm Hg(II) = 0.498 meq Hg(II)
Weight of resin used was 0.2 g.

**pH 3 was taken as the reference point.

Table 12. Difference in base added (Δ meq) between titration of OM with 100 ppm Hg(II) and the sum of the separate titrations on 100 ppm Hg(II) and OM.*

pH	Total chloride concentration, moles/l				
	0	10^{-4}	10^{-3}	10^{-2}	10^{-1}
			Δ meq		
3.0*	0.000	0.000	0.000	0.000	0.000
3.5	-0.206	-0.137	0.044	0.050	0.075
4.0	-0.350	-0.212	0.075	0.062	0.113
4.5	-0.387	-0.237	0.106	0.069	0.106
5.0	-0.412	-0.250	0.100	0.100	0.119
5.5	-0.425	-0.238	0.100	0.087	0.112
6.0	-0.438	-0.206	0.156	0.112	0.131
6.5	-0.419	-0.188	0.206	0.131	0.131
7.0	-0.431	-0.181	0.300	0.244	0.125
7.5	-0.450	-0.194	0.219	0.381	0.169
8.0	-0.444	-0.194	0.212	0.456	0.275
8.5	-0.444	-0.225	0.194	0.456	0.437
9.0	-0.544	-0.250	0.056	0.355	0.500
9.5	-0.387	-0.294	0.025	0.200	0.344
10.0	-0.344	-0.312	-0.012	0.081	0.163
10.5	-0.275	-0.362	-0.037	0.019	0.088
11.0	-0.219	-0.450	0.019	0.031	0.088

*Titration rate was 0.0375 meq per minute
100 ppm Hg(II) = 0.498 meq Hg(II)
Weight OM used was 1.5g.

**pH 3 was taken as the reference point.

In both cases, the resin and peat, the same trends are evident (Tables 11 and 12). It is interesting to note that the Δ meq values for the resin titrations (Table 11) are more negative where no chlorides were added as compared to the corresponding Δ meq values for the peat titrations (Table 12). However, at 10^{-3}, 10^{-2}, and 10^{-1} M total chloride concentration, the Δ meq values for the resin titrations were more positive as compared to the peat titrations. This observation will be elaborated on in the section dealing with acidity sources. In both cases, maximum Δ meq values were obtained in the pH range where the chloride complexes in solution are being titrated at the corresponding total chloride concentrations. The fact that the Δ meq values were positive was rather unexpected and together with the change in gradients between the Hg(II) titration in the presence of chlorides alone and the titrations of Hg(II) in presence of chlorides and resin or peat (Figures 25, 26, and 27) indicates that additional secondary acidity sources are involved. This conclusion is based on the observation that in the absence of chlorides or low chloride concentrations, complexation between Hg(II) and organic functional groups decreases Δ meq values and that all additive acidity sources should cancel out due to the subtractions made when Δ meq values were determined. This means that the Δ meq values should either be negative or zero. Furthermore, if some of the Hg(II) did complex with the organic functional groups at the onset of the titration, one would expect a steeper gradient than the Hg(II)-chloride titration if the binding energy is larger than that of the Hg(II)-chloride complex. If the binding energy of the organo-Hg(II) complex is the same or smaller than the Hg(II)-chloride complex, the same gradient would be expected. The unexpected observation at the higher chloride concentrations surfaces problems in interpreting the data quantitatively and to some degree even at a qualitative level.

In order to explain the obtained data at least to some degree, an attempt was made to identify the main possible acidity sources during the course of the titrations. These acidity sources are discussed in the following section.

Possible acidity sources during titrations:

Competition between ligands:

In the presented titration systems there are effectively three ligands competing for Hg(II) - namely, organic functional groups, chloride, and hydroxyl ions. The functional groups in the case of the resin are carboxylic weak acid groups. These groups are believed to be also the main functional sites in the peat, since the two sets of titrations display great similarity.

In the absence of chlorides the potentiometric titrations will detect the degree of complexation between Hg(II) and organic functional groups. The negative Δ meq values given in the first column in Tables 11 and 12 show the effectiveness of such complexation and may represent an approximate quantitative measure of the amount of Hg(II) complexed by the organic groups. Since the Δ meq values are obtained by subtracting the individual titrations of Hg(II) and organic forms from the titration of Hg(II) in the presence of organic forms, the amount of Hg(II) complexed by the organic forms can be assumed to be equal to

Δ meq/2. This assumption seems to be appropriate because, when the resin or peat and Hg(II) are titrated separately over the same pH range, each component displays acidity when neutralized.

The Δ meq values in the second column indicate that a total chloride content of 10^{-4} M (3.5 ppm) was effective in reducing the amount of Hg(II) complexed by the organic forms (Tables 11 and 12).

The nature of the titration curves (Figures 25-27) and the positive Δ meq values (Tables 11 and 12) at total chloride concentrations of 10^{-3}, 10^{-2}, and 10^{-1} M/l cannot be explained offhand. First of all, if the resin or peat would have complexed Hg(II) in the presence of chlorides prior to commencement of the titration, negative Δ meq values would have been obtained at pH values below the pH where the Hg(II)-chloride complex is titrated. However, this was not the case at 10^{-3}, 10^{-2}, and 10^{-1} M total chloride concentrations, except for a few negative Δ meq values at 10^{-2} M total chloride concentration in the case of the resin (Tables 11 and 12). These negative values are assigned to experimental error and are regarded as insignificant. Secondly, as mentioned earlier, if the weaker acid groups complexed Hg(II) prior to the titration and such complexed Hg(II) would be released (titrated) in the same pH range where Hg(II)-chloride complexes are being titrated, a gradient steeper than or equal to the gradient of the titration of Hg(II)-chloride complexes alone, would have been expected. As shown by the respective gradients in Figures 25-27, the opposite was the case. The gradients of the titrations on Hg(II)-chloride in the presence of resin or peat were less than those obtained with the titrations of Hg(II)-chloride complexes alone at 10^{-3}, 10^{-2}, and 10^{-1} M total chloride concentrations.

After a fruitless and rather escalating endeavor to find an explanation or at least similar examples in the literature, the abovementioned observations were related to systems where Hg(II) complexation with carboxylic groups takes place during the course of a titration. The reason for this approach was that if such complexation during the titration takes place, protons must be released which would account for additional acidity. Since no stability constants for Hg(II) complexes with the resin or peat could be obtained, it was decided to use nitrilotriacetic acid (NTA). The stability constant of Hg(II)-NTA complex is $10^{12.7}$ (Kolthoff _et_ _al_., 1969). Stability constants of organic fractions in soils have not been established without pH dependency (Stevenson and Ardakani, 1972). However, as an analogy NTA will serve the same purpose. The calculations performed with NTA are given in Table 13 and contain α-terms as described by Ringbom (1963), which means that they are based on conditional stability constants. The concentration of Ba^{++} for the computation of the α-values was taken as the amount of Ba^{++} added in the form of chloride plus the amount added as base. The latter component was based on pOH values and not actual amounts of base added. The concentration of NTA was arbitrarily taken as 10^{-2} M/l. No more significance should be attached to the calculations given in Table 13 than merely a demonstration of possible complexing behavior during the course of such titrations.

Table 13 Predicted distribution of Hg(II) in the presence of NTA, chloride, and hydroxyl ions.*

pH	$[Cl^-] = 10^{-3}$ M/l			$[Cl^-] = 10^{-2}$ M/l			$[Cl^-] = 10^{-1}$ M/l		
	fr_{NTA}	$\bar{n}_{Cl}$	$\bar{n}_{OH}$	fr_{NTA}	$\bar{n}_{Cl}$	$\bar{n}_{OH}$	fr_{NTA}	$\bar{n}_{Cl}$	$\bar{n}_{OH}$
3.0	0.0004	2.01	0.00	0.0000	2.08	0.00	0.0000	2.88	0.00
3.5	0.0016	2.00	0.00	0.0000	2.08	0.00	0.0000	2.88	0.00
4.0	0.0054	2.00	0.00	0.0001	2.08	0.00	0.0000	2.88	0.00
4.5	0.0172	1.97	0.00	0.0002	2.08	0.00	0.0000	2.88	0.00
5.0	0.0526	1.90	0.00	0.0005	2.08	0.00	0.0000	2.88	0.00
5.5	0.1486	1.69	0.01	0.0016	2.07	0.00	0.0000	2.88	0.00
6.0	0.3391	1.23	0.10	0.0049	2.04	0.00	0.0000	2.88	0.00
6.5	0.4892	0.57	0.46	0.0136	1.88	0.01	0.0000	2.88	0.00
7.0	0.3671	0.14	1.13	0.0296	1.15	0.14	0.0000	2.88	0.00
7.5	0.1535	0.02	1.67	0.0318	0.24	0.83	0.0000	2.87	0.01
8.0	0.0412	0.00	1.92	0.0088	0.03	1.75	0.0000	2.79	0.07
8.5	0.0074	0.00	1.98	0.0011	0.00	1.97	0.0000	2.15	0.50
9.0	0.0010	0.00	2.00	0.0001	0.00	2.00	0.0000	0.66	1.54
9.5	0.0001	0.00	2.00	0.0000	0.00	2.00	0.0000	0.08	1.94
10.0	0.0000	0.00	2.00	0.0000	0.00	2.00	0.0000	0.01	1.99
10.5	0.0000	0.00	2.00	0.0000	0.00	2.00	0.0000	0.00	2.00
11.0	0.0000	0.00	2.00	0.0000	0.00	2.00	0.0000	0.00	2.00

*NTA = nitrilotriacetic acid 10^{-2} M/l

α- values for NTA were included in calculations.

At a chloride ion concentration of 10^{-3} M/1, with increase in pH, chloride complexes disappear (see $\bar{n}_{Cl}$ values, Table 13) and NTA complexes form (fr_{NTA} values increase), and only at a later stage do the Hg(II)-hydroxy complexes ($\bar{n}_{OH}$ values) predominate. Incidentally, complexation with NTA falls within the pH range where Hg(II)-chloride complexes are being titrated at 10^{-3} M total chloride concentration. However, here again, this coincidence should not be taken as being comparable quantitatively, but merely as an example of possible complexation during the course of titrations, since the concentrations of functional groups may be quite different for the resin and peat. The main aim of this example is to show the possibility of an additional source of acidity when such complexation takes place during the course of the titrations. The quantitative aspect of this effect may be expressed by the following reaction sequence:

$$\begin{array}{rll}
\text{Initial phase:} & R(COOH)_2 + HgCl_2 & \\
\begin{array}{r}\text{Step 1}\\ \text{at lower pH}\end{array} & \Big\downarrow \quad + Ba(OH)_2 & \\
\text{Intermediate phase:} & R(COO^-)_2Hg + BaCl_2 + \overbrace{2H^+ + 2OH^-}^{2H_2O} & [24] \\
\begin{array}{r}\text{Step 2}\\ \text{at higher pH}\end{array} & \Big\downarrow \quad + Ba(OH)_2 & \\
 & R(COO^-)_2Ba + BaCl_2 + Hg(OH)_2 & [25]
\end{array}$$

The above sequence shows that more acidity is produced than if the reaction $HgCl_2 \rightarrow Hg(OH)_2$ takes place by itself. The amount of additional acidity produced will depend on the degree to which Hg(II) replaces additional H^+ from the organic functional groups since, some may merely replace already bound Ba^{++} originating from the $BaCl_2$ added.

The increase in acidity produced will further depend on how many weak acid groups complex with the Hg(II) which are otherwise not titrated at that particular pH when organic forms are titrated in the absence of Hg(II) at the corresponding total chloride concentrations.

The data in Table 13 indicate that the additional acidity due to complexation of Hg(II) with organic functional groups during the course of the titration would be more prevalent at lower total chloride concentrations. The data also show that the titrations of Hg(II) in the presence of chlorides and organic functional groups may be grossly misinterpreted. Although, the base consumed may be in the pH range where Hg(II)-chloride complexes are titrated, it may not represent the actual conversion of the Hg(II)-chloride complex to the hydroxide form.

The observation that the Δ meq values were lower at zero and 10^{-4} M total chloride concentrations and higher at the 10^{-3} M total chloride concentration for the titrations of Hg(II) in the presence of the resin than in the presence of peat, may partially substantiate the occurrence of the above-mentioned acidity source which in turn may be responsible for the positive Δ meq values.

Buffer action of Ba^{++} and organic functional groups:

Since positive Δ meq values were encountered even at very high total chloride concentrations (Tables 11 and 12), other possible sources of acidity need consideration. As mentioned before, the Δ meq values are obtained by addition of amounts of base added during the separate titrations of Hg(II) and resin or peat and subtracting the sum from the titration of Hg(II) in the presence of resin or peat. This was done for all total chloride concentrations. At the higher chloride concentrations this procedure may have significant consequences since, in the case of the titration of Hg(II) in the presence of resin or peat, more $Ba(OH)_2$ is added as compared to the separate titrations on Hg(II) and resin or peat. The resultant buffer action which may account for the positive Δ meq values is illustrated by the following equations.

When Hg(II) and resin or peat are titrated separately at the different chloride concentrations, then the following reactions take place.

$$HgCl_{\bar{n}} + Ba(OH)_2 \rightleftarrows Hg(OH)_2 + Ba^{++} + \bar{n}_{Cl^-} \quad [26]$$

and $$R(COOH)_2 + Ba(OH)_2 \rightleftarrows R(COO^-)_2\,Ba + H_2O. \quad [27]$$

In the case where Hg(II) is titrated in the presence of organic functional groups the overall reaction will be

$$R(COOH)_2 + HgCl_{\bar{n}} + 2Ba(OH)_2 \rightleftarrows$$
$$R(COO^-)_2Ba + Hg(OH)_2 + Ba^{++} + \bar{n}\ Cl^-. \quad [28]$$

Equations [26], [27], and [28] are assumed to be stoichiometric. Equation [28] is in this case the sum of equations [26] and [27] and is based on the assumption that the Ba^{++} does not react any further. However, since Ba^{++} has a tendency to complex with the RCOOH groups, even though they may normally not be neutralized at that pH by the added base, the additional $Ba(OH)_2$ required to titrate the Hg-Cl complexes may form an additional $R(COO^-)_2Ba$ group with the subsequent release of H^+. The degree to which this process takes place will depend on the formation constant for $R(COO^-)_2Ba$ groups and the additional Ba^{++} concentration present.

Designating the amount of Ba^{++} complexed in this manner as Δ meq, then the following relationship will hold during the course of the titration:

$$(1+\Delta)\ [R(COOH)_2] + HgCl_{\overline{n}} + 2Ba(OH)_2 \rightleftarrows$$

$$(1+\Delta)\ [R(COO^-)_2Ba] + Hg(OH)_2 + (1-\Delta)\ Ba^{++} + \overline{n}_{Cl^-} + \Delta H^+ \qquad [29]$$

Equation [29] unlike [28] does not represent the sum of equations [26] and [27] and contains an additional acidity term. The additional acidity term may, therefore, account for any additional acidity represented by positive Δ meq values in Tables 11 and 12 at the higher chloride concentrations and in the absence of complexation effects discussed in the previous section. The additional acidity encountered in the model described by equation [29] will be produced during the course of the titration until either all the Hg(II)-chloride complexes have been converted to $Hg(OH)_2$ or if the complexation of the Ba^{++} with organic functional groups ceases. The mechanism has been termed buffer action of Ba^{++} and organic functional groups, since acidity is produced which will tend to lower the pH during base addition.

Effect of salt concentration on ionization:

The concentration of the supporting electrolyte has a marked effect on the ionization or degree of dissociation of carboxylic acid groups (Gregor *et al.*, 1955; Gregor *et al.*, 1957; Michaeli *et al.*, 1957; Schnitzer *et al.*, 1970). The salt effects are most likely responsible for the different titration curves obtained for the resin and peat in the absence of Hg(II) at the different chloride concentrations. However, it is highly unlikely that the salt concentrations (in this study $BaCl_2$) had much effect on the Δ meq values. This statement is based on the fact that salt effects should cancel out with the procedure adopted in obtaining the Δ meq values.

Although the salt effects have obtained much attention, especially in the presence of polyelectrolytes such as polyacrylic acid and polymethacrylates resulting in rigorous mathematical formulations, the main objectives were to describe ionization and complexation of metal ions with such polyelectrolytes at different pH values. Such systems are rather different from the ones used in this study where Hg(II) was in competition with three complexing agents, namely organic forms, chlorides and hydroxyl ions. It is, therefore, postulated that the effects discussed in the previous two sections account for most of the positive Δ meq values obtained.

SUMMARY AND CONCLUSIONS

Computations on the distributions of the hydroxy species show that hydrolysis of Hg(II), Pb(II), Zn(II) and Cd(II) increases markedly with increase in pH above pH 1, 5, 7, and 8, respectively. Formation of chloride complexes of the corresponding metal ions becomes important above 10^{-8}, $10^{-2.5}$, 10^{-2} and 10^{-2} M Cl^-, respectively. Competition between hydroxy and chloride complexes of Hg(II) takes place at all pH values and chloride ion concentrations encountered in natural waters. In the case of Zn(II), Pb(II) and Cd(II) such competition is possible only at chloride ion concentrations above 10^{-2} M (350 ppm) and at pH values greater than 7, 5, and 8, respectively. These values are subject to the accuracy of the selected constants employed in the computations.

Cation and anion hydrolysis as well as chloride complexation affect the solubilities of sparingly soluble compounds to such an extent that salt effects can be overshadowed by a substantial factor. Solubilities of the sparingly soluble compounds may increase by deca-orders depending on the degree of hydrolysis or complex formation with chlorides. The magnitude to which these complexation effects may affect solubilities clearly demonstrates that any calculations, based on activities obtained from stoichiometric concentrations without accounting for complexes present, are rather meaningless. This does not apply only to chloride and hydroxy complexes but also to any other possible complexes that may be present. The fact that other complexes may participate, was the reason why in this study the distributions and related topics were treated as representing effects rather than exact models.

The intrinsic solubilities of the hydroxides of Hg(II), Zn(II) and Pb(II) are greater than the solubilities obtained from the corresponding solubility products.

Investigations on the nature of Hg(II) adsorption on clays were performed by two studies. The first experiment was conducted at higher Hg(II) concentrations (25-1000 ppm) and more or less uniform chloride concentrations (between 10^{-4} and 10^{-3} M) in the equilibrium solutions. In the second experiment lower Hg(II) concentrations (0.1-5 ppm) were used at two levels of chloride concentrations ($\simeq 10^{-3}$ and 0.44 M Cl^-).

At the higher Hg(II) levels no detectable amount of Hg(II) was found to be adsorbed on montmorillonite, illite, kaolinite and vermiculite as determined by the flame atomic absorption technique, although Hg(II) concentrations were taken up to 1000 ppm. The pH and pCl values of the equilibrium solutions when related to the corresponding species distributions indicated that practically all Hg(II) present in the respective equilibrium solutions were in the form of $HgCl_2^o$. The results indicate that the complexes in the solution phase are the prime factor controlling the adsorption of Hg(II) on clays. Furthermore, the surface charge of the clays had no apparent significant influence on the dissociation of the $HgCl_2^o$ complex at these suspension concentrations. The practice of attempting to rank Hg(II) in preferential adsorption series with other cations that do not form inorganic complexes seems to be unfounded and misleading.

Adsorption studies of Hg(II) at lower Hg(II) concentrations (0.1, 0.5, 2.5 and 5.0 ppm) were performed by utilizing the flameless atomic absorption technique. The main purpose was to attempt detection of possible adsorption by molecular species and repulsion by negatively charged complexes. At pCl ≃ 2.8, Hg(II) adsorption increased with increase in Hg(II) concentration. The largest amount adsorbed was obtained with vermiculite and the smallest amount with kaolinite although, the latter had a suspension concentration of 182 mg/10 ml as compared to ≃ 50 mg for vermiculite and montmorillonite. The highest percentage of added Hg(II) adsorbed was at the 0.5 ppm level for both montmorillonite and vermiculite and at 2.5 ppm level for kaolinite. pH and pCl values for the equilibrium solutions of montmorillonite and vermiculite indicated that 75 percent of Hg(II) existed as $Hg(OH)_2^o$ and 25 percent as $HgCl_2^o$. In the case of kaolinite 90 percent existed as $HgCl_2^o$ and 10 percent as $Hg(OH)_2^o$. Therefore, the difference in adsorption on kaolinite as opposed to vermiculite and montmorillonite could not be assigned solely to differences in clay mineral structure.

At 0.44 M Cl^- in the equilibrium solution there was a strong tendency for negative adsorption. The pH and pCl conditions in the equilibrium solution allowed for all Hg(II) to be present as $HgCl_4^=$.

Potentiometric titrations were considered to be effective in assessing the interaction between Hg(II) and organic functional groups at the different chloride concentrations. The assumption was that possible soluble organo-metal-ion complexes could not interfere with the actual determinations. Therefore, an itterative procedure was derived by which the nature of the titrations on Hg(II)-chloride complexes could be predicted at any Hg(II) and chloride concentrations. After this was established by titrations on Hg(II)-chloride solutions, titrations were performed with Hg(II) in the presence of resin and peat at different chloride concentrations. Although the effect of chlorides could be detected the titrations accounted for acidity sources which were unexpected. Two sources of acidity have been proposed. One source of acidity is assigned to the possibility that Hg(II), in the presence of chlorides, may complex and decomplex with the organic groups during the course of the titration. The second source of acidity is thought to result from displacement of hydrogen ions from the weaker carboxylic acid groups by a proportion of the additional Ba^{++} added as base to titrate the Hg(II)-chloride complex. This would proceed until carboxylic acid groups cease to ionize or when the titration of Hg(II)-Cl complexes is completed.

Whatever the nature of the additional source of acidity is, it seems reasonable to assume that whenever the base additions of the titration on Hg(II) in the presence of organic matter is greater than the sum of base additions of the individual titrations on Hg(II)-chloride and organic matter at the pH concurrent with the endpoint of the Hg(II)-chloride titration, chlorides compete with organic groups for Hg(II).

BIBLIOGRAPHY

Abott, W. and C. E. Dawson. 1971. Physical, chemical, and biological characteristics of estuaries. In L. L. Ciacco (ed.). Water and water pollution handbook Vol. 1: Marcel Dekker, Inc., New York. 449 p.

Allison, L. E. 1964. Salinity in relation to irrigation. Advan. Agron. 16: 139-180.

Andersson, A. A. 1967. Kvicksilvret i marken. Grundförbättring 20: 95-105.

Babcock, K. L. and G. M. Marion. 1972. Effect of ion-pair formation on the solubility product. Soil Sci. Soc. Amer. Proc. 36: 689-691.

Barr, A. J. and J. W. Goodnight. 1971. Statistical analysis system. Department of Statistics, North Carolina State University, N. C. Project No. FR-00011.

Beckwith, R. S. 1955. Metal complexes in soils. Aust. J. Agr. Res. 6: 685-698.

Beckwith, R. S. 1959. Titration curves of soil organic matter. Nature 184: 745-746.

Bjerrum, J. 1941. Metal amine formation in aqueous solutions. P. Haase and Sons, Copenhagen. 296 p.

Bower, C. A. 1959. Cation-exchange equilibria in soils affected by sodium salts. Soil Sci. 88: 32-35.

Bubeck, R. C., W. H. Diment, B. L. Deck, A. L. Baldwin, and D. S. Lipton. 1971. Runoff of deicing salt: Effect on Irondequoit Bay, Rochester, New York. Science 172: 1128-1131.

Butler, J. N. 1964. Ionic equilibrium: A methematical approach. Addison-Wesley Publishing Company Inc., Reading, Massachusetts. 547 p.

Cairns, J., J. S. Crossman, K. L. Dickson, and E. E. Herricks. 1971. The recovery of damaged streams. The ASB Bulletin (The Quarterly Publication of the Association of Southeastern Biologists) 18: 79-106.

Cranston, R. E., and D. E. Buckley. 1972. Mercury pathways in a river and estuary. Environ. Sci. Tech. 6: 274-278.

Dewan, H. C., and C. I. Rich. 1970. Titration of acid soils. Soil Sci. Soc. Amer. Proc. 34: 38-44.

D'Itri, F. M. 1972. Mercury in the aquatic ecosystem. Institute of Water Research, Michigan State University. Technical Report No. 23. 87 p.

Durum, W. H. 1971. Chemical, physical and biological characteristics of water resources. In L. L. Ciacco (ed.). Water and water pollution handbook, Vol. 1. Marcell Dekker Inc., New York. 449 p.

Feick, G., R. A. Horne, and D. Yeaple. 1972. Release of mercury from contaminated fresh water sediments by the runoff of road deicing salts. Science 175: 1142-1143.

Fleischer, M. 1970. Summary of the literature on the inorganic geochemistry of mercury. In Mercury in the environment. Geological Survey Professional Paper 713. 67 p.

Furukawa, K., T. Suzuki, and K. Tonomura. 1969. Decomposition of organic mercurial compounds by mercury resistant bacteria. Agr. Biol. Chem. 33: 128-130.

Gamble, D. S. 1970. Titration curves of fulvic acid: The analytical chemistry of weak acid polyelectrolyte. Can. J. Chem. 48: 2662-2669.

Gamble, D. S., M. Schnitzer, and I. Hoffman. 1970. Cu^{2+}-fulvic acid chelation equilibrium in 0.1 M KCl at 25.0° C. Can. J. Chem. 48: 3197-3204.

Gapon, E. N. 1933. Theory of exchange adsorption in soils. J. Gen. Chem. USSR. 3: 144-152.

Gilmour, J. T., and M. S. Miller. 1973. Fate of a mercuric-mercurous chloride fungicide added to turfgrass. J. Environ. Quality 2: 145-148.

Ginzburg, I. I. 1960. Principles of geochemical prospecting techniques of prospecting for non-ferrous ores and rare metals. Pergamon Press, New York. 311 p.

Gregor, H. P., and M. Frederick. 1957. Potentiometric titrations of polyacrylic and polymethacrylic acids with alkali metal and quaternary ammonium bases. J. Polymer Sci. 23: 451-465.

Gregor, H. P., L. B. Luttinger, and E. M. Loebl. 1955. Metal-polyelectrolyte complexes. I. The polyacrylic acid-copper complex. J. Phys. Chem. 59: 34-39.

Hanes, R. E. 1970. Chloride reactions in soils. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg. 131 p.

Hanes, R. E., L. W. Zelazny, and R. E. Blaser. 1970. Effect of de-icing salts on water and biota. Nat'l. Coop. Highway Res. Program Rep. 91. Highway Research Board, National Academy of Sciences, Washington, D.C. 70 p.

Harvey, H. W. 1955. The chemistry and fertility of sea waters. University Press, Cambridge, Mass. 240 p.

Hem, J. D. 1970. Chemical behavior of mercury in aqueous media. In Mercury in the environment. Geological Survey Professional Paper 713. 67 p.

Huling, E. E., and T. C. Hollochner. 1972. Groundwater contamination by road salt: Steady state concentrations in east central Massachusetts. Science 176: 288-290.

Hutchinson, G. E. 1957. A treatise on limnology. Vol. 1. John Wiley and Sons, New York. 1015 p.

Jackson, M. L. 1956. Soil chemical analysis - advanced course. Published by author, Soils Department, University of Wisconsin, Madison. 991 p.

Jensen, S., and A. Jernëlov. 1969. Biological methylation of mercury in aquatic organisms. Nature 223: 753-754.

Jernëlov, A. 1969. Conversion of mercury compounds. In M. W. Miller and G. G. Berg (eds.). Chemical fallout. Charles C. Thomas Publisher, Illinois, U.S.A. 531 p.

Joensuu, O. I. 1971. Fossil fuels as a source of mercury pollution. Science 1972: 1027-1028.

Jonasson, I. R., and R. W. Boyle. 1971. Geochemistry of mercury. In Proceedings special symposium on mercury in man's environment. Royal Society of Canada, Ottawa, Ontario. 201 p.

Kagawa, I., and H. P. Gregor. 1957. Theory of the effect of counter-ion size upon titration behavior of polycarboxylic acids. J. Polymer. Sci. 23: 477-484.

Khan, S. U. 1969. Interaction between the humic acid fraction of soils and certain metallic cations. Soil Sci. Soc. Amer. Proc. 33: 851-854.

Khanna, S. S., and F. J. Stevenson. 1962. Metallo-organic complexes in soil: I. Potentiometric titration of some organic matter isolates in the presence of transition metals. Soil Sci. 93: 298-305.

Kimura, Y., and V. L. Miller. 1964. The degradation of organomercury fungicides in soil. J. Agr. Food Chem. 12: 253-257.

Klein, L. 1959. River pollution. I. Chemical analysis. Butterworths, London. 206 p.

Kolthoff, I. M., E. B. Sandell, E. J. Meehan, and S. Bruckenstein. 1969. Quantitative chemical analysis. Fourth ed. Collier-McMillan Ltd., London. 1199 p.

Krauskopf, K. B. 1956. Factors controlling the concentration of thirteen rare metals in seawater. Geochim. et. Cosmochim. Acta 9: 1-32B.

Lagerwerff, J. V. 1967. Heavy metal contamination of soils. In N. C. Brady (ed.). Agriculture and the quality of our environment. Amer. Assoc. Adv. Sci. Pub. 85: 343-364.

Lagerwerff, J. V. 1972. Lead, mercury, and cadmium as environmental contaminants. In J. J. Mortvedt. Micronutrients in agriculture. Soil Sci. Soc. Amer. Inc. 666 p.

Lagerwerff, J. V., and G. H. Bolt. 1959. Theoretical and experimental analysis of Gapon's equation for ion exchange. Soil Sci. 87: 217-222.

Lagerwerff, J. V., and D. L. Brower. 1972. Exchange adsorption of trace quantitites of cadmium in soils treated with chlorides of aluminum, calcium and sodium. Soil Sci. Soc. Amer. Proc. 36: 734-737.

Lagerwerff, J. V., and D. L. Brower. 1973. Exchange adsorption or precipitation of lead in soils treated with chlorides of aluminum, calcium and sodium. Soil Sci. Soc. Amer. Proc. 37: 11-13.

Laitinen, H. A. 1960. Chemical analysis. McGraw-Hill Book Company, New York. 611 p.

Landner, L. 1971. Biochemical model for the biological methylation of mercury suggested from methylation studies in vivo with Neuraspora crassa. Nature 230: 452-454.

Matijevic, E., M. B. Abramson, R. H. Ottewill, K. F. Schulz, and M. Kerker. 1961. Adsorption of thorium ions on silver iodide sols. J. Phys. Chem. 65: 1724-1729.

Matijevic, E., M. B. Abramson, K. F. Schulz, and M. Kerker. 1960. Detection of metal ion hydrolysis by coagulation: II. Thorium. J. Phys. Chem. 64: 1157-1161.

Matijevic, E., K. G. Mathai, R. H. Ottewill, and M. Kerker. 1961. Detection of metal ion hydrolysis by coagulation. III. Aluminum. J. Phys. Chem. 65: 826-830.

Martin, A. E., and R. Reeve. 1958. Chemical studies of podzolic illuvial horizons. III. Titration curves of organic matter suspensions. J. Soil Sci. 9: 89-100.

Michaeli, I., and A. Katchalsky. 1957. Potentiometric titrations of polyelectrolyte gels. J. Polymer Sci. 23: 683-696.

Norvell, W. A. 1972. Equilibria of metal chelates in soil solution. In J. J. Mortvedt (ed.). Micronutrients in agriculture. Soil Sci. Soc. Amer. Inc. 666 p.

Oliff, W. D. 1963. Hydrobiological studies on the Tugela River system. III. The Buffalo River. Hydrobiologica XXI: 355-379.

Reitemeier, R. F., and L. A. Richards. 1944. Reliability of the pressure-membrane method for extraction of soil solution. Soil Sci. 57: 119-135.

Rhoades, J. D., and L. Bernstein. 1971. Characteristics of irrigation and soil water. In L. L. Ciacco (ed.). Water and water pollution handbook, Vol. 1. Marcell Dekker, Inc., New York. 449 p.

Ringbom, A. 1963. Complexation in analytical chemistry. Chemical analysis. Vol. XVI. Interscience Publishers, New York/London. 395 p.

Schnitzer, M., and E. H. Hansen. 1970. Organo-metallic interactions in soils: 8. An evaluation of methods for the determination of stability constants of metal-fulvic acid complexes. Soil Sci. 109: 333-340.

Schnitzer, M., and S. I. M. Skinner. 1963. Organo-metallic interactions in soils: 1. Reactions between a number of metal ions and the organic matter of a podzol B_h horizon. Soil Sci. 96: 86-93.

Sillen, L. G., and A. E. Martell. 1964. Stability constants of metal-ion complexes. Chem. Soc. London. Spec. Pub. 17. 754 p.

Smith, E. E., and K. S. Shumate. 1971. Pilot study of acid mine drainage. U.S. Government Printing Office, Washington, D.C. 84 p.

Stevenson, F. J. and M. S. Ardakani. 1972. Organic matter reactions involving micronutrients in soils. In J. J. Mortvedt (ed.). Micronutrients in agriculture. Soil Sci. Soc. Amer. Inc., Madison, Wisconsin, USA. 666 p.

Stumm, W., and J. J. Morgan. 1962. Chemical aspects of coagulation. J. Amer. Water Works Assoc. 54: 971-994.

Stumm, W., and J. J. Morgan. 1970. Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters. Wiley-Interscience, John Wiley and Sons Inc., New York. 583 p.

Stumm, W., and C. R. O'Meila. 1968. Stoichiometry of coagulation. J. Amer. Water Works Assoc. 60: 514-539.

Voege, F. A. 1971. Levels of mercury contamination in water and its boundaries. In Proceedings special symposium on mercury in man's environment. Royal Society of Canada, Ottawa, Ontario. 201 p.

Warren, C. B., and E. J. Malec. 1972. Biodegradation of nitrotriacetic acid and related imino- and amino acids in river water. Science 176: 277-279.

Wershaw, R. L. 1970. Sources and behavior of mercury in surface waters. In Mercury in the environment. Geological Survey Professional Paper 713. 67 p.

White, D. E., M. E. Hinkle, and I. Barnes. 1970. Mercury contents of natural, thermal and mineral fluids. In Mercury in the environment. Geological Survey Professional Paper 713. 67 p.

Wood, J. M., F. S. Kennedy, and C. G. Rosen. 1968. Synthesis of methylmercury compounds by extracts of a methagenic bacterium. Nature 220: 173-174.

APPENDIX

Table 14. Analysis of variance values for Hg(II) adsorption study (Hg(II) concentration range 0.1-0.5 ppm).

Source	Probability > F	
	% Hg(II) adsorbed	μmole Hg(II)/100g clay
Clay	0.0271	0.0002
Hg(II)	0.0018	0.0001
$[Cl^-]$	0.0001	0.0001
Clay x Hg(II)	0.1427	0.0118
Clay x $[Cl^-]$	0.6662	0.0002
Hg(II) x $[Cl^-]$	0.6178	0.0001

Table 15. Interactions at confidence levels above P = 0.05 (units of the values are μmoles Hg(II) adsorbed per 100g clay).

Hg(II) x [Cl$^-$] interaction*

[Cl$^-$] moles/l	Hg(II) concentrations (ppm) 0.1	0.5	2.5	5.0
0.001	3.7	30.0	120.3	201.1
0.440	-2.5	2.0	- 9.3	- 14.9

Hg(II) x clay interaction**

Clay	Hg(II) concentrations (ppm) 0.1	0.5	2.5	5.0
Montmorillonite	0.8	17.7	79.8	117.9
Vermiculite	0.7	28.9	72.1	137.0
Kaolinite	0.2	1.5	14.6	24.4

Clay x [Cl$^-$] interaction***

[Cl$^-$] moles/l	Montmorillonite	Vermiculite	Kaolinite
0.001	103.8	132.4	30.1
0.440	4.3	- 13.0	- 9.8

*LSD's: (0.01) = 33; (0.05) = 24; (0.10) = 20: P>F = 0.0001
**LSD's: (0.01) = 40; (0.05) = 30; (0.10) = 24: P>F = 0.0118
***LSD's: (0.01) = 28; (0.05) = 20; (0.10) = 17: P>F = 0.0002

The two page vita has been removed from the scanned document. Page 1 of 2

The two page vita has been removed from the scanned document. Page 2 of 2

ABSTRACT

Significance of pH and pCl in Heavy Metal Ion Reactions and Mercury(II) Adsorption by Soil Materials

by

Hermann C. H. Hahne

A computational approach was utilized to evaluate the degree to which Zn(II), Cd(II), Hg(II), and Pb(II) hydrolyze and complex with chlorides at pH and chloride concentration levels encountered in natural waters and soil solutions. The significance of hydroxy and chloride complexes of these heavy metal ions is discussed in relation to solubilities of sparingly soluble salts, Hg(II) adsorption on clays, and Hg(II) interactions with organic functional groups.

Occurance of and competition between Hg(II) hydroxy and chloride complexes is important at all pH and chloride concentrations encountered in natural waters. Hydrolysis of Pb(II), Zn(II), and Cd(II) increases markedly above pH 5, 7, and 8, respectively, and the chloride complexes are important above chloride concentrations of approximately 10^{-2}M.

Hydrolysis and chloride complexation increases the solubilities of sparingly soluble salts of these heavy metal ions by deca-orders depending on the degree of complexation. Intrinsic solubilities of the heavy metal hydroxides are greater than the solubilities obtained from the corresponding solubility products, except for $Cd(OH)_2$. The effects due to complexation may in many cases overshadow salt effects.

Studies on Hg(II) adsorption by Montmorillonite (53 mg/10 ml), vermiculite (47 mg/10 ml), and kaolinite (182 mg/10 ml) showed that at Hg(II) levels of 0.1, 0.5, 2.5, and 5.0 ppm adsorption was low but increased with increase in Hg(II) concentration. Highest amount of Hg(II) adsorbed was 0.3 mmoles per 100 g clay at the 5 ppm level and in the presence of vermiculite. Lowest adsorption was with kaolinite. Equilibrium pH and pCl measurements indicate that $Hg(OH)_2^{\circ}$ was the main species present. Lower adsorption by kaolinite could not be assigned solely to clay difference since the proportion of $HgCl_2^{\circ}$ in the equilibrium solution was higher than for the other two clays. Highest percentage of added Hg(II) adsorbed was attained at 0.5 ppm level for montmorillonite and vermiculite and at 2.5 ppm level for kaolinite. When Hg(II) existed as $HgCl_4^{=}$ in the equilibrium solution there was a tendency towards negative adsorption (repulsion). At Hg(II) levels of (25-1000 ppm) $HgCl_2^{\circ}$ in the equilibrium solution did not exchange any significant amounts of exchangeable Ca.

Potentiometric titrations were performed first on Hg(II)-chloride solutions after an itterative procedure was developed for predicting such titrations. Titrations of Hg(II) in presence of different chloride concentrations were quantitative and followed the predicted course. The titrations of Hg(II) in presence of resin and peat at various chloride concentrations indicated that chlorides compete effectively with the organic functional groups for Hg(II). However, at the same time unexpected acidity sources were apparent at the higher chloride concentrations. Possible origin of such acidity has been postulated.

The potentiometric titrations showed that more research is required in order to obtain a full understanding of the various acidity sources especially when organic and inorganic complexes are present.