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SPECIATION OF HEAVY METALS IN HIGHWAY DRAINAGE SYSTEMS

BY

Lee P. Wiseman
B.S., University of Central Florida, 1982

THESIS

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for the Master of Science degree
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ABSTRACT

A trace metal speciation scheme proposed by Batley and
Florence (1976) was applied to determine the
physiochemical forms of zinc, cadmium, lead and copper in
two Central Florida highway drainage systems. The
linearity and limitations of the ASV technique were also
examined. The measurements showed that (a) more than 70%
of the soluble Zn and Cd in all of the waters analyzed
existed as labile ionic metal (b) lead was divided between
labile and non-labile inorganic forms, but one particular
form, $PbCO_3$, predominated (c) a substantial fraction of
copper is associated with organic colloids if humic
substances are present. In addition a computerized
chemical model for trace and major element speciation was
applied to the waters in both drainage systems using
measured average water quality for input parameters. A
comparison between metal species measured by ASV and those
predicted by the computer model are presented. There
appears to be good agreement between the metal fractions
measured in the water samples by ASV and those predicted
by the chemical model.

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CHAPTER 1

SCOPE AND OBJECTIVES

Introduction

When rain falls on an area of significant urban
development it tends to flow overland. As it travels,
this "stormwater runoff" accumulates impurities deposited
on the ground surface. These impurities include organic
and inorganic compounds, nutrients and heavy metals.
Currently there are increasing concerns about the impact
of stormwater runoff from highways and bridges on
receiving water bodies.

Stormwater runoff from highway bridges is discharged
directly through scupper drains into lakes, streams or
floodplains located beneath them or diverted to adjacent
swales and detention/retention ponds prior to disposal
into receiving waters (Yousef et al. 1984). Highway
stormwater runoff contains significantly higher
concentrations of trace metals particularly lead (Pb),
zinc (Zn), iron (Fe), cadmium (Cd), chromium (Cr), nickel
(Ni), and copper, than the adjacent water environment
(Yousef et al. 1982). As these metals reach our
ecosystems, they will undergo physical, chemical, and
biological transformations. They may be absorbed on clay

particles, taken up by plant and animal life or remain in solution. Particulate fractions will settle to the bottom sediments, and heavy metals may resuspend or redissolve back into solution when the environmental conditions permit. The distribution of a trace metal between all possible forms will be dependent upon the type and concentration of the trace element, pH, Eh, and types and concentration of organic ligands and availability of colloidal surfaces (Benes et al. 1979; Shuman and Woodward 1976). The environmental scientist realizes that the total concentration of a particular metal in natural waters can be very misleading. A water with high total metal concentration may be in fact less toxic than a similar water with a lower concentration or a different form of that metal. For example, ionic copper is far more toxic towards aquatic organisms than organically-bound copper (Allen et al. 1980). An understanding of trace metal speciation is therefore necessary to realize the impact of these heavy metals on existing biota.

Two approaches have been used in attempts to better the understanding of trace metal speciation. The first approach is the use of physical and chemical separation coupled with highly sensitive analytical procedures, to

provide a direct measurement of metal species. The second approach is through chemical modelling of the system.

Analytical Procedures

Chemical speciation of trace metals in solution is a very difficult analytical problem and reliable methods are needed to differentiate between the various chemical forms existing in natural waters. Only in the last few years have analytical techniques become available to measure metals below the microgram per liter level and to subdivide each concentration into several forms. The fact that contamination problems are extreme and the purity of all reagents used is critical, complicate the problem of analysis. However, there are a number of voltammetric techniques which can be used for this analysis. The most sensitive and convenient to use for trace metal analysis is Differential Pulse Anodic Stripping Voltammetry (DPASV). The upper concentration limit is about 10^{-6} to 10^{-5} moles/liter and the lower concentration limit is 10^{-8} to 10^{-9} moles/liter which corresponds to about 0.1 ug/l (Christian 1977).

There are several of heavy metal speciation schemes for modelling natural water systems (Batley and Florence 1976; Figura and McDuffie 1980; Hart and Davies 1981; Laxen and Harrison 1981). Each scheme followed specific

assumptions which resulted in its own advantages and limitations. The scheme developed by Batley and Florence, which applied ASV techniques, was utilized in this study.

Chemical Modelling

The second approach utilizes chemical modelling of the system using equilibrium calculations to include interactions with organic and inorganic ligands and more recently, adsorbing surfaces (Jenne 1979). More than a dozen computerized chemical models based on equilibrium calculations in aqueous systems, especially natural waters, are available and reviewed by Nordstrom et al. (1979). Some of these models incorporate trace metals such as Pb, Zn, Cu, Fe, Ni, Cr, and Cd. Of course, all methods have limitations and only by pursuing both analytical methods and chemical modelling will a sufficient understanding be developed to permit the prediction of trace metal speciation in a particular aquatic system.

Objectives

The relationship between the concentration of trace metals in highway runoff and their bioavailability are of particular interest if we want to protect the environment. It is important to know whether the

introduction of these trace metals into adjacent surface

and groundwaters by rainfall and runoff will make them

available for solution of whether chemical processes such

as complex formation, precipitation and adsorption can

greatly vary their concentration. The overall scope of

this research is to determine the various trace metal

species in stormwater runoff and their receiving waters.

The specific objectives of this study are:

1) To collect water samples of; 1) rainfall, stormwater runoff, and the detention pond receiving the runoff from the Maitland Interchange and I-4 site and, 2) bridge runoff and Shingle Creek at U.S. 17-92 site. These samples will be analyzed for their major constituents of anions, cations, and trace metals. Also metal fractions associated with organics, inorganics, and particulates will be determined.

2) To predict changes in speciation of trace metals by applying available computer programs. A widely used model (WATEQ2) to assess the actual form of trace elements existing in natural waters has been adapted to the IBM system in Gainesville.

3) To utilize analytical analysis and computer models to examine changes in trace metal species as a result of changes in environmental parameters such as changing pH values, and other cations and anions normally present in natural waters.

4) To apply an available technique, Anodic Stripping Voltammetry (ASV), and a previously developed speciation scheme to the water samples described

in (1) for the dissolved metals Pb, Zn, Cn and
Cd. The linearity of the ASV system during
analysis and the effect of pH on available metal
concentrations will be investigated.

CHAPTER II

LITERATURE SURVEY OF ANALYTICAL PROCEDURES

Introduction

Man's activities related to mining for mineral ore,
industrial processes, and motor vehicles have resulted in
an apparent increase of heavy metals in the surrounding
environment. Metal contamination such as lead (Pb), zinc
(Zn), copper (Cu), iron (Fe), nickel (Ni), chromium (Cr),
and cadmium (Cd) in natural waters, bottom sediments, and
aquatic biomass are of particular concern because of their
deleterious effects. A common method of monitoring these
metals in the environment is to measure their total
concentration. However, when total metal is used to
assess the toxicity of the water towards aquatic organisms
contradicting results may occur. A water with a high
total metal concentration may be less toxic than another
water with a lower concentration. For example many
researchers (Shaw and Brown 1974; Andrew, Biesenger and
Glass 1977; Wagemann and Barica 1979; Allen, Hall and
Brisbin 1980) have concluded that ionic copper is far more
toxic towards aquatic organisms than complexed copper, and
that the more stable the copper complex, the lower its

toxicity. Similar conclusions have been reached for lead (Davies et al. 1974), cadmium (Bellavere and Gorbi 1981) and zinc (Peterson 1982).

Laboratory experiments designed to measure the concentration of a heavy metal toxic to aquatic organisms will have little meaning unless the chemical forms of the metal in the test water are known. Extrapolation of results from an experimental test to a natural water system (lake, pond or river) may not be possible if the chemical speciation of the metal being studied is unknown in the natural system. When evaluating the environmental impact of the discharge of heavy metal compounds into an aquatic environment, it is important to determine the extent and rate at which the incoming metal species equilibrate with the natural pool of dissolved chemical species in the receiving water. Unless the chemical distribution of the polluting metal is known, predictions cannot be made about its effect on aquatic organisms.

Some of the most sensitive analytical techniques, atomic absorption and emission spectrophotometry, are not applicable to trace metal speciation studies because they measure only the total metal concentration. Anodic Stripping Voltammetry (ASV) is perhaps the only technique able to directly and accurately measure heavy metal

species at low concentrations. Initially ASV was used for the primary distinction, in filtered samples, between species which are "labile" or "bound" (non-labile) under the specified conditions of the experiment (Chau 1974).

In this chapter different heavy metal speciation schemes based on the conventional labile-bound discrimination using ASV, but combined with simple sample treatments will be reviewed. The results of each speciation scheme will permit the quantification of metal species in discrete groups. Each scheme follows specific assumptions which result in its own advantages and limitations. Also, existing information on contribution of metal loadings from highway runoff and their fate in the surrounding environment will be reviewed and presented.

Dissolved Metal Speciation Schemes

The term refers to the particular physical and chemical forms in which an element occurs; and environmental researchers are becoming aware of the need for reliable methods which can differentiate between various forms of trace metals, especially the toxic heavy metals, in natural waters. Measuring the total concentration of a particular metal in a water sample can be very misleading because, depending on the chemical

forms of the metal, a water with high total metal concentration may be, in fact, less toxic than another water with a lower total metal concentration. The study of a chemical speciation of trace heavy metals in natural waters is obviously a very complex analytical problem, and subdividing each metal concentration into several fractions is a task of considerable difficulty. Contamination problems are extreme, and the purity of all reagents used is critical.

Methods used to differentiate between the various chemical forms of metals range from simple procedures which discriminate between weakly and strongly complexed forms of the metal to comprehensive analytical schemes. A general speciation scheme may be based on the particle size fractionation. However, three major questions must be answered:

1) Is the soluble metal present as complexed species or hydrated ions?

2) Are the species charged?

3) What is the size of each metal species?

Differentiation of metals in the free state and bound form was impossible until the resurgence of voltammetric

techniques in the early 1970s. There are currently a number of techniques which can be employed. However, the most sensitive for trace metals is Differential Pulse Anodic Stripping Voltammetry (DPASV) which measures metal concentrations as low as 10^{-8} or 10^{-9} moles/liter (mol/l). Metal speciation schemes have been developed for the modelling of natural water systems and a brief explanation of three commonly used schemes and the assumptions that were made during their development will follow:

Batley and Florence Speciation Model

This model was developed in 1976 and divided metal species into seven discrete groups. However, it should be kept in mind that the speciation scheme is based on behavioral differences; and there may well be some overlap between species. The concentration of each species is calculated from measurements using water samples which are: (a) filtered; (b) irradiated by ultraviolet (UV) light; (c) passed through a chelating resin (Chelex) column; and (d) UV irradiated, then passed through a chelating resin column. Description of the analytical scheme and method of calculations are presented in Chapter III since it is used in this study.

In 1978 Batley and Gardner applied the Batley and Florence (1976) heavy metal speciation scheme to the Port Hacking Estuary (NSW, Australia). The study was undertaken in order to fully evaluate the potential of the scheme to reflect differences in metal distribution within a water body. An estuarine system was chosen because it represented an area of dynamically variable conditions with continual mixing of fresh and saline waters, both through tidal changes and temporal changes of fresh water input, giving rise to large fluctuations in oxidation-reduction potential, pH, and salinity. Such changes were reflected in changes in the speciation of heavy metals.

The scheme proposed by Batley and Florence (1976) differentiates between four classes for soluble metals in water samples which include seven different species. These classes include labile and non-labile compounds. The labile compounds are divided into organic colloidal and inorganic soluble colloidal compounds. The non-labile compounds are divided into soluble and colloidal organic and soluble and colloidal inorganic compounds. Examples of possible chemical forms in each class are presented in Table 1.

Florence (1977) analyzed water samples collected from Woronora Reservoir, Woronora River, and tap water from

Lucas Heights. Pb, Cu, and Cd speciation are presented in Table 2. It is interesting to notice that Cu in tap water showed the highest measured concentration and more than half of the Cu are non-labile forms.

The data indicates that copper is associated mainly with organic species in natural water systems, probably organic colloids. Also, most of the samples contained both organic and inorganic lead species in significant fractions. However, cadmium exists primarily as free ions or simple complexes and very little or none may be associated with organic colloids or strong organic chelators.

Hart and Davies Speciation Model

This model was developed in 1979 to separate heavy metals into four fractions by molecular size, using membrane filtration, chelex resin, and dialysis. The concentration of each species is calculated from measurements using DPAV for a total and filtered metal sample. The filtered sample can be broken down further into four fractions.

According to Hart and Davies (1981) the ion-exchangeable fraction will include ionic forms, together with that associated as labile complexes (organic

TABLE 1

EXAMPLES OF POSSIBLE FORMS FOR EACH OF THE SEVEN CLASSIFICATIONS FOR HEAVY METALS IN WATER SAMPLES DEVELOPED BY BATLEY AND FLORENCE

Possible Chemical Forms

	Labile			Non-Labile		
Organic	Inorganic		Organic	Organic	Inorganic	
Colloidal	Soluble	Colloidal	Soluble	Colloidal	Soluble	Colloidal
Cu-humate	Zn^{+2}	$Pb\text{-}Fe_2 O_3$	Zn citrate	Cu-humate	PbS	Pb MnO_2
	$CdCl^{-4}$		Cd-cysteine		$ZnCO_3$	
	Cu-glycinate				$Cu(HO_2)CO_3$	

TABLE 2

SPECIATION OF METALS IN FRESH WATER SAMPLES AFTER·FLORENCE (1977)

Location and Sample Date	Metal	% Metal Speciation								Dissolved Metal ug/l
		Labile				Non-Labile				
		Organic		Inorganic		Organic		Inorganic		
		Dissolved	Colloid	Soluble	Colloid	Soluble	Colloid	Soluble	Colloid	
Woronora Reservoir 04/12/76	Pb	0	0	33	0	5	0	62	0	0.42
	Cu	3	0	3	0	66	28	0	0	0.32
	Cd	3	0	73	0	21	3	0	0	0.29
Woronora Reservoir 07/19/76	Pb	12.5	0	6	0	44	12.5	25	0	0.16
	Cu	5	0	2	0	10	50	33	0	0.39
	Cd	0	0	92	0	0	0	8	0	0.15
Woronora Reservoir 07/28/76	Pb	8	0	4	0	20	24	44	0	0.25
	Cu	13	0	33	0	0	54	0	0	0.24
	Cd	0	0	78	0	0	0	22	0	0.09
Tap Water	Pb	0	0	33	33	0	0	23	11	1.72
	Cu	0	0	28	0	11	13	45	3	61
	Cd	0	0	55	45	0	0	0	0	0.38

and inorganic) whose stability constant is less than that resulting from the combination of the trace metal with the chelex. The bound fraction will generally include colloidally bound metal species, the dialyzable fraction, and ion-exchangeable species with molecular weights less than approximately 1,000. All fractions were measured in a two-molar acetate buffer, with pH of 5.2.

In 1981 Hart and Davies applied their scheme to three Victorian Lakes (Australia): Lake Tarli Karng, Tarago Reservoir, and East Basin Lake. The water of Lake Tarli Karng was extremely clear; low in dissolved solids, suspended solids, and dissolved organic carbon; and near neutral. Water in the Tarago Reservoir was slightly acidic; low in dissolved salts, containing 5 to 6.5 mg/l dissolved organic carbon; and high in suspended solids concentration of which less than 10 percent is organic. The water was also colored by humic substances. The water of East Basin Lake was alkaline, saline, and contained a high concentration of filterable organic carbon and suspended solids.

Most of the filterable Cd in each lake (70 to 90 percent) was ion exchangeable; and in lakes Tarago and East Basin, over 90 percent of this ion exchangeable was also dialyzable. This data is consistent with the

conclusion that Cd in natural waters generally exists in the free ionic form and as simple inorganic and possible organic complexes (Florence 1977; Batley and Gardner 1978). The filterable Zn fraction in Tarago Reservoir and Lake Tarli Karng also consisted mainly (76 percent) of ion exchangeable species. This contrasted with East Basin Lake where only 35 to 40 percent of the filterable Zn was ion exchangeable. The Tarago Reservoir exhibited speciations results similar to Woronora Reservoir (Florence 1977). The filterable copper concentration in water samples contained approximately 75 percent in ion exchangeable forms for Tarli Karng water and 70 to 80 percent in bound forms for East Basin Lake water. Hart and Davies (1981) felt that copper-organic complexes, together with colloidal $CuCO_3$ absorbed in organic compounds, existed in East Basin Lake water. Filterable lead contained more than 60 percent exchangeable forms in waters from the three lakes tested. A considerable amount of filterable Pb in natural waters appears to be associated with organics; however, Hart and Davies (1981) believed that Pb-fulvic acid complexes would be determined as part of the ion exchangeable fraction in their speciation scheme.

Figura and McDuffie's Model

This speciation scheme was developed in 1980 and divided soluble heavy metals in environmental water samples into four categories. Trace metal species are classified as "very labile" which includes free and hydrated metal ions, "moderately labile," "slowly labile," and "inert." The non-labile fraction includes metal bound in complexes or absorbed on colloidal material with a slow rate of dissociation to the free metal. Examples of "moderately labile" fractions might be Cd-NTA (Cd-nitrilotriacetate) or Cu-humate. Also, some examples of "slowly labile" fractions might be Cd-, Pb-, and Zn-EDTA (Zn-ethylenediaminetetraacetic acid) complexes.

Figura and McDuffie (1980) applied their scheme to St. Lawrence and Susquehanna River waters and Hudson River Estuary samples. The estuary samples were distinctly higher in Cd, Cu, Pb, and Zn content than samples from the St. Lawrence and Susquehanna rivers. The soluble lead represented only 11 to 46 percent of the total metal. Most of the Cd and Zn in all the samples existed as "very labile" or "moderately labile," with a small percentage of "slowly labile" and no "inert" fractions. In contrast, both Cu and Pb existed in forms which are less labile. Copper was found almost entirely in the "moderately

labile" and "slowly labile" categories. Similarly, a small percentage of lead (30 percent) was in the "very" or "moderately labile" fractions. The results presented by Figura and McDuffie (1980) were consistent with other investigators.

Laxen and Harrison Speciation Model

This model which was developed in 1980 utilized the particle size fractionation approach. Samples were filtered through Nucleopore filters with the following pore sizes; 12, 1.0, 0.4, 0.08 and 0.015 um. Information on the species within the different size fractions was gained using the following techniques:

A) ASV at the natural pH of the sample to differentiate ASV-labile and non-labile species;

B) Metal titrations in conjunction with (A) to indicate metal complexation;

C) Chelex exchange resin in a batch technique to determine chelex-labile metals with slower dissociation kinetics;

D) U.V. irradiation to destroy organics and to release previously non-labile organically associated metals in a labile form. The range of possible metal species classified according to their particle size association is presented in Table 3.

TABLE 3

METAL FORMS OF WATER ACCORDING TO THE SCHEME PROPOSED BY LAXEN AND HARRISON

Size	.001um	.01um	.1um	1um
	S o l u b l e		C o l l o i d a l	P a r t i c u l a t e
Metal Species	Free Metal Ions	Inorganic Ion Paris; Organic Chelates	Organic Complexes	Metal Species Bound to High Molecular Weight Organic Material	Metal Species Adsorbed on Colloids	Mineral Incorporated with Organic Particles and Remains of Living Organisms	Mineral Solids; Metals Adsorbed on Solids; Precipitates Co-Precipitates
Example	Pb^{2+}	$PbHCO_3$ + Pb-Fulvic Acid			Pb-Humic Acid	$Pb-Fe(OH)_3$	Pb-Organic
Pb-Clay		Pb-EDTA Acid			$Pb-MnO_2$	Solids	$PbCO_3$

Laxen and Harrison (1981) applied their scheme to two freshwater rivers in NW England, Pendle River and Irwell River. The Pendle River water sample was taken during a period of low flow and in consequence there was a low suspended solids loading. Additionally, the water was high in dissolved solids, contained about 6.0 mg/l total organic carbon, near neutral pH and moderate alkalinity (90 mg/l as $CaCO_3$). In contrast, the sample taken from the Irwell River was collected during the rising stage of storm and threfore yielded a much higher suspended solids loading. This water also had a high solids loading, contained 6.3 mg/l total organic carbon, a pH of 7.5 and a moderate alkalinity. It should be noted that stormwater runoff from a motorway was discharging into the Irwell River directly upstream of the collection point. Consequently, the Irwell River contained higher concentrations of the metals Pb, Cu, Cd, Fe and Mn.

The speciation patterns of the two samples were similar. However, a greater percentage of each metal in the Irwell River was in the particulate form. This was attributed to a higher suspended solids loading in the Irwell River. Also greater than 90 percent of the total concentration of lead and iron in the Irwell River was in the particulate form.

The greatest difference between the speciation patterns of the two waters was observed in the cases of copper and iron. There was a much higher percentage of colloidal iron and copper in the Pendle River than the Irwell River. This was thought to be due to either the conditions of the water or an impact of the different sources contributing to the river.

It is also interesting to note that of the four metals Cd, Pb, Cu, and Fe, generally less than 30 percent of the total concentrations were chelex labile. Also no ASV-labile forms were detected for the metals tested.

In summary, speciation schemes have been developed for Cd, Zn, Pb, and Cu in natural waters; and other metals are still under development. Cd and Zn exist as free ions and more labile species, while Pb and Cu exist as more bound complexes and less labile species.

A Comparison of Speciation Models

Of the schemes presented in the previous sections, only two of them were reasonably comprehensive and systematic; the Batley and Florence (1976) model and the Laxen and Harrison (1981) model. The Batley and Florence model was the first model derived and many separate applications of the individual components were used by other investigators, for instance the use of Anodic

Stripping Voltammetry (Duinker and Kramer 1977); ion exchange resins (Figura and McDuffie 1979); and U.V. irradiation to destroy organic matter and release organic non-labile organically associated metal (Florence and Batley 1977). In a number of investigations components have been combined to provide partial schemes, such as the use of filtration and ion exchange resin (Hart and Davies 1981) and ASV and ion exchange resin by Figura and McDuffie (1980). The second comprehensive speciation model was presented in 1981 by Laxen and Harrison. They utilized the processes of ion exchange, ASV, u.v. irradiation and filtration. However, the filtration process employed a series of uniform diameter nucleopore filters. Based on these different filter sizes the metals were divided in fractions based on particle size.

Each of the schemes, however, have limitations that warrant mention. The usage of a single membrane filter to distinguish between "dissolved" metal and "particulate" metal is not totally accurate. Membrane filters are depth filters which trap particles within the membrane (Laxen and Harrison 1981). They do not act as absolute size selective filters in their retention properties. Furthermore, they present a considerable surface area for

adsorption. Nucleopore filters, on the other hand, are much closer to absolute screen filters.

A component of the two comprehensive speciation schemes was the use u.v. irradiation for the destruction of organics Laxen and Harrison (1981) reported that u.v. irradiation created a two-fold problem; 1) an increase in pH was observed, with a simultaneous loss of ASV-labile metal and 2) the formation of a brown solid on the bottom of the sample container. It was theorized that the increase in pH was a result of an increase in temperature (around 50 to 60°C) and a subsequent loss of CO_2. The brown precipitate was believed to be hydrous iron oxides which were associated with organic colloidal material. The u.v. light oxidized the organic coating allowing the iron oxides to coagulate and precipitate. This was believed to impact lead and copper concentrations, since both metals have a strong adsorption tendency towards hydrous iron oxide, and would likely be removed from the soluble phase with the precipitating hydrous iron oxides. Laxen and Harrison observed this effect in waters with total iron concentrations as low as 0.8 ug/ml.

In addition to the above-mentioned limitations, each scheme was limited by the metal measuring technique, ASV, as discussed in the following sections.

An Overview of ASV

Anodic Stripping Voltammetry is a very accurate and powerful technique for measuring trace metal concentrations in natural waters. However, it is imperative that the limitations and operational characteristics are understood before the technique is applied to natural water samples, but first a quick overview of the technique needs to be presented.

A small volume of sample is placed in a non-reactive cell along with a small volume of $Hg(NO_3)_2$ and a buffered electroyte solution. The sample is then deoxygenated with some inert gas, e.g. nitrogen, for a specific time period to allow for maximum mercury deposition during the next step. Then a slight positive potential is applied to the working electrode (+0.15V), thus depositing a thin film of mercury on the electrode. Next a negative potential (in the range of -1.2V) is applied to the working electrode and all metals with more positive redox potential simultaneously deposit on the mercury film. It is imperative that the solution be stirred continuously during deposition. This step is followed by a quiescent period, which allows the amalgam to reach equilibrium. During the next step, the stripping process, the potential is scanned anodically and the

current is measured. A peak is generated in a current versus potential curve with its peak potential (E_p) a qualitative indication of the identity of the metal ion and the peak height (i_p) a quantitative measure of its concentration in the solution. The procedure is then repeated for accuracy and precision. Next, a known volume and concentration of standard is added to the solution and the procedure is repeated again. The concentration of each metal measured in solution is then calculated by the method of standard additions as discussed in Chapter III.

Influences and Limitations of ASV

While ASV is a useful and versatile technique, its limitations and possible interferences appear to be inadequately appreciated when applied to natural waters. The oxidation peak current changes with variations in pH, complexing capacity and redox potential.

The analysis of natural waters requires that the pH of the sample during the analysis be kept as close as possible to the original sample pH. A change in the pH would cause the metal ion activity and the oxidation peak current to decrease (Schonberg and Pickering 1980). Also, a shifting of the peak potential accompanies a change in pH (Sinko and Dolezal 1970). Deaeration of unbuffered solutions drives off CO_2, thus increasing the pH of the

solution. The suitability of an acetate buffer as a base electrolyte for natural water analysis is widely accepted (Florence 1977; Hart and Davies 1981; Laxen and Harrison 1981). In dilute acetate buffer solutions, the oxidation peak currents for Zn, Cd, Pb and Cu were found to be independent of the pH in the acid range up to 7 (Sinko and Dolezal 1970).

Another interference which affects the measurement of Cu and Zn in the pH range of 5 to 7 is intermetallic compound formation. Several Cu-Zn intermetallic compounds can be formed during the ASV analysis of solutions containing Cu and Zn. There are three soluble compounds with copper to zinc ratios of 1:1, 1:2 and 1:3 which can be formed (Shuman and Woodward 1976). The formation of these compounds decreases the ASV zinc oxidation current and increases the copper current. This interference in the determination of Cu and Zn by ASV is most serious with thin film electrodes, where a small mercury volume leads to very high amalgam concentrations. Intermetallic compound formation generally does not cause problems in natural waters because copper and zinc concentrations are not commonly found in the 1 ppm range.

In natural waters there are miscellaneous organic compounds which can form complexes with metal ions as well

as form organo-metallics. In addition, metals can be strongly adsorbed on colloidal particles. These organic compounds are commonly called humic substances.

Sorption of these substances can effect both diagnostic parameters (i_p and E_p) used in ASV. E_p may shift to more positive values if a sorbed molecule coats the electrode and renders the metal oxidation irreversible by creating a barrier to ion diffusion. Sorption affects peak current in two ways: by preventing metal deposition (a sorbed organic layer may hinder metal ion diffusion to the surface of retard chemical steps prior to electron transfer and by changing the reversibility of the metal oxidation reaction (Brezonik et al. 1976).

A method for determining whether complexing agents are interfering with ASV analysis of a natural water sample has been described by Benes (1979). By comparing the slope of the calibration curve for each metal in distilled/DI water and the slope of the calibration curve for each metal in the suspected natural sample. If the slope obtained in the natural sample is lower, it can be assumed that the natural water sample contains components that bind that particular metal added or block the electrode active surface.

When the iron concentration in natural waters is in the range of 1-10 mg/l and the sample is analyzed using DPASV, significant interference effects are noted (Bonelli et al. 1978).

Iron (III) contributes to the stripping peak current and oxidizes at the peak potential of copper, clearly a standard additions procedure will not compensate for the interference. The relative error introduced by the interference however, can be decreased by increasing the deposition time. A direct experimental method of correction that minimizes the required analysis time can also be used. Since the peak current from iron is independent of deposition, a zero deposition time voltammogram is obtained and algebraically subtracted from a normal stripping voltammogram for samples and standards alike. This method compensates for the current contribution from iron and also for the limited copper deposition during the rest and potential scan periods.

For a river water sample containing 1 mg/l of Fe^{+2} (a typical concentration in natural waters) leads to an error for copper of over 100% at the 10 ug/l level (Bonelli 1978).

CHAPTER III

FIELD AND LABORATORY PROCEDURES

Study Sites

Two sites were selected to investigate the consequential species of heavy metals in highway stormwater runoff. The sites were selected on the basis of accessibility, abundance of existing information, traffic volume and proximity to the laboratory for analysis. Sampling sites for this study are located at:

a) the intersection of Interstate 4 and Maitland Interchange; and

b) the intersection of U.S. 17-92 and Shingle Creek, south of Kissimmee.

The traffic on I-4 at the Maitland site exceeds 50,000 vehicles per day and on U.S. 17-92 at the Shingle Creek site exceeds 12,000. The average daily traffic (ADT) count at each site for the past three years was provided by David Harrell (1984) and is presented in Table 4. The ADT at I-4 in the vicinity of the Maitland site increased by more than one-third between 1981 and 1983. However, the ADT at the Shingle Creek site appeared to remain fairly constant at U.S. 17-92, south of the Kissimmee city limit.

TABLE 4

DAILY TRAFFIC COUNT FOR SELECTED SITES TO STUDY
CONSEQUENTIAL SPECIES

Site Location	Traffic Lanes	Average Daily Traffic		
		1981	1982	1983
NE I-4 and Maitland Interchange	East Bound	36,013	38,717	51,454
	West Bound	35,430	39,288	50,023
SW I-4 and Maitland Interchange	East Bound	45,207	47,546	54,482
	West Bound	43,705	50,008	52,810
Maitland Avenue at SR 427	East Bound	12,506	14,305	15,833
	West Bound	12,896	13,965	15,683
U.S. 17-92 and Shingle Creek, St. #3, SW Kissimmee City Limit	Combined	12,856	12,117	12,254

Maitland Interchange Site

The site for this investigation is located at the

Interstate 4 and Maitland Boulevard Interchange, north of

the City of Orlando, Orange County, Florida. Maitland

Boulevard crosses over Interstate 4 by means of a bridge

overpass created during the construction of the

interchange in 1976. The traffic lanes on the interstate

are separated by a 6.0 m grassy median, as they approach

the interchange, which widen to 13.5 m through the

interchange. The Maitland Boulevard bridge consists of two sections, one carrying two lanes of east bound traffic plus one exit lane, with the other section carrying two lanes of west bound traffic plus one exit lane. The section carrying west bound traffic spans 168 m with a 16 m roadway and also a 16 m horizontal clearance. The section carrying east bound traffic spans 163 m, also having a 16 m roadway and a 16 m horizontal clearance. The traffic volume on Maitland Boulevard approximates 15,000 ADT.

Interstate 4 has three lanes of through traffic east and west bound through the Maitland Interchange. The traffic volume on Interstate 4 through the Maitland Interchange is over 50,000 ADT in each direction, east bound and west bound, as presented in Table 4.

Three borrow pits were dug to provide fill for the construction of the overpass, as depicted in Figure 1, and remain in existence, serving as stormwater detention/retention facilities. The total design drainage areas for those three ponds are shown in Table 5 (Yousef, Harper, Wiseman and Bateman 1984).

TABLE 5

TOTAL DESIGN DRAINAGE AREAS FOR PONDS
LOCATED AT MAITLAND INTERCHANGE

Pond	Location of Pond	Total Drainage Area (ha)
A	Southwest (west)	19.8
B	Northeast	48.6
C	Northwest	10.1

Stormwater runoff from the interstate is delivered by overland flow over grassy swales to storm drain inlets or detention Ponds A, B, and C. Stormwater runoff from the Maitland Boulevard bridge crossing over Interstate 4 is conveyed directly off the roadway surface through stormwater inlets to culverts that discharge directly into Pond A. The ponds are interconnected so that the water from the two northernmost ponds flows into the southwest pond (referred to hereafter as the west pond) when they reach a certain design level. The water from the west pond flows over a wood weir at its southern end which is connected to Lake Lucien by means of a culvert and a short, densely vegetated ditch.

The west pond is triangular in shape, with a surface area of approximately 3 acres or 1.2 ha. The eastern side is parallel to I-4, the northern side is parallel to the
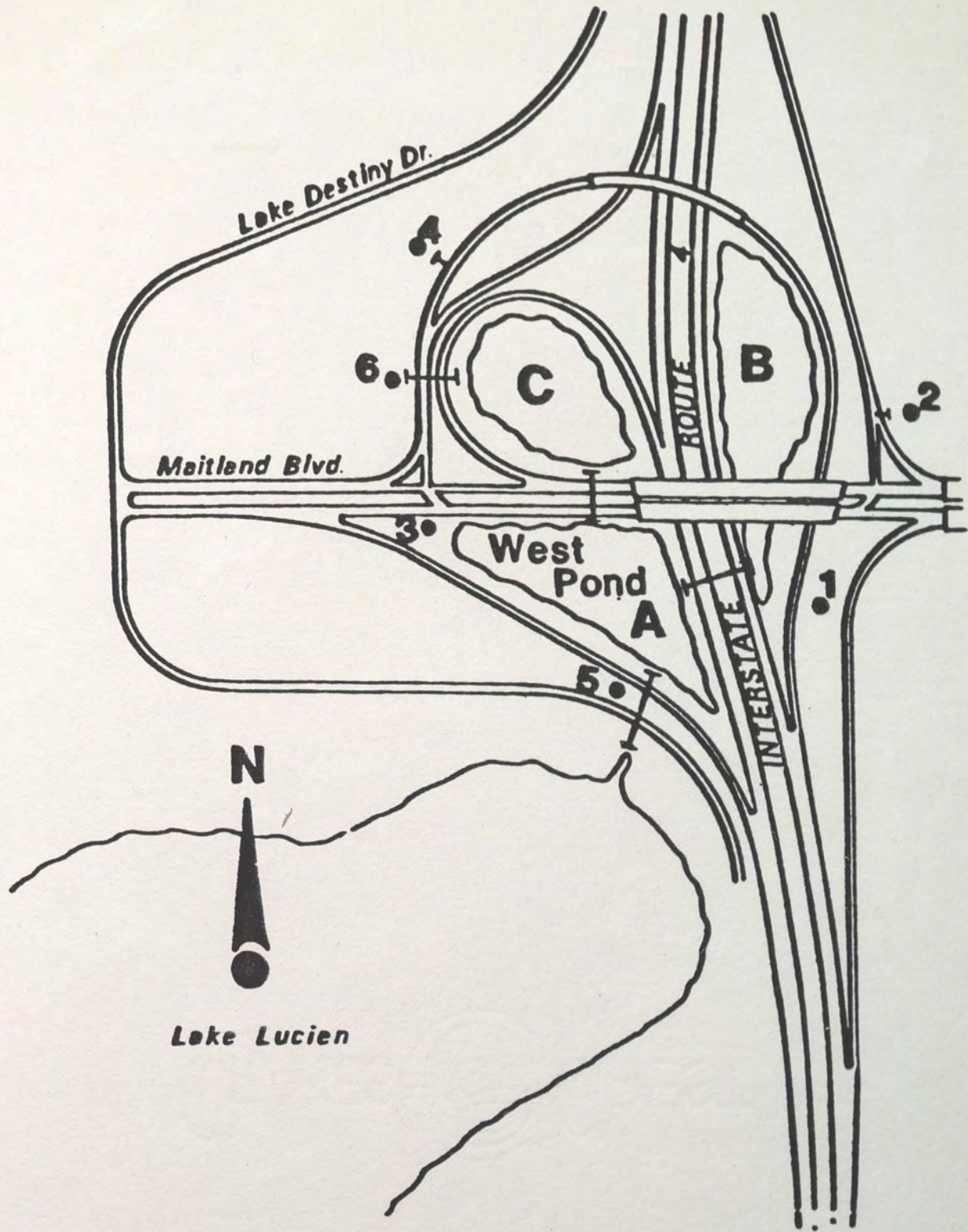
Figure 1. Sampling Site for Highway Runoff at Maitland
Interchange and Interstate 4.

Maitland Interchange, and the third side is parallel to ramp A leading from the Maitland Interchange to I-4 west. Water and sediment samples were collected from the west pond for heavy metal analysis. Also, water samples were collected from the surrounding drainage area to investigate heavy metal speciation in highway runoff water.

U.S. 17-92 and Shingle Creek Site

U.S. 17-92 crosses over Shingle Creek south of the Kissimmee city limit, approximately one mile from Lake Tohopekaliga. The roadway is a two-lane undivided highway with an average daily traffic count of 12,254 vehicles during 1983. The bridge which crosses over Shingle Creek is approximately 97 meters long and 8 meters wide. The area beneath the bridge is a low wetland area which is inundated several times per year when Shingle Creek overflows its banks. Stormwater runoff is removed from the bridge area by a system of numerous 10 cm scupper drains which drain directly onto the underlying wetland areas. In some locations, small channels have eroded in the soil and the drainage from some scuppers is transported directly into Shingle Creek.

Sampling locations, shown in Figure 2, were selected beneath the bridge from the scupper drains (S-1) and from the Shingle Creek water near the bridge site (S-2).

Field Sampling

Water and sediment samples were collected from various sites in the study areas and brought to the Environmental Engineering Laboratory and the Chemistry Department at the University of Central Florida (UCF) for analyses. Also, portions of selected water samples were sent to the United States Geological Survey, Water Resources Laboratory at Ocala, Florida, for quality assurance. All samples were brought to the laboratory, stored, and refrigerated according to U.S. EPA Methods for Chemical Analysis of Water and Wastes, 1974. Speciation of dissolved heavy metals in water samples was determined by Anodic Stripping Voltammetric (ASV) measurements at the Environmental Engineering Laboratory, UCF.

Water Samples

The Maitland Interchange stormwater sampling program covered an eight-month period between August 1982 and March 1983. Sampling stations shown in Figure 1 were included in the program: Station #2 - direct highway runoff from Maitland Boulevard; Station #3 - direct bridge and highway runoff from Maitland Boulevard flowing into detention Pond "A"; Station #4 - direct highway runoff from an I-4 exit ramp. A total of seventeen storm events were included in the stormwater sampling program and a
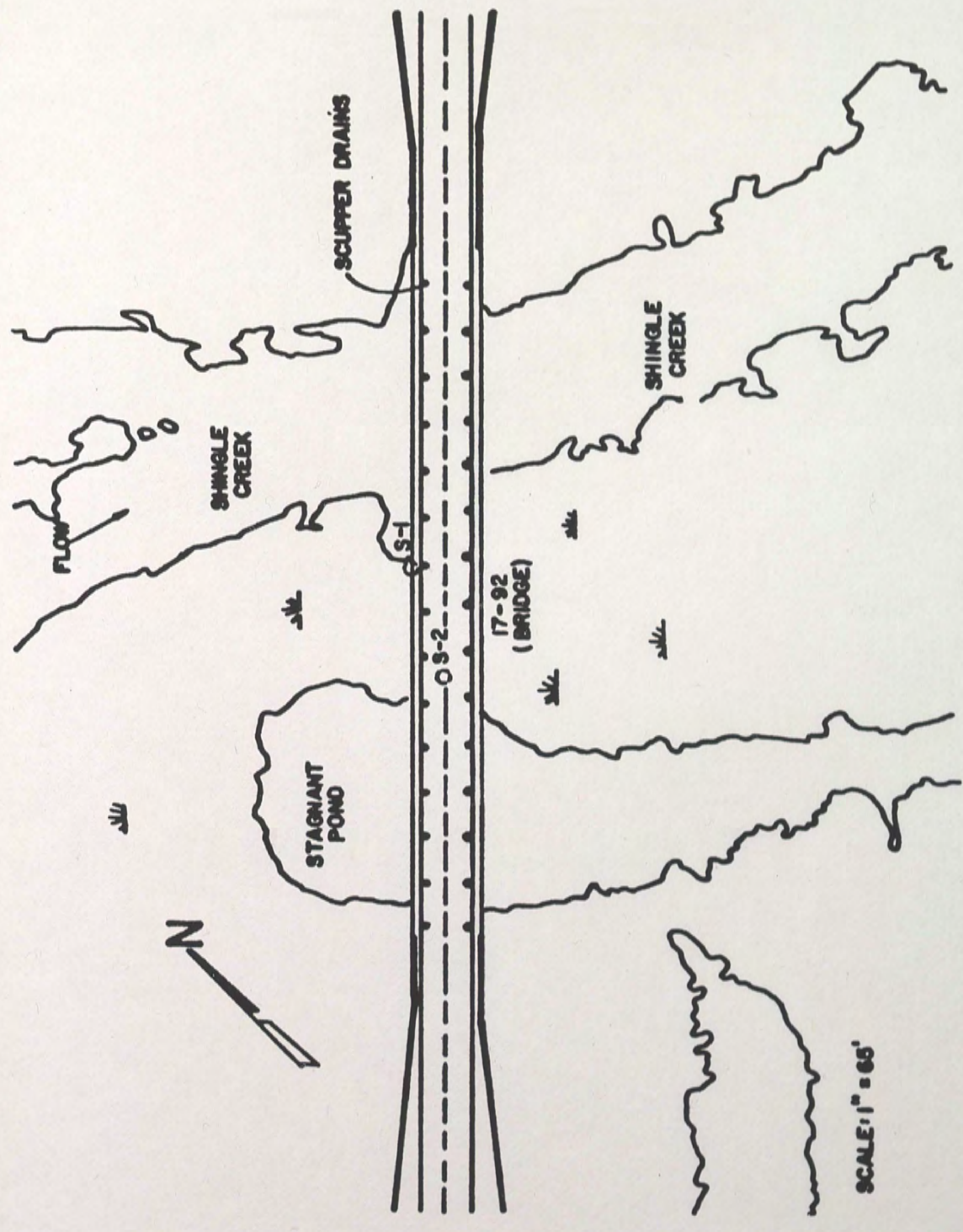
Figure 2. Locations of Sample Sites at U.S. 17-92 and Shingle Creek.

various number of samples were taken at each station.
Collection of these samples should assist in
differentiating between total and soluble metals in
highway runoff. The above samples were collected from
surface runoff intercepted by a plexiglass collector
connected to Tygon tubing leading to a polyethylene
sampling bottle.

Also, selected water samples were collected from
highway runoff, Station #3 at Maitland Interchange site,
using an ISCO refrigerated automatic sampler Model 1680R.
The samples were collected on a volume proportional basis
from highway runoff flowing through stormwater pipe
discharging to the west Pond "A," as shown in Figure 3.
The ISCO sampler was housed inside a mobile trailer and
activated by a Liquid Level Sample Actuator Model 1640,
which allows collection of up to twenty-eight separate
sequential samples representative of predetermined volumes
of runoff. The sampler actuator was placed downstream
from the stormwater culvert at a distance of approximately
1 meter from the pipe facing and housed in a prefabricated
wooden box with a $90^{o}V$ notch at one end of the box to
allow for the calibration of stormwater flow. The total
runoff volume could be compared to rainfall depth which is
continuously recorded by a rain gauge, Texas Electronics.
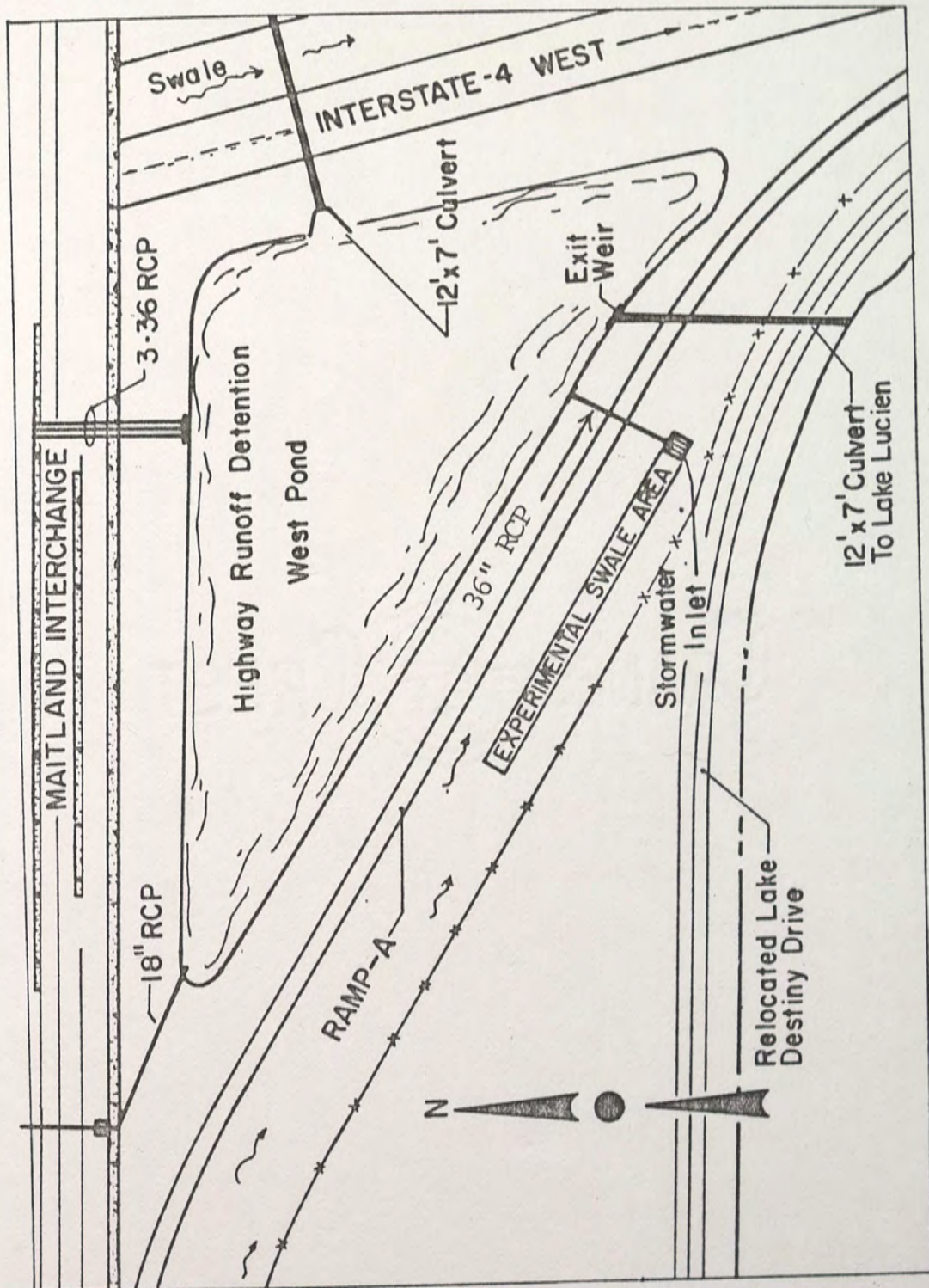
Figure 3. Location of Mobile Trailer Housing Isco Sampler for Stormwater Collection.

Rainfall samples were also collected only by wet deposition using MIC Precipitation Collector Type AI placed on the top of the mobile trailer.

Highway bridge runoff samples were collected at the Shingle Creek and U.S. 17-92 site. The bridge at this site was equipped with scuppers, and rainfall excess was collected directly into a funnel as it drained through the scupper, to be stored in a 25 liter polyethylene container (Figure 4). The larger size of the stormwater collection vessels allowed the rainfall excess from several storms to be collected and stored so that, when the samples were retrieved from the field, they represented a composite sample of all storm events during the collection period. It was felt that this technique would more accurately represent, both in terms of stormwater quality and assessment of environmental effects, an "average" response which would tend to minimize fluctuations due to an isolated extreme event. Also, composite Shingle Creek water samples were collected near the bridge areas using a plexiglass 4 liter Kemmerer water sampler.

Water samples collected were filtered and prepared in the field using 0.45 micron millipore filter discs and suction created by a GEO Filter Peristaltic Pump Model #004 manufactured by Leonard Mold & Die Works, Inc.,

Figure 4. Bridge Stormwater Collection System on U.S. 17-92.

Denver, Colorado, 80221. The samples were preserved and stored in the refrigerator until analysis, as specified in U.S. EPA Methods for Chemical Analysis of Water and Wastes, 1974.

Dissolved Metal Speciation

The dissolved metal speciation scheme involved ASV measurements of labile and total metal concentration in sample filtrate using:

a)   raw water;

b)   water after passing through a chelating resin column;

c)   uv-irradiated water; and

d)   uv-irradiated water after passing through a chelating resin column.

A schematic representation for water sample preparation required for metal speciation by ASV is shown in Figure 5. A minimum of eight different subsamples were analyzed for every water sample collected and filtered in the field. Each subsample was treated differently, as shown in the figure, before analysis by ASV. The various treatment steps are briefly discussed as follows.

325 ml of Water Sample

25 ml for Total Metal Analysis

300 ml Filtered Sample

Filtered 100 ml to pass through Chelex-100

25 ml for Total Metal Analysis

25 ml for Labile Metal Analysis

Filtered 150 ml to be irradiated by UV

Reject 50 ml

50 ml

25 ml for Labile Total

25 ml for Labile Total

100 ml to pass through Chelex-100

50 ml

25 ml for Labile Total

25 ml for Labile Total

reject 50 ml

25 ml for Labile Total

25 ml for Labile Total
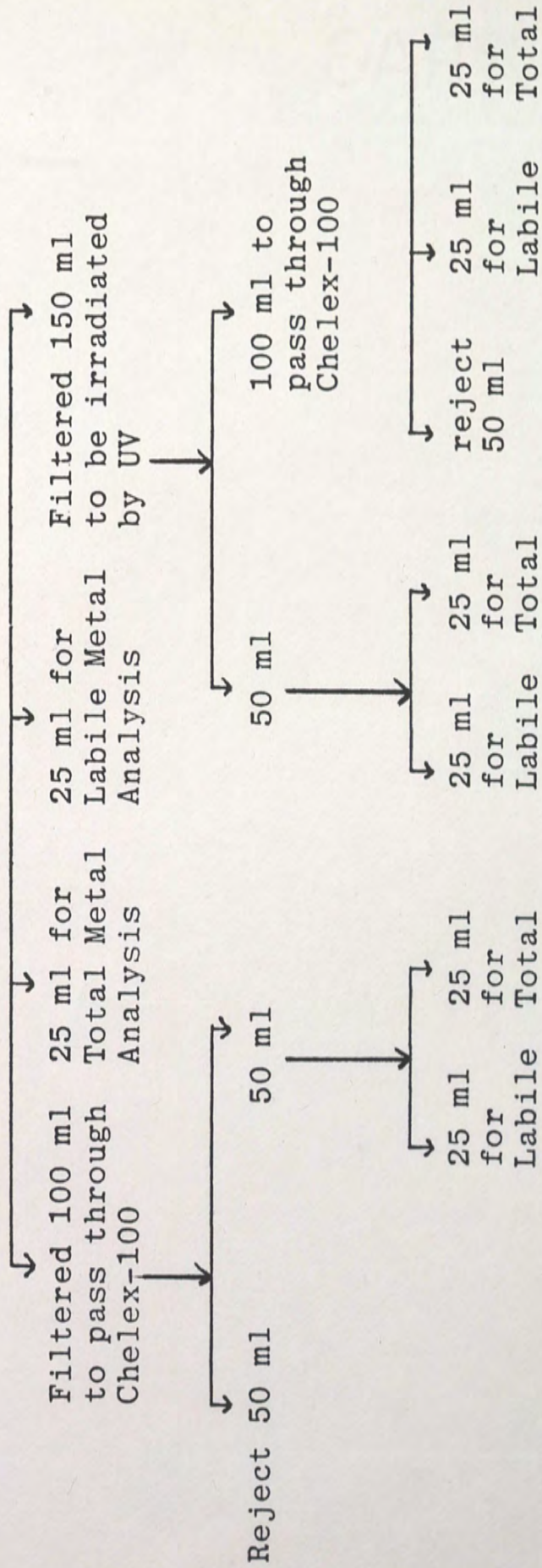
Figure 5. Schematic For Metal Analysis of Runoff Samples by Anodic Stripping Voltammetry (ASV).

Chelating Resin Separation

The function of the chelating resin separation is to differentiate between species retained by the resin and those associated with colloidal complexes. The resin used is Chelex 100, 100-200 mesh and is manufactured by Bio-Rad Laboratories in California. It has a molecular weight exclusion limit of 500, which corresponds to a port size of 15^OA. The resin should remove free metal ions and weak complexes which are easy to dissociate. Florence (1977) conducted studies using hydrated iron oxide colloidal suspension and concluded that little, if any, adsorption of colloids occurs on the surface of the resin beads. The adsorbed complexes by the resin may be organic or inorganic in nature.

Chelex-100 resin was supplied in the sodium form and was suspended in a two-mole solution of nitric acid (2M HNO_3) from Fisher Ultrex to saturate the resin with hydrogen rather than sodium. The H^+ saturated Chelex-100 was loaded into a 15 cm long glass column with a 0.9 cm diameter. The resin was washed again with five column bed volumes of 2.0 M HNO_3, followed by five bed volumes of deionized-distilled water. The resin was then converted to the NH_4^+ form by passing five bed volumes of 2M NH_4OH (MCB Suprapur) and washed with water

until the pH of the effluent was below 8.0. The ammonium form of the resin was used in preference to the sodium form. The pH of the sample effluent from an NH_4^+ form column was 7.0-7.5.

A volume of 100 ml of each filtered sample, at laboratory temperature of approximately $25^{\circ}C$, was passed through a chelating resin column at a rate of 1-2 ml/min. The first 50 ml of effluent was discarded, and the second 50 ml was divided into two subsamples for analysis of labile and total metal content, as shown in Figure 5.

UV Irradiation

Destruction of organic matter was achieved by irradiating 150 ml aliquots of each water sample under an Ultra-Violet Products, Inc., (R-52G) shortwave uv lamp (Florence 1977). This lamp produced high intensity illumination, of 1,250 uW/cm^2 at 15 cm. Each 150 ml sample was irradiated for 10 hours. One 50 ml aliquot from each irradiated sample was divided into equal portions for a labile and total metal analysis. The remaining 100 ml of the irradiated sample was then passed through a chelating resin column. The first 50 ml of the effluent was discarded, and the second 50 ml was divided for analysis of labile and total metal.

Labile Metal

The use of the term "labile metal" in ASV analysis requires a statement of the exact experimental conditions under which the measurement is made. In our work, measurements were made in a 0.1 molar solution of acetate buffer, pH = 6.0; and the labile metal analysis broadly represented hydrated metal ion, organic, and inorganic complexes which are completely or partially dissociated from colloidal particles.

All labile metal samples were prepared by placing 25 ml of treated or untreated water sample in a 50 ml disposable plastic beaker covered with parafilm. These samples were stored in a refrigerator at $4^{\circ}C$ until analysis.

Total Metal

To insure that all metal is converted to the ionic state before ASV analysis, it was found necessary to completely destroy organic matter and solubilize inorganic colloids. Oxidation of samples was achieved by adding 0.1 ml of concentrated HNO_3 (Fisher Ultrex) to 25 ml of sample in a 125 ml Ehrlenmeyer flask. The sample was placed on a hot plate and evaporated to a volume of 5-10 ml. The sample was then neutralized with NaOH and brought back up to its initial volume.

ASV Analysis

Anodic Stripping Voltammetric measurements were performed using a Rotating Glassy Carbon Electrode (RGCE), IBM-EC 219, in conjunction with an IBM Voltammetric Analyzer (EC 225) and Electrochemical Sequencer (EC 229). The glassy carbon electrode was used in conjunction with a saturated Calomel Electrode (IBM) and a platinum wire (IBM) as the counter electrode. A photographic picture of the instruments used is shown in Figure 6.

The following instrumental settings were determined empirically to optimize the sensitivity and resolution: operating mode, differential pulse; current range 100 uA full scale; electrode rotating speed, 3,600 RPMs; pulse amplitude, 50 mV; voltage scan rate, 10 mV/sec; pulse time, 0.3 sec; initial (deposition) potential, -1.3 V; deposition time, 5.0 min; conditioning time, 2.0 min; conditioning potential, +0.15 V. Following proper setting of the instruments, the filtered water samples were analyzed as follows.

Place 10.0 ml of sample, 2.0 ml of 0.1 M acetate buffer (pH = 6.0), and 300 ul of .0062 M $Hg(NO_3)_2$ in the voltammetric cell. The electrochemical sequencer was then set at four repetitions, and then the setup automatically initiated the stripping process. At the
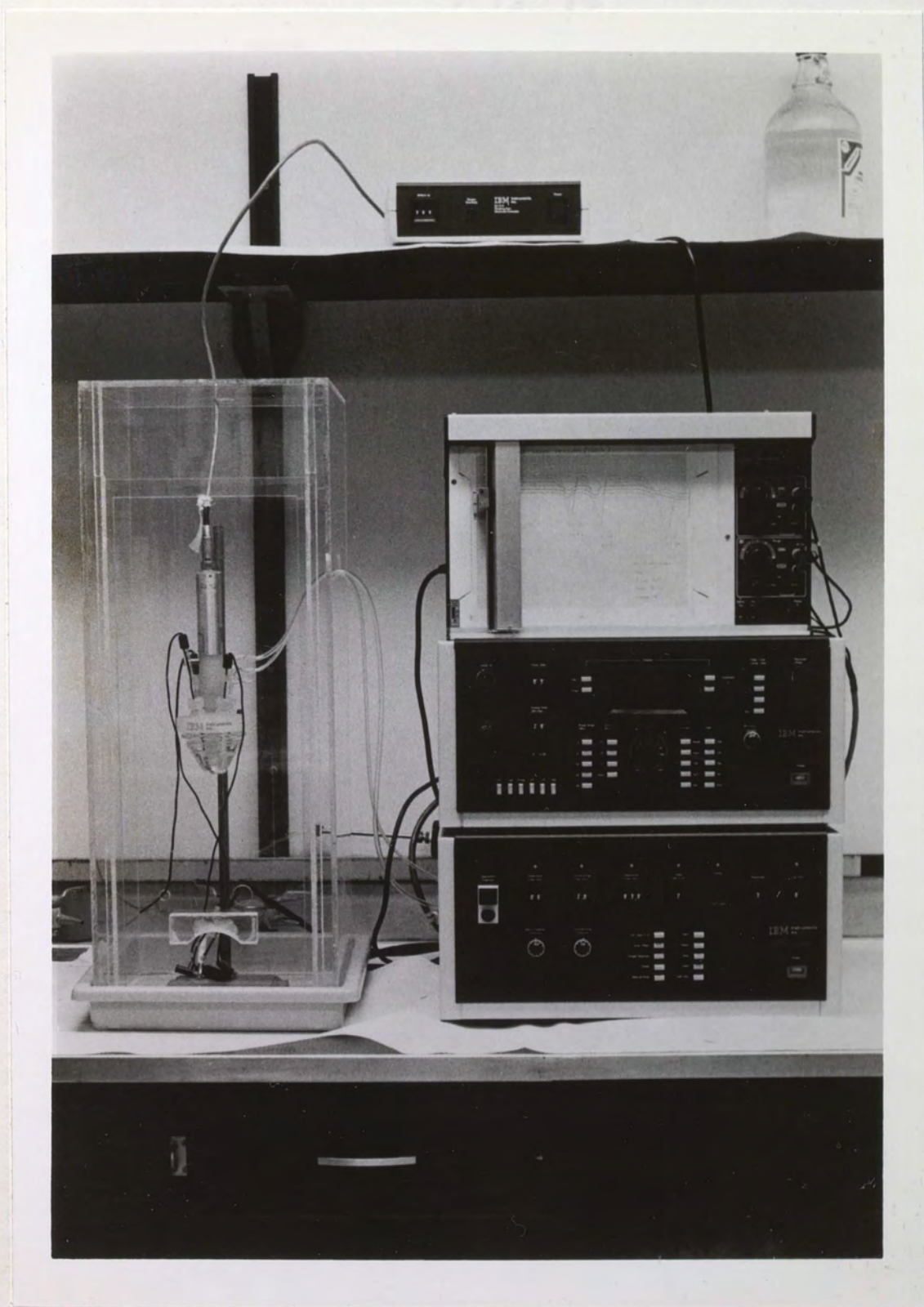
Figure 6.   Instrumentation for Anodic Stripping
            Voltammetry (ASV).

finish of each cathodic deposition, each metal was anodically stripped one at a time from the mercury film which was applied to the RGCE. As the redox potential of a particular metal was reached, the current (transfer of e^-) was measured between the glassy carbon electrode and the platinum wire electrode. This will produce a peak in the I-E (Current-Voltage) curve with its peak potential (E) serving as a qualitative indication of the identity of the metal ion and the peak height (I) a quantitative measure of its concentration in the solution. This automated process was continued three more times after rejecting the first run.

After three sample stripping I-E curves had been obtained, the sample was spiked with a combined metal standard and reanalyzed three more times. In summary, there should be three stripping curves, representing the concentration of Zn, Cd, Pb, and Cu in the sample. In addition, there should also be three more stripping curves, representing the concentration of sample plus spiked standard. Typical stripping curves are shown are shown in Figures 7.

Calculation of Metal Species

The relative sample and metal standard peak heights are determined to aid in the calculation of the metal
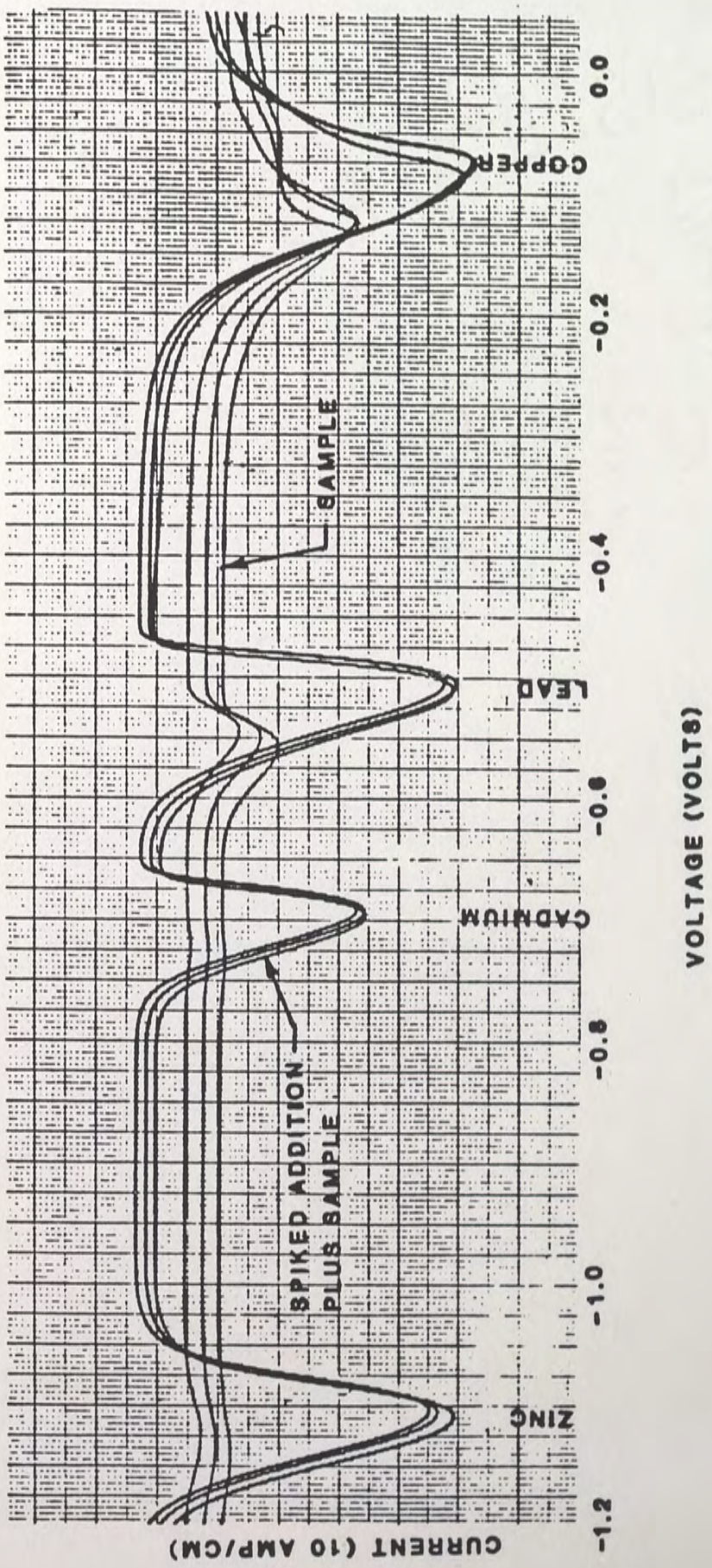
Figure 7. Typical ASV Analysis of Dissolved Metals in Water Samples Collected from the West Pond at the Maitland Interchange.

concentration by the equation of standard additions as follows (Neirotti 1982):

$$C_S = \frac{V+v}{V_S} \quad \frac{I_1 \, v \, C_{std}}{(I_2 - I_1) V + I_2 v}$$

where: C_{std} concentration of standard solution spiked

C_S concentration of the analyte (metal) in the original sample

V volume of supporting electrolyte + volume of analyte aliquot

v volume of standard spiked

V_S volume of analyte aliquot

I_1 peak height of sample

I_2 peak height of sample + standard

For a measurement of a metal concentration, the spiked standard plus sample peak height (I_2) must be at least twice the peak height of the sample (I_1) alone.

Even though ASV is the only analytical technique available that can be used in conjunction with metal speciation schemes, it has its drawbacks. If there is an excess of complexing agents in the natural water, some of the spiked standard will be complexed, thus reducing the peak height. This causes the metal concentration to appear higher than it actually is. Secondly, this technique is very sensitive to even the slightest

contamination. Every aspect of preparation and analysis must be meticulously carried out.

Speciation Scheme

After each pretreated subsample has been analyzed, the speciation scheme can be developed. The classification scheme applied for the ASV technique was developed by Batley and Florence (1976). The scheme permits the quantitative measurement of seven different heavy metal species in natural waters. Table 6 describes the speciation scheme classifications. The different species are calculated as shown in Table 7. As a final note, it should be mentioned that there is some overlap between the species and the analysis time on the voltammeter approaches hours for each sample collected.

Humic-Like Substances

The characterization and determination of humic substances is of prime importance if the nature and capacity of water for complexation of metals is desired. However, much information is lacking about their formation, chemical structures, and reactions. Standard methods for the determination of humic acids (HA) or fulvic acids (FA), which constitute fractions of the

TABLE 6

SPECIATION OF HEAVY METALS IN NATURAL WATERS

Part. Metal	Soluble Metal			
	ASV Labile Metal		Bound Metal	
	Class 1	Class 2	Class 3	Class 4
	free metal ion (M) labile organic complexes (ML_1) labile inorganic complexes (MA_1)	labile organic complexes and labile metal adsorbed on organic (ML_2) labile inorganic complexes and labile metal adsorbed on organic (MA_2)	non-labile organic complexes (ML_3) non-labile inorganic complexes (MA_3)	non-labile organic complexes and non-labile metal adsorbed on organic (ML_4) non-labile inorganic complexes and non-labile metal adsorbed on inorganic (MA_4)
Retained by 0.45 um filter	Not retained by 0.45 um filter			
	Direct ASV in Ac$^-$ Buffer		Total Metal Minus Labile Metal	
	Removed by Chelex 100	Not Removed by Chelex 100	Removed by Chelex	Not Removed by Chelex
		Released by UV irradiation / Not released by UV irradiation	Released by UV irradiation / Not Released by UV irradiation	Released by UV irradiation / Not Released by UV irradiation

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TABLE 7

CALCULATIONS FOR THE HEAVY METAL SPECIATION SCHEME PROPOSED
BY BATLEY AND FLORENCE (1976)

Treatment	Effect of Treatment	Measured in Solution After Treatment	
		(a) Labile Metal	(b) Total Metal

MEASUREMENTS:

Treatment	Effect of Treatment	(a) Labile Metal	(b) Total Metal
1) Filtration (0.45 um)	Removes Particulate Metal	M ML_1, ML_2 MA_1, MA_2	M ML_1, ML_2, ML_3, ML_4 MA_1, MA_2, MA_3, MA_4
2) Chelex-100	Removes $M, ML_1,$ ML_3, MA_1, MA_3	ML_2, MA_2	ML_2, ML_4 MA_2, MA_4
3) UV Irradiation	Releases metal from ML_1, ML_2, ML_3, ML_4	M ML_1, ML_2, ML_3 ML_4, MA_1, MA_2	M ML_1, ML_2, ML_3, ML_4 MA_1, MA_2, MA_3, MA_4
4) UV Chelex-100	Removes Metal released from ML_1, ML_2, ML_3, ML_4	MA_2	MA_2, MA_4

Calculations:

$M + M_1 + MA_1 = 1a - 2a$

$MA_2 = 4b - 4a$

$MA_4 = 4b - 4a$

$ML_2 = 2a - 4a$

$ML_4 = 2b - 2a - MA_4$

$MA_3 = 1b - 3a - MA_4$

$ML_3 = 3a - 1a - ML_4$

humic-like materials found in natural waters, apparently do not exist.

There are methods presented in the Standard Methods for Examination of Water and Wastewater (1980) for analysis of tannin-lignin materials. These materials contain aromatic hydroxyl groups similar to those present in HA and FA. The determination yields results which should be reported as "tannin-like," "lignin-like," or "hydroxylated aromatic-like" compounds.

Published books by Schnitzer and Khan (1972) and Gjessing (1976) describe knowledge available about humic substances and include analytical methodology to determine functionality, etc. Determination of HA and FA at low concentration levels is not included. The determination of FA by ultraviolet spectroscopy has been considered by Wilson (1959) and Lawrence (1980); and we have elected to utilize the method of Wilson, which is relatively rapid. It is not selective for FA. HA substances and FE (III) are known interferences. We have not been able to acquire a pure FA sample from a commercial source but do have available one HA standard from which standard solutions can be prepared. We, therefore, have used this HA sample for calibration purposes and base results for "humic-like" acids on this single standard. This approach has severe

limitations and, combined with previously mentioned
interferences associated with the uv method, suggests that
reported results may be valid only to establish the order
of magnitude for HA/FA concentrations.

CHAPTER IV

ANALYSIS OF HEAVY METAL SPECIATION

Introduction

Water samples were collected from rainfall, highway
runoff, and a detention pond at Maitland Interchange and
I-4 for analysis of particulate and dissolved metal
content. Similar analysis was performed on water samples
collected from highway bridge runoff and receiving stream
at U.S. 17-92 and Shingle Creek. Various metal species of
Pb, Zn, Cu, and Cd in solution were determined using ASV
techniques which followed the proposed scheme by Florence
and Batley (1976) described in Chapter III. These metals
are the most abundant in highway runoff and received the
most study (Wilber and Hunter 1977). Together, these
accounted for approximately 90 to 98 percent of the total
metals observed, with Pb and Zn accounting for 89
percent. Speciation of other metals using the same scheme
have not been fully developed. However, available
computer programs may assist in the determination of
various species of additional metals that exist under a
known set of environmental parameters.

The data collected during the course of this study from water quality analysis and heavy metal speciation are presented in this chapter.

Water Analysis

Water samples of the Maitland pond, rainfall, Shingle Creek, and runoff at each site were collected in duplicate, filtered in the field, and stored inside ice-packed chests. Five sets of the water samples, collected on 4/6, 5/13, 6/7, 7/5, and 8/1/85 were analyzed by both the USGS Water Resources Laboratory in Ocala and the Chemistry and Environmental Engineering Laboratories at the University of Central Florida (UCF). The analysis included major anions, cations, and trace metals. The results received from USGS laboratory are presented in Table 8, and those measured at UCF are presented in Table 9. Overall averages of the results from USGS and UCF are presented in Table 10.

The average pH values from rainfall samples are slightly higher than 5; however, other samples from highway runoff, bridge runoff, Maitland Pond, and Shingle Creek water were close to neutral. The acidic rainfall is generally neutralized as it flows over the drainage basin. Also, runoff water picks up dissolved solids, which is evident from the increase in specific conductance

TABLE 8

AVERAGE DISSOLVED WATER QUALITY PARAMETERS ANALYZED BY USGS

Parameter	Maitland Interchange Rainfall x̄	σx	Maitland Interchange Runoff x̄	σx	Maitland Interchange Pond x̄	σx	U.S. 17-92 & Shingle Creek Shingle Creek x̄	σx	U.S. 17-92 & Shingle Creek Runoff x̄	σx
pH (lab)	5.2	0.7	6.9	0.2	6.8	0.2	6.8	0.2	7.2	0.2
Sp. Cond (umho/cm)	18.0	4.0	123.0	52.0	186.0	21.0	210.0	64.0	237.0	101.0
Color Units	1.0	2.5	10.0	9.0	10.0	7.0	220.0	69.0	50.0	36.0
Dissolved Solids	9.8	2.1	75.9	39.9	113.3	10.4	159.9	40.8	173.3	95.4
Alk(CaCO$_3$)	1.0	1.0	44.4	16.2	50.4	9.5	40.4	15.4	74.5	22.1
TH(CaCO$_3$)	4.3	2.1	48.8	25.6	70.8	9.9	60.6	12.6	95.5	49.2
HCO$_3$	1.5	1.3	54.2	20.2	61.7	12.0	49.2	19.1	92.0	26.9
SO$_4^=$	3.0	1.1	11.8	10.5	29.8	2.0	24.4	8.1	24.7	15.5
Cl$^-$	1.9	0.45	2.9	1.5	5.6	0.9	23.2	6.0	11.5	8.8
TN as N	0.66	0.50	0.79	0.18	0.51	0.16	1.37	0.42	3.15	2.16
Organic N as N	0.27	0.13	0.32	0.18	0.38	0.14	1.02	0.45	1.78	1.38
NH$_4$-N	0.09	0.12	0.06	0.05	0.04	0.03	0.07	0.02	0.57	1.02
NO$_2$-N	0.01	0.0	0.02	0.01	0.01	0.0	0.01	0.0	0.07	0.07
NO$_3$-N	0.29	0.29	0.4	0.3	0.07	0.08	0.27	0.3	0.73	0.98
TP-P	0.02	0.0	0.05	0.01	0.01	0.0	0.22	0.13	0.12	0.03
OP-P	0.02	0.0	0.04	0.02	0.01	0.0	0.20	0.12	0.09	0.04
Ca^{++}	1.3	0.7	17.7	8.4	20.8	3.4	17.0	3.7	36.5	18.8
Mg^{++}	0.2	0.1	1.1	1.4	4.5	0.5	4.0	0.9	1.4	0.9
Na^{++}	1.1	0.3	2.4	2.0	5.3	0.4	13.1	6.2	4.1	2.7
K$^+$	0.3	0.2	2.1	2.0	5.6	0.6	3.1	1.0	5.4	6.5
SiO$_2$	0.1	0.1	2.1	1.5	0.9	1.3	4.5	1.5	3.0	0.7

All concentrations are expressed in mg/l.

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TABLE 9

AVERAGE DISSOLVED WATER QUALITY PARAMETERS ANALYZED BY UCF
(ALL CONCENTRATIONS ARE IN mg/l)

| Parameter | Maitland Interchange | | | | | | U.S. 17-92 & Shingle Creek | | | |
| | Rainfall | | Runoff | | Pond | | Shingle Creek | | Runoff | |
	$\bar{x}$	σ_x	$\bar{x}$	σ_x	$\bar{x}$	σ_x	$\bar{x}$	σ_x	$\bar{x}$	σ_x
$SO_4^=$	2.1	2.3	11.2	9.9	22.6	6.6	21.4	5.8	32.7	48.1
Cl^-	1.0	0.6	2.8	1.8	4.5	0.7	19.4	3.6	9.8	11.8
NH_4-N	0.15	0.1	0.12	0.08	0.08	0	0.27	0.3	0.84	1.24
NO_3-N	0.35	0	0.24	0.19	0.08	0.12	0.25	0.14	0.15	0.19
OP-P	0.03	0	0.03	0	0.03	0.03	0.26	0.05	0.09	0.06
Ca	2.2	1.6	16.2	8.1	20.2	4.0	25.0	5.5	16.1	14.8
Mg	0.2	0.1	1.2	1.5	4.4	0.4	4.4	1.3	0.4	0.3
Na	4.4	4.1	3.5	2.8	5.9	1.3	24.4	12.0	2.9	0.2
K	0.8	0.7	1.1	0.9	2.6	0.4	1.9	0.4	0.7	0.5
SiO_2	0.2	0	1.6	1.4	1.5	1.2	4.6	2.3	3.1	1.1
Homic Acids	1	0.5	5	4	4	2	18	14	10	9

TABLE 10

OVERALL AVERAGE DISSOLVED WATER QUALITY PARAMETERS

| Parameter | Maitland Interchange | | | | | | U.S. 17-92 & Shingle Creek | | | |
| | Rainfall | | Runoff | | Pond | | Shingle Creek | | Runoff | |
	$\bar{x}$	σ_x	$\bar{x}$	σ_x	$\bar{x}$	σ_x	$\bar{x}$	σ_x	$\bar{x}$	σ_x
pH (lab)	5.2	0.7	6.9	0.2	6.8	0.2	6.8	0.2	7.2	0.2
Sp.Cond (umho/cm)	18.0	4.0	123.0	52.0	186.0	21.0	210.0	64.0	237.0	101.0
Color Units	1.0	2.5	10.0	9.0	10.0	7.0	220.0	69.0	50.0	36.0
Dissolved Solids	9.8	2.1	75.9	39.9	113.3	10.4	159.9	40.8	173.3	95.4
Alk($CaCO_3$)	1.0	1.0	44.4	16.2	50.4	9.5	40.4	15.4	74.5	22.1
TH($CaCO_3$)	4.3	2.1	48.8	25.6	70.8	9.9	60.6	12.6	95.5	49.2
NCH($CaCO_3$)	3.3	2.2	8.0	6.6	20.2	2.4	20.2	5.3	23.5	24.9
HCO_3	1.5	1.3	54.2	20.2	61.7	12.0	49.2	19.1	91.0	26.9
$SO_4^=$	2.7	1.4	11.9	10.2	26.6	5.5	23.3	7.0	28.1	30.2
Cl^-	1.6	0.7	2.9	1.5	5.1	1.0	21.8	5.3	10.8	9.3
TN as N	0.66	0.50	0.79	0.18	0.51	0.16	1.37	0.42	3.15	2.16
Organic N as N	0.27	0.13	0.32	0.18	0.38	0.14	1.02	0.45	1.78	1.38
NH_4-N	0.11	0.10	0.09	0.07	0.04	0.02	0.14	0.19	0.69	1.03
NO_2-N	0.01	0.0	0.02	0.01	0.01	0.0	0.01	0.0	0.07	0.08
NO_3-N	0.31	0.26	0.33	0.26	0.15	0.26	0.26	0.24	0.48	0.77
TP-P	0.02	0.0	0.05	0.01	0.01	0.0	0.22	0.13	0.12	0.03
OP-P	0.01	0.0	0.03	0.02	0.0	0.0	0.22	0.10	0.09	0.04
Ca^{++}	1.6	1.0	27.0	28.3	20.5	3.4	17.3	4.1	27.8	19.2
Mg^{++}	0.2	0.1	1.17	1.34	4.5	0.4	4.2	1.0	0.9	0.9
Na^{++}	2.2	2.6	2.9	2.3	5.6	0.9	17.3	9.9	3.7	2.2
K^+	0.5	0.4	1.7	1.6	4.3	1.6	2.6	1.0	3.9	5.6
SiO_2	0.1	0.1	1.9	1.4	1.2	1.2	4.5	1.7	3.0	0.8
Humic Acids	1	0.5	5	4	4	2	18	14	10	9

All concentrations are expressed in mg/l.

and dissolved solids measurements between rainfall and runoff samples. Rainfall samples averaged approximately 10 mg/l of dissolved solids, while runoff samples were averaging between 76 and 173 mg/l. There were very little differences between values measured in runoff water and those measured in receiving water. Dissolved solids concentrations can be expressed in terms of specific conductance. The dissolved solids concentration to specific conductance ratio averaged 0.54, 0.62, 0.61, 0.76, and 0.73 for rainfall, highway runoff, Maitland Pond, Shingle Creek water, and bridge runoff, respectively. Water characteristics for the Maitland site appear to show distinct differences from those for the Shingle Creek site. However, dissolved solids, alkalinity, and total hardness in the Maitland Pond water are higher than the same parameters in runoff water, presumable due to their concentration by evaporation of the pond water.

It is interesting to notice that the average total nitrogen (TN) and total phosphorus (TP) concentrations in Maitland Pond water are lower than those in rainfall and runoff waters. Inorganic nitrogen is the major fraction in rainwater and organic nitrogen is the major fraction in pond water. The average inorganic nitrogen and total

phosphorus concentrations in Maitland Pond water did not exceed 30 percent of the average concentrations in highway runoff water. The pond appears to be very efficient in the removal or inorganic nitrogen and phosphorus species from highway runoff water. The same conclusions were reached during a detailed analysis of the pond by Hvitved-Jacobsen et al. (1984).

Total nitrogen in the bridge runoff was higher than total nitrogen in Shingle Creek water; however, total phosphorus was lower. Shingle Creek is a flowing stream receiving municipal wastewater effluent, agricultural runoff, and urban runoff. It is highly colored, averaging 220 color units caused by humic substances from the decay of vegetation. The average humic substance concentration averaged 18 mg/1 in Shingle Creek water and 4 mg/1 in Maitland Pond water. Similarly, SiO_2 concentration averaged much higher values in Shingle Creek water than Maitland Pond water.

The analysis indicates that rainwaters wash off deposits on highway surfaces and dissolve contaminants during surface overflow. Major cations, particularly Ca, Mg, Na, and K, are dissolved in surface runoff water. The quality of runoff appears to be improved by retention/detention in Maitland Pond. Calcium

concentration in the pond water is lower than runoff water; however, Mg, Na, and K concentrations were higher in the pond water than in the runoff water. Calcium is reduced by precipitation and removal and other cations are concentrated by evaporation.

Heavy Metal Speciation

Dissolved heavy metal species in water samples collected from Maitland Interchange and I-4 and from Shingle Creek and U.S. 17-92 were determined by the ASV technique, following Florence and Batley's (1976) speciation scheme. Also, speciation of heavy metals in bottom sediments of the retention/detention pond receiving highway runoff of Maitland Interchange was investigated.

ASV Calibration of Selected Heavy Metal

Standard for Cd, Pb, and Cu were calibrated using the following operational conditions:

1) Rotating Disc Electrode Controller IBM EC 219 was set at 3,600 rpm for the glassy carbon electrode.

2) IBM 7424M, X-Y Recorder was set at a current range of 10 microampere/volt (10 ua/V) full scale. The X axis was set at 0.05 V/cm and the Y axis was set at 0.5 V/cm.

3) IBM Voltammetric Analyzer EC225 was set for:

a) Deposition potential = -1.3 v

      b)   Conditioning potential = +0.15 v

      c)   Sweep rate = 25 mv/sec

      d)   Timer = 0.30 sec

    4)   IBM Electrochemical Sequencer EC 229 was set for:

      a)   Deposition time = 3.0 min

      b)   Conditioning time = 2.0 min

      c)   Deaeration time = 5 min

      d)   Delay time = 20 sec

These operational parameters were kept constant throughout this study. Also, the linearity of this equipment was checked using three or four different concentrations of each metal within the range of 0.1 ug/1 and 20 ug/1. The results seem to indicate that the voltammetric analyzer is linear for Cd, Pb, and Cu within the range tested, as shown in Figure 8. A near perfect correlation seems to exist between the peak height and the actual metal concentration for Cd, Pb, and Zn solution in deionized water at a controlled pH value of 6.0 in acetate buffer 0.1 molar solution. A current-output curve is developed for each sample, where the peak height indicates the metal concentration and the peak location identifies the qualitative description of each metal.
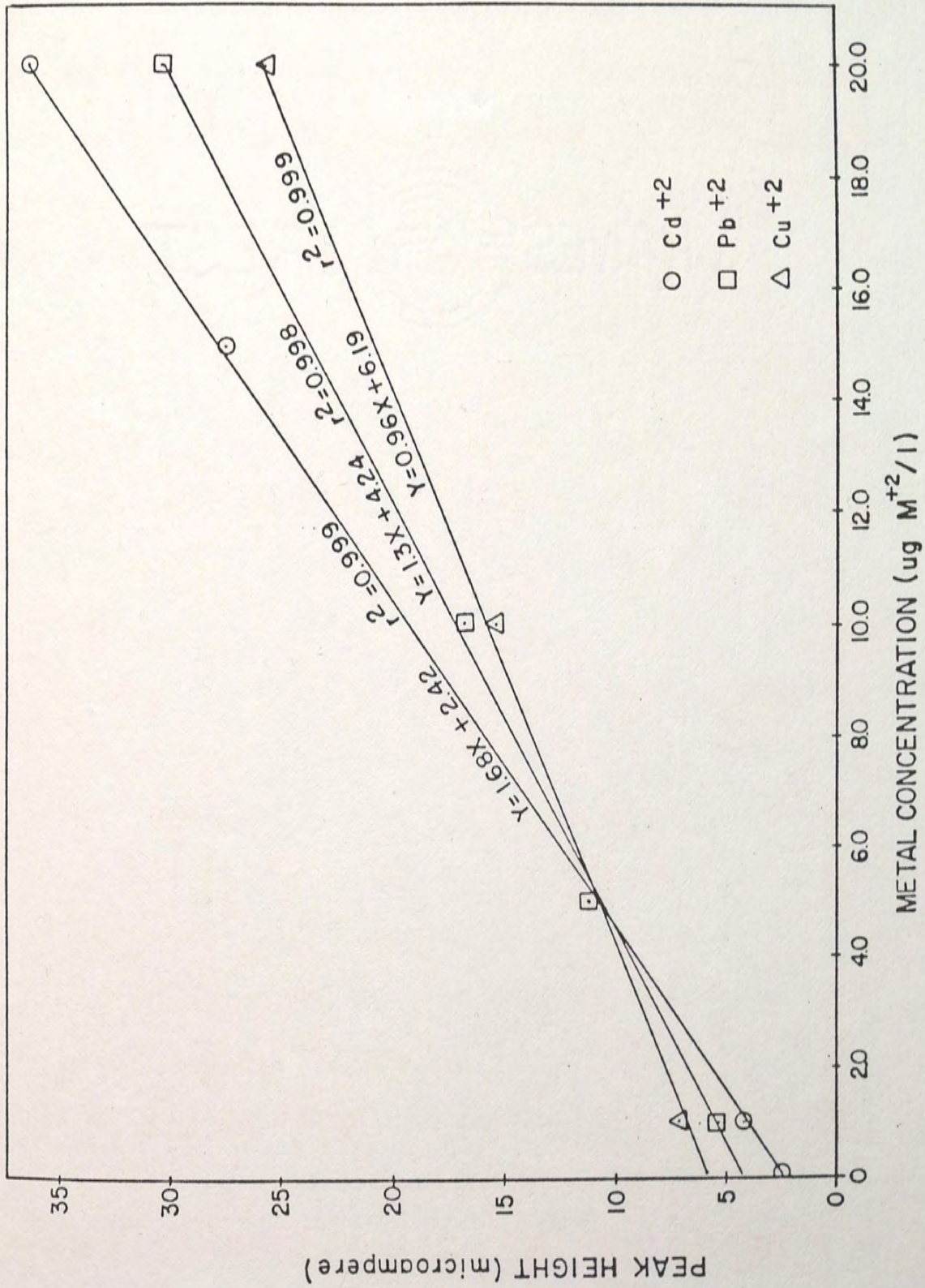
Figure 8. Calibration of Heavy Metal Standards Using Anodic Stripping Voltammetry.

Metal Speciation in Water Samples

Analytical procedures have been developed for dissolved species of Zn, Cd, Pb, and Cu in water samples using ASV. However, reliable and sensitive methods for additional metals are still in the process of development. Therefore, the analytical analysis is limited to the four listed trace metals dissolved in water samples. Those metals constitute more than 90 percent of the total metal content in highway runoff. The analysis followed the speciation scheme discussed in Chapter III, which required several treatment steps to separate the various species of labile and non-labile trace metals. Labile species may include organic colloidal and inorganic soluble and colloidal forms. Also, non-labile species may include organic soluble and colloidal and inorganic soluble and colloidal forms. The peak heights measured from current (I) versus voltage (E) diagrams for Zn, Cd, Pb, and Cu in water samples before and after Chelex-100 treatment and before and after exposure to uv light should allow us to calculate concentrations of various species, as outlined in Tables 6 and 7.

Concentrations of various species in the water samples are presented in Tables A-1 through A-11 in the Appendix. These tables show calculated concentrations of various

species, summation of concentrations for aggregate
species, filterable metal concentration, and total
concentration for nonfiltered samples. The added
concentration of aggregate species should be close to the
concentration of the metal in a filtered water sample.
Occasionally, considerable differences were found between
the calculated and measured dissolved metal
concentrations, and it was decided not to use these
samples in the analysis of results. The reported data in
Tables A-1 through A-11 indicate that a maximum difference
of 4 percent exists between summation of measured
aggregate species and the total filterable concentration.
This remarkable agreement enhances the credibility of the
scheme used and the extra cautious techniques developed
through this analysis. Also, the data indicate that the
soluble metal fraction in rainfall, runoff, Maitland Pond,
bridge runoff, the Shingle Creek water samples averaged:
86, 86, 100, 78 and 71 percents for Zn; 100, 85 96, 76,
and 89 percents for Cd; 79, 57, 85, 47, and 82 percents
for Cu; and 45, 38, 28, 23, and 51 percents for Pb. Zn,
Cd, and Cu fractions in solution appear to be much greater
than lead fractions. Zn and Cd appear to be the most
soluble in waters tested.

The data presented in the appendix are summarized in
Tables 11 through 15. These data indicate that the
average concentration in Maitland rainfall, runoff, and
pond water were 2.49, 1.61, and 1.05 ug-Cd/l; 8.15, 23.0,
and 10.8 ug-Zn/l; 8.7, 40.7, and 20.4 ug-Pb/l; and 66.1,
26.6, and 16.6 ug-Cu/l, respectively. Also, Shingle Creek
water and bridge runoff averaged 1.76 and 2.92 ug-Cd/l;
14.5 and 15.3 ug-Zn/l; 18.8 and 27.7 ug-Pb/l and 8.86 and
18.6 ug-Cu/l, respectively. It is interesting to notice
that the average metal concentrations in Maitland Pond
water are lower than those detected in rainfall and runoff
water. The pond is efficient in metal removal which
accumulate in the bottom sediments (Yousef, Harper,
Wiseman and Bateman 1984). Similarly, the average metal
concentrations in the Shingle Creek water are lower than
those detected in highway bridge runoff crossing over the
creek at U.S. 17-92.

The relative distribution of various dissolved species
of trace metals detected in water samples collected during
this study is presented in Table 16. The data shows that
labile, organic, and colloidal fractions average 82.0,
5.3, and 3.2 percents for Cd; 92.9, 0.3, and 42.7 percents
for Zn; 60.9, 22.1, and 55.6 percents for Pb; and 63.7,
48.9, and 69.8 percents for Cu in all water samples

TABLE 11

SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN RAINFALL WATER FROM MAITLAND SITE

Metal	Parameter	Labile Organic Coll.	Labile Inorganic Sol.	Labile Inorganic Coll.	Non-Labile Organic Sol.	Non-Labile Organic Coll.	Non-Labile Inorganic Sol.	Non-Labile Inorganic Coll.	Total Dissolved Metal
Cd	n	4	4	4	4	4	4	4	4
	$\bar{x}$(ug/l)	0.01	1.69	0.44	0.003	0.015	0.32	0.015	2.49
	σ_x	0.02	0.53	0.12	0.005	0.017	0.12	0.017	0.61
	%	0.4	67.8	17.7	0.1	0.6	12.8	0.6	100
Zn	n	2	2	2	2	2	2	2	2
	$\bar{x}$(ug/l)	0.0	3.90	3.73	0.0	0.0	0.52	0.0	8.15
	σ_x	0.0	0.7	0.83	0.0	0.0	0.06	0.0	1.59
	%	0.0	47.9	45.8	0.0	0.0	6.3	0.0	100
Pb	n	3	3	3	3	3	3	3	3
	$\bar{x}$(ug/l)	3.6	9.67	11.4	1.03	0.83	3.07	7.97	37.6
	σ_x	1.78	4.3	3.21	0.31	0.23	1.29	1.27	8.72
	%	9.6	25.7	30.3	2.8	2.2	8.2	21.2	100
Cu	n	4	4	4	4	4	4	4	4
	$\bar{x}$(ug/l)	14.9	16.0	24.6	10.4	0.01	0.2	0.01	66.1
	σ_x	16.1	7.12	23.3	12.0	0.03	0.23	0.03	57.7
	%	22.6	24.2	37.2	15.7	0.0	0.3	0.0	100

Dissolved Metal Fraction

TABLE 12

SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN RUNOFF WATER FROM MAITLAND SITE

| | | Dissolved Metal Fraction | | | | | | | Total Dissolved |
| | | Labile | | | | Non-Labile | | | |
Metal	Parameter	Organic Coll.	Inorganic Sol.	Inorganic Coll.	Organic Sol.	Organic Coll.	Inorganic Sol.	Inorganic Coll.	Metal
Cd	n	6	6	6	6	6	6	6	6
	$\bar{x}$(ug/l)	0.02	0.81	0.53	0.05	0.0	0.16	0.16	1.61
	σ_x	0.03	0.28	0.28	0.0	0.0	0.14	0.023	
	%	1.2	50.5	33.0	3.1	0.0	10.0	2.2	100
Zn	n	3	3	3	3	3	3	3	3
	$\bar{x}$(ug/l)	0.06	15.87	5.36	0.1	0.0	1.64	0.01	23.04
	σ_x	0.05	5.84	4.84	0.17	0.0	0.95	0.02	3.85
	%	0.3	68.9	23.3	0.4	0.0	7.1	0.0	100
Pb	n	5	5	5	5	5	5	5	5
	$\bar{x}$(ug/l)	0.33	19.9	9.34	1.01	4.91	1.93	3.25	40.7
	σ_x	0.43	4.64	1.57	0.26	4.07	2.54	1.31	7.66
	%	0.8	48.9	23.0	2.5	12.1	4.7	8.0	100
Cu	n	6	6	6	6	6	6	6	6
	$\bar{x}$(ug/l)	2.37	4.29	5.55	0.81	11.9	1.4	0.28	26.6
	σ_x	1.12	1.03	4.73	0.59	15.3	0.92	0.26	22.5
	%	8.9	16.1	20.9	3.0	44.7	5.3	1.1	100

TABLE 13

SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN POND WATER FROM MAITLAND SITE

Metal	Parameter	Dissolved Metal Fraction							Total Dissolved Metal
		Labile			Non-Labile				
		Organic	Inorganic		Organic		Inorganic		
		Coll.	Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	
Cd	n	8	8	8	8	8	8	8	8
	$\bar{x}$(ug/l)	0.005	0.59	0.31	0.03	0.008	0.095	0.01	1.05
	σ_x	0.008	0.27	0.19	0.05	0.014	0.12	0.009	0.49
	%	0.5	56.3	29.5	2.9	0.8	9.1	0.9	100
Zn	n	4	4	4	4	4	4	4	4
	$\bar{x}$(ug/l)	0.03	1.37	9.04	0.0	0.0	0.4	0.0	10.84
	σ_x	0.06	0.82	2.74	0.0	0.0	0.22	0.0	2.09
	%	0.3	12.6	83.4	0.0	0.0	3.7	0.0	100
Pb	n	7	7	7	7	7	7	7	7
	$\bar{x}$(ug/l)	0.53	4.0	6.76	0.66	2.34	4.68	1.4	20.4
	σ_x	0.48	0.95	3.06	0.42	0.93	2.17	0.5	5.74
	%	2.6	19.6	33.2	3.2	11.5	23.0	6.9	100
Cu	n	8	8	8	8	8	8	8	8
	$\bar{x}$(ug/l)	6.16	3.93	2.86	0.2	2.24	0.32	0.28	16.6
	σ_x	1.07	0.69	0.56	0.15	0.39	0.27	0.23	2.16
	%	38.5	24.6	17.9	1.3	14.0	2.0	1.7	100

TABLE 14

SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN SHINGLE CREEK WATER

Metal	Parameter	Dissolved Metal Fraction								Total Dissolved Metal
		Labile				Non-Labile				
		Organic		Inorganic		Organic		Inorganic		
		Coll.	Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Sol.	Metal
Cd	n	6	6	6	6	6	6	6		6
	$\bar{x}$(ug/l)	0.015	0.67	0.64	0.2	0.02	0.21	0.008		1.76
	σ_x	0.023	0.38	0.29	0.19	0.02	0.21	0.01		0.72
	%	0.9	38.0	36.3	11.3	1.1	11.9	0.5		100
Zn	n	3	3	3	3	3	3	3		3
	$\bar{x}$(ug/l)	0.03	8.5	4.47	0.0	0.0	1.53	0.01		14.54
	σ_x	0.01	1.81	0.91	0.0	0.0	0.86	0.02		0.55
	%	0.2	58.5	30.8	0.0	0.0	10.5	0.0		100
Pb	n	5	5	5	5	5	5	5		5
	$\bar{x}$(ug/l)	1.03	4.97	6.64	0.34	2.26	1.3	2.28		18.8
	σ_x	0.82	0.62	0.53	0.26	0.51	1.57	0.39		0.61
	%	5.5	26.4	35.3	1.8	12.0	6.9	12.1		100
Cu	n	6	6	6	6	6	6	6		6
	$\bar{x}$(ug/l)	1.51	0.76	2.07	0.93	3.07	0.11	0.41		8.86
	σ_x	1.74	0.18	1.03	1.0	1.14	0.15	0.32		3.1
	%	17.0	8.6	23.4	10.5	34.7	1.2	4.6		100

TABLE 15

SUMMARY OF DISSOLVED HEAVY METAL SPECIATION IN BRIDGE RUNOFF FROM U.S. 17-92 AND SHINGLE CREEK SITE

Metal	Parameter	Dissolved Metal Fraction							Total
		Labile			Non-Labile				Dissolved
		Organic	Inorganic		Organic		Inorganic		Metal
		Coll.	Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	
Cd	n	5	5	5	5	5	5	5	5
	$\bar{x}$(ug/l)	0.03	1.24	1.01	0.04	0.03	0.52	0.05	2.92
	σ_x	0.03	0.51	1.3	0.05	0.05	0.33	0.04	2.0
	%	1.0	42.5	34.6	1.4	1.0	17.8	1.7	100
Zn	n	2	2	2	2	2	2	2	2
	$\bar{x}$(ug/l)	0.045	9.66	4.4	0.0	0.0	1.15	0.005	15.26
	σ_x	0.007	2.04	0.92	0.0	0.0	0.22	0.007	3.18
	%	0.3	63.3	28.9	0.0	0.0	7.5	0.0	100
Pb	n	4	4	4	4	4	4	4	4
	$\bar{x}$(ug/l)	1.88	2.65	7.62	3.18	7.11	2.86	2.4	27.7
	σ_x	0.39	0.16	2.35	3.59	2.91	1.13	0.5	4.13
	%	6.8	9.5	27.5	11.5	25.7	10.3	8.7	100
Cu	n	5	5	5	5	5	5	5	5
	$\bar{x}$(ug/l)	0.27	4.56	6.12	0.92	5.02	1.57	0.11	18.6
	σ_x	0.26	1.97	4.69	0.82	4.38	1.93	0.01	11.3
	%	1.4	24.6	33.0	5.0	27.0	8.4	0.6	100

tested, respectively. The organic fraction for dissolved copper in water samples was the highest among all metals tested. The organic fraction in all metals tested followed a decreasing order for Cu Pb Cd Zn. Similarly, the labile fraction followed a decreasing order for Zn Cd Cu Pb. Also, the colloidal fraction followed a decreasing order Cu Pb Zn Cd. It can be concluded that Zn and Cd are more reactive in natural environments than Cu and Pb. Zn and Cd may exist in ionic forms and are more readily available to biota in natural systems.

Effects of Influences and Interferences

Due to the complex nature of natural water samples, interferences in the analysis of a particular ion of interest are bound to occur. This was noted during the ASV analysis of Zn, Cd, Pb and Cn. Organic ligands such as fulvic and humic acids will complex with Cd, Pb and Cu under the proper conditions. During the analysis, when the metal standards were added to the water sample the peak height of Cd, Pb and Cu decreased with time and each subsequent run. This was probably attributable to the formation of metal-organic complexes. This subsequently decreases the metal ion concentration in solution, thus reducing the peak height. This would overestimate the

TABLE 16

RELATIVE DISTRIBUTION FOR VARIOUS DISSOLVED SPECIES OF
TRACE METALS IN WATER SAMPLES

		Percentage in Water From				
		Maitland Interchange			U.S. 17-92	
Metal	Form	Rainfall	Runoff	Pond	Bridge Runoff	Shingle Creek
Cd	Labile	85.9	84.7	86.3	78.1	75.2
	Non-Labile	14.1	15.3	13.7	21.9	24.8
	Organic	1.1	4.3	4.2	3.4	13.3
	Inorganic	98.9	95.7	95.8	96.6	86.6
	Colloidal	19.3	36.4	31.7	38.3	38.8
	Non-Colloidal	80.7	63.6	68.3	61.7	61.2
Zn	Labile	93.7	92.5	96.3	92.5	89.5
	Non-Labile	6.3	7.5	3.7	7.5	10.5
	Organic	0.0	0.0	0.3	0.3	0.2
	Inorganic	100	99.3	99.7	99.7	99.8
	Colloidal	45.8	23.6	83.7	29.2	31.0
	Non-Colloidal	54.2	76.4	16.3	70.8	69.0
Pb	Labile	65.6	72.7	55.4	43.8	67.2
	Non-Labile	34.4	27.3	44.6	56.2	32.8
	Organic	14.6	15.4	17.3	44.0	19.3
	Inorganic	85.4	84.6	82.7	56.0	80.7
	Colloidal	63.3	36.7	54.2	68.7	54.9
	Non-Colloidal	36.7	63.3	45.8	31.3	45.1
Cu	Labile	84.0	45.9	81.0	58.7	49.0
	Non-Labile	16.0	54.1	19.0	41.3	51.0
	Organic	38.3	56.6	53.8	33.4	62.2
	Inorganic	61.7	43.4	46.2	66.6	37.8
	Colloidal	59.8	75.6	72.1	62.0	79.7
	Non-Colloidal	40.2	24.4	27.9	38.0	20.3

metal concentrations measured in each sample. However, zinc was not affected by organic content of the water.

Iron could present a problem if the metal exists at levels higher than 0.8 ppm in water samples. This would have an impact on the copper concentration measured in solution by increasing the copper stripping peak. However, highway runoff from Maitland Interchange and Shingle Creek sites generally contained less than 0.8 mg/l of dissolved iron.

Probably the biggest impact on the metal speciation scheme was the use of u.v. irradiation to measure the metal fraction associated with organics. A brown precipitate was noticed in most of the samples which were treated with u.v. light. This indicates that the organic coating associated with ferrous colloidal material was probably oxidized, thus precipitating iron, manganese lead and some copper. However, the magnitude of the loss of the metals lead and copper was not quantified.

CHAPTER V

PREDICTION OF METAL SPECIATION

The speciation of trace elements in natural waters is important in assessing the potential for biological uptake. Most of our analytical techniques measure gross parameters such as total dissolved lead or copper but give us no clue as to the actual form of their existence in the environment. One of the methods to attempt to gain insight in this area is the use of computer modelling. One widely used model is WATEQ2 (Ball et al. 1980, Jenne 1979).

WATEQ2

This is a computerized chemical model for trace and major element speciation and mineral equilibria of natural waters. It is a PL/1 program and is adapted to run on the IBM in Gainesville.

The program has resulted from extensive additions to and revisions of WATEQ model (Truesdell and Jones 1973, 1974). The model is limited by available literature and thermochemical data pertinent to chemical reactions of selected elements. A U.S. geological survey, Water Resources Investigation 78-116, published by Ball, Nordstorm, and Jenne (1980), makes available the details

of the reactions added to the model and their sources.
Also, the report lists details of the program operation
and a brief description of the output of the model.

Prediction of Metal Species

To test the validity of the computer program WATEQ2,
the average water quality characteristics for rainfall,
runoff, and detention/retention pond water from the
Maitland site and bridge runoff and Shingle Creek site
were utilized to predict trace metal speciation in these
waters. The parameters presented in Table 10 were used as
input data to predict species of Zn, Cd, Pb, Cu, and Ni.
Predicted heavy metal species are presented in tables 17
through 21.

It is interesting to notice that half of the Cu metal
or better is associated with organic complexes of humic
substances in all waters tested. This appears to be
consistent with measured values presented in Table 16.
Also, most of the Zn and Cd metals are present in ionic
species as Zn^{+2} or Cd^{+2}. These species are labile and
readily available for biological forms. More than 95
percent of the Zn, Cd, Pb, and Ni are metal ion, metal
carbonate, and bicarbonate species. This is in agreement
with the measured inorganic forms presented in Table 16.
Inorganic factions measured for Cd and Zn exceeded 95

TABLE 17

PREDICTED METAL SPECIES FOR MAITLAND RAINFALL

Metal	Measured Dissolved Conc. mg-M/l	Predicted Dissolved Species	Predicted Conc. mg-M/l	% M of Measured Concentration
Zn	0.0082	Zn^{+2}	0.0081	99.1
		$ZnHCO_3^+$,	0.0001	0.9
		$ZnSO_4$		
Cd	0.0025	Cd^{+2}	0.002463	98.5
		$CdHCO_3^+$,	0.000033	1.3
		$CdCl^+$,		
		$CdSO_4$		
		Cd-Fulvate		
Pb	0.038	Pb^{+2}	0.03663	96.4
		$PbHCO_3^+$	0.00065	1.7
		$PbSO_4$	0.00049	1.3
		$PbCO_3$,	0.00023	0.6
		$PbOH^+$		
Cu	0.066	Cu^{+2}	0.03439	52.1
		Cu-Fulvate	0.03003	45.5
		Cu-Humate	0.00105	1.6
		$CuOH^+$,	0.00053	0.8
		$CuHCO_3^+$,		
		$CuSO_4$		
Ni	0.001	Ni^{+2}	0.00099	99.0
		$NiHCO_3^+$,	0.00001	1.0
		$NiCO_3$,		
		$NiSO_4$		

TABLE 18

PREDICTED METAL SPECIES FOR MAITLAND RUNOFF

Metal	Measured Dissolved Conc. mg-M/1	Predicted Dissolved Species	Predicted Conc. mg-M/1	% M of Measured Concentration
Zn	0.023	Zn^{+2}	0.019	82.6
		$ZnHCO_3^+$	0.0023	10.0
		$ZnCO_3$	0.00115	5.0
		$ZnSO_4$	0.00032	1.4
		$AnOH^+$, $Zn(OH)_2$, $ZnSO_4$	0.00023	1.0
Cd	0.0016	Cd^{+2}	0.00128	80.5
		$CdHCO_3^+$	0.00016	10.0
		$CdCO_3$	0.0001	6.2
		$CdSO_4$	0.00003	1.7
		Cd-Fulvate	0.00002	1.1
		$CdCl^+$	0.00001	0.5
Pb	0.041	Pb^{+2}	0.00565	13.8
		$PbCO^3$	0.03026	73.8
		$PbHCO_3^+$	0.00435	10.6
		$PbSO_4$, $PbOH^+$	0.00074	1.8
Cu	0.027	Cu^{+2}	0.00243	9.0
		Cu-Fulvate	0.01612	59.7
		$CuCO_3$	0.00389	14.4
		$Cu(OH)_2$	0.00243	9.2
		$CuHCO_3$	0.00119	4.4
		Cu-Humate	0.00057	2.1
		$CuOH^+$, $CuSO_4$	0.00032	1.2
Ni	0.003	Ni^{+2}	0.00087	29.0
		$NiCO_3$	0.002	66.4
		$NiHCO_3$	0.00012	4.0
		$NiSO_4$, $Ni(CO_3)_2^{-2}$	0.00001	0.6

TABLE 19

PREDICTED METAL SPECIES FOR MAITLAND POND

Metal	Measured Dissolved Conc. mg-M/l	Predicted Dissolved Species	Predicted Conc. mg-M/l	% M of Measured Concentration
Zn	0.011	Zn^{+2}	0.00931	84.6
		$ZnHCO_3^+$	0.00094	8.5
		$ZnCO_3$	0.00036	3.3
		$ZnSO_4$	0.00034	3.1
		$ZnOH^+$,	0.00005	0.5
		$Zn(OH)_2$,		
		$ZnCl^+$		
Cd	0.001	Cd^{+2}	0.00082	82.0
		$CdHCO_3^+$	0.00008	8.3
		$CdSO_4$	0.00004	4.2
		$CdCO_3$	0.00005	4.5
		Cd-Fulvate	0.00001	1.0
Pb	0.020	Pb^{+2}	0.00376	18.8
		$PbCO_3$	0.01296	64.8
		$PbHCO_3^+$	0.00238	11.9
		$PbOH^+$	0.00038	1.9
		$PbSO_4$	0.00034	1.7
		$PbCl^+$,	0.00018	0.9
		$Pb(CO_3)_2^{-2}$		
Cu	0.016	Cu^{+2}	0.00182	11.4
		Cu-Fulvate	0.00976	61.0
		$CuCo_3$	0.00192	12.0
		$Cu(OH)_2$	0.00121	7.5
		$CuHCO_3$	0.00072	4.5
		Cu-Humate	0.00035	2.2
		$CuOH^+$,	0.00022	1.4
		$CuSO_4$		
Ni	0.002	Ni^{+2}	0.00076	38.0
		$NiCO_3$	0.00113	56.5
		$NiHCO_3^+$	0.00008	4.0
		$NiSO_4$	0.00002	1.0
		$NiOH^+$,	0.00001	0.5
		$Ni(CO_3)_2^{-2}$		

TABLE 20

PREDICTED METAL SPECIES FOR SHINGLE CREEK

Metal	Measured Dissolved Conc. mg-M/l	Predicted Dissolved Species	Predicted Conc. mg-M/l	% M of Measured Concentration
Zn	0.015	Zn^{+2}	0.01278	85.2
		$ZnHCO_3^+$	0.00123	8.2
		$ZnCO_3$	0.00048	3.2
		$ZnSO_4$	0.00041	2.7
		$ZnOH^+$, $ZnCl^+$	0.0001	0.7
Cd	0.0018	Cd^{+2}	0.00144	80.0
		$CdHCO_3^+$	0.00013	7.0
		$CdCo_3$	0.00006	3.5
		$CdCl^+$	0.0006	3.5
		$CdSO_4$	0.00005	2.5
		Cd-Fulvate	0.00006	3.5
Pb	0.019	Pb^{+2}	0.00369	19.4
		$PbCO_3$	0.01214	63.9
		$PbHCO_3$	0.00224	11.8
		$PbOH^+$	0.00038	2.0
		$PbSO_4$	0.0003	1.6
		$Pb(OH)_2$, $PbCl^+$	0.00025	1.3
Cu	0.009	Cu^{+2}	0.00034	3.8
		Cu-Fulvate	0.00769	85.5
		$CuCO_3$	0.00034	3.8
		$Cu(OH)_2$	0.00023	2.5
		Cu-Humate	0.00028	3.1
		$CuHCO_3^+$	0.00012	1.3
Ni	0.003	Ni^{+2}	0.00117	39.0
		$NiCO_3$	0.00168	56.0
		$NiHCO_3^+$	0.00012	4.0
		$NiSO_4$	0.00003	1.0

TABLE 21

PREDICTED METAL SPECIES FOR SHINGLE CREEK RUNOFF

Metal	Measured Dissolved Conc. mg-M/1	Predicted Dissolved Species	Predicted Conc. mg-M/1	% M of Measured Concentration
Zn	0.015	Zn^{+2}	0.01132	75.5
		$ZnHCO_3^+$	0.00173	11.5
		$ZnCO_3$	0.00163	10.9
		$ZnSO_4$	0.00021	1.4
		$ZnOH^+$	0.00011	0.7
Cd	0.003	Cd^{+2}	0.00215	71.7
		$CdCO_3$	0.00040	13.5
		$CdHCO_3^+$	0.00032	10.8
		Cd-Fulvate	0.00006	2.0
		$CdSO_4$	0.00005	1.5
		$CdCl^+$	0.00002	0.5
Pb	0.028	Pb^{+2}	0.00182	6.5
		$PbCO_3$	0.0238	85.0
		$PbHCO_3^+$	0.00176	6.3
		$PbOH^+$	0.00045	1.6
		$PbSO_4$,	0.00017	0.6
		$Pb(CO_3)_2^{-2}$	0.00017	0.6
Cu	0.019	Cu^{+2}	0.00076	4.0
		Cu-Fulvate	0.01083	57.0
		$Cu(OH)_2$	0.00323	17.0
		$CuCO_3$	0.00313	16.5
		$CuHCO_3$	0.00048	2.5
		Cu-Humate	0.00038	2.0
		$CuOH^+$	0.00019	1.0
Ni	0.003	Ni^{+2}	0.00045	15.0
		$NiCO_3$	0.00246	82.0
		$NiHCO_3$	0.00007	2.3
		$NiSO_4$	0.00002	0.7

percent of the total dissolved metal concentration. However, it was estimated to be around 80 percent only for Pb in most water samples. The scheme presented by Florence and Batley (1976) resulted in more than 15 percent of the Pb associated with organic complexes and the predicted values from WATEQ2 did not show any. Perhaps accurate reactions and thermodynamic data for Pb-organic complexes are not available in literature.

Generally, the WATEQ2 could be a useful tool to predict the major metal species in natural water samples of known characteristics. Of course, modifications and improvements of the chemical reactions and input of thermodynamic data should continue.

WATEQ2 Sensitivity Analysis

A base case and twelve effect cases were run. The base case was configured to simulate a typical central Florida surface water. The input values of the parameters were:

Major Parameters

	mg/l		mg/l
Conductivity= 300 umhos	Ca^{+2} = 35		Cl^- = 3
TDS = 220mg/l	Mg^{+2} = 2		SO_4^{-2} = 1
DOC = 5 mg/l	Na^+ = 20		HCO_3^- = 10
Temp = 20°C	K^+ = 5		Fe(tot) = 3
pH = 7.0	NH_4^+ = 0.5		PO_4^{-3} = 1.0
DOX = 6.0			NO_3^- = 1.0
			SiO_2^{-2} = 0.0

Trace Elements (mg/l):

Ag^{+1} = 0.10		Ni^{+2} = 1.0
Ba^{+2} = 1.0		Pb^{+2} = 2.0
Cd^{+2} = 0.005		Zn^{+2} = 0.50
Cu^{+2} = 0.050		$Fulvate^{-2}$ = 1.0
Mn^{+2} = 0.50		$Humate^{-2}$ = 1.0

Values for pH, PO_4^{-3}, NO_3^-, DOX, HCO_3^-,
$fulvate^=$, NH_4^+, temperature, $SO_4^=$, and $SiO_2^=$
were varied; and the effects on the distribution of trace
metal species were observed. It was found that the most
significant parameters were pH and HCO_3^-
concentration. Changing pH by ±1 unit had major effects
on copper, nickel, lead, zinc, and cadmium speciation.

Changing HCO_3^- concentration from 100 to 150 mg/l (at constant pH had major effects on copper, lead, and nickel speciation. Changing fulvate concentration from 1.0 to 10.0 mg/l caused a substantial change in copper species distribution with minor changes in cadmium and silver. Changing the temperature from 20° to $25^\circ C$ caused minor changes in several elements.

None of the trace elements showed any change when we changed the concentrations of dissolved oxygen, PO_4^{-3}, NO_3^{-1}, NH_4^{+1}, SO_4^{-2}, or SiO_2^{-2}.

Also, the trace elements silver, manganese, and barium were very insensitive to any changes in any of the tested parameters, at least over the range that were included in the trials.

From the above results, it was concluded that careful measurements of pH and HCO_3^- concentration must be included with the sampling of the natural water. The temperature at the time of sampling should also be recorded. Total fulvate and humate concentrations should also be included because copper, cadmium, and silver can all form soluble fulvates and humates; and these may be important to organic uptake of these elements.

Effect of pH on Metal Speciation

The fractions of various metal species predicted in
WATEQ2 in water samples from Maitland Pond and Shingle
Creek over a pH range of 5 to 9 are presented in figures 9
through 18. Water quality characteristics for Maitland
Pond and Shingle Creek were kept constant while pH values
were changed. For the heavy metals Zn and Cd, the free
metal ion forms dominate over the pH range of 5 to 8 for
both the Maitland Pond and Shingle Creek water samples, as
shown in figures 9, 10, 14, 15. Above pH 8, the majority
of zinc is divided between $ZnCO_3$ and $Zn(OH)_2$; but
cadmium exists mainly in the form of $CdCO_3$.

The speciations of Pb and Ni are also very similar in
water samples from the Maitland Pond and Shingle Creek.
Lead exists mainly as the free metal ion and bicarbonate
forms between a pH range of 5 to 6, as presented in
figures 11 and 16. On the other hand, nickel exists
mainly as free metal ion and bicarbonate accounts for less
than 10 percent of the total nickel concentration from pH
5 to 6.5, as shown in figures 13 and 18. Above pH 6.5,
the carbonate form increases rapidly for both lead and
nickel and dominates over the rest of the pH range.

Copper was the only metal in which the free metal ion
did not dominate at any point over the pH range of 5 to 9
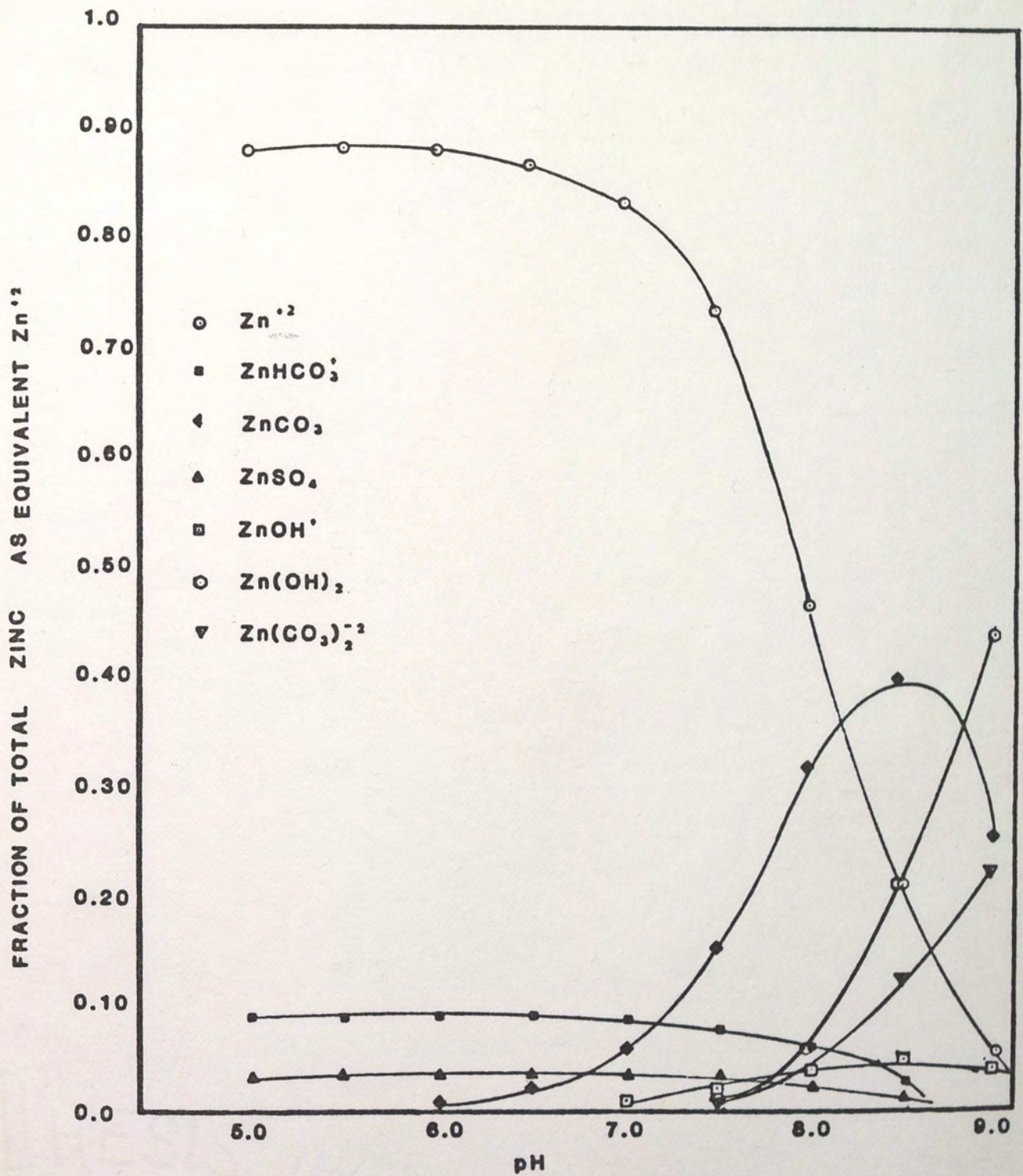
Figure 9. Zn Speciation vs pH for Pond Water from the Maitland Site at 20°C. (Predicted by WATEQ2)
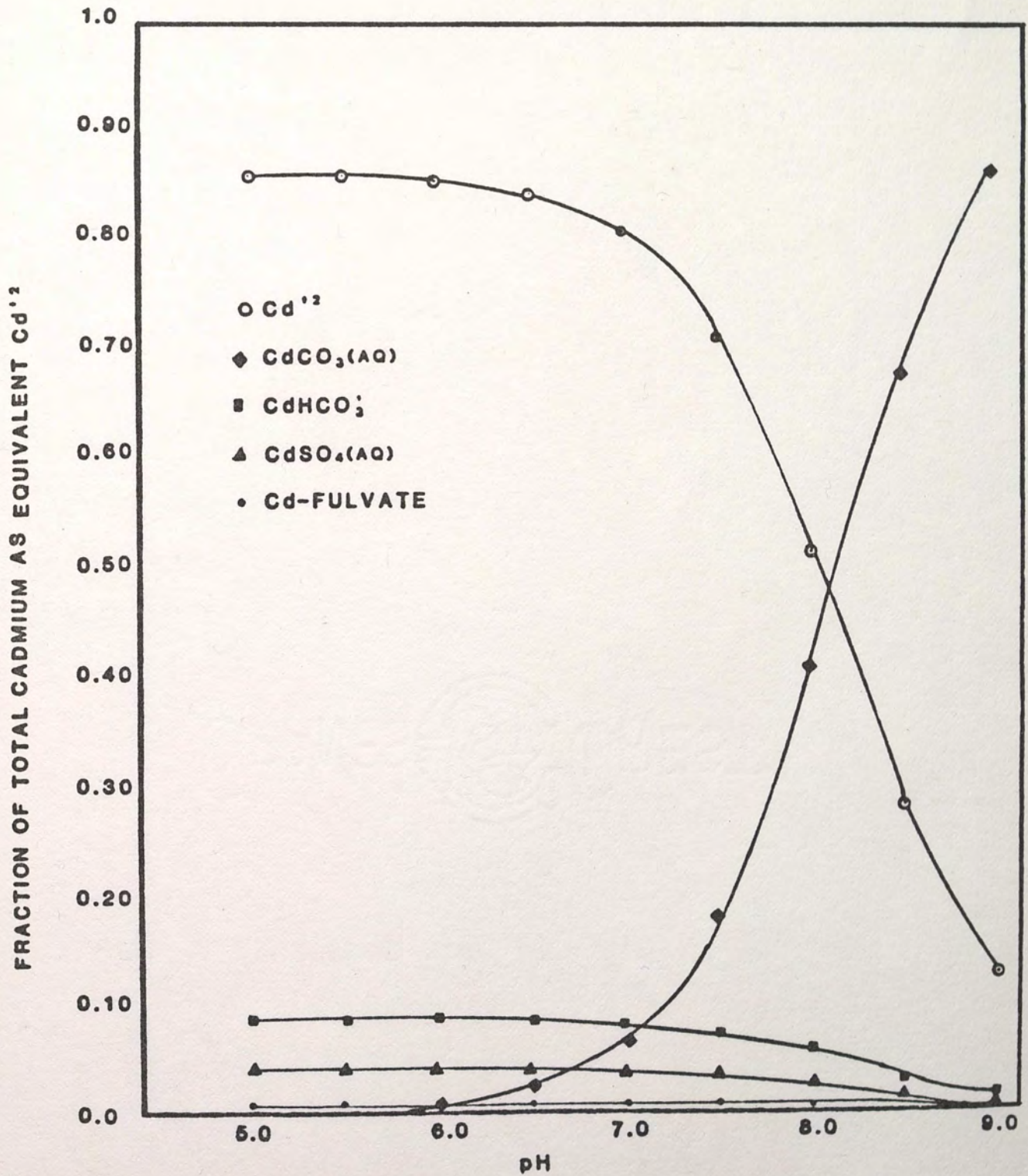
Figure 10. Cd Speciation vs pH for Pond Water from the Maitland Site at 20°C. (Predicted by WATEQ2)
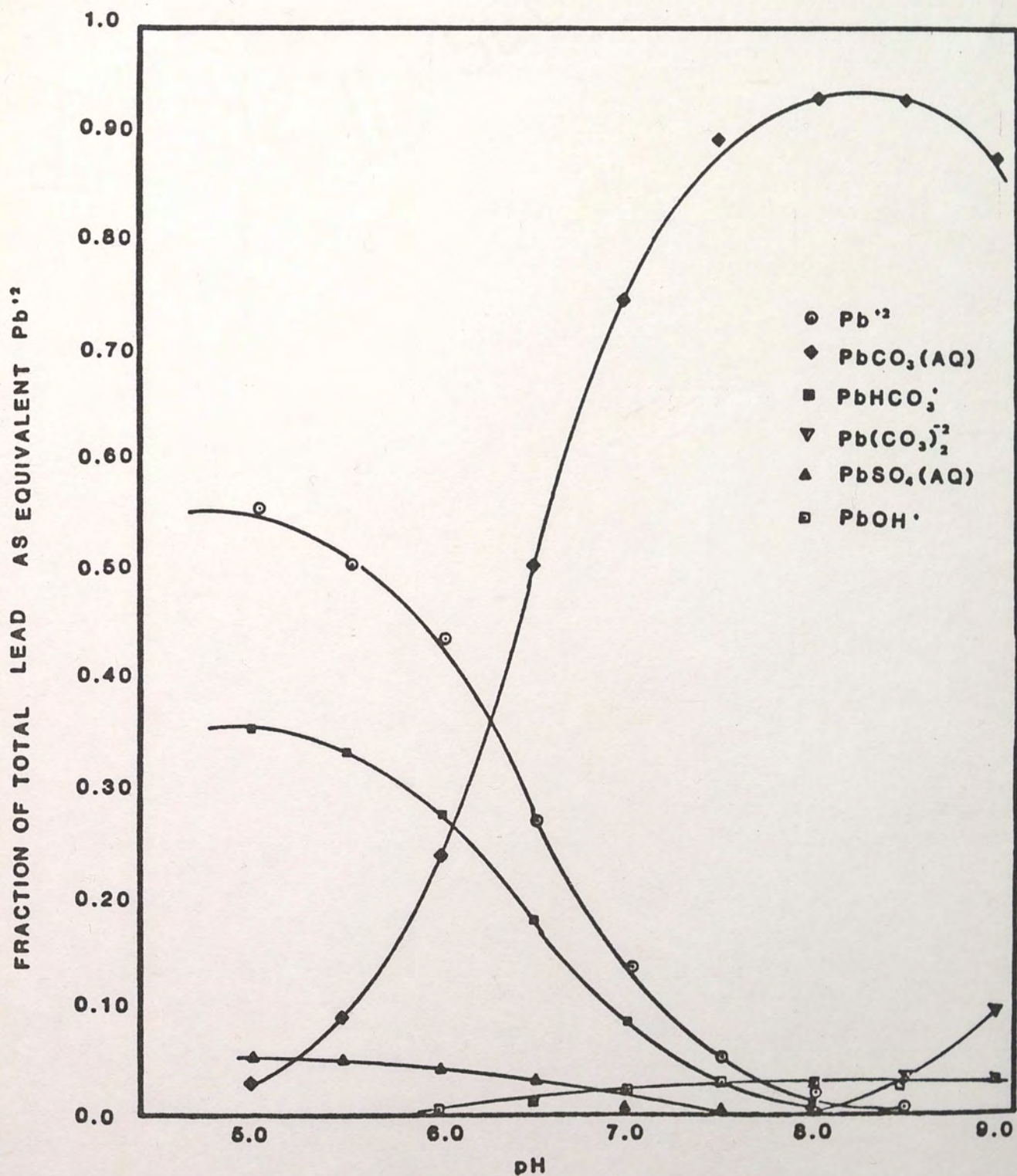
Figure 11. Pb Speciation vs pH for Pond Water from the Maitland Site at 20°C. (Predicted by WATEQ2)
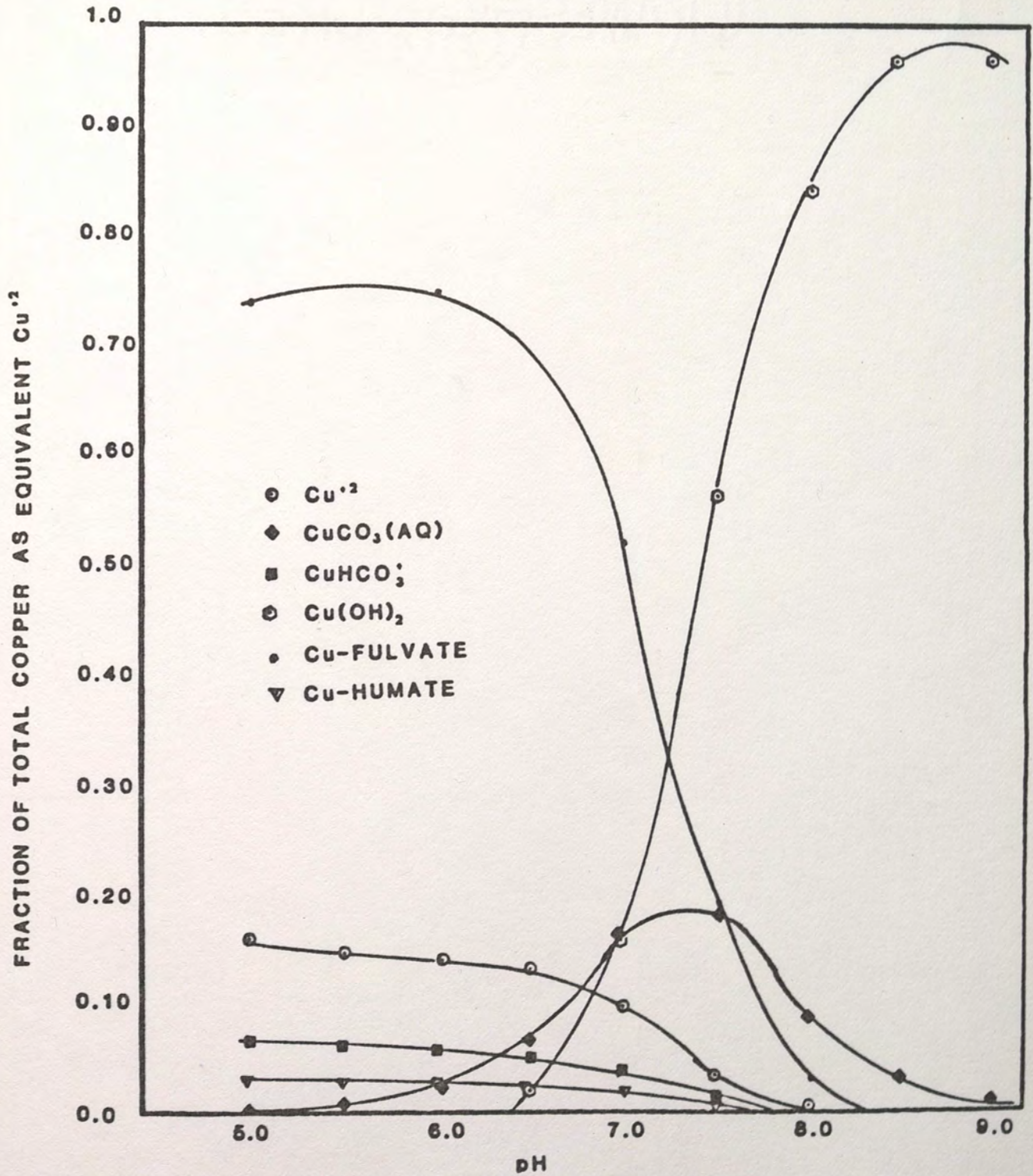
Figure 12. Cu Speciation vs pH for Pond Water from the Maitland Site at 20°C. (Predicted by WATEQ2)
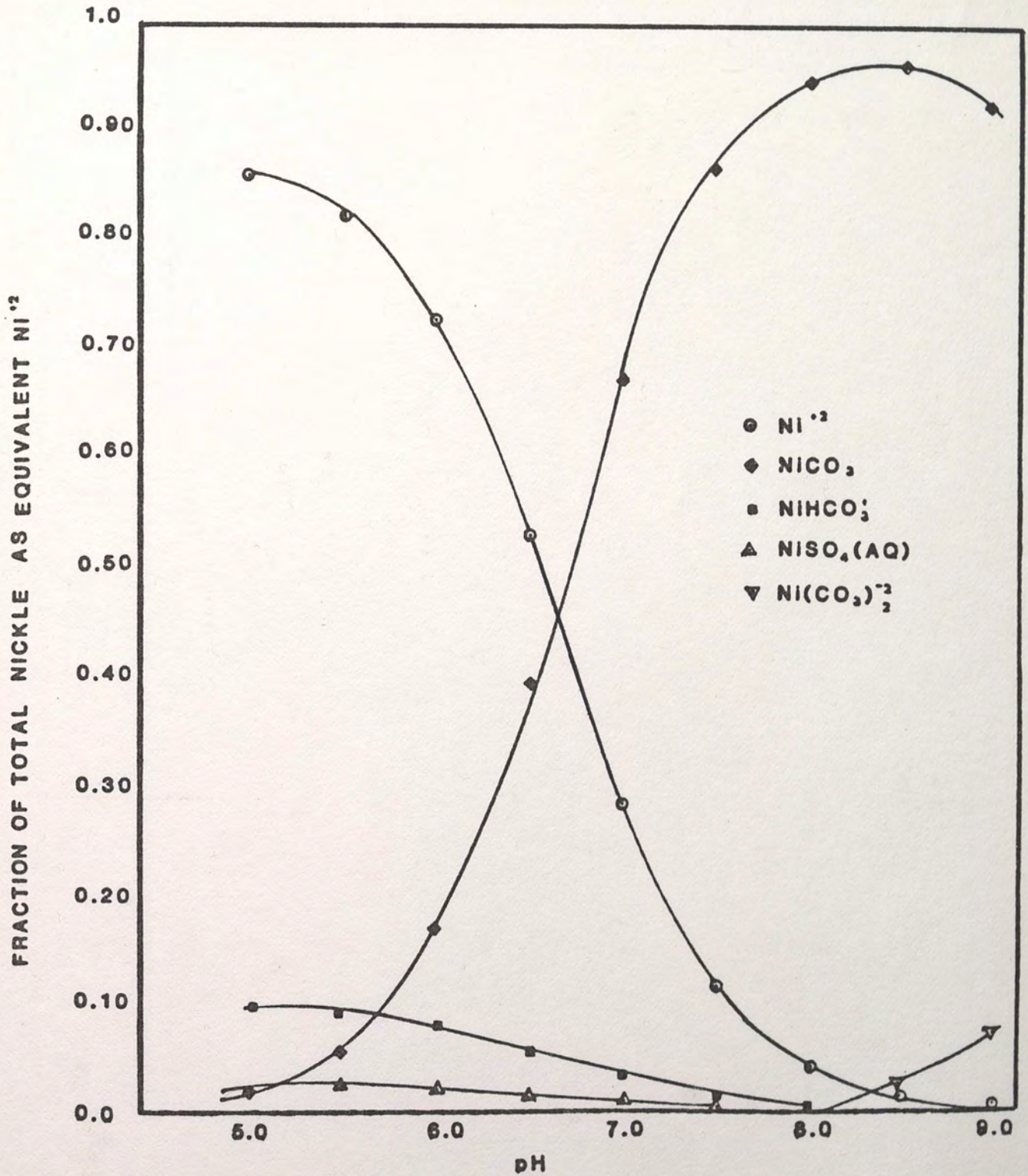
Figure 13.   Ni Speciation vs pH for Pond Water from the
             Maitland Site at 20°C. (Predicted by WATEQ2)
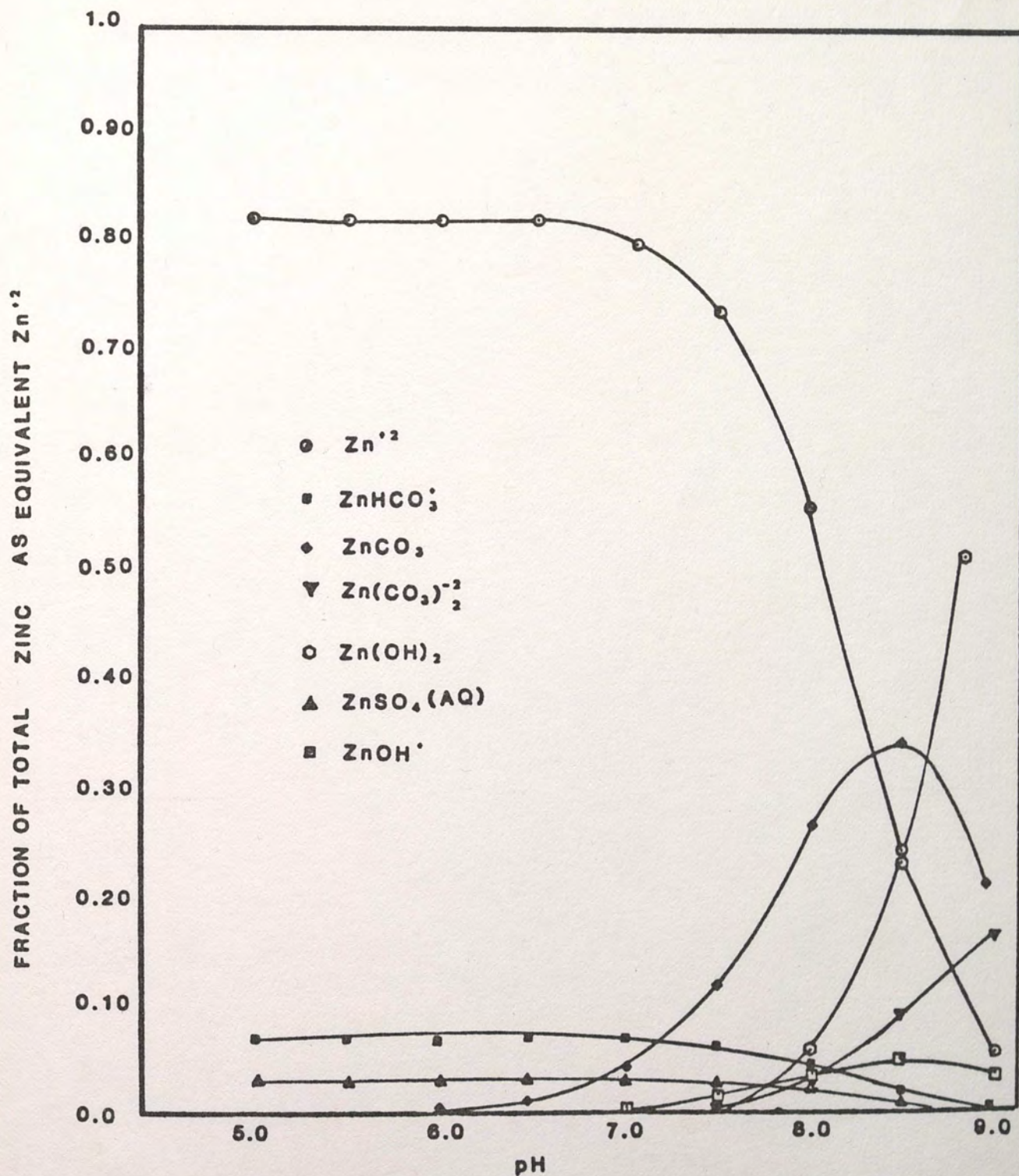
Figure 14. Zn Speciation vs pH for Shingle Creek Water from the Shingle Creek Site at 20°C. (Predicted by WATEQ2)
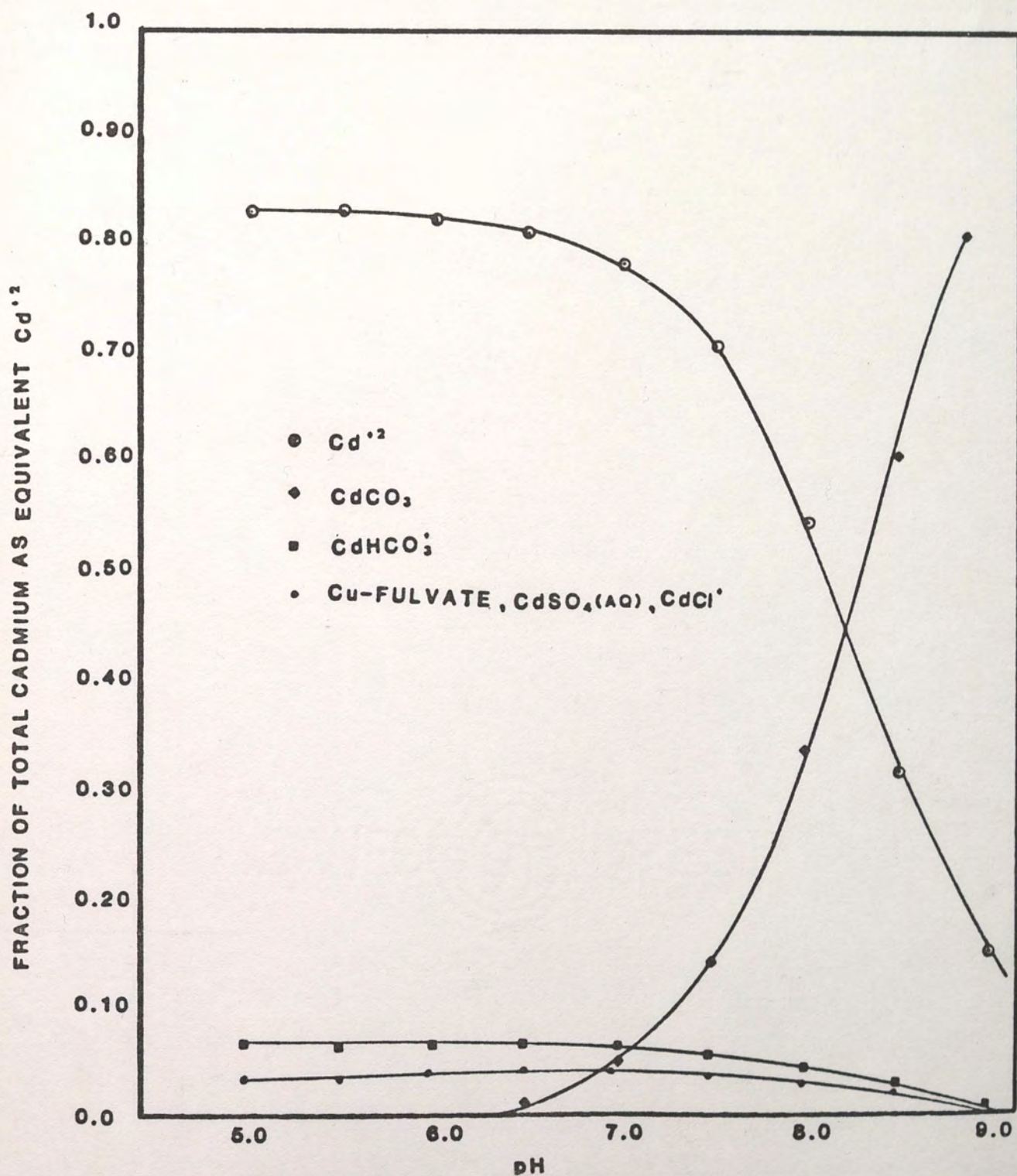
Figure 15. Cd Speciation vs pH for Shingle Creek Water from the Shingle Creek Site at 20°C. (Predicted by WATEQ2)
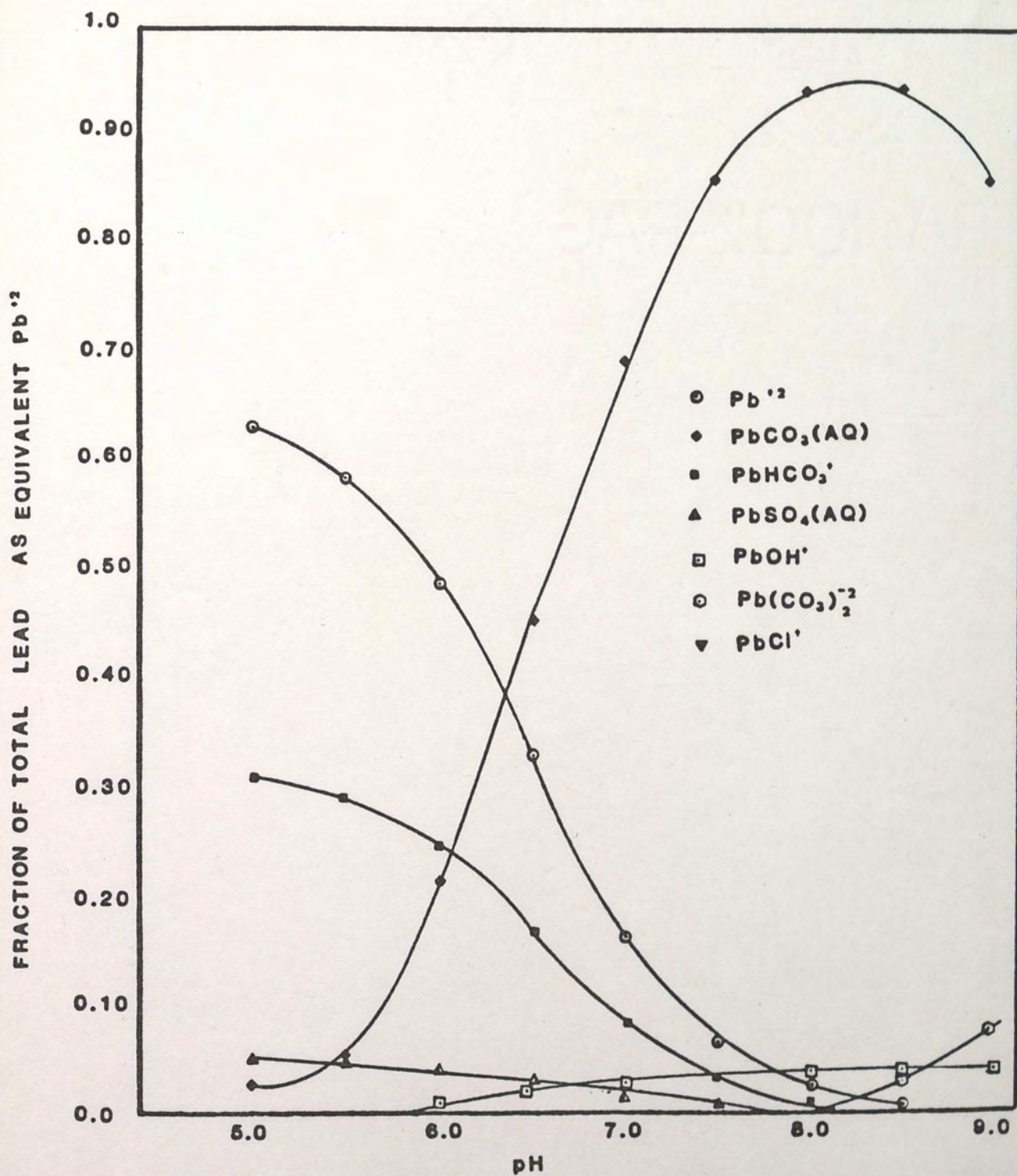
Figure 16. Pb Speciation vs pH for Shingle Creek Water
from the Shingle Creek Site at 20°C. (Predicted
by WATEQ2)
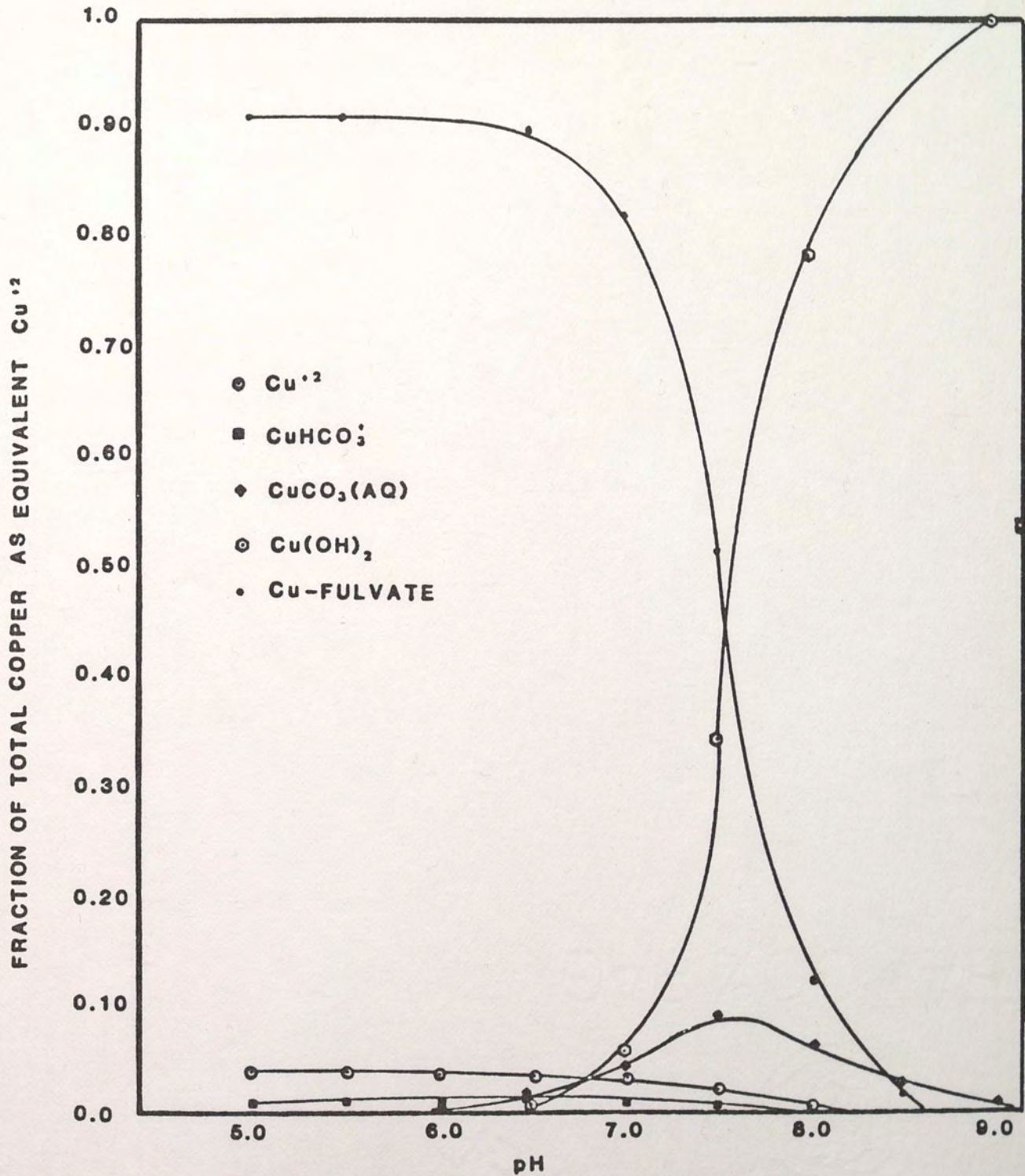
Figure 17. Cu Speciation vs pH for Shingle Creek Water from the Shingle Creek Site at 20°C. (Predicted by WATEQ2)
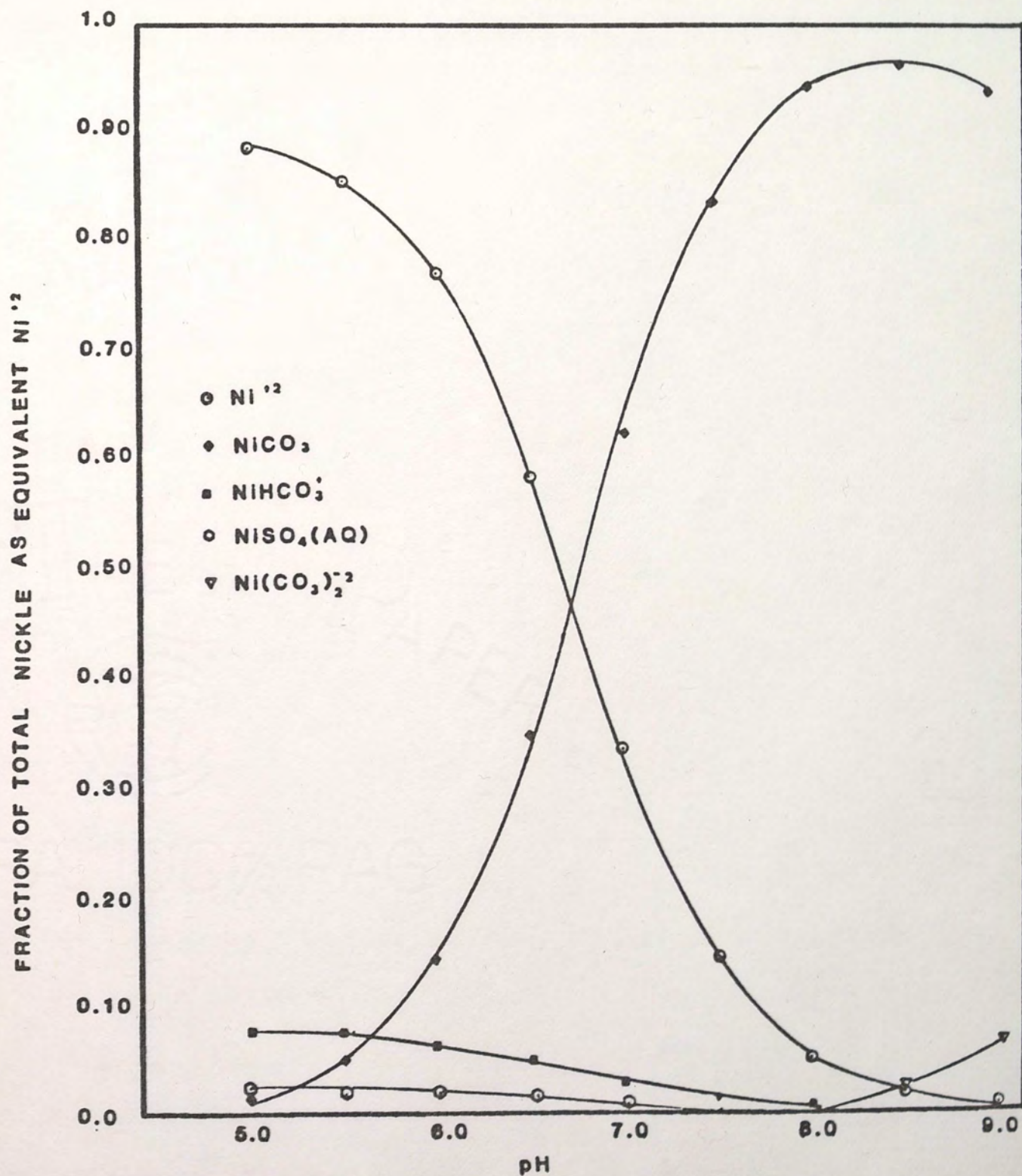
Figure 18. Ni Speciation vs pH for Shingle Creek Water
from the Shingle Creek Site at 20°C. (Predicted
by WATEQ2)

(see figures 12 and 17). Over the pH range of 5 to 7, Cu-Fulvate was the dominant form in both water samples. However, from pH 7.5 to 9.0, copper exists mainly as $Cu(OH)_2$ with Cu-fulvate decreasing rapidly with increasing pH and ultimately precipitating around pH 8.5.

It appears that the predicted heavy metal speciation in water samples collected from Maitland Pond and Shingle Creek are very similar. The water quality parameters that seem to have the greatest impact on the heavy metal speciation are carbonates (MCO_3, $MHCO_3^+$, $M(CO_3)_2^{-2}$) and fulvates.

Effect of Alkalinity on Metal Speciation

A slightly higher total carbonate fraction associated with all of the heavy metals was observed in the water sample from Maitland Pond. This would be expected since the HCO_3^- concentration is higher in Maitland Pond than in Shingle Creek (61.7 and 49.2 mg/l, respectively). For the computer simulation, the HCO_3 concentration was varied between 50 and 10 mg/l for Maitland Pond and between 25 and 75 mg/l for Shingle Creek. Over the ranges tested, the varying HCO_3^- concentrations had a minor effect on the heavy metals Zn, Cd, and Cu. However, increasing the HCO_3^- from 50 to 75 mg/l decreases the free metal ion concentration of lead by 35 percent and

nickel by 27 percent in both water samples, as presented in tables 22 and 23. It appears then that the speciation of lead and nickel are controlled by pH and total carbonate concentration.

Effects of Humic Substances

For this study, humic substances were measured to be 4 and 18 mg/1 for Maitland Pond and Shingle Creek, respectively. From this, the fulvate concentration was estimated to be around 90 percent of these values for each sample and used in the computation of Figures 11 through 18. It was observed that only fulvic acid had any substantial impact on the heavy metal speciation. Based on this, a study was conducted in which the fulvate concentration was varied between 1 and 50 mg/1 while holding the pH, temperature, and bicarbonate concentration constant (average conditions) for both water samples. Since there were no formation constants built into the program for Zn, Cd, and Pb, no changes in the speciation were observed. While cadmium did have a formation constant built into the program, the speciation did not change substantially for fulvate concentrations between 1 and 10.0 mg/1. However, the Cd-fulvate form increased about 11 percent between a fulvate concentration of 1 and 50 mg/1.

TABLE 22

EFFECT OF BICARBONATE CONCENTRATION ON THE SPECIATION OF
HEAVY METALS IN POND WATER FROM THE MAITLAND SITE

HCO_3^- Conc., mg/l	Metal Species	% of Total Dissolved Metal				
		Zn	Cd	Pb	Cu	Ni
50.0	M^{+2}	86.4	83.9	21.8	11.6	42.7
	MCO_3	2.8	3.5	62.3	10.1	51.8
	$MHCO_3^+$	7.0	6.9	11.3	3.8	3.8
	$M(OH)_2$	0.0	0.0	0.0	7.6	0.0
	M-Fulvate	--	0.9	--	63.4	--
	M-Humate	--	0.0	--	2.3	--
75.0	M^{+2}	82.4	79.9	16.1	10.9	33.6
	MCO_3	3.9	4.9	66.0	14.2	60.5
	$MHCO_3^+$	9.8	9.8	12.4	5.3	4.5
	$M(OH)_2$	0.0	0.0	0.0	7.1	0.0
	M-Fulvate	--	0.9	--	58.9	--
	M-Humate	--	0.0	00	2.1	--
100.0	M^{+2}	79.6	76.3	12.8	10.4	27.8
	MCO_3	4.9	6.2	69.8	17.8	66.0
	$MHCO_3^+$	12.4	12.4	13.1	6.7	4.9
	$M(OH)_2$	0.0	0.0	0.0	6.7	0.0
	M-Fulvate	--	0.8	--	55.0	--
	M-Humate	--	0.0	--	1.9	--

TABLE 23

EFFECT OF BICARBONATE CONCENTRATION ON THE SPECIATION OF HEAVY METALS IN SHINGLE CREEK WATER

HCO_3^- Conc., mg/l	Metal Species	% of Total Dissolved Metal				
		Zn	Cd	Pb	Cu	Ni
25.0	M^{+2}	93.0	83.3	34.7	3.5	59.5
	MCO_3	1.4	0.0	49.0	1.5	35.9
	$CHCO_3^+$ 3.6		3.4	9.0	0.6	2.7
	$M(OH)_2$	0.0	0.0	0.0	2.3	0.0
	M-Fulvate	--	4.2	--	87.9	--
	M-Humate	--	0.0	--	3.2	--
50.0	M^{+2}	86.7	79.4	22.1	3.5	43.1
	MCO_3	2.7	3.2	61.3	3.0	51.5
	$MHCO_3^+$ 6.9		6.5	11.3	1.1	0.8
	$M(OH)_2$	0.0	0.0	0.0	2.3	0.0
	M-Fulvate	--	3.9	--	86.0	--
	M-Humate	--	0.0	--	3.1	--
75.0	M^{+2}	80.0	75.9	16.2	3.5	33.9
	MCO_3	3.9	4.6	69.4	4.5	60.2
	$MHCO_3^+$ 9.8		9.2	12.4	1.7	4.5
	$M(OH)_2$	0.0	0.0	0.0	2.2	0.0
	M-Fulvate	--	3.7	--	85.0	--
	M-Humate	--	0.0	--	3.1	--

Copper appears to be the only metal significantly affected by fulvates. As the concentration of fulvate is increased from 1 to 25 mg/l, Cu-fulvate increases to 66 percent. This increase in Cu-fulvate causes the species of $CuCO_3$, $CuHCO_3^-$, $Cu(OH)_2$, and Cu^{+2} to decrease accordingly, thus changing the copper equilibrium in both samples, as presented in tables 24 and 25.

Comparison Between Predicted and Measured Speciations

Predicted speciation shows that Zn and Cd exist mainly as free ions below pH 8 and are controlled by carbonates at higher pH values (pH = 8). Pb exists as free ions, bicarbonate, and carbonate forms below pH 6.5 and is controlled mainly by the carbonate concentration above pH 7. Ni exists mainly as the free metal ion below pH 6, is divided between free ion form and $NiCO_3$ between pH 6 and 7.5, and is controlled solely by carbonate concentration above pH 7.5. Finally, copper exists mainly as Cu-fulvate between pH 5 and 7, is divided between Cu-fulvate and $Cu(OH)_2$ between pH 7 and 8, and is controlled by $Cu(OH)_2$ exclusively above pH 8.

Predicted species for water samples collected during this study are presented in tables 17 through 21. However, measured species are presented in Chapter IV. The predicted species show specific compounds based on

TABLE 24

EFFECT OF FULVATE CONCENTRATION ON THE SPECIATION OF Cd AND Cu IN POND WATER FROM THE MAITLAND SITE

Fulvate Conc., mg/l	Metal Species	% of Total Diss.Metal		Fulvate Conc., mg/l	Species	% of Total Diss.Metal	
		Cd	Cu			Cd	Cu
1.0	M^{+2}	82.5	21.2	25.0	M^{+2}	77.8	2.4
	MCO_3	4.2	22.9		$MCO3$	3.9	1.0
	$MHCO_3^+$	8.4	8.5		$MHCO_3^+$	7.9	0.9
	$M(OH)_2$	0.0	13.9		$M(OH)_2$	0.0	1.6
	M-Fulvate	0.0	31.1		M-Fulvate	6.0	92.3
5.0	M^{+2}	81.7	9.2	50.0	M^{+2}	73.5	1.3
	MCO_3	4.1	9.9		MCO_3	3.7	1.0
	$MHCO_3^+$	8.3	3.7		$MHCO_3^+$	7.4	0.5
	$M(OH)_2$	0.0	6.0		$M(OH)_2$	0.0	0.8
	M-Fulvate	1.2	70.0		M-Fulvate	11.2	95.6
10.0	M^{+2}	80.7	5.4				
	MCO_3	4.1	5.8				
	$MHCO_3^+$	8.2	2.2				
	$M(OH)_2$	0.0	3.5				
	M-Fulvate	2.5	82.3				

TABLE 25

EFFECT OF FULVATE CONCENTRATION ON THE SPECIATION OF
Cd AND Cu IN SHINGLE CREEK WATER

Fulvate Conc., mg/l	Metal Species	% of Total Diss.Metal Cd	Cu	Fulvate Conc., mg/l	Species	% of Total Diss.Metal Cd	Cu
1.0	M^{+2}	82.7	22.7	25.0	M^{+2}	78.0	2.4
	MCO_3	3.3	19.3		$MCO3$	3.1	2.1
	$MHCO_3^+$	6.7	7.2		$MHCO_3^+$	6.3	0.8
	$M(OH)_2$	0.0	14.8		$M(OH)_2$	0.0	1.6
	M-Fulvate	0.0	33.6		M-Fulvate	5.9	92.9
5.0	M^{+2}	81.9	9.5	50.0	M^{+2}	73.7	1.3
	MCO_3	3.3	8.1		MCO_3	2.9	1.1
	$MHCO_3^+$	3.6	3.0		$MHCO_3^+$	5.9	0.4
	$M(OH)_2$	0.0	6.2		$M(OH)_2$	0.0	0.8
	M-Fulvate	1.2	72.1		M-Fulvate	11.2	95.9
10.0	M^{+2}	80.9	5.5				
	MCO_3	3.2	4.7				
	$MHCO_3^+$	6.5	1.7				
	$M(OH)_2$	0.0	3.6				
	M-Fulvate	2.5	84.0				

thermodynamic data and the measured species are grouped in classes based on behavioral characteristics. However, for the purpose of comparison, it may be assumed that free metal ion is represented by the measured class of soluble labile, and fulvate-humate compounds represent the organic fractions measured by ASV. The predicted and measured speciation indicated that Zn and Cd existed mainly as free metal ion in natural waters. Cu is strongly influenced by organic matter present and exists mainly as organic complex. However, organic Pb complexes are measured by ASV and are not predicted by WATEQ2 due to the lack of sufficient thermodynamic data for organic compounds.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Highway stormwater runoff from bridges is either discharged directly through scupper drains into streams, lakes or floodplains located beneath them or diverted to adjacent swales and detention/retention ponds prior to disposal into receiving waters. The runoff water contains higher concentrations of the metals Zn, Cd, Pb, Cu, Fe, Ni, and Cr than the surrounding receiving water environment. These metals may be concentrated in the surrounding soils, assimilated by plant and/or animal life or remain in solution. Particulate metal fractions may deposit on the bottom of these systems or redissolve back into solution depending upon the various environmental conditions (Yousef, Harper, Wiseman and Bateman 1984).

Upon reaching the receiving water these metals may be removed by the sediments (Yousef et al. 1984), adsorbed by colloids, or transformed either chemically or biologically from one metal species to another. One method of assessing the distribution of a heavy metal within a natural aqueous system is the application of a classification scheme. There are several dissolved heavy metal speciation schemes which can be used in identifying

potential available toxic species to aquatic organics.
The available metal concentration, rather than the total
metal concentration, controls the biotoxicity within a
particular water.

During this study, water samples were collected from
rainfall, highway runoff, and a retention/detention pond
at the I-4 and Maitland Interchange site, and from bridge
runoff and the receiving stream at the Shingle Creek and
U.S. 17-92 site. The water samples were anlyzed for metal
speciation by ASV, following a scheme recommended by
Florence and Batley (1976). Similarly, a computer program
WATEQ2 was utilized to predict various metal species in
natural waters based upon solubility constants and
thermodynamic data.

In evaluating the environmental impact of the
discharge of heavy metal compounds into a receiving water,
hydraulic considerations, as well as stream water quality
and the characteristics of the bottom sediments must be
considered. All of these considerations determine the
phsyiochemical form of species of a particular metal in
the receiving water. A comparison between metal species
measured by ASV and those predicted by WATEQ2 is presented
in Table 26. From the table, it appears that more than 70
percent of Cd and Zn exists in ionic forms (M^{+2}) in all

of the samples, which accounts for 75 percent to 100 percent of the labile fractions measured by ASV. These fractions are probably reactive and biologically available. Conversely, a much lower fraction of Pb and Cu exists in ionic form. Pb is predicted to exist as $PbCO_3$ and Cu to be associated with humic and fulvic substances.

There appears to be good agreement organic fraction measured in water samples by ASV and those predicted by WATEQ2, as shown is Table 26. Note that a fraction of lead in the water samples was associated with organic complexes as measured by ASV. However, the chemical model WATEQ2 did not include thermodynamic data for lead organic complexes. It is difficult to find in literature thermodynamic data on metals associated with humic and fulvic substances in the natural environment. As more information on thermodynamic data becomes available, the program can be modified and improved. The organic Pb complexes varied between 15 percent and 44 percent of the metal in solution measured by ASV. The labile Pb fraction appears to include ionic forms, as well as organics and inorganic complexes. Most of the labile fraction of Cu in the aquatic environment may be associated with organic complexes.

TABLE 26

COMPARISON BETWEEN PREDICTED METAL SPECIES BY WATEQ2 AND MEASURED
FRACTIONS BY ASV

Sample	Species	Predicted %				Measured %			
		Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
Rainfall	M^{+2}	99.1	98.5	96.5	52.1	--	--	--	--
	Labile	--	--	--	--	93.7	85.9	65.6	84
	Organic	--	0.2	--	47.1	0	1.1	14.6	38.3
Highway Runoff	M^{+2}	82.6	80.5	13.8	9.0	--	--	--	--
	$MHCO_3^+$	10.0	10.0	10.6	4.4				
	Labile	--	--	--	--	92.5	84.7	72.7	45.9
	Organic	--	1.1	--	61.8	0.7	4.3	15.4	56.6
Maitland Pond	M^{+2}	84.6	82.0	18.8	11.4	--	--	--	--
	$MHCO_3^+$	8.5	8.3	11.9	4.5				
	MCO_3	3.3	4.5	64.8	12				
	Labile	--	--	--	--	96.3	86.3	55.4	81.0
	Organic	--	1.0	--	63.2	0.3	4.2	17.3	53.8
Shingle Creek	M^{+2}	85.2	80.0	19.4	3.8	--	--	--	--
	$MHCO_3^+$	8.2	7	11.8	--				
	MCO_3	3.2	3.5	63.9	3.8				
	Labile	--	--	--	--	89.5	75.2	67.2	49.0
	Organic	--	--	--	88.6	0.2	13.3	19.3	62.2
Bridge Runoff	M^{+2}	75.5	71.7	6.5	4.0	--	--	--	--
	$MHCO_3^+$	11.5	10.8	6.3	2.5				
	MCO_3	10.9	13.5	85.0	16.5				
	Labile	--	--	--	--	92.5	78.1	43.8	58.7
	Organic	--	2.0	--	59.5	0.3	3.4	44.0	33.4

The specific conclusions reached during this study can be outlined as follows:

1. The average pH of rainfall measured at both highway sites was about 5, and the average pH of highway and bridge runoff is near neutral. It appears that the rainfall is neutralized while traveling over the drainage basin.

2. The average dissolved solids concentrations in highway runoff water samples, the detention/ retention pond at the Maitland site, and Shingle Creek are similar.

3. More than 70 percent of the solube Zn and Cd in rainfall, highway runoff, Maitland Pond water and Shingle Creek water exists as ionic metal. Most of the lead exists as $PbCO_3$ and a substantial fraction of Cu is associated with organic complexes if humic substances are present.

4. Labile fractions determined by ASV show higher fractions for Cd and Zn than Pb and Cu in all water samples tested. This indicates that a higher fraction of Cd and Zn may be available in more chemically reactive species and hence, be biologically available.

5. The average soluble Zn, Cd, Pb and Cu measured in Maitland Pond and Shingle Creek water are lower than Federal Primary and Secondary Drinking Water Standards. This implies that these metals exist in concentrations that have no deleterious effects on the surrounding environment.

6. ASV is an accurate method of measuring low concentrations of metals in freshwater samples, however, the operational characteristics must be fully understood.

7.   The method of standard additions used in
      conjunction with D.P.A.S.V. when applied to
      natural waters with a high organic content over
      estimates the actual concentration of the metals
      Cd, Pb and Cu.   The measured concentrations of
      Cu, Pb and Cd may have been overestimated in some
      samples by as much as 20, 5 and 2 percents,
      respectively.

8.   U.v. irradiation is not a suitable technique for
      the quantitative determination of the
      organo-metallic fraction in freshwater samples.

CHAPTER VII

RECOMMENDATIONS

1. Recommended standards for trace metals should take into consideration the chemically reactive species and their bioavailability. Parameters which affect these reactive species should be considered in the generation of these standards.

2. Excess organic ligands should be complexed by metal titrations before the application of standard additions.

3. Pretreatment methods such as ozone or addition of hydrogen peroxide should be employed to replace the u.v. irradiation if quantification of the organo-metallic fraction if desired.

APPENDIX

TABLE A-1

SPECIATION OF ZINC FOR WATER SAMPLES FROM I-4 AND MAITLAND INTERCHANGE

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic Total		Organic		Inorganic				
		Coll.	Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Maitland Rainfall	7/5/83	0.0	4.4	4.31	0.0	0.0	0.56	0.0	9.27	9.27	10.8
	8/1/83	0.0	3.41	3.14	0.0	0.0	0.47	0.0	7.02	7.02	
x̄		0.0	3.90	3.73	0.0	0.0	0.52	0.0	8.15	8.15	10.8
σx		0.0	0.7	0.83	0.0	0.0	0.06	0.0	1.59	1.59	
Maitland Runoff	1/12/83	0.0	22.2	0.0	0.3	0.0	0.7	0.0	23.2	23.2	
	7/5/83	0.08	14.7	9.4	0.0	0.0	2.6	0.04	26.82	26.8	27.2
	8/1/83	0.1	10.7	6.7	0.0	0.0	1.6	0.0	19.1	19.1	
x̄		0.06	15.87	5.36	0.1	0.0	1.64	0.01	23.04	23.04	27.2
σx		0.05	5.84	4.84	0.17	0.0	0.95	0.02	3.86	3.85	
Maitland Pond	11/29/82	0.0	0.8	10.2	0.0	0.0	0.7	0.0	11.7	11.7	
	11/29/82	0.0	1.0	10.2	0.0	0.0	0.3	0.0	11.5	11.4	
	7/5/83	0.01	2.59	4.95	0.01	0.0	0.2	0.0	7.76	7.76	10.3
	8/1/83	0.12	1.1	10.8	0.0	0.0	0.4	0.0	12.42	12.4	
x̄		0.03	1.37	9.04	0.0	0.0	0.4	0.0	10.84	10.84	10.3
σx		0.06	0.82	2.74	0.0	0.0	0.22	0.0	2.09	2.08	

TABLE A-2

SPECIATION OF ZINC FOR WATER SAMPLES FROM U.S. 17-92 AND SHINGLE CREEK

		Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic		Organic		Inorganic				
Sample	Date	Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Shingle Creek	2/16/83	0.04	10.43	3.43	0.0	0.0	0.6	0.0	14.5	14.5	
	7/7/83	0.04	8.22	5.14	0.0	0.0	1.7	0.04	15.14	15.1	19.4
	8/1/83	0.02	6.85	4.83	0.0	0.0	2.3	0.0	14.0	14.0	
	x̄	0.03	8.5	4.47	0.0	0.0	1.53	0.01	14.54	14.54	19.4
	σx	0.01	1.81	0.91	0.0	0.0	0.86	0.02	0.57	0.55	
Bridge	2/16/83	0.05	11.1	5.05	0.0	0.0	1.3	0.0	17.5	17.5	
Runoff	7/7/83	0.04	8.21	3.75	0.0	0.0	0.99	0.01	13.0	18.3	18.3
	x̄	0.045	9.66	4.4	0.0	0.0	1.15	0.005	15.26	15.26	18.3
	σx	0.007	2.04	0.92	0.0	0.0	0.22	0.007	3.28	3.18	

TABLE A-3

SPECIATION OF CADMIUM FOR WATER SAMPLES FROM I-4 AND MAITLAND INTERCHANGE

| | | Labile (ug/l) | | | Non-Labile (ug/l) | | | | Total Dissolved Metal (ug/l) | | Total Metal (ug/l) |
| | | Organic | Inorganic | | Organic | | Inorganic | | | | |
Sample	Date	Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Maitland Rainfall	4/6/83	0.04	1.71	0.53	0.0	0.04	0.22	0.04	2.58	2.55	
	6/7/83	0.0	2.11	0.07	0.01	0.0	0.48	0.01	2.98	2.91	2.91
	7/5/83	0.0	0.94	0.3	0.0	0.01	0.35	0.01	1.61	1.56	1.57
	8/1/83	0.0	2.0	0.55	0.0	0.01	0.24	0.0	2.8	2.77	
	x̄	0.01	1.69	0.44	0.003	0.015	0.32	0.015	2.49	2.45	2.24
	σx	0.02	0.53	0.12	0.005	0.017	0.12	0.017	0.61	0.61	0.95
Maitland Runoff	1/2/83	0.03	0.77	0.22	0.21	0.0	0.07	0.07	1.37	1.38	
	4/6/83	0.0	0.62	0.63	0.03	0.0	0.43	0.03	1.74	1.67	
	5/13/83	0.08	0.89	0.52	0.04	0.0	0.03	0.04	1.62	1.62	1.66
	6/7/83	0.0	1.13	0.47	0.0	0.0	0.2	0.0	1.80	1.76	2.08
	7/5/83	0.0	0.37	0.33	0.0	0.0	0.12	0.03	0.85	0.83	1.18
	8/1/83	0.02	1.06	1.03	0.0	0.01	0.09	0.04	2.25	2.24	
	x̄	0.02	0.81	0.53	0.05	0.0	0.16	0.035	1.61	1.58	1.64
	σx	0.03	0.28	0.28	0.08	0.0	0.14	0.023	0.47	0.46	0.45

TABLE A-4

SPECIATION OF CADMIUM FOR WATER SAMPLES FROM MAITLAND POND AT I-4 AND MAITLAND INTERCHANGE

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic		Organic		Inorganic				
		Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Maitland Pond	11/29/82	0.01	0.38	0.18	0.0	0.0	0.07	0.01	0.65	0.6	
	11/29/82	0.0	0.34	0.22	0.03	0.0	0.03	0.0	0.62	0.6	
	1/12/83	0.02	0.32	0.11	0.01	0.01	0.13	0.01	0.61	0.61	
	4/6/83	0.01	0.84	0.29	0.02	0.0	0.11	0.02	1.29	1.29	
	5/13/83	0.0	0.81	0.27	0.03	0.01	0.38	0.0	1.5	1.49	1.49
	6/7/83	0.0	0.46	0.42	0.0	0.0	0.02	0.0	0.9	0.86	0.87
	7/5/83	0.0	0.51	0.29	0.0	0.0	0.2	0.02	0.83	0.83	0.88
	8/1/83	0.0	1.03	0.72	0.14	0.04	0.0	0.02	1.95	1.94	
	$\bar{x}$	0.005	0.59	0.31	0.03	0.008	0.095	0.01	1.05	1.03	1.08
	σx	0.008	0.27	0.19	0.05	0.014	0.12	0.009	0.49	0.5	0.36
Anaerobic	2/21/83	0.0	0.29	0.26	0.02	0.0	0.06	0.04	0.67	0.66	0.36

TABLE A-5

SPECIATION OF CADMIUM FOR WATER SAMPLES FROM U.S. 17-92 AND SHINGLE CREEK

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/1)
		Organic	Inorganic		Organic		Inorganic				
		Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Shingle Creek	2/16/83	0.01	0.86	0.6	0.027	0.03	0.1	0.0	1.37	1.34	
	4/8/83	0.06	1.24	1.04	0.1	0.06	0.59	0.03	3.12	3.12	
	5/13/84	0.0	0.16	0.24	0.53	0.02	0.07	0.0	1.02	0.98	1.18
	6/8/83	0.0	0.8	0.53	0.2	0.0	0.1	0.0	1.63	1.57	2.00
	7/7/83	0.0	0.68	0.09	0.07	0.02	0.08	0.0	1.75	1.75	2.48
	8/1/83	0.02	0.79	0.54	0.0	0.01	0.34	0.02	1.72	1.67	
x̄		0.015	0.67	0.64	0.2	0.02	0.21	0.008	1.76	1.74	1.89
σx		0.023	0.38	0.29	0.19	0.02	0.21	0.01	0.72	0.73	0.66
	2/26/83	0.02	1.49	0.18	0.03	0.12	0.09	0.06	1.99	1.99	
	4/8/83	0.0	0.9	0.78	0.13	0.0	0.55	0.05	2.41	2.41	
	5/13/83	0.06	0.79	0.31	0.0	0.0	0.62	0.0	1.78	1.76	2.0
	6/8/83	0.01	1.0	0.49	0.0	0.05	0.36	0.03	1.94	1.94	2.3
	7/7/83	0.05	2.02	3.3	0.03	0.0	0.97	0.1	6.47	6.44	7.0
x̄		0.03	1.24	1.01	9.04	0.03	0.52	0.05	2.92	2.91	3.77
σx		0.03	0.51	1.3	0.05	0.05	0.33	0.04	2.0	1.99	2.8

TABLE A-6

SPECIATION OF LEAD FOR WATER SAMPLES FROM I-4 AND MAITLAND INTERCHANGE

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic		Organic		Inorganic				
		Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Maitland Rainfall	4/6/83	5.6	4.7	7.7	0.7	0.7	1.6	6.5	27.5	27.5	
	6/7/83	2.2	12.3	13.5	1.1	1.1	4.0	8.6	42.8	42.8	111.2
	7/5/83	3.0	12.0	13.0	1.3	0.7	3.6	8.8	42.4	42.4	76.8
x̄		3.6	9.67	11.4	1.03	0.83	3.06	7.97	37.6	37.6	94
σx		1.78	4.3	3.21	0.31	0.23	1.29	1.27	8.72	8.72	24
Maitland Runoff	1/12/83	0.19	26.55	8.76	1.29	4.11	0.46	4.04	45.4	45.4	
	4/6/83	0.15	23.15	10.7	0.95	4.05	0.3	4.5	43.8	43.8	
	5/13/83	1.1	16.3	11.3	1.1	12.0	6.2	1.1	49.1	49.1	74
	6/7/83	0.11	17.03	8.26	0.6	2.0	2.37	3.43	33.8	33.8	120
	7/5/83	0.1	16.7	7.7	1.1	2.4	0.3	3.2	31.5	31.5	109
x̄		0.33	19.9	9.34	0.01	4.91	1.93	3.25	40.7	40.7	101
σx		0.43	4.64	1.57	0.26	4.07	2.54	1.31	7.66	7.66	24

TABLE A-7

SPECIATION OF LEAD FOR WATER SAMPLES FROM MAITLAND POND I-4 AND MAITLAND INTERCHANGE

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic Total		Organic		Inorganic		Calculated	Measured	
		Coll.	Sol.	Coll.	Sol.	Coll.	Sol.	Coll.			
Maitland	11/29/82	0.12	3.24	2.5	0.16	1.22	3.31	0.85	11.4	11.4	
Pond	11/29/82	0.55	4.54	5.51	0.3	2.0	5.89	0.91	19.7	19.7	
	1/12/83	0.04	3.88	3.19	0.84	2.65	4.52	1.58	16.7	16.7	
	4/6/83	0.45	2.75	8.1	1.15	3.45	5.1	2.0	23.0	23.0	
	5/13/83	4.5	5.4	10.4	1.2	1.7	7.7	1.3	29.2	29.2	126.4
	6/7/83	0.48	3.4	8.52	0.68	3.62	5.42	2.08	24.2	24.2	46.8
	7/5/83	0.59	4.81	9.1	0.29	1.71	0.8	1.1	18.4	18.4	82.1
x̄		0.53	4.0	6.67	0.66	2.34	4.68	1.4	20.4	20.4	85
σx		0.48	0.95	3.06	0.42	0.93	2.17	0.5	5.74	5.74	40
Anaerobic	2/21/83	0.4	4.3	8.0	2.0	1.4	5.2	1.9	23.2	23.2	

TABLE A-8

SPECIATION OF LEAD FOR WATER SAMPLES FROM U.S. 17-92 AND SHINGLE CREEK

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic Coll.	Inorganic Total Sol.	Coll.	Organic Sol.	Coll.	Inorganic Sol.	Coll.	Calculated	Measured	
Shingle Creek	2/16/83	0.11	5.39	7.5	0.51	2.29	0.2	2.5	18.5	18.5	
	4/8/83	1.4	5.2	6.2	0.1	3.0	0.2	2.5	18.6	18.6	
	5/13/83	0.21	5.2	6.29	.016	2.44	3.86	1.64	19.9	19.9	
	6/8/83	1.8	3.87	2.79	0.13	1.77	1.74	2.16	18.4	18.4	37.4
	7/7/83	1.5	5.2	7.4	0.7	1.8	0.5	2.6	18.7	18.7	121
x̄		1.03	4.97	6.64	0.34	2.26	1.3	2.28	18.8	18.8	79
σx		0.82	0.62	0.53	0.26	0.51	1.57	0.39	0.61	0.61	59
Shingle Creek Runoff	2/16/83	1.99	2.42	5.26	0.0	10.25	1.22	1.88	23.02	23.0	
	4/8/83	2.33	2.77	6.0	0.83	7.57	3.8	2.1	25.4	25.4	
	5/13/83	1.4	2.7	10.1	7.9	3.2	3.3	2.6	31.2	31.2	
	6/8/83	1.8	2.7	9.1	4.0	7.4	3.1	3.0	31.1	31.1	60.5
x̄		1.88	2.65	7.62	3.18	7.11	2.86	2.4	27.7	31.1	60.5
σx		0.39	0.16	2.35	3.59	2.91	1.13	0.5	4.13	4.13	58

TABLE A-9

SPECIATION OF COPPER FOR WATER SAMPLES FROM I-4 AND MAITLAND INTERCHANGE

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic		Organic		Inorganic				
		Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Maitland	4/6/83	0.89	9.33	4.31	0.02	0.05	0.45	0.0	15.05	15.0	
Rainfall	6/7/83	1.23	11.1	4.5	0.0	0.0	0.35	0.05	17.23	17.23	39.3
	7/5/83	27.3	24.7	44.0	22.0	0.0	0.0	0.0	118.0	117.0	131
	8/1/83	30.3	18.8	45.4	19.5	0.0	0.0	0.0	114.0	117.0	
$\bar{x}$		14.9	16.0	24.6	10.4	0.01	0.2	0.01	66.1	65.8	85
σ_x		16.1	17.12	23.3	12.0	0.03	0.23	0.03	57.7	57.4	65
Maitland	1/12/83	1.0	3.86	3.5	1.22	5.02	1.45	0.35	16.1	16.1	
Runoff	4/6/83	1.99	2.48	3.03	1.12	4.48	1.20	0.5	14.8	14.8	
	5/13/83	1.99	4.21	3.8	1.52	7.28	0.70	0.2	19.7	19.7	36.2
	6/7/83	2.45	4.91	2.94	0.11	8.19	0.84	0.16	19.6	19.6	34.5
	7/5/83	2.4	4.97	4.93	0.1	3.7	1.03	0.06	17.2	17.2	27.9
	8/1/83	4.4	5.3	15.1	0.8	43.0	3.2	0.7	72.5	72.5	
$\bar{x}$		2.37	4.29	5.55	0.81	11.0	1.4	0.28	26.6	26.6	32.9
σ_x		1.12	1.03	4.73	0.59	15.3	0.92	0.26	22.5	22.5	4.4

TABLE A-10

SPECIATION OF COPPER FOR SAMPLES FROM MAITLAND POND I-4, MAITLAND INTERCHANGE, U.S. 17-92, AND SHINGLE CREEK SITES

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/1)
		Organic	Inorganic		Organic		Inorganic				
		Coll.	Total Sol.	Coll.	Sol.	Coll.	Sol.	Coll.	Calculated	Measured	
Maitland	11/29/82	6.9	3.6	2.9	0.13	2.17	0.17	0.13	16.0	16.0	
Pond	11/29/82	7.25	3.3	2.95	0.0	2.09	0.05	0.35	15.99	15.8	
	1/12/83	4.7	3.5	2.0	0.43	1.77	0.84	0.46	13.7	13.7	
	4/6/83	6.16	3.74	2.82	0.05	2.53	0.0	0.61	16.01	16.0	
	5/13/83	4.51	3.54	2.3	0.25	1.7	0.51	0.0	12.81	12.8	20.3
	6/7/83	6.04	3.79	2.77	0.14	2.26	0.33	0.27	15.6	15.6	16.2
	7/5/83	7.36	4.7	3.44	0.4	2.8	0.29	0.21	19.2	19.2	19.7
	8/1/83	6.37	5.3	3.73	0.17	2.63	0.33	0.07	18.6	18.6	18.7
$\bar{x}$		6.16	3.93	2.85	0.2	2.24	0.32	0.27	16.0	16.0	18.7
σ_x		1.07	0.69	0.56	0.15	0.39	0.27	0.23	2.16	2.16	2.2
Anaerobic		0.0	0.37	1.87	0.33	0.21	1.03	0.24	4.05	4.04	

TABLE A-11

SPECIATION OF COPPER FOR WATER SAMPLES FROM U.S. 17-92 AND SHINGLE CREEK

Sample	Date	Labile (ug/l)			Non-Labile (ug/l)				Total Dissolved Metal (ug/l)		Total Metal (ug/l)
		Organic	Inorganic		Organic		Inorganic		Calculated	Measured	
		Coll.	Total Sol.	Coll. Sol.	Coll. Sol.	Sol.	Coll. Sol.	Coll.			
Shingle Creek	2/16/83	0.86	0.75	1.34	0.89	3.08	0.04	0.6	7.56	7.56	
	4/8/83	0.75	0.87	1.85	0.06	3.13	0.0	0.42	7.08	7.03	
	5/13/83	1.0	0.61	2.12	0.52	3.54	0.13	0.76	8.68	8.68	21.5
	6/8/83	0.91	0.5	1.56	0.79	3.05	0.1	0.63	7.54	7.54	9.1
	7/7/83	0.51	0.89	1.45	2.88	1.07	0.39	0.05	7.24	7.24	19.8
	8/1/83	5.04	0.96	4.1	0.44	4.56	0.0	0.0	15.1	15.1	
$\bar{x}$		1.51	0.76	2.07	0.93	3.07	0.11	0.41	8.86	8.86	16.8
σ_x		1.74	0.18	1.03	1.0	1.14	0.15	0.32	3.1	3.11	6.7
Shingle Creek Runoff	2/16/83	0.01	1.46	1.49	0.07	1.37	1.1	0.1	5.6	5.6	
	4/8/83	0.19	4.62	4.09	0.02	2.61	1.36	0.11	13.0	13.0	
	5/13/83	0.17	5.23	6.3	1.19	5.81	4.88	0.12	23.7	23.7	29.8
	6/8/83	1.3	4.59	4.8	1.61	3.0	0.5	0.1	14.9	14.9	18.5
	7/7/83	0.7	6.9	13.9	1.7	12.3	0.0	0.1	25.1	35.1	42.1
$\bar{x}$		0.27	4.56	6.12	0.92	5.02	1.57	0.11	18.6	18.6	30.1
σ_x		0.26	1.97	4.69	0.82	4.38	1.93	0.01	11.3	11.3	13.3

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