

U.S. Department of the Interior
U.S. Geological Survey

Prepared in cooperation with the
FEDERAL HIGHWAY ADMINISTRATION

An Overview of the Factors Involved in Evaluating the Geochemical Effects of Highway Runoff on the Environment

Open-File Report 98-630

A Contribution to the
NATIONAL HIGHWAY RUNOFF DATA AND METHODOLOGY SYNTHESIS



U.S. Department of the Interior
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By OWEN P. BRICKER

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Northborough, Massachusetts
1999

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

For additional information write to:

Chief, Massachusetts-Rhode Island District
U.S. Geological Survey
Water Resources Division
10 Bearfoot Road
Northborough, MA 01532

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286
Denver, CO 80225-0286

PREFACE

Knowledge of the characteristics of highway runoff (concentrations and loads of constituents and the physical and chemical processes which produce this runoff) is important for decision makers, planners, and highway engineers to assess and mitigate possible adverse-impacts of highway runoff on the Nation's receiving waters. In October, 1996, the Federal Highway Administration and the U.S. Geological Survey began the National Highway Runoff Data and Methodology Synthesis to provide a catalog of the pertinent information available; to define the necessary documentation to determine if data are valid (useful for intended purposes), current, and technically supportable; and to evaluate available sources in terms of current and foreseeable information needs. This paper is one contribution to the National Highway Runoff Data and Methodology Synthesis and is being made available as a U.S. Geological Survey Open-File Report pending its inclusion in a volume or series to be published by the Federal Highway Administration. More information about this project is available on the World Wide Web at <http://ma.water.usgs.gov/fhwa/runwater.htm>

Fred G. Bank
Team Leader
Natural and Cultural Resources Team
Office of Environment and Planning
Federal Highway Administration

Patricia A. Cazenas
Highway Engineer
Natural and Cultural Resources Team
Office of Environment and Planning
Federal Highway Administration

Gregory E. Granato
Hydrologist
U.S. Geological Survey

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

| Symbol | When You Know | Multiply By | To Find | Symbol | When You Know | Multiply By | To Find | Symbol |
|-------------------------------------|----------------------------|----------------------------|------------------------|-------------------|--------------------------------|-------------|----------------------------|--------------------|
| LENGTH | | | | | | | | |
| in | inches | 25.4 | millimeters | mm | millimeters | 0.039 | inches | in |
| ft | feet | 0.305 | meters | m | meters | 3.28 | feet | ft |
| yd | yards | 0.914 | meters | m | meters | 1.09 | yards | yd |
| mi | miles | 1.61 | kilometers | km | kilometers | 0.621 | miles | mi |
| AREA | | | | | | | | |
| in ² | square inches | 645.2 | square millimeters | mm ² | square millimeters | 0.0016 | square inches | in ² |
| ft ² | square feet | 0.093 | square meters | m ² | square meters | 10.764 | square feet | ft ² |
| yd ² | square yards | 0.836 | square meters | m ² | square meters | 1.195 | square yards | yd ² |
| ac | acres | 0.405 | hectares | ha | hectares | 2.47 | acres | ac |
| mi ² | square miles | 2.59 | square kilometers | km ² | square kilometers | 0.386 | square miles | mi ² |
| VOLUME | | | | | | | | |
| fl oz | fluid ounces | 29.57 | milliliters | ml | milliliters | 0.034 | fluid ounces | fl oz |
| gal | gallons | 3.785 | liters | L | liters | 0.264 | gallons | gal |
| ft ³ | cubic feet | 0.028 | cubic meters | m ³ | cubic meters | 35.71 | cubic feet | ft ³ |
| yd ³ | cubic yards | 0.765 | cubic meters | m ³ | cubic meters | 1.307 | cubic yards | yd ³ |
| MASS | | | | | | | | |
| oz | ounces | 28.35 | grams | g | grams | 0.035 | ounces | oz |
| lb | pounds | 0.454 | kilograms | kg | kilograms | 2.202 | pounds | lb |
| T | short tons (2000 lb) | 0.907 | megagrams | Mg | megagrams (or "metric ton") | 1.103 | short tons (2000 lb) | T |
| TEMPERATURE (exact) | | | | | | | | |
| °F | Fahrenheit temperature | 5(F-32)/9 or (F-32)/1.8 | Celsius temperature | °C | Celsius temperature | 1.8°C + 32 | Fahrenheit temperature | °F |
| ILLUMINATION | | | | | | | | |
| fc | foot-candles | 10.76 | lux | lx | lux | 0.0929 | foot-candles | fc |
| f | foot-Lamberts | 3.426 | candela/m ² | cd/m ² | candela/m ² | 0.2919 | foot-Lamberts | f |
| FORCE and PRESSURE or STRESS | | | | | | | | |
| lbf | poundforce | 4.45 | newtons | N | newtons | 0.225 | poundforce | lbf |
| lb/in ² | poundforce per square inch | 6.89 | kilopascals | kPa | kilopascals | 0.145 | poundforce per square inch | lb/in ² |

NOTE: Volumes greater than 1000 l shall be shown in m³.

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

An Overview of the Factors Involved in Evaluating the Geochemical Effects of Highway Runoff on the Environment

By Owen P. Bricker

Abstract

Materials washed by rain and snowmelt from highways into adjacent surface waters, ground waters, and ecosystems can pollute water and affect biota. To understand the chemical behavior of any one of these materials and its effects on the environment requires knowledge of the chemistry of the material and how it interacts with other components in the local geochemical system. An integrated watershed approach, therefore, would be the most effective method to assess the effects of highway runoff on local receiving waters. Analysis of one or a few specific contaminants will provide limited and incomplete information and may be misleading in terms of environmental effects. This report addresses the background geochemistry required to model highway runoff and to make realistic assessments of the potential effects of runoff on the environment.

INTRODUCTION

Highway runoff contains a variety of chemical constituents that include deicing chemicals; metals; organic compounds in gasoline, oil, grease, and hydraulic fluids; tire and brake-lining residues; components of gasoline additives; and materials from catalytic converters. Many of these constituents are harmful to the environment and are washed from roads by rain and snowmelt into adjacent surface waters, ground waters and ecosystems where they can pollute water and damage biota, including man. To understand the behavior of any one of these materials and its effects on the environment requires knowledge of the chemistry of the material and how it interacts with

other components in the system. Policies and procedures for planning, designing, and maintaining the Nation's highways as outlined by the Intermodal Surface Transportation Efficiency Act (ISTEA) are beneficial for and compatible with watershed-based environmental management (Bank, 1996). Geochemical knowledge of the watershed environment surrounding the highway is an important factor in evaluating the effects of highway runoff on local waters, the effectiveness of best management practices (BMPs), the quality of available information, and normalizing measured differences between sites in a national database.

Metal concentrations that cause toxic effects in stream biota are related to surface-water hardness (a gross measure of the geochemical environment in a watershed), which varies considerably between watersheds across the country (Driscoll and others, 1990). Wilde (1994) noted several important geochemical effects on surface and ground water near stormwater BMPs. Most notable of these is the dissolution of non-native building materials (rock aggregate) in a BMP structure, which releases magnesium, nickel, and possibly chromium into infiltrating stormwater (Wilde, 1994). Another example is the eutrophication of a small lake in Vermont, which was caused by sulfur from the weathering of freshly exposed highway construction materials (Morgan and others, 1984). The sulfur coprecipitated natural iron in lake water that had previously scavenged available phosphate into insoluble ferric phosphate precipitates. Deicing chemicals also may be a continuing source of sulfur to feed this process, because sulfate is the largest contaminant of sodium chloride road salt by mass (Granato, 1996). Much of the inorganic sediment washed off roadways is representative of the local geology (Gupta and others, 1981); therefore, natural soils may be a substantial source of measured constituents. Shacklette and

Boerngen (1984) examined 1,318 soil samples collected at 20 centimeters (cm) depth about every 80 kilometers (km) along the Nation's highway system and found that background soil concentrations of chromium, copper, iron, lead, and zinc varied by 2 to 4 orders of magnitude (1-2,000; <1-700; 100-100,000; <10-700; and 5-2,000 parts per million, respectively). The quality and comparability of data can be evaluated by using geochemical interpretations. Sansalone and Buchberger (1997) demonstrated that the partitioning of metals between suspended solids and the dissolved phase in untreated samples of pavement runoff over a 24-hour period was driven by the geochemical characteristics of the individual metals. Their data also indicate that the proportion of dissolved metals in pavement runoff may be higher than expected because the metals were not in geochemical equilibrium with available sediments.

The purpose of this report is to examine the geochemistry of highway runoff, the techniques for sample collection and analysis, and the interpretation and modeling of data pertinent to understanding the consequences of highway runoff on the environment. Gupta and others (1981) observed that "Much of the street contaminants are representative of local geology and, to a lesser extent, products abraded from the roadway surfaces, and are largely inorganic." In this report, therefore, emphasis is placed on the inorganic aspects of highway runoff geochemistry.

BACKGROUND OF CHEMICAL PROCESSES

Assessment of the effects of highway runoff on the environment requires knowledge of the chemical behavior of the runoff components and their interactions with other components of the system into which they are introduced. The chemical behavior of substances, either natural or those introduced by human activities into the environment, depends on the

intrinsic properties of these substances and the types and concentrations of other constituents in the system with which they may interact. Major processes driving geochemical interactions include:

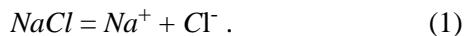
-
- Dissolution
 - Precipitation
 - Activity and concentration
 - Ion-exchange
 - Adsorption and desorption
 - Oxidation and reduction (redox), and
 - Complexation.
-

In an ideal world, when two or more substances interact, the end state of the reaction is a condition of thermodynamic equilibrium. Given the appropriate thermodynamic data, the equilibrium state for any reaction can be calculated. This equilibrium state will be the one that the system will react to. In the real world, more frequently than not, the reaction will not reach the true equilibrium state in a finite time because of kinetic hindrances. Equilibrium thermodynamics is a useful tool for predicting the direction a reaction will take and the final state of the system given infinite time. Kinetics provides information on the rate at which a reaction will proceed, the rate-limiting steps, and the time necessary to achieve the equilibrium state.

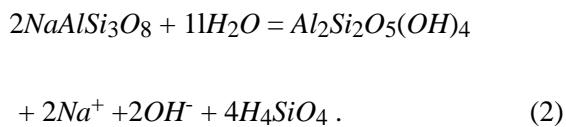
Many of the chemical constituents of interest are sensitive to the acidity (pH) and (or) the oxidation-reduction (redox) conditions of the system in which they occur. Changes in these variables may control the concentration, form, and availability of the constituent and its effect on the environment. Two variables that are useful in quantitatively describing such interactions are Eh (redox potential relative to the hydrogen half-cell) and pH (activity of the hydrogen ion). These variables are so useful in describing chemical reactions that they have been referred to as "master variables" (Sillen, 1967). A third variable necessary to quantify chemical reactions in aqueous solutions is the ionic strength of the medium in which the reactions are taking place.

Dissolution of Substances

Substances may dissolve in several ways. When sodium chloride is placed in water it dissolves completely, forming sodium and chloride ions in solution:



This type of solution behavior is termed "congruent solution" and is exhibited by many compounds. The solid dissolves completely, leaving no residual. In contrast to congruent dissolution, some compounds dissolve by releasing a part of their constituents to solution but retaining others in the form of a new solid phase. This type of solution behavior is termed "incongruent solution", and is commonly exhibited by the silicate minerals:



Precipitation of Substances

Compounds precipitate from solution when the solution is saturated with respect to the solid. Ideally, precipitation occurs when the solution reaches saturation with the compound. In homogeneous systems where there are no nuclei, a high degree of supersaturation is generally required to initiate nucleation. In heterogeneous systems, other particles often serve as nuclei and precipitation occurs at saturation values very close to the thermodynamically predicted value.

The precipitation-dissolution behavior (solubility) of compounds can be described by the law of mass action. For a general reaction of the type,

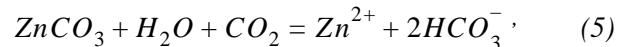
$$aA + bB = cC + dD , \quad (3)$$

the distribution of species is given by

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} , \quad (4)$$

where K_{eq} is the thermodynamic equilibrium constant and A , B , C , and D are the activities of the respective species raised to their stoichiometric coefficients a , b , c , and d .

If the equilibrium constant, K_{eq} , is known for a reaction, the distribution of all of the species involved in the reaction can be calculated. Equilibrium constants for a large number of reactions have been tabulated in earlier literature (for example, Sillen and Martell, 1964, 1967; Martell and Smith, 1974–1989). Equilibrium constants may also be calculated directly, provided thermodynamic data are available for the species involved at the temperature and pressure of interest (for example, Robie and others, 1978; Wagman and others, 1982; Woods and Garrels, 1987). If zinc carbonate ($ZnCO_3$) is placed in water open to the atmosphere, for example, the resulting solution composition can be calculated



and

$$K_{eq} = \frac{[Zn^{2+}][HCO_3^-]^2}{[ZnCO_3][H_2O]P_{CO_2}} \quad (6)$$

where

K_{eq} is the equilibrium constant for the reaction,

[species] is the thermodynamic activity of the respective species, and

P_{CO_2} is the partial pressure of CO_2 (in this case, the partial pressure of CO_2 in the atmosphere).

The equilibrium constant for the reaction (K_{eq}) can be calculated from thermodynamic data using the following relation

$$\Delta G_R^\circ = -RT \ln K_{eq} , \quad (7)$$

where

- ΔG_R° is the standard Gibbs free energy of the reaction,
- R is the gas constant,
- T is the temperature in degrees K, and
- $\ln K_{eq}$ is the natural log of the equilibrium constant.

For conditions of one atmosphere total pressure and 25 degrees Celsius ($^{\circ}\text{C}$), and converting from natural logs to logs to the base 10, the relation in units of kilocalories is

$$\Delta G_R^\circ = -1.364 \log K_{eq} . \quad (8)$$

The ΔG_R° is the sum of the standard free energies of the reaction products minus the sum of the free energies of the reactants

$$\begin{aligned} \Delta G_R^\circ &= \left[\Delta G_{\text{Zn}^{2+}}^\circ + \Delta G_{\text{HCO}_3^-}^\circ \right] \\ &\quad - \left[\Delta G_{\text{ZnCO}_3}^\circ + \Delta G_{\text{H}_2\text{O}}^\circ + \Delta G_{\text{CO}_2}^\circ \right] . \end{aligned} \quad (9)$$

Referring to a table of standard free energy values (Robie and others, 1978),

$$\begin{aligned} \Delta G_R^\circ &= [(-35.19) + 2(-140.26)] \\ &\quad - [(-174.83) + (-56.67) + (-94.26)] . \end{aligned} \quad (10)$$

$$\Delta G_R^\circ = + 10.05 \text{ Kcal} . \quad (11)$$

then

$$\log K_{eq} = -7.37 . \quad (12)$$

Since PCO_2 in the atmosphere is $10^{-3.5}$, then

$$\text{Zn}^{2+} = 10^{-3.82} , \text{ and} \quad (13)$$

$$\text{HCO}_3^- = 10^{-3.79} . \quad (14)$$

It is important to understand what these calculations are based on and how they are made, because this type of calculation forms the basis on which geochemical models are built, for example, WATEQ (Truesdell and Jones, 1974), PHREEQE (Parkhurst and others 1980), SOLMINEQ (Kharaka and others 1988), and EQ 3/6 (Wolery, 1992a).

The degree to which a compound or mineral approaches thermodynamic equilibrium is termed the saturation state. The saturation state is derived by first calculating the ion activity product (IAP) for the reaction and dividing by the equilibrium constant (K_{eq}). For the mineral calcite (calcium carbonate, CaCO_3), the IAP would be the activity of Ca^{2+} times the activity of CO_3^{2-} in the solution divided by the product of those activities at equilibrium

$$Q = \frac{IAP}{K_{eq}} . \quad (15)$$

When Q (the saturation state) is < 1 , the solution is undersaturated; when Q is 1, the solution is at equilibrium; and when Q is > 1 , the solution is supersaturated. This ratio is referred to as the saturation index (SI) when it is expressed in logarithmic form

$$SI = \log \left(\frac{IAP}{K_{eq}} \right) . \quad (16)$$

When SI is < 0 , the solution is undersaturated; when SI is 0, the solution is at equilibrium; and when SI is > 0 , the solution is supersaturated. SI and Q both provide the same type of information about the state of the system relative to the solid phase of interest. If the solution is undersaturated, the solid phase should dissolve, but it cannot precipitate. If the solution is supersaturated, the solid phase may precipitate but it cannot dissolve. If the solution is saturated, the solid phase should neither precipitate nor dissolve. This information is useful in predicting the evolution of the solution. Geochemical programs, such as WATEQ, can be used to calculate the SI for a large number of mineral phases for each water analysis provided.

Activity and Concentration of Ions in Solution

Calculations that use thermodynamic data, including most geochemical models, provide information on the activities of species in the system. Results of laboratory analyses provide data in terms of concentrations, generally expressed in units of weight or molar concentration. Thermodynamic activity represents the quantity of a species in the system that is available to react; concentration is the total amount of the species in the system. At infinite dilution, activity and concentration are essentially equivalent; as concentration increases, however, the divergence between concentration and activity increases. The divergence between concentration and activity is largely due to electrostatic effects, as the interactions among charged particles increases in relation to increasing numbers of particles. Lewis and Randall (1923) coined the term ionic strength to describe the electrostatic atmosphere in a solution of charged particles. Ionic strength is defined as

$$I = \frac{1}{2} \sum m_i Z_i^2 , \quad (17)$$

where

- I is the ionic strength,
- m_i is the molality of the i^{th} species, and
- Z_i^2 is the charge squared of the i^{th} species.

It is necessary to convert analytically determined concentrations to activities in order to make realistic chemical calculations. The activity of a dissolved species is related to its concentration by

$$A_i = \varphi_i m_i , \quad (18)$$

where

- A_i is the activity of the i^{th} species,
- φ is the activity coefficient of the i^{th} species, and
- m_i is the concentration (molality) of the i^{th} species.

One of the most frequently used approximations for activity corrections is the Debye–Hückel approximation

$$-\log_{10} \varphi_i = \frac{Az_i^2 \sqrt{I}}{1 + ai^\circ B \sqrt{I}} , \quad (19)$$

where

- φ is the activity coefficient of the i^{th} species,
- I is the ionic strength of the entire solution,
- A, B are the constants characteristic of the solvent at temperature and pressure,
- ai° is the effective diameter of the i^{th} species in solution, and
- z is the charge on the i^{th} species.

Examples of the deviations between activity and concentration as a function of ionic strength for some common monovalent and divalent cations are shown in figure 1. The difference between activity and concentration increases with increasing ionic strength and with increasing charge on the ion. Activity of the ion, rather than analytical concentration, must be used for all thermodynamic calculations, if valid answers are to be realized. All of the current geochemical models incorporate a routine for activity correction as an integral part of the model (for example, Plummer and others, 1976; Parkhurst and others, 1980; Parkhurst, 1995). In addition to ionic strength effects, the activities of ions in solution may be reduced by complexing with other ions in the solution. For example, the activities of the calcium (Ca^{2+}) ion and sulfate (SO_4^{2-}) ion may be reduced by the formation of the calcium sulfate ($CaSO_4^\circ$) ion pair. The formation of ion pairs is treated in a parallel manner to the solubility of a compound.



and

$$K_f = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4^\circ]} \quad (21)$$

where

- K_f is the formation constant for $CaSO_4^\circ$,
- $[Ca^{2+}]$ is the activity of calcium in solution,
- $[SO_4^{2-}]$ is the activity of sulfate in solution, and
- $[CaSO_4^\circ]$ is the activity of the calcium sulfate ion pair in solution.

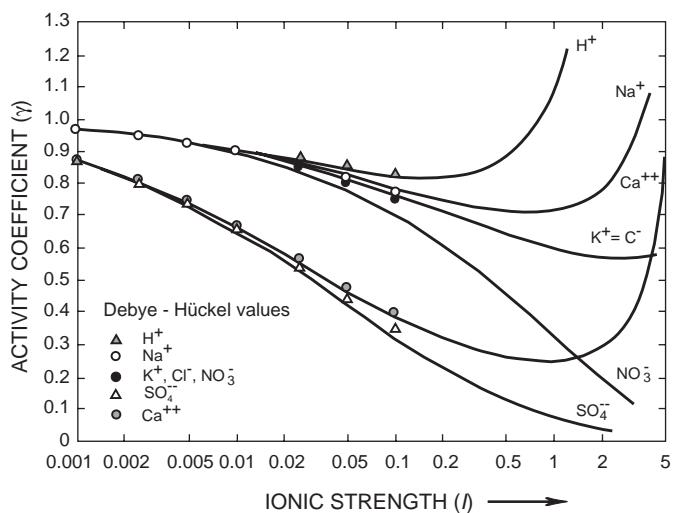


Figure 1. Single ion activity coefficient as a function of ionic strength for some common ions. Solid lines represent values calculated by the mean salt method. Debye-Hückel values were calculated using equation 19. (From Garrels and Christ, 1965).

One effect of the formation of ion pairs is not only to reduce the activities of the individual ions in solution, but to increase the total dissolved concentrations of these elements. For example, when (Ca^{2+}) and (SO_4^{2-}) form the ion pair, $(CaSO_4)$, the activities of Ca^{2+} and (SO_4^{2-}) are reduced and $(CaSO_4)$ is increased. This permits more of the solid phase to dissolve to bring the activities of (Ca^{2+}) and (SO_4^{2-}) to equilibrium, and the total concentration of these elements in the solution is increased. The solubility of gypsum is an example of the importance of ionic-strength corrections and ion-pair formation to the composition of electrolyte solutions. Calculation of the amount of gypsum that will dissolve in water when these corrections are ignored results in 0.86 grams per liter (g/L). If the ionic-strength correction and ion-pair formation are considered, the actual value is 3.15 g/L—more than three and a half times the amount calculated without considering the corrections (Appelo and Postma, 1993). Data from urban-and highway-runoff studies have indicated increased solubilities of metals by ion-pair formation in surface and ground waters affected by runoff pollution (Morrison and others, 1990; Warren and Zimmerman, 1994; Granato and others, 1995). A realistic assessment of the chemistry of most natural

waters, which are complex electrolyte solutions, requires consideration of ionic-strength effects and ion-pair formation. Examples of other common ion pairs in natural waters are calcium carbonate ($CaCO_3$), calcium bicarbonate ($CaHCO_3$), aluminum fluoride (AlF_2), and aluminum hydroxide ($Al(OH)_4$).

Ion Exchange

Many solids, including zeolites, clay minerals, oxyhydroxides, colloids, and natural organic compounds exhibit ion-exchange behavior. Ion exchange is a process in which ions associated with a solid, held by forces ranging from very weak to very strong, are replaced by other ions as the composition of the electrolyte solution in which they are bathed changes. A classic example of ion exchange resulting from electrostatic forces is exhibited by clay minerals. Ionic substitution in the alumino-silicate framework of these minerals creates a charge imbalance leading to a negative charge on the framework. This negative charge is neutralized by sorption of cations on the surface of the mineral or in interlayer sites. The amount of charge and, thus, the capacity of the mineral to sorb cations is called the cation-exchange capacity (CEC). The CEC can vary depending on a particular clay mineral, the nature of the ions occupying exchange sites, and the pH of the solution. CEC values for some typical clay minerals are shown in table 1 (Drever, 1997). The exchange equilibrium can be expressed by the mass action expression



$$K_{AB} = \frac{[B-clay][A^+]}{[A-clay][B^+]}, \quad (23)$$

or

$$\frac{a_{A-clay}}{a_{B-clay}} = K_{AB} \frac{a_{A^+}}{a_{B^+}}, \quad (24)$$

where

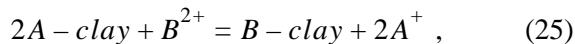
a_{A-clay} and a_{B-clay} are the activities of A and B on the exchange sites,
 a_{A^+} and a_{B^+} are the activities of A^+ and B^+ in solution, and
 K_{AB} is the exchange constant.

Table 1. Cation-exchange capacities of clay materials

[From Drever, 1997. <, actual value is less than value shown]

| Clay materials | Cation-exchange capacity (millequivalents per 100 grams) |
|--------------------|--|
| Smectites | 80-150 |
| Vermiculites | 120-200 |
| Illites..... | 10-40 |
| Kaolinite..... | 1-10 |
| Chlorite..... | <10 |

The same form of equation can be written for divalent-divalent ion exchange. For monovalent-divalent exchange, the expression is written



$$K_{AB} = \frac{[B - clay][A^+]^2}{[A - clay]^2[B^{2+}]}, \quad (26)$$

or

$$\frac{a_{A-clay}^2}{a_{B-clay}} = K_{AB} \frac{a_{A+}^2}{a_{B^{2+}}}. \quad (27)$$

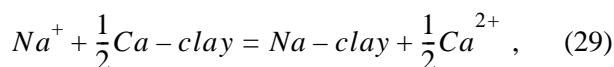
If the above equations are written with equivalent fractions instead of activities to represent the solid phases, and concentrations instead of activities to represent the aqueous ions, then

$$\frac{X_{A-clay}}{X_{B-clay}} = K_{AB}^1 \frac{m_{A+}}{m_{B+}}, \quad (28)$$

and

K_{AB}^1 is the selectivity coefficient.

Three conventions are commonly used in ion exchange investigations. For homovalent exchange, there is little difference among the conventions, but for heterovalent exchange the convention chosen can make a significant difference. For the exchange of sodium (Na^+) for calcium (Ca^{2+}) on clay, the reaction may be written



$$K_{\frac{Na}{Ca}} = \frac{[Na - clay][Ca^{2+}]^{0.5}}{[Ca - clay]^{0.5}[Na^+]} = \frac{B_{Na}[Ca^{2+}]^{0.5}}{B_{Ca}^{0.5}[Na^+]} \quad (30)$$

When B is the equivalent fraction for ion i ,

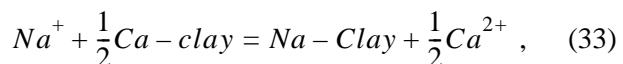
$$B_i^{eq} = \frac{meq[i - clay] per 100 g clay}{CEC}, \quad (31)$$

where CEC is the cation-exchange capacity, the above expression conforms to the Gaines and Thomas (1953) convention.

When B is the molar fraction for ion i ,

$$B_i^m = \frac{mmol[i - clay] per 100 g clay}{TEC}, \quad (32)$$

where TEC is the total exchange capacity, the above expression conforms to the Vanselow convention (Vanselow, 1932). If the activities of sorbed ions are assumed to be proportional to the number of exchange sites on the clay that are occupied by the ion, the reaction is written



$$K_{\frac{Na}{Ca}}^G = \frac{[Na - clay][Ca^{2+}]^{0.5}}{[Ca - clay]^{0.5}[Na^+]}, \quad (34)$$

which corresponds to the Gapon convention (Gapon, 1933). All of these conventions are used in exchange studies, and the choice of a particular one is a matter of goodness of fit of the data being examined. There is little difference among the three conventions at low solute concentrations.

In general, divalent cations are favored on exchange sites of clay minerals in freshwater systems. When clays are transported to the marine environment, the divalent cations are exchanged for sodium because of the high sodium to divalent cation activity ratio in seawater. Ion exchange has been identified as an important process in affecting the composition of waters in areas where road salt is applied for deicing purposes (Shanley 1994; Granato and others, 1995). Runoff from highways to which road salt is applied is concentrated in sodium (Na^+), and this may promote the exchange of sodium (Na^+) for calcium (Ca^{2+}) and other metals if the sodium to calcium (Na^+/Ca^{2+}) ratio

in runoff is high. In addition to its effect on water composition, the type of ion occupying exchange sites may have a significant effect on the physical properties of the clay. Clays whose exchange sites are primarily occupied by calcium (Ca^{2+}) are generally permeable and granular whereas clays with sites primarily occupied by sodium (Na^+) tend to be cohesive and impermeable (Krauskopf, 1967).

Drever (1997) has pointed out that ion exchange is an important process in the control of water chemistry wherever water is in contact with sediments. As an example, he cites an aquifer with a CEC of 5 milliequivalents per 100 grams (meq/100 g) and a porosity of 20 percent. In this system, the exchange capacity of the solids is on the order of 500 milliequivalents per liter (meq/L) of water, a number larger than the concentration of cations in dilute water. Thus, the exchangeable ions can strongly influence the composition of the water.

Adsorption and Desorption

When a solid is placed in an aqueous solution, adsorption occurs at the interface. Adsorbed ions may be held by forces that range from weak to very strong depending upon the characteristics of the surface and the sorbed ion. Sorption plays an important role in controlling the behavior of trace elements in the environment and may be one of the most important chemical processes affecting the movement of contaminants in natural water systems (Drever, 1997). For example, the concentrations of heavy metals in natural waters are commonly far lower than would be predicted from mineral solubility calculations. The low concentrations are usually the result of sorption of these metals onto particulate matter, such as iron and manganese oxyhydroxides, or organic matter. Prediction of the movement of heavy metals in soils and ground water requires the quantitative description of sorption processes. The fundamental theory applicable to sorption on particles is the electrical double layer, of which two types are recognized (Berner, 1971; van Olphen, 1977). In the first type, sorption results from imperfections or ionic substitutions within the crystal lattice, which produces an electrical charge on the surface of the particle. This charge is balanced by an excess concentration of ions

of opposite charge called counterions attracted to the surface from the surrounding solution. The charged surface is the fixed layer and the counterions form the mobile layer. Together they make up the electrical double layer. The clay minerals with their fixed surface charge arising from imperfections and ionic substitution in the crystal lattice and broken bonds along crystal edges are good examples of this type of sorbant particle.

Another type of double layer occurs when, due to specific chemical forces, ions are sorbed at the surface of a particle causing it to become charged. The sorbed ions are called potential determining ions and make up the fixed layer. In this type of double layer, the fixed charge on the surface is not constant but will vary as the composition of the solution changes. Thus, the sorption capacity will vary with solution composition. The counterions balancing the charge on the fixed layer constitute the mobile layer. Most particulates exhibit this type of sorption behavior.

Extensive theoretical treatments of double layer theory can be found in Overbeek (1952), Sparnaay (1972), van Olphen (1977), and Adamson (1990). Summary discussions and examples of applications of the various theories are presented in Appelo and Postma (1993), Stumm and Morgan (1996), and Drever (1997). In practice, it is usually very difficult or impossible to distinguish among various types of sorption and ion exchange in environmental systems, and empirical approaches are used to describe sorption. The most simple of these is the linear adsorption isotherm (K_d), expressed as

$$m_{i(ads)} = K_d m_{i(sol)}, \quad (35)$$

where

$m_{i(ads)}$ is the concentration of the sorbed species i ,

$m_{i(sol)}$ is the concentrations of species i in solution, and

K_d is the distribution coefficient.

When the adsorption isotherm is used in computer codes for geochemical modeling, the i in solution is expressed in terms of its thermodynamic activity (a_i) instead of concentration (m_i) and the K_d is called an activity distribution coefficient.

Two other isotherms commonly used in adsorption studies are the Freundlich isotherm and the Langmuir isotherm. The Freundlich isotherm is similar to the linear isotherm with the addition of an exponent on the solution concentration term

$$m_{i(ads)} = K_f m_{i(sol)}^n . \quad (36)$$

The n exponent is usually less than one and leads to curvature of the isotherm at higher concentrations. The Langmuir isotherm, originally developed to describe the adsorption of gas on a solid surface, can be used to describe adsorption in aqueous systems (Stumm, 1992). It is assumed that a fixed number of adsorption sites are on the surface of the adsorbent. Then the maximum concentration of sites available is $m_{i(ads, max)}$, the concentration of sites occupied by sorbed i is $m_{i(ads)}$, and the concentration of sites not occupied by i is $m_{(vacant\ sites)}$. The adsorption expression is

$$\text{vacant site} + i = \text{occupied site}, \quad (37)$$

and the equilibrium constant expression is

$$K_{lang} = \frac{m_{i(ads)}}{m_{i(sol)} m_{(vacant\ sites)}} , \quad (38)$$

or

$$m_{i(ads)} = m_{i(ads, max)} \frac{K_{lang} m_{i(sol)}}{1 + K_{lang} m_{i(sol)}} . \quad (39)$$

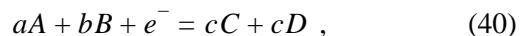
Adsorption, like ion exchange, is important with respect to the fate of materials released to the environment. If a potentially toxic material in aqueous form is adsorbed or exchanged onto sediment particles, it will be transported with the sediment either until conditions change and cause desorption (for example, freshwater entering brackish or saline waters) or until it is effectively removed from the system upon burial with the sediment. If conditions upon burial are favorable, the material will remain with the sediment as long as the sediment is not disturbed or resuspended and the geochemical conditions of the sediment remain the same (for example, oxic to anoxic). If conditions

change upon burial, the sorbed or exchangeable material may be released and may diffuse into the water column.

Oxidation and Reduction (Redox)

Oxidation-reduction reactions involve the transfer of electrons. In an oxidation reaction, an element loses electrons; in a reduction reaction, an element gains electrons. There cannot be an oxidation without a corresponding reduction and vice versa. A number of elements can occur in more than one oxidation state. The most abundant elements displaying this behavior are oxygen (O), hydrogen (H), carbon (C), sulfur (S), and nitrogen (N). These elements generally drive redox reactions in natural systems. Two other elements, iron (Fe) and manganese (Mn), although less abundant, are major participants in redox reactions in some natural systems. The behavior of many of the minor elements in the environment, of concern because of their toxicity, is dependent on their redox state. The redox state of an element determines its chemical and biological behavior, including toxicity, as well as its mobility in the environment. For example, if water in a BMP designed to collect contaminated sediments, such as a retention/detention pond, catchbasin, or storm-sewer sedimentation tank, becomes anoxic between storms, metals will be mobilized in the water column or, in the case of ponds, into infiltrating ground waters, only to be flushed out with flow from the next storm.

Redox reactions can be written as half-reactions or half-cells which, when combined, form the whole reaction. The general form of the half-reaction, written as a reduction reaction is represented by



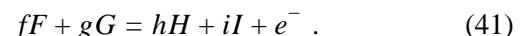
where

A and B are the oxidized species,

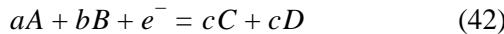
C and D are the reduced species, and

e^- is the number of electrons transferred in the reaction.

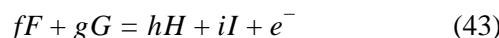
A reduction half-reaction cannot proceed without being coupled to an oxidation half-reaction



When the half-reaction



and the half reaction



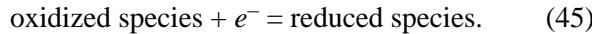
are added, the whole reaction



results and the electrons cancel mathematically.

Because a single half-reaction cannot take place in the absence of a corresponding opposite half-reaction, the absolute potential of a half-reaction cannot be measured. For most purposes, it is not necessary to know the absolute potential of half-reactions, but only differences in potential. By convention, the potential of the hydrogen half-reaction has been set at zero, and the potentials of other half-reactions are measured against it. This potential, usually measured in volts or millivolts, is referred to as *Eh*—the potential of the half-reaction relative to the hydrogen-half reaction. By normalizing against the hydrogen half-reaction, the differences in potential between redox half-reactions can be quantified. When the activities of all of the participating species in a reaction are unity, the potential of the reaction is the standard potential. Standard potentials for a large number of half-reactions are tabulated (Latimer (1952), Sillen and Martell (1964), Wagman and others (1982), and Bard and others (1985) and also may be calculated from thermodynamic data. If the activities of the participating species are different from unity, the redox potential of the reaction is given by the Nernst equation that relates the standard potential of the reaction to the activities of the participating species at thermodynamic equilibrium.

Consider the half-reaction



The Gibbs free energy expression for this half reaction is

$$\Delta G_R = \Delta G_R^\circ + RT \ln \frac{[\text{reduced species}]}{[\text{oxidized species}]} . \quad (46)$$

The Gibbs free energy of the reaction (ΔG_R) is related to the redox potential (*Eh*) by the equation

$$\Delta G_R = -nFEh , \quad (47)$$

where

- n* is the number of electrons transferred in the reaction, and
- F* is the Faraday constant.

By dividing equation (46) by $-nF$, the result is

$$\frac{-\Delta G_R}{nF} = \frac{-\Delta R^\circ}{nF} + \frac{RT}{nF} \ln \frac{[\text{reduced species}]}{[\text{oxidized species}]} . \quad (48)$$

By substituting equation (47) in equation (48),

$$Eh = E^\circ - \frac{RT}{nF} \ln \frac{[\text{reduced species}]}{[\text{oxidized species}]} , \quad (49)$$

where

Eh is the redox potential of the reaction,

E[°] is the standard potential of the reaction when all species are at unit activity,

R is the gas constant,

T is the absolute temperature in K,

F is the Faraday constant,

n is the number of electrons transferred in the reaction,

[oxidized] represents the sum of all oxidized species taking part in the reaction, and

[reduced] represents the sum of all reduced species taking part in the reaction.

By converting to log to the base 10,

$$Eh = E^\circ + \frac{2.303RT}{nF} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]} . \quad (50)$$

At 25 degrees Celsius

$$Eh = E^\circ + \frac{0.0592}{n} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]} . \quad (51)$$

Equation (51) is the form of the Nernst equation most commonly used in geochemical calculations. Another way of expressing the redox state of a system is with the variable *pE*. The *pE* is defined as the negative log of the electron activity. It is related to *Eh* by the following expression

$$pE = \frac{nFEh}{2.303RT} \text{ or at } 25^\circ\text{C} \frac{Eh}{0.0592} . \quad (52)$$

Diagrams to describe relations among redox-sensitive elements may be constructed by using either *Eh* or *pE* as the redox variable; the geometry will be the same. Because protons are commonly involved in redox reactions, such diagrams are usually constructed with a redox variable on one axis and pH on the other axis, and are referred to as *Eh*-pH or *pE*-pH diagrams.

So many reactions of interest in natural systems involve both *Eh* and pH that these variables have been called “master variables” (Sillen, 1967). Theoretical *Eh*-pH diagrams provide a useful way to visualize the aqueous speciation and dominant solid phases of redox-sensitive elements.

The *Eh*-pH diagram in figure 2 (Bricker, 1965) depicts stability relations in the system manganese, oxygen, water ($Mn-O_2-H_2O$) at 25°C and one atmosphere total pressure. It can be seen at a glance that the manganous ion is the major dissolved component, with the manganese hydroxide ($Mn(OH)_3^-$) aqueous complex only dominant over a narrow range of *Eh* at elevated pH. If carbon (C) and sulfur (S) are added to the system (fig. 3; Hem 1985), the stability fields of rhodochrosite ($MnCO_3$) and alabandite (MnS) appear and begin to encroach on the pyrochroite ($Mn(OH)_2$) field, but manganous ion (Mn^{2+}) remains the dominant dissolved species, and manganese oxides the dominant solid phases over most of the *Eh*-pH conditions that are usually observed in natural waters. Similar diagrams can be drawn for any element of interest provided that appropriate thermodynamic data are available.

There is a widespread perception that *Eh* may be easily measured in environmental systems by simply inserting an electrode into the system and reading the potential. In fact, *Eh* is difficult or impossible to measure in most natural systems by using electrodes. A number of conditions must be met if a thermodynamically meaningful *Eh* is to be measured by using an electrode (Bricker, 1982). The electrode must be inert; both the oxidized and reduced species of the half cell being measured must be electroactive at the surface of the electrode; the redox reaction must be reversible at the surface of the electrode; the concentrations of both the oxidized and reduced species must be high enough to be measured by the electrode; and the oxidizing half reaction must be coupled with the reducing half reaction and not with another half reaction that may be more electrochemically advantageous. When the oxidation half reaction of one reaction is coupled to the reduction half reaction of another reaction or the reverse, a mixed potential results. Mixed potentials are not interpretable

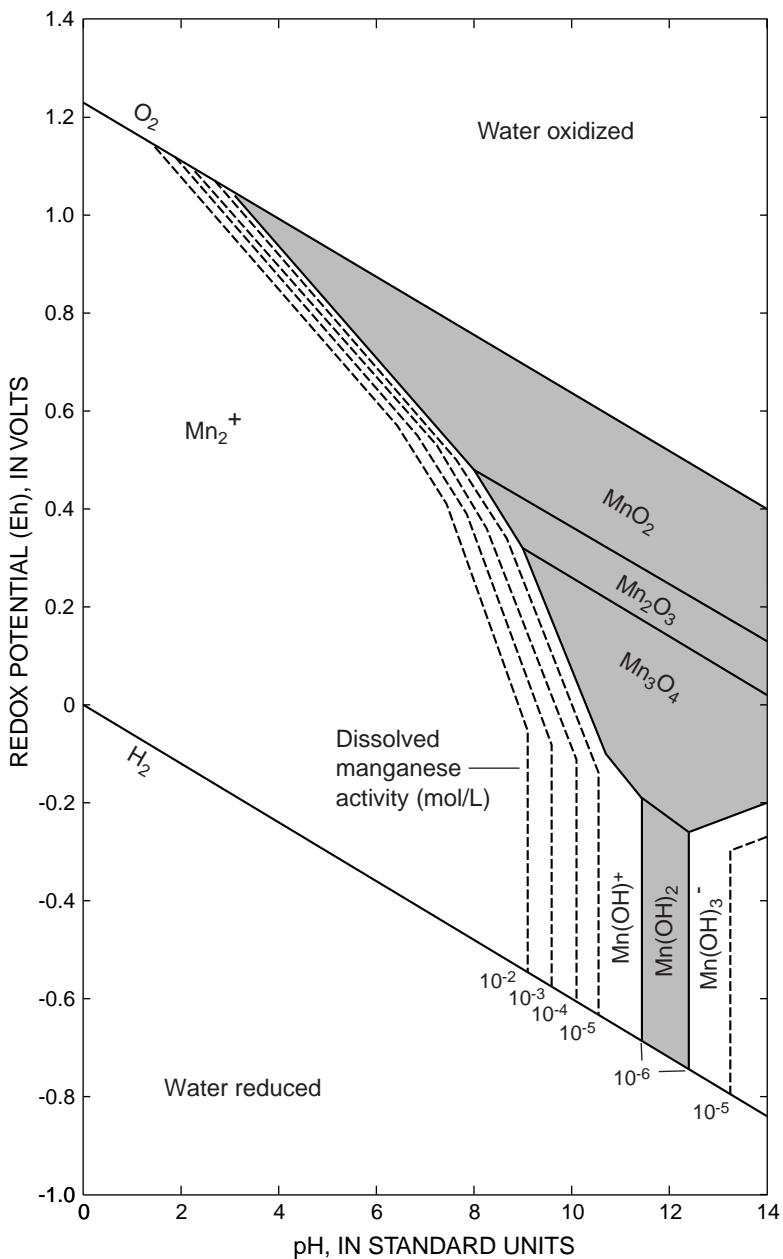


Figure 2. *Eh*-pH diagram showing stability relations among some manganese oxides and pyrochroite at 25°C and one atmosphere total pressure. Boundaries between solids and dissolved species are drawn at activity of dissolved species = 10^{-6} contour of $A_{Mn^{2+}}$ is at 10^{-4} . (Modified from Bricker, 1965.)

thermodynamically but commonly occur when *Eh* measurements are attempted in natural systems that contain more than one redox couple (Bricker, 1982; Stumm and Morgan, 1996). For that reason, it is best to measure the concentrations of the reduced and oxidized species, when possible, and calculate *Eh* by using the Nernst equation.

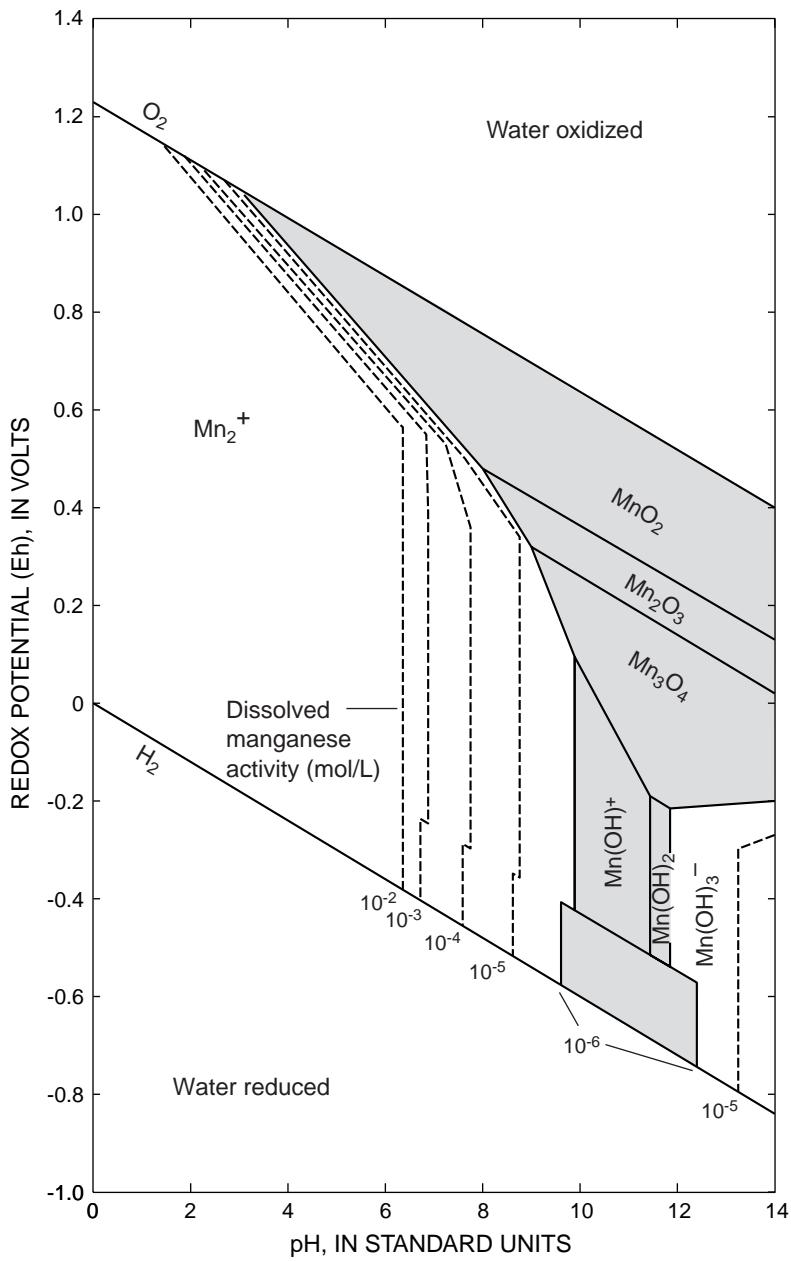


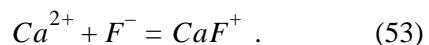
Figure 3. *Eh-pH diagram showing stability relations among some manganese solids at 25°C and one atmosphere total pressure. Activity of sulfur species is 96 mg/L as SO_4^{2-} and carbon dioxide species 61 mg/L as HCO_3^- . (Modified from Hem, 1985.)*

Another problem arises in trying to establish the *Eh* of a natural system. Many redox reactions are kinetically slow; thus, when several redox couples are present in a system, they may not be in equilibrium. Measurement of one couple may give a different value of *Eh* than measurement of another couple. The *Eh*

measured by an electrode will be that of the couple most reactive at the electrode surface (or it may be a mixed potential). Regardless of the difficulties of measuring *Eh* in natural systems, the concept of *Eh* and the construction of *Eh-pH* diagrams can be extremely useful in understanding the chemistry of these systems. *Eh-pH* calculations will provide information about the state of the system at equilibrium and will indicate the direction of reactions in systems that have not reached equilibrium. The classic work on the construction and application of *Eh-pH* diagrams can be found in Garrels and Christ (1965). Additional information on the theory, application, construction and use of *Eh-pH* diagrams is detailed in Bricker (1965), Cloke (1966), Pourbaix (1966), Brookins (1988), Stumm and Morgan (1996), Drever (1997), and Langmuir (1997).

Complexation

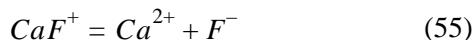
In natural systems, the majority of trace elements and many major elements form complexes (Langmuir, 1997). Complexation increases the apparent dissolved concentrations of elements in solution and can increase their transport by reducing the potential for removal by contact with soils and sediments that are stationary or may settle (or be filtered, in the case of subsurface waters) out of solution. The formation of aqueous complexes and ion pairs is usually described by an equilibrium constant expression. For the formation of the complex CaF^+ , the expression is written



The equilibrium constant expression is

$$K_{eq} = \frac{[CaF^+]}{[Ca^{2+}][F^-]} \quad (54)$$

Another convention is sometimes used for describing complexes. In this convention, the reactions are written as dissociation reactions



The dissociation constant for this reaction is

$$K_{diss} = \frac{[Ca^{2+}][F^-]}{[CaF^+]} \quad (56)$$

This is the inverse of the equilibrium constant and has the same numerical value but the opposite sign.

Complexing affects the behavior of dissolved elements in a number of ways. Most importantly, complexing may have a profound effect on the toxicity and the bioavailability of an element. The speciation of an element in solution is often much more important with respect to its toxicity than its total concentration. Uncomplexed aluminum (*Al*) ion in waters affected by acid rain is toxic to fish, whereas the same total concentration of dissolved *Al* in the form of organic complexes or *F* complexes is much less toxic (Driscoll and others, 1984). Metals, such as copper (*Cu*), lead (*Pb*), cadmium (*Cd*), and mercury (*Hg*), which are very toxic in their uncomplexed ionic forms, are much less toxic (at the same concentration of total metal) when present as complex species (complexed dissolved components such as $CuCl_2^-$). The bioavailability of elements is also a function of speciation (Morel and Hering, 1993), as are the sorption characteristics. Simple uncomplexed ionic forms of elements usually are strongly sorbed relative to carbonate, sulfate, or chloride complexes of those elements. Hydroxyl and phosphate complexes, on the other hand, often are sorbed readily. This behavior has implications for the mobility and transport of elements. Free ions and complexed ions that have little tendency to sorb onto surfaces will be transported with the aqueous phase. Elements that sorb onto particulates will be transported with them and deposited where sediments accumulate. Elements exhibiting this behavior may be removed effectively from interaction in the system as long as they remain sorbed to particles. If chemical conditions change during transport or after deposition (for example, changes in salinity along a river or redox state after burial in the sediments), the elements may be released, perhaps in a toxic form, and become available to interact with biota or other components of the system. Complexing may significantly increase the concentration of an element in solution beyond its calculated solubility in the absence of a complexing agent. Complexing, in addition to the effect of ionic

strength on activity, may lead to the solubilization and transport of much larger amounts of an element than would be predicted from solubility constant considerations alone. To understand how an element will behave with respect to solubilization, mobilization and transport, sorption, and bioavailability and toxicity to biota, its speciation in the system of interest must be known. This entails knowledge of all of the components of the system and how they interact (not just an analysis of a few regulated compounds).

This background section provides a brief sketch of some basic geochemical principles that are necessary to understand environmental systems. More detail on this material can be found in books by Garrels and Christ (1965), Appelo and Postma (1993), Stumm and Morgan (1996), Drever (1997) and Langmuir (1997).

SAMPLE COLLECTION

Investigating highway runoff and its effects on ecosystems and the environment entails the collection of appropriate samples to answer the questions posed. In addition, the techniques that are used to collect samples are critical to the success of a monitoring or research program. If proper techniques are not employed, the samples may be compromised during collection. If this occurs, subsequent analyses of the samples, no matter how good, will only provide compromised data, which at best may be misleading. Remedial or mitigative actions that are based on these data may not provide the desired results and may waste valuable resources.

A number of problems must be confronted when collecting samples. The first objective is to collect a representative sample of the system of interest. If the system is homogeneous, a sample taken from anywhere in the system will be representative of the entire system. In the real world, however, this is seldom the case. Virtually all natural systems are heterogeneous, and a sample from one part of the system will not be representative of the entire system (Hem, 1985). One approach to sampling this type of system is to aggregate (integrate) a series of subsamples taken systematically throughout the system. The larger the number of subsamples, the more representative the aggregate (integrated) sample will be of the system. Another problem arises if the system

changes with time—often the defining factor in stormwater studies of urban and highway runoff. Highway runoff during snowmelt is one example, with the initial runoff commonly more concentrated in deicing compounds than subsequent runoff. For instance, changes in the concentration of dissolved sodium chloride ($NaCl$) will affect ion exchange, sorption, and complexing reactions. In this example, the runoff likely would undergo systematic changes in composition along its flow path through dilution by mixing with other waters and reaction with materials with which it comes into contact. In cases where knowledge of the temporal and spatial changes in the runoff is important, the sampling program must be designed to provide that information.

Other problems are associated with methods that are used for sampling and for control checks on the quality of the resulting data. One of the most obvious and frequently encountered problems is contamination of the sample by the sampling equipment. This can be a particularly serious problem when trace elements are the object of investigation. Trace elements typically are present in very small concentrations, so any changes in concentration due to contamination or sorption on the sampling equipment or storage container can lead to large errors (Schock and Schock, 1982; Bricker-Good and Schroder, 1984; Benoit and others, 1997). Collection equipment or sample containers constructed of inappropriate materials or the improper cleaning of these items can lead to substantial contamination (Schroder and Bricker, 1985; Horowitz and others, 1994; Shelton, 1994). For example, Windom and others (1991) and Horowitz (1997) observed that some of the earlier sampling equipment and techniques commonly used by the U.S. Geological Survey and other water-sampling agencies resulted in biased values for some trace metals (cadmium, Cd ; copper, Cu ; lead, Pb ; zinc, Zn) in surface waters for data reported before 1990. Subsequent studies resulted in the implementation of ultra-clean sampling techniques and quality-assurance procedures for collecting trace-element samples. Often, contamination comes from unlikely sources. In the early days of the National Acid Deposition Assessment Program, rain samples were frequently contaminated with sulfate. This contamination was finally traced to the rubber seals that were used on the lids of the

collecting buckets (Gordon and others, 1998). If improper techniques are used, each step in the sample collection, handling, and analysis process can contribute a substantial proportion of the trace element concentrations measured, even in a contaminated urban stream (Benoit and others, 1997).

Sampling techniques should distinguish between dissolved and particulate material. Dissolved species are generally more available to biota and to reaction with other components of the system than are particulates. When particulate matter occurs in large-size fractions, there is little problem in separating it from the solution. As the size of the particulate decreases and approaches colloidal size, separation becomes increasingly difficult. The standard practice is to define as dissolved the material that passes through a 0.45- micron membrane filter. This is strictly an operational definition, and many colloidal particulates will pass through such a filter (Kennedy and others, 1974; Horowitz, 1997). When these filtrates containing colloids are acidified for analysis, the colloids will dissolve and be analyzed with the dissolved fraction. Colloids frequently contain coprecipitated or sorbed metals that are released when the colloid is dissolved. Colloidal materials and dissolved species each exhibit different characteristics relative to bioavailability and toxicity, and metals associated with colloids are not easily available to the biota. Thus, misidentifying colloids as dissolved components could lead to exaggeration of the potential environmental effects of a discharge. Where the presence of colloidal materials is suspected, filtration through 0.1-micron or finer membrane filters, or high-speed centrifugation techniques for separation, may be required (Rostad and others, 1998). Pressure filtration, by using a peristaltic pump or an inert gas, is preferred to vacuum filtration, which may degas the sample, causing loss of volatiles, changes in pH, and possibly precipitation of solid phases such as calcite. Filtration also may be a source of contamination if the filters contain leachable materials (Jay, 1985).

Runoff from highways may infiltrate soils and eventually reach the water table. Special techniques are required for obtaining samples of soil water and ground water. Soil solutions are frequently collected by using tension lysimeters, but some potential problems may

arise in using them (Severson and Grigal, 1976; Schimmmack and others, 1984; Grossman and others, 1987). The porous section of the lysimeter (the frit) is made of material that may not be inert. If this is the case, reaction of the pore waters with the frit may contaminate the solution, or such reactions may change the pH of the solution causing precipitation and loss of the element of interest. The large surface area of the frit may lead to sorption of the element of interest. The vacuum imposed on the tension lysimeters may significantly disturb the gas balance of the sample and cause changes in the pH and other chemical parameters. Other methods for collecting soil water samples include zero-tension lysimeters and expression of soil waters from soil cores by squeezing or displacement techniques. Each method has its drawbacks and limitations, and careful consideration should be given to the information needed before choosing a sampling method. Ground-water sampling presents an additional set of problems. Wells are needed to obtain ground-water samples, and contamination may be caused by disturbance during the drilling, the introduction of drilling fluids, packing materials, or well casings (Koterba and others, 1995; Lapham and others, 1995; Lapham and others, 1996). These effects can be mitigated by using appropriate methods and materials in drilling and finishing the well and by properly flushing the well before sampling.

Often, ground waters and even some soil waters are in a reducing state. When waters of this type are encountered, care must be taken so that samples are not exposed to oxygen during collection. Exposure of the water sample to the atmosphere may cause significant changes in chemistry as a result of precipitation of oxidized phases or changes in speciation of aqueous species (Ivanhenko and others, 1996). Should this occur, subsequent analysis of the water will not reflect the *in situ* chemistry. In summary, the sampling program must be designed to provide information that addresses the problem of concern, the sampling and collection equipment must not affect the chemistry of the medium being sampled, and the sampling techniques must preserve the *in situ* composition of the sample. Appropriate experimental controls and, in particular, quality assurance/quality control (QA/QC) procedures are required to ensure the quality and utility

of the data collected (especially if the data are intended to be combined and (or) compared in a national database).

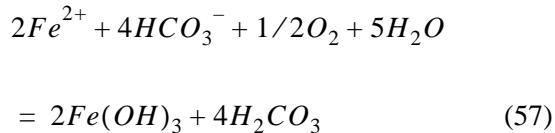
SAMPLE ANALYSIS

After a representative sample has been collected, it must be analyzed for the component of interest, and for all other components of the system that may affect the behavior of that component. Historically, many studies of water chemistry have been inadequate because samples were analyzed for only one or a few components of interest (Davis, 1988). The minimum set of data necessary for geochemical studies includes the major ions (sodium, Na^+ ; potassium, K^+ ; magnesium, Mg^{2+} ; calcium, Ca^{2+} ; sulfate, SO_4^{2-} ; nitrate, NO_3^- ; bicarbonate, HCO_3^- ; chloride, Cl^-) temperature, conductivity, and pH (Mather, 1997). Although many major ions are often neglected in contaminant studies because of the small additional cost and because they are not regulated compounds (Davis, 1988), analysis of samples for the major ions is important because the composition of the major ions in solution will commonly control the partitioning of trace constituents between the dissolved and available solid phases (Appelo and Postma, 1993).

Specific conductance can be used as a gross measure of ionic strength and as a quality-control check on water-quality analysis (Rossum, 1949; Lind, 1970; Hem, 1982). The specific conductance and, therefore, ionic strength of highway stormwater runoff has been demonstrated to vary by several orders of magnitude within and between storm events (Church and others, 1996). Thus, specific conductance measurements in samples facilitate the analysis and interpretation of discrete and composite samples of highway and urban runoff, and a continuous record of measured specific conductance in stormwater flows will put sample analysis into a context with storm runoff processes. Concentrations of major ions and values of pH and specific conductance are required to calculate the ionic strength and other solution characteristics that influence the behavior of all of the dissolved constituents in the system. Concentrations of nutrients and sources of oxygen demand in highway and urban runoff can be substantial (Smith and Lord,

1990; Makepeace and others, 1995). Measurement of dissolved oxygen (DO), nutrients, and measures of oxygen demand are important to assess the geochemical status and potential effects of runoff. The analytical methods that are used must provide the precision and accuracy needed for interpretation and modeling of the species of interest in the system. In the last decade, rapid developments in analytical methods have decreased detection limits for many elements to unprecedented low levels (Horowitz, 1997). This has significantly increased the capability to model the behavior of trace constituents in environmental systems.

The objective of analysis is to represent, as closely as possible, the *in situ* chemical composition of the system of interest. Some parameters are quite sensitive to change if a sample is removed from the system. These parameters, including pH, redox potential, DO, specific conductance and, in some cases, alkalinity, are best measured in the field. For example, if carbon dioxide (CO_2) degasses from the sample after collection, the pH will increase. This, in turn will cause changes in the speciation of hydrogen ion (H^+) sensitive constituents. If the sample is close to calcite saturation, a change in pH may induce precipitation of that phase, which will cause concomitant changes in the calcium (Ca^{2+}), the alkalinity, the specific conductance, and the total dissolved inorganic carbon. The chemistry of a water sample can change from exposure to the atmosphere after collection and ingress of oxygen, which changes the redox potential and causes oxidation of species such as ferrous iron (Fe^{2+}), hydrogen sulfide (H_2S), and other reduced constituents. For example, the following reaction will take place in water samples containing ferrous iron (Fe^{2+}) and carbonate alkalinity when exposed to the atmosphere:



If the water initially contains 20 parts per million ferrous ion (20 ppm Fe^{2+}), equivalent to 0.36 millimoles per liter (0.36 mmol/L), virtually all of the Fe will be removed in the solid phase, twice that amount of bicarbonate (HCO_3^-), equal to 0.72 mmol/L will be removed, and carbonic acid will be produced, which will significantly change the chemistry of the sample (Appelo and Postma, 1993). Any trace metals in the sample will likely be scavenged from solution by the freshly precipitated ferric hydroxide.

It should be pointed out that measurements using electrochemical techniques, such as pH, ion-specific electrode determinations, or Eh should be done on separate aliquots of the sample, which are then discarded. These electrochemical techniques depend upon controlled leakage of electrolyte from the reference electrode to establish electrical continuity with the solution; thus, the sample aliquot will be enriched in the components of the reference electrolyte. As discussed above, Eh measurements using electrode techniques in natural systems are qualitative at best. Except under unusual conditions, they will not provide data that are thermodynamically meaningful, but might reflect the general redox state of the system relative to whether it is oxidizing or reducing (Bricker, 1982; Appelo and Postma, 1993; Stumm and Morgan, 1996).

The parameter pH is of major importance in the quantitative calculation of mineral stability and in other aspects of geochemical modeling. It is, therefore, important to have accurate pH data. With care, pH can be measured to within plus or minus 0.02 unit, the error margin associated with certified buffer solutions. Measurement of pH requires careful consideration of the nature of the sample. A number of problems may cause difficulty in accurately determining pH. If the sample is supersaturated with carbon dioxide (CO_2) relative to equilibrium with the atmosphere (commonly the case with stream, lake, soil, and ground waters), degassing is likely to occur after the sample is taken, especially if samples are collected with automatic samplers that require suction to withdraw the samples.

This will cause pH to increase as carbon dioxide (CO_2) evolves. The pH will rise during measurement until equilibrium with atmospheric carbon dioxide (CO_2) is achieved, then stabilize at a value not representative of the *in situ* value. If the water is near saturation with calcium carbonate ($CaCO_3$) initially, precipitation may be induced, changing the calcium and inorganic carbon concentration of the sample (Suarez, 1987). Similar problems can arise if the water contains reduced species, such as ferrous iron. In this case, if the water is exposed to the atmosphere during measurement, the iron will oxidize, causing the pH to decrease. In addition to change in pH, the precipitated ferric hydroxide may scavenge trace metals and other constituents from the sample. Effects of this type can usually be avoided if the measurements are made *in situ* (directly in the water body of interest) or in a closed vessel with no air space.

Another common problem in measuring pH arises from the liquid junction between the reference electrode and the sample. Electrical continuity must be established between the electrode system and the sample. This is usually accomplished by the use of a fiber wick or a porous frit in the reference electrode, which allows the reference electrolyte to contact the solution being measured. A liquid junction potential will be established across the wick or frit, and the magnitude of the potential will vary with the composition of the solution being measured. In dilute waters, the liquid junction potential can lead to significant errors in pH measurement even though the electrodes respond correctly in buffer solutions. Techniques for calibration and use of pH electrodes in dilute waters are discussed by Neal and Thomas (1985), Davison (1987), and Busenberg and Plummer (1987).

The chemical analysis for most other constituents in water is usually done in the laboratory. Numerous analytical methods are available, and the method of choice depends on the constituent being analyzed, its range of concentration in the system, and

whether the total concentration or concentration of each of the species of the constituent in the sample is desired. Currently, the most commonly used methods for cations are flame or flameless atomic adsorption spectrometry (AA), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). A comparison of detection limits for selected elements is shown in table 2. For anions, one of the most commonly used chemical analysis methods currently is ion chromatography. This method also has been used in the analysis of cations, but not as commonly as for anions. Detection limits for selected anionic species are shown in table 3. The number of techniques available for specialized analyses is too large to cover in detail. A few of the newer types of analytical capabilities that may be useful in characterizing the chemistry of specific materials in highway runoff include:

- (1) sedimentation, field flow fractionation-inductively coupled plasma mass spectrometry for the separation of submicrometer size particles and determination of their composition, including surface adsorbed trace elements (Taylor and Shiller, 1997);
- (2) static secondary ion mass spectrometry (SIMS) for the detection of sorbed contaminants on the surface of soil and sediment particles (Ingram and others, 1997);
- (3) hydride generation in combination with atomic fluorescence spectrometry for determination of a number of trace elements (for example, *As*, *Bi*, *Ge*, *Sb*, *Se*, *Te*) (Ping, Zhou and Guo, 1997);
- (4) scanning electron microscope with electron dispersive x-ray spectroscopy (Goldstein and others, 1992);
- (5) electron probe (Reed, 1996); and
- (6) x-ray fluorescence techniques (Glanzman and Closs, 1997).

The analytical methods selected must be based on the questions to be answered and must provide data that have the necessary accuracy and precision to address those questions.

Table 2. Atomic spectroscopy detection limits for a representative series of elements in natural waters

[From Perkin Elmer Corporation, 1995. AA, atomic absorption; GFAA, graphite furnace atomic absorption; Hg, mercury; ICP, inductively coupled plasma; ICP-MS, inductively coupled plasma–mass spectrography. All values in microgram per liter; <, actual value is less than value shown]

| Element | Flame AA | Hg/ Hydride | GFAA | ICP emission | ICP-MS | Element | Flame AA | Hg/ Hydride | GFAA | ICP emission | ICP-MS |
|---------|-------------|----------------|-------|-----------------|---------|---------|-------------|----------------|-------|-----------------|---------|
| Ag | 1.5 | | 0.02 | 0.9 | 0.003 | Mo | 45 | | 0.08 | 3 | 0.003 |
| Al | 45 | | 0.1 | 3 | 0.006 | Na | 0.3 | | 0.0 | 3 | 0.003a |
| As | 150 | 0.03 | 0.2 | 50 | 0.006 | Nb | 1,500 | | | 10 | 0.0009 |
| Au | 9 | | 0.15 | 8 | 0.001 | Nd | 1,500 | | | 2 | 0.002 |
| B | 1,000 | | 20 | 0.8 | 0.0 | Ni | 6 | | 0.3 | 5 | 0.005 |
| Ba | 15 | | 0.35 | 0.09 | 0.002 | Os | 120 | | | 6 | |
| Be | 1.5 | | 0.008 | 0.08 | 0.01 | P | 75,000 | | 130 | 30 | 0.3 |
| Bi | 30 | 0.03 | 0.25 | 30 | 0.0005 | Pb | 15 | | 0.06 | 10 | 0.001 |
| Br | | | | 0.2 | | Pd | 30 | | 0.8 | 3 | 0.003 |
| C | | | 75 | 150 | | Pr | 7,500 | | | 2 | <0.0005 |
| Ca | 1.5 | | 0.01 | 0.02 | 0.05a | Pt | 60 | | 2.0 | 10 | 0.002 |
| Cd | 0.8 | | 0.008 | 1 | 0.003 | Rb | 3 | | 0.03 | 30 | 0.003 |
| Ce | | | 5 | 0.0004 | | Re | 750 | | | 5 | 0.0006 |
| Cl | | | | 10 | | Rh | 6 | | | 5 | 0.0008 |
| Co | 9 | | 0.15 | 1 | 0.0009 | Ru | 100 | | 1.0 | 6 | 0.002 |
| Cr | 3 | | 0.03 | 2 | 0.02 | S | | | | 3 | 70 |
| Cs | 15 | | | 0.0005 | | Sb | 45 | 0.15 | 0.15 | 10 | 0.001 |
| Cu | 1.5 | | 0.1 | 0.4 | 0.003 | Sc | 30 | | | 0.2 | 0.02 |
| Dy | 50 | | | 2 | 0.001 | Se | 100 | 0.03 | 0.3 | 50 | 0.06 |
| Er | 60 | | | 1 | 0.0008 | Si | 90 | | 1.0 | 3 | 0.7 |
| Eu | 30 | | | 0.2 | 0.0007 | Sm | 3,000 | | | 2 | 0.001 |
| F | | | | 10,000 | | Sn | 150 | | 2.0 | 60 | 0.002 |
| Fe | 5 | | 0.1 | 2 | 0.005a | Sr | 3 | | 0.025 | 0.03 | 0.0008 |
| Ga | 75 | | | 4 | 0.001 | Ta | 1,500 | | | 10 | 0.0006 |
| Gd | 1,800 | | | 0.9 | 0.002 | Tb | 900 | | | 2 | <0.0005 |
| Ge | 300 | | | 20 | 0.003 | Te | 30 | 0.03 | 0.4 | 10 | 0.01 |
| Hf | 300 | | | 4 | 0.0006 | Th | | | | | <0.0005 |
| Hg | 300 | 0.009 | 0.6 | 1 | 0.004 | Ti | 75 | | 0.35 | 0.4 | 0.006 |
| Ho | 60 | | | 0.4 | <0.0005 | Tl | 15 | | 0.15 | 30 | 0.0005 |
| I | | | | 0.008 | | Tm | 15 | | | 0.6 | <0.0005 |
| In | 30 | | | 9 | <0.0005 | U | 15,000 | | | 15 | <0.0005 |
| Ir | 900 | | 3.0 | 5 | 0.0006 | V | 60 | | 0.1 | 0.5 | 0.002 |
| K | 3 | | 0.008 | 20 | 0.015a | W | 1,500 | | | 8 | 0.001 |
| La | 3,000 | | | 1 | 0.0005 | Y | 75 | | | 0.3 | 0.0009 |
| Li | 0.8 | | 0.06 | 0.3 | 0.0001a | Yb | 8 | | | 0.3 | 0.001 |
| Lu | 1,000 | | | 0.2 | <0.0005 | Zn | 1.5 | | 0.1 | 1 | 0.003 |
| Mg | 0.15 | | 0.004 | 0.07 | 0.007 | Zr | 450 | | | 0.7 | 0.004 |
| Mn | 1.5 | | 0.035 | 0.04 | 0.002 | | | | | | |

Table 3. Minimum detection limits for the determination of anions by ion chromatography—EPA Method 300.0

[From Pfaff et al, 1991. mg/L, milligram per liter]

| Analyte | Minimum detection limit (mg/L) |
|------------------------|--------------------------------|
| Fluoride..... | 0.01 |
| Chloride..... | 0.02 |
| Nitrite–N..... | 0.004 |
| Nitrate–N..... | 0.002 |
| Bromide..... | 0.01 |
| Ortho-Phosphate–P..... | 0.003 |
| Sulfate..... | 0.02 |
| Chlorite..... | 0.01 |
| Chlorate..... | 0.003 |
| Bromate..... | 0.02 |

GEOCHEMICAL MODELING

The major objective of investigating highway runoff is to determine the effects on the environment of materials that are contained in runoff waters that are derived from highway operations, local soils, and natural and anthropogenic inputs from local atmospheric deposition. Predictions of the effects of these runoff materials on surface and ground water and biota can be made when knowledge and understanding of how the system functions is more complete. Understanding system function and making quantitative statements about processes require the application of theoretical analysis and can effectively be done through the development of models. Geochemical models can be used to assess the bioavailability and mobility of contaminants in a particular geochemical environment by predicting the behavior of the contaminants based on the chemical and physical properties of local soils, sediments, and solutions (precipitation and surface and ground waters). This type of geochemical information also is critical for the evaluation of appropriate BMPs for a given site. For example, much of the work

demonstrating the effectiveness of swales and infiltration structures to remove metals has been done in areas with soils containing high cation exchange capacities, but these same BMPs may contribute to the contamination of ground water in sand and gravel aquifers because of the lower capacity of these materials to retain the contaminants (Granato, 1996).

Depending on the system and the questions to be addressed, models can range from quite simple paper and pencil calculations to those requiring advanced computer capabilities. In most cases, highway runoff consists of relatively complex aqueous solutions and is most easily interpreted through the use of geochemical computer models. A number of these models have been developed for different applications, but they are all based on the processes outlined in the background section of this report. The quality and completeness of the water analyses that are used to develop the models are critical to the model output. If the analyses are inaccurate or incomplete, the model results have a high probability of being meaningless or misleading. Even with good quality analyses, the model results should not be accepted blindly but should be carefully examined to determine if they are consistent with what is known about the system being modeled and the assumptions inherent in the models. Following are examples of some of the better known and more widely used types of geochemical models.

Speciation Models

Speciation models are used to calculate the partitioning of an element among different aqueous species and complexes. They also calculate, to the extent of the thermodynamic information in the program, the saturation state of the solution with respect to solid phases and gases. The thermodynamic database must be internally consistent and must contain data for all of the species present in the system being modeled if reliable results are to be obtained.

Because the thermodynamic databases as well as the aqueous species and mineral phases considered commonly differ among models, care must be exercised in choosing the model that best suits the system of interest. Most existing models will simulate solutions comparable to seawater (salinity of 35 parts per thousand) in ionic strength. For more concentrated waters, such as brines, other models must be used. Widely accepted ranges for the salinities of freshwater, brackish water, and brines are 0–1, 1–35, and greater than 35 parts per thousand, respectively (Bates and Jackson, 1987). Speciation models provide data that aid in the interpretation of the relative importance of aqueous complexes and the toxicity of contaminated waters. Current models provide good approximations for speciation of the major elements but are not as good for speciation of trace metals. Thermodynamic data for many trace metal species are not easily available and often are not of the same quality as data for major ion species. Nordstrom (1996) discusses trace metal speciation and compares computational versus analytical techniques for assessing trace metal speciation in natural waters. Examples of speciation models are WATEQF (Plummer and others, 1976) and WATEQ4F (Ball and Nordstrom, 1991).

Mass-Transfer Models

Mass-transfer models are used to simulate changes in solution chemistry caused by mass-transfer processes. They are useful in modeling the mixing of two waters, evaporation, boiling temperature and pressure changes, dissolution and precipitation, ion exchange and adsorption and, ingassing and outgassing processes, and are commonly used in reaction-path modeling. Such models can be used to predict the overall geochemical behavior of contaminants and whether reactions in a system will go to equilibrium. As in the speciation models, these models have routines for speciating aqueous solutions. Some drawbacks of these models are that they do not consider solid-solution mass transfer, and they are restricted in the area of mass transfer due to ion exchange and adsorption. The models EQ3/6 (Wolery, 1992a, 1992b) and the Geochemist's Workbench (Bethke, 1994, 1996) include routines for specifying rate laws and mass-transfer kinetics, and keep track of water mass. Other models, such as PHREEQE (Parkhurst and others, 1980), PHRQPITZ (Plummer and others, 1988), and

MINTEQA2 (Allison and others, 1991), do not contain these options; however, they are extremely useful for many modeling applications. Other models of this type are SOLMNEQ.88 (Kharaka and others, 1988), MINEQL+ (Schecher and McAvoy, 1991), MINTEQ(4.00) (Eary and Jenne, 1992), and PHREEQC (Parkhurst, 1995).

Mass-Balance Models

Mass-balance models are used to simulate the net changes in the masses of reactants and products in waters along a flow path. Given the initial and final water compositions and the mineral phases present in the system, these models calculate how much of each phase must dissolve or precipitate to account for the observed difference in the water compositions. The models are independent of any assumptions about thermodynamic equilibrium or reaction kinetics and are based solely on mass-transfer considerations. Most of these models, such as NETPATH (Plummer and others, 1991, 1994) contain a routine that speciates the water and calculates saturation indices (SI) for each of the minerals in the data bank. It is incumbent upon the user to determine which of the phases that have SIs less than 0 are likely to dissolve and which that have SIs greater than 0 are likely to precipitate in the system. Usually, a number of plausible conceptual solutions are found for the system of interest, and the user must choose, based on his or her knowledge of the mineralogy, geochemistry, and hydrology, the conceptual solution that is most realistic. These types of models also can incorporate isotopic data for both the waters and minerals, if available, and the use of these data may help to eliminate unrealistic solutions. A major strength of these models is that they aid in identifying and quantifying the most important geochemical processes controlling the evolution of the chemistry of the waters.

Geochemical Mass-Transport Models

Geochemical mass-transport models can be used to simulate hydrodynamic advection and dispersion of dissolved species in porous media, as well as speciating the aqueous solution and determining geochemical mass transfer. Currently, a major drawback of the models is that they generally assume steady-state,

one-dimensional flow fields in homogeneous media with simple boundary conditions. These constraints are seldom, if ever, found in real natural systems. Nevertheless, such models can be valuable in providing insights into the processes that are responsible for the chemical evolution of natural waters and for designing BMP's and strategies for cleanup of contaminated sites. Some examples of this type of model are CHMTRNS (Noorishad and others, 1987), PHREEQM-2d (Nienhuis and others, 1994) and PHREEQC (Parkhurst, 1995). For some examples of the application of geochemical transport models, see Appelo and Postma (1993, chap. 10).

The modeling field is developing rapidly, and geochemical models are becoming more powerful and realistic in terms of the detail with which they can simulate real systems. It must always be kept in mind, however, that these are models and are only as good as (1) their ability to represent real processes and (2) the accuracy and completeness of the data that are entered into them. Even the best models today are not reliable for predicting future changes. Their greatest value is in providing insights into the way systems function, identifying gaps in our knowledge of the systems of interest, and indicating the kinds of data that are needed to fill these gaps. Many of the latest versions of the U.S. Geological Survey software and documentation for geochemical and hydrological models are posted on the Internet and can be downloaded at no charge (U.S. Geological Survey, 1998). Additional information on the location of models can be obtained on the appropriate Agency homepages (for example, U.S. Geological Survey, U.S. Environmental Protection Agency) and in Langmuir (1997).

DISCUSSION

This report is an attempt to provide a brief overview of the factors that must be considered in evaluating the geochemical effects of highway runoff on the environment. It should be apparent that focusing on a single component and examining total concentrations of that component will usually provide incomplete and potentially misleading information about its role in the system. Both the toxicity and the bioavailability of metals in waters depend on the aqueous speciation or complexation of the metals. For example, if an element such as aluminum is present as the trivalent aluminum (Al^{3+}) ion in water, its toxicity

to fish will be much greater than if it is present as an organo-aluminum complex (Driscoll and others, 1984). Therefore, an analysis of the total aluminum concentration of the water may provide misleading information about the toxicity of the water. To obtain an accurate picture of the role of aluminum (Al) in the system, the complete chemistry of the waters, including all of the other components that might interact with Al , must be considered. This is true for the evaluation of any constituent of interest in the system (Davis, 1988). In general, the toxicities of metals such as cadmium (Cd^{2+}), copper (Cu^{2+}), mercury (Hg^{2+}), nickel (Ni^{2+}), lead (Pb^{2+}), zinc (Zn^{2+}), and others, are a function of the aqueous activities of the metal ions and their complexes and not of total metal concentrations (Makepeace and others, 1995; Morel and Hering, 1993; Manahan, 1994).

Failure to consider the effects of aqueous speciation on toxicity may result not only in incomplete understanding of the system but also in unnecessarily restrictive and expensive regulations for controlling metal discharges (Lee and Jones, 1990; Lee and Jones-Lee, 1996). For instance, until recently, the U.S. Environmental Protection Agency did not take into account the relation between metal speciation and toxicity in its water-quality assessments (Hall and Raider, 1993). Just as the speciation of metals affects their toxicity, it also affects their bioavailability. The ability of plants to use essential metals, for instance, is related to the speciation of the metals in solution (Morel and Hering, 1993). Another type of process, often referred to as speciation, is the partitioning of metals between the aqueous and solid phases. This partitioning is a result of sorption or ion exchange processes and plays a major role in determining the bioavailability of trace metals in the environment. A number of investigations have addressed the partitioning of trace pollutants between the aqueous and solid phase. Gjessing and others (1984) found that significant amounts of the toxic inorganic and organic pollutants in highway runoff in Norway are strongly adsorbed to the particulate matter. Harrison and Wilson (1985a, b) investigated metal concentrations in runoff from a highway in England and found that the metals were strongly associated with the particulate matter. They observed that metal concentrations on particulates increased with decreasing particle size (increasing surface area), and that the suspended particulates in highway runoff contained higher overall

metal concentrations than road surface dusts. This was attributed to the preferential mobilization and transport of the finer particulates from the road surface during storm washoff. The strong association of metals with particulate street dust also was observed by Gibson and Farmer (1984) in urban Glasgow and by Hamilton and others (1987) in a suburb of London. The metals are adsorbed on both inorganic and organic particulate matter and may be released to aqueous solution if they encounter different chemical conditions in the receiving waters or soils or if the organic matter is decomposed. Morrison and others (1984) investigated the physicochemical speciation of zinc, lead, cadmium, and copper in stormwater from urban catchments in England and Sweden and found that zinc and cadmium preferentially partition into the aqueous phase, lead onto the particulate phase, and copper is about equally divided between the aqueous and particulate phases. They also observed that the high metal concentration associated with the particulate phase may be easily released on contact with receiving waters and is a major source of bioavailable metals.

Another source of trace constituents to the environment is the application of deicing salts to highways (Granato, 1996). Although deicing salts are relatively pure, because of the large amounts applied to roads, the small amounts of impurities translate into significant amounts of trace constituents being introduced into a watershed. The major constituents of deicing chemicals, in addition to adversely affecting water quality by increasing total dissolved solids, play a role in the mobilization of metals by promoting processes such as ion exchange, desorption, complexing, acidification and mineral dissolution (Amrhein and Strong, 1990; Shanley, 1994; Granato and others, 1995). These investigations, including those by Davis and others (1993), which addresses geochemical and hydrologic parameters affecting metal transport in ground water systems, and by Breault and others (1996), which examines the speciation and binding of copper by organic matter in contaminated streamwater, all point to the necessity of considering all of the components in a system in order to understand the behavior of any individual component.

Recently, the use of catalytic converters for vehicle emission control has introduced platinum, palladium, and osmium into the environment. Concentrations of these metals in road dusts along highways have increased concern relative to their

environmental and human health implications (Farago and others, 1997; Pearce and others, 1997; Schaefer and Puchelt, 1997). The road dusts are transported by storm runoff and winds to adjacent soils and surface waters, where they may become solubilized and enter the food chain. Platinum is a good example of the importance of speciation to toxicity; although platinum in metallic form is inert, some platinum compounds are known to be cyclotoxic and have mutagenic and carcinogenic effects. They also affect micro-organisms at very low concentrations. Charged platinum complexes that contain reactive ligand groups, particularly chloride, appear to be the most toxic (Farago and others, 1997).

One of the most productive approaches to examining the effects of contaminants on the environment is through the study of small watershed systems (Bricker and Kennedy, 1997; Peters and others, 1997). This approach was extensively used in the National Acid Precipitation Assessment Program (NAPAP) to investigate and document the effects of acid deposition on the environment and was used recently to examine the transport and fate of atmospherically deposited trace elements in a forested watershed in central Maryland (Church and others, 1997). In the NAPAP program, small watersheds in settings with minimal influences from human activities, except those from atmospheric deposition, were chosen for long-term monitoring and research (Bricker and others, 1983; Bricker, 1986). The watershed approach addresses the entire watershed system and allows evaluation of the relative importance of the inputs of constituents, both natural and anthropogenic, on system function (Velbel, 1985; Swank and Waide, 1988; Bricker and Rice, 1989; Moldan and Cerny, 1994). Also, watershed-level studies are key to support watershed-based environmental management, which has potential benefits within national surface transportation planning policies and procedures (Bank, 1996).

The effects of road salt on the chemistry of some small watersheds in central Maryland (Katz and others, 1985) and in Vermont (Shanley, 1994) have been discussed in the context of watershed systems. A synopsis of recent developments in solute modeling in watershed systems is provided by Trudgill (1995).

The watershed approach would potentially have direct application to the investigation of the environmental effects of highway runoff. In the ideal situation, where a road traverses across a watershed, investigation of the upstream and downstream portions

of the system would permit evaluation of the effects of the road. Alternatively, the use of paired watersheds, one containing a road and a hydrological similar, but roadless watershed, would provide valuable information on the effects of highways. In a region where a new highway is planned, study of the watershed prior to, during, and after road construction would provide invaluable information on the effects of the construction process and the subsequent use of the highway. For example, the use of upstream and downstream water-quality monitoring around several streams and ponds, as well as monitoring in an unimpacted subwatershed during a watershed study before, during, and after highway construction along I-84 in Danbury, Connecticut, showed that protective highway-construction BMPs were successful and the main sources of contaminants were from other construction activities in the watershed (Maguire, 1985). Investigations at the watershed level give an integrated picture of system behavior that cannot be obtained from fragmented studies of specific parts of the system.

CONCLUSION

The first step in assessing the impact of highway runoff on the environment is the collection of representative samples. If the samples do not accurately represent the chemical compositions of the system at the time of study, or are compromised by improper sampling techniques, subsequent chemical analyses will provide data that are misleading or worthless. The second step is the chemical analyses of the samples using methods that have the appropriate sensitivity and detection limits for each component of the sample. The analyses should provide as complete a chemical characterization of the sample as possible, including all of the major constituents as well as the specific contaminant species of interest. This is essential to provide the information necessary to calculate the ionic strength of the water and the activities and speciation of the dissolved constituents, both major and minor. If the analyses are incomplete for the major dissolved constituents (even though these may not be of interest from the toxics standpoint), it will not be possible to evaluate the behavior of the contaminant species in terms of solubilities, speciation, complexing, sorption, ion exchange, ion pairing, mobilization, and transport- all of the processes that determine toxicity and bioavailability. Analyses of

samples only for the total concentrations of selected elements of interest provide, at best, limited information and almost certainly will give a misleading picture about the effects of those elements on the ecosystem. Geochemical modeling, whether it is a simple pencil and paper effort or a sophisticated and complex computer project, requires chemical analyses as complete as possible, beginning with the data on major dissolved constituents that determine the electrolyte characteristics of the water.

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Bricker—AN OVERVIEW OF THE FACTORS INVOLVED IN EVALUATING THE GEOCHEMICAL EFFECTS OF
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District Chief,
Massachusetts—Rhode Island District
U.S. Geological Survey
Water Resources Division
10 Bearfoot Road
Northborough, MA 01532