

FUNDAMENTAL ENVIRONMENTAL CHEMISTRY

Martina Schmeling

Loyola University Chicago, Chicago, Illinois, U.S.A.

Joseph H. Aldstadt

University of Wisconsin–Milwaukee, Milwaukee, Wisconsin, U.S.A.

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Summary

The survival of humans relied on accurate interpretation of the surrounding environment gained by experience and observation. In ancient times, people were limited to the observation of the environment and making correct decisions to sustain the community. Examples are the meticulous study of the heavens to predict the changing seasons, the study of mineral types to predict soil fertility, as well as the development of a vast knowledge of plant and animal diversity and behavior. Nowadays, sophisticated instruments allow observations and provide knowledge about every aspect of human activities — including our future on this planet.

Environmental chemistry as a distinct discipline, however, is rather new and emerged only in the last decades of the 20th century. Environmental chemistry investigates the effects different elements, molecules or chemical products have on the environment and the species living within it. The four major pillars of the environment are the biosphere, the atmosphere, the hydrosphere, and the geosphere. Whereas chemical reactions occur in each “sphere” separately, without interaction among the four spheres the environment would not function properly. The most prominent examples for the interaction among different environmental “compartments” are the global water cycle and the elemental nutrient cycles of carbon, phosphorous, and nitrogen.

This chapter will introduce the reader to several major topics in environmental chemistry. After a brief introduction into the compartments and basic chemical and physical principles, major environmental issues for each compartment will be discussed. Special emphasis is placed on recent developments and findings as well as on representative examples to provide more concrete illustrations of these far-ranging topics. At the end of the chapter a conclusion and perspective section will summarize the subject.

1. Introduction

1.1. Environmental Compartments

To begin our discussion of the “Fundamentals of Environmental Chemistry”, a useful starting point will be to consider the environmental chemist’s perspective. To understand the abundance and distribution as well as the transport, reactivity, and fate of pollutants and nutrients, it is useful to view the environment as divided into “compartments”. These compartments represent the gas, liquid, and solid phases of matter that form heterogeneous matrices (or “spheres”) in which pollutants and nutrients are found and through which they move. While describing the gases that envelope the Earth as “the atmosphere” is common (from the Greek *atmos* for vapor and *sphaira* for globe), other “spheres” may be less familiar terms: the geological features such as rocks, soils, and sediments that represent the “lithosphere” (from the Greek *lithos* for stone), water in all of its forms that creates the “hydrosphere” (from the Greek *hydor* for water), and the vast diversity of living organisms that comprise the “biosphere” (from the Greek *bios* for life, course or way of living). These compartments are clearly interrelated and interdependent. Consider the schematic diagram of a freshwater lake

shown in Figure 1, where the complex intertwining of the lithospheric (sediment, soil), hydrospheric (surface water, ground water, water vapor), and atmospheric compartments are depicted.

Not surprisingly, the perspectives of biologists and geologists may differ and result in alternative classification schemes. Nevertheless, the classification scheme described above is accepted widely and will be useful as a model for understanding the basics of environmental chemistry.

The complexity of the four major compartments is important to appreciate. The *lithosphere* encompasses the earth's crust and the upper region of the mantle, extending to ~50 km below the surface. The primary matrices in the lithosphere are inorganic rock formations, soils (the uppermost layer of the crust) and sediments (including freshwater, estuarine, coastal, and harbor sediments, as well as dredged material thereof). That soils and sediments contain organic material is of great importance in that many matrices in the lithosphere, such as river sediments or freshwater bogs, have a high content of organic material (i.e., humic material or peat, respectively). The primary structure of the *atmosphere* is four-fold: the troposphere, stratosphere, mesosphere, and thermosphere, with the upper boundary of the latter at a distance of >100 km. Boundaries between these regions are known as the tropopause, stratopause, and mesopause, respectively. Additional structural distinctions are made for the ozone layer (found in the stratosphere), the ionosphere (that region containing ionic species, encompassing the mesosphere and thermosphere), and the exosphere (where the atmosphere thins out into space). The main components of the *hydrosphere* are the oceans, where 97.61% of the water on Earth resides, polar ice and glaciers (2.08%), groundwater (0.30%), freshwater and saline lakes (each ~0.01%), with rivers, soil moisture, and atmospheric water vapor comprising the remainder. The *biosphere* permeates the other compartments; organisms have been found just about everywhere that biologists have looked – from thermophiles such as *Pyrococcus* that live at > 80°C in hydrothermal vents to primitive microbes such as *Arthrobacter* which have been found in ~500 m deep drilling cores.

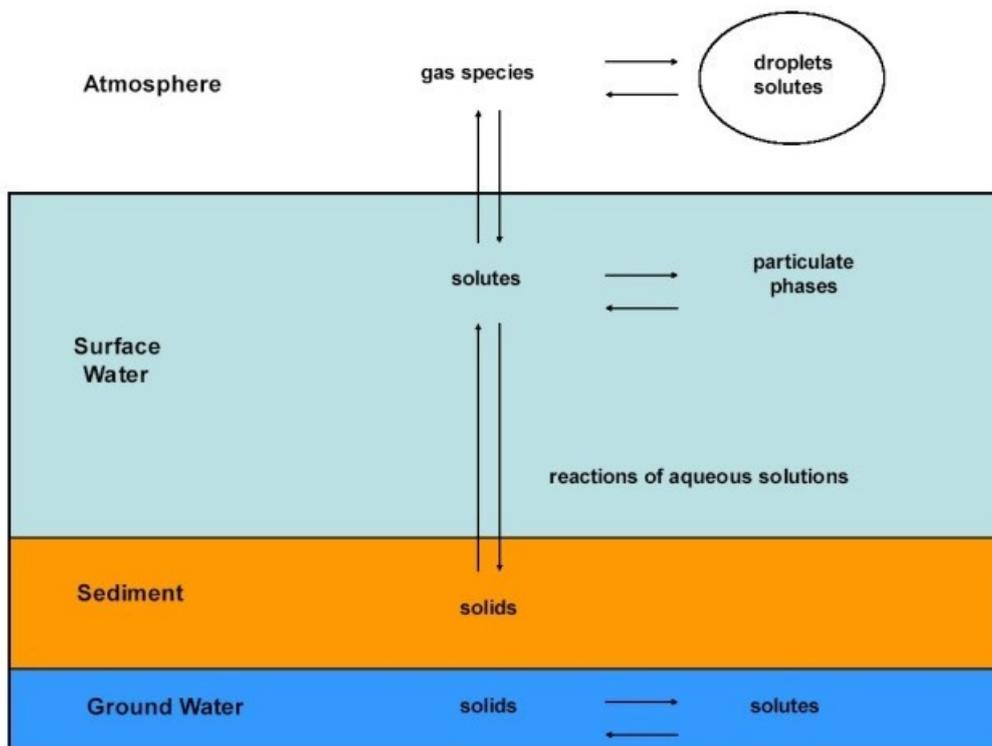


Figure 1. Cross-sectional diagram of a body of surface water

Processes that occur between these compartments are a key area of interest to the environmental chemist. Study of the movement and transformations occurring at these interfaces (e.g., air : water) is crucial in developing an understanding of transport and fate in particular. In Figure 2, the dynamic cycling of trace elements in the same type of limnological system as depicted in Figure 1 is shown. The geochemical make-up of the sediment is a source of iron and manganese oxides, upon reduction yielding relatively large amounts of dissolved Fe and Mn to the surface water, and often lesser amounts of other metal ions (including toxic species). Upon reaching the oxic zone of the water column, Fe and Mn can undergo oxidation and precipitation as they cycle back to the sediment. Association of trace metals to the metal oxides that are formed (e.g., the adsorption and subsequent co-precipitation of arsenate with iron oxides) can occur as well. Meanwhile, atmospheric deposition (e.g., rain, snow) and run-off (from soil and man-made structures, for example) provides further routes of input of trace metals to the system. A multitude of chemical reactions (e.g., acid-base, reduction-oxidation, precipitation, and complexation) and physical processes (e.g., phase changes, partitioning, adsorption, etc.) are taking place — from chelation by ligands such as dissolved humic material (derived largely from plant decomposition) to incorporation and ultimately precipitation with dead biological tissue.

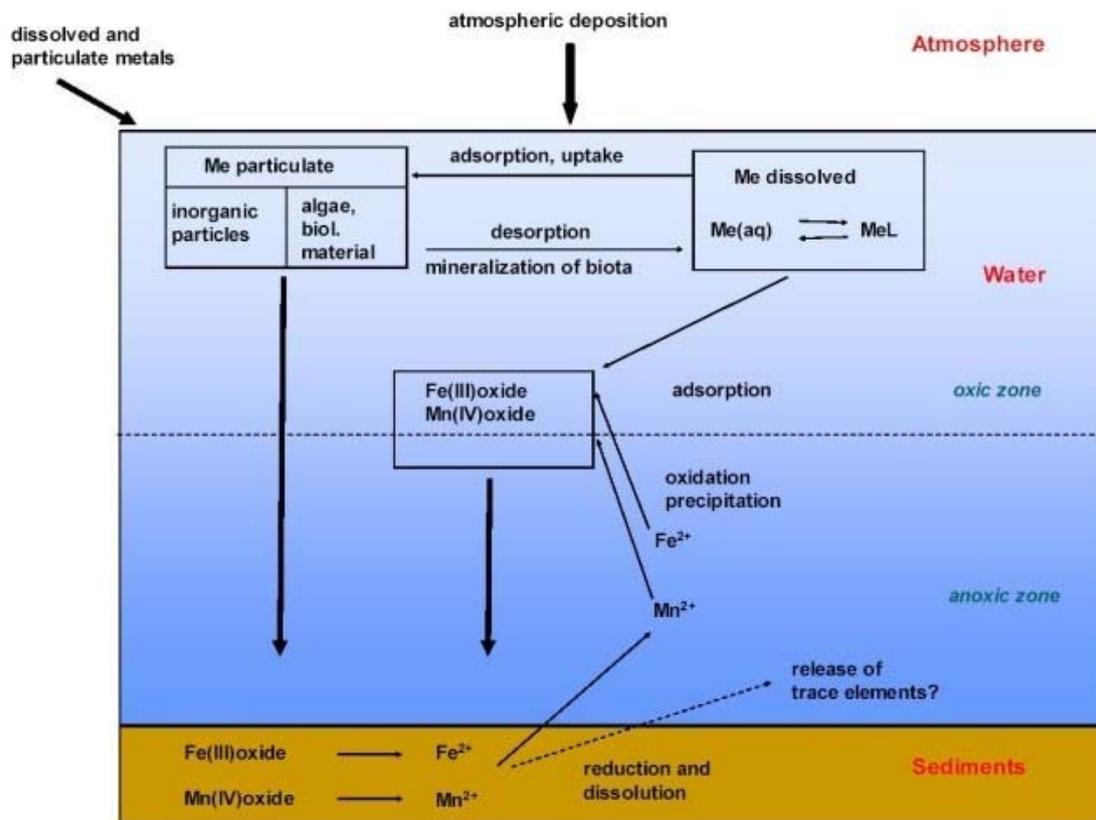


Figure 2. Trace element cycling in a freshwater lake (Me = metal and L = ligand)

1.2. Basic Physical and Chemical Principles

All chemical species present in the environment are cycled among the different compartments —atmosphere, hydrosphere, lithosphere, and biosphere — according to basic chemical and physical principles. During these cycling processes, chemical reactions convert species by reduction/oxidation, acid/base, precipitation, or complex formation and physical processes are responsible for phase changes, adsorption and partitioning. The time scale at which these different processes happen varies greatly — between millions of years for tectonic uplifting in the lithosphere to less than a second for photochemical reactions in the atmosphere. A good example of the exchange of species between compartments is the hydrological cycle. The processes responsible for water cycling are mostly physical in nature, including evaporation from rivers, streams and oceans into the atmosphere, and condensation into liquid water during cloud and rain formation, which can of course freeze when conditions are favorable. The glaciers and ice caps contain water in its solid form and melting releases it into the environment. Other species such as carbon or nitrogen are cycled between the compartments by a complex system of chemical and physical processes, including the conversion into biologically accessible forms and the precipitation of solid species for deposition in soil and sediments.

All reactions occurring are equilibrium reactions and follow the basic thermodynamic principles — though few are in a state of *true* equilibrium (*vide infra*). The First Law of

Thermodynamics (Eq. (1)) states that the change in internal energy (ΔE) of a system is the sum of heat flow into the system (q) and work done on the system (w), thus describing the ΔE that a given system experiences:

$$\Delta E = q + w \quad (1)$$

The Second Law of Thermodynamics (2) refers to the fact that all spontaneous reactions are accompanied by a net increase in entropy (S) or disorder of the universe.

$$\Delta S > 0 \quad (2)$$

An example highlighting how the First and Second Laws of thermodynamics are implemented can be found in the hydrological cycle, when considering the evaporation of water from a water body — thus the phase change of water from liquid to vapor. The evaporation process is based on heat flow into the system by solar radiation and work done on the water molecules to break the hydrogen bonds of liquid water (as described by the First Law). An increase in S results from this process as water in the form of vapor has a higher S than liquid water (as expected from the Second Law). Some environmental reactions are energetically favored to form product(s), but most need to have a source of energy (like the sun for the case of water evaporation) to make them happen. The parameter which relates ΔE and S of a system to each other and ultimately defines whether a reaction happens spontaneously under given conditions is the Gibbs Free Energy (G). The Gibbs-Helmholtz equation (3) describes the change in G for a reaction at constant pressure and instead of ΔE , which is pressure independent, we use enthalpy (ΔH) in equation (3) defining the heat flow for a reaction at constant pressure. A reaction is product-favored when ΔG is negative, and it proceeds in the opposite direction when the Gibbs free energy change is positive. In case ΔG is zero, the system is in equilibrium. Some reactions can be forced to form product(s) by changing the temperature, but others do not. For instance the evaporation of water at ambient atmospheric pressure is a spontaneous process for temperatures above the boiling point at 373K or 100°C.

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

As mentioned above, all environmental reactions are equilibrium reactions and can occur in both directions – towards the products or towards the reactants. The quantity which defines whether a reaction is happening in a forward or reverse direction is the equilibrium constant (K). In general, for a reaction between A and B to products C and D the equilibrium expression is:



$$K = \frac{C * D}{A * B} = \frac{\text{products}}{\text{reactants}} \quad (5)$$

The equilibrium constant determines in which direction a reaction proceeds under given pressure, temperature and concentration of reactants and products. Acid/base reactions,

redox reactions and solubility reactions are all equilibrium reactions each having a specific K to describe it. When a change in conditions occurs, such as the addition or removal of products or reactants, a new equilibrium will be established (Le Châteliers Principle). A good example is the mobilization of aluminum in natural waters with a change in pH, i.e.,:



$$K_{\text{sp}} = [\text{Al}] \times [\text{OH}^-]^3 = 10^{-33} \quad (7a)$$

An increase in acidity forces the reaction in the direction of product formation because of the reaction of H^+ with OH^- . Usually the aluminum ion (Al^{3+}) concentration in natural water is very low, because of a neutral to slightly basic pH. However, the addition of acid, for instance by atmospheric deposition (see *Acid Deposition*), can increase the solubility of aluminum significantly. When considering solid Al(OH)_3 as the major aluminum compound in natural waters at neutral pH, the aluminum ion concentration can be found as follows:

$$10^{-33} = [\text{Al}] \times [\text{OH}^-]^3 \quad (7b)$$

At pH=7 the hydroxyl ion concentration is $10^{-7} \text{ mol L}^{-1}$, hence the aluminum ion concentration will be $10^{-12} \text{ mol L}^{-1}$. Lowering the pH by two units from 7 to 5 decreases the hydroxyl ion concentration in the water to $10^{-9} \text{ mol L}^{-1}$. In order to satisfy the equilibrium conditions, the aluminum ion concentration has to increase to $10^{-6} \text{ mol L}^{-1}$, therefore making aluminum much more soluble at lower pH.

Chemical reactions proceed at different rates. In the environment, some reactions are extremely slow (like the weathering of rock), while other reactions are very fast (such as the conversion of ozone into oxygen molecules by reaction with nitrous oxide in the troposphere). The rate law describes how fast a reaction proceeds towards its products (Eq. (8)) and reactions can be first, second or higher order with respect to each species. Summarizing the orders provides the overall order of a reaction. The reaction order is determined experimentally and the rate law can be found from this. An important parameter derived from the rate law is the half-life of a reaction, $t_{1/2}$, which describes the time required until one-half of a reactant has disappeared (Eq. (9)). Equation (9) refers to the half-life for a “first order” reaction. Half-lives are important quantities in environmental chemistry because they determine how long it takes until one-half of a radioactive substance, for instance, has decayed. The half-life of ^{239}Pu produced in nuclear reactors is approximately 6580 years.

$$\text{rate} = k [\text{A}] \times [\text{B}] \quad (8)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (9)$$

Partitioning between the different compartments (phases) is another important process, referring to the amount of a substance present in a given phase for reaction or

metabolization. Partitioning depends on various parameters including the species concentration and partial pressure as well as the presence of other species. Henry's and Raoult's Laws define the degree of partitioning a species experiences between the gas and the liquid phase. Henry's Law is applied to determine the amount of a gas dissolved in a liquid (Eq. (10)) at a given pressure whereas Raoult's Law (Eq. (11)) specifies the vapor pressure of a species above a solution.

$$c_{\text{g}} = k_{\text{H}} \times p_{\text{g}} \quad (10)$$

$$p_{\text{g}} = x_{\text{g}} \times p_{\text{g}}^{\text{pure}} \quad (11)$$

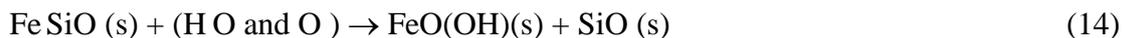
The Henry's constant (k_{H}) for the species of interest and the mol fraction of the solvent in the solution (x_{g}) are key parameters. Both laws find wide application to environmental processes. Henry's Law, for example, describes the solubility of carbon dioxide and oxygen in water — both of which are fundamentally important species for aquatic ecosystems. An application of Raoult's Law can be found when comparing frost points of fresh water and seawater. Seawater contains a significantly higher mol fraction of ions than does fresh water, which has a frost point of -3°C as opposed to 0°C for fresh water.

Important chemical processes in all environmental compartments are acid/base, precipitation, and redox reactions. Acid/base reactions involve hydronium ions (H_3O^+) and require proton donors and proton acceptors. In precipitation reactions, an insoluble product is formed. During redox reactions electrons are transferred from one species to another, thereby changing the oxidation state of each species. A good example of an acid/base reaction involving a weak base and weak acid is the carbonate-water equilibrium. The principle reaction and equilibrium expression is shown in Eqs. (12) and (13). Here the carbonate ion serves as proton acceptor (weak base) and water as proton donor (weak acid). The equilibrium constant for this reaction is 4.69×10^{-11} — heavily favored toward the reactants. The carbonate/water equilibrium is also mainly responsible for the buffering capacity of natural waters, describing the water's ability to withstand changes in pH.



$$K_{\text{a}} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} \quad (13)$$

Other common acid/base reactions are hydrolysis reactions of metal ions, which increase or decrease their mobilities in the system. Redox reactions also play a vitally important role in the environment. Photosynthesis and the conversion of nitrogen(III) to nitrogen(V) as catalyzed by bacteria are good examples of redox reactions. Other redox reactions that illustrate their importance are the conversion of organic material with oxygen molecules to carbon dioxide and water and the erosion of rocks with oxygen and water.



When considering chemical reactions in the four major compartments, in most cases concentrations can be used to calculate the amount of species present and formed. In certain situations, however, the concentrations vary and electrostatic interactions between ions cannot be neglected (as described by Debye and Hückel in the early 20th century). In such cases the concentrations have to be converted into activities, which take into account the charge, size and concentration of ions – and their effects on their neighboring ions and neutral molecules (e.g., water). Concentration (c) and activity (A) are related to each other by the activity coefficient γ :

$$A = \gamma \times c \quad (15)$$

Correcting c with A becomes more important for solutions of ionic strength greater than approximately 100 mM.

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Biographical Sketches

Martina Schmeling received her Diploma chemistry in 1992 from Westfaelische Wilhelms University in Muenster, Germany and her Ph.D. in 1997 from University of Dortmund, Dortmund, Germany. In 1997 she moved to University of Antwerp, Antwerp, Belgium to work for one year as Visiting Professor. After that she spent a year as a postdoctoral researcher at Princeton University, Princeton, New Jersey, USA. In 1999 she was appointed an Assistant Professor of analytical chemistry at Loyola University Chicago, Chicago, Illinois, USA. She is a member of several professional societies like German Society of Chemistry, American Chemical Society, American Geophysical Union, German Society for Aerosol Research and American Meteorological Society. Her main research interests are focused on the study of atmospheric aerosols, their chemical composition (organic and inorganic) and their effects on climate and human health and she has published number of scientific articles in this research area. Her teaching duties include General Chemistry, Elemental Quantitative Analysis, Environmental Chemistry as well as Atmospheric Chemistry. Her recent research project involves collecting aerosols with high temporal resolution (1 hour) at the "Loyola University Chicago Air Monitoring Station" (LUCAS) and their analysis for different species. To perform this, a procedure of aerosols chemical characterization based on total reflection X-ray fluorescence (TXRF) was developed. The high time resolution in combination with local meteorology provided information about daily transport patterns of air masses. In addition, this station is also equipped with an UV photometric spectrometer for ozone analysis and a chemiluminescence analyzer for NO-NO₂-NO_x analysis.

Joseph H. Aldstadt received his Ph.D. degree from Ohio University, Athens, Ohio, USA. At present he is an Associate Professor of analytical chemistry at University of Wisconsin-Milwaukee, Milwaukee, Wisconsin, USA. His research activities encompass fundamental studies of analytical instrument design

and applied studies in environmental trace analysis. His research group is currently developing: (a) new methods for determining trace levels of semi-volatile organics (e.g., PCBs) in a wide variety of biological tissues using GC-MS/MS; (b) *in situ* monitoring instruments based on continuous flow analysis within forged microconduits; (c) novel stationary phases for solid-phase extraction (SPE) based on molecular imprinting for specific organoarsenicals (phenyl arsonic acids, e.g., Roxarsone); and (d) the development of a prototype "Photon Trapping Spectrometer" in collaboration with Prof. Geissinger's group for sensitivity enhancement in visible spectroscopy.

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