Water-Quality Principles
QW1022–TEL

Lesson 8—Environmental Organic Chemistry

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Organic Constituents

(p.151)

The intimate relationship between water in the hydrologic cycle and living matter and its waste products ensures that all natural water contains organic material. The amounts present in most waters are small compared with dissolved inorganic solute concentrations, but even small amounts can have significant effects on the chemical properties of aqueous systems. For example, various organic solutes form complexes that affect metal solubilities, participate in redox reactions, serve as nutrients for microbiota that mediate chemical processes, and influence both physical and chemical properties of solid–liquid or liquid–gas interfaces. When present in large enough concentrations, organic solutes may need to be considered in the analytical cation-anion balance, and even small concentrations of certain organic solutes can render a water unsuitable for use by humans or toxic to aquatic or other life forms.

Naturally occurring organic solutes are generally assumed to be somewhat similar to the organic material present in soils—however, their chemical properties remain incompletely understood.

Approximate determinations of the total concentration of organic material in a water sample include measurements such as "dissolved organic carbon" (DOC) and "total organic carbon" (TOC). Less specific information also may be obtained by measuring color intensity or total oxidizable material.

The properties of dissolved organic material may be evaluated in a general way by ancillary measurements

such as acid-base titration and capacity for complex formation with metal ions. Techniques involving chromatographic separation and selective uptake by ion-exchange resins can be used for segregating portions of the organic solutes and concentrating them for further study. Solvent-extraction techniques also have been used for such purposes. Finally, the fractionated material can be analyzed by means of a mass spectrograph to identify specific compounds.

Dissolved and Total Organic Carbon

The determination of organic carbon is done by converting all carbon species present to carbon dioxide and correcting the subsequent determination of CO_2 for any dissolved CO_2 species that were initially present. The DOC concentration in river water has been reviewed by Meybeck (1981, 1982). He calculated an average DOC for all rivers of 5.75 mg/L, noting that the rivers of the subarctic zone have a relatively high average (19 mg/L) compared with those of tropical regions (6 mg/L) and those of temperate and arid or semiarid zones (3 mg/L). The total organic carbon transported to the ocean by rivers is from 1 to 2 percent of the primary production (through photosynthesis) of organic carbon. There is, of course, a substantial range in DOC in any given stream as well as wide differences from one drainage basin to another.

Organic-carbon concentrations in ground water normally are smaller than those in surface water, but information on actual concentrations is still scarce, and what is available refers generally to systems that have been affected by pollution. Ground water is characteristically exposed to a very large area of rock surface per unit water volume as it moves from points of recharge to points of discharge. Organics that may be present in recharge can be lost by adsorption. Evidence of adsorption of organics by stream sediment and bed material is plentiful, but available surface areas per unit volume of water in river systems are much smaller than in ground water systems.

Some ground waters may contact organic debris along the flow path to add DOC, and both dissolved and solid-phase material may serve as reactants in such processes as sulfate reduction. Thorstenson and others (1979) reported TOC values for water from the Fox Hills–basal Hell Creek aquifer of the western Dakotas ranging from 1.9 to 20 mg/L. In this area the sulfate content of the water is greatly depleted by reduction as the water moves through the system. It is evident, however, that the TOC data do not correlate with apparent loss of sulfate, suggesting that organic material from the aquifer is the principal reductant source.

Indirect Evaluation of DOC Effects

Participation of dissolved organic matter in ground water in metal oxide reduction can help explain increases in manganese and(or) iron in water withdrawn from wells near organic-carbon sources. A high DOC concentration is likely to be characteristic of leachate from landfill waste dumps (Baedecker and Back, 1979).

A substantial effect on minor metal concentration can be expected through formation of metal-organic complexes. The nature of organic compounds in solution generally is not well enough known to permit using the type of rigorous mathematical model that is being used to predict inorganic complexing and speciation, although a start in this direction was made by Mattigod and Sposito (1979). Two general approaches have been used to avoid this difficulty. One may use the actual water of interest and evaluate its interaction with added metal ions, using ion specific electrodes, or polarography to identify complexing (Sunda and Hanson, 1979). This may be appropriate for natural waters of constant composition. The second approach has been to use a model compound which is available as a pure substance and bears enough resemblance to the natural organics that it may give results similar to those observable in the field. Tannic acid has been used, for example, as a means of evaluating some features of iron chemistry in the presence of organic solutes (Theis and Singer, 1974).

In some waters organic solutes are major constituents. For example, short-chain aliphatic acid anions such as acetate, propionate, and butyrate in some places occur in water associated with petroleum (Willey and others, 1975). In such waters these ions will be partly titrated by strong acid added during the determination of alkalinity and may be erroneously reported as an equivalent amount of bicarbonate.

Color

The determination of color that is sometimes included in water analyses represents an evaluation of a physical property and has no direct chemical significance. The color of natural water usually results from leaching of organic debris. The color ranges from a pale yellow to a dark brown, and it can generally be matched fairly well by dilutions of a mixture of cobalt chloride and potassium chloroplatinate solutions. An arbitrary standard solution containing 1 g of cobalt chloride, 1.245 g of potassium chloroplatinate, and 100 mL of concentrated hydrochloric acid in a total volume of 1 L has a color rating of 500. Permanently colored glass discs are commonly used as standards with which tubes of a specific depth, containing samples of water, are compared in a color-matching device. The intensity of color is rated numerically, a color of 5 being equivalent to one-hundredth that of the standard. The color number has no direct connection

with the actual amount of organic material causing the color.

Intensely colored waters occur in many different environments where vegetation is plentiful, as in swamps and bogs, from the tropical Amazon to Alaskan tundra. The materials causing the color can hardly be chemically identical in all those places. It is also rather unlikely that such materials are identical to the organic material extracted by standard soil-analysis techniques. However, the nomenclature used in soil chemistry has been carried into this aspect of water chemistry and requires consideration here. The organic fraction of soils can be partly brought into solution by treating the soil with a sodium hydroxide solution. The colored extract is further treated by acidification, which causes part of the organic material to precipitate. This acid-insoluble fraction is termed "humic acid." The acid-soluble organic matter is termed "fulvic acid" (Black and others, 1965, p. 1414–1416). These terms do not denote definite chemical compounds but are operational definitions that might imply that the materials obtained from different soils by one kind of treatment have some chemical similarity. Other names are applied by soil chemists to certain other fractions of the organic extract that can be separated using organic solvents. These are not of concern in water chemistry.

The terms "humic" and "fulvic" are widely used to refer to colored organic material in water. Without more specific identification of chemical composition and structure, such terminology conveys little useful information. Studies to characterize the materials more specifically have been made by several investigators.

Black and Christman (1963b, p. 897) reported the colored materials in water they studied were mostly of the fulvic-acid type, and they described them as polyhydroxy aromatic methoxy carboxylic acids. They found most of the colored material was particulate (Black and Christman, 1963a, p. 766) having diameters between 4.8 and 10 nm, as determined by membrane filtration and dialysis. This size range indicates that some or all the material could represent single or polymerized molecules. The equivalent weight of the material, defined as the molecular weight per mole of carboxylic plus phenolic hydrogen, was found to range from 89 to 138 (Black and Christman, 1963b). This value is in approximate agreement with some others for probably similar material. Pommer and Breger (1960), for example, reported a value of 144 for humic acid. However, the literature contains a wide range of values for molecular weights for these materials.

Continuing research on the chemistry and structure of these organics has shown that fractionation of the material by adsorption on synthetic resin may aid in characterization (Thurman and Malcolm, 1981). Lamar and Goerlitz (1966) identified 13 organic acids in colored water by gas chromatography. Most of the colored material, however, was not sufficiently volatile to be identifiable by this technique.

Complexing and adsorptive behavior of dissolved organic coloring matter toward metal ions has been of considerable interest, but it is difficult to evaluate because of the ill-defined nature of the organics. An empirical approach was used by Schnitzer (1968), who determined stability constants for a suite of metals complexed with fulvic acid extracted from a podzolic soil. It should be noted, however, that the stability constants reported by Schnitzer are applicable only to solutions having certain specified pH values. Also, the composition and behavior of fulvic or humic acid extracted from different soils may be different. Consequently, the reporting of stability constants for combinations of metal ions with these rather ill-defined organic solutes does not provide a complete understanding of the behavior of organic solutes in natural water toward metal cations. More information on the chemical composition and structure of the organic material as well as the complexes must eventually be obtained to achieve an understanding comparable to that which has been attained for many inorganic complexes. Jenne (1975) reviewed the literature on trace-element interactions with these materials.

The color of some streams in the Southeastern United States that drain swamps exceeds 200 units at times. Color below 10 units is barely noticeable to the casual observer.

Synthetic Organics

The chemical industries of the United States and other developed nations have produced and continue to produce enormous amounts of synthetic organic materials. Many of these substances do not occur naturally. Besides the various intermediate and end products of industry, substantial volumes of exotic organic wastes are generated.

End uses of many of these products tend to disperse them in the environment. The production and waste-disposal sites also can be expected to release synthetic organic chemicals and their decomposition products into the atmosphere and hydrosphere. Presence of these materials in water and the hazards thus produced have been of increasing concern in the United States during the 1980's. Programs to rectify effects of unwise waste-disposal practices have received much public attention.

Obviously, the first line of defense here should be minimizing the escape of these materials into surface and, especially, underground waters. Coping with existing and inevitable future problems relating to these materials

will require a reasoned approach. The total number of potential organic chemical compounds that might escape is enormous. However, the number that pose any significant threat to potable water supplies is much smaller.

Factors that should be considered in connection with these compounds, in addition to their toxicity, include quantities produced and released, stability of the compound in aqueous systems, especially those in which organisms that might attack and consume or alter them are present, the degree to which the material might dissolve in water or be adsorbed on sediment, and such chemical properties as complexing behavior toward other solutes, especially metal ions, and interaction with hydrogen and hydroxide ions.

Over the years, attention has been directed toward various organic compounds that tend to be stable in natural aqueous systems. Phenol and cyanide (the latter is not usually considered an organic substance) were recognized as toxic pollutants and limits were fixed for them in drinking water standards established early in the 20th century.

Halogenated organics are among the more stable species in water. This was thought an advantageous feature of the persistent pesticides such as DDT and chlordane. Other substances such as the polychlorinated biphenyls (PCB's) once widely used in electrical equipment and elsewhere were purposely designed to be chemically inert. Low-boiling materials in refrigeration systems (freon, for example) or related compounds used as propellants for aerosol sprays and as dry-cleaning solvents have been widely disseminated in air and water and have even been suggested as possible hydrologic tracers or dating tools (Russell and Thompson, 1981). Specific methods have been developed for identifying compounds of these types. Most of them are hydrophobic; they have low aqueous solubilities and tend to associate with particulate surfaces. In the later 1970's, it was discovered that undesirable chlorinated hydrocarbons could be formed when waters containing natural organic solutes were treated with chlorine in the process of disinfection and sterilization.

Techniques for fractionation of organic constituents in water using ion-exchange resins followed by various elution procedures (Leenheer and Huffman, 1979) can be used to segregate organic compounds that have similar chemical properties. These procedures are useful in developing methods for analysis and in improving our understanding of both natural and synthetic organics.

In the late 1970's the U.S. Environmental Protection Agency, under the terms of a Federal court settlement, proposed a list of toxic materials termed "priority pollutants" for which it was to provide effluent limitations and guidelines. This list includes 113 specific organic compounds, 13 inorganic elements (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc) and 3 general categories including fibrous asbestos, total cyanides, and total phenols. Some aspects of the development of the list of materials and possible means of analyses were described by Keith and Telliard (1979). The priority pollutant list is an initial effort to cope with the very difficult problems posed by synthetic organic materials in the environment.