Kirk-Othmer Encyclopedia of Chemical Technology.

WATER, SOURCES AND QUALITY ISSUES

The physical effectiveness of water moving through the hydrologic cycle, as a means of modification of surface topography, is impressively demonstrated in such geographic erosional features as the Grand Canyon of the Colorado River. Besides the physical movement of erodible material, however, the chemical attack of circulating water on rock minerals over time brings into solution a wide variety of elements that are transported to the oceans by rivers.

In the early years of development of the science of geochemistry there was a strong interest by investigators Goldschmidt and Vernadski in Europe and Clarke in the United States in the significance of chemical composition of river water and how the observed composition was reached through water-rock chemical reaction. There also were direct practical motivations of studies of river water composition. For example, during the nineteenth century the settlement of the interior of the United States was continuous. The growing major cities commonly were located on navigable streams, or at the shoreline of other surface water bodies, that could be used both as sources of water supplies and for disposal of wastes as well as for transportation. That these uses were commonly not compatible became clear as populations of cities increased.

Evaluation of water for its fitness to be used as a public supply, the procedures generally termed “sanitary analysis,” involve such determinations as dissolved oxygen, biochemical oxygen demand, testing for presence of various forms of bacteria, and related evaluations, are described in “Standard Methods” (1) and are discussed only briefly in this article. The evaluation of river water for possible industrial uses is generally concerned with determination of major dissolved constituents in filtered sample aliquots. Samples must be taken at intervals frequent enough to show the degree of variability of these concentrations over a range of flow rates.

Ideally the historical record of stream water quality would extend back to a time when human activities in the drainage basin had no significant effects. This “pristine” condition had probably already passed in most U.S. rivers before any organized water quality studies were made, as concern about apparent stream pollution was commonly a motivating factor in starting such studies (see Water, pollution).

1. Factors Affecting Stream Water Quality

1.1. General Principles of Stream Water Geochemistry

The composition of pristine stream water can range from nearly that of rainwater, a very dilute solution containing up to a few tens of milligrams per liter of dissolved material, to concentrations of as much as several thousand milligrams per liter, which mainly are found in semiarid regions where saline springs contribute chemical constituents derived from readily soluble rock strata. In general, however, the dissolved-solids concentrations of principal streams in humid and subhumid regions of the conterminous United States have a narrower range. Analyses showing maximum and minimum concentrations for a recent 3-year period for 29 stream-sampling sites in the United States recently were published (2). Seven of these sites had maximum total dissolved-solids concentrations greater than 1000 mg/L; these high concentrations are attributable to natural saline inflows, although human activities probably intensified their effects.

Chemical analyses of stream water that have been published since the early years of this century generally include determinations for four positively charged ions (cations)—calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{2+}), and potassium (K^+)—and five negatively charged ions (anions)—bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), and nitrate (NO_3^-)—and uncharged dissolved silicic acid (generally reported in terms of silica, SiO_2). These are the major constituents in most natural stream water and are those given principal attention in this article. Minor constituents, present at concentrations substantially less than 1 mg/L, include a wide variety of inorganic and organic constituents, and although these constituents commonly are the result of human activities, they are not considered in detail in this article because few reliable measurements were made until the 1970s. Short-term trends for these constituents have been evaluated using statistical techniques (3).

1.1.1. Chemical Reactions that Govern Stream Composition

Weathering is a general term for mechanical and chemical alteration of rock minerals that are exposed to the atmosphere and circulating water at and near the land surface. Chemical reactions that occur during weathering produce both water-soluble and nonwater-soluble products; those that are water soluble are transported from the reaction site in surface runoff or in moving groundwater. To a certain extent, at least, the concentrations of dissolved elements would be expected to reflect the relative abundance of the elements in the rocks exposed at the reaction site. Such a broad generalization has some validity for silicon (Si) and the four elements that form the major cations of most natural stream water. These five elements are among the eight most abundant elements, with oxygen being the most abundant, in igneous and sedimentary rocks of the Earth's outer crust. The other two of the most abundant elements—aluminum (Al) and iron (Fe)—form oxides or hydroxides of very low solubility during normal rock weathering and, therefore, generally are not present in large amounts in stream water. On the other hand, major anions in stream water display a more complex relation to rock composition. In the average stream water sample, the five most abundant anions represent the nonmetallic elements carbon, sulfur, chlorine, fluorine, and nitrogen. Also, oxygen is included in three of the anions of these elements.

Oxygen is by far the most abundant element in crustal rocks, composing 46.6% of the lithosphere (4). In rock mineral structures, the predominant anion is O^{2-}, and water (H_2O) itself is almost 90% oxygen by weight. The nonmetallic elements fluorine, sulfur, carbon, nitrogen, chlorine, and phosphorus are present in lesser amounts in the lithosphere. These elements all play essential roles in life processes of plants and animals, and except for phosphorus and fluorine, they commonly occur in earth surface environments in gaseous form or as dissolved anions.

In a very broad general sense, then, the major cationic constituents of stream water tend to reflect the composition of associated rocks and the relative resistance of the rock minerals to weathering. The anions, which must be present in these water solutions in electrochemical balance with the cations, tend to reflect the influence of various chemical and biochemical processes that have broken down the rock minerals as well as the chemical, biochemical, and physical processes taking place in the aquatic and surrounding environments. The predominance of bicarbonate anions in most stream water is related to cycling of carbon dioxide (CO_2) from air and to biological processes in soil. Dissolution of carbon dioxide in water produces carbonic acid (H_2CO_3) that attacks rock minerals. Bicarbonate anions are formed in solutions participating in such reactions in amounts equivalent to the amount of cations that are released.

Sulfur and nitrogen participate in biologically mediated oxidation reactions producing hydrogen ions (H^+) that become available for weathering of rock minerals. For example, pyrite (FeS_2) can be converted to dissolved ferrous iron and sulfate as a result of oxidation of sulfur by dissolved oxygen, and the hydrogen ion is a major by-product. Carbonate or sulfate in sedimentary rocks (eg, limestone and gypsum) can be taken directly into solution and can add substantially to the bicarbonate and sulfate contents in water that is in contact with such rocks.

Chlorine plays a less significant role in chemical weathering processes than do sulfur and carbon. Most geochemists believe that much, or most, of the chloride in stream water in coastal areas is derived from sea salt that is carried landward or deposited by rainfall. Farther inland, however, a major part of the chloride loads in streams is the result of human activities.

The final composition of stream water is the product of the weathering reactions and related processes outlined above. However, the chemical processes are influenced and controlled by an intricate combination of environmental factors that are characteristic for each drainage system. Therefore, the composition of the bedrock in an area and the residual material left at the surface as soil and subsoil exert a strong influence on the chemical composition of runoff from the area. The reactions of water with this material are the ultimate geological control and are the source of soluble weathering products.

Most igneous and metamorphic rocks are composed predominantly of aluminosilicate minerals, including feldspar such as albite ($NaAlSi_3O_8$) or anorthite ($CaAl_2Si_2O_8$) and crystalline forms of silica such as quartz (SiO_2). Various mixed metal-plus-silicon oxides such as olivine [$(Mg,Fe)_2(SiO_4)$] and pyroxene [$Mg_2(SiO_3)_2$] can be major constituents in darker colored igneous rocks that are relatively low in total silicon.

Rocks that were deposited as sediment can consist of unaltered fragments of a precursor rock body and are represented by sandstone and conglomerate. The finer grained sedimentary rocks, such as shale or siltstone, also can contain some unaltered particles but also usually have high proportions of slightly soluble alteration products, such as clay minerals, formed during weathering of resistant silicate minerals. Such rocks are classified as hydrolyzates. Another class of sedimentary rock of major importance is the precipitates, such as limestone and dolomite, which are predominantly composed of calcium carbonate and calcium plus magnesium carbonate, respectively. Evaporites are sedimentary rocks produced by extensive evaporation of water from weathering solutions. Common examples are gypsum and anhydrite, primarily composed of calcium sulfate, or halite (rock salt), primarily composed of sodium chloride. Obviously the more readily soluble minerals of evaporite or precipitate rocks can dissolve rapidly when exposed to circulating water. Carbonates also can act as cementing material between the mineral grains of resistate and hydrolyzate rocks.

The extent to which minerals are attacked and dissolved from igneous and metamorphic terranes depends in large part on the availability of reaction sites on solid surfaces and the length of time the solution–solid contact is maintained. The effects of weathering are controlled by kinetic factors, such as the rates of the chemical reactions and the general rates of water and sediment movement, and biological factors that include the effects of biotic growth in the weathering zone. Also, the hydrologic properties of the drainage system (precipitation, evaporation, runoff, slope of the area), the relative permeability of rocks and soils, and the degree to which the surface drainage system is coupled to the groundwater reservoirs are important modulating forces. In rocks that contain more soluble minerals such as calcite, the degree to which solids are dissolved and carried off in the runoff is more likely to be governed by chemical thermodynamic factors, and in carbonate systems a state of chemical equilibrium could be closely approached.

Mineral dissolution reactions of importance generally require a continuous supply of hydrogen ions in the incoming solution. To some degree, reacting hydrogen ions are supplied from the water itself, which always includes, to some extent, water molecules that have broken apart (dissociated) into hydrogen and hydroxide ions. Under standard conditions (25°C and 1 atm pressure), the effective concentration (activity) of hydrogen ions in pure water is $10^{-7.00}$ mol/L. (A mole of a chemical element is a quantity in grams numerically equal to the atomic weight. For hydrogen, $10^{-7.00}$ moles/L is equivalent to 0.1 μg/L.)

The pH scale commonly used to express acidity is defined as the negative base-10 logarithm of the activity of hydrogen ions in a solution. At neutrality under the conditions defined in the preceding paragraph, the pH therefore will be 7.00. A change of 1 pH unit represents a 10-fold change in hydrogen ion activity. The activity of a dissolved ion is exactly equal to its concentration only in very dilute solutions. This topic has been discussed and explained more extensively elsewhere (5).

In natural systems the most effective sources of hydrogen ions generally are chemical reactions involving dissolved constituents. An important source is carbon dioxide gas, which is present in weathering solutions as a result of contact with air; it is produced in larger quantities by plant root respiration and decay of soil organic matter and by the metabolic processes of various organisms in water and sediment. equation 1 shows that some of the carbon dioxide that dissolves forms carbonic acid (note that in the following equations the arrows indicate the direction in which the reaction normally proceeds; reactants are on the left side and products on the right; double arrows indicate that reactions can proceed in either direction):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (1)$$

equation 2 shows that the acid dissociates to form bicarbonate ions and hydrogen ions:

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad (2)$$

and carbonate anions can be formed in a second dissociation step:

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad (3)$$

The H^+ that is supplied by reactions in Eqs. 2 and 3 can react with silicate minerals such as the sodium-bearing form of feldspar:

$$2\ NaAlSi_3O_8 + 2\ H^+ + 9\ H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + 4\ H_4SiO_4(aq) + 2\ Na^- \qquad (4)$$

albite hydrogen water kaolinite silicic acid sodium

to produce the clay mineral kaolinite, undissociated silicic acid (H_4SiO_4 which also can be written as SiO_2), and sodium ions. This is essentially an irreversible process (note the single arrow) in that albite is not readily synthesized from the reaction products under ordinary natural weathering conditions, and the reaction will continue to proceed to the right as long as reactants are available.

The hydrogen ion flux that is provided by carbonic acid dissociation also can attack calcite ($CaCO_3$):

$$CaCO_3 + H^+ \rightleftharpoons HCO_3^- + Ca^{2+} \qquad (5)$$

This reaction is relatively fast and readily reversible so that in drainage basins in carbonate-dominated terranes the stream water commonly will have near-equilibrium concentrations of hydrogen, bicarbonate, and calcium ions. At equilibrium, the rates of forward and reverse processes represented in equation 5 are equal.

In effect, the forward progress of reactions such as is shown in equations 4 and 5 will be controlled by the availability of hydrogen ions, but the final result, as indicated by the chemical composition of stream water from any given drainage basin, will be influenced by a complicated set of interrelated physical factors that influence the volume and rate of water movement, ecologic and climatic factors that control the type and density of plant and bacterial growth and soil development, and the human development of water and land resources. Thus, the geochemistry of stream water in any given drainage basin is unique to that basin. The historical record of water chemistry in a specific basin cannot be interpreted without giving proper attention to the way various hydrologic and other environmental factors in the basin have influenced the chemical composition of the water. An extensive body of research on the topic of global stream water geochemistry is summarized in Ref. 6, who agree with the need expressed in this paragraph for a broad consideration of cause and effect when evaluating stream water chemistry.

1.1.2. Effects of Human Activities

A considerable part of the currently existing motivation for organized long-term water quality studies has been public concern that human activities in many drainage basins have induced destructive changes in stream water quality. From examples cited in this article, such effects can indeed be documented. Also, in some basins water quality management has succeeded in correcting some of the human-caused deterioration and is substantially restoring the quality of the water. The concept of sustainability is relevant, and the development goal for drainage systems is to maintain suitable water quality while permitting levels of water use that will sustain the basin's existing and reasonable future economic development.

Human activities that alter stream flow characteristics and thus cause water quality changes include the building of structures that impound or regulate rates of stream flow, diversion of water from one drainage basin to another, irrigation of land adjacent to streams, and lowering of tributary groundwater tables by pumping from wells. Waste disposal, directly or indirectly, into streams also influences water quality by adding chemicals and suspended matter. Disposal of untreated organic waste into streams was common in urban and rural areas of the nation until the early twentieth century. Besides pathogenic bacteria in the waste, large amounts of organic chemicals and suspended material depleted the dissolved oxygen of receiving waters and killed much of the aquatic biota in some streams. Thus, the concentration of dissolved oxygen in stream water also is considered a contamination index. Normally, the dissolved-oxygen content is near the saturation level that can be calculated for water that is in contact with air at ambient temperature, but oxidizable material in solution, especially organic waste, can substantially deplete the dissolved-oxygen content. Additionally, phosphate (PO_4^{-3}) concentrations are indicative of contamination from waste sources. Phosphate is a constituent of domestic and industrial waste, in part, because of the widespread use of phosphate compounds as detergent additives.

Land use changes and related developments also can affect stream water quality. Examples include urbanization, clearing of forests, various agricultural practices, such as use of fertilizers and pesticides and return flow of drainage water from irrigated fields, and industrialization. Urbanization and industrialization lead to various side effects. Mining for coal and metals generally contaminates water during and after the mining activity. The smelting of ores to recover metals and the burning of coal to generate power release pollutants into the air, and eventually some of these pollutants find their way into water supplies. Metal ores, coal, and other organic fuels commonly contain, or are associated with, reduced sulfur. Oxidation of the sulfur by burning the fuel and smelting the ores and oxidation in the mines or in waste dumps when sulfides are exposed to air constitute major sources of sulfur in stream water. High metal concentrations commonly are found in streams draining metal-mining areas, and sodium chloride and calcium chloride are dispersed widely by salt and sand mixtures used to melt ice from highways.

1.2. Circulation Rates of Elements

The concept of cycling of individual elements, in part coupled to the hydrologic cycle, has been developed and quantified over the past half century. Besides the total quantities of the elements present in various reservoirs—bedrock (the lithosphere), soils, all forms of living matter (the biosphere), the oceans, the atmosphere, and fresh water—the rates of exchange and mechanisms of movement from one reservoir to another are considered in the cycle. This concept is highly relevant in developing a frame of reference for evaluating possible environmental effects of energy technology.

A simplified diagram representing the various reservoirs and transport mechanisms and pathways involved in the cycles of nutrient elements at and above the surface of the Earth is given in Figure 1. The processes are those considered to be the most important in the context of this article, but others of lesser significance can be postulated. For some of the elements, notably carbon, sulfur, chlorine, and nitrogen, considerable research has been done to evaluate (quantitatively) the amount of the various elements in the reservoirs and the rates of transfer.

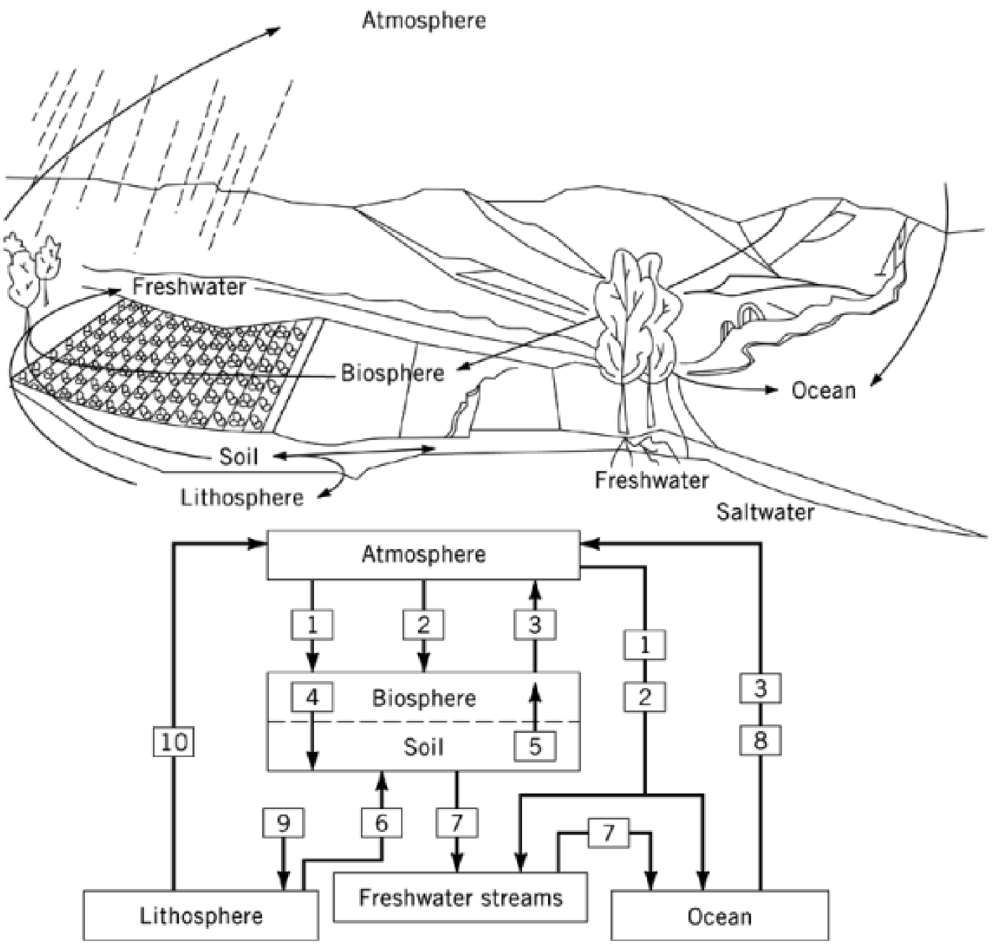

Fig. 1. Generalized cycle of the various reservoirs and transport mechanisms and pathways involved in the circulation of nutrient elements. The numbered arrows represent processes by which elements transfer among the reservoirs. Processes shown are those considered to have the most important influence on stream water quality. (Modified from Ref. 7.)

1.2.1. Carbon

Most of the Earth's supply of carbon is stored in carbonate rocks in the lithosphere. Normally the circulation rate for lithospheric carbon is slow compared with that of carbon between the atmosphere and biosphere. The carbon cycle has received much attention in recent years as a result of research into the possible relation between increased atmospheric carbon dioxide concentration, most of which is produced by combustion of fossil fuel, and the "greenhouse effect," or global warming. Extensive research has been done on the rate at which carbon dioxide might be converted to cellulose and other photosynthetically produced organic compounds by various forms of natural and cultivated plants. Estimates also have been made of the rate at which carbon dioxide is released to soil under optimum conditions by various kinds of plant cover, such as temperature-zone deciduous forests, cultivated farm crops, prairie grassland, and desert vegetation.

The efficiency of the weathering of rocks in using carbonic acid produced in the carbon cycle is affected by various hydrologic, environmental, and cultural controls. The fact that the principal anion in fresh surface water worldwide almost always is bicarbonate attests to the overriding importance of this process. Exceptions are systems in which evaporite minerals are available for dissolution by groundwater or where human activities are major sources of sulfate or chloride inflow.

Quantitative estimates of the magnitude of the carbon cycle, based mainly on a compilation in Ref. 8, suggest that the total amount of carbon dioxide converted to organic matter during a year might be as great as 7–9 tons/acre in midlatitude deciduous forests and about a tenth that amount in native grassland. Cultivated farm crops presumably convert somewhat more carbon dioxide per unit area than might be expected in native grassland. Respiration of carbon dioxide by plant roots is at a rate equal to about 25% of the total carbon dioxide used by the plants, and the potential supply of carbon dioxide from vegetation for weathering rock is about 1.65 tons/acre/yr on the average, over the whole land area of the Earth (8). This is equivalent to about 1060 tons/mi^2/yr of carbon dioxide. If all this carbon dioxide were dissolved in water and the resulting carbonic acid reacted with silicate minerals to maintain near-neutral pH, the annual bicarbonate yield could be as great as 1500 tons/mi^2. A drainage basin in a limestone terrane theoretically could produce bicarbonate at an even higher rate, as the reaction between dissolved carbon dioxide and solid carbonate minerals produces two bicarbonate ions per reacting dissolved carbon dioxide molecule.

As might be expected, the average rates of bicarbonate yield in drainage basins of the world are far below these numbers, as only a relatively small proportion of the carbon dioxide released in soil is likely to participate in rock weathering. A general indication of the role of dissolved carbon dioxide in weathering processes in streams can be obtained by calculating the average annual bicarbonate yield from average concentration of dissolved bicarbonate, average water discharge, and drainage basin area. Examples of this type of calculation can be obtained from published literature. Ref. 9 studied 56 drainage basins in the conterminous United States and Hawaii to determine the relative importance of stream temperature, human population density, atmospheric precipitation, and predominant type of bedrock (limestone, sandstone, or crystalline) as controls of constituent yield. Of the 19 limestone basins, the Kalamazoo River at Saugatuck, Michigan, had the maximum annual bicarbonate yield, which was about 324 tons/mi^2. However, in the other basins, annual bicarbonate yields were substantially lower—15 had less than 225 tons/mi^2, and the average yield for the 19 limestone basins was 114 tons/mi^2.

In general, bicarbonate yields reported in Ref. 9 were much smaller for basins in crystalline (noncarbonate) rock terranes than for those in limestone or sandstone terranes. Other investigators have reported relatively large bicarbonate yields for certain igneous terranes. For example, Ref. 10 reports large bicarbonate yields from igneous drainage basins in the Pacific Northwest. Among studies referred to is a study for a basin having an active glacier in the northern Cascade Mountains of Washington (11). In this basin, the annual bicarbonate yield was near or slightly greater than 100 tons/mi^2.

The high bicarbonate yield in some of the Pacific Northwest streams could be the result of glacial action and mechanical erosion of rock material in basins having steep slopes that produce large amounts of relatively freshly fractured and fine-grained sediment that would participate readily in dissolution and alteration reactions. The rate at which such reactions would proceed is a function of net surface area of sediment available per unit volume of runoff and the length of time such material was exposed to water in the runoff process. Therefore, the efficiency of solvent erosion under conditions in the Pacific Northwest region could be considerably increased by such factors.

The chemical analyses tabulated in this article identify “alkalinity” as a property of the water rather than a simple constituent. Alkalinity has been more broadly defined as “capacity for acid neutralization” (12, 13). Common practice in water analysis is to report alkalinity in terms of bicarbonate and carbonate concentrations, although other ionic species also may contribute by reacting with the titrating acid.

1.2.2. Sulfur

The cycle of sulfur in weathering environments is affected by a more diverse set of reactions than for carbon. As is the case with carbon, most of the Earth’s supply of sulfur is stored in the lithosphere (5). Although some sulfur actually is taken up by vegetation, the growth and decay of plants does not tie up large proportions of the total sulfur supply. The element's geochemical behavior in the environment is summarized in Ref. 14. In igneous and metamorphic rocks, sulfur generally is present in the chemically reduced sulfide form (S^{2-}) and commonly is associated with metals. Polysulfide minerals in which the nominal valence of sulfur is between -2 and 0 also are common. An example is pyrite (FeS_2), which commonly occurs in association with coal seams and other sediments laid down under conditions where free oxygen was not available.

In weathering environments where oxygen is continuously available, negatively charged reduced forms of sulfur are converted to positively charged oxidized forms such as sulfate (SO_4^{2-}) in which the sulfur is in the fully oxidized (S^{6+}) state. Oxidation and reduction reactions of sulfur commonly are bacterially mediated. The calcium sulfate minerals gypsum ($CaSO_4{\cdot}2H_2O$) and anhydrite ($CaSO_4$) are common constituents of evaporite rocks, and in semiarid regions where such rocks are near the land surface, stream water can contain substantial concentrations of sulfate. However, streams in humid regions generally carry relatively low concentrations of sulfate unless human activities have intervened. Weathering reactions that involve oxygen are important in the development of soils, especially in humid and subhumid climates. Commonly, oxygen is in relatively short supply at shallow depths in the soil zone, having been depleted by oxidation of organic matter. In wetland soil and submerged sediments, oxygen can be in very short supply and sulfur is in reduced form. However, as noted in Refs. 15 and 16, the sulfur in aerated soil is principally a component of organic compounds. In any event, any reduced species of sulfur may be converted to sulfate by oxidation when wetlands are drained or soils are converted from their natural state to agricultural cropland. All these processes can increase the availability of sulfate for transport by streams and cause increased sulfate loads in areas affected by development.

Geochemical studies of sulfate in streams have been approached in various ways. For example, Ref. 17 is a review of literature on sources of sulfate in the dissolved loads of streams, especially in areas where development effects are likely to be strong. It was concluded that for North America as much as 60% of the average yield of sulfate carried to the ocean is related to human activities. This study assigned a higher proportion of the total yield of sulfate in European streams to human sources, but for other continents it was thought the effects of human activities to be relatively minor.

Some of the compounds produced in the sulfur cycle are gases. For example, combustion of fossil fuels, especially coal, produces sulfur dioxide gas (SO_2), which is further oxidized in the atmosphere to sulfur trioxide (SO_3) that combines with water to form sulfuric acid (H_2SO_4). Reduction of sulfate in anaerobic soils and sediment produces hydrogen sulfide (H_2S) gas that also is reoxidized to sulfate in the presence of air. As a result, precipitation from the atmosphere is a major source of sulfate in streams in parts of North America and Europe. The estimate for human sources includes both sulfur dioxide and hydrogen sulfide reaction pathways (17). A compilation by the U.S. Environmental Protection Agency (18), summarizing research on acidic deposition, quoted estimates and measurements of "excess sulfate" yields in precipitation and in lakes and streams in the northeastern United States and southeastern Canada. Among measured data cited was a wet-plus-dry annual sulfate deposition rate for a site in the Adirondacks that ranged from about 8.2 to 16 tons/mi^2. Although a wide range of values was observed, these rates probably can be considered reasonable for much of the eastern half of the United States. The term "excess sulfate" is defined as the amount "over and above that supplied by sea salt cycling." Ref. 9 estimates that, on average, 60% of the sulfate yield observed for the stream basins he studied was assignable to atmospheric sources.

Another source of sulfur in the global hydrologic cycle that is not related to human activities is gaseous emission of hydrogen sulfide and sulfur dioxide from volcanoes and other geothermal sources. Although effects of these emissions can be locally intense, they generally are thought to be much less significant on a global scale than the human sources.

Sulfate concentration in streams and changes over time are discussed later in this article as one of the principal indices of human influences on stream water composition. Also, it will be shown that differences and similarities in sulfate yields help in attaining a reasonable perspective on the importance of various hydrologic and geochemical characteristics of individual drainage systems.

1.2.3. Chlorine

Nearly all chlorine compounds are readily soluble in water. As a result, the major reservoir for this element in Figure 1 is the ocean (5). Chloride, as noted earlier, is naturally present at low levels in rain and snow, especially over and near the oceans. Widespread increases in chloride concentration in runoff in much of the United States can be attributed to the extensive use of sodium chloride and calcium chloride for deicing of streets and highways. Ref. 19 points out the importance of the increased use of deicing salt as a cause of increased chloride concentrations in streams of the northeastern United States and the role of this factor in the chloride trends in Lake Ontario. Increases in chloride concentration also can occur as a result of disposal of sewage, oil field brines, and various kinds of industrial waste. Thus, chloride concentration trends also can be considered as an index of the alternation of streamwater chemistry by human development in the industrialized sections of the world. Although chlorine is an essential element for animal nutrition, it is of less importance for other life forms.

1.2.4. Nitrogen

About three-fourths of the Earth's nitrogen is present in the atmosphere as nitrogen gas. Because of its importance as an essential element in plant and animal nutrition, nitrogen, in its various oxidation states and its yield and concentration, is of considerable interest in studies of human influences on stream water composition. Certain small- and medium-sized streams in the intensively developed agricultural areas of the United States have been strongly affected by nitrogen-bearing runoff from fertilized soil. However, because of its use by aquatic vegetation, the amount and form of nitrogen tend to be seasonally variable, and especially for larger streams, it is more difficult to use than sulfate or chloride as an index of human effects on water composition. Although nitrate concentrations are reported in some of the streams, no attempt at interpretation of the nitrogen chemistry is made here; however, Ref. 20, using mainly U.S. Geological Survey (USGS) data, evaluates nitrogen trends since 1905 in the Mississippi River at St. Francisville, Louisiana.

2. Stream Water Quality Trends

2.1. Data Available

The first comprehensive nationwide study of the chemical composition of surface water in the United States was begun by the USGS in 1905. This program received cooperative support from state agencies in Illinois, Minnesota, Kansas, California, Oregon, and Washington and entailed collection of daily samples of water at or near gaging station sites on principal streams for a period of about one year. The daily samples were combined into 10-day composites, which were filtered to remove suspended material and analyzed for principal dissolved constituents using standard "wet-chemical" procedures. As a result of decreased funding and related factors, this work was substantially curtailed after 1907; however, the studies did produce compilations of analyses for about 100 stream-sampling sites east of the 100th Meridian (21) and for about another 55 sites in the western part of the country (22). Somewhat more detailed reports for each of the six cooperating states also were issued in the USGS Water-Supply Paper series, and Clarke (23) used many of the analyses from the program in his summary of the composition of river and lake waters of the United States.

From about 1914 to 1940 studies of river water quality were carried on at only a few sites in the United States. A revival of interest began in the 1940s, however, and by the 1960s, a much larger number of sampling sites were in operation than had existed at the height of the 1905–1907 program. The available historical data base for most U.S. sampling stations has no water quality measurements for the 1910–1940 period.

Stream water quality commonly varies greatly in response to water discharge; thus, a single year of record is not adequate for reliable extrapolation, and in any exacting comparison of historical data, this factor needs to be taken into account. From the beginning, it has been a general policy in the USGS surface water quality program to locate sampling sites at or near gaging stations where records of stream flow are obtained. Until about 1970, many of the USGS water quality records were based on daily sampling, generally with determinations of specific electrical conductance (an indicator of total cation and anion concentration) on each sample, but with extensive analyses performed only on composited daily samples. Composites usually contained 10 daily samples. However, where stream discharge and other factors caused substantial day-to-day changes in specific conductance, the composite period was shortened to prevent mixing of chemically dissimilar samples and to give a clearer indication of the stream chemistry variability. Annual averages of these analyses, weighted by time or discharge, were used to summarize the records. After 1970, complete analyses were done on single samples collected at various time intervals ranging from semimonthly to quarterly, and analyses of composite samples were no longer made. Analytical procedures changed from time to time as improved instrumentation and techniques became available.

In order to identify and consider the importance of the various sources and controlling factors that operate in specific drainage basins in the United States to produce water having hydrochemical properties that are characteristic of each basin, four drainage basins having long-term hydrologic and water chemistry records were chosen for study in the original version of this article (24)—the Great Lakes—Upper St. Lawrence River at and near Ogdensburg, New York, and Cornwall, Ontario, Canada; the Columbia River at and upstream from the Dalles, Oregon; the Allegheny River upstream from Pittsburgh, Pennsylvania; and the lower Mississippi River at and upstream from New Orleans, Louisiana. However, these discussions are beyond the scope of this article. The Great Lakes study is given here as an example. For more details, refer to Ref. 24.

The historical records mentioned above are compared with more recent data for each of the drainage basins in order to detect and explain major differences between water composition observed early in the twentieth century and that observed more recently. Sulfate, as mentioned earlier, is one of the principal indicators of the effects of human activities on stream water composition, and it is the principal indicator used in the following discussions. The records selected for study display general trends in concentrations and yields that appear to be well-enough defined to outweigh the influences of different sampling frequencies and changing compositing practices. Trends that can be detected in the data collected in the past 20 years generally are too subtle to be evaluated closely by the methods used in this article and are more appropriately studied by the more sophisticated procedures which are described in Refs. (3, 25), and 26.

Selected analytical and related data for the example drainage basin are given in Tables 1 and 2. Apparent trends with time are evaluated by various means described in the text. The annual minimum and average constituent concentrations and annual yields of sulfate in tons per unit area of drainage basin are the focus of the discussion.

2.2. Other Constituents of Stream Water

The records reported in Refs. 21 and 22 were obtained for the primary purpose of evaluating the suitability of surface water resources of the United States for utilization by industry and for irrigation of agricultural lands in the western part of the country. These stream waters also provide public water supplies for many municipalities. Evaluations of water quality for the latter purpose emphasize constituents that were not given detailed consideration in Refs. 21 and 22 summaries, although there are references in Ref. 21 to work done in various state health laboratories and municipal treatment plants.

2.3. Surface Water Ecology

Ecologic studies of contaminated and uncontaminated streams have been the subject of extensive research. Those streams that have been subjected to contaminant additions through disposal of industrial and other forms of waste generally show substantial decreases in the diversity and abundance of instream biota. These effects are often first observed in decreases of native game fish such as brook or rainbow trout, but more

Table 1. Chemical Composition of Water and Related Data for St. Lawrence River, Representing Outflow from Lake Ontario, Selected Years (1906–1990)

	Ogdensburg, N.Y.	Cornwall, Ontario, Canada		Ogdensburg, N.Y.		Cornwall, Ontario, Canada		
Constituent property, and related data	1906–1907[a] (1)	1935[b] (2)	1940[b] (3)	1956[c] (4)	1969[d] (5)	1977[b] (6)	1980[b] (7)	1990[e] (8)
silica (SiO_2)	6.6	6.9	4.1	3.5	0.6	0.2	0.5	
calcium (Ca)	31	33	36	36	39	38	36	
magnesium (Mg)	7.2	7.9	8.5	8.2	7.3	8.0	7.8	
sodium (Na)	{6.3[f]	7.3[f]	7.5[f]	9.7	12	13	13	
potassium (K)				1.5	1.3	1.6	1.4	
alkalinity as bicar-bonate (HCO_3) (property)	122	110	97	112	110	110	99	
sulfate (SO_4)	12	19	21	25	28	27	26	27
chloride (Cl)	7.7	15	16	21	26	27	26	
fluoride (F)				0.1	0.1	0.1	0.2	
nitrate (NO_3)	0.3	0.6	1.0	1.0	0.3	0.53	0.49	
dissolved solids	134	156	158	179	169	169[g]	160[h]	
specific conductance, μS at 25°C (property)				299	314	370	270	300
pH units (property)		8.0	8.0	6.8–7.9	7.3–8.0	7.8	7.1	
drainage area, mi^2	295,200	298,800	298,800	295,200	295,200	298,800	298,800	298,800
average discharge, ft^3/s	242,300	192,000	226,000	257,000	270,000	250,000	296,000	264,800

Note: Concentration values are in milligrams per liter unless otherwise noted. Data from the Ogdensburg, N.Y., and Cornwall, Ontario, Canada, stations are considered equivalent. *Sources:* column 1, ref. 21; columns 2, 3, ref. 36; column 4, ref. 34; column 5, ref. 35; columns 6, 7, ref. 2; column 8: U.S. Geological Survey, New York District office written communication, 1991.

[a] Average of 11 monthly samples, Sept. 1906–Jan. 1907, March–Aug. 1907.

[b] Single sample collected on Aug. 30, 1935 (col. 2), Aug. 22, 1940 (col. 3), June 27, 1977 (col. 6), and Sept. 29, 1980 (col. 7).

[c] Average of 10-day composite samples collected during water year 1969.

[d] Average of 10 individual monthly samples collected during water year 1969.

[e] Average of 5 bimonthly samples collected between October 1989 and July 1990.

[f] Sodium and potassium not determined separately; value reported is total $Na + K$ expressed as an equivalent amount of sodium.

[g] Maximum total dissolved solids for period 1977–1980.

[h] Minimum total dissolved solids for period 1977–1980.

Table 2. Estimated Annual Yield of Constituents (t/mi^2), St. Lawrence River Outflow from Lake Ontario, Selected Years (1906–1990)

			Ogdensburg, N.Y.		Cornwall, Ontario, Canada		
Constituent or property	Ogdensburg, N.Y., 1906–1907 (1)	Cornwall, Ontario, Canada, 1937 (3)	1956 (5)	1969 (6)	1977 (7)	1980 (8)	1990 (9)
calcium (Ca)	25.0	24.2	30.9	35.1	31.3	35.1	na
sodium (Na)	5.1[a]	6.7[a]	8.3	10.8	10.7	12.7	na
bicarbonate (HCO_3)	98.6	75.9	96.0	99.0	90.6	96.5	na
sulfate (SO_4)	9.7	14.8	21.4	25.2	22.2	25.4	23.6
chloride (Cl)	6.2	10.8	18.0	23.4	22.2	25.4	na

Note: Calculated from data in Table 1 using the equation tons per square miles = annual average constituent concentration in milligrams per liter × annual average stream discharge in cubic feet per second × conversion factor 0.9844 divided by drainage area in square miles. Column numbers are those used in Table 1. na, data not available for calculation.

[a] Equivalent amount of sodium from combined sodium and potassium.

extensive research has shown many more subtle changes. A compilation (27) includes summaries of ecologic studies in 12 river basins in North America.

The drainage basin of the Clark Fork, an eastern tributary of the Columbia River, has been affected for long distances by the copper mining and ore treatment processes that were conducted at Butte and Anaconda, Montana, for about 125 years, ending in 1982. Conditions in this stream have been described (28). A more recent paper (29) pointed out that many streams in mineralized areas had relatively high metal concentration prior to the beginning of mining activity.

2.4. Means for Summarizing Dissolved-Material Contents

Water analyses traditionally have included a summarizing value termed "total dissolved solids." A determined value specified as "residue on evaporation" (ROE) is obtained by evaporating a measured volume of the water sample to dryness in a dish whose weight is known exactly, drying the residue at a specified temperature (in USGS practice at 180°C for 1 h), and weighing the dish and its contents after cooling in a moisture-free atmosphere. The more modern analyses also include electrical conductance, which is related to the total concentration of dissolved cations and anions, and electronic determination of pH, which is a measure of the acidity or hydrogen ion (H^+) activity. Although the ROE procedure appears to be simple and direct, it has complicating factors. The bicarbonate in solution in the original sample is converted to carbonate by drying, with loss of an equivalent amount of carbon dioxide gas. However, some types of water, such as those having high concentrations of dissolved calcium and sulfate, can deposit residues that contain water incorporated in crystalline minerals such as gypsum ($CaSO_4 \cdot 2H_2O$). To avoid this problem, a calculated total dissolved solids (SUM) commonly is reported for water containing more than about 1000 mg/L total constituent concentration. The SUM calculation is made by adding reported concentrations for all the major constituents, with a correction factor converting dissolved bicarbonate to an equivalent carbonate content of the dried residue.

3. Example: Great Lakes–Upper St. Lawrence River

The St. Lawrence River, at the outlet of Lake Ontario, represents the drainage from the Great Lakes basin and has a relatively constant chemical composition, owing to the large storage capacity of the lakes and their efficiency in mixing of inflow. The water surface of the Great Lakes makes up a substantial fraction of the basin area. The basin also has a relatively constant water discharge. These characteristics make it a good site for study of water quality trends. Data from two water-quality-sampling and stream-flow-gaging stations—Cornwall, Ontario, Canada, and Ogdensburg, New York (40 miles upstream from Cornwall)—are used to show constituent change over time. Although the two stations are 40 miles apart and there is a small amount of tributary inflow between them, the chemical composition of the water at the sites does not differ significantly and thus can be used for comparison of data over time. At Cornwall, the drainage area of the St. Lawrence River is 298,800 mi^2 and the long-term average discharge is 245,000 ft^3/s, as reported by the U.S. Geological Survey (30).

Data from these stations are summarized briefly in Table 1, where each of the columns represents data for a particular year progressing from 1906–1907 to 1990. The data show that principal dissolved-ion concentrations in the river were nearly constant during the period 1969–1980 and that most of the change occurred between 1907 and 1956. Data for some major ions for samples from Lake Ontario that were presented (31) indicate that relatively continuous increases occurred until the 1960s. An illustration in Ref. 2 based on a graph from Ref. 32 suggests that sulfate concentration in Lake Ontario steadily increased from 12–14 mg/L in 1906 to 28–30 mg/L in the 1970s. However, during the 1980s, the sulfate concentration in the lake as represented by the St. Lawrence River at Cornwall did not show any further upward trend, and it seems likely that the sulfate concentration had stabilized. Samples taken at 1- or 2-month intervals during water years

1981–1985 had sulfate concentrations of 28 mg/L or more on 11 occasions. During water years 1986–1990 no sulfate concentrations greater than 27 mg/L were observed at Cornwall.

Behavior of chloride concentration during the period of record was somewhat similar to that of sulfate—about a threefold increase compared to the doubling of sulfate. Data in Table 1 indicate that a long-term decrease in bicarbonate of 10–20 mg/L is a reasonable estimate.

Refs. 32 and 33 attribute the historical changes in water composition of the Great Lakes to human activities, which have increased as the population of the drainage basins of the lower four lakes has increased since the beginning of the twentieth century. Industrial waste and incompletely treated sewage are thought to be major sources of sulfate and chloride. Other nonpoint sources are agricultural fertilizers and fossil fuel combustion and urban runoff that add sulfate and sodium and calcium chlorides used for deicing highways. The decrease in alkalinity of the water leaving Lake Ontario can possibly be explained as a direct consequence of the low pH of rain that falls on all the lakes. However, because the loss of bicarbonate alkalinity is only about two-thirds as great as the gain in sulfate, the observed changes cannot be simply assigned to sulfuric acid in this rainfall. It seems more likely that some of the acidity in the rain that falls over the tributary drainage is neutralized by reaction with sedimentary rock minerals, as calcium and sodium show increases.

During the 1960s there was much concern about the increasing rate of eutrophication of Lake Erie. The limiting nutrient for aqueous microbiota in the Great Lakes was perceived to be phosphorus (33), and household synthetic detergents containing sodium phosphate were thought to be an important source. Consequently, a concerted effort was made to decrease the sale of detergents containing phosphate and to improve sewage treatment processes. By the 1980s, some declines in phosphate concentration had occurred in Lake Erie and Lake Ontario (33).

An accompanying effect of eutrophication that is more readily observable in Table 1 is a decrease in silica concentration in Lake Ontario. Some decline in dissolved silica apparently has occurred in all of the lakes except Lake Superior. This decline is brought about by the growth of diatoms, a species of aquatic microorganisms in the upper layers of lake water that is widespread in all types of water impoundments where the water is clear and exposed to the sun. The silica is used by these microorganisms to form their skeletons and is later precipitated and becomes part of the bed sediment.

Silica determinations on the 1906–1907 St. Lawrence samples (Table 1, col. 1) might have been affected by inadequate filtration, and possibly some silica was dissolved from the glass sample bottles during storage before analysis. Thus, the average silica concentration of 6.6 mg/L might be too high. However, a rather well-defined downward trend is observable in more recent silica concentration records for the St. Lawrence at Ogdensburg and Cornwall that has greater experimental certainty. Determinations of dissolved silica on individual samples collected during water year 1956 ranged from 1.1 to 6.8 mg/L (34). A record of once-monthly samples from water year 1969 (35) shows silica concentration that ranged from a low of 0.0 (below the minimum reporting limit) to a maximum of 1.9 mg/L. Samples taken during water years 1977–1980 show concentrations of 0.2 and 0.5 mg/L (Table 1, cols. 6, 7).

The Lake Superior drainage basin is underlain predominantly by metamorphic and igneous rocks, whereas most of the Great Lakes drainage area eastward to the outlet of Lake Ontario is underlain by carbonate-rich sediment. It would be expected, therefore, that the water of Lake Superior would have different chemical characteristics than those of the other Great Lakes because it has a different set of geochemical controls. Also, the major ion composition of water in Lake Superior has not changed significantly during the period of record.

Additional insight into changes in dissolved material flowing from the lakes over time can be obtained by calculating average annual yields of major constituents observed in the Great Lakes–St. Lawrence basin (Table 2). Ref. 9 contains calculations of the annual yields of principal constituents for 56 drainage basins and evaluated the degree of correlation with four environmental factors—bedrock type, annual precipitation, population density, and average stream temperature. The study shows that in basins dominated by limestone bedrock, the average annual yield for calcium was 36.0 tons/mi^2 and for bicarbonate was 114.2 tons/mi^2. Calcium yields listed in Table 2 for the 1956–1980 period are close to the averages reported by Peters (9) and

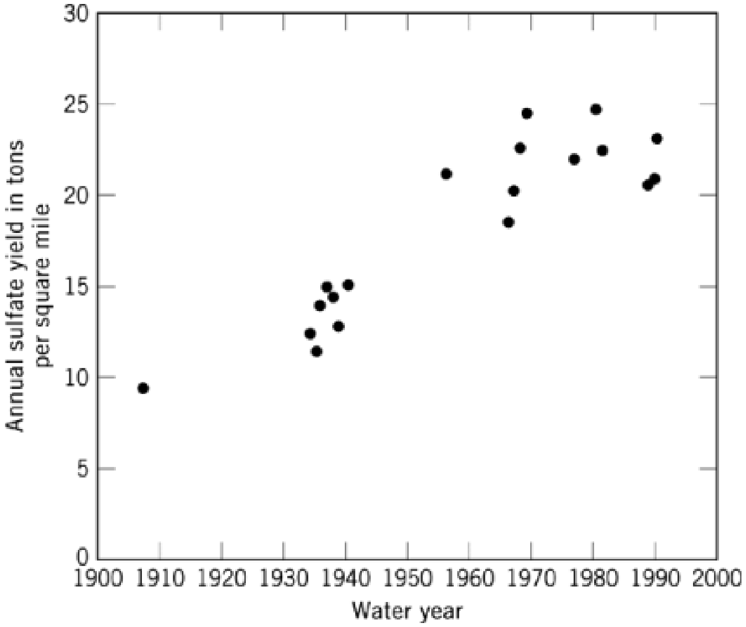

Fig. 2. Annual sulfate yields of the St. Lawrence River at Cornwall, Ontario, Canada, 1906–1990. (Calculated from data in U.S. Geological Survey water-resources records and Ref. 36.)

are significantly higher than yields for 1906–1907. However, the bicarbonate yields indicated in Table 2 are lower than the average reported by Peters and show no well-defined trend. Eight of the 56 streams studied by Peters are tributaries of the Great Lakes–St. Lawrence system, and the average of the annual sulfate yield reported for these eight streams was 28.5 tons/mi^2. This finding agrees approximately with the sulfate yield of 25.4 tons/mi^2 given in Table 2 (col. 8) for Cornwall during water year 1980, considering the rather wide range of annual sulfate yields in the eight basins that were selected.

Although the substantial effects of human activities on the composition of the Great Lakes water is well documented by the data cited here, the system as a whole in recent years has shown a substantial ability to maintain a relatively high degree of chemical stability. The effect of acidic precipitation, for example, has not significantly depleted the capacity of the system to neutralize acid as has occurred in smaller lakes and streams in noncarbonate terranes in other parts of the northeastern United States. Although further increases in sulfate concentration in the lower Great Lakes have been predicted by various investigators (33), the concentrations of sulfate and chloride in the St. Lawrence River just downstream from the outlet of Lake Ontario appear to have remained the same or perhaps declined slightly since about 1980 (26).

The annual yields of sulfate during 1906–1990 for the St. Lawrence–Great Lakes basin (Fig. 2) are influenced considerably by differences in water discharge from year to year. The maximum values of about 25 tons/mi^2 in 1969 and 1980 and 23 tons/mi^2 in 1990 represent discharges substantially above the long-term average. The minimum yield for 1960–1970, 18.8 tons/mi^2, occurred in 1966, a year that had below-normal discharge. However, the yield more than doubles between 1906 and 1956 and has an upward trend through about 1970.

4. Summary

Under pristine conditions, that is, in the absence of human civilization and development, the chemical composition of inland stream and lake waters is, ideally, controlled by the alteration of rock minerals through chemical weathering processes, which liberate soluble products. These processes in turn are controlled or influenced by climatic factors such as rainfall, air temperature, and evaporation and by associated biological or biochemical processes, such as photosynthesis and transpiration by plants, decay of vegetative debris, and the effects of aquatic life processes. Circulation of essential nutrient elements, including carbon, sulfur, chlorine, and nitrogen, generally is bound to elemental oxygen from the atmosphere and provides most anionic species occurring in natural water, such as bicarbonate, sulfate, chloride, and nitrate. Other constituents of natural surface waters, including calcium, magnesium, sodium, and potassium, can be correlated in general with the chemical composition of rocks and soils in a given drainage basin and are found as principal cationic species and are in electrochemical balance with anions in these waters.

The influence of human activities in a stream drainage basin can be relatively simple and direct, as in the disposal of soluble organic and inorganic waste, or more subtle and complex, as in the conversion of prairie or forest land to agricultural use. Such effects can be expected to increase as population density and agricultural, industrial, and mining activities increase.

In the Great Lakes–Upper St. Lawrence River basin, for example, the yield of sulfate in tons per square mile per year in the St. Lawrence River nearly doubled between 1905 and 1956 and continued to increase, but at a lesser rate, until about 1970, when the yield leveled off or perhaps even declined slightly. The continuing yield of between about 19 and 25 tons/mi^2 indicates that the basin may have reached a steady state between the natural and human-induced loading of sulfur to the basin and its removal by the St. Lawrence River. In contrast, sulfate concentrations in the upper Columbia River basin at Northport, Washington, show less clearly defined trends in sulfate concentrations and yields during the century (24). These data indicate that human-induced effects are largely masked by the large amount of runoff available in the Columbia River basin and by the effects of storage and mixing in lakes and reservoirs.

Coal mining was extensive in the Allegheny River drainage basin in Pennsylvania in this century, and sulfate concentrations in the river near Pittsburgh increased substantially between the early 1900s and 1962 as a result of drainage from many active and abandoned coal mines. The operation of flood control and multipurpose reservoirs in the basin has caused a nearly 50% decline in sulfate concentration in the Allegheny River near Pittsburgh at low flow, as shown in analysis of samples collected in 1947 and compared to samples collected in 1975 and 1989 (24). This flow augmentation by timed reservoir releases has had a beneficial effect on the quality of the Allegheny River.

The Mississippi River drains more than 1,125,000 mi^2 of the conterminous United States and integrates the effect on stream water quality of a large range of human activities across a large continental area. The calculation of sulfate yield in the basin has many uncertainties because water quantity and water quality data are incomplete, and the effects of flow control and water diversions are difficult to measure. However, from the available data it can be estimated that sulfate concentrations in the lower Mississippi River at and upstream from New Orleans, Louisiana, probably have doubled between 1905–1906 and 1989; most of this increase seems to have occurred before 1980 (24). Estimates of the increase in annual sulfate yield due to human activities since 1905 ranging from about 9 to about 14 tons/mi^2 are consistent with the increase in sulfate yields in the Great Lakes–St. Lawrence River system. In both instances, yields seem to have leveled off around 1970 or 1980 and to have remained fairly stable since. Possibly, both drainage systems have reached a steady state, and the natural and human-induced sulfate loading to the basins, much of it from atmospheric deposition, is now stable. Data for total SO_2 emissions for each state from 1965 to 1980 (37) show that in most states adjacent to the Great Lakes the emission rates decreased significantly after 1970.

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