Evaluation of Environmental Factors Affecting Yields of Major Dissolved Ions of Streams in the United States



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# Evaluation of Environmental Factors Affecting Yields of Major Dissolved Ions of Streams in the United States

By NORMAN E. PETERS

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## Evaluation of Environmental Factors Affecting Yields of Major Dissolved Ions of Streams in the United States

#### By Norman E. Peters

#### Abstract

The seven major dissolved ions in streams sodium, potassium, magnesium, calcium, chloride, sulfate, and bicarbonate—and their sum dissolved solids from 56 basins in the conterminous United States and Hawaii were correlated with bedrock type, annual precipitation, population density, and average stream temperature of their respective basins through multiplelinear-regression equations to predict annual yields. The study was restricted to basins underlain by limestone, sandstone, or crystalline rock. Depending on the constituent, yields ranged from about 10 to 100,000 kilograms per square kilometer. Predicted yields were within 1 order of magnitude of measured yields.

The most important factor in yield prediction was annual precipitation, which accounted for 58 to 71 percent of all yields. Rock type was second in importance. Yields of magnesium, calcium, bicarbonate, and dissolved solids from limestone basins were 4 to 10 times larger than those from sandstone or crystalline basins as a result of carbonate weathering. Population density was an ineffective indicator of all constituents except sodium and chloride; it accounted for 13 percent of the annual sodium yield and 20 percent of the annual chloride yield. Average stream temperature was significant only for calcium and bicarbonate in limestone basins. Its relationship with yields was consistently negative. Either carbonate dissolution increases at low temperatures, or weathering in northern basins, which contain glacial deposits and have the lowest stream temperatures, is greater than in southern basins.

Average ion contributions from atmospheric deposition accounted for 30 percent of the sodium and chloride and 60 percent of the sulfate in annual yields. The amount of sulfate derived from atmospheric contributions was higher in sandstone and crystalline basins (65 and 80 percent, respectively) than limestone basins (38 percent). This disparity is attributed to the lack of available sulfate in crystalline rock and the chemical precipitation of sulfate in the sandstone basins, most of which are in semi-arid or arid areas.

#### **INTRODUCTION**

Streamwaters of the United States differ widely in chemical composition (Clarke, 1924; Livingston, 1963; Briggs and Ficke, 1977), especially in the major cations (potassium, sodium, magnesium, and calcium) and major anions (chloride, sulfate, and bicarbonate). The annual yields of dissolved ions in stream water are derived mainly from only a few sources. Three major ones are the rocks and soils of the drainage basin, atmospheric deposition, and substances derived from man's activities (Hem, 1970). These sources, in turn, are affected by four main environmental factors-climate, geology, topography, and biota-and by time (Gorham, 1961; Gibbs, 1970; Hem, 1970). Because the relationships between the amount of dissolved ions contributed by specific sources and the amount actually transported in streams are complex and variable, the influence of a specific source on a stream or drainage system is difficult to quantify.

The studies described below indicate a certain consistent relationship between concentration or transport of a dissolved constituent in streams and various basin characteristics. Streams in basins underlain by noncalcareous and nonevaporitic bedrock generally have low dissolved-solids concentrations; streams draining sedimentary terrain generally have high dissolved-solids concentrations. In basins adjacent to an ocean or containing no major internal source of a given constituent, atmospheric deposition may be a direct and major contributor of that constituent to streams. Basins having large annual precipitation quantity generally yield large quantities of dissolved material. Also, areas receiving large amounts of precipitation generally contain more organic material than arid regions and, therefore, through the supply of carbonic acid from organic decay, undergo more intense weathering, which in turn affects stream composition. Man's activities also contribute a variety of constituents to streams; these contributions are related to the type of activity and population density and may be independent of climate or basin lithology.

#### **Purpose and Scope**

This study was conducted to delineate the relationships between the environment and the sources and yields of major dissolved ions in streams. Through multiplelinear-regression analysis, annual ion yields from basins in the conterminous United States and Hawaii were examined as a function of the four major environmental factors: (1) rock type underlying a drainage area, (2) amount of annual precipitation, (3) population density, and (4) average stream temperature.

Although the purpose was to quantify the effects that these factors have on stream-water chemistry, the results may also be used in investigations of crustal and oceanic evolution to determine transport of major dissolved ions to ancient oceans and by water-resource planners to select long-term stream monitoring sites for assessing changes in the chemical composition of streams.

#### **Previous Studies**

Many aspects of stream chemistry have been addressed in previous studies. Results of these studies are summarized for the following factors: bedrock type, precipitation quality, precipitation quantity, stream temperature, and human activity.

#### Relationship between Bedrock and Ion Concentration in Streams

The type of rock underlying a drainage basin is a major influence on the chemical composition of stream water draining that basin (Miller, 1961; Garrels, 1967; Douglas, 1968; Reeder and others, 1972; Johnson and Reynolds, 1977).

Many investigators have been able to identify rock types within drainage areas from the dissolved-solids concentration in streamflow. Dissolved-solids concentration is a summation of all dissolved ions and is, therefore, a measure of the contribution from all sources. Of the dissolved solids carried to the ocean by streams, 95 to 99 percent consists of the major ions noted above plus silica (Mackenzie and Garrels, 1966; Meybeck, 1977).

Conway (1942) related waters with salinity (dissolved solids minus organic matter) of less than 50 mg/L to crystalline (igneous) rock basins, and waters with salinity exceeding 200 mg/L to sedimentary terrains. He attributed salinity values between 50 and 200 mg/L to a combination of both rock types. He also noted that, as salinity in-

creases toward 200 mg/L, the percentage of calcium, magnesium, and carbonate in these waters increases in relation to the other ions, a phenomenon he ascribed to the weathering of carbonate minerals within the sedimentary rocks.

In a study comparing the chemical character of streams in the Sangre De Cristo Range, N.Mex., Miller (1961) reported that the ratio of dissolved-solids concentration in streams draining quartzite basins to that in granite basins was 1:2.5 and to that in sandstone basins was 1:10. He attributed the higher dissolved-solids concentration in the sandstone basins to the weathering of carbonate cement and thin limestone interbeds and also noted that the size of the drainage basin did not affect the dissolvedsolids concentration of these streams.

In a similar study of headwater streams in Vermont and New Hampshire, Johnson and Reynolds (1977) observed that the lowest dissolved-solids concentrations in streams (12.8 to 18.6 mg/L) were associated with basins underlain by plutonic (granitic) rock and that basins containing metamorphic and sedimentary bedrock had substantially higher dissolved-solids concentrations (32 to 224 mg/L). They also noted that the bedrock types could be identified on the basis of combined ion percentages in stream water.

In a study of relationships between net dissolvedsolids yields (dissolved solids minus precipitation contribution) and discharge in streams draining basins of various rock types in the Northeastern United States, Feltz and Wark (1962) found that the lowest dissolved-solids yields were associated with basins underlain by granite or sandstone and that the highest were associated with basins underlain by limestone or dolomite. They also reported that the smallest change in net dissolved-solids concentration for a unit change in discharge was in a stream draining granite.

Biesecker and Leifeste (1975) examined the relationship between maximum TDS concentration and average annual runoff (average volume of water discharged by a stream per year divided by the basin drainage area) for streams draining single rock types in the United States. The intercept from the relationship was larger and the slope steeper for granite and sandstone basins than for either limestone or volcanic basins. They suggested that granite or sandstone is less permeable than limestone or volcanic rock; that, because low permeability results in longer residence time of waters within the rocks, the maximum dissolved-solids concentration of waters from granite or sandstone is higher than that of waters derived from limestone or volcanic rocks. Biesecker and Leifeste also found that mineral dissolution is slower in the granite or sandstone basins and that, as precipitation and runoff increase, water draining granite and sandstone basins becomes more diluted than water from limestone or volcanic basins.

Hack (1960), in a study of streams in the Shenandoah River Valley, found the lowest concentrations of solutes to be in streams draining quartzite basins and the highest to be in streams from carbonate basins. Also, the ratio of magnesium plus calcium to sodium plus potassium was lower in waters draining the quartzite basins than in those draining the carbonate basins, which corroborates Conway's (1942) observation that waters with high salinity are associated with carbonate mineral weathering.

Reynolds and Johnson (1972), in a study of stream waters, rocks, and soils of the Northern Cascade Mountains, suggested that the composition of streamwaters there is controlled by bedrock composition and not by precipitation, aerosol infall, or evaporation.

A multivariate statistical analysis of 101 water samples from streams in the MacKenzie River basin, Canada, by Reeder and others (1972), indicated rock type to be the major factor controlling the solute concentration of streams draining that basin. In that region the principal rock types controlling stream composition were evaporates and carbonates, marine shales, noncalcareous shales, and igneous and metamorphic rocks.

In summary, associations made between streamwater composition and the type of rock underlying the drainage basin suggest that, aside from dilution by atmospheric precipitation, rock type is a major control on the chemical composition of streamwaters. In general, streams having the lowest dissolved-solids concentration drain noncalcareous and nonevaporitic terrains, whereas those with the highest dissolved-solids concentration drain sedimentary terrains.

Relationship between Atmospheric Precipitation Quality and Ion Concentration or Transport in Streams

Many investigators have related the composition and transport of constituents in streams to the quality and quantity of atmospheric precipitation. The atmosphere is a major source of ions in stream water. Although no adequate network of precipitation-quality monitoring stations had been established over the United States at the time of this study (October 1971–March 1978), atmospheric contributions of the major ions have been measured in some watersheds, and some regional trends have been discerned.

Within basins underlain by rocks containing stable mineral assemblages, such as granites or quartzites, the ions found in streamwater are derived mostly from atmospheric precipitation (Conway, 1942; Hembree and Rainwater, 1961; Miller, 1961; Feth, Roberson, and Polzer, 1964; Gambel and Fisher, 1966; Juang and Johnson, 1967; Fisher, 1968; Fisher and others, 1968; Meade, 1969; Cleaves and others, 1970; Gibbs, 1970; Janda, 1971; Reynolds and Johnson, 1972; Likens and others, 1977; Ceasar and others, 1976). In particular, waters draining many basins composed of stable weather-resistant minerals reflected large atmospheric contributions of sulfate and chloride. In many of these, the atmospheric contributions were equivalent to the entire chloride and sulfate yields from the basins (Fisher and others, 1968; Cleaves and others, 1970; Likens and others, 1977).

The highest concentrations of sodium, potassium, and chloride in precipitation occur in coastal regions (Conway, 1942; Eriksson, 1955; Junge and Gustafson, 1957; Junge and Werby, 1958; Gorham, 1961; Carroll, 1962; Whitehead and Feth, 1964; Douglas, 1968; Fisher, 1968; Goudie, 1970; Baldwin, 1971); these substances are derived largely, although not solely, from marine aerosols. Conway (1942) attempted to quantify the average concentration of chloride in precipitation as a function of distance from the coast of the Northeastern United States and found a reasonable relationship within distances of 100 mi. Beyond 100 mi, chloride concentrations stabilized at 0.2 to 0.3 mg/L, an order of magnitude less than the concentrations nearer the coast.

In a study of the chemical mass balance between and oceans, Mackenzie and Garrels (1966) rivers suggested that the dominant sources of atmospheric sulfate are sea spray, industrial activities, and oxidation by photochemical processes of hydrogen sulfide (H<sub>2</sub>S) formed by the decomposition of organic matter. The burning of fossil fuel and smelting of metal sulfides releases to the atmosphere gaseous sulfur dioxide  $(SO_2)$ , which is subsequently converted to sulfate through oxidation and hydrolysis and then washed out of the atmosphere by precipitation (Robinson and Robins, 1970; Berner, 1971; Likens, 1976; Hales, 1977). Studies have suggested that in the Northeastern United States, localized industrial areas are the source of most sulfate found in streams draining rocks made up of stable mineral assemblages (Fisher and others, 1968; Gambel and Fisher, 1968; Likens, 1976; Likens and others, 1977).

In the Southwestern United States, where industrial emissions are relatively small, Junge and Werby (1958) observed high concentrations of sulfate in precipitation, and attributed this predominantly to the oxidation of  $H_2S$  produced by decaying organic matter.

#### Relationship between Atmospheric Precipitation Quantity and Ion Concentration or Transport in Streams

The amount of annual precipitation affects weathering rates. A qualitative assessment of North American river basins by Clarke (1924), which addressed the interplay between biota, rainfall, and basin lithology, suggested that streams in regions having abundant rainfall and fertile soil typically contain high concentrations of bicarbonate and carbonate, whereas streams in arid regions tend to have higher concentrations of sulfate and chloride than bicarbonate. In that study, Clarke attributed the high carbonate concentrations of streams in humid regions to the reaction of carbonic acid (formed by the hydrolysis of  $CO_2$  produced through decomposition of organic matter) with rocks and soils, which results in the addition of bicarbonate and carbonate ions to solution. In contrast, chemical precipitation of calcite in soils of arid regions (caliche) reduces the amount of carbonate in solution, which results in relatively higher concentrations of sulfate and chloride.

The amount of dissolved material transported annually by a stream is related to the amount of runoff (precipitation minus evapotranspiration). Langbein and Dawdy (1964) found that the annual dissolved-solids yield (mass per unit area) carried by rivers in the United States increased directly with annual runoff up to 7.6 cm/yr, at which point the dissolution rate of the rock-forming minerals becomes a limiting factor. Therefore, as runoff increases beyond 7.6 cm/yr, the increase in dissolved-solids yield is small, and dissolved-solids yield approaches a constant.

#### Relationship between Stream Temperature and Ion Concentration or Transport in Streams

Although few field studies have specifically addressed the effect of stream temperature on stream chemistry, the effect of temperature on mineral solubility has been investigated and summarized by Garrels and Christ (1965), Stumm and Morgan (1970), and Garrels and Mackenzie (1971). As water temperature increases, mineral solubility generally increases, but the relationship is complicated by the effects of carbonic acid on mineral weathering.

At low temperatures, water in equilibrium with a given amount of gaseous carbon dioxide  $(CO_2)$  contains more  $CO_2$  than at higher temperatures. Thus, cold water may have more carbonic acid available for weathering than warm water. In a chemical weathering study of a temperate glacial environment in the Northern Cascade Mountains, Reynolds and Johnson (1972) confirmed that carbonation reactions proceed more vigorously in cold regions than in warm regions. This hypothesis is complicated, however, by the production of  $CO_2$  by decomposition of organic matter, (Clarke, 1924), the mass of which increases in relation to the humidity (annual precipitation) of an area.

An additional effect of stream temperature on stream-water composition, also related to the gaseous up-take of  $CO_2$ , is that carbonate mineral dissolution is favored more at low temperatures than at high temperatures

(Stumm and Morgan, 1970). In a study of waters draining limestone in northern England, Sweeting (1966) observed an increase in carbonate-mineral dissolution with decreasing stream temperature and also observed that pH decreased with decreasing stream temperature.

Finally, air temperature as reflected by stream temperatures, combined with precipitation quantity may indirectly affect the dissolution rate of minerals. In areas receiving similar amounts of precipitation, high air temperatures result in higher evaporation and lower runoff than low temperatures (Blatt, Middleton and Murray, 1972); higher evaporation and lower runoff, in turn, would result in higher dissolved-solids concentrations but smaller dissolved-solids yields.

#### Relationship between Human Activity and Ion Concentration or Transport in Streams

Human activities have been shown to influence the ion concentration of streams both indirectly and directly. Activities having indirect effects include quarrying or agricultural operations, in which disaggregation of rocks and soils increases the surface area of weatherable material; and emissions of sulfur and nitrogen oxides and particulate fly ash from the combustion of fossil fuel. These gases and aerosols undergo changes in the atmosphere (for example,  $SO_2 \rightarrow SO_4$ ) and are subsequently returned to the lithosphere, often at a considerable distance from the basin from which they were derived (Miller and others, 1978; Sampson and others, 1978). Direct influences (point sources) include sewage and wastewater disposal, urban runoff, and the release of industrial effluents to surface waters. The ways in which human activity affects the composition and loads of dissolved constituents in streams are the subject of many reports, a few of which are described below.

Clarke (1924) addressed the composition of North American rivers and noted that river water represents the average of all its tributaries plus rain and ground water, and that many rivers contain effluents from towns and factories. He also stated that the greatest compositional differences are found among small streams, which are presumably more sensitive to local conditions than large streams.

Conway (1942), in attempting a mass balance for chloride transported by rivers in the United States, quantified three main chloride sources resulting from human activity: salt production or salt mining, human excretion (sewage), and combustion of fossil fuel with chloride volatization. He was able to attribute only 10 percent of the river chloride to these sources, however. In contrast, he found that 44 percent came from atmospheric precipitation and 11 percent from rock weathering. He could not account for the remaining 35 percent. Since Conway's study, a principal source of sodium and chloride in streams in the northern latitudes has been road salting for removal of snow and ice (Hanes and others, 1970). The amount of salt used is related to climate, miles of roadway, and traffic density, which in turn are related to population density. Some site-specific studies have evaluated the changes in sodium and chloride loads during selected time periods and calculated what part of the noted increases may be attributed to road salt (Frost, 1976; Lipka and Aulenbach, 1976; Peters and Turk, 1981). For example, Peters and Turk (1981) detected a 145-percent chloride increase in the Mohawk River, N.Y., from the 1950's to the 1970's and attributed 96 percent of this increase to the use of road salt in the basin.

Musser and Whetstone (1964) monitored streamwater chemistry in the Beaver Creek basin, Kentucky, before and during strip-mining operations. The disturbance of the land surface of one of the basins placed unweathered, fine-grained, pyrite-rich sandstone, siltstone, and claystone at or near the surface, and streams draining this exposed area contained noticeably higher concentrations (and loads) of chemical constituents (notably sulfate) than streams draining undisturbed basins.

Anderson and Faust (1965), in a study of the dissolved-solids concentration of the Passaic River, N.J., found that the dissolved-solids concentration per volume of water discharged by the river increased from 1947 to 1964, whereas dissolved oxygen decreased over the same period. They attribute these changes to the disposal of increasing volumes of municipal and industrial wastewaters within the river basin.

Ceasar and others (1976) studied the mass transport of the major ions plus phosphorus in the Merrimack River in New England. They first measured the atmospheric contributions, then applied population density as a master variable to represent the contributions from man's activities. They then summed the contributions and subtracted the total from the actual river yield to obtain the contribution from weathering. They found that population density correlated well with all constituents transported in the river except phosphorus and silica.

Lystrom and others (1978) predicted yields of various nitrogen and phosphorous species from streams in the Susquehanna River basin through multiple-linear-regression equations. They related water-quality characteristics of 80 subcatchments to 57 basin chacteristics within the major categories of climate, topography, geology, soils, streamflow, and land use. They found that land use recurred most often in these equations, particularly agricultural land use, because farming is the dominant feature of that basin.

In summary, human activities affect the composition of streams by contributing constituents directly through both point and nonpoint sources and indirectly by altering the soils and underlying rocks. Both population density and land-use data have been used successfully to assess the impact of man's activities on the composition of streams.

#### METHODS

Gaged streams within 56 areas of the conterminous United States and Hawaii that have drainage basins underlain by sandstone, limestone, or crystalline (igneous and metamorphic) rocks were selected for study. For each basin, the following data sets were compiled: (1) annual yields of major dissolved ions (sodium, potassium, magnesium, calcium, chloride, sulfate, bicarbonate, and dissolved solids), (2) annual precipitation quantity, (3) population density, and (4) average stream temperature. These data were computed from basin and stream characteristics gathered from the literature and U.S. Geological Survey water-data computer files. Relationships among these factors were calculated through linear- and multiple-linear-regression equations to predict dissolved-ion yields for each basin. The following paragraphs describe methods of basin selection, methods of estimating basin and stream characteristics, and the application of multiple linear regression to predict yields of the major dissolved ions.

#### **Basin Selection**

The basins were selected from the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) (Ficke and Hawkinson, 1975) and National Benchmark Network (Cobb and Biesecker, 1971). Primary considerations for selection were that the basin be underlain predominantly by a single bedrock type and that at least 2 years of concurrent streamflow quality and quantity data be available. Sites were selected throughout the United States to provide a wide range in stream-water temperatures and precipitation quantities. Gage-site locations and rock type of the drainage basin are indicated in figure 1; corresponding basin and streamflow characteristics are summarized in table 1.

The rock types were chosen to represent extremes in the range of type and quantity of chemical-weathering products expected in streamflow. Limestone was selected because it is composed primarily of easily weathered calcium and magnesium carbonate minerals and because it is relatively abundant. (Limestone constitutes 20 percent by volume of the world's sedimentary rocks, which in turn make up 75 percent of the rocks exposed at the Earth's surface (Pettijohn, 1957).) Sandstone containing little or no carbonate was chosen because it generally consists of silicate minerals, which are more resistant to weathering



**Figure 1.** Locations of gaged stream sites for drainage basins underlain by single bedrock types. (Corresponding gage site locations and basin characteristics are listed in table 1.)

than carbonates. Crystalline rock, igneous and metamorphic, constitutes 75 percent by volume of the Earth's crust and was chosen for contrast with the other two types; also it has the widest range in composition and mineral texture. Crystalline basins containing marble were eliminated because marble and limestone are similar in composition. Of the 56 basins selected, 19 were limestone, 12 were sandstone, and 25 were crystalline.

The type of bedrock underlying a basin was determined initially from national and State geologic maps and more thoroughly from the literature (References to basin geology are listed in the appendix). Many of the large basins contain a mixture of rock types. Basins designated as limestone were those in which more than 50 percent of the bedrock contained carbonate. Basins designated as sandstone were those in which carbonate minerals were virtually absent. (Sandstone basins may contain lenses of carbonates, but the strata containing them constitute less than 10 percent of the bedrock. Both limestone and sandstone basins also contained shale in varying quantities.) Basins designated as crystalline contained more than 80 percent metamorphic or igneous rock.

## Estimates of Basin and Stream Characteristics

#### **Atmospheric Precipitation**

Annual precipitation-quantity data were obtained from a computer file of basin characteristics maintained by the U.S. Geological Survey. These data were compiled by an isohyetal method (Linsley and others, 1975) from longterm averages for some basins. (The isohyetal method consists of contouring the precipitation-quantity data and, in part, accounts for both orographic effects and the density of measurement stations in an area.) For basins where these data were unavailable, values were calculated from the arithmetic average of monthly quantity data published by U.S. National Oceanic and Atmospheric Administration (1970–78).

#### Table 1. Basin and streamflow characteristics of sites studied.

[Rock type and location of sites is shown in figure 1]

				Drafan	Popula-	Prostate		Average
			Period of		density	tation		slieam temper→
Site	Station		record used	area	(persons/	quantity	Runoff	ature
No.	No.	Station name	in study	(km <sup>2</sup> )	km <sup>2</sup> )	(cm/yr)	(cm/yr)	(C°)
	Limestone Bedrock							
1	2313000	Withlacoochee River near Holder, Fla.	04/01/72 03/31/77	4.727.0	8.5	137.4	13.6	21.94
2	2320500	Suwanee River at Branford, Fla.	10/01/71 09/30/76	20,047.0	12.7	124.0	37.2	20.41
3	2329000	Ochlockonee River at Havana, Fla.	10/01/71 09/30/76	2,953.0	15.4	130.3	41.3	19.34
4	2368000	Yellow River at Milligan, Fla.	10/01/71 09/30/76	1,616.0	17.9	148.8	82.6	19.00
5	3085000	Monongahela River at Braddock, Penn.	04/01/72 03/31/77	19,003.0	61.7	133.6	65.3	15.11
6	* 3254000	Licking River at Butler, Ky.	04/01/75 03/31/77	8,741.0	13.3	111.8	35.6	14.11
7	3290500	Kentucky River at Lock 2 at Lockport, Ky.	04/01/73 03/31/78	16,006.0	28.7	116.8	57.1	14.88
8	3425000	Cumberland River at Carthage, Tenn.	02/01/75 01/31/77	27,687.0	14.8	132.1	65.0	14.22
9	3543005	Tennesee River at Watts Bar Dam, Tenn.	10/01/74 09/30/77	44,833.0	35.7	129.2	59.9	16.15
10	35/1850	Tennessee River at South Pittsburg, Tenn.	04/01/75 03/31/78	58,638.0	36.2	149.7	68.8	16.49
11	* 3593005	Tennessee River at Pickwick Landing Dam, Tenn.	10/01/74 09/30/78	85,004.0	36.6	149.7	64.0	18.26
12	4045500	Tahquamenon River near Tahquamenon, Mich.	04/01/75 03/31/77	2,046.0	4.0	76.2	38.5	9.00
13	* 4057004	Manistique River at Manistique, Mich.	10/01/75 09/30/7/	3,756.0	1.2	76.2	45.1	9.22
14	× 4108690	Kalamazoo River at Saugatuck, Mich.	04/01/74 03/31/78	5,232.0	70.8	86.4	36.0	11.54
15	= 412652U	Manistee River at Manistee, Mich.	04/01/75 03/31/77	5,180.0	4.6	/8./	42.9	9.99
10	* 4132052	Cheboygan River at Cheboygan, Mich.	04/01/75 03/31/77	3,900.0	8.3	/6.2	35.6	9.6/
17	4165500	Clinton River at Mt. Clemens, Mich.	04/01//4 03/31/7/	1,901.0	116.0	/8./	37.8	11.00
18	8103900	South Fork Rocky Creek near Briggs, Tex.	04/01/72 03/31/77	87.6	.0	74.9	17.4	19.41
19	13018300	Cache Creek near Jackson, Wyo.	04/01//2 03/31//6	25.0	.0	/0.2	50.1	3.60
	Sandstone Bedrock							
1	1545600	Young Homong Crock soon Bonous Bono	04/01/72 02/21/77	119 2	0.0	102 6	72 2	9.06
2	* 30/9625	Allegheny River at New Konsington Ronn	04/01/72 03/31/77	29 800 0	23 4	113.0	44 6	12 07
3	3237280	linner Twin Creek at McGraw Obio	04/01/72 03/31/78	23,000.0	JJ.4	109.2	35.6	13.40
4	6439300	Chevenne River at Cherry Creek, S. Dak.	10/01/72 09/30/76	61.901.0	2.1	43.7	.9	10.60
Ś	64 52 000	White River near Oacoma, S. Dak.	04/01/74 03/31/78	26.418.0	1.4	43.2	1.6	10.59
6	6478500	James River near Scotland, S. Dak.	04/01/75 03/31/77	55.815.0	3.5	49.0	.4	12.50
7	7026000	Obion River at Obion. Tenn.	04/01/75 03/31/78	4.797.0	25.9	127.0	51.4	15.67
8	7231500	Canadian River at Calvin, Okla.	10/01/71 09/30/76	72.396.0	4.6	55.9	1.9	17.37
9	7232500	Beaver River near Guymon, Okla.	10/01/71 09/30/75	5,540.0	2.6	40.9	.1	14.52
10	7234000	Beaver River at Beaver, Okla.	10/01/71 09/30/76	20,603.0	1.2	48.3	.3	15.20
11	7237500	North Canadian River at Woodward, Okla.	11/01/74 10/31/76	30,016.0	1.6	51.6	.1	15.85
12	7245000	Canadian River near Whitefield, Okla.	10/01/71 09/30/76	123,222.0	6.6	61.2	5.1	16.03
		Crystal	line Bedrock					
	1050/00			0 107 0	10.0	120 7		0 60
1	1059400	Androscoggin River near Auburn, Maine	11/01//5 10/31///	8,430.0	18.0	132.7	/3.2	9.30
2	1066000	Saco Kiver at Cornish, Maine	10/01/74 09/30/78	3,302.0	4.9	40.0	39.3	7.60
د ۸	4014500	Saptism River near beaver Bay, Minn.	10/01/74 09/30/76	505.0	1.4	66 0	26.4	8 93
2	5124400	Rawishiwi kivet heat biy, ninh.	04/01/72 03/31/77	199 2	.0	66.0	52 4	4 18
6	7311200	Blue Beauor Creek poar Cashe Okla	04/01/72 03/31/77	63.0	.0	68 6	18.2	15.11
7	8431700	limnia Creek above Rt. Davie, Tex.	10/01/72 09/30/76	135.7	.0	52.9	2.5	22.31
8	9352900	Vallecito Creek near Bayfield, Colo.	10/01/71 09/30/76	184.6	.0	116.8	70.6	4.33
9	9430600	Mogollon Creek near Cliff. N. Mex.	10/01/75 09/30/77	176.6	.0	29.2	4.2	12.30
10	9508300	Wet Bottom Creek near Childs, Ariz.	10/01/71 09/30/76	93.2	.0	63.5	11.6	16.92
11	10396000	Donner und Blitzen River near Frenchglen. Oreg.	04/01/75 03/31/77	518.0	.0	35.6	23.6	6.98
12	11264500	Merced River near Yosemite, Calif.	04/01/72 03/31/77	468.8	.0	137.2	62.1	6.87
13	12447390	Andrews Creek near Mazama, Wash.	04/01/72 03/31/78	56.6	.0	88.9	55.8	2.82
14	13169500	Big Jacks Creek near Bruneau, Idaho	04/01/72 03/31/78	647.7	.0	33.0	.7	10.25
15	1 3 3 3 1 5 0 0	Minam River at Minam, Oreg.	04/01/72 03/31/77	614.4	.0	95.5	72.5	6.53
16	14048000	John Day River at McDonald Ferry, Oreg.	04/01/75 03/31/77	19,632.0	.6	48.3	37.0	11.60
17	14103000	Deschutes River at Moody near Biggs, Oreg.	11/01/74 10/31/76	27, 195.0	2.0	55.9	21.2	11.26
18	14113000	Klichetat River near Pitt, Wash.	10/01/72 09/30/78	359.0	2.6	91.4	45.7	9.61
19	16031000	Waimea River near Waimea, Kauai, Hawaii	10/01/75 09/30/77	150.0	.0	172.7	46.4	22.76
20	16213000	Waikele Stream at Waipahu, Oahu, Hawaii	05/01/72 04/30/78	118.0	302.0	182.9	23.7	22.53
21	16229300	Kalihi Stream at Kalihi, Oahu, Hawaii	04/01/75 03/31/78	13.0	1,600.0	264.4	35.6	22.34
22	16400000	Halawa Stream near Halawa, Molokai, Hawaii	04/01/75 03/31/78	12.0	.0	233.7	142.1	20.25
23	16618000	Kanakuloa Stream near Honohohau, Maui, Hawaii		9.0	•0	228.8 266 7	67 3	20.13
24	16/04000	Walluku Kiver at Piihonua, Hawali, Hawali	04/01//3 03/31//8	324.0	•0	200./	375 2	18 43
20	10/1/000	nonolli Stream near rapaikou, Hawali, Hawali	04/01/12 03/31///	29.1	••	437.2	212.2	10.43

\* Water-quality stations with discharge estimated from another station. The corresponding discharge station names, locations, and areas are listed below.

Water-quality station	<u>Drainage area (km²)</u>	Name and location	Discharge station	Drainage area (km²)
3049625	29,800	Allegheny River at Natrona, Penn.	3049500	29,550
3254000	8,741	Licking River at Catawaba, Ky.	3253500	8,547
3593005	85,004	Tennessee River at Savannah, Tenn.	3593900	85,830
4057004	3,756	Maniatique River near Manistique, Mich.	4056500	2,849
4108690	5,323	Kalamazoo River near Fennville, Mich.	4108500	4,144
4126520	5,180	Manistee River near Manistse, Mich.	4126000	4,610
4132052	3,900	Cheboygan River at Cheboygan, Mich.	4130000	2,240

Methods 7

Within the last few years, precipitation quality in several areas in the United States, particularly the Northeast, has been monitored. However, standards for collection and analysis have not been uniform; in addition, the areas in which precipitation quality has been documented form only a fraction of the area considered in this study. Therefore, the data used in this study were taken from published records (Junge and Werby, 1958), which present average annual concentrations (contoured) of sodium, potassium, calcium, 1954 and 1955 at 200 sites distributed uniformly over the conterminous United States.

In this study, annual direct atmospheric contribution of each constituent within each of the 49 basins in the conterminous United States was calculated by multiplying average annual concentration of bulk precipitation by annual precipitation quantity. (The seven basins in Hawaii were eliminated from this analysis because the precipitation collectors were located only in the continental United States.) Percent atmospheric contribution of each ion to annual yield in streamflow was then calculated and averaged for each rock type.

#### Stream Temperature

Stream temperatures fluctuate seasonally. A simple arithmetic mean of the temperature data might not accurately represent the mean annual stream temperature because inaccessibility and other factors could result in a nonrepresentative distribution of data. Therefore, the temperature data were fitted to a sine curve with an annual wavelength, a technique known as harmonic analysis (Steele, 1979). Adjusting the curve both horizontally along the time axis and vertically along the temperature axis to produce a best fit for the data yielded a mean temperature about which the seasonal values oscillate (table 1).

#### **Population Density**

Population density (in persons per  $km^2$ ) was determined from the 1970 population census (U.S. Bureau of Census, 1972) and basin drainage area.

#### Major-Dissolved-Ion Yields

Average annual yields (kg/km<sup>2</sup>) were calculated for sodium, potassium, magnesium, calcium, chloride, sulfate, bicarbonate, and for their sum, dissolved solids by multiplying the respective arithmetic-mean concentration by the total volume per unit area of streamwater discharged and then dividing by the number of years represented (table 2). Discharge, major-ion concentration, and stream temperature were retrieved from the National Water Data and Retrieval System (WATSTORE), a computer file maintained by the U.S. Geological Survey (Hutchinson, 1975).

For basins in which water-quality and discharge data were obtained from two adjacent stations rather than a single station, the discharge was area-weighted to correspond with the basin area above the water-quality station.

#### Prediction of Dissolved-Ion Yields

To evaluate the effect that rock type, population density (persons/km<sup>2</sup>), annual precipitation quantity (cm), and average stream temperature (°C) have on annual dissolved-ion yields (kg/km<sup>2</sup>), empirical relationships between ion yields and these factors were calculated. Although several multivariate statistical techniques are available to determine the correlation between these independent variables and yields, the linear and multiple linear regressions used in this study were judged most suitable to provide quantitative information on the relationship between characteristics and yields (Lystrom and others, 1978).

The general form of the multiple-linear-regression relationship is

$$Y_i = a + b_1 X_1 + b_2 X_2 + \dots + b_n X_n;$$
(1)

where

 $Y_i$  = the annual yield of a major dissolved ion, i, and

 $X_1, X_2$ , etc. = the basin and stream characteristics.

The method for computing the regression coefficients is described by Edwards (1979). Computations, data transformations, linear- and multiple-linear-regression analyses, and other statistical tests were performed on a computer through a set of programs from the Statistical Analysis Systems (SAS) (Barr and others, 1976).

The reliability of multiple-linear-regression equations to accurately represent the relationship among variables is diminished by nonnormal distributions of the variables through unequal weighting by extreme values (Daniel and Wood, 1971; Edwards, 1979). Extreme values may also diminish the value of simple linear-regression relationships (Daniel and Wood, 1971).

The distributions of yields, annual precipitation quantity, and population density were nonnormal, as determined by the Kolomogorov-Smirnov test at the 95-percent level of significance (Davis, 1973). Furthermore, they were positively skewed; that is, values smaller than the mean were more common than values larger than the mean, which is typical of hydrologic data (Gray, 1970). Accordingly, these data groups were transformed through the common (base 10)

#### Table 2. Annual yields in streams of the major dissolved ions from basins in the conterminous United States and Hawaii.

#### [Annual yields are in kilograms per square kilometer, except dissolved solids, which are in 1,000 kilograms per square kilometer]

Site No.	Station No.	Sodium	Potassium	Magnesium	Calcium	Chloride	Sulfate	Bicarbonate	Dissolved solids
				Limes	tone Bedrock				
1	2313000	726.0	54.6	609.0	6 600 0	1 410.0	3 720.0	17 196.0	30.3
2	2320500	1,690,0	246.0	1.800.0	9,700.0	2 140.0	4,470.0	31,500.0	51.5
3	2329000	3,980.0	698.0	804.0	2,220,0	5,940.0	2,130,0	7,265,0	23.0
4	2368000	1,800.0	420.0	906.0	4,970.0	2.980.0	1.340.0	18,100.0	30.5
5	308 5000	13,600.0	1,600.0	5,690.0	21.600.0	8,320.0	79,400.0	16,700.0	146.9
6	3254000	1,403.8	896.1	2,266.2	12,975.9	1,745.7	10,023.3	37,555.0	66.9
7	3290500	4,170.0	1,380.0	3,930.0	19,800.0	6,010.0	19,800.0	53,500.0	108.6
8	3425000	1,820.0	838.0	2,740.0	13,800.0	1,710.0	11,900.0	40,500.0	73.3
9	3543005	3,210.0	868.0	2,690.0	11,800.0	3,940.0	7,580.0	47,900.0	78.0
10	3571850	1,470.0	379.0	1,100.0	5,020.0	1,700.0	3,260.0	16,900.0	29.8
11	3593005	2,978.5	960.9	2,227.4	12,742.8	3,936.8	10,282.3	40,922.0	74.1
12	4045500	599.0	292.0	2,150.0	8,210.0	845.0	5,100.0	31,300.0	48.5
13	4057004	821.0	409.2	3,626.0	16,446.5	1,157.7	15,255.1	53,872.0	91.6
14	4108690	11,914.0	979.0	9,272.2	29,785.0	14,063.7	21,108.5	113,442.0	200.6
15	4126520	6,578.6	678.6	5,231.8	25,589.2	23,724.4	5,335.4	78,736.0	145.9
16	4132052	1,113.7	292.7	4,532.5	15,462.3	1,476.3	3,729.6	68,894.0	95.5
17	4165500	17,800.0	1,720.0	8,070.0	28,300.0	28,800.0	24,100.0	94,400.0	203.2
18	8103900	1,349.4	290.1	4,247.6	9,686.6	1,955.4	2,874.9	48,174.0	68.6
19	13018300	1,108.5	318.6	6,656.3	21,859.6	492.1	3,289.3	98,938.0	132.7
				Sands	tone Bedrock				
1	1545600	613.8	650.1	3,193.5	2,952.6	960.9	5,076.4	7,772.6	21.2
2	3049625	8,029.0	1,341.6	4,869.2	16,938.6	9,375.8	49,728.0	16,912.7	107.2
3	3237280	1,305.4	872.8	2,051.3	2,615.9	973 <b>.</b> 8	11,577.3	6,708.1	26.1
4	64 <b>393</b> 00	1,720.0	114.0	647.0	1,620.0	445.0	8,170.0	1,840.0	14.6
5	6452000	648.0	40.2	27.9	229.0	210.0	635.0	1,520.0	3.3
6	6478500	393.0	66.0	231.0	545.0	203.0	1,840.0	1,240.0	4.5
7	7026000	2,900.8	1,015.3	1,186.2	3,133.9	2,268.8	3,185.7	15,565.9	29.3
8	7231500	2,440.0	102.0	573.0	1,460.0	4,250.0	1,830.0	4,280.0	14.9
9	7232500	38.8	7.0	34.2	66.6	20.7	71.2	366.7	0.6
10	7234000	1,160.0	23.0	170.0	341.0	1,840.0	978.0	586.0	5.1
11	7237500	353.0	9.3	58.2	228.0	502.0	570.0	314.0	2.0
12	7245000	1,840.0	172.0	528.0	1,620.0	2,980.0	1,460.0	5,440.0	14.0
				Crysta	lline Bedrock				
1	1059400	7,511.0	704.5	616.4	4,221,7	8,054.9	7,485.1	12,328.4	40.9
2	1066000	2,305.1	505.0	360.0	2,266.2	3,082.1	3,418.8	7,640.5	19.6
3	4014500	1,230.0	175.0	1,340.0	4,160.0	1,214.0	3,960.0	14,600.0	26.7
4	5124480	323.7	106.2	367.8	1,023.0	238.3	1,333.8	3,574.2	7.0
5	6623800	1,206.9	538.7	787.4	3,936.8	471.4	2,421.6	17,171.7	26.5
6	7311200	2,385.4	305.6	787.4	2,874.9	1,486.7	2,481.2	13,571.6	23.9
7	8431700	161.6	76.4	106.4	287.5	66.6	546.5	1,960.6	3.2
8	9352900	800.3	450.7	1,307.9	6,578.6	603.5	5,905.2	20,512.8	36.2
9	9430600	246.0	34.4	102.6	466.2	60.1	647.5	1,701.6	3.3
10	9508300	1,642.1	111.4	678.6	2,362.1	849.5	955.7	12,069.4	18.7
11	10396000	1,080.0	291.0	708.0	1,860.0	229.0	725.0	10,800.0	15.7
12	11264500	1,137.0	217.6	162.4	1,442.6	1,585.1	1,023.0	5,646.2	11.2
13	12447390	1,248.4	282.3	497.3	3,470.6	341.9	1,279.5	15,824.9	22.9
14	13169500	75.1	27.7	19.2	82.9	32.9	50.0	417.0	U./
15	13331500	1,750.8	/89.9	1,090.4	4,558.4	660.4	1,665.4	21,/81.9	32.3
16	14048000	1,080.0	180.0	854.0	1,830.0	201.0	66/.0	11,500.0	10.3
1/	14103000	1,990.0	3/3.0	1,000.0	1,000.0	454.0	590.U	10 001 1	17.0
10	14113000	1,841.0	1.160	1,434.9 / / ag o	J,1J7.0 2 / 10 0	029.4 5 /00 0	1,040.2	31 257 0	51 0
19	16031000	3,807.3	531.5	4,428.9	J,418.8 J /70 /	J,470+0	1,021.J	15 177 /	53 0
20	16223000	12,043.5	191.1	1,92/.0	2,4/8.0	12,//3.1	4,/91.0	31 090 0	64 9
21	16400000	0,493.2	49/.3	J,211.0	J,027.J 2 101 1	15 000 6	57059	10 / 37 7	46 8
22	1661 2000	9,9/1.0	1 030 5	1,143.1 2 602 6	2,171.1 6 656 Q	11 577 3	4 014 5	27.454.0	59.7
23	16704000	1 818 7	33/ 1	2,073.0 Q63 5	7 157 3	1 999.5	1.771.6	11,292.4	20.3
25	16717000	9,816.1	1,258.7	7,899.5	14,711.2	11,266.5	8,547.0	82,362.0	135.9
	·		-	•	-				

logarithm (Gray, 1970). Average stream temperatures were also log transformed to provide uniform data for assessing the relative effect of each characteristic on yields. In addition, because the logarithm of zero is undefined and 21 of the basins had zero population, a constant of 1.0 was added to each population density value. Rock type was treated as a class variable in the multiple-linear-regression analysis of the data. (A class variable is one that has discrete values for each member of the class.) The form of the equations developed was

 $\log Y_i = \log a + b_1 X_1 + b_2 \log X_2 + b_3 \log X_3 + b_4 \log X_4 \quad (2)$ 

where

Y = constituent yield,

 $X_1 = rock$  type,

and

 $X_{2,}$  etc. = remaining basin and stream characteristics

The accuracy of yield prediction from the regression equations was judged from the standard error of estimate of the equation (Snedecor, 1949; Ezekiel and Fox, 1959). The standard error of estimate was derived from the relationships of log-transformed data and is presented as both the standard error in log units and an average percentage for the backtransformed empirical relationships according to the method described by Riggs (1968). The best fitting equations derived for each ion included variables with partial correlation coefficients that were statistically significant at the 95-percent level according to Student's t-test of significance (Draper and Smith, p. 305, 966). The overall closeness of fit of the regression equation was determined from a t-test on R, the coefficient of multiple correlation (Edwards, 1979). The coefficient of multiple determination,  $R^{2}$ , used herein, is equal to the fractional percent of the variance in a log-transformed yield that is explained by the regression relationship (Edwards, 1979).

It is important to compare the effects that selected independent variables have on the yield of a constituent so that those having a direct relationship can be identified. The regression coefficients of the multiple-linear-regression equations do not provide this information directly because their magnitude and range differ among the variables (Davis, 1973). To assess the sensitivity of these variables to predicting yields, all were standardized by subtracting the mean from each value and dividing the remainder by the standard deviation (Edwards, p. 23, 1979). The multiple-linear-regression equations were then recomputed, and the regression coefficients, more appropriately called regression weights, were compared. Each standardized variable then has a mean of zero and a standard deviation of 1. The reliability of multiple-linear-regression equations is also diminished by relationships among presumed independent variables. Although no relationship between population density and average stream temperature is apparent (fig. 2A), a noticeable trend between population density and annual precipitation is evident in basins having a population density greater than zero (fig. 2B).

To compensate for possible colinearity among annual precipitation quantity and population density, an additional approach was used to assess the relationship between yield and annual precipitation quantity from basins containing no permanent population. Linear relationships were developed between the transformed yields and annual precipitation; yields associated with annual precipitation were estimated from these relationships, and their percentages of the total yields were calculated. These amounts will be referred to henceforth as indirect amounts estimated from the relationship between yield and annual precipitation. These amounts may reflect both the direct contribution from atmospheric deposition and the transport from within the basin of solutes which are derived from weathering and human activities.

#### **RESULTS AND DISCUSSION**

Yields of the major dissolved ions in streams can be predicted by multiple-linear-regression equations with a standard error of estimate of about 0.4 logarithmic units. Annual yields measured in this study ranged generally from 10 to 100,000 kg/km<sub>2</sub> depending on the ion (table 3), and can, therefore, be predicted to within an order of magnitude of the observed values.

The factors that had the greatest effect on ion yields in this study were annual precipitation quantity (which represents climate) and rock type, the predominant source of most constituents. Population density and average stream temperature had less effect on yields of most constituents, although a direct relationship with certain constituents was apparent. The following discussion describes the relationships between annual yields and the respective sources, or environmental factors, and evaluates the ion contributions from each source as a percentage of total yield in streams draining the respective basin. The factors examined are rock type, atmospheric precipitation, population density, and stream temperature.

#### Effect of Rock Type on Yields

Rock type had a significant effect on solute yields from all basins. The statistical evaluation of differences in mean yields among rock types (table 3) indicates that the yields of all constituents except sodium were larger in



Figure 2. Population density in relation to (A) average stream temperature; and (B) annual precipitation, within drainage basins underlain by single bedrock types in the United States.

limestone basins than in sandstone or crystalline basins and that yields of calcium, bicarbonate, and dissolved solids were larger in crystalline basins than in sandstone basins. The multiple-linear-regression results (table 4) suggest that these differences are significant only in predicting yields of magnesium, calcium, sulfate, bicarbonate, and dissolved solids. Furthermore, the antilog of the rock-type coefficient from these logarithmic relationships suggests that yields of magnesium, calcium, and bicarbonate in limestone basins were about 10 times greater than those in sandstone basins. Also, magnesium, bicarbonate, and dissolved-solids yields were about 4 times greater in limestone basins than in crystalline basins, and calcium yields were about 6 times greater. The larger yields of magnesium, calcium, and bicarbonate from limestone basins reflect the greater solubility of carbonate minerals over aluminosilicate minerals, which make up the sandstone and crystalline basins.

In limestone basins, calcium and bicarbonate yields were much larger than those of the other constituents (table 3) and generally contributed the most to dissolvedsolids yields. In this study, the dissolved-solids yield in limestone basins was about 4 times greater than that in sandstone and crystalline basins. This difference is comparable to results for average dissolved-solids concentration in streams draining sandstone and granite in the Sangre De Cristo Range, N. Mex., (Miller, 1964). The sandstone in that study behaved similarly to the limestone in this study, presumably because the sandstone contained carbonate cement and thin limestone interbeds (Miller, 1964).

The coefficients for sulfate by rock type from the multiple-linear-regression relationships indicate that the sulfate yields in limestone basins were 3 times greater than those in crystalline basins and that yields in sandstone basins were twice those in the crystalline basins. Reasons for these differences are discussed in the section "Sulfate."

Although the mean yields of potassium and chloride were higher in limestone basins than in sandstone or crystalline basins, they could not be differentiated between sandstone and crystalline basins. How other factors may affect these constituents is more thoroughly discussed in the section "Sodium, Chloride, and Potassium."

#### Table 3. Summary statistics of annual yields, basin characteristics, and statistical comparison of yields among rock types.

[Yields are reported in kilograms per square kilometer per year, except dissolved solids, which are in 1,000 kilograms per square kilometer per year. Mean values are reported as the mean (antilog) of the log-transformed values]

					Compari	son of log-t	ranaformed	yields
		Rock type	\/			among roch	typea	Marra M
Constituent	Limestone (LS)	(minimum-maximum Sandstone (SS)	Crystalline (XX)	All basins		<u>P test</u> ª/	t test	Waitney U test
Sodium	(630-15,800)/2,500	(40-7,900)/1,000	(79-12,600)/1,600	(40-15,800)/1,600	LS-SS LS-XX SS-XX	NS NS NS	P<.05 N9 NS	P≺.1-0 NS⇒ NS
Potassium	(50-1,600)/500	(6-1,300)/126	(25-1,260)/320	(6-1,600)/320	LS-SS LS-XX SS-XX	P<.01 P<.05 P<.05		P<.05 P<.10 NS
Magnesium	(630-10,000)/2500	(25-5,000)/400	(20-7,900)/790	(20-10,000)/1,000	LS-SS LS-XX SS-XX	P<.01 P<.05 NS	 NS	P<.01 P<.01 NS
Calcium	(2,000-32,000)/12,600	(63-15,800)/1,000	(79-15,800)/2,000	(63-32,000)/3,200	LS-SS LS-XX SS-XX	P<.01 NS P<.10	 P<.01	P<.01 P<.01 P<.10
Chloride	(500-25,000)/3,200	(20-10,000)/790	(32-15,800)/1,000	(20-25,000)/1,600	LS-SS LS-XX SS-XX	NS P<.05 NS	P<.01	P<.05 P<.05 NS
Sulfate	(1,300-79,000)/6,300	(63-50,000)/2,000	(50-7,900)/1,600	(50-7,900)/3,200	LS-SS LS-XX SS-XX	P<.05 NS P<.10	P<.01	P<.05 P<.0} NS
Bicarbonate	(7,900-100,000)/40,000	(320-15,800)/2,500	(400-79,000)/10,000	(320-100,000)/12,600	LS-SS LS-XX SS-XX	P<.05 NS NS	 P<.01 P<.01	P<.01 F<.01 P<.01
Dissolved solids	(25-200)/79	(0.6-100)/10	(0.6-126)/20	(0.6-200)/25	LS-SS LS-XX SS-XX	F<.01 P<.05 NS	 P<.10	P<.01 P<.01 P<.10
Population density (persons/km <sup>2</sup> )	(0-126)/13	(0-32)/4	(0-1600)/2.5	(0-1600)/5				
Annual precipitation (cm)	(79-160)/100	(40-126)/63	(32-500)/100	(32-500)/100				
Temperature (°C)	(4-22)/13	(9-17)/13	(3-23)/11	(3-23)/12				

a/ p test is for determining equality of variances for the selected rock type pairs with the null hypothesis, Ho:variances are equal. No indicates nonsignificant. Mann Whitney V test and t test are for determining equality of means for the selected rock type pairs with the null hypothesis, H<sub>0</sub>:means are equal. Dashes under the t-test indicate that test is inappropriate because variances are unequal. NS indicates nonsignificant.

<u>b/</u>

Table 4. Multiple-linear-regression equations for the prediction of major-dissolved-ion yields derived from basins underlain by single bedrock types in the United States.

[Back-transformed equations are in the form  $Y = a \ 10^{b_1^X} \cdot X_2^{b_2} X_3^{b_3} \cdot X_4^{b_4}$  where Y is annual yield, in kilograms per square kilometer (except dissolved solids, which are in 1,000 kilograms per square kilometer); a is the regression constant; X1 is rock type; X2 is annual precipitation quantity, in centimeters; X<sub>3</sub> is basin-population density, in persons per square kilometer; X<sub>4</sub> is average stream temperature, in degrees Celsius. No value indicates the partial correlation of that particular coefficient was not statistically significant at the 95 percent level and that the variable was, therefore, not included in the multiple-linear-regression relationship]

		bj		b2	bg	bą	a			Percentage
	Rock Lype		Annual precipitation	Average Population stream		Regression	Standard error of estimate		variance explained	
Constituent	Limestone	Sandstone	Crystalline	quantity	density	temperature	constant	(logarithmic units)	(percent)	(100R <sup>2</sup> )
Sodium				1.09	0.26		7.8	0.38	107	52
Potassium				1.43	.23	-0.98	3.8	.38	107	56
Magnesium	3.6	0.32	1.00	1.14			3.8	.47	150	48
Calcium	6.3	.63	1.00	1.23		-1.00	83.2	.36	99	69
Chloride			-	1.59	.36		0.60	.45	140	62
Sulfate	3.3	2.3	1.00	1.20	.20	86	44.	.42	124	53
Bicarbonate	4.0	.46	1.00	1.15		83	400.	.37	102	67
Total dissolved solids	3.9	.93	1.00	1.26		70	3.1	.35	96	63

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#### Effect of Atmospheric Precipitation on Yields

Of the factors investigated, annual precipitation quantity had the strongest correlation with constituent yields. Graphs showing the relationship between yields and annual precipitation for basins with zero population and for all basins combined are displayed respectively as pairs in figures 3-10 for sodium, potassium, magnesium, calcium, chloride, sulfate, bicarbonate, and dissolved solids. For basins with zero population, least-squares linear relationships of the log-transformed variables, henceforth referred to as logarithmic relationships, were statistically significant at the 99-percent level, except for calcium and bicarbonate, which were significant at the 90-percent and 95-percent level, respectively (table 5). The slopes are slightly less than or equal to 1.0 for all constituents except sodium and chloride, which have considerably larger slopes. The positive relationship for all constituents implies that the greater the quantity of water running over or through a soil-rock system, the more effective is the transport of constituents from that system. (For sodium and chloride, the rate of increase in yield becomes larger with increasing annual precipitation, but for the other constituents the rate of increase remains constant or diminishes slightly.)

This trend is supported by the slopes associated with annual precipitation from the multiple-linear-regression equations (exponents of the back-transformed equations), which were greater than 1.0 for all constituents (table 5). This suggests that the rate of increase in yield becomes larger with increasing annual precipitation.

The apparent increase in transport rate of dissolved solutes with increasing mean annual precipitation may be related to more effective carbonic acid weathering in humid regions than in dry regions. Areas receiving large amounts of atmospheric precipitation have, in general, a higher biological productivity (Clarke, 1924). The release of  $CO_2$  in soils from the decay of organic material produces more carbonic acid in the soil water than in water in equilibrium with the atmosphere, and this increasing acid-ity promotes more active weathering (Berner, 1978).

#### **Annual Runoff**

The relationship between annual precipitation quantity and runoff (fig. 11) aids in explaining the high correlation between ion yields and precipitation. As annual precipitation increases, the amount of water entering streams (runoff) also increases. The distribution of points about



Figure 3. Annual dissolved-sodium yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.



Figure 4. Annual dissolved-potassium yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.



Figure 5. Annual dissolved-magnesium yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.

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Figure 6. Annual dissolved-calcium yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.



Figure 7. Annual dissolved-chloride yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.



Figure 8. Annual dissolved-sulfate yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.



Figure 9. Annual dissolved-bicarbonate yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.

#### 16 Environmental Factors Affecting Yields of Major Dissolved Ions of Streams



Figure 10. Annual dissolved-solids yield of streams in relation to annual precipitation within drainage basins underlain by single bedrock types in the United States. A, basins with zero population; B, all basins combined.

**Table 5.** Relationship between constituent yield and pre-cipitation quantity for basins having no permanent resi-dents.

[Equation is of the form  $\log Y = a + b \cdot \log X$  where Y = annual yield, in kilograms per square kilometer (except dissolved solids, which are in 1,000 kilograms per square kilometer),  $X = annual precipitation quantity, in centimeters, and <math>100R^2$  yield explained by the relationship between yield and precipitation quantity]

Constituent	<u>a1</u> /	<u>b1</u> /	100R <sup>2</sup>	Number of observations
Sodium	0.55	1.27**	64	21
Potassium	.50	.98**	54	21
Magnessium	.62	1.16**	37	21
Calcium	1.75†	.821	26	21
Chloride	82	1.87**	77	21
Sulfate	1.391	.94**	39	21
Bicarbonate	2.27**	.89*	30	21
Dissolved solids	72	1.02**	41	21

1/ † indicates statistical significance a<0.10

indicates statistical significance a<0.05</li>

\*\* indicates statistical significance a<0.01

the logarithmic relationship in figure 11 suggests that the relationship is curvilinear, particularly for the sandstone basins. The slope of the relationship is high at low annual precipitation and is low at high annual precipitation. Basins receiving low annual precipitation and having low runoff are in the far Midwest and Southwest, (table 1 and fig. 1), where much of the precipitation either returns to the atmosphere through evaporation or leaves the basins as ground water, without discharging to a stream. Indeed, high evaporation has been observed in this area (U.S. Environmental Science Service Administration, 1968). The percentage of water leaving these basins as streamflow, in general, is much smaller than that in regions receiving greater precipitation, and the transport of constituents from soils and rocks into streams is further inhibited by evaporation. In the southwest, this phenomenon is exemplified by the formation of caliche.

Because increases in precipitation cause a greater increase in basin runoff in areas having low annual precipitation than in areas with high annual precipitation, the relationship between yield and runoff for sandstone basins is also curvilinear, as shown qualitatively for dissolved solids in figure 12. The distribution of dissolved-solids yields





Figure 11. Annual runoff in relation to annual precipitation quantity within drainage basins underlain by single bedrock types in the United States.

Figure 12. Annual dissolved-solids yield of streams in relation to annual runoff within drainage basins underlain by single bedrock types in the United States.

in sandstone basins suggests that as annual runoff increases, the rate of change in yield increases until annual runoff reaches 3 to 4 cm. Above this level, the rate of change in yield decreases with increasing runoff. In contrast, the rate of change in dissolved-solids yields in crystalline basins decreases with increasing annual runoff (slope <1.0) over the full range of observed runoff. An assessment of dissolved-solids yields from rivers worldwide by Meybeck (1976) yielded the same result as that observed for crystalline basins.

In a study of streams in the United States, Langbein and Dawdy (1964) observed the same general configuration for dissolved-solids yields and runoff as described above for sandstone basins. They attributed the relationship to a general increase in transport with increasing runoff until a point is reached at which the rate of dissolution becomes a controlling factor and transport approaches a constant. This would also apply in part to the yields from crystalline basins because a slope less than 1 on this type of log-log plot indicates that increases in runoff diminishes the rate at which yield increases.

It is also possible that where annual precipitation increases, the amount of water infiltrating the soils and rocks decreases in relation to the amount entering streams as surface runoff. If this is true, the flow paths along which water travels to the streams would be an additional controlling factor on stream composition.

A possible explanation for the increase in dissolvedsolids yields with low runoff in sandstone basins could be chemical precipitation of minerals as a result of evaporation. As runoff increases slightly, yields will increase disproportionately until all soluble precipitated salts are depleted. Thus, in areas where evaporation is high and runoff low, slight annual changes in climate could produce a considerable change in the transport of dissolved constituents by streams.

The dissolved-solids yields from limestone basins show no relationship to annual runoff (fig. 12). However, the range in runoff within limestone basins is small compared with that for either sandstone or crystalline basins, which makes a general comparison, from which the effects of runoff in limestone basins could be judged, virtually impossible.

It is possible that the relationships between the variables and the yields investigated in this study are distinct for each rock type. An evaluation of these relationships for basins in this study cannot give meaningful results, however, because the basins within each rock type are too few and the values of the independent variables are not comparable among rock types because of their range, as exemplified by dissolved-solids yields from limestone basins.

In conclusion, the relationship between annual runoff and precipitation quantity suggests that precipitation may be a surrogate for the amount of water transported out of the basin as streamflow. Furthermore, chemical denudation is predominantly controlled by the amount of water a basin receives from precipitation.

#### Sodium, Chloride, and Potassium

The direct contribution of atmospherically derived sodium to stream yields averaged 26 percent for all basins and was consistent among rock types (table 6). Direct chloride contributions to stream yield averaged 28 percent for all basins; they were lowest in limestone basins (17 percent), intermediate in sandstone basins (26 percent), and highest in crystalline basins (42 percent). These direct values are a little less than 50 percent of the indirect amount estimated from the relationship between yield and annual precipitation quantity (table 6). The positive relationship between population density and precipitation quantity (fig. 2) suggests that the remaining contribution of sodium and chloride may have been derived mainly from human activities.

Previous estimates of the contribution of atmospheric sodium to river yields worldwide are 35 percent (Garrels and Mackenzie, 1971) and 46 percent (Livingston, 1963b). Estimates for chloride are 55 percent (Garrels and Mackenzie, 1971) and 44 percent (Conway, 1942). These estimates of direct contributions are higher than those calculated in this study but are slightly lower than the indirect amounts of 63 percent for sodium and 62 percent for chloride estimated from the relationship between yield and annual precipitation quantity (table 6). A possible explanation for the low estimates of direct contributions in this study is that they were made solely for basins in the conterminous United States, only a few of which were in coastal areas (fig. 1), where direct atmospheric contributions to streams are large (Conway, 1942).

The mean direct contribution of atmospherically derived potassium to stream yields was 45 percent for all basins (table 6); the indirect estimate of potassium yield from the relationship between yield and precipitation was 67 percent. Garrels and Mackenzie (1971) estimated 15 percent to be directly contributed from atmospheric deposition. Cycling of dust at inland sites may explain the disparity among estimates. The highest average direct contribution (70 percent of the stream yield) occurred within sandstone basins, and most of these basins are in arid to semiarid areas, where dust may contribute a significant amount to the total bulk deposition. Average concentrations of potassium in bulk atmospheric precipitation were very low, ranging from 0.1 to 0.3 mg/L (Junge and Werby, 1958). The insensitivity of these data therefore could produce errors as large as 100 percent in the estimated contributions.

#### Magnesium, Calcium, Bicarbonate, and Dissolved Solids

The direct atmospheric contribution of calcium to stream yields averaged 34 percent for all basins (table 6) and was much lower in limestone basins (7 percent) than in sandstone basins (69 percent) or crystalline basins (40 percent). Weathering of carbonate minerals that are high in calcium could account for this difference. Although magnesium and bicarbonate were not reported by Junge and Werby (1958), the direct atmospheric contribution of these two constituents would probably also be extremely small because they are products of carbonate mineral dissolution. The same would be true for dissolved solids because calcium and bicarbonate are the principal constituents.

The indirect amount of calcium estimated from the relationship between yield and annual precipitation was 53 percent for all basins (table 6). For calcium, more than any other constituent, there was a pronounced difference in limestone basins between the indirect estimate and the amount contributed directly from atmospheric deposition. Thirty percent of the total stream yield was indirectly related to precipitation quantity, whereas the direct contribution from atmospheric deposition accounted for only 7 percent. Furthermore, a worldwide estimate of the amount of calcium atmospherically recycled from the oceans by rivers is only 0.7 percent (Garrels and Mackenzie, 1971). The difference between that estimate and estimates presented in this study-the 34-percent direct atmospheric contribution estimated for all basins and even the 7-percent direct atmospheric contribution estimated for limestone basins-is significant. The estimates herein suggest that more calcium may be recycled from the oceans annually than had been estimated by Garrels and Mackenzie (1971).

If these estimates represent the true atmospheric recycling of calcium, then the time estimated by Garrels and Mackenzie (1971) for calcium transported in streams, which is derived from weathering, to attain the current amount in the oceans may be low by more than an order of magnitude. They estimate this time to be  $1.24 \times 10^6$ years. Adjusting this for the order-of-magnitude difference noted for atmospheric recycling would make it comparable to the 10.7 x  $10^6$  years that they estimated for magnesium. The estimates of atmospherically recycled calcium in this study are probably high, however, because dust may contribute significant amounts of calcium to bulk atmospheric precipitation (Galloway and Likens, 1976). Table 6. Percentages of annual constituent yields from streams in the conterminous United States related directly to atmospheric deposition and indirectly to annual precipitation quantity.

[The indirect amount was determined from the relationship between yield and precipitation quantity for basins with zero population density; the direct, or atmospherically derived, contribution was determined from precipitation-quality data (Junge and Werby, 1958). Contributions exceeding stream yields are reported as 100 percent]

Site	Station	Sodi	um	Potas	sium	Calc	ium	Chlo	oride	Sulf	ate
No.	No.	Indirect	Direct	Indirect	Direct	Indirect	Direct	Indirect	: Direct	Indirect	Direct
					Li	mestone Bed	rock				
1	2313000	100	100	100	100	56	10	00	07	70	5 5
2	2320500	100	37	100	50	30	10	56	57	55	50
2	2320000	25	16	57	10	100	23	20	40	100	50
ر د	2323000	100	50	100	15	100	23	52	20	100	100
4	3085000	100	3	100	33	16	2	16	30	100	100
5	3254000	14	16	20	12	20	2	10	12	21	ر ۱۱
7	3290500	37	10	25	8	20	3	18	15	21	11
,	3435000	100	22	2.J //8	16	25	2	10	4	11	11
0	35/3005	100	12	40	10	25	4	22	15	25	17
9	2571850	100	12	100	20	20	12	32	19	100	20
10	3571050	75	15	100	16	34	12	40	10	100	22
11	4045500	100	13	45	10	17	13	40	14	22	42
12	4045500	100	15	50	10	17	6	50	14	22	45
15	4037004	50	1	25	19	6	2	5	10	6	14
14	4100090	13	1	20	12	0	2	2	1	22	12
16	4120520	71	7	JZ 71	26	0	5	40	8	22	44 61
10	4132032	,1	,	12	20	5	2	40	0	5	11
19	8103000	57	28	70	20	14	15	20	11	29	50
10	13019300	71	20	65	26	14	3	100	31	3%	52
19	10101000										
Maan nam	aant +										
nean per	deutetten	66136	20422	57+29	25122	20+20	7+5	45+22	17+22	20+22	20125
scandard	deviation	00-30	20-23	57 420	2 3 + 2 2	30-30	1 = 5	45 <u>+</u> 52	1/ = 2 3	30-133	30 - 23
					6.	ndotono Pod	l no ok				
					38	indscone bec	FOCK				
,	1545600	100	100	1.6	24	77	28	0/	61	26	61
1	2040625	100	100	40	13	16	20	11	04 د		7
2	3237280	100	4	25	13	97	20	100	22	17	25
5	6439300	20	8	91	100	34	54	58	15	6	2.5
4	6452000	51	20	100	100	100	100	100	31	70	100
6	6478500	100	37	100	100	100	100	100	36	30	80
7	7026000	60	13	38	13	100	61	55	14	80	64
8	7231500	20	5	100	100	57	77	9	2	37	55
ő	7232500	100	100	100	100	100	100	100	100	100	100
10	7234000	34	8	100	100	100	100	16	100	55	100
10	7234000	100	20	100	100	100	100	10	15	100	100
11	7237300	21	29	100	71	100	76	14	13	100	75
12	7243000										
Maan nor	cont +										
et and ard	deviation	61+36	28+35	77+31	70+41	78+30	69+34	60+39	26+29	49+33	65+34
Scanuaru	deviation	01_50	20135	<u>,,,,,,,</u> ,,	/0141	70130	07134	00137	2012)	47.55	05.54
					Cry	vstalline Be	drock				
					02)	bearrine be	uroen				
1	1059400	25	5	58	19	83	16	16	7	37	50
2	1066000	71	16	73	24	100	27	38	16	70	100
3	4014500	56	11	100	40	29	17	42	6	25	35
4	5124480	100	41	100	62	100	65	100	28	66	99
5	6623800	53	11	32	12	28	17	100	14	37	55
6	7311200	28	6	59	45	41	36	34	7	38	50
7	8431700	100	100	100	100	100	100	100	100	100	100
8	9352900	100	29	77	52	43	62	100	19	38	59
9	9430600	73	24	100	100	60	100	100	97	37	81
10	9508300	36	12	100	86	43	81	53	11	87	100
11	10396000	23	26	28	12	21	10	83	31	45	49
12	11264500	100	36	100	95	100	29	87	43	100	100
13	12447390	80	28	88	94	52	13	100	100	100	100
14	13169500	100	100	100	100	100	100	100	100	100	100
15	13331500	64	22	34	12	44	10	100	29	97	86
16	14048000	36	31	65	27	35	13	100	60	80	87
17	14103000	25	17	38	15	.52	17	82	37	100	100
18	14113000	57	30	41	14	60	14	100	44	97	89
Mean per	cent +										
standard	deviation	63+29	30+27	72+28	50+36	61+29	40+34	80+29	42+35	70+29	80+23
								· · · · · · · · · · · · · · · · · · ·			
Total me	an percent +										
standard	deviation	63+33	26+28	67+29	45+36	53+35	34+36	62+35	28+30	52+34	60+32
-				-							

20 Environmental Factors Affecting Yields of Major Dissolved Ions of Streams

#### Sulfate

Sulfate derived from atmospheric deposition has received considerable attention in the last few years because it is a major component of acid precipitation (Likens, 1976). Watershed studies in Tennessee, an area rich in limestone (Kelly, 1980), indicate that about 4 times more sulfate is deposited from the atmosphere than is transported in streams. In contrast, atmospheric contributions to basins underlain by granitic to calcareous rock types in Norway (Wright and Johannessen, 1980), to a granitic basin in Nova Scotia (Kerekes, 1980), and to three granitic basins in the Adirondack Mountains of New York (Galloway and others, 1980) were found to approximately equal the amounts in streams.

The amount of atmospheric sulfate deposited that was calculated herein equaled a substantial percentage of the total sulfate yields in streams and averaged 60 percent for all basins (table 5). Furthermore, 39 of the 49 basins in the conterminous United States received greater direct contributions from atmospheric deposition than the indirect amounts estimated from the relationship between sulfate yield and annual precipitation. In contrast to sodium and chloride yields, of which about 30 percent was directly contributed from atmospheric deposition and more than 60 percent was indirectly related to annual precipitation quantity, the relationship between sulfate yield and annual precipitation suggests that a significant fraction of the sulfate yield in streams is derived directly from atmospheric deposition.

An analysis by rock type of the average percent sulfate contribution derived directly from atmospheric deposition reveals that contributions to total yield were largest in crystalline basins, averaging 80 percent (table 6); 11 of the 19 crystalline basins received contributions exceeding 85 percent. Direct atmospheric contributions in sandstone basins averaged 65 percent, and 4 of the 12 basins had contributions exceeding 85 percent. The atmospheric sulfate contribution to yields in limestone basins averaged only 38 percent, much less than that in either the sandstone or crystalline basins, and only 1 of the 19 limestone basins had a contribution exceeding 85 percent.

The availability of sulfur minerals for weathering can partly explain these results. In general, sedimentary rocks contain more sulfur than crystalline rocks. Clarke (1924), in summarizing weight percent  $SO_3$  in rocks indicated that limestones and sandstones contain about 0.1 percent and that igneous rocks (excluding some highly sulfurous extrusives) generally contain variable amounts, usually much less than 0.1 percent. These values are consistent with the observations above. These observations are further supported by the abundance of sulfur in shales (averaging 0.7 weight percent  $SO_3$ ), because shales are present in most of the limestone and sandstone basins.

The sulfate yields from limestone basins are generally larger than those from sandstone basins (table 3). This may be related to both climate and farming practices. The limestone basins studied generally have a higher population density and higher annual precipitation than the sandstone basins (table 3). The high precipitation in limestone basins may bring in or release larger quantities of sulfate to streams than occurs in the more arid sandstone basins, where low precipitation coupled with proportionately higher evaporation may enhance retention of sulfate through chemical precipitation. This possibility is supported by the abundance of gypsum in soils in arid to semiarid regions (Donner and Lynn, 1977). Also, fertilizer application and disaggregation of soils and rocks through farming and construction in the more humid limestone basins may have provided proportionately more sulfate than atmospheric deposition to the total yield in streams than in sandstone basins.

#### Effect of Human Activity on Yields

Results of the multiple-linear-regression analysis suggest that the effect of human activities, as measured by basin-population density, on the yields of the major dissolved ions in streams is generally not as important as climate or rock type. The only constituents for which population density was a valid predictor were sodium, chloride, potassium, and sulfate (table 4). For potassium and sulfate, population density was an even less significant factor than average stream temperature, as determined by the regression weights (table 7). Thus, human activities were indicated to be a major source of contributions only for sodium and chloride (figures 13 and 14).

Human contributions to the total yield of sodium and chloride in streams probably result from road salting, which is used in northern latitudes for snow and ice removal, and from the disposal of sewage and industrial wastes. The contributions from human activities were quantified by calculating the population-related yield from a logarithmic relationship between residual yield and population density; residual yield was determined by subtracting the amount related to precipitation from the total yield. These relationships and the average estimated contributions from population are listed in table 8.

The average contribution from human sources to all basins was 13 percent of the sodium yield and 20 percent of the chloride yield. The exponents of these back-transformed equations (table 8) are considerably larger than those in the multiple-linear-regression equations (table 4) so that estimates of population-related contributions derived from equations developed from residual yields are higher than those derived from multiple-linear-regression equations. The results indicate that, even in extreme cases, the contributions of sodium and chloride from human activities are small, yet, as noted in previous studies, human influences on local stream composition may actually be quite large (Peters and Turk, 1981).

## Table 7. Regression weights for coefficients of standardized log-transformed independent variables.

[These coefficients correspond to the multiple-linear-regression equations in table 4. Annual constituent yields are in kilograms per square kilometer (except dissolved solids, which are in 1,000 kilograms per square kilometer); annual precipitation quantity is in centimeters; population density is in persons per square kilometer, and temperature is in degrees Celsius. No value indicates that the partial correlation of that particular coefficient was not statistically significant at the 95 percent level and that the variable was, therefore, not included in the multiple-linear-regression relationship]

••••••••••••••••••••••••••••••••••••••	Indepo	e	
<u>Constituent</u> (minimum-maximum)	Precipitation (29-559)	Population (0-1,600)	Temperature (2.8-22.8)
Sodium (39-17,800)	0.53	0.36	
Potassium (7-1,720)	.68	.30	-0.36
Magnesium (19-9,270)	.48		
Calcium (66-29,800)	.52		-0.33
Chloride (21-28,800)	. 59	. 38	
Sulfate (50-79,400)	.54	.25	30
Bicarbonate (314-113,442)	.49		27
Diaaolved solids (0.60-203)	.59		26

Therefore, the use of population density as an indicator of sodium and chloride yields may have only limited validity in most regional studies.

One possible reason population density failed to provide valid estimates of ion contribution to stream yield is that population density does not correlate directly with land use. Even though an increase in population of an area is almost certain to cause an increase in solute yields, either directly through waste disposal or indirectly through disturbance of the land surface, land use is probably a far more reliable indicator of both the amount and the types of solutes transported in streams from these areas. For example, if the population of a given basin is concentrated in an industrial-urban center at the downstream end of the drainage area, the stream will contain primarily industrial substances, whereas a mostly agricultural basin with a similar population will yield substances characteristic of farmland. Also, major urban areas contribute constituents directly to streams through sewage and industrial wastedisposal systems so that their impact on a stream is sewage through leach fields, contribute these substances more gradually. This may explain the good correlations between yield and population density that Ceasar and others (1972) found in the Northeastern United States, where population is concentrated in urban centers.

#### Effect of Average Stream Temperature on Yields

In the multiple-linear-regression equations, average stream temperature was important in predicting yields for five of the constituents studied-potassium, calcium, sulfate, bicarbonate, and dissolved solids (table 4). The regression weight for temperature in these equations was comparable to, or slightly higher than, that for population density, which indicates that the importance of stream temperature in predicting yields is about as limited as population density. In all equations, however, the temperature coefficient was negative, which suggests that, as temperature increases, the yield of these constituents decreases. Also, for the constituents having a temperature coefficient less than 1 (magnesium, chloride, and sodium), a unit increase in temperature will produce a greater reduction in yield at low temperatures than at high temperatures. Although these relationships indicate temperature has some importance in predicting yields (table 7), average stream temperature displays a strong relationship only with calcium (fig. 15) and bicarbonate (fig. 16) yields from limestone basins.

As indicated in figures 15 and 16, calcium and bicarbonate yields from limestone basins decrease with increasing stream temperature, which may support the hypothesis that mineral weathering occurs more rapidly at low temperatures than at high temperatures because  $CO_2$  is more soluble at low temperatures (Reynolds and Johnson, 1972).

A positive relationship between stream temperature and annual precipitation is apparent for limestone basins (fig. 17). The higher biological productivity in areas receiving high annual precipitation would seem to contribute little to the weathering of carbonate minerals. Rather, the greater solubility of gaseous  $CO_2$  at low temperatures than at high temperatures would seem to be a dominant factor in aiding the release of constituents to streams in limestone basins. However, the limestone basins having the lowest stream temperatures are in Michigan and Wyoming (fig. 1 and table 1), where they are glaciated. Because glacial deposits are generally more permeable and have fresher mineral faces available for weathering than nonglaciated bedrock, they could presumably release more constituents to streams than soils and bedrock in nonglaciated areas.

#### USES AND LIMITATIONS OF THE MULTIPLE-LINEAR-REGRESSION EQUATIONS FOR PREDICTING DISSOLVED-ION YIELDS

The Mohawk River at Cohoes, N.Y., provides an example of how the multiple-linear-regression equations may be used to estimate constitutent yields. This basin contains limestone, shale, and crystalline bedrock. The area underlain by limestone and shale constitutes 82 percent of the drainage basin. In the crystalline part of the basin, population density is 1 person per square kilometer, temperature



Figure 13. Annual dissolved-sodium yield of streams in relation to basin-population density within drainage basins underlain by single bedrock types in the United States.

**Table 8.** Average percentage of total annual sodium and chloride yield attributed to basin-population density and the relationships between annual yield and population density.

[Values are in percent. Annual yields are in kilograms per square kilometer. Population density is in persons per square kilometer]

Constituent	Limestone basin	Sandstone basin	Crystalline basin	All basins
Sodium	14 <u>+</u> 9	17 <u>+</u> 27	10 <u>+</u> 21	13 <u>+</u> 19
Chloride	23 <u>+</u> 19	24 <u>+</u> 30	17 <u>+</u> 28	20 <u>+</u> 25

Annual Soc	iium Yield	-	30(Population	density)0.82
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Annual Chloride Yield =  $20(Population density)^{1.21}$ 

averages about 9°C, and annual precipitation is about 140 cm. In the limestone and shale part of the basin, population density is 70 persons per km<sup>2</sup>, stream temperature averages about 13°C, and annual precipitation is about 105 cm. The annual chloride yield may be computed by using the appropriate equation in table 4 and adding the yields associated with the fractional area of the basin underlain by a specific bedrock type. For this example, limestone



Figure 14. Annual dissolved-chloride yield of streams in relation to basin-population density within drainage basins underlain by single bedrock types in the United States.

and shale were grouped together and treated as limestone. Because only precipitation and population density are needed, the computation is as follows:

$$Y_{C1} = 0.18(0.6)(140)^{1.59}(1.0)^{0.36} + 0.82(0.6)(105)^{1.59}(70)^{0.36} = 279 + 3,714 = 3,993 kg/km2$$

The computed yield compares well with the observed chloride yield,  $3,040 \text{ kg/km}^2$  for 1952-53 and 7,450 for 1970-74, estimated by Peters and Turk (1981) for the basin. (Almost all of the chloride increase from the 1950's to the 1970's was attributed to increased use of road salt for snow and ice removal (Peters and Turk, 1981.))

A similar computation for sulfate, using all variables, and grouping the limestone and shale as limestone, is as follows:

$$Y_{SO4} = 0.18(1.00)(44)(140)^{1.20}(1.0)^{0.20}(9.0)^{-0.86} + 0.82(3.3)(44)(105)^{1.20}(70)^{0.20}(13)^{-0.86} = 450 + 8,170 = 8,620 kg/km2$$



Figure 15. Annual dissolved-calcium yield of streams in relation to average stream temperature within basins underlain by single bedrock types in the United States.

Figure 16. Annual dissolved-bicarbonate yield of streams in relation to average stream temperature within basins underlain by single bedrock types in the United States.

The computed sulfate yield is about 50 percent lower than that estimated for 1970–74 by Peters and Turk (1981), but it is within the order of magnitude (862 to  $86,200 \text{ kg/km}^2$ ) accuracy determined for the equation.

As noted in the example, yields estimated from the multiple-linear-regression equations compare well with the observed yields. Discretion should be used, however, when estimating yields and interpreting their results because the standard error of estimate of these equations (table 4) suggests that the predicted yield will be only within an order of magnitude of the actual yield. Furthermore, estimated yields may not be accurate for drainages where other major constituent sources, such as evaporite minerals or cultural and industrial contributions, are known.

Also, application of these equations to basins that have values of the independent variables (annual precipitation, population density, or average stream temperature) outside the range of values for which these equations were derived may yield erroneous results because the relationship may not be valid. The equations, however, could be used to provide an initial estimate of yields, particularly in areas where stream chemistry data are unavailable.

#### **CONSIDERATIONS FOR FUTURE STUDIES**

Results of this study indicate that, of the four factors analyzed, annual precipitation and the type of rock underlying a basin are the most important in determining the yields of dissolved major ions in streams. Consequently, a more refined analysis to assess the interaction between climate and rock types in relation to stream composition would provide data on assessing how climatic changes affect the weathering of basin materials. Such an analysis could also address contributions of constituents from the atmosphere, which, as results of this study suggest, may be substantial in most basins. It would be preferable to use basins underlain by single rock types having comparable and known ranges in mineral composition so that deviations in the relationships could be attributed to the correct source(s).

The use of population density to assess contributions of human activities to streams, which was only partly successful in this study, could be replaced with a more specific measure, such as land use, which can be divided into categories that correspond to known types of contributions.



**Figure 17.** Average stream temperature in relation to annual precipitation within basins underlain by single bedrock types in the United States.

Results from this study indicate that yield of all constituents is an exponential function of precipitation quantity. Yet, the method of averaging yields and the use of average precipitation from long-term data may have compounded the error associated with assessing the relationship between yield and precipitation quantity. An investigation of the relationship between annual precipitation and annual yield over a long period of record at basins representing a wide range in climatic conditions should be made to assess the associated errors.

#### SUMMARY

The yields in streams of the seven major dissolved ions—sodium, potassium, magnesium, calcium, chloride, sulfate, and bicarbonate—and yields of dissolved solids from basins can be predicted to within about 0.4 logarithmic units through multiple-linear-regression equations combining data on rock type, annual precipitation, basin-population density, and average stream temperature. The range in annual yields of these constituents was 3 to 4 orders of magnitude—10 to 100,000 kg/km<sup>2</sup>. The equations presented herein can be used to predict the yield of a constituent to within an order of magnitude of the observed yield.

The most important basin characteristics for predicting yields were annual precipitation quantity and rock type. Average yields from limestone basins were larger than those from sandstone or crystalline basins. Only the yields of calcium, bicarbonate, and dissolved solids could be differentiated between sandstone and crystalline basins. In limestone basins, the dissolved-solids yields were dominated by contributions of calcium and bicarbonate from carbonate minerals weathering. In sandstone basins, dissolved-solids yields were dominated by bicarbonate and sulfate; in crystalline basins, dissolved-solids yields were dominated by bicarbonate.

The regression coefficients in the multiple-linear-regression equations indicate that the ratio of constituent yields in limestone basins to those in crystalline basins and in sandstone basins was as follows: magnesium, 11:3:1; calcium, 10:1.6:1; sulfate, 1.4:0.4:1; bicarbonate, 8.7:2.2:1; and dissolved solids, 4.2:1.1:1.

The percentage of yield that could be related to annual precipitation quantity averaged between 58 and 71 for all basins. Smaller percentages for most constituents, particularly calcium, were associated with limestone basins, which are rich in carbonate minerals, so that a larger percentage of yield is derived from the rock than from the atmosphere. As a consequence, these appear relatively unaffected by precipitation quantity.

An assessment of direct atmospheric contributions of sodium, potassium, calcium, chloride, and sulfate from precipitation-quality data (Junge and Werby, 1958) suggests that 30 percent of the sodium and chloride yield and 60 percent of the sulfate yield could be derived from precipitation. In this study, the sulfate percentage was greater in crystalline basins (80 percent) than in limestone basins (38 percent), presumably because crystalline rocks contain less sulfur. Although the atmospheric contribution of calcium averaged 34 percent of the annual yields of all basins, the amount contributed to yields from limestone basins was small (7 percent), which suggests that most of the calcium is derived from weathering of carbonate minerals within the basin.

Population density was effective in predicting only the yields of sodium, potassium, chloride, and sulfate in consort with other variables. In each case population density was of lesser importance than precipitation quantity, rock type, or average stream temperature. Annual precipitation and population density combined were the most reliable predictors of sodium and chloride yields, however. The amount of these constituents in annual yields that could be attributed directly to population density averaged only 13 percent for sodium and 20 percent for chloride.

The relationship between average stream temperature and yields indicated that temperature has a negative effect on the yields of potassium, calcium, sulfate, bicarbonate, and dissolved solids. This effect is most pronounced for calcium and bicarbonate yields from limestone basins and may result from increased dissolution of carbonate minerals at low temperatures as well as from the large weathering potential of glacial deposits in northern basins, where stream temperatures were the lowest.

The prediction of a constituent yield may be improved by determining the amount contributed from atmospheric deposition. Yield prediction may also be improved by replacing population density in the multiple-linear-regression equations with a more specific measure of contributions from man's activities, such as land use. Also, multiple-linear-regression relationships developed for each rock type separately might improve yield prediction because the effect that these environmental factors have on yield is probably partly related to basin mineralogy.

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### APPENDIX

Published References to Basin Geology

- A. By rock type and USGS station number. (Locations are given in fig. 1 and table 1.)
- B. By author, in alphabetical order.

11565	· · · · · · · · · · · · · · · · · · ·	
station identifi-		Limestone basins
number	Station name and location	References
02313000	Withlacoochee River near Holder, Fla.	Carr and Alverson, 1956; Espenshade and Spencer, 1963; Vernon, 1951; Vernon and Puri, 1965.
02320500	Suwanee River at Branford, Fla.	Georgia Geological Survey, 1891; Lawton and others, 1976; Vernon and Puri, 1965.
02329000	Ochlockonee River at Havana, Fla.	Brantly, 1916; Georgia Geological Survey, 1917; Lawton and others, 1976; Pascale and others, 1978; Sellards, 1917; Sellards and Gunter, 1918; Veatch and Stephenson, 1911.
02368000	Yellow River at Milligan, Fla.	Alabama Geological Survey, 1926; Turner and Scott, 1968; Vernon and Puri, 1965.
03085000	Monongahela River at Braddock, Pa.	Cardwell and others, 1968, Pennsylvania Topographic and Geologic Survey, 1960.
03254000	Licking River at Butler, Ky.	Hall and Palmquist, 1960; Palmquist and Hall, 1960.
03290500	Kentucky River at Lock 2 at Lockport, Ky.	Jillson, 1954; Newell, 1977; Newell and Rice, 1977.
03425000	Cumberland River at Carthage, Tenn.	Douglas and others, 1965; Miller, 1974; Miller and others, 1966.
03543005	Tennessee River at Watts Bar Dam, Tenn.	Georgia Department of Mines, Mining and Geology, 1939; Miller, 1974; Miller and others, 1966, North Carolina Department of Conservation and Development, 1958; Stuckey and Conrad, 1958; Virginia, Department of Conservation and Development, 1963.
03571850	Tennessee River at South Pittsburg, Tenn.	Georgia Department of Mines, Mining and Geology, 1939; Lawton and others, 1976; Miller, 1974; Miller and others, 1966, North Carolina Department of Conservation and Development, 1958; Virginia, Department of Conservation and Development, 1963.
03593005	Tennessee River at Pickwick Landing Dam, Tenn.	Alabama Geological Survey, 1926; Georgia Department of Mines, Mining and Geology, 1939; Miller, 1974; Miller and others, 1966; North Carolina Department of Conservation and Development, 1958; Stuckey and Conrad, 1958; Virginia, Department of Conservation and Development, 1963.
04045500	Tahquamenon River near Tahquamenon, Mich.	Bergquist, 1931, 1936; Dorr and Eschman, 1970; Hussey, 1952; Martin, 1936, 1955; Nellist, 1908; Smith, 1936.
04057004	Manistique River at Manistique, Mich.	Bergquist, 1936, Dorr and Eschman, 1970; Hussey, 1952; Martin, 1936.
04108690	Kalamazoo River at Saugatuck, Mich.	Dorr and Eschman, 1970; Leverett, 1929; Martin, 1936, 1955, 1957; Nellist, 1908.
04126520	Manistee River at Manistee, Mich.	Dorr and Eschman, 1970; Leverett, 1929; Martin, 1936, Nellist, 1908.
041320 <b>52</b>	Cheboygan River at Cheboygan, Mich.	Dorr and Eschman, 1970; Landes and others, 1045; Martin, 1936; Nellist, 1908; Smith and Kelly, 1947.
04165500	Clinton River at Mt. Clemens, Mich.	Bay, 1938; Dorr and Eschman, 1970; Martin, 1936, 1955, 1957; Nellist, 1908; Wisler and others, 1952.
08103 <b>9</b> 00	South Fork Rock Creek near Briggs, Tex.	Darton and others, 1937; Hill, 1899; Paige, 1911; Renfro and others, 1973; Spencer and others, 1912; Taft and Leverett, 1892.

Appendix A. Published references to basin geology, by rock type and USGS station number [Full citations are given in part B.]

USGS station identifi-		Sandstone basins
cation number	Station name and location	References
13018300	Cache Creek near Jackson, Wyo.	Love, 1956; Love and Love, 1978, Love and others, 1955.
01545600	Young Womans Creek near Renovo, Pa.	Chance, 1880; Denny, 1956; Elbright, 1952; Sherwood, 1880.
03049625	Allegheny River at New Kensington, Pa.	Caster, 1934; Fisher and others, 1970; Kimmel and Schiner, 1970; Laird, 1941; Legette, 1936; Pennsylvania Topographic and Geologic Survey, 1960; Platt and Platt, 1877; Willard, 1962.
03237280	Upper Twin Creek at McGraw, Ohio	Bownocker, 1947; Goldthwait and others, 1961; Pepper and others, 1954.
06439300	Cheyenne River at Cherry Creek, S. Dak.	Darton, 1951; Dobbins and others, 1957; Love and others, 1955; Sharp and Gibbons, 1964; South Dakota Geological Survey, 1971; Whitcomb, 1965.
06452000	White River near Oacoma, S. Dak.	Burchett, 1969; Darton, 1951; Nebraska Geological Survey, 1969; South Dakota Geological Survey, 1971.
06478500	James River near Scotland, S. Dak.	Carlson, 1969, Darton, 1951; South Dakota Geological Survey, 1971.
07026000	Obion River at Obion, Tenn.	Miller, 1974; Miller and others, 1966.
07231500	Canadian River at Calvin, Okla.	Dane and Bachman, 1965; Darton and others, 1937; Gould, 1906, 1907; Johnson, 1972; Johnson and Gonzales, 1978; Johnson and others, 1972; Miser, 1957.
07232500	Beaver River near Guymon, Okla.	Baldwin and Muehlberger, 1959; Dand and Bachman, 1965; Darton and others, 1937; Gould, 1907; Johnson, 1972; Johnson and Gonzales, 1978; Johnson and others, 1972; Miser, 1957; Renfro and others, 1973; Schoff, 1943.
07234000	Beaver River at Beaver, Okla.	Baldwin and Muehlberger, 1959; Dane and Bachman, 1956, Darton and others, 1937; Gould, 1907; Johnson, 1972; Johnson and Gonzales, 1978; Johnson and others, 1972; Miser, 1957; Renfro and others, 1973; Schoff, 1943.
07237500	North Canadian River at Woodward, Okla.	Baldwin and Muehlberger, 1959; Dand and Bachman, 1965; Darton and others, 1937; Gould, 1907, Johnson, 1972; Johnson and Gonzales, 1978; Johnson and others, 1972; Kansas State Geological Survey, 1964; Miser, 1957; Renfro and others, 1973; Schoff, 1943.
07245000	Canadian River near Whitfield, Okla.	Dane and Bachman, 1965; Darton and others, 1937; Gould, 1906; Johnson, 1972; Johnson and Gonzales, 1978; Johnson and others 1972; Miser, 1957; Renfro and others, 1973; Schoff, 1939.
01059400	Androscoggin River near Auburn, Maine	Billings, 1928, 1955; Hussey and others, 1967.
01066000	Saco River at Cornish, Maine	Billings, 1955; Henderson, 1950; Hussey and other, 1967; Pirsson and Rice, 1911; Quinn, 1953; Smith and others, 1939.
04014500	Baptism River near Beaver Bay, Maine	Elftman, 1894; Grout and Schwartz, 1925, 1939; Leverett, 1929; Olcott and others, 1976; Van Hise and Leith, 1911.
05124480	Kawishiwi River near Ely, Maine	Bath and others, 1965, Green, 1972; Green and others, 1966; Leverett, 1929; Morey and others, 1970; Van Hise and Leith, 1911.

Appendix A. Published references to basin geology, by rock type and USGS station number-Continued

USGS					
station identifi-	Crystalline basins				
cation number	Station name and location	References			
06623800	Encampment River above Hog Park Creek near Encampment, Wyo.	Atwood, 1937; Burbank and others, 1935; Henderson and others, 1932; Love and others, 1955; Spencer, 1904; Tweto, 1976.			
07311200	Blue River Creek near Cache, Okla.	Dane and Bachman, 1965; Govin, 1928; Hoffman, 1930; Johnson and others, 1972; Miser, 1957.			
08431700	Limpia Creek above Ft. Davis, Tex.	Baker and Udden, 1918; Darton and others, 1937; Jones, 1938; Renfro and others, 1973.			
09352900	Valleciio Creek near Bayfield, Colo.	Atwood and Mather, 1932, Baker, 1969; Burbank and others, 1935; Cross and others, 1905, 1935; Henderson and others, 1932; Larsen and others, 1956; Steven and others, 1969; Tweto, 1976.			
09430600	Mogollon Creek near Cliff, N. Mex.	Gillerman, 1964; Ratte, 1975; Weber and Willard, 1959.			
09508300	Wet Bottom Creek near Childs, Ariz.	Wilson and others, 1959, 1969.			
10396000	Donner und Blitzen River near Frenchglen, Oreg.	Piper and others, 1939, Renound and Newton, 1972; Walker, 1977; Walker and King, 1969; Waring, 1909.			
11264500	Merced River at Happy Isles Bridge near Yosemite, Calif.	Calkins, 1970; Jennings and others, 1977; Matthes, 1930; U.S. Geological Survey and California Division of Mines and Mining, 1966.			
12247390	Andrews Creek near Mazama, Wash.	Huntting, 1961; Smith and Calkins, 1904; Weissenborn, 1969.			
03169500	Big Jacks Creek near Bruneau, Idaho	Malde and others, 1963; Ross and Forrester, 1959; Weissenborn 1964.			
13331500	Minam River at Minam, Oreg.	Kranskopf, 1943; Renound and Newton, 1972; Smith and others, 1941; Walker, 1977; Walker and King, 1969.			
14048000	John Day River at McDonald Ferry, Oreg.	Brown and Thayer, 1977; Collier, 1914; Hodge, 1932; Renound and Newton, 1972; Robinson, 1975; Thayer, 1940; Walker, 1977.			
14103000	Deuschutes River at Moody near Biggs, Oreg.	Hodge, 1932, 1940; Moore, 1937; Renound and Newton, 1972; Robinson, 1975; Swanson, 1968; Walker, 1977; Walker and King, 1969; Wells and Peck, 1967, Wilkinson, 1940.			
14113000	Klichetat River near Pitt, Wash.	Huntting, 1961; Weissenborn, 1969.			
16031000	Wiamea River near Waimea, Kauai, Hawaii	Hinds, 1930; MacDonald and others, 1960.			
16213000	Waikele Stream at Waipahu, Oahu, Hawaii	MacDonald, 1940; Stearns, 1939, Winchell, 1947.			
16229300	Kalihi stream at Kalihi, Oahu, Hawaii	Bennison, 1974; Stearns, 1939; Winchell, 1947.			
16400000	Halawa stream near Halawa, Molokai, Hawaii	Stearns and MacDonald, 1947.			
16618000	Kahakuloa stream near Honohohau, Maui, Hawaii	Stearns and MacDonald, 1942; Yamanaga and Huxel, 1969, 1970.			

Appendix A. Published references to basin geology, by rock type and USGS station number-Continued

USGS station identifi-	Crystalline basins			
number	Station name and location	References		
16704000	Wailuku River at Piihonau, Hawaii, Hawaii	MacDonald, 1949, Stearns and MacDonald, 1946.		
16717000	Honolii stream near Papaikou, Hawaii, Hawaii	MacDonald, 1949; Stearns and MacDonald, 1946.		

Appendix A. Published references to basin geology, by rock type and USGS station number-Continued

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#### **Conversion Factors and Abbreviations**

The following factors may be used to convert the International System of units (SI) of measure used in this report to inch-pound units.

Multiply	by	<u>To obtain</u>
	Length	
millimeter (mm)	0.0394	inch (in)
centimeter (cm)	0.394	inch (in)
meter (m)	3.28	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km²)	0.3861	square mile (mi <sup>2</sup> )
square meter (m²)	10.76	square foot (ft²)
	Volume	
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.0610	cubic inch (in <sup>3</sup> )
	Mass	
gram (g)	0.0353	ounce (oz)

#### Other abbreviations used in this report:

kg/km<sup>2</sup>, kilograms per square kilometer persons/km<sup>2</sup>, persons per square kilometer °C, degrees Celsius cm/yr, centimeters per year