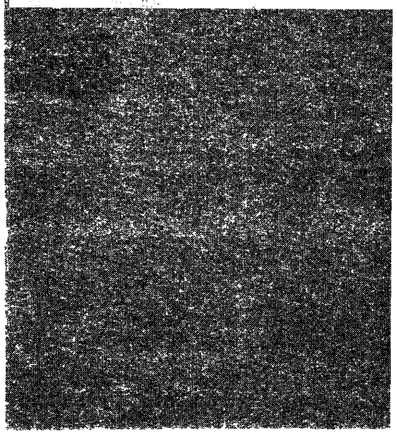
Chloride in Natural Continental Water—A Review



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Chloride in Natural Continental Water— A Review

By J. H. FETH

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FOREWORD

This publication (Water-Supply Paper 2176) is the first in the Geological Survey's Water-Supply Paper (WSP) series to be published in a recently adopted new format. The larger page size (8½ × 11 inches) will permit greater flexibility in presentation of information, especially of tables and illustrations. Lower printing costs and more expeditious publication schedules also are anticipated. Consequently, we will be able to achieve timely release of important water information through the familiar, widely distributed and archived Water-Supply Paper series rather than through the less familiar and locally distributed informal publications series used in recent years. Water Supply Papers will continue to emphasize subjects of nationwide interest. Data compilations, which are now released in other ways, will not normally be a part of this series.

The first Geological Survey Water-Supply Paper was published in 1896. In the preface to that report F. H. Newell, Hydrographer-in-Charge, stated that the purpose of this publication series was to:

> * * * afford an opportunity for prompt publication of short reports, generally popular in character, relating to the water resources and the methods of utilizing these. To reply to questions arising in various parts of the country regarding the progress of the investigation of water resources and the facts relating to the available supply of water for irrigation, power, or domestic use, it is necessary to have pamphlets which can be sent out * * *, and which, in order to answer the particular needs of individuals or communities, will not be too general in character.
>
> It is not intended to bring together simply a lot of obvious facts and inferences relating to the water resources of the country, but to extend the bounds of knowledge in directions where exact information will have the greatest future value. It should be recognized that progress in new fields can never be so rapid as traveling over the old paths. It is only by bringing together clearly and concisely what is already known and building upon this that progress can be made in the utilization of the water resources of the country.

Eighty-five years later, Mr. Newell's words still hold true. Over the years, the Survey has published numerous reports, including more than 2,100 Water-Supply Papers, that cover all aspects of water resources and hydrology. We are continously seeking ways to improve our dissemination of water-resources information, and we hope this new, improved Water-Supply Paper series will help us reach, more effectively, an ever-increasing diversified audience.

Doyle G. Frederick

Doyle G. Frederick
Acting Director

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Chloride in Natural Continental Water—A Review

By J.H. Feth

Abstract

Chlorine is the 15th most abundant element in the outer lithosphere but is the most abundant in the hydrosphere, which is dominated by the oceans. Chloride (Cl) ranks 5th in abundance among the ions in average river water. Cl is probably present in all natural waters, although below detection limits in some. The geochemistry of chlorine is largely that of the Cl ion. The ready solubility of Cl salts and general noninvolvement in oxidation-reduction reactions makes chlorine one of the more mobile of elements.

The concentrations of chlorine in rocks are poorly known. Estimates suggest that in igneous rocks concentrations are less than 500 ppm (parts per million), in sedimentary rocks, excluding evaporites, from 10 or less to about 1,500 ppm. In a few individual minerals such as sodalite, apatite, mica, and hornblende, where chlorine replaces hydroxyl, and in scapolite, the concentration may reach 50,000 ppm or more. I found virtually no information about concentrations of chlorine in metamorphic rocks except those containing scapolite.

Cl is present in the tissues of all plants and in all animals where it exercises important physiological controls. Concentrations in living tissue are estimated to range from 100 to 1,000 ppm.

In the oceans, the average concentration of Cl^- is about 19,000 mg/L, its mass about 270×10^{14} metric tons. Its mass in the hydrosphere other than the sea is unknown but probably insignificant by comparison. Concentrations of Cl in precipitation range from less than 0.02 to more than 200 mg/L (milligrams per liter) in samples taken on exposed sea coasts during storms. In surface waters the concentrations range from less than 1 to more than 280,000 mg/L, in ground waters the range is from less than 1 to more than 200,000 mg/L.

Cl is the ion that dominates most discussion of "cyclic salts." Unquestionably there is a Cl cycle in which Cl from the sea is incorporated in masses of moving air—then in precipitation—then runoff and ground water—and finally in water discharged from the continents back to the sea. The magnitude of the Cl contribution from precipitation to runoff and ground water remains uncertain. Where surface and ground waters contain less than 5 or 10 mg/L Cl, atmospheric sources may be the major contributors. But where high concentrations of Cl are involved, the data available indicate that continental sources can supply almost all the Cl load.

A problem is posed by those numerous places where, year after year, ground water carries a virtually constant concentration of Cl, large or small There is implication in those occurrences of a supply that either releases Cl ions at constant rate or that is itself renewed at a constant rate. Understanding of Cl contributions from the atmosphere to both surface and ground water requires, among other things, that we learn a great deal more about the volume of aqueous precipitation and especially about the chemical character of precipitation, including rain, dry fallout, and bulk precipitation, the geochemically active mixture of aqueous precipitation and dry fallout.

There are various obvious sources from which Cl gets into natural water. These include salt particles and brine droplets airborne from the sea, beds of halite, saline crusts of desert basins, magmatic gases, and human and animal wastes. These obvious sources do not seem adequate to explain Cl concentrations found in water in many areas. They do not, for instance, seem to explain the fact that many fault-zone springs have high Cl concentrations. Existing information on the chlorine content of rocks—and what little we know of Cl in soils—does not suggest that weathering of rocks and leaching of soils would supply the quantities of Cl found (and continually renewed) in surface and ground water

Studies of rock leaching and of the thermal-water systems of New Zealand suggest that hydrothermal alteration of volcanic rocks may be supplying all the Cl in the New Zealand thermal waters. In some areas scapolitic rocks might possibly be a source for Cl in water.

Because stations were abandoned and practices of sampling and compositing of samples changed drastically, a statistical analysis of Cl records from 1957 (used as a base year for this study) against those of 1975 (a "normal" year in which environmental cleanup effects might have been discovered) and 1977 (a drought year) appeared unwarranted. Records suggest, however, that the effect of the drought could be seen in high concentrations but low Cl loads at some river stations in Texas and Oklahoma, especially.

With respect to ground water, certain regions, of which Alabama is one, are characterized by many sources that yield water with concentrations of less than 10 mg/L Cl; others such as the northern Great Plains have wells that commonly yield Cl in concentrations of hundreds or even thousands of milligrams per liter. Examples from Utah show that Cl concentrations from the same geologic formation may span five orders of magnitude. Although water from springs tended to have low concentrations, depth of wells proved to be an unreliable criterion for predicting concentration.

A study of 30 shallow wells on Long Island, N.Y., showed that in about one-half, Cl concentration fluctuated only a few milligrams per liter over a year, whereas in the other half the fluctuation was from 20 to nearly 300 mg/L One-half the wells showed maximum concentrations in winter, the other half in summer.

Discharge of saline ground water from springs adds an incalculable tonnage of Cl to streams worldwide. Individual sources in Texas (300,000 to 330,000 t/yr), Arizona (150,000 t/yr) and Idaho (14,000 t/yr) suggest the magnitude of the occurrence.

The geochemistry of chlorine is dealt with only sketchily in this report.

There are two stable isotopes of chlorine, ^{35}Cl which makes up about 75 percent of that found in nature, and ^{37}Cl. The radioactive isotope, ^{36}Cl, which has a half-life of 300,000 years, is produced naturally by action of cosmic rays, and perhaps more abundantly by irradiation of sea spray during thermonuclear tests.

Under natural conditions, Cl generally does not participate in oxidation or reduction reactions. Its main exchange activity is between solid sodium chloride and the chloride ion.

In virtually all waters having 20,000 mg/L dissolved solids or more, the dominant anion is Cl. Thus most oil-field brines and other brines of high concentration are Cl brines.

The derivation of many subsurface brines with dissolved solids in the range of 50,000 to 200,000 mg/L involves difficult geochemical puzzles. Several explanations have been offered. The explanation in current favor for many such brines includes concentration of ions below shale or clay layers that act as semipermeable membranes, permitting passage of water molecules but retarding the passage of ions dissolved in the water. It seems to explain many occurrences where water, presumably having an original concentration closely analogous to that of modern seawater, has been converted into brine with 100,000 mg/L or more dissolved solids. The hypothesis is deficient where Br/Cl ratios are either exceptionally large or exceptionally small. The "book" on Cl is far from closed.

INTRODUCTION

> The geochemistry of chlorine is essentially that of the chloride ion. There is a definite chlorine cycle * * *. Chlorine (chloride) is being introduced into the hydrosphere by the weathering of rocks and by volcanic activity. This chlorine (chloride) eventually winds up in the sea where a small part of it is deposited in the sediments. The chlorine cycle is completed by return of the chlorine (chloride) to the continents by rain.
>
> (Hoering and Parker, 1961, p. 193)

Chloride (Cl) may well be the ion most commonly determined in water analyses. It is generally conservative, traveling through the hydrologic cycle with less involvement in oxidation-reduction reactions, adsorption, or the life processes of plants or animals than is true of most common ions. Therefore, Cl has been considered to be a good tracer. Increasing concentrations with time may indicate seawater intrusion of aquifers or contamination of surface and ground water by industrial or domestic wastes. Periodic Cl determinations are used to monitor water sources for contamination. Cl concentration limits the usefulness of water in various industrial processes and hence is routinely monitored in industry. Cl is among the constituents determined in many routine and all detailed analyses of water.

The present Analytical Service and Research Coordinator (W. A. Beetem, oral commun., Sept. 12, 1979) said that the U.S. Geological Survey alone makes more than 90,000 Cl determinations per year on samples collected in the Survey's water-quality networks of surface- and ground-water stations and project studies. Its research investigations add an unknown number to that total. Considering similar activities in other nations, by States, municipalities, other governmental agencies, and by industry, it seems not unreasonable to estimate that worldwide, one million to several million water samples are analyzed for Cl each year. Most of those analyses are not published. Many published analyses are unrelated to the environment or so vaguely related that they defy interpretation. Nevertheless, the volume of manipulatable data on Cl in water is fantastically large. This paper will deal with only a fraction of the data. Most examples to be discussed and most of the references cited are from the United States. However, the principles that govern the distribution and behavior of Cl in water are universal, and those that can be stated with any degree of confidence have carryover value throughout the world.

Despite the quotation that opened this paper, this is not a review of the geochemistry of chlorine. Rather, it is the purpose of this report to discuss something of the hydrogeochemistry of Cl and to illustrate some of the gaps in our knowledge, omitting perhaps the basic problem—the origin of the vast quantity of Cl in the oceans. The most detailed considerations of the sources of Cl in the sea remain those of Conway (1942), Rubey (1951), and Correns (1956). The report also omits estuaries, the interfaces between continental water and the sea.

The geochemistry of chlorine was discussed by Rankama and Sahama (1950), Correns (1956), and briefly by Hem (1970); of these only Hem concentrated attention upon Cl in water.

Some aspects of the hydrologic cycle of Cl will be considered in sections such as the following: Problems of balance—"cyclic salts"; sources of Cl; distribution of Cl in surface and ground water; and hydrochemical behavior of Cl. Necessarily there is overlap among the topics. Indeed, as the hydrologic cycle is a continuum that includes continental water and the hydrochemical cycle, the topical subdivisions basically are artificial. They seem desirable as devices to focus attention on individual aspects of the whole.

ABUNDANCE OF CHLORINE AND CONCENTRATIONS OF CHLORIDE

Abundance

Chlorine occurs in virtually all rocks in measurable concentrations. It is seldom sought in rock analyses, however, because the determination requires a separate procedure and because, in most rocks, the concentrations are so small that they fall well within the fraction of a 1-percent margin of error characteristic of rock analyses—even the good ones. However, on the basis of admittedly scanty data, some estimates of abundance have been made.

Chlorine, with a mean concentration of 314 g/t (grams per metric ton), is the 15th most abundant element in the outer lithosphere according to Rankama and Sahama (1950, p. 40-42). Sodium ranks 4th, calcium is 5th, magnesium 7th, potassium 8th, and sulfur 13th. Others have ranked the elements differently, using various bases and sources of data. Taylor (1964, p. 1280-1281), for example, ranked chlorine 19th in abundance (mean concentration 130 ppm = g/t), sulfur 15th, sodium 6th, and calcium, magnesium, and potassium as above. A critical review and summary of various estimates of crustal abundance of the elements was published by Parker (1967). In the sea, which dominates the hydrosphere, the rankings and average concentrations of the appropriate ions are as follows:

Rank	*Ion*	*Concentration (mg/L)*
1	Cl	19,300
2	Na	10,600
3	SO_4	2,560
4	Mg	1,270
5	Ca	400
6	K	380

Thus Cl is greatly enriched in the hydrosphere relative to the abundance of chlorine in the lithosphere.

Rankama and Sahama (1950, p. 286) estimated the mass of the oceans to be about $14{,}100 \times 10^{20}$ g. On that basis, and assuming a Cl concentration of 19,000 mg/L, the mass of chlorine in the oceans (as chloride) is about 270×10^{20} g, or roughly 270×10^{14} metric tons. The mass of Cl in the rest of the hydrosphere cannot be estimated, but is probably insignificant in comparison.

Concentrations

Livingston (1963, p. 40-41) gave the following estimate of the mean composition of river waters of the world:

Rank	*Ion*	*Concentration (mg/L)*
1	HCO_3	58.4
2	Ca	15
3	SiO_2	13.1
4	SO_4	11.2
5	Cl	7.8
6	Na	6.3
7	Mg	4.1
8	K	2.3

Livingston cited Cl concentrations in surface water ranging from less than 1 to 280,000 mg/L (milligrams per liter), the latter in the Dead Sea. White and others (1963) showed Cl concentrations in ground water ranging from less than 1 to more than 200,000 mg/L. The lower values are in water from igneous rocks, the higher from waters associated with halite deposits.

Cl is present in the tissues of all plants (Rankama and Sahama, 1950, p. 761-762), and in all animals where the greatest concentrations (not stated quantitatively) are in the lower marine organisms; smallest concentrations occur in some freshwater species. Cl is a factor in plant growth, a constituent of gastric juices, and a complexing element in the transport of metals. Along with sodium, it determines the quantity of water in living tissues and the osmotic pressure in tissue fluids. Correns (1956, p. 228) estimated the concentration of Cl in living tissue to range from 100 to 1,000 mg/L.

Although chlorinated organic compounds are outside the scope of this paper, as they are nearly all man-made, the fact of their occurrence in measurable quantities in water is of great public-health concern. The origin of most is known or inferred to be in pesticides or industrial materials or the waste compounds resulting from their manufacture.

Concentrations in Relation to Use of Water

Threshold or limiting concentrations of Cl recommended for various uses of water have been reported by McKee and Wolf (1963, p. 91-161). The limits for drinking water recommended by the World Health Organization (1971) and by the Environmental Protection Agency (1977) are as follows (concentrations in mg/L):

	WHO International	*EPA*
Maximum limit	600	250
Recommended limit	200	—

The taste threshold varies with individuals, most detecting a salty taste when the concentration of Cl is about 400 mg/L, but some at about 100 mg/L and others not until 700 mg/L; harmful effects on humans appear at concentrations of 900-1,000 mg/L in hot, dry areas where ingestion of water is large (McKee and Wolf, 1963, p. 160).

Animals are generally more tolerant of Cl, harmful limits cited by McKee and Wolf (1963, p. 161) being as follows:

	Cl *(mg/L)*
All livestock	4,000
Cattle, sheep, swine, chickens	1,500
Trout	400
Various fish	2,000
Bass, pike, perch	4,000
Carp eggs	4,500-6,000
Small bluegills	8,000-10,500

For various industrial uses, McKee and Wolf (1963, p. 88–109) cited the following as threshold or limiting concentrations:

	Cl *(mg/L)*
Brewing (beer)	60–100
Carbonated beverages	250
Dairy industry (cleanup water)	<30
Food-equipment washing	250
Food canning and freezing	600–900(approx)
Photographic processes	<25
Paper mills (process water)	4.5–200
Sugar manufacturing	20
Textile manufacturing	100
Irrigation water	20–700

It is apparent from the foregoing that for some uses Cl concentrations must be found or controlled at quite low levels. The range of concentrations found in natural water has been mentioned.

A FEW PROBLEMS IN BALANCE— "CYCLIC SALTS"

The idea that the Cl content of continental water can be explained by air-borne sea salt seems to have originated with Posepny in 1877. Since then, the cyclic-salt concept has been championed and developed by many writers, for example Eriksson (1955).

Admittedly there is a cycle in which Cl moves from the ocean, through the atmosphere to continental waters, and back to the sea. The process by which the importance of cyclic Cl has, at times, been blown out of proportion can be illustrated by the following example.

Clarke (1924, p. 118–119) prepared a table showing average percentage composition of lake and river water of the world, on the basis of data whose inadequacy he pointed out in meticulous detail. He said that major rivers in Canada and Alaska were not represented by any data, that he based his estimates for Asian rivers on "feeble clues," and that for Africa he used analyses of water of the Nile and for the rest of the continent made estimates by analogy with South America. In that fashion, the final average was at best a rough approximation, as Clarke clearly pointed out.

Sverdrup and others (1942, p. 213–214) repeated Clarke's table and added a column showing percentage composition of seawater, and another showing river-water composition recalculated on the assumption that all Cl is cyclic and other constituents are adjusted according to their proportion in seawater. They said that "a considerable proportion of the dissolved material carried to the sea by rivers is 'cyclic salt'—that is, salt that has been carried inland by the atmosphere and then deposited or carried down by rain or snow." They then discussed mineral increments derived from weathering and leaching of rocks and soil and concluded, "If we assume that all of the chloride in the river-water is cyclic, the amounts of the other elements must be modified in the proportions in which they occur in seawater. It is hardly possible that this assumption is entirely correct * * *."

Rankama and Sahama (1950, p. 274) repeated the Sverdrup table, commenting that it shows "the composition of the solids in river-water, corrected with reference to the cyclic salts carried from the ocean to the atmosphere by spraying and deposited by precipitation on the continental areas. This analysis is according to Sverdrup, Johnson, and Fleming (1942), who believed that all the chloride in river-water is cyclic." Thus, by a process of dropping modifying statements and failing to state assumptions, the thesis is stated in a major reference work in geochemistry that all Cl in river water is cyclic.

Mason (1952, p. 170) used the cyclic concept in a modified sense, including both airborne Cl and that leached from sedimentary rocks, as in either case the Cl probably came originally from the ocean. In that sense, Cl derived from second- or later-generation igneous rocks might be considered "cyclic" also.

The Cycle at Low Concentrations

It is instructive, perhaps, to consider first the degree to which airborne salts determine the Cl concentration of continental waters. Two quite opposite pictures seem to emerge.

Juang and Johnson (1967) studied the cycling of Cl in two small forested watersheds in New England. Weighted-average Cl concentration in precipitation was 0.21 mg/L and in streamflow was 0.51 mg/L in one watershed and 0.50 mg/L in the other. During the study period, September 1965 through August 1966, two-thirds of the Cl input was from wet removal of atmospheric Cl. The authors attributed the remaining one-third to dry removal of gaseous chlorine or particulate Cl by impaction or adsorption in the forest canopy. They concluded that chemical weathering and activities of man did not contribute measurably to the Cl budget.

Kennedy and others (1979) observed that the ratio Cl:Na in precipitation at rural Petrolia some 200 miles north of San Francisco was that of seawater at concentrations ranging from 0.02 to 38 mg/L. At Menlo Park on San Francisco Bay, the Cl:Na ratio was about that of seawater above 0.5 mg/L, but at smaller concentrations Cl was in excess, indicating influence of anthropogenic sources of Cl.

Gorham (1961, p. 804) compared average Cl concentration in precipitation (1-year averages) with average or minimum concentrations in lakes or streams in areas near the precipitation-sampling stations concerned. In those comparisons, the average Cl concentration in precipitation in Newfoundland was 8.9 mg/L, and the winter average in ponded waters on granite in Nova Scotia was 7.7. Precipitation in Wisconsin averaged 0.2 mg/L Cl, and the minimum lake-water concentration in Wisconsin was 0.1. Precipitation at a station in northern Sweden averaged 0.7 mg/L Cl, and the minimum concentration in lake water in northern Sweden was 0.4.

Feth and others (1964a, p. 144–145) observed similar conditions in the Sierra Nevada where the mean concentration of Cl in 79 samples of snow was 0.5 mg/L, that in snowmelt runoff was 0.4; among 56 perennial springs, 7 had Cl concentrations equivalent to the average found in snow and 28 springs had smaller concentrations. Those writers inferred that some Cl was adsorbed—probably on kaolinite which has the capacity to adsorb anions and which is known to be present in the environment.

The Cycle at Higher Concentrations

The foregoing examples all deal with low to very low concentrations of Cl. When large river systems are considered, and Cl concentrations and loads attain major proportions, quite a different picture appears. There the Cl contribution by precipitation is inadequate to explain the loads found in runoff.

The Cl balance in streams is most usefully examined on the basis of loads rather than of concentrations. The available data are plagued with uncertainties and with gaps in the record. They include inadequate knowledge of the following: (1) Precipitation, both as to volume and chemical content; (2) volumes of water lost by evapotranspiration and degree of consequent concentration of mineral content of the water; (3) volumes and concentrations of diversions and return flows; and (4) sources from which minerals in solution are added to the system.

The runoff and Cl concentrations of the Rio Grande in 1945 were given by Cunningham and others (1953, p. 1166), and Cl loads are calculated for this paper as follows:

Station	*Discharge (hm^3)*	*Cl (mg/L)*	*Cl (metric tons)*
Otowi Bridge, near Santa Fe, N. Mex	1,400	5.0	7,000
San Marcial, N. Mex	1,000	32	32,000
Elephant Butte Dam	1,040	35	36,000
Caballo Dam	1,090	50	54,000
El Paso, Tex	702	120	85,000
Hudspeth County Line, Tex	346	550	190,000
Fort Quitman, Tex	256	640	165,000

It is clear that most of the water in the system originates in the headwaters—most of the mineralization occurring downstream. Van Denburgh and Feth (1965) estimated that less than 5 percent of the Cl load was brought in by precipitation. The last two station records suggest that Cl is building up in soils between the two stations as a result of irrigation practices.

A considerable part of the Cl load in the lower Rio Grande basin is brought in by the Pecos River and by return flows from irrigation water (Winslow and Kister, 1956, p. 46), and some is probably added from saline-water sources in valley fill along the river, especially near El Paso (Foster *in* Sayre and Livingston, 1945, p. 48–55).

Van Denburgh and Feth (1965) considered the Cl balance in 11 river basins of the Western United States. Maps (scale 1:2,500,000) of the drainage basins of the rivers were divided into irregular areas by superimposing isohyetals (from U.S. Weather Bureau publications) and precipitation isochlors from Junge and Werby (1958, fig. 1). The areas of the irregular sections were determined by planimeter and the load of Cl brought into each basin calculated. The load carried out of each basin was determined by averaging records of the U.S. Geological Survey for appropriate gaging and sampling stations over a 10-year period. The isohyetals were based on the usual Weather Bureau averaging period. The isochlors were derived from a single year of sampling. Inconsistencies in the data are immediately apparent. But the records used are the best available, and the resulting calculations are presumably significant in establishing trends and general orders of magnitude.

The study indicated that tonnages of Cl brought by rain and snow into the 11 river basins made up from about 2 to nearly 20 percent of the Cl tonnages removed from those basins in an average year. The Pecos River, with its abundant near-surface deposits of halite but low precipitation and runoff, yielded an estimate of 1.6 percent; the Willamette and Rogue River basins, underlain by much less soluble and less chlorine-rich rocks but near the ocean, yielded estimates of 16 percent and 17 percent respectively. The average for the 11 river basins was 8.5 percent.

The inadequacy of sampling volumes of precipitation is suggested by the fact that for the Willamette River the gaged runoff was somewhat more than 100 percent of the calculated precipitation. Granting differences in periods of averaging, nevertheless the discrepancy suggests that precipitation rates in the higher mountains are incompletely known. The inadequacy of our knowledge of the chemical character of precipitation is even more evident. The Junge and Werby record is for 1 year only, and about 60 stations were operated to cover the entire United States.

Whatever the deficiencies of the record, it appears that, in general, far more Cl leaves the drainage basins of major western rivers than can be explained by Cl brought in with precipitation.

Gambell and Fisher (1966) and Fisher (1968) reported that in four North Carolina river basins Cl in precipitation accounted for about one-fourth the load of Cl carried out of the basins in each of 2 years. Fisher (1968) reported that total sales of salt in the area approximately amounted to the difference and attributed the increased load largely to the activities of man.

Gorham (1961, p. 802) cited a few comparable estimates: Estimates from Finland suggested that 30 to 50 percent of the Cl in river water is brought in by rain; an estimate from Japan is that 14 percent of the Cl in a river drainage basin is brought in by rain and 41 percent by dry fallout. However, in another Japanese study, Tsunogai (1975) found that only 20 percent of the Cl was attributable to dry fallout.

Anderson (cited by Gorham, 1961, p. 817) observed the rainfall-runoff relations of five Australian rivers and measured the chemical content of rain over the river drainage basins for 8 years. From those data, he calculated the mean Cl concentrations to be expected in each river. The calculated values were compared with concentrations measured in the river waters, giving close agreement. According to those data, dry fallout and capture of salt particles by vegetation have little effect on the Cl concentrations of the rivers chosen for study, "in marked contrast," as Gorham says, "to results elsewhere." We do not know, however, from the information given, whether Anderson collected and analyzed samples of bulk precipitation or of rain (as defined by Whitehead and Feth, 1964).

Following a meticulous study in the basin of the Mattole River, a coastal stream in northern California, Kennedy and Malcolm (1977) reported that about 85 percent of the Cl discharged was of oceanic origin, and in that sparsely populated basin, the remainder was from rock weathering. Dry fallout in the summer contributed perhaps 10 percent, but during windy winter storms between rains, deposition of dry aerosols added material quantities. The authors cited the conclusion by Tsunogai and others (1975) that Cl in oceanic rain or maritime air increases by a factor of 10 for each 4–7 meters per second increase in wind velocity.

Moderate rain causing little runoff brought large tonnages of Cl to the Mattole basin, and much of the ion was stored in the upper soil in intergranular water and by adsorption on the acid soil particles. Later, during heavy, dilute rain causing much runoff, some of the Cl retained in the soil was removed and an increment was transmitted downward to appear as ground-water-supported runoff during the dry summer.

Four soil profiles showed maximum storage in the upper 30 cm and rapid decrease to 90 cm, the maximum depth sampled. A decrease of about 15-fold was found at all depths with increasing distance (1.5–21 km) from the coast.

Garrels and Mackenzie (1971, table 14.8) estimated that 55 percent of the Cl in river water is cyclic. The derivation of their estimate was not given.

It is abundantly clear that differing assumptions, areas of study, and types and accuracy of data, lead to widely varying estimates. The differences will not be reconciled until a great deal of additional reliable information is in hand. Whatever the worldwide average percentage of airborne (cyclic) Cl in streamflow ultimately turns out to be, present data strongly indicate that there are wide variations in that percentage from region to region, depending on variables such as climate, urban development, nearness to the sea, and geology of the river basin.

The Cycle in Ground Water

The effect of the Cl concentration in precipitation on that of ground water remains largely unexplored. Feth and others (1964a, table 2) attempted to evaluate that effect upon the generally dilute ground water of granitic terrain in the Sierra Nevada. The average concentration of Cl in water from all 56 perennial springs was about twice that found, on the average, in Sierra snow, but the median was virtually identical. In contrast, the ratio for silica averages was 150:1, calcium 26:1, and sodium 10:1. In a study in North Carolina, Laney (1965, p. C189) found an average Cl concentration of 0.2 mg/L in 33 samples of rain and average concentration of 0.9 mg/L and 1.0 mg/L, respectively, in 28 ground-water samples ranging from 9 to 20 mg/L in dissolved solids and 27 ground-water samples ranging from 21 to 30 mg/L in dissolved solids.

Striking a Cl balance in a ground-water system would require at the minimum thorough knowledge of volume and chemical character of precipitation over the area tributary to an aquifer; volume and chemical character of water that becomes recharged; and volume and chemical character of yearly discharge from the aquifer. If specific sources of Cl other than precipitation were sought, it would further be necessary to know the concentrations of chemical constituents at various places, laterally and vertically, within the aquifer.

In a series of articles, four authors (Cooper and others, 1964) described a Cl cycle that occurs in coastal aquifers of high permeability such as the Biscayne aquifer in Florida and basaltic aquifers in Hawaii. From observations and theory alike, they demonstrated that seawater intrudes the lower part of the aquifer in the form of a blunt-nosed wedge. Overlying the wedge, a zone of diffusion is formed where seawater and fresh ground water mix, and above that zone freshwater moves through the upper part of the aquifer. In response to changes in tidal stage and recharge to the aquifer, the wedge moves at times seaward, at times farther inland into the aquifer. Those dynamic forces are responsible for dispersion of seawater into the zone of mixing. The cycle is completed as water from the zone of diffusion is entrained in movement of the overlying freshwater and returned to the sea. In the Biscayne aquifer, near the coastline, the interface between freshwater and saltwater ranges from land surface to about 30 m below.

On the basis of limited temperature data from oil-test wells that suggest a negative geothermal gradient (ground-water temperatures decrease with depth to about 910 m below sea level in coastal areas) Kohout (1967) postulated a deeper cyclic system. Near the coast, water temperature at -910 m is about 21°C; near the axis of the Floridian Plateau at equivalent depth, temperatures are near 42°C. Kohout suggested that cold seawater enters cavernous dolomite whose presence is known from drilling, moves landward becoming gradually warmed by upward flow of geothermal heat, and rises as the added heat decreases its density. The upward movement brings the seawater in contact with fresh water in the Floridan aquifer, where the two water bodies partly mix. The diluted seawater flows seaward with the freshwater to complete the cycle.

SOURCES OF CHLORIDE

General Considerations

In the strict sense, there is probably only one primary source for the Cl in continental water, namely the chlorine or hydrochloric acid discharged to the developing atmosphere during degassing of the primordial earth. However, in this section we are concerned with water presently in streams, lakes, and aquifers and will consider sources in a "now" sense of time.

In that context there are various obvious sources from which surface and ground waters unquestionably obtain part of their Cl content. These include salt particles and brine droplets airborne from the sea, beds of halite, saline crusts of desert basins—both those at present land surface and older deposits buried in the valley fill—magmatic gases, brines, and human and animal wastes. The obvious sources, however, do not seem to explain Cl concentrations found in water in many areas.

The continuing release of Cl at rates that cause modest and virtually constant concentrations in some natural waters pose problems of supply mechanism that remain unanswered—indeed largely unexplored. The common Cl salts are highly soluble in water. Where present in soil or in shallow aquifer materials, rapid solution should (1) cause higher concentrations of Cl than are observed, and (2) cause geologically rapid exhaustion of the supply of Cl ions. There is the implication of a renewable source, but the most obvious one, the atmosphere, seems to be inadequate in many places.

There are a few alternative explanations: Steady entrainment of small volumes of concentrated brine in large volumes of dilute water—a process that would greatly extend the life of the Cl source, or comparatively small, local sources of solid Cl salts where small volumes of water in passage become virtually saturated with Cl ions which then diffuse and are mixed with large volumes of dilute water in an extensive aquifer. But these possibilities are hypothetical; actual examination of appropriate examples has not been made with the exception of a few studies of seawater-freshwater interfaces. In those, the entrainment process seems to occur, effects are generally local, and the processes cannot explain the presence of Cl in aquifers remote from the sea.

High concentrations of Cl are found in many fault-zone waters, whether thermal or not. In some places, the Cl is thought to come from a magma body still cooling and degassing at depth. In the Sierra Nevada, however, some saline thermal springs rise where for kilometers around there is no indication of magmatic activity later than formation of the Sierra Nevada batholith. The last plutons of the batholith were intruded probably in Late Cretaceous time. Larsen (1945) estimated that the southern California batholith, comparable in age and size to that of the Sierra Nevada, cooled to 600°C and crystallized to a depth of about 13 km in about 3 million years, and to a depth of 18 km in some 7 million years. Perhaps ten times 7 million years has elapsed since emplacement of the batholiths, and it is inconceivable that degassing of those intrusive rocks is supplying Cl to thermal springs in the Sierra Nevada.

Why in general are fault-zone waters higher in Cl and SO_4 than springs in adjacent areas that are not located on fault zones? Why are not all fault-zone waters in a given geologic province equally enriched in Cl and SO_4? Some are not.

These, then, are a few of the vexing problems that pertain to the discussion of sources of Cl in the paragraphs that follow.

Oceanic and Atmospheric Sources of Aerosols

Oceanic and atmospheric sources are so closely related that they are here considered together. Many details were given earlier in discussion of cyclic salts.

There is a large literature on the subject of oceanic salt in the atmosphere. Much of it was summarized by Gorham (1961) and by Junge (1963). The following three paragraphs are abstracted and paraphrased largely from the latter source, the numbers in parentheses being page references.

Chlorine occurs in the air in gaseous, liquid and particulate forms. The gas may be in the form of Cl_2 or HCl—perhaps both. Its origin has variously been ascribed to reaction of ozone with sea-salt particles in the atmosphere and to reaction of NaCl and H_2SO_4. Valach (1967) took issue with those hypotheses on the basis of calculations that led him to conclude that such reactions would yield only 5-50 percent of the gaseous chlorine observed. He suggested that volcanic emanations probably supply the rest. Limited studies suggest that the quantities of gaseous chlorine and of Cl in the atmosphere are comparable in magnitude (p. 91–92; 166). Undoubtedly some of the Cl in precipitation is from the gaseous source, whatever its origin. The removal of gaseous and particulate aerosols from the atmosphere is imperfectly understood. However, at least three mechanisms are involved, namely wet removal in precipitation, dry sedimentation, and dry impaction (impingement) on surfaces that impede the flow of air (p. 290, 307).

The oceans are the largest single source of aerosols, and Na and Cl naturally are the most abundant ions in air masses over the sea (p. 157–159). The Cl concentration is expectably high near sea coasts but decreases rapidly, almost exponentially, with increasing distance inland. The effect is attributed to vertical mixing of air masses resulting from convective eddy diffusion. The concentration of Cl aerosols reaches a fairly steady level where mixing is complete and only small concentrations remain in layers of air below cloud base. The result is that over inland areas, Cl in precipitation declines to a relatively constant value that persists across large regions. Some approximate average concentrations are shown in the following table (p. 321):

Concentrations of Cl *in precipitation*

Region	*Distance from coast (km)*	*Concentration (mg/L)*
England	30	7
Holland	50	3.5
Australia	150	1
Sweden	290	.4
United States of America	500	.15

The concentration of gaseous chlorine (as Cl_2) at 116 stations in northwestern Europe was reported by deBary and Junge (1963) from data published from 1954 to 1959 in *Tellus*. The summer average ranged from 1.2 to 114 and the winter average from 1.4 to 82.9 $\mu g/m^3$ (micrograms per cubic meter).

During exceptional events, coastal rainfall contains large concentrations of Cl. Anderson and George (1966, p. G6) reported 200 mg/L Cl during tropical storms Helene (Sept. 28, 1958) and Donna (Sept. 12, 1960). At the same times, but 24 km inland, Cl concentrations were about 5 mg/L. Woodcock and Spencer (1961) estimated that where streams of molten lava flow into the ocean, the rate of production of raindrop nuclei (as sea-salt particles) is 1 to 6 million times greater per unit of surface from steaming lava than from the ordinary sea surface.

Woodcock and others (1953) gave one of the earlier, more colorful, and convincing accounts of how sea-salt aerosols originate. Using high-speed motion pictures, they demonstrated that as bubbles burst on the ocean surface, tiny jets of water are spurted into the air. Raindrop and snowflake impacts have the same result. It is assumed that the jets are in part entrained in air moving across the oceans; the water evaporates if the relative humidity is low and salt crystals remain suspended in the air. Thus a solid-gas aerosol is formed. The salt crystals may become nuclei for raindrop or snow-crystal formation. If relative humidity of the air mass is high, however, the droplets may remain liquid, and a liquid-gas aerosol is formed. Duce (1979) reaffirmed the process described by Woodcock and others.

At the First International Symposium on Acid Precipitation and the Forest Ecosystem, Yue and Mohnen (1976, p. 181-203) presented a theoretical model for formation of HCl in clouds by interaction of atmospheric trace gases and droplets containing NaCl. Their theory proposed global production of 173 million t/yr to 932 million t/yr of HCl as a probable upper limit. The symposium participants, however, presented no actual observations of HCl in precipitation (Dochinger and Seliga, 1976). N and S species were cited by many as the sources of acidity with Cl suspect but not demonstrably involved. Cogbill (1976, p. 368) calculated components of acidity at three stations in New York and two in New Hampshire as 62 percent H_2SO_4, 32 percent HNO_3, and 6 percent HCl.

Earlier, Gorham (1958) observed a correlation between Cl and acidity in samples of urban precipitation where pH was less than 5.7. Correlation between H ions and SO_4 was not significant. He suggested that HCl might be a cause of acidity. But apparently neither Yue and Mohnen nor Gorham nor anyone else has demonstrated its presence.

Continental Sources of Aerosols

Junge (1963, p. 182) remarked that knowledge of natural continental sources of aerosols is meager, but suggested (p. 322) that in arid regions salts deposited at land surface by evaporation of precipitation or evaporation of rising ground water may be a source of Cl aerosols.

Gambell (1962) used the ratio Ca/Cl to infer that, except in immediate coastal areas, continental aerosols provide the larger part of soluble material brought down in precipitation. He concluded that Cl derived by deflation of arid-land basins exerts only small influence on the Cl content of rainfall. His data were drawn from Junge and Werby (1958), hence, they are governed by the distribution of Junge and Werby's sampling points and by the fact that their samples were of rain and did not include dry fallout. Sampling stations in the more arid parts of the southwest were few.

Eardley (1969, p. 21) estimated, on the basis of 1-year samples from five collecting stations supplemented by snowpack profile analyses, that about 14,000 t of Cl are brought to the Great Salt Lake watershed each year from the Pacific Ocean, and some 28,000 t found in precipitation are of local derivation, thus recycled within the basin. Wedman (1964, p. 66-67) calculated that on the average 30,000 t of salt are removed by deflation yearly from the Sebkra Sedjoumi, a saline playa southwest of Tunis, Tunesia, and that a layer less than 1 mm thick over the surface of the 28 km^2 area of the salt flat would supply that quantity. He remarked that dust storms occur commonly and the dust has a salty taste. Data from Wedman's table 4 (p. 65) suggest that nearly one-third of the total load might be Cl.

In summary, aerosols contribute measurable quantities of Cl to precipitation almost everywhere; many such aerosols originate from the ocean, and their effect is most evident in coastal areas. We know less about the continental sources, but areas within range of the influence of aerosols derived by deflation of continental salt deposits might be strongly influenced by such airborne salts.

Precipitation

Chloride Load

The preceding section reviewed evidence for presence of Cl-bearing liquid-gas and solid-gas aerosols and suggested some of their sources. Most Cl aerosols generated over the oceans return by gravity or rainout to the sea and do not reach land. Nevertheless, large quantities of Cl—most of it probably of oceanic origin—are brought down to continental watersheds by precipitation. A sampling of estimates is given in the following table, with initial data calculated to conformable units for this paper:

Locality	*Cl input per year (t/km^2)*	*Reference*
Taita, New Zealand	12	Miller (1961).
New Hampshire, U.S.A	0.27-0.28	Juang and Johnson (1967).
Geneva, N.Y	1.8	Collison and Mensching (1932).
Lower Rio Grande Valley, Tex.	5.6 -17	Fanning and Lyles (1964).
Four river basins in North Carolina.	0.42	Gambell and Fisher (1966).
Israel (arid areas)	0.10-0.20	Yaalon (1961).
Southern Sweden	0.25-4.4	Eriksson (1955).
11 river basins, Western U.S.A.	0.03-0.47	Van Denburgh and Feth (1965).

Some, perhaps most, of the variation in estimates given above results from location of the areas with reference to the sea. But some almost surely reflects varying procedures in sampling and analysis of samples, problems that are discussed in the next section.

Sampling, Methods of Analysis, and Interpretation of Results

The literature is somewhat contradictory with reference to the influence of dry fallout on the Cl concentrations in continental water, partly, at least, because of varying methods of defining and sampling "precipitation." Speaking of the inland, arid parts of Israel, Yaalon (1961, p. 13) said "the * * * precipitated salt will be mainly by deposition of dry salts." Junge and Gustafson (1957, p. 164) reported tests at Boston, Mass., where "two collectors were exposed side by side; one open to precipitation only, and the other open continuously. On the average, the open gauge collected twenty-five percent more Cl as a result of the dry fallout." Koyama and others (1965, p. 3) calculated that the increment from dry fallout was 2.3 times the increment from precipitation excluding dry fallout for the islands of Japan, but Tsunogai (1975) estimated that only 20 percent of Cl brought landward from the sea was deposited as dry fallout.

In the northern European network, samples are collected in plexiglass funnels that drain into polyethylene bottles housed in boxes, heated as appropriate when frozen precipitation is expected. The collectors are continuously exposed and each sample represents precipitation, rain or snow plus dry fallout, for one month. Junge and Gustafson (1956, p. 244; 1957, p. 165) designed a 1-year study in the United States with procedures "to be identical with that of the Scandinavian and European network," except that the funnel was protected in dry weather. Miller (1961, p. 847) collected samples in a continuously exposed vessel changed at approximately monthly intervals. Miller titrated for Cl, using 0.02N silver nitrate. For the network samples, European and United States, Cl "was turbidimetrically determined after addition of silver nitrate to an acidic solution. An accuracy of about ± 15 per cent was achieved for concentrations less than 1 mg/L" (Junge and Gustafson, 1957, p. 165).

In contrast, Larsen and Hettick (1956) collected samples of individual rainstorms and, on occasion, consecutive samples during a single rainfall. They used a stainless steel pan draining to a borosilicate glass bottle. The pan was covered except during precipitation events, and, prior to sampling, pan and drain tube were rinsed with deionized water. The mercuric nitrate procedure of Clarke (1950) was used, and a high degree of accuracy was reported (Larson and Hettick, 1956, p. 193). The samples reported as rain versus bulk precipitation by Whitehead and Feth (1964, p. 3319) were taken on a semirigid sheet of polyethylene drained through a polyethylene funnel into a borosilicate bottle. Bulk-precipitation samples were those taken when the collecting surface had been exposed to dry fallout between rains; rain samples were those taken immediately after the collector, funnel, and bottle had been thoroughly cleaned. The Cl determination was that of Iwasaki and others (1952), using mercuric thiocyanate and ferric ion, and in the range 1-5 mg/L Cl has an indicated accuracy (20 ml aliquot) of ±2-10 percent (C. E. Roberson, oral commun., 1968).

Kennedy and others (1979) used a sampler that allowed analysis of individual increments of rain during a single storm. The device was used both in an urban (Menlo Park, Calif.) and in a rural (Petrolia, Calif.) environment. Results showed rather consistently that Cl concentration was commonly but not invariably inversely related to rates of rainfall and that the concentration within a single storm might range across three orders of magnitude. For instance a storm on January 22, 1972, at Petrolia showed a range from 0.02 to 3.0 mg/L Cl. A sample of hail had 38 mg/L Cl, the highest concentration by far of any sample analyzed.

The foregoing examples suffice to show that variations in sampling and in analytical procedures inevitably produce results that cannot be rigorously compared from one study to another. Those studies that report results alone, without defining methods of collection and analysis, leave the reader in even more of a quandary with regard to interpretation and comparison.

The studies also show that whether by gravitative settlement or by impingement on solid surfaces that impede the flow of air, or by both processes, dry particles reaching the land surface ultimately contribute Cl to continental water and must be considered in any input-output studies of the ion.

Chloride in Rain and Snow

By far the greatest accumulation of chemical data on precipitation so far is that of the Scandinavian-Northern European network. The data relating to sulfur and Cl from the network during the years 1954-59 were summarized by deBary and Junge (1963). The records for each of the more than 100 stations were calculated to average concentrations of Cl for the 6-year period, broken down into summer rain (May to October) and winter precipitation (November to April). The summer minimum average Cl concentration was 0.18 mg/L; the maximum average was 42.36 mg/L. The winter minimum average was 0.20 mg/L and the maximum average 83.29 mg/L. The stations were not the same for the seasonal extremes. In coastal areas subject to winter storms, the Cl concentrations in winter are 2-3 times those in summer precipitation (deBary and Junge, 1963, p. 379).

Overall, there is much less information on the chemical content of precipitation identified specifically as snow than there is on rain. Table 1 presents a sampling of data from various publications.

The foregoing paragraphs indicate something of the variation in Cl content in rain and snow—principally as a function of location, and in a rather long time frame. Eriksson (1952, p. 289-293) discussed influences governing concentration of Cl at individual locations in a short time span, as within a single storm. In general, concentration varies inversely with quantity (depth) of rainfall in a single storm, decreasing to a lower limit. Kennedy and others (1979, p. 689) reported the same general relationship. However, changes in wind speed and direction may invalidate the trend, bringing new supplies of Cl. Such effects are probably most important in coastal areas and in areas within range of sources of industrial pollution. Eriksson also summarized reports showing seasonal variations and concluded that they reflect prevailing wind directions that change with the seasons. Marked variation was reported by Rossby and Egner (1955, p. 118) between Cl in precipitation from arctic or polar continental air masses where concentrations were negligible, and precipitation from air masses reaching Sweden from the south or southeast. Whitehead and Feth (1964, table 1) reported variations in concentration ranging from fractions of a milligram per liter to several milligrams per liter in successive samples collected during several single-day continuous rainfall events. In the coastal-industrial environment of their study, variations were erratic with time.

We may conclude that rain, snow, hail, and dry fallout all contribute Cl to continental water. The concentrations vary widely in space and with time. The oceans are the principal source of Cl-bearing aerosols. But if precipitation is perhaps the most universal and obvious source of Cl in continental water, it is not the only source and in many places seems to contribute less of the total Cl load found in water than do other sources.

Rocks and Minerals

In considering rocks and minerals as sources of Cl in water, we must consider at least two phenomena; first, the abundance of chlorine in the materials, and second, release as the ion from the rocks and minerals into water. The two will be taken up separately.

As stated in the introduction, chlorine is not included in most rock analyses. Available data, then, are scanty and not altogether consistent. For example, Johns and Huang (1967, p. 36), selecting from the literature those analyses for which rock samples were "sufficiently characterized" and those for which the accuracy of the analytical method was stated, emerged with only 1,134 separate analyses from which to characterize the chlorine content of all terrestrial rocks. Their value for shale of 50-450 ppm (p. 43) was challenged by Billings and Williams (1967, p. 2247) on the basis of analyses of 77 surface samples of shale and 13 subsurface core samples. Billings and Williams determined water-soluble Cl to range from 7 to 110 ppm in surface samples, but from 45 to 2,450 ppm in the core samples. Recognizing that whole-rock analyses should

Table 1.—*Chloride concentrations in precipitation*

Place	*Cl concentration (mg/L)* Max	Mean	Min	*Remarks and reference*
Univ. Illinois	3.5	--	0.07	62 individual samples of rain, nonindustrial area, 10-month period (Larson and Hettick, 1956, fig. 3).
New Zealand	26	8.1	.4	3 years, monthly composite samples, bulk precipitation; six miscellaneous samples after 3-year sequence omitted (Miller, 1961, table 1).
N. European network	42.4	--	.2	6-year averages of monthly composite samples, bulk precipitation, May-October, 106 stations (deBary and Jung, 1963, table 1).
Do	83.3	--	.2	As above, but November-April (table 2).
Menlo Park, Calif	23	3.1	.0	56 samples individual rains, 2 years.
Do	30	7.3	.2	25 individual samples, bulk precipitation, 2 years (Whitehead and Feth, 1964, tables 1, 2).
Wahnsdorf, Germany	--	1.6	--	99 individual samples of "shower" rain, 8 years.
Do	--	1.5	--	188 individual samples of "rain," 8 years (Mrose, 1966, p. 267).
North Carolina and Virginia	15.8	--	.2	1-year monthly composite samples, bulk precipitation, 27 stations, coastline to about 390 km inland (Gambell and Fisher, 1966, fig. 1).
Mojave desert region, Calif	90	5.8	.2	39 individual samples, bulk precipitation, 11 months, 12 stations (Feth, 1967, p. C225).
New Hampshire	.32	.21	.04	1-year monthly averages of weekly samples, bulk precipitation, 2 collectors (Juang and Johnson, 1967, table 1, 2).
Menlo Park, Calif. MG Building.	15	--	.05	64 samples from six storms November-December 1971; samples taken sequentially in increments of 1.35 mm of rain (Kennedy and others, 1979, table 1).
Building 3	8.5	--	.05	37 samples from four storms December 1971, taken in increments of 2.65 mm of rain (Kennedy and others, 1979, table 2).
Petrolia, Calif	8.3	--	.02	51 samples, January 1972, taken in increments of 2.65 mm of rain. A 52nd sample including hail had 37.8 mg/L Cl (Kennedy and others, 1979, table 3).
Honeydew, Calif	5.9	--	.02	35 samples, January 1972, taken in increments of 5.4 mm of rain. A 36th sample including hail had 28 mg/L Cl. Honeydew is about 11 km inland from Petrolia (Kennedy and others, 1979, table 4.)
Sierra Nevada, California and Nevada.	1.6	.5	.0	78 samples of snow collected over two winters from various localities (Feth and others, 1964b, table 2).
Antarctica	.027	--	--	One sample of "snow mine" snow estimated to be about 100 yr. old. Sampled 13 m below surface (Wilson and House, 1965, table 1).
Alaska	210	34	.6	31 individual samples of snow, Point Barrow coastline to about 10 km inland (Duce and others, 1966, p. 246).
Canada	15	4.8	2.0	One composite snowmelt sample from each of 10 sites in southeastern Ontario, Dec. 27, 1965 to April 1, 1966 (Rutherford, 1967, table 2).
Leige, Belgium	12	--	5.3	16 samples from a single snowfall; industrial pollution suspected for higher concentrations (Batta and Leclerc, 1934).
Northern Norway	5.3	--	.0	20 samples of snow (Kohler, 1937).
West Germany	31	--	1.6	59 samples of snow in area where pollution from city of Worms was expected.
Do	--	26	1.9	Nine samples from agricultural area where industrial effects were presumed to be absent (Menzel, 1948).

show higher contents than water-soluble determinations alone, Billings and Williams calculated from both sets of data that their surface samples should have about 80 ppm of nonsoluble chlorine. Adding that value to the average water-soluble Cl of their subsurface samples, those authors concluded that the average chlorine content of shale is 1,466 ppm, assuming that subsurface shale effectively equals total shale volumetrically. They did not discuss the possibility that saline ground water contributed Cl to their core samples but concluded that chlorine values in the literature generally are too low because analyses were made of surface samples from which much of the water-soluble Cl had been leached.

Nonevaporites

Table 2 is intended to show the general range of concentration of chlorine in various rocks and minerals, omitting evaporites. The variations in estimates from

Table 2.—*Chlorine in some rocks and minerals.*
[Concentrations are in parts per million by weight]

Rock or mineral	*Rankama and Sahama (1950 table 5.52)*	*Correns (1956, various tables)*	*Parker (1967, table 19)*	*Johns and Huang (1967, table 7)*	*Shaw (1960 p. 218)*	*Gulbrandsen (1966, table 1)*
Igneous rocks undiff.	314	--	--	--	--	--
Ultramafic rocks	--	340-1,000	50-85	40-300	--	--
Basalt, andesite	--	20-1,100	50-60	50-400	--	--
Granitic rocks	--	80-800	100-240	130-800	--	--
Rhyolitic rocks	--	20-150	--	--	--	--
Obsidian, pitchstone	--	80-1,280	--	--	--	--
Syenite	--	200-970	520	400-2,170	--	--
Clay and shale	--	50-450	160	47-180	--	--
Shale	--	--	180	--	--	--
Sandstone, wacke	trace to 20-100	10	20, 70	--	--	--
Carbonate rocks	200	20-2,000	150	130-660	--	--
Phosphorite	--	--	--	--	--	100-400
Apatite	--	530-58,000	--	--	--	--
Fluorite	--	170 (p. 188)	--	--	--	--
Hornblende	--	210-6,000	--	--	--	--
Mica	--	20-3,000	--	--	--	--
Scapolite	--	--	--	--	500-33,000	--
Sodalite	--	70,000 (p. 188)	--	--	--	--

column to column reflect variations in source references used by the different compilers, in use of ranges or averages, and probably other factors as well. Perhaps most of all, they reflect the continuing uncertainty as to the content of chlorine in rocks and minerals.

Nevertheless, table 2 implies that weathering of common rocks and minerals is not a likely source for Cl in water beyond rather small concentrations. The studies by Correns, Parker, and Johns and Huang (table 2) reflect extensive compilations of data from many individual investigators. Other compilations and individual studies such as those of Lamar and Shrode (1953) on dolomite and limestone, Gillberg (1964) on mica and amphibole, or Steuber and others (1968) on ultramafic rocks, do not materially change the concentration ranges shown in table 2 nor add appreciably to the types of rocks and minerals already cited. Reed and Allen (1966) reported chlorine in chondritic meteorites to range from less than 1 to about 770 ppm, but their effect on continental water must be negligible.

Evaporites

Evaporite minerals are of great importance in industry and agriculture and have been extensively searched for and studied. The more exotic deposits, such as the large concentration of boron-bearing evaporites mined at Kramer, Calif., and the extensive beds of trona in Wyoming are of major geochemical interest as their formation must have required exceptional—and as yet unexplained—chemical environments. However, they are not significant with respect to Cl. Various evaporite minerals contain Cl in negligible to appreciable proportions, but halite (NaCl) is so overwhelmingly important (Stewart, 1963, p. Y10, tables 22-26), both for its content of Cl—about 60 percent of the pure mineral (Hill and others 1967, p. 164)—and for its worldwide distribution in great abundance, that this discussion will focus on halite to the exclusion of all others.

The attention that has been given to evaporite minerals—and among them principally halite—is suggested by the occurrence of at least four major symposia on salt within the period 1950-68, two in Ohio, one in Texas, and one in Hannover, Germany.

As an aside, it is interesting that G. I. Atwater (in Mattox, 1968, Foreword, not paginated) remarked on the significance of studies of salt to a variety of disciplines. He mentioned interpretation of geologic history, disposal of radioactive wastes, use as raw materials for industry, and control by salt deposits over occurrence of oil and natural-gas deposits. He did not mention salts as contributors of Cl pollution of water. Doubtless he was accentuating the positive.

Halite—like other evaporites—forms from evaporation of water. There are thick and extensive deposits of halite of both marine and saline-lake origins. Kozary and others (in Mattox, 1968, p. 43-57) said that deposition of salt (halite) and other evaporites took place on all continents, possibly excepting Antarctica, from late Precambrian to the present, and showed their distribution in a series of maps. They reported (p.44-45) that about one-fourth of the continental areas may be underlain by evaporites, and that about 60 percent of these areas are underlain by salts that contain Cl. Most saline deposits are in the northern hemisphere where more than one-half the areas underlain by nonevaporite sedimentary rocks also are underlain by evaporites (fig. 1).

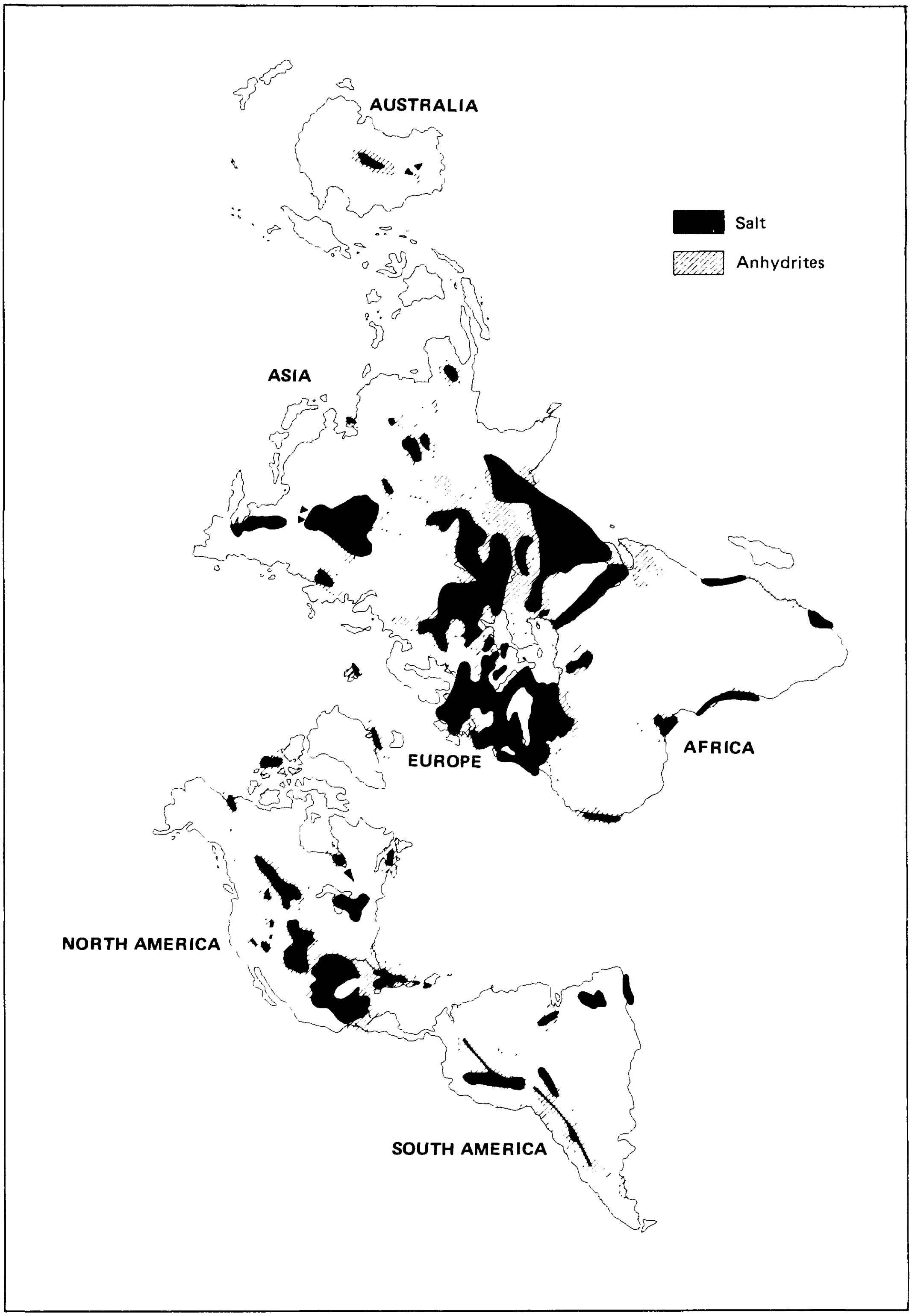


Figure 1.—Composite distribution of evaporites worldwide (Kozary and others, 1968, *in* Mattox fig. 10). The authors considered the map preliminary and indicative rather than definitive (W. E. Humphrey, written commun., March 27, 1969).

Pierce and Rich (1962) reviewed the occurrence of rock salt in the United States. The deposits of marine origin range in thickness from a few meters to a few thousand meters in bedded deposits and in salt domes to 3,000 or 6,000 meters. Lacustrine deposits of halite were reported to range from a few feet to a few hundred feet in individual deposits (p. 67).

From those data it is evident that halite is a widespread and virtually limitless source from which Cl may get into ground water in areas of sedimentary rocks. Halite, as daily household experience shows, is readily soluble in water. The fact that there are, virtually worldwide, freshwater aquifers depends on the fortunate circumstance that most halite occurs at considerable depth beneath land surface, or—where surficial—commonly lies at the down-gradient end of ground-water systems.

Although halite is most impressive, perhaps, where it occurs in discrete and virtually pure masses or as separate beds within evaporite sequences, the mineral occurs also in other environments. It is widely disseminated as grains in clastic sedimentary rocks, and in outcrop its former presence commonly is marked by cubical imprints or molds (Pettijohn, 1957, p. 217). Halite also is the cement in some sandstone and argillaceous sandstone, according to Waldschmidt (1958, p. 871-872) who reported core samples that ranged from sandstone with negligible quantities of halite cement to virtually pure halite with minor quantities of disseminated sand. Minute grains of halite also occur in cracks in some minerals, notably scapolite (O.C. Ingamells, oral commun., 1968).

It is clear from the foregoing discussion that halite is a widespread and ready source from which Cl ions enter natural water. Ground water probably accumulates Cl in greater quantities by solution of halite than does surface water. However, where rock salt crops out, as along reaches of the Sevier River, Utah, and near the Dead Sea, precipitation causing direct runoff also must dissolve appreciable quantities of halite and add Cl directly to surface water.

Release of Chloride to Water

The release of Cl from evaporite minerals is by solution. The process is direct and commonly rapid. Where Cl is released from disseminated grains of halite, as in sandstone, solution is the process also, but rate of release may be retarded by slow movement of water through the rock. Similarly, in limestone or dolomite, where Cl may be present in fluid inclusions, release depends on the rate at which the inclusions are exposed by solution of the surrounding carbonate minerals. The solution of NaCl ceases where brines reach saturation with respect to the mineral.

Release of Cl from nonevaporite minerals involves processes other than solution of NaCl and generally is slow. In those rather rare minerals—chiefly sodalite, scapolite, and chlorapatite—where Cl is an integral part of the mineral molecule, release probably is by hydrolysis. Frederickson (1951) explained the process as penetration of the H ion into the mineral lattice. At each penetration site the electrical neutrality of the molecule is destroyed, and an atom of one of the mineral constituents is displaced to compensate for the entering H. A parallel, but different, reaction takes place where Cl ions occupy exchange sites on minerals such as mica (especially biotite) and hornblende (Rankama and Sahama, 1950, p. 785; Greenland and Lovering, 1966, p. 969). There OH ions displace the adsorbed Cl ions, releasing the latter to solution.

The chlorine content of 102 samples of silicic volcanic glass was reported (Powers, 1961) to range from 0.05 to 0.25 percent, to be generally uniform among samples from single ash beds, and seemingly to be independent of geologic age. However, Noble and others (1967) found appreciable loss of Cl from silicic volcanic rocks as a result of (1) hydration of glassy material, and (2) crystallization. They reported that comparison of glassy and crystallized parts of the same rock mass showed an average loss of 80 percent of the Cl during crystallization. Changes by hydration were inferred to result from reaction of the glass with ground water over long periods of time. A comparable observation was made by Ross and Smith (1955, p. 1086) who reported that the smallest quantities of Cl in volatiles extracted from volcanic glass were from "pitchstone," namely, hydrated obsidian.

The rate at which Cl may be released by solution of halite is suggested by examples from Oklahoma and Texas. Springs that discharge from halite-bearing rocks of Permian age in northwestern Texas and western Oklahoma contain 20,000-200,000 mg/L Cl (Ward, 1960). The halite in the section occurs both bedded and disseminated in shale. Where bedded, according to Ward, removal of halite has caused development of "lows" on the surface of the bedded salines and formation of solution and collapse features at the land surface.

The quality of water in the Brazos River, east-central Texas, is materially impaired by saline inflows in headwater reaches upstream from Possum Kingdom Reservoir. Springwater, emerging from rocks also of Permian age, contains as much as 160,000 mg/L Cl and, at low flow, Na and Cl make up about 90 percent of the dissolved solids (Baker and others, 1964) in the Salt Fork Brazos River. The occurrence of highly saline inflows, alternative methods of eliminating or diminishing the problem, and data records of the upper Brazos basin were further presented by Rawson and others (1968).

In contrast, study of a small watershed in New Hampshire underlain by gneissic rocks showed a discharge-weighted average concentration of 0.50 mg/L

Cl (Juang and Johnson, 1967, tables 1 and 2). In large areas of the Western States, Cl concentrations in streams that drain a wide variety of rock terrains is less than 10 mg/L (Feth, 1965a, sheet 4). Similar low concentrations prevail in ground water in many places, for example Alabama (see Avrett, 1968).

Exceptional Cases

The foregoing section implies that—excepting evaporites—rocks and minerals are not a ready source of Cl ions. Two exceptional cases have appeared that warrant special discussion. One deals with Cl in, and Cl leached from, rocks of New Zealand; the other describes the distribution and Cl content of scapolitized rocks. They will be discussed in the order named.

In the New Zealand study (Ellis and Mahon, 1964, 1967) rock samples were leached in the laboratory at 150°C to 600°C and at pressures of as much as 100,000 kilopascals. Leaching removed silica, alkalies and noteworthy concentrations of Cl, F, B, and NH_3, suggesting that those constituents exist to a large degree on intergranular surfaces within the rock and not within the structure of the silicate minerals. The rocks used in the runs were pumice, obsidian, ignimbrite, rhyolite, dacite, andesite, basalt, and graywacke. Analyses of the rocks showed chlorine to range from 12 ppm in graywacke to 990 ppm in pumice (table 4).

Release of the ions was rapid, implying (1) the ions were not contained in the mineral structures, and (2) available supplies of the ions were depleted rapidly.

Making certain assumptions about the circulation patterns of the thermal-springs system on the islands, Ellis and Mahon concluded that hydrothermal alteration of the volcanic rocks—known to be proceeding—could supply all the Cl and B found in New Zealand thermal-water systems if the rock/water ratio is about 10 in active volcanic hydrothermal areas; hydrothermal alteration under the same assumptions would supply more than enough F, SO_4, Ca, and Mg, and much more than enough silica and alkalies to satisfy the requirements of the thermal-water system. The hydrologic aspects of the Ellis-Mahon model were not described, hence the problem of attaining rock-water contact that would allow continuing removal of ions from the rocks, most of which appear to offer only minor permeability, cannot be evaluated.

Overall there was a tendency for a yield of Cl to increase with increasing temperature to about 400–450°C and then to level off. The authors inferred that the leveling-off point represented final removal of Cl from crystal surfaces and microfissures and said that more than 50 percent of the Cl was removed from most of the samples of all the rocks by leaching and 75–100 percent was removed from pumice, dacite, andesite, and basalt.

The geochemistry of scapolites was discussed by Shaw (1960). The scapolites are silicate minerals forming an isomorphous series analogous to the plagioclase feldspars, which scapolites commonly replace. Chlorine makes up as much as 3.3 percent of some scapolites and seems to average about 1 percent. The minerals form preferentially by metamorphism of rocks originally fairly high in calcium. Formation of scapolite may also occur by passage of normal ground water or thermal water through the host rock.

Noteworthy regional occurrences of scapolitized rocks were reported by Shaw from the Precambrian Grenville province of New York and Canada, the Kiruna and other iron-ore districts in Sweden, parts of Norway, the Swiss Alps, and the Precambrian of Australia. In the Grenville province of Ontario, Quebec, and New York, scapolitic rocks are abundant over 200,000 km^2. In the Kiruna district, many rocks contain 50 percent scapolite which, in turn, contains as much as 3 percent Cl. In Australia, the scapolite probably is formed by sodium-metasomatism of calcareous shale and associated rocks. The resulting granulites have an average Cl content of 1.34 percent, or about 38 kg of Cl per cubic meter of rock. For two main granulite bands in the region this required introduction of 37 million metric tons of Cl. The total Cl in the metamorphic rocks of the province may be about 450 million metric tons.

In general, Cl is bound tightly in the scapolite molecule. During hydrothermal alteration, as of scapolitized dolomite, scapolite goes over to muscovite, releasing part of the Cl (Anna Heitanen-Makela, oral commun., 1966), but in normal weathering processes scapolite probably breaks down at about the same rate as feldspar. She reported having seen soil in Idaho developed by complete breakdown of parent dolomite where there were numerous residual crystals of scapolite.

In summary, we know surprisingly little about the Cl content of rocks and minerals, partly because most rock analyses are virtually in balance without consideration of Cl. The evaporites, especially halite, are widespread, prolific, and ready sources of Cl for water. But the rate of release of Cl from nonevaporites probably is slow. Nevertheless, the studies of hydrothermal leaching of New Zealand rocks and studies of scapolitization suggest that, in some areas at least, we should look searchingly at nonevaporite rocks as sources for significant quantities of Cl in excess of that brought into the system by precipitation.

Soils

Although the Cl content of soils ranges from zero (Morris and others, 1959, p. 88) to many thousands of parts per million (Thompson, 1929, p. 67; Dyer, 1965, fig. 2), soils cannot be considered as a source of Cl except where they are leached by irrigation. Inasmuch as soils form from weathering of rock in place, or after transport and deposition of weathered-rock material, it might be assumed that soil material must have a Cl content no greater—and probably less—than the rocks from which it was derived.

The high concentrations of Cl found in some soils can be attributed to various processes of accumulation. Among them are dry fallout and evaporation of precipitation in arid areas; evaporation of ground water where the water table is shallow or on "wet" playas at the terminal ends of closed-basin artesian systems; deposition of salt by evaporation of water from saline springs; adsorption by acid soil; and evapotranspiration of water applied for irrigation. In all those circumstances, the soil is an accumulator of Cl brought in from other sources. Even if subsequently leached, by a change in natural regimen or intentionally by irrigation, the soil itself is not the source of Cl.

Brines

Feth and others (1965) showed that about two-thirds of the area of the 48 conterminous United States is known to be underlain by ground water having dissolved-solids concentrations of 1,000 mg/L or more. Of nearly 1,050 analyses used, more than 35 percent were of sodium chloride type water. No other chemical type was as prevalent. Virtually all water containing more than 20,000 mg/L dissolved solids had Cl as the dominant anion. A few decades ago, the chemistry of saline water was extensively studied by the petroleum industry in hope of using water-quality variations as a guide to oil. Selected references from the resulting, rather extensive, literature were cited by Feth (1965b).

Such studies as those mentioned—and many others—indicate that vast reservoirs of saline water—some with concentrations of dissolved solids measured in hundreds of thousands of milligrams per liter—underlie much of the United States, and other countries as well. Locally, the salty water is at, or near, land surface. More commonly it is overlain by freshwater aquifers. The freshwater aquifers may receive increments of Cl by slow, upward movement of brine where potentiometric gradients favor such movement. They definitely receive slugs of Cl-rich water in places where wells are heavily pumped and cones of mineralized water are induced into the freshwaters. A special case of the freshwater-salt water interface is found on islands, such as those of the Hawaiian group, where the rocks are highly permeable and the fresh ground water floats in generally lens-shaped configuration on seawater, because of the density difference between the two.

Except where the saline aquifers have direct, present connection with the sea and the water in those aquifers has effectively the same composition as seawater, or where solution of halite can be demonstrated, the origin of the brines remains in the realm of speculation. Some of the speculations will be given later in discussion of the geochemistry of Cl.

In any event, the origin and diagenesis of deep-seated brine occupying an aquifer composed of geologically young, marine sand, those of a brine found in cavernous limestone of Paleozoic age, and those of a brine at depth in a topographically closed, arid-climate basin whose aquifers consist of unconsolidated alluvium, can hardly be the same.

Magmatic Emanations

Magmatic gases—fumeroles, volcanic throats, geysers—have long been looked to as major sources of Cl. Correns (1956, p. 201) summarized estimates of the annual yield of gaseous chlorine from some magmatic sources:

Source	*Chlorine produced (grams per year)*
Kilauea	3×10^{10}
Valley of Ten Thousand Smokes (1919)	1.3×10^{12}
Norris Geyser Basin, Yellowstone National Park	1×10^{9}
Steamboat Springs, Nev	3.5×10^{9}
Arima, Hyogo Prefecture, Japan	1.5×10^{9}

Although the quantities are impressive, some—as the Valley of the Ten Thousand Smokes—are transient. Correns found them inadequate to begin to explain the total supply of gaseous chlorine needed yearly to keep the lithosphere-biosphere-hydrosphere system of the Earth in balance with respect to Cl. The composition of volcanic emanations was summarized by White and Waring (1963) who presented data showing that HCl made up 0.0 percent (table F) to 87 percent (table C) of the "active" gases sampled. "Active" gases are those exclusive of H_2O, O_2, N_2, and Ar (White and Waring, 1963, p. K1).

Cadle and others (1979) reported that explosive volcanoes inject significant quantities of solids and gases into the troposphere, including "particulate and gaseous chlorine-containing compounds." SO_2 and H_2SO_4, however, were reported to be vastly more important.

Miscellaneous Sources

The occurrence and role of Cl in hydrothermal fluids, especially those related to ore deposits, was discussed by various authors in a volume edited by H.L. Barnes (1967) as follows: C.W. Burnham (p. 73) showed, on theoretical grounds, that Cl, in various states and combinations with other elements, is discharged from a cooling body of magma. H.L. Barnes and G.K. Czamanske (p. 347–350; 353–368) discussed the role of Cl in relation to ore-mineral solubility, and H.D. Holland (p. 382–387; 402–417) examined the relation of gangue minerals to Cl content of hydrothermal fluids. A.J. Ellis tabulated (p. 488–489) Cl concentrations ranging from 31 (Iceland) to 184,000 mg/L (Salton Sea area, California) in water condensates from wells in hydrothermal areas. Edwin Roedder (p. 538) mentioned Cl as a major constituent of fluid inclusions in minerals, and D.E. White (p. 580–581; 615–616) gave examples of Cl concentrations in water related to mercury deposits and discussed evidence that brines of the Na-Ca-Cl type may be the dominant base-metal ore solutions.

Hydrothermal solutions—ore-bearing or not—may locally influence the chemical composition and Cl content of ground water. However, such solutions probably are rarely in contact with aquifers used by man and merit mention as special cases, but not extensive discussion, in a general review such as this.

Man

The Waste Maker redistributes Cl. Man's activities impose loads of millions of tons of Cl yearly on streams and ground-water supplies, and—without belaboring the point exhaustively—a few examples may be appropriate.

According to McMillion (1965), Texas accumulated at land surface on the order of 3.6×10^8 m^3 of salt water yearly. Of the total brine in 1961, about one-fifth was disposed into unlined earthen pits whence much overflowed or seeped out to contaminate streams or ground water. About four-fifths was put underground through disposal or repressuring wells—presumably back to saline-water aquifers.

Krieger and Hendrickson (1960) reported that, prior to August 1958, water in the Green River at Munfordville, Ky., had an average Cl concentration of less than 10 mg/L. A small oil field in the drainage basin was developed very rapidly, and within months, daily Cl concentrations at Munfordville commonly exceeded 1,000 mg/L. In water year 1957, the Green River at Munfordville discharged 10,600 tons of Cl, but in water year 1959, discharge was 305,000 tons. Recharge from the contaminated river apparently caused increased Cl concentrations in ground water detectable 100 miles downstream from the area of principal petroleum production.

I have no quantitative estimates of the effect of other Cl brines used and disposed of by man. But the industrial consumption of muriatic acid (commercial-grade HCl), and the use of salt in processing foods such as pickles and corned beef, suggests that the loads must be large. Atmospheric pollution by industrial HCl fumes was discussed by Gorham (1958) with reference to Britain, and doubtless that pollution introduces some Cl into water.

Most public water supplies in the United States are treated with chlorine (as Cl_2 or hypochlorites) to insure sanitary acceptability. Comparison of same-day samples of raw and finished water, reported by Durfor and Becker (1964), suggests that chlorination adds, generally, from 0.5 to 2.0 mg/L to the Cl concentration but that in some cities (Durfor and Becker, 1964, p. 136, 184) the increment is 5 to nearly 25 mg/L. And domestic use adds 20–50 mg/L Cl to the water before it is discharged as sewage (California Department of Water Resources, 1961, p. 52). Sewered domestic wastes—with or without treatment, and with no significant change in Cl content—normally are discharged to streams or to the sea. The effluent from cesspools or septic tanks in many places adds to the Cl content of ground water. Examples were given by deLaguna (1964, p. D36–D38). Walker (1969, p. 34) showed that discharge of water-softener waste brine caused an increase of nearly 700 mg/L Cl in ground water in areas near the place of brine disposal.

Other activities of man directly or indirectly add Cl to continental water, such as implacement of "sanitary land fills" (Anderson and Dornbush, 1967; California State Water Pollution Control Board, 1961), melting of highway ice with chloride salts (Dowst, 1967; Bingham and Rolston, 1978), and doubtless many others. But perhaps the point is made.

Summary of Sources

The ultimate "source" of Cl in continental water presumably is the Cl_2 and HCl discharged during degassing of the primitive earth. However, that is so far removed in time, that "sources" are considered in the context of contributions to continental water now moving on or beneath the land surface.

Aerosols, derived principally from the sea, are an all-pervasive, worldwide source of Cl in aqueous precipitation. The concentrations are generally small, ranging down to fractions of a milligram per liter over large areas of North America, for example. Dry fallout and impaction of aerosol particles also contribute Cl to continental water. These processes seem adequate to explain the Cl concentrations in surface water in some places. In others—especially where concentrations become appreciable—Cl brought in by precipitation probably makes up less than 20 percent of the concentration in stream water. Wide variations in definition of precipitation, and in obtaining and analyzing samples, make it difficult to evaluate existing data.

Rocks and minerals, other than evaporites, are not sources of readily available Cl, although areas undergoing hydrothermal alteration and areas rich in scapolite may be exceptions. Soils store and, under special circumstances such as leaching by irrigation, release Cl, but being composed largely of residual rock-weathering products, are not significant sources. Evaporite minerals, notably halite, are broadly distributed, readily soluble, and locally add large quantities of Cl to water.

Brines of various origins also affect materially the Cl content of streams and of ground water. Magmatic gases, hydrothermal fluids, and other miscellaneous sources probably are of minor moment in explaining the Cl content of natural water. Man redistributes Cl in huge quantities and imposes heavy loads of Cl on natural water by disposal of oil-field brine, sewage, and other wastes.

OCCURRENCE IN SURFACE WATER

Cl is probably ubiquitous in natural water. Zero concentrations have been reported many times, but the information presented earlier in this paper implies that lack of detection resulted from use of analytical methods insensitive to minute concentrations rather than from complete absence of Cl. However, there are many sources of error in sampling and analysis, and most data on Cl in surface water, and other water for that matter, are in part ambiguous. The sampling problems stemming from variations in concentration with time, place in cross section of the stream, and other variables have been discussed by Hem (1970, p. 60–73) and by the Pacific Southwest Interagency Committee (1966, p. 114–122). Three decades ago, Hem (1948, p. 82) showed that Cl concentrations in the Pecos River, New Mexico, changed hourly with fluctuating discharge, and that the change over a 24-hour period was almost 150 mg/L. Hem commented that "The causes of the chloride fluctuations during this study are complex, involving changes in the amount of river water available to dilute saline ground water inflows in the area of study, solution of salt deposits along the river channel by the increased flow, and other factors."

The variability in Cl concentrations in surface water with time is further illustrated by the record of Salt Croton (Dove) Creek which is in the upper drainage basin of the Brazos River, Texas. In water year 1957, Cl concentrations ranged from 6,800 mg/L to 158,000 mg/L (U.S. Geological Survey, 1961a, p. 338). The creek receives a rather steady inflow of brine from a series of small springs and seepages. The higher concentrations represent that ground-water discharge, and the smaller concentrations represent samples taken when the ground-water flow was diluted by rainwater. This example approaches an extreme in concentration for flowing surface water, but the wide range does not. The Dolores River near Cisco, Utah, yielded concentrations of Cl that ranged from 12 to 2,910 mg/L, the Little Snake River near Lily, Colo., 2.5-100 mg/L, and the Eagle River at Gypsum, Colo., 5.0–160 mg/L, for example (U.S. Geological Survey, 1961b, p. 25–26, 70–71).

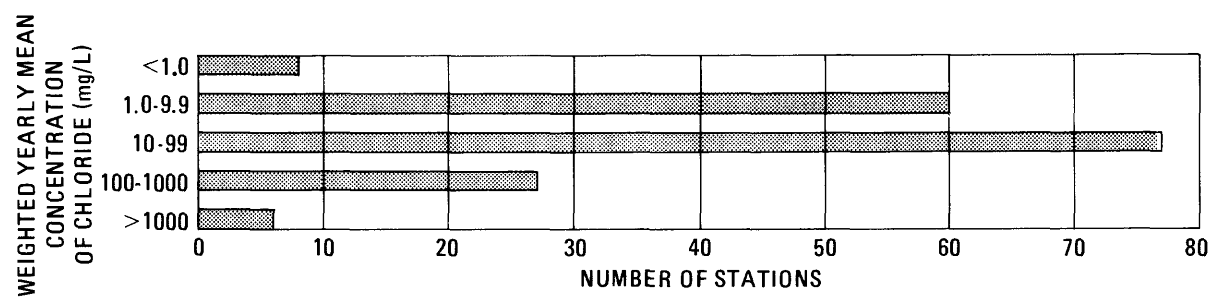
Figure 2 shows distribution by concentration ranges of weighted yearly mean Cl concentrations at 178 stream stations in the conterminous United States in water year 1957, the reference year selected for 20-year comparisons and one of the last years for which nationwide weighted means are available. The overall low Cl concentration indicated is impressive.

Table 3 represents an attempt to observe effects of environmental cleanup on the one hand and of the drought of the late 1970's on the other, assuming that comparison of 1957 data with those of 1975 (both "normal" years) would show effects of environmental cleanup; comparison of data between 1975 and 1977 would reveal drought effects.

The data from the Little River both in Arkansas and Oklahoma, from the Ouachita River in Louisiana, and from the Canadian River in Oklahoma suggest that oilfield brines are being more consistently disposed of by reinjection than they were in 1957. Records for western rivers generally, and for those of Texas and Oklahoma especially, suggest that higher concentrations of Cl were found in the drought year. The familiar dependence of high load upon high discharge can be seen also, the load being generally more dependent on discharge than on concentration. The prevalent relation is shown in figure 3 where greatly increased volume of discharge overrides reduced concentration, and dissolved-solids discharge (load per unit time) increases with increasing water discharge. The units are immaterial to demonstration of the principle. The letters on the abscissa reflect the months of the water year, which starts October 1 and ends September 30 of the following year and is designated by the year in which it ends.

The numbers in table 3 must be used as suggestions only and are presented with full knowledge that the data may not represent true central tendencies in some cases. In 1957 the Geological Survey commonly took daily samples from a stream and analyzed them on the basis of 10-day composites. In the East the composites were usually made up of 10 equal parts of each of the daily samples (time weighted). In the West, the composites were normally made of 10 parts, each daily contribution being proportional to the discharge determined for that day (discharge weighted). The practice of compositing was phased out in the 1960's and early 1970's.

In 1975 and 1977, sampling practices varied widely. One average (Humboldt River near Rye Patch, Nev.) represents for 1975 only three grab samples. Many sites were sampled once per month – some more often. Those averages footnoted in the table are derived from daily values for specific conductance against which Cl was calculated from regression relationships established for each station. Hem's (1948) Pecos River studies, men-



NOTE: Only 13 stations had mean concentrations exceeding 250 mg/L but many more exceeded that concentration at times during the year. Maximum mean was 77,300 ppm at Salt Croton (Dove) Creek near Aspermont, Texas. Minimum mean was 0.2 mg/L at Embarrass River at Embarrass, Minnesota. Median mean concentration is 11 mg/L

Figure 2.—Weighted yearly mean concentration of Cl in stream water in the conterminous United States, water year 1957.

tioned earlier (p. 63), may represent an extreme case, but they underline other uncertainties in the numbers in table 3.

Data for 1957 in table 3 are from U.S. Geological Survey publications. Those for 1975 and 1977 are from tables furnished by the Water Resources Division of the Survey in the several States.

Low loads per unit area tend to be related to low rates of water discharge (table 3). The Columbia River, however, has a high rate of water discharge per unit area. The low Cl load reflects the (1) low concentration of Cl, characteristic of precipitation over the continental interior, (2) minimal concentration by evaporation, (3) the paucity of available Cl in the rocks of the drainage basin, and (4) absence of loading by wastes.

The low loads in North Dakota reflect the interaction of low rates of runoff, modest Cl concentration in precipitation, and small ground-water inflow to the streams, as much of the ground water in that area contains appreciable concentrations of Cl.

Table 3.—*Comparison of mean discharge per unit area, Cl concentration, and Cl load per unit area of selected high-load and low-load streams whose records permit comparison among records for 1957, 1975 ("normal" years), and 1977 (drought year)*

[Streams are arranged in order of decreasing discharge per unit area in 1957, adjusted for changes in contributing area reported in 1975 water-year records]

Explanation of Data

Top line of data: 1957 discharge, Cl concentration, and load
Middle line of data: 1975 discharge, Cl concentration, and load
Bottom line of data: 1977 discharge, Cl concentration, and load

River and station (km² contributing)	*Discharge (dm³/s)/km²*	*Cl concentration (mg/L)*	*Cl load (t/km²)/yr*
Little nr Horatio, Ark. (6,894)	24.9	33	26
	24.8	10	7.7
	12.6	7.8	3.1
Clear Boggy (Creek) nr Caney, Okla. (1,860)	21.8	33	23
	--	--	--
	5.90	58	11
Columbia at International Boundary (155,500)	17.5	.3	.16
	17.6	1.10	.61
	15.6	.83	.41

Table 3.—*Unit-area discharge, Cl concentration, and unit-area Cl load—Continued*

River and station (km² contributing)	*Discharge (dm³/s)/km²*	*Cl concentration (mg/L)*	*Cl load (t/km²)/yr*
Ouachita at Monroe, La. (39,622)	14.8	240	110
Do	28.1	24.3	22
at Columbia Lock and Dam nr Riverton, La. (1977)	7.54	47.2	11
Little nr Sasakwa, Okla. (2,240)	13.0	1020	420
	6.67	290	61
	1.42	520	23
Sabine nr Tatum, Tex. (9,047)	12.0	37	14
	14.2	[1]29	13
	7.87	[1]33	8.1
Oswego at Minetto, N.Y. (13,200)	11.7	207	76
Do	16.3	234	120
at Lock 7, Oswego, N.Y.	16.2	188	96
(1977 not drought year in N.Y.)			
Deep Fork nr Beggs, Okla. (5,227)	10.4	47	15
	12.1	112	43
	.984	174	5.3

Table 3.—*Unit-area discharge, Cl concentration, and unit-area Cl load—Continued*

River and station (km^2 contributing)	*Discharge $(dm^3/s)/km^2$*	*Cl concentration (mg/L)*	*Cl load $(t/km^2)/yr$*
Red at Alexandria, La. (159,450)	8.31	121	32
	10.9	65	22
	4.15	115	15
Red at Shreveport, La. (141,600)	8.09	117	30
above Shreveport	8.96	78	22
above Shreveport	4.04	142	18
Arkansas at Little Rock, Ark. (351,694)	5.79	85	16
"nr"	6.23	79	15
"nr"	1.86	76	4.6
Brazos nr Whitney, Tex. (43,900)	4.04	126	16
	1.42	[1]400	18
	.984	[1]350	11
Red nr Denison, Tex. (87,498)	3.50	258	28
	3.17	[1]250	25
	1.31	[1]250	16
Brazos nr Graford, Tex. (34,470)	3.39	119	13
	.874	[1]760	21
	.328	[1]860	8.8
Canadian nr Whitefield, Okla. (98,047)	3.28	134	14
	3.06	[1]54	5.3
	.437	[1]67	.91
Red Gainesville, Tex. (64,351)	3.28	283	29
	2.19	[1]400	28
	1.20	[1]660	25
Cimarron at Perkins, Okla. (33,478)	2.95	629	59
	3.06	1300	130
	.656	[1]2800	58
Arkansas nr Tulsa, Okla. (160,770)	2.51	392	31
	2.73	[1]330	27
	.874	[1]530	15
Arkansas at Ralston, Okla. (121,340)	2.19	208	13
	2.19	[1]276	19
	.546	[1]300	5.3
Rio Grande nr San Ildefonso, N. Mex. (29,420)	1.75	5.9	.33
	1.42	[1]4.9	.22
	.546	[1]7.8	.13
Salt Fork Brazos nr Aspermont, Tex. (5,340)	1.53	1360	66
	.328	[1]6000	62
	.328	[1]5500	57
Republican nr Hardy, Nebr. (37,680)	.437	4.6	.063
nr Guide Rock, Nebr	.109	18	.063
nr Guide Rock, Nebr.	.076	19	.046
Republican at Milford, Kans. (64,500)	.328	11	.11
at Clay Center, Kans. (63,564)	.219	[1]41	.28
at Clay Center, Kans.	.219	[1]32	.22
Sheyenne at Lisbon, N. Dak: (11,970)	.328	24	.25
(6,459)	1.20	32	1.2
Do	.109	50	.17
Humboldt nr Rye Patch, Nev: (35,480)	.109	67	.23
(41,700)	.238	130	1.3
Do	.087	173	.49
Souris nr Westhope, N. Dak: (45,600)	.109	18	.06
(17,100)	1.75	30	1.6
Do	.0437	29	.039
Pecos nr Artesia, N. Mex. (39,600)	.0874	624	1.7
	.0984	[1]1020	3.2
	.0656	[1]798	1.6

[1] Mean Cl concentration calculated by regression from daily specific conductance values. Other mean values are arithmetic averages of from 3 to 37 spot samples for 1975 and 1977; 1957 values are time or discharge weighted.

OCCURRENCE IN GROUND WATER

The occurrence and behavior of Cl in ground water has been referred to throughout earlier discussions in this paper. Concentrations range from <1 to >200,000 mg/L. The Cl cycle in ground water was shown to be incompletely understood, except where seawater intrudes cavernous aquifers. Constant-rate release of Cl to ground water was mentioned as a possible but unexplained phenomenon. The variation of Cl concentrations in fault-zone springs was considered with reference to possible sources. Halite was cited as a potential and actual source of Cl in ground water, notably in Texas and Oklahoma where some springs have concentrations of Cl ranging from 20,000 to 200,000 mg/L. Feth and others (1965) showed large areas of the United States to be underlain by mineralized ground water and that 35 percent of nearly 1,050 analyses studied had sodium and chloride as the dominant ions. Virtually all samples having more than 20,000 mg/L dissolved solids had Cl as the dominant anion. Those Cl-rich waters locally overlie freshwater aquifers but more commonly underlie them. The origin and diagenesis of the saline waters are not simply explained.

We shall now show by use of examples how Cl in ground water varies by geographic location, by geologic formation, by depth—but not consistently—and over time. The presentation is indicative only, not exhaustive.

Avrett (1968) presented chemical analyses of ground water in Alabama collected over many years and representing thousands of sources. The data were tabulated by counties. Those for Talladega County were from more than 270 sources. The reported range in Cl is 0-272 mg/L, and only 33 have concentrations in excess of 10. A quick review of Avrett's 103 pages of tables suggests that the above ratio might approximately hold for all the State except for Mobile, Marengo, and Sumpter Counties, where higher concentrations prevail. In contrast, samples from 15 wells in the Grand Forks area, North Dakota, showed a Cl range of 106-16,700 mg/L, and only three wells had concentrations lower than 1,000 mg/L (Benz and others, 1961).

Cl concentrations in water from bedrock sources in Utah range from a "trace" to 250,000 mg/L, spanning five orders of magnitude and entering a sixth. Although there are certain elements of order, as will be shown, the 645 analyses reported from 542 different sources are, above all, characterized by scatter when plotted against characteristics that suggest the possibility of order, such as geologic formation, geographic region, or depth of well. The data are from Feltis (1966, tables 2-4). The water samples are from diverse sources such as drill-stem tests of oil wells, free-flow tests, pumped wells, and springs. Analyses were made by 15 different laboratories with varying standards for analysis and reporting of results. Not all samples were collected and analyzed under carefully controlled conditions nor for identical purposes, and therefore they are not strictly comparable one with another. Individual values may be open to question, but in the aggregate the story they tell is unmistakably clear. Cl concentrations vary almost unpredictably and across a range that spans many orders of magnitude within a given region.

For example, 47 samples are reported from aquifers in the Navajo Sandstone, 70 from the Green River Formation, and 65 from sedimentary rocks of Mississippian age. Figure 4 shows that water from none of the formations spans the entire range in concentration, but water from each of the three spans five orders of magnitude. Of the three, the Navajo is most likely to yield water of potable quality—on the basis of these data—and the Mississippian rocks least likely. This distinction depends in part on the fact that the Navajo is at or near surface in much of the region and many samples are from springs, whereas the Mississippian rocks generally are deeply buried and some contain connate water.

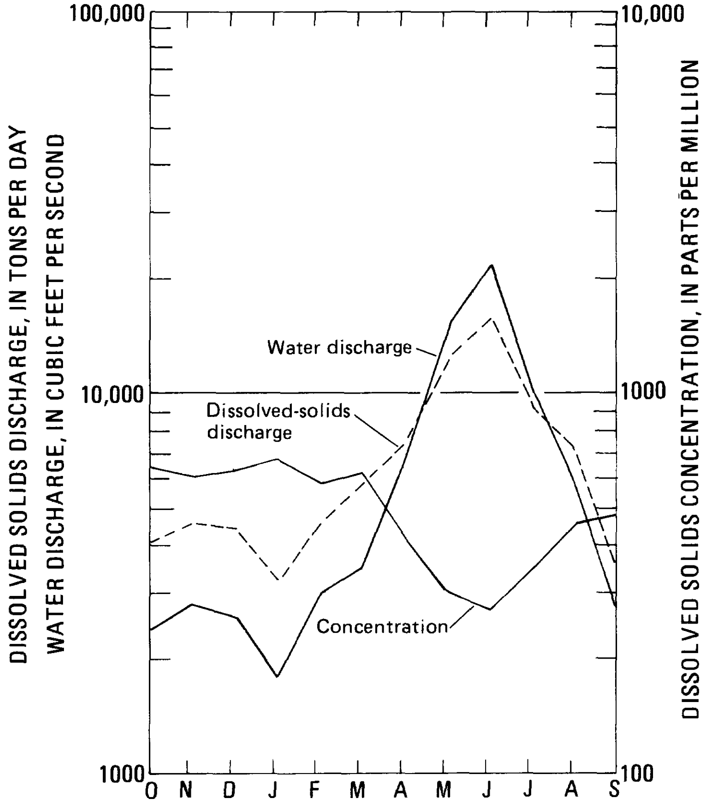


Figure 3.— Dissolved-solids concentration and discharge and water discharge, Green River near Ouray, Utah, 1951 water year (Iorns and others, 1965, p. 23)

Feltis divided his area of study into the Uinta Basin, Canyon Lands, and High Plateaus sections. The range of Cl concentrations in those subregions is shown in figure 5. The Canyon Lands samples show concentrations of Cl in a range of six orders of magnitude. The extreme range and the large number of samples result from the fact that this, more than the other two, is an area of exploration for petroleum. But even in the High Plateaus section, which yielded the highest proportion of samples with low ranges of concentration, many samples are from oil wells and some yielded water with 20-50 mg/L Cl from depths of >1,500 meters.

The Cl concentration of most springs in the Colorado Plateaus in Utah is less than 100 mg/L (fig. 6); the concentration in wells definitely tends to be higher where well depth exceeds about 300 m. But even from the deeper wells, 14 percent of the samples have less than 100 mg/L Cl and 39 percent less than 1,000. Of the 18 samples where concentration exceeded 100,000 mg/L, 17 were from depths greater than about 1,500 m; the depth of the 18th sample was not stated.

Fluctuations in concentration over time are illustrated from a study (Katz and others, 1978) of water from 30 wells in Nassau and Suffolk Counties, New York, and are selectively illustrated in figure 7. The

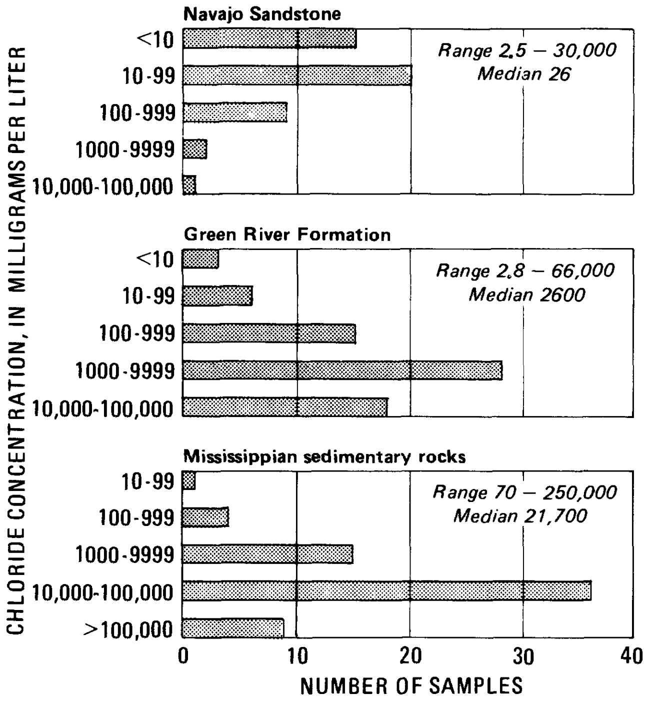


Figure 4.—Distribution of Cl concentrations in samples from selected aquifers in the Colorado Plateaus (Data from Feltis, 1966, tables 2-4). Where more than one sample was taken from a single well, the highest concentration was plotted. In some wells, concentration increased with depth; in others, concentration decreased with depth.

general pattern discovered in 16 of the wells is shown by their well N 8789 (fig. 7) where in the period of study, Cl concentration changed only a few milligrams per liter. In contrast, 14 wells showed fluctuations (see their well S 46914) ranging from 20 to nearly 300 mg/L. The authors reported no correlation between fluctuation range and either depth to water, which ranged from 3 to 105 ft, or location in sewered or unsewered areas, but they attributed the Cl to sources such as agricultural fertilizer, septic-tank effluent, or road salt. Half the wells showed maximum Cl concentrations in the winter, half in summer.

Discharge of saline ground water from springs adds a large tonnage of Cl to surface waters of the world. It is not feasible to estimate the magnitude of that tonnage, but a few examples may be suggestive, admitting that large examples have been selected. Table 3 of this paper cites discharge and area of the drainage basin of the Salt Fork Brazos River near Aspermont, Texas. Using the 2 years of minimal discharge, it is reasonable to assume that virtually all the Cl calculated as load at that station in those years was derived from ground water. On that basis, springs contributed not less than 300,000 t, and perhaps more than 330,000 t, of Cl to the river in the 1975 and 1977 water years. Blue Spring, near the mouth of the Little Colorado River in Arizona, discharges about 5,700 L/s (liters per second), and the Cl concentration is about 820 mg/L (Feth and Hem, 1963, tables 4,5). The calculated discharge of Cl is about 150,000 t/yr. The discharge of Utah Hot Springs near Ogden, Utah, is about 60 L/s, the Cl concentration is about 14,000 mg/L (Feth and others, 1966, p. 50, 61), and the discharge totals about 25,000 t/yr. That discharge reaches Great Salt Lake where it mingles with water of even higher concentration. Even where concentrations are small, discharge of large volumes of ground water contribute noteworthy tonnages of Cl to streams. The Thousand Springs in the valley of the Snake River, Idaho, have an average discharge of about 34,000 L/s. Cl concentrations average about 13 mg/L. The discharge of Cl is about 14,000 t/yr from that single group of springs (data from files of the U.S. Geological Survey, Boise, Idaho, Janet Crockett, Oct. 19, 1979, oral communication).

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The geochemistry of Cl is overall unexciting. Hem (1970, p. 172) summarized the situation as follows:

> The chemical behavior of chloride in natural water is very tame and subdued compared to the other major ions. Chloride ions do not significantly enter into oxidation or reduction reactions, form no important solute complexes with other ions, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles. The circulation of chloride ions in the hydrologic cycle is largely through physical processes.

In the same vein, Piper and others (1953, p. 85-90) discussed native and contaminated ground water in the Long Beach-Santa Ana area, Calif., mentioning that "* * * most of the contaminated waters of the area have been profoundly modified by chemical reactions which involve all the major constituents other than chloride." With respect to criteria for identifying proportions of original waters of differing types in a mixture of two such waters, they said further, "* * * only chloride probably remains chemically inert in the zones of contamination. Hence the amount of this constituent can be taken to indicate the proportion of the mixture."

Although Cl has two naturally occurring stable isotopes, ^{35}Cl and ^{37}Cl, the two seldom if ever fractionate in nature, and ^{35}Cl makes up about 75 percent of the total (Hoering and Parker, 1961). Those authors measured the Cl-isotope ratios in 81 samples, including seawater from several locations, oil-field brines, and rocks and minerals, and found virtually no variation in the ratio. ^{36}Cl, the radioactive isotope, has a half-life of 300,000 years, is formed naturally by cosmic rays, and has in the recent past been found in the atmosphere and in seawater following nuclear-test explosions (Schaeffer and Davis, 1956).

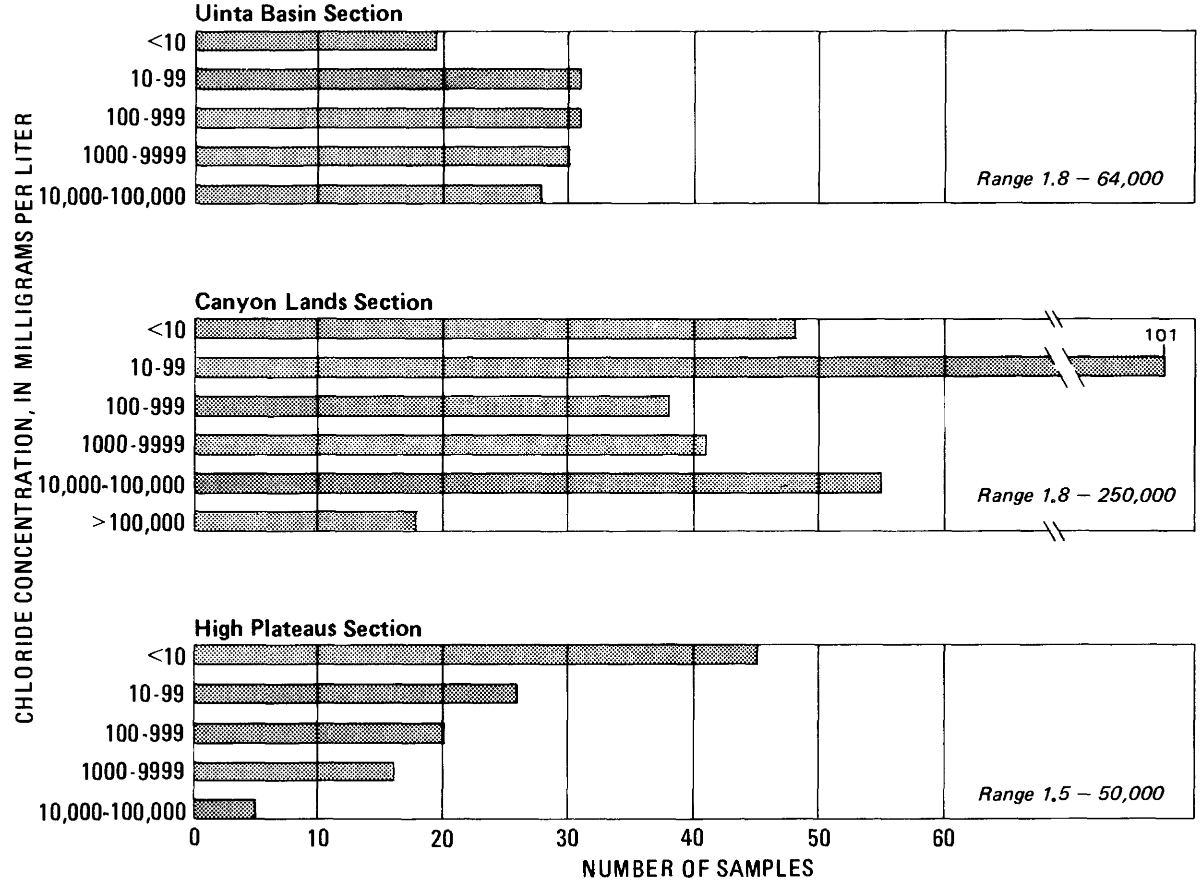


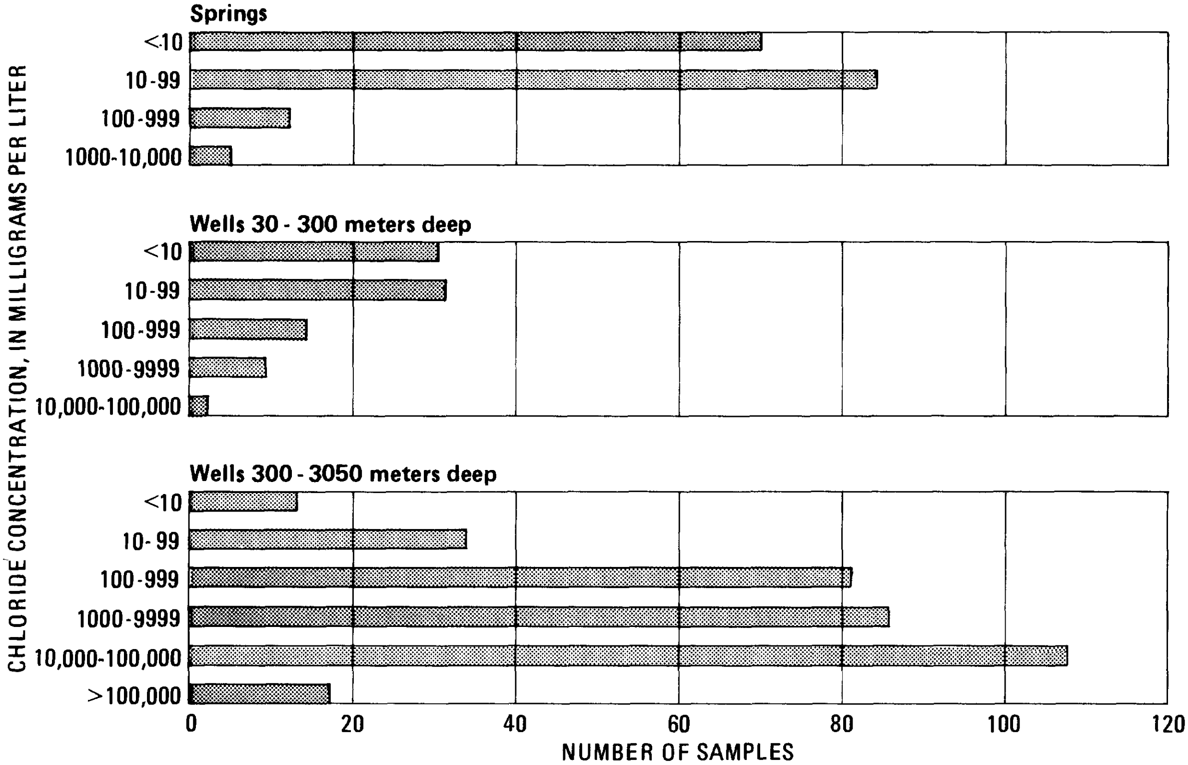
Figure 5.—Distribution of Cl concentrations by subdivisions of the Colorado Plateaus, Utah. (Data from Feltis, 1966, tables 2-4.)

As reported earlier in this paper, Cl may be removed from ground water by adsorption although the quantities so removed appear to be small. Carroll (1959) said that the reaction requires exposure of OH ions either on planar surfaces or on exposed edges of clay micelles. Kaolinite and halloysite have OH ions exposed on both sites and, along with hydrous oxides of Fe and Al present in some soils, provide optimal conditions for adsorption of Cl. Acid pH (range not stated) favors removal of Cl from dilute solutions. Adsorption is not known to be an important factor in the behavior of Cl in water.

Cl-dominated water occurs across a wide range in pH. At one extreme, White and others (1963, table 19) reported a water having 20,000 mg/L Cl and a pH of 0.4 from Yakeyama, Niigata Prefecture, Honshu, Japan, a volcanic environment. Other pH values reported in the same table for Cl-dominated waters range from 1.7 to 3.2, also from volcanic or crater-lake environments. At the other extreme is Aqua de Ney, a small nonthermal spring in north-central California, that had 7,200 mg/L Cl, nearly 4,000 mg/L SiO_2, a pH of 11.6, and numerous other strange chemical characteristics when reported by Feth and others (1961). The spring was restudied by Ivan Barnes (oral commun., October 17, 1979) who said the pH was remeasured at 12.0. Barnes includes Aqua de Ney in the class of springs (Barnes and O'Neil, 1969) of high pH that emerge at sites where ultramafic rocks are metamorphosing to serpentine in the near-surface environment. Complexion Spring, Lake County, Calif., is another example of the same class, having a pH of 12.07 and Cl concentration of 18,000 mg/L (Barnes and others, 1972, p. 265).

Hoering and Parker said (1961, p. 193-195), "The most general type of exchange reaction for chlorine in nature is exemplified by the exchange between solid sodium chloride and chloride ion. * * * The lack of isotope ratio variations in evaporite deposits * * * is probably the result of the lack of isotope fractionation in this exchange. * * * The oxidation and reduction reactions which, in the case of sulphur and carbon, have large isotope effects, are absent in the geochemical cycle of chlorine."

We have, then, an element that is characterized by its existence in ionic form, and one that is stable with respect to chemical reactions that greatly influence the behavior of many other common elements. The implication is one of extreme mobility, especially in the



NOTE: Four wells less than 30 meters deep yielded water with chloride in the range 22-4,030 mg/L. Eight wells more than 3,000 meters deep yielded water with chloride in the range 3,200-130,000 mg/L. Thirty-seven samples were not identified as to depth. The chloride range was 2-2,700 mg/L

Figure 6.—Distribution of Cl concentrations in samples from springs and samples from wells by depth zones. Where a well sample was drawn from several producing zones, the deepest was chosen for plotting. (Data from Feltis, 1966, tables 2-4.)

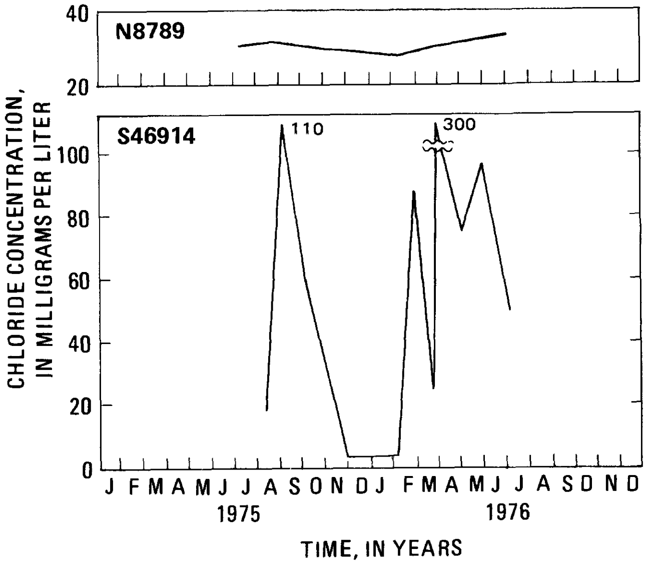


Figure 7.—Negligible and material fluctuations in Cl concentration over time in Long Island, N.Y. (Adapted from Katz and others, 1978, fig. 8-A.)

hydrosphere where—as we have seen earlier—chloride is greatly enriched relative to its abundance in the lithosphere.

Part and parcel of the mobility of chloride is the high degree of solubility of its salts. Beyond a limit of about 6,000 mg/L dissolved solids, natural water tends to have Cl as by far the most abundant anion. The trend increases with increasing concentration, Cl making up more than 75 percent of the anions in virtually all waters having 20,000 mg/L dissolved solids or more.

Sea water, of course, has a dissolved-solids concentration of about 35,000 mg/L, of which more than 19,000 is Cl. Yet, in many places where oil-field brines, for instance, have been analyzed, the total concentration is in the hundreds of thousands of milligrams per liter, and the Cl concentration 150,000 mg/L or more. If the water was originally seawater, entrapped during deposition of the sediments, then some process(es) must have operated to concentrate further the saline content. Various explanations have been offered for the phenomenon. The three that perhaps have led the running are concentration by evaporation of water and its entrainment (as vapor) in expanding natural gas (Mills and Wells, 1919), concentration and density stratification by molecular settling (Russell, 1933), and that which seems currently to be most likely, ionic filtration through natural membranes such as clay and shale.

This hypothesis is, in brief, that where types of shale or clay are suitable and where conditions of hydraulic, or perhaps osmotic (Young and Low, 1965), head permit, the fine-grained sediments act as semipermeable membranes, allowing passage of water molecules but retarding the passage of ions. It is thought that electrostatic charges on the sediment particles repel anions, causing them to lag on the high-pressure side of the membrane. Considerations of chemical balance then require that an appropriate number of cations remain with the anions. A concentration by filtration thus results. Adsorption also plays a part in the concentration process.

The bare bones of the theory were proposed by deSitter in 1947. The literature remained largely silent on the matter for about a decade until Chave (1960) discussed post-depositional changes in relation to oil-field brine composition. His paper, however, is perhaps more noteworthy for discussion of the inadequacy of sampling and of sample descriptions with reference to oil-field brines.

Nearly simultaneously there was an outburst of papers on ion filtration through membranes, on the basis of laboratory studies, field relations, and mathematical models. A sampling of the literature follows: McKelvie and others (1959); Bernstein (1960); Berry and Hanshaw (1960); Kemper (1960); McKelvie and Milne (1962); Bredehoeft and others (1963).

By the time of a symposium in 1964, White (1965) was able to present, in words and diagrams, a coherent and comprehensive account of the hypothesis of concentration by filtration through semipermeable clay- or shale-dominated membranes. The concept has been widely accepted but may require modification or indeed be inappropriate in environments where brines having very low Br/Cl ratios suggest dissolution of evaporites; conversely where the Br/Cl ratio is exceptionally high, residual bitterns remaining after precipitation of salts must be considered (Y.K. Kharaka and D. E. White, oral communs., October 22, 1979). The membrane-filtration hypothesis is attractive and useful but probably is not the last word in explaining all occurrences of subsurface brines.

Despite the attention that has been—and is being—given to the chemistry of atmospheric precipitation, our knowledge of its importance in determining the Cl concentrations found in surface and ground water is far from complete. Knowledge of continental sources of Cl and their importance remains almost negligible. There still is no explanation for the release of Cl to ground water at what appear to be steady rates. Where concentrations are sufficiently high, Cl may not be completely dissociated. If that is so, it may affect processes by which brines are concentrated in aquifers and result in inaccurate determination of Cl concentration. The book on Cl is far from closed.

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Metric Conversion Factors

The International System of units (SI) is used in this report. For readers who prefer the inch-pound system of units, the conversion factors for the terms in this report are listed below:

Multiply SI unit	*By*	*To obtain inch-pound unit*
ha (hectare	2.471	acre
hm^3 (cubic hectometer)	810.7	acre-ft (acre-foot)
L/s (liters per second)	15.85	gal/min (gallons per minute)
m (meter)	3.281	ft (foot)
m^3 (cubic meter)	35.31	ft^3 (cubic foot)
m^3/s (cubic meter per second)	35.31	ft^3/s (cubic foot per second)
$(dm^3/s)/km^2$ (cubic decimeter per second per square kilometer)	.09149	$(ft^3/s)/mi^2$ (cubic foot per second per square mile)
kg (kilogram)	2.205	lb (pound)
kPa (kilopascal)	.1450	lb/in^2 (pounds per square inch)
km (kilometer)	.6214	mi (mile)
km^2 (square kilometer)	.3861	mi^2 (square mile)
t (metric ton)	1.102	ton
t/km^2 (metric ton per square kilometer)	2.855	ton/mi^2 (ton per square mile)

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