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HYDROCHEMISTRY OF THE ONEIDA LAKE BASIN, NEW YORK

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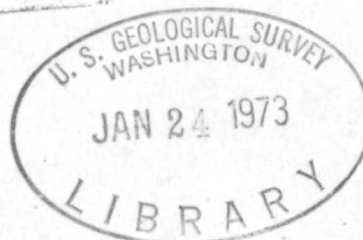
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HYDROCHEMISTRY OF THE ONEIDA LAKE BASIN, NEW YORK

by

F. J. Pearson, Jr., and George S. Meyers

ABSTRACT

Oneida Lake, the largest lake within New York State, supports massive algae blooms that interfere with one of its major uses, recreation. As part of a study of the algae problem, a chemical balance for the lake and its drainage basin has been made. The quantities of major dissolved species entering the lake are determined for each of the hydrochemically homogeneous terrains comprising the basin. The largest terrain, the Tug Hill terrain to the north of the lake contributes more than half the total streamflow to the lake, but is underlain by chemically unreactive bedrock and glacial deposits and its mean annual dissolved-solids contribution is only 0.25 t per d per sq mi (tons per day per square mile). Adjacent to Oneida Lake and extensive to the south and west is the Lake Plain terrain, underlain by sediments from ancestral Oneida Lake and contributing dissolved solids to streams at the moderate rate of 0.57 t per d per sq mi. At the foot of the Appalachian Upland escarpment is the Salina Group terrain, underlain by gypsiferous shales and carbonate rocks, and contributing more dissolved solids than any other terrain--32 t per d per sq mi. Within the Appalachian Upland, in the extreme southern part of the basin are two terrains underlain by glacial sand and gravel and by glacial till and bedrock. Their contributions are 0.58 and 0.85 t per d per sq mi, respectively. Throughout the basin, the dissolved-solid contribution of precipitation is 0.06 t per d per sq mi. Lake input is balanced by lake output for all major species except sulfate and possibly calcium and magnesium, which are retained in the lake.

Stream nitrogen loads are about 0.0016 t per d per sq mi throughout the basin, a value lower than that typical of undeveloped grassland and forest. In the southern part of the basin, this load is increased to 0.0020 t per d per sq mi by sewered wastes. Nitrogen loads leaving balance those entering the lake.

Phosphate loads are consistent with the geology of the several terrains and range from 0.0006 to 0.0034 t per d per sq mi. Domestic and industrial wastes, lakeshore cottages, and boaters and recreationists probably contribute not more than 30 percent of the phosphate entering the lake. Phosphate is strongly retained in the lake.

INTRODUCTION

Oneida Lake, the largest lake wholly within New York State, is beset from time to time with extensive growths of planktonic algae that interfere with its recreational use. Such growths occur only in lakes whose water contains sufficient quantities of dissolved chemicals in the proper proportions to support the algae. As part of understanding the algae regimen in the lake, the chemistry of the lake water and factors affecting it must be known.

The chemicals in the lake are ultimately derived from its drainage basin and tributary streams. They may be transported through or be trapped and accumulate in the lake. Additional chemicals may be added to the lake water from atmospheric precipitation on the lake's surface, from lake bottom sediment interactions, by direct ground-water flow to the lake, or by the activities of man on the lake shore.

This study had the following objectives:

- (1) To measure the chemistry of the streams tributary to Oneida Lake, and to describe the characteristics of the basin that give rise to the observed stream chemistry;
- (2) To use the basin characteristics derived from the observed stream chemistry to compute the chemical loads entering Oneida Lake through its tributaries; and
- (3) To compare measured lake outlet loads with computed stream input loads to determine whether sources other than streams are contributing significant quantities of chemicals to the lake.

Most of the data on which this report is based were collected from June 1967 through July 1968 specifically for this study. During this period, biological and other chemical data were also collected from Oneida Lake itself. Lake-data collection is continuing, but a preliminary discussion has been prepared (Greenson and Meyers, 1969). Other data collected by the U.S. Geological Survey and by the Onondaga County Department of Health were also used in preparing this report. The individual analyses and discharge measurements are not given in this report, but will be published separately in the Geological Survey's annual series of reports on water data for New York State (for example, U.S. Geol. Survey, 1967).

Acknowledgments

The authors are grateful to a number of people who have added much to this study with their assistance in data collection and analysis. They include Irwin H. Kantrowitz, Phillip E. Greeson, Lawrence A. Cerrillo and Blair F. Jones, U.S. Geological Survey; Henry C. Carroll, New York State Division of Water Resources; and M. C. Lehne, Onondaga County Department of Public Works. The laboratory analyses were performed in the Albany laboratory of the U.S. Geological Survey by Gael A. Hallenbeck, who was also of great assistance in making and checking many of the calculations in the report.

This study was a cooperative venture of the New York State Division of Water Resources, F. W. Montanari, Director, and the ~~New York District, Water Resources Division, U.S. Geological Survey, Gerald G. Parker, former District Chief, under the immediate supervision of Kenneth I. Darmer, Chief, Hydro-~~logic Studies Section.

Basis of Defining Lake Balances

Several methods could have been used to get the information needed to describe the chemical and water budgets of Oneida Lake. One approach would have been to measure the dissolved-solids contents and discharges of the major tributaries and of the lake outlet for a sufficiently long time that their average values could be found. The input to the lake then would be the sum of the measured tributary average values plus an estimated term for the contribution of smaller, unmeasured streams and areas draining directly to the lake. This method was not suitable for this study for several reasons. First, insufficient time was available to collect enough chemical data to get average stream values. Second, the streams entering the lake contain water from large areas of the basin, so knowledge of their chemistry alone would provide little information on the characteristics of the basin itself. Finally, the need to estimate the unmeasured contribution to the lake introduces an uncertainty in the balance itself that is undesirable.

To overcome these difficulties, the basin was divided into five regions, called terrains, each internally homogeneous and yielding equal loads of dissolved solids per square mile throughout its extent. The input to the lake was then found by adding the total contributions from each of these terrains. This procedure eliminated the need to estimate any unmeasured contribution to the lake and provided information on the characteristics of the basin itself, thus overcoming two of the objections to the first approach mentioned. The third difficulty was eliminated by the method used to determine characteristic terrain loads, as described below.

A brief discussion of the hydrochemical cycle is necessary to follow the rationale behind the procedure used to determine the characteristic loads per square mile of the various terrains.

The source of the water in Oneida Lake is precipitation, rain or snow, that falls on the basin and drains into the lake. Some of this precipitation is returned to the atmosphere by plant transpiration and by evaporation from the ground surface and the surface of water bodies in the basin. The remainder flows through the basin into Oneida Lake and leaves the lake by the Oneida River. Part runs over the ground surface directly into the streams during periods of heavy rainfall or during spring snowmelt. This overland flow causes the high streamflows that commonly occur during the spring of the year and during or following rainstorms. Because of its relatively rapid flow through the top soil layers or over the ground surface, overland flow is little exposed to soluble or otherwise chemically reactive earth materials before it enters the stream system. Its dissolved-solids content, therefore, tends to be rather low, as are the dissolved-solids contents of streams during periods of high flow.

The final part of the total precipitation falling in the basin percolates through the soil zone into the underlying sediments to become ground water. Ground water is not lost from the basin's hydrologic system, because it, like water in streams, tends to flow to the lowest level available to it. For example, water entering a ground-water system on a hill will tend to flow toward neighboring valley bottoms to be discharged into their streams. For the whole basin, the lowest level to which water can flow is Oneida Lake itself, which is, therefore, the discharge area for ground water that does not reach the streams directly. The actual points of ground-water discharge to streams may be springs or, artificially, wells, but more commonly are areas of almost imperceptibly slow seepage either to streambeds directly or to swampy regions bordering them. Because the rate of movement of ground water is slow compared to that of water running over the ground's surface, the ground-water system continues to discharge to streams long after a rain-storm or period of snowmelt has passed. It is ground-water discharge that maintains the flow of streams during prolonged periods of fair weather.

Ground water is in intimate contact with earth materials for relatively long periods of time and so is able to dissolve and react with them. Its dissolved-solids content is, therefore, higher than that of overland runoff from the same region, and the various dissolved species may be differently distributed. The differing mineral contents of the ground water maintaining the lower flows of streams and of the overland runoff responsible for the higher flows produce a general relationship between stream discharge and dissolved-solids content. This relationship is extensively used in this study and so warrants further discussion.

A graph of the ideal relationship between stream discharge and stream chemistry is shown in figure 1. Over a wide range of low discharges, the amount of material dissolved in the stream water remains essentially constant (B-B'). In this range, the flow of the stream is being maintained by ground-water discharge which, in this idealization, is assumed to be from a chemically homogeneous source. At higher flows, overland runoff of lower dissolved-solids content contributes an increasingly greater proportion of the total stream discharge, and the concentration of dissolved material in the stream water correspondingly decreases (A-A').

The volume of precipitation may vary from year to year as may temperature and, hence, evaporation and transpiration so the amount of water in transit through the basin also will vary. With data for many years, it is possible to arrive at average yearly discharge values for streams in the basin and at the lake outlet. For many streams, long periods of continuous records are available from which mean annual flow and flows at other time intervals can be derived. Even for ungaged streams or those for which only a few instantaneous discharge measurements are available, the same type of information can be inferred by a variety of methods (Hunt, 1963; Riggs, 1968). Thus, streamflow data and interpretive techniques permit reliable estimates of discharge to be made for most points on most streams.

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Figure 1. -- Ideal relationship between stream discharge and dissolved-solids content.

Long-term data and interpretive methods are not available for the chemistry of most streams in the basin, so it is necessary to use indirect procedures to evaluate such parameters as mean annual chemical loads and loads at other recurrence intervals. The method used in this study was to define the discharge versus dissolved-solids content relation at significant points on many streams in the basin. Long-term stream-discharge data were then used with this relationship to determine the mean annual dissolved-solids contents or those at any streamflow values. For example, suppose figure 1 represents the experimentally determined discharge versus dissolved-solids content relationship for a point on a stream. From streamflow data, the mean annual stream discharge might be A, and that equaled or exceeded 95 percent of the time B. From the curve, the dissolved-solids concentration, represented perhaps by specific conductance values, are found to be A' and B', respectively.

To construct such curves requires a number of simultaneous discharge and chemical measurements. These measurements need not be spread over many years, because time variations are implicit in the stream-discharge records used with these curves. The measurement pairs must represent a wide range of instantaneous discharges to define as much of the curve as possible. In practice, measurements made biweekly or monthly and at times of extreme high or low flows for about a year suffice.

To determine the loads characteristic of the terrains comprising the basin, sites for regular chemical sampling and discharge measurements were established on various streams in the basin. Ideally, these sites would represent drainage from only one type of terrain, so data from them would give the characteristics of the terrain directly. In practice, such sites were not available for all terrain types and it was necessary to take data from several sites, each representing drainage from two or more terrain types, and from this compute the individual terrain yields.

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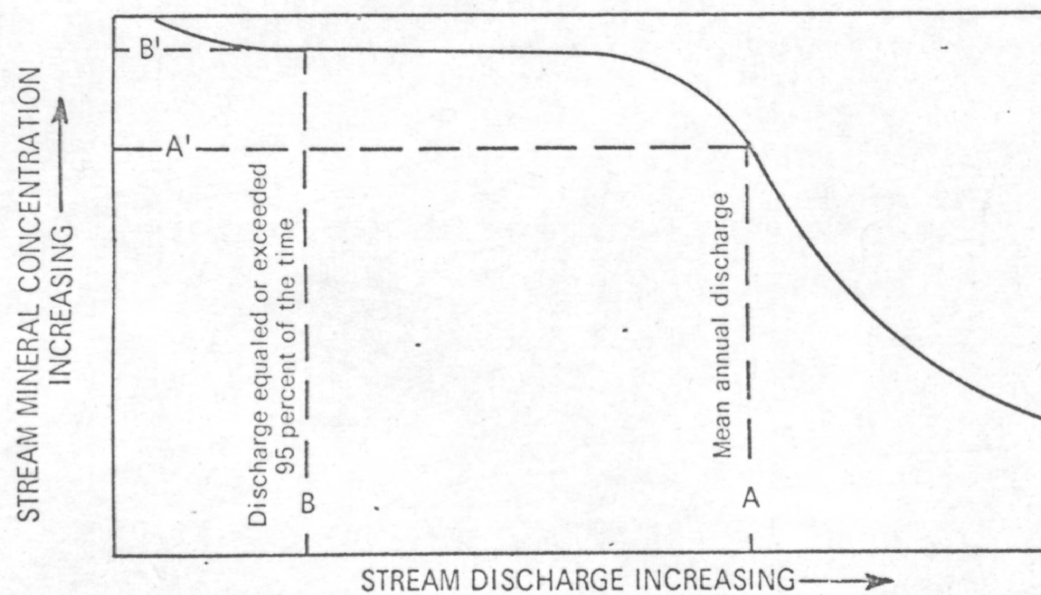


Fig. 1

The various terrain-yield values can be used to cover the entire basin or to find the load of any stream within the basin. For example, consider a stream with a drainage area of 100 square miles, consisting of 25 square miles type X, 35 square miles type Y, and 40 square miles type Z terrains, and with known precipitation. If the yield of these terrains are 1, 2, and 3 t per d per sq mi (tons per day per square mile), respectively, and the load of the precipitation is 0.01 t per d per sq mi, the total average load carried by the stream will be:

$$L_s = (25 \times 1) + (35 \times 2) + (40 \times 3) + (100 \times 0.01) = 216 \text{ tons per day.}$$

If the average discharge of the stream is, say 100 cfs (cubic feet per second), known either from streamflow records or from a reasonable estimate, the average concentration will be $216 / (100 \times 0.0027) = 800 \text{ mg/l}$ (milligrams per liter). By the same procedure, knowing the areas and yields of all terrains in the basin and atmospheric precipitation, the chemical loads entering Oneida Lake can be found.

PHYSIOGRAPHY AND GEOLOGY OF THE BASIN

Oneida Lake is located in the Erie-Ontario Lowland physiographic province (Muller, 1965). This is a relatively flat region at an elevation of about 400 ft, which includes the plains bordering Lake Ontario and is coextensive east of Oneida Lake with the lowlands through which flow the Mohawk and Hudson Rivers (figure 2). The basin south of the lake includes part of the Appalachian Upland. This province, which is continuous southward to Georgia, here consists of gently southward dipping rock forming a plateau region with elevations of as much as 2,000 feet. Along the north-facing escarpment in the Oneida Lake basin, however, the Upland is deeply channeled by glacial and stream action, so its plateau structure is not obvious, and the region appears rather one of north-trending valleys and hills. North of Oneida Lake is the Tug Hill Upland, a region similar to the Appalachian Upland, but with lower peak elevations and with no dominant trend to its valley and hill appearance.

The consolidated rock underlying Oneida Lake basin is all of sedimentary origin and of Paleozoic age (Broughton and others, 1961; Kantrowitz, in press). The rocks of the Tug Hill region are chiefly sandstones, which are highly resistant to physical erosion. This resistance is responsible for the region's elevation and relief. Further, these sandstones are made up of only sparingly soluble minerals and so chemical weathering and erosion also is slow.

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Figure 2. -- Oneida Lake basin and the physiographic units of New York State. (After Muller, 1965, fig. 1).

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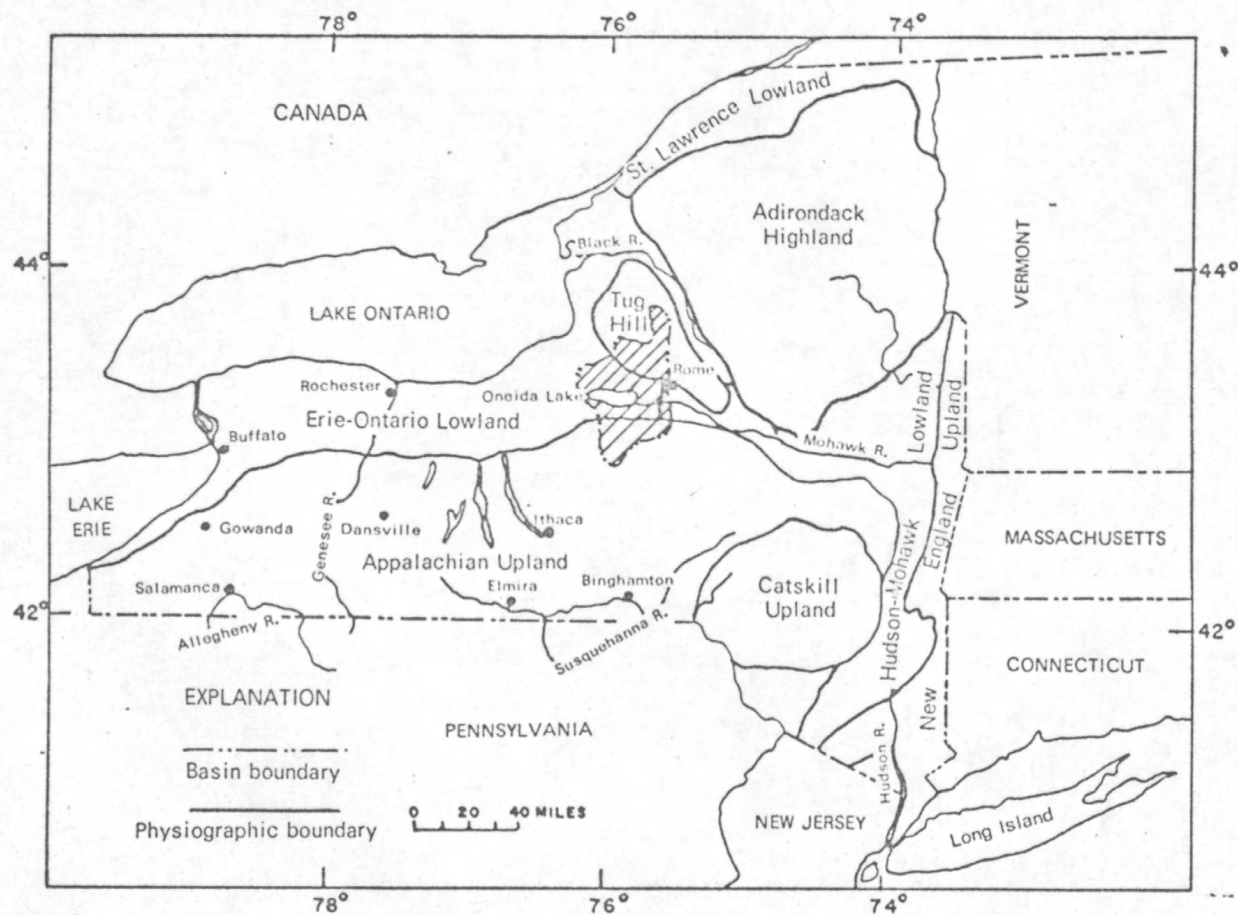


Fig. 2

The rocks of the Appalachian Upland are primarily limestones, shales, and siltstones. Some of these rocks, too, are resistant to physical erosion, particularly the massive beds that form the crest of the escarpment. All, however, are considerably more chemically reactive than those in the Tug Hill region.

In the Lake Plain Lowland region surrounding Oneida Lake, the consolidated rocks are shales, limestones, and sandstones, which have varying resistance to erosion. However, over most of the lowland, the consolidated rock is covered with up to 100 feet of younger unconsolidated material, and thus, the surface topography does not reflect the erosional characteristics of the deeper material.

All except one of the consolidated rock units in the basin have little or no direct effect on the chemistry of streams and so need no more detailed discussion here. The Salina Group has a profound effect on stream chemistry, and must be given special attention.

The Salina Group, which consists of the Vernon Shale, Syracuse Salt, Camillus Shale, and Bertie Limestone, in this area ranges from about 700 - 900 feet in thickness (Kantrowitz, in press; Leutze, 1964). It is present at land surface at the lower edge of the Appalachian Upland escarpment, and may be found along the sides and bottoms of some of the deeper valleys cut into the escarpment. The Salina Group extends under the unconsolidated material in the lowland region south of Oneida Lake, where, because of this cover, its northern edge cannot be seen at the ground surface. The position of this edge may be inferred and drawn with some confidence, however, using the topography of the buried consolidated rock which is known from bore hole records (Kantrowitz, 1964). The Salina Group terrain is easily erodible, whereas its northern neighbor is more resistant limestone and forms a buried east-west chain of low hills. The extent of the Salina Group is shown in plate 1. The southern exposed contact is taken directly from the Geologic Map of New York State (Broughton and others, 1961). The northern buried contact has been drawn slightly to the north of its position on the New York State map to better follow the buried topography.

The Salina Group is made up of shales with some subsidiary carbonate rock (dolomite, $\text{CaMg}(\text{CO}_3)_2$). The shales contain lenses and disseminated grains of the mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This is a highly soluble mineral -- a saturated solution of it contains about 530 mg/l calcium and 1,280 mg/l sulfate -- and its presence greatly affects the chemistry of streams flowing over the shales. In addition, the Syracuse Salt of this group contains rock salt (NaCl), but this is present only deep beneath the Appalachian Upland, and no salt can be found where the rocks are now exposed. It is probable, though, that some sodium and chloride are contributed to the streams in the basin by deep moving ground water discharging to the lowland after moving through the Appalachian Upland and being in contact with the buried salt. The total quantity of this salt in the streams is much less than that of the gypsum.

The extent, configuration, and type of unconsolidated material in the Oneida Lake basin was, for the most part, determined by glaciers, or ice sheets, which from time to time, have covered this region from the north. Although at their maximum glaciers extended far to the south of the Oneida

Lake basin, it is the period during which the front of the last glacier was retreating northward across the basin (Muller, 1964, 1965) that is of interest to this study.

Sediments deposited by glaciers may be divided into two broad categories: those moved and deposited by the action of solid ice under and on the flanks of a glacier, and those deposited by flowing water associated with the glacier. For the purposes of this report, the distinction between them rests on the sorting of the grains of the resulting sediments. That is, ice-laid deposits consist of particles of a wide variety of shapes, sizes, and compositions indiscriminately jumbled together. On the other hand, the action of moving water tends to separate material it is carrying by particle size because of the greater ease with which smaller sized material can be transported. Within a single water-laid deposit, therefore, the individual grains have a fairly uniform size range, although the sizes themselves may vary widely from deposit to deposit. Also, it is likely that water-laid materials will contain less soluble rock than ice-laid materials because of the solution action of the depositing water.

As the glaciers advanced southward over the basin, rock was picked up, crushed, and deposited as till by the moving ice over almost the entire consolidated rock surface. Much of this till remained as the glacier retreated, and there is now present over much of the uplands a veneer of ice-laid surficial material. In general, this material was not transported far from its source, and has not been greatly modified chemically by its movement. Thus, the chemistry of streams flowing over ice-laid deposits is not significantly different from that of those flowing over the consolidated source rock.

There are two types of water-laid deposits in the basin that are significant within the content of this study. Both are associated with the melting, retreating phase of the last glaciation. As the glacial front wasted northwards near and across the escarpment of the Appalachian Upland, volumes of melt water deposited thick sequences of sand and gravel in the north-south valleys of the escarpment. These sequences, the Valley Heads Moraine (Muller, 1965), form the southern drainage boundary of the basin in the valleys, and cover the floors of these valleys northward beneath the present streams. The deposits of this type that are important to the water chemistry of the basin are shown in plate 1 as the sand and gravel terrain.

As the ice front retreated across the lowland north of the Appalachian Upland, the melt water covered much of the present plains around Oneida Lake. As the volume of melt water decreased and ice dams blocking drainage to the east and west were opened, the level of this lake fell until it became the present Oneida Lake. As the ancestral lake fell, the surficial material now present in the lowlands was deposited. This includes areas of fine-grained material transported by moving water and deposited under quiet lake conditions. Shoreline features such as dune and bar-shaped sand bodies, and an area of peaty, organic detrital material in swampy regions were left as the level went down. Of the lake deposits on the lowland, only the last is likely to affect the water chemistry; because of its rich organic nature, it is an important source of nutrient chemicals to streams entering Oneida Lake.

DATA COLLECTION AND ANALYSIS

Collection-Site Selection

After perusal of chemical and other hydrologic data previously collected in the basin, and a reconnaissance of the basin, certain sites were chosen where streamflow and stream chemical data would be collected routinely. The location of these sites and the boundaries of the areas draining to them are shown in plate 1.

Within the basin there are seven continuous-recording stream-gaging stations, as well as one at the lake outlet at Caughdenoy (pl. 1). These stations have varying periods of record, the longest being East Branch Fish Creek at Taberg (2425), in operation since 1923; the shortest is Scriba Creek near Constantia (2458.4) in operation since March 1966. These stations are listed in table 1, and their detailed records are given in various publications of the U.S. Geological Survey (1958, 1962b, 1963, 1964a, 1964b, 1965, 1966, and 1967).

There are also four stations (2455, 2438, 2437, and 2435.3) at which a large number of instantaneous discharge measurements have been made since 1964. These stations are also listed in table 1 and their locations shown in plate 1. The individual measurements at these sites are published by the U.S. Geological Survey (1965, 1966, and 1967).

A consideration in selecting sites for routine chemical sampling was preexisting flow data at that site. During project planning, though, it became clear that while chemical data at all partial-record sites and northern gaging stations would be desirable, only one southern gaging station, Butternut Creek near Jamesville (2452), would yield useful chemical information. The other three southern stations, Chittenango Creek near Chittenango (2440), Limestone Creek at Fayetteville (2450), and Oneida Creek at Oneida (2435) drain several types of terrain and so would not be particularly useful in determining individual terrain contributions, nor are they close enough to the lake to provide data on total input to it.

As will be shown, most of the dissolved-solids load entering Oneida Lake is derived from the southern part of the basin. To provide a better analysis of the terrains in this region, three partial-record stations were established for this study. These stations, Sconondoa Creek at Vernon Center (2433.9), Chittenango Creek at Rippleton (2438.8), and West Branch, Limestone Creek near Manlius (2449.9) are listed in table 1 and their locations shown in plate 1.

Collection Procedures

An instantaneous stream-discharge value accompanied each chemical sample collected so that the relation between stream discharge and the chemical constituents could be defined. Most discharge values were determined by current-meter measurement at the time of sample collection, but for those gaged sites and long-term partial-record stations where a stable stage-discharge relation is known, a discharge value based on the stream stage at the time of sample collection sometimes was used.

Laboratory chemical analyses were made on each sample for: silica (SiO_2), calcium (Ca^{+2}), magnesium (Mg^{+2}), strontium (Sr^{+2}), sodium (Na^{+}), potassium (K^{+}), alkalinity (HCO_3^{-} plus CO_3^{-2}), sulfate (SO_4^{-2}), chloride (Cl^{-}), fluoride (F^{-}), total phosphate (PO_4^{-3}), the nitrogen-bearing species ammonia (NH_4^{+}), nitrite (NO_2^{-}), nitrate (NO_3^{-}), organic nitrogen, pH, and specific conductance. Concentrations of dissolved solids were computed from the sum of the concentrations of the analyzed constituents. The analytical procedures were those in common use in U.S. Geological Survey laboratories as described by Rainwater and Thatcher (1960). The metals were analyzed using atomic absorption spectroscopy (Fishman and Downs, 1966).

To insure that chemical analysis data correspond as closely as possible to the true compositions of the streams, a combination of field and laboratory procedures was used. Specific conductance and temperature of each stream were measured in the field and a 2-liter sample pressure filtered through a 0.45 micron pore-size medium. An alkalinity titration and pH measurement were performed on each filtered sample in the field, and the remainder of the filtered sample split into three or four fractions as follows: 500-ml (milliliter) sample with 2 ml of a 10 percent mercuric chloride (Hg_2Cl_2) solution added was collected in a polyethylene bottle on which analyses for the nitrogen species were performed. The Hg_2Cl_2 solution was intended to preserve the natural ratios of the nitrogenous species, which ratios are known to be unstable during normal sample storage. A second 300-ml sample for analysis for total phosphate was collected in a soft-glass bottle. Glass was used because polyethylene is known to adsorb phosphate. The remainder of the analyses were performed on a 1-liter sample, collected in a polyethylene bottle. Streams south of the lake were often saturated with calcite (CaCO_3), which could precipitate in the sample bottle, especially if it was warmed appreciably, and so give erroneously low analyzed calcium concentrations. For these streams, an additional 50-ml sample was taken and acidified in the field to prevent calcite precipitation. Calcium then was determined in the laboratory on this sample.

Although a preservative was used in the samples analyzed for nitrogen species, not much confidence can be placed in the individual specific analyses. To use the data, therefore, the nitrogen species analyses were recalculated in terms of their equivalent milligrams per liter nitrogen, these values added, and a single sum of total nitrogen as N used for each sample.

Streamflow-Data Analysis

The purpose of this study is to describe those phenomena that give rise to the present chemical characteristics of Oneida Lake. Because the volume of the lake is large compared to the amount of water flowing through it, changes in the chemistry of the water in the tributary streams are not rapidly reflected in the chemistry of the lake itself. The primary consideration was, therefore, to define the mean annual streamflow and its chemical properties.

For consistency among the flow records for stations with varying periods and types of records, all were adjusted to correspond to the period 1931-60, the present standard reference period for hydrologic data (Busby, 1963). The adjusted flow values in tables 2 and 4 were determined by O. P. Hunt (oral commun., 1968) using graphical-regression procedures (Hunt, 1963; Riggs, 1968) to extend the records at short-term gaging stations and partial-record stations. The annual flow values for all gaging stations and the four older partial-record sites should be well within 10 percent of the true values for the base period.

Precipitation in the Oneida Lake basin is shown in figure 3. The lines on this figure are taken from a larger map of the entire Oswego River basin, based on U. S. Weather Bureau data for the standard period 1931-60 (R. A. Gardner, written commun., 1968). From this figure, the mean annual precipitation in the area draining at the various streamflow measuring stations was found (tables 2 and 4).

Precipitation and evapotranspiration values calculated for contiguous gaged areas were used to estimate the mean annual streamflow at the three new partial-record sites. The number of measurements at these sites is too few for the usual correlation methods to be completely effective. However, what correlation was possible showed that the estimated values are quite reasonable.

Chemical-Data Analysis

The data-analysis technique adopted made use of the reliable streamflow data at the sites sampled and the relationship between stream discharge and stream chemistry. Instantaneous discharges at the time of sampling were plotted against specific conductance, a parameter related to dissolved-solids content. From these graphs, the specific conductance at any discharge could be read. From the analyses of water from each site, a group of additional graphs of specific conductance versus individual ion contents also was made. From these, the composition of the dissolved solids at any specific conductance could be estimated. These synthetic compositions are the basis for the discussions below.

Unfortunately, some of the dissolved constituents of greatest interest in this study, the nitrogen-bearing species and phosphate, cannot be treated by this method, because their concentrations are normally independent of specific conductance. To find the average loads of these constituents, the load corresponding to each sample, based on its analysis and the discharge

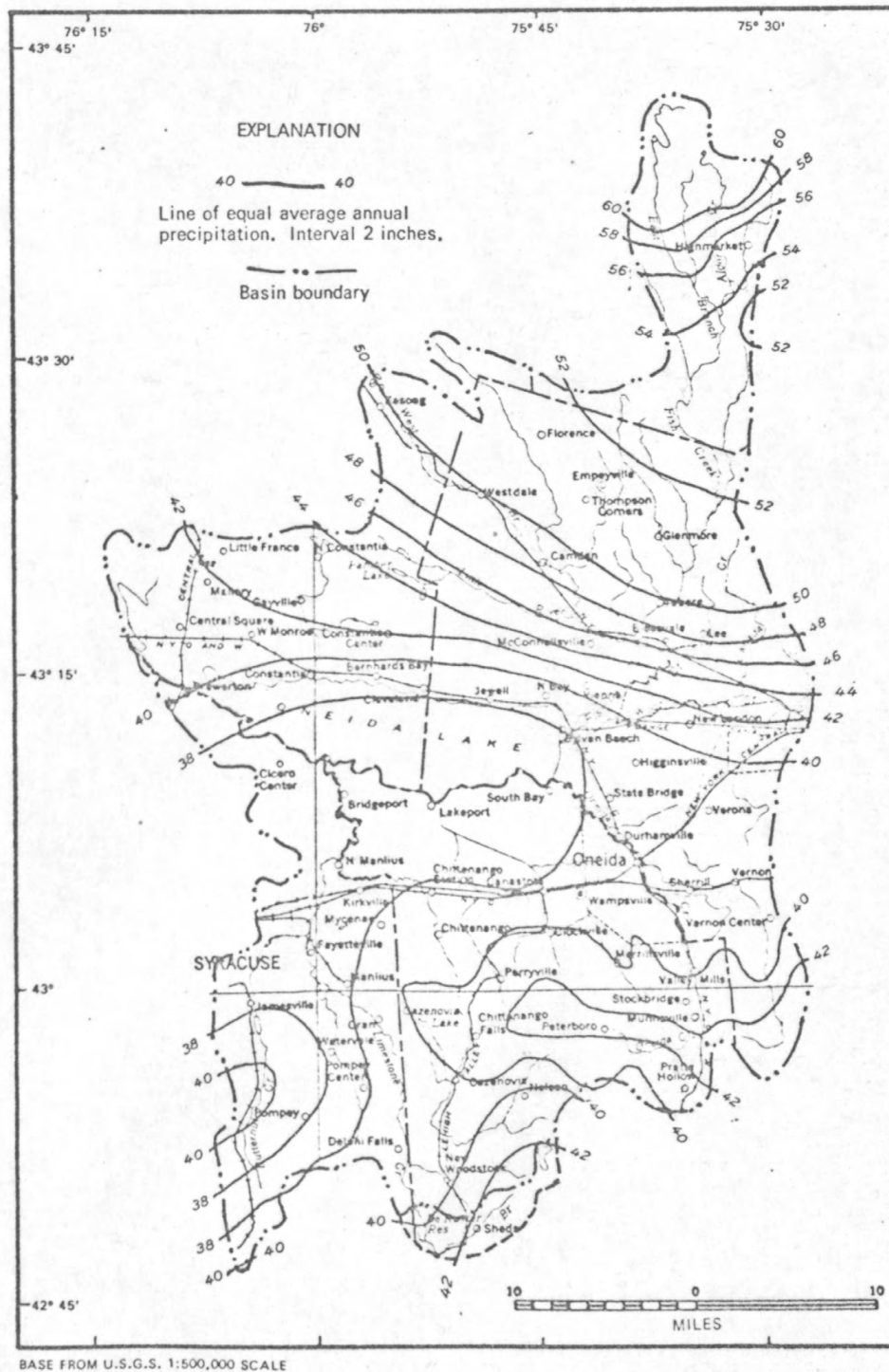
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Figure 3.--Average annual precipitation, in inches,
in the Oneida Lake basin, 1931-60.
(After R. A. Gardner, written commun., 1968).

at time of collection, were plotted by date. Total nitrogen values are those resulting from this study, while phosphate values include also data collected from 1964 through 1966 for the Onondaga County Department of Public Works by M. C. Lehne. Mean annual loads were estimated from these graphs.

TOP



SOURCES OF CHEMICALS DISSOLVED IN STREAMS

The rocks and sediments within the Oneida Lake basin have diverse hydrologic and chemical properties, many of which have been mentioned previously. In this section, the details of the effects of this diversity on the chemistry of streams in the basin are discussed.

The physiography and geology of the basin are such that the basin can be divided into five hydrochemically distinct and internally homogeneous terrains, excluding Oneida Lake itself. The largest of these is the Tug Hill terrain which includes almost all of the region north of the lake (pl. 1). This terrain has the highest precipitation in the basin, but is underlain by chemically unreactive earth materials so that although it contributes more than half the water entering the lake, it contributes only about 10 percent of the dissolved-solids load. South of Tug Hill in the Erie-Ontario Lowland physiographic region is the Lake Plain terrain. This is a flat lying, in places swampy terrain underlain by sediments from the bottom of ancestral Lake Oneida. Because of their organic nature, these sediments contribute more than 35 percent of the phosphate load entering the lake, although they cover only 21 percent of the basin's area. South of the lake plain, and also of low relief, is the Salina Group terrain. Because of the various soluble minerals in the bedrock here, this terrain alone contributes 50 percent of the dissolved-solids load to the lake. Finally, in the Appalachian Upland, two terrains are present, distinguished from one another by the type of surficial glacial material present. In the upper reaches of the major streams and extending down their valley floors are extensive water-laid sand and gravel deposits. This sand and gravel terrain yields large amounts of ground water with a relatively low dissolved-mineral content. The intervening hills and smaller valleys, on the other hand, are mantled by ice-laid, poorly sorted till, exposed bedrock, and small areas of low yielding sand and gravel which yield lesser amounts of more highly mineralized water to the streams. The locations of these terrains are shown in plate 1, and the areas of each contributing to the various streams and the entire lake are given in table 1.

Precipitation

Precipitation is the source of all water in the Oneida Lake basin and also contributes small but significant amounts of dissolved material to the streams of the basin. It therefore is appropriate to discuss the contribution of precipitation before taking up those of the various terrain types.

The general pattern of wind and storm movement in the basin is roughly parallel to the long axis of Oneida Lake, from west to east off the Great Lakes. Storms moving in this direction, are forced to rise over the higher ground surface in the Tug Hill Upland and the escarpment of the Appalachian Upland. This lifting causes cooling of the air masses and results in higher precipitation over the upland than in the lowland in which Oneida Lake is located (fig. 3). The western part of the Tug Hill Upland receives especially high precipitation because it is the first elevation of any consequence over which moisture-laden air moving eastward off the Great Lakes must rise.

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Table 1.--Drainage areas at sampling stations and areas of contributing terrains

Number	Stream and location	Sand and gravel		Till		Saline Group		Lake plain		Tug Hill		Lake surface		Total	
		sq mi	per-cent	sq mi	per-cent	sq mi	per-cent	sq mi	per-cent	sq mi	per-cent	sq mi	per-cent	sq mi	per-cent
2458.4	Scriba Creek near Constantia (continuous record since 1966, partial record since 1964)							1	2	37	98			38.4	3
2412.	West Branch Fish Creek at Blossvale (continuous record since 1965, partial record since 1964)									204	100			204	15
2425.	East Branch Fish Creek at Taberg (continuous record since 1923)									188	100			188	13
2428.	Wood Creek near New London (partial record since 1966)							66	72	25	28			90.5	6
2435.3	Oneida Creek at Oneida Valley (partial record since 1964)	16	12	44	33	47	35	26	20					133	10
2437.	Cenaseraga Creek near N. Chittenango (partial record since 1964)			8	42	12	58							20.1	1
2438.	Cowaselon Creek at Oniontown (partial record since 1964)	3	4	18	27	42	61	6	8					69.2	5
2455.	Chittenango Creek at Bridgeport (partial record since 1964)	63	20	166	53	81	26	4	1					314	22
	Unaged area					10	4	194	75	55	21			259	19
	Oneida Lake surface											80	100	80	6
2466.01	Oneida River at Caughdenoy (continuous record since 1947 - station no. 4-2465)	82	6	236	17	192	14	297	21	509	36	80	6	1,396	100

STATIONS WITHIN AREAS ABOVE

2433.9	Sconondoa Creek at Vernon Center (partial record, 1967-68)			12	48	13	52							24.9	2
2438.8	Chittenango Creek at Rippleton (partial record, 1967-68)	15	46	17	54									31.8	2
2449.9	West Branch Limestone Creek near Manlius (partial record, 1967-68)			19	100									18.8	1
2452.	Butternut Creek near Jamesville (continuous record since 1958)	10	30	22	70									32.2	2

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There are significant quantities of chemical matter introduced into the basin from the atmosphere. This matter may be dissolved in precipitation or may be fine particles--aerosols--in the atmosphere, which settle on the ground surface during periods of no precipitation or are washed down by precipitation at the beginning of storms. Routine data on the atmospheric contributions to the chemistry of water in New York State are collected by exposing containers to the atmosphere for monthly periods and analyzing the combination of precipitation and settled aerosol matter collected in them. These analyses combined with measured precipitation data give the total loads contributed by the atmosphere. For convenience the values calculated are called here precipitation loads, although they actually include both precipitation and aerosol contributions.

From routine sampling it has been found that, except quite close to large industrial complexes such as New York City or the Buffalo-Tonawanda area, the pattern of precipitation chemistry throughout the State is quite constant. Thus, no special precipitation chemistry stations were set up in the Oneida Lake basin. Instead, relations developed for all of rural upstate New York were taken as representing the precipitation contribution to the basin's water chemistry.

The nitrogen-bearing species in precipitation are ammonium (NH_4^+) and nitrate (NO_3^-). These ions, especially ammonium, are relatively unstable and their individual concentrations can change rapidly during the period of collection or later storage. Thus here, as elsewhere in the report, the individual nitrogen species are not differentiated but are expressed in terms of the total nitrogen contributed by both.

The chemical loads in precipitation in rural, upstate New York, as derived from the statewide sampling network are shown in figure 4. As this figure shows, the loads of some species vary with precipitation and others do not. The nonvariant species--magnesium, potassium, sodium, chloride, and total nitrogen--probably result from the settling of solid aerosol particles, which should be at a constant rate and independent of precipitation amount.

Of the variant species, sulfate results in part from the solution in precipitation of various gaseous oxides of sulfur which are present in the atmosphere, and in part also from the solution of soluble calcium sulfate aerosols. Thus, sulfate and calcium loads should indeed vary with precipitation. The dissolved-solids content, primarily sulfate ions also varies with the amount of precipitation.

To find the chemical contribution of precipitation to streams, the stream drainage area and the average precipitation over that area must be known. The values used here (tables 2 and 4) were found by drawing the drainage boundaries on a larger version of figure 3, and measuring the areas between the equal precipitation contours within each area. These average precipitation values, used with figure 4, give unit area loads, which can be multiplied by total area to give total loads.

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Figure 4.--Average chemical loads in precipitation in rural
upstate New York.

Contributions of Terrain Types

The chemical loads contributed by each type of terrain were determined from measured loads of streams draining them, as described above. Details of stream measurement site selection and the results of the terrain contribution calculation are given here.

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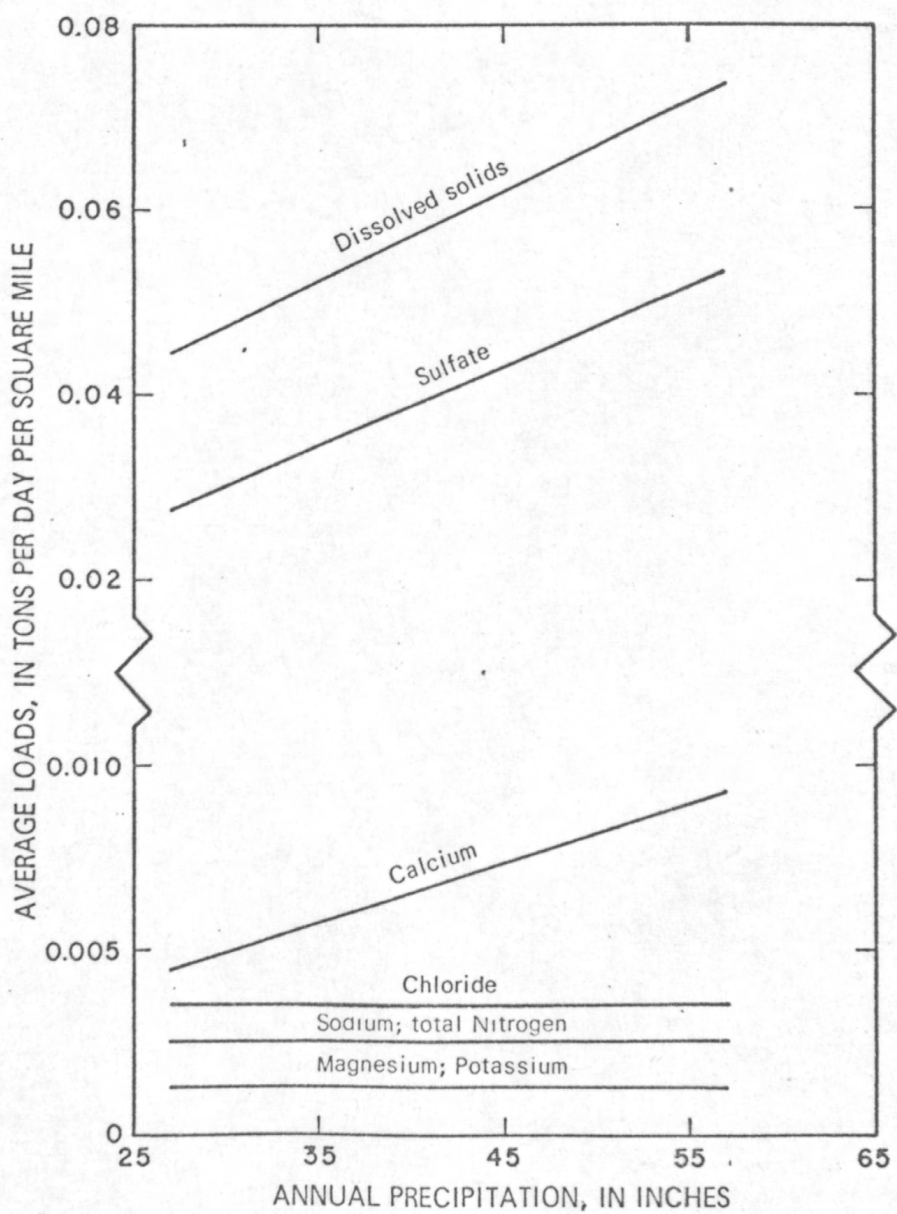


Fig 4

Appalachian Upland Terrain

The Appalachian Upland part of the basin is made up of two terrain types, designated here as the sand and gravel terrain and the till terrain. The former includes the well-sorted, water-laid glacial deposits of the Valley Heads Moraine (Kantrowitz, in press; Muller, 1964, 1965) and glacial and post-glacial deposits of the same type in the floors of some of the major valleys. The terrain is characterized by its high ground-water storage and yield to streams during fair weather, and by its relatively low content of soluble or chemically reactive mineral matter. The areal extent of this terrain, as shown in plate 1, was based on the delineation of areas of high ground-water yield in this region by Kantrowitz, (in press).

The till terrain is the remaining part of the Appalachian Upland region north to the outcrop belt of the Salina Group. It is made up of poorly sorted, ice-laid glacial deposits, small areas of sand and gravel, and exposed bedrock. Its ground-water yield is less than that of the sand and gravel terrain and contains more soluble minerals (Kantrowitz, in press).

The hydrochemistry of these terrains was determined using discharge and chemical data from stations on Chittenango Creek at Rippleton (2438.8), West Branch Limestone Creek near Manlius (2449.9), and Butternut Creek near Jamesville (2452). The locations and drainage basins of these stations are shown in plate 1, and the contributions of the two terrain types to their total areas in table 1. Analysis of water samples and discharge data at each station were used to define the relationships between stream dissolved-solids content and discharge shown in figure 5.

Two discharge values are marked for each stream in figure 5. They are the mean annual flow, used in calculating the average water and dissolved-solids loads budget, and the approximate discharge that will, on the average, be equaled or exceeded 95 percent of the time. In this region, this is about equal to the flow that can be expected to occur on the average for seven consecutive days every two years. In figures 5, 8, 9, 10, and 11 this flow is designated as 7 day-2 year. The reason for considering this flow as well as the mean annual is that at flows as low as the 7 day-2 year, the streams are generally almost completely ground-water fed. Stream data at these flows, therefore, given information about regional ground-water yields and chemistry (La Sala, 1967). On the graphs in figure 5, these flows are on relatively flat parts of the conductance curves, showing that ground water is the major contributor to the streams.

The mean annual flows, per square mile, of West Branch Limestone Creek (2449.9) and Butternut Creek (2452) are about the same, 1.4 cfs per sq mi (cubic feet per second per square mile) and that of Chittenango Creek at Rippleton (2438.8) slightly higher, 1.6 cfs per sq mi. This higher value is due to the greater amount of precipitation falling on the area drained at this station (table 2).

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Figure 5.--Specific conductance versus discharge for streams
draining the Appalachian Upland terrain.

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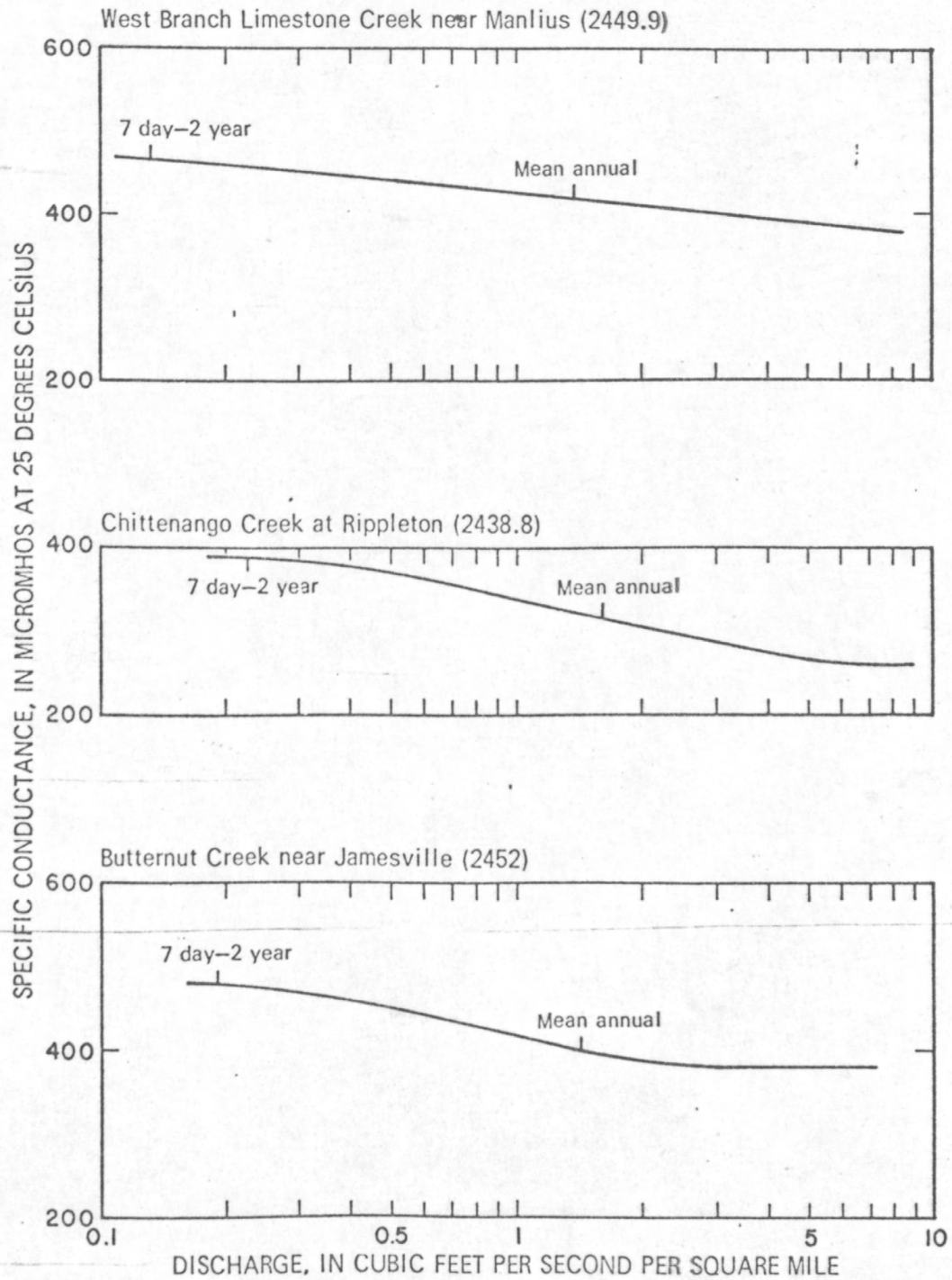


Fig. 5

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Table 2.--Examples of terrain net-yield calculations

Station and terrain drained	Drainage area (sq mi)	Flow (cfs)	Precipitation (inches)		MEAN ANNUAL							
					Dissolved solids (mg/l) (t/d/sq mi)		Calcium (Ca) (mg/l) (t/d/sq mi)		Sulfate (SO ₄) (mg/l) (t/d/sq mi)	Chloride (Cl) (mg/l) (t/d/sq mi)		
Chittenango Creek at Rippleton 46 Percent Sand and gravel; 54 Percent Till	31.8	51	40.6	Total Precipitation Net	180 .06 .72	0.78 .06 .72	48 .01 .20	0.21 .01 .20	18 .039 .039	8 .039 .039	0.035 .004 .031	
West Branch Limestone Creek near Manlius 100 Percent Till	18.8	26	38.0	Total Precipitation Net	240 .06 .84	.90 .06 .84	72 .01 .26	.27 .01 .26	29 .037 .071	9 .037 .071	.034 .004 .030	
Butternut Creek near Jamesville 30 Percent Sand and gravel; 70 Percent Till	32.2	44	39.0	Total Precipitation Net	225 .06 .77	.83 .06 .77	61 .01 .21	.22 .01 .21	25 .038 .054	9 .038 .054	.033 .004 .029	
Sand and gravel terrain from figure 6						.58		.13			.050	.030
Till terrain from figure 6						.85		.25			.075	.030
Sconondoa Creek at Vernon Center 48 Percent Till; 52 Percent Salina Group	24.9	34	41.1	Total Precipitation Net	590 .06 2.11	2.17 .06 2.11	140 .01 .51	.52 .01 .51	250 .04 .88	11 .04 .88	.040 .004 .036	
Salina Group yield = (measured yield -0.48 Till yield)/0.52						3.27		.75		1.62		.042
Canaseraga Creek near North Chittenango 42 Percent Till; 58 Percent Salina Group	20.1	29	40.0	Total Precipitation Net	580 .06 2.20	2.26 .06 2.20	140 .01 .53	.54 .01 .53	240 .04 .89	16 .04 .89	.062 .004 .058	
Salina Group yield = (measured yield -0.42 Till yield)/0.58						3.18		.73		1.48		.078
Salina Group terrain average of 2 Salina Group values						3.22		.74		1.55		.060
Scriba Creek near Constantia 2 Percent Lake Plain; 98 Percent Tug Hill	38.4	80	44.6	Total Precipitation Net	46 .06 .20	.26 .06 .20	9.0 .007 .044	.051 .007 .044	12 .067 .039 .028	2.5 .067 .039 .028	.014 .004 .010	
West Branch Fish Creek at Blossvale 100 Percent Tug Hill	204	499	48.8	Total Precipitation Net	52 .06 .28	.34 .06 .28	9.8 .007 .058	.065 .007 .058	11 .073 .044 .029	3.3 .073 .044 .029	.022 .004 .018	
East Branch Fish Creek at Taberg 100 Percent Tug Hill	188	555	55.1	Total Precipitation Net	42 .07 .26	.33 .07 .26	8.3 .007 .059	.066 .007 .059	9 .071 .050 .021	1.3 .071 .050 .021	.010 .004 .006	
Tug Hill terrain, average of above 3 net values						.25		.054			.028	.011
Wood Creek near New London 72 Percent Lake Plain; 28 Percent Tug Hill	90.5	140	43.4	Total Precipitation Net	130 .06 .48	.54 .06 .48	27 .007 .105	.112 .007 .105	20 .083 .040 .043	16 .083 .040 .043	.067 .004 .063	
Lake Plain terrain; yield = (measured yield -0.28 Tug Hill yield)/0.72						.57		.12		.050		.083

The low-flow discharges per square mile show greater variation among the three streams, from the 0.13 cfs per sq mi of West Branch Limestone Creek to the 0.23 cfs per sq mi of Chittenango Creek (fig. 5). These differences are related to the ground-water yields of the sand and gravel and the till terrains. The stream with lowest flow drains only the low yielding till terrain, while, as expected, the other streams have flows higher in proportion to the amount of sand and gravel terrain drained by them (fig. 7).

The dissolved solids and individual ion concentrations corresponding to mean annual and low flow specific conductances from figure 5 were found from specific conductance versus concentration graphs for each station. From these concentrations and their associated discharges, mean annual and low-flow loads per square mile were found. Examples of these values are shown in table 2. The precipitation loads contributing to the streams were calculated as described above and subtracted from the stream load to give net terrain yields, in tons per day per sq mi for dissolved solids and selected individual ions. Precipitation loads were not considered when making low-flow load calculations.

The period of data collection at these stations, except that for flow data at the station on Butternut Creek (2452), is less than a full year, so precise mathematical treatment of quantities derived from these data is not appropriate, and a simple graphical method was used. The net yields of various species at the three stations were plotted against the proportion of each contributing terrain, as shown in figures 6 and 7. From such graphs, the yields of the two types of terrain can be read directly. An advantage of the graphical solution is that the amount of departure of the data points from straight lines is an indication of the consistency and, presumably, of the reliability of the assumptions and techniques used to arrive at the plotted data. The mean annual load values (fig. 6) show good internal agreement, while the low-flow values (fig. 7) are more scattered. The former values, though, are based on more reliable discharge values, so the different scatter in the two sets is not surprising. Also, because the mean annual yields for each terrain are used below in constructing the materials balances for the lake system, their reliability is more important than that of the low-flow loads which are meant to indicate only generally the chemistry of the ground-water component of streamflow.

The net mean annual yields of the sand and gravel and the till terrains of the Appalachian Upland, determined in this manner and used below in the lake-balance calculations, are given in table 6. The low-flow yields are given in table 3.

As mentioned, the mean annual discharges per square mile of these Appalachian Upland terrains are not greatly different, so the loads in figure 6 and tables 2 and 6 are closely proportional to the concentrations of the dissolved species. From these loads, it is clear that the dissolved-solids content of streams draining the till terrain is considerably higher than that of streams draining the sand and gravel terrain. This is as expected from the geologic differences between the two terrains, for

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Figure 6.--Mean annual stream loads of selected chemical species
as functions of areas of contributing
Appalachian Upland terrain.

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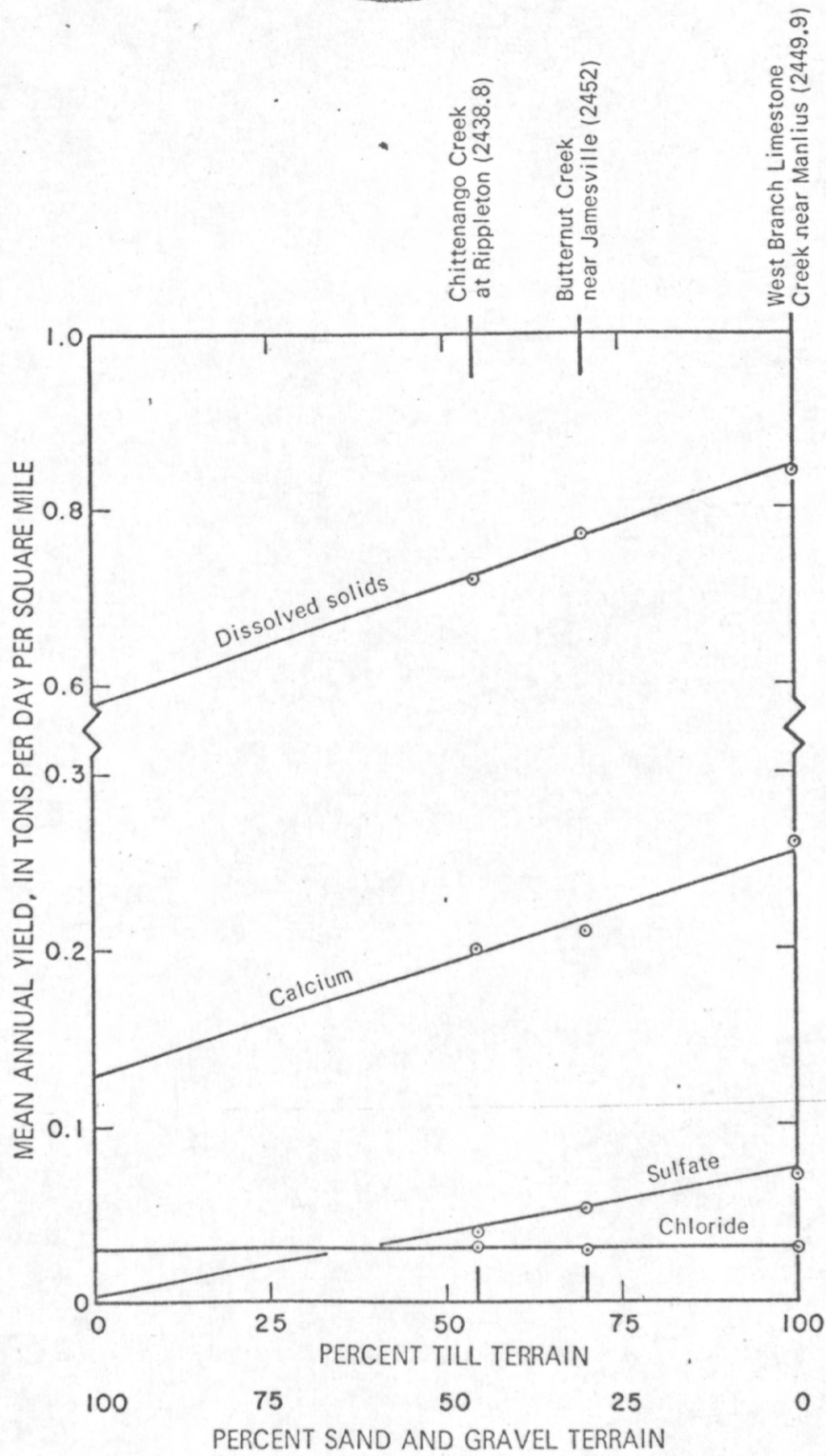


Fig. 6

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Figure 7.--Low-flow (approximate 7 day-2 year) loads of selected chemical species and discharge as functions of areas of contributing Appalachian Upland terrain.

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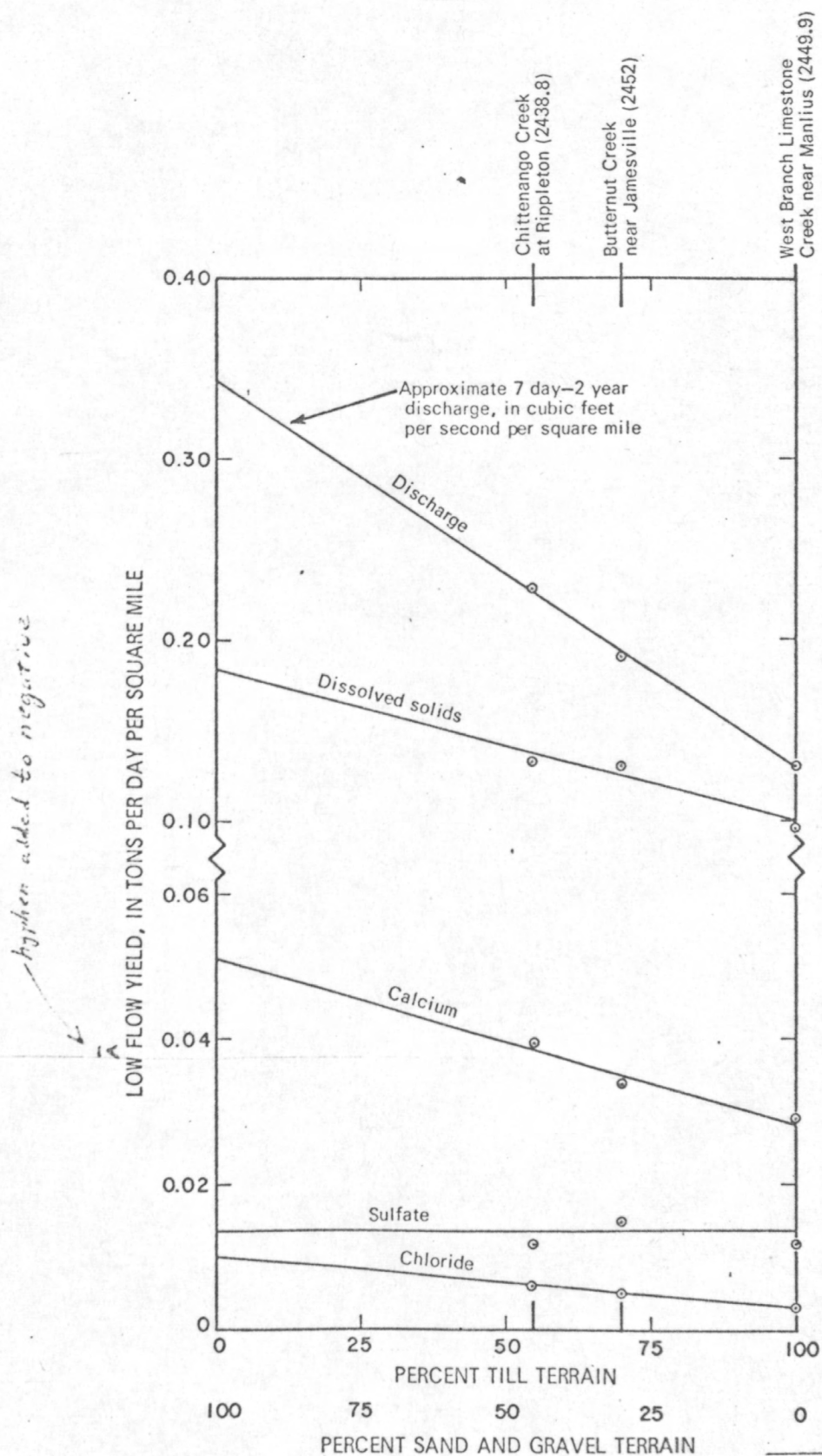


Fig. 7

Table 3.--Appalachian Upland and Salina Group
terrain yields at low streamflow

		Sand and gravel	Till	Salina Group
Dissolved solids	mg/l t/d/sq mi	215 0.20	275 0.10	1,210 0.59
Calcium (Ca)	mg/l t/d/sq mi	60 .06	80 .03	290 .14
Magnesium (Mg)	mg/l t/d/sq mi	14 .013	17 .006	54 .026
Strontium (Sr)	mg/l t/d/sq mi	.1 .0001	.2 .00007	8.7 .0042
Sodium (Na)	mg/l t/d/sq mi	4 .004	4 .0015	13 .006
Potassium (K)	mg/l t/d/sq mi	1 .0010	1 .0003	3 .001
Bicarbonate (HCO ₃)	mg/l t/d/sq mi	225 .21	260 .10	320 .16
Sulfate (SO ₄)	mg/l t/d/sq mi	11 .015	37 .013	730 .35
Chloride (Cl)	mg/l t/d/sq mi	16 .010	9 .003	20 .010

the water-laid sand and gravel deposits are likely to have retained fewer soluble minerals than the ice-laid till or the bedrock. Differences between individual ion loads (table 6) substantiate this conclusion. As mentioned, glacial materials in this region probably were not transported far from their source areas so that material from the nearby Salina Group was likely to have been incorporated into the deposits of these terrains. It is probable, therefore, that sulfate minerals characteristic of the Salina Group are present to some extent in the till terrain, but, because of their solubility are absent or sparse in the sand and gravel terrain. This accounts for the observed higher sulfate and calcium loads from the till terrain (fig. 6 and tables 2 and 6).

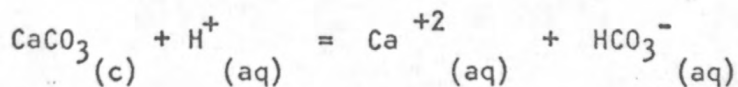
Under low-flow conditions (fig. 7) the relative magnitude of the net yields from the two terrain types is reversed. This is not due to more highly mineralized ground water issuing from the sand and gravel than from the till, but from the greater amount of water discharged by the former. The low-flow discharges of the three stations draining these terrains also

are shown in figure 7. From these graphs low flows per square mile characteristic of the individual terrains can be found as were their characteristic chemical loads. The values so found are 0.34 cfs per sq mi and 0.13 cfs per sq mi for the sand and gravel and the till terrains, respectively. The former value is a reasonable 7 day-2 year flow from high yielding sand and gravel deposits, but the latter is high for ice-laid deposits--true tills. The till terrain as the term is used here, though, is not exclusively till, but also includes some smaller areas of sand and gravel. These tend to raise the low flows to the value observed.

These discharges can be used with the loads of the various dissolved species to calculate back to the species' concentrations in the ground water that feeds the streams under these flow conditions. These concentrations in milligrams per liter, along with the low-flow loads in tons per day per square mile are shown in table 3.

The inferred ground-water compositions substantiate the statements made above about the mineral makeup of the two terrains. The two waters are not greatly different, showing that the deposits containing them are of similar mineralogy. Water from till terrain has a higher dissolved-solids content (275 mg/l) than that from the sand and gravel terrain (215 mg/l), the significant additional dissolved material being calcium, bicarbonate, and sulfate. The source of sulfate and part of the calcium is the mineral gypsum, derived from glacially transported Salina Group rock. Higher sulfate in till terrain water suggests the presence of more unreacted Salina material there than in the sand and gravel terrain. This agrees with the geological conclusions above.

The source of bicarbonate and calcium in waters of both terrains is the solution of limestone, primarily the mineral calcite (CaCO_3), which makes up much of the bedrock of the Appalachian Upland and, hence, of the glacial deposits derived from it. A simple way of describing this solution is by the reaction:



c - crystalline

aq - in aqueous solution

As this reaction shows, if a solution is saturated with calcite at a given temperature, the calcium and bicarbonate concentrations and pH ($= -\log \text{H}^+$) will be fixed relative to one another. If any two of the three quantities are known, it is possible to calculate the third (Garrels and Christ, 1965, chapt. 3). The pH calculated for low-flow sand and gravel terrain water at saturation is 8.0 at 0°C and 7.4 at 25°C; for low-flow till terrain water, the pH is 7.9 at 0°C and 7.3 at 25°C. If the actual stream pH values agree with those calculated, the streams are saturated with respect to calcite, while if the observed pH is higher than the calculated, the streams are oversaturated.

The pH of the terrain waters cannot be calculated from the stream data as were other constituents because it is not an additive property of water mixtures. The general range of pH, however, can be estimated from the stream data as being from 7.5 to 8.0 in both the mean annual and low-flow waters. These values suggest that ground waters from both terrains are saturated or slightly undersaturated at low temperatures, and probably supersaturated at higher temperatures. Under most conditions of stream-flow, the ground water will be diluted with less mineralized overland flow water, and the resulting mixture less than saturated. During summer low flows, though, the supersaturation is relieved by calcite precipitation. Such precipitation occurs in both sample bottles and along the stream. On the bed of Butternut Creek near the measuring and sampling site, for example, irregular masses of calcite are found containing leaves and other streambed debris to attest to their recent formation. The pH values also show that at all temperatures the till terrain waters are more highly saturated than those from the sand and gravel terrain. This is as it should be for not only is the till likely to contain more calcite, but its hydraulic properties are such that water in it will have longer contact time for solution to occur.

Salina Group Terrain

This terrain includes that part of the basin south of Oneida Lake where the Salina Group is not overlain by other bedrock units. This unit has been described above, and its boundaries are shown in plate 1.

The stations on Sconondoa Creek at Vernon Center and on Canaseraga Creek near North Chittenango represent streams draining only Salina Group and till terrains. Their locations and drainage areas are shown in plate 1 and the contributions of the two terrain types to their total areas in table 1. Samples and discharge data at each station were used to find the relationships between dissolved-solids content and discharge shown in figure 8. The mean annual and approximate 7 day-2 year flows are also shown. Mean annual and low-flow chemical loads per square mile in the streams and mean annual chemical loads from precipitation were determined. Examples of values calculated are given in table 2.

The period of chemical data collection at both stations and of stream discharge data on Sconondoa Creek was about 11 months. Instantaneous discharge measurements have been made on Canaseraga Creek for several years.

The ratios of the areas of the two types of terrain drainage at each station are similar, so a graphical technique, as used for the Appalachian Upland terrains, or simultaneous solution of mass-balance equations to determine the net yields of the two terrains would give results that could have large errors as a consequence of small errors in the area ratios. Therefore, it was assumed that the till terrain yields determined above are correct, and these yields were used in the station mass-balance equations to calculate the Salina Group yields reflected at each station. For example, the sulfate mass-balance equation for Sconondoa Creek at Vernon Center is $(0.075 \text{ tons per day per square mile}) \times 48 \text{ percent} + (X \text{ tons of SO}_4 \text{ per day per square mile}) \times 52 \text{ percent} = 0.88 \text{ tons of SO}_4 \text{ per day per square mile} \times 100 \text{ percent}$ where X is the net yield of sulfate from the Salina Group terrain.

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Figure 8.--Specific conductance versus discharge for streams draining the Salina Group and till terrains.

Examples of the results of these calculations for some constituents are shown in table 2. Except for chloride, there is good agreement between the values at the two stations. This difference in chloride values, which also occurs in the sodium values for the two streams, is discussed below. Because the other constituents agree, the characteristic mean annual yield of the Salina Group terrain was taken as the average of the two stream values. These were used in the lake balance calculations and are shown in table 6.

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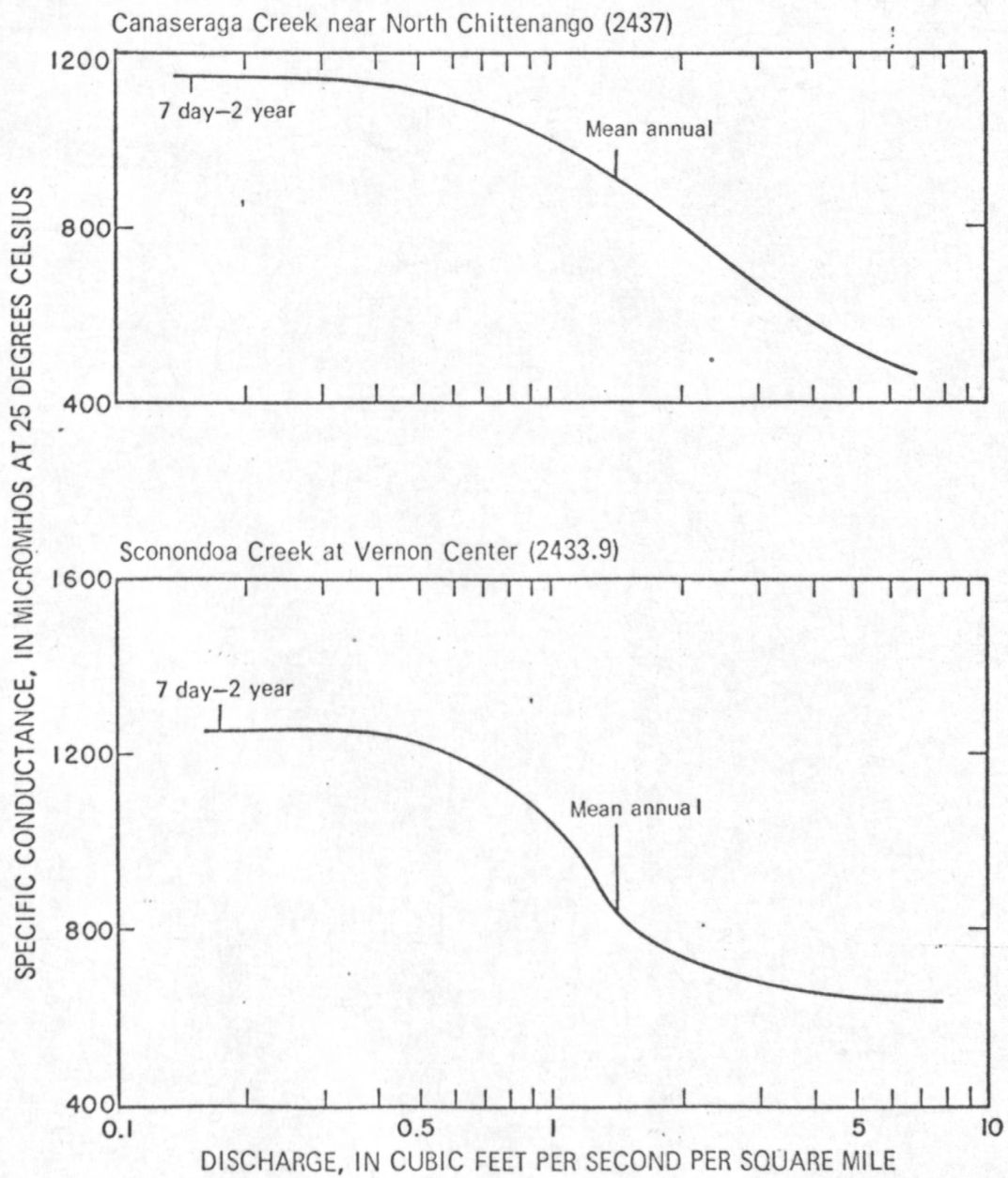


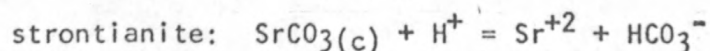
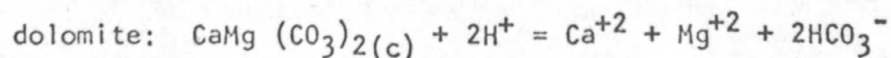
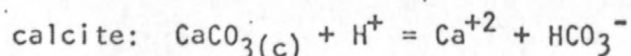
Fig. 8

It is clear from table 2 that the chemical yields per square mile of the Salina Group terrain are far higher than those of any other terrain. This is in keeping with the far higher amounts of soluble minerals here than in other parts of the basin. In particular, the high sulfate is a product of the solution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) present in the bedrock and the glacial material derived from the bedrock. Magnesium, and some of the calcium and bicarbonate, are derived from the solution of dolomite ($\text{Ca, Mg}(\text{CO}_3)_2$), another mineral far more common in the Salina Group than elsewhere in the basin. Calcium also is present from solution of gypsum, but probably also is due to solution of calcite, as is some of the bicarbonate. Strontium is found in significant concentrations only in waters from this terrain. Strontium-bearing minerals are not mentioned in geologic descriptions of the Salina Group (Leutze, 1964), but in dolomites and gypsiferous shales elsewhere, the minerals celestite (SrSO_4) and strontianite (SrCO_3) commonly are present. Solution of either or both of these minerals could produce the observed strontium.

The ground-water (low-flow) loads of the Salina Group terrain are shown in table 3. The two stream records from which they were calculated do not agree as well as do the mean annual values. Because the low-flow loads are not used in the lake budget determinations, but merely as general indicators of shallow ground-water chemistry, this disagreement is not disqualifying. The differences between mean annual and low-flow stream chemistry are of quantity rather than quality, so the conclusions about aquifer mineralogy drawn above are not changed.

Saturation calculations on the low-flow water are useful to check the conclusions about minerals responsible for the water chemistry.

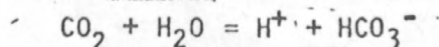
The carbonate minerals calcite, dolomite, and strontianite may be the ones influencing the calcium, magnesium, and strontium content of the ground water. To check this, the pH of water with the calculated composition was determined by the method given above for the reactions:



The pH of the Salina Group terrain low-flow water, were it saturated with calcite, would be 7.4 at 0°C and 6.8 at 25°C . The actual pH of the streams draining this terrain is much higher, about 8.0. A comparison of the actual pH with the calculated lower values shows that the water is greatly supersaturated with respect to calcite. Calculated pH values for dolomite and strontianite saturation are 6.5 and 5.0, respectively, indicating that the water is supersaturated with respect to these minerals as well. The degree of supersaturation is not as great as the calculated low pH values suggest, though, because the effects of complexing in the solution were not considered in the calculations. In solutions as concentrated as the Salina Group terrain low-flow water, large proportions of the ions in solution are not present as free ions, calcium ions for example, but are chemically bound in such complex dissolved species as

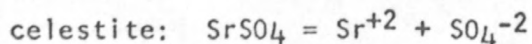
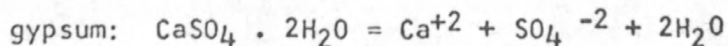
$\text{CaSO}_4^\circ(\text{aq})$ or $\text{CaHCO}_3^+(\text{aq})$. This reduces the effective concentration of the free ions in the solution, which is the concentration used in calculating the saturation pH values. This, in turn, produces higher calculated pH values, in better agreement with those of the streams. The subject of complexing in solutions is discussed at length by Garrels and Christ (1965, Chap. 4).

Although the stream pH values are about 8.0, it is likely that those of the ground water are lower than this, and in better agreement with those calculated. Surface waters, such as overland flow, shallow streams, and the upper levels of lakes, are exposed to a carbon dioxide partial pressure (P_{CO_2}) equivalent to that of the atmosphere, about $10^{-3.5}$ atmospheres. In the soil zone, because of plant respiration and decay, the P_{CO_2} is higher than that of the free atmosphere (Ingerson and Pearson, 1964). Ground water, having passed through the soil zone, may have its dissolved carbonate species distributed so as to reflect high soil P_{CO_2} values. The effect of this high P_{CO_2} is to make the water more acid by the reaction:



Because of complexing and higher ground water P_{CO_2} values, the degree of supersaturation of this Salina Group water is probably not as great as the calculated pH differences would suggest.

The other two possible controlling minerals are the sulfate minerals gypsum and celestite, which dissolve by the reactions:



Saturation calculations on these reactions show that this water is undersaturated with respect to gypsum and celestite.

This mineral saturation information lends confidence to the assertions made above about the mineralogical controls on the chemistry of the Salina Group terrain water. In summary, it appears that solution of the sulfate minerals, gypsum and celestite, to almost their saturation values set the calcium, strontium, and sulfate contents of the water. The calcium and strontium values so set are probably near or above their saturation levels with respect to the carbonate minerals, calcite, dolomite, and strontianite, while the water is in the ground. When the ground water enters the lower P_{CO_2} environment of a stream, its pH rises and it becomes supersaturated with these minerals. This supersaturation probably is relieved not by precipitation of the minerals but by dilution with overland runoff during periods of normal streamflow, or by less concentrated water from upstream terrains during periods of low flow.

Tug Hill Terrain

Most of the area north of Oneida Lake is of the Tug Hill terrain type (pl. 1). This terrain is characterized by higher precipitation than elsewhere in the basin, and is underlain by chemically unreactive sandstones and shales, and glacial material derived from them. The high rainfall and inert earth materials produce low dissolved-solids contents (0.26 t per d per sq mi) in the streams of this terrain.

The stations used to find the chemical yield of this terrain were those on East Branch Fish Creek at Taberg (2425), West Branch Fish Creek at Blossvale (2412), and Scriba Creek near Constantia (2458.4). The locations and areas drained by these stations are shown in plate 1 and their drainage areas are given in table 1. Water samples and discharge data were used to find the relationship between discharge and mineral content shown in figure 9.

The mean annual flows at each station are marked in figure 9. They are about 2.0 to 2.8 cfs per sq mi, much higher than corresponding values for the southern streams. As table 2 shows, though, the average rainfall on the areas drained at these stations is also higher than elsewhere. The low-flow values were not considered for this terrain because water from it contains so little dissolved material that no useful information about mineralogical controls would have been gained.

Mean annual chemical loads per square mile in the streams and resulting from precipitation were calculated as above. Examples of these loads are given in table 2.

These stations are all continuous recording gaging stations with from 2 to 45 years of record. They were sampled at least at monthly intervals for a year during this study, and additional data from Scriba and East Branch Fish Creeks were available from a previous study (Shampine, written commun., 1968). The three streams each drain essentially 100 percent Tug Hill terrain areas (table 1) and the agreement between their loads of various species is reasonably good (table 2). The yield of this terrain used in the lake balance calculations has therefore been taken to be the average of the three streams.

As tables 2 and 6 show the yields of this terrain are much smaller than those of any other in the basin, even though the streamflow is higher. This indicates that the bedrock and glacial material of the area are indeed as free of reactive minerals as the regional geology suggests.

Lake Plain Terrain

The area immediately adjacent to the lake is the Lake Plain terrain (pl.1). It is an area of low relief underlain by sediments deposited in and around the higher level lake ancestral to the present Oneida Lake. These include sand and clay lake sediments, shoreline dunes and bars, and areas of highly organic peaty sediments. Much of the region is poorly drained and swampy.

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Figure 9.--Specific conductance versus discharge of streams
draining the Tug Hill terrain.

(TOP)

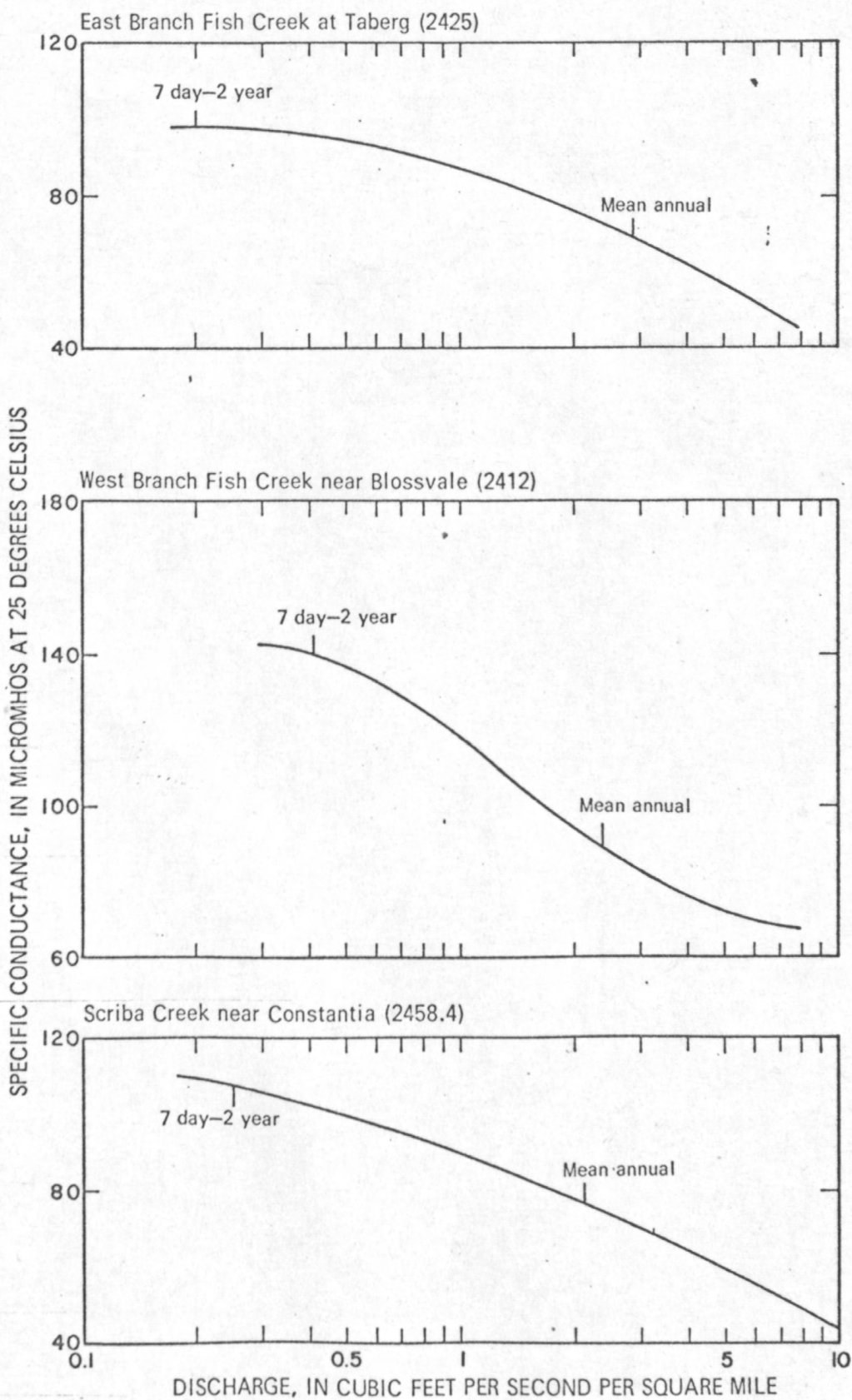


Fig. 9

The station on Wood Creek near New London (2428) was used to find the characteristic yield of this terrain. Its location and drainage basin are shown in plate 1, and the contributions of the terrains drained by it in table 1.

This site was sampled for chemical analysis and measured for discharge for about one year, and there are additional earlier discharge data available. From these data, the relationship between discharge and dissolved-solids content was drawn and is given in figure 10. The mean annual discharge shown in this figure is the same range as those of the streams draining the southern part of the basin.

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Figure 10.--Specific conductance versus discharge for stream draining the Tug Hill and Lake Plain terrains.

The dissolved solids and individual ion concentrations corresponding to mean annual specific conductance from figure 10 were found from a specific conductance versus concentration graph for the station. From these concentrations and their associated discharge, mean annual loads per square mile were found. Examples of these values are shown in table 2. The precipitation loads contributing to the streams were calculated and subtracted from the stream load to give net terrain yields, in tons per day per square mile, for dissolved solids and individual ions.

The loads characteristic of the Lake Plain terrain were calculated from the measured Wood Creek loads using the ratio of Tug Hill to Lake Plain terrain at the station and the Tug Hill loads calculated above. Examples of the calculations and loads are given in table 2, and the yields of all species used in the lake balance calculations are given in table 6.

TOP

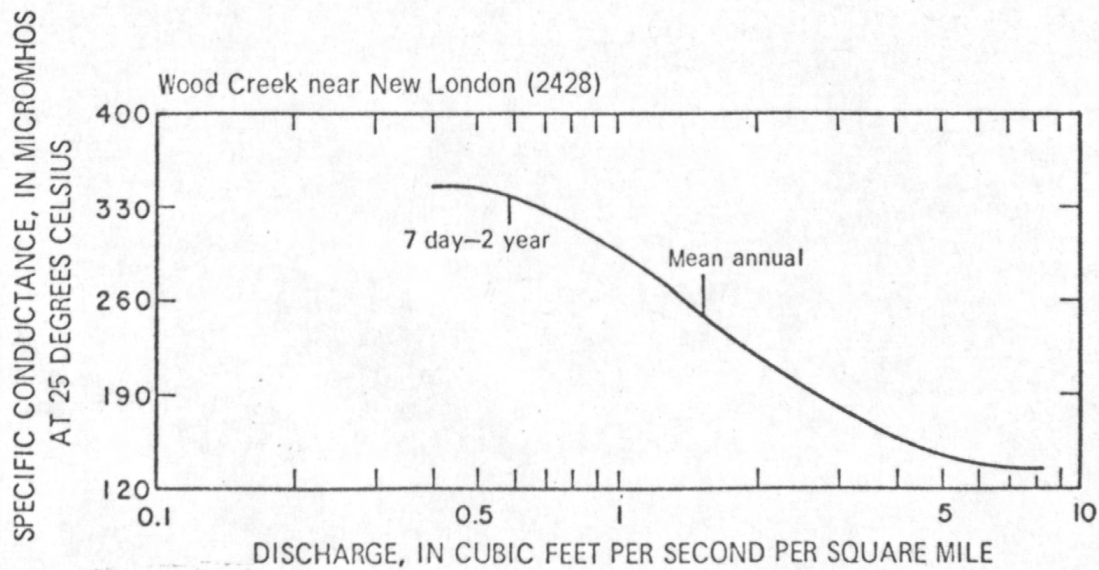


Fig. 10

957-15
100-10

As table 6 shows, the Lake Plain terrain yields are moderate, as expected from its geology. The only species that are present in anomalously high amounts are sodium and chloride. These species are discussed below. Because of the amount of organic matter in some of the sediments of this terrain, it is an important source of nutrients to the lake. These too are discussed below.

Loads of Large Streams Near Oneida Lake

In addition to the stations already used to determine terrain yields, three stations on large streams south of Oneida Lake also were sampled and the discharge measured. These stations, Chittenango Creek at Bridgeport (2455), Cowaselon Creek at Ontiontown (2438), and Oneida Creek at Oneida Valley (2435.3) are shown in plate 1 with their drainage basins. Their drainage areas and the contributions of the various terrains to them are given in table 1.

A number of discharge measurements have been made at these stations since 1964, so their flow characteristics are fairly well known. In addition, they have been sampled frequently for phosphate, pH, and alkalinity by Onondaga County Department of Public Works personnel (M. C. Lehne, written commun., 1967), so phosphate loads can be found for them. Their greatest utility, aside from the phosphate information, is that their measured loads can be used to check the loads calculated from the yields determined above.

From the discharge data and samples taken during this study, the relationships between discharge and chemical content shown in figure 11 were developed.

The total dissolved solids and individual ion concentrations corresponding to mean annual specific conductances from figure 11 were found from specific conductance concentration graphs for each station. From these concentrations and their associated discharges, mean annual loads were found and are shown in table 4. This table also shows the loads for each stream calculated from the yields and contributing areas of the individual terrains.

For Chittenango Creek at Bridgeport (2455), the agreement between measured and calculated loads and the derived concentrations is excellent. The only significant differences are for chloride and sodium for which the measured loads exceed the calculated by 9.8 and 4.9 tons per day, respectively. This difference is discussed below.

The calculated and measured loads of the other two streams, however, do not agree. In particular, the measured dissolved-solids loads of Cowaselon Creek (2438) are 10 to 20 percent higher than those calculated, whereas the reverse is true for Oneida Creek (2435.3). The drainage areas of the two streams are contiguous, and if the load values for them are added, that is, if the streams are considered to be two outlets from a single larger drainage area, these differences disappear.

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Figure 11.--Specific conductance versus discharge for
southern streams near Oneida Lake.

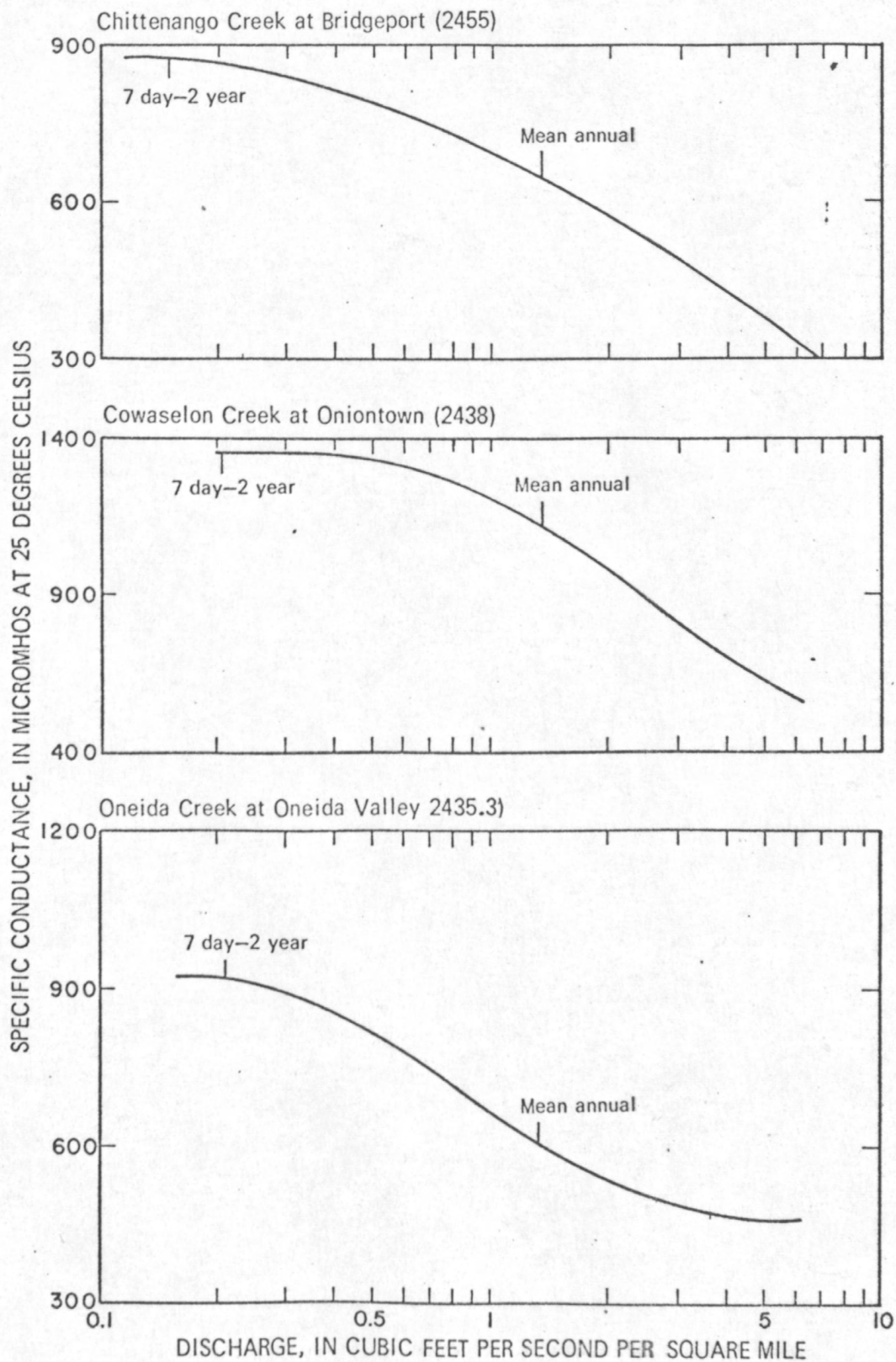


Fig. 11

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Table 4. -- Comparison of measured and calculated large stream mean annual loads of chemical constituents

Station	Terrain	Drainage area (sq mi)	Dissolved solids t/d	Calcium t/d	Magnesium t/d	Strontium t/d	Sodium t/d	Potassium t/d	Bicarbonate t/d	Sulfate t/d	Chloride t/d	Fluoride t/d	Silica t/d
Chittanooga Creek at Bridgeport	Sand and gravel	63	36	8	2.2	0.1	1.0	0.7	33	0	1.9	0.03	0.9
	Till	166	141	42	8.3	.2	2.5	1.0	146	12	5.0	.07	2.5
	Salina Group	81	261	60	13.0	1.9	2.1	.5	85	126	4.9	.09	1.2
	Lake Plain	4	2	0	.1	.0	.2	.0	2	0	.3	.00	.1
Precipitation: (39.1 inches)		--	18	2	.4	--	.8	.4	0	12	1.1	--	--
Sum		314	458	112	24.0	2.2	6.6	2.6	266	150	13.2	.19	4.7
			398 (mg/l)	98 (mg/l)	21 (mg/l)	1.9 (mg/l)	5 (mg/l)	2.3 (mg/l)	230 (mg/l)	130 (mg/l)	11 (mg/l)	.2 (mg/l)	4.1 (mg/l)
Measured: (Discharge 425 cfs)		314	448	110	27	1.6	11.5	2.0	242	150	23.0	.2	4.6
			390 (mg/l)	96 (mg/l)	18 (mg/l)	1.4 (mg/l)	10 (mg/l)	1.7 (mg/l)	210 (mg/l)	130 (mg/l)	20 (mg/l)	.2 (mg/l)	4.0 (mg/l)
Cowaselon Creek at Ontonowaga	Sand and gravel	3	2	0	.1	.0	.0	.0	2	0	.1	.00	.0
	Till	18	15	4	.9	.0	.3	.1	16	1	.5	.01	.3
	Salina Group	42	135	31	6.7	1.0	1.1	.3	44	65	2.5	.05	.6
	Lake Plain	6	3	1	.2	.0	.2	.0	2	0	.5	.00	.1
Precipitation: (39.8 inches)		--	4	0	.1	--	.2	.1	0	3	.2	--	--
Sum		69	159	36	8.0	1.0	1.8	.5	64	69	3.8	.06	1.0
Measured: (Discharge 96 cfs)		69.2	181	43	8.3	.9	3.9	.5	70	78	6.5	.05	1.2
			200 (mg/l)	165 (mg/l)	32 (mg/l)	3.5 (mg/l)	15 (mg/l)	2.0 (mg/l)	270 (mg/l)	300 (mg/l)	25 (mg/l)	.2 (mg/l)	4.7 (mg/l)
Oneida Creek at Oneida Valley	Sand and gravel	16	9	2	.6	.0	.2	.1	8	0	.5	.01	.2
	Till	44	37	11	2.2	.0	.7	.2	39	3	1.3	.02	.7
	Salina Group	47	151	35	7.5	1.1	1.2	.3	49	73	2.8	.05	.7
	Lake Plain	26	15	3	.7	.0	1.0	.1	10	1	2.2	.01	.4
Precipitation: (40.5 inches)		--	8	1	.1	--	.3	.1	0	5	.5	--	--
Sum		133	220	52	11.1	1.1	3.4	.8	106	82	7.3	.09	2.0
Measured: (Discharge 175 cfs)		133	184	42	9.9	.8	4.7	.9	102	59	7.3	.09	1.8
			390 (mg/l)	88 (mg/l)	21 (mg/l)	1.7 (mg/l)	10 (mg/l)	1.9 (mg/l)	215 (mg/l)	125 (mg/l)	16 (mg/l)	.2 (mg/l)	3.8 (mg/l)
Calculated sum: Cowaselon and Oneida Creeks		202	379	88	19.1	2.1	5.1	1.3	170	151	11.1	.15	3.0
			518 (mg/l)	120 (mg/l)	26 (mg/l)	2.9 (mg/l)	7.0 (mg/l)	1.9 (mg/l)	232 (mg/l)	205 (mg/l)	15 (mg/l)	.1 (mg/l)	4.1 (mg/l)
Measured Sum Cowaselon and Oneida Creeks		202	365	85	18.2	1.7	8.6	1.4	172	137	13.8	.14	3.0
			498 (mg/l)	116 (mg/l)	25 (mg/l)	2.3 (mg/l)	11.7 (mg/l)	1.9 (mg/l)	235 (mg/l)	187 (mg/l)	19 (mg/l)	.1 (mg/l)	4.1 (mg/l)

The agreement between the sums, but not individual loads, for these streams suggests that the position of the drainage divide between them in plate 1 may be in error. Such an error is likely in the region just west of Oneida, where even on detailed topographic maps, the location of the divide is not obvious. Only a small error would be needed to cause these differences. If, for instance, 9 square miles of Salina Group terrain, here assigned to Oneida Creek, were actually draining into Cowaselon Creek, the calculated total dissolved-solids loads would then be 191 and 188 tons per day -- values in good agreement with those measured. This is the probable explanation for the discrepancies, rather than failure of the contributing terrain concept or gross errors in the net yield values used.

The differences between the calculated and measured sodium and chloride loads both for Chittenango Creek at Bridgeport (2455) (table 4) and calculated for the Salina Group terrain from Canaseraga Creek near North Chittenango (2437) and Sconondoa Creek at Vernon Center (2433.9) (table 2) require further discussion. In the earlier description of the Salina Group, the presence of rock salt (NaCl) within this unit at depth was mentioned. Although this salt is not found at the surface, it approaches the surface more closely in the western part of the basin than in the eastern part (Kantrowitz, in press). Therefore, ground water can pick up sodium chloride at shallower depths to the west than to the east, and if the effective depth of ground-water circulation is the same throughout the southern part of the basin, the western streams should receive more sodium and chloride than those in the east. This agrees with the observations. Canaseraga Creek, to the west, has more chloride and sodium than has the otherwise quite similar Sconondoa Creek to the east. Likewise, Chittenango Creek contains more sodium and chloride than calculated using average values for the entire Salina Group terrain. The conclusion that solution of the rock salt is responsible for the addition is supported by the fact that the differences between the measured and calculated sodium and chloride loads, when expressed as chemical equivalents, are in a 1:1 ratio. Although of interest to the basin chemistry, this areal difference in sodium and chloride loads within the Salina Group terrain need not be taken into account in determining the lake input, for the latter is set by the average terrain yields shown in tables 2 and 6.

CHEMICAL BALANCES FOR ONEIDA LAKE

Basin Outflow

Differences between the quantities of chemical substances entering Oneida Lake from its drainage basin and the quantities leaving the lake through its outlet, the Oneida River, are the result of chemical or biological processes occurring within the lake itself. The loads leaving the lake were determined by sampling the Oneida River at Caughdenoy (pl. 1). Because the lake outflow is controlled by dams and its chemistry is fixed by that of the lake, the relationship between stream discharge and chemistry, as described for the streams of the basin, does not hold here. Therefore, to find the mean chemical composition and dissolved-solids loads of water leaving the basin, the following procedure was used.

The volume of Oneida Lake is large relative to the volume of water moving through it, so its chemistry, and hence, the chemistry of its outlet, changes slowly. The analyzed compositions of samples from the Oneida River, therefore, were plotted by date of collection. These include samples taken for this study and analyses made of composited daily samples taken during the period October 1957 to September 1958 (U.S. Geol. Survey, 1962a). Examples of these plots are given in figure 12. The agreement between the two sets of samples is reasonably good except for chloride and sodium (not plotted). From similar graphs for all the dissolved constituents, the monthly mean concentrations were read, taking the approximate average of all the data. For chloride and sodium only the monthly averages for the 1967-68 data were used. From these concentrations and from monthly mean stream-discharge data adjusted to the standard period 1931-60 (U.S. Geol. Survey, 1958, 1964) monthly mean chemical loads were computed. The average of these is the mean annual load. Examples of these monthly values are shown in table 5, and the mean annual loads used in developing the lake budget are shown in table 6.

The pattern of the regulation of the lake's outflow is apparent from the monthly average discharges in table 5. The lake is held at a constant high level during the late spring, summer, and early fall months to maintain proper depth in the New York State Barge Canal which passes through it. In the late fall, after the Barge Canal is closed, the lake level is lowered and kept low throughout the winter and early spring. The high discharge in December marks the fall lowering, while the spring discharges, although high because of snow runoff in the basin, are probably not as high as they would be naturally, because some of the runoff is held back to refill the lake.

The year-round constancy of the lake water's composition compared with those of its tributaries also is evident from table 5 and figure 12. Only during March and April, when the lake is receiving spring runoff and refilling, does its dissolved-solids content drop appreciably. Because the lake water is so constant, the loads leaving it directly reflect the variations in discharge (table 5).

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Figure 12.--Chemistry of Oneida Lake outlet by months.

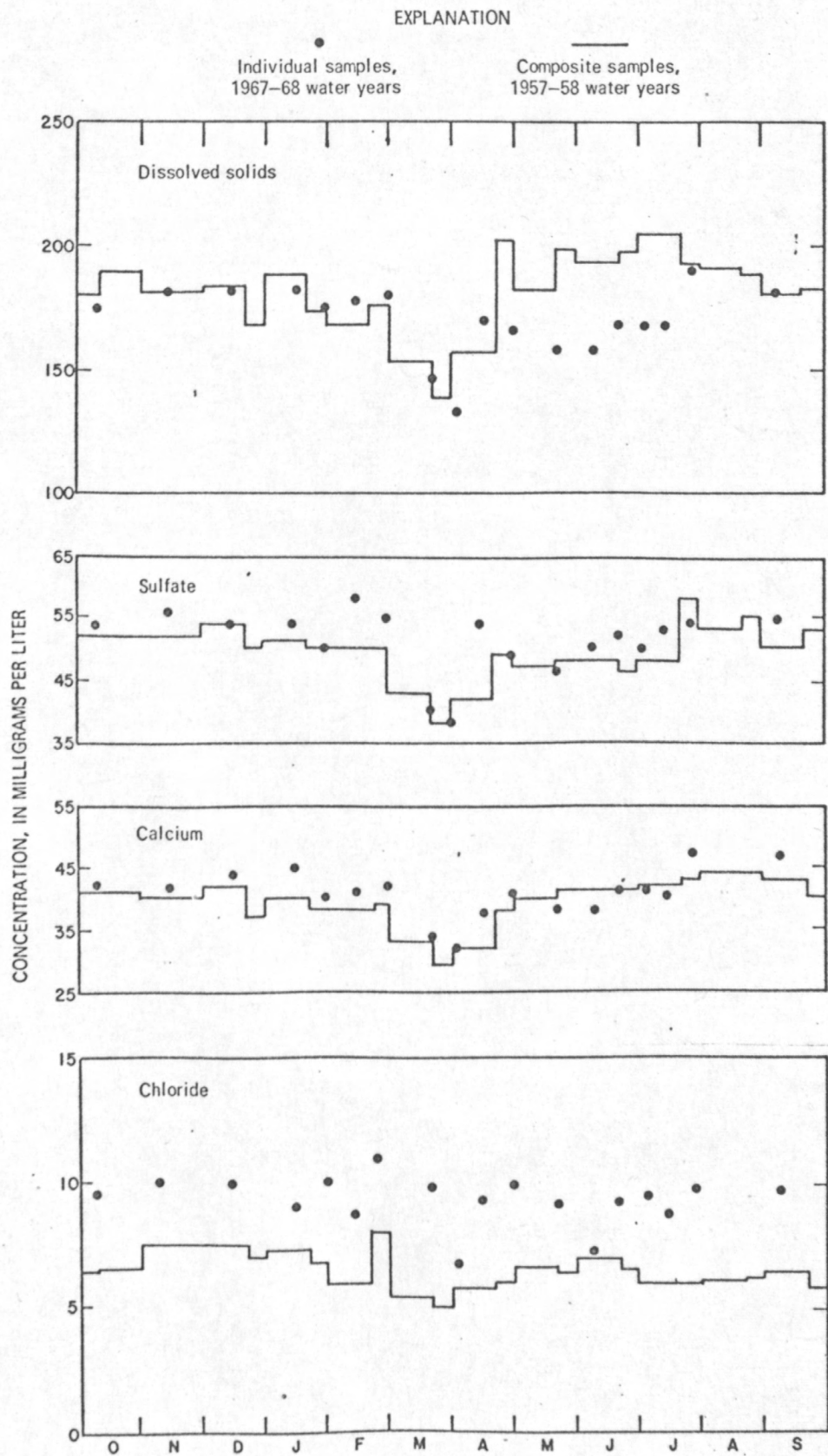


Fig. 12

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Table 5.--Examples of dissolved chemical loads leaving Oneida Lake at Caughdenoy

Month	Mean daily discharge		Dissolved solids				Total nitrogen as N						Total phosphate as PO ₄				
	cfs	Per-cent (total)	mg/l	t/d	Per-cent (total)	Calcium mg/l	t/d	Sulfate mg/l	t/d	Chloride mg/l	t/d	mg/l	t/d	Per-cent (total)	mg/l	t/d	Per-cent (total)
October	1,090	4	180	530	4	42	124	53	156	9.5	28	0.17	0.5	2	0.16	0.5	4
November	1,910	7	180	930	7	42	217	54	278	10.0	52	.32	1.6	6	.17	.9	8
December	3,690	13	180	1,790	14	43	428	53	528	10.0	100	.42	4.2	16	.28	2.8	24
January	3,260	11	180	1,580	12	43	378	53	466	9.5	84	.48	4.2	16	.26	2.3	20
February	2,940	10	175	1,390	10	41	325	53	421	10.0	79	.46	3.7	14	.14	1.1	10
March	3,820	13	160	1,650	12	37	382	48	495	8.5	88	.38	3.9	14	.18	1.9	16
April	5,300	19	155	2,220	17	36	515	47	673	8.0	114	.32	4.6	17	.07	1.0	9
May	2,920	10	175	1,380	10	40	315	50	394	9.5	75	.22	1.7	6	.04	.3	2
June	1,360	5	175	640	5	41	151	52	191	9.0	33	.24	.9	3	.04	.1	1
July	960	3	185	480	4	43	111	54	140	9.0	23	.30	.8	3	.08	.2	2
August	590	2	185	290	2	44	70	54	86	9.5	15	.22	.3	1	.10	.2	2
September	840	3	180	410	3	43	98	54	122	9.5	22	.18	.4	2	.13	.3	2
Yearly average	2,390	100	170	1,100	100	40	260	51	329	9.1	59	.34	2.2	100	.16	1.0	100

Balances of Major Chemical Species

The total input to the lake is the sum of the contributions of the terrains comprising the basin, the load from precipitation on the basin and lake surface, direct ground-water inflow to the lake, and whatever is contributed directly to the lake by cottages and settlements on the lake shore and by man's activities on the lake itself. The ground-water hydrology of the region is known well enough (Kantrowitz, in press), that the direct ground-water contribution to the lake's chemistry can be estimated. At maximum, this could not amount to more than 1 percent of the total load entering the lake and probably is closer to 0.1 percent (Kantrowitz, ~~oral~~ commun., 1967). Thus, the direct ground-water contribution to the lake can be neglected.

The contribution of man's activities around and on the lake to the chemical species discussed in this section is also so small as to be negligible when compared with the stream loads. For example, Mt. Pleasant and others (1962) report that the bicarbonate (alkalinity) load from this source is at most 1.7 tons per day, again less than 1 percent of the stream load (table 6). However, note that the contribution of nitrogen and phosphate species, discussed below, may not be negligible.

The input from the basin to Oneida Lake was calculated using the mean annual loads per square mile characteristic of the terrains in the basin, multiplied by the total area of the terrain. The sum of these terrain loads plus those in precipitation on the basin is the input to the lake. The terrain yields, total contributions, and sums, and the lake outflow loads for the major dissolved species are shown in table 6. Two other substances of interest, total nitrogen and phosphate, are discussed separately below.

As table 6 shows, there is good agreement between calculated input and output for some species, but an apparent loss of other species in the lake. Although the probable errors in these data cannot be found using rigorous statistical techniques, during manipulation of the data one gains the impression that the various values in table 6 should be within 10 percent of their true values, except for those species present in only small amounts. Thus the major species silica, chloride, bicarbonate, and sodium, with small percentage differences, pass through the lake without change, as do the minor species strontium, potassium, and fluoride, with small absolute differences.

The species that are affected by passage through the lake and whose fate, therefore, must be considered in detail are sulfate, and probably, magnesium and calcium. The differences in the last two are close to the estimated error and, therefore, may not be real, but there is no difficulty in discovering a mechanism by which they could be lost. In the earlier discussion of the contributing terrains, calcite saturation calculations are described by which saturation pH values can be found. If these calculations are made on the lake outflow, as representing the average lake chemistry, the pH values at which the lake would be calcite saturated are found to be 8.6 at 0°C and 8.0 at 25°C. The actual pH, both at the outlet and in the lake, ranges from about 7.5 to over 8.4 during the summer. Thus

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Table 6.--Terrain yields, lake outflow loads, and basin chemical balance

Terrain type	Drainage area		Dissolved solids			Calcium		Magnesium		Strontium		Sodium		Potassium		Bicarbonate		Sulfate		Chloride		Fluoride		Silica	
	Sq mi	Per- cent	t/d	t/d/mi ²	Percent (total)	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²	t/d	t/d/mi ²
Sand and gravel	82	6	48	0.58	4	11	.13	3	0.035	0.1	0.001	1.2	0.015	1.0	0.012	43	0.52	0	0.005	2	0.030	0.0	0.0004	1.1	0.014
Till	236	17	201	.85	16	59	.25	12	.050	.2	.001	3.5	.015	1.4	.006	208	.88	18	.075	7	.030	.1	.0004	3.5	.015
Salina Group	192	14	618	3.22	50	142	.74	31	.16	4.6	.024	5.0	.026	1.2	.006	202	1.05	298	1.55	12	.060	.2	.0011	2.9	.015
Lake Plain	297	21	166	.56	13	36	.12	8	.028	.2	.0008	11.9	.040	1.2	.004	113	.38	15	.050	25	.083	.1	.0003	4.5	.015
Tug Hill	509	36	132	.26	10	29	.057	10	.019	.1	.0002	3.0	.006	.5	.001	107	.21	13	.025	6	.012	.3	.0007	11.2	.022
Lake Surface	80	6	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PRECIPITATION (43 inches)	--	--	84	.060	7	10	.0070	2	.0012	--	--	3.5	.0025	1.7	.0012	0	.00	57	.041	5	.0035	--	--	--	--
SUM	1,396	100	1,249	.90	100	287	--	66	--	5.2	--	28	--	7.0	--	673	--	401	--	57	--	.7	--	23	--
LAKE OUTFLOW	1,396	--	1,100	--	--	260	--	58	--	3.7	--	27	--	6.5	--	660	--	330	--	59	--	.6	--	24	--
Percent change in lake	--	--	-12	--	--	-9	--	-12	--	-30	--	-41	--	-7	--	-2	--	-18	--	+3	--	-14	--	+3	--

the lake is sometimes oversaturated with calcite, which could precipitate, lowering the calcium and coprecipitated magnesium content of the lake water. If there is indeed calcium and magnesium loss in the lake, it is probably due to chemical precipitation.

The single species that is unquestionably retained in the lake is sulfate, which is lost at the rate of about 70 tons per day (table 6). This loss cannot be accounted for as inorganic precipitation of such sulfate minerals as gypsum, for not only is there no equivalent calcium loss, but the lake is greatly undersaturated with respect to this mineral.

The lake sediments are the only sink into which this amount of sulfate could disappear. Although no work on the lake sediments was done as part of this study, a great deal is known about intrasediment reactions, and the probable fate of the sulfate can be described (Berner, 1964; Siever, Beck, and Berner, 1965). In most sediments, there is a certain amount of organic debris, even when, as in Oneida Lake, measurable dissolved oxygen concentrations commonly occur even in the deepest lake water (Greeson and Meyers, 1969) and hence oxidizing conditions exist at the sediment-water interface. As the sediments are buried, the organic material decays and reducing conditions set in. Under these conditions, the sulfate in the interstitial sediment water is reduced to such species as elemental sulfur, hydrogen sulfide and, primarily, sulfide ion. This last species usually reacts with iron to form various iron sulfide minerals that remain in the sediments.

The best way to check this hypothesis would be to examine the mineralogy and chemistry of lake-bottom sediments and the chemistry of their interstitial water. The appearance of sulfides in the sediments, or, better, a decrease in the sulfate content of the interstitial waters would be direct evidence that sulfate reduction occurs. In any future work on Oneida Lake the sediment and its interstitial water should be examined, the former by X-ray diffraction and optical mineralographic techniques, the latter by the methods used by Siever, Beck, and Berner (1965).

Nitrogen and Phosphate

Loads of nitrogen species and phosphate in transit through the basin were found by a different method than used for the major dissolved solids. Neither substance is present in large amounts in any streams in the basin, the total nitrogen species (nitrate, nitrite, ammonium, and organic nitrogen) as N being generally 2 mg/l or less, and total phosphate 1 mg/l or less. Also, their concentrations are responsive to seasonal plant-growth factors rather than to stream-water sources as are the major constituents. Therefore, the mean annual loads of these substances were found by plotting instantaneous loads against date of collection for the various sampling sites. From these graphs, the average monthly or seasonal loads were estimated and the yearly average computed.

Examples of these plots in figure 13 show the amount of scatter typical of the data. In spite of this scatter, the calculated mean annual load values are consistent from stream to stream and are in good agreement with generally accepted values in waters elsewhere (table 7).

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Strip in figure 13 here
(a film negative is furnished)

Figure 13.--Stream phosphate and nitrogen loads by months.

The total nitrogen and phosphate loads entering Oneida Lake also were computed differently from the loads of the other species. Instead of finding loads representative of the terrain types, the loads of the large streams measured close to their mouths were summed. In this sum, the contributions of the ungaged parts of Tug Hill and Lake Plain terrains were estimated. The averages of the yields per square mile of the stations on Fish and Scriba Creeks were used for the ungaged Tug Hill region. The

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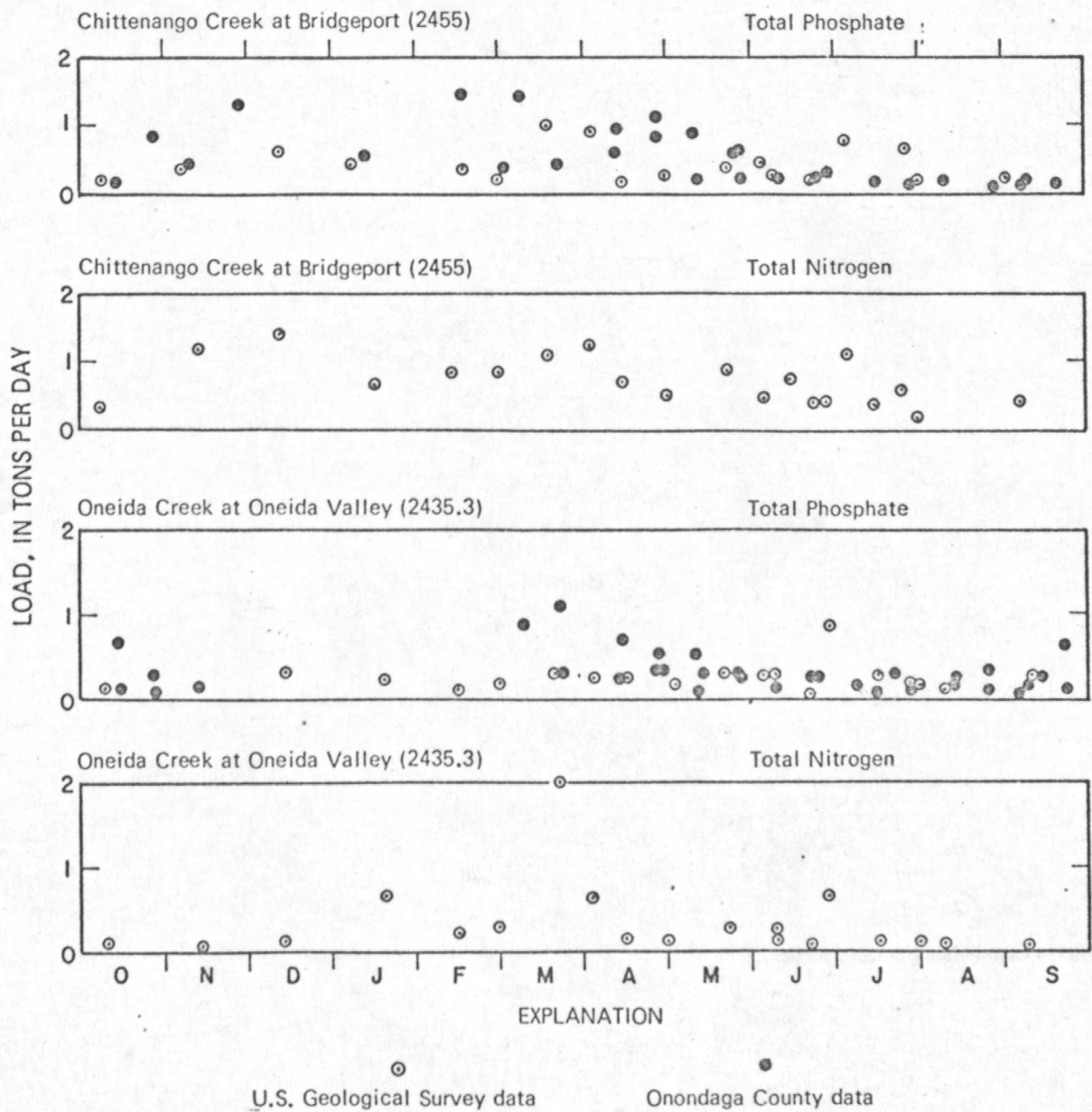


Fig. 13

values for the Lake Plain were calculated from the measured Wood Creek loads, using the average Tug Hill loads and the ratio of the terrains contributing to the site as was done for the other constituents (table 2). As with the loads of the major species, the probable errors in the nitrogen and phosphate loads cannot be determined rigorously, but manipulating the raw data suggests that error in the mean annual values should not be much greater than about 15 percent.

Before discussing the data for the Oneida Lake basin, it is useful to review briefly the load data and conclusions of other studies. Table 7 gives average nitrogen and phosphate loads in waters of various types. The values are taken from a recent summary of nitrogen and phosphorous chemistry (American Water Works Association, 1967) which should be consulted for further details. As this table shows, the nitrogen load per square mile from nonagricultural land (forest and unfertilized grassland) is slightly less than that of atmospheric precipitation. This effect, which is well documented (Fisher, 1968), is probably due to plant and soil uptake of nitrogenous species or to the direct return to the atmosphere of gaseous nitrogen compounds. Phosphate loads in precipitation are less well known, but probably are not a major source of phosphate in natural streams. Rather, phosphate in nonagricultural areas comes from solution of various phosphate minerals that are present in small amounts in most rocks.

Agricultural land yields more nitrogen and phosphate than equivalent noncultivated land. This is due mostly to the incomplete retention on the land of fertilizers applied to it. Finally, the per capita loads in domestic sewage also are shown. The nitrogen in this material results primarily from metabolic wastes, while the phosphate is primarily from detergents. The values given refer to loads commonly found in sewage treatment plant effluent.

Table 7.--Typical nitrogen and phosphate loads
in various waters

Source	Total Nitrogen as N	Total Phosphate as PO ₄	Unit
Domestic sewage <u>1/</u>	0.011-.017x10 ⁻³	0.006-.017x10 ⁻³	t/capita/d
Agricultural land <u>1/</u>	.006	.001	t/d/sq mi
Nonagricultural land <u>1/</u>	.002	.0008-.002	t/d/sq mi
Atmospheric precipitation	.0025	.0001-.001	t/d/sq mi

1/ Data from American Water Works Association, 1967.

The Oneida Lake basin, although primarily rural, is not undeveloped. In the Tug Hill and Appalachian Upland regions, dairy farming is common as is truck farming in the Lake Plain terrain south of Oneida Lake. Further, there are communities in the basin with an aggregate sewered population of at least 34,700 (Federal Water Pollution Control Administration, 1968, table 7) in areas not draining directly to the lake, but at least 90 percent of this population is in the southern part of the basin.

The nitrogen and phosphate loads within and leaving the Oneida Lake basin are given in table 8. The nitrogen loads reflect the population and land use differences within the basin. Streams draining the relatively undeveloped northern and western parts of the basin have average nitrogen loads of about 0.0016 t per d per sq mi, while those draining the southern part average about 0.0020 t per d per sq mi. If the average nitrogen load is 0.012×10^{-3} t per capita per d (table 7) from the southern region's sewered population of about 27,000 (Federal Water Pollution Control Administration), the resultant stream load would be 0.0004 t per d per sq mi. Thus, the average stream nitrogen load, exclusive of sewered domestic wastes, is about 0.0016 t per d per sq mi in the southern streams, the same as the loads of the northern streams in which sewered domestic wastes are insignificant.

This basinwide nitrogen yield, exclusive of sewered wastes, of 0.0016 t per d per sq mi includes the contributions of all natural sources, of runoff from cultivated land, and of nonsewered domestic wastes, yet it is about the same as that of nonagricultural land alone elsewhere (0.002 t per day per sq mi). Thus, it appears that the contributions of nonsewered domestic wastes and of agriculture to streams in the basin is small.

In determining the total nitrogen input to the lake, the contribution of precipitation on the lake's surface and of human activities on the lake's surface and its shores must be included with the stream loads. The precipitation contribution can be found, but that of human activities can only be roughly estimated. The population, all unsewered, of communities on the lake shore is about 5,000 (Federal Water Pollution Control Administration) and the isolated cottage population and population equivalent of boat traffic may be as much as twice this figure. The maximum contribution from these 15,000 people will be that of domestic sewage, 0.012×10^{-3} t per capita per d, or a total of 0.2 t per d.

The total nitrogen input to the lake, including the estimated lake shore contribution is 2.8 t per d, about 20 percent higher than the 2.2 t per d load leaving the lake in the Oneida River (table 8). The difference of 0.6 t per d must not be taken too seriously, however, because the errors associated with the stream and river data may be as much as 15 percent (0.3 t per d) and the estimate of the lake shore contribution may be several hundred percent in error. Oneida Lake is highly productive; therefore, large quantities of nitrogen will be used by the biota of the lake (Greeson and Meyers, 1969). Some of this nitrogen could be removed from the lake water by incorporation into organic sediments. Greeson and Meyers (1969) show that the lake and lake sediment surface are generally under oxidizing

Table 8.--Loads of nitrogen and phosphate in streams of the Oneida Lake basin

Number	Station	Drainage area (sq mi)	Total Nitrogen as N		Total Phosphate	
			(t/d/sq mi)	(t/d)	(t/d/sq mi)	(t/d)
2455	Chittenango Creek at Bridgeport	314	0.0019	0.60	0.0020	0.63
2437	Canaseraga Creek near Chittenango	20	.0030	.06	.0015	.03
2438	Cowaselon Creek at Ontiontown	69	.0017	.12	.0017	.12
2435.3	Oneida Creek at Oneida Valley	133	.0018	.24	.0027	.36
2428	Wood Creek near New London	90	.0021	.19	.0027	.24
2425	East Branch Fish Creek at Taberg	188	.0018	.34	.0007	.13
2412	West Branch Fish Creek at Blossvale	204	.0014	.29	.0006	.12
2458.4	Scriba Creek near Constantia	38	.0013	.05	.0003	.01
	Ungaged Tug Hill <u>Terrain</u>	79	.0016	.13	.0006	.05
	Ungaged Lake Plain Terrain	181	.0022	.41	.0034	.61
	Lake Surface (precipitation)	80	.0025	.20		
	Boats and cottages (estimated)			.20		.2
	SUM: Inflow to lake	1,396	.002	2.8	.002	2.5
	Concentration at mean annual flow:		.43 (mg/l)		.39 (mg/l)	
	Outflow at Caughdenoy	1,396	.0016	2.2	.0007	1.0
	Concentration at mean annual flow:		.34 (mg/l)		.15 (mg/l)	

conditions, so it is likely that biologically bound nitrogen is oxidized and recycled into the lake waters rather than being accumulated to any great extent in the bottom sediments. Thus, errors in the lake input and output values are likely to be such that the difference between the two values is magnified.

There is considerably more variation in the stream phosphate loads than in their nitrogen loads (table 8), but the variation is explicable in terms of the basin's geology, physiography, and culture. The lowest phosphate loads are present in the streams draining the northern part of the basin, the Tug Hill region, where the average yield is about 0.0006 t per d per sq mi. This is as expected, for the rocks underlying this region contain very few soluble minerals, such as phosphates, and their natural phosphate contribution to the streams therefore should be low. Likewise, because the region is not densely settled, there should be little phosphate of human origin.

The streams draining the lake plain and southern part of the basin have considerably higher phosphate loads than the northern streams (table 8). These higher loads are due not only to the greater amount of sewered domestic wastes here, as were the region's higher nitrogen loads, but also are due to differences between the geology of the southern and northern parts of the basin. Wood Creek has one of the highest yields (0.0027 t per d per sq mi) measured, yet no sewered communities are within its drainage basin (Federal Water Pollution Control Administration, 1968, table 7; plate 1). Wood Creek drains only Tug Hill and Lake Plain terrains. The Tug Hill terrain phosphate yield is known from the loads of the streams draining it, so the load contributed to Wood Creek by the Lake Plain terrain can be calculated as described above. The Lake Plain terrain phosphate load so calculated is about 0.034 t per d per sq mi. As mentioned above, this terrain includes areas of peaty sediments from the ancestral Oneida Lake bottom which are likely to yield large quantities of phosphate as they oxidize. The presence of this material is the probable cause of the high phosphate loads in streams draining this terrain.

The average load of the southern part of the basin, excluding the Lake Plain terrain, is about 0.0021 t per d per sq mi, as calculated from the loads of streams draining this part of the basin. Some of this phosphate is certainly from domestic sewage, as was some of the nitrogen from the southern part of the basin. A phosphate load of 0.012×10^{-3} t per capita per day (table 7) from a sewered population of 27,000 (Federal Water Pollution Control Administration) is equivalent to a stream load of about 0.0006 t per d per sq mi. Thus, the net phosphate load from the southern part of the basin, excluding sewered wastes and the Lake Plain terrain, is about 0.0015 t per d per sq mi. Because phosphate minerals commonly occur in limestones and shales, and this part of the basin is underlain by such rock types, natural phosphate loads higher than those from the Tug Hill region are to be expected.

In addition to the stream loads, the contributions of boats and cottages directly to the lake must be included in the lake input value. This contribution, from 15,000 people at 0.012×10^{-3} t per capita per d, is 0.2 t per d, a maximum value. As the lake balance (table 8) shows, there is significantly less phosphate leaving Oneida Lake than entering it. The loss in the lake could take place by accumulation in the bottom sediments of phosphate either in organic debris or as inorganic precipitates. The fact that the lake is an oxidizing environment argues against the first possibility, as does the lack of significant nitrogen loss in the lake. Precipitation of inorganic phosphates in the sediments, therefore, probably accounts for the phosphate loss.

There are a number of naturally occurring phosphate minerals that could precipitate in Oneida Lake. The least soluble of these, and so most likely to be precipitated, are the apatites, which have compositions ranging from $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ to $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Calculations of the theoretical solubilities of these minerals show that the lake is oversaturated by several powers of ten, but it is known that a number of processes occur in natural waters that have the effect of increasing the apparent solubility of the minerals. These processes, primarily surface complexing, have been described by Chaverri and Black (1966), who also give information on observed versus theoretical solubilities. Using their observed solubilities reduces the apparent oversaturation to only one or two powers of 10. Although some of the analyzed phosphate may be tied up by organic species and not available for inorganic reactions, there is little doubt that the lake is oversaturated with apatite and that it or similar phosphate minerals are precipitating out in the lake bottom sediments.

Further work on Oneida Lake should include studies of the lake bottom sediments to see if, among other things, phosphate minerals can be discovered in them. To recognize such minerals by X-ray diffraction or optical techniques would be difficult, and, therefore, not finding them would not necessarily mean they do not occur.

The sources of nitrogen and phosphate to Oneida Lake, based on this study, are given in table 9. Phosphate loads listed by the Federal Water Pollution Control Administration (1968) are included for comparison, as are loads calculated from values typical of nonagricultural land elsewhere as summarized by the American Water Works Association (1967) and shown in table 7. The division of sources is as described above; that is, the loads from sewered populations have been separated from rural runoff, and the basin separated into regions, each with characteristic rural runoff loads. These regional loads include natural loads from precipitation, and dissolved from rock and sediment, and the loads from such human activities as farming and nonsewered waste disposal.

The nitrogen loads from rural areas of the Oneida Lake basin are lower than loads typical of nonagricultural areas elsewhere, although the loads from this basin include agricultural and rural domestic sources. This implies that nonnatural contributions to the rural areas of the basin are small when compared with the natural loads. The significant human-controlled sources of nitrogen to the lake are sewered wastes, and boats and cottages,

Table 9.--Summary of sources of nitrogen and phosphate input to Oneida Lake

	Nitrogen as N			Phosphate as PO ₄			
	This study (tons/day)	(percent)	Typical 1/ (tons/day)	This study (tons/day)	(percent)	Typical 1/ (tons/day)	FWPCA 2/ (tons/day)
Region north of lake	0.82	29	1.0	0.31	12	} 1.2 }	1.50
Lake Plain terrain	.48	17	.6	.94	38		
Region south of lake (except Lake Plain)	.82	29	1.0	.73	29	.8	.47
Sewered wastes (region south of lake)	.32	11	.3	.32	13	.3	.68
Direct to lake							
Precipitation on lake surface	.20	7	.2	--	--	--	--
Boats and cottages	<.2	<7	<.2	<.2	<8	<.2	.17
Total Input	2.84	100	3.3	2.51	100	2.5	2.82

1/ Calculated from typical loads elsewhere (table 7).

2/ From Federal Water Pollution Control Administration, 1968, figure 10.

which may contribute as much as 23 percent of the total input. The yearly average concentration of nitrogen in the lake water, using total input and average flow data, is about 0.43 mg/l. If the human controlled 23 percent were eliminated, the average concentration would drop to about 0.33 mg/l, still well above that needed to support algae (Greeson and Meyers, 1969).

The phosphate load from the region north of the lake and the Lake Plain terrain agree with those typical of nonagricultural lands elsewhere and, within the estimated error, with those reported by the Federal Water Pollution Control Administration (1968, fig. 10). Likewise, the sums of the three sets of values--the total input to the lake--also are in essential agreement. The total loads from the region south of the lake, excluding the Lake Plain (that is, the sum of the sewered wastes and rural runoff) are about 1.1 t per d, based on the three sets of values. However, the distribution of this total into its rural and sewered waste portions reported by the Federal Water Pollution Control Administration is significantly different from the results of this study and from that typical of work elsewhere. If the Federal Water Pollution Control Administration distribution is correct, it implies a land-runoff load of only about 0.001 t per d per sq mi and a sewered-waste load per capita of 0.018×10^{-3} t per capita per d. This load per capita is higher than has been reported elsewhere (table 7), and the rural runoff load is lower than is typical of other regions of similar geology (above, American Water Works Association, 1967). Thus, the sewered waste contribution from this region to the basin is probably closer to the 18 percent found by this study than the 24 percent reported by the Federal Water Pollution Control Administration.

The yearly average concentration of phosphate entering the lake from all sources is about 0.39 mg/l. If the contributions from human-controlled sewered wastes and boats and cottages as found in this study were eliminated, the phosphate concentration would drop to about 0.29 mg/l. If the waste load eliminated were as high as that reported by the Federal Water Pollution Control Administration, the concentration would be about 0.32 mg/l. These contributions are still far above those needed to support algae growth (Greeson and Meyers, 1969).

SUMMARY AND CONCLUSIONS

The chemistry of waters of the Oneida Lake basin is shown in table 6 and can be summarized as follows: (1) the quantities of the major species dissolved in the streams of the basin and in Oneida Lake are set by the relative areas of hydrochemically homogeneous terrains drained by them, and by the chemistry of atmospheric precipitation on the basin; (2) the hydrochemical terrains, and their characteristics, are:

- (a) Tug Hill terrain, to the north of the lake. Because of its size and high rainfall, it contributes more than half the total streamflow to the lake, but it is underlain mainly by chemically unreactive bedrock and glacial deposits, so its mean annual dissolved-solids contribution is only about 0.26 t per d per sq mi, primarily calcium and bicarbonate.
- (b) Lake Plain terrain, immediately adjacent to the lake and extensive to the west and south. It is underlain by relatively inert sediments from the bottom of ancestral Oneida Lake, and contributes dissolved solids to the lake at the moderate rate of 0.56 t per d per sq mi, again primarily calcium and bicarbonate.
- (c) Salina Group terrain, in the southern part of the physiographic Lake Plain and at the foot of the Appalachian Upland. It is underlain by gypsiferous shales and carbonate rocks and contributes dissolved solids to streams at the extreme rate of 3.2 t per d per sq mi, of which calcium, bicarbonate, and sulfate are the major species.
- (d) Appalachian Upland terrains, including the sand and gravel and the till terrains, in the extreme southern part of the basin. The former is underlain by water-laid deposits from which highly soluble minerals are absent. Its contribution of dissolved solids to streams is therefore relatively low, 0.58 t per d per sq mi, and is mostly calcium and bicarbonate. The till terrain is made up of ice-laid deposits (till) and of exposed bedrock, containing more soluble mineral matter and so contributing dissolved solids to the streams at the higher rate of 0.85 t per d per sq mi, again primarily calcium and bicarbonate.

(3) The contribution of dissolved solids by atmospheric precipitation to the basin is about 0.06 t per d per sq mi, primarily sulfate. (4) Lake input is balanced by lake output for all major species except sulfate and possibly calcium and magnesium. The latter two species could be lost into the lake sediments by inorganic precipitation—the former probably is reduced to sulfide within the sediments.

The nitrogen and phosphate chemistry of the Oneida Lake basin can be summarized as follows:

- (1) Nitrogen loads of streams draining rural areas throughout the basin are similar and are about 0.0016 t per d per sq mi. This value is lower than that typical of streams draining undeveloped forest and grassland and lower than the contribution of atmospheric precipitation to the basin. Thus, what human activities do occur in the rural reaches of the basin cannot be contributing enough nitrogen to the stream to be a significant addition to the natural loads.
- (2) In the southern part of the basin, sewered wastes increase the total stream nitrogen load to an average of 0.002 t per d per sq mi. These sewered wastes and man's activities on and around the lake contribute as much as 23 percent of the total nitrogen input to the lake.
- (3) Nitrogen loads leaving Oneida Lake are approximately the same as, or only slightly smaller than, those entering the lake. Nitrogen accumulation within the lake and its sediments, therefore, is insignificant.
- (4) Phosphate loads of streams draining rural areas are consistent with the geology of those areas and range from 0.0006 t per d per sq mi in the Tug Hill region to 0.0034 t per d per sq mi in the peaty Lake Plain.
- (5) Sewered wastes contribute phosphate to the streams in the southern part of the basin sufficient to raise their loads from a rural level of 0.0015 t per d per sq mi to 0.0021 t per d per sq mi. These wastes and man's activities on and around the lake may contribute between 25 and 30 percent of the total phosphate input to the lake.
- (6) Considerably more phosphate enters Oneida Lake than leaves it, suggesting phosphate accumulation within the lake and its sediments. This probably takes place by the inorganic precipitation of phosphate minerals, such as apatite, with respect to which the lake water is highly oversaturated.

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