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The chemical composition of lakes in the north-central United States¹

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Abstract

Lake waters of the north-central U.S.A. are classified into five groups, based on increasing specific conductivity and changes in ionic composition from east to west, from Wisconsin through Minnesota to North and South Dakota. The most dilute group of waters has specific conductivities $<29 \mu\text{mhos} \cdot \text{cm}^{-1}$ at 25°C ; the most concentrated group has specific conductances that range from 7,000 to 73,000 μmhos . As conductivity increases all major ions increase, but there is a shift in cation dominance from Ca^{2+} to Mg^{2+} to Na^+ , and in anion dominance from HCO_3^- to SO_4^{2-} . This shift partly reflects a westward increase in climatic aridity, and partly a westward sequence of glacial drifts from noncalcareous to calcareous and thence to calcareous with abundant sulfur-bearing minerals. Levels of pH, K, Cl, F, B, and SiO_2 also show a distinct westward increase. Concentrations of NO_3^- and Mn increase from east to west, but the trend is less distinct. Concentrations of Fe vary widely without any trend over the range of conductivity. Color, mostly from dissolved organic matter, is controlled chiefly by lake depth, except for lakes with extensive peatlands in their drainage basins.

Investigators have treated environmental controls of surface-water chemistry in different ways. Some have chosen areal treatments, at geographical scales from global (Clarke 1924; Conway 1942; Gibbs 1970) to regional (Clarke 1924; Gorham 1955; Reeder et al. 1972) to local (Mackereth 1957; Gorham 1957*a,b*; Garrels and MacKenzie 1967). Others have examined environmental factors separately (Gorham 1961), discussed individual elements one by one (Hem 1970), or provided a strongly theoretical treatment (Stumm and Morgan 1981). We examine here the chemistry of lake waters in the north-central states of Wisconsin, Minnesota, North Dakota, and South Dakota, classify them into chemical categories, and relate their concentration and composition to environmental factors.

We thank G. Glass for water samples from the Boundary Waters Canoe Area of Minnesota and the U.S. Geological Survey for analyzing most of the samples on which we report. R. H. Hofstetter assisted in analyzing Minnesota waters. G. H. Harrach assisted in generating computer plots. We are grateful for criticisms by R. E. Hecky, W. M. Lewis, D. A. Livingstone, J. Turk, T. C. Winter, and G. E. Groschen.

Description of the region

The study area is centered on 96°W , 45°N . It is about 1,000 km wide from Lake Michigan in the east to the Missouri River in the west by about 700 km from the Canadian border on the north to the Wisconsin border on the south. Elevations range from about 240 m asl in eastern Wisconsin to about 550 m in north-central Wisconsin, northeastern Minnesota, and western South Dakota (Winter 1977; Petri and Larson 1971).

Geology—Lakes in this region are mostly in glacial till and outwash or gla-

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cial lake sediments, although bedrock basins in crystalline igneous and metamorphic rocks are common in northeastern Minnesota and occasionally elsewhere.

The bedrocks exposed in northeastern Minnesota and northern Wisconsin are igneous Precambrian granite, gabbro, diabase, and basalt together with metamorphosed igneous and sedimentary rocks (Winter 1974; Poff 1970). Consolidated Paleozoic sandstone, dolomite, and limestone underlie much of the southern half of Wisconsin and southeastern Minnesota. Poorly consolidated Cretaceous shale is found in western Minnesota, especially in the southern part. Poorly consolidated Cretaceous and Tertiary shale, siltstone, and sandstone predominate in the Dakotas (Sloan 1972).

Glacial drift overlies most of the bedrock and includes ground- and end-moraines, outwash deposits, and glacial lake sediments. Glaciers brought calcareous, silty and clayey gray and buff drift into the region from the northwest, and non-calcareous sandy red drift from the northeast. The thickness of drift in areas of large end-moraines in northwestern Wisconsin, southwestern Minnesota, and the Dakotas may be as much as 150 m (Winter 1974).

Groundwaters—Dilute calcium-magnesium bicarbonate groundwaters with $<250 \text{ mg} \cdot \text{liter}^{-1}$ of total dissolved solids are common in much of Wisconsin and Minnesota. Groundwaters in western Minnesota and the Dakotas are of four main types, calcium-magnesium sulfate, sodium bicarbonate, sodium chloride, and sodium sulfate (Winter 1974, 1977), and may have as much as $3,000 \text{ mg} \cdot \text{liter}^{-1}$ total dissolved solids in the Dakotas. The saline calcium-magnesium sulfate groundwaters are derived from glacial drift rich in gypsum and iron sulfide from Cretaceous sedimentary rocks. The sodium bicarbonate groundwaters are usually deep and are products of ion exchange. Sodium chloride groundwaters are common in Cretaceous and Paleozoic bedrock aquifers in the Dakotas. Sodium sulfate groundwaters are believed to be caused by the mixing of sulfate-rich

waters from glacial drift with waters rich in sodium chloride in underlying Cretaceous sedimentary rocks or by cation exchange in clayey deposits. All of these saline groundwaters may move for long distances before surfacing to influence lake water chemistry (Winter 1974, 1977).

Climate—Northeastern Minnesota and much of Wisconsin have a positive balance of precipitation over evaporation, whereas western Minnesota and the Dakotas have a distinct negative balance (Bright 1968; Petri and Larson 1971). The range is from a 10-cm excess in northeastern Minnesota to a 50-cm deficit near the Missouri River (Winter 1977). Mean annual temperature ranges from about 3°C in the north to 8°C in the south (Bright 1968).

Vegetation—Northern Wisconsin and northeastern Minnesota are covered by mixed coniferous-deciduous forest. Deciduous forest predominates in southern Wisconsin and as a band westward of the mixed forest, narrow in the northwest and broadening toward southeastern Minnesota. The Dakotas east of the Missouri River are covered by cultivated prairies that extend narrowly into northwestern Minnesota and broadly across the southernmost part of the state. A generalized vegetation map is presented by Wright (1969).

Sources of data

In selecting data on ionic composition we have excluded waters in which analyses for total cations and total anions were not within 5% of one another, except for very dilute samples (specific conductivity $< 29 \mu\text{mhos} \cdot \text{cm}^{-1}$ at 25°C) for which differences up to 10% were accepted (only 18 of more than 50 dilute lake waters analyzed met this criterion). Most of our data for Wisconsin come from Poff (1967); the rest (13 very dilute waters) were collected by us and analyzed by the U.S. Geological Survey. Many Minnesota samples were collected and analyzed by us; many more analyses are from Maderak (1963), some northern waters were collected by G. Glass and were analyzed by the USGS, and a few analyses are from Bright (1968)

and Tarapchak (1973). The data for the Dakotas are from Petri and Larson (1971), Mitten et al. (1968), and the U.S. Geological Survey (1964–1969). Most samples were analyzed by standard methods of the USGS (Rainwater and Thatcher 1960; Brown et al. 1970). Our own Minnesota samples were analyzed by the techniques of Mackereth (1963). Because sample storage, analytical methods, etc. undoubtedly varied considerably within and among sample sets, pH and nitrate values may only be approximate.

Most data for Wisconsin and Minnesota lakes represent single samples collected at various times throughout the ice-free season, whereas many data from the Dakotas are averages of several samples collected during ice-free seasons over >1 year. Considerable seasonal and annual variations of chemical composition in the western lakes are to be expected due to severe and lengthy droughts (Mitten et al. 1968).

We have compiled measurements of specific conductivity—closely correlated with salinity (*see Fig. 4*)—for 1,133 samples, and analyses of major ions— Ca^{2+} , Mg^{2+} , Na^+ , K^+ , alkalinity, SO_4^{2-} , Cl^- —for 219 samples. Many of the latter have been analyzed for pH, NO_3^- , F, B, Fe, Mn, SiO_2 , and color. Individual data are given by Gorham et al. (1982).

Chemical classification of surface lake waters

The data for specific conductivity allow construction of an empirical chemical classification of lake waters in the north-central United States, which we shall consider in relation to ionic composition and surficial geology. Figure 1 shows frequency distributions of specific conductivity (at logarithmic intervals) for 1,133 lakes. The distributions reveal four modal groups that overlap but can be separated at approximately 28, 141, and 7,079 μmhos . Figure 1 also suggests another boundary at 501 μmhos , marked by the slight overlap of Wisconsin and Dakota lakes and by a “shoulder” on the middle Minnesota group; the reality of this boundary is confirmed by changes in ion-

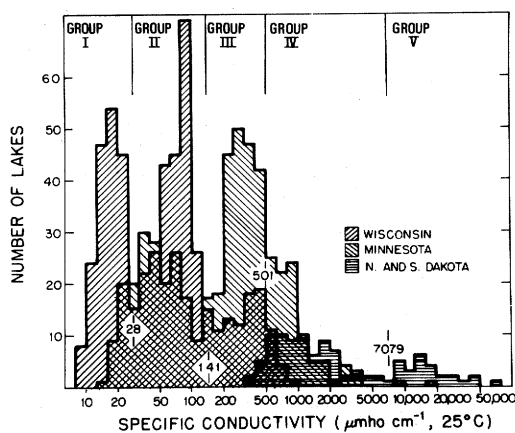


Fig. 1. Frequency distributions of specific conductivity at logarithmic intervals for 1,133 lakes in Wisconsin, Minnesota, and the Dakotas.

ic proportions (*see Fig. 9*). Five groups of lakes can thus be distinguished and are numbered I to V in order of increasing conductivity.

The main controls of lake water salinity in the north-central United States, as will be discussed below, are the east-west gradients in geology and climate. Because the conductivity boundaries were determined empirically, they should not be taken as generally valid and may not apply in other geologically and climatically different regions.

Group I lakes are small, with more than half <20 ha and 80% <100 ha (Juday and Birge 1941; Glass and Loucks 1980). They occur on coarse, noncalcareous sand and gravel in northern Wisconsin and Minnesota (Fig. 2) or in watersheds on exposed igneous rock. Many have small drainage areas and no outlets, and were called seepage lakes by Juday and Birge (1933, 1941) and perched lakes by Hawkinson and Verry (1975) to distinguish them from drainage lakes with outlets. Many others are headwater lakes. The waters of group I lakes are derived largely from rapid surface runoff over terrain resistant to weathering, and the most dilute among them are close to atmospheric precipitation in total ionic concentration. Table 1 provides representative analyses of both precipitation and extremely dilute lake waters.

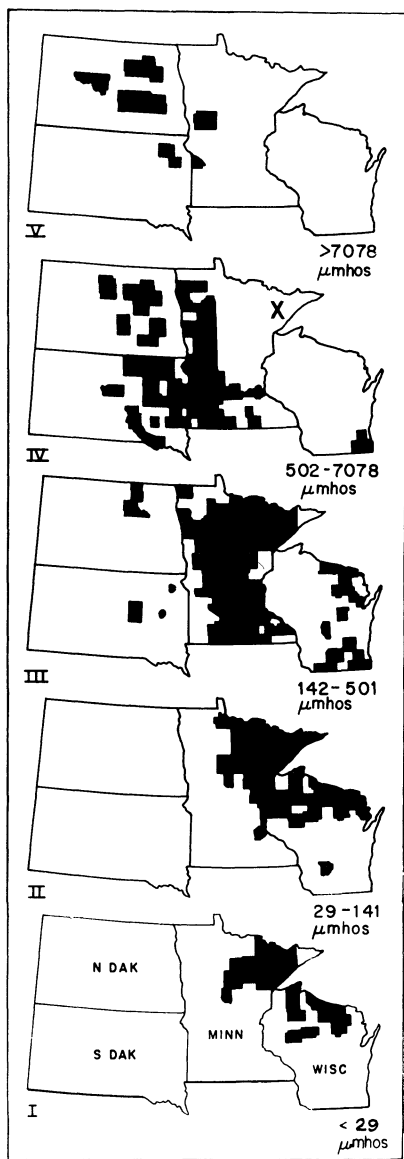


Fig. 2. Geographical distribution (by county) of lakes in the north-central United States, grouped (I-V) in order of increasing conductivity. In group IV, X marks Lake Manganika, partly filled by mine spoil.

Group II lakes also occupy drainage basins in noncalcareous substrates in northern Wisconsin and Minnesota (Fig. 2), but many are larger and have active outlets. Their drainage basins generally have more weathered soil, and therefore

Table 1. Volume-weighted mean ionic composition of atmospheric precipitation in northeastern Minnesota, compared with the composition of the four most dilute group I lakes.

	Rain, Hovland, Minn.*	Mean, four dilute lakes, Wis.
	(meq·liter ⁻¹)	
H ⁺	0.0215†	0.0050‡
Ca ²⁺	0.0200	0.0663
Mg ²⁺	0.0108	0.0267
Na ⁺	0.0061	0.0033
K ⁺	0.0033	0.0179
NH ₄ ⁺	0.0371	not done
Total cations	0.0988	0.1192
Alkalinity	nil	0.0250
SO ₄ ²⁻	0.0394	0.0745
Cl ⁻	0.0262	0.0162
NO ₃ ⁻	0.0207	0.0
Total anions	0.0863	0.1157

* Munger (1982). Chloride values are too high.

† pH 4.67.

‡ pH 5.30.

the lakes have higher concentrations of dissolved material.

Group III lakes are on calcareous substrates, predominantly in Minnesota (Fig. 2). All but the most dilute of these deposit marl in their profundal sediments (Dean and Gorham 1976; Megard 1968). The exceptions are a few lakes on the Anoka sand plain north of Minneapolis, where weathering profiles are deep and the surface horizons of the very sandy soils are now depleted of calcium carbonate.

Group IV lakes occur chiefly in western Minnesota and the Dakotas (Fig. 2). The few group IV lakes in southeastern Wisconsin probably represent the more saline tail of the distribution of group III lakes overlapping the distribution of group IV lakes, just as the few group III lakes in the Dakotas probably represent an overlapping dilute tail of the distribution of group IV lakes (Fig. 1). Lakes in group IV occur on calcareous substrates rich in the sulfur-bearing minerals gypsum and pyrite derived from Cretaceous shale (Winter 1974, 1977). As a result, sulfate increases sharply with increasing conductivity and dominates

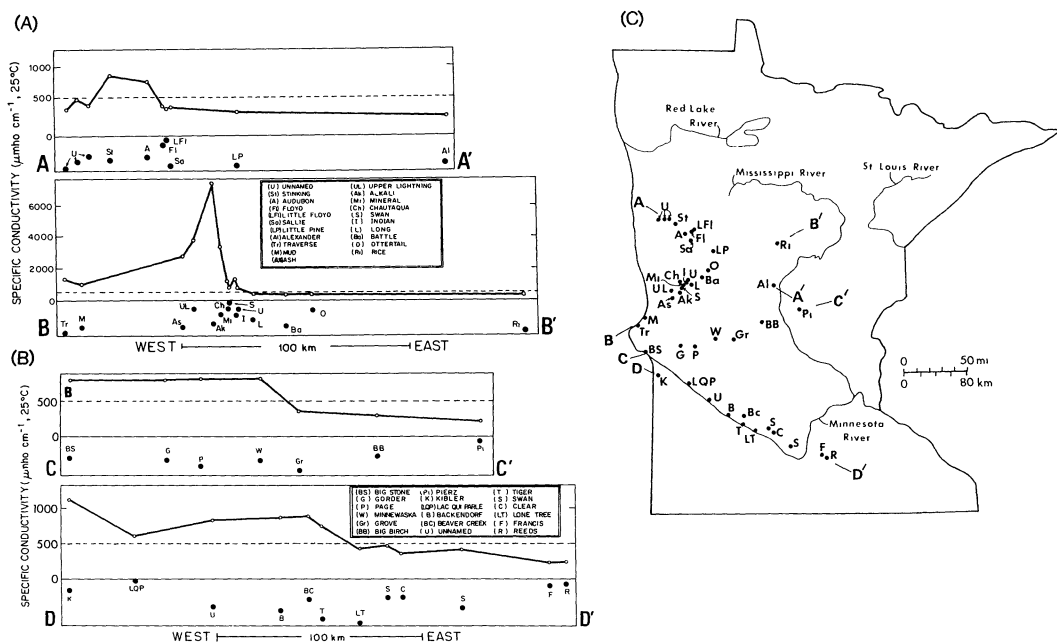


Fig. 3. Belt transects of specific conductivity in lake waters of western Minnesota. A. Two northern transects. B. Two southern transects. C. Map locations of the four transects. Dashed lines in panels A and B separate lakes of group III (below) and group IV (above). ●—Geographic positions of the lakes sampled within the belt transects.

strongly over bicarbonate and carbonate in the most concentrated waters.

The westward increase in climatic aridity is the main cause of the increase in conductivity between group III and group IV lakes and contributes to the shift of ionic dominance toward sulfate as marl is precipitated from increasingly concentrated bicarbonate waters during photosynthesis in summer (Megard 1968). However, the boundary must also mark a change in geological substrate or a different source or degree of groundwater input (cf. Winter 1974). Figure 3 shows four belt transects of specific conductivity in lakes from east to west in western Minnesota. If the boundary between group III and group IV lakes were the result solely of a gradual climatic shift in the balance between precipitation and evaporation, a continuous westward increase of specific conductivity would be expected. In fact there is a sharp discontinuity (also observed on four other tran-

sects) which strongly suggests that a geological boundary has been crossed or that a different source or amount of groundwater has been tapped.

Group V lakes are in the Dakotas and western Minnesota (Fig. 2). Their waters are highly saline, dominated by sodium and sulfate ions, and concentrations fluctuate greatly. The most saline lakes precipitate hydrated sodium sulfate (mirabilite) during winter (Mitten et al. 1968; cf. Rawson and Moore 1944). Sloan (1972) noted that the most saline potholes in North Dakota occur at low elevation in glacial outwash deposits.

Concentrations and ionic proportions

The waters in groups I–V exhibit striking differences both in ion concentrations and in cation and anion proportions.

Total cations and anions—Total cations range from 0.098 meq·liter⁻¹ in northern Wisconsin to 1,570 in North Dakota; total anions range from 0.095 to 1,580

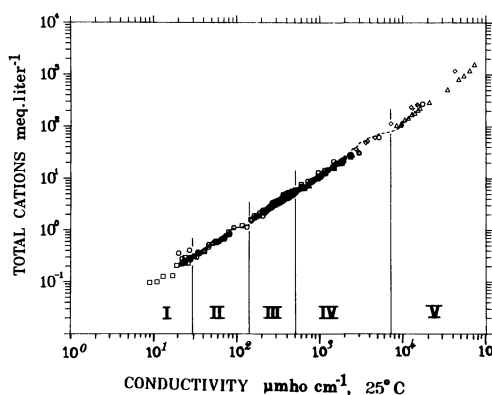


Fig. 4. \log_{10} relationship between total cations and specific conductivity. Vertical lines mark separation of lake groups. For this and following figures, dashed line is a 21-point, weighted moving average of the raw data. Minnesota—○; Wisconsin—□; North Dakota—△; South Dakota—◇.

$\text{meq} \cdot \text{liter}^{-1}$. The \log_{10} relationship between total cations and conductivity is approximately linear (Fig. 4). The ratio of conductivity to ion concentration decreases from about 100:1 in the most dilute waters to an average of 54:1 in the six most concentrated waters, owing to lesser dissociation of dissolved salts.

Trends in ionic concentration—Most dissolved substances increase in concentration with increasing specific conductivity, but the patterns of increase vary (Figs. 5–8).

Values of pH (Fig. 5) increase with increasing conductivity. The minimum is pH 5 in a dilute group I lake, the maximum pH 9.6 in a saline group V lake.

Calcium concentration (Fig. 6A) is closely related to conductivity in groups I–III, rising from about $0.05 \text{ meq} \cdot \text{liter}^{-1}$ to about 2.2 at the group III/IV boundary. Above about $2 \text{ meq} \cdot \text{liter}^{-1}$ the waters are supersaturated with calcium and carbonate ions so that marl precipitates (cf. Dean and Gorham 1976). The relationship of magnesium concentration (Fig. 6B) to conductivity is similar to that of calcium concentration but only a few saline waters show marked depletion of magnesium owing to precipitation as carbonate.

Sodium (Fig. 6C) is very low in the most

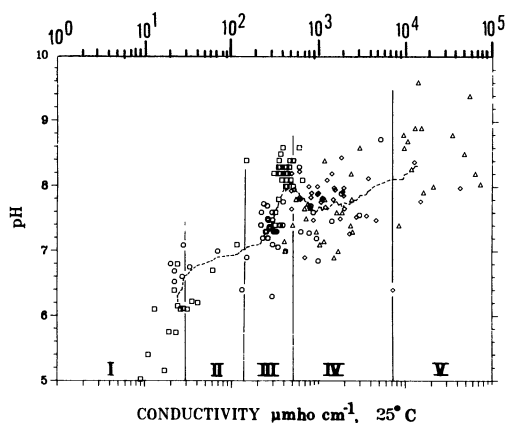


Fig. 5. As Fig. 4, but between pH and \log_{10} specific conductivity.

dilute Wisconsin lakes of group I and increases sharply with increasing conductivity to the group II boundary. Sodium increases very little within group II because the salinity increase there is dominated by the leaching of calcium and magnesium from noncalcareous soils. Thereafter sodium increases steadily, reflecting the accumulation of sodium salts in arid soils. Potassium distribution (Fig. 6D) resembles that of sodium except that group I waters have potassium concentrations similar to those of group II.

Alkalinity distribution (Fig. 7A) resembles that of calcium, increasing to the group III/IV boundary after which marl is precipitated. Sulfate distribution (Fig. 7B) resembles that of potassium, showing little change in concentration in lakes on noncalcareous substrates. In lakes with calcareous drainage basins, sulfate increases steadily with increasing conductivity. Chloride (Fig. 7C) is at or near the limit of detection in many waters from groups I to III and increases sharply as the lakes of group IV are reached. Nitrate concentration (Fig. 7D) shows little relationship to conductivity. There is a tendency for low concentrations in lakes on noncalcareous, forested substrates, an increase in group III where agriculture is important, and little change beyond.

Fluoride data (Fig. 8A) are few in

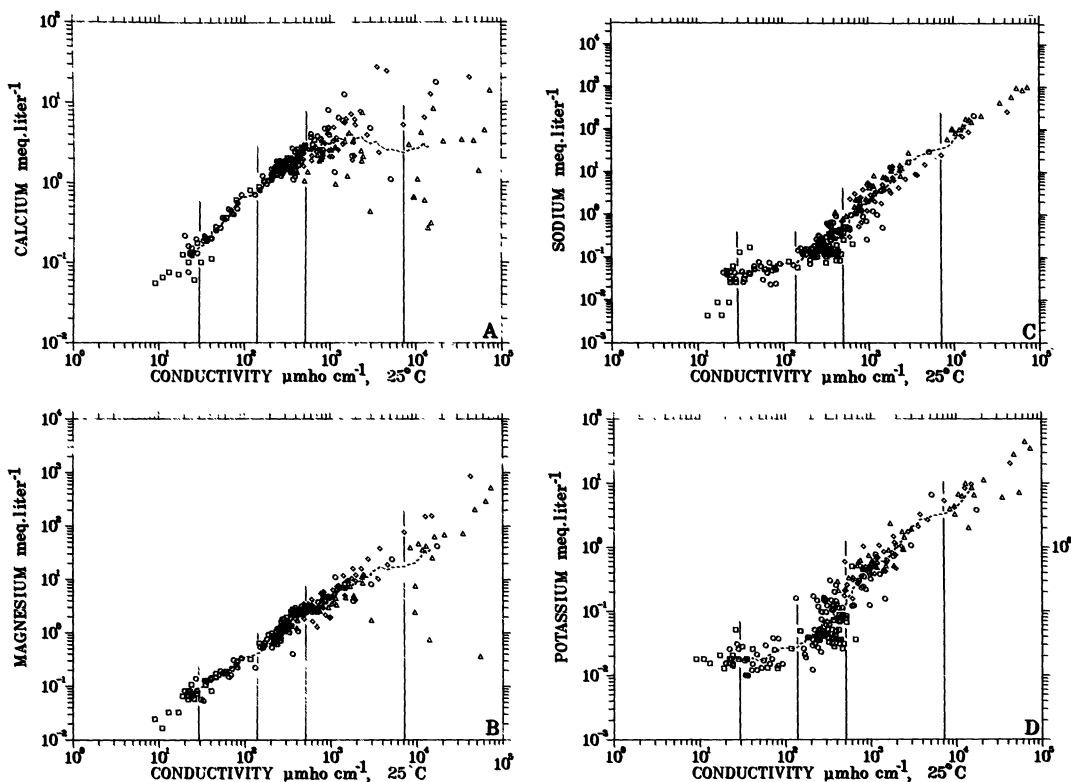


Fig. 6. As Fig. 4, but between specific conductivity and calcium (A), magnesium (B), sodium (C), and potassium (D).

groups I and II where the concentration is lowest; concentrations tend to increase up to the boundary between groups III and IV and then to level off. Boron (Fig. 8B) is usually below detection limits in dilute waters. In groups III–V, boron is correlated strongly with conductivity.

Iron (not shown), with few analyses in groups I and II, shows no relationship to conductivity. The concentration ranges from 0.01 to 0.7 ppm and is probably controlled by redox conditions in surrounding soils, groundwaters, and littoral sediments, as well as the degree to which sediments are resuspended in the water by turbulence, especially in shallow lakes. Waterlogged, peaty drainage basins may contribute substantial amounts of iron to some lakes, probably chelated by dissolved organic matter. Manganese concentration (Fig. 8C) also shows little re-

lationship to conductivity for the same reasons. However, waters of groups II (two samples) and III tend to be lower than those of groups IV and V.

Silica (Fig. 8D) is low in group I waters, among which the most dilute consist of rainwater little altered by addition of weathered materials (Table 1). It increases in groups I–III as weathering products of silicate minerals are added and then levels off.

Trends in ionic composition—Although most dissolved materials increase in concentration with rising conductivity, their proportions relative to one another and to total ions change radically owing to differences in mineral weathering and evaporative precipitation (Fig 9).

Calcium (Fig. 9A) accounts for half or more of total cations in group I and II lakes on substrates mapped as noncalcar-

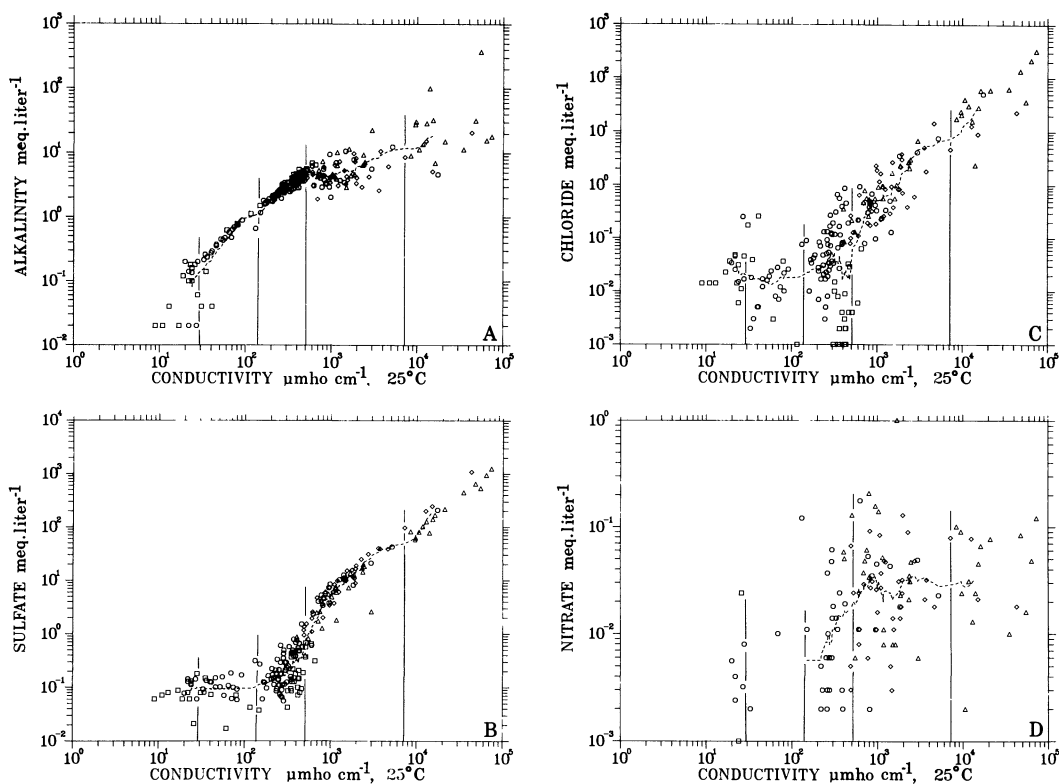


Fig. 7. As Fig. 4, but between specific conductivity and alkalinity (A), sulfate (B), chloride (C), and nitrate (D).

eous and also in the more dilute group III lakes on calcareous substrates. As conductivity increases and calcium carbonate precipitates, calcium decreases to <10% of total cations in saline group V waters. Magnesium accounts for about 30% of total cations in group I and II waters, increases to about 50% in the more concentrated group III waters because of calcium carbonate precipitation, and then declines (but with great variability) to about 30% in saline group V waters as sodium becomes dominant. Sodium is variable in dilute waters and declines in importance as calcium and magnesium are weathered from noncalcareous substrates and added to the more concentrated group II waters. It remains proportionally low in the group III lakes on calcareous substrates and then increases rapidly once the sulfur-bearing substrates of group IV lakes are reached. Sodium is clearly dom-

inant in the most saline waters of groups IV and V. Potassium is the least concentrated of the major cations and is highest proportionally in group I waters; it declines in proportion to other cations through groups II and III, increases slightly in group IV, and declines slightly in group V.

Alkalinity (Fig. 9B) is extremely low in many group I waters, as it is in atmospheric precipitation. According to Munger (1982) precipitation is distinctly acid in northeastern Minnesota, with a mean volume-weighted pH of 4.7; in northwestern Minnesota the mean precipitation pH is 5.0, in southeastern North Dakota 5.3. However, as rainwater dissolves noncalcareous soil minerals it is enriched in bicarbonates of calcium and magnesium and transformed into group II water, which is increasingly dominated by bicarbonate as it becomes more saline. In group III

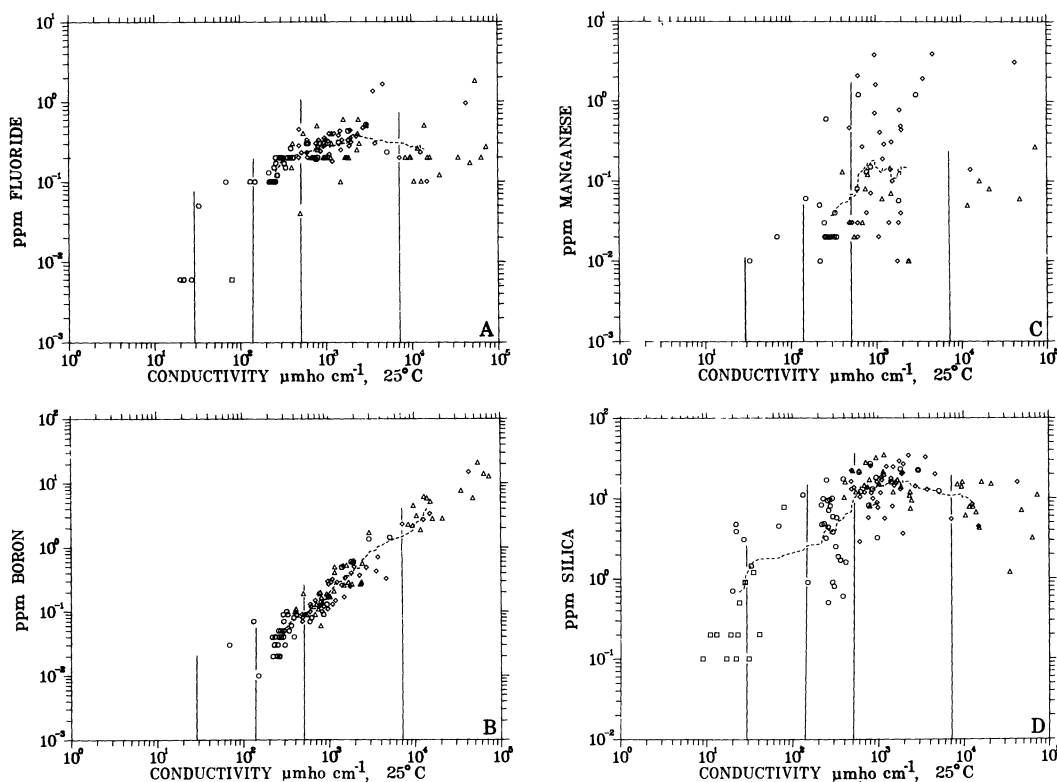


Fig. 8. As Fig. 4, but between specific conductivity and fluoride (A), boron (B), manganese (C), and silica (D).

waters, alkalinity averages close to 90% of total anions. Group IV waters drain calcareous substrates rich in sulfur-bearing minerals, and this—combined with precipitation of calcium carbonate—results in a striking proportional decline of alkalinity in group IV waters, from about 90% of total anions near the group III/IV boundary to about 20% of total anions near the group IV/V boundary. The proportional decrease in calcium and increase in magnesium, in response to precipitation of calcium carbonate, occurs within group III waters at a conductivity well below that at which alkalinity declines and sulfate increases (cf. Fig. 9A and B). The empirical boundary for precipitation of calcium carbonate, based both on water chemistry (Fig. 9A) and its presence in the sediments (Dean and Gorham 1976), is at a specific conductivity of about 190 μmhos (about 2 meq·liter⁻¹ total cations).

Between this empirical boundary and the group III/IV boundary, the Mg:Ca ratio increases, but these two cations are clearly dominant. A major change does not occur until the group III/IV boundary, where both sodium and sulfate increase markedly to become dominant in the more saline group IV waters.

Sulfate (Fig. 9B) is a mirror image of alkalinity. It accounts for >60% of total anions in some group I waters and declines sharply as alkalinity increases in group II. In group III lakes on calcareous substrates, sulfate is commonly <10% of total anions. Group IV lakes are greatly enriched by weathering of abundant sulfur-bearing minerals. Partly for this reason, and partly owing to marl precipitation, sulfate accounts for about 65% of total anions in the most concentrated group IV waters. Even higher percentages are observed in group V waters.

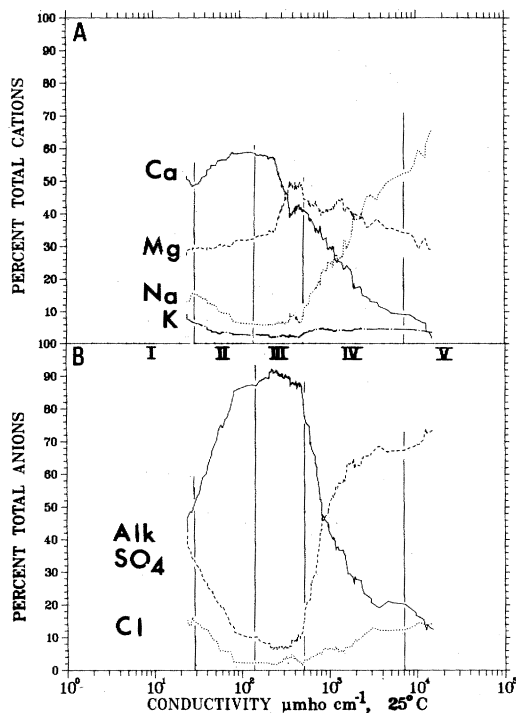


Fig. 9. A. Relationship of individual major cations, as a percentage of total cations, to \log_{10} specific conductivity. B. As panel A, but of individual major anions.

Chloride (probably from road salt) dominates three dilute waters on noncalcareous substrates, but in general it is not abundant. Chloride declines from about 15% of total anions in group I waters to <5% in group III waters, increasing again to about 15% in the saline waters of group V (Fig. 9B).

Nitrate is proportionally most abundant in group I waters and declines to very slight importance in the saline group V. Fluoride is likewise most significant in dilute waters. In contrast, boron (where detectable) does not change proportionally as conductivity increases. Silica tends to be proportionally low in both group I and group V waters, where weathering products of silicate minerals contribute least to salinity.

Q-mode factor analysis—We sought an objective confirmation of the validity of our lake classification, and an alternative examination of relationships among vari-

ables, by Q-mode factor analysis using the CABFAC program of Klován and Imbrie (1971). \log_{10} data for the four major cations and three major anions in 209 lakes were scaled to range from 0 to 1 so that variables with larger means and variances would not determine the outcome.

After varimax rotation 93% of the variance was accounted for by two factors. A plot of varimax loadings from factor 1 vs. conductivity was similar to the plots of proportions of calcium and alkalinity for lakes in groups I–III and the plot of proportions of Mg for lakes in groups IV and V (Fig. 9). A plot of varimax loadings from factor 2 vs. conductivity was similar to the plot of proportions of sulfate (Fig. 9B).

The Q-mode factor loadings can be thought of as composite variables, so that the original seven variables have been reduced to two factor loadings, each an attribute of water chemistry expressing a synthesis of several measured variables. Correlation analyses among factor loadings and the original seven measured ions showed that factor 1 is mainly a measure of calcium and alkalinity with a minor contribution from magnesium. Factor 2 is mainly a measure of sodium, potassium, chloride, and sulfate.

The Q-mode analysis confirmed in a general way the lake classification based on specific conductivity and the chemical characteristics of the five groups. However, the Q-mode analysis recognized only two main groups, one with calcium bicarbonate waters and a second with sodium, potassium, chloride, and sulfate waters; it was not capable of resolving as detailed a classification as we have presented. Moreover, the Q-mode analysis did not show the details of interionic associations that are particularly evident in Fig. 9.

Another confirmation of our conductivity classification was attempted early in our study by applying the agglomeration techniques of Orloci (1967) to 82 Minnesota lakes for which concentrations of seven major ions were available. The resulting dendrogram confirmed the conductivity boundaries between groups II and III and groups III and IV for the

Minnesota lakes, which gave us confidence in applying our empirical techniques across a broader geographical area.

Temporal variability in concentration and composition—Lakes in arid western Minnesota and the Dakotas fluctuate in concentration and composition. Samples taken at extreme high and low water can have conductivities (and compositions) so different as to place them in different lake groups. For instance, Sully Lake near Onida, South Dakota, had a conductivity of 4,800 μmhos on 19 November 1959 and 155 μmhos on 7 April 1960 (Petri and Larson 1971). In late 1959 Sully Lake would have been classified as high group IV. In the spring of 1960 it received a great deal of dilute inflow and rose more than 3 m, which changed it to low group III. By April 1961 the water level had declined enough so that the lake crossed the conductivity boundary into group IV again and remained there until May 1964 when analyses ceased. The most concentrated waters of Sully Lake were 16-fold richer in calcium, 45-fold richer in magnesium, and 119-fold richer in sodium than the most dilute waters, and 9-fold richer in alkalinity, 84-fold richer in sulfate, and 119-fold richer in chloride.

Unusual situations—Certain lakes are unusual because of natural circumstances. Elk Lake (group IV) in Grant Co., Minnesota, has an exceptionally high ratio (>7) of magnesium to calcium and appears to form sedimentary dolomite as a diagenetic alteration of high-magnesium calcite (Dean and Gorham 1976). The extremely saline East Stump Lake in North Dakota precipitates mirabilite (Mitten et al. 1968).

There are also regional differences between the group V lakes in North and South Dakota. Waters in North Dakota are generally richer in sodium and chloride, and to a lesser degree in alkalinity, than those in South Dakota. Concentrations of calcium, magnesium, and sulfate are generally higher in South Dakota. Presumably these differences reflect the influence of different types of groundwater (Winter 1974).

Pollution may also shift a lake into a

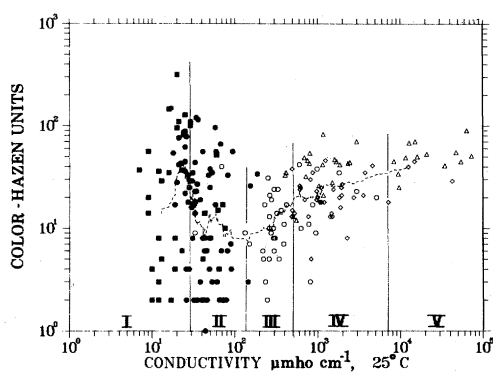


Fig. 10. As Fig. 4, but between color (Hazen Pt-Co scale) and specific conductivity. Symbols as in Fig. 4; Glass and Loucks 1980, Minnesota—●; Juday and Birge 1933, Wisconsin—■.

more saline group. Lake Manganika in the Iron Range of northern Minnesota has group IV water rich in sulfate (Maderak 1963) and lies far to the east of other northern group IV waters (Fig. 2). A large part of the lake has been filled in with mine spoils. Some lakes are strongly polluted; Farquar Lake in Dakota Co., Minnesota, had 7.5 ppm of nitrate in October 1961, and in Big Stone Lake at Ortonville, Minnesota, nitrate levels range up to 9 ppm because of agricultural drainage. A few group III lakes in the vicinity of Minneapolis and St. Paul had, in October 1961, chloride concentrations ($0.5\text{--}0.8\text{ meq}\cdot\text{liter}^{-1}$) somewhat higher than normal for their conductivities ($300\text{--}400\text{ }\mu\text{mhos}$) because roads were salted in winter.

A much greater pollution threat—acid rain—faces group I (and to a lesser extent group II) lakes in northern Wisconsin and Minnesota. The pH of atmospheric precipitation in northeastern Minnesota is now 4.67 (Table 1), close to the level at which damage to lakes and their fisheries has been observed in Scandinavia (Wright and Gjessing 1976).

Color

Water color—a useful measure of dissolved organic matter (Juday and Birge 1933)—was not measured in most of our dilute lakes. However, simultaneous color and specific conductivity data are

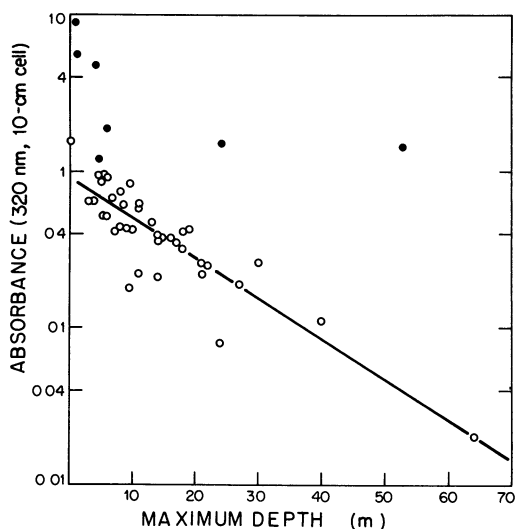


Fig. 11. Relationship of \log_{10} water color (absorbance at 320 nm in a 10-cm silica cell) to maximum lake depth. Lakes with peaty drainage—●; lakes with normal drainage—○.

available for such lakes (Juday and Birge 1933; Glass and Loucks 1980) and have been treated together with our data in Fig. 10.

Color is extremely variable in group I and II waters, ranging from 1 to 300 Hazen units. Very low values represent surface runoff over coarse, sandy and gravelly soils with thin acid humus layers, whereas high values represent drainage from acid peat deposits that are uncommon on calcareous substrates in this region. The most dilute group III lakes have relatively little color (averaging <10 units) and there is a steady increase to the most saline group V lakes (≈ 50 units).

Absorbance (at 320 nm in a 10-cm silica cell) was measured in 39 of the Minnesota lakes as another estimate of color and dissolved organic carbon (Gorham 1957c; Mackereth 1963). Most of these lakes are in groups II, III, and IV, with one each in groups I and V. The waters were filtered quickly through a coarse paper.

Highly colored waters (absorbance > 2) were found only in lakes on peaty, non-calcareous substrates. If lakes receiving peaty drainage are excluded, \log_{10} color correlates very closely ($r = -0.88$) with

maximum lake depth. The inverse relationship of color (and dissolved organic matter) to depth (Fig. 11) is probably explained by the interaction of several factors: shallow lakes are more productive per unit volume than deep lakes, hence the secretion of extracellular metabolites and the release of dissolved organic matter by decomposition of dead plankton is greater in shallow lakes; the ratio of sediment area to water volume is higher in shallow than in deep lakes, leading to a relatively greater release of dissolved organic matter to the overlying water by decay in the sediments; evaporative concentration per unit volume is greater in shallow than in deep lakes; and residence times are likely to be shorter in shallow than in deep lakes, allowing less photooxidation and microbial breakdown of dissolved organic matter. Decreasing depth is probably an important factor in the increase of color (Fig. 10) from the most dilute group III lakes to the most saline group V lakes.

Discussion

It is clear from our results that the chemistry of lake waters in the north-central United States—like the chemistry of groundwaters (Winter 1977) and of profundal lake sediments (Dean and Gorham 1976)—can be understood largely in terms of the interaction of climatic and geologic factors, although human influences are discernible. Our data are in accord with—and provide a detailed background to—the broad generalization by Clarke (1924) that there is a pronounced shift from bicarbonate-dominated waters in the humid forests east of the Mississippi to sulfate-dominated waters that precipitate calcium carbonate in the more arid prairie regions of the west. In addition we have shown that changes in geologic substrate are also important. Our data are broadly compatible with the model presented by Gibbs (1970) for the control of global water chemistry by atmospheric deposition, rock weathering, and the evaporation/precipitation process. He observed that the most dilute surface waters, which have ionic com-

positions close to rainwater, have high ratios of sodium to calcium and of chloride to bicarbonate. These ratios decline sharply toward the middle range of salinity where rock and soil weathering is the predominant source of ions, and rise again as evaporation leads to further ion concentration and the precipitation of calcium carbonate. Generally similar relationships occur in the north-central United States (Fig. 9), but the ratio of sodium to calcium is not nearly so high as that observed by Gibbs (1970), who included a number of rivers strongly influenced by sea spray. Likewise, the ratio of chloride to alkalinity never reaches the high levels observed by Gibbs at either end of the salinity range, where again sea salt plays a predominant role. The distribution of the ratio of sulfate to alkalinity in the north-central United States is similar to the distribution of the ratio of chloride to alkalinity presented by Gibbs; both are low in the middle range of salinity (Fig. 9B).

Contrary to the view of Bright (1968), water chemistry is not closely related to vegetation type. The boundary between group II and III lakes is generally east of the boundary between coniferous and deciduous forests shown by Wright (1969), whereas the boundary between groups III and IV is usually west of the forest-prairie boundary.

According to Hall (1972) the composition of Minnesota lake waters approximately fits a model in which rainfall enriched by soil-derived carbon dioxide reacts with calcite, dolomite, gypsum, illite, and sodium feldspar at 5°C and 1 atmosphere total pressure. He suggested that the waters become saturated with calcite at about 5 meq·liter⁻¹ total cations (specific conductivity about 450 μ mhos·cm⁻¹) and with respect to calcite and dolomite at about 8.9 meq·liter⁻¹ total cations (specific conductivity about 750 μ mhos). This does not agree with our empirical boundary (Dean and Gorham 1976) for carbonate precipitation at 190 μ mhos (about 2 meq·liter⁻¹ total cations). Hall also suggested that dissolution of gypsum becomes progressively more important as

salinity increases above 5 meq·liter⁻¹ total cations, which is consistent with Figs. 7B and 9B. Our data also show (Fig. 9B) that sulfate begins to dominate the anions above about 10 meq·liter⁻¹ total cations (specific conductivity about 900 μ mhos). Hall (1972) suggested further that isothermal evaporation of waters in the lakes of southwestern Minnesota should produce highly alkaline magnesium-calcium sulfate waters that he claimed were typical of closed-basin lakes in the Dakotas. However, he did not account for the sodium sulfate waters that are characteristic of the most concentrated closed-basin lakes in those states and begin to appear as salinity increases above about 30 meq·liter⁻¹ (specific conductivity about 2,200 μ mhos). Our data, moreover, indicate that at concentrations where sulfate begins to dominate over alkalinity (specific conductivity about 900 μ mhos; Fig. 9B), sodium is already a significant cation, approaching calcium in concentration (Fig. 9A).

According to Sloan (1972) the sodium sulfate waters of North Dakota do not require bedrock sources of saline water but are the result of an evaporation sequence in which waters are dominated successively by calcium bicarbonate, magnesium bicarbonate, calcium and magnesium sulfate, and sodium sulfate. Mitten et al. (1968) noted that runoff from the Big Coulee at Church's Ferry into the markedly saline Devils Lake chain in North Dakota is dominated by calcium, magnesium, and bicarbonate ions except during periods of low flow when sodium and sulfate ions predominate. As the salts dissolved in runoff are concentrated by evaporation, the alkaline-earth carbonate minerals precipitate, so that the waters stored in the chain of lakes come to be dominated strongly by sodium and sulfate ions, chloride increases markedly, and calcium decreases to only a few percent of total cations.

The work reported here does raise questions for further study by hydrogeologists, glacial geologists, and soil scientists. For example, several group III lakes occur on glacial deposits mapped as non-

calcareous red drift (e.g. west of Mille Lacs, Minnesota: Winter 1974). Presumably these lakes are tapping calcareous material underlying rather shallow red drift. Likewise group II lakes may occur as western outliers on deposits mapped as calcareous gray drift (e.g. several lakes in Itasca State Park, northwestern Minnesota). These lakes are small and usually occur on sandy, gravelly material that has undergone substantial surface depletion of calcium carbonate by soil leaching. The larger lakes in the area that drain deeper weathering profiles have normal group III waters.

The boundary between group III and group IV lakes raises a hydrogeological problem. We do not know how closely that boundary reflects mineralogical and chemical differences in the respective glacial deposits and how far it may be influenced by regional vs. local groundwater flow (Winter 1974, 1977).

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