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Chemical geology of  
ground and surface waters  
in Finnish Lapland

by Pertti Lahermo

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CHEMICAL GEOLOGY  
OF GROUND AND SURFACE WATERS  
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PERTTI LAHERMO

WITH 49 FIGURES AND 9 TABLES IN TEXT AND TWO APPENDICES

GEOLOGINEN TUTKIMUSLAITOS  
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## ABSTRACT

Chemical analyses were made of 1 300 water samples collected in Finnish Lapland.

The geological structure and petrographic composition of the Quaternary deposits and the underlying crystalline bedrock, together with the texture of the subsoil, are the dominant factors regulating the chemical composition of the ground and surface waters. An increase in subsilicic mineral constituents in the geological environment causes a rise in the total electrolyte content, especially the Ca and  $\text{HCO}_3$ , and in the pH level of the waters. The ground water occurring in the fractures of the bedrock contains more dissolved matter than does the ground water percolating through the Quaternary strata. The latter are chemically similar to the flowing surface waters. This is due to the circumstance that the main source of the brook and river waters in winter and in dry seasons is the ground water discharged from Quaternary deposits.

In waters contaminated by agricultural settlement, the geological regulation of the chemical composition is overshadowed by the increase in the electrolyte content.  $\text{NO}_3$ , Cl,  $\text{KMnO}_4$ -consumption and the alkali metals, particularly K, are sensitive indicators of contamination.

Of atmospheric origin in natural waters are, for the most part, the  $\text{NO}_3$  and Cl, to some extent the K and Na, and, in dilute waters a major part of the  $\text{SO}_4$ .

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### ERRATA

p. 33 Addendum to Fig. 9: The smaller figures indicate the number of determinations.

p. 33 l. 5 *for* strongest *read* most evident.

p. 37 l. 8 *for* most *read* least

Addendum to Appendix 2: The linear correlation used in the calculation of correlation matrix.

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The author has participated in the general ground-water investigations carried out in conjunction with the mapping of Quaternary deposits by the Geological Survey of Finland in central and northern Finnish Lapland in the region covered by the present study. Since the year 1962, the author served at first as what is called a »summer assistant» and later as a geologist. A large part of the material the author collected during an eight-year period is utilized in this work.

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*Pertti Lahermo*

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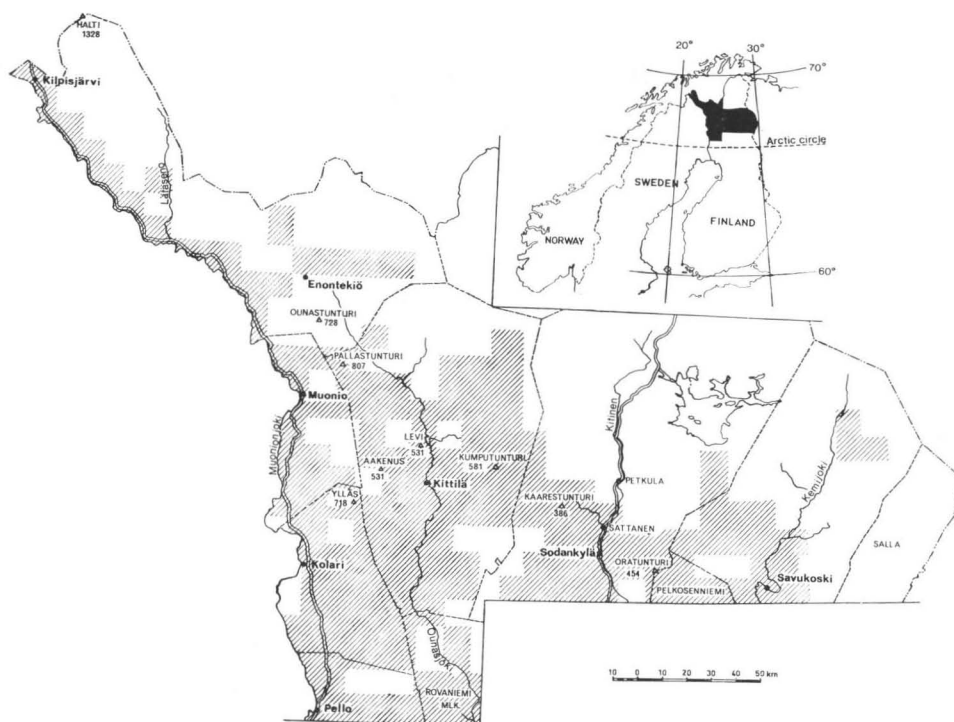


FIG. 1. Area from which the water samples were collected, indicated by the slanting lines. Location of the study area is shown in the inserted map.

## INTRODUCTION

The crystalline Precambrian bedrock of Finland contains little ground water. The Quaternary deposits consist predominantly of till, which, together with clay, is generally only slightly permeable to water. Besides, these deposits are partly overlain by peat (about 30 % of the land area). The most general thickness of the surficial deposits averages only between three and four meters (see Okko 1964, pp. 242—243). Thus the amounts of ground water to be obtained from them in Finland are inconsiderable. The accumulations of glaciofluvial material are likely to contain more ground water, but they account for only a small part of the total area.

Ground-water investigations carried out in Finland up to the 1920's are few (see Hausen 1968, p. 126). Later, various engineering firms have done much work to ascertain the quantities and quality of available water supplies. In addition, the Geological Survey has initiated ground-water investigations of a general nature in areas being surveyed for maps of Quaternary deposits. So far the results obtained for the map sheets of the Kerava (Hyypä, J. 1959), Tampere (Virkkala 1962), Joensuu (Rainio 1969), Hämeenlinna (Hyypä, J. 1969) and Riihimäki (Hyypä, J. 1969) areas have been published as part of the explanatory texts accompanying the maps of Quaternary deposits. Brief studies on certain chemical properties of ground water have been published by Sandelin (1936), Vuorinen (1944) and Lahermo (1969). From a number of samples of water obtained from wells and mines, Wilska (1952) analyzed the trace element contents. Marmo (1958) used pH determinations from well water in geochemical ore prospecting. Several summary reports on the occurrence and chemical quality of ground water in various geological environments (Natukka 1960, 1963; Laakso 1966) have been made on the basis of the extensive material gathered by one engineering firm in the course of making ground-water investigations and drilling wells into bedrock. The Board of Agriculture and the Board of Health have jointly investigated the quality of the household water by establishing a sampling network covering the whole of Finland (Väre 1959, 1960, 1961).

The region investigated for the present study covers most of central and north-western Finnish Lapland (Fig. 1). The region belongs to the northern coniferous forest zone and, in its northwestern part, to the subarctic tundra zone. It is very sparsely settled. The settled areas are concentrated along the lakes and streams and motor highways, between which lie vast stretches of forests and peat lands. It is for



these reasons of accessibility that the samples making up the material of this study were collected in terrain lying close to the road network.

By virtue of the sparse settlement, the natural state of the ground water and of the surface bodies of water in the region has not been significantly affected by human activity. Therefore, the region affords good opportunities to study the influence of geological factors, notably the mineral composition and the grain-size distribution of Quaternary deposits and the composition of the bedrock on the chemical contents of natural waters. The relative amounts of elements and compounds contained in the ground and surface waters depend on the susceptibility of the different minerals and rocks to weathering — hence the study also throws light on local weathering phenomena.

Elsewhere in the country, the ground and surface waters are rapidly becoming contaminated as a result of the spread of settlement, agriculture and industrial activity. In the near future, the drainage and fertilization of bogs and forest lands as well as regulation and construction programs involving the major lakes and rivers will extend their effects to the ground and surface waters also in broad areas of Lapland, altering their original nature. By now, the ground water in the area investigated shows in places signs of contamination by settlement. This condition allows the study of the effect of the first stages of contamination on the chemical composition of intact water. In addition to the data on intact waters, an analysis of the present-day trends of contamination should be useful in evaluating the future changes in natural waters.

## RESEARCH METHODS

### Sampling

Collecting samples of water was the main part of the field work. Because twenty different chemical determinations were to be made (see p. 9—11), the samples were poured into three one-liter polyethene bottles. Into one of the bottles, intended for the determination of iron and manganese only, a small amount of hydrochloric or sulfuric acid was added to prevent the precipitation of these components.

The samples of water were mainly collected during the months of June, July and August between 1962 and 1968 and in the months of March and April in the year 1968. The sampling sites, the majority of which represent discharges of ground water from springs in uninhabited forest areas, were selected on the basis of aerial photographs and their interpretation. The places where ground water is discharged are generally situated at the base of wooded hills, river banks and eskers in the border zone between tracts of mineral soil and surrounding peat land. Ground water is capable of nourishing richer vegetation than that of surrounding areas. This can be perceived upon stereoscopic examination of an aerial photograph in the form of a pale groove running in the direction of the flow on bog surfaces. In many cases, the

brook originating as a discharge of ground water appears in the photograph as a dark band. By means of topographic and geological observations, it can further be determined where springs might be expected, even though the sites cannot be directly detected in aerial photographs. Water samples were also taken from drilled wells in bedrock and wells dug out of Quaternary deposits, which serve household needs, as well as from surface waters such as small rivers and brooks, esker pools and ponds.

The discharges from springs were measured by using a Thompson-model measuring weir. It was not always feasible to use this device because of unfavourable conditions in the terrain; in such cases, the discharge was estimated visually. In order to obtain a general idea of the composition of the Quaternary deposits in the study area, a considerable number of samples of these deposits were collected for mechanical grain-size analysis. In addition, geological maps of the Quaternary deposits were consulted. No separate observations of the bedrock were made for the purposes of the present study, for reliance was placed on the previously published maps of rocks.

### Chemical methods of analyzing water

The pH and specific electrical conductance values were determined from the water samples in the morning of the day after sampling. Laboratory determinations could be started only three or four days after the samples had been collected. In the pH determinations made in the field, a small BDG comparator with a carton of buffer tubes was used in the beginning of the investigations; later use was made of Beckman's model GS and Radiometer's »pH-meter 24» potentiometric apparatus equipped with glass and calomel electrodes. In addition, a Beckman Model N-meter was used in laboratory work. Electrical specific conductance was measured in the field with a Normameter RW and in the laboratory with a Philips GN 4249/01 Wheatstone bridge. In the present study use has been made of the pH and specific conductance values measured in the laboratory.

The chemical water analyses were done in the laboratory by applying the generally used standard methods <sup>1)</sup> under prevailing temperatures of +20 to 23 °C.

The results of the chemical analysis are reported in milligrams per liter, specific conductance in  $10^6 \times \text{Ohm}^{-1} \times \text{cm}^{-1} = \mu S$ , alkalinity in meq = mg-equivalents and total hardness in dH° = German degree.

Carbon dioxide dissolved in water, or free carbon dioxide, was analyzed in the laboratory immediately after the delivery of the samples by titration with 0.05-n NaOH

<sup>1)</sup> \*. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (1954). Verlag Chemie. GMBH. Veiheim.

\*\*. Juoma- ja talousveden fysikaaliset ja kemialliset analyysimenetelmät (Physical and chemical methods of analyzing drinking and household water) (1955). Elintarviketutkijain seura, ry. (Food Investigators' Society, Inc.) Helsinki.

\*\*\*. Methods for collection and analysis of water samples (1960). F. H. Rainwater, L. Thatcher, U. S. Geol. Survey Water- Supply Paper, 1454.

\*\*\*\*. Standard methods for the Examination of Water and Wastewater (1965). American Public Health Association, Inc. New York.

solution and, as indicator, phenolphthalein (pH 8.3) (\*\* p. 23, \*\*\* p. 82). The alkalinity was titrated with 0.1-n HCL solution, using methyl orange as indicator (pH 4.5) (\*\* p. 20). The bicarbonate content was calculated from the alkalinity value.

The total hardness was determined by adding an indicator tablet (Merck) and 1 ml of conc. ammonia to 50 ml of a solution titrated with 0.01-m complexon III. Also calcium was determined complexometrically with the same titrant, but 5 ml of 2-n KOH and, as indicator, calconcarbonic acid were added to the 50 ml sample. The magnesium was calculated in accordance with the foregoing as follows:

$$\text{Mg} = \frac{\text{total hardness} - 0.14 \times \text{Ca}}{0.231}$$

For the determination of the  $\text{KMnO}_4$ -consumption, to the 100 ml sample were added 10 ml of 0.01-n  $\text{KMnO}_4$ -solution (or more, as needed) and 10 ml of 25 %  $\text{H}_2\text{SO}_4$ . The mixture was kept heated by a boiling water bath for 40 minutes until the organic or other oxidizable substances in the water oxidized. After this an equal amount of 0.0125-n  $\text{Na}_2\text{C}_2\text{O}_4$  solution was added. The remaining permanganate oxidizes part of the added oxalate, the unoxidized portion of which is titrated with the 0.01-n  $\text{KMnO}_4$  solution at a temperature of  $+50 - +60^\circ\text{C}$ . This procedure yields slightly higher values than those commonly obtained, in which an 0.01-n  $\text{Na}_2\text{C}_2\text{O}_4$  solution is used.

The ammonia was determined colorimetrically by the Nesslerization method (\* p. 70, \*\*\* p. 211). The color is obtained by means of a Seignette salt solution and a Nessler reagent and it is compared visually with standard ammonia solutions. If the solution being examined was colored in itself or contained abundant iron, the sample was distilled from a phosphate solution buffered to pH 7.4, and the determination was made from the distillate (\*\* p. 39). In the nitrite determination a mixture of  $\alpha$ -naphthylamine, sulphanilic acid and tartaric acid was used, upon which there results in the presence of nitrite a red azo dye (\* p. 52). This was compared visually in Nessler tubes after a period of 30 minutes with standard solutions made in the same way. The nitrate color reaction was obtained by adding to the sample being examined a brucine solution and conc.  $\text{H}_2\text{SO}_4$  (\*\* p. 50, \*\*\*\* p. 198). The visual color comparison was performed 5 minutes later in Nessler tubes. The humus of colored surface waters was precipitated before the determination of nitrite and nitrate with  $\text{CuSO}_4$  in NaOH-bearing solution.

The chlorides were determined argentometrically by titration with an 0.02-n  $\text{AgNO}_3$  solution and  $\text{K}_2\text{Cr}_2\text{O}_7$  as indicator (\*\* p. 52). The fluorides were determined colorimetrically (\*\*\* p. 166, \*\*\*\* p. 141). A red-violet hue is produced with an alizarine-zirconium solution in an HCl- and  $\text{H}_2\text{SO}_4$ -bearing solution; the visual comparison of colors was carried out after an hour. In colored surface waters, the humus was eliminated in the same way as in the determination of nitrite and nitrate. The sulphate was determined gravimetrically with  $\text{BaCl}_2$  (\* p. 44, \*\*\* p. 283). Phosphate was determined

colorimetrically with ammonium-molybdate (\*\*\*\* p. 234). The resultant phosphomolybdate was reduced with  $\text{SnCl}_2$  into a blue complex compound, the color comparison of which was performed visually after 15 minutes, using Nessler tubes. Silicate was determined colorimetrically as molybdenum blue (\*\*\* p. 259). The color reaction is brought about by adding to the HCl-bearing solution of the sample ammonium molybdate,  $\text{Na}_2\text{EDTA}$  and  $\text{Na}_2\text{SO}_3$ . The resulting blue color was measured after 30 minutes with a Beckman Model B spectrophotometer.

Sodium and potassium were determined with an Eel Model A flame photometer. To standard sodium solutions of a hundred milliliters was added a 1 ml KCl solution, which was made by diluting a saturated solution 1: 9. In the determination of potassium, a corresponding amount of NaCl solution was added to the standard potassium solutions. The iron was determined colorimetrically with KSCN, the intense red hue resulting from which was compared visually in Nessler tubes (\*\* p. 67). Before the determination, ferrous iron was oxidized to produce ferric iron in an acid solution with  $\text{H}_2\text{O}_2$ . Also manganese was determined colorimetrically by oxidizing it with  $\text{K}_2\text{S}_2\text{O}_8$  into permanganate (\*\* p. 70). The disturbing influence of chloride was prevented by adding an amount of 0.02-n  $\text{AgNO}_3$  solution corresponding to the chloride content. The color comparison was performed visually after heating in Nessler tubes.

In the oxygen determinations, bottles of a known capacity with glass stoppers were used; and in conjunction with the taking of samples, a solution of 50 %  $\text{MnCl}_2$  and then one of 33 % NaOH were added (Winkler method, \* p. 97, \*\*\* p. 234). The oxygen in the water oxidizes the  $\text{Mn}(\text{OH})_2$  into  $\text{MnO}(\text{OH})_2$ . Added KJ reduces it back in acid solution after which an amount of released iodine corresponding to the  $\text{O}_2$ -content of the water is titrated with an 0.01-n  $\text{Na}_2\text{S}_2\text{O}_3$  solution, starch acting as indicator.

### **On the reliability of analytical methods**

In order to obtain an over-all picture of the natural ground and surface waters in the extensive study area, it was necessary to do a large number of water analyses. Consequently, one of the criteria in choosing the methods of analysis was speed. Maximum accuracy was not a requirement, for the ion balance of ground and, in particular, surface waters is labile, depending decisively on, among other things, the sampling site, amount of precipitation and the season of the year. The majority of the colorimetric determinations were done visually, using a Nessler tube. Accordingly, in the determination of iron, for example, the optimum reliability of comparison is no better than 5 %, and often only 10 % (\*\*\*\* p. 159). As simple methods, however, they do reliably give the order of magnitude of the contents in question. In those surface waters in which the color derived from the humus interfered with the colorimetric determination ( $\text{NO}_2$ ,  $\text{NO}_3$  and F), the humus was removed by precipitation with copper sulfate in an NaOH-bearing solution.

The precision of the bicarbonate content determined as alkalinity, was estimated to be better than  $\pm 1.5$  mg per l. In dilute ground waters, this causes considerable distribution of determinations; but in the average bicarbonate contents of the natural waters of the study area (median: 21 mg per l), the relative distribution is less than 10 %. There is a tendency for the titration to yield excessively high values because of the gradual nature of the indicator's (methyl orange, pH 4.5) change of color. Moreover, the bicarbonate content is liable to change significantly during the transportation and storage of the samples (see p. 75).

The precision of the complexometric determinations of calcium and total hardness is better than  $\pm 0.2$  mg per l and  $\pm 0.02$  dH°. By means of the method, it is possible to observe calcium contents of even 1 mg per l and total hardness of 0.2 dH°, though values as low as these are scarcely ever met with in the waters of the study area. These determinations are mostly disturbed by heavy metals, of which only iron is notably present in the waters investigated. The error induced by iron in the determinations of the calcium and total hardness of the ground water discharged from Quaternary deposits is negligible. Although the iron content of the ground water occurring in the bedrock is significantly higher, the proportional error resulting in the calcium determinations in consequence of it is nevertheless noteworthy in only 5 % of these samples. Iron occurs in the largest amounts in the surface waters, where, however, the consequent proportional error is noteworthy in the case of only 10 % of the surface-water samples. The magnesium was determined arithmetically from the difference between the total hardness and the calcium contents. This method is apt to result in errors in the magnesium determinations, owing to the inaccuracy of either or both of the factors, especially if there is present an abundance of iron to disturb the complexometric titration.

The sensitivity limits of the rodanide and persulfate methods used in the determinations of iron and manganese are about 0.005 mg per l. In most cases, the iron and manganese contents of the waters of the study area are below this figure. At its most accurate, the visual method is in the content range of 0.005—0.100 mg per l, and this is the range within which most of the waters investigated that exceed the determination limit mentioned fall.

The colorimetric determination of nitrite with sulfanilicamide by diazotization is a fast and convenient procedure (see, e.g. Koroleff 1969, p. 107). The minimum contents clearly observable visually are about 0.0025 mg per l. Practically all the nitrite concentrations in the natural waters of the study area fall below this limit, and they are low even in contaminated waters. The ammonia determinations carried out in the present work are only orientative. The difficulty of the Nesslerization method used is — besides the matter of obtaining sufficiently pure reagents and water — that the air in the laboratory also is a source of contamination (see Koroleff 1969, p. 110). The sensitivity limit of the brucine method applied in the determination of nitrate is c. 0.01 mg per l and its accuracy is satisfactory up to 10 mg per l. The nitrate contents of the natural waters of the study area are nearly invariably below 1 mg per l. Iron disturbs the

determination when it occurs in concentrations of higher than 1 mg per l, but such instances were met with in only a small number of the samples. More uncertainty results from the tendency of nitrogen compounds, notably ammonia and nitrite, to undergo changes of concentration during transportation and storage than from the errors inherent in the analytic methods applied (see p. 68).

The determination of fluoride by the zirconium-alizarin method is most sensitive in the case of low contents up to 0.05 mg per l. The fluoride concentrations of the waters of the study area are regularly considerably below 1 mg per l, which means that the visual method referred to is applicable. The argentometric chloride determination used in the study is not accurate in the case of low concentrations owing to the gradual nature of the color change. Thus the average chloride content of 2.1 mg per l obtained for natural waters is probably somewhat in excess of what it actually is (see also Holmberg 1935, p. 11).

By the molybden-blue method, using the spectrophotometer, silica contents of even 0.1 mg per l can be detected. In the study area, however, the concentrations are regularly higher, ranging on both sides of the level 10 mg per l, where the accuracy is still good. Phosphate contents of as low as 0.005–0.01 mg per l can be detected by the phosphomolybdate method. Most of the phosphate contents of the samples taken registered below this determination level. The contents are liable to decrease during the transportation and storage of the samples (see p. 72).

The sodium and the potassium were determined with the relatively inaccurate Eel flame-photometer. The apparatus was nevertheless calibrated with care and repeatedly to standards, by virtue of which the results may be regarded as mutually comparable and satisfactory.

### **Treatment of analytical results**

Nearly 15 000 chemical determinations were made from the some 1 300 numbered samples of water. The samples were divided into thirty-two groups, each of which represents ground water or surface water occurring in various geological environments. By combining these groups, it was possible to obtain combinations representing larger unified types of geological environments. The grouping is to be seen in Table 1.

The till and the sorted drift have been transported varying distances from the parent rock (see p. 22, 39). This circumstance was taken into account in the classification of the ground and surface waters according to the composition of the local bedrock in each case. Only the areas of formation of ground water and the drainage areas of surface waters situated several kilometers inside the limits of extensive bedrock zones composed of similar rock are classified according to the rocks in question (e.g., groups 2, 3, 6 and 7) or, more broadly, according to silicic (e.g., groups 1–4 and 23) and subsilicic bedrock zones (e.g., groups 5–8 and 24). Water samples taken from transitional rock zones or areas characterized by a varying composition of the bedrock are placed in intermediate groups (e.g., groups 9 and 25).

TABLE 1.  
The geological division of the water sampling sites.

Groups	Water sampling sites	State of water	Quaternary deposits	Bedrock		
1	ground-water discharges (springs)	natural	till	silicic and intermediate	quartzites, quartzose and leptite gneisses	
2					granites, granite gneisses	
3					mica schists, Al <sub>2</sub> O <sub>3</sub> -rich mineral bearing schists (partly unknown rocks)	
4					diorites, syenites, granodiorites	
5				subsilicic	limestones	
6					black schists	
7					greenstones, amfibolites, agglomerates	
8					other subsilicic rocks, as gabbros and ultramafic rocks	
9				mixed	in the borders of silicic and subsilicic rocks and mixed rocks	
10				stratified drift	silicic	
11			subsilicic			
12	perched water	till or strat. drift				
13	ground-water springs			slightly polluted	silicic	
14					subsilicic	
15	ground water in bedrock (household wells drilled in bedrock)			nearly natural	silicic	
16				slightly polluted	subsilicic	
17					mixed	
18					silicic	
19	subsilicic					
20	household well water			nearly natural	silicic	
21				strongly polluted	subsilicic	
22	surface water in brooks and small rivers			natural	silicic	
23					subsilicic	
24					mixed	
25	surface water in (esker) pools and ponds and small lakes			till	silicic	
26		strat. drift	subsilicic			
27			silicic			
28			subsilicic			
29	standing or running water on bogs and peatlands					
30	water discharged from deposits overlain by peat	till or strat. drift	silicic	subsilicic		
31						
32						



The ground water is classified as contaminated in every case where the area of its formation is within the sphere of agricultural settlement. Wherever the ground water is discharged out of Quaternary deposits as springs, the contamination is usually slight by virtue of the rapid percolation of the water (groups 13—14). In wells where waste matter is liable to find its way and the water is nearly stagnant, the contamination was in many instances observed in the field to be fairly high (group 22). In addition, this field classification according to the degree of contamination has been verified by nitrate and chloride determinations.

In the case of single groups and larger combinations, a computer was used to calculate the frequency distributions, arithmetic mean values and standard deviations of the chemical determinations. In order that the chemical compositions of the ground and surface waters of different geological environments might be visually compared, the distributions are presented in graphic form as cumulative curves. In addition, a matrix of the correlation between the determined properties and dissolved components of water was worked out. Where the correlation was a close one, the linear or logarithmic regression models of a single variable were calculated. These models are presented with observation points, as correlation diagrams.

## OUTLINE OF THE STUDY AREA

### Relief

The highest elevations occur in the northwestern part of the study area, where the loftiest summits rise more than 1 300 meters above sea level and the relative differences in altitude are as much as 300 to 600 meters. The rest of the study area as a whole, from the Lätäseno valley to the east and southeast, consists of mainly hilly country dissected by a few chains of fells and some isolated fells. The greatest of these is the Ounas—Pallas—Ylläs (Ounasselkä) fell zone extending from Enontekiö to Kolari, in which the highest summits rise 700 to 800 meters above sea level and between 400 and 500 meters above the surrounding terrain. In the center of Kittilä commune there is another, smaller chain of fells, the highest of them being known as Aakenustunturi and Levitunturi. The eastern portion of the commune of Kittilä is relatively flat and boggy; the most prominent rise is the isolated Kumpunturi. The center of Sodankylä commune is hilly country, the highest fells being Oratunturi and Kaarestunturi, but the northern part is to a large extent boggy and flat. In the eastern section of the study area, consisting of the Savukoski district, there are several fells rising 400 to 450 meters above sea level, although the terrain is mainly flat.

According to Tanner (1938, pp. 111—125), the area covered by this study consists, with the exception of the northwest corner, of a peneplain as far as its general physiographic character is concerned. Out of the peneplain rise erosion remnants and horst-like hills, which are composed of either quartzites highly resistant to chemical weath-

ering or, more uncommonly, granites and amphibolites (see, e.g., Tanner 1938, pp. 126—147; Niini 1964). In Enontekiö the peneplain is at a 300—400 m level; in Kolari, Kittilä and Savukoski at 150—200 m; and in Pello, in the southwestern part of the study area, at an elevation of 80 to 100 m. It slopes southward c. 1.3 m per km (Kujansuu 1967, p. 14). The levellest and most deeply eroded areas are zones of schist and greenstone. Tectonic fracture lines, which are generally dozens of kilometers long separate the peneplane of bedrock into blocks, as pointed out by Kujansuu (1967, p. 17). The influence of the Quaternary deposits on the relief is slight, with the exception of some chains of large eskers and tracts of hummocky moraines. The Quaternary deposits are of significance to the relief mainly as a levelling factor in valleys and basins.

### Hydrology and climate

The study area belongs for the most part to the Kemijoki (Kemi river) drainage area, which is situated on the southern side of the primary divide. The boundary in the west against the Tornio—Muoniojoki (Tornio—Muonio river) watershed consists in the main of the Ounasselkä fell zone. Lakes cover less than 5 per cent of the total area; only in the Muonio district, in the western section, do they amount to between 5 and 10 per cent of the area (see Granö 1931, p. 102). The lakes have generally formed in tectonic depressions or in basins created by glacial abrasion and in many cases dammed up by glacial outwash. The largest rivers have found their way into preglacial valleys or they follow elongated tectonic forms in the bedrock depressed below the level of the surrounding land. The smaller watercourses likewise essentially adhere to the mosaic structure of the bedrock (Marmo 1959, p. 96; Penttilä 1961, p. 30).

Lapland largely belongs, according to Köppen's (1931, pp. 265—276) classification, to a zone characterized by a humid climate with cold winters (Df), but the north-western part of Enontekiö represents the tundra climatic zone (ET). The mean annual temperature is 0 — —1 C° and the mean temperature of the warmest month, July, is c. +15 C° and that of the coldest month, February, —13 — —15 C° (Kolkki 1960, section 5, cartogram 1—3).

The division of precipitated water into surface water and ground water depends chiefly on the ratio between precipitation and evaporation. The average annual precipitation, according to observations made during a 30-year period, is 350 mm to 500 mm in central and northwestern Lapland (HVK 1968, appendix V). According to observations recorded for a period of 50 years, 66 per cent of the annual precipitation falls between May and September, and the precipitation maximum is in July, at the same time as the temperature maximum (Simojoki 1966, p. 5). Evaporation is thus strongest in summer. The average annual evaporation in the area of the investigation is between 150 mm and 200 mm (Siren 1955, p. 6).

The proportion of water precipitated in the form of snow is important from the standpoint of spring floods. Lavila (1949, pp. 102—103) reports that the snowfall

in Lapland amounts to over 200 mm (40—50 per cent of the total precipitation), of which from 80 to 90 per cent remains on the ground on March 15. At this juncture the snow cover, converted into water, amounts to 130—140 mm (see HVK 1968, appendix VI). The rapid melting of the snow causes remarkably high fluctuations in the runoff values from the mean level, which is 9—11 l per s. per sq. km (Siren 1955, p. 8).

### Bedrock

The area investigated belongs to the zone of Precambrian bedrock and for the most part to the schist belt of central Lapland, which extends from the commune of Enontekiö to the commune of Savukoski and beyond the area to the southeast (Simonen 1960). This schist belt, which is an extension of the Karelidic range northward, is bounded on the north and the northeast by a granulite formation and pre-Karelidic granite gneiss, and on the south and southwest by the large granite area of western Lapland (Figs. 2 and 3. Mikkola 1936, 1937, 1941). The northwestern corner of the study area extends to the margin of the Caledonides consisting of Cambrosilurian schists (Matisto 1959).

The schist belt of central Lapland contains many kinds of metasediments and metavolcanics, some of which form homogeneous areas of broad extent. The most homogeneous of these is the extensive greenstone massif in the center of the schist belt. Situated mostly in the eastern part of the commune of Kittilä and extending into the western portions of Sodankylä, this vast massif, with its many branches, consists of volcanites representing different degrees of metamorphism; their chemical composition corresponds to iron-rich basalts. The greenstones are mainly albite-amphibolite and albite-chlorite rocks. Associated with them are numerous albite diabases, which, however, are small of size. Characteristic of the chemical composition of the greenstones are high contents of iron, magnesium and calcium as well as the predominance of sodium, among the alkalis (Table 2, Analysis 1). In the outermost, elongated branches of the massif, the greenstones grade over into comagmatic amphibolites, and their composition corresponds in the main to that of the greenstones (Analysis 2). As in the case of the greenstones, they likewise contain considerably more sodium than potassium, and the chief mineral constituents are amphiboles and plagioclases.

In the sequence extending from the village of Petkula to Kolari, there occur black schists associated mainly with greenstones. They are chlorite schists, carbonaceous and sulfidebearing phyllites and tremolite schists. These rocks contain abundant iron and moderate amounts of alkali earths and sodium, and their potassium content is also greater than that of greenstones and amphibolites (Analysis 3). The chief minerals are albite, chlorite, biotite and quartz, and the carbon content is apt to be as high as from one to three per cent. The chloritebearing black schists grade over in places into graywackes or conglomerates.

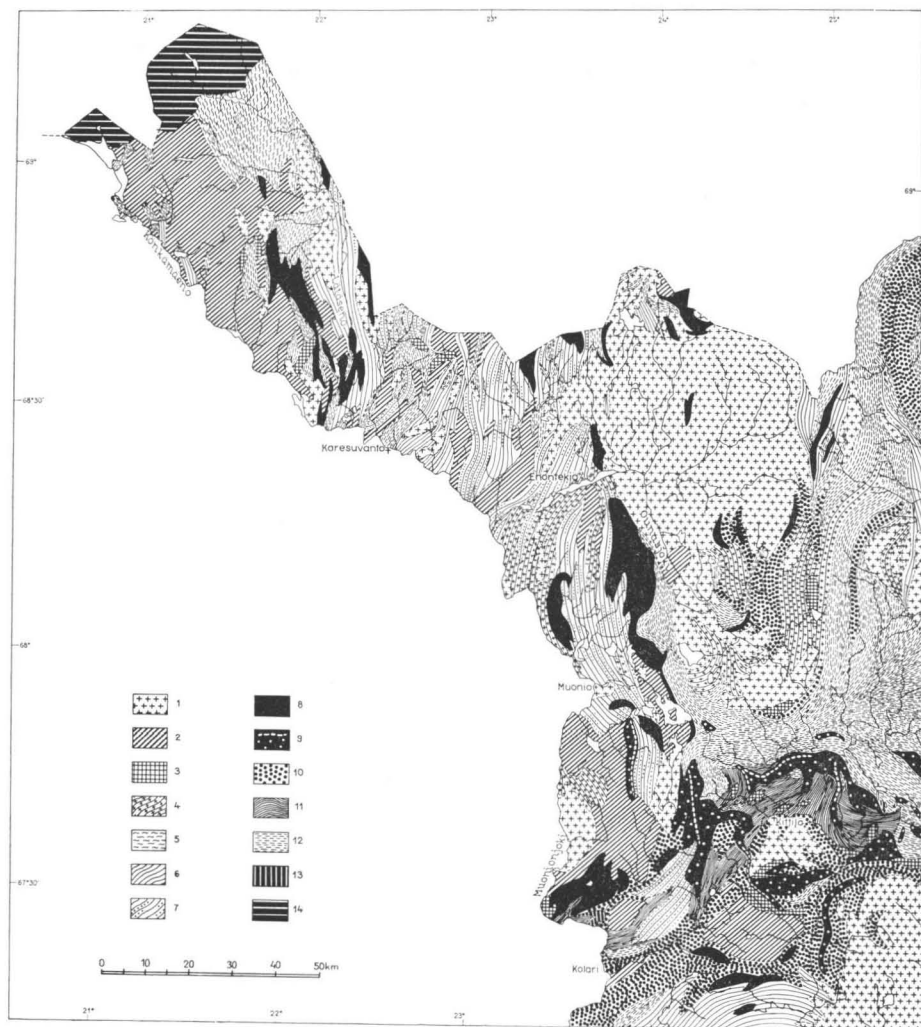


FIG. 2. Pre-Quaternary rocks in western Lapland according to Mikkola (1936, 1937), Matisto (1959) and Meriläinen (1965). 1) Granites, 2) quartz diorites and granodiorites, 3) diorites, gabbros and ultramafic rocks, 4) migmatites, 5) banded granite gneisses, 6) gneisses (and schists) of different kinds, 7) sillimanite gneisses, 8) quartzites, 9) quartzites and conglomerates of the Kumpu—Oraniemi series, 10) quartz feldspar schists, partly unknown because of lack of outcrops, 11) black schists and phyllites, 12) greenstones and amphibolites, 13) carbonate rocks, 14) Paleozoic rocks. The bedrock of the southwestern part of the study area is not shown: the dominant rocks there are granites and gneisses as well as, in some places, mica schists (Hackman 1910, 1918). From Kujansuu 1967, p. 16.

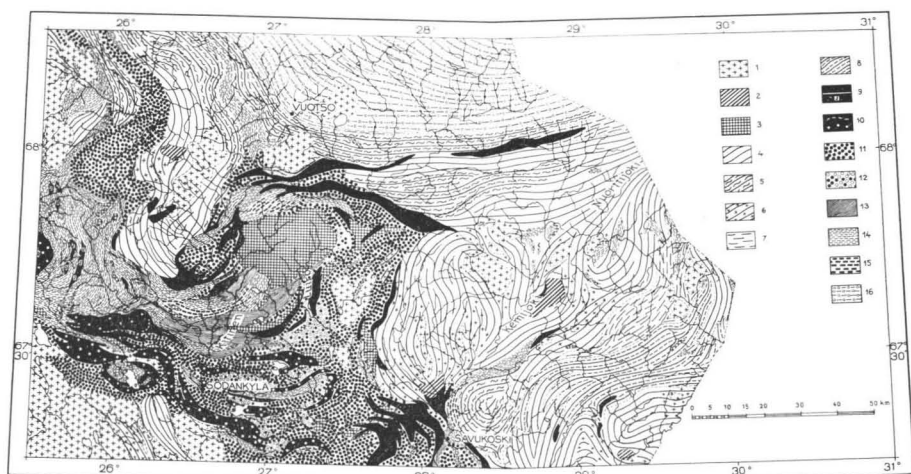


FIG. 3. Pre-Quaternary rocks in central and eastern Lapland according to Mikkola (1936, 1937). 1) Granites, 2) quartz diorites and granodiorites, 3) diorites, gabbros and ultramafic rocks, 4) granite gneisses and gneissose granites, 5) banded and mylonitic granite gneisses, 6) migmatites, 7) gneisses of Korvatunturi with subsilicic intercalations, 8) mica schists and mica gneisses of Tunta—Savukoski series, 9) quartzites and jasper quartzites, 10) quartzites and conglomerates of the Kumpu—Oraniemi series, 11) quartz feldspar and mica schists, partly alternating with subsilicic schists (or unknown because of lack of outcrops), 12) andalusite, staurolite and distenebearing mica schists, 13) phyllites and black schists, 14) greenstones and amphibolites, 15) agglomerates and pillow lavas, 16) granulites. Courtesy of R. Kujansuu and S. Leskelä.

Especially in the eastern parts of the greenstone massif, the metavolcanics are associated with minor occurrences of ultramafic plutonic rocks. They are mainly serpentinites and soapstones, which in places contain amphibole and olivine in abundance. On the eastern side of the greenstone massif there occur amphibole-chlorite rocks, which in certain spots undergo a transition into ultramafic rocks and agglomerates. Besides a substantial iron content, the amphibole-chlorite rocks are characterized by a high magnesium and rather low calcium content (Analysis 4).

Metasediments of residual character, among them the Sirkka and Kumpu conglomerates, overlie the greenstone and belong to the so-called Kumpu—Oraniemi formation. Along with the associated quartzites, they extend from the southern edge of the schist belt in Muonio commune to the middle of Sodankylä commune. The cobbles of the conglomerates consist of various schists and greenstones. The matrix contains predominantly quartz and, in addition, minor amounts of chlorite, plagioclase and carbonate. In the middle of the greenstone area there occur small-grained and dense jasper quartzites and associated stratified hematite iron ores. The jasper quartzites consist almost solely of quartz stained red by iron-oxide pigment. Occurring in association with them are also black schists and carbonate rocks. The quartzites of the schist area, which antedate the Kumpu—Oraniemi formation, are small-grained

and stratified. They are found in the eastern border zone up against the pre-Karelidic granite gneiss as well as elsewhere, like, among other places, the proximity of the syenite area of Central Lapland and the Kumpu—Oraniemi formation. These quartzites in many instances contain sericite and feldspar. The quartzites occurring in the eastern part of the schist area and known as Vasaniemi schists contain diopside, epidote and hornblende.

Along the middle course of the LUIRO and KEMI rivers and, as a narrow zone, in the southern part of the schist belt, there occur mica schists and gneisses containing  $Al_2O_3$ -rich minerals: staurolite, andalusite, garnet, sillimanite and kyanite. These rocks contain more magnesium than calcium and a slightly greater amount of potassium than sodium, the principal minerals being quartz, plagioclase, biotite and muscovite (Analysis 5). In western Lapland, there are large areas of sillimanite gneisses, which in places grade over into quartzites. Among the alkaline earths and alkali metals, the most abundant are magnesium and potassium; and in addition to the main mineral, quartz, there are slight amounts of microcline and biotite (Analysis 6). In the eastern part of the study area, there occur mylonitic mica-gneisses belonging to the Tuntsa—Savukoski supracrustal formation as well as, in many spots, aplitic, fine-grained quartzitic schists rich in mica.

The most noteworthy uniform limestone occurrence in the study area is at the mouth of Äkäsjoki in the commune of Kolari, its material consisting of nearly pure calcite. The smaller occurrences of limestone in central and eastern Lapland, on the other hand, are mainly composed of dolomites. The  $CaCO_3$  and  $MgCO_3$  contents of the calcite limestones are 79 to 95 % and 1.3 to 3.9 %, the corresponding contents of the dolomites being 24 to 61 % and 19 to 46 % (Mikkola 1941, pp. 213—214).

Plutonic rocks, the composition of which varies from granites to gabbros penetrate the schist belt of central Lapland in many places. Hornblende and pyroxene gabbros are common especially in association with greenstones and black schists. In addition to their notable iron content, they contain abundant magnesium and their principal mineral constituents are amphiboles, pyroxenes and plagioclases (Analysis 7). In western Lapland and in the northwestern stretch of Enontekiö, there are extensive areas containing granodiorites, syenites and diorites. Characteristic of their chemical composition are a high sodium and a moderate calcium content (Analysis 8). The principal minerals are the plagioclases, quartz, microcline and hornblende.

Taken as a whole, the pre-Karelidic granite gneiss in the east is quite a uniform formation, which consists of markedly gneissose rocks with a granitic composition. This formation has long forks extending to the northern side of the schist belt. Large granite areas occur on the southern and southwestern sides of the schist sequence and also in the northern part, with its so-called Hetta granite. The composition of the granites is marked by dominant amounts of potassium in comparison with the sodium and the alkaline earths (Analysis 9). Their principal mineral constituents are quartz, plagioclase, microcline and micas.

TABLE 2.

The chemical composition and mode of the chief rocks in the study area.

Analyzed	Mean values, %								
	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO <sub>2</sub> .....	49.9	49.4	55.7	42.7	56.0	85.0	50.5	64.8	73.7
Al <sub>2</sub> O <sub>3</sub> .....	13.2	14.1	14.2	6.9	22.3	8.6	16.3	14.5	13.7
Fe <sub>2</sub> O <sub>3</sub> .....	2.6	2.3	1.3	4.0	4.2	0.4	1.3	2.4	0.9
FeO .....	10.6	12.0	11.3	8.3	4.8	0.9	7.1	3.2	0.9
MnO .....	—	0.2	0.12	0.2	0.06	0.02	0.13	0.09	0.02
MgO .....	7.1	6.1	4.5	23.0	2.2	1.0	8.0	1.5	0.3
CaO .....	8.0	10.5	1.3	7.3	0.8	0.1	12.5	3.6	1.2
Na <sub>2</sub> O .....	3.2	2.3	3.7	0.5	2.2	0.5	1.8	4.5	3.5
K <sub>2</sub> O .....	0.6	0.6	1.6	0.3	3.1	2.4	0.2	3.4	4.6
TiO <sub>2</sub> .....	2.5	1.7	2.6	0.9	1.4	0.2	1.0	0.9	0.4
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	—	—	—	0.13	0.3	0.09
Mode									
microcl. ....						3—20		2—27	20—25
plagiocl. ....	27—35	24	13—48	0—4	0—31	0—5	22—40	26—63	33—38
quartz .....	0—11		11—33		19—36	62—84	0—1	2—35	28—42
muscovite ....					12—60	2—3			3—4
biotite .....		2	15—24		0—16	4—6			1—4
chlorite .....	5—23		0—48	20—48	3—11		0—1		
epidote .....	1—10						1—4		
amphibole ....	28—57	70	0—21	45—73			33—59	6—26	
pyroxene .....							0—23	0—7	
carbonate .....	0—3		0—1	0—3					
titanite .....	0—8	2						0—2	0—1
pyrite .....			0—13						
apatite .....				0—0.5				0—2	0—1

1. Greenstone, according to 8 analyses (Mikkola 1941, p. 260). Mode is based on 4 analyses (Hackman 1927, pp. 18, 23; Mikkola 1941, pp. 245, 247).
2. Amphibolite, according to one analysis (Mikkola 1941, p. 257).
3. Black schists, according to 4 analyses (Hackman 1927, p. 47; Mikkola 1941, pp. 206—210).
4. Amphibole-chlorite rocks, according to 3 analyses (Rankama 1939, p. 8; Mikkola 1941, pp. 238—239).
5. Felsic, mica-bearing schists, according to 3 analyses (mode according to 10 analyses) (Hackman 1927, p. 52; Mikkola 1941, p. 219—222).
6. Sillimanite gneisses, according to 3 analyses (Mikkola 1941, pp. 201—202).
7. Hornblende gabbros and pyroxene gabbros, according to 3 analyses (Hackman 1927, p. 24; Lokka 1934, pp. 26—27).
8. Syenites, granodiorites, diorites and Kangosjärvi gneiss, according to 6 analyses (mode according to 11 analyses) (Hackman 1927, p. 14; Rankama 1939, p. 9; Mikkola 1941, pp. 268—276).
9. Granites, according to 5 analyses (Hackman 1918, p. 76; 1927, p. 12; Lokka 1934, pp. 56—57; Mikkola 1941, p. 278).

## Ground water

### Ground water in till

Ground moraines are the commonest Quaternary deposits in the study area (Penttilä, Kujansuu 1964; Kujansuu 1966, 1967). Throughout the region, the till is rich in fine and medium sand; the content of finer fractions is rather slight (Fig. 4



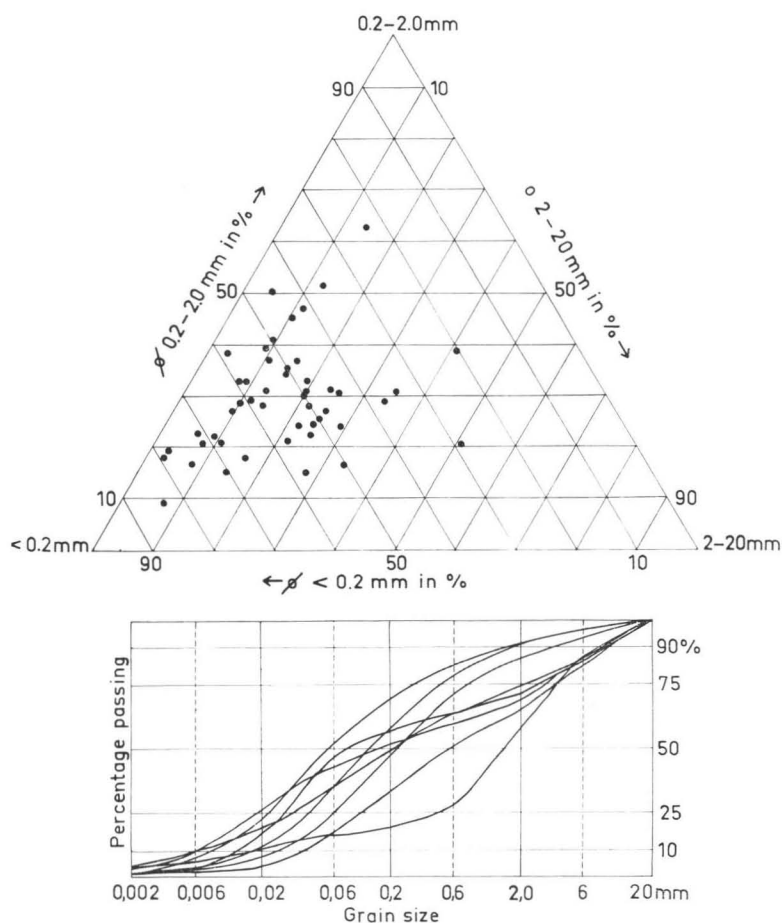


FIG. 4. Mechanical composition of till plotted in the triangle diagram and as selected cumulative curves.

and Kujansuu 1967, p. 20). The clay fraction ( $\phi < 2 \mu$ ) generally accounts for only a small percentage of the material.

On the average, the till has traveled but a short distance from its source, which means that in broad, uniform bedrock areas it reflects the petrographic composition of the bedrock (Okko 1944, p. 42). The tills can thus be classified into petrographic types corresponding to the varieties of rock composing the bedrock. Examples are the granitic till and greenstone till types (see Tanner 1915, pp. 14—15; Okko 1941, p. 632; 1946, Fig. 1). The till cover averages only from three to five meters in thickness (Hyypä E. 1960, p. 27). The thickest deposits are generally met with at the foot of hills, in river valleys and in other low-lying portions of the terrain, where

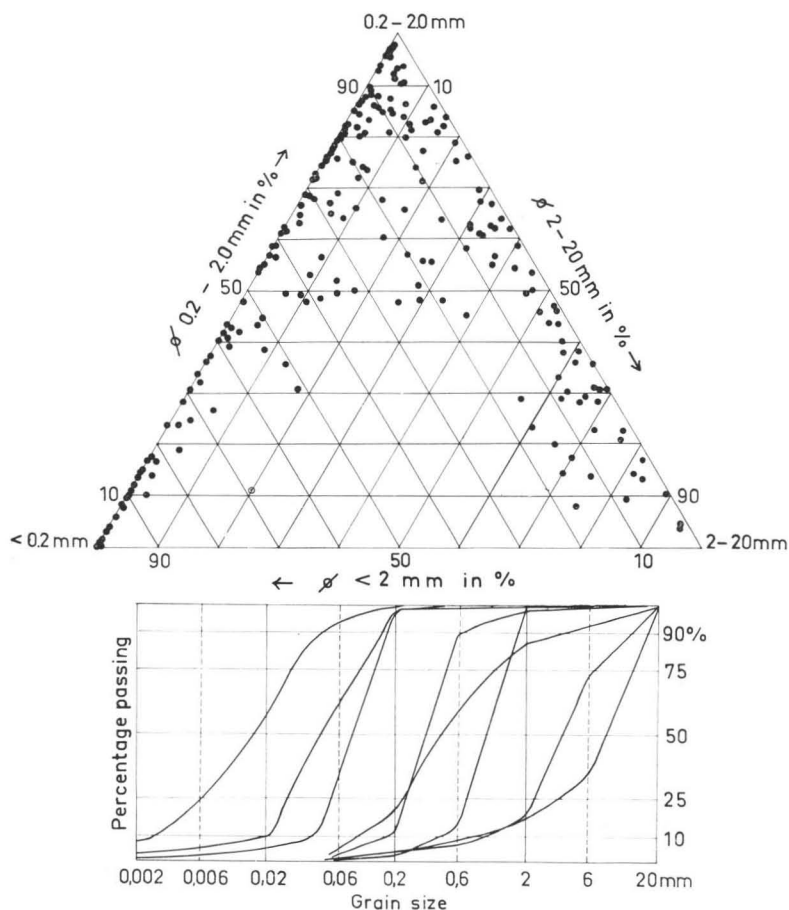


FIG. 5. Mechanical composition of glaciofluvial drift plotted in the triangle diagram and as selected cumulative curves.

the accumulations are likely to be dozens of meters thick. The till cover grades over into the underlying remains of the weathering crust and on the upper slopes of the hills, as the deposits thin out, into block fields. Especially in Enontekiö, there occur in many places independent accumulation forms of till, in which the glacial drift in many instances is coarse and contains lenses composed of sorted material, too (Kujansuu 1967, p. 18).

In the ground moraines, layers of sorted material quite commonly occur between till deposits of different ages (Kujansuu 1967, pp. 30—31). These layers extend in some places over quite broad stretches of ground, and along with the low content of fine fractions in the till, they make possible the abundant occurrence of ground water

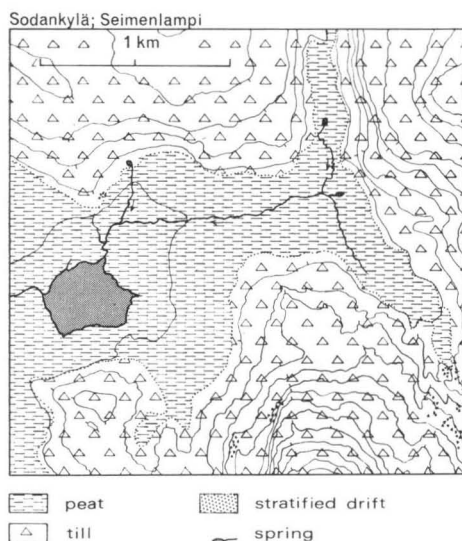


FIG. 6. Ground-water springs feeding brooks and lakes in hilly till-covered terrain.

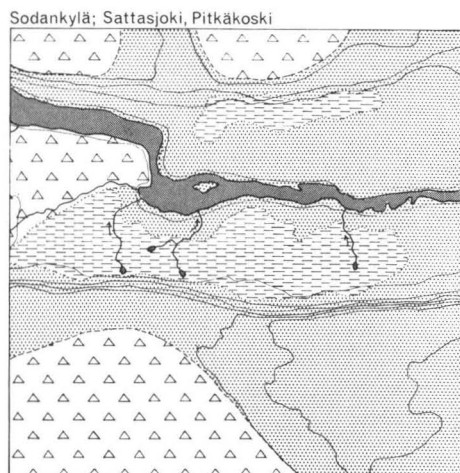


FIG. 7. Ground-water springs occurring at the foot of a glaciofluvial outwash plain.

in spots. The intercalated strata of sorted material in the till collect the ground water and act as aquifers. The ground water flowing in them is discharged at the base of hills or riverbanks, either as springs feeding brooks or as rather extensive seepage belts (Figs. 6, 8b and 8d). Groundwater surfacing as springs usually discharges at a rate of 1 to 4 l per sec, but when the intake area is extensive, the rate is apt to be as high as 10 to 20 l per sec. Zones of ground-water seepage occur everywhere at the foot of hills where the ground-water table meets the surface of the ground.

The ground water discharging in the peat lands from Quaternary deposits overlain by the peat cover is under slight pressure and usually forms pools extending down through the peat beds all the way to the minerogenic substratum (Fig. 8d). The peat borders of the crater-like pools measure in diameter as much as 10 m and may rise 0.5–1.0 m above the surrounding bog. They are grown over with mosses and stunted spruces requiring a favorable habitat. Springs of this kind are apt to be situated in a bog hundreds of meters from any hillside, and the flow away from the spring occurs either underneath the peat or as surface seepage on the bog.

Few studies have been made of the amounts of ground water occurring in till and obtainable from it. According to Vanhala (1960, p. 49), the quantity of ground water derived from till deposits (containing only minor quantities of fractions below 0,074 mm) is at least 15 per cent of the yearly precipitation. By determining in the study area the yield of springs discharging from the lower slope of a hill and measuring the intake areas of ground water, it may be estimated that at least 20 per

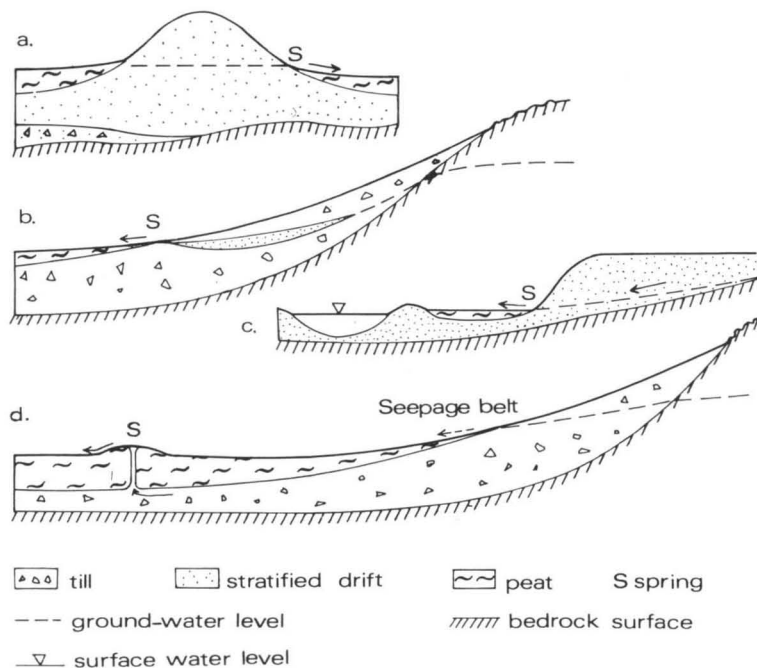


FIG. 8. Schematic cross sections showing how springs occur in the study area. b and d) Springs at the foot of a till-covered hill near the margin of a bog. Ground water collects into lenses composed of sorted glaciofluvial material within the till deposits (b). If the till is homogeneous, ground water seeps through to the surface in a broad belt, and, farther out in the bog, the ground water is apt to rise under slight pressure to form craterlike springs (d). a and c) Ground water is discharged at the foot of glaciofluvial outwash plains (c) and eskers (a) likewise over the lowest edge of the surrounding peat cover.

cent of the annual precipitation in a region with a till mantle is filtered to produce ground water.

According to Troedsson's (1955, p. 175) investigations in Central Sweden, the filtering of rain water to produce ground water does not take place on a broad front throughout an entire bed of till; rather do the rain and the gravitational water percolate down to the ground water table via the channels formed by plant roots and the more permeable boundary surface between the bedrock and its cover as well as through the portion of the till composed of blocks or sorted material. The evidence collected by Troedsson (1955, p. 151) indicates that the passage of water is locally influenced by, e.g., the porosity, the moisture content and grain size of the soil, the density of the illuvial horizon and the topography.

### Ground water in glaciofluvial deposits

The most notable amounts of ground water in the study area occur in eskers as well as deltas and sandurs composed of glaciofluvial material and forming in places extensive outwash plains in preglacial river valleys (see Kujansuu 1967, Fig. 6). The eskers follow in the main the direction of movement of the last glaciation from the ice divide. In advancing, the ice sheet followed the path of least resistance and cleared the tectonic fracture valleys and other low-lying tracts in the terrain. Meltwaters later collected in these valleys and deposited the material of the eskers at the bottom or along their sides. Only in rare instances do the eskers cross the higher uplands or hills. They vary greatly in structure and material composition (Kujansuu 1967, pp. 38—39). The components vary from fine sand to boulders. A typical material is medium sand and gravel containing some pebbles and blocks (Fig. 5 and Kujansuu 1967, Fig. 8). In quite a few cases, the material is poorly sorted or the ridge formation is overlain by till.

In the eskers of small size and consisting of deposits of poorly sorted material, there is generally ground water in scanty quantities. In the event that an esker stands on a base of till or rock above the ground-water table, it cannot accumulate ground water, either. By contrast, considerable amounts of ground water are likely to occur in large esker formations of highly sorted material situated in valleys. The esker kettles in such formations often contain pools of clear water, which indicate the level of the ground-water table. An esker situated in a valley tends to collect the ground water from higher surroundings. The ground water flowing over the peat rim at the foot of the esker forms in places springs (Fig. 8a), discharging as much as 10—20 l per sec.

Significant areas of occurrence of ground water are alluvial plains composed of outwash — which dates back to the stage of deglaciation. They fill the lower-lying places in the terrain and fracture zones and, especially, preglacial river valleys. Along the margins of large rivers, these formations occur as extensive flat fields, the thicknesses of the strata of which vary from a few meters to several dozens of meters. On the whole, the typical thicknesses are in the order of 10 to 20 meters. Underlying the sorted material are till deposits, which often contain boulders or, then, without intervening strata, more or less weathered bedrock. The river beds, which have dug their way through easily eroded deposits of sand and gravel, form rapids in many places. The grain size of the outwash material varies greatly, but fine material nevertheless occurs more abundantly than in the eskers. The average composition is that of medium sand and of gravelly sand. The deposits out of which the eskers and alluvial plains are built are generally loosely packed, but their density increases with depth.

Extensive outwash plains, which occur in the river valleys and surrounding terrain, are apt to contain abundant ground water. This calls, however, for a sufficient thickness of the deposits beneath the ground-water table. An outwash plain of the valley-

filling type tends, like the eskers, to collect the ground water from higher surroundings when the ground water flow takes place in the direction of the river (see Hausen 1948, Fig. 1). Yet, it is common for the deposits to be situated at a level above the water table of the river or the ground-water table on a poorly permeable base of till or bedrock, over which a thin layer of subsurface water flows, forming springs at the foot of the river bank (Fig. 7 and 8c). Water-table springs of the type described also occur in alluvial sand-gravel deposits of valleys in Norway (Skjeseth 1957 Fig. 3A).

In the Sodankylä area, the proportion of the annual precipitation producing ground water in sand and gravel has been observed to range from 42 to 61 % (J. Hyypä 1962, p. 25). In southern Finland, the percentage is 22 to 28 in areas covered with sand and gravel of a stony character (Vanhala 1959, p. 16). In the case of eskers, in general, the figure is 50 % or lower in Finland (Sederholm 1909, p. 15). According to Brömssen's (1968, p. 107)<sup>1</sup> calculations, it lies below 70 % in Sweden.

### Ground water in bedrock

In western and central Lapland, the bedrock is nearly everywhere overlain by Quaternary deposits and peat beds. Only in the Enontekiö uplands and elsewhere in the fell country are there extensive uncovered tracts of bedrock. Very little rock with an unbroken surface is met with, for mechanical weathering has generally shattered it to form block fields (see Tanner 1938, pp. 665—666; Ohlsson 1964). Such block fields occur not only in the fells but also on the summits of wooded hills and even on level tracts. Remains of the preglacial weathering crust are encountered in many places in central Lapland. Such remains occur most commonly in sheltered places like the bases of fells and hills or in tectonically depressed areas, where the ground has escaped glacial abrasion (Kujansuu 1967, pp. 23—24). In places the weathering crust is apt to reach down to a depth of 50—100 meters (Tanner 1938, p. 456, 662; Virkkala 1955, p. 395).

The solid bedrock contains only 0.5 to 1.0 per cent of pore water (Holmsen 1953, p. 10). The occurrence of ground water in bedrock is made possible, however, by the existence of the weathering crust and, especially, networks of fissures and fractures (Nordenskjöld 1896; Hausen 1948, Fig. 6; Skjeseth 1955, Fig. 3). Ground water can be obtained most abundantly out of thoroughly shattered bedrock, especially fracture zones broken up to considerable depths by tectonic movements. Three types of fracturing chiefly occur in the bedrock: irregular fissures, believed to originate from temperature variations on the surface, horizontal jointing, known as skeeting, and tectonical jointing (Holmsen 1956, p. 41). As far as the occurrence of ground water is concerned, the latter two types are the more important. The weathering crust and the block fields greatly promote the filtering of rain water in the production of gravitational and ground water.

Settlement in Lapland has predominantly gravitated to the banks of rivers and the shores of lakes, which are largely situated in fractured and depressed bedrock zones

or their marginal areas. The wells drilled into the bedrock have generally yielded ground water. Only very seldom has the bedrock proved to be so solid as to be barren of ground water. In river valleys it has first been necessary in many places to dig through a soil cover — most commonly composed of till — several dozen meters thick in the quest for ground water in the bedrock. The average depth of over 200 bored wells in the study area is 33 meters (the average thickness of Quaternary deposits, 6.9 m) and the mean yield 2 000 liters an hour. The largest yield amounts to 7 000 l per h. The pumping tests have almost invariably been of short duration, however, and the capacity of the pump has not always sufficed to measure the total yield. In comparison, the average depth and mean yield of more than 1 100 drilled wells in Precambrian bedrock in different parts of Finland, calculated according to the material presented by Laakso (1966), are 68 m and 2 460 l/h, respectively. The corresponding figures in Norway (Holmsen 1953, p. 10; Bryn 1961, Fig. 5) and southern Sweden (Wenner 1951, p. 1102) are approximately 40–48 m and between 700–2 170 l/h.

In the area covered by the present study, no noteworthy variations in yield caused by the rock composition of the bedrock were observed. In Norway, Skjeseth (1953, p. 22) has observed soft schists to yield ground water in only very limited amounts, whereas the yield from harder quartzites and sandstones is abundant; and Bryn (1961, p. 19) has found that more ground water can be obtained from bedrock consisting of gneiss than from massive granites. When the surficial part of the bedrock is particularly weathered, the yield may be considerable. In the study area no correlation could be perceived between yield and depth. This is understandable because the fissures and fractures occur irregularly in bedrock and begin to be closed after a depth of between 80 and 100 meters (see Troedsson G. T. 1936, p. 434), which means that deeper down the chances of obtaining ground water diminish.

### Variations in ground-water table and the temperature of ground water

The vertical movements of the ground-water table in the study area and elsewhere in Finland fairly consistently follow a certain annual rhythm controlled by the winter, spring and summer seasons (Hyyppä, J. 1962, p. 39; Johansson, Soveri 1965, p. 19; see also Okko 1967, p. 49). The winter season begins with the freezing of the ground and the cessation of the abrupt fluctuations of the ground-water table caused by the fall rains. During the winter season, the ground-water table steadily sinks lower. The spring season begins after the ground has lost its snow cover and thawed out; it is then that the water percolating down into the ground causes a vigorous rise of the ground-water table. The spring season accounts for the extremes in the fluctuations of the ground-water table. The summer season begins with the spring peak and terminates with the start of the winter season. The summer season is generally the most restless time in the movements of the ground-water table.



The timing of the different seasons depends not only on climatic factors but also on the topography, exposure conditions, vegetation, geological structure and grain size of the Quaternary deposits and bedrock and the occurrence of frost. In the study area the depth of the ground frost in sand and gravel covered by snow usually varies between 70 and 120 cm (Kaitera, Helenelund 1947, p. 392; Karjalainen 1965, p. 48), but in northern Sweden it has been calculated to reach even depths of 4.9 m in gravel and 2.2 m in sand (see Janson 1968, p. 60). Ground frost binds considerable quantities of gravitational water; accordingly, it likewise has the effect of lowering the level of the ground-water table. In the spring, the slow thawing of the thick ground-frost layer prevents in places the passage of meltwaters and floodwaters into the part of the ground occupied by ground water; but, on the other hand, as the frost does melt it adds to the quantity of ground water, causing the table to rise. The ground frost thaws out in the study area Sodankylä at the turn of the months of May and June (HVK 1968, 19, p. 89), which means that the ground-water table is apt to be on the rise as late as the end of May or the first half of June (see Hyyppä, J. 1962; Johansson, Soveri 1965, p. 20). Slight rainfall in the summer, when the rate of evaporation is high, does not significantly affect the movements of the ground-water table. Fall rains do have a significant effect, because evaporation during this season is substantially lighter.

In the area investigated, the fluctuations of the ground-water table are generally greater in till deposits than in sorted material. Larsson (1962, p. 47) has made similar observations in southern Sweden. In the study area the amplitude of the fluctuations in the ground-water table in flat ground or in gentle slopes seldom exceeds two meters (see Hyyppä 1962; Johansson, Soveri 1965, Table 2).

It is generally held that the temperature of the ground water in Finland is close to the mean annual atmospheric temperature. At 176 sampling sites in the region investigated, the temperature of the ground water discharged from Quaternary deposits overlying the bedrock was in half the measurements  $+3.1^{\circ}$  or below (see the tabulation below), which is a couple of degrees above the mean annual temperature.

Min	10 %	25 %	50 %	75 %	90 %	Max
$1.7^{\circ}$	$2.4^{\circ}$	$2.8^{\circ}$	$3.1^{\circ}$	$3.7^{\circ}$	$4.3^{\circ}$	$5.0^{\circ}\text{C}$

Some of the measurements were made in the winter, and no fundamental differences from those made in summer could be perceived (23 determinations, min.  $2.2$ , median  $2.8$ , max  $4.0^{\circ}\text{C}$ ). According to Kahri's (1963, Fig. 1) studies, the temperature of the ground water in central Finnish Lapland is around  $+3.5^{\circ}\text{C}$  or slightly below.

## CHEMICAL COMPOSITION OF GROUND AND SURFACE WATERS AND CONTRIBUTING FACTORS

### Specific conductance, pH, bicarbonate and total hardness (calcium and magnesium)

#### Distribution

The specific conductance of natural fresh water is directly proportional to the amount of electrolytes dissolved in the water. The effect of different ions on specific conductance, however, differs to some extent (see Freier 1958, pp. 161—165). The composition of the waters in the study area is uniform to the extent that the specific conductance may be regarded as an accurate measure of the electrolyte content. The components that do not occur in ion form in water, such as the monomeric or complex colloidal compounds of iron, silica and humus, have no significant effect on specific conductance.

The combined content of bicarbonates and carbonates was determined as total alkalinity by titrating to the pH value of 4.5 (p. 10). In water below this pH value, bicarbonates no longer occur significantly, for they decompose into carbonic acid and free carbon dioxide. Theoretically, in water with a certain carbonate content, at pH reading of 6.4 the  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3 + \text{CO}_2$  contents are equal (Hutchinson 1957, p. 657, Krauskopf 1967, p. 49—50). Roughly between pH 6 and pH 9, bicarbonate is of greatest quantitative significance. The dissociation of bicarbonate into carbonate is effective but largely above the last-mentioned pH value (Davis, de Wiest 1966, p. 107). Because pH values higher than 9 hardly occur in the study area, alkalinity in practice represents exclusively the bicarbonate content.

The total hardness is chiefly produced by salts of calcium and magnesium, which, being elements of a similar chemical character, generally occur together. Therefore the cumulative distribution curves of total hardness, calcium and magnesium in the waters of the study area are quite similar in shape (Figs. 12—14). The curves show that the correlation between total hardness and calcium is notably more distinct than that between total hardness and magnesium. Hence calcium seems to play a bigger part in determining the level of total hardness. However, the possible inaccuracy in determinations of magnesium (see p. 12) may have a decreasing effect on the correlation. Abundant iron has this effect too, although only in a minor part of the samples of humus-rich surface waters and ground water occurring deep in bedrock.

The specific conductance, pH, bicarbonate content and total hardness of the natural waters of the study area stand in close correlation to each other: hence the cumulative distribution curves are quite similar in shape (Figs. 9—12). In this paper the collective expression »main factors» is used to depict the significance of these properties.

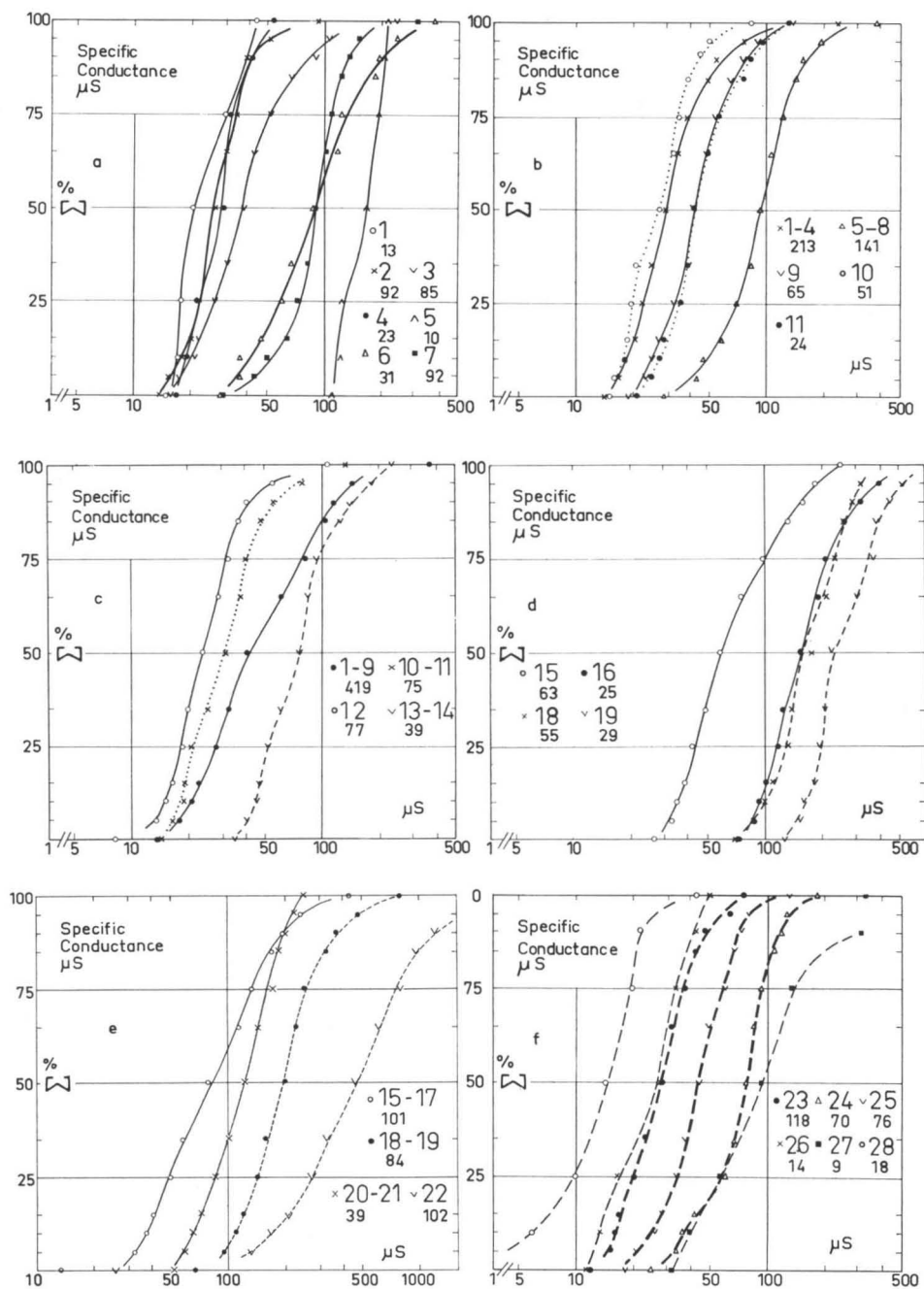
The values of each of the main factors of ground water discharged from till deposits are on the average at their lowest level in the quartzite areas (group 1, Figs.

9—12, a, and appendix 1) and slightly higher in the granite (group 2), granodiorite and diorite areas (group 4). In the bedrock areas composed chiefly of silicic schists (group 3), the values are on a higher level than in the foregoing areas. In bedrock areas composed of black schists (group 6) and greenstones (group 7), the values of the main factors in ground water are higher than in the different areas of silicic bedrock. The highest values of the main factors occur in the ground water of the limestone areas (group 5). The standard deviations of the determinations are slightest in ground water of granite areas (group 2, appendix 1); in areas of black schists they are greater (group 6) than in areas of greenstones (group 7).

The specific conductance values and bicarbonate contents of ground water discharged from till deposits in subsilicic bedrock areas (groups 5—8, Figs. 9—14, b, and appendix 1), are roughly 3-fold, the pH about 0.75 unit higher and the calcium and magnesium contents approximately 5 and 2.5 times, respectively, higher in comparison with the ground water of silicic bedrock areas (groups 1—4). Like the concentrations, also the standard deviations of the determinations are greater in ground water of subsilicic bedrock areas (groups 5—8, appendix 1). The values of the main factors of ground water discharged from glaciofluvial material (group 10 and 11, Figs. 9—12, b, are likewise greater in subsilicic bedrock areas, although the differences are not as great as in the ground water in till deposits. The values of the main factors of the ground water occurring in till deposits (groups 1—9, Figs. 9—12, c) are distinctly on a higher level than those of ground water contained in sorted glaciofluvial material (groups 10—11). Also the standard deviations of these determinations are greater in the case of ground water occurring in till deposits (groups 1—9, and appendix 1). The differences in the composition of ground water occurring in till and glaciofluvial material are most marked in areas of subsilicic bedrock (groups 5—8 and 11, Figs. 9—12, b). The values of the main factors of the perched water or ground water occurring near the surface of the ground (group 12, Figs. 9—12, c) are lower than those of ground water proper.

Compared to the ground water occurring in the fissures and fractures of silicic bedrock (group 15, Figs. 9—14, d, and appendix 1), the specific conductance values of ground water occurring in subsilicic bedrock (group 16) are approximately 2.5-fold, the pH values about 0.60 unit higher, the bicarbonate content 2-fold, and the calcium and magnesium contents 5 and 2 times greater. Also the standard deviations of the determinations are larger in ground water of subsilicic bedrock (group 16, appendix 1).

The specific conductance and total hardness values of ground water slightly contaminated by agricultural settlement, ascertained with the aid of nitrate and chloride concentrations (see p. 15), are significantly greater than those of intact ground water occurring in a corresponding geological environment (groups 13—14, Figs. 9, 12 c, Bicarbonate, by contrast, is not a constituent that strongly increases along with contamination (groups 13—14, Fig. 11, c). In slightly contaminated ground water occurring in bedrock (group 18 and 19, Figs. 9—12, d), the main factors are still distinctly greater in subsilicic rocks; in heavily contaminated waters (group 22), the



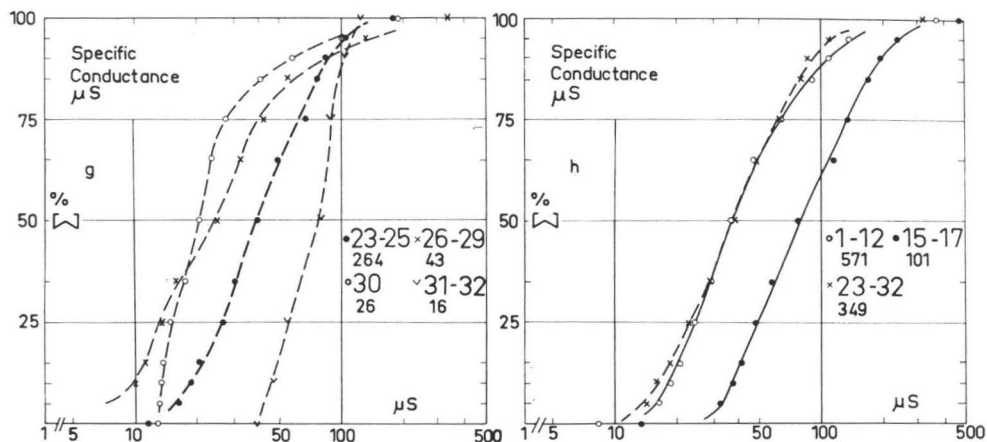


FIG. 9. Cumulative curves showing the frequency distribution of specific conductance values of ground and surface waters.

Continuous line = natural ground water discharged from till deposits and occurring in bedrock. Dotted line = natural ground water discharged from glaciofluvial deposits. Broken line (closely spaced) = ground water contaminated by agricultural settlement. Broken line (sparsely spaced) = surface water.

The diagrams show the distribution in different group combinations. For details, see Table 1 and text on p. 30—35.

effect of the rocks is not discernible. As the concentrations indicating the contamination rise, the values of main factors increase markedly, except the pH values, which decrease slightly (groups 13—14, 18—19 and 22, Figs. 9—12). With increasing contamination, also the standard deviations of determinations become greater (appendix 1). It is only natural that contamination should be strongest in electrolyte-poor, acid ground waters (group 18).

Compared to areas of silicic bedrock (group 23, Figs. 9—14, f, and appendix 1), the specific conductance values of brook and river waters discharged from subsilicic bedrock areas (group 24) is approximately 3-fold, the pH 0.50 unit higher, the bicarbonate content 2-fold and calcium and magnesium contents roughly 3 and 2 times higher, respectively. The standard deviations of the determinations are greater in more electrolyte-bearing waters (group 24, appendix 1) than in dilute waters (group 23). The same kind of correlation is observed in more stagnant surface waters, such as small lakes and ponds (group 26 and 27, Figs. 9—10, f). On the average, the lowest values of the main factors occur in the esker pools and ponds of areas of silicic bedrock (group 28, Figs. 9—12, f). The standard deviations of the determinations of the specific conductance and pH values are substantially higher in lake and pond waters (groups 26—29, appendix 1) than in flowing surface waters, such as small rivers and brooks (groups 23—25). This is due to the equalizing effect of flow on the concentration differences in water.

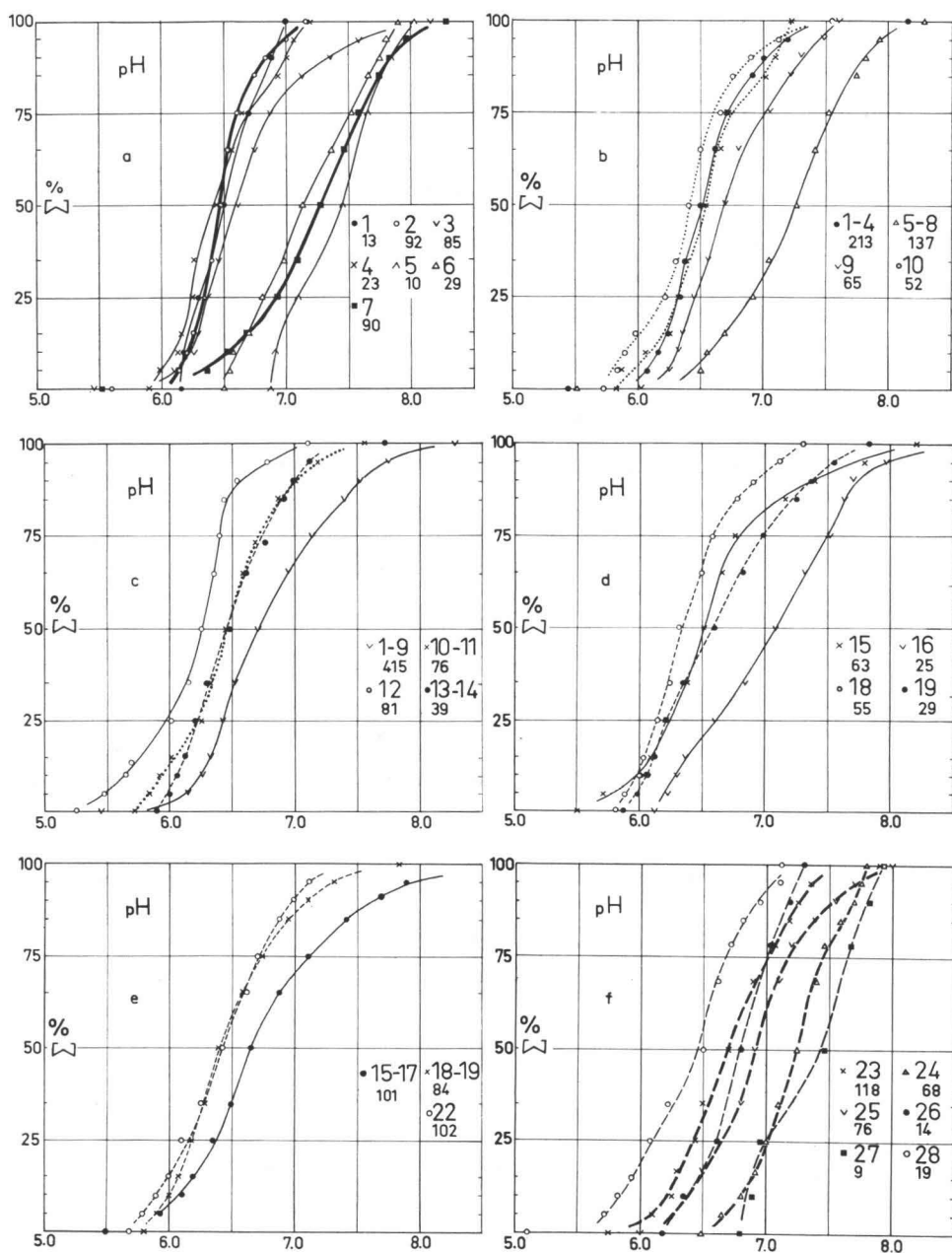


FIG. 10. Continued on next page.

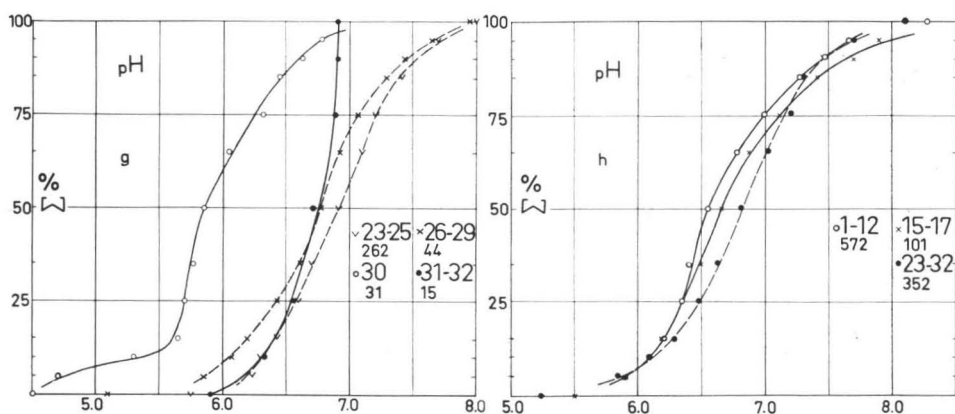


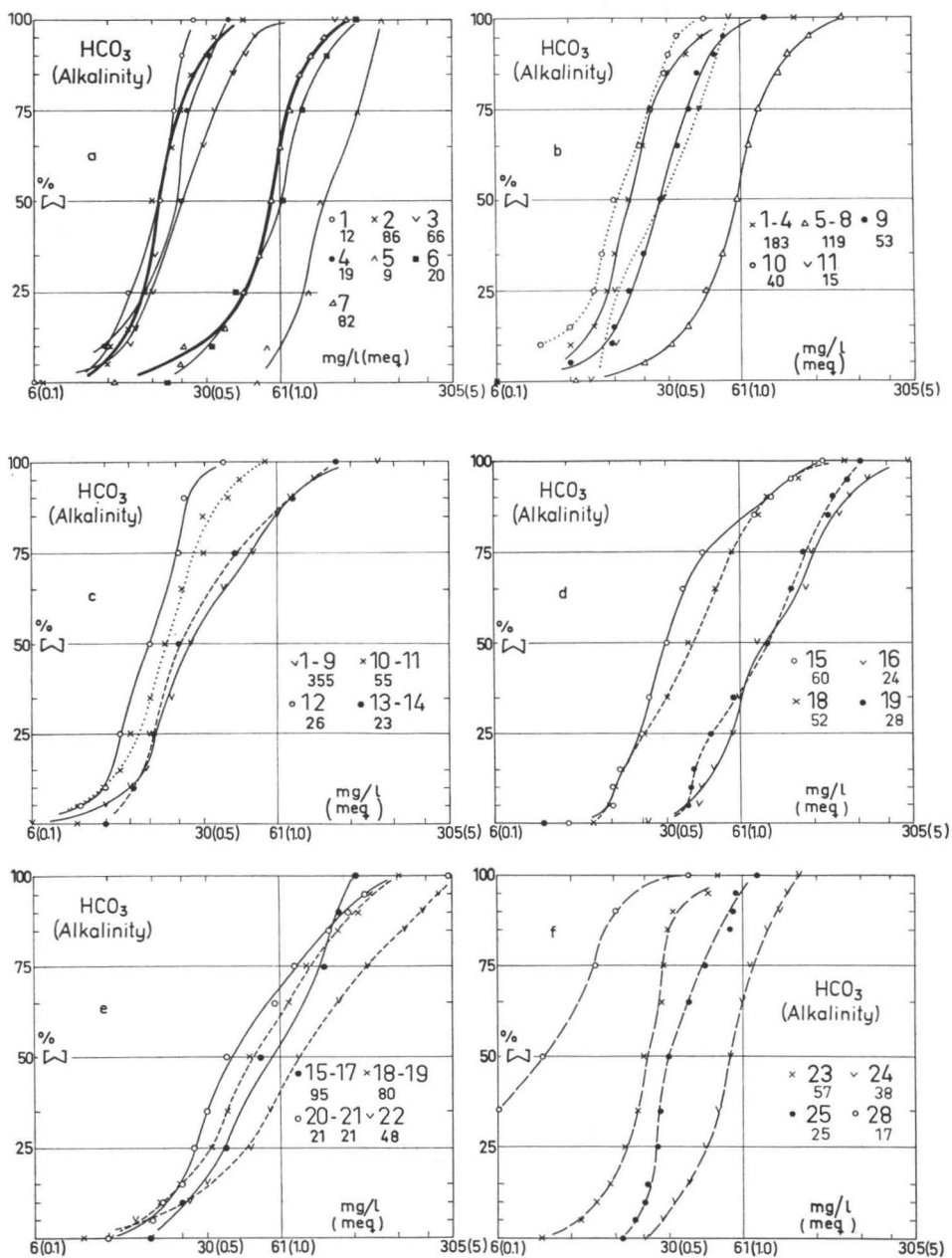
FIG. 10. Cumulative curves showing the frequency distribution of pH values of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 30—35.

The water standing or flowing on the surface of bogs is quite poor in dissolved ionic matter and has a low pH value (group 30, Figs. 9—10, g). By contrast, the ground water discharged from underneath peat beds into bog drainage trenches contains substantial amounts of electrolytes (groups 31—32, Fig. 9, g), although this water is also mixed with humus-bearing waters from the bog surface.

The values of the main factors of ground water discharged from all the Quaternary deposits sampled correspond in magnitude to the values of surface waters (groups 1—12 and 23—32, Figs. 9—12, g, h). The standard deviation of the determinations is nevertheless slightly larger in ground water (groups 1—12, appendix 1); hence the local concentration peaks or minima of ground water level out in surface waters (groups 23—32). The equality of the medians of the main factors in discharged ground water (groups 1—12, appendix 1) and surface waters (group 23—32) suggests that no actual weakening of the concentrations takes place at the change from ground water into surface water. The main factors of the ground water occurring in the fissures and fractures of the bedrock (groups 15—17, Figs. 9—12, g, h), as well as, the standard deviations (appendix 1) are greater than those of both ground water discharged from Quaternary deposits (groups 1—12) and surface waters (groups 23—32).

### Factors contributing to the specific conductance values

In the humid climate prevailing in Lapland (p. 16), physical weathering is an intensive process (see Ohlsson 1964). Combined with glacial abrasion, it has paved the way for chemical weathering by pulverizing the mineral matter. The dissolved oxygen and carbon dioxide as well as humus material promote weathering by participating in the reactions and reducing the pH value of the gravitational and ground water.





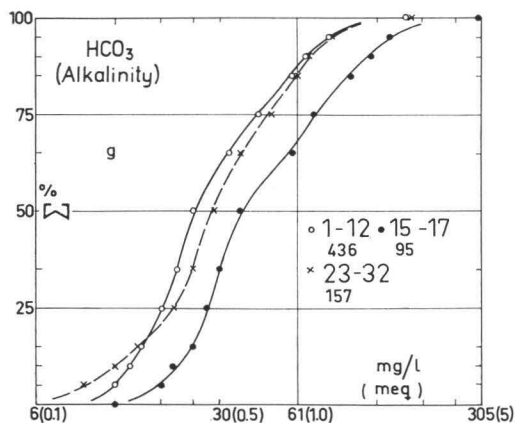


FIG. 11. Cumulative curves showing the frequency distribution of bicarbonate concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 30—35.

The chemical weathering is at its most intense in the surficial portion of the ground, where the action of the foregoing factors is most effective (see, e.g., Tamm 1930; Aaltonen 1935; Eriksson E., Khunakasem 1968, Fig. 1). It takes place in many different ways, depending on the nature of the mineral undergoing the process and the environmental factors (see, e.g., Reiche 1950; Keller 1957; Barshad 1964, pp. 35—41).

The weathering sequence of the different silicate minerals, or the relative »stability principle», follows in the main Bowen's reaction series in that the minerals that had crystallized at the highest temperatures are the most resistant (see, e.g., Goldich 1938, p. 56, Pettijohn 1941, p. 618, Loughnan 1962, p. 288). Thus, according to the stability principle the mafic minerals are more susceptible to weathering than are the felsic minerals. So mafic minerals form more weathering products, the soluble components of which are released into gravitational, ground and surface waters.

Soluble weathering products are removed as ions, molecules and colloids, whereas the insoluble matter remains in place or is carried away in suspension. In humid conditions, the clay minerals of the kaolinite group are considered to be decomposition products of feldspars and micas (Goldschmidt 1922, p. 30, E. Eriksson, Khunakasem 1968, p. 112). In the fine-grained material of clays and tills in Finland, however, the amounts of these minerals have been observed to be scanty, the main portion being hydrous micas, illites, vermiculites and chlorites (Soveri 1956; Soveri, Hyyppä J. M. 1966). Ferric iron, aluminum and silica released in weathering are partly retained in soil (see, e.g., Aaltonen 1935; Jauhiainen 1969).

The amount of mafic minerals, which are rather susceptible to weathering, in the bedrock and Quaternary deposits determine predominantly the amount of dissolved matter in the natural waters of the area investigated. Thus a characteristic feature of ground water of granite areas, which contain mafic minerals in only small amounts, is their low specific conductance value, that is, low electrolyte content. The same feature has also been observed elsewhere in other granite areas, e.g., in Sierra Nevada

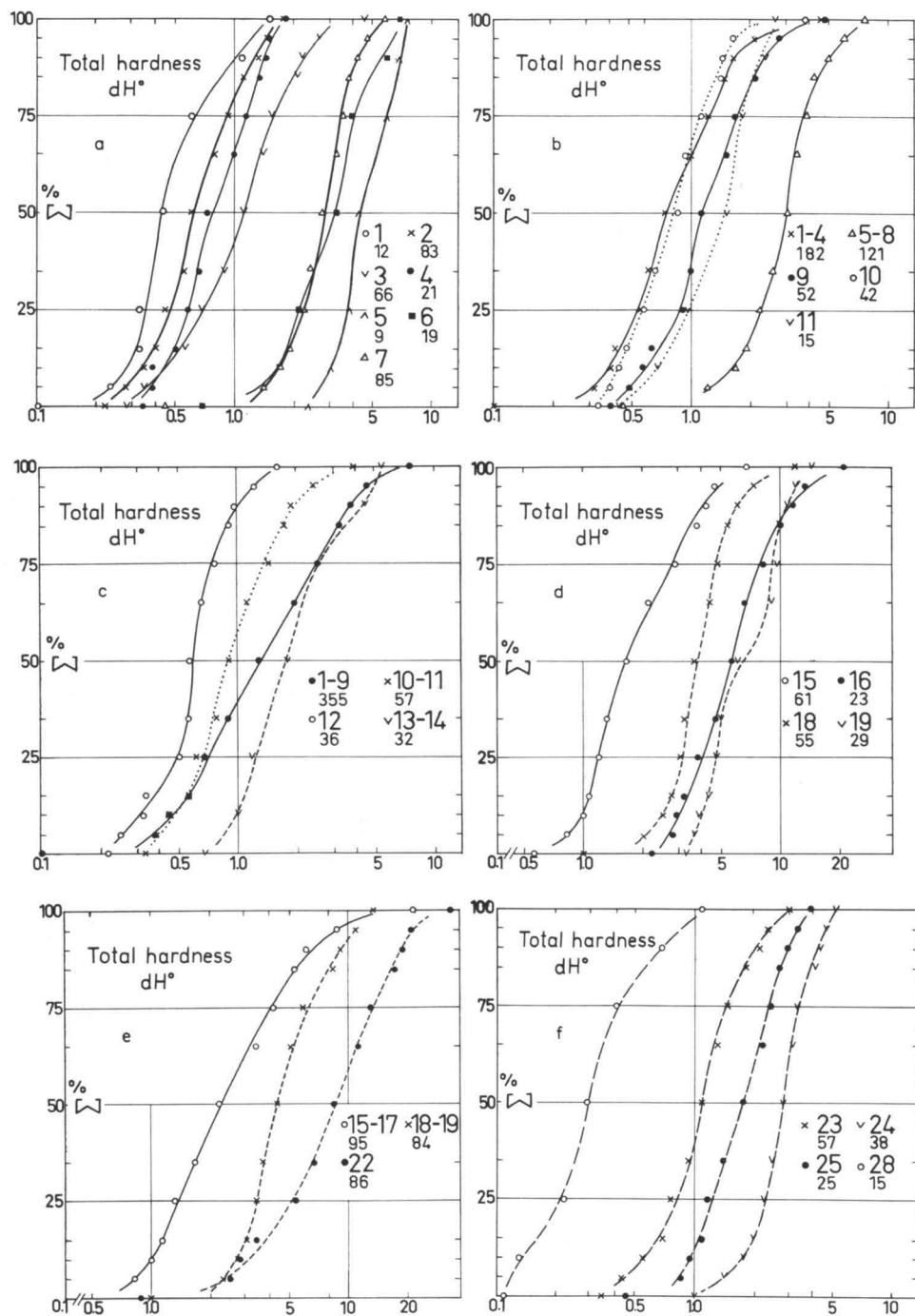


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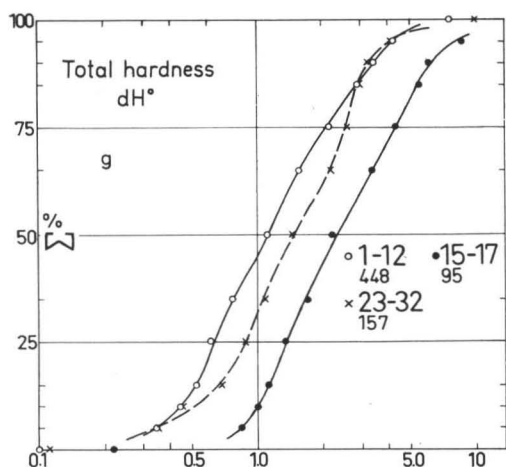


FIG. 12. Cumulative curves showing the frequency distribution of total hardness values of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 30—35.

(Feth, Roberson, Polzer 1964, p. 1, 16). The ground water of subsilicic greenstone and black schist areas in Central Lapland, on the other hand, contains many times more electrolytes than that of granite areas. Vuorinen (1944, Tables 7—9); J. Hyypä (1959a, p. 64) and Lahermo (1969) likewise report that in localities where the bedrock and the overlying deposits consist of subsilicic rocks, the ground waters are appreciably higher in electrolyte content than in areas characterized by silicic varieties of rock. Viro's (1955, p. 33) calculations dealing with river waters also show that leaching affects subsilicic rocks more than silicic rocks. According to Troedsson (1952, Table 3, 1955, pp. 95—96), this is especially true of the bedrock areas containing carbonates.

In black schists and greenstones, the carbonates and sulfides occurring in dissemination or as substantial deposits cause an increase in the electrolyte content of the ground water. The strength of the carbonation is revealed in the high content of dissolved ionic matter in the ground water of limestone areas. In areas of mainly silicic schists (group 3), the greater electrolyte content of ground water, as compared to areas of quartzites and granites, is influenced by inclusions of amphibolites and gabbros, or less frequently, carbonates occurring within these schists.

The glaciofluvial material, having been transported from afar, represents a mixture of different varieties of rock (Virkkala 1958; Matisto 1961). For this reason and because of the low content of fine-grained fractions in the material, the electrolyte content of ground water discharged from sorted material does not reflect the composition of the local bedrock as closely as does ground water occurring in till deposits, which better represent the local rock complex. Besides, sorted material generally no longer contains carbonates or other easily weathered minerals in abundance (see Repo, Winterhalter 1968, p. 122).

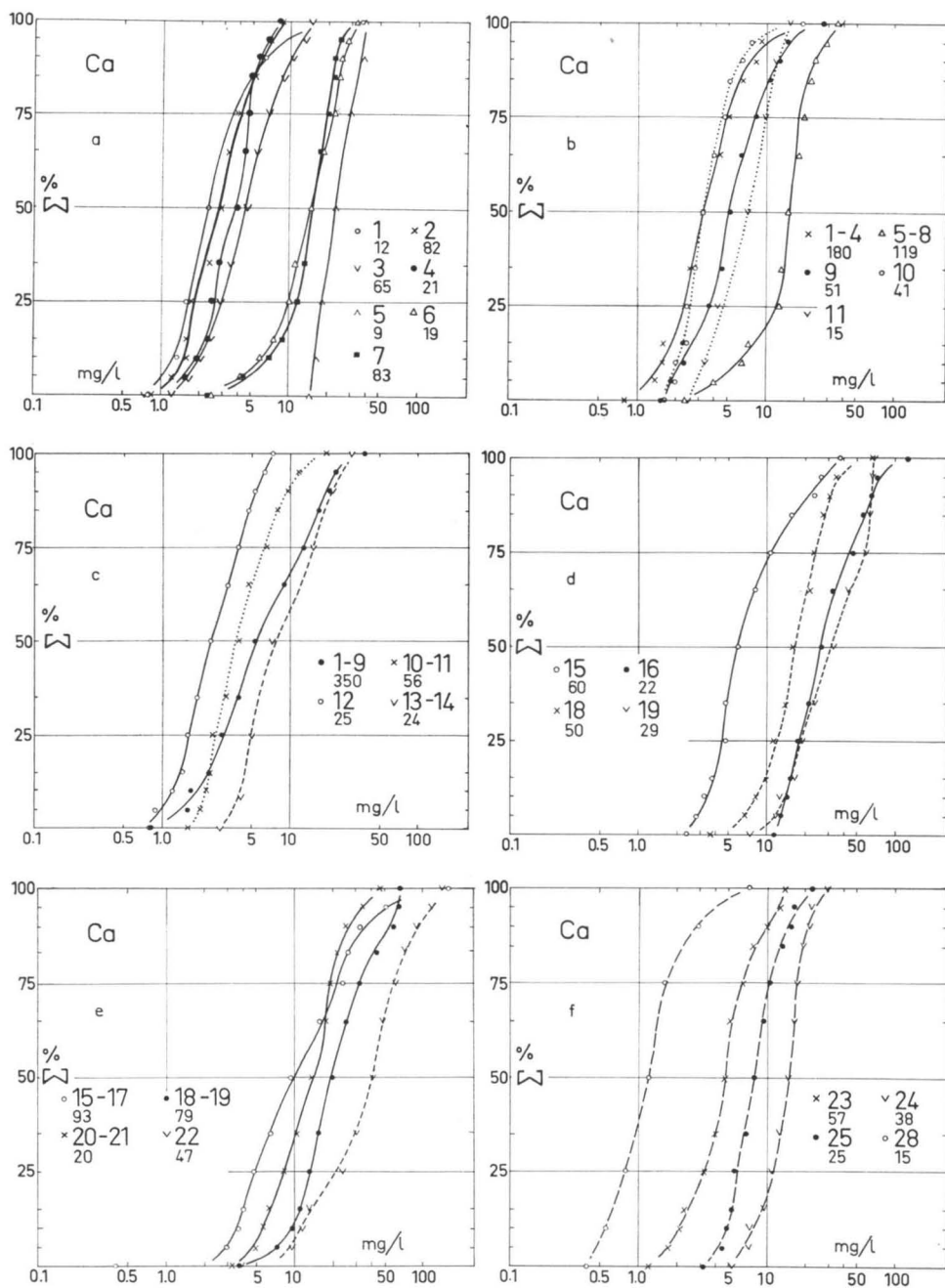


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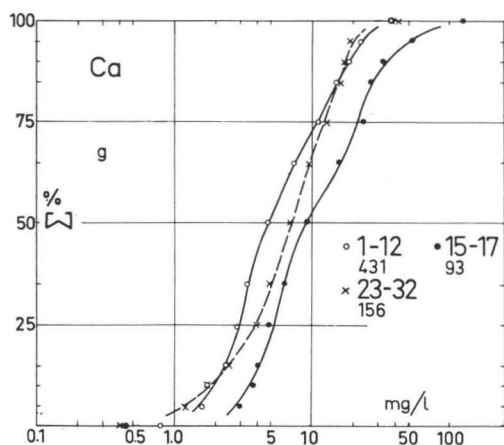


FIG. 13. Cumulative curves showing the frequency distribution of calcium concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 30–35.

With decreasing grain size, the specific surface of the mineral grains increases markedly, whereby the weathering action becomes intensified. Therefore, a higher content of fine-grained fractions in till material in the study area is reflected in the higher electrolyte content of ground water compared with ground water in stratified drift. Also Natukka (1960, 1963); Hyypä J. (1969 b, p. 91) and Lahermo (1969) have observed the ground water occurring in eskers and other glaciofluvial deposits to be poorer in dissolved ionic matter than that contained in till deposits. In the study area, this is true especially of subsilicic bedrock areas, whereas there is no great difference in the electrolyte contents of ground water occurring in till and in sorted glaciofluvial material in areas of silicic bedrock. Hence the texture or the degree of sorting undergone by material composed predominantly of felsic minerals is not of significance in regulating the quality of ground water. In silicic bedrock areas the water in esker pools and ponds contains exceptionally few electrolytes; accordingly, the texture of deposits is of significance in determining the electrolyte content of surface waters too.

In the study area, the low electrolyte content of perched and ground water occurring in the surface layer of the ground is affected by the weathering undergone by the eluvial horizon and, furthermore, the rapid percolation of water. According to Aaltonen (1937, p. 31), the surface of the ground is slightly weathered and leached as deep as 1.0 meter. Moreover, rains dilute the ground water near the surface more than deeper down. The water standing or flowing on the surface of bogs is quite poor in dissolved ionic matter, because it predominantly collects directly from rain water. The ground water occurring underneath the peat cover percolates quite slowly in places, which gives plenty of time for the dissolving process. The prevailing reducing conditions and the humus materials released from the peat promote the solution of, among other components, ferrous iron. Troedsson (1955, p. 64) has

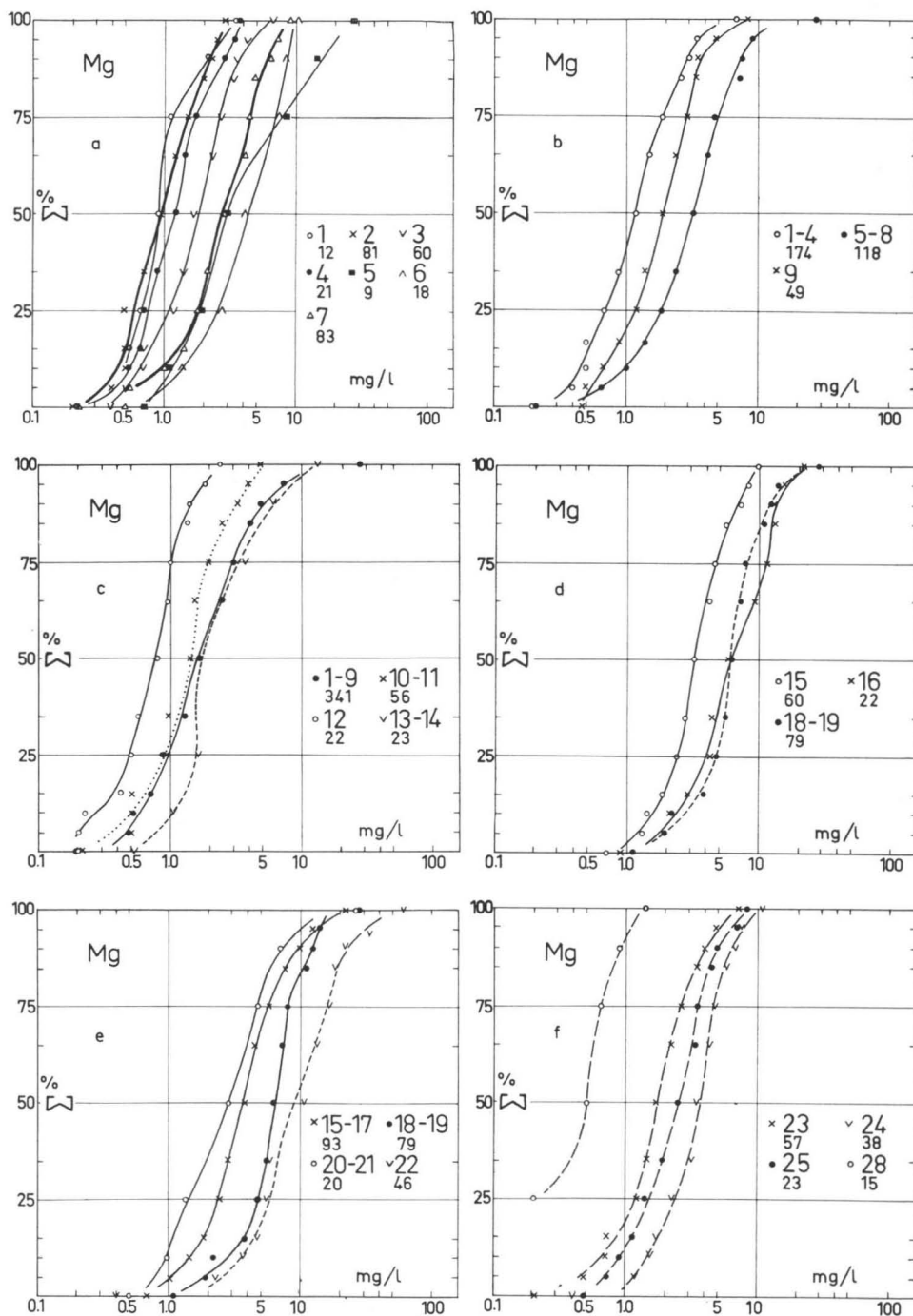


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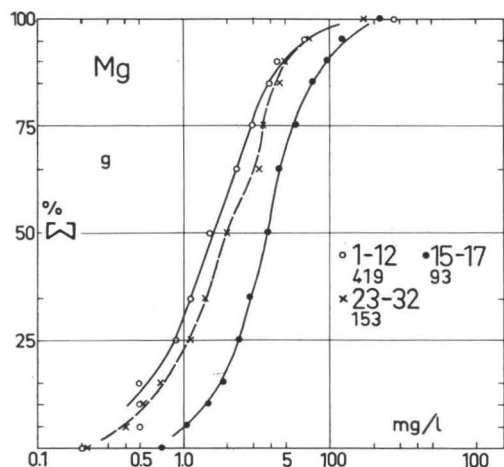


FIG. 14. Cumulative curves showing the frequency distribution of magnesium concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 30–35.

likewise observed the electrolyte content of the ground water to increase in peat-covered areas.

The most fundamental of the factors influencing the high electrolyte content of ground water occurring in fissures and fractures of bedrock is, besides the rock composition, the »time factor». In many places, an actual balance in the ion exchange is possible between almost stagnant ground water and the mineral constituents of the bedrock. The significance of the time factor in increasing the electrolyte content is also stressed by Chebotarev (1955, p. 210). It should be kept in mind that ground water which has found its way into the network of fissures and fractures in the bedrock has a relatively high content of electrolytes, having at first percolated through the cover of Quaternary deposits. Arrhenius (1954) and Laakso (1966) have observed the content of dissolved ionic matter in household well waters from Quaternary deposits to be smaller than in the ground water of bedrock. According to Gorham (1961, p. 821), the effect of geology on the quality of water is clearest in deep-well waters that have had a long time to equilibrate. In slightly contaminated ground water occurring in bedrock the influence of the rock environment on the electrolyte content is not as distinct as in intact waters. In heavily contaminated ground waters, the geological factors are completely obscured by the abundance of foreign matter introduced by the contaminating process.

The sameness of the electrolyte content in discharged ground water and flowing surface waters in similar bedrock areas indicates that brooks and small rivers during dry summer seasons and in winter derive mainly from ground water discharged from Quaternary deposits. It is therefore natural that the composition of the bedrock in the study area is clearly reflected in the content of dissolved ionic matter in the surface waters too. This is not, however, so marked as in the case of ground water

discharged from till deposits. Troedsson (1955, p. 174) has reported ground and brook waters of areas covered with till in Central Sweden to be very much alike in composition. Further, Hofman—Bang (1904) and J. V. Eriksson (1929) in Sweden as well as Holmberg (1935) and Viro in Finland (1955) have noted that the rock composition of surficial deposits and the bedrock is an important factor in regulating the chemical composition of river waters. The great differences in the concentrations justify the conclusion that the slowly circulating ground water contained in bedrock is of minor importance as a source of the electrolytes occurring in ground water discharged from Quaternary deposits and in surface waters.

### Factors contributing to the pH values

Silicate minerals, being salts between weak silicic acid and strong bases, form basic water solutions upon hydrolytically decomposing. This has also been experimentally observed by suspending mineral matter in distilled water or water saturated with carbon dioxide and measuring the abrasion pH values. The results achieved by Stevens and Carron (1958, p. 37), Keller (1957, p. 25) and Keller, Balgord and Reesman (1963, p. 195) indicate that the abrasion pH values of mafic silicate minerals and carbonates are on the average considerably higher (pH 8—11) than those of the minerals occurring abundantly in silicic rocks (pH 6—10). According to Tamm's studies (1934, p. 11), the pH values of the hydrolysis reactions of artificially pulverized potash feldspar and oligoclase are at most 10.8 and 11.1 respectively. The solution of carbon dioxide in water, which normally occurs abundantly in nature, however, considerably reduces the abrasion pH values.

The pH values of the natural waters in the study area show a fairly direct dependence on the mafic minerals in the Quaternary deposits and the bedrock. Stevens states (1934, p. 2) that, in view of the abundance of silicates, there seems little doubt that they greatly affect the pH of underground waters and in deep-seated waters the silicates would have a major influence. According to Krauskopf (1967, p. 115), too, any solution in contact with silicate minerals cannot long remain acid, but the solution must eventually become alkaline. A slight increase in the content of subsilicic minerals is not, however, reflected very sensitively as an increase in the pH value of ground water. On the other hand, even a slight carbonate content in the till is made evident in a rise in the pH value of ground water, which has been observed elsewhere by, e.g., Troedsson (1952, Table 3, 1955, p. 95).

The highest sulfate contents of ground water in the study area occur in tracts of subsilicic bedrock, where the pH of ground water generally varies between 7.0 and 8.0. Also in the areas of sulfide-bearing black schists, the ground waters are clearly alkaline, so the effect of the sulfuric acid, resulting from the weathering of sulfide minerals, on the pH value is slight (see p. 85). However, in the light of their investigations in southern Finland, Sandelin (1936, pp. 109—110) and Marmo (1958, pp. 65—66) reported that the sulfuric acid is capable of substantially reducing the pH of ground



water. In addition, ground water discharged into pyrite mines is often highly acid, as at Outokumpu, eastern Finland, where the pH of mine waters is in certain places 3.6 to 3.9 (Wilska 1952, p. 70).

The reason for the rather low pH level of the ground water contained in glacio-fluvial material and, especially, of the perched water in the area investigated is slight weathering of the mineral matter in leached topsoil and the washing of acid humus-rich water into the subsurface water. In the surficial portion of humus-bearing and weathered soil there prevails a low pH (see Aaltonen 1937), with the result that the low pH value of the acid rain and gravitational water is preserved. The water standing or flowing on the surface of bogs has a low pH value, because it collects predominantly straight from rain water.

In contaminated ground water in the study area, the effect of the rock environment in regulating the pH is obscured by the organic waste matter forcing down the pH. The higher pH of surface waters in comparison with discharged ground water is due partly to the release of carbon dioxide and, possibly, the activity of micro-organisms assimilating the carbon dioxide. This latter factor is viewed by Hutchinson (1957, p. 687) as being of general significance in lake waters. The effect of the two factors is stronger than the tendency of the acid humus waters discharged from surrounding peat lands into flowing surface waters to lower the pH value.

### **Factors contributing to the bicarbonate and carbon dioxide concentrations**

Bicarbonates are generated most readily through the weathering of carbonate minerals, through the process of carbonation. Magnesite weathers more easily than calcite, which in turn is more susceptible to weathering than is dolomite. At room temperature, calcium carbonate dissolves in distilled water only to the extent of 12 to 13 mg per liter (Hutchinson 1957, p. 661; Freier 1958, p. 4) but in CO<sub>2</sub>-bearing water very intensely as bicarbonate (see, e.g., Keller 1957, p. 43; Hem 1959, p. 71).

In addition to the bound carbonic acid consumed in the formation of bicarbonates, an excess of free attached carbonic acid is needed in order that the bicarbonates remain in solution (Hutchinson 1957, p. 688). If the attached carbonic acid is removed, part of the bicarbonate is precipitated back as carbonate, releasing carbon dioxide as a new attached carbonic acid. The supply of carbon dioxide in a humid climate, as in the study area, is generally secured by the rain water filtering down through the humus-rich surface portion of the ground. In the electrolyte-poor waters of the study area, bicarbonates do not occur in nearly the amounts made possible by the abundant free carbonic acid content.

In the study area, the weathering of the carbonates in black schists and greenstones increases the bicarbonate content of the ground water. This is to be observed in the high bicarbonate content of the ground water in till deposits of the limestone areas. Carbonates do not, however, occur everywhere in areas of subsilicic bedrock in sufficient abundance and even distribution to explain the bicarbonate content of

ground water. The conclusion then remains that the bicarbonates of natural waters originate in the main in conjunction with the weathering of silicate minerals. Also Stevens states (1934, p. 1) that the abundantly present silicate minerals are more significant factors in producing alkalinity, consequently bicarbonates, in ground water than are the carbonates. Accordingly, the markedly high bicarbonate content of ground water in areas of subsilicic bedrock indicates that among the mafic minerals susceptible to weathering considerably more bicarbonates are produced and fed into ground and surface waters than in the case of the more stable felsic minerals. The amounts of weathering products, especially bicarbonates, are slight in perched water and in ground water occurring near the surface, in spite of the considerable carbon-dioxide content deriving from the humus layer of the soil.

In the atmosphere there occurs 0.03 % by volume of carbon dioxide, only 0.8—1.0 mg per liter of which can dissolve in water under normal pressure (Ohle 1934, p. 430; Freier 1958, p. 5). Consequently, in ground and surface waters it is generated as the final product of the decomposition of the organic matter in the ground, in which the carbon-dioxide content is many times that of the air. According to Franz (1960, p. 179), the carbon-dioxide content of the air in the surface layer of the ground is 0.3 to 1.6 % but in the poorly aerified deeper layers as much as 8 vol. % — and, according to Romell (1922), a maximum of 2.8 % in forest soil with hard-pan zones and 5 to 6 % in very wet soils. Further, Bear (1955, p. 205) presents that the carbon dioxide content in soil varies from 0.3 to 10 per cent. In dissolving in water, it forms to some extent carbonic acid, the total amount of which is, however, only 0.1 to 0.6 % of the carbon-dioxide content of water in molecular form (Hutchinson 1957, p. 655; The carbonic acid becomes further dissociated to a slight extent into bicarbonates (Ohle 1934, p. 430). The amount of bicarbonates thus generated in ground and surface waters remains, however, insignificantly slight.

According to nearly a hundred laboratory determinations, the carbon-dioxide contents of the ground and surface waters of the study area varied between 3 and 89 mg per liter, the median value being 11 mg per liter (Table 3). The carbon-dioxide contents of ground water discharged from till deposits are notably higher in slightly acid (groups 1—4) than in slightly basic (groups 5—8) waters, which is in agreement with the correlation between the carbonic acid-bicarbonate system and the pH (p. 84).

TABLE 3.  
The carbon-dioxide contents of ground and surface waters.

Groups	Number of determ.	Min mg/l	25 % mg/l	50 % mg/l	75 % mg/l	Max mg/l
1—4 .....	26	3	11	17	21	39
5—8 .....	18	3	4	6	9	11
1—14 .....	59	3	7	9	15	39
15—21 .....	29	4	10	19	27	89
23—29 .....	9	3	—	7	—	11

The ground water occurring in bedrock and in household wells dug into Quaternary deposits (groups 15—21) is appreciably more CO<sub>2</sub>-bearing than is the ground water discharged from Quaternary deposits. This is due to the higher partial pressure of the carbon dioxide in deep ground layers and in nearly stagnant water. The carbon-dioxide contents of surface waters (groups 23—29) are slight, owing to, for instance, the low partial pressure of the carbon dioxide in the air, the aerification resulting from flow and the biological activity consuming carbon dioxide.

The carbon-dioxide concentrations in ground and surface waters are greater in natural conditions, apparently, than the analytic results indicate. This is partly due to the following conditions: As the ground water is discharged to the surface, the partial pressure of the carbon dioxide diminishes and the temperature of the water rises, reducing the amount of dissolved carbon dioxide. Contributing to the same effect is the aerification of the water during the taking of the sample and its transportation.

### **Factors contributing to calcium and magnesium concentrations and Ca/Mg ratio**

The higher alkaline-earth content of subsilicic rocks as compared to silicic rocks (see p. 21) results clearly in regional differences in the contents of calcium and magnesium in natural waters. The abundance of mafic minerals in the Quaternary deposits and the bedrock is thus a predominant factor in regulating the alkaline-earth content of both ground water and related surface waters. In addition, the differences in the alkaline-earth content between the ground water in subsilicic and silicic bedrock areas are furthered by the greater susceptibility of mafic minerals to weathering (see Hem 1959, p. 7). When artificially pulverized minerals are extracted in CO<sub>2</sub>-bearing water, calcium is obtained in greatest abundance from hornblende and augite, the chief minerals of subsilicic rocks, while magnesium is obtained abundantly from biotite (Keller, Balgord, Reesman 1963, p. 195).

In the study area, carbonates have mainly a local significance as a source of alkaline earths. However, the local influence of limestone upon the composition of ground water and surface waters is striking. This is no exception, for where limestone is present waters are as a rule greatly enriched in, besides bicarbonate, also calcium and in places magnesium. (see e.g., Eriksson J. V. 1929, pp. 84—88; Troedsson 1955, pp. 83—97; Skjeseth 1956, p. 67). The amount of dissolved carbon dioxide controls the dissolution of the alkaline earths as well as bicarbonates (White, Hem, Waring 1963, pp. 3—4). According to Hem (1959, p. 70, 79), calcium and magnesium are normally present in solution in ionic form as bicarbonates.

According to four rock analyses (p. 21), the Ca/Mg ratio of the granites of the study area varies between 3.0 and 4.0. Approximately the same ratio prevails in the ground water of the granite areas (group 2, Fig. 15). This indicates that in the weathering process the alkaline earths enter the ground water in roughly the same proportions as they are present in silicic bedrock. In black schists (4 analyses, mean Ca/Mg 0.39) and greenstones (8 analyses, mean Ca/Mg 1.3), the Ca/Mg ratio is lower than in

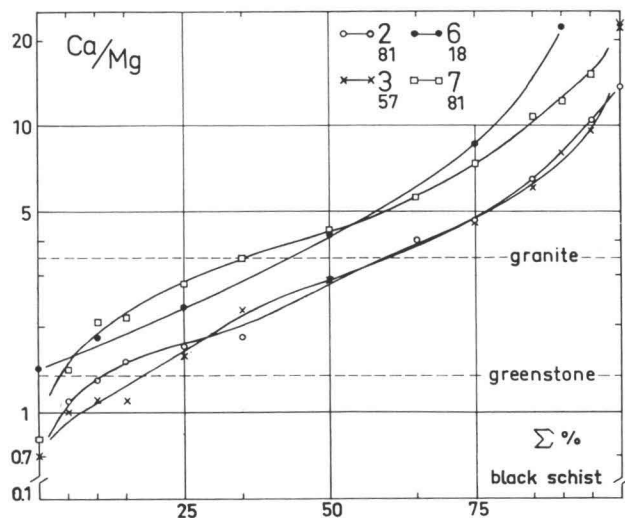


FIG. 15. Cumulative curves showing the frequency distribution of the Ca/Mg ratio in natural ground water discharged from till deposits. Group 2, bedrock composed of granites; group 3, silicic schists; group 6, black schists; and group 7, greenstones. The average Ca/Mg ratio in the different varieties of rock in the area investigated is shown by the horizontal dash lines.

granites. In the ground water in the areas of black schists and greenstones, the corresponding ratio, however, appreciably exceeds that in the bedrock (group 6 and 7, Fig. 15) and is even greater than in the ground water of the granite areas. In the areas of subsilicic bedrock, the content of calcium in proportion to magnesium in ground water is thus higher than the ratio in the bedrock would presuppose. It is evident that this is due to the greater tendency of calcium to be released during weathering than other elements in mafic minerals. Another factor which may lower the ratio is the possible fixation of magnesium in weathering products (see Loughnan 1963, p. 288).

The Ca/Mg ratio of the surface waters in the areas of silicic bedrock (group 23, Fig. 16) is on the same order of magnitude as in ground water (group 1—4). This also supports the view that, besides having a tendency to migrate during the weathering process, calcium remains highly stable in solution (see Eriksson J. V. 1929, p. 51; Davis, de Wiest 1966, p. 102). In the areas of subsilicic bedrock, on the other hand, the ratio in over half of the determinations is higher in ground water (groups 5—8) than in surface waters (group 24).

Mattson (1942) and Gorham (1955, p. 132) are of the opinion that adsorbed monovalent ions in a soil-water system should be strongly displaced into solution by divalent ions as the system is diluted, causing a great decrease in the percentage of calcium. The magnesium, on the other hand, remains equal. In addition to the geo-

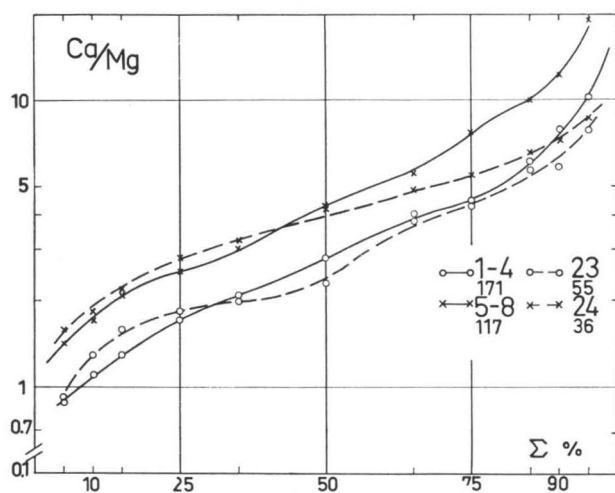


FIG. 16. Cumulative curves showing the frequency distribution of the Ca/Mg ratio in natural ground and surface waters. Groups 1—4, ground water discharged from till deposits in silicic bedrock areas; groups 5—8, in subsilicic bedrock areas. Group 23, surface water in silicic bedrock areas; group 24, in subsilicic bedrock areas.

logical factors, this is apt to lead to the slight calcium content of dilute waters of silicic bedrock areas and thereby to the low Ca/Mg ratio. In the study area, with an increase in the electrolyte content, the Ca/Mg ratio in ground water and surface waters rises only slightly (Fig. 17).

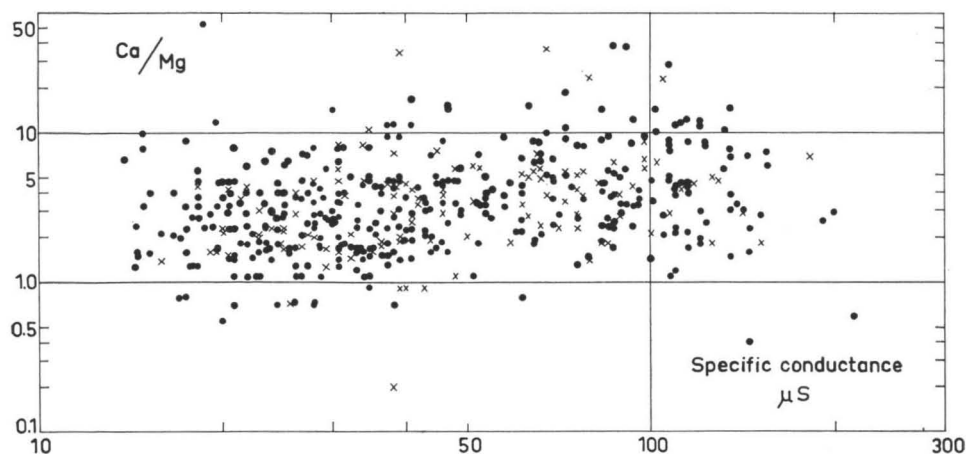


FIG. 17. Correlation between Ca/Mg ratio and specific conductance values of natural ground (·) and surface (×) waters (groups 1—12 and 23—32).

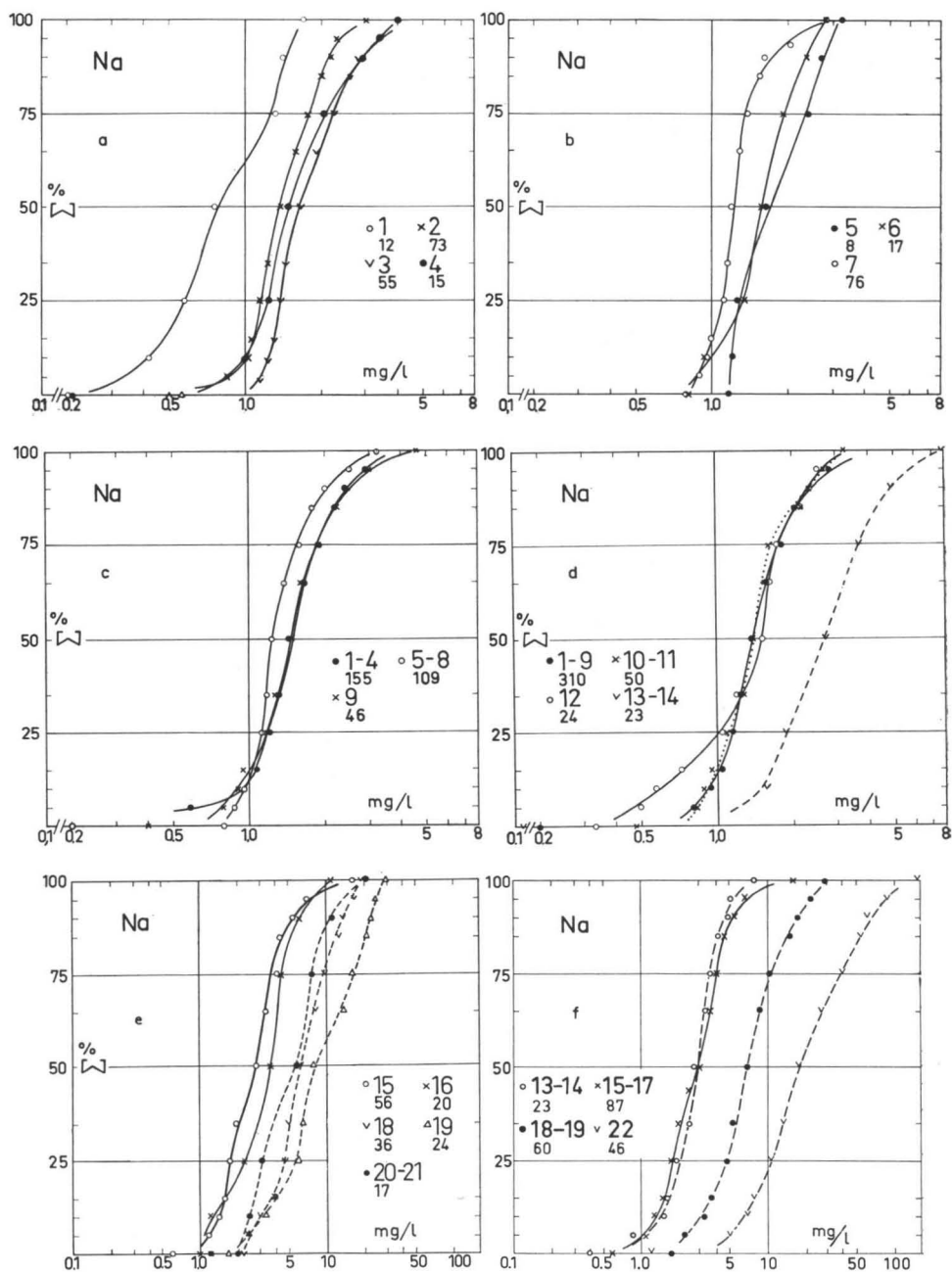


FIG. 18. Continued on next page.

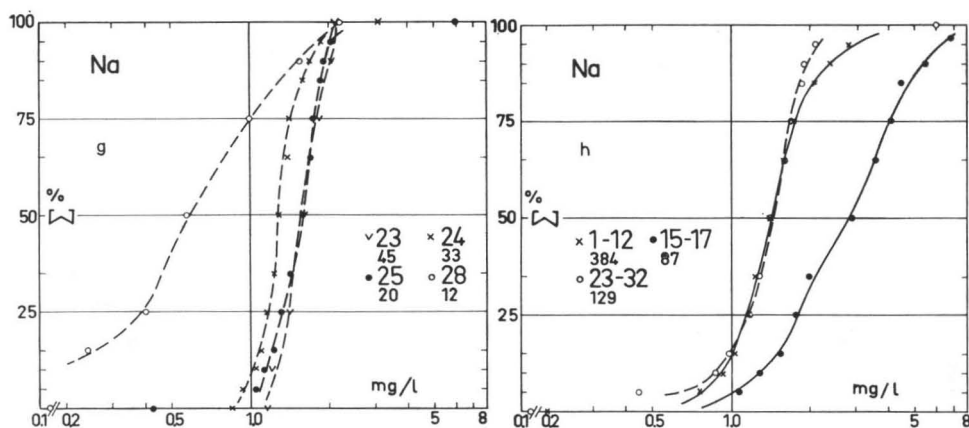


FIG. 18. Cumulative curves showing the frequency distribution of sodium concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 51—53.

## Sodium and potassium

### Distribution

Sodium and, in smaller concentrations, potassium are invariably present in ground and surface waters in the study area. In the ground water discharged from till deposits, the lowest alkali, especially sodium, concentrations occur in quartzite areas (group 1, Figs. 18—19, a, and appendix 1). Concentrations are lower in localities characterized by granitic rocks (group 2) than in areas of mainly silicic schists (group 3) and intermediary rocks (group 4). Further, the alkali contents of ground water are distinctly smaller in areas of greenstones (group 7, Figs. 18—19, b) than in areas of black schists (group 6). The standard deviations of the determinations are smallest in ground water of granite areas (group 2, appendix 1). Like concentrations in ground water, also standard deviations are smaller in areas of greenstones (group 7) compared with black schists (group 6).

As a whole, the sodium concentrations in ground water discharged from till deposits and the standard deviation are greater in silicic (groups 1—4, Fig. 18, c, and appendix 1), than in subsilicic bedrock areas (groups 5—8), whereas the potassium contents are in the same order of magnitude in areas of both silicic and subsilicic bedrock (groups 1—4 and 5—8, Fig. 19, c). Nearly equal amounts of alkalis occur in the ground water contained in till (groups 1—9, Figs. 18—19, d) and glaciofluvial material (groups 10—11), though the standard deviation in the ground water occurring in till deposits (groups 1—9, appendix 1) is substantially larger. The alkali contents of electrolyte-poor perched water and ground water occurring near the surface (group 12, Figs. 18—19, d) are nearly the same as in the ground water proper with a higher content of electrolytes. Sodium and potassium concentrations of ground water

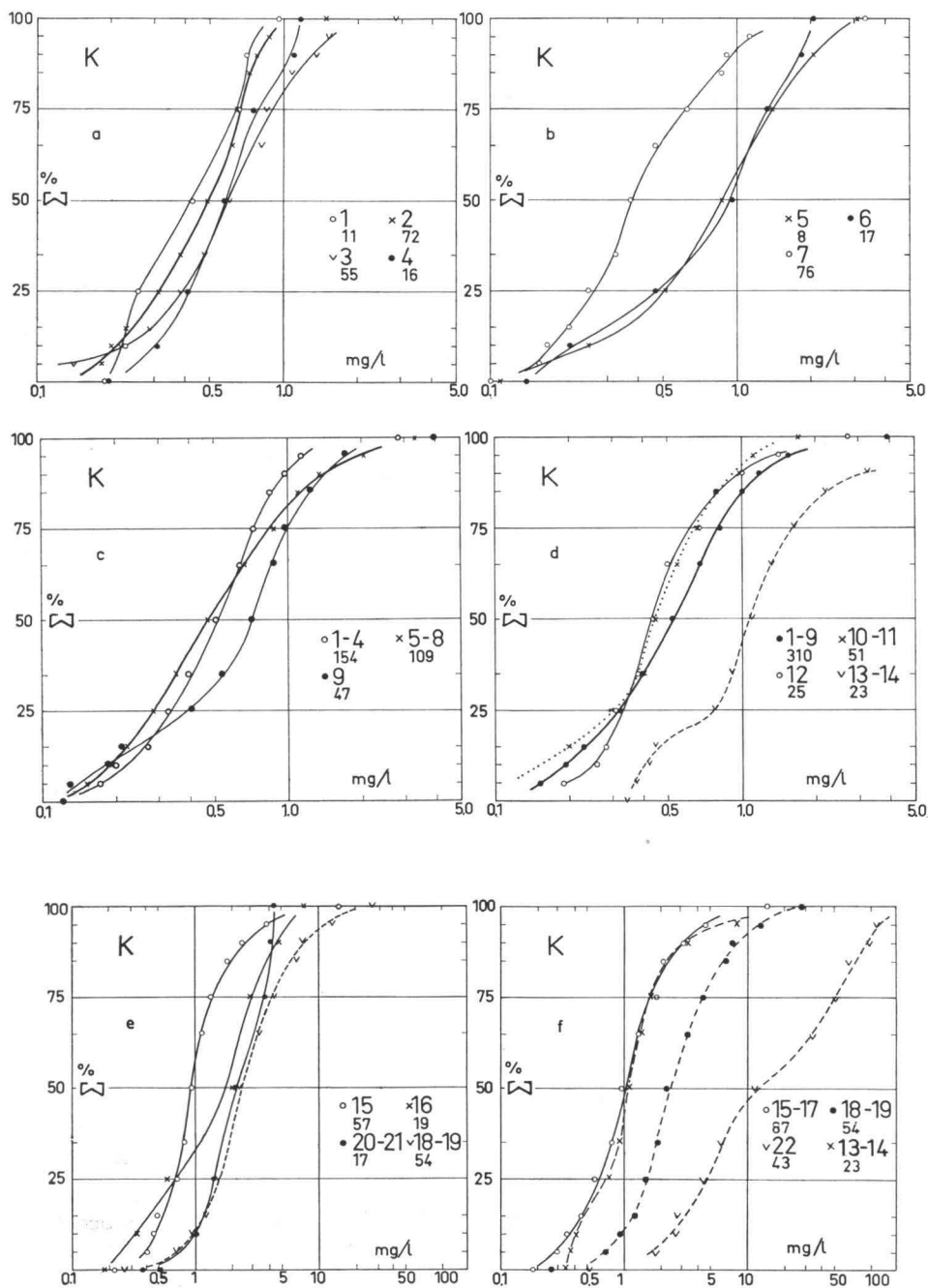


FIG. 19. Continued on next page.



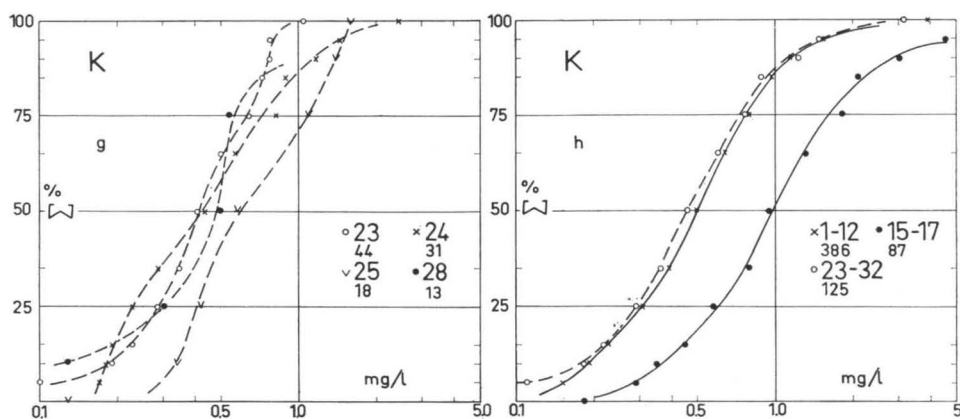


FIG. 19. Cumulative curves showing the frequency distribution of potassium concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 51—53.

stored in bedrock (group 15 and 16, Figs. 18—19, e) are on the average greater in areas of subsilicic rocks.

The alkali concentrations of slightly contaminated ground water discharged from Quaternary deposits (groups 13—14, Figs. 18—19, d) are high compared to intact ground water. As the contamination increases, the concentrations and their standard deviations increase steeply (groups 13—14, 18—19 and 22, Figs. 13—14, f, appendix 1). The alkali metals thus strongly indicate the contamination of ground water caused by agricultural settlement. In this respect, potassium is appreciably more sensitive than sodium.

In flowing surface waters, the potassium concentrations do not clearly reflect lithological changes (group 23 and 24, Figs. 18—19, g), but sodium occurs in surface waters more abundantly in silicic bedrock areas (group 23); this is true also with regard to ground water. In the electrolyte-poor waters of esker pools and ponds (group 28, Figs. 18—19, g), the potassium contents are of the same order of magnitude as in the ground water containing more dissolved matter whereas the sodium concentrations are small.

The alkali contents of ground water discharged from Quaternary deposits (groups 1—12, Figs. 18—19, h) and surface waters (groups 23—32) are nearly the same. The slight standard deviation in the sodium contents of surface waters (see appendix 1) indicates the equalization of the extreme contents of ground water changing into surface waters, although no significant weakening takes place in the average alkali concentrations. The sodium and potassium concentrations of ground water occurring in bedrock and the standard deviation of the determinations (groups 15—17, Figs. 18—19, h, see appendix 1) are substantially higher than those in ground water discharged from Quaternary deposits and in surface waters.

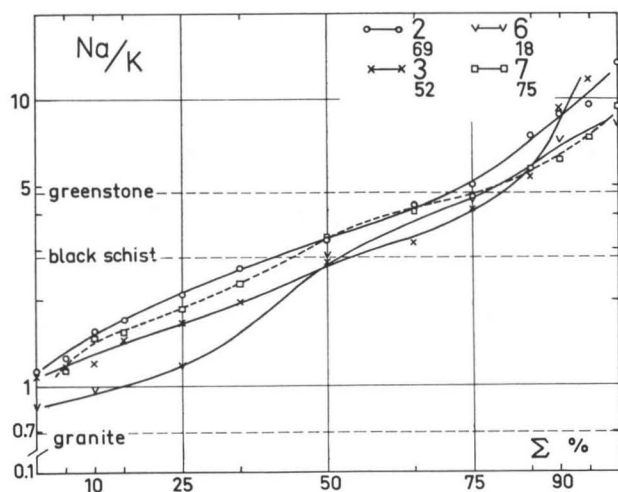


FIG. 20. Cumulative curves showing the frequency distribution of the Na/K ratio in natural ground water discharged from till deposits. Group 2, bedrock composed of granites; group 3, silicic schists; group 6, black schists; and group 7, greenstones. The average Ca/Mg ratio in the different varieties of rock in the area investigated is shown by the horizontal dash lines.

### Contributing factors and Na/K ratio

The sodium contents of subsilicic rocks are on the average slightly greater than those of silicic rocks (p. 21), in the areas of which, except for the quartzites, the ground water nevertheless contains more sodium. The probable reason for the low sodium concentrations in the ground water discharged from till deposits in areas of subsilicic greenstone is the great resistance of Na-rich albite to weathering. On the other hand, the amphiboles that occur in small amounts in silicic rocks are relatively richer in sodium than amphiboles in subsilicic rocks (Rankama, Sahama 1949, Table 5.23). This partly accounts for the greater sodium content of ground water in silicic bedrock areas. The laboratory experiments of Keller, Balgord and Reesman (1963, p. 195) show that  $\text{CO}_2$ -bearing waters extract the most sodium from pulverized microcline, one of the chief minerals of silicic rocks. This supports the results obtained in the present study. In addition, in laboratory conditions sodium is also extracted quite abundantly from hornblende, labradorite, muscovite and augite which are dominant in subsilicic rocks.

Potassium occurs in fair abundance in silicic rocks (p. 21). According to Keller, Balgord and Reesman (1963, p. 195),  $\text{CO}_2$ -bearing water extracts the most potassium from pulverized microcline and micas of silicic rocks, substantially less from hornblende and exceedingly little from other mafic minerals. Tamm (1934, p. 25) has

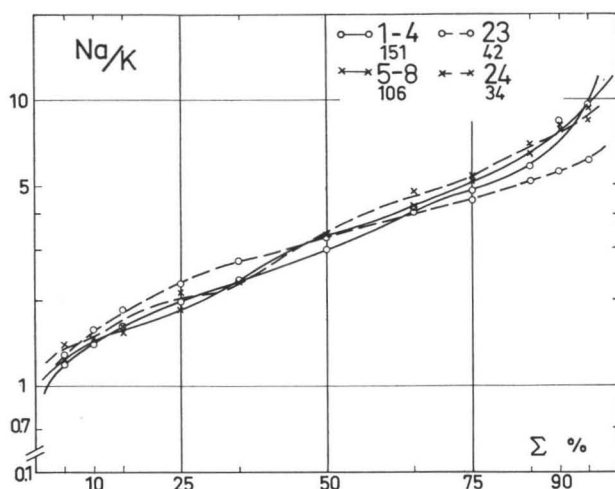


FIG. 21. Cumulative curves showing the frequency distribution of the Na/K ratio in natural ground and surface waters. Groups 1—4, ground water discharged from till deposits in silicic bedrock areas; groups 5—8, in subsilicic bedrock areas; group 23, surface water in silicic bedrock areas; group 24, in subsilicic bedrock areas.

observed in his weathering studies that potassium is extracted in significant amounts in a pH 3—6 from feldspar and biotite fractions of smaller than  $0.5 \mu$ . Subsilicic rocks weather more easily, however, so that nearly as much potassium is released from the K-bearing minerals occurring more scantily in them as from silicic rocks. This is indicated in the study area by the almost equal concentrations of potassium in ground and surface waters of both silicic and subsilicic bedrock areas. The only difference in concentrations induced by the rock composition is the slight potassium content of the ground water occurring in areas of K-poor greenstones.

In greenstones the Na/K ratio averages 4.8 (8 analyses, p. 21) and in black schists 2.5 (4 analyses). Correspondingly, in ground water discharged from till deposits, the alkali ratio is distinctly higher in greenstone areas (group 7, Fig. 20) than in the areas of black schists (group 6). In granites the alkali ratio averages 0.7 (3 analyses) and in silicic schists 0.6 (3 analyses). The Na/K ratios of ground water in areas composed of granites and silicic schists are nevertheless much higher (group 2 and 3), being of the same order of magnitude as in areas characterized by subsilicic bedrock (group 6 and 7). It may therefore be stated that the average alkali ratio of ground water in areas of silicic rocks is markedly Na-dominant compared to the bedrock. In the flowing surface waters, the distribution of the Na/K ratio is quite the same (group 23 and 24, Fig. 21) as in ground water (group 1—4 and 5—8), the ratios being nearly independent of the composition of the bedrock. The alkali ratio varies,

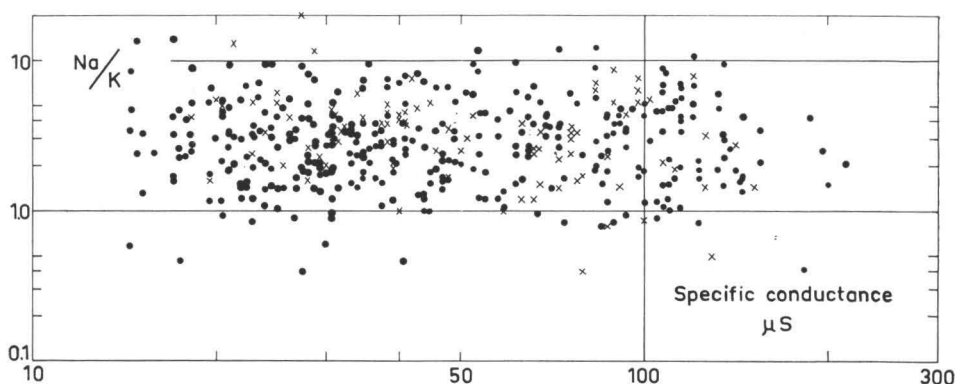


FIG. 22. Correlation between the Na/K ratio and specific conductance values of natural ground (·) and surface (×) waters (groups 1—12 and 23—32).

however, in the surface waters within slightly narrower limits than in ground water discharged from Quaternary deposits. This is due to the equalization of extreme alkali contents of ground water discharged into flowing surface waters.

The remarkably high Na/K ratio of dilute slightly acid ground and surface waters (in silicic bedrock areas) as compared to the alkali ratio in the bedrock is due to the immobility of potassium. At the weathering stage or in ground and surface waters, it has a tendency to be preserved in non-exchangeable form or become bound to the clay minerals and other weathering products (see e.g. Rankama, Sahama, 1949, p. 431, Wilska 1952, p. 62, Gorham 1955, p. 138, Feth, Roberson, Polzer 1964, p. 67). As a whole, the Na/K ratios in both dilute and more concentrated ground and surface water are roughly equal (Fig. 22). However, between the sodium and potassium contents there exists only a slight correlation (Fig. 46). In electrolyte-poor perched water and esker ponds and pools, the potassium concentrations are in the same order of magnitude as in waters containing abundant soluble weathering products. This suggests that the potassium contained in natural waters is not solely a product of weathering but the matter brought down from the atmosphere by rain is a significant additional source (p. 82).

## Silica

### Distribution

The mineral constituents of the bedrock and the Quaternary deposits of the study area are almost wholly various complex silicates; hence it is only natural that significant amounts of silica also occur in the ground and surface waters. The silica content is less variable than any of the other major dissolved constituents of natural water (Davis

1964, p. 890), generally occurring in the natural waters of the study area in 10–12 mg/l amounts.

The silica content (determined as  $\text{SiO}_2$ ) of the ground water discharged from till deposits in the study area is lowest in the quartzite areas (group 1, Fig. 23, a, and appendix 1). In areas characterized by granites (group 2), mainly silicic schists (group 3) and intermediary rock types (group 4), there are no clear mutual differences between the silica concentrations. In greenstone areas (group 7, Fig. 23, b), the ground water contains somewhat greater amounts of silica than in areas of black schists (group 6), but there the content is on the average lower than in limestone areas (group 5).

The silica contents of ground water discharged from till deposits as well as the standard deviation of the determinations are substantially greater in areas of silicic (groups 1–4, Fig. 23, c, see appendix 1) than of subsilicic rock types (groups 5–8). Further, they are greater on the average in ground water discharged from till deposits (groups 1–9, Fig. 23, d) than from glaciofluvial material (groups 10–11). The silica content of electrolyte-poor perched water and ground water occurring near the surface of the ground is considerably lower (group 12) than in the foregoing cases. In the ground water contained in fissures and fractures of bedrock, silica occurs on the average in slightly higher amounts in areas of silicic (group 15, Fig. 23, e) than of subsilicic types of rocks (group 16), even though the latter have registered more individual high concentrations.

In ground water slightly contaminated by human activity (groups 13–14 and 18–19, Fig. 23, d, e), the silica content is in the same order of magnitude as in intact water, and in highly contaminated household well water (group 22), too, the content is only a trifle higher. The contaminating influence of agricultural settlement on ground water thus appears only in exceedingly contaminated cases as a slight increase in the silica concentrations.

Similar to the occurrence of silica in ground water of till deposits and bedrock, the silica content in flowing surface waters is higher in silicic (group 23, Fig. 23, f) than in subsilicic bedrock areas (group 24). The lowest silica concentrations have been registered in electrolyte-poor esker pools and ponds in areas of silicic bedrock (group 28).

In ground water discharged from Quaternary deposits and surface waters (groups 1–12 and 23–32, Fig. 23, g), the amounts of silica are approximately the same. The levelling out of the sporadic extreme silica concentrations of ground water discharging into surface waters is most clearly to be observed in comparing the standard deviations of ground and surface waters in areas of silicic bedrock (groups 1–4 and 23, appendix 1). However, no fundamental weakening of the mean silica concentrations can be detected upon the change from ground water discharged from Quaternary deposits into surface waters. On the average, the silica content and the standard deviation of the determinations are the highest in the ground water occurring in fissures and fractures of the bedrock (groups 15–17, Fig. 23, g).

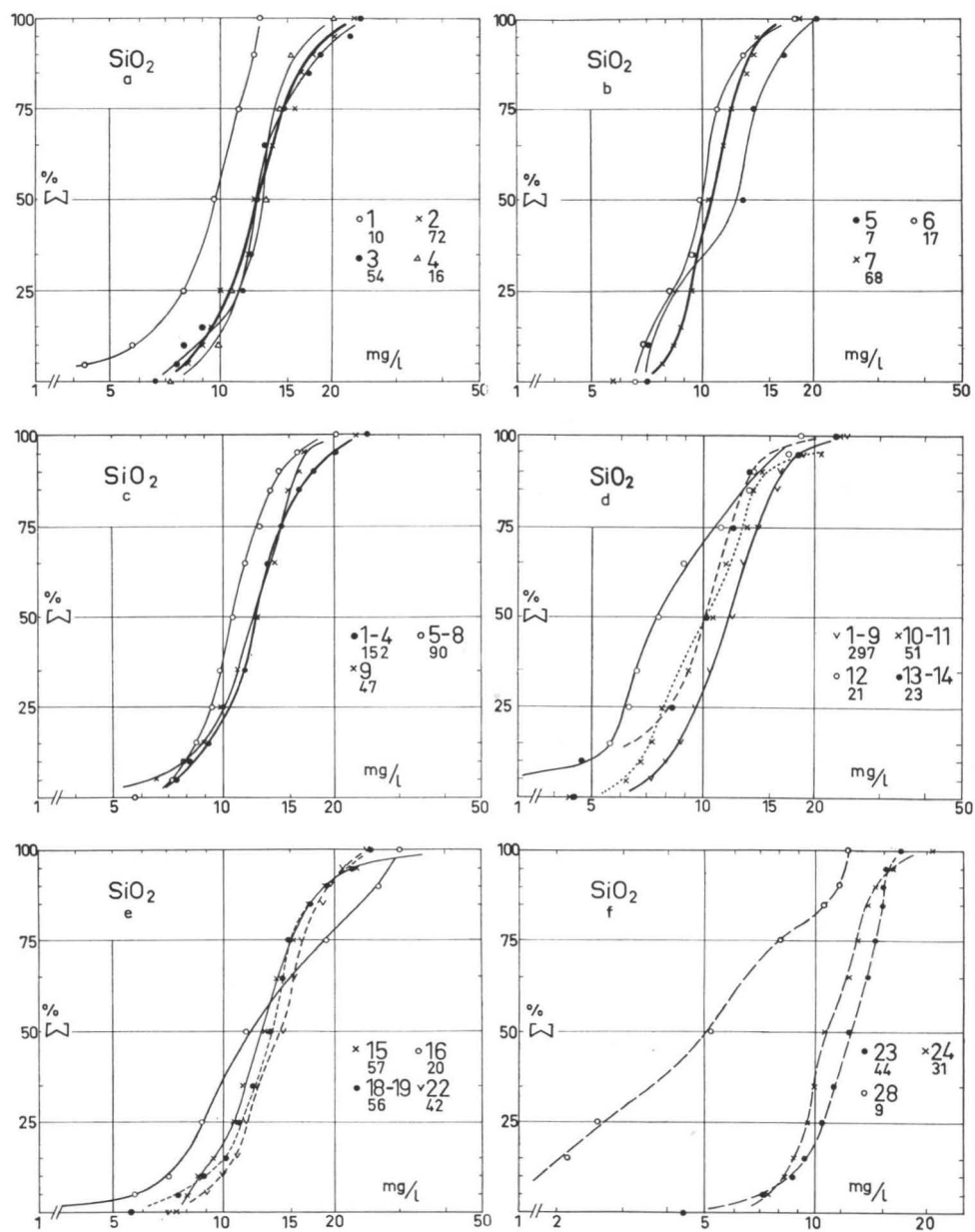


FIG. 23. Continued on next page.

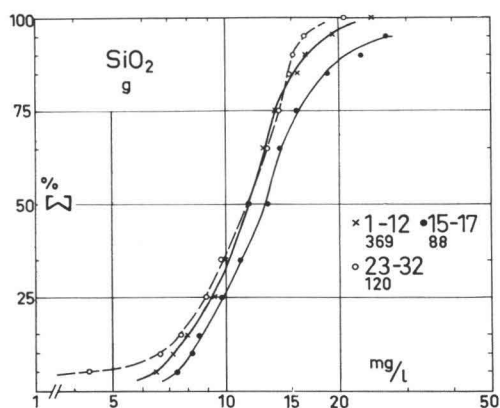


FIG. 23. Cumulative curves showing the frequency distribution of silica concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 56—57.

### Contributing factors

The most important factor controlling the silica in ground water is the type of rock in contact with the water (Davis 1964, p. 870; Polzer 1967, p. 508). The silica contents of the silicic rocks of the study area, calculated in terms of  $\text{SiO}_2$ , are substantially higher (in granites over 70 %, in quartzites over 90 %) than those of subsilicic rocks, in which the silica content is around 50 % or less (p. 21). Although in silicic varieties of rock, the main part of the silicates occurs as quartz, which dissolves only with extreme difficulty, or as K-feldspars, the ground and surface waters of the study area in such areas contain more silica than in the areas of subsilicic bedrock. The silica of subsilicic rocks almost invariably occurs in more easily decomposed mafic minerals and Ca-plagioclases, in the weathering of which, however, less silica is released into natural waters.

Experiments have revealed that water in equilibrium with fine-grained quartz powder will have 6 to 12 mg per liter of silica in solution (Polzer 1967, p. 508). The dissolving of quartz in the study area is slighter than these experimental values would suggest, for in the Quaternary deposits the amounts of fine fractions of crushed quartz in them are quite small. Moreover, the accomplishment of the solubility equilibrium between quartz and water requires much time. The main part of the dissolved silica must derive from silicate minerals, chiefly feldspars (see Brickel and Carrels 1967, p. 460).

Investigating the weathering of feldspars, Tamm (1934, p. 25) observed that in water suspension they release significant amounts of silicic acid, and according to Hem (1959, p. 205) felsic silicates rich in alkalies are likely to release more silica than do the ferromagnesian Ca-rich mafic minerals. This is in accordance with the higher silica content of electrolyte-poor waters in silicic bedrock areas in the area investigated. On the other hand, Keller, Balgord, Reesman (1963, p. 195) observed, when

leaching pulverized minerals in distilled and  $\text{CO}_2$ -bearing water, that the most silica released derives from mafic minerals, but the  $\text{CO}_2$  content of water augments the solubility of the minerals considerably, notably equalizing the solubility difference between mafic and felsic minerals in relation to silica.

In the study area, acid  $\text{CO}_2$ -bearing ground water is a more effective solvent of silica than is electrolyte-bearing water with its higher pH. According to Pickering (1962, p. 1201), too, ground water containing slight amounts of dissolved matter is effective in leaching silica from silicate rocks under both stagnant conditions and good drainage, and the rate of dissolution of silica increases as the pH is reduced. No significant correlation exists, however, between the pH and the  $\text{SiO}_2$  content of the waters of the study area, although as the pH increases the silica content slightly diminishes and the range of variation narrows (Fig. 47). Loughnan (1962, Fig. 1) reports that, independent of pH, silica maintains a low but fairly constant solubility. By contrast, Keller (1957, p. 26) and Krauskopf (1967, pp. 167—168) present that the solubility of silica increases with an increase in the pH value.

Also elsewhere in the world in areas of subsilicic bedrock the silica content of ground and surface waters is low. In Hawaii, Patterson and Roberson (Table 219.2) found only a few mg per liter of silica in water from weathered basalt (cf., greestones in the study area, p. 17), which contained abundant clay minerals or other product of weathering. According to Krauskopf (1967, pp. 115—116), in areas of subsilicic bedrock, part of the silica, especially from minerals of the amphibole and pyroxene groups, may not dissolve at all but remain as amorphous residues of the original crystal structure.

The current view is that silica dissolved as a weathering product in water occurs in the usually prevailing pH range as a monomeric orthosilicic acid (Krauskopf 1956, p. 23; Polzer 1967, p. 506). To some extent the silicates dissolved in water occur as a negative hydrosol, which in an electrolyte-bearing solution containing cations in abundance is apt under suitable conditions to coagulate. S. Davis (1964, p. 877) reports a relatively low silica content in waters containing abundant calcium. Also in the electrolyte-bearing waters of the study area in which calcium occurs in fair abundance, the average silica content is smaller than in dilute waters poor in calcium.

## Iron and manganese

### Distribution

Iron and slight amounts of manganese occur almost consistently in ground and surface waters under natural conditions. In the study area the iron and manganese contents of the ground water do not show any close relationship to the composition of the bedrock. This is especially true of the oxygen-rich ground water discharged from till deposits, where the amounts of iron and manganese are insignificant and



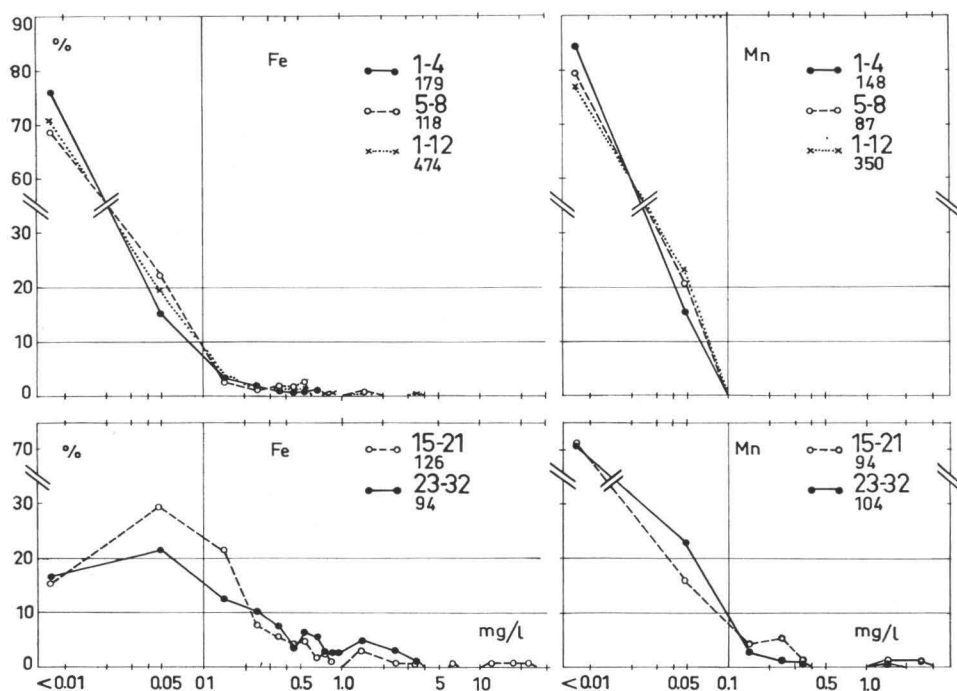


FIG. 24. The frequency distribution of iron and manganese concentrations in natural ground and surface waters. The diagrams show the distributions in different group combinations. For details, see Table 1 and text on p. 60—61.

roughly the same in areas of both silicic and subsilicic bedrock (groups 1—4 and 5—8, Fig. 24, and appendix 1). The iron and manganese contents of ground water stored in bedrock and in household wells (groups 15—21) and of surface water (groups 23—32) are substantially higher than in the ground water discharged from Quaternary deposits (groups 1—12). The iron contents of surface waters vary within more narrow limits than those of ground water occurring in bedrock, where more high contents were sporadically registered. The ground water discharged from deposits underlying peat beds into drains (dug for the purpose of drying out bogs) is often quite rich in iron and manganese (groups 31—32, appendix 1). The iron is rapidly precipitated, however, on the bottom and sides of drainage ditches as abundant reddish deposits. That manganese remains principally in solution is evident from the analytical results (Fe, 7 determinations, median 0.06 mg per l, Mn, 5 determinations, median 0.10 mg per l). The iron remaining in the water is mainly suspended in the form of a fine-grained or flaky precipitate.

### Contributing factors

Principal sources of the iron and manganese in Quaternary deposits and bedrock are mafic minerals. According to Keller, Reesman and Balgord (1963, p. 195), pulverized biotite upon being extracted in distilled water yields many times more iron than do other mafic minerals. Sulfide minerals, which are more susceptible to weathering than the silicate minerals (Smirnow 1954, p. 39), are locally notable sources of iron. They occur in the main in subsilicic rocks and, as far as the study area is concerned, particularly in black schists (p. 12). According to Skjeseth (1956, p. 67), the high iron content of the ground water obtained from wells drilled into bedrock is due to the presence of pyrite and pyrrhotite. Hem (1960, p. 71) likewise reports that the pyrite in soil and bedrock can be an important source of iron in ground waters. On the other hand, the oxide minerals of iron are exceedingly resistant to weathering (Pettijohn 1941, p. 618; Smirnow 1954, p. 77) and therefore do not contribute iron significantly to natural waters. According to Eriksson E. and Khunakasem (1968, p. 105), iron and manganese in most cases originate in the illuvial horizon of the soil profiles, where there are good supplies of iron and manganese and organic matter, the latter being a necessary prerequisite for releasing these elements into ground water.

Iron-bearing silicate and sulphide minerals undergo weathering through oxidation and related hydration and hydrolysis reactions (see, e.g., Reiche 1950, Keller 1957, p. 39). When ferrous iron is oxidized into ferric iron, the spatial requirements of the ferrous ion and the electrostatic neutrality of the crystal lattice of ferromagnesian and sulfide minerals are altered. This causes a weakening of the entire structure and thus promotes weathering (Barshad 1964, p. 32). Some of the iron and a great deal of the manganese released during weathering remain precipitated in ground levels situated above the ground-water table, notably the illuvial and gley horizons of the soil (see, e.g., Aarnio 1915, Tamm 1930, Aaltonen 1935, Barshad 1964, p. 67, Jauhainen 1969). In addition to the pH and prevailing redox potential of the surrounding ground, the electrochemical properties of the iron and humus colloids have a bearing upon the precipitation process (see Mattson 1933).

In oxygen-bearing natural waters, the oxidation result of ferrous iron in a usually predominantly pH area is a highly insoluble ferric hydroxide, the solubility product of which limits the ferric ion content of water to a very small quantity (see, e.g., Hem 1959, p. 59, Hem, Cropper 1959). On the other hand, under conditions deficient in oxygen, iron is apt to be present quite abundantly as soluble ferrous hydroxide or, in CO<sub>2</sub>-bearing waters, as ferrous bicarbonate (see, e.g., Rutner 1962, p. 101). The rise in the pH value of the water and an abundant HCO<sub>3</sub>-content reduce the solubility of ferrous iron (see Larson, King 1954, Fig. 8; Hem 1960, p. 54). The redox potential is roughly in direct proportion to the oxygen content and diminishes as the pH value rises. Thus, in addition to the content of bicarbonate, the redox potential is the factor that most forcefully regulates the behavior of the iron present in natural waters

TABLE 4.  
The oxygen content of ground and surface waters.

Groups	No. of determinations	O <sub>2</sub> , mg/l	O <sub>2</sub> , median mg/l	Degree or saturation
1—14 .....	19	7.8—13.5	11.2	0.87
15—18 .....	20	2.3—13.0	9.8	0.77
23—31 .....	8	5.9—13.8	13.2	0.98

(White, Hem, Waring 1963, p. 3). Strongly reducing conditions are required to bring iron into solution, but manganese is not as susceptible as the ferrous iron to oxidation (Rutner 1962, p. 105, Morgan 1967, pp. 614—615; Eriksson E., Khunakasem 1968, p. 97). For this reason, manganese is apt to occur in solution even in waters with a moderate oxygen content.

The ground waters discharged from Quaternary deposits in the study area are almost saturated with oxygen (groups 1—14, Table 4). Owing to the abundant oxygen, the redox potential of the ground water discharged from Quaternary deposits is high, and it cannot contain dissolved iron in any significant amounts. In areas of subsilicic bedrock, where iron is to be obtained abundantly from the mineral matter, rich in oxygen, together with the higher pH of the waters, promotes the precipitation of iron. The result is, as already pointed out, that the iron content of the ground water is hardly higher than in areas of silicic bedrock.

The ground water occurring in fissures and fractures of bedrock has often been found to be deficient in oxygen (groups 15—18, Table 4) and thus to possess, in some degree, reducing conditions. The oxygen deficiency is reflected in elevated iron and manganese contents. It may be mentioned that household well waters in Finland generally contain iron in noticeable amounts (see Johansson, Veijola 1955, p. 273, Väre 1961, p. 20), and this is especially true of ground water occurring in deposits overlain by clay beds (Natukka 1960, p. 22) and bearing only little oxygen.

The remarkable iron content of the surface waters in the study area, in spite of abundant dissolved oxygen (groups 23—31, Table 4), may be explained by the fact that the iron evidently occurs as complexes with humus compounds. Accordingly, in the surface waters of the area investigated there exists a marked correlation between the KMnO<sub>4</sub>-consumption, indicating the average humus content, and the iron content (see p. 91). The same mode of occurrence of iron in humus-bearing waters is mentioned by many researchers, e.g., Aschan (1906); Aarnio (1915) and Oden (1922). Lohammar (1938, p. 175) has found in northern Sweden, that iron is most abundant in dilute humus-rich waters. The iron in the bogs is not precipitated in an acid environment but is carried away in the form of iron humates, thereby adding to the iron content of the surface waters (Väre 1962, p. 13). For the same reason, the margins of peatlands and bogs are, as a consequence of the presence of organic matter of

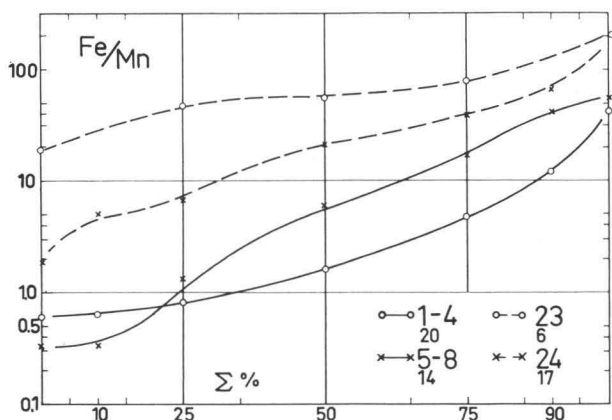


FIG. 25. Cumulative curves showing the frequency distribution of the Fe/Mn ratio in natural ground and surface waters. Groups 1—4, ground water discharged from till deposits in silicic bedrock areas; groups 5—8, in subsilicic bedrock areas. Group 23, surface water in silicic bedrock areas; group 24, in subsilicic bedrock areas.

humic acid character, most likely the sources of iron and manganese in ground water (Eriksson and Khunakasem 1968, p. 105). Ferric iron may also be present, bound to the clay minerals suspended in the water (Carrol 1958, p. 25).

Rather little is known about the state of the manganese contained in natural waters. In surface waters the manganese evidently occurs and travels, like the iron, as humic complexes or as colloidal hydroxides of different state of oxydation stabilized by humus (see Aschan 1932; Rankama, Sahama, 1949, p. 647; Morgan 1967, p. 561). Since manganese is not particularly susceptible to oxydation, in an acid or neutral environment, it is likely to occur also as a divalent ion in complex compounds.

Certain bacteria utilize the energy released by iron and manganese in oxidizing and thereby act as oxidizers or, also, as reducers (see Hutschinson 1957, p. 715; Taylor 1958, p. 110). The activities of micro-organisms are for that reason of great importance in bringing iron into solution from soils and from mixtures of soils and organic matter (Oborn, Hem 1961, p. 233). The significance of microbiologic factors in the study area has not, however, been investigated.

The occurrence of iron in natural waters is generally regarded to be associated with the concomitant occurrence of manganese. In the study area there exists, however, no significant correlation between iron and manganese in the ground and surface waters (see p. 91). Neither did Plochniewsky (1966, p. 870), in his studies carried out in northern Poland, find any close relation between Fe and Mn in ground waters discharged from Quaternary deposits.

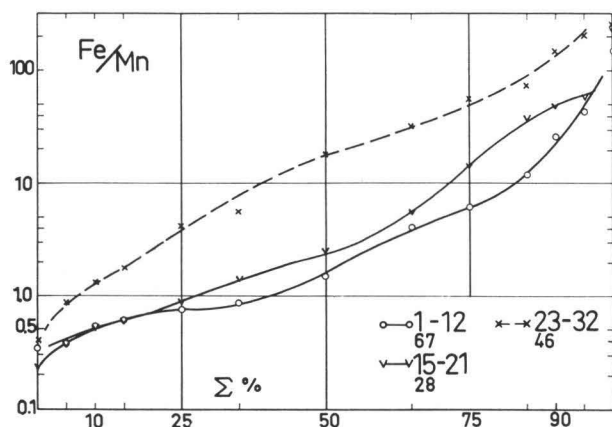


FIG. 26. Cumulative curves showing the frequency distribution of the Fe/Mn ratio in natural ground and surface waters. Groups 1—12, ground water discharged from Quaternary deposits; groups 15—21, ground water occurring in the bedrock; groups 23—32, surface waters.

The Fe/Mn ratio in igneous rocks of both subsilicic and silicic varieties averages 50—60 (Rankama and Sahama 1949, p. 643). In the present study area, it is on the average higher in silicic (Fe/Mn = 100) than in subsilicic (Fe/Mn = 70) rocks (p. 21), but it varies in broad limits. This difference is reflected in the Fe/Mn ratio of surface waters occurring in silicic (group 23, Fig. 25) and subsilicic bedrock areas (group 24), whereas in ground water discharged from till deposits the ratio is higher in areas of subsilicic (group 5—8) than silicic bedrock (group 1—4). On the whole, the Fe/Mn ratio of the ground water is considerably lower (groups 1—12 and 15—21, Fig. 26) than that of surface waters (groups 23—32), which in the case of the latter approaches the ratio prevailing in the bedrock.

The low Fe/Mn ratio of ground water is partly due to the circumstance of iron's being more likely to oxidize and become precipitated than manganese, the proportional content of which thus increases in the solution. This likewise explains the relatively high manganese content of ground water discharged into ditches from underneath beds of peat, as compared to the iron content (p. 61). More mobile than iron, manganese is released from weathering mineral matter first. As the weathering process advances the Fe/Mn ratio in the ground water is likely to increase (Eriksson E., Khunakasem 1968, p. 97, 100). The fluctuations of the ground-water table also produce changes in the relative contents of iron and manganese (see p. 76). The higher Fe/Mn ratio of surface waters is partly due to the tendency of iron to form soluble humic complexes.

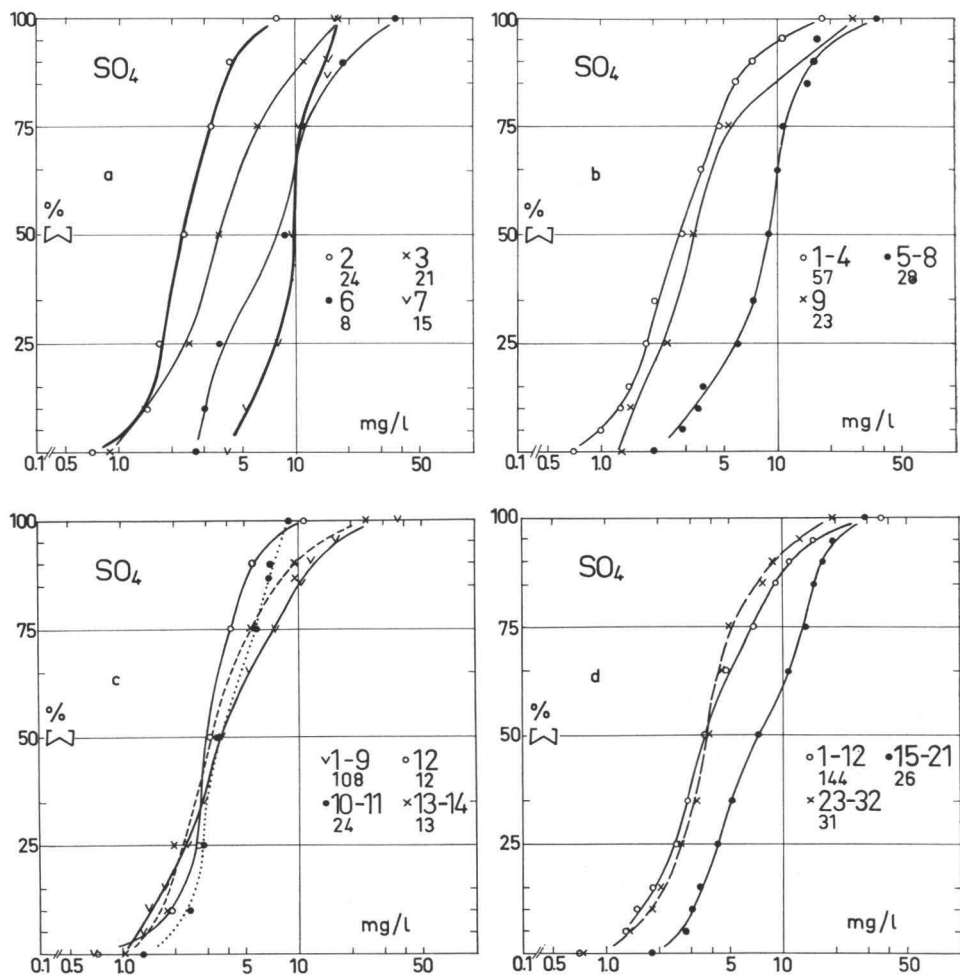


FIG. 27. Cumulative curves showing the frequency distribution of sulfate concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 66—67.

## Sulfate

### Distribution and contributing factors

In the region investigated, the sulfate content of the ground water discharged from till deposits is quite low in the granite areas (group 2, Fig. 27, a, and appendix 1), whereas in the areas of mainly silicic schists (group 3) the content is substantially higher. In the areas of subsilicic black schists (group 6) and greenstones (group 7), no noteworthy differences are to be observed in the sulfate contents of the ground water. More sporadic high concentrations occur in the areas of black schists, however, with

the result that also the standard deviation of the determinations is greater (see appendix 1). As a whole, the sulfate content and the standard deviation of the determinations of the ground water are appreciably higher in areas of subsilicic (groups 5—8, Fig. 27, b) than in those of silicic bedrock (groups 1—4).

The sulfate content of the ground water discharged from glaciofluvial drift (groups 10—11, Fig. 27, c) is on the same order of magnitude as in the ground water contained in till deposits (groups 1—9). However, higher sporadic concentrations are to be observed in the latter, also reflected in a higher standard deviation (see appendix 1). The sulfate content of ground and perched water occurring near the surface (group 12) does not fundamentally differ from the contents found in the ground water proper (groups 1—9), any more than that of slightly contaminated ground water, either (groups 13—14). The contamination of ground water in the study area does not appear as any significant increase in the sulfate content.

The sulfate concentrations of ground water discharged from Quaternary deposits (groups 1—12, Fig. 27, d) is of the same order of magnitude as those of surface waters (groups 23—32). The greater standard deviation of the determinations in the ground water (see appendix 1) indicates that the extreme concentrations in ground water discharged from Quaternary deposits become levelled down with the change into surface waters. The sulfate contents of ground water occurring in fractures and fissures of bedrock and in household wells dug in Quaternary deposits (groups 15—21), are higher than the concentrations in discharged ground water and surface waters.

The main source of sulfates in natural waters is in the sulfide minerals of Quaternary deposits and the bedrock. In the study area the higher sulfide content of subsilicic rocks, especially black sedimentogenic schists, is reflected in the notable sporadic sulfate concentrations in the ground water.

Sulfates that are the final oxidation products of sulfurous compounds occur in water in ionic-form. They remain nearly quantitatively in solution (Hem 1959, p. 100), as indicated also in the study area by the similar concentrations of sulfate in discharged ground water and surface waters. It is known that under natural conditions ground and surface waters are apt to carry sulfate-reducing bacteria, which utilize the oxygen from sulfate ions (see Hutchinson 1958, p. 754, Davis, de Wiest 1966, p. 109). Bacteria are likely to occur both in soil horizons and even at considerable depths under anaerobic conditions decreasing the sulfate content of ground water.

### **Ammonia, nitrite and nitrate**

#### **Distribution and contributing factors**

The flowing, humus-bearing surface waters contain on the average higher concentrations of ammonia (63 determinations, median 0.1—0.2 mg per l) than do ground water discharging from Quaternary deposits (278 determinations, median

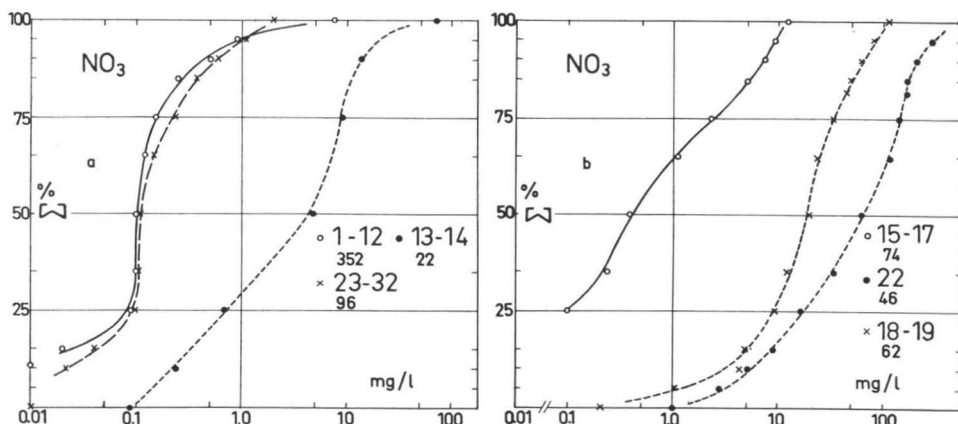


FIG. 28. Cumulative curves showing the frequency distribution of nitrate concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 68.

0.05—0.1 mg per l). The nitrite contents of natural waters were almost invariably below the limit of determination (0.0025 mg per l).

Because ammonia and nitrite are easily released as gases or become oxidized during the transportation of samples (Roberson, Whitehead 1961, p. 10), the low contents registered in laboratory analyses may reflect these phenomena. Furthermore, the content of ammonia is known to diminish notably during the preservation of water samples in polyethylene bottles (Koroleff 1969, p. 105).

The nitrate content of natural waters in the study area is slight (groups 1—12 and 23—32, Fig. 28, a, and appendix 1), but it is tens of times higher in even slightly contaminated ground water (groups 13—14). Its concentrations and the standard deviation of the determinations rise considerably as the contamination increases (groups 18—19 and 22, Fig. 28, b, and appendix 1). It is thus a sensitive indicator of the contamination of waters with a moderate or rich oxygen content, by far more sensitive than ammonia and nitrite. It should be pointed out, however, that the analytical method used to determine the nitrate content is not very accurate (p. 12). Moreover, nitrate may become reduced during the transportation and preservation of water samples.

The contents of nitrogen compounds in the bedrock itself are exceedingly small. For this reason, the nitrogen compounds occurring in natural water have made their appearance when organic, nitrogen-bearing substances oxidized and decomposed, or they are of atmospheric origin, as discussed in more detail on p. 82. According to Taylor (1949, p. 144), vegetable matter, by oxidation in the soil, yields nitrous compounds in very small amounts, while animal matter yields a large amount. Consequently, the contamination of water brings about a rise in the nitrate content. At the first stage, ammonia appears, oxidizing into nitrite and — as the final oxidation



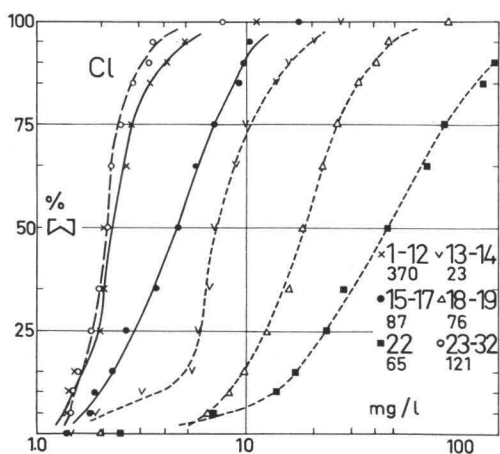


FIG. 29. Cumulative curves showing the frequency distribution of chloride concentrations of ground and surface waters. Symbols as in Fig. 9.

See also Table 1 and text on p. 69—70.

product — into nitrate (see e.g., Hutchinson 1957, pp. 865—866). The oxidation of nitrogen compounds takes place not only through the agency of oxygen dissolved in water but also through the action of proteolytic bacteria. On the other hand, certain bacteria are capable of reducing nitrates back into nitrites. Ammonia, nitrite and nitrate occur principally as ion-form in the pH range usually predominating in ground and surface waters (see Hem 1959, p. 115; Becking, Kaplan, Moore 1960, p. 249). There is a likelihood that ammonia may be bound to humus matter to form complex compounds (Ohle 1934, p. 593), which explains the higher ammonia concentrations of humus-rich surface waters in the study area in comparison with ground waters.

### Chloride and fluoride

#### Distribution

Chlorides and, to a slighter extent, fluorides regularly occur in ground and surface waters under natural conditions. In the light of the analytical results, the chloride content of the ground water discharging from Quaternary deposits and occurring in fissures and fractures of bedrock of the study area is independent of the rock composition. In natural ground and surface waters, it is low (median 2.1 mg per l) and varies within narrow limits (groups 1—12 and 23—32, Fig. 29, and appendix 1). The lowest chloride contents occur in the electrolyte-poor water of esker pools and ponds (13 determinations, median 1.8 mg per l).

The influence of agricultural settlement on the ground water discharged from the Quaternary deposits (groups 13—14) appears as a distinct increase in the chloride

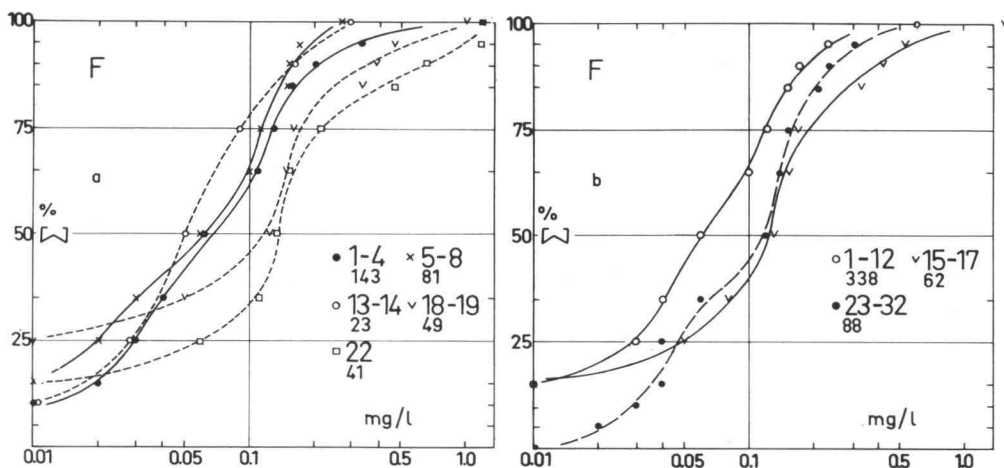


FIG. 30. Cumulative curves showing the frequency distribution of fluoride concentrations of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 70.

content. The chloride content is remarkably high also in slightly contaminated ground water occurring in bedrock (groups 18—19) and this is particularly true of highly contaminated household well water (group 22).

In the ground water discharged from till deposits the fluoride content is richest in granite areas (68 determinations, median 0.08 mg per l) and least in the areas of black schists (14 determinations, median 0.04 mg per l). As a whole the fluoride content and the standard deviations of the determinations are a trifle higher in silicic (groups 1—4, Fig. 30, a, and appendix 1) than in subsilicic bedrock areas (groups 5—8). The fluoride contained in electrolyte-poor perched water and esker pools and ponds is roughly the same (32 determinations, median 0.06 mg per l) as in waters containing dissolved matter in abundance. The contamination of natural waters does not essentially affect the fluoride content (groups 18—19 and 22, Fig. 30, a). Consequently, fluoride is practically independent of the contamination of ground water. The fluoride content of ground water discharged from Quaternary deposits (groups 1—12, Fig. 30, b) is lower than the corresponding contents of ground water contained in fissures and fractures of bedrock (groups 15—17) and of surface waters (groups 23—32).

### Contributing factors

Rankama and Sahama report (1949, p. 756) that the chloride content of igneous rocks averages 0.03 % (by weight). Kuroda and Sandel (1953, p. 879) estimate the average content of chloride in granites and gabbros to be 0.022 %. A large fraction of the total chloride in common igneous rocks, is understood to occur in biotite

and hornblende, which may contain several tenths of a per cent of chloride. Apatite, which occurs in general in amounts of less than 2.0 % in the bedrock of the study area (p. 21), may nevertheless account for much or most of the minerogenic chloride. The chloride content of the bedrock is so slight, however, that the amounts appearing in natural waters can derive only to an insignificant degree from the weathering of mineral matter. The source of the chlorides thus seems to be salts contained in rain. An atmospheric origin is also indicated by the circumstance that the chloride content of dilute natural waters is roughly equal to that of natural water containing abundant dissolved matter.

The results of this study show that as the contamination of ground water increases, the chloride contents increase substantially. They are sensitive indicators of the contamination resulting from agricultural settlement. The sewage of settled areas is apt to contain large quantities of chlorides (see Clarke 1924, p. 6), the effect being that ground water in the sphere of contamination has many times higher a chloride content than has water in a natural state. The chloride content in ground water for this reason increases in general towards centers of population (Taylor 1958, p. 140). According to the studies of Väre (1960, p. 25), household well water in Finland as a whole contains an average of 12 mg per l of chloride — for the most part the consequence of contamination. It is noteworthy that near the coast, chlorides occasionally occur in quite high amounts in the ground water of bedrock (Hyypä J. 1963, p. 61; Salmi 1963, p. 57) and poorly pervious deposits overlain by clay beds (Natukka 1960, pp. 22—23). In the view of a number of researchers, the phenomenon involves relict salinity dating back to postglacial marine stages.

In bedrock, fluoride is present mainly in the apatite and fluorite components as well as, to a small extent, in hornblende and micas. According to Rankama and Sahama (1949, p. 756), the average fluoride content of igneous rocks is 0.06 % (by weight). Although it is higher than the corresponding chloride content, the fluoride content of natural waters is very low compared to that of chloride. The occurrence of fluorides in water limits the slight solubility of apatite and fluorite (Hem 1959, p. 112); yet, the higher fluoride content of granites compared to other rocks (Sahama 1945, p. 7) is reflected in the study area by the slightly higher fluoride content of ground water in till deposits of the granite areas. A corresponding phenomenon has been observed by Väre (1959, p. 161; 1960, p. 25) and Natukka (1963, p. 22), who ascertained that the fluoride content of ground water in the rapakivi areas of Finland is distinctly greater than that in the rest of the county. This reflects the higher fluoride content of rapakivi than other granites.

### **Phosphate**

#### **Distribution and contributing factors**

In ground water discharged from till deposits, 58 per cent of (122) determinations in silicic bedrock areas and 52 per cent of (60) determinations in subsilicic bedrock

areas yielded less than 0.005 mg phosphate per liter. The phosphate contents are almost independent of the composition of the bedrock regardless of the fact that subsilicic rocks contain more phosphate than do silicic rocks (see Goldschmidt 1954, p. 457). The concentrations are roughly equal in amount both in ground and surface waters (62 per cent of 336 determinations below 0.005 mg per l).

The results of this study show that the amounts of phosphate borne into ground and surface waters by the weathering process are very slight. The content of phosphate in the fresh waters does not generally exceed a few micrograms, as shown in the analyses presented by Clarke (1924).

The sole phosphoric mineral of significance in the study area is disseminated apatite. Both the accessory mode of occurrence of apatite in the bedrock and its high resistance to weathering (see, e.g., Pettijohn 1941, p. 618; Krauskopf 1967, p. 89) contribute to the slight concentrations of phosphate in natural waters. The solubility of apatite is promoted, however, by the carbon dioxide and humus contents of water (see Rankama, Sahama 1949, p. 589). In his soil studies, Tamm reported (1930, p. 282) that apatite is, after all, rather susceptible to weathering. Also the tendency of phosphate to become bound together with iron, aluminum and calcium as insoluble complex compounds (see Tamm 1920, p. 121, Viro 1951, p. 15) is a reason for its small concentrations. Humus has been found, however, to impede the precipitation of phosphate by calcium (see Swain 1963, p. 92). Furthermore, the reduction of concentrations during the transportation and preservation of water samples in polyethene bottles may lead to a lowering of the phosphate content (see Koroleff 1969, p. 105).

An important source of phosphate is the waste water from farms and industrial plants; the ground waters contaminated are liable to have a comparatively high content of phosphates (Taylor 1958, p. 142). The effect of contamination on the phosphate content of the ground and surface waters in the study area was not investigated. Chlorides and nitrites, which occur in greater amounts, are more sensitive indicators of contamination than is phosphate (see Taylor 1958, p. 142—143).

### **Permanganate consumption**

#### **Distribution and contributing factors**

The values for permanganate consumption are proportional to the amounts of oxidizable constituents in water, the most important of which are the colloidal humus materials dissolved or suspended in the water. The permanganate consumption is further augmented by the nitrogen compounds at a lower level of oxidation as well as by the ferrous and manganous compounds. Owing to their low contents in the natural oxygen-bearing ground and surface waters of the study area, other oxidizable constituents than the humus matter account for only a very small part of the permanganate consumption. Therefore, permanganate consumption represents a pro-

portional index of the humus content. Because organic matter in water does not oxidize completely and, furthermore, because different types of organic matter oxidize with different intensities, the permanganate consumption values do not give information on the quality or total amount of the organic matter present (Taylor 1958, p. 152).

The permanganate consumption values of ground water discharged from till deposits are higher in areas of silicic (groups 1—4, Fig. 31, a, and appendix 1) than of subsilicic rocks (groups 5—8). The permanganate consumption values of ground water discharged from glaciofluvial material (groups 10—11, Fig. 31, b) or perched water (group 12) are higher than those of ground water discharged from till deposits (groups 1—9).

The permanganate consumption values of oxygen-bearing ground water slightly contaminated by agricultural settlement (groups 13—14) do not fundamentally differ from those of intact ground water (groups 1—9). On the other hand, these values are high in slightly contaminated and, in places, oxygen-poor ground water occurring in bedrock (groups 18—19, Fig. 31, c), as well as, in particular, in heavily contaminated well water (group 22). Permanganate consumption is not, however, as sensitive an indicator of contamination induced by agricultural settlement as are nitrate and chloride (see p. 68, 69—70).

The humus content of flowing surface waters is high, varying according to, among other things, the intensity of paludification of the area and meteorological factors like the amount of precipitation and evapotranspiration. Therefore, there is no reason to assume any correlation between the permanganate consumption of natural water and the local composition of the rocks. The present research material nevertheless indicates that the permanganate consumption values of surface waters flowing across an area of silicic rocks (group 23, Fig. 31, d) and the standard deviation of these values (see appendix 1) are substantially higher than in the case of waters flowing through areas characterized by rocks of subsilicic composition (group 24).

On the average, the permanganate consumption values are lower in ground water discharged from Quaternary deposits (groups 1—12, Fig. 31, e) than in ground water occurring in fissures and fractures of bedrock (group 15—17). The permanganate consumption level and standard deviation of the determinations registered for surface waters (groups 23—32) are high by comparison with the ground water.

In ground water discharged from Quaternary deposits, the lower the pH, the higher the permanganate consumption and thereby the humus content (Table 5). This applies also to surface waters containing an abundance of humus. The main reason for the lower humus content of basic waters containing abundant electrolytes is the precipitating effect of cations on humus (see Hiidenheimo 1963, p. 44). The rather high level of permanganate consumption in ground water occurring near the surface of the ground is due to the filtering of humus-rich water into Quaternary deposits. Arrhenius (1954, p. 327) has likewise observed the permanganate consumption of the water in shallow wells to be on the average higher than that of ground water occurring at greater depths. The rather high permanganate consumption values

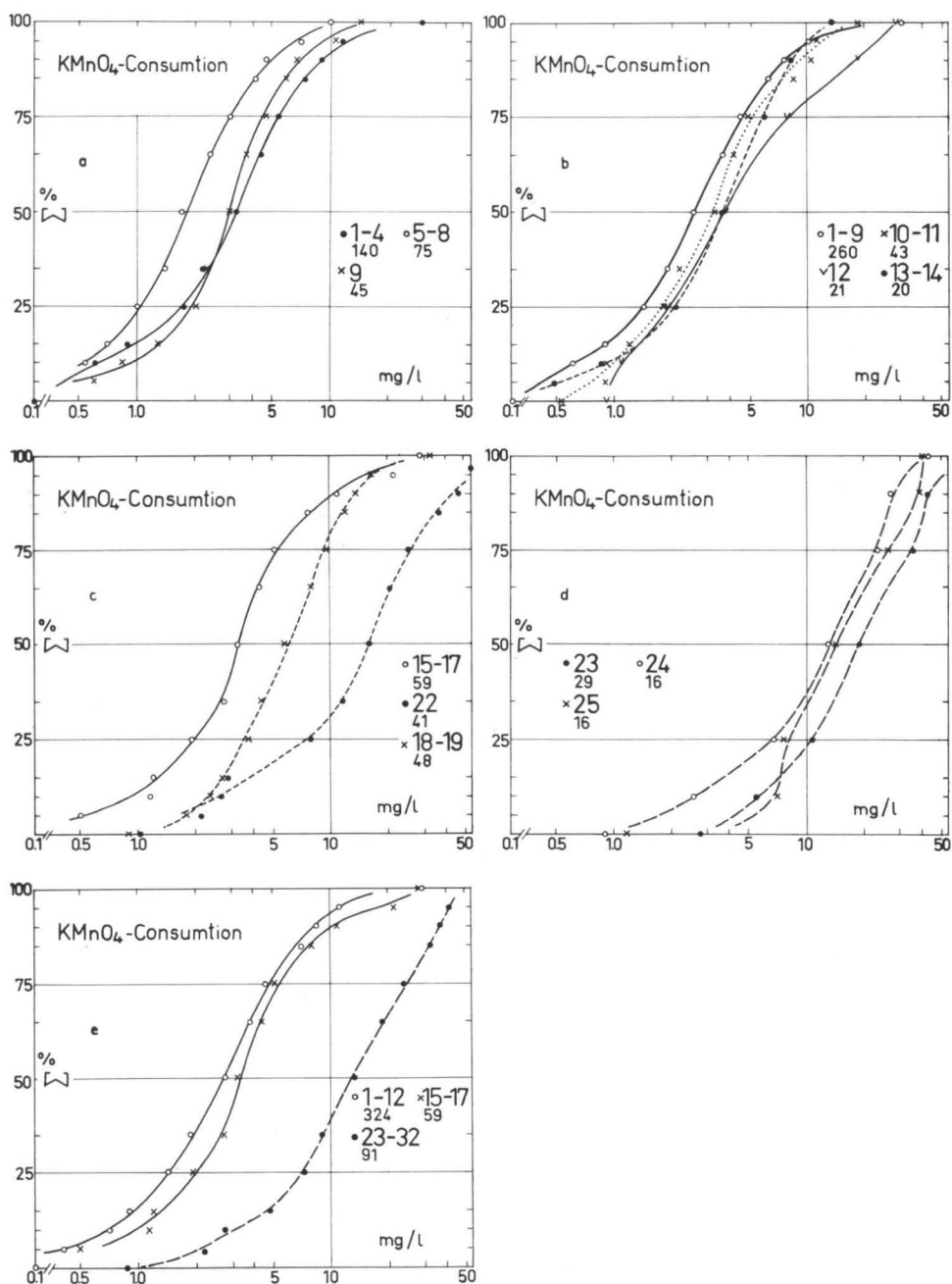


FIG. 31. Cumulative curves showing the frequency distribution of  $\text{KMnO}_4$ -consumption values of ground and surface waters. Symbols as in Fig. 9. See also Table 1 and text on p. 73.

TABLE 5.  
Correlation of the  $\text{KMnO}_4$ -consumption of ground and surface waters to the pH-level.

	Groups	pH (median)	$\text{KMnO}_4$ -consumption (median)	S Standard deviation
Ground water .....	12	6.25	3.9 mg per l	8.4
	10—11	6.45	3.3	3.8
	1—4	6.50	3.3	4.3
	9	6.70	3.1	3.2
	5—8	7.25	1.7	2.1
Surface water .....	23	6.70	19.3	15.4
	25	6.91	14.4	12.9
	24	7.25	12.9	11.7

of ground water occurring in fissures and fractures of bedrock may be attributed to, e.g., ferrous iron occurring under reducing conditions. The highest permanganate consumption values are due to oxidizable waste matter containing, e.g., nitrogen compounds and chlorides, in contaminated waters.

#### Alteration of certain properties during transport and storage of water samples

Many chemical properties of water are apt to change as a function of time during the transportation and preservation of water samples. According to Hem (1961, p. 11) the pH values measured in the field and later in the laboratory differ from each other in the range of  $\pm 0.3$  pH units. Feth, Roberson and Polzer (1964, Table 1) have found that, besides the pH values, also the alkalinity determined in the field averages higher than the laboratory results. Further, Roberson, Feth, Seaber and Anderson (1963) have investigated the changes in the pH and bicarbonate (alkalinity) values. Also these studies showed that field determinations are generally higher than the laboratory determinations, and that field determinations are more representative of water in its natural environment. These researchers observed that the changes are most marked in weakly buffered water samples having a low dissolvedsolid content, like the waters in the study area.

As in these studies, also in the study area the pH values measured in the field are considerably higher, whereas the values for the specific conductance change only slightly during the transportation and preservation of the samples (Table 6). A part

TABLE 6.  
The pH and specific conductance values measured in the field and in the laboratory.

	No. of deter- minations	Measured in the field, mean	Measured in the laboratory, mean
pH .....	447	6.87	6.73
specific conductance .....	361	70—75	76

of the dissolved gaseous carbon dioxide is released from water readily when the pressure prevailing in the sphere of ground water is lowered and the temperature rises. In the waters of the study area the effect of this phenomenon on the pH value is insignificant, however, as shown by the lowering of this value during the transport of the samples. Roberson, Feth, Seaber and Anderson (1963, p. 213) report that waters with a low content of different carbonate species, like the dilute waters in the area investigated, tend to gain carbon dioxide showing a decrease in pH. Further, in the event that iron is precipitated in waters with an abundant iron content, the pH and specific conductance values are appreciably lowered (see Hem 1959, p. 60). Both of these phenomena may lower the pH level in the waters of the study area during the transportation of samples.

In surface waters stored several months in plastic bottles, a significant factor altering the equilibrium of dissolved materials is photosynthesis (see Slack, Fischer 1965), wherein the consumption of carbon dioxide causes a slight increase in the pH. Moreover, the consumption of carbon dioxide may upset the carbonic acid-bicarbonate equilibrium, bringing about a rise in the pH. If, however, the water is not exposed to light, the decay from the death of organisms releases carbon dioxide, which, in turn, lowers the pH value.

### Periodic variations

The pH and the amount of dissolved ionic matter in ground water discharged from Quaternary deposits, as in large springs in the study area, remain relatively unchanged throughout the year (Fig. 32). The values of permanganate consumption are greatest during the period while the ground is thawed out, for then the abundant surface runoff results in the washing of humus substances from the boggy surroundings into the ground water. Also in Sweden, Troedsson (1952, 1955) observed that the chemical composition of ground water occurring in Quaternary deposits remains relatively unchanged, although in winter, sometimes also in the middle of summer, the content of dissolved matter is usually higher than in spring. In the ground water contained in fissures and fractures of the bedrock the electrolyte content is likewise nearly constant all year (Fig. 33).

The iron, manganese and potassium contents are quite unstable in the ground water discharged from Quaternary deposits and in the ground water stored in bedrock. The variations in the concentrations of iron and manganese are partly due to the changes in the ground-water table. As the level of the ground water rises, the iron and manganese compounds that had become precipitated in the ground are likely to redissolve under reducing conditions. As a result, the iron and manganese concentrations in the ground water are apt to vary according to the fluctuations in the ground-water table — and thus according to the seasonal variations (see Scheider 1952, pp. 61—62. Eriksson E., Khunakasem 1968, pp. 99—100). Of the alkaline earths, magne-



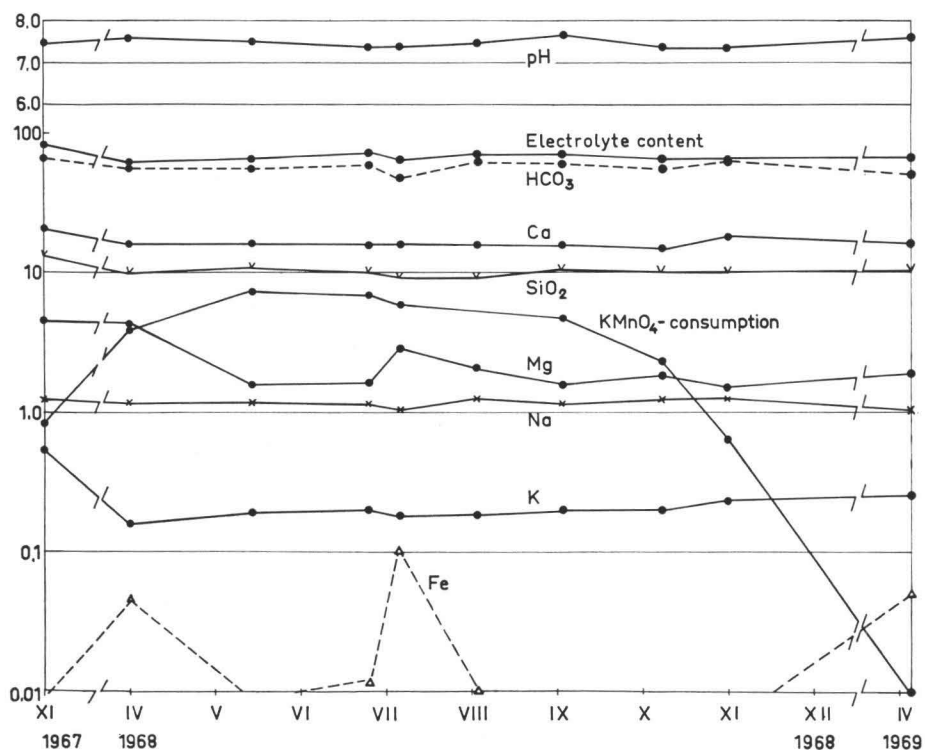


FIG. 32. Periodic variations in the chemical composition of ground water discharged from till deposits (a great spring in Nuokkioselkä, Kittilä). The average electrolyte content is calculated from the specific conductance value by multiplying by 0.75.

sium is more susceptible to change than calcium, which has also been noticed by Feth, Roberson and Polzer in Sierra Nevada (1964, Fig. 10).

At different seasons of the year, the composition of the surface water in the area investigated varies considerably more than that of the ground water (Figs. 34—35). In the spring, when the snow melts and the ground frost thaws out, there are large amounts of streaming water, and as a consequence the contents of substances dissolved in the water and the pH yield lower values. The relative amounts of the different substances remain approximately constant even with low concentrations, as in the case of ground water, too. Exceptions are iron, manganese and potassium, which often increase in amount as other contents diminish and the pH value falls. The increase in iron and manganese is caused by the greater solubility made possible by the lowered pH and, further, the washing away from boggy areas by floodwaters of iron-bearing water rich in humus matter. The last-mentioned conclusion is supported by the simultaneous increase in the  $\text{KMnO}_4$ -consumption.

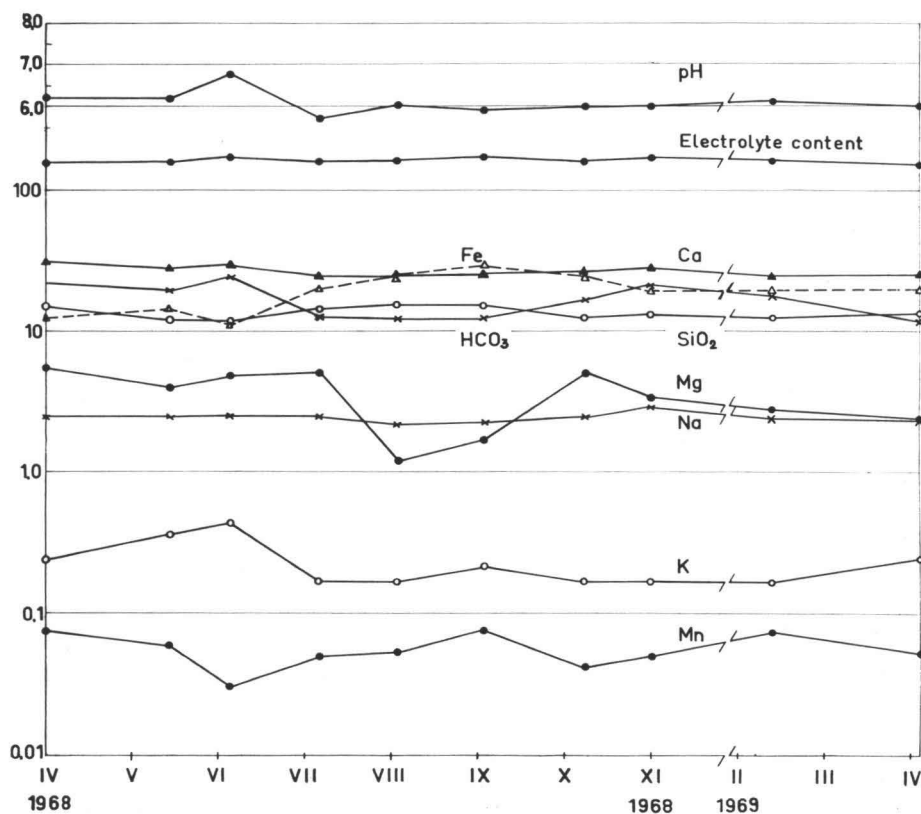


FIG. 33. Periodic variations in the chemical composition of ground water occurring in the bedrock (a well drilled in bedrock in Riikonkumpu, Kittilä).

Studies by other researchers concerning the variations in the composition of river waters in northern Finland have yielded similar results. In Kemijoki and Lismaoja (the latter in Sodankylä commune) the content of dissolved matter is greatest in March and April and lowest during the flood season brought on by the melting of the snow (see Holmberg 1935, Väre 1961), which J. V. Eriksson (1929, pp. 79—84), too, has observed in Sweden. The  $\text{KMnO}_4$ -consumption values are the highest in summer and lowest in winter, which, according to Hiidenheimo (1963, p. 44), is a circumstance dependent on the precipitative effect on humus material of an increasing electrolyte content. The contents of iron and manganese in Kemijoki vary greatly at different seasons of the year and even on the same day at observation points situated close together (Karjalainen 1965, pp. 98—99): The highest contents of iron and manganese occur during the late winter, although, to be sure, also during the flood period there is a slight maximum brought about by acid, iron-rich humus waters washed down from boggy tracts and peat lands.

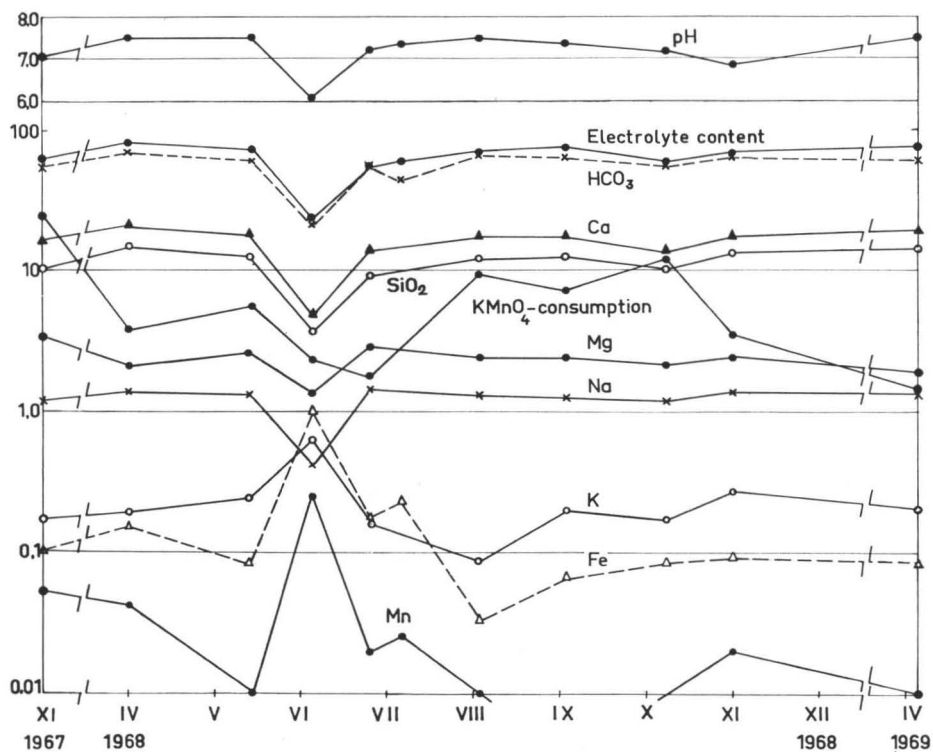


FIG. 34. Periodic variations in the chemical composition of surface water (The upper course of Ala-Vaalojoki, a river in Sodankylä).

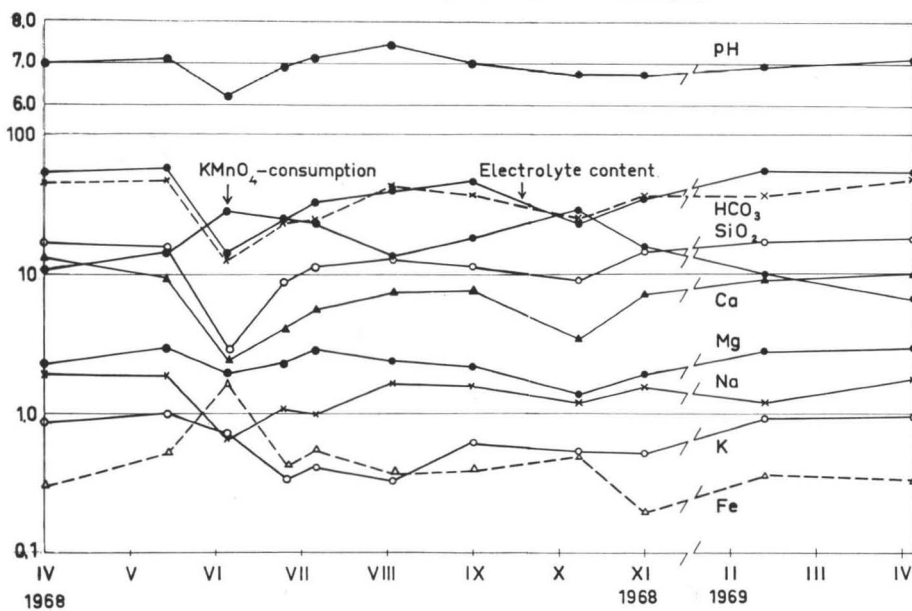


FIG. 35. Periodic variations in the chemical composition of surface water (The upper course of Loukinen, a river in Kittilä).

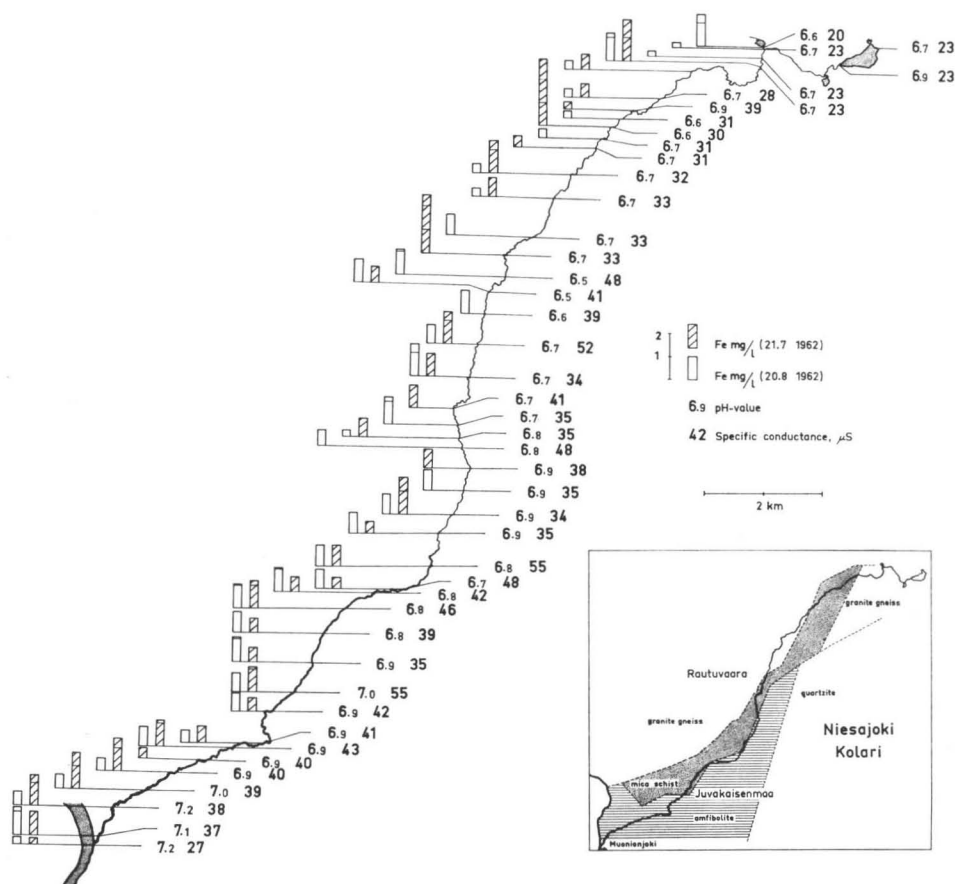


FIG. 36. Variations in the pH, specific conductance values and iron-value along the whole course of the Niesajoki on July 21, 1962. The iron contents were likewise measured, on August 20, 1962.

The author made a local study of the variations of the pH and specific conductance values and iron concentrations in the Niesajoki (a small river in Kolari commune) during a single 24-hour period (July 21, 1962) over the whole course of the river. The pH and specific conductance values vary within rather narrow limits (Fig. 36). They rise somewhat in the amphibolite area of the lower course of the river; thus the influence of the bedrock is slightly brought to bear. The iron content varies quite markedly, particularly in the upper and middle courses of the river, where the bedrock consists of silicic rocks, the banks are boggy and the current slow. The iron content averages highest in the amphibolite belt of the lower course, and there it is also most consistent by virtue of the swift current of the series of rapids. The iron contents

measured on two different sampling occasions (July 21 and August 20, 1962) varied greatly at the same point. Variations of content in flowing surface waters are affected not only by variations in the petrographic composition of the rocks, the redox potential and the pH but also by the rate of flow and the quality of the water contributed by tributary streams.

The seasonal variations in the chemical composition of the surface waters are many times greater than in ground water. The effect of runoff on surface waters is greatest in spring. The data obtained in the present study show that the water of small rivers and brooks in winter and during dry summer periods consists of ground water discharged from Quaternary deposits.

### Atmospheric precipitation as a source of inorganic matter

Gorham (1961, p. 795) has emphasized in his studies that the amounts of matter introduced from the atmosphere into natural waters by rain have been underestimated in relation to the total quantity of matter dissolved in water. The content of matter in rain varies greatly, however, and it depends on, among other things, the density of settlement, industry, the amount of rain and the length of the rainy seasons as well as the distance to the sea (see e.g., Rankama, Sahama 1949, p. 312).

The chemical composition of rain water in four Fennoscandian areas is shown in Table 7. The pH value of rain water is generally 4.3—5.9 (see Tamm 1953; Gorham 1955, Table 1; Carrol 1962, p. 8); in Sodankylä the average figure is 5.4.

In Table 8, section B presents the ratios of inorganic matter derived from the atmosphere in the ground water discharged from till deposits and in the surface waters of areas characterized by silicic (section d) and subsilicic bedrock (section e). The chief factor of uncertainty in these calculations is the inaccuracy of the amount of

TABLE 7.  
Content of inorganic matter in rain water.

	Salinity mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	SO <sub>4</sub> mg/l	NO <sub>3</sub> mg/l	SiO <sub>2</sub> mg/l
1. ....	4—7	0.5	0.1	0.5	0.2	0.6	3.5	0.06	
2. ....	6	0.4	0.2	0.3	0.4	1.0	0.7		0.5
3. ....						0.3	1.8		
4. ....	4	0.4		0.6	0.3				0.4

1. Mean composition of rain-water samples collected monthly in Sodankylä, in the study area, during the years 1956—1964. According to data kindly made available by Dr. Koroleff. The Institute of Marine Research, Helsinki. (Years 1956—1960 in appendices published quarterly in »Tellus»).
2. Composition of the water from single snow samples, taken from ten sampling sites representing the main part of Finland in 1952 and 1953 (Viro 1955, p. 36).
3. Mean composition of rain water in northern Finland in 1955—1957 (Eriksson E. 1960, p. 81, 86).
4. Mean composition of rain water collected from an open space in central Sweden during several short periods in 1951 and 1952 (Tamm 1953, pp. 88—90).

TABLE 8.

Calculated average ratios, in per cent, of inorganic matter borne by rain both in ground water discharged from till deposits and in surface waters (section B) in areas of silicic (d) and subsilicic (e) bedrock. Section A represents the composition of ground (1—4, 5—8) and surface water (23, 24) in areas of silicic (a) and subsilicic (b) bedrock. Estimated composition of rain water (c).

Content of inorganic matter in ground and surface waters			Electrolyte content	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>2</sub>
			medians, mg/l								
A	a	groups 1—4	29	3.2	1.2	1.4	0.5	2.1	2.9	0.1	12.3
		and 23	29	4.8	1.7	1.6	0.4	2.1	3.1	0.1	12.4
	b	groups 5—8	91	15.2	3.3	1.2	0.5	2.1	9.0	0.1	10.6
		and 24	78	14.4	3.4	1.3	0.4	2.1	7.8	0.1	10.6
Content of inorganic matter in rain water	c		estimated, mg/l								
			5	0.5	0.1	0.5	0.2	0.6	1.0—3.0	0.06—0.1	0.4
Calculated average ratios of atmospheric inorganic matter in ground and surface waters	B		%								
	d	$\frac{c}{a} \cdot 100\%$	15—20	10—15	5—10	30—35	40—50	30	30—100	60—100	5
	e	$\frac{c}{b} \cdot 100\%$	5—7	5	5	40	40—50	30	10—40	60—100	5

matter contained in rain water (section c); relatively low values were estimated on the basis of the determinations presented in Table 7. According to the calculation, a noteworthy proportion of the matter contained in the ground and surface waters of the study area derives from atmospheric precipitation. Naturally, in the acid, electrolyte-poor waters of silicic bedrock areas (section d), the ratio is higher than in the waters of subsilicic bedrock areas containing electrolytes in abundance (section e). It is only in dilute waters that matter derived from the atmosphere has any significant effect on the calcium and magnesium contents (section d). All natural waters in the study area receive quite significant alkali replenishments from the atmosphere, which contributes nearly half the potassium (sections d and e).

Owing to the fact that the routine analytic method applied in this study (p. 13) tends to give excessive values in the case of small concentrations, the ratio of atmospheric chloride is apparently considerably higher than the figures in Table 8 would presuppose. Particularly in waters of silicic bedrock areas (section d), sulfate is mainly derived from the atmosphere. Regardless of the electrolyte content of natural waters, nearly all the nitrate comes from the atmosphere. The main part of the electrolytes of ground and surface waters in the study area consists of bicarbonates, which are almost totally lacking in acid rain waters. Thus, rain water does not add notably to the total electrolyte content of ground and surface waters.

The discharge coefficient of the Kemijoki river is 0.64—0.77 (Saarinen 1966, p. 16). Consequently, the evaporation ranges from 23 to 36 per cent. If this is considered in the calculations presented in the Table 8 the portion of the inorganic matter derived from the atmosphere into natural waters increases respectively.

According to Viro (1955), appreciable amounts of chloride, nitrogen compounds and alkali metals of river waters are brought by precipitation. Gorham's calculations (1961, p. 805), which are partly based on Viro's material (1955), indicate that 22 to 40 % of the calcium and 10 to 11 % of the magnesium contents of the Vuoksi and Kymi rivers in southern Finland as well as 17 to 25 % of the sodium and 11 to 22 % of the potassium contents originate in the atmosphere. The corresponding proportions of chlorides and sulfates are 31 to 50 % and 53 to 71 %. Similarly, according to Carrol (1962, p. 1), in humid regions the important amounts of Ca, Mg, Na and K added by rain may be expected to influence the composition of the natural waters. Further, E. Eriksson (1960, pp. 82—83, 86) reported that in Sweden and Finland the ratios of chloride in precipitation to chloride in river run-off varies from 0.15 to 0.76 being on the average 0.30 and the proportion of sulfate being correspondingly 0.50 to 0.80. In central Sweden the sulfate content of rain water is in some places twice as high as that of the water flowing in rivers.

Troedsson (1955, pp. 78, 92) ascertained through his investigations that the rain water remaining on the surface of the ground fairly rapidly achieves an ion equilibrium with the mineral matter and thereby nearly the same composition as the ground water proper. Eriksson E. and Khunakasem (1968, p. 90) remarked that soil can hardly contribute much to the chemistry of ground water and its composition is therefore largely determined by the composition of precipitation and the fraction re-evaporated. According to Laney (1965, p. 187), the change in the character of the dissolved constituents from rain water to ground water is apparently rapid. The outstanding difference in chemical composition of the two kinds of water results from the solution of magnesium, sodium and silica in the ground, and from the removal of sulfate by anion exchange with clay minerals or bacterial reduction.

### **Correlation between properties and chemical components of water**

Many of the properties and chemical components of water are closely correlated. For this reason, correlation calculation and regression analysis were applied to gain a clearer picture of these correlations. The regression lines and total correlation coefficients were worked out for the properties selected with respect to observed correlation of the ground water discharged from Quaternary deposits jointly with the surface waters (groups 1—12 and 23—32). These correlations are presented as graphic correlation diagrams, in which the lines obtained have also been drawn (Figs. 37—47). The correlation matrix was computed in smaller combinations of groups (I—VI, see appendix 2) to clarify the nature of the correlation in more detail, these being as follows:

	Groups	
I .....	1—4	ground water discharged from till deposits in areas of silicic bedrock
II .....	5—8	ground water discharged from till deposits in areas of subsilicic bedrock
III .....	1—9	ground water discharged from till deposits in general
IV .....	15—17	ground water occurring in bedrock
V .....	13—14	ground water occurring in Quaternary deposits
	18—22	and bedrock, contaminated by agricultural settlement
VI .....	23—32	surface waters

The pH of natural waters shows a clear correlation to the bicarbonate contents and total hardness (Figs. 37—38). The pH correlates to these better in ground water discharged from till deposits (III,  $r = 0.72$ ,  $r = 0.72$ , see appendix 2) than in the ground water of bedrock (IV,  $r = 0.53$ ,  $r = 0.40$ ) or in surface waters (IV,  $r = 0.51$ ,  $r = 0.49$ ). The pH correlates to calcium more closely (III,  $r = 0.69$ ,  $r = 0.53$ ) than to magnesium (III,  $r = 0.47$  and VI,  $r = 0.24$ ). In contaminated ground water, on the other hand, there is no noteworthy correlation between the pH value and bicarbonate or total hardness.

In view of the fact that bicarbonate and calcium are by far the most abundant ionic constituents of the natural waters of the study area (Fig. 49), the foregoing correlations show the  $\text{Ca}(\text{HCO}_3)_2$ -content to be an important factor in regulating the pH value. This applies particularly to the ground water discharged from till deposits, though not equally unambiguously to the ground water contained in bedrock or to surface waters. In the ground water occurring in bedrock, there is not the same abundance of bicarbonates in relation to the other constituents (groups 15—17, Fig. 49); and under the reducing conditions in places the behaviour of iron as a function of the redox potential also influences the pH value (p. 76). In surface waters the pH is regulated by, in addition to the bicarbonate, the photosynthesis of organisms in the water (p. 76). In contaminated ground waters, again, the decomposition products of organic waste matter influence the pH value more than does the bicarbonate, which occurs in relatively small amounts (group 22, Fig. 49). This influence is opposite to that of bicarbonate; that is, it tends to lower the pH value.

In acid waters there is generally an abundance of dissolved free carbon dioxide (p. 46), which is of significance in regulating the pH. Although the  $\text{CO}_2$  determinations in the laboratory are inaccurate (p. 47), owing to the tendency of carbon dioxide to be released from water as gas, there exists a slight negative correlation between the  $\text{CO}_2$  concentrations and the pH in ground water (100 determinations,  $r = 0.30$ ). In more basic bicarbonate-bearing waters, the relatively slight carbon dioxide content has no essential effect on the pH values. The bicarbonate and carbon dioxide contents thus have an opposite influence on the pH.

The pH values of ground water discharged from till deposits and the surface waters have a slight negative correlation to the permanganate consumption (III,



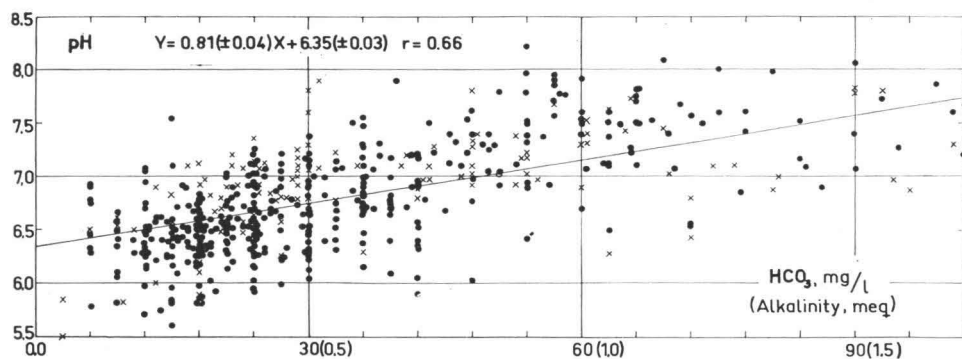


FIG. 37. Correlation between pH-values and bicarbonate concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

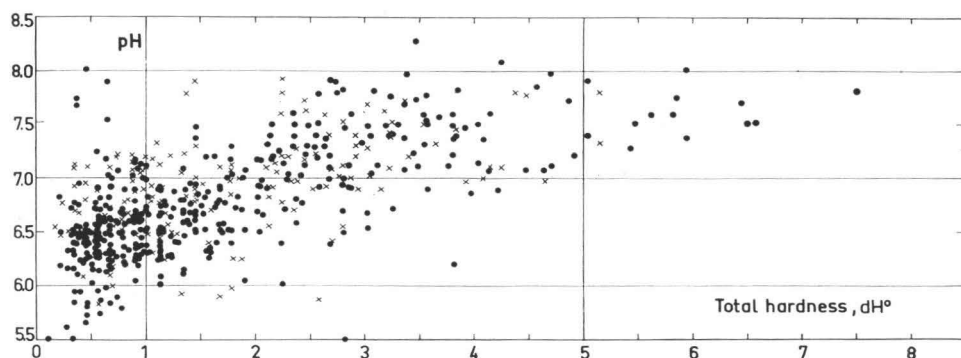


FIG. 38. Correlation between pH and total hardness values in natural ground (·) and surface (×) waters (groups 1—12 and 23—32).

$r = -0.38$  and VI,  $r = -0.29$ ). Unexpectedly enough, a rich humus content induced by the flow of acid humus-bearing waters from peat lands has less of an effect in lowering the pH value of surface waters than of ground water. Nor does the sulfate, which indicates sulfuric acid generated by weathering, cause any drop in the pH level (III,  $r = 0.37$ ).

A marked correlation prevails between the bicarbonate content and total hardness. The correlation is most conspicuous in the ground water discharged from till deposits and in surface waters (III,  $r = 0.94$  and VI,  $r = 0.92$ ), but it is noteworthy also in the ground water contained in bedrock and in contaminated ground water (IV,  $r = 0.70$  and V,  $r = 0.71$ ). The bicarbonate correlates to calcium more closely (III, VI,  $r = 0.85$ ,  $r = 0.94$ ) (Fig 39) than to magnesium (III,  $r = 0.70$  and VI,  $r = 0.67$ ). In the light of the foregoing, calcium, in particular, and also magnesium occur in natural ground and surface waters in the form of bicarbonates. This observation likewise applies to contaminated ground waters.

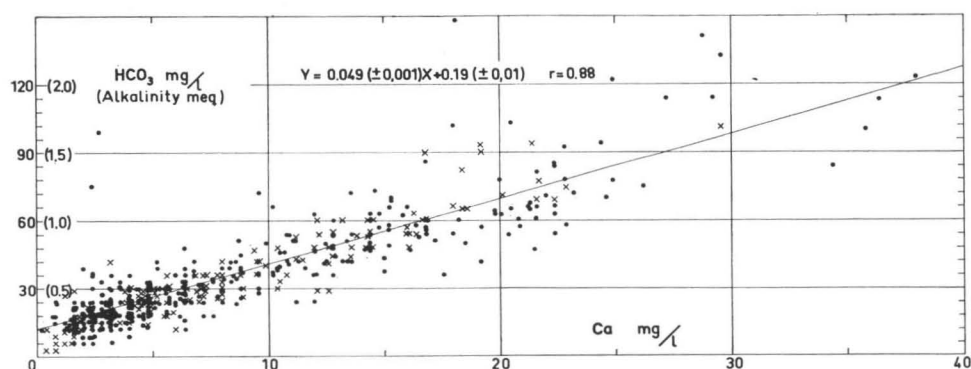


FIG. 39. Correlation between bicarbonate and calcium concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

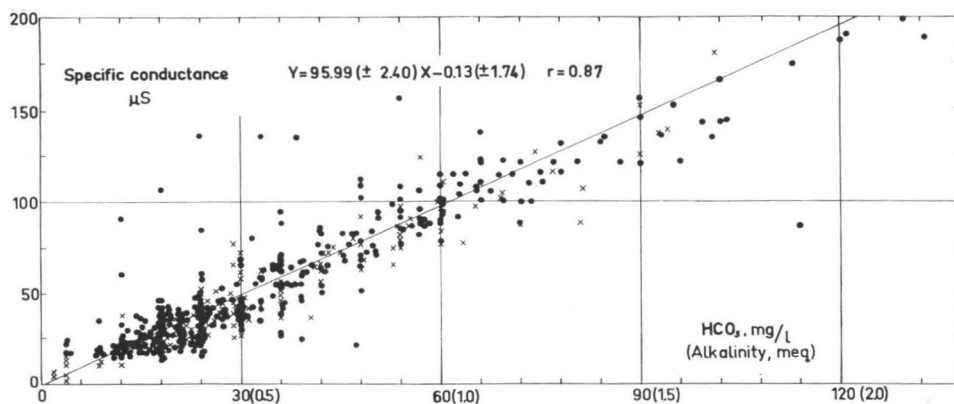


FIG. 40. Correlation between specific conductance values and bicarbonate concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

The specific conductance correlates strongly to bicarbonate content (Fig. 40) and total hardness, more markedly in surface waters (VI,  $r = 0.95$ ,  $r = 0.95$ ) than in ground water (III,  $r = 0.86$ ,  $r = 0.85$  and IV,  $r = 0.85$ ,  $r = 0.79$ ). It is notable that the correlation is stronger in dilute ground waters (I,  $r = 0.80$ ,  $r = 0.79$ ) than in water containing electrolytes in greater abundance (II,  $r = 0.69$ ,  $r = 0.66$ ). Specific conductance correlates more closely to calcium (VI,  $r = 0.95$  and III,  $r = 0.77$ ) (Fig. 41) than to magnesium (VI,  $r = 0.70$  and III,  $r = 0.62$ ). In contaminated ground waters, the correlation between specific conductance and total hardness is closer (V,  $r = 0.83$ ) than between specific conductance and bicarbonate content (V,  $r = 0.60$ ). Specific conductance correlates to sulfate less markedly (III,  $r = 0.50$ ) than to bicarbo-

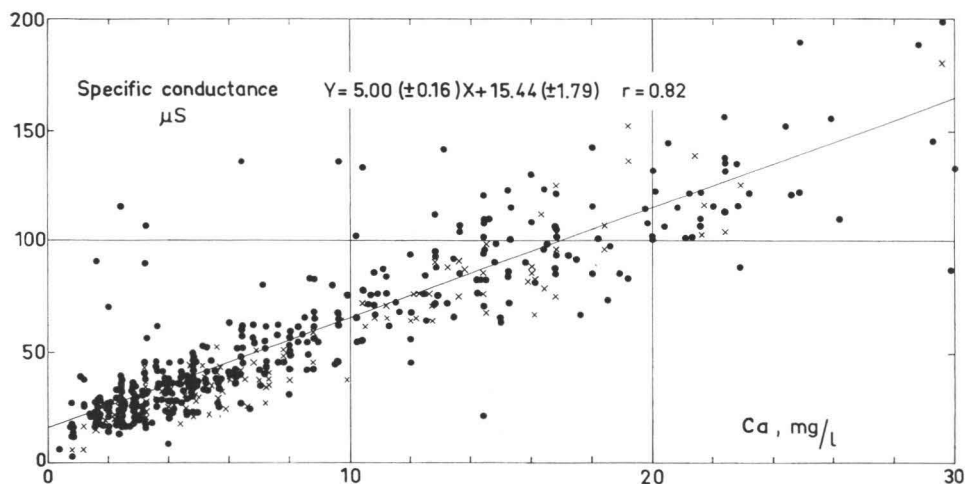


FIG. 41. Correlation between specific conductance values and calcium concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

nate and total hardness, and the correlation is weakest in ground water containing electrolytes in abundance (II,  $r = 0.25$ ). There is a slight negative correlation between specific conductance and permanganate consumption values (III,  $r = -0.24$  and VI  $r = -0.21$ ).

To summarize the foregoing, the  $\text{Ca}(\text{HCO}_3)_2$ , which occurs more abundantly than other constituents in natural waters, and, to a lesser extent, the  $\text{Mg}(\text{HCO}_3)_2$  regulate not only the pH but also the level of the specific conductance. The effect of sulfate in augmenting the specific conductance is most marked in dilute waters, although taken as a whole its contribution in this respect is slight. A rise in the humus content of water induces a slight reduction of the specific conductance, which may be partly due to the formation of complexes between the cations and the humus. On the other hand, acid electrolyte-poor surface waters have been found to contain the greatest abundance of humus (p. 73).

Inasmuch as the quantity of a  $\text{Ca}(\text{HCO}_3)_2$  is the main factor regulating the pH and the specific conductance, the clear correlation between them is understandable (Fig. 42). The correlation is more marked in the ground water of till deposits (III,  $r = 0.60$ ) than in surface waters (VI,  $r = 0.47$ ) and the ground water stored in bedrock (IV,  $r = 0.43$ ). On the other hand, it is stronger in dilute waters of an acid character than in slightly basic waters containing electrolytes in greater abundance (I, II,  $r = 0.52$ ,  $r = 0.26$ ). Any increase in the quantity of electrolytes has no essential effect on the pH value of waters in areas characterized by subsilicic bedrock. In contaminated ground waters, there is no correlation between the pH and the specific conductance.

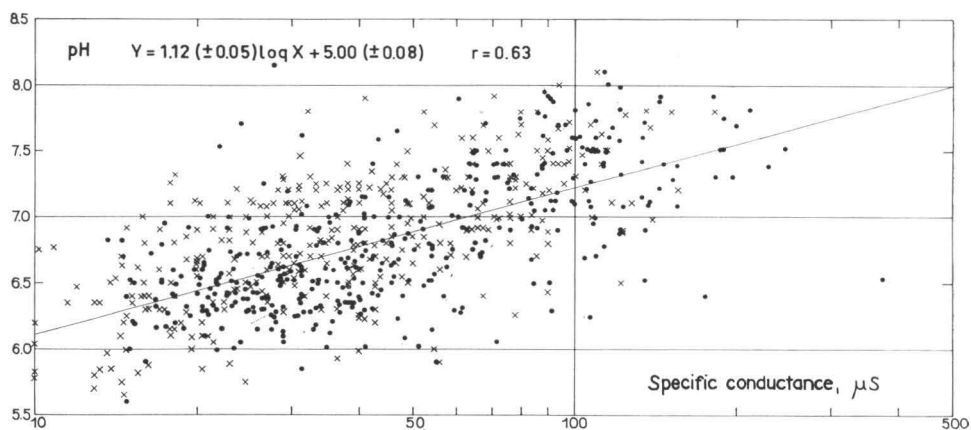


FIG. 42. Correlation between pH and specific conductance values of natural ground (·) and surface (×) waters (groups 1–12 and 23–32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown, sented at the top of the diagram.

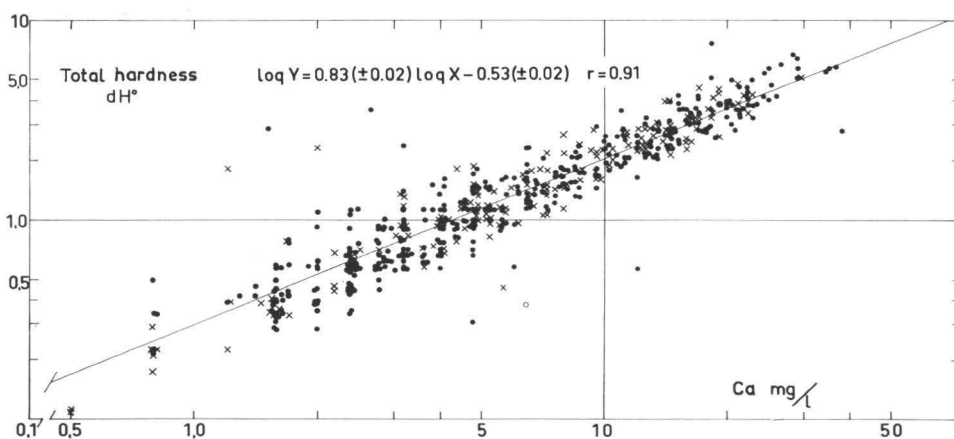


FIG. 43. Correlation between total hardness values and calcium concentrations of natural ground (·) and surface (×) waters (groups 1–12 and 23–32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

The correlation between total hardness and calcium in ground and surface waters (III,  $r = 0.90$ , VI,  $r = 0.94$  and V,  $r = 0.86$ ) is stronger than between total hardness and magnesium (III,  $r = 0.74$ , VI,  $r = 0.84$  and V,  $r = 0.68$ ) (Figs. 43–44). The correlation between total hardness and calcium is much closer in slightly basic than in dilute acid waters (II,  $r = 0.86$  and I,  $r = 0.49$ ). The influence of calcium on total hardness, occurring as it does abundantly, is thus appreciably more significant than that of magnesium. This applies especially to the waters of areas characterized by subsilicic bedrock, which waters contain electrolytes in abundance. In estimating the

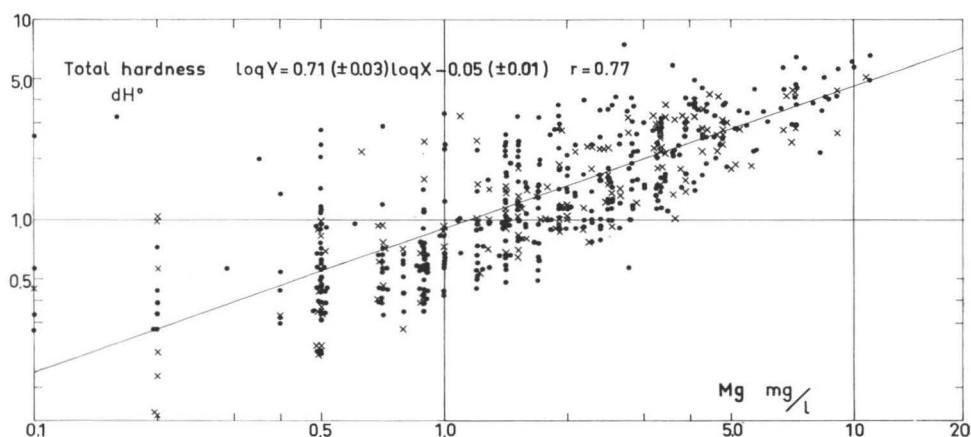


FIG. 44. Correlation between total hardness values and magnesium concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

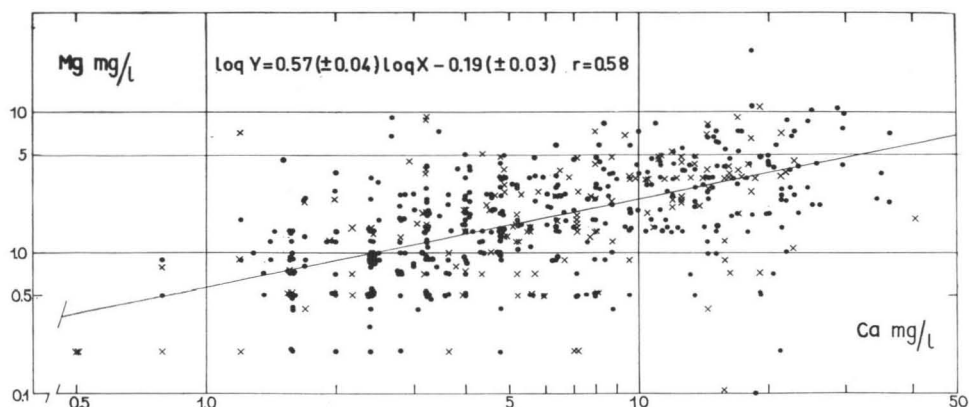


FIG. 45. Correlation between magnesium and calcium concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

meaning of correlation coefficients, one must keep in mind, as previously mentioned (p. 12), the influence of the inaccuracy in the determinations of magnesium in particular. Calcium correlates only slightly with magnesium (Fig. 45), which means that the concomitant occurrence of alkali earths is not necessary.

Among the alkali metals, potassium correlates only slightly to specific conductance in dilute acid ground waters and surface waters (I,  $r = 0.49$  and VI,  $r = 0.47$ ). In contaminated ground waters, by contrast, sodium and potassium correlate closely to specific conductance (V,  $r = 0.90$ ,  $r = 0.86$ ). The alkali metals thus increase

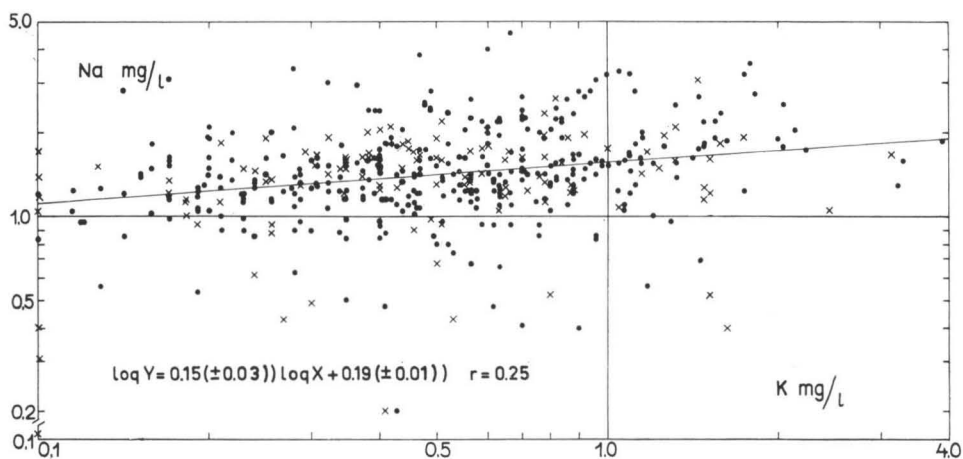


FIG. 46. Correlation between sodium and potassium concentrations of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

markedly as the electrolyte concentration induced by contamination increases, and serve, as already noted (p. 53), as sensitive indicators of contamination. Likewise, the correlation between sodium and potassium is marked only in contaminated ground water (V,  $r = 0.90$ ), but it is slight in intact ground and surface waters (Fig. 46).

The other indicators of contamination, chlorides, nitrates and permanganate consumption, correlate distinctly to specific conductance in contaminated ground waters (V,  $r = 0.85$ ,  $r = 0.69$ ,  $r = 0.47$ ). As the coefficients of correlation show, chloride seems to be a more sensitive indicator of increasing contamination than is nitrate, the permanganate consumption being in this respect the least sensitive. The higher correlation coefficient of chloride probably is perhaps partly due to its more accurate determination compared with nitrate. Moreover, sodium and potassium, while indicating contamination, correlate clearly to nitrate (V,  $r = 0.66$ ,  $r = 0.62$ ) and to chloride (V,  $r = 0.75$ ,  $r = 0.68$ ). The coefficient of correlation between nitrate and chloride is nevertheless small (V,  $r = 0.44$ ), so that the contamination of ground water appears variably, depending on the origin of the pollutants, as an increase in the content of chloride or nitrate or both.

The silica content of natural ground and surface waters is virtually independent of the other properties or dissolved components of the water. In dilute ground water contained in till deposits, it correlates only slightly to the bicarbonate content and total hardness (I,  $r = 0.34$ ,  $r = 0.37$ ) and in slightly basic waters containing more dissolved salts to the sodium and, negatively, to the pH values (II,  $r = 0.49$ ,  $r = -0.21$ ). The lastmentioned correlation is in agreement with the slight negative correlation between silicate content and pH level (Fig. 47).

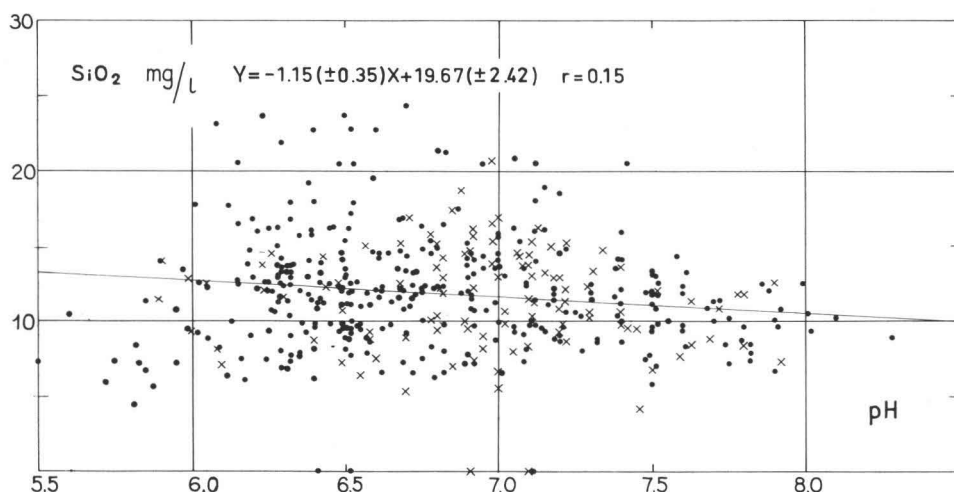


FIG. 47. Correlation between silica concentrations and pH values of natural ground (·) and surface (×) waters (groups 1—12 and 23—32). The equation of the regression line, also drawn out in the diagram, and the coefficient of correlation are shown.

In oxygenated ground water discharged from till deposits, the iron and manganese are nearly independent of the other components, but in surface water iron correlates slightly to the humus content indicated by the permanganate consumption (VI,  $r = 0.54$ ). This is in agreement with the marked iron concentrations observed in humic surface waters (p. 63). In contaminated waters, the manganese correlates to the ions indicating contamination, as with sodium and potassium (V, 0.50, 0.56). The occurrence of iron and manganese in contaminated ground waters is associated principally with the prevalence of conditions short on oxygen. Also the correlation between iron and manganese is most conspicuous in contaminated ground waters (V,  $r = 0.54$ ), but somewhat less so in the ground water occurring in bedrock (IV,  $r = 0.43$ ). In the oxygenated ground water occurring in till deposits, it is low (III,  $r = 0.22$ ). Thus these metals do not necessarily occur concomitantly (p. 64).

## DISCUSSION AND CONCLUSIONS

The cumulative curves presented in Fig. 48 provide a graphic basis of comparison of the amounts of dissolved matter in the waters of the study area. The numbers of determinations vary, so that the curves are not altogether mutually comparable; nevertheless, they do reveal the orders of magnitude and relative quantities. Curves represent both natural and contaminated ground and surface waters, and for this reason the range of variation of their contents is wide.

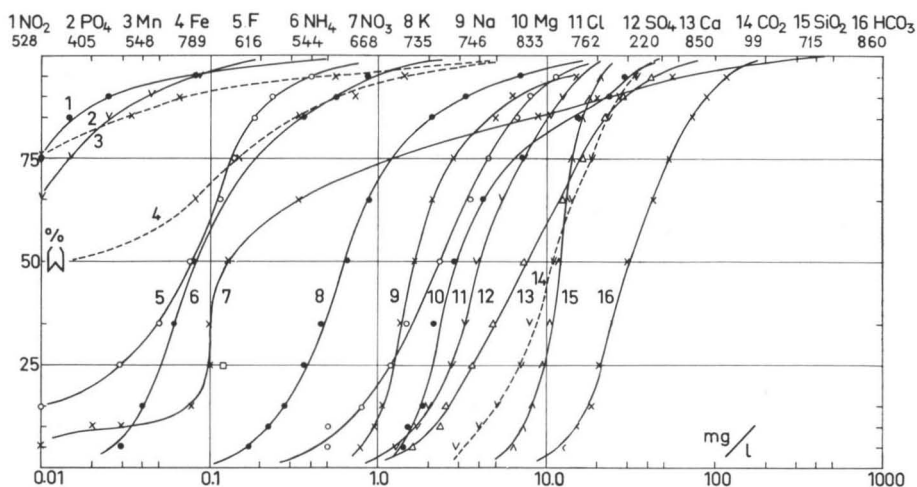


FIG. 48. Cumulative curves showing the frequency distribution of the chemical components of all the investigated waters, both natural and contaminated. The numbers attached to the curves refer to the numbering of the components listed at the top of the diagram. The figures under the components show the number of determinations.

Of the elements and compounds dissolved in water, the most abundant by far is bicarbonate (curve 16). Of the other anions, silica (curve 15) occurs in amounts in the same order of magnitude as free carbonic acid (curve 14), but the range of variation of silica is narrower than that of any components dissolved in water. Sulfate (curve 12) is present in smaller amounts than the aforementioned substances, and phosphate occurs in exceedingly small quantities (curve 2). The wide range of variation in the chloride (curve 11) and nitrate (curve 7) contents is due to the high concentrations of these components in contaminated waters. Fluorides (curve 5) regularly occur in smaller amounts than chlorides.

Calcium (curve 13) occurs in manifold quantities compared to the other cations. Magnesium (curve 10) and sodium (curve 9) are present in roughly equal amounts, but there is appreciably less potassium (curve 8). The great variation in alkali contents is due to the high concentrations found in contaminated ground waters. In oxygen-bearing waters, the amounts of iron (4) and manganese (3) are small compared to alkaline earths and alkali metals. Only in oxygen-poor ground water occurring in bedrock and in contaminated ground waters are there instances of abundant iron. Manganese usually occurs in lower concentrations than iron.

In order to produce a fuller picture of the chemical composition of the ground and surface waters in the area investigated, the proportional distribution of the mg-equivalents of the most important cations and anions is presented as graphic ion-roses in Fig. 49. The figure shows that ground and surface waters in a natural environment are predominantly  $\text{Ca}(\text{HCO}_3)_2$  waters. Conway (1942, pp. 134—135) has observed



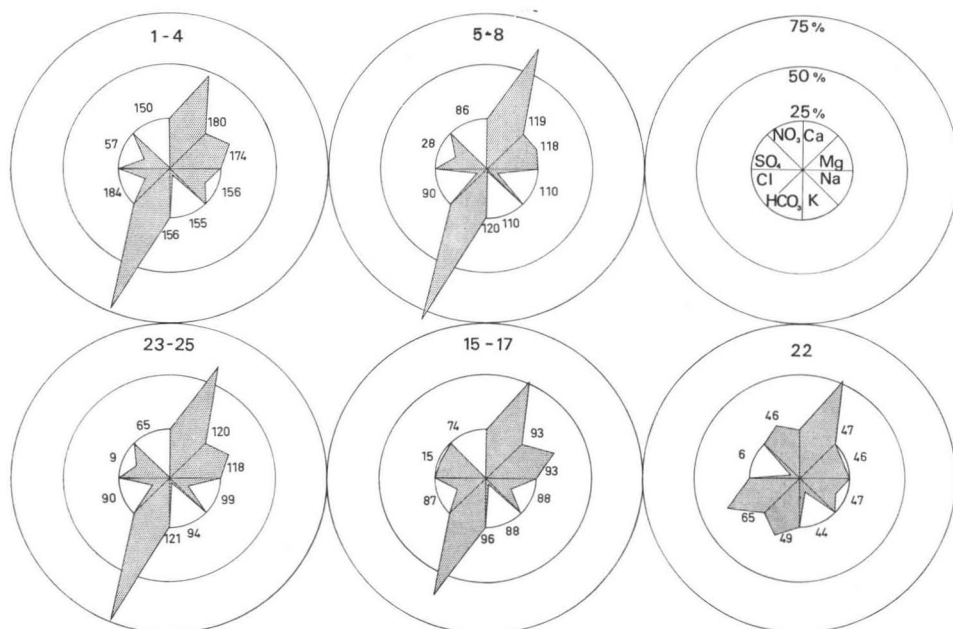


FIG. 49. Percentage of the mg-equivalents of the most important anions and cations presented as ion-roses. Groups 1—4, ground water discharged from till deposits in areas of silicic bedrock. Groups 5—8, ground water discharged from till deposits in areas of subsilicic bedrock. Groups 15—17, ground water occurring in bedrock; group 22, ground water strongly contaminated by agricultural settlement; groups 23—32, surface water. The smaller figures indicate the number of determinations.

the same circumstance to prevail generally in the dilute surface waters that originate in drainage areas composed of igneous rocks. In the ground water discharged from till deposits in the study area, the relative content of  $\text{Ca}(\text{HCO}_3)_2$  is distinctly higher in ground waters of subsilicic bedrock areas containing abundant electrolytes (groups 5—8) than in acid dilute ground waters of silicic bedrock areas (groups 1—4). The relative contents of magnesium and sodium, which occur in much smaller amounts than calcium, are higher in acid dilute waters (groups 1—4). Flowing surface waters (groups 23—32) do not essentially differ in their ion contents from ground water discharged from Quaternary deposits. Hence in dry seasons and in winter the water flowing in brooks and small rivers is mainly water discharged from Quaternary deposits.

In the ground water occurring in fissures and fractures of the bedrock (groups 15—17), the amounts of magnesium and sulfate relative to the bicarbonate content are slightly greater than in the ground water of Quaternary deposits. In highly contaminated well water (group 22), bicarbonates do not occur in proportionally as large amounts as in ground waters in a natural environment, for chlorides and nitrates introduced by contamination occur in abundance. The calcium content remains

TABLE 9.

The relative mobility sequence of common elements, calculated from their median concentrations in natural water and their mean abundance in rocks. All the figures, except those in columns (I), (II) and (III), are weight-percentages.

	a	b	c	groups 1—12, 23—32	(I) W/R <sub>a</sub>	groups 1—4, 23	(II) W/R <sub>b</sub>	groups 5—8, 24	(III) W/R <sub>c</sub>
	%	%	%	%		%		%	
Si .....	31.5	32.4	23.5	19.2	0.6	27.0	0.8	7.9	0.4
Fe .....	3.3	3.3	9.1	—	—	—	—	—	—
Mg .....	1.0	0.7	5.6	6.3	6.2	6.7	9.6	5.2	0.9
Ca .....	2.4	1.3	4.7	21.3	8.9	18.5	14.2	23.3	5.0
Na .....	2.2	2.3	2.0	5.0	2.3	7.0	3.0	2.0	1.0
K .....	2.9	2.9	0.7	1.7	0.6	2.1	0.7	0.7	1.0

a = Average composition of Finnish bedrock (Sederholm 1925).

b = Mean composition of silicic igneous and sedimentogenic rocks in the study area, according to 16 rock analyses (p. 21).

c = Mean composition of subsilicic igneous and sedimentogenic rocks in the study area, according to 17 rock analyses (p. 21).

1—4, 23 = Median composition of dissolved matter in ground water discharged from till deposits and surface water in areas of silicic bedrock. (Calculations are based on electrolyte content = specific conductance multiplied by 0.75).

5—8, 24 = Median composition of ground water discharged from till deposits and surface water in areas of subsilicic bedrock.

1—12, 23—32 = Median composition of ground water discharged from Quaternary deposits and of surface water.

W/R<sub>a-c</sub> = The relative mobility sequence.

nearly unchanged in contaminated water, but there is slightly less magnesium, while a concomitant of contamination is a steep rise in the potassium and sodium content. On the average, the same equivalent proportions of major ions as in the ground and surface waters of the study area prevail in the large rivers of Finland (see Viro 1955, Table 2; Gorham 1961, p. 798 and the fresh waters of the world in general (see Clarke 1924, p. 119; Conway 1942, Table 5, Rankama, Sahama 1949, Table 6. 7).

Since a large part of the soluble weathering products is washed into ground and surface waters, their content indicates roughly the intensity of the weathering process. It is by comparing the concentrations of common elements in the natural ground and surface waters (as weight percentages of total electrolytes) with the corresponding percentages observed in the rocks that one obtains the relative mobility sequence (W/R) (Feth, Roberson, Polzer 1964, p. 49):

$$W/R = \frac{\text{percentage of element in water}}{\text{percentage of element in rock.}}$$

It represents the weathering sequence of the elements involved, i.e., their susceptibility to becoming dissolved and preserved in water out of the mineral lattice.

The relative mobility sequence values of the commonest elements in the area investigated are calculated in Table 9. According to this table, the relative mobility sequence (in ground and surface waters) in different areas of bedrock is as follows:

(I) .....	Ca > Mg > Na > K = Si > Fe
(II) .....	Ca > Mg > Na > Si = K > Fe
(III) .....	Ca > K = Na = Mg > Si > Fe

In the sequence (I) representing the »average Finnish bedrock», the relative mobility sequence of alkaline earths and alkali metals is the same as the sequence of weight-proportion in which these elements occur in ground and surface waters (Fig. 48). Calcium is by far the most mobile element. In silicic, principally granitic bedrock areas (II), noteworthy is the slightly greater mobility of silica than potassium and in areas of subsilicic bedrock (III), the nearly equal mobility of magnesium and the alkali metals. Iron remains in the soil nearly quantitatively. Gorham (1961, p. 823) warns that the method does not give reliable results unless the salt content of rain water is taken into account. In the event that the dissolved inorganic matter passing from the atmosphere into the ground and surface waters in the study area (p. 82) is deducted, the potassium takes its place in the first series after the silica, while in the third series the order of the potassium and the magnesium is reversed.

Viro's data (1955, Table 3) on the water of Kemijoki yield the same mobility sequence as (I). Differences in the composition of the bedrock and in the climatic conditions elsewhere in the world may bring about different results. However, Miller (1961, p. 19) reported the same weathering sequence from the granite areas of New Mexico as the first series (I) of the present study area, whereas, in granitic areas of different parts of the USA, Smyth (1913), Polynov (1937, p. 162), Feth, Roberson and Polzer (1964, p. 48) arrived at the following weathering sequence: Ca > Na > Mg > Si > K > Fe. According to Anderson and Hawkes (1958, p. 210), however, in the granite areas of New England, the magnesium is released before the other elements. Aluminum and iron are, according to all these researchers, the last of the weathering products to be released.

## SUMMARY

Several factors contribute to the chemical properties and composition of the ground and surface water in Finnish Lapland. The role of the different factors, as deduced from the chemical data and the geological interpretation of the sample material, will be summed up in this final chapter.

### *Factors contributing to the chemical composition*

*Rock composition.* The composition of the bedrock influences not only the chemical composition of the ground water occurring in fissures and fractures of the bedrock but also the composition of the ground water in Quaternary deposits. This is understandable because the till has travelled on the average but a short distance from its

source, reflecting the petrographic composition of the bedrock. The glaciofluvial material may have been transported from afar, but in large areas of uniform bedrock, however, the petrographic composition of the glaciofluvial material corresponds to that of the bedrock and the more local till.

In winter and dry summer periods surface waters — brooks and small rivers — consist of ground water discharged out of the Quaternary deposits. Thus surface waters likewise reflect in their chemical composition the variations in the bedrock environment — though only, to be sure, in extensive, homogeneous bedrock areas.

An abundant occurrence of mafic minerals in the subsilicic bedrock and in related Quaternary deposits is best revealed by an increase in the specific conductance, bicarbonate content and total hardness of ground and surface water, and less so by a rise in the pH level. Also the sulfate concentrations of ground and surface waters are greater in areas of subsilicic bedrock, in accordance with the proportional occurrence of sulfide minerals. Generally, in the areas of subsilicic bedrock, ground and surface waters contain 2 to 4 times more dissolved matter than in silicic bedrock areas.

Calcium and bicarbonate are by far the most abundant constituents in the natural ground and surface waters of the area investigated. Their relative content is distinctly higher (as mg-equivalents) in waters of subsilicic bedrock areas containing abundant electrolytes than in slightly acid dilute ground waters of silicic bedrock areas.

In subsilicic black schist, greenstone and gabbro areas, where the concentrations of material dissolved in natural waters are relatively high, the standard deviation of the determinations proved to be large. By contrast, in the case of dilute waters in silicic, especially granite areas, the standard deviation of the determinations was exceptionally small. This signifies that the composition of the waters there varies in narrower limits.

All differences in the chemical composition of natural water induced by the rock environment are most clearly seen in ground water discharged from till deposits. Variations in the petrographic composition of the bedrock are only weakly reflected in the alkali, silica, phosphate and fluoride contents of natural waters.

The sodium and silica contents of ground water are slightly higher in areas of silicic than of subsilicic bedrock. The low sodium content of ground water occurring in albite-rich greenstones areas is due to the resistance of albite to weathering. The lower silica content of the ground and surface waters of subsilicic bedrock areas, compared with silicic bedrock areas, is due either to the possible formation of weathering residuals or clay minerals or to the precipitation of the silica colloids in electrolyte-bearing waters.

Fluorides occur most abundantly in the ground water of silicic bedrock areas. Their occurrence in natural water is chiefly regulated by the abundance of apatite and fluorite in the bedrock and overlying deposits, a fact also earlier observed in ground water in rapakivi tracts in southern Finland containing unusual amounts of fluorite.

The occurrence of iron and manganese in natural waters depends more on the prevailing pH and the oxygen content, i.e., on the redox potential regulated by these properties, than on the geological factors. Iron is abundantly present in ground water of a low oxygen content occurring in bedrock as well as in highly contaminated ground water. An appreciable iron content in surface waters is attributable to the formation of complex compounds involving iron and humus.

The  $\text{KMnO}_4$ -consumption values, which mainly represent the humus content, are substantially higher in the ground and surface waters of silicic than of subsilicic bedrock areas. This may be due to the fact that in waters containing electrolytes in abundance, the humus probably is partly precipitated as humates.

*Time factor.* Ground water occurring deep down within Quaternary deposits, where it has remained for a relatively long time, has a higher electrolyte content than does perched water or ground water occurring near the surface and undergoing more rapid percolation. The nearly stagnant ground water occurring deep in fissures and fractures of the bedrock overlain by Quaternary deposits contains dissolved material in the largest amounts. This supports the view that, besides the geological environment, also the time factor is of great significance in determining the chemical composition of ground water.

*Texture of Quaternary deposits.* The abundance of fine-grained constituents in Quaternary deposits diminishes the rate of flow of ground water and thereby, according to the contribution of the time factor, affects its chemical composition. In addition, weathering is more intensive in fine-grained mineral matter. Accordingly, the results of the present study show that the ground water contained in fine-grained till has a higher concentration of electrolytes than has the easily percolating ground water of sorted glaciofluvial material.

The differences in the electrolyte content of the ground water caused by the texture of the material composing the subsoil are most considerable in tracts of subsilicic bedrock. In areas of silicic bedrock, where the ground waters are dilute by their very nature, on the other hand, the extent of sorting undergone by the Quaternary deposits is not a significant factor in regulating the amounts of dissolved ionic matter.

*Contamination.* The contaminating influence of agricultural settlement on ground water is evidenced by a strong increase in specific conductance and by a slight but clear drop in the pH level.

True indicators of contamination are chlorides and the final oxidation products of nitrogen compounds, nitrates. In contaminated waters their concentrations increase as much as several hundreds of times compared to intact waters. For this reason the standard deviation of the determinations of the nitrate in contaminated waters proved to be greater than that of any other dissolved substances.

Also the sodium and, especially, potassium were found to increase greatly as a consequence of contamination, but the calcium and magnesium contents somewhat less. In waters containing little humus, an increase in  $\text{KMnO}_4$ -consumption likewise indicated contamination, although not so sensitively as the chlorides, nitrates and alkali metals. The bicarbonate was found to increase rather slightly and the silica hardly at all with a rise in the degree of contamination. The local abundance of iron and manganese in contaminated waters is generally associated with the low oxygen content of these waters.

*Matter derived from the atmosphere.* The chlorides and nitrates occurring in the natural ground and surface waters of the study area are mainly derived from the atmosphere. A notable proportion of the potassium and of the sulfate occurring in dilute waters can likewise be traced to precipitation.

Acid rain waters do not contain significant amounts of bicarbonates, which are among the principal constituents of ground and surface waters. Accordingly, rain waters do not add notably to the total electrolyte content of the natural ground and surface waters occurring in the study area. The dilute perched waters and esker pools and ponds of the study area closely resemble rain water in composition.

*Periodic variations.* Besides the regional variations in the chemical composition of waters caused by the geological environment, also seasonal factors alter the composition of both ground water and, particularly, surface waters.

The composition of ground water discharged from Quaternary deposits as large springs remains fairly constant throughout the year, but in small springs the variations are greater, and the total electrolyte content of the ground water is apt to diminish as a result of dilution by melting snow in the spring. Flood water also brings with it more than the usual amount of humus matter from the humus layer of soil and from surrounding peat lands.

The composition of the ground water occurring deep in fractures and fissures of bedrock is little or not at all susceptible to seasonal variation.

By contrast, it is only natural that the composition of flowing surface waters should vary greatly during the period the ground is not frozen, depending on the amount of precipitation and the runoff. With the dilution of the concentrations of dissolved matter, the pH level also falls. The relative contents of the different components remain fairly unchanged, but exception are the iron and potassium, which frequently increase in amount when the other contents diminish. An increase in the iron content is influenced by a lowering of the pH level, as a consequence of which the iron is apt to occur more in soluble form. An additional factor is the washing of iron-bearing acid humic waters from boggy tracts.

i The pH and specific conductance values measured during a single 24-hour period in summer from the source to the mouth of a river (Niesajoki in the commune Kolari) was seen to vary only slightly. In the same river, the iron contents vary quite considerably, so that no clear correlation with the rock environment is discernible.

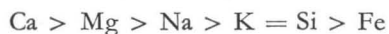
### *Relation between some chemical properties*

The electrolyte contents indicated by the specific conductance, pH level and bicarbonate content as well as total hardness are closely correlated in the natural waters. The correlation between total hardness and bicarbonate content is due to the fact that the calcium and magnesium are present mainly as bicarbonates. Since the latter elements are also the principal cationic and anionic components of water, their correlation with specific conductance is understandable.

According to the observed correlations, the most important factor determining the pH level of the natural waters in the study area is the carbon dioxide-bicarbonate equilibrium. The higher pH level of the slightly basic waters containing electrolytes in abundance is due to the high bicarbonate content, whereas in dilute acid waters the free carbonic acid causes a substantial lowering of the pH value. The sulfate content (indicating sulfuric acid as a result of weathering of sulfide minerals) has no significance, generally speaking, as a factor contributing to a lowered pH level in the waters of the study area. The humus contained in surface waters (indicating acid humus-rich waters from peat lands) no longer influences their pH.

### *Relative mobility sequence*

By comparing the proportional contents of the elements and compounds dissolved in water with the corresponding components of the bedrock, one could draw conclusions concerning the tendency of these substances to be released and preserved in water during weathering. With the average composition of Finnish bedrock as a basis, the following relative mobility sequence is obtained for the most important elements occurring in the waters of the study area:



In areas of silicic bedrock, however, the silica is apt to be released into and preserved in water during weathering somewhat more readily than the potassium. In areas of subsilicic bedrock, again, the alkali metals are more mobile than the magnesium. The iron is consistently last in the relative mobility sequence, for it is precipitated almost quantitatively in conjunction with weathering or subsequently, when the ground water comes into contact with oxygen.

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		1	2	3	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
		pH	Specific conductance	HCO <sub>3</sub>	Total hardness	KMnO <sub>4</sub> -consumption	NH <sub>4</sub>	NO <sub>2</sub>	NO <sub>3</sub>	Cl	F	SO <sub>4</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	Ca	Mg	Na	K	Fe	Mn
2	Specific conductance	I	0.52																	
		II	0.26																	
		III	0.60																	
		IV	0.43																	
		V	0.04																	
		VI	0.47																	
3	HCO <sub>3</sub>	I	0.48	0.80																
		II	0.54	0.69																
		III	0.72	0.85																
		IV	0.53	0.86																
		V	0.32	0.60																
		VI	0.51	0.95																
5	Total hardness	I	0.46	0.79	0.82															
		II	0.52	0.66	0.91															
		III	0.72	0.85	0.94															
		IV	0.40	0.79	0.70															
		V	0.07	0.83	0.71															
		VI	0.49	0.95	0.92															
6	KMnO <sub>4</sub> -consumption	I	−0.37	−0.11	−0.04	−0.06														
		II	−0.37	−0.19	−0.19	−0.12														
		III	−0.38	−0.24	−0.23	−0.22														
		IV	−0.22	−0.03	−0.02	−0.03														
		V	−0.18	0.47	0.34	0.26														
		VI	−0.29	−0.21	−0.13	−0.17														
7	NH <sub>4</sub>	I	0.09	−0.11	−0.04	−0.09	−0.08													
		II	−0.28	−0.05	−0.19	−0.10	0.63													
		III	−0.09	−0.14	−0.13	−0.15	0.04													
		IV	0.02	−0.13	−0.11	−0.07	0.07													
		V	−0.04	0.28	0.42	0.17	0.38													
		VI	−0.21	−0.13	−0.11	0.03	−0.08													
8	NO <sub>2</sub>	I	−0.03	−0.04	0.02	−0.01	0.07	0.25												
		II	0.15	−0.01	0.10	0.13	−0.17	−0.09												
		III	0.08	0.04	0.10	0.10	−0.0005	0.12												
		IV	0.20	0.33	0.39	0.21	−0.06	−0.01												
		V	−0.14	0.54	0.08	0.36	0.26	0.11												
		VI	0.06	0.24	0.34	0.19	0.05	−0.06												
9	NO <sub>3</sub>	I	−0.06	0.04	−0.04	−0.01	0.22	−0.10	0.05											
		II	−0.10	0.01	−0.16	−0.08	0.36	0.28	−0.05											
		III	−0.04	0.04	−0.05	−0.004	0.21	−0.002	−0.002											
		IV	−0.11	−0.02	−0.14	0.03	0.11	−0.16	−0.01											
		V	−0.16	0.69	0.07	0.42	0.38	0.08	0.58											
		VI	0.06	0.13	0.22	0.08	0.07	0.02	0.35											
10	Cl	I	−0.07	0.07	0.14	−0.01	−0.05	0.12	0.05	0.06										
		II	−0.22	0.32	0.09	0.13	0.01	0.08	−0.14	0.39										
		III	−0.16	0.10	0.03	−0.01	0.06	0.11	−0.01	0.26										
		IV	0.02	0.37	0.19	0.21	0.13	−0.05	−0.04	0.36										
		V	−0.12	0.85	0.51	0.70	0.36	0.27	0.51	0.44										
		VI	−0.03	0.03	−0.02	0.04	−0.06	0.27	0.04	−0.08										
11	F	I	−0.09	0.08	0.13	0.10	0.13	0.03	0.41	−0.0004	−0.04									
		II	−0.28	−0.20	−0.10	−0.16	0.29	−0.05	−0.13	−0.04	−0.17									
		III	−0.16	−0.07	−0.05	−0.08	0.14	0.05	0.18	−0.01	−0.04									
		IV	0.20	0.24	0.26	0.11	−0.01	−0.09	0.18	−0.14	−0.10									
		V	−0.10	0.29	0.07	0.18	0.48	−0.01	0.15	0.28	0.20									
		VI	−0.03	0.02	0.06	0.05	0.32	0.02	0.07	0.25	−0.09									
12	SO <sub>4</sub>	I	0.27	0.57	0.35	0.51	−0.18	−0.24	−0.11	−0.02	−0.15	−0.24								
		II	0.27	0.25	0.25	0.50	−0.09	−0.06	0.09	−0.16	0.05	0.04								
		III	0.37	0.50	0.46	0.62	−0.13	−0.20	0.002	0.02	−0.03	−0.11								
		IV	0.60	0.40	0.31	0.36	−0.59	−0.28	0.09	0.03	0.57	0.31								
		V	−0.15	0.40	0.19	0.48	0.40	−0.04	0.18	0.31	0.26	0.33								
		VI	0.07	0.26	0.14	0.23	−0.32	−0.14	−0.05	−0.18	−0.04	−0.09								
13	PO <sub>4</sub>	I	0.06	−0.13	−0.09	0.002	−0.02	−0.04	−0.07	0.02	−0.15	−0.10	0.18							
		II	0.08	−0.07	−0.04	−0.02	0.20	−0.08	0.01	−0.02	−0.04	−0.02	−0.35							
		III	0.05	−0.07	−0.04	−0.01	0.04	−0.02	−0.02	−0.004	−0.08	−0.06	−0.06							
		IV	0.01	−0.01	0.12	−0.05	−0.19	0.05	0.53	−0.11	−0.26	0.11	−0.30							
		V	−0.01	−0.13	−0.15	−0.13	−0.04	−0.01	−0.10	−0.13	−0.14	0.04	−0.03							
		VI	−0.09	0.10	0.07	0.10	−0.19	−0.06	−0.06	−0.02	0.21	−0.11	−0.10							
14	SiO <sub>2</sub>	I	0.01	0.23	0.34	0.37	−0.05	−0.01	−0.002	−0.01	−0.03	0.12	0.25	0.11						



