

QUALITY OF BEDROCK GROUNDWATER IN WESTERN FINLAND, WITH SPECIAL REFERENCE TO NITROGEN COMPOUNDS

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Monitoring of bedrock aquifers utilized for water supply in the Vaasa region, western Finland, suggests slight changes in the chemical composition of groundwater resulting both from natural and anthropogenic factors. Applying the permissible limits for parameters in drinking water reveals that the groundwater quality is generally good. Groundwater occurring in fractures and fissures of the crystalline bedrock is protected from anthropogenic pollution by clay and till deposits with low permeability. Temporally, the contents of nitrogen compounds in groundwater exhibit a decreasing trend. Reducing conditions prevailing in bedrock aquifers are reflected in elevated ammonium, iron and manganese contents in water.

Key words: water supply, ground water, aquifers, bedrock, drilled wells, water quality, hydrochemistry, nitrogen, pollution, atmospheric precipitation, Ostrobothnia, South Ostrobothnia, Finland

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INTRODUCTION

In the present study the occurrence of nitrogen compounds in bedrock groundwater is briefly discussed on the basis of hydrochemical data collected from the Vaasa region (Fig. 1). The paper describes the results of the investigation of the bedrock groundwater at shallow and medium depths, i.e. the local flow zone, which according to Salmi (1985) extends to a depth of about 200 m in Finland. The results of analyses of water samples from 23 drilled wells (from 19 locations, Fig. 1) were extracted from the database compiled by the

West Finland Regional Environment Center. Data interpreted here show a large spread in terms of sampling intervals and sampling frequencies. At some waterworks the water quality has been monitored during the last 20–30 years (6–10 analyses), but from others only 1–3 analyses are available. The depth of the wells ranges from 20 to 150 meters and the amount of abstracted groundwater is generally some tens of m³/d. Groundwater chemistry is compared to the quality standards set by the Ministry of Social Affairs and Health (Anonymous 1994).

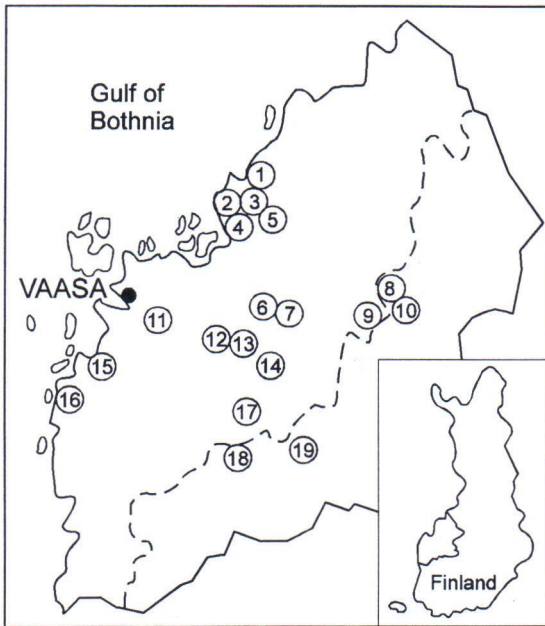


Fig. 1. Schematic map of Western Finland showing the location of the studied bedrock aquifers: 1-Stranden, 2-Monäs, 3-Munsala Källan, 4-Hirvlax, 5-Silvast, 6-Ko-sola, 7-Rintakangas, 8-Lappajärvi, 9-Ylipää, 10-Poke-la, 11-Ruto, 12-Isokyrö, 13-Lavo, 14-Munkkila, 15-Norrby and Petalax, 16-Harrström, 17-Ryöskölä, 18-Luopa, 19-Peräseinäjoki. Dotted line marks the highest limit of the postglacial Litorina Sea.

GENERAL GEOLOGICAL SETTING OF AREA

The bedrock of the Vaasa region is composed of folded and metamorphosed Svecofennidic mica schists, phyllites and mica gneisses intruded by granitoids (Simonen 1980). The principal system of faults and fractures in the crystalline bedrock was already established in the course of extensive tectonic activity before the Middle Proterozoic (Niini 1987). The ancient structural pattern of the bedrock underwent some modifications during the Quaternary glaciations (Talvitie 1979). Because of the glacial abrasion the topography of the area is relatively smooth and the weathering zone between the soil and the bedrock is practically absent. The relief varies between 0 and 200 m a.s.l. In topographical heights the bedrock is exposed

or commonly overlain by a few meters of soil. Topographical depressions form valleys in which the soil cover is thicker. The most widely distributed soil type is till, which overlies the bedrock as a thin, discontinuous layer. Other commonly found sediments are glaciofluvial sands and gravels, as well as marine and lacustrine clays and silts, sometimes measuring up to tens of meters in thickness. As these deposits usually occupy topographic depressions they have frequently been subject to paludification and are overlain by peat.

The evolution of groundwater conditions over the entire region has been controlled by recurring continental glaciations in the course of the Pleistocene. The evolutionary stages of the Baltic Sea with their different extents and the salinity of inundating waters have influenced the development of the chemical composition of groundwater. The present chemical character of shallow groundwater is a result of the infiltration of fresh atmospheric water modified by bedrock/soil and groundwater interaction.

GROUNDWATER QUALITY AND THE DISTRIBUTION OF NITROGEN COMPOUNDS IN GROUNDWATER

When studying the bedrock groundwater of the Vaasa region from the point of view of quality requirements, it can be stated that these are generally fulfilled. The limits for NO_2 (0.01 mg/l) and NO_3 (25 mg/l) in groundwater are exceeded only in a few cases. Ammonium contents above the limit of 0.5 mg/l are recorded more frequently, suggesting reduced conditions prevailing in some aquifers. The groundwater is also characterized by high Fe and Mn content and high KMnO_4 consumption value. As extensive areas of the Vaasa region were inundated by waters of the Litorina Sea, chloride concentrations higher than 100 mg/l have been detected in four monitored wells (Isokyrö, Ruto, Hirvlax and Monäs). Selected parameters of groundwater analyses are summarized in Table 1.

Mean concentrations of nitrogen compounds of the Vaasa region (columns 1) and the analytical

Table 1. Selected hydrochemical properties of bedrock groundwater in the Vaasa region compared to the limit values set by standard.

	pH	EC mS/m	KMnO ₄ mg/l	NH ₄ mg/l	NO ₂ mg/l	NO ₃ mg/l	Fe mg/l	Mn mg/l	F mg/l	Cl mg/l
Mean	6.8	41	16	0.25	0.03	2.2	2.97	0.35	0.5	45
Median	6.8	29	12	0.10	0.01	0.8	1.34	0.20	0.3	22
Maximum	8.5	121	53	2.10	0.50	58.0	15.00	2.00	1.7	260
Minimum	5.5	4	1	0.01	0.00	0.0	0.00	0.00	0.1	0
n	89	83	75	88	86	89	89	79	43	79
Limit value*	7.0–8.8	< 40	< 12	0.50	0.10	25.0	0.20	0.05	1.5	100

* Groundwater quality standards set by the Ministry of Social Affairs and Health (Anonymous 1994).
EC = electrical conductivity, KMnO₄ = KMnO₄ consumption

results obtained in some earlier investigations (columns 2–8) are schematically presented in Fig. 2. A comparison of the values plotted in the diagram shows that the mean contents of nitrogen compounds in bedrock groundwater are on the same order of magnitude in both the present and earlier studies (Laakso 1966, Rönkä 1983, Hyypä 1984, Lahermo et al. 1990, Korkka-Niemi et al. 1993). The abundance of NO₂ in groundwater is exactly the same (0.03 mg/l) in most of the compared results, except for the Laakso's (1966) mean of the whole country (column 3). Thus, regionally there appear to be no differences between the concentrations of NO₂ in bedrock groundwater. Its low concentration indicates that nitrite is unstable and tends to oxidize to nitrate or to reduce to ammonium quite quickly.

Mean NO₃ values in bedrock groundwater in Finland as a whole have increased from 1960s to 1990s (Laakso 1966, Lahermo et al. 1990). However, according to the results by Korkka-Niemi et al. (1993), no increase in nitrogen compounds in bedrock groundwater was observed. The data available from the Vaasa area show the lowest mean NO₃ concentration compared to the results of earlier studies. The median values of NO₃ in the Vaasa aquifers and in the bedrock wells covered by the nation-wide water survey are approximately the same, 0.8 and 1.0 mg/l, respectively (Korkka-Niemi et al. 1993). The corresponding value in bedrock wells is much higher (2.4 mg/l) according to the results of hydrochemical mapping

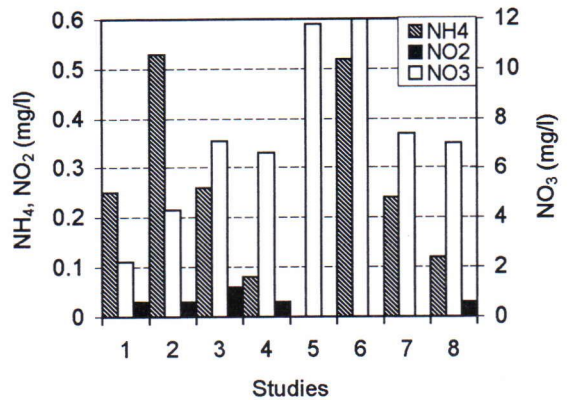


Fig. 2. Concentrations of nitrogen compounds in bedrock groundwater. 1 – Vaasa region (present study); 2 – former Vaasa county (Laakso 1966); 3 – Finland as a whole (Laakso 1966); 4 – Middle Finland, Savo, Vehmaa and Helsinki district (Rönkä 1983); 5 – Finland as a whole (Lahermo et al. 1990); 6 – Finland as a whole, < 100 m deep drilled wells (Hyypä 1984); 7 – Finland as a whole, > 100 m deep drilled wells (Hyypä 1984); 8 – Finland as a whole (Korkka-Niemi et al. 1993). Columns represent the mean values of the concentrations.

carried out by the Geological Survey of Finland (Lahermo et al. 1990).

Hyypä (1984) calculated the mean and median chemical composition of groundwater samples from <100 m and >100 m deep drilled wells. A remarkable depletion in the content of nitrogen compounds in bedrock groundwater with increasing depth can be observed (Fig. 2, columns 6 and

7). The median values of NH_4 and NO_3 content in the >100 m deep wells (0.10 and 1.0 mg/l, respectively) are close to those detected in present study (Table 1). However, there is no obvious relationship between the concentration of nitrogen compounds and well depth in the Vaasa region.

Relative concentrations of ammonium and nitrate depend on the degree of nitrification. The NO_3/NH_4 ratio in the bedrock groundwater of the Vaasa area (8.8) is considerably lower compared to that in the Finnish bedrock groundwater as a whole. Based on the results of investigations referred to above, the NO_3/NH_4 ratio in the Finnish bedrock groundwater varies from 25 to 58. The results of the present study as well as Laakso's (1966) data from the Vaasa region, refer to reducing conditions prevailing in the bedrock groundwater of this area. The nitrogen compounds in water tend to occur in the most reduced states.

POTENTIAL SOURCES OF NITROGEN COMPOUNDS

The natural geochemistry of bedrock groundwater is closely related to the geology of its host rock. The amount of nitrogen compounds in the bedrock itself is practically nil. According to Taylor (1964), the mean nitrogen content of igneous rocks is 20 ppm or 0.002% by weight. This nitrogen appears to be in chemical combination, mainly as ammonium nitrogen. The possible substitution of K^+ (ionic radii 133 pm) by NH_4^+ (143 pm) might offer a possibility of explaining the manner of occurrence of nitrogen in rocks. Stevenson (1962) has shown that nitrogen may exist as ammonium ions held in structures of micas and feldspars and only little, if any, of the nitrogen in igneous rocks is in organic combination. Oxidized nitrogen is absent in rocks and insignificant amounts of nitrogen compounds are liberated from rocks during weathering. Thus, their presence in groundwater results largely from the decomposition of organic matter in surficial deposits, atmospheric deposition and various anthropogenic sources.

Shallow hard rock systems are particularly susceptible to pollution from a variety of agricultural

and industrial pollutants. The buffering capacity of hard rock groundwaters is generally poor and they are susceptible to acid inputs from acid deposition. Insufficient information is available, however, to understand the role of such rocks in buffering groundwater and attenuating pollution.

Groundwater pollution incidents can be divided into two broad types on the basis of the source and mode of propagation of pollutants. Point-source pollution occurs where pollutants are derived from a discrete, often readily identifiable source such as a factory, farm, leaking tank or waste disposal site. Diffuse pollution occurs where pollutant input is widely distributed and cannot be pin-pointed precisely. Examples are the ammonium fertilizers used in agriculture and forestry and acid rain, which may be distributed on a regional or national scale.

Bedrock groundwater is in continuous motion and participates in the annual hydrologic cycle. Groundwater is most mobile in the surface parts of the Finnish bedrock and its movement slows down with increasing depth (Salmi 1985). In Norway, transmissive fractures in the upper 12 m of a granite led to hydraulic conductivities two orders of magnitude higher than the hydraulic conductivity in the background granite (Banks et al. 1992). According to Rönkä (1983), the best average yields (46 m^3/d) are given by drilled wells in the depth range of 41–50 m. The fact that fresh groundwater is obtained almost invariably from drilled wells extending down to a depth of 200 m in Finland indicates that groundwater circulation may extend deep in the bedrock. Hyyppä (1984) has demonstrated that groundwater in fracture zones (drilled wells >60 m deep) contains more nitrogen than that in areas of unbroken bedrock. Jacks (1973) has found the amount of total nitrogen to decrease in bedrock groundwater with increasing depth. In a study carried out by Pirhonen (1990) in the coastal areas of southern Finland an increase in NH_4 concentration with depth in bedrock groundwater has been recorded.

In an area of exposed bedrock, the groundwater table corresponds to topography as does the groundwater table in the overburden, being somewhat deeper in uplands than in lowlands. In the

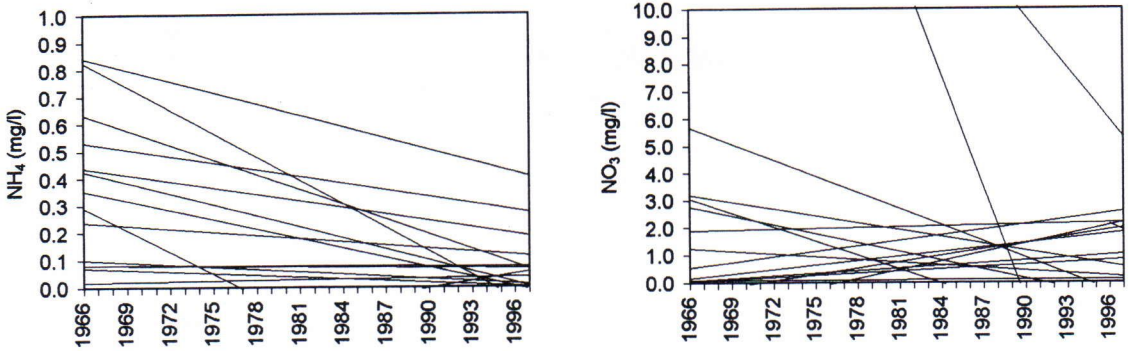


Fig. 3. Trendlines of data series representing the temporal increase or decrease of NH_4 and NO_3 concentration in bedrock groundwater.

Vaasa region groundwater levels are generally close to the ground surface. Thus the unsaturated zone provides little protection and pollutants will rapidly reach the water table. Infiltration from soil into bedrock occurs at specific sites where suitable combinations of geological and hydrological variables exist (Olofsson 1994), e.g. in cases where conductors in the bedrock, such as fractures and fracture zones, are hydraulically connected with a groundwater reservoir in permeable soil or with horizons of permeable and conductive material in heterogeneous soil. The hydraulic conditions of the contact zone between soil and rock are of particular importance for infiltration, even a thin layer of silt on the bedrock surface may block the water flow.

Point-source pollution

It is supposed that an increase in abundances of dissolved components, including nitrogen compounds, occurs in groundwater as a result of human activities. In the case of point-source pollution the changes in groundwater chemistry can be locally large, if the sediment is permeable. Due to the quite low concentration of nitrogen compounds, the presence of anthropogenic pollution may be clearly recognized only in a few of the studied areas. The changes in groundwater quality can be attributed to the point-source pollutants in the Norrby and Stranden waterworks (Fig. 1). Both wells are situated adjacent to farms (100–200 m) and the fluctuating content of NH_4 and

NO_3 in the Norrby aquifer have exceeded the limit values set by the standard. Furthermore, the highest NO_3 concentration (58.0 mg/l) has been detected in Norrby, too.

In spite of some elevated concentrations of NH_4 and NO_3 the general depletion of these ions in the Vaasa groundwater is commonplace. Trendlines of plotted NH_4 and NO_3 values show the general temporal changes in concentrations of these components in groundwater (Fig. 3). Most of the NH_4 abundances in the monitored drilled wells exhibit a declining trend. In the case of very low NH_4 concentrations the trendlines are approximately horizontal referring to natural conditions prevailing in the aquifers. On the NO_3 plot both declining and slightly ascending trendlines are presented. The two deeply declining lines represent the decrease of NO_3 abundances in the Norrby and Hirvliax groundwater. The decreasing trend may be partly explained by earlier agricultural activity, resulting in the accumulation of nitrogen compounds in the soil. When the pumping of groundwater basin progressed, the amount of dissolved matter, including nitrogen compounds, diminished with time (Fig. 3). As a consequence of acceleration of groundwater flow, pure groundwaters from more distal parts of aquifer are mixed with slightly polluted water. In the case that groundwater is pumped constantly, the quantity of dissolved matter attains the level characteristic of the groundwater basin in question. Variations in it, again, depend particularly on changes in the utilization of water, variations in the hydrometeorological

factors and possible contamination of the recharge area of groundwater.

Atmospheric deposition

The studied waterworks are influenced by long-term effects from relatively low concentrations of atmospheric deposition. In rural areas the infiltration of precipitation might, besides decomposition of organic matter in surficial deposits, be the only source of nitrogen compounds in bedrock groundwater. Major nitrogen compounds present in the atmosphere are nitrogen oxides (NO_x) and ammonia (NH_3). Normally, most of the nitrogen compounds added to the soil via precipitation and dry deposition will be adsorbed and transformed in the humus-rich soil zone and taken up by vegetation. If nitrogen compounds are deposited via precipitation more than what the vegetation can utilize, then surplus will seep through the topsoil and overburden into the bedrock groundwater.

The effects of acid deposition on groundwater quality have been studied by Hrkal (1992) in the metamorphic rocks and granites of the Bohemian Massif. The extensive use of the poor quality fossil fuels has led to a five fold increase in the average concentration of NO_3 (from 4 mg/l to 19 mg/l) in groundwater over a 25 year period. Changes in Sweden and Finland appear to be less pronounced than those in Bohemia (Swedberg 1989, Knutsson 1994, Soveri 1992, Lahermo 1991, 1994, Ruoho-Airola et al. 1998). Nitrates occur in rainwater in concentrations of 0.3–0.5 mg/l in southern Finland

and 0.1–0.3 mg/l in northern Finland (Järvinen 1986, Ruoho-Airola et al. 1998). Precipitation-weighted annual mean values for ammonium are 0.2–0.4 mg/l in the southern and 0.05–0.20 mg/l in the northern part of the country (Ruoho-Airola et al. 1998). Mean concentrations of NH_4 and NO_3 in snow samples collected from the Vaasa region were 0.2–0.3 and 1.6–1.8 mg/l, respectively (Soveri & Peltonen 1996). The highest mean nitrate content (2.5 mg/l) was recorded in the southern part of the area. The deposition level of NO_3 has been reported to be relatively stable during the 18 year observation period (1976–1993). The contents of NH_4 and NO_3 in most of the aquifers included into the present study are less than 0.3 and 2.0 mg/l, respectively. Considering the median values of nitrogen compounds (Table 1), the similarity between the chemical composition of rainwater/snow and bedrock groundwater occurring under natural conditions is evident.

CORRELATIONS BETWEEN CHEMICAL PARAMETERS

Pearson correlation matrix was computed for the geochemical parameters determined in this study (Table 2). The matrix is presented for the whole data. The data sets of separate wells are insufficient (3–10 series of analyses) to calculate significant correlation coefficients. Therefore, the r-values express some general geochemical relationships within the entire studied region.

Table 2. Correlation matrix for the hydrochemical parameters.

	pH	EC	O_2	KMnO_4	NH_4	NO_2	NO_3	Fe	Mn
EC	0.49								
O_2	0.13	-0.63							
KMnO_4	-0.17	-0.01	0.88						
NH_4	0.01	0.24	-0.67	0.20					
NO_2	0.09	0.15	-0.35	-0.07	0.06				
NO_3	-0.25	0.13	0.08	0.18	0.18	0.12			
Fe	0.05	-0.15	-0.47	0.10	0.43	0.10	-0.16		
Mn	0.05	0.31	-0.61	0.04	0.57	0.03	0.07	0.45	
Cl	0.54	0.85	-0.59	-0.10	0.08	-0.04	0.06	-0.20	0.19

EC = electrical conductivity.

KMnO_4 = KMnO_4 consumption.

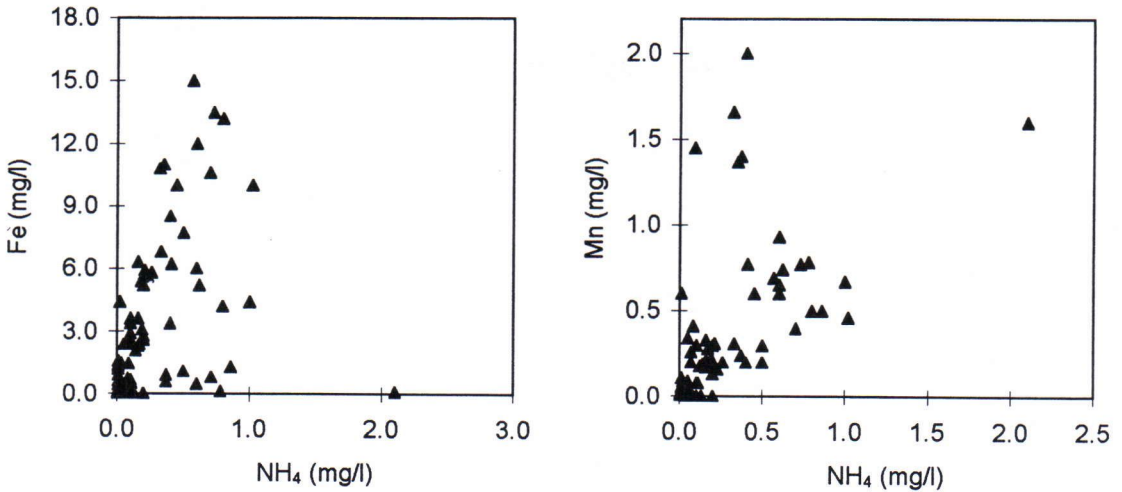


Fig. 4. The concentrations of Fe and Mn plotted against ammonium concentration.

Under reducing conditions deficient in oxygen, nitrogen compounds occur in part in the low oxidation states, as nitrite and ammonium, whereas under oxidizing conditions they occur mainly as nitrate. When water becomes anoxic and the environment gets reduced, Fe and Mn dissolve in the water. The observed iron concentrations in the Vaasa region range from nil to a maximum of 15.0 mg/l. The corresponding figures for manganese are nil and 2.0 mg/l, respectively. In 75 % of the monitored aquifers the iron content has been higher than the limit value (0.2 mg/l), and in some wells (Röyskölä, Harrström, Peräseinäjoki, Rintakangas, Kosola, Lavo) the Fe concentrations ranging between 3.0 to 7.0 mg/l are quite common. As to the extremely high iron contents, the conditions prevailing in the aquifer must be highly reduced; consequently, some of the dissolved total nitrogen occurs as ammonium and there are very small amounts of nitrate (Fig. 2, columns 1).

The formation of NH_4 -humus complexes explains the simultaneous occurrence of ammonium and iron in groundwater (Hem 1970). This is indicated by positive correlation between the ammonium and the iron concentrations ($r = 0.43$) as well as between the ammonium and the manganese contents ($r = 0.57$) in bedrock groundwater (Fig. 4). However, the correlation between NH_4 and KMnO_4 -consumption value is not significant ($r =$

0.20). The occurrence of iron in natural waters is generally regarded to be associated with the concomitant occurrence of manganese. In the Vaasa area there exists a moderate positive correlation between iron and manganese in groundwater ($r = 0.45$).

The most sensitive inorganic indicators of human activities in groundwater are NO_3 and Cl (Lahermo 1988, Lahermo et al. 1990, Korkka-Niemi et al. 1993). There exists no correlation between these compounds in the study area, thus the abundance of chlorides in the bedrock water cannot be attributed to any noteworthy extent to pollution. Only in Norrby and Petalax the increase of nitrogen compounds was followed by the simultaneous increase of Cl concentration in groundwater. Electrical conductivity correlates strongly with the concentration of chlorides ($r = 0.85$) (Fig. 5). Relict salts, originating from the postglacial Litorina Sea which inundated large coastal areas 5000 to 7000 years ago (Fig. 1), are the probable sources of high Cl concentrations in coastal aquifers.

Nitrate has a slight negative correlation with the pH value ($r = -0.25$). Approximately the same result ($r = -0.28$) was derived from the hydrogeochemical study of Finnish groundwater (Lahermo et al. 1990). The application of ammonium fertilizers and/or acid atmospheric deposition is reflected in some decline in the pH values. Ammo-

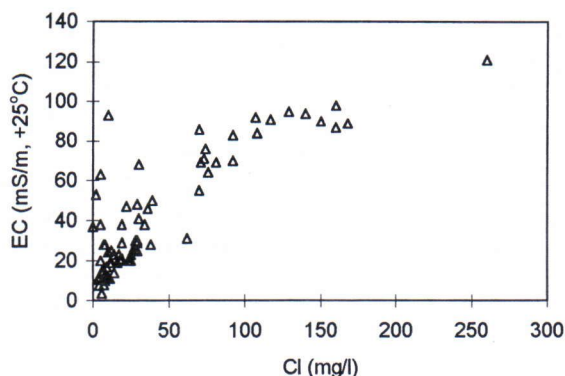


Fig. 5. The values of electrical conductivity (EC) as a function of the chloride concentration.

nium displaces exchangeable calcium from soils. Some of this Ca will be lost in infiltrating water, and the exchangeable ammonium is nitrified releasing H^+ . The nitrate formed is either lost by leaching or is taken up by the crops (Mather 1993). The other reasons for the slight declining pH level of groundwater may be the washing of acid humus-rich soil water from surrounding peatlands into the aquifers and the chemical weathering of primary sulfides in the soil and bedrock.

CONCLUSIONS

The groundwater quality in the terms of nitrogen compounds is good in the studied bedrock aquifers. Maximum permissible concentrations of NH_4 and NO_3 in water set by Finnish and international standards have been exceeded only in few samples. Decreasing trends of NH_4 and NO_3 abundances in bedrock wells can be observed during the last 30 years. A clear effect of anthropogenic sources on the groundwater chemistry is not evident, although it may be recognized in the Norrby and Stranden water plants as a point-source pollution. The atmospheric deposition of nitrogen species and the decomposition of organic matter in humus-rich soil are assumed to be the main sources of nitrogen compounds in groundwater.

The Vaasa area is characterized by reducing conditions prevailing in clay-covered bedrock aquifers. The oxygen deficiency is reflected in the

elevated iron and manganese contents in groundwater. Consequently, the amount of nitrate in groundwater is low compared with bedrock groundwater of Finland as a whole.

Chloride abundances close to 100 mg/l (in 6 of 23 monitored wells) increase electrical conductivity of groundwater. The elevated Cl concentration cannot be attributed to intrusion of sea water into aquifers. The distances from the recent coastline to the Isokyrö and Ruto water supply plants, where the highest Cl contents were recorded, are 20 and 12 km, respectively. Leaching of fossil marine salts or relict sea water preserved in fractures of bedrock are plausible sources of the salinity of groundwater.

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