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Long-term changes in groundwater chemistry in four coastal water supply plants in southern Finland

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Monitoring of four glacial outwash aquifers that have been utilised during the last 30 years for municipal water supply of Espoo community, southern Finland, reveals changes in chemical composition of groundwater. A 1.5 to 2.0-fold increase in electrical conductivity and in concentrations of main cations and anions in abstracted groundwater reflect primarily the geological impact of Litorina deposits. Relict seawater trapped in deeper parts of aquifers and leaching of fossil salts from postglacial clay and silt deposits have a marked effect on the chemistry of groundwater.

Introduction

During late phases of deglaciation the Baltic basin was occupied by a larger water body than the present sea. Owing to eustatic changes in sea level and the concomitant isostatic uplift of the central part of the Baltic Shield, the basin gradually diminished in size until it reached its present areal extent. The most saline seawater phase of the Baltic, called Litorina Sea, started in southern Finland about 7 300 to 7 400 years BP (Eronen *et al.* 1979, Hyvärinen *et al.* 1988). It covered a large coastal area of Finland as shown in Fig. 1.

An increase in the dissolved components in the groundwater, especially chloride and sodium, has been observed in many wells drilled into overburden and bedrock along coastal regions of Finland (Hyyppä 1984, Lahermo and Lampén 1987, Lahermo 1991, Mitrega and Lahermo 1991, Korkka-Niemi 1994). This phenomenon has been attributed primarily to relict salts left deep in glaciomarine deposits and within fractures and fissures of bedrock during the Litorina stage (about 7 500–5 000 years ago). It has been estimated by Eronen *et al.* (1979) that the salinity of the Litorina Sea was 5‰–10‰. This is considerably higher than that of the present-day Baltic Sea, which ranges from 4‰ to 6‰ (Pietikäinen *et al.* 1978, Perttilä *et al.* 1980).

The preservation of relict salinity could be explained by the sluggish exchange of water in the formations involved, which has diminished

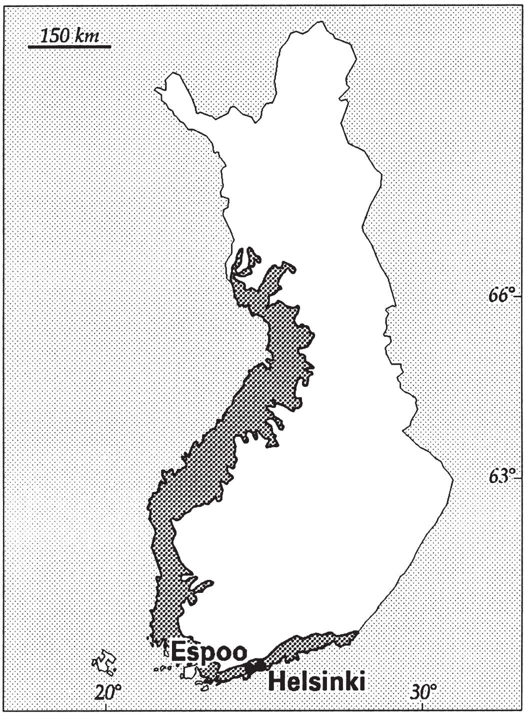

Fig. 1. Map of Finland showing location of Espoo. Coastal area covered by the Litorina Sea some 7000 years ago is highlighted.

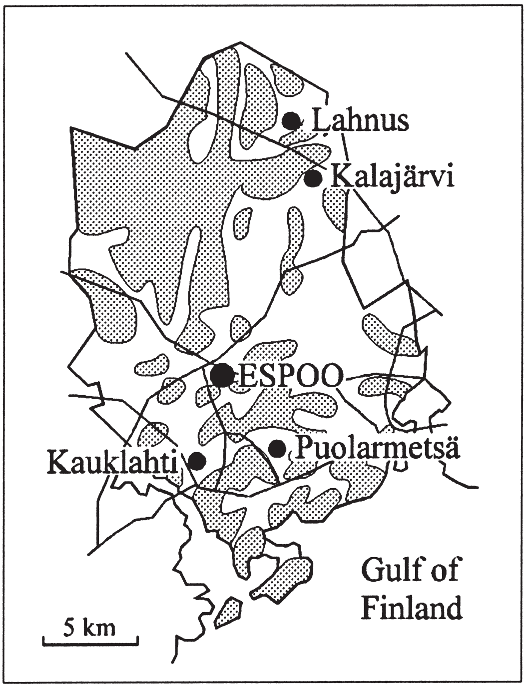

Fig. 2. Location of the four studied groundwater supply plants in Espoo community. Dotted areas represent bedrock terrains (surficial deposits less than 1 m thick).

the effect of dilution by a later less saline stage of the present Baltic Sea and by a very slow circulation of groundwater, that have been capable of storing seawater for many thousands of years (Lahermo 1971). Pumping an aquifer changes the mass-balance of the aquifer and thus the groundwater flow. As the influence area of pumping increases, the leakage from surrounding sediments and fractured bedrock is accelerated and an increasing proportion of dissolved salts or relict seawater may be captured by groundwater intake.

The purpose of this study is to gather information on the long-term changes in groundwater chemistry in coastal glaciofluvial aquifers and to evaluate the possible causes of the increase in the content of dissolved solids in groundwater.

Study sites and observation data

Espoo community is located in the western part of the Helsinki metropolitan area and has a population of about 196 000 people (Fig. 1). The economical activity has been concentrated in the southern parts of the approximately 300 km^2 area of Espoo, while the northern parts have remained rural areas and some nature preserves.

In Espoo, the bedrock consisting mainly of granites, migmatic gneisses and amphibolites is covered by till and clay deposits. In topographical highs the bedrock is exposed or covered by a few meters of sediments, while in topographical depressions the overburden is much thicker. Groundwater is mainly stored in volumetrically small glacial outwash deposits and in fissured bedrock. In the Helsinki region the highest Litorina shoreline is about 30 m above the present sea level (Eronen 1983), which means that extensive areas of Espoo were submerged during the Litorina stage.

Four glacial outwash aquifers utilised for municipal water supply are deposited in topographic depressions associated with fracture zones and are generally confined by clay deposits. The chemical composition of groundwater has been monitored during the last 30 years from wells drilled into these aquifers representing both urbanised (Kauklahti, Puolarmetsä) and rural (Lahnus, Kalajärvi) areas (Fig. 2). The depth of wells in water supply plants range between 15 to 25 meters. The amount of abstracted groundwater varied from year to year, between 100 to 300 m^3 d^{-1}.

The investigation is based on the groundwater monitoring data collected during years 1956 to 1995. Water samples were taken and the analyses were performed by the Espoo Water and Sewage Works. Groundwater was analysed for pH, electrical conductivity, anions (HCO_3, SO_4, Cl), cations (Ca, Mg, Na, K), nitrogen compounds, $KMnO_4$ number and some heavy metals, for a total of 23 parameters listed in Table 1. Unfortunately, determinations of all these components were not consistently available for the first 5 to 10 observation years. For the older data set 1 to 3 analyses per year are available. The sampling frequency was higher during the last 10 years, when on average 10 to 12 samples were analysed each year. Groundwater quality is compared to quality standards set by the Ministry of Social Affairs and Health of Finland (Anon. 1994).

Temporal changes in groundwater chemistry

Comparison of the mean and median concentrations of major cations and anions in 1956 to 1979 and 1991 to 1995, respectively, does not reveal dramatic changes in water quality (Table 1). However, some variations in groundwater composition are discernible during the last 25 years or more. The maximum permissible concentrations of major components in water set by the Ministry of Social Affairs and Health of Finland or international standards have been exceeded only in few samples. In both rural and urban parts of Espoo, the SO_4, NH_4, NO_2, NO_3 and F abundances were clearly below the limit values. The values of electrical conductivity (EC) indicate an increase of dissolved ion (Cl, SO_4, Na, Mg) content in groundwater. The pH of groundwater has slightly de-

Table 1. Chemical composition of groundwater in Espoo water supply plants. m = mean, md = median.

Parameter	Unit	Limit values	Groundwater supply plants															
			Puolarmetsä				Kauklahti				Kalajärvi				Lahnus			
			1959–70		1991–95		1956–70		1991–95		1971–79		1991–95		1975–79		1991–95	
			m	md	m	md	m	md	m	md	m	md	m	md	m	md	m	md
pH		6.5–8.8	6.7	6.6	6.3	6.2	6.6	6.5	6.4	6.3	5.9	5.9	5.8	5.8	6.6	6.6	6.4	6.4
EC	mS m^{-1}	40	14	15	31	30	20	19	24	24	18	17	30	29	20	19	33	32
O_2	mg l^{-1}		3.9	4.5	0.5	0.1	1.3	1.4	2.2	2.2	5.8	5.8	4.9	4.9	8.2	8.2	5.9	5.8
$KMnO_4$	mg l^{-1}	12	3.2	3.0	3.5	3.5	5.4	4.0	5.7	5.7	3.4	3.6	3.4	3.4	2.5	2.5	2.5	2.4
Alkalinity	mmol l^{-1}		0.7	0.8	1.6	1.6	0.8	0.7	1.3	1.3	0.5	0.3	0.3	0.3	0.6	0.6	0.8	0.8
HCO_3	mg l^{-1}		47	46	100	98	42	41	78	79	17	17	20	20	36	38	50	48
CO_2	mg l^{-1}		23	25	56	54	29	30	34	36	52	52	32	35	15	12	20	21
Ca	mg l^{-1}	100	15	16	24	24	16	13	17	16	11	12	12	12	18	16	22	22
Mg	mg l^{-1}	50	5.1	5.4	9.5	9.3	5.9	4.2	6.5	6.4	3.2	3.1	3.2	3.2	5.0	5.1	6.9	7.0
Na	mg l^{-1}	150	12	12	15	15	21	22	17	17	15	15	31	32	10	11	16	15
K	mg l^{-1}	12	3.1	2.9	4.0	3.9	4.0	4.0	2.5	2.6	3.3	3.0	2.2	2.1	5.2	4.5	7.9	7.9
SO_4	mg l^{-1}	150	16	22	42	44	16	20	32	31	12	13	21	19	14	14	24	22
Cl	mg l^{-1}	100	13	13	21	20	31	28	17	17	31	33	63	63	27	27	54	54
F	mg l^{-1}	1.5	0.38	0.40	0.56	0.58	0.17	0.20	0.14	0.16	0.16	0.17	0.12	0.12	0.12	0.12	0.10	0.10
SiO_2	mg l^{-1}		14	14	11	14	16	18	16	17	13	13	11	12	14	14	13	13
NH_4	mg l^{-1}	0.5	0.042	0.010	0.010	0.009	0.063	0.050	0.004	0.003	0.032	0.018	0.004	0.004	0.045	0.045	0.004	0.005
NO_2	mg l^{-1}	0.1	0.007	0.000	0.004	0.003	0.010	0.000	0.004	0.003	0.000	0.000	0.003	0.003	0.014	0.014	0.003	0.003
NO_3	mg l^{-1}	25	1.99	1.75	0.63	0.66	3.21	2.00	0.82	0.80	6.30	6.00	3.53	3.36	16.05	16.05	11.04	10.60
Al	µg l^{-1}	200	13	10	27	30	10	10	13	10	33	40	48	40	13	10	8	10
Fe	µg l^{-1}	200	195	100	247	110	107	100	76	80	64	55	26	10	267	100	61	20
Mn	µg l^{-1}	50	38	20	88	90	77	65	132	140	21	22	22	20	7	6	11	10
Cu	µg l^{-1}	300	30	25	11	10	10	10	14	10	6	6	12	10	13	18	11	10
Zn	µg l^{-1}	3000	175	85	11	10	105	100	11	10	24	20	11	10	47	40	11	10

creased and the content of free CO_2 has increased. The acidity of bedrock is the most important reason for low pH of the groundwater. Aquifers are covered by clay, which together with the long distances from recharge areas has contributed to relatively high concentrations of iron and manganese and low oxygen content.

The lower concentrations of Cl, SO_4, Na and Mg observed during first years of water abstraction indicate that the initial groundwater composition is only marginally influenced by marine components. Long distances from the present shoreline (Kauklahti 1.5 km, Puolarmetsä 3.5 km, Kalajärvi and Lahnus 18–19 km) suggest that direct infiltration of saline seawater is highly unlikely (Fig. 2).

The correlation analyses of chemical parameters.

Correlation matrices were computed for the geochemical parameters determined in this study and are shown in Table 2.

During the first years of groundwater abstraction the pH values had a positive correlation with HCO_3 concentrations (Lahnus $r = 0.87$) and a negative one with free CO_2 content (Kauklahti $r = -0.39$, Lahnus $r = -0.87$, Puolarmetsä $r = -0.57$). The covariation of the presented parameters shows that the pH values of the surficial groundwaters were mainly controlled by CO_2-HCO_3 equilibrium. These correlations are not seen in Table 2, where all the members of the data series are included. The weak negative correlations between pH and the content of SO_4 can be observed (Table 2). When sulphide-rich fine-grained sediments are exposed to the air, sulphur compounds oxidise quickly to sulphates with the result that the pH values decrease. In Puolarmetsä and Lahnus pH values have a weak negative correlation with Al. Low pH values accompanied by the low alkalinity values and high Al concentrations have been recorded from the Kalajärvi groundwater (Table 1).

Electrical conductivity (EC) correlates strongly with concentrations of the main anions and cations, i.e. HCO_3, Cl, SO_4, Ca, Mg, Na and K (Table 2). Positive correlations are especially strong with Cl and Na. Weak negative correlation between EC value and NO_3 concentrations indicates that the possible anthropogenic contamination does not notably increase the amounts of dissolved electrolytes.

Dissolved O_2 has a weak negative correlation with CO_2 (Puolarmetsä $r = -0.58$), $KMnO_4$ consumption and the main anions and cations. Concentrations of dissolved O_2 are lower in aquifers covered with clay and silt deposits, where conditions favour higher CO_2 content in water. The thickness of clay cover in Puolarmetsä and Kauklahti areas is approximately 5 m which is also reflected in the groundwater chemistry of confined aquifers concerned (Table 1). Dissolved CO_2 shows a weak negative correlation with pH and a slight positive correlation with the main anions and cations (expect Cl and Na), indicating a relationship with CO_2 as a factor promoting silicate weathering. These correlations are strongest in Puolarmetsä aquifer.

Concentrations of HCO_3 correlate moderately with the value of EC and the content of Ca and Mg in Puolarmetsä, Kauklahti (not with EC) and Lahnus (not with Ca), but weakly with EC and Mg in Kalajärvi groundwater. In Lahnus and Kalajärvi HCO_3 is not a dominant anion in groundwater, as the concentrations of Cl has been approximately the same (Lahnus) or higher (Kalajärvi) throughout the whole observation period (Table 1). Only during the first years of groundwater abstraction did the content of HCO_3 dominate over Cl and SO_4 in all aquifers.

Sulphates correlate moderately with EC, Ca (Puolarmetsä, Kauklahti), Mg (not in Kalajärvi) and K (only Puolarmetsä). In Puolarmetsä and Lahnus plants moderate positive correlation exists with Cl ($r = 0.43$ and 0.57 respectively), which might point to marine origin of some sulphates.

Chlorides correlate strongly with EC, moderately with Na and Mg, which indicates that the marine salts significantly increase the ion content of groundwater. Positive correlation exists also with K (Kalajärvi) and Ca (Puolarmetsä). Total hardness of groundwater, resulting from the presence of dissolved calcium and magnesium salts, is also positively correlated with Cl. The increase of Cl content in groundwater during water abstraction is followed by a decrease in oxygen content in Lahnus and Puolarmetsä plants ($r = -0.51$ and

–0.41, respectively) and in some increase of Mn and Fe. Groundwater retained in deep portions of glacial deposits and in bedrock is deficient in oxygen and is apt to contain considerable amounts of dissolved components (including Cl). Slight negative correlation between Cl and NO_3 (Kalajärvi and Puolarmetsä) points also to the intrusion of groundwater derived from more anoxic deeper horizons.

Fluoride concentrations are relatively independent of other water-soluble components. Nevertheless some slight and mainly positive correlations exist in Puolarmetsä (Table 2), where the F content in groundwater together with the main cations and anions has increased during water abstraction. Generally, the increase of other substances does not essentially lead to an increase in the F content.

The content of silicic acid (SiO_2) is less variable than any of the other major dissolved constituents of natural water (Davis 1964), generally occurring in the groundwater of the study area in amounts of 12–18 mg l^{-1}. Silicic acid exhibits slight negative correlation with EC and main cations and anions in the groundwater of northern part of Espoo (Table 2). Silica is released in conjunction with the weathering of silicate minerals and its concentration in seawater is low, according to Rankama and Sahama (1950) about 7 mg l^{-1}. The observed slight decrease in SiO_2 in the groundwater may indicate the influence of silica-poor ancient seawater to groundwater chemistry.

Lahermo (1988) observed, that potassium, together with NO_3, and generally also Cl, seems to be a more sensitive indicator of pollution than other alkali metals and alkali earths. There appears to be no positive correlation between these components in the Espoo study area. Nitrate tends to correlate negatively with main ions of groundwater (Table 2) and these correlations are strongest in Puolarmetsä, where the most remarkable depletion in O_2 content has occurred. The general decline in all nitrogen compounds (Table 1) and the lack of positive correlations between nitrogen compounds and the other components (Table 2) indicate that the anthropogenic sources have no clear impact on groundwater chemistry in observed aquifers. The source of NH_4 and NO_2 in the groundwater of the coastal areas may be organic compounds deposited during Litorina Sea stage. However, anthropogenic sources of N-compounds cannot be excluded.

Calcium and magnesium, the main cations of fresh groundwater, correlate positively with EC, HCO_3 and SO_4, especially in Puolarmetsä and Kauklahti areas. The moderate correlation of Mg with Cl (in all plants) and Na (Lahnus) points to some marine source for Mg. Two alkali earths are also in positive correlation with K in Kauklahti and Lahnus areas. Mutual covariation between Ca and Mg appears stronger in southern Espoo (r = 0.62–0.78) when compared to the northern part of the study area (r = 0.32–0.45). Total hardness is closely correlated with the Ca (r = 0.88–0.95) and Mg (r = 0.64–0.93) contents. There exists no clear correlation, however, between total hardness and bicarbonate in groundwater (except in Puolarmetsä, r = 0.64), because in coastal region like Espoo the hardness may be associated with the occurrence of chloride and sulphate. Total hardness is in positive correlation with the Cl content, especially in the southern part of study area (Table 2).

Sodium correlates positively with EC and Cl. Correlations between Na and Cl are strongest in Kalajärvi (northern Espoo), where the highest mean and median Cl content together with lowest mean and median SO_4 and HCO_3 contents were recorded (Table 1).

Potassium, like sodium, correlates moderately with EC, but only in southern Espoo. The best correlation of K with other main cations and Cl (positive) and with SO_4 and HCO_3 (negative) was found to be in Kauklahti groundwater (Table 2). Alkali metals do not exhibit a clear mutual correlation. According to Lahermo (1971) the correlation between K and Na diminishes as the content of dissolved solids in groundwater increases (groundwater of bedrock and of deposits overlain by clay beds).

Heavy metals show only a few meaningful correlations. Iron and manganese, the elements with similar chemical properties, do not correlate with each other. Slight correlation of Mn with $KMnO_4$ consumption values can be observed (r = 0.16–0.54) and might be explained by the complexing of Mg with dissolved humic matter.

Table 2. Correlation matrices for the properties and concentrations of dissolved constituents; *r*-values below significance level $p = 0.05$ are not presented, n = number of analyses.

Puolarmetsä (1959–1995)
$n = 185$

	pH	EC	Alkal.	HCO_3	Tot.h.	O_2	$KMnO_4$	CO_2	Ca	Mg	Al	Mn	Fe	Cu	Zn	K	Na	NH_4	NO_2	NO_3	F	Cl	SiO_2
EC	–0.36																						
Alkal.	–0.46	0.79																					
HCO_3	–0.40	0.74	0.95																				
Tot.h.	–0.48	0.86	0.73	0.64																			
O_2	0.48	–0.61	–0.63	–0.58	–0.79																		
$KMnO_4$	–0.25	0.25	0.15		0.35	–0.15																	
CO_2	–0.57	0.54	0.44	0.27	0.65	–0.58	0.22																
Ca	–0.33	0.66	0.59	0.46	0.95	–0.63		0.54															
Mg	–0.26	0.63	0.51	0.44	0.83	–0.71	0.21	0.37	0.62														
Al	–0.23	0.19	0.19	0.19	0.20	–0.23	0.16			0.24													
Mn	–0.35	0.45	0.51	0.50	0.28	–0.30	0.26			0.29	0.41												
Fe	–0.13				–0.18						–0.21												
Cu		–0.17	–0.20	–0.18	–0.26	0.40		–0.14	–0.17	–0.23													
Zn	0.26	–0.36	–0.35	–0.32	–0.38	0.28	–0.22	–0.28	–0.42	–0.14		–0.19											
K	–0.17	0.35	0.15	0.13	0.30	–0.35	0.38	0.20			0.28	0.57	0.17		–0.23								
Na		0.38	0.55	0.51	0.36	–0.23			0.24	0.13		0.19			–0.17								
NH_4	0.29	–0.18	–0.19	–0.19	–0.25	0.30		–0.29	–0.36	–0.54	0.13						0.17						
NO_2		0.13				–0.41				0.28	0.30	0.45	0.17	–0.15	–0.23	0.37		–0.15					
NO_3	0.38	–0.59	–0.50	–0.50	–0.54	0.44	–0.19	–0.46	–0.55	–0.68		–0.26		0.21	0.84	–0.13	–0.19	0.15	–0.14				
F	–0.16	0.32			0.14	–0.16	0.27			0.37	0.55	0.48				0.58	–0.18		0.36	–0.32			
Cl	–0.45	0.57	0.56	0.56	0.69	–0.41		0.45	0.53	0.59	0.33	0.33			–0.18		0.19	–0.19		–0.39	0.33		
SiO_2					0.17	–0.32		0.20	0.18		–0.50			0.16			–0.29			0.15	–0.14	0.15	
SO_4	–0.26	0.61	0.50	0.50	0.69	–0.49		0.43	0.50	0.44	0.13	0.28		–0.19	–0.27	0.65	0.33	–0.21	0.35	–0.33	0.43	0.44	

Kauklahti (1956–1995)
$n = 169$

	pH	EC	Alkal.	HCO_3	Tot.h.	O_2	$KMnO_4$	CO_2	Ca	Mg	Al	Mn	Fe	Cu	Zn	K	Na	NH_4	NO_2	NO_3	F	Cl	SiO_2
EC	0.24																						
Alkal.		–0.13																					
HCO_3		–0.13	0.99																				
Tot.h.		0.75																					
O_2	–0.16	–0.19																					
$KMnO_4$	–0.30	–0.23	0.53	0.53	–0.15																		
CO_2		0.17	0.53	0.53	0.20		0.32																
Ca		0.56	0.46	0.46	0.94	0.24	0.23	0.49															
Mg	–0.14	0.66	0.36	0.36	0.93	0.33	0.27	0.41	0.78														
Al	0.16	0.19				–0.23	–0.15	–0.15	–0.14	–0.23													
Mn	–0.17		0.54	0.54	0.27	0.20	0.54	0.22	0.48	0.42	0.14												
Fe		0.22	–0.28	–0.28	0.27		–0.25	–0.16		0.20	0.25	–0.24											
Cu	0.13										0.43	0.22											
Zn	0.13	0.49	–0.52	–0.52	0.57		–0.45	–0.31	0.29	0.34	0.37	–0.14	0.62										
K	0.34	0.69	–0.57	–0.57	0.72	–0.22	–0.37		0.45	0.55		–0.22	0.31		0.72								
Na	0.42	0.61	–0.33	–0.33	0.24		–0.38			0.17		–0.35			0.22	0.49							
NH_4	0.37	0.15	–0.54	–0.54	0.28		–0.21	–0.31	0.14			–0.23	0.48	0.13	0.66	0.47	0.27						
NO_2	–0.13	–0.42	0.15	0.15	–0.36	0.16	0.26		–0.25	–0.21		0.30	–0.16		–0.32	–0.39	–0.46						
NO_3	0.13	–0.25	–0.51	–0.51				–0.33	–0.32	–0.40		–0.25			0.44	0.49		0.38	0.24				
F	–0.16		–0.22	–0.22	–0.19	–0.16		–0.21		–0.13		–0.29					0.20		0.24				
Cl	0.21	0.79	–0.60	–0.60	0.74	–0.14	–0.54	–0.19	0.28	0.54	0.15	–0.28	0.47		0.71	0.87	0.63	0.42	–0.41	0.14			
SiO_2	0.20				0.17	–0.21					–0.26						–0.36		–0.32		–0.16		
SO_4		0.39	0.57	0.57	0.23			0.44	0.42	0.40	0.29	0.33		0.20	–0.33	–0.30		–0.29	–0.30	–0.68	–0.30		

Lahnus (1975–1995)
n = 131

	pH	EC	Alkal.	HCO_3	Tot.h.	O_2	$KMnO_4$	CO_2	Ca	Mg	Al	Mn	Fe	Cu	Zn	K	Na	NH_4	NO_2	NO_3	F	Cl	SiO_2
EC																							
Alkal.		0.41																					
HCO_3		0.41	0.99																				
Tot.h.		0.36	0.30	0.30																			
O_2		–0.29	–0.31	–0.31	–0.42																		
$KMnO_4$					0.37	–0.23																	
CO_2																							
Ca					0.88	–0.32	0.38																
Mg		0.53	0.39	0.39	0.67	–0.39	0.19		0.32														
Al	–0.28				–0.23				–0.34														
Mn	–0.17	0.17	0.25	0.25	0.26	–0.35	0.33		0.21	0.18													
Fe					–0.24	0.18			–0.31														
Cu		0.24				–0.19				0.21	–0.20	0.24	0.31										
Zn		–0.33			–0.29	0.29		–0.19	–0.18	–0.32			0.28	0.41									
K		0.16			0.36			0.19	0.26	0.37		0.16			–0.47								
Na		0.74	0.51	0.51	0.27	–0.19		–0.22		0.45		0.17			–0.26	0.25							
NH_4		–0.30	–0.29	–0.29	–0.38	0.29	0.23	0.21	–0.32	–0.35	0.61			–0.20	0.35	–0.25	–0.27						
NO_2						0.25	–0.18			–0.19	–0.23	–0.19			0.20								
NO_3	0.20				–0.39	0.20			–0.39	–0.24	–0.20		0.13		0.28				0.16				
F	0.18	–0.25			–0.28	0.18	–0.25			–0.46	–0.17	–0.22			0.32		–0.22	–0.12		0.21			
Cl	–0.25	0.81	0.51	0.51	0.44	–0.51		–0.20	0.22	0.59		0.37		0.24	–0.28	0.16	0.61	–0.32			–0.27		
SiO_2	0.37	–0.46	–0.30	–0.30	–0.23			–0.28		–0.49	–0.32	–0.28	–0.37	–0.22			–0.31				0.37	–0.41	
SO_4	–0.28	0.54			0.38	–0.48	0.21	0.16	0.19	0.64		0.25	0.51	0.24	–0.34		0.17	–0.20	–0.17	–0.28	–0.18	0.57	–0.45

Kalajärvi (1971–1995)
n = 139

	pH	EC	Alkal.	HCO_3	Tot.h.	O_2	$KMnO_4$	CO_2	Ca	Mg	Al	Mn	Fe	Cu	Zn	K	Na	NH_4	NO_2	NO_3	F	Cl	SiO_2
EC																							
Alkal.		0.27																					
HCO_3		0.27	0.99																				
Tot.h.																							
O_2																							
$KMnO_4$						–0.16																	
CO_2			–0.25	–0.25		–0.26	0.20																
Ca					0.94																		
Mg		0.23	0.33	0.33	0.64		–0.35		0.45														
Al		0.23			–0.20					–0.36													
Mn					0.16		0.16				0.39												
Fe		–0.27	–0.16	–0.16							–0.37												
Cu	0.16		0.17	0.17																			
Zn		–0.39					–0.35				–0.35												
K		–0.18	–0.37	–0.37			0.21	0.22				0.27		–0.18	0.21								
Na		0.43			0.23	–0.41			0.16	0.19	0.26		–0.25		–0.40								
NH_4		–0.38	–0.17	–0.17			0.31	0.23		–0.19				–0.21		0.48	–0.22						
NO_2	–0.25	0.19	0.21	0.21		0.25	–0.19	–0.40			0.45	–0.20			–0.17	–0.51		–0.25					
NO_3	0.16	–0.38	–0.16	–0.16		0.32				0.16	–0.34				0.38	0.24	–0.36	0.22	–0.30				
F					0.25				0.17		0.16	0.17	0.24	–0.22	0.34		–0.31			0.22			
Cl		0.59	0.18	0.18	0.33	–0.17		–0.26	0.24	0.32	0.39	0.17	–0.34		–0.52		0.78	–0.26	0.25	–0.42	–0.30		
SiO_2		–0.75	–0.33	–0.33						–0.17	–0.21		0.28	0.25	0.40		–0.24			0.34		–0.29	
SO_4	–0.18	0.59	0.38	0.38	–0.29			–0.36	–0.28						–0.24	–0.61		–0.30	0.48	–0.51			–0.61

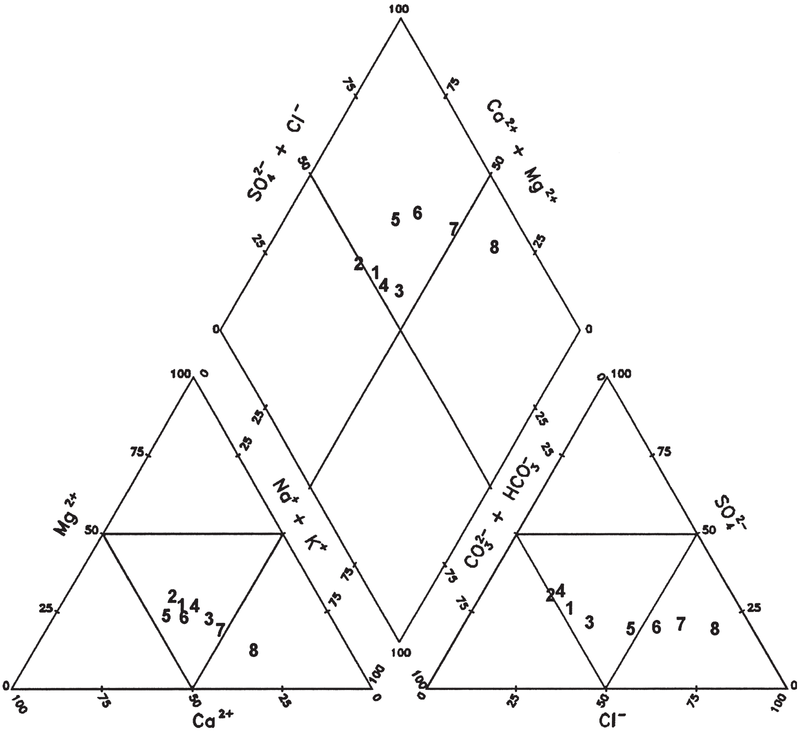

Fig. 3. Trilinear diagram showing groundwater chemistry changes in four Espoo aquifers: Puolarmetsä (from 1 to 2), Kauklahti (3–4), Lahnus (5–6) Kalajärvi (7–8). Numbers 1 – 8 refer to the mean values calculated for sampling intervals listed in the head of Table 1.

Relict seawater as one source of dissolved components in groundwater

Low concentrations of ions and the limited number of analysed components complicates the examination of possible sources of salinity in the groundwater. However, available data suggests that ancient seawater may have altered the chemistry of the groundwater.

Major ion chemistry of sampled groundwater is examined as a whole using the Piper diagram (Fig. 3). It shows slight change in relations between main cations and anions in all aquifers. The change towards the more Na-Cl- (Lahnus and Kalajärvi) or Mg-SO_4-dominating (Puolarmetsä and Kauklahti) groundwater is evident.

Some ion ratios used to interpret the origin of groundwater are presented in Table 3. Samples of groundwater taken near the present-day sea level (Puolarmetsä and Kauklahti) are characterised by higher ratios of SO_4:Cl, Na:Cl, Mg:Cl, Ca:Cl and lower ratios of Ca:Mg than those taken further

Table 3. Selected cation:anion ratios.

		SO_4:Cl	Na:Cl	Mg:Cl	Ca:Cl	Ca:Mg
Puolarmetsä	1959–79	1.88	0.86	0.50	1.24	2.70
	1980–95	2.16	0.79	0.48	1.28	2.70
Kauklahti	1957–79	0.54	0.48	0.25	0.67	2.81
	1980–95	1.59	1.05	0.33	0.88	2.69
Kalajärvi	1971–79	0.34	0.51	0.14	0.45	3.56
	1980–95	0.30	0.52	0.05	0.19	3.75
Lahnus	1975–85	0.50	0.31	0.16	0.57	3.57
	1986–95	0.46	0.31	0.14	0.44	3.26
Seawater *		0.14	0.56	0.07	0.02	0.30

* Rankama and Sahama 1950.

inland. The ion ratios in northern Espoo (especially in Kalajärvi area) are closer to those in seawater, compared to the southern part of investigated area. Mg:Cl and Ca:Cl ratios show a general decreasing trend and approach the values found in seawater (Fig. 4). Ratios of cation and chloride concentrations in southern Espoo are similar to values calculated for groundwater in Finnish bedrock (Hyyppä 1984). In Sweden, groundwaters with Na:Cl ratios of 0.29–0.90 and Mg:Cl ratios of 0.05–0.08 have been interpreted as relict Baltic water (Nordström 1983).

Scatter diagrams for the most significant parameters are presented in Fig. 5a–e. The Na:Cl plot shows that the groundwater in Lahnus water works is depleted in sodium relative to seawater (Fig. 5a). Groundwaters sampled in Kalajärvi and Puolarmetsä are located roughly on seawater dilution line (SDL). The depletion of Na relative to seawater in Kauklahti plant occurs at higher Cl concentrations. The distribution of data is quite linear, suggesting a mixing trend of a more saline water with dilute meteoric water.

Magnesium lies close to the SDL with respect to Cl in Kalajärvi, with small deviations to either side (Fig. 5c). This indicates that Mg has a marine component, modified to some extent (mainly at lower Cl values) by precipitation and dissolution/weathering reactions.

Calcium and potassium are enriched in the groundwaters relative to seawater and their concentrations are fairly independent of Cl concentrations as shown in Fig. 5d and e. The fact that the points lie mainly above the SDL (K, Mg, Ca) reflect the high-solubility of K-, Ca- and Mg-rich weathering products.

If we consider the increase in concentration of different ions and the evolution of their ratios during pumping, it is possible to evaluate the sources of the increasing salinity. Fig. 6 shows the ratios of Na:Cl, Mg:Cl and SO_4:Cl as a function of the chloride concentration from Kauklahti and Kalajärvi well fields. In addition to dissolution/leaching from glaciomarine deposits sodium and magnesium can be derived from weathering of rocks and minerals. Thus it might be expected that the Na:Cl- and Mg:Cl-ratios in the sampled groundwater would always remain higher than respective ratios in seawater. However, the Na:Cl- and Mg:Cl-ratios in groundwater have decreased when compared with the same ratios in seawater as salinity has increased. This may be due to preferential adsorption and ion-exchange of Na and Mg ions on clay minerals. Clay minerals have a net negative charge and are therefore unlikely to adsorb anions. Cationic attraction to the basal planes of lattices in clay particles increases with higher valence and decreasing hydrated ionic radii. This leads to an enrichment of polyvalent cations in adsorbed positions relative to the ionic com-

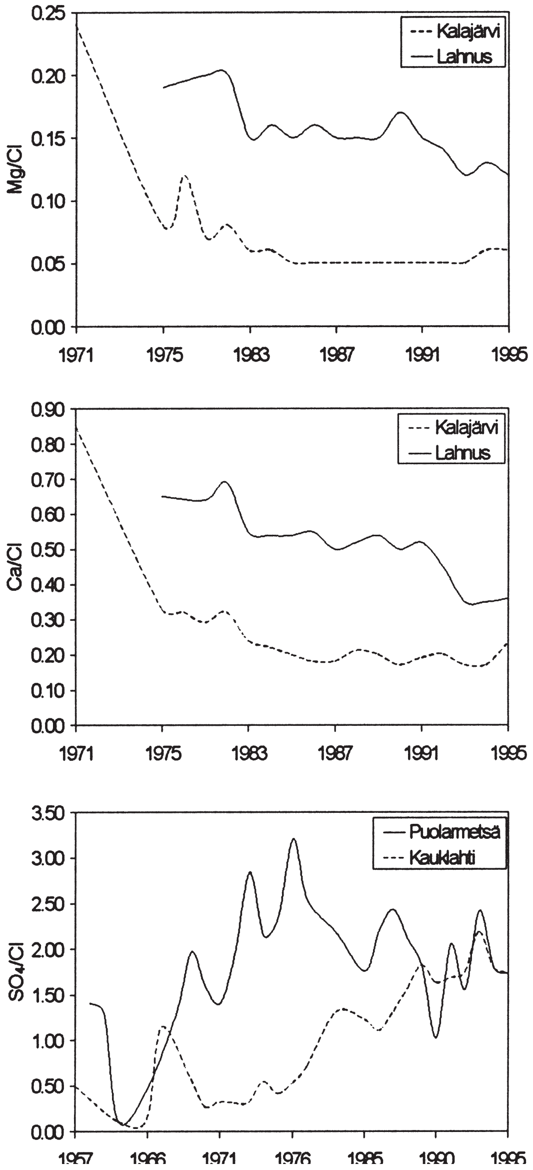

Fig. 4. Time series of some obviously increasing or decreasing ion ratios.

position in the liquid phase (Van Olphen 1977). Studies conducted in Norway indicate an elevated concentration of Na in relation to Cl in the pore water of marine clay samples, and that adsorbed cations are enriched in Mg and Ca compared with Na (Hilmo *et al.* 1992). Further, use of salt for de-icing on roads may disturb natural balance of Na and Cl in groundwater.

Temporal chances in SO_4:Cl ratios in Kauklahti and Puolarmetsä show the increasing weight of SO_4 in groundwater chemistry (Fig. 4). On the SO_4:Cl plot most of the points lie above the seawater dilution line suggesting geological sources (sulphide-sulphate-rich clay) for the majority of the sulphate (Fig. 5b). Generally, sulphate in groundwater originates from: 1) weathering of sulphides and secondary sulphate-minerals, 2) the marine environment and 3) infiltration of anthropogenically contaminated precipitation. Sources 1) and 3) best explain the high concentrations of sulphate and the high SO_4:Cl ratios at low Cl concentrations. In groundwater which has higher salinity, the SO_4:Cl ratio approaches the value found in Standard Seawater indicating a marine origin of salinity (Fig. 6).

Conclusions

1. Changes in groundwater chemistry in coastal glacial outwash aquifers have occurred during 30 to 35 years of water abstraction. The 1.5 to 2.0-fold increase of EC and concentration of cations and anions existing in abundance in seawater (Na, Mg, Cl, SO_4) is observed. The pH of groundwater and its content of O_2 has decreased. However, the maximum permissible concentrations of components in water set by national or international standards have rarely been exceeded. Water quality problems are associated with elevated Cl (all observed aquifers) and SO_4 (southern Espoo) concentrations.
2. Groundwater chemistry is controlled by a complicated system of anthropogenic and natural factors. The main source of dissolved load in

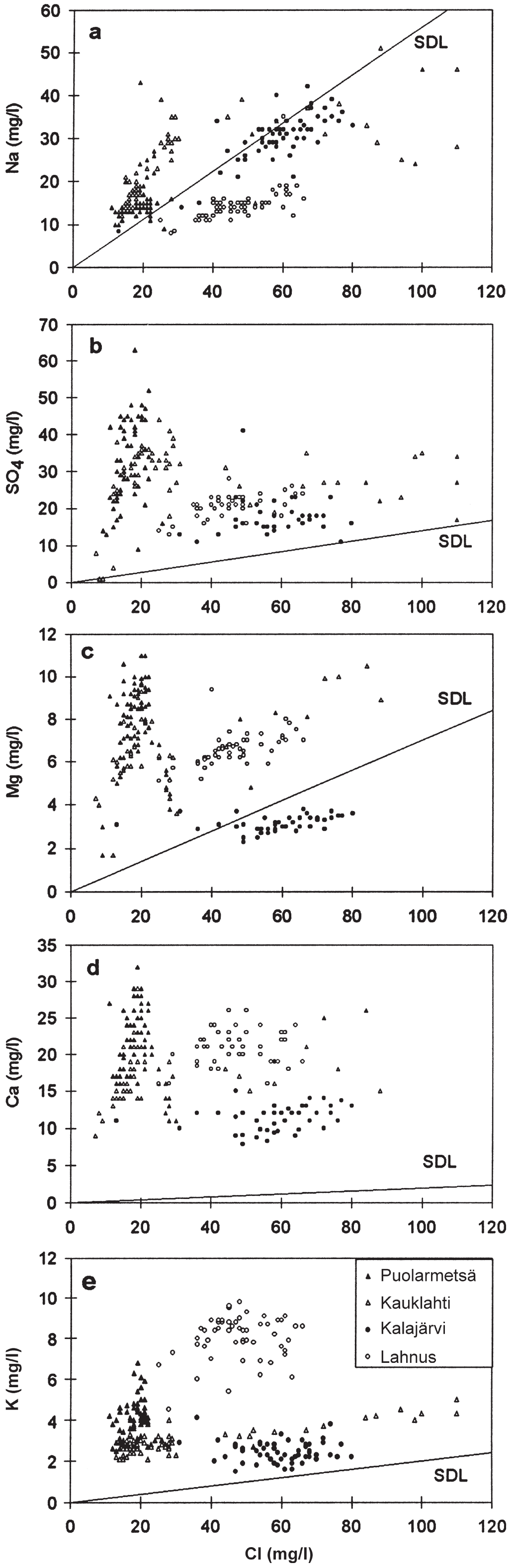

Fig. 5 (on the left). The concentrations of various ions plotted against chloride concentration. SDL = seawater dilution line.

groundwater is the weathering of bedrock and overburden. In coastal aquifers, relict seawater trapped in isolated sand/gravel layers and within fractures of bedrock and fossil salts leached from clay and silt deposits dating back to Litorina or later marine phases are the second important sources of ions. Due to the low pumping rates (100–300 m^3 d^{-1}) direct intrusion of seawater into aquifers with consequent implications for water quality does not exist. The main portion of anthrophogenic matter entering the groundwater could be derive from increasing traffic, particularly from the dissolution of de-icing salts (NaCl), and from dry and wet deposition. Because the alkalinity of groundwater has not decreased there is no clear impact of acid deposition on groundwater quality. Low concentration of sensitive indicators of contamination (N-compounds, K) and the results of correlation analyses indicate that agricultural activity has no polluting influence regarding groundwater quality. Real marine components are, however, difficult to distinguish from the geological and anthropogenic end members.

3. Prolonged groundwater withdrawal has shifted the ion ratios of groundwater closer towards to those found in Standard Seawater. The decrease in SO_4:Cl, Mg:Cl and Ca:Cl ratios in the aquifers of northern Espoo points to additional marine source of Cl. In the southern aquifers studied the increase in SO_4:Cl ratio is remarkable. Possible source of elevated SO_4 content is relict sulphide- and sulphate-rich marine clay and silt deposits. Also preferential adsorption and ion-exchange of cations on clay minerals control ion ratios in groundwater. Chlorine, sodium and magnesium contents exhibit the mutual positive correlation and correlate strongly with the values of electrical conductivity. Relict marine salts significantly increase the ion content of groundwater.
4. Water sampling during test-pumping and the first years of groundwater utilisation may give some misleading results on the chemical character of water, as compared with continuous long-term pumping of coastal aquifers. Considering the changes in water chemistry at present yields, estimated safe yields for Espoo aquifers (up to 400–700 m^3 d^{-1}) might turn out to be qualitatively overvalued.

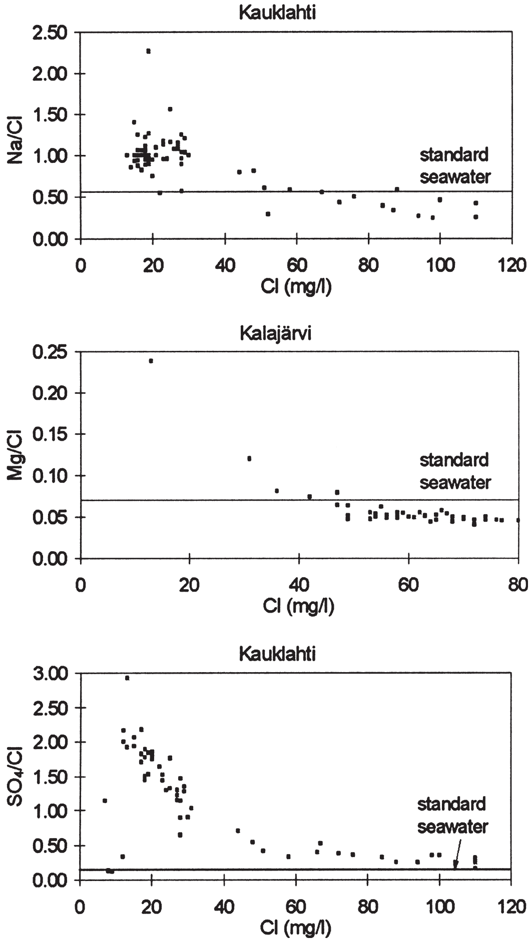

Fig. 6. Ratios of Na:Cl, Mg:Cl and SO_4:Cl as a function of the chloride concentration.

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