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# Evaluation of the quality of groundwater sampling: Experience derived from radioactive waste disposal programmes in Sweden and Finland during 1980-1992

**J.A.T. Smellie**  
Conterra AB, Uppsala

**M. Laaksoharju**  
Intera, Sollentuna

**M.V. Snellman**  
Posiva Oy

**P.H. Ruotsalainen**  
Fintact Oy

**September 1999**

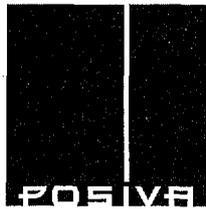
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**POSIVA OY**

Mikonkatu 15 A, FIN-00100 HELSINKI, FINLAND

Phone (09) 2280 30 (nat.), (+358-9-) 2280 30 (int.)

Fax (09) 2280 3719 (nat.), (+358-9-) 2280 3719 (int.)



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Tiivistelmä – Abstract  Existing Finnish and Swedish hydrogeochemical field data from the 1980s and the early 1990s have been closely examined in the light of other influencing activities, such as geology and hydrology, which form an integral part of site-specific investigations. The report has considered data relating to the monitoring of groundwater chemical trends and groundwater sampling and analysis. These data have been used to simulate the effects of important parameters on groundwater quality and representativeness, to generate recommendations to improve the standard of hydrogeochemical sampling and analyses, and to discuss these results in the broader context of future site-specific investigations.	
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Tiivistelmä – Abstract  Befintliga finska och svenska hydrogeokemiska data från 1980-talet och tidigt 1990-tal har noggrant undersökts mot bakgrund av andra inverkanse faktorer såsom geologi och hydrogeologi, vilka bildar en integrerad del av platsspecifika undersökningar. Studien har tagit i beaktande data relaterade till monitoreringen av grundvattenkemiska trender samt provtagning och analys av grundvatten. Dessa data har använts för att simulera effekterna av viktiga parametrar för grundvattnets kvalitet och representativitet, i syfte att utveckla en detaljerad rekommendation för att förbättra standarden i hydrogeokemisk provtagning och analys samt för att diskutera dessa resultat i ett vidare sammanhang för framtida platsspecifika undersökningar.	
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Tiivistelmä – Abstract  Suomen ja Ruotsin ydinjätteiden loppusijoittamisen paikkatutkimuksista 1980-luvun ja 1990-luvun alun aikana saatujen pohjavesikemian kenttämittausaineistojen edustavuutta on arvioitu muiden tutkimusalojen, esimerkiksi geologian ja hydrologian aiheuttamien häiriöiden kannalta. Raportissa tarkastellaan pohjavesikemian kenttämittauksia sekä eri näytteenotto- ja analyysimenetelmiä hydrokemian laadunarvioinnissa. Aineiston avulla on simuloitu merkittävien muuttujien vaikutus pohjavesikemian näytteiden laatuun ja edustavuuteen sekä esitetty suosituksia pohjavesikemian analyysitulosten luotettavuuden lisäämiseksi, varsinkin tulevissa paikkakohtaisissa tutkimuksissa.	
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## 1 BACKGROUND

The main purpose of a hydrogeochemical site characterisation for repository containment is to establish the chemistry of the different groundwater types, their origin, their evolution, the dominant reactions and reactive processes within the host bedrock that determine the chemical and isotopic character of the groundwaters, the degrees of groundwater mixing and, ultimately, to trace the groundwater flow patterns. Only when this has been achieved is it possible to predict the long-term hydrochemical stability of a radioactive repository system in the event of potential climatic change (i.e. glacial scenario), and the influence this would have on the near- and far-field chemical controls acting on radionuclide mobility and transport in the event of radionuclide leakage and dispersion from a breached waste package.

Reliability of groundwater quality and representativeness of the bedrock levels sampled, are essential prerequisites for any hydrogeochemical programme of study. This has long been recognised in the field of contaminant hydrogeology (e.g. Pennino 1988, Garner 1988 and references cited therein) and within national programmes for the long-term disposal of high-level radioactive waste (e.g. Smellie et al. 1985, 1987a; Andrews et al. 1988; Gascoyne et al. 1988; Pearson et al. 1989; Graham & Johnson 1991), where the stability of the chosen host rock and the chemistry of the groundwaters has to be guaranteed for thousands to hundreds of thousands of years, until the wastes no longer pose a threat to the environment. In this latter context, high quality groundwater data are required as input for: a) hydrogeochemical classification and characterisation of groundwater types, b) geochemical equilibrium modelling of water-rock interactions, c) conceptual hydrogeological modelling of the groundwater flow paths, and d) modelling parameters considered important for repository safety performance assessment.

Of course, depending on the scale or degree of interpretation required, some data need not be as quantitative for some purposes as others. As pointed out by Smellie & Laaksoharju (1992): "If the overall purpose is to describe the large-scale distribution of the major chemical constituents (i.e. the global approach), often very useful for general modelling requirements or as a back-up for hydrogeological interpretation, then the quality of data (i.e. analytical precision) need not be more than qualitative. If, however, the purpose of the exercise is to describe the natural undisturbed hydrogeochemical system, then carefully sampled representative groundwaters are a necessary prerequisite to obtain precise values for master variables such pH, Eh and the minor element concentrations, which form, for example, the basis for radionuclide solubility and speciation modelling in assessing repository performance. The various levels of ambition can often be accommodated if proper planning of the borehole activities are carried out well in advance, so that unnecessary contamination and perturbation of the groundwater environment, prior and during sampling, can be avoided".

In the Basement Shield environment of Sweden and Finland, where groundwater flow through crystalline bedrock is controlled by complex systems of fractures, experience has shown that every fracture system is unique and, depending on its hydraulic properties, may reflect, in terms of contamination, a history of borehole activities prior to sampling. This

was clearly illustrated in the early SKB site investigations (Smellie et al. 1985, 1987a) and later at Äspö (Smellie & Laaksoharju 1992) and Laxemar (Laaksoharju et al. 1995). Drilling, borehole clearance, geophysical logging, hydraulic testing (injection and interference) and eventually groundwater sampling can all contribute to reduced groundwater quality and a lack of representativeness for the bedrock level under investigation.

This report represents an evaluation of existing hydrogeochemical data from the Finnish and Swedish radioactive waste site-specific programmes during the 1980s and the early 1990s. Previous reports in this area include the compilation of existing Finnish and Swedish groundwater data (Lampén et al. 1992) and attempts to classify these data into groundwaters considered representative or otherwise for the locations sampled (Laaksoharju et al. 1993). The reader is therefore referred to these reports (and the references therein) for background details on site characterisation hydrochemical studies in Sweden and Finland at that time. The main objective of this present review is to recommend improvements in sampling and analytical techniques (leading to increasing the quality of groundwater data) which may be implemented in future site-specific investigations.

Although the first draft of this report was written already in 1993, the observations and conclusions are still valid in spite of more advanced sampling technology and methods nowadays available both in the Swedish and the Finnish site characterisation programmes.

## 2 AIMS AND METHODS

This study has closely examined Finnish and Swedish hydrogeochemical data from approximately 1980-1992 in the light of other influencing activities (e.g. geology, hydrology etc.) which form an integral part of site-specific investigations. By this multidisciplinary approach, it has been possible to:

1. Use existing data to simulate the effects of important parameters on the quality and representativeness of groundwater samples, and
2. Recommend improved standards of hydrogeochemical sampling and analysis, which may be used in future site-specific investigations.

The study has considered three main categories: a) monitoring groundwater chemical trends, b) groundwater sampling, and c) groundwater analyses. Each category has been structured according to the outlined scheme below (Table 1).

*Table 1. Categories considered.*

Previous Experience	Monitoring chemical trends	Sampling	Analyses
<b>Objectives</b>	Groundwater mixing trends based on monitoring parameters, e.g. pH, Eh, Temperature (T), Electrical Conductivity (EC).	Effects of borehole hydraulics and extraction pump rates.	Correct choice of parameters and reliability of analyses.
<b>Available data</b>	Selected Swedish and Finnish sites.		
<b>Results</b>	Description of trends.		
<b>Implications</b>	Significance in future planning for detailed site characterisation.		

It should be made clear at this juncture that much of the data presented and described below have not been derived systematically using similar sampling and analytical protocols and techniques. Most of the data is from sampling or analyses under field conditions (usually mobile field laboratory). Wide discrepancies in approach have been employed, often integrated with the testing and development of new methods and equipment. In some cases drilling water has been obtained from surface localities (streams and lakes), with the potential of introducing considerable contamination into the bedrock zones to be sampled (e.g. oxic conditions, organics). In other cases, this contamination has been minimised by using formational groundwaters from the local bedrock. At different occasions both iodine (NaI) and uranine (Na-fluorescein) have been used to spike the drilling water. Sometimes monitoring and sampling extraction rates have been based on a detailed understanding of the hydraulics of the zones being sampled; more commonly, however, sampling is based on the simple philosophy: "If there's water, let's collect it".

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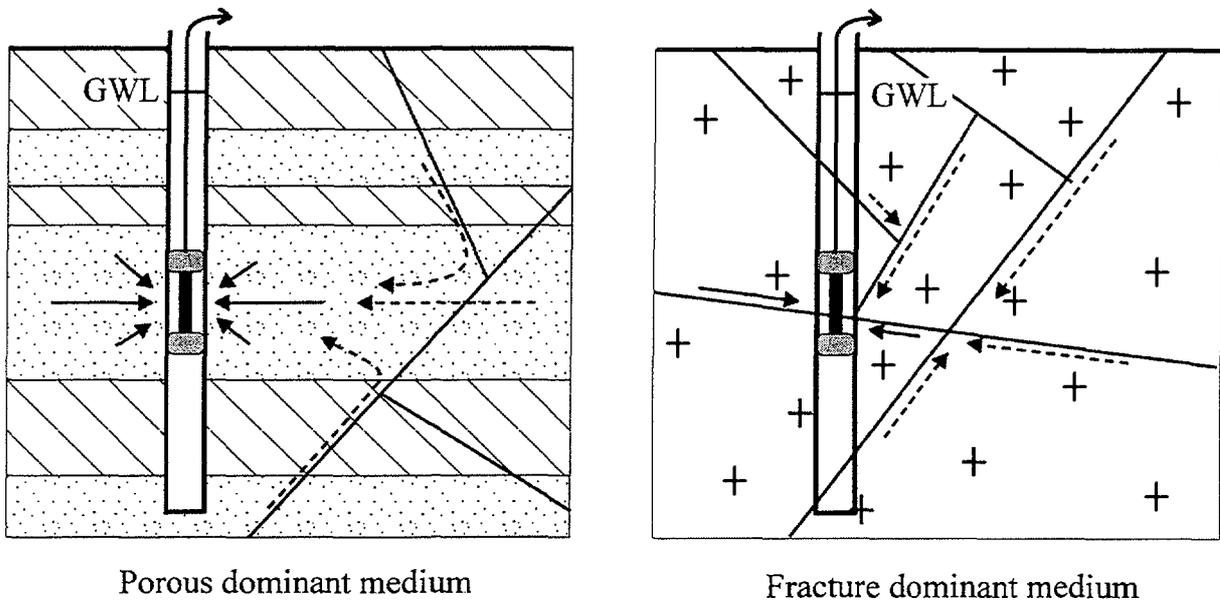
### 3 MONITORING TREND EXPERIENCE

In this section the term monitoring represents the continuous recording of some key chemical parameters (e.g. EC, T, Eh and pH) prior to sampling of groundwater; monitoring trends during groundwater sampling are discussed in section 4. Such data, collected over periods of up to several weeks from isolated, packed-off borehole sections, sometimes show fluctuations indicating sudden or gradual changes in chemistry. The explanation for this may be several-fold.

The vast majority of sedimentary groundwater aquifers exhibit chemical variation, particularly a vertical stratification, but also lateral changes along the groundwater flow direction. Pumping from an isolated borehole section will initially remove water with a characteristic composition for that depth. When the aquifer is sufficiently large, and when the rate of extraction is equal to, or less than, the inflow of formational groundwater into the sampling borehole section (i.e. a function of the hydraulic conductivity of the aquifer host-rock), then even with prolonged pumping the groundwater composition remains stable and can therefore be considered "representative" for the level sampled. If this balance is in any way upset, for example when using excessive extraction pump-rates, then formational groundwaters from higher or lower bedrock horizons, or from more lateral localities, may be pulled in, resulting in a heterogeneous mixture of groundwater types being sampled from the borehole section. These sampled groundwaters cannot therefore be considered representative (Figure 1).

This hydraulic imbalance at the sampled borehole section between groundwater inflow and extraction rate is even more sensitive in a fractured host-rock media, where integrated networks of fractures may provide direct pathways from the sampled borehole section to greater (e.g. more reducing) and shallower (e.g. more oxidising) depths in the bedrock, causing rapid and significant changes in the groundwater chemistry during extraction (Figure 1). Such changes are illustrated in Chapter 4.

In many cases the duration of pre-sampling monitoring is somewhat arbitrary, being governed more by tight time schedules of the site investigation programmes rather than by hydrochemical criteria. To know whether or not a balance between borehole hydraulic properties and groundwater extraction rates has been achieved, can be therefore critical to the sampling of representative groundwater samples, and adequate time should be allocated. Moreover, every section to be sampled is unique, and monitoring should be given equal priority at each sampling locality.



*Figure 1. Schematic illustration of possible effects in porous and fractured bedrock media resulting from excessive groundwater extraction rates.*

### 3.1 Objectives

The main objective is to identify groundwater mixing trends from existing data, collected in the 1980s and the early 1990s, relate them to potential causes, and illustrate their implications in future studies.

### 3.2 Available Data

Monitoring data exist from both Finnish and Swedish site-specific studies. In Sweden, monitoring (i.e. Electrical Conductivity (=EC), T, pH, Eh, O<sub>2</sub>, pS) was carried out for periods up to 10 days prior to hydrogeochemical sampling, and a further period of time during sampling which normally varied from 2-4 weeks depending on the problem being tackled. It was during this latter period that groundwater samples were selected for complete chemical characterisation. In Finland, initial pumping has been conducted for periods of 1-2 weeks prior to monitoring and sampling. This was followed by field monitoring ranging from 3-4 days to even 4 months before sampling for complete hydrogeochemical characterisation was carried out. To underline what was mentioned previously, ideally the duration of monitoring times should be dependant on the borehole history (e.g. loss of drilling fluid, borehole cleaning and logging, hydraulic testing etc.) and not restricted by the time constraints of the overall investigation programme.

All Swedish data are stored in the GEOTAB database (Eriksson & Sehlstedt 1991; Eriksson et al. 1992). In contrast, the Finnish field monitoring and chemical data are stored in different databases (except for the field data gained during the sampling period; see Lampén & Snellman (1993)) which presents difficulties when comparing and combining field data

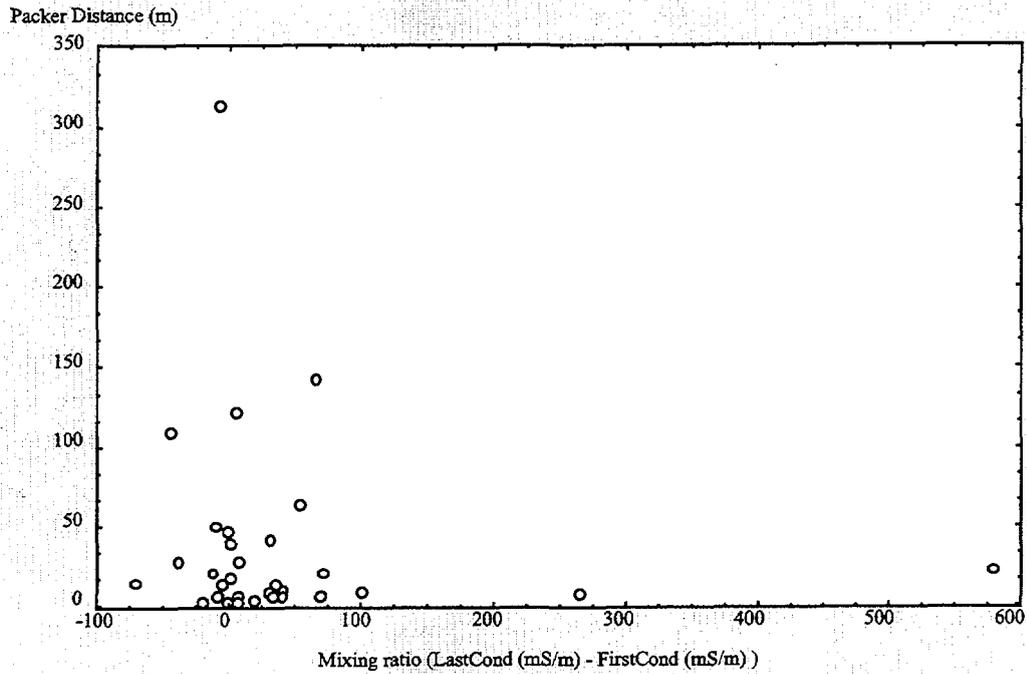
(e.g. geology, hydrogeology) with chemical data. Since the latter single database approach can be potentially dangerous due to miss-use of correlations, it was deemed preferable to identify suitable areas of study from the Swedish GEOTAB database.

### **3.3 Observed Trends**

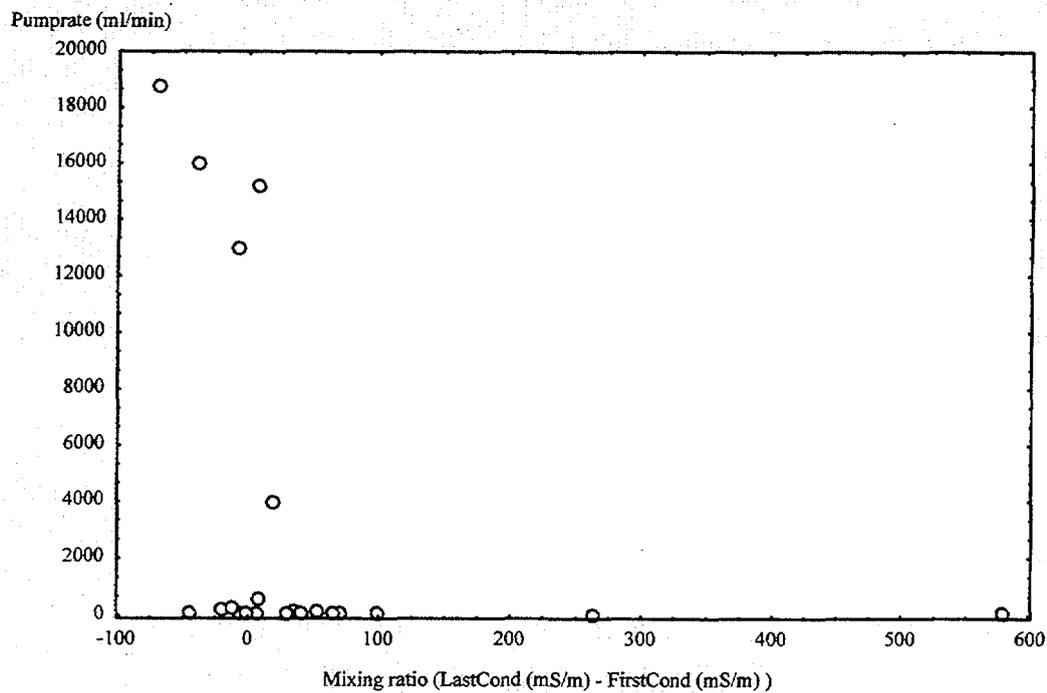
#### **3.3.1 General database**

As a first step, a very general, objective attempt was made to detect possible correlations between different borehole parameters that may influence monitored hydrochemical trends. No prior effort was made to group or classify the data. For example, groundwater mixing ratios (based on the difference between the initial and final electrical conductivity values) were related to the packer straddle length (Figure 2) and to the extraction pump-rate (Figure 3). Figure 2 is based on the assumption that the longer the straddle length, the greater the number of potentially conductive fracture zones that are likely to occur along the borehole section being sampled. Figures 2 and 3 indicate no direct correlation between high or low mixing ratios, long or short straddle lengths and high or low pump-rates. The highest mixing values are related to short straddle lengths; this may indicate that the borehole section being sampled contains fractures with low hydraulic conductivities, such that short-circuiting of contrasting groundwater chemistry may have occurred around the packer systems caused by high extraction pump-rates, or, may also be due simply to natural complex mixing processes within the surrounding bedrock. However, Figure 3 clearly shows that at these locations a low pump-rate has been used. This may still indicate low hydraulically conductive borehole sections and short-circuiting processes, or, may also reflect residual contaminated waters remaining in the section from borehole activities. Due to the many possible explanations hydraulic conductivity does not help to resolve these questions.

As a second step, a general plot of EC vs. cumulative number of observations (i.e. with time) was produced (Figure 4). Despite the fact that some of the variation shown may have no hydrochemical significance, reflecting only instrumental fluctuations, some promising profiles showing systematic trends are indicated, and these were subsequently verified on closer examination.



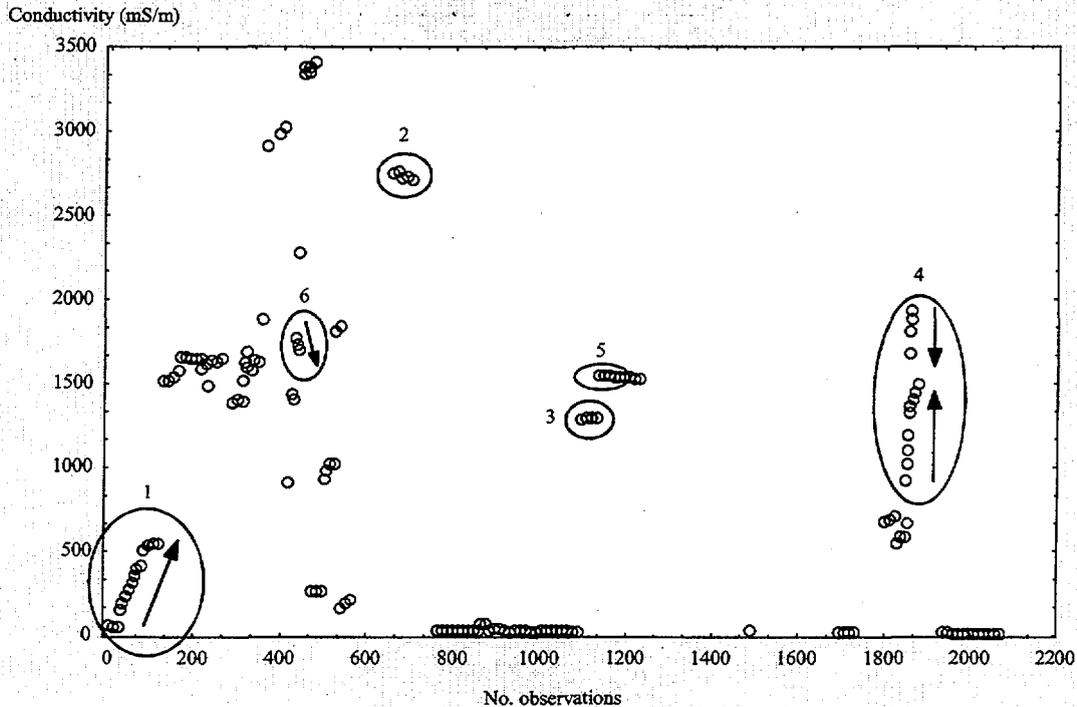
**Figure 2.** Groundwater mixing ratios (based on the difference between the initial and final changes of Electrical Conductivity values) versus packer straddle distance (source: GEOTAB). Low values indicate a small tendency to mix.



**Figure 3.** Estimation of groundwater mixing ratios (based on the difference between the initial and final changes of Electrical Conductivity values) versus extraction pump-rate (source: GEOTAB). Low values indicate a small tendency to mix.

### 3.3.2 Site-specific database

Profile 1, representing borehole BF101 from the Finnsjön study site, was selected from Figure 4 on the basis of a clear systematic variation in chemistry, suggested by the increasing EC. The trend is reproduced in Figure 5. The Finnsjön database was used to plot Eh versus cumulative number of observations (Figure 6).



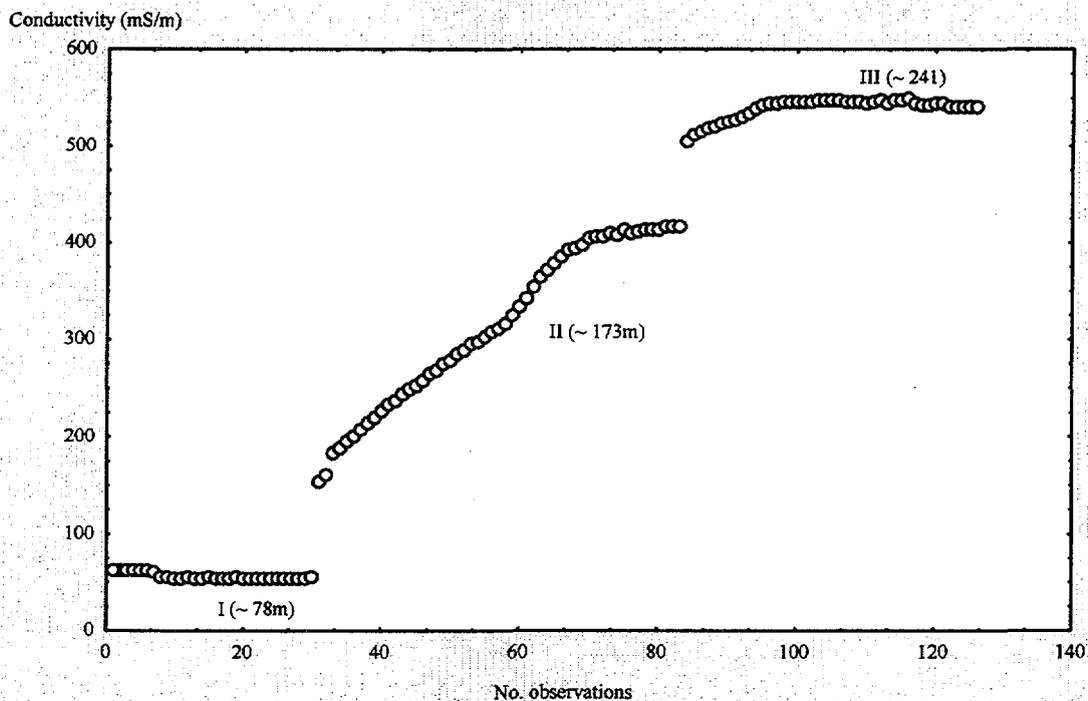
**Figure 4.** Plot of electrical conductivity versus cumulative number of observations with time from the Swedish site investigations [source: GEOTAB). Arrows denote increasing/decreasing chemical trends. [1= Finnsjön (BF101); 2= Ävrö (KAV01); 3= Forsmark (KFR01); 4= Laxemar (KLX01); 5= Forsmark (KFR10); 6= Äspö (KASO3)].

Borehole Section II (at 173 m depth) shown in Figure 5 was chosen for illustration because of the clearly systematic variation in chemistry (salinity) prior to and during sampling. As only a small change in the groundwater extraction rate during monitoring was recorded (range of 21-36 mL/min), certainly not enough to cause the dramatic change in chemistry, the illustrated changes need an alternative explanation.

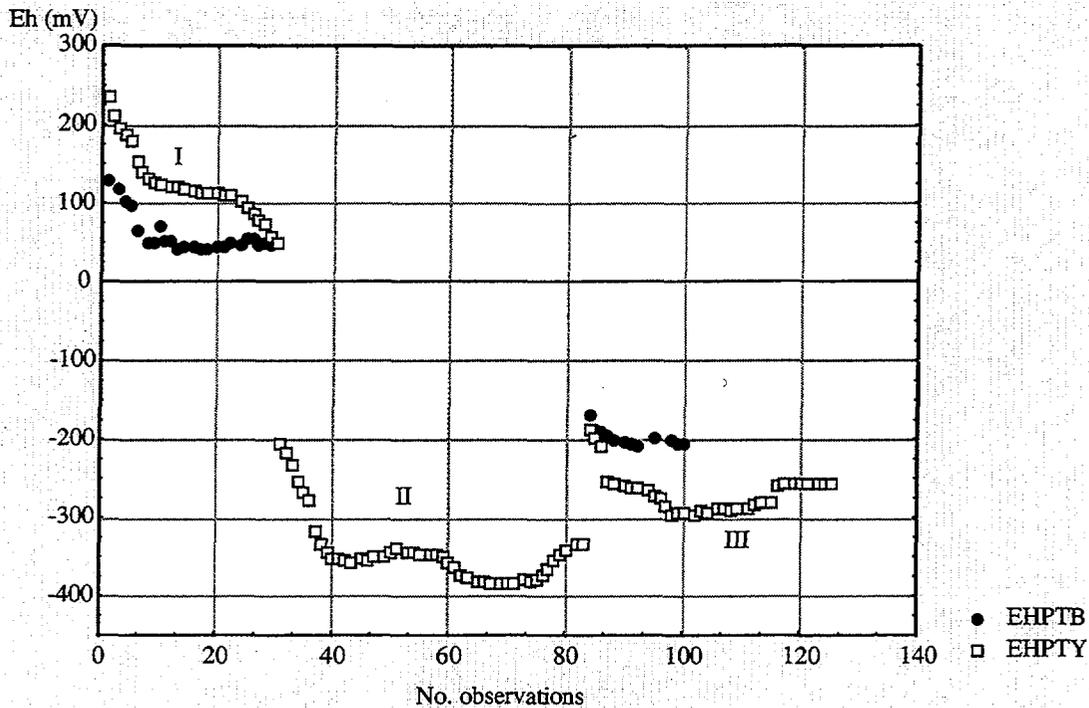
Studies in the Finnsjön area (Smellie & Wikberg 1991) show that the sampled level is located in a non-saline aquifer which is separated from a deeper, highly saline aquifer by a shallow dipping conductive fracture zone (Zone 2). This fracture zone produces a "hydraulic cage" effect whereupon downward penetrating non-saline, meteoric groundwaters preferentially spread out along the upper, more conductive levels of Zone 2, rather than continuing to deeper levels to mix with the older saline groundwaters. Essentially, Zone 2 "is a horizon along which groundwaters of considerably contrasting age and chemistry

come into contact and partially mix with one another” (Smellie & Wikberg op. cit.). The increase in salinity at level 173 m, even at such low extraction rates, is believed to be due to short-circuiting around the packer system via a system of interconnected fractures in the adjacent bedrock, such that water deeper in the borehole and/or formation water from greater depths in the bedrock (i.e. saline sources) is drawn into the sampling section of the borehole where it increasingly dominates. The eventual levelling out of the profile indicates that a mixing equilibrium between the non-saline/saline groundwater types has been reached.

Figure 6 also shows the disparity of Eh measurements (surface vs. downhole) which is not unexpected (see Section 4). For example, in the shallow groundwater environment (Section I: ~78 m), lower downhole values are indicated until after a period of 9 days when both electrodes registered values of around +40 mV. The downhole trend at depth (Section III: ~240 m), however, is uncertain and incomplete because of a malfunctioning electrode. No downhole data are available for Section II (~173 m).



**Figure 5.** Electrical Conductivity versus cumulative number of observations with time for three different sections (Profiles I-III, Figure 5) along borehole BF101 (Finnsjön). (Profile I: 9 days; II: 18 days; III: 23 days)



*Figure 6. Eh versus cumulative number of observations with time for the three different sections (See Figure 5 for Profiles I-III) along borehole BF101 (Finnsjön). (EHPTB= downhole platinum Eh measurements; EHPTY= surface platinum Eh measurements).*

### 3.4 Implications

Although the evidence presented here is sometimes ambiguous, and in many cases incomplete, it demonstrates, nevertheless, that groundwater samples collected for hydrogeochemical characterisation are not always representative for the bedrock depth under investigation. Comparison of data is often impossible, given that all zones do not have similar hydraulic properties and therefore the residual drilling water may not have been totally removed from each zone. As a general conclusion, however, in sampled sections showing less than 5% drilling water contamination, observed changes in EC are attributed to residual foreign waters (i.e. from earlier open-hole effects prior to isolating the borehole section) or natural mixing of groundwaters from the host bedrock caused by extraction pumping.

The main implication is that there is a general absence of systematic studies to determine optimum sampling conditions prior to quantitative groundwater characterisation, and there has been a lack of appreciation that every horizon to be sampled is unique. To approach optimum conditions, the following conditions should be met: a) specifying extraction pump-rates based on the hydraulic properties of the isolated zone to be sampled, b) ensuring the complete removal (at least to <1%) of drilling water tracer (this means often pumping 2-3 times or more the total volume of water in the packer section and in the tube flow system of the sampling instrument) and c) monitoring key hydrochemical parameters (EC, T, Eh,

pH, O<sub>2</sub>, S<sup>2-</sup> and tritium activity) until uniform stable values are obtained. These conditions can only be achieved by subjecting every demarcated horizon to a systematic study, where extraction pump-rates are varied, hydrochemical trends monitored, and then, subsequently, a final decision is made. By observing such trends prior to sampling enables the situation to be immediately addressed and subsequently remedied before it is too late.

## 4 SAMPLING EXPERIENCE

From the above discussions it is clear that changes in groundwater chemical parameters within the isolated borehole section during sampling can be the result of:

- a) Continued removal of residual contaminated groundwaters (i.e. drilling water; open-borehole water; injection test water),
- b) High groundwater extraction rates (sometimes combined with restricted hydraulic conductivity of the surrounding bedrock) leading to short-circuiting and access to different water sources (i.e. higher and lower bedrock horizons; higher and lower sections in the sampled borehole; lateral connection with other open boreholes) causing mixing in the borehole section, and
- c) Long transport times under low extraction rates from the borehole section to the bedrock surface (i.e. encouraging biogeochemical and gas-uptake or degassing reactions) causing changes in groundwater chemistry produced by variations in pH and Eh.

In addition, the early recognition of technical problems encountered during measurements is an important factor in the quantitative evaluation of groundwater data.

This section provides data from sampling experience resulting from site-specific investigations supporting the above conclusions. Some suggestions are also given as to how the sampling protocol can be improved.

### 4.1 Objectives

The main objectives are to illustrate from existing data: 1) changes in groundwater chemical composition caused by high and/or low extraction rates, 2) instrument malfunction during monitoring or sampling, and 3) suggestions to minimise such effects.

### 4.2 Available Data

Data are available from four main sources:

- a) From the Swedish site investigations - GEOTAB
  - Figure 3, already referred to, compares pump-rate with the groundwater mixing values;
  - Figures 7 and 8 compare surface and downhole Eh and pH measurements, respectively.
  - Figures 9a and 9b represent CO<sub>2</sub> degassing and up-take in the Äspö Hard Rock Laboratory (HRL).

- b) From the Finnish site investigations - TVODATAC
- Figure 10 compares field and laboratory pH measurements (Lampén & Snellman 1993),
- c) Specific experimental runs to test the effects of pump-rate on groundwater chemical parameters:
- Taavinunnanen, Sweden (Figure 11; Smellie 1983),
  - Olkiluoto, Finland (Figure 12 a,b; Laaksoharju et al. 1994),
- d) General examples illustrating instrumental problems:
- Figure 13 compares Eh measurements using glassy carbon and platinum electrodes;
  - Figure 14 shows Eh vs. time during downhole and surface measurements (Wikberg 1992). Figure 15 a-d shows monitoring plots of EC, Eh and O<sub>2</sub> from Olkiluoto which illustrate irregularities in measured values.

## 4.3 Results

### 4.3.1 Swedish GEOTAB data

Figure 7, plotting surface versus downhole Eh(Pt), shows a relatively linear relationship within  $\pm 100$  mV. There are, however, no general systematic trends; sometimes the downhole Eh values are more negative (which might be expected) but examples exist which show the reverse trend. In other cases anomalous values which occur at depth are also reflected at the surface. More detailed studies relating measured Eh with, for example, the controlling Fe<sup>2+</sup> and Fe(tot) redox couple, are required to calculate a more representative Eh (Grenthe et al. 1992). Positive Eh values in Figure 7 can often be related to the initial phase of the sampling programmes, when extraction pumping has pulled in oxygenated groundwaters from shallower bedrock levels, or from higher levels in the borehole containing surface-derived groundwaters.

Figure 8, plotting surface versus downhole pH, is interesting as it shows that both high (>8.2) and low pH (<6.8) values deviate from a linear relationship; an error of one pH unit represents the spread in values. This may be explained by the uptake of CO<sub>2</sub> in deeper groundwaters during pumping up to the surface (i.e. downhole “high risk area” with pH >8.2) and CO<sub>2</sub> degassing at shallower depths (i.e. surface “high risk area” with pH <6.8). These areas compare with the central “low risk area” where the groundwater is close to CO<sub>2</sub> saturation. This means that pH determinations are particularly difficult when either deep or shallow groundwaters are measured. It also underlines the disparity between surface and downhole measurements of pH due to degassing or ingassing of CO<sub>2</sub> (depending on the original CO<sub>2</sub> partial pressure, PCO<sub>2</sub>) which occurs when the groundwaters are pumped slowly to the surface through polyamide tubing. Degassing of CO<sub>2</sub> from the groundwater probably occurs due to the pressure difference between downhole and the bedrock surface; the CO<sub>2</sub> is lost by diffusion through the polyamide tubing. Additional degassing or ingassing of CO<sub>2</sub> may occur at the bedrock surface due to differences of partial pressure in the sample compared to the atmosphere; in this case CO<sub>2</sub> loss or uptake may occur via the

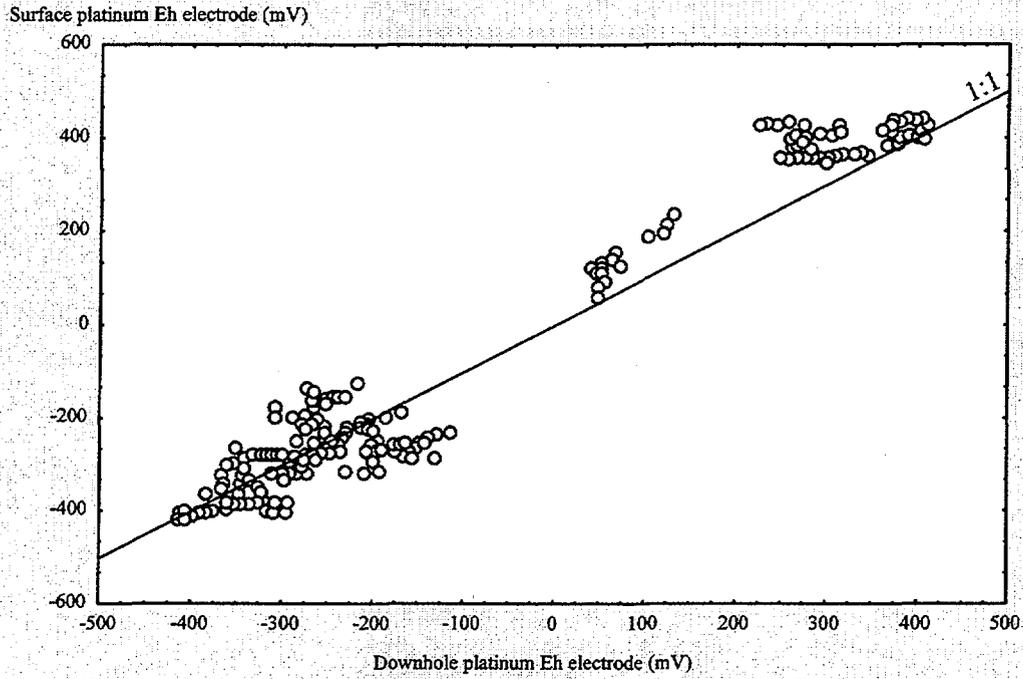


Figure 7. Downhole versus surface Eh(Pt) measurements (source: GEOTAB).

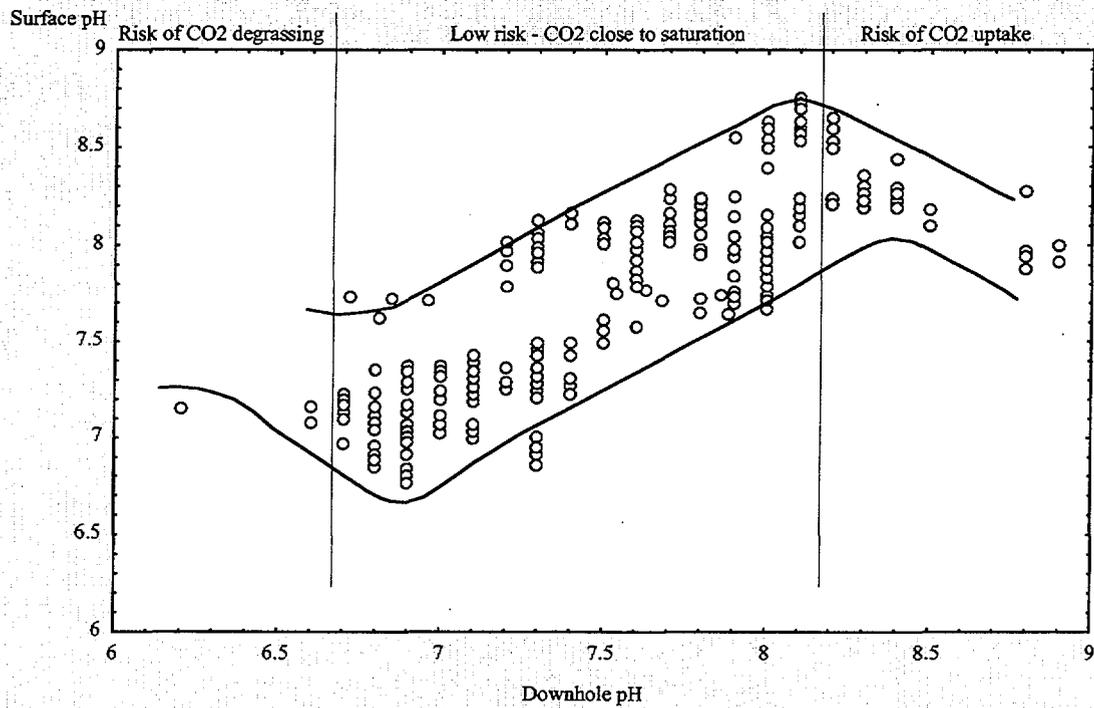


Figure 8. Downhole versus surface pH measurements (source: GEOTAB).

flow-through cell equipment at the surface. At depth all  $\text{CO}_2$  is dissolved whereas it is evacuated as gaseous  $\text{CO}_2$  during pumping.

All parameters in the alkalinity determining system (including also  $\text{CaCO}_3$ ) might be “disturbed” during sampling. Especially sensitive are those groundwaters at great depth with very low alkalinity (and low  $\text{PCO}_2$ ), as even small amounts of  $\text{CO}_2$ -ingassing will disturb the system. The resulting pH decrease due to the  $\text{CO}_2$ -uptake does not influence the total alkalinity of the solutions, if no other processes, such as dissolution of particulate  $\text{CaCO}_3$ , is occurring during alkalinity titration resulting in erroneously high of alkalinity values. As the deep groundwaters generally are oversaturated with respect to calcite, there is a risk for particulate  $\text{CaCO}_3$  in the pumped groundwater.

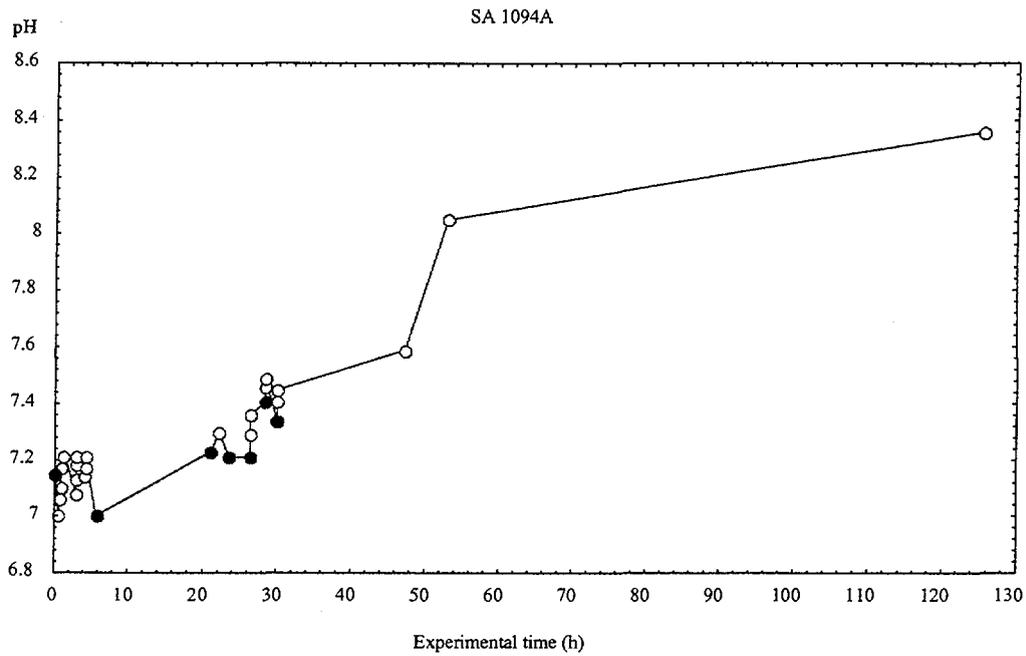
On the other hand, some groundwaters in granitic environments may be under-saturated with respect to the carbonate species and therefore also some ingassing of atmospheric  $\text{CO}_2$  through the sampling tubing may take place, if the hydrological conductivity of the sampling section is very low and the transport time of the sample is consequently long.

The  $\text{HCO}_3^-$  concentration is also an important parameter in this estimate, since  $\text{PCO}_2$  is a function of it, as well as  $\text{SI}_{\text{calcite}}$  and pH. It is possible to have groundwaters, which are equally stable in both “risk” areas, if the  $\text{HCO}_3^-$  is at the suitably high or low level.

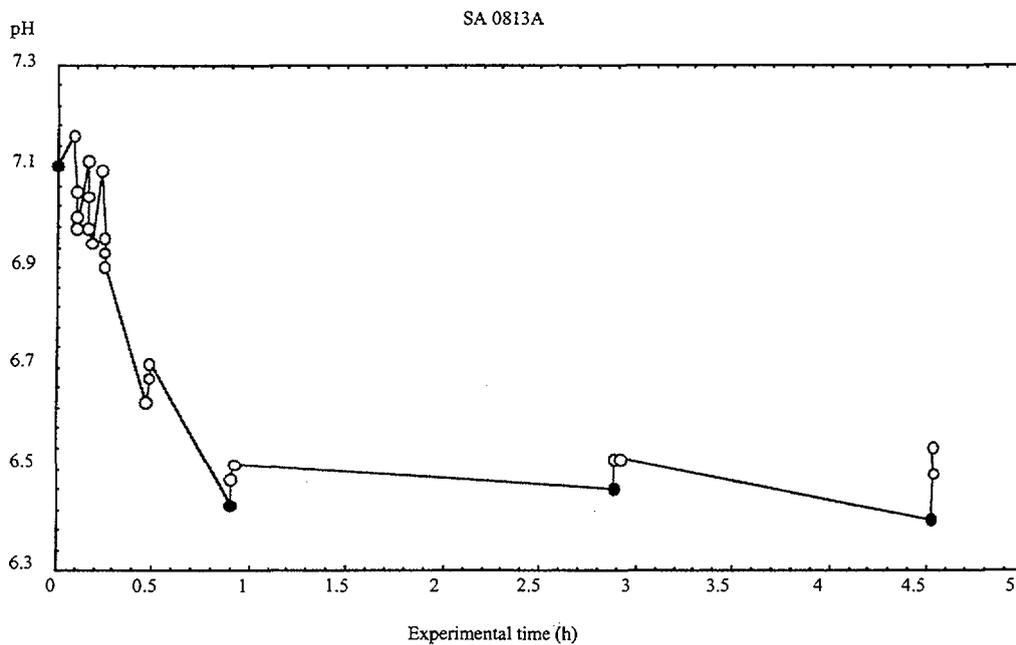
Figures 9a and 9b illustrate the contrasting variations of pH with time as measured at two locations (with an initial similar groundwater pH) along the access tunnel to the Äspö Hard Rock Laboratory (HRL). At one location shallow groundwaters (high  $\text{PCO}_2$ ) are equilibrating with the atmosphere and giving rise to degassing and a corresponding increase in pH (Figure 9a). At another location deep groundwaters (lower  $\text{PCO}_2$ ) are equilibrating giving rise to  $\text{CO}_2$  up-take and a corresponding decrease in pH (Figure 9b). The  $\text{HCO}_3^-$  levels are probably of minor importance, unless they are in very low concentrations. Despite the difference in time periods (130 vs. 5 hours), Figure 9a shows > 1 pH unit increase during the experimental time; in contrast, Figure 9b shows within the first 5 hours of the experiment a half order of magnitude decrease in pH with time.

#### 4.3.2 Finnish Data

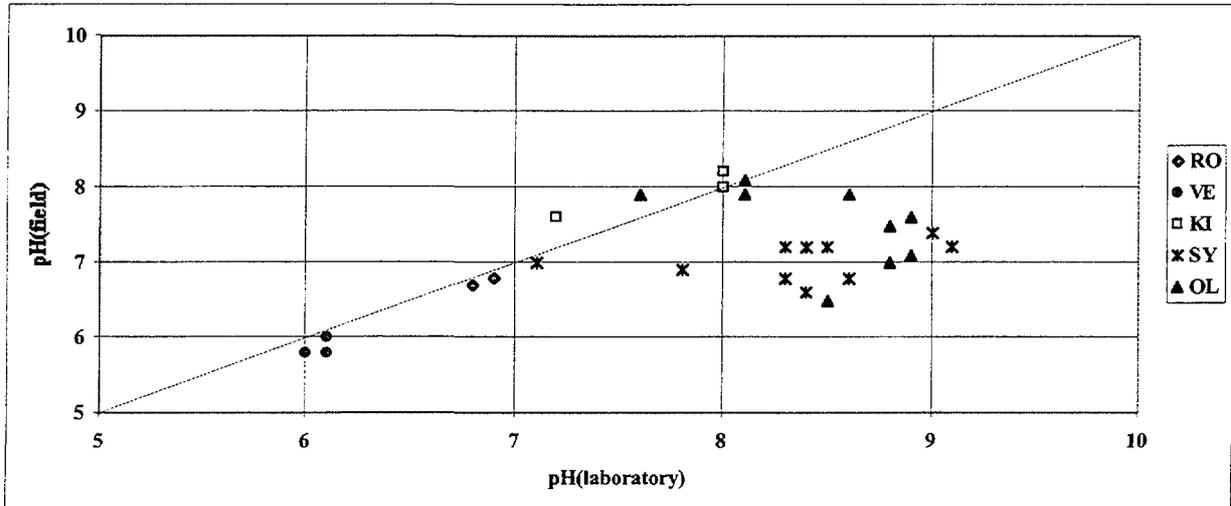
Figure 10 compares laboratory and field-derived pH values from five sites. Some of the plotted values show a general linear relationship; however, a clear cluster of values plot separately indicating much lower field pH values when compared to the laboratory measurements. Little difference between field and laboratory pH is observed when the fresh (TDS far below 1 g/L; salinity classification according to Davis 1964) groundwaters of Romuvaara (RO), Veitsivaara (VE) and Kivetty (KI) are involved. These are fairly well buffered (fairly high alkalinity) neutral or slightly alkaline groundwaters containing mostly  $\text{N}_2$  and  $\text{CO}_2$  as dissolved gases. These groundwaters represent the low risk area (close to  $\text{CO}_2$  saturation) in Figure 8. Most deviance occurs at Syyry (SY) and Olkiluoto (OL) where the deeper brackish (TDS between 1 and 10 g/L) and saline (TDS between 10 and 100 g/L) groundwaters contain abundant dissolved reducing gases (e.g.  $\text{CH}_4$  and  $\text{H}_2$ ). The high pH values measured and the fairly low alkalinity of the groundwaters indicate the risk for  $\text{CO}_2$  up-take (see Figure 10).



**Figure 9a.** Variation of pH measured at one location in the Äspö HRL access tunnel (sample SA 1094A) where values are increasing with time ( $\text{CO}_2$  degassing) when a shallow groundwater sample is in contact with the atmosphere (Filled circles represent the first measurement following calibration).



**Figure 9b.** Variation of pH measured at one location in the Äspö HRL (sample SA 0813A) access tunnel where values are decreasing ( $\text{CO}_2$  up-take) with time when a deep groundwater sample is in contact with the atmosphere (Filled circles represent the first measurement following calibration).



**Figure 10.** Laboratory versus field pH measurements from selected Finnish sites (RO = Romuvaara, VE = Veitsivaara, SY = Syyry, KI = Kivetty and OL = Olkiluoto; source: TVODATAC).

#### 4.3.3 Experimental test cases

Experimental runs, aimed at identifying changes of groundwater chemistry with changes in extraction pump-rates, are reproduced in Figures 11 (Taavinunnanen) and 12 (Olkiluoto). It can be clearly seen from both figures that the groundwater physico-chemical parameters (in addition to the colloid fraction chemistry at Olkiluoto) are significantly affected by changes in pump-rate. In both cases high extraction rates have drawn unrepresentative groundwater types (or “drilling debris” in the case of the “colloid” compositions at Olkiluoto from the fracture surfaces) by short-circuiting either from higher or lower parts of the borehole to the borehole section, or from other higher or lower levels in the surrounding bedrock.

At Taavinunnanen (Smellie, 1983), a surface flow-through electrode cell system was used to monitor Eh, pH, and  $O_2$  over a period of 35 days. The first 21 days illustrated in Figure 11 represent a normal sampling campaign; the first 4 days of the sampling period represent the removal of residual contaminating water from the connecting tube and thereafter from the packed-off borehole section. From day 4 to 8, however, there is evidence of an influx of more oxidising water. This was interpreted as suggesting short-circuiting from around the packers to higher levels in the borehole. This was followed by an unscheduled pump-stop. With renewed pumping there was a gradual increase in more reducing-type groundwaters, probably reflecting the system being flushed out by more representative groundwaters. Continued pumping, however, showed yet again more oxidising water entering the system towards the end of the sampling period at 21 days, i.e. beginning to return to similar conditions as indicated after day 4.

The period from day 27 to 35 represents the experimental phase when the water extraction rate was controlled, starting from 260 mL/min at the beginning of the run, and then

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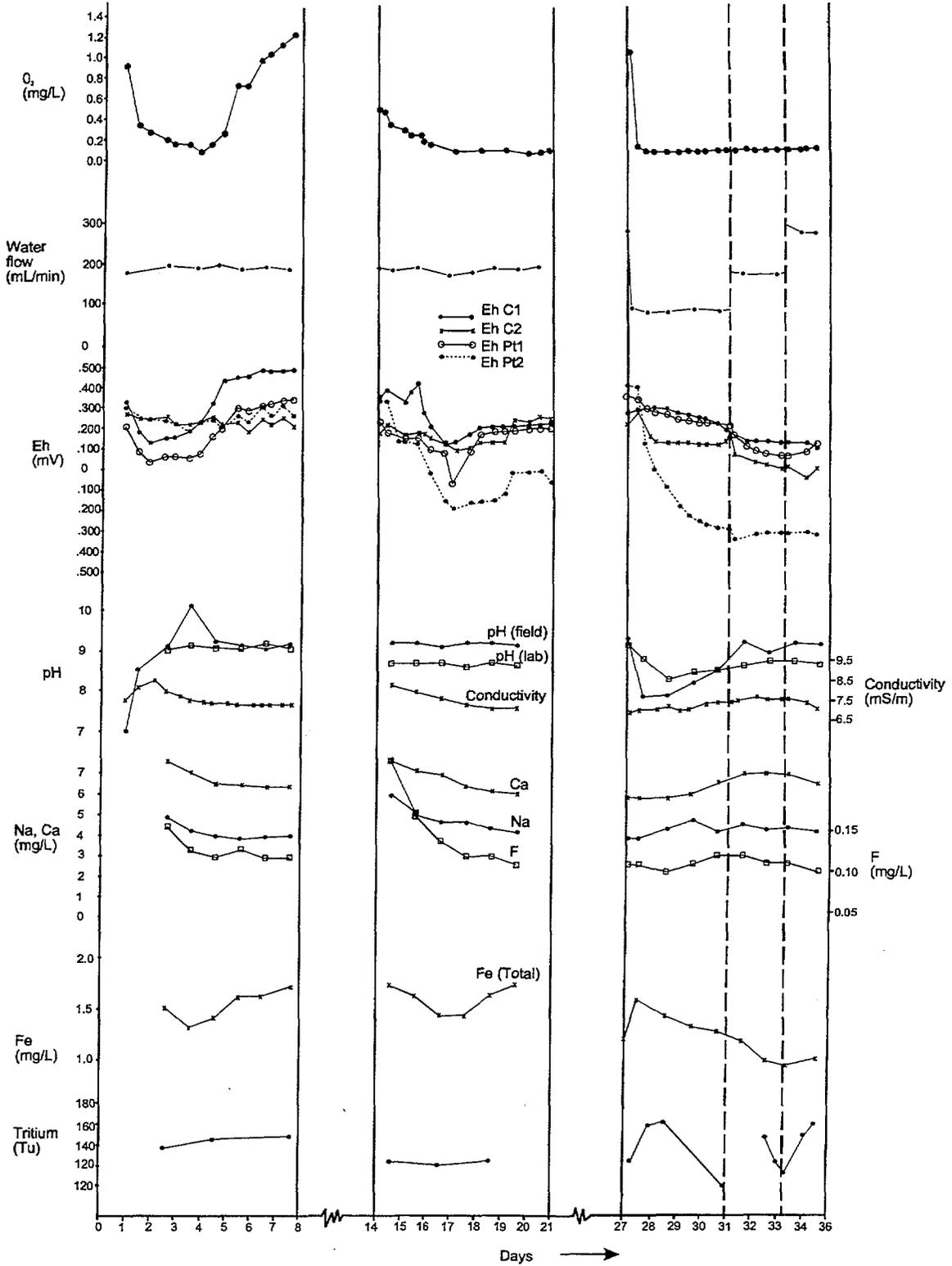
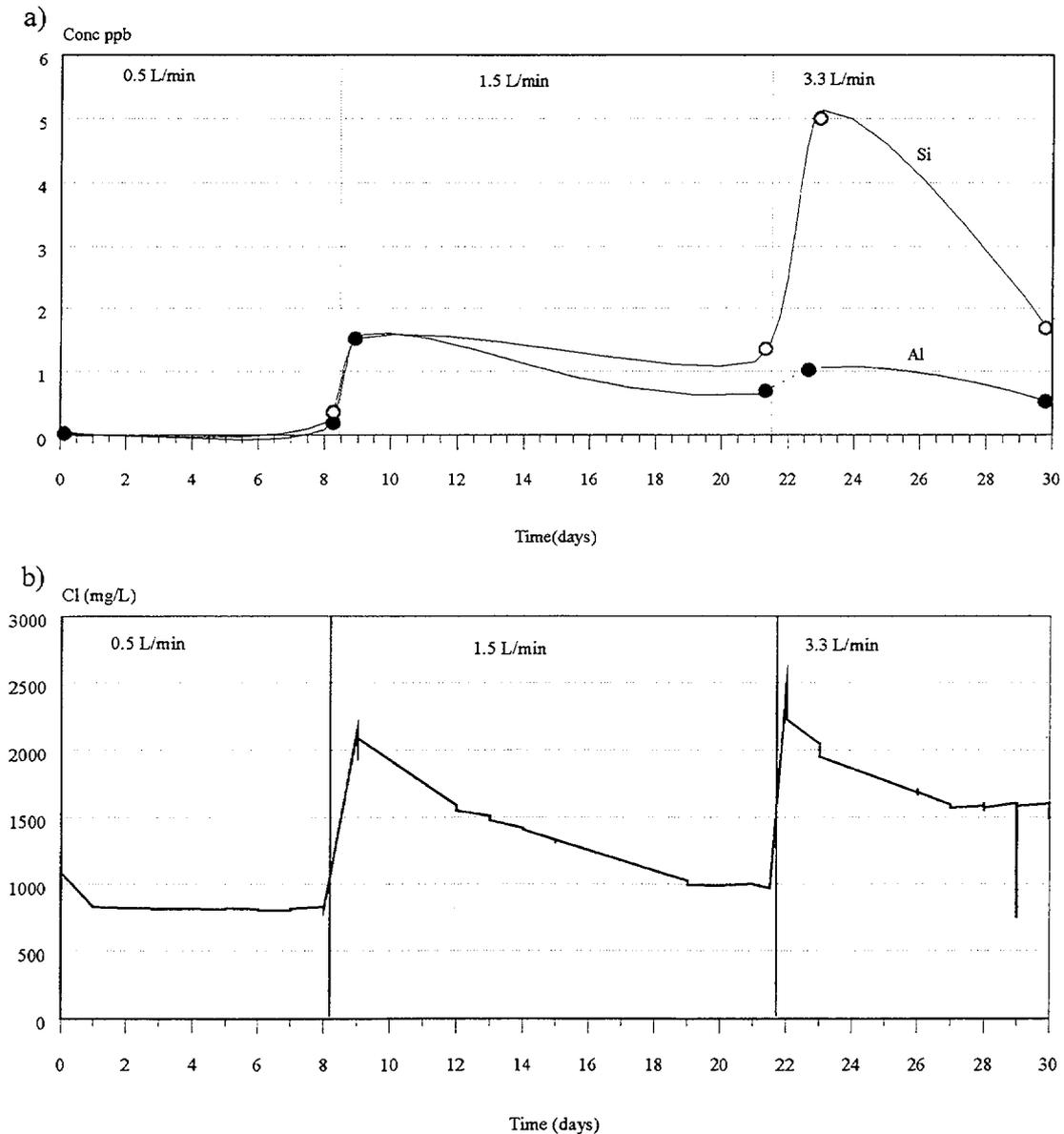


Figure 11. Variation in groundwater physico-chemical parameters with changes in extraction pump-rate from the Taavinunnen test site (from Smellie 1983).

decreasing to 60 mL/min; subsequently, the rate was increased to 150 mL/min and then back to 260 mL/min. The trends show that at lower extraction rates (60-150 mL/min) the groundwater encountered was more stable and reducing than any of the earlier sampling periods, and probably most representative for this borehole section. By increasing the extraction rate back to 260 mL/min, there is a suggestion that conditions were reverting back to an increasing influx of more oxidised water. This can be seen, in particular, from changing trends in Eh and EC. An extra 5 days or so would have been desirable.

At Olkiluoto (Figures 12a and 12b; Laaksoharju et al. 1994), an interesting feature is the initial Cl peak resulting from changes in the extraction pump-rate. It is followed by a levelling out of the Cl content during the pumping period, although the level of Cl is consistently higher at each increase in pump-rate. In this case there is a known hydraulic



**Figure 12.** a) Variations of Al and Si in the colloid fraction (400 nm), and b) groundwater Cl, caused by changes in the extraction pump-rate at the Olkiluoto test site (from Laaksoharju et al. 1994).

connection to a higher level in a nearby open borehole, where the chloride contents are lower. At each increased change of pump-rate there is a sudden pulse of higher chloride groundwater, more characteristic of the deeper levels, pulled into the studied borehole section. However, this is quickly equilibrated by short-circuiting dilute groundwater from the nearby open borehole. This hydraulic connection appears to be limited, since successively higher chloride waters are being collected at higher extraction rates, i.e. compare around 700 mg/L Cl at 0.5 L/min with over 1500 mg/L Cl at 3.3 L/min at the end of each experimental run.

Furthermore, Finnish observations have shown a relation between low extraction rates and high TOC values (Lampén & Snellman 1993). This is most likely due to contamination from the polyamide material of the tubing due to long contact times (Snellman et al. 1995), a phenomenon recognised and reported also from the Swedish Stripa study (Andrews et al. 1988).

#### 4.3.4 Instrumental problems

During many of the site investigations in Sweden and Finland, field measurements of Eh(Pt): (Pt= Platinum), Eh(C): (C= Glassy Carbon), pH, EC, dissolved O<sub>2</sub> and T have been continuously monitored at the ground surface during sampling. There appear to be differences in the sensitivity of these measurements to sudden changes in the chemistry. EC is, perhaps, the most reliable indicator to chemical changes, whilst Eh(Pt) seems to be more sensitive to (even minor) disturbances caused by pump failure or calibration pauses. Furthermore, accumulation of some precipitation on the electrode surface during long pumping periods and even extremely small amounts of oxygen have caused problems.

Some of the observed changes can also be due to technical problems. Instrumental problems with pH measurements have been already mentioned in association with groundwaters which are both saline and contain abundant dissolved gases. Other problems surround the choice of Eh electrode for redox measurements. The Finnish data (Figure 13), measured using a surface flow-through cell system, indicate that in most cases Eh(C) shows a more positive trend than Eh(Pt); in Olkiluoto and Kivetty both measured Eh systems agreed reasonably well with each other.

Within the Swedish programme, considerable attention has been given to field measurements of redox potential. Experimental and field data (Figure 14) comparing downhole and surface Eh measurements using different electrode types have been summarised by Wikberg (1992):

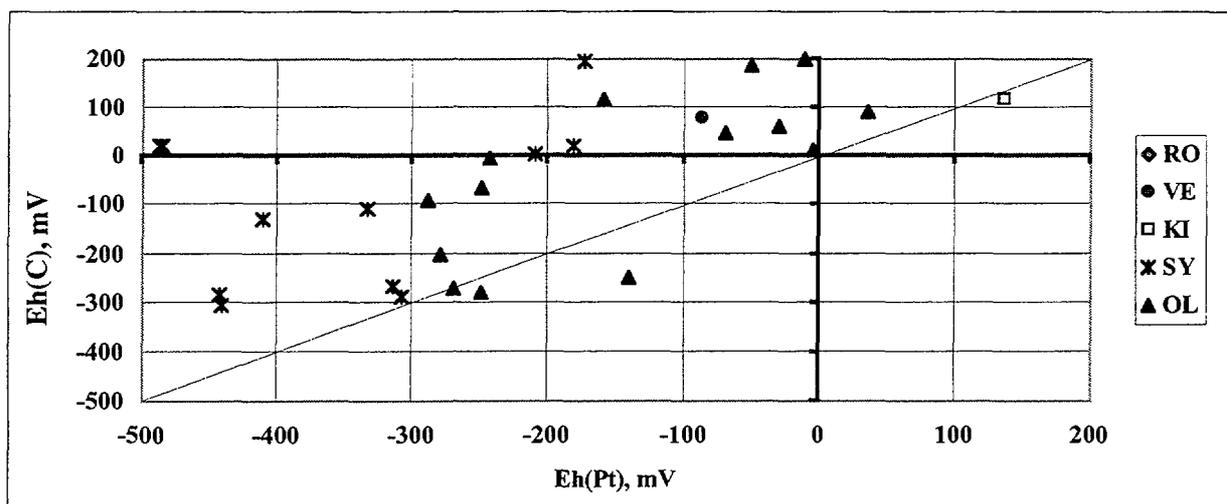
- In poorly buffered natural groundwaters it takes a long time to obtain stable Eh-readings on the inert electrodes.
- Different types of electrodes give initially different readings, but as the drift of them level out, they are constant to within a couple of tens of mV. The initially diverging potentials are likely to be due to impurities (O<sub>2</sub>) on the electrode surfaces.

- Measurements in a flow-through cell at the surface will give as reliable readings as the downhole probe, but they are much more sensitive to disturbances caused by atmospheric  $O_2$ .
- Given adequate time the readings on all three inert electrode materials (Au, Pt, C) eventually agree at a constant value. This value is presented as the Eh value of the groundwater.

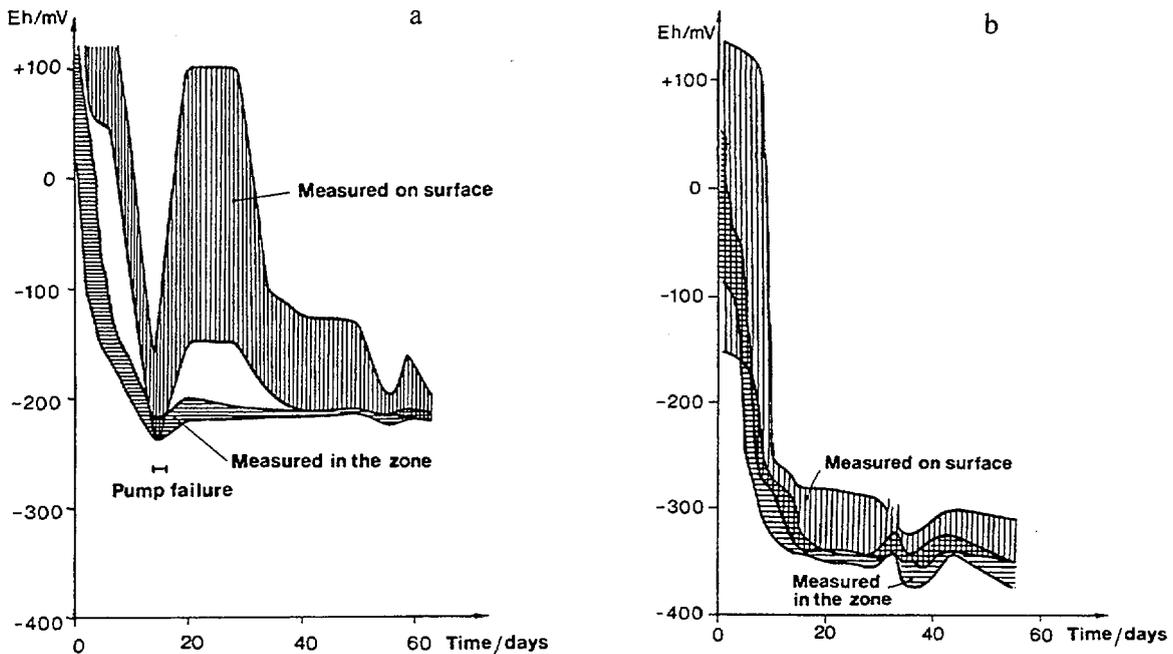
Caution should be exercised when measuring Eh(Pt) in deep groundwaters containing significant amounts of dissolved sulphide at a specific Eh/pH range. This can lead to a reaction between the electrode and the  $S^{2-}$  forming PtS, which causes the probe to cease being a measure of Eh, becoming instead a measure of the sulphide content (Whitfield 1974). Furthermore, there is some risk that porous carbon electrodes may adsorb oxygen which might also account for such discrepancies. However, this would not be expected with the glassy, non-porous carbon electrodes used in the field measurements (Wikberg 1996). The sulphide poisoning of the Pt electrode may explain some of the discrepancies encountered at Olkiluoto.

Oxygen measurements are, perhaps, most liable to technical problems. The semi-permeable membrane of the Clark's cell quite often needs replacement together with the addition of a new fresh electrode solution (KCl). This essentially means that the monitoring of dissolved  $O_2$  can be very suspect, if not meaningless, if frequent calibrations are necessary.

To illustrate some of the typical technical problems encountered during groundwater sampling, Figures 15a to 15d show a series of surface monitoring plots from borehole OL-KR3 (388-393m depth) at Olkiluoto, highlighting Eh, EC,  $O_2$  and pH. The monitoring period was over 17 days, with one gap in the data logging. The Eh plot (Figure 15a) shows, after an initial stabilising period from 0 to 1000 observations, two sudden jumps: the first after 1000 observations and later again at 3700 observations to lower mV values. These Eh-jumps are not reflected in the  $O_2$  profile (Figure 15b) which instead shows a clear



**Figure 13.** Comparison of surface Eh measurements using Pt and C electrodes from the Finnish site investigations. Site codes as in Figure 10 (source: TVODATAC).



**Figure 14.** Eh versus time during downhole and surface measurements made in flowing groundwater from different boreholes (after Wikberg 1992). The shaded areas represent the maximum difference between the different electrodes (Au, Pt, C). Figure 14a represents low pH (6.9) and high iron concentration (1.0 mg/L) whilst Figure 14b represents high pH (9.0) and low iron concentration (<0.005 mg/L). In Figure 14b, sulphide has buffered the water despite the low iron concentration. Furthermore, because of the low iron content, the Eh has taken time to stabilise. (Iron concentration and pH were stable throughout the experimental period).

instrumental disturbance at around 2700 observations, decreasing rapidly to values below detection limit. The generally increasing values of electrical conductivity (Figure 15c) exhibit much fluctuation due to minute bubbles of evacuating dissolved gases disturbing the measurement. The pH values (Figure 15d) initially show a general slight decrease before levelling off with time. The high fluctuation of pH readings not only reflect the above-mentioned effects of the evacuated gases, but also daily “cyclic” trends in temperature. It should be noted, however, that the pH-scale in Figure 15d is very narrow, so actually, the fluctuation has no practical importance. The high dissolved gas contents (mostly CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and higher hydrocarbons; Snellman 1991) generally found in the deep groundwaters at Olkiluoto, is degassing during transport to the surface and causing difficulties in field measurements in a two-phase solution. These evacuated gases explain the high fluctuation in the EC and pH measurements, but the Eh jumps are apparently due to more reducing groundwaters entering the isolated borehole section during pumping.

In the Posiva groundwater monitoring equipment (Rouhiainen et al. 1992) used during the preliminary site investigations in 1987-1992, groundwater first enters the Eh-cell with the O<sub>2</sub>-cell situated “up-flow” in the constructed flow-through cell system. The O<sub>2</sub> instability is believed to have been caused by short-term technical problems in the sensor. The Eh

jumps may also reflect technical problems in the electrodes, but could also be explained by changes in the groundwater redox controlling couples. For example, changes in groundwater composition are indicated from the steadily increasing conductivity profile (i.e. change to a deeper derived groundwater). Based on hydrogeochemical interpretation, pyrite-groundwater interaction controlled redox conditions have been proposed for the water sampled at the end of the monitoring period (sample with Eh = -250 mV; Pitkänen et al. 1992). This has been later shown (based on a new comprehensive dataset) to be related to the microbially mediated oxidation of organic carbon and reduction of sulphate under anaerobic conditions, as a consequence of which pyrite precipitates if ferrous iron is present (Pitkänen et al. 1996). However, even in such a case, the electrode reactions may still be due to the oxidation and reduction of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . (Wikberg 1996).

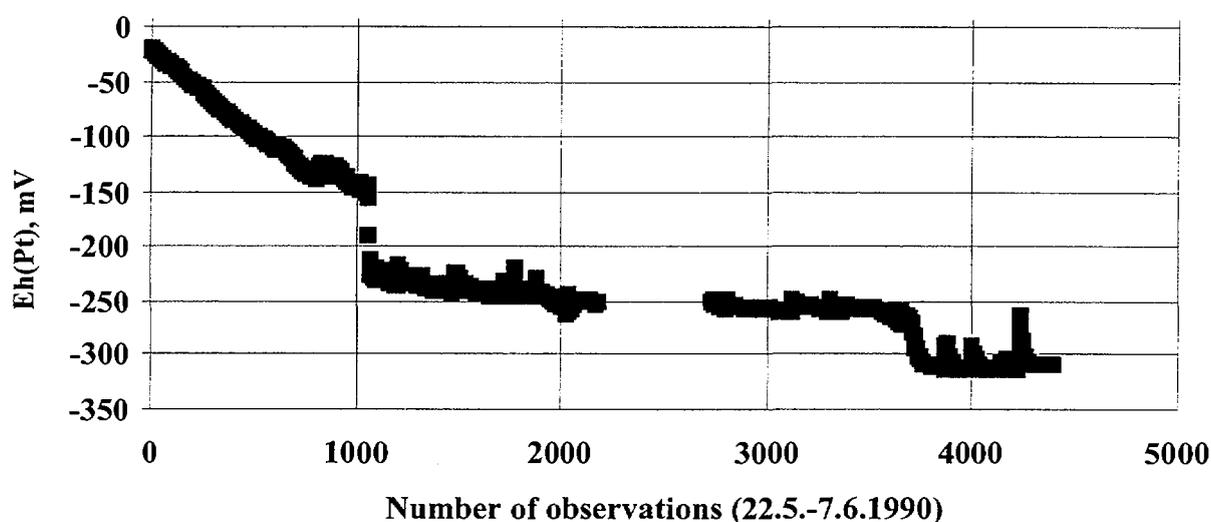


Figure 15a. Eh monitoring plot from Olkiluoto (OL-KR3, 388-393m, 25.5.-7.6.1990).

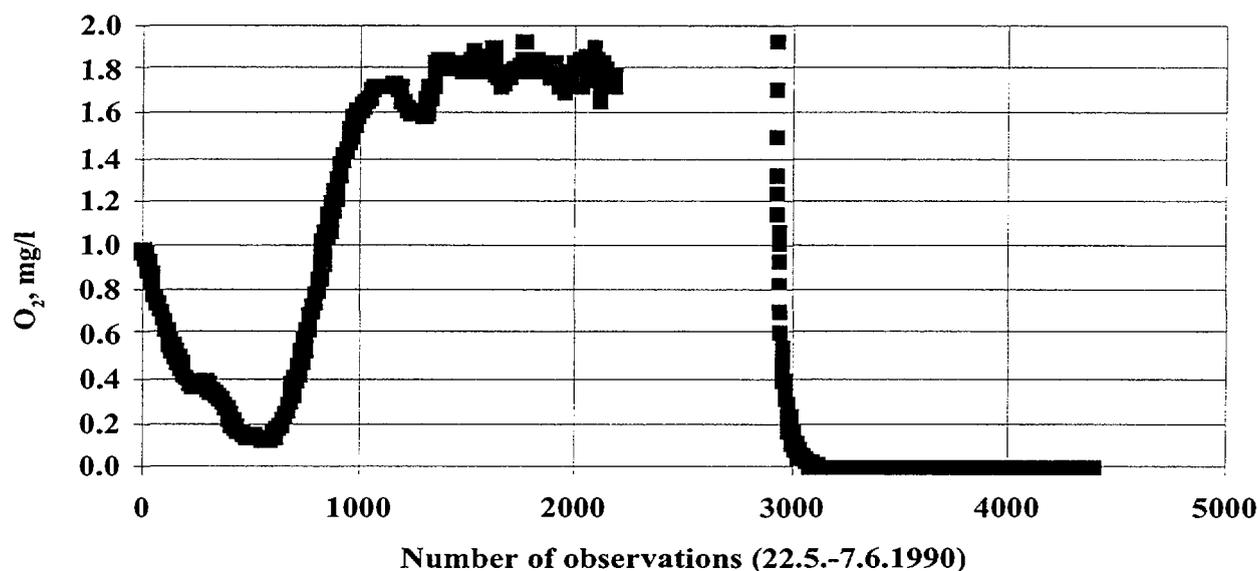
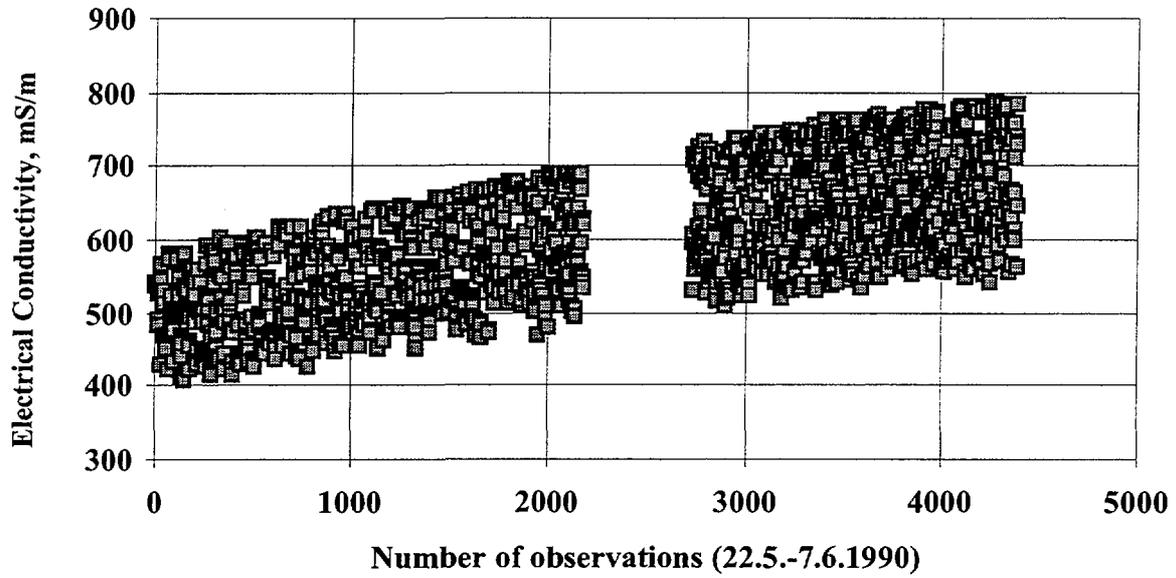
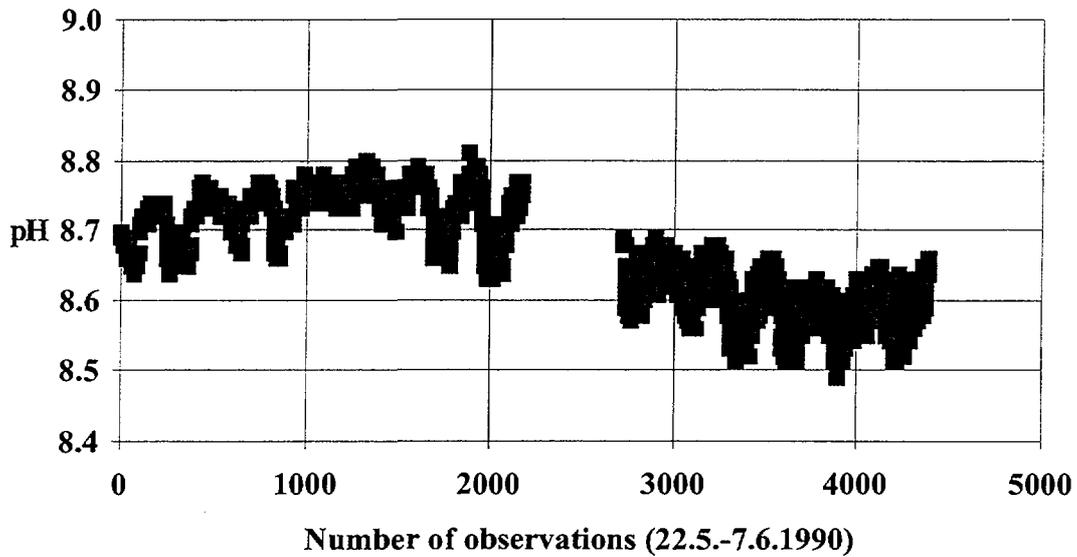


Figure 15b. Dissolved  $\text{O}_2$  monitoring plot from Olkiluoto (OL-KR3, 388-393m, 25.5.-7.6.1990).



*Figure 15c. Electrical conductivity monitoring plot from Olkiluoto (OL-KR3, 388-393m, 25.5.-7.6.1990).*



*Figure 15d. pH monitoring plot from Olkiluoto (OL-KR3, 388-393m, 25.5.-7.6.1990).*

#### 4.4 Implications

The implications from the presented topics are several-fold. There is evidence that many of the inconsistencies described above can be adequately explained by instrumental (e.g. sensor-specific) problems, and by the effects of residual drilling water and waters resulting from intra-borehole flow. It has also been shown that extraction pump-rates can be a major influence on the quality and representativeness of the groundwaters sampled. These issues underline the necessity to monitor several parameters in parallel so that natural chemical variations in the groundwater can be distinguished from instrumental malfunction.

As suggested from the monitoring trends described in Section 3, pre-sampling testing or monitoring of the isolated borehole section is essential to ensure the removal of residual drilling and open borehole waters and to establish optimum pump-rates. Logically, these rates should be as low as possible, in order to approach the natural groundwater flow-rate to the borehole section. It should also be borne in mind that too low a flow-rate can also influence the pH and Eh, if measured at the surface due to the long residence times in the connecting tubing (in extreme cases up to several hundreds of hours; Snellman et al. 1995). Such influences include degassing of CO<sub>2</sub> (most important, but also other gases) at shallower levels, CO<sub>2</sub> up-take at deeper levels, increase in TOC or DOC from the polyamide material of the tubing, and microbial activity (potentially iron or sulphur-reducing bacteria) from the borehole section and within the polyamide tubing, as well as effect on trace element concentrations (e.g. redox active Fe<sup>2+</sup> and S<sup>2-</sup>).

Experience has also shown that with care, reliable Eh and pH measurements can be obtained both downhole and at the surface, but adequate time is required to obtain stable and consistent values.

## 5 ANALYTICAL EXPERIENCE

Before sampling and analysing groundwaters, the correct choice of parameters and the precision, accuracy and reliability required must be established. In addition to those major ions and environmental isotopes needed to characterise and classify the main groundwater types, input requirements are also necessary for other groups who subsequently will use the data for various modelling purposes.

### 5.1 Objectives

The main objective is to provide high quality chemical input for: a) hydrogeochemical classification and characterisation of groundwater types, b) conceptual hydrogeological modelling of the groundwater flow paths, c) geochemical equilibrium modelling of water-rock interactions, d) modelling of groundwater evolution, and e) modelling parameters considered important for repository safety performance assessment. In order to address points (c) and (d), much of the groundwater analytical data has to interface with mineral chemical data.

### 5.2 Available Data

A considerable amount of major element analytical data has been compiled from both the Swedish and Finnish site investigations during the 1980s and the early 1990s. With only the exception of a few ions, these data are of high quality. Four main groups of data are available: on-line, *in situ*, on-site and off-site. The following breakdown (Table 2) is a compilation of parameters analysed within the Swedish and Finnish programmes; note, all parameters are not available for each of the studied sites.

The absence of any worthwhile trace element data (e.g. Cr, Co, Pb, Cu, Zn, REEs etc.) is noticeable in the Swedish programme. In contrast, the Finnish programme has given more attention to this area with trace element data dating back to 1987. More trace element data are necessary as there are indications from some of the major element data (e.g. Mn, Mg) that the host bedrock chemistry can play an important role in producing different groundwater types characteristic of different rock types. Furthermore, trace element compositions may be used to directly test solubility and speciation calculations that form a central part to radionuclide migration models used in safety performance assessment.

**Table 2.** Available analytical data from the Swedish and Finnish site investigations during the 1980s and the early 1990s.

Parameters	In situ	On-line	On-site	Off-site
Physico-chemical	Eh, pH	Eh, pH, EC, T, pS, Diss. O <sub>2</sub>	pH	pH, EC, Alkalinity, Acidity, COD, Tot. hardness, Colour, Solid matter, Turbidity
Anions			HCO <sub>3</sub> , CO <sub>3</sub> , Cl, F, Br, SO <sub>4</sub>	As "On site" + I
Cations			Ca, Mg, Na, K, Si	As "On site" + Al, Sr, Li
Trace elements			S <sup>2-</sup> <sub>tot</sub> , NO <sub>3</sub> , NO <sub>2</sub> , PO <sub>4</sub> , NH <sub>4</sub> , Fe <sup>2+</sup> , Fe <sub>ox</sub> , Mn	B, Ba, Be, Cr, Cs, Cu, Co, Hg, Mo, Ni, Pb, Th, Ti, U, Zr, V
Organics			Uranine (tracer)	TOC, DOC, Humic acids, Fulvic acids
Isotopes				<sup>2</sup> H, <sup>3</sup> H, <sup>18</sup> O, <sup>226</sup> Ra, <sup>222</sup> Rn, <sup>13</sup> C, <sup>14</sup> C, <sup>234</sup> U, <sup>238</sup> U, <sup>32</sup> S, <sup>34</sup> S
Gases	Sampling for dissolved gases	Sampling for evacuated gases		N <sub>2</sub> , O <sub>2</sub> , CO <sub>2</sub> , CO, CH <sub>4</sub> ...C <sub>3</sub> H <sub>8</sub> , H <sub>2</sub> , He, Ar
Particles and colloids				0.45-0.02 μm fractions of Ca, Al, Mg, Mn, Si, Fe and S

### 5.3 Results

Hydrogeochemical evaluation of groundwater studies in the 1980s and the beginning of the 1990s at the Swedish and Finnish sites is well documented in the literature and need not be repeated here (e.g. Smellie et al. 1985, 1987a; Smellie & Wikberg 1991; Wikberg 1992; Smellie & Laaksoharju 1992; Pitkänen et al. 1992; Lampén & Snellman 1993; Laaksoharju et al. 1995). Some discrepancies, however, do exist. For example, the unreliability of Al analysis due to several sources of contamination (e.g. drilling equipment and debris; atmospheric input; colloidal Al), and the lack of adequate environmental isotopic data for <sup>3</sup>H and <sup>14</sup>C. In addition, the detection level for <sup>3</sup>H conducted for the site studies is often too high (> 8 TU) to be of any use when only small amounts of near-surface mixing are suspected. In addition, problems with TOC or DOC analysis at high chloride contents have been recognised (Snellman 1991; Lampén & Snellman 1993).

The measurement of Eh and pH, two important parameters in any modelling exercise, has received considerable attention, especially in the Swedish programme. Certain difficulties (see Chapter 4) still remain which are gradually being resolved.

Problems are also encountered due to the long transport times from depth to the surface due to the low hydraulic conductivity of the studied packer section and partly also due to the small diameter of the polyamide tubing. This has been shown to result in enhanced TOC

contents (e.g. at Olkiluoto and Stripa) and also provides a large surface area for microbiological growth that can alter the iron or sulphur redox chemistry of the groundwater. This in turn may affect the surface Eh measurements and gas contents of the groundwaters.

#### 5.4 Implications

The difficulty surrounding the acquisition of reliable groundwater aluminium data requires to be resolved because of its importance in geochemical equilibrium modelling of Al-silicates (i.e. major minerals such as feldspars); for similar reasons, the reliability of redox and pH measurements must be assured. In this latter respect, downhole measurements would go a long way in solving problems of CO<sub>2</sub> degassing and therefore pH uncertainty, and also avoiding diffusion of O<sub>2</sub> into the groundwater when it is approaching the surface and entering the flow-through cell equipment. In the case of Al, the necessity of maintaining a contamination-free environment from sampling to analysis is of the utmost importance.

Alternatively, rather than try to measure aluminium, other workers (Gascoyne 1994) prefer to assume clay mineral control (+ calcite, gypsum etc.) and use [SiO<sub>2</sub>] and the cation concentration to predict the relevant clay mineral. Furthermore, as most of these low temperature minerals (i.e. clays, calcite, gypsum etc.) do not require redox Eh values for predictive calculations, there is no need for quantitative groundwater redox data. However, for repository performance assessment calculations, quantitative Eh and pH values are of major importance.

It should also be recognised that for geochemical equilibrium modelling and groundwater evolution studies, more detailed data on fracture minerals (both qualitative and quantitative) are needed. Specifically selected minerals (e.g. sulphides, carbonates, clays etc.) should be analysed for the most important environmental isotopes and lanthanides.

More environmental isotope samples are required during the sampling campaigns to test for groundwater mixing; this bears important consequences for groundwater quality evaluation. Identifying drilling water contamination is also important in this context. It is recommended that in addition to tagging the drilling water with uranine (previously also with NaI), which is routinely carried out in both the Swedish and Finnish programmes, analysis of other parameters of significance (particularly environmental isotopes) should also be carried out on a regular basis during the drilling campaigns.

Table 3. Recommended protocol for groundwater and mineral analysis.

	In-situ	On-line	On-site	Off-site
<b>Precautions</b>	Borehole section properly isolated. Use of optimum pump rate.	Optimum pump rate, tubing material. Insulation of tubing from borehole. Atmospheric and T protection. Shielding of flow-through cell and glove box with high purity N <sub>2</sub> (6.0). Use of constant through-flow line. Sampling using a T-connection fitted with a valve.	Clean-lab + air conditioning + air filters. Double doors ("Star Trek" air lock) entrance. Shoe covers or lab shoes.	Reliable and speedy transportation.
<b>Sampling</b>	Gas, microbe, colloid and redox species (e.g. Fe <sup>2+</sup> ) sampling using a shut-off container. Groundwater sampling sections identified with the Posiva flow meter.	Pre-filtering (0.45 µm) of nearly all samples.	Detailed protocol concerning: Preparation of samples. Sampling under N <sub>2</sub> shield. Optimum sample volumes. Sequence of sampling. Reserve samples and their preparation. Samples for QA (blind, reference etc).	
<b>Ground-water analysis</b>	Down-hole Eh, pH, T	Flow-through-cell measurements of pH, Eh, T, EC, flow rate, diss. O <sub>2</sub>	Detailed protocol concerning: Sequence of analysis. Rapid analysis needed for alkalinity and acidity, uranine, Fe <sup>2+</sup> , Fe <sub>tot</sub> , Cl, SO <sub>4</sub> , NO <sub>2</sub> , NO <sub>3</sub> , NH <sub>4</sub> , PO <sub>4</sub> . Possible field analysis (by IC) for F, Br, Cl, SO <sub>4</sub> , NO <sub>2</sub> , NO <sub>3</sub> , NH <sub>4</sub> , PO <sub>4</sub> , Na, K. Analyses of alkalinity and acidity under N <sub>2</sub> shield.	Guidance analyses of <sup>3</sup> H and uranine at an early stage. Detailed protocol concerning: Sequence of analysis. Rapid analysis needed for** (see below). QA procedures (charge balance, geochemical modelling).  <u>Analytical Programme</u> <b>Phys.-chem.:</b> pH**, EC**, COD**, Density**, DIC**, DOC (attention in saline gws). <b>Anions:</b> S <sup>2-</sup> **, PO <sub>4</sub> ** , F, I, Br (needs a lower detection limit) <b>Cations:</b> Ca, Mg, Na, K, Si, Mn, Al, Sr <b>Trace elem.. PA-related:</b> U, Th, Ra, Se, Mo, Sn, Cu, Rb, Zr, Ni, U <sup>4+</sup> /U <sup>6+</sup> **, lanthanides; <i>Evolution related:</i> U, Th, Ra, Li, Ba, B. <b>Isotopes:</b> <sup>2</sup> H, <sup>3</sup> H**, <sup>18</sup> O(H <sub>2</sub> O, SO <sub>4</sub> , DIC, DOC), <sup>13</sup> C & <sup>14</sup> C(DIC, DOC, gases), <sup>222</sup> Rn**, <sup>234</sup> U/ <sup>238</sup> U, <sup>34</sup> S(SO <sub>4</sub> , S <sup>2-</sup> ), <sup>87</sup> Sr/ <sup>86</sup> Sr, USD, <sup>40</sup> Ar/ <sup>36</sup> Ar, <sup>37</sup> Cl, <sup>15</sup> N <b>Gases**:</b> N <sub>2</sub> , O <sub>2</sub> , CO <sub>2</sub> , CO, CH <sub>4</sub> ...C <sub>3</sub> H <sub>8</sub> , H <sub>2</sub> , He, Ar. <b>Organics**:</b> TOC/DOC(attention in saline gws), humics, fulvics. <b>Colloids**:</b> 0.45-0.02 µm fractions of Ca, Al, Mg, Mn, Si, Fe, S. <b>Microbes**:</b> Fe and S reducing or oxidising bacteria etc.
<b>Analysis of fracture minerals in contact with sampled ground-water</b>				Qualit. and quantit. mineralogical analysis. Detailed analysis of specific minerals, e.g. sulphides, carbonates, clays. <b>Isotopes:</b> <sup>13</sup> C, <sup>14</sup> C, <sup>87</sup> Sr/ <sup>86</sup> Sr, <sup>18</sup> O, <sup>34</sup> S, USD. <b>Lanthanides</b>

## 6 SUMMARY AND DISCUSSION: IMPLICATIONS FOR SITE-SPECIFIC INVESTIGATIONS

Swedish and Finnish experience has shown that the real hydrochemical character of formation groundwater can be easily perturbed during borehole activities such as drilling, borehole testing and sampling. Furthermore, there is not yet a well tested or fixed strategy which can be applied when sampling groundwater. The reason is that the representativeness of groundwater samples is a function of many interacting variables such as borehole location, sampling depth, in-situ groundwater composition, pump rate, and economic and time constraints. In addition, the success of sampling can only be evaluated using expert judgement based on expected groundwater compositions at the sampling depth. There are no samples from totally undisturbed downhole conditions which can be used as reference samples for the actual sampling. Nevertheless, based on Fennoscandian experience, important guidelines can be provided for future site-specific characterisation programmes.

Using Swedish and Finnish hydrochemical data from the 1980s and the early 1990s this report has underlined the advantages of establishing optimum pump extraction rates to sample groundwaters, and also the value of downhole probes to measure pH and Eh. The extraction rate depends on the hydraulic properties of the borehole section to be sampled; ideally, just slightly in excess of the natural flow-rates at any hydrostatic head. Excessive pumping can cause short-circuiting (and access to different groundwater chemistries) around the installed packer systems to the open borehole and/or to higher or lower levels in the host bedrock via interconnected fracture systems. Although this may also occur even at the very low extraction rates advocated, at these low rates the radius of influence will tend to be more restricted, therefore minimising the risk.

A potentially greater problem when using low extraction rates is the time-lag of transporting groundwater to surface Eh and pH monitoring installations, where erroneous pH readings may result from the up-take and degassing of CO<sub>2</sub> through the polyamide tubing which connects the borehole section to the surface measuring equipment. Similar pH discrepancies were noted within the Canadian programme by Gascoyne et al. (1988). Comparison of redox potential measurements conducted from surface and downhole probes also show some variability. Furthermore, enhanced TOC or DOC contents may occur from excessive contact between groundwater and polyamide tubing in the sampling equipment (Andrews et al. 1988; Holm et al. 1988; Lampén & Snellman 1993), and also bacterial activity (particularly for iron and sulphur species) may be encouraged. An optimum pump-rate must therefore be chosen which provides a balance between minimising the risk of contamination through short-circuiting, and avoiding excessively long groundwater transport times from the borehole section to the bedrock surface. This can only be accomplished during a period of careful pumping and monitoring (i.e. pH, Eh, EC, T, drilling water tracer) prior to sampling.

Also of importance, but only briefly referred to so far, is the pre-monitoring stage, i.e. the initial location of the boreholes, the drilling techniques employed, whether sampling should be carried out both during and subsequent to drilling, and borehole activities conducted prior to the main sampling programme (e.g. hydraulic testing; geophysical logging). These

topics have been fully summarised by Laaksoharju et al. (1993). Taken collectively, it is strongly felt that the integrity of hydrogeochemical studies would benefit considerably from: a) first locating a deep borehole(s) (1000 m) solely to establish the reference hydrogeochemistry (reference source term), b) establishing a routine protocol of pre-monitoring, monitoring, sampling and analysis for the hydrogeochemical borehole, and c) establishing a routine protocol of pre-monitoring, monitoring, sampling and analysis for all subsequent boreholes.

## 6.1 Hydrogeochemical Borehole

The main purpose of a hydrogeochemical borehole(s) is to establish a reference groundwater chemistry of maximum quality that is representative for the site under investigation. To ensure these requirements, attention and priority should be given to each of the following stages: borehole location, drilling activities, pre-monitoring phase, monitoring phase, and the sampling and analysis phase.

Hydrogeochemical studies should also include other sampling points at, and in the near-vicinity of the site. This would include annual monitoring of precipitation and the collection of groundwaters and surface waters from the overburden and the upper part of the bedrock (springs, brooks, rivers, lakes, domestic borehole wells; specifically drilled shallow boreholes).

### 6.1.1 Location

Initially a regional hydrogeological reconnaissance of the terrain demarcated of interest should be carried out to establish major groundwater flow directions. This should include, for example, the use of existing topographical maps and available well or borehole groundwater level measurements. Regional hydrogeochemical evaluations, depending on available data, can also be used to support the hydrogeological reconnaissance studies. Such data may comprise:

- a) Existing groundwater chemical analyses (e.g. domestic well inventories; other borehole investigations in the near-vicinity),
- b) Selective sampling and analysis (e.g. for EC, T, pH, Cl, Br,  $^3\text{H}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ) of environmental reference samples (e.g. lakes, streams and springs or seepages),
- c) The drilling and sampling of shallow boreholes, based on a regular grid-system, through the overburden to the bedrock, to characterise the groundwater input to the system, and
- d) An attempt to use these data to predict groundwater compositions (i.e. by using  $\text{PCO}_2$ ; Laaksoharju et al. 1993) to the depths expected to be drilled (i.e. 1000 m).

These data require to be integrated fully to finally locate the best position of the hydrogeochemical borehole in relation to the hydrology of the potential site area. Ideally two boreholes would be required, representing recharge and discharge conditions respectively, and one borehole should be central to the site area. If not possible for economic reasons, a

borehole central to the site is preferred. Furthermore, the borehole should be placed within the recharge part of the site area (if possible to establish) to ensure minimum contamination of the borehole during the subsequent site-specific investigations.

### 6.1.2 Pre-monitoring phase

The most suitable drilling methods to be used are still open for discussion. In Sweden, "Telescopic Borehole" methods (Almén & Zellman 1991) may be compared to "Reverse Flushing" techniques (Ljunggren 1993) and "Triple Tube" drilling. Reverse Flushing is best employed only when hydraulic zones are intercepted, being more efficient in preventing the penetration of flushing water and drilling debris along the fractures. Triple Tube is preferred when fracture infilling is required for mineralogical characterisation, especially friable clay-rich phases, gouge etc. In any case the main emphasis should be to minimise the penetration of flushing water, air and drilling debris into any fracture system that will subsequently be sampled for hydrogeochemical characterisation, and also to preserve the fracture infilling mineralogy of the extracted drillcore material. The upper 200-250m of bedrock, being normally the most hydraulic conductive part in Fennoscandia, also should be treated with caution. Perhaps only percussion techniques (or reverse-flushing) should be used for this part and more conventional methods at greater depths as concluded from the "Booster Hole" study conducted at Finnsjön (Smellie et al. 1987b; Smellie & Wikberg 1991). In this study, casing of the upper bedrock interval was also advocated to prevent near-surface derived groundwaters from continuously discharging into the borehole.

The effects of drilling on hydrochemical sampling at the Hanford feasibility site for radioactive disposal have been quantitatively detailed by Graham & Johnson (1991). Based on mass balance calculations they pointed out that extensive borehole development was required before most of the complex water-based drilling fluids introduced to maximise drilling efficiency (which included different mud types) was removed from the bedrock formation. Such drilling methods were shown to influence most measured physico-chemical parameters of the formation groundwaters adjacent to the borehole. Both the SKB and Posiva programmes strive to limit flushing water to formation groundwaters (although usually only representative of the upper 100-150 m) or, if not possible, to surface waters from nearby lakes and streams (increased susceptibility of contamination due to oxidation and organic material). Because of the adverse influence on natural colloidal, microbial and organic contents in the groundwaters, drilling mud is never used by SKB and Posiva as a medium for lubrication or removal of rock debris.

Sampling for major hydrogeochemical characterisation is recommended during drilling; this can either take place when a hydraulically active fracture zone is breached (e.g. observed as a sudden loss of flushing water and/or changes in drilling penetration), or, at predetermined depths (e.g. every 50 or 100 m) when no obvious marked variation occurs. This has the advantage of: a) reducing the monitoring times to ensure a representative sample (i.e. less time for foreign waters to penetrate into the borehole section to be sampled), and b) less possibility of mixing of different types of groundwaters via hydraulic connections with deeper borehole sections. This was often a problem in earlier site-specific investigations.

Following drilling, confirmation of the sections sampled and the location of any additional favourable hydraulic sections for sampling can be carried out by logging the borehole. The most suitable methods, chosen to give the maximum resolution of borehole fractures and their hydraulic properties, whilst causing minimal perturbation to the borehole and the borehole groundwaters, include geology (drillcore lithological mapping; fracture frequency), TV-imagery/radar measurements (fracture orientation), spinner or flowmeter (hydraulic conductivity of difference and cross flow measurements; Rouhiainen 1993; 1994) and EC (salinity). Hydraulic head measurements are also essential to calculate the total water budget for each sampled section (water in vs. water out).

### 6.1.3 Monitoring phase

Monitoring should commence as soon as the borehole section is isolated and involve the measurement of Eh(Pt), pH, EC, T and drilling water tracer; Eh and pH should preferably be measured downhole. Low-key pump-tests, based on knowledge of the hydraulic properties of the borehole section to be sampled and the transport distance to the bedrock surface, should be carried out to establish the optimum extraction rate suitable for the section being investigated. Using the optimum pump extraction rate, continuous monitoring should be carried out until the key parameters have stabilised.

### 6.1.4 Sampling and analysis

Analytical data presently available from the Swedish and Finnish site investigations are listed in Table 2. A recommended protocol for groundwater sampling and *in situ*, on-line, on-site and off-site groundwater or mineral analysis is detailed below in Table 3. In particular, it should be emphasised that specialised sampling for colloids, microbes, dissolved gases and organic material should be carried out preferably *in situ* and in parallel with the major hydrogeochemical sampling campaign, and that mineral selection and identification should be conducted in the same fractures or borehole sections sampled for groundwater characterisation. This will ensure that the colloid compositions, for example, can be directly correlated with all the other measured groundwater parameters, and that data input to geochemical equilibrium modelling, for example, relates to groundwater and fracture minerals in contact with each other.

## 6.2 Boreholes for Site-specific Investigations

Earlier site-specific investigations conducted by SKB and Posiva have not included deep boreholes, intended mainly for hydrogeochemical studies. In most cases these programmes involved up to 15 cored boreholes per site (SKB; down to maximum depths of 700-800 m) and up to 5 cored boreholes at each of five sites (Posiva; one hole to 1000 m at each site, the others up to 500 m), for complete site characterisation. Because of rigid time schedules, the low priority given to hydrochemistry, and the lack of experience in recognising the sensitivity of groundwaters to borehole activities, the hydrogeochemical programmes normally constituted the final stages of the investigations, with the result that many of the boreholes were contaminated to varying degrees prior to sampling.

Regrettably it is considered often impractical and costly to plan a complete site characterisation around hydrogeochemical requirements. However, it is strongly advocated that following complete characterisation of the hydrogeochemical borehole, the additional shallower boreholes (100-700m), whose principle aim will be to further characterise in greater detail the geology and hydrogeology of the site, should be at least monitored during drilling and at any other suitable occasion (e.g. during interference pumping). Hydrogeochemistry need not be neglected; with proper planning and integration, all interests can be satisfied.

### **6.2.1 Additional sampling**

The site investigation boreholes will probably be drilled using conventional rotary core water flushing techniques, with the flushing water suitably tagged. Monitoring and periodic sampling of the flushing water output during drilling is recommended as it may provide useful indications of major groundwater types encountered during drilling. Provision should therefore be made to monitor and sample groundwater compositions during drilling (i.e. flushing/formation water) and at a later stage during interference pump tests (formation water). Parameters required during monitoring should include EC, T, pH, Eh, Cl, Br,  $^3\text{H}$ ,  $^2\text{H}$  and  $^{18}\text{O}$ . These parameters should provide direct input into the hydrogeological interpretation of the site.

Based on a conceptualism of groundwater flow in the site area, an additional 5-10 strategic borehole sections should be identified for full hydrogeochemical characterisation. Isolation of suitable sections, monitoring and sampling and analysis should follow the same protocols as described for the hydrogeochemical borehole. Selection should be facilitated by predictive modelling using the reference data from the hydrogeochemical borehole. All these data can be used to support the hydrogeochemical and hydrogeological modelling of the site.

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## 7 FINAL COMMENT

Despite the difficulties mentioned in this report it is important to note that the groundwater sampling conducted within the Swedish and Finnish programmes during the 1980s and 1990s contributed considerably to the understanding of the origin, mixing processes and major reactions taking place in the Fennoscandian Shield groundwater systems. This experience subsequently has been integrated into the planning and execution of more recent hydrochemical programmes in both countries, to the extent that hydrogeochemical studies are now approaching the status and priority they deserve. Now, groundwater sampling is of such quality that groundwaters, ranging from modern precipitation to deep saline varieties with an age of more than 1.5 Ma, have been accurately traced and quantified. This has helped to unravel known palaeo or modern events such as de-glaciation, different marine signatures, land uplift, tunnel construction, organic and inorganic reactions and effects from microbiological processes (e.g. Smellie et al. 1995; Laaksoharju & Wallin, 1997; Pitkänen et al. 1998).

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## 9 REFERENCES

- Almén, K-E. & Zellman, O. (1991). Äspö Hard Rock Laboratory. Field investigation methodology and instruments used in the pre-investigation phase, 1986-1990. SKB Tech. Rep. (TR 91-21), Stockholm.
- Andrews, J., Fontes, J-C., Fritz, P. & Nordstrom, K. (1988). Hydrogeochemical assessment of crystalline rock for radioactive disposal: The Stripa experience. Stripa Project Tech. Rep. (TR 88-05), Stockholm.
- Davis, S.N. (1964). The chemistry of saline waters. In: Krieger, R.A., Discussion. Groundwater, Vol 2(1), p. 51.
- Eriksson, E. & Sehlstedt, S. (1991). Description of background data in the SKB database GEOTAB. Version 2. SKB Tech. Rep. (TR 91-06), Stockholm.
- Eriksson, E., Johansson, B., Gerlach, M., Magnusson, S., Nilsson, A-C., Sehlstedt, S. & Stark, T. (1992). GEOTAB: Overview. SKB Tech. Rep. (TR 92-01), Stockholm.
- Garner, S. (1988). Making the most of field-measurable ground water quality parameters. Ground Water Monitoring Review. Summer, 60-66.
- Gascoyne, M., Ross, J.D. & Watson, R.L. (1988). Geochemical and isotopic characterisation of flow in fractured rocks: Examples from the Canadian Shield. Proceedings of the 4th Canadian/American Conference on Hydrogeology, Banff, Alberta, Canada (June 21-24, 1988).
- Gascoyne, M. (1994). Personal communication.
- Graham, D.L. & Johnson, V.G. (1991). Effects of fluid rotary drilling on hydrochemical sampling results from deep boreholes in fractured Columbia River Basalt. J. Hydrol., 128, 171-212.
- Grenthe, I., Stumm, W., Laaksoharju, M., Nilsson, A-C. & Wikberg, P. (1992). Redox potentials and redox reactions in deep groundwater systems. Chemical Geology, 98, 131-150.
- Hansson, K. (1993). Personal communication.
- Holm, T.R., George, G.K. & Barcelona, M.J. (1988). Oxygen transfer through flexible tubing and its effects on ground water sampling results. Ground Water Monitoring Review. Summer, 83-89.
- Laaksoharju, M., Smellie, J.A.T., Lampén, P.H. & Snellman, M.V. (1993). An approach to quality classification of deep groundwaters in Sweden and Finland. SKB Tech. Rep. (TR 93-27), Stockholm.

Laaksoharju, M., Vuorinen, U., Snellman, M., Allard, B., Pettersson, C., Helenius, J. & Hinkkanen, H. (1994). Colloids or artefacts? A TVO/SKB co-operation project in Olkiluoto, Finland. Nucl. Waste Comm. Finn. Power Co. Tech. Rep. (YJT-94-01), Helsinki.

Laaksoharju, M., Smellie, J., Nilsson, A-C. & Skårman, C. (1995). Groundwater sampling and chemical characterisation of the Laxemar deep borehole KLX02. SKB Technical Report TR 95-05, Stockholm.

Laaksoharju, M. & Wallin, B. (eds.) (1997). Evolution of the groundwater chemistry at the Äspö Hard Rock Laboratory. Proceedings of the second Äspö International Geochemistry Workshop, June 6-7, 1995. SKB International Co-operation Report ISRN SKB-ICR-91/04-SE. ISSN 1104-3210 Stockholm, Sweden.

Lampén, P.H., Laaksoharju, M. & Smellie, J.A.T. (1992). SKB/TVO joint project for groundwater chemistry, Phase I. A compilation of existing Finnish and Swedish groundwater data. TVO/Site Investigations, Int. Rep. (92-51).

Lampén, P.H. & Snellman, M.V. (1993). Summary report on groundwater chemistry. Nuclear Waste Commission of Finnish Power Companies, Report YJT-93-14, Helsinki.

Ljunggren, C. (1993). Core drilling by reverse flushing – a new drilling concept for small diameter boreholes. SKB Tech. Rep. TR 93-30. SKB, Stockholm, Sweden.

Pearson, J. et al. (1989). Chemistry of waters in the Böttstein, Weiach, Riniken, Schafisheim, Kaisten and Leuggern boreholes: A hydrochemically consistent data set. Nagra Tech. Rep. (86-19), Nagra, Baden, Switzerland.

Pennino, J.D. (1988). There's no such thing as a representative ground water sample. Ground Water Monitoring Review. Summer, 4-9.

Pitkänen, P., Snellman, M., Leino-Forsman, H. & Front, K. (1992). Ground water chemistry and water-rock interaction at Olkiluoto. Nucl. Waste Comm. Finn. Power Co. Tech. Rep. (YJT-92-02), Helsinki.

Pitkänen, P., Snellman, M. & Vuorinen, U. (1996). On the origin and chemical evolution of groundwater at the Olkiluoto site. Report POSIVA-96-04.

Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. & Vuorinen, U. (1998). Geochemical modelling of groundwater evolution and residence time at Olkiluoto site. Helsinki, Finland: Report POSIVA 98-10.

Rouhiainen, P. (1993). TVO-Flowmeter. Nuclear Waste Commission of Finnish Power Companies. Report YJT-93-1.

Rouhiainen, P. (1994). Difference flow measurements with the TVO flowmeter, methodological and instrumental specification. TVO/Site investigations, Work report PATU-94-24 (in Finnish with an English abstract).

Rouhiainen, P., Lampén, P., Snellman, M. & Helenius, J. (1992). Water sampling equipment. Technical description and operating instructions. Rev. III. TVO/Site investigations. Work report PATU-92-71 (in Finnish with an English abstract).

Smellie, J.A.T. (1983). Groundwater pump flow-rate and its effect on some physico-chemical parameters: a controlled experiment carried out at Taavinunnanen, Norrbotten. SKBS/KBS Status Rep. (AR 83-45), Stockholm.

Smellie, J., Larsson, N-Å., Wikberg, P. & Carlsson, L. (1985). Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions. Experience from the SKB test-sites in Sweden. SKB Tech. Rep. (TR 85-11), Stockholm.

Smellie, J., Larsson, N-Å., Wikberg, P., Puigdomènech, I. & Tullborg, E-L. (1987a). Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Klipperås test-site, Småland, Southern Sweden. SKB Tech. Rep (TR 87-21), Sweden.

Smellie, J.A.T., Gustavsson, E. & Wikberg, P. (1987b). Groundwater sampling during and subsequent to air-flush rotary drilling: hydrochemical investigations at depth in fractured crystalline rock. SKB Status. Rep., (AR 87-31), Stockholm.

Smellie, J.A.T. & Wikberg, P. (1991). Hydrochemical investigations at Finnsjön, Sweden. *J. Hydrol.*, 126, 129-158.

Smellie, J.A.T. & Laaksoharju, M. (1992). The Äspö Hard Rock Laboratory: Final evaluation of the hydrogeochemical pre-investigations in relation to existing geologic and hydraulic conditions, SKB Tech. Rep. (TR 92-31), Stockholm.

Smellie, J.A.T., Laaksoharju, M. & Wikberg, P. (1995). Äspö, S.E. Sweden: A natural groundwater flow model derived from hydrogeochemical observations. *J. Hydrol.*, 172, 147-169.

Snellman, M. (1991). Summary report on groundwater chemistry at Olkiluoto, Eurajoki. Teollisuuden Voima Oy. Site investigations, Work Report 91-34.

Snellman, M., Helenius, J., Sellge, R. & Rajala, R. (1995). Testing of the field measurement equipment for evaluating Eh and O<sub>2</sub> observations (in Finnish with an English abstract). Teollisuuden Voima Oy. Site investigations, Work Report PATU-95-51.

Whitfield, M. (1974). Thermodynamic limitations of the use of the platinum electrode in Eh measurements. *Limnol. Oceanogr.*, 19, 857-865.

Wikberg, P. (1992). Laboratory Eh simulations in relation to the redox conditions in natural granitic groundwaters. Presented at a Workshop on Sorption Processes, Interlaken (October, 1991).

Wikberg, P. (1996). Personal communication.

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