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Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters



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## **RAPPORT**

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28 groundwater samples have been collected from boreholes in bedrock aquifers in Trøndelag, Hvaler and other areas around Oslofjord. A clear relationship between many chemical parameters and lithology/geographical location is demonstrated. The parameters Rn, U, Th, Si, Al, Fe, Na, Cd, Cu, Zn, Cr, V, F, Cl, SO<sub>4</sub>=, Y, Be, Mo, Bi, La, E.C., Tl, Zr, Pb and B have generally higher values in the Iddefjord Granite of Hvaler, while Ca, Mg, Sr, Rb, Cs, pH and alkalinity are highest in Trøndelag. Several parameters such as Rn, U, F, Na, Fe and possibly Al exceed drinking water norms on Hvaler. Measured values of parameters compare very well (except F) with the Dutch "A" values, although the authors warn against uncritical use of norms developed in lands with other dominant lithologies than Norway.

28 grunnvannsprøver er hentet fra borebrønner i fast fjell i Trøndelag, Hvaler og andre deler av Oslofjord. En klar sammenheng mellom mange kjemiske parametre og litologi/geografisk lokalisering er påvist. Parametre som Rn, U, Th, Si, Al, Fe, Na, Cd, Cu, Zn, Cr, V, F, Cl, SO<sub>4</sub>-, Y, Be, Mo, Bi, La, ledningsevne, Tl, Zr, Pb og B har høyeste konsentrasjoner i Iddefjordgranitten ved Hvaler, mens Ca, Mg, Sr, Rb, Cs, pH og alkalitet har høyeste verdier i Trøndelag. Flere parametre overskrider drikkevannsnormer på Hvaler inkl. Rn, U, F, Na, Fe og muligens Al. Målte verdier samsvarer overraskende bra med Nederlandske "A" verdier (med unntak av F), men det advares allikevel mot ukritisk bruk av "normer" utviklet i land med andre bergarter enn Norge.

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## 1. INTRODUCTION

A pilot study has thus been initiated to assess the feasability of a background mapping of Norwegian bedrock groundwater chemistry. Its primary aim was to establish background concentrations of the radioactive elements radon, uranium and thorium (Banks and others 1993c). The analyses performed at the Norwegian Air Research Institute (NILU) and the Geological Survey of Norway (NGU) also provided a data set on some 40 additional parameters, with very low detection limits.

This paper sets out to document and interpret the results of these analyses, in the hope that they will encourage environmental investigators to consider the wide range of background concentrations which can occur in the geological environment.

Increasing political emphasis on environmental protection in many nations has led to strict pollution laws and, in many cases the compilation of registers of contaminated land (Misund and others 1991). This has in turn led to a huge demand for site investigations of degree of contamination of soil and groundwater. It should be an axiom amongst environmental geologists that it is impossible to assess the degree of contamination in the geoenvironment unless one has suitable natural background values to compare with, a point repeatedly emphasized by Bølviken (1990), among others.

Some nations, notably the Netherlands, have made some progress in defining background and action concentrations for some contaminants in soils and water. These have, however, been rather uncritically used by environmental organizations in other lands, often with rather different geological situations. In particular, one might suspect that "background" concentrations for many metals and radionuclides in groundwater which have been developed in nations abstracting groundwater from Quaternary deposits, may seriously underestimate the natural background levels of such parameters in bedrock groundwaters widely exploited by lands underlain by crystalline bedrocks, such as the Scandinavian nations, the Czech republic and many African nations. If such limits are legally enforced in an uncritical manner in such "hard rock" nations, it may prove extremely costly or even impossible to treat water to meet unrealistic action concentrations.

In some nations, such as the Czech Republic, contamination may have reached such an extent that it is no longer possible to measure true background concentrations, even in hard rock groundwaters (see e.g. Hrkal 1992). In Norway, however, anthropogenic impact is far less advanced (although the South is becoming increasingly affected by atmospheric deposition of contaminants) and a survey of bedrock groundwater chemistry provides an ideal opportunity for quantifying background levels and, possibly more importantly, the variation in background levels with lithology and other factors.

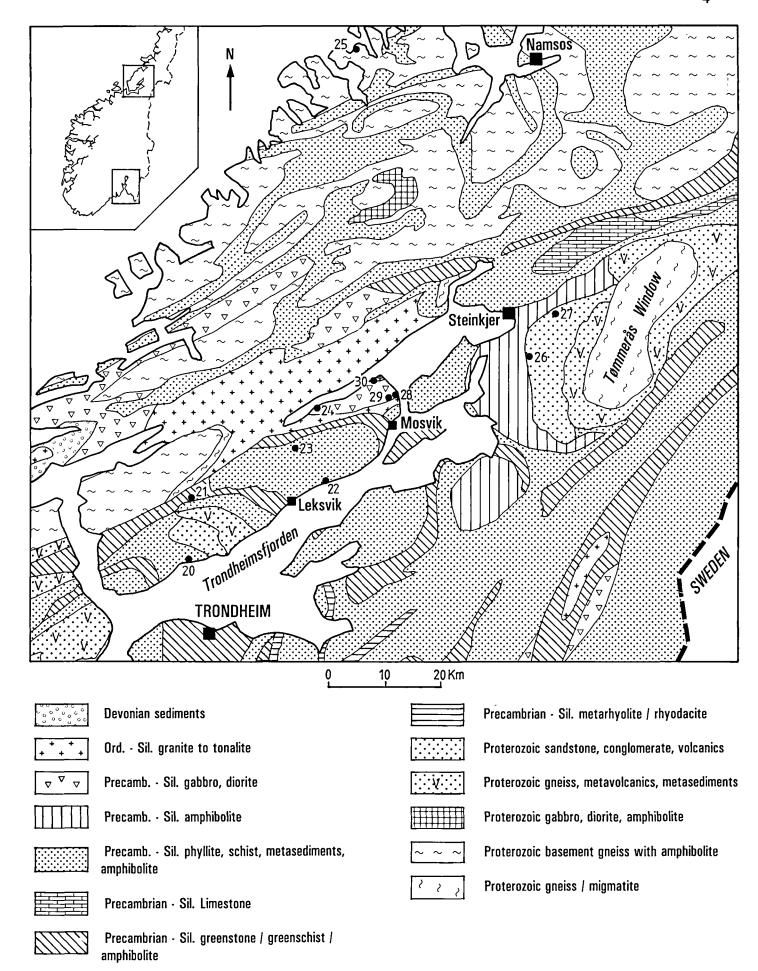


Figure 1. Map of Trøndelag showing sampling locations. Inset shows location of Trøndelag and Oslofjord in Norway.

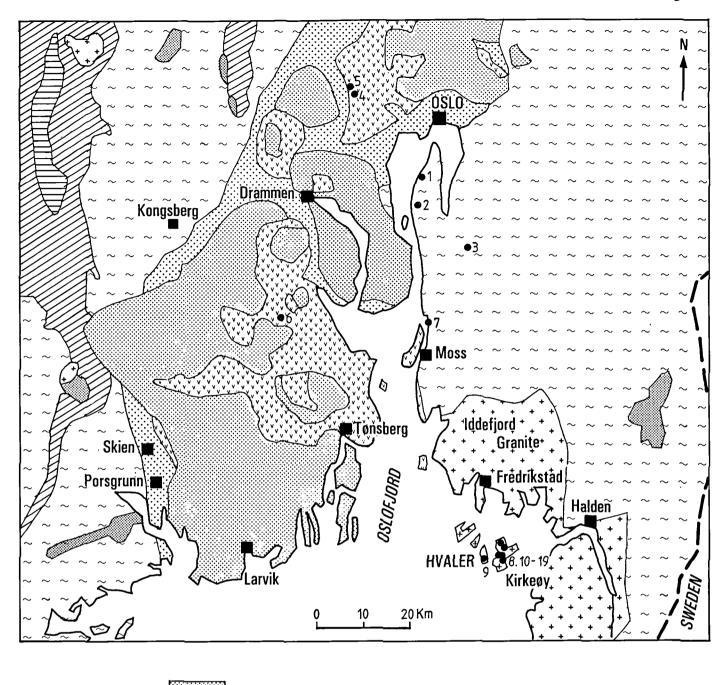




Figure 2. Map of Oslofjord showing sampling locations.

## 2. THE STUDY AREAS

28 bedrock boreholes from two geographical regions were chosen for sampling in autumn 1992 and winter 1992-93. The two study regions were chosen according to the following criteria: (i) ease of accessibility and existing groundwater projects in progress (ii) lithological variation (iii) presence of lithologies suspected to be "high risk". The county north of Trondheim (Nord-Trøndelag) and the area around Oslofjord were chosen.

## 2.1 Nord-Trøndelag

A simplified geological map of the county of Nord-Trøndelag is shown in Fig. 1. The area can be subdivided very coarsly into three:

- 1) The Caledonian mountain belt consisting of a sequence of nappe-piles of gneisses, metasediments and metavolcanics of Precambrian to Lower Palaeozoic age.
- 2) The Proterozoic (so-called "basement") gneisses occurring west of the Caledonian belt. Although sometimes considered as parautochthonous, these are often also regarded as belonging to the lower allochthons of the nappe sequence.
- 3) Windows of Proterozoic "basement" gneisses and metasediments (e.g. the Tømmerås Window).

A dominant tectonic feature is the Møre and Trøndelag fault zone, which largely controls the "grain" of Trondheimsfjord. In several localities in inner Trondheimsfjord, narrow hydrothermal thorium-bearing breccia zones occur (Grønlie and Staw 1987).

## 2.2 Oslo Region

The region (Fig.2) is tectonically dominated by the Oslo rift, of Carboniferous-Permian age. Within the rift can be found sedimentary rocks of Precambrian to Silurian age, including the uranium-rich Alun Shales. These are overlain by volcanics and sediments of Carboniferous-Permian age, and intruded by igneous rocks of largely Permian age. To the east and the west of the Oslo rift can be found autochthonous Precambrian basement, consisting of gneisses and granites dating from the Sveconorvegian orogeny or earlier.

In the extreme southeast of the area lies the Precambrian Iddefjord granite, the Norwegian extension of the major Swedish Bohus granite batholith. It is known to be rich in incompatible elements, including U and Th (Banks and others 1993c, Killeen and Heier 1975). The hydrogeology and major-element hydrochemistry of the Iddefjord granite are relatively well known from the Hvaler group of islands and are described in papers by Banks and others (1993a,b), and thus the Hvaler islands were focussed on during the sampling programme as a third subarea.

## 3. METHODS AND EQUIPMENT

Bedrock boreholes or wells were chosen (Table 1) with emphasis being given to the following criteria:

- (i) borehole should be in regular use or should be naturally overflowing, such that "fresh" groundwater is sampled.
- (ii) borehole should not be newly drilled. Investigations (Banks and others 1993b) have indicated that newly exposed rock surfaces and drilling cuttings can substantially affect water chemistry.
- (iii) borehole should give low possibility for degassing, i.e. sampling points at borehole head, or sampling points which are part of a closed system (e.g. pressure tank) were preferred.
- (iv) the water should not contain particulate matter or humus.

In practice, however, some boreholes did not satisfy all criteria (i.e. minor infringements of (iii) and (iv)). In particular, sample 13 came from a relatively newly drilled (7 month old) borehole which still contained a sufficient particulate load to prevent filtering and field acidification. All results quoted below for this borehole refer thus to the unfiltered sample. Sample 12 came from a borehole with a permanent problem of particulate and humic matter in the water, but which could be filtered in the field.

Two samples of groundwater from wells in Quaternary sediments were also taken as controls (samples 19 and 27) from Trøndelag and Hvaler, making a total sample set of 30.

It can, of course, not be excluded that some parameters (e.g. metals such as Cu, Zn etc.) may be derived from contact with pipework. The sampling procedures and criteria employed would help to minimise such an effect. If, however, such "contamination" is of any importance, results would not be expected to exhibit any regional or geological correlation.

Prior to sampling, the tap was allowed to run for at least 5 minutes. All polythene flasks were rinsed thoroughly three times with groundwater, and twice with filtered (0.45  $\mu$ m Millipore filter) water before sampling.

The following samples were then taken in polythene bottles with screw caps.

- (a) 2 x 100 ml unfiltered, unacidified
- (b) 2 x 100 ml filtered (0.45  $\mu$ m Millipore filter and polythene syringe) and acidified (10 drops 65% Ultrapur nitric acid) in the field.
- (c) 1 x 500 ml unfiltered, unacidified

One quantum of sample (a) was analysed at the Geological Survey of Norway (NGU) for 7 anions (F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>--</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>) by ion chromatography. One quantum of sample (b) was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) at NGU for Si,

Al, Fe, Ti, Mg, Ca, Na, K, Mn, P, Cu, Zn, Pb, Ni, Co, V, Mo, Cd, Cr, Ba, Sr, Zr, Ag, B, Be, Li, Sc, Ce, La and Y (although many of these have inappropriately high detection limits).

The second quanta of samples (a) and (b) were analysed at the Norwegian Institute for Air Research (NILU) by ICP Mass Spectrometry (ICP-MS) for Pb, Cd, Cu, Zn, Cr, Ni, Co, Fe, Mn, V, As, Ba, Sr, Al, Sb, Bi, Tl, U, Th, Be, Li, Rb, Cs, Mg, Ca, Mo, Y and La. The standard method used at NILU was employed - 10 ml of each sample was taken, and  $100\mu l$  1% HNO<sub>3</sub> was added.  $50 \mu g/l$  Sc, Re and In were also added to the sample as an internal standard. The ICP-MS instrument is calibrated against reference standards provided by SPEX Industries, and calibration allows a maximum of 10% deviation for a concentration of  $10 \mu g/l$ .

The 500 ml sample (c) was used for laboratory determinations at NGU of pH, electrical conductivity and alkalinity. Standard methods employed at NGU are described by Ødegård and Andreassen (1987).

For sampling of radon, a plastic funnel was inserted below the running sampling tap such that the tap mouth was under water and there were no air bubbles in the funnel. Using an adjustable automatic pipette, with disposable tips, a quantum of 10 ml water was taken from the funnel and injected slowly into a 20 ml vial containing 10 ml of prefilled scintillation liquid (Lumagel). The ampule of scintillation liquid was then sealed and shaken. The liquid gelifies on contact with water, immobilising the radon. Flasks were delivered to the Norwegian Radiation Protection Authority (Statens Strålevern - NRPA) within 3 days and analysed using an LKB Wallac 1215 scintillation counter, calibrated using a standard radium solution. Results were back adjusted for radioactive decay to give a radon concentation in Bq/l at time of sampling. The overall uncertainty in the method is estimated to be around 20 % at the 95 % confidence level, and the lower limit of detection is 1 Bq/l.

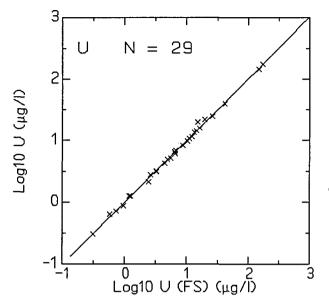
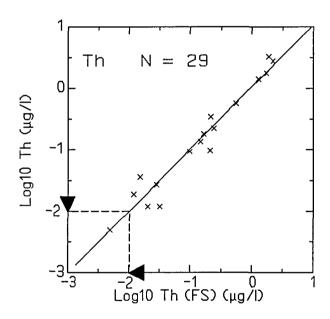


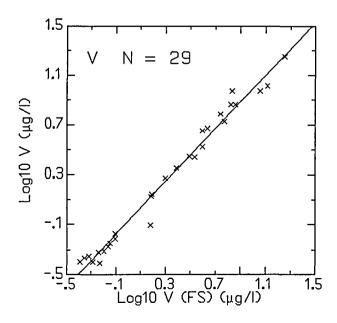
Figure 3. Plots showing effect of field acidisation on results of ICP-MS analyses for U, Th and V. Sample 13 is excluded (not filtered/acidified in field). FS = field filtered and acidified. Black triangles show detection limits, where relevant.

Correlation coefficients of Log<sub>10</sub> parameters

 $U: r^2 = 0.997$ Th:  $r^2 = 0.977$ 

 $V: r^2 = 0.982$ 





## 4. RESULTS

## 4.1 Analytical Comments

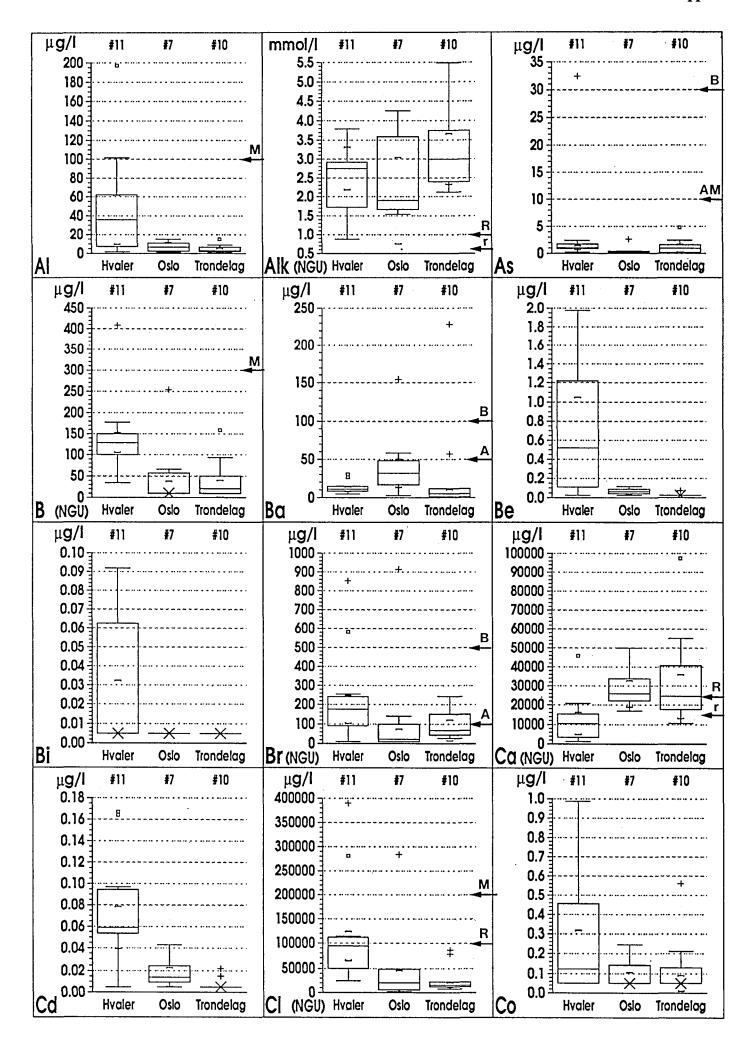
It cannot be overemphasized that analytical results will depend not only on the total content of an element in a solution, but also its form (complexed, colloidal, particulate), the sampling methodology, preservation techniques, storage conditions and time and analytical equipment and methodologies. The duplicate analyses made on many elements at NGU and NILU, and the analyses by ICP-MS on field-acidified and field-unacidified samples allowed independent control of many parameters. In the case of most parameters, field filtration and acidification did not dramatically affect the analysis outcome (Fig. 3). A few parameters were more sensitive to field preservation, including Fe, Mn, Bi and to a lesser extent Pb, Al, La, Y, Cd and Cu.

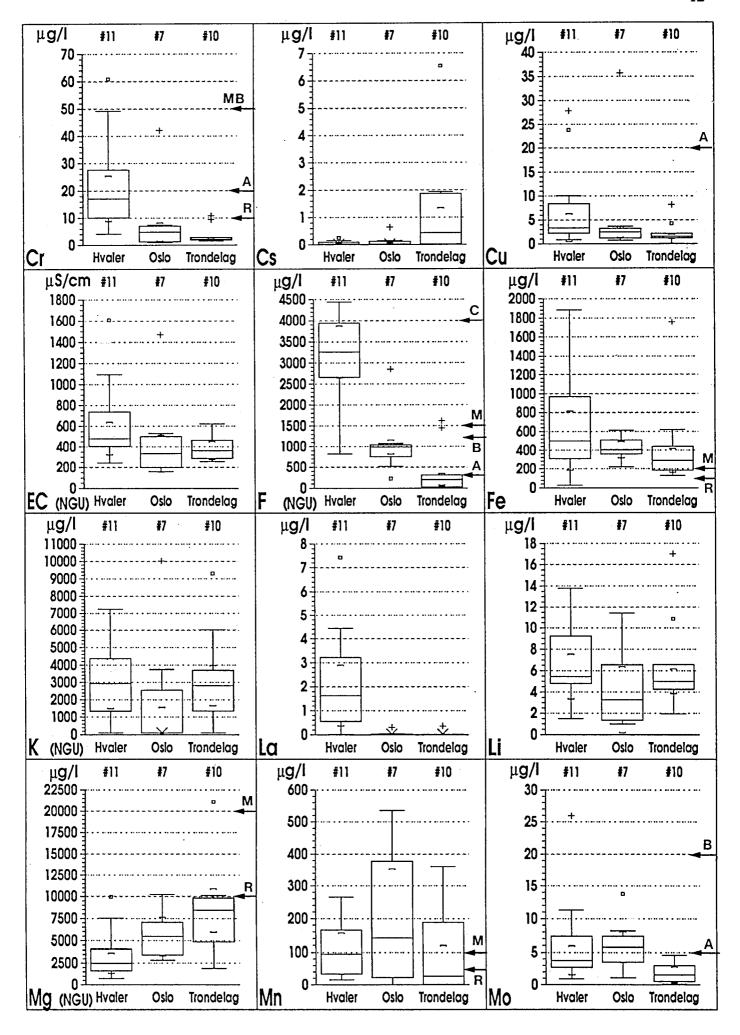
A few discrepancies were discovered between ICP-OES and ICP-MS analytical results. These concerned particularly a few elements which are sensitive to pH and redox conditions (and thus to filtering, storage and sample preparation), such as Fe and Al (see below). In addition, Cr and V are known to be problematic for ICPMS methods in high salinity solutions due to interference with Cl. In a similar manner, high Ca concentrations will interfere with Fe and Ni. Therefore, ICPMS results ranged up to 20 and 61 ppb for vanadium and chromium, whereas ICP analyses indicated that all samples contained < 5 ppb V and < 10 ppb Cr. Discrepancies in ICP-OES and ICP-MS analytical results were also obtained for Mo and, to a lesser extent, Li. Rather good correspondence between ICP-OES and ICP-MS results was found for the elements Ca, Mg, Ba, Cu, Zn, Sr and Y. For the other elements, the values obtained by ICP-MS lay under the ICP-OES detection limits, or were not analysed by ICP-OES. For a further discussion of these questions the reader is referred to Appendices 1 & 2.

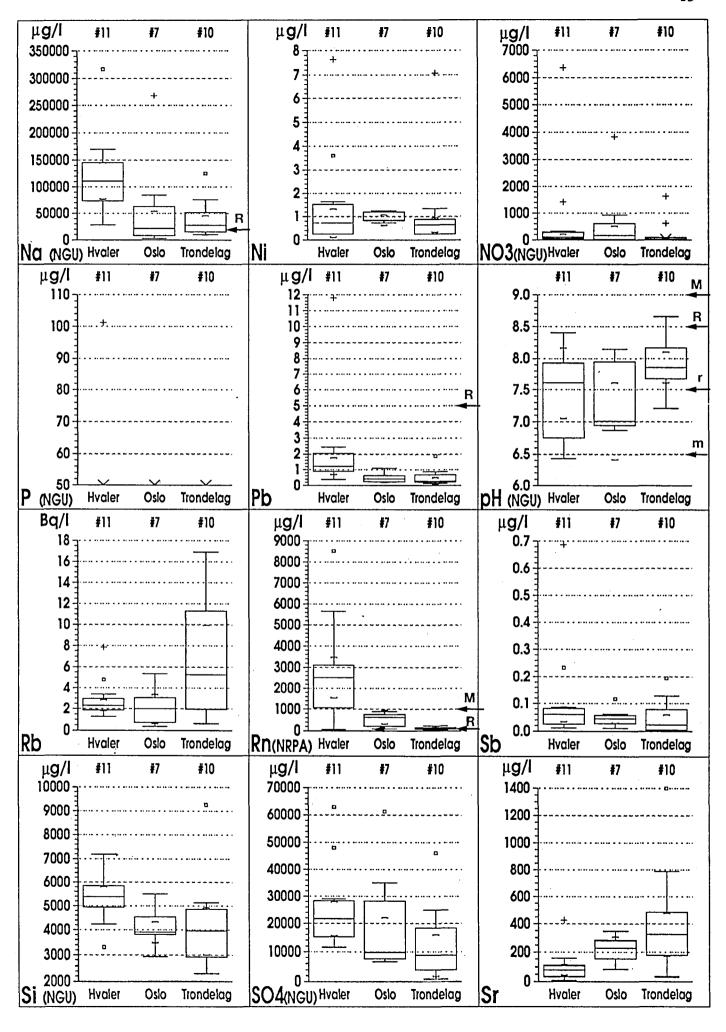
In the following analysis, ICP-OES values for major elements (Na, K, Ca, Mg and elements not analysed by ICP-MS, such as Zr) are used, while ICP-MS results for field acidified samples are used for trace elements (including Cr and V). Analysis results below the detection limit were set to half the detection limit for the purposes of statistical analysis.

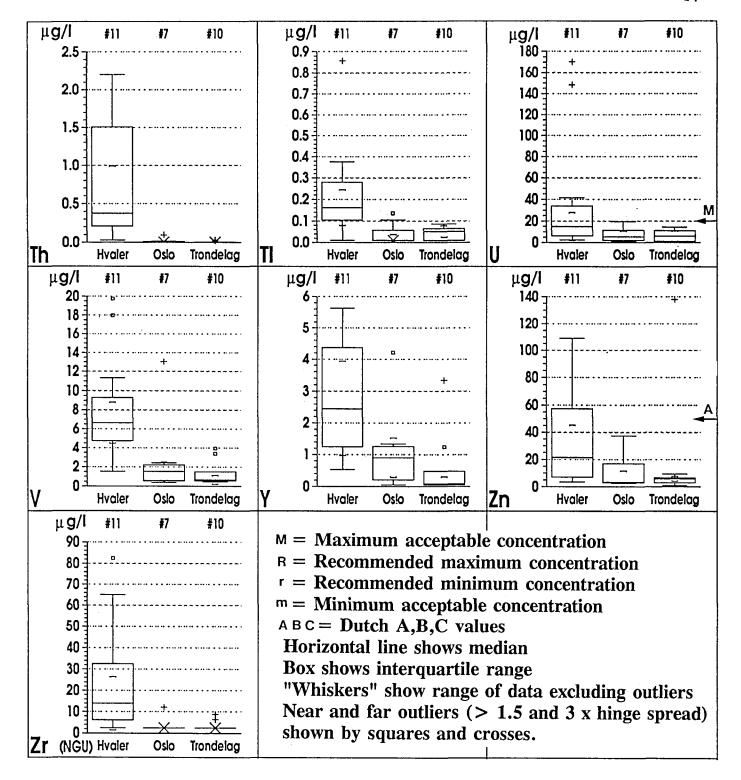
## 4.2 Water types

Ionic balances were calculated for all samples on the basis of major ions, fluoride, nitrate, manganese, iron (designated +II) and aluminium (designated +III). Two thirds of the samples exhibited cation/anion imbalances of less than 5 %. Only 4 samples exhibited imbalances of more than 10 %, and none more than 15 %. Groundwaters from the Iddefjord Granite of Hvaler were all either Na-HCO<sub>3</sub> or Na-Cl waters (Appendix 3). The samples from rhomb porphyry lavas were calcic in character: Ca-HCO<sub>3</sub>-(Cl). The samples from Trøndelag are typically Na-HCO<sub>3</sub>-(Cl) or Ca-HCO<sub>3</sub> in character, reflecting their more non-marine character.









Groundwater from Oslofjord's Precambrian gneisses ranges from Ca-HCO<sub>3</sub> through Na-HCO<sub>3</sub> to NaCl. The Quaternary samples are of Ca-HCO<sub>3</sub> type (Trøndelag) and Na-Cl type (Hvaler).

The results of the F, Ca, NO<sub>3</sub>, Cl, and Na analyses for each borehole are given in Table 1. Cl can be regarded as an indicator of marine influence, the parameter Na - Cl as a coarse indicator of water-rock interaction (Banks and others 1993b), and nitrate as one indicator of anthropogenic impact.

### 4.3 Trends among geographical provinces

The wells are divided up into three geographical groups which reflect geological provinces: (a) = Hvaler, (b) = Oslo region (excluding Hvaler) and (c) = Trøndelag. Maximum, median, minimum and mean values of all parameters for the three geographical areas are shown in Table 2. All major and trace elements have been examined using box plots (Fig. 4) for each of the three geographical groups, and it is revealed that many parameters show considerably higher concentrations in the Hvaler area than otherwise in the Oslo area, with the Trøndelag area often showing the lowest concentrations. Parameters which follow this pattern are Rn, U, Th, Si, Al, Fe, Na, Cd, Cu, Zn, Cr, V, F, Cl, SO<sub>4</sub>-, Y, Be and Mo. Parameters such as Bi, La, E.C., Tl, Zr, Pb and B show elevated levels for the Hvaler area, but little significant difference between Oslo and Trøndelag.

Parameters which show the opposite trend, with highest concentrations in the apparently more calcareous geological environment of Trøndelag include Ca, Mg, Sr, Rb, Cs, pH and alkalinity.

Other parameters, namely Br, Li, Mn, K, P, NO<sub>3</sub>, Sb, Ba, As and Ni, appear to show no systematic trend between the three areas.

### 5. CORRELATION STUDIES

## 5.1 Correlations with lithology

In order to interpret the data, the wells been divided into 8 lithological groups as follows:

- 1 = Quaternary wells
- 2 = rhomb porphyry basalts (Oslofjord)
- 3 = metadiorite (Trøndelag)
- 4 = metasediments (schists, meta-arkose, Trøndelag)
- 5 = granodiorite gneiss (Trøndelag)
- 6 = Precambrian gneiss (Trøndelag)
- 7 = Precambrian gneiss (Oslofjord)
- 8 = Iddefjord granite (Hvaler)

The lithologies are chosen such that they exhibit a general increase in acidity and thus in expected incompatible element content. Fig. 5 illustrates that similar trends to those mentioned above can be noted for the eight lithological subdivisions. Correlation coefficients have been calculated for the logs of the various parameters with lithology number, and the highest correlations are found ( $r \ge 0.7$ ) for Rn, B and Na. Weaker correlations with lithology number ( $r \ge 0.5$ ) are found for U, Th, Y, F, V, Cl, Cr, Cd, Br, Zr, EC, Pb, Tl, La, Be (in order of descending r).

What such analyses of lithological and geographical trends do not reveal, however, are the hydrogeological reasons for elevated concentrations of many elements in the Hvaler/Iddefjord granite area. Although none of the geographical areas are located far from the coast, the Trøndelag wells are least marine dominated and Hvaler (being an island group) is most coastal in character. Chloride concentrations, for example, are not derived from lithology (as demonstrated in Banks and others 1993b) but are marine-related. Species such as sulphate will be largely marine-related, but also be influenced by elevated levels of anthropogenic fallout in southeast Norway as compared to Trøndelag. There are thus at least three separate controlling trends from Trøndelag through Oslofjord region to Hvaler:

- (i) Increasing geological occurrence of incompatible elements
- (ii) Increasing marine influence
- (iii) Increasing fallout from atmospheric contamination

Any correlation between the measured parameters and lithology may therefore:

(i) be purely coincidental (i.e. non-geological), such as that between Cl and lithology

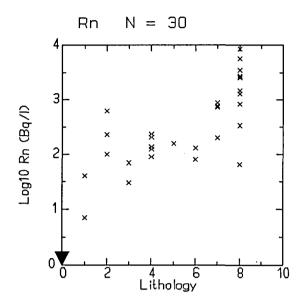
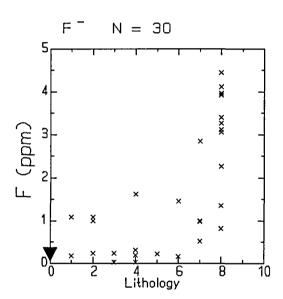
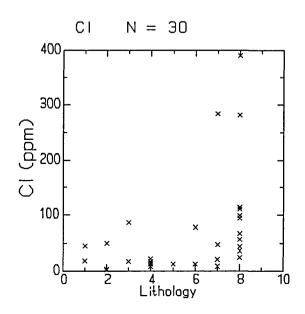


Figure 5. Variation of Rn, F and Cl with lithology number. Black triangles show limits of detection, where relevant.

An explanation of the lithology number can be found in the text.





- (ii) reflect a covariation in element concentrations with respect to geological environment covariations between "incompatible" late-melt elements in acidic rocks. This is probably at least partly true for those parameters displaying the stronger correlations with lithology number (Rn, B, Na, F, U, Y and Th). The lithological derivation of Na, F and B is revealed from more detailed studies of the Iddefjord Granite (Banks and others 1993b).
- (iii) reflect a direct causitive relationship, e.g. expected relationships between U and Rn (the one being derived from the other), between HCO<sub>3</sub> and U (if the one complexes with and mobilises the other), between pH and many heavy metals (decreased pH mobilising heavy metals in the aquifer or from metal pipework), or between Ca and F (the limiting solubility of fluorite CaF<sub>2</sub> potentially leading to an inverse correlation between these elements).
- (iv) be due to analytical interference (e.g. Cr or V with salinity).

Correlation matrices have been produced between all elements, for the entire data set (N = 30) and for purely the Iddefjord granite lithology (N = 11), for both untransformed and log-transformed data. Correlation coefficients over 0.7 are arbitrarily regarded as "relatively high" for the purposes of this paper.

#### **5.2 Radioactive elements**

Generally speaking, the radioactive elements U, Th and Rn showed only rather weak correlations with other elements (Banks and others 1993c,d). The strongest, most persistent correlations were found between Th and Bi, La and Y (the latter two being chemically analogous to the actinides). Weaker, but persistent, correlations were found for Rn with F, B and Zr. Uranium showed moderate correlations with Mo, As and Sb (Fig. 6). These correlations probably reflect covarying degrees of enrichment in the host rocks (i.e. type ii above). No significant or persistent correlations were found between uranium and major parameters which might be expected to affect mobility, such as alkalinity, Cl, V or pH (i.e. type iii above).

Surprisingly, only rather weak correlations between U, Rn and Th themselves were found, and these correlations only occurred within the entire data set, reflecting the coarse-scale covariation in host rock contents of these elements. Within a single lithology (the Iddefjord Granite) these correlations disappear, indicating that the hydrochemistry is dominated by hydrodynamic factors and interaction between various dissolved species, rather than purely by lithological content of U and Th (Banks and others 1993c).

## 5.3 Major elements

Strong correlations were found between the members of the marine-related parameter group, namely Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, Mg, Na and B. Banks and others (1993b) have demonstrated that B, Na and

Mg have both a marine and lithological component. A lesser degree of intercorrelation was also found among the alkaline-earth elements; Sr, Ca, Mg, Ba and Rb, and also Cs. These were found both for the total (N=30) data set and the (N=11) set from Hvaler.

A strong correlation was found between pH and alkalinity for Hvaler, but a lower one (r = c.0.65) for the total set, indicating that the correlation is not just due to covariation with lithology. For the Hvaler data, correlations ( $r \ge 0.7$ ) were found for alkalinity with B and F. A weaker correlation was also found between alkalinity and Na. This may illustrate production of HCO<sub>3</sub> during weathering of Na, B and F-containing minerals in the granite by CO<sub>2</sub>.

Some parameters show little correlation with other parameters or lithology. Among these is nitrate, concentrations of which are significantly higher in southern Norway than mid-Norway (Fig. 4). This indicates that a significant component is probably derived from anthropogenic fallout ("acid deposition") or possibly by diffuse agricultural activity (although this is probably equally dominant in Trøndelag as around Olsofjord). Outliers above 1 mg/l may indicate a more immediate source of contamination from e.g. agriculture or sewer leakage.

## 5.4 Minor parameters

For the Hvaler data set, fluoride shows relatively high correlations with B, pH, alkalinity, and a weaker correlation with Na, indicating its lithological origin. The correlation with pH has been interpreted (Englund and Myhrstad 1980, Banks and others 1993b) as evidence of anion exchange at high pH with OH on amphiboles and sheet silicates. A negative correlation of -0.51 was found between Ca and F for Hvaler, possibly indicating fluorite (CaF<sub>2</sub>) solubility as a control on fluoride concentrations in the Iddefjord Granite.

For the data set as a whole, a correlation (r = c.0.7) between Rn and F was found, indicating that the two health-related parameters are often associated with similar lithologies.

#### 5.5 Trace elements

For the entire data set, good correlations were found between the members of the group of metals Cr, Cd, V, Pb and Tl. Cr, Tl and V also show relatively high correlation with members of the marine group of parameters. The following relatively high correlations were also noted: La with Pb, Cd, Bi, Be and Y; Sb with Mo and As; Fe with Ni; Al with Co; Zr with Tl.

The correlations of Cr, Tl and V with marine parameters appear at first sight to be merely coincidental; i.e. the metal rich Iddefjord Granite lies in a marine environment. However, within the Hvaler set of data alone, the correlations persist as strongly as ever, and include now Cu and Cd in addition to Cr, V and Tl, thus negating this hypothesis. Thus, three further hypotheses can be suggested:

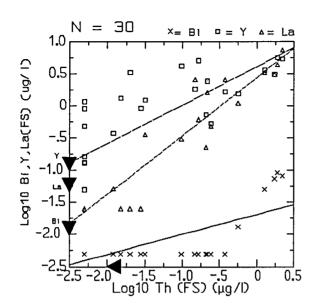


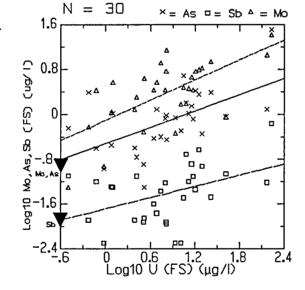
Figure 6. Plots displaying covariation of (a) Th with Bi, La and Y; (b) of U with Mo, As, Sb and (c) of Rn with F and B. Black triangles show limits of detection, where relevant.

Correlation coefficients (Log<sub>10</sub> parameters)

Bi:Th 
$$r = 0.73$$
  
Y:Th  $r = 0.78$   
La:Th  $r = 0.95$ 

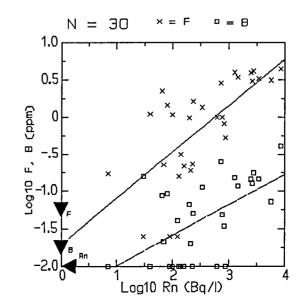
Correlation coefficients (Log<sub>10</sub> parameters)

As:U r = 0.56Sb:U r = 0.41Mo:U r = 0.65



Correlation coefficients (Log10 parameters)

Rn:F r = 0.67Rn:B r = 0.56



- (i) that the metals Cr, Tl, V, Cu and Cd are complexed/mobilized by one or more of the marine parameters.
- (ii) that the metals are derived from seawater. This hypothesis can be rejected immediately from the fact that the most saline water on Hvaler was c. 2 % seawater, and by multiplying concentrations of these metals in standard seawater (e.g. Horne 1969) by 0.02.
- (iii) that the analysis of these metals is subject to interference in chloride-rich groundwaters (i.e. an analytical artifact).

The analytical discrepancies between ICP-OES and ICP-MS data suggest that the last explanation is the most probable, at least for the elements Cr and V.

Within the Hvaler data set alone the same general correlations as mentioned above can be observed: intercorrelation between Cd, Cu, Cr, V and Tl; correlation of La with Y, Bi, Pb, Tl, Al; of Sb with As, Mo, Rb and Cs; of Mo with Sb, As, Li and Rb. Negative correlations of F with Zn, Ni, Co and Ba are observed. Negative correlations (with r > 0.4) are also observed between pH and Co, Fe, Ba, Mn, Al, Y, La, Zn and Ni, possibly reflecting higher solubility at low pH.

# 6. BACKGROUND CONCENTRATIONS IN A HEALTH CONTEXT

Table 3 indicates the Norwegian drinking water standards (SIFF 1987) for many of the analysed parameters. Where Norwegian limits are not specified, European Community limits are quoted. Dutch A,B,C values for assessing contamination of groundwater are also given. These limits are shown, where appropriate on Figure 4.

It will be noted that a significant proportion of the water samples from the 28 bedrock boreholes exceed accepted drinking water standards for several parameters.

### 6.1 Major parameters

36 % of the boreholes on Hvaler exceed 100 mg/l chloride, reflecting the coastal environment. All of the boreholes at Hvaler and over 50 % of the boreholes around Oslofjord and in Trøndelag exceed 20 mg/l sodium. This is one of the most problematic parameters for groundwater in bedrock aquifers, particularly in coastal areas. Comparison of box-plots for sodium and chloride reveals, however, that the sodium is not entirely derived from marine influence, but that a significant component comes from dissolution of sodium-bearing minerals such as plagioclase.

As regards calcium, the majority of boreholes fall outside the 15 - 25 mg/l guidelines. In Hvaler, the majority are too low in calcium; in Oslo and Trøndelag rather too high. As regards alkalinity, almost all boreholes exceed the 1 mmol/l guideline limit, alkalinities, particularly in Trøndelag commonly reaching as high as 3 - 5 mmol/l. pH values fall almost entirely within the SIFF (1987) guideline range of 6.5 - 9, although many boreholes in Hvaler and Oslofjord fall below the guideline value of 7.5 for good drinking water.

Sulphate, magnesium, nitrate and potassium satisfy drinking water standards for all samples.

## **6.2 Minor parameters**

The majority of boreholes in the Hvaler and Oslofjord areas exceed the 100  $\mu$ g/l limit for acceptable quality for manganese. The large majority of boreholes on Hvaler exceed 1.5 mg/l fluoride, a fact noted previously in Hvaler area (Banks and others 1993b), where concentrations of up to 6.5 mg/l have been measured. Even higher concentrations, and examples of dental fluorosis, have been documented in crystalline bedrock groundwater in other areas of Norway (Prof. Kjell Bjorvatn, pers. comm.).

As regards iron and aluminium, an evaluation depends on which analysis results one accepts. According to ICP-MS results from NILU, almost all samples exceed the upper limit of 200  $\mu$ g/l

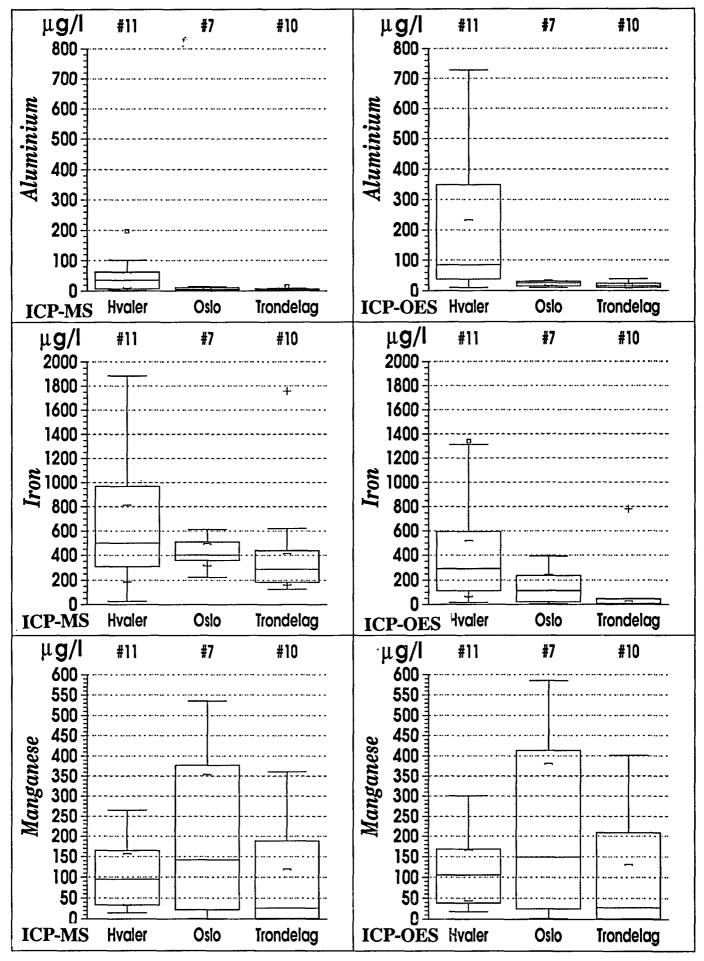


Figure 7. Plots comparing Fe, Al and Mn determinations using differing analytical techniques.

for iron. According to ICP results from NGU, the majority of waters from Hvaler exceed this limit, while over 50 % of those from Oslofjord exceed the lower limit of 100  $\mu$ g/l. For aluminium, the majority of groundwaters do not exceed 100  $\mu$ g/l. In Hvaler, however, according to NGUs results, almost half of the samples do exceed this, the median lying at 84  $\mu$ g/l (Fig. 7).

### **6.3 Trace parameters**

The majority of samples satisfy drinking water standards for elements such as Pb, Cu, Zn, Cd, Ni, Sb, Ba and As, although individual outliers exceed the recommended limits for e.g. As and Pb. Around 36 % of samples from the Hvaler area do, however, appear to exceed the lower guide limit for good drinking water of 20  $\mu$ g/l chromium, according to ICP-MS results (see above). For the other two geographical areas, chromium is unproblematic. As discussed above, however, the disturbingly high values in the ICP-MS data set for Cr and V are likely to be due to analytical interference in high salinity groundwaters (see Fig. 8). The ICP-OES data, giving values of < 10 ppb and < 5 ppb, respectively, for all samples are more believable for these elements.

For many trace components, including known toxins such as Be and Bi, no drinking water standards have been developed, and an assessment of the significance of the concentrations recorded in this study is not possible at this juncture.

### 6.4 Dutch A,B,C values

Considering that the Dutch A,B,C values are developed in a completely different geological context to Norway, there is a surprising correspondance between the A (background) value and typical concentrations in bedrock groundwater for elements such as Mo, Zn, Cr, Ba and Br. For others, such as Cu, As, Cd and Co, the A value overestimates measured concentrations. The only real conflict arises with fluoride at Hvaler, where the majority of samples exceed the B value and some exceed the C value.

#### Independent variable: NGU

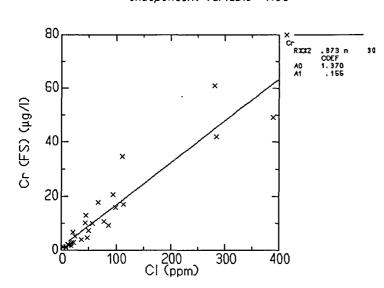
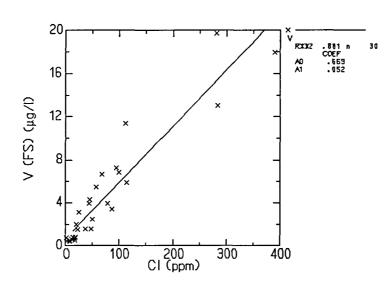
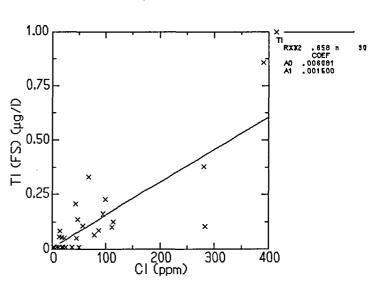


Figure 8. Plots of (a) Cr vs. Cl, (b) V vs. Cl and (c) Tl vs. Cl. Metal analyses by ICP-MS, Cl analyses by NGU. Best fit lines are shown. Detection limit for Tl is  $0.02 \mu g/l$ .

Independent variable : NGU



Independent variable: NGU



## 7. CONCLUSIONS

A data set of 28 groundwater samples from groundwater boreholes in crystalline bedrock have been collected from the Trøndelag, Oslofjord and Hvaler areas of Norway. The most serious problems with regard to drinking water standards have been discovered in the Hvaler area, where the majority of samples exceed standards for the health-related parameters fluoride (up to 4.5 mg/l), radon (up to 8500 Bq/l) and uranium (up to 170  $\mu$ g/l). Infringement of aluminium standards may also be common, but difficulty has been experienced in obtaining consistent analysis results. Elevated values of other potentially toxic parameters such as Be (up to 2  $\mu$ g/l) and Th (up to 2.2  $\mu$ g/l) are also noted, although drinking water standards are not fixed for these. Infringements of the more "aesthetic parameters" alkalinity, iron, and manganese occur for many samples in all areas. Calcium values are too low with respect to standards in Hvaler and generally too high in the other areas.

The parameters Fe, Al, Cr and V have shown significant discrepancies between ICP-MS and ICP-OES data sets. The degree of discrepancy can, in the case of Fe, Al and Cr affect whether the water satisfies drinking water standards or not. It is thus of the utmost importance to recognize that sample preparation, storage and analytical methodology affect analytical results. In the case of Cr and V, high values obtained using ICPMS techniques appear to be caused by interference in high salinity waters.

Most parameters show systematic variations with geological/geographical province. Many parameters, including Rn, U, Th, Si, Al, Fe, Na, Cd, Cu, Zn, Cr, V, F, Cl, SO<sub>4</sub>-, Y, Be, Mo, Bi, La, E.C., Tl, Zr, Pb and B exhibit generally higher concentrations in the Precambrian Iddefjord Granite of Hvaler, which is rich in late-melt incompatible elements and is a marine dominated environment. Many of these parameters show lowest concentrations in the Trøndelag area. The apparently more calcareous metasediments and gneisses of Trøndelag yield groundwater with elevated values of Ca, Mg, Sr, Rb, Cs, pH and alkalinity. The gneisses and rhomb prophyry lavas of Oslofjord typically yield intermediate concentrations for many parameters.

Correlation studies provide tentative evidence for covariance in groundwater within groups of elements such as (Na, B, F, alkalinity), (Ca, Sr, Mg, Ba, Rb, Cs), (Cl, EC, Br, SO<sub>4</sub><sup>-</sup>, Na, B), (As, Sb, Mo, Rb), (Th, Bi, La, Y, Be), (Cu, Cd, Cr, Pb, V, Tl). There is also tentative evidence that a marine environment may lead to mobilisation (e.g. complexing with chloride) of Cr, Tl, Cu, V and Cd, although this is more likely to be an artifact of analytical interference.

Dutch A,B,C values for groundwater seem to function surprisingly well in the Norwegian bedrock groundwater environment, the A value often corresponding with typical measured concentrations. The only serious discrepancy is with fluoride, which can exceed the C value on Hvaler. The results of the study nevertheless show that host-rock lithology has a major influence on hard-rock groundwater composition. To avoid problems with unsuitable drinking water standards it would be

desirable to establish a larger database of groundwater compositions in various Norwegian hard-rock lithologies.

The results suggest that it may be dangerous to work with fixed "action level" values for groundwater in general. This could easily result in quite a large number of boreholes being classified as unsuited for human consumption although the water may, in many respects, be healthier than most surface waters. Similar problems have been encountered with action levels for soils which have been established without taking account of lithology (e.g. Reimann 1989). Further research should focus on defining realistic action levels for toxic elements, where geological pragmatism and cost-effectiveness is balanced against toxicological data, and on documenting regional trends in hard-rock groundwater composition.

## 8. ACKNOWLEDGMENTS

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Note: Out of respect for limited distribution of data on private water supplies, the raw data from this study is documented in a confidential NGU report (Banks 1993).

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Table 1. Details of samples taken during the Norwegian pilot study. Samples 8 - 19 from Hvaler, 1 - 7 Oslofjord, 20 - 30 Nord Trøndelag. \* = angled borehole.

Sample nr.	Lithology (Class)	Depth (m)	F (ppm)	NO <sub>3</sub> - (ppb)	Ca <sup>++</sup> (meq/l)	Na <sup>+</sup> (meq/l)	Cl <sup>-</sup> (meq/l)
1	Precambrian gneiss	60 m	0.52	< 50	1.21	0.57	0.23
2	Precambrian gneiss	90 m	0.99	< 50	2.5	1.80	1.34
3	Precambrian gneiss		0.98	< 50	1.01	3.7	0.58
4	Permian rhomb porphyry	60 m	1.1	170	1.29	0.13	0.07
5	Permian rhomb porphyry	25 m	0.23	3800	1.96	0.93	1.39
6	Permian rhomb porphyry		1.0	930	1.42	0.14	0.09
7	Precambrian gneiss	65-100 m (2 wells)	2.9	300	0.84	11.7	8.0
8	Iddefjord granite		3.1	< 50	0.52	3.1	1.03
9	Iddefjord granite		3.4	250	1.04	2.6	0.69
10	Iddefjord granite	c.70 m	3.1	130	0.25	4.1	1.90
11	Iddefjord granite	80 m	4.4	330	0.67	13.8	11.0
12	Iddefjord granite	80 m	2.3	99	0.14	3.3	2.8
13	Iddefjord granite	80 m *	1.4	1400	2.3	7.3	7.9
14	Iddefjord Granite	101 m	3.9	< 50	0.18	5.1	2.7
15	Iddefjord granite	70 m	0.82	6400	0.69	1.23	1.23
16	Iddefjord granite	c. 45 m	4.0	63	0.07	4.8	1.61
17	Iddefjord granite	60 m	4.1	62	0.16	7.4	3.2
18	Iddefjord granite	c. 80 m	3.3	< 50	0.84	5.3	3.1
19	Quaternary sand.	2.5 m	0.17	< 50	0.20	0.82	1.27
20	Precambrian-cambrian garnet-mica schist	52 m	<0.05	1600	1.12	1.00	0.40
21	Precambrian-cambrian garnet-mica schist	120 m	0.19	< 50	0.74	2.3	0.36
22	Precambrian-cambrian quartz and garnet-mica schist	25.5 m	1.6	620	0.92	1.78	0.49
23	Precambrian-cambrian mica schist	75 m	<0.05	< 50	4.9	0.43	0.63
24	Ordovician(?) metadiorite	80 m	< 0.05	88	0.53	5.4	2.4
25	Precambrian gneiss	80 m	1.5	< 50	0.88	3.3	2.2
26	Late Pre€-palæozoic metaarkose	120 m	0.31	< 50	2.7	0.45	0.22
27	Quaternary sediments	1 m	1.1	8700	2.7	0.37	0.52
28	Ordovician(?) metadiorite	119 m	0.23	< 50	2.0	1.42	0.50
29	Pre€€. granodioritic gneiss	100 m	0.22	< 50	1.69	0.86	0.34
30	Precambrian granitic gneiss	71 m	0.16	< 50	1.34	0.67	0.34

Table 2. Statistical characteristics of each parameter measured in the pilot study of groundwater from bedrock boreholes. For each box:

All samples Hvaler
N = 28 N = 11

Oslofjord Trøndelag
N = 7 N = 10

	Maximur	n	Median		Minimu	m	Mean		St.Dev.	
Ag-NGU ppb	All samp	All samples contain less than 10 ppb								
Al-NGU	730	730	26	84	<20	<20	93	210	170	230
ppb	31	39	25	<20	<20	<20	23	18	9	10
Al-NILU	200	200	6.7	36	<1	1.8	23	49	42	59
μg/l	15	15	6.6	3.1	1.4		7.2	4.8	5.4	4.4
Alk-NGU	5.49	3.79	2.76	2.75	0.88	0.88	2.74	2.42	1.05	0.96
mmol/l	4.25	5.49	1.90	3.00	1.54	2.12	2.60	3.19	1.16	1.00
As-NILU	32	32	0.89	1.0	<0.1	0.25	2.2	4.0	6.0	9.4
μg/l	2.6	4.8	0.36	0.96	<0.1	0.11	0.63	1.3	0.90	1.4
B-NGU	410	410	58	130	<20	35	86	140	91	97
ppb	250	160	<20	21	<20	<20	58	42	89	49
Ba-NGU	210	22	7.5	7.5	<2	2.6	24	9.0	45	6.5
ppb	140	210	32	3.2	<2	<2	42	29	46	65
Ba-NILU	230	30	10	11	0.1	5.1	28	13	50	8.0
μg/l	150	230	32	5.3	3.0	0.1	46	32	51	71
Be-NILU	2.0	2.0	0.063	0.52	<0.05	<0.05	0.29	0.68	0.52	0.68
μg/l	0.12	0.073	0.064	<0.05	<0.05	<0.05	0.066	0.030	0.034	0.015
Bi-NILU μg/l	0.092 <0.01	0.092 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.015 <0.01	0.031 <0.01	0.025	0.036
Br-NGU	920	850	78	180	<20	<20	170	250	230	250
ppb	920	240	22	68	<20	27	170	98	330	78
Ca-NGU	97	46	19	10	1.3	1.3	24	12	20	13
ppm	50	97	26	25	17	11	29	34	12	26
Ce-NGU ppb	All samp	les contain le	ss than 50	ppb						
CI-NGU	390	390	40	95	2.4	25	72	120	95	110
ppm	280	86	21	16	2.4	7.8	59	28	100	29
Cd-NILU μg/l	0.17 0.043	0.17 0.022	0.019 0.014	0.059 <0.01	1	<0.01 <0.01	0.038 0.019		0.045 0.013	0.050 0.006
Co-NILU	0.99	0.99	<0.1	0.13	<0.1	<0.1	0.20	0.32	0.26	0.37
μg/l	0.25	0.56	<0.1	<0.1	<0.1	<0.1	0.10	0.13	0.077	0.16
Cr-NILU	61	61	6.0	17	0.94	4.2	12	22	16	18
μg/l *	42	11	4.8	2.2	0.94	1.6	9.2	3.7	15	3.4
Cs-NILU	6.5	0.26	<0.05	<0.05	<0.05	<0.05	0.49	0.072	1.3	0.075
μg/l	0.65	6.5	<0.05	0.43	<0.05	<0.05	0.14	1.2	0.23	2.0
Cu-NILU μg/l	36 36	28	2.3 2.5	3.4 1.6	<0.1 0.75	0.89	5.5	7.7 2.2	8.8	9.4 2.4

							T :		1	
EC-NGU μS/cm	1610 1470	1610 620	430 340	480 360	160 160	240 260	510 480	650 390	350 460	400 130
F-NGU ppm	4.4 2.9	4.4 1.6	1.0	3.3 0.21	<0.05 0.23	0.82 <0.05	1.6 1.1	3.1 0.43	1.5 0.84	1.2 0.59
Fe-NGU	1.3	1.3	0.070	0.29		0.016	0.25	0.46	0.37 0.15	0.48 0.24
ppm	0.39	0.78	0.11	<0.01	ļ	<0.01	0.15	0.092	<u> </u>	
Fe-NILU mg/l +	1.9 0.61	1.9 1.8	0.39 0.40	0.50 0.29	<0.05 0.22	<0.05 0.13	0.53	0.69 0.44	0.45	0.54 0.48
K-NGU ppm	10 10	7.3 9.3	2.5 <0.2	2.9 2.8	<0.2 <0.2	<0.2 <0.2	2.9 2.2	3.2 3.2	2.7 3.7	2.2
La-NILU µg/l	7.4 0.31	7.4 0.36	<0.05 <0.05	1.6	<0.05 <0.05	<0.05 <0.05	0.93 0.069	2.3 0.059	1.8	2.2 0.11
Li-NILU µg/l	17 11	14 17	5.1 3.3	5.4 5.0	1.0	1.5 1.9	6.2 4.5	7.0 6.4	4.1	4.0
Mg-NGU	21	10	5.0	2.5	0.73	0.73	5.8	3.5	4.3	2.9
ppm	10	21	5.5	8.4	2.8	1.9	5.6	8.4	2.7	5.3
Mn-NGU ppb	590 590	300 400	69 150	110 28	<2 <2	18 <2	140 230	110 110	160 240	90 160
Mn-NILU μg/l	540 540	260 360	63 140	95 27	<1 <1	15 <1	130 210	100 100	150 220	82 140
Mo-NILU	26	26	2.9	3.7	0.12	0.91	4.7	6.5	5.3	7.2
μg/I	14	4.6	5.8	1.5	1.1	0.12	6.1	1.8	4.2	1.5
Na-NGU ppm	320 270	320 130	55 21	110 28	3.0	28 9.9	78 62	120 40	78 95	78 36
Ni-NILU μg/l +	7.6 1.3	7.6 7.1	0.77 0.84	0.72 0.64	<0.5 0.72	<0.5 <0.5	1.3 0.98	1.6 1.2	1.8 0.23	2.2 2.1
NO <sub>3</sub> -NGU	6.4 3.8	6.4 1.6	0.063 0.17	0.099	<0.05	<0.05 <0.05	0.59 0.76	0.80 0.25	1.4	1.9 0.52
ppm P-NGU ppb			L			Ivaler with 1	<u> </u>	· · · · · · · · · · · · · · · · · · ·		
PO <sub>4</sub> 3-NGU ppb		es contain le			pie Hoili i	Ivaici with I	.от рро			
Pb-NILU	12	12	0.68	1.2	0.12	0.38	1.2	2.3	2.2	3.2
μg/l	1.1	1.9	0.68	0.28	0.12	0.12	0.49	0.51	0.34	0.54
pH-NGU	8.7 8.2	8.4 8.7	7.7 7.0	7.6 7.9	6.4 6.9	6.4 7.2	7.6 7.4	7.4 7.9	0.61 0.59	0.72 0.40
Rb-NILU μg/l	17 5.4	7.9 17	2.5 2.0	2.3 5.3	0.38 0.38	1.3 0.63	4.0	2.9 6.4	3.9 1.8	1.9 5.3
Rn-NRPA Bq/l	8500 890	8500 240	290 630	2500 130	30 100	65 30	1200 510	2700 130	1900 320	2500 63
Sb-NILU	0.69	0.69	0.048	0.060	<0.01		0.079		0.13	0.20
μg/l	0.12	0.20	0.045	0.000	0.011	<0.012	1	0.052	0.035	0.064
Sc-NGU ppb	All sample	es contain le	ss than 2 p	ppb						
Si-NGU	9.3	7.2	4.6	5.4	2.3	3.3	4.7	5.3	1.5	1.0
ppm	5.5	9.3	3.9	4.0	2.9	2.3	4.2	4.3	0.82	2.0
SO <sub>4</sub> =-NGU	63 61	63 46	15 9.8	22 8.8	0.82 6.6	12 0.82	20 21	26 13	17 20	16 14

Sr-NGU	2900	360	160	76	9.8	9.8	290	92	540	99
ppb	310	2900	210	300	77	34	200	560	85	840
Sr-NILU	1400	430	170	80	10	10	250	100	290	120
μg/l	350	1400	230	320	86	32	220	430	95	400
Th-NILU	2.2	2.2	0.018	0.38	<0.01	=	0.33	0.81	0.63	0.81
μg/l	0.097	0.032	<0.01	<0.01	<0.01		0.021	0.009	0.034	0.009
Ti-NGU μg/l	All sampl	es contain le	ess than 10	ppb						
TI-NILU	0.86	0.86	0.062	0.16	<0.02		0.12	0.23	0.18	0.24
μg/l	0.14	0.086	<0.02	0.052	<0.02		0.042	0.044	0.055	0.031
U-NILU	170	170	7.6	15	0.59	2.4	20	41	40	60
μg/l	20	14	5.5	5.9	0.74	0.59	7.6	6.5	7.4	5.3
V-NILU	20	20	2.2	6.6	0.41	1.5	4.4	8.2	5.3	5.9
μg/l *	13	4.0	1.5	0.66	0.41	0.48	2.9	1.3	4.5	1.3
Y-NILU	5.6	5.6	0.92	2.5	<0.1	0.53	1.6	2.8	1.8	1.9
μg/l	4.2	3.3	0.91	<0.1	<0.1	<0.1	1.2	0.56	1.4	1.0
Zn-NILU	140	110	5.9	21	0.93	3.6	24	38	36	37
μg/l	37	140	3.4	5.9	2.5	0.93	12	18	15	42
Zr-NGU	83	83	<5	14	<5	<5	12	25	20	27
μg/l	12	8.8	<5	<5	<5	<5	3.9	3.5	3.6	2.2

Table 2. Statistical characteristics of each parameter measured in the pilot study. For each box, top left = whole sample group of bedrock boreholes (N=28), top right = Hvaler (N=11), bottom left = Oslofjord (N=7), bottom right = Trøndelag (N=10).

- -NILU = ICP-MS analysis
- -NGU = analysis at NGU
- -NRPA = analysis at NRPA
- + = subject to intereference with Ca
- \* = subject to intereference with Cl

ICP-OES analyses (NGU) give V < 5 ppb and Cr < 10 ppb for all samples.

Table 3. Drinking water limits, and Dutch contamination characterization values for a range of toxic elements.

Parameter	Drinking water limits	Dutch A,B,C values
A 1111-14		, ,
Alkalinity	0.6 - 1.0 mmol/l (SIFFG)	
Aluminium	< 0.1 mg/l* (SIFF)	
Antimony	$< 10 \ \mu g/l \ (EC)$	
Arsenic	$< 10 \mu g/l (SIFF)$	10, 30, 100 μg/l
Barium	< 1 mg/l (SIFF)	50, 100, 500 μg/l
Bromide		100, 500, 2000 μg/l
Boron	$< 300 \mu g/l (SIFF)$	
Cadmium	$< 1 / 5 \mu g/l$ (SIFFG/A)	1, 2.5, 10 μg/l
Calcium	15 - 25 mg/l (SIFFG)	]
Chloride	< 100 / 200 mg/l (SIFFG/A)	
Cobalt		20, 50, 200 μg/l
Copper	< 100 / 300 μg/l (SIFFG/A)	20, 50, 200 μg/l
Chromium	< 10 / 50 μg/l (SIFFG/A)	20, 50, 200 μg/l
Fluoride	< 1.5 mg/l (SIFF)	0.3, 1.2, 4.0 mg/l
Iron	< 100 / 200 μg/l (SIFFG/A)	
Lead	< 5 / 20 μg/l (SIFFG/A)	20, 50, 200 μg/l
Magnesium	< 10 / 20 mg/l (SIFFG/A)	
Manganese	$< 50 / 100 \mu g/l (SIFFG/A)$	
Molybdenum		5, 20, 100 μg/l
Nickel	< 50 μg/l (EC)	20, 50, 200 μg/l
Nitrate	< 11 / 44 mg/l (SIFFG/A)	
Potassium	< 12 mg/l (EC)	
pH	7.5-8.5 / 6.5-9.0 (SIFFG/A)	
Radon	< 100 / 1000 Bq/l (Sweden)***	
Sodium	< 20 mg/l (SIFFG)	
Sulphate	< 100 mg/l (SIFF)	
Uranium	< 20 μg/l (Canada)***	
Zinc	< 300 μg/l (SIFF)	50, 200, 800 μg/l

<sup>\* =</sup> after chemical treatment \*\* = see Banks and others (1993c)

SIFF = Norwegian maximum value, SIFFG = Norwegian recommended value for good drinking water SIFFG/A = Norwegian recommended and maximum acceptable values. All after SIFF (1987)

EC = European Community Standard

Dutch A level implies uncontaminated background concentration, B level implies contamination present and further investigation required, C implies significant contamination present and cleanup required

# Appendix 1. Examples of effect of field acidification on samples for ICP-MS analysis

FS = field filtered and acidified.

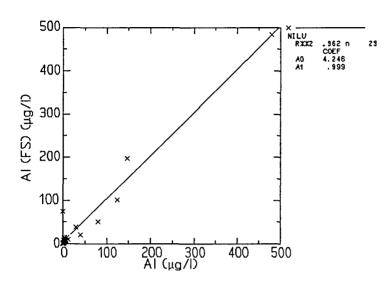
N = 29 (sample 13 omitted - not filtered/acidified in field)

Detection limits - NILU (ppb)

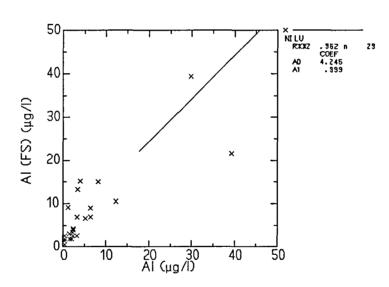
Al	1
As	0.1
Ba	0.05
Be	0.05
Bi	0.01
Ca	-
Cd	0.01
Co	0.1
Cs	0.05
Cu	0.1
Cr	-
Fe	50
La	0.05
Li	-
Mg	-
Mn	1
Mo	0.1
Ni	0.5
Pb	-
Rb	-
Sb	0.01
Th	0.01
T1	0.02
U	-
Y	0.1
Zn	0.5

<sup>- =</sup> detection limit below lowest measured sample

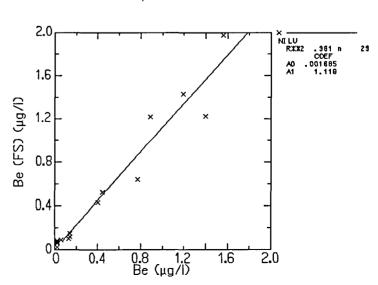
Independent variable: NILU

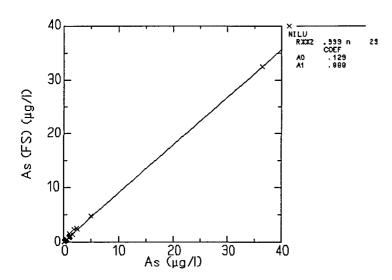


Independent variable : NILU

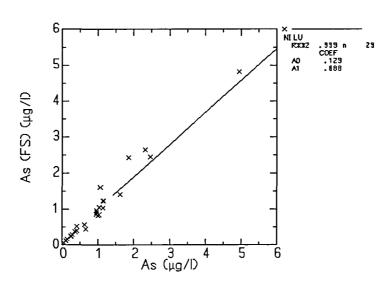


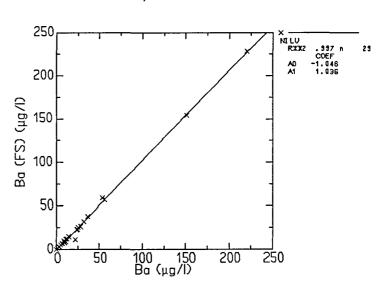
Independent variable: NILU

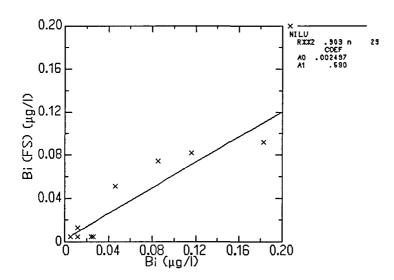




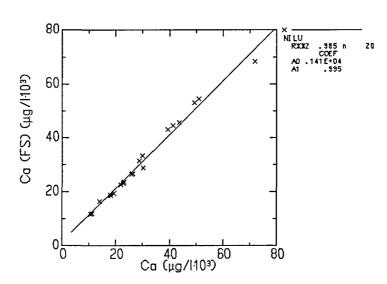
## Independent variable: NILU

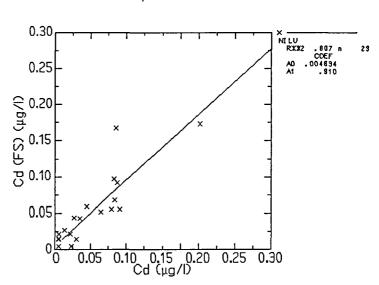


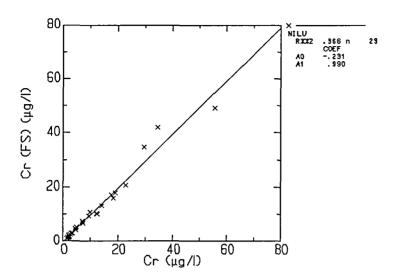




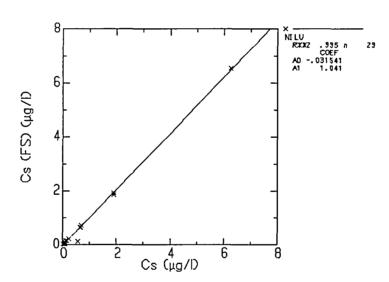
#### Independent variable: NILU

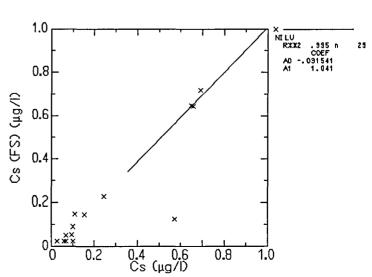


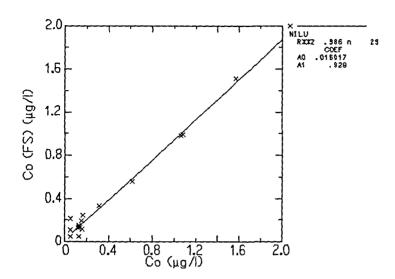




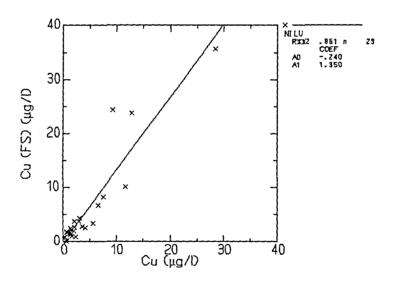
## Independent variable : NILU

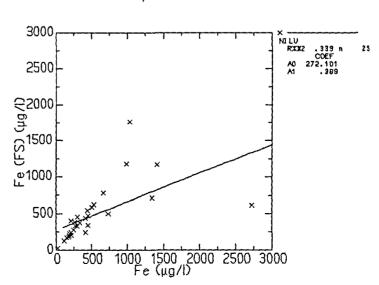


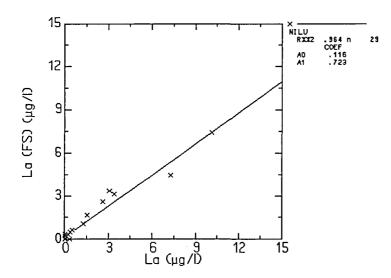




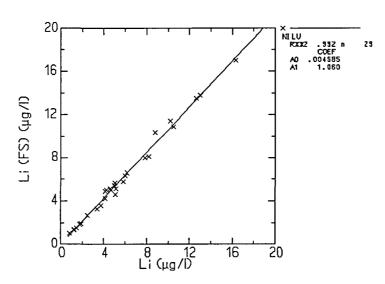
#### Independent variable: NILU

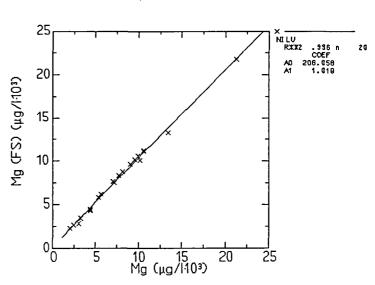


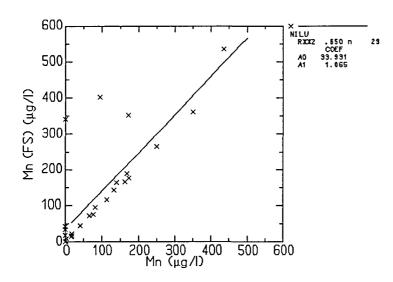




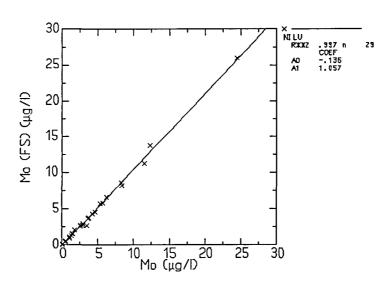
## Independent variable: NILU

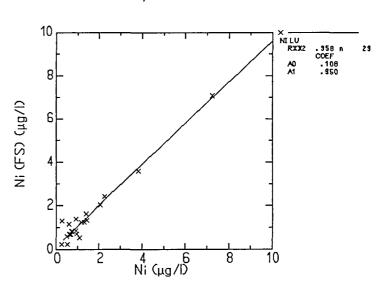


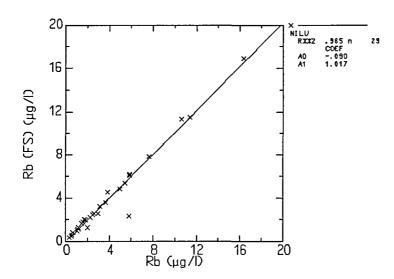




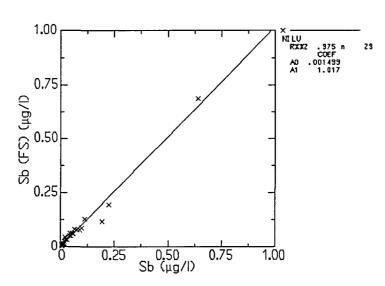
## Independent variable: NILU

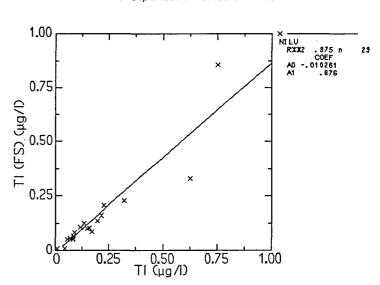


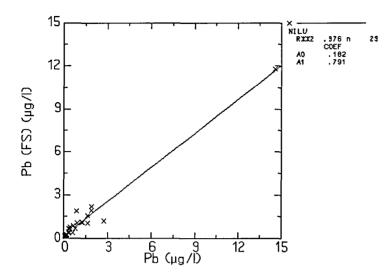


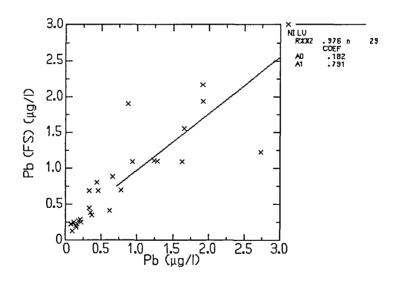


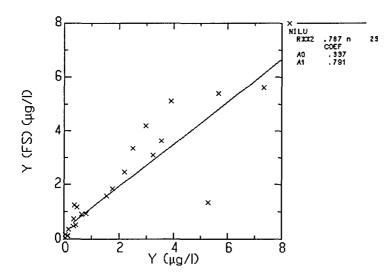
#### Independent variable: NILU

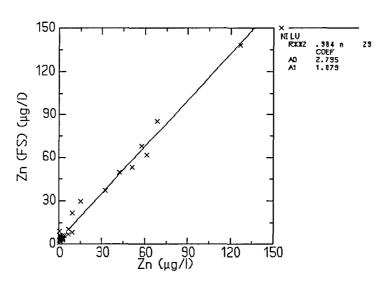












# Appendix 2. Comparison of results by ICP-OES with results by ICP-MS for selected elements.

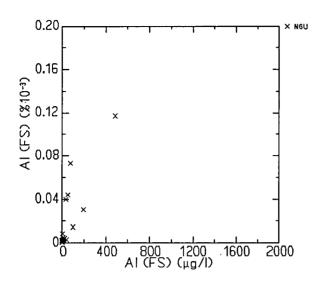
$$N = 30$$
 ICP-OES = y-axis, ICP-MS = x-axis

(All samples field filtered and acidified, except sample 13).

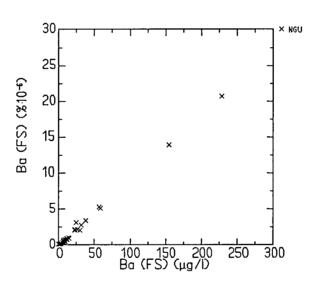
Limits of detection (ppb)	ICP-OES	ICP-MS
Al	20	1
Ba	2	0.05
Ca	20	-
Cu	2	0.1
Fe	10	50
Li	2	-
Mg	50	-
Mn	2	1
Mo	10	0.1
Sr	2	-
Y	2	0.1
Zn	5	0.5

<sup>- =</sup> detection limit below lowest measured sample

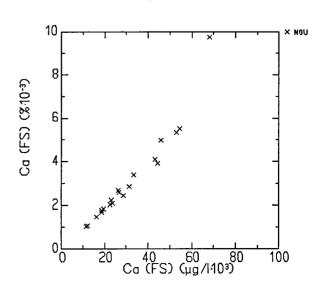
Independent variable : NILU

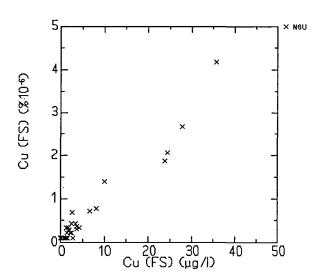


Independent variable : NILU

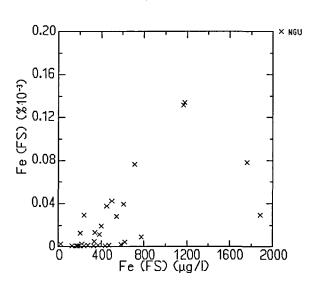


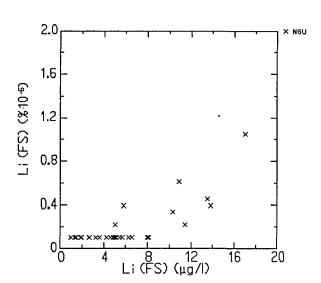
Independent variable : NILU



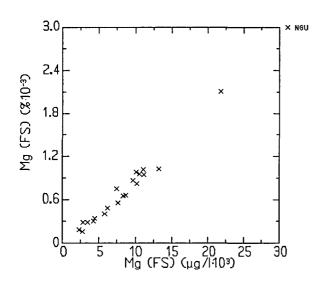


#### Independent variable : NILU

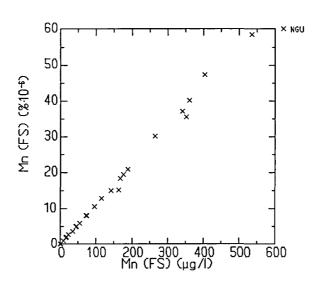




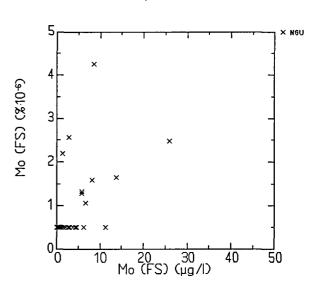
Independent variable: NILU



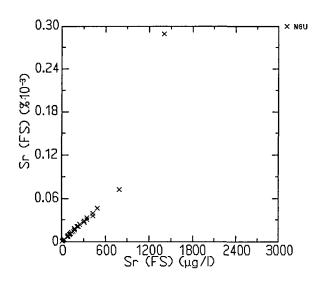
Independent variable : NILU



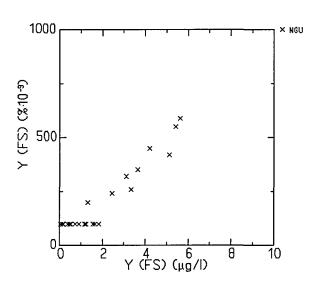
Independent variable: NILU



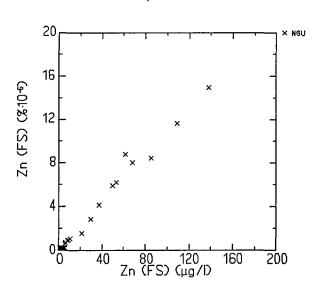
Independent variable : NILU



Independent variable : NILU

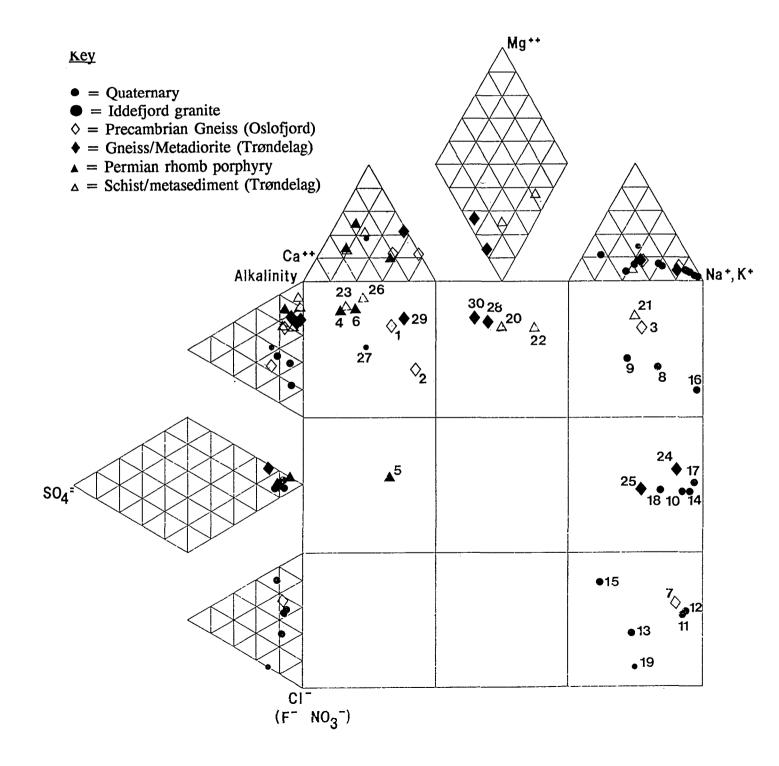


Independent variable : NILU



## Appendix 3. Piper type plot showing water-types according to main species present.

Each apex of the triangular plots represents 100 % of that parameter as a proportion of total anions or cations. Triangular plots are subdivided into intervals of 10 %. Numbers refer to sample number - Table 1.



Appendix 4. Error in ion balance for all samples.

Calculated as { Anions - Cations } \* 2 \* 100 % / { Cations + Anions }

Sample no.	Error in ion balance (%)
1	1.5
2	11.3
3	1.3
4	7.3
5	3.0
6	5.5
7	-3.4
8	6.8
9	5.6
10	-9.5
11	6.6
12	15.3
13	0.5
14	5.6
15	12.4
16	-0.1
17	-1.5
18	0.5
19	12,1
20	-1.2
21	-0.1
22	1.5
23	-2.5
24	4.8
25	6.2
26	0.4
27	0.7
28	1.2
29	1.0
30	-0.8