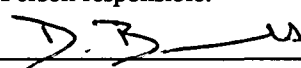


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Kola Ecogeochemistry: Groundwater
investigations

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Summary: <p>The chemical composition of 185 groundwater samples collected from two catchments in the extreme NE of Norway and NW of Russia over the period April 1994 to November 1995 is reported in terms of Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Li, Mg, Mn, Mo, Na, Ni, NO₃, P, Pb, PO₄, Rb, S, Sb, Se, Si, SO₄, Sr, Th, Ti, Tl, U, V and Zn concentrations (as determined by ICP-MS, ICP-AES and IC), pH and electrical conductance. One catchment (C2) is located in Russia 5 km downwind of the nickel-copper ore smelting industry in Monchegorsk, which is a major SO₂ and trace metal emission source, the other (C5) is located in Norway 30 km off-wind from the nickel-copper ore smelter in Nikel and 52 km off-wind from the nickel-copper ore roasting plant of Zapoljarniy, which are also significant emitters of inorganic atmospheric pollutants. Groundwater chemistry mostly reflects the mineralogical composition of the gabbro aquifer in C2 and the Quaternary deposits in C5, although groundwater in C2 also shows signs of incipient contamination from surface waters (heavy metals, sulphate, chloride). However, only the median value of Ni concentration in groundwater from C2 exceeds published 'background' groundwater compositions. WHO, CEC and U.S. EPA drinking water standards are all (well) above any detected concentration in C2 or C5 groundwater, except for Al, Fe and Mn. Groundwater in C2 has been acidified by S-compounds emitted from Monchegorsk, but the groundwater's capacity to neutralise incoming acidity has not been exhausted. In C5, groundwater has not been acidified to any extent and has a high acid neutralising capacity. This study demonstrates that the geological substrate of a catchment is a fundamental control on how groundwater responds to anthropogenic manipulation, even of the most severe magnitude.</p>				
Keywords: Groundwater		Hydrogeochemistry		Weathering
Contamination		Acidification		Bedrock aquifer
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ABSTRACT

The chemical composition of 185 groundwater samples collected from two catchments in the extreme NE of Norway and NW of Russia over the period April 1994 to November 1995 is reported in terms of Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Li, Mg, Mn, Mo, Na, Ni, NO₃, P, Pb, PO₄, Rb, S, Sb, Se, Si, SO₄, Sr, Th, Ti, Tl, U, V and Zn concentrations (as determined by ICP-MS, ICP-AES and IC), pH and electrical conductance. One catchment (C2) is located in Russia 5 km downwind of the nickel-copper ore smelting industry in Monchegorsk, which is a major SO₂ and trace metal emission source, the other (C5) is located in Norway 30 km off-wind from the nickel-copper ore smelter in Nikel and 52 km off-wind from the nickel-copper ore roasting plant of Zapoljarniy, which are also significant emitters of inorganic atmospheric pollutants. Groundwater chemistry mostly reflects the mineralogical composition of the gabbro aquifer in C2 and the Quaternary deposits in C5, although groundwater in C2 also shows signs of incipient contamination from surface waters (heavy metals, sulphate, chloride). However, only the median value of Ni concentration in groundwater from C2 exceeds published 'background' groundwater compositions. WHO, CEC and U.S. EPA drinking water standards are all (well) above any detected concentration in C2 or C5 groundwater, except for Al, Fe and Mn. Groundwater in C2 has been acidified by S-compounds emitted from Monchegorsk, but the groundwater's capacity to neutralise incoming acidity has not been exhausted. In C5, groundwater has not been acidified to any extent and has a high acid neutralising capacity. This study demonstrates that the geological substrate of a catchment is a fundamental control on how groundwater responds to anthropogenic manipulation, even of the most severe magnitude.

1. INTRODUCTION

The Central Kola Expedition (CKE) and the Geological Surveys of Finland (GTK) and Norway (NGU) are carrying out a major, cooperative regional geochemical mapping project of a 188,000 km² area north of the Arctic Circle on the Kola Peninsula (NW Russia) and in adjacent areas in Finland and Norway (see World Wide Web at URL: <http://www.ngu.no/Kola>). One of the aims of the project is to assess the environmental impact of the nickel smelting and other heavy industry in Nikel, Zapoljarniy and Monchegorsk.

As one part of the project, element concentrations in various sampling media (rain, snow, stream water, groundwater, moss, different soil horizons, Quaternary deposits and bedrock) was determined and/or monitored in eight selected catchments (watersheds) located at various distances from the smelters, and in different geological settings (Fig. 1). Four of these catchments are situated in Russia (C1: Zapoljarniy, C2: Monchegorsk, C3: Kirovsk and C4: Kurka), one in Norway (C5: Skjellbekken) and three in Finland (C6: Kirakka, C7: Naruska and C8: Pallas).

This paper presents the results from groundwater studies in the Monchegorsk (C2) and Skjellbekken (C5) catchments. The composition of the groundwater is reported rather comprehensively (pH, electrical conductance, concentration of 40 elements/species) making use of state-of-the-art analytical methods (ICP-MS) with detection limits in the part per trillion range (Stetzenbach et al., 1994). The major, minor and trace element composition of groundwater is a function, among other factors, of the geochemical and mineralogical properties of the aquifer hosting it (e.g. Garrels and MacKenzie, 1967, Frapé et al., 1984, Bricker and Jones, 1995, Mather, 1997), and of its pathway through the catchment (e.g. Caritat and Saether, 1997). Here, the two groundwaters studied are from different types of aquifers (C2: bedrock; C5: Quaternary deposits), occurring in lithologically distinct provinces. In addition, extreme industrial pollution and ensuing environmental contamination are found at one site (C2), whilst relatively uncontaminated conditions characterise the other (C5). At both sites, natural or background processes (weathering, etc.) dominantly control the composition of the groundwater, but signs of incipient contamination can be discerned in groundwater from C2. In this paper, the composition of the two groundwaters is described and interpreted in terms of element levels and sources, and acidification status, and it is compared with surface water composition; time-series will be reported separately (Storrø et al., in prep.).

2. CATCHMENT DESCRIPTION

2.1. *Monchegorsk (C2)*

C2 covers an area of 22.38 km², ranges in elevation between 128 and 507 m above sea level, received 391 mm of precipitation in 1994 (normal range 400 to 600 mm), and is described as a «technogenic desert» (Alexeyev, 1993, Kryuchkov, 1993) with some birch shrubs subsisting in remaining soil pockets; its outlet coordinates are 67°50'30'' north and 32°54'48'' east (Fig. 1). The main bedrock types present are (1) gabbro/gabbro-norite (40% areal coverage), (2) andesite/tuff (32%), (3) pyroxenite (16%), and (4) (grano-)diorite (Fig. 2). Quaternary overburden is principally represented by (1) till (76%), (2) glacio-fluvial (9%), (3) eluvial (8%), and (4) glacio-lacustrine (4%) deposits (Fig. 2).

C2 is located 5 km south and downwind from the major SO₂ and trace element pollution source of the Monchegorsk nickel-copper ore smelter complex (Fig. 1). Official figures for emissions from Monchegorsk in 1994 are ca. 98,000 tonnes SO₂, 1619 tonnes Ni, 934 tonnes Cu, 82 tonnes Co, 341 tonnes Cl and 1267 tonnes NO₂ (data from Murmansk Region Committee of Ecology and Nature Resources, see Reimann et al., 1997). Deposition in 1994 over C2 was estimated to be 654 kg S/km², 845 kg Ni/km², 494 kg Cu/km² and 60 kg Co/km² (Chekushin et al., in prep.).

2.2. *Skjellbekken (C5)*

C5 covers an area of 34.56 km², ranges in elevation between 80 and 297 m above sea level, received 422 mm of precipitation in 1994 and 581 mm in 1995 (1961-1990 mean: 440 mm), and is vegetated by typical north taiga pine forest with birches; its outlet coordinates are 69°21'25'' north and 29°27'25'' east (Fig. 1). The main bedrock types present are (1) andesite/andesitic volcanoclastic schist (40% areal coverage), (2) tholeiitic basalt/tuff (30%), (3) black schist (20%), and (4) other rock types including ultramafic/mafic intrusions (5%), minor carbonates and quartzite (Fig. 3). Surface covers consists of (1) till (71%) and (2) glacio-fluvial (15%) Quaternary deposits, (3) water bodies (6%), and (4) outcrop (5%) (Fig. 3).

C5 is located 30 km west-southwest (perpendicular to the dominant wind direction) of the Nikel nickel-copper ore smelter, 52 km west-southwest of the Zapoljarniy nickel-copper ore roasting plant, and 48 km south-southwest of the Kirkenes iron ore mine and pelleting works (Fig. 1). Official figures for emissions from Nikel/Zapoljarniy in 1994 are ca. 198,000 tonnes

SO₂, 297 tonnes Ni, 163 tonnes Cu and 11 tonnes Co (data from Murmansk Region Committee of Ecology and Nature Resources, see Reimann et al., 1997). Deposition in 1994 over C5 was estimated to be 164 kg S/km², 6 kg Ni/km², 4 kg Cu/km² and 0.17 kg Co/km² (Chekushin et al., in prep.).

3. SAMPLING

3.1. *Monchegorsk (C2)*

In C2, groundwater was sampled from one monitoring hardrock well situated in the upper part of the catchment (see Fig. 2). The well penetrates ca. 5 m of fine sand and silt, and ca. 45 m of the underlying fractured gabbro (Fig. 4). The upper 10 m of the well is cased with a steel pipe (diameter 127 mm), whereas the lower part is uncased (diameter 59 mm). The yield of the well is 1 l.sec⁻¹. A small ABS electric pump (Eijkamp™ submersible pump type Whale) was installed at 5 m depth for sampling the groundwater.

The groundwater was sampled weekly from 30 April 1994 to 8 November 1994, then monthly until 28 February 1995. Temperature, EC, pH and water level were measured in the field. Some well water was pumped out and discarded before taking the sample for analysis. The stream draining C2 was sampled weekly over the period 23 March 1994 to 2 June 1995 (monthly in winter).

Each groundwater and stream water sample comprised two subsamples. The first subsample consisted of 100 ml of water filtered (0.45 µm Millipore™ membrane filters) and acidified (ultrapure nitric acid) in the field and stored in a cool room before dispatching to the laboratory for cation analysis. The second subsample consisted of 500 ml of unfiltered, unacidified water for anion, pH and electrical conductance (EC) analyses.

3.2. *Skjellbekken (C5)*

Nine groundwater monitoring wells were drilled in mid-August 1994 at three different locations in the Quaternary deposits of the lower part of C5 (see Fig. 3). These deposits consist of 6 to 11 m of glaciofluvial to glaciolacustrine sediments (fine sand to sand) overlying coarser esker sediments (gravel). At each location, a deep ('Level 1', 7 to 12 m), an intermediate ('Level 2', 5 to 9 m) and a shallow ('Level 3', 2 to 3 m depth) well was drilled and cased with white PE tubing (diameter 50 mm) (Fig. 5). Thus, both the deeper gravel

aquifer (Loc. 42 Level 1, 43/1, 44/1 and 44/2) and the shallower sand aquifer (42/2, 42/3, 43/2, 43/3 and 44/3), which are hydraulically distinct only at Loc. 44 (see Fig. 5), were sampled. The casing of the wells was slotted through the monitored interval and the annulus was sealed with bentonite. Sediment samples were collected at all levels during drilling. A small electric pump of the same type as described above was installed in each of the nine wells for sampling.

Groundwater was sampled for the first time on 20/21 September 1994, and the second time on 9 February 1995. Groundwater was then sampled weekly from 11 April to 6 July 1995, and thereafter monthly until 7 November 1995. The groundwater level was measured in each well before sampling. A volume of water equivalent to at least two well shaft volumes was pumped out and discarded prior to collecting the sample for analysis. Surface water samples were collected weekly at the outlet of the catchment from Skjellbekken, the main stream draining the catchment, from 18 March 1994 to 7 November 1995 (sampling frequency was reduced to monthly in winter 1994/95 and from July to November 1995). For sampling and preservation of the samples, the same procedures as in C2 apply here.

4. ANALYSIS AND QA/QC

4.1. Analysis

All chemical analyses were carried out at the GTK Laboratory, except for the determination of pH, EC, alkalinity and anion concentration of the first two sampling rounds in C5 (20-21 September 1994 and 9 February 1995), which was performed at NGU. The analytical programme at GTK consisted of quantitative determination of cation concentrations by inductively coupled plasma-atomic emission spectrometry (ICP-AES: Ca, Mg, Na, P, S, Si) and inductively coupled plasma-mass spectrometry (ICP-MS: Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, Tl, U, V, Zn), of anion concentrations by ion chromatography (IC: Br, Cl, F, NO₃, SO₄) and spectrophotometry (PO₄), and pH and EC (at 25°C) by potentiometry.

4.2. Quality assurance/quality control

When using ICP-MS techniques with detection limits in the low ppt-range, contamination at any stage of the sample's analytical cycle poses a serious threat to the quality of the data obtained.

In terms of field equipment used, and especially sample bottles for water samples, there are widely diverging opinions as to how best to avoid contamination and/or adsorption to the bottle walls. Some researchers claim that only factory new teflon bottles (very expensive) will give reliable results, others prefer laborious and time-consuming pre-washing methods of all field equipment used (e.g. Stetzenbach et al., 1994).

We consider the chance of introducing chemical contamination in the laboratory a real threat, and thus opted against pre-washing methods. Instead, brand new field equipment (gloves, syringes, filter capsules, PE-bottles) was used throughout the project, and all field teams in all three countries were equipped with sufficient amounts of the same brand of equipment coming from the same manufacturing batch to carry out the whole project. This way, comparability between our results from the different areas was already guaranteed. PE-bottles from new manufacturing batches were regularly checked for contamination by using acidified sample blanks, and no problems were reported. The acid used for acidification of the samples in the field came from the same manufacturing batch for all teams as well, and was checked for contamination. Field teams had to follow a strict and clear sampling protocol in the field (Äyräs and Reimann, 1995).

The chemical laboratory at the Geological Survey of Finland is equipped with clean room technology and accredited to meet the requirements of the EN 45001 standard and the ISO Guide 25. The ICP-MS calibration was confirmed by artificial multielement calibration method and QC solutions from Spex™ and Merck™. International reference material used was Riverine Water Reference Materials SLRS-2 and SLRS-3 from the National Research Council, Canada, and Standard Reference Materials 1643c and 1643d (Trace Elements in Water) from the National Institute of Standards and Technology, USA.

Quality control procedures for water analysis followed generally the methods suggested by Reimann and Wurzer (1986), and included frequent analysis of an in-house water standard, sample blanks and the duplicate analysis of every tenth sample. Using these methods, a source of Zn contamination in the laboratory was detected, giving occasional very high, spurious Zn results in our data. Our Zn data should consequently be treated with care, although this potential problem is not discussed further herein. The most likely source of this contamination is the wearing off of the teflon coating on rubber fittings in a dispenser.

Reported precision was generally excellent for the elements presented here and in other reports of water analyses obtained within the Kola Ecogeochemistry project according to the same rigorous protocol (Äyräs et al., 1995, Reimann et al., 1997, Caritat et al., 1996a,b). The very low analytical results obtained for most typical contaminants in the background areas indicate that no low level contamination problem was encountered using the described approach. The high analytical values from the most contaminated catchments are well in agreement with the levels reported by other workers from the same general area.

5. RESULTS

Tables 1 and 2 summarise the data obtained for groundwater and stream water in both catchments. Minimum, median (50th percentile), mean, standard deviation and maximum reported values are given. Where results below the detection limit were encountered, half the detection limit value was used for the statistical treatment. The variance of the data results from (1) the contrasting hydrogeological setting of the two groundwater reservoirs (overburden vs. hardrock aquifer), (2) the different levels sampled in C5 (shallow, intermediate and deep), and (3) the natural time-dependent variation in groundwater composition throughout the hydrological year (see Storrø et al., in prep.).

Figure 6 shows that the groundwaters from C2 are mainly of the Ca-SO₄-Cl-(HCO₃) type, and those from C5 mainly of the Ca-Na-HCO₃-(Cl) type.

6. DISCUSSION

6.1. Comparison of C2 and C5

6.1.1. Boxplots

Figure 7 shows the difference in chemical composition of the groundwaters collected from the two catchments in terms of pH, EC, and Al (note the log scale), As, Ca, Cl, Cu, K, Li, Mg, Mo, Na, Ni, Si, SO₄ and Sr concentrations. Groundwaters from C5 are subdivided with respect to sampling level 1 to 3 (see Fig. 5). A few of these parameters are commented hereafter.

We can see that groundwater from C2 generally has a lower pH than in C5, though shallow groundwater in C5 comes close to C2 groundwater; in any case the pH values recorded are dominantly circum-neutral or even alkaline. In C2, this reflects the effective mineral neutralisation that occurs when the rain, acidified by massive industrial emissions of SO₄ (rainwater median pH = 4, SO₄ = 5 mg/l, see Reimann et al., 1997), comes in contact with the soil, overburden and finally mafic bedrock. In C5, the rain is much less affected by airborne anthropogenic emission (rainwater median pH = 4.5, SO₄ = 1 mg/l, quite similar to background control areas, see Reimann et al., 1997), and the influence of basic substrate, including carbonates, in the catchment is also very important here.

The effect of the mineral-water interactions near the landscape surface also is reflected by the EC values. In C5, median EC near 3 mS/m was recorded in the shallowest wells, whilst it

climbed to 4 and 9 mS/m in the intermediate and deepest wells. In C2, EC reached 11 mS/m. Rainwater has median EC values of 1.1 mS/m in C5 and 4.6 mS/m in C2 (Reimann et al., 1997). This is consistent with evaporative upconcentration and with the idea that the deeper the groundwater is abstracted from, the longer its residence time has been, i.e. the longer it has been in contact, and has had the potential to interact, with minerals. These interactions commonly consume acidity and yield free cations and alkalinity, resulting in progressively higher pH and EC values (e.g. Drever, 1997). Episodic infiltration of surface water into the aquifer at C2 may have occurred, as suggested by few samples with very low Si concentrations.

There has been some discussion as to the origin of As in natural waters in C5 (Caritat et al., 1996a), primarily because of the concern that airborne As originating from industrial emissions in Russia may be deposited in Norway (Hagen et al., 1995). Observation of the levels of As at the different levels within the aquifer(s) at C5 shows that the highest levels of As (median As = 1.45 µg/l) come from the deeper wells and some intermediate wells. More detailed scrutiny reveals that the high As concentrations (>0.25 µg/l) are from Loc. 44/1, 44/2, 43/1, 42/1; all four wells are screened within the deep gravel/moraine aquifer. This confirms the earlier interpretation (Caritat et al., 1996a, Chekushin et al., in prep.) that As in C5 primarily has a geogenic source in this area, with a secondary anthropogenic (atmospheric) origin (Sivertsen et al., 1994, Hagen et al., 1995).

Calcium similarly shows that in C5 the deep gravel/moraine aquifer (same four wells as above) yields the highest concentrations (10 to 26 mg/l). This can suggest that labile Ca-bearing minerals are found predominantly in that layer of the overburden cover, or it can reflect longer residence time. In C2, the high Ca levels (13 mg/l) reflect also weathering of labile Ca-minerals in the overburden and in the gabbroic bedrock (plagioclases, pyroxenes).

The pattern displayed by Cl is very interesting: given the much closer proximity to the sea of C5 relative to C2, one would expect to see higher Cl concentrations in groundwater from the former than from the latter area. However, the opposite is observed (2.5 and 9.5 mg/l, respectively), and we interpret this to be a consequence of the important Cl emissions reported from the Monchegorsk industrial complex (341 tonnes in 1994, Murmansk Region Committee for Ecology and Natural Resources, 1995, quoted in Reimann et al., 1997).

Higher concentrations of Cu and Ni in groundwater from C2 than from C5 presumably reflect mostly the different geological settings (gabbro vs. andesite bedrock). However, the high emissions of these heavy metals from Monchegorsk (934 and 1619 tonnes, respectively, in 1994, Murmansk Region Committee for Ecology and Natural Resources, 1995, quoted in Reimann et al., 1997) are unlikely to have left aquatic ecosystems only 5 km downwind from

the smokestacks completely unaffected. Indeed, surface waters are known to be quite seriously contaminated in heavy metals, sulphur and aluminium (Moiseenko et al., 1995, Caritat et al., 1996a,b), and the time-series for Ni in C2 clearly demonstrates that the groundwater here is affected by the heavy metal peak occurring during springtime snowmelt (Fig. 8). This peak in the groundwater is delayed by about 1 month compared to the stream water, but its magnitude is in both waters of a factor 10 (from about 100 to 1000 µg/l in surface water, and from about 2 to 20 µg/l in groundwater).

Lithium, Mg, Mo, Na, Si and Sr are elements of predominantly geogenic origin, and their overall increasing concentration from shallow to deeper wells can be taken as a measure of the progress of mineral-water interaction, or weathering particularly of silicate and carbonate minerals.

Sulphate concentrations in groundwater can reflect weathering/oxidation of sulphide minerals and/or the infiltration of anthropogenic sulphate from the surface. In C5, groundwater sulphate (median $\text{SO}_4 = 3.6 \text{ mg/l}$) probably mostly has a geogenic source (sulphur deposition is at or close to background levels, see Chekushin et al., in prep.; in addition, groundwater sulphate increases with depth), in agreement with the finding that both Quaternary deposits and bedrock in C5 are rich in S (Pavlov et al., 1996). In C2, however, the situation is less clear-cut; sulphate in groundwater (median = 20.1 mg/l) can have a dual source, geogenic and anthropogenic. Rainwater and stream water here have median sulphate concentrations of 5 and 27.5 mg/l (Reimann et al., 1997, Caritat et al., 1996a), whilst Quaternary deposits and bedrock are relative rich in S (Pavlov et al., 1996). We conclude that S/ SO_4 in groundwater from C2 probably has a dual, natural and anthropogenic, origin, without quantifying this further at this stage.

6.1.2. Scatterplots

The relationships between the two groundwaters also can be illustrated by XY-diagrams. Median values in groundwater (Tab. 1, Fig. 9a) are higher in C5 than C2 for (parameters are ranked in order of decreasing ratio, and if ratio < 2 the parameter is given in parenthesis) Al (by a factor of 6.1), U (> 6), Pb (3.2), (V), (K), (Mo), (B), (pH), (Si) and (Cd), whilst higher in C2 than C5 for Ni (10.3), Fe, SO_4 , S (5.3), NO_3 , Co (4), Cl, Ca, Mg (2.8), Mn, EC, (Ba), (Rb), (Cu), (Li), (Sr) and (Na).

The single greatest difference between the two groundwaters is for Ni, which is more than 10 times more abundant in C2 than in C5. In C2, this element can have both a geogenic source

(gabbro bedrock present in the catchment, but no Ni-mineralisation known) and an anthropogenic source (Ni emissions from the smelter). The median Cu:Ni ratio in groundwater (0.18) is closer to the value of this ratio in the emission data (0.6; Reimann et al., 1997) or the deposition data (0.6; Chekushin et al., in prep.) than in the normal 'background' groundwaters (2 to 5.9) of Allard (1995).

Figure 10 illustrates the different composition of groundwaters from C2 and C5 in a Ni-Cu-As ternary diagram. Except for a few results, the groundwater in C2 is clearly more enriched in Ni (relative to Cu and As) than that from C5. These exceptions when Cu:Ni is unusually high in C2 groundwaters occur, interestingly, mostly in May 1994 or about a month after the snowmelt-related flood in the springtime and the remarkable Cu:Ni peak in stream water discussed by Caritat et al. (1996b). This leads to two important observations: 1) percolating surface water in C2 takes about 1 month to reach the groundwater table, so this can be a first approximation of the recharge delay, 2) the groundwater is clearly affected by the downward advection of water and its dissolved constituents from the surface, making it potentially vulnerable to contamination from polluted streams in the vicinity of the Monchegorsk smelter (Moiseenko et al., 1995, Caritat et al., 1996a).

Other elements also part of the ore being smelted at Monchegorsk (Cu, Co, S) are similarly higher in groundwater from C2 than from C5. Absence of known mineralisation within C2 and high industrial emission and deposition again suggest incipient groundwater contamination from anthropogenic pollutants, though part of the relatively elevated concentrations are natural.

The relatively high median SO_4 (20 mg/l) and Cl (9.5 mg/l) values in C2 groundwater are also taken as evidence supporting the infiltration of contaminants down from the surface, since these elements are not abundant in rock-forming minerals in C2 and both have high emission values from neighbouring Monchegorsk (see above).

High cation (Ca, Fe, Mg) concentration and EC in C2 can be mainly attributed to weathering of basic silicates, which reactions may be accelerated under extreme SO_2 loading ('acid deposition'), together with some direct deposition effects as seen in snow meltwater and rainwater (Äyräs et al., 1995, Caritat et al., in prep., Reimann et al., 1997, Chekushin et al., in prep.). The solubility of Fe is controlled by redox conditions. Nitrate levels (0.9 mg/l) in groundwater at C2 also reflect elevated N emissions from Monchegorsk.

Groundwater from C2, being collected from a steel cased well (see above), can be contaminated, e.g. with Fe and heavy metals from the pipe. The degree to which this source of

contamination influences groundwater composition is uncertain. The heavy metal composition of the steel is unknown.

Al and U, which are more enriched in C5 than C2 groundwater, are likely to have a geogenic source here. Relatively elevated Pb concentrations in C5 groundwater has a problematic origin as no Pb(-Zn) mineralisation is known within C5. C2 receives 10 times more Pb deposition than C5, which appears to be at, or only slightly above, background Pb deposition levels (Chekushin et al., in prep.) and which has a well-developed humus layer that would effectively bind most deposited Pb (Lewis, 1977, Wang et al., 1995). Therefore, some minor subsurface source(s) (war relics or waste from a small industrial development) could play a role here. The simultaneous, relatively high concentrations of Al, U and Pb point towards some particular physico-chemical (Eh-pH) conditions within the aquifer favouring a high solubility.

The Na-Cl relationship for the groundwater from C2 and C5 (Fig. 11a) illustrates that both waters are off the seawater dilution line: C2 waters are enriched in Cl, presumably through anthropogenic emissions of Cl (see above), and C5 waters are enriched in Na, presumably because of Na release from mineral (plagioclase, etc.) weathering.

In terms of Ca-SO₄, groundwaters from both C2 and C5 are enriched in Ca relative to the seawater dilution line (Fig. 11b). In C2, the elevated Ca concentrations can be interpreted as reflecting (a) the leaching of Ca-minerals by water-rock interaction, possibly enhanced by very acid precipitation (high SO₄ loadings, see Reimann et al., 1997, Chekushin et al., in prep.), (b) the mobilisation of Ca due to cation exchange in the soil, and (c) possibly the direct deposition of Ca (carbonates used as flux in the smelting process?). In C5, only the shallow groundwater is influenced somewhat by seaspray, as shown by the relative proximity to the seawater dilution line. The deeper groundwater is enriched both in Ca and SO₄ compared with the shallow groundwater. This is presumably related to weathering of Ca-minerals and oxidation of sulphides.

The S-Ni systematics of groundwater (Fig. 11c) from C2 show a relatively stable S-content and widely varying Ni concentrations (0.3 to 18 µg/l), which are time-dependent (see Fig. 8). In C5, Ni concentrations are restricted to a much narrower range (mostly 0.1 to 2 µg/l), and S (but not Ni) increases generally with depth/residence time, as seen above for SO₄.

The groundwater from C2 is overall considerably more enriched in Ni than in Cu (Fig. 11d): the median Cu:Ni ratio is 0.14. The Cu:Ni ratio recorded in rainwater, which is either between 6 and 8 or between 2 and 3 in C2, depending on which type of ore, Norilsk ore with a higher Cu:Ni or local (Pechenga) ore with a lower ratio, is being smelted in Monchegorsk (Reimann

et al., 1997). This means that as rainwater infiltrates down to the aquifer and becomes groundwater, the Cu:Ni ratio drops dramatically. As both Ni and Cu concentrations also drop (median Ni = 57 µg/l and Cu = 231 µg/l in rainwater versus median Ni = 5.8 µg/l and Cu = 1 µg/l in groundwater), this implies that Cu is much more effectively immobilized in the upper soil layers than Ni. This is consistent with the conclusion of Niskavaara et al. (1996) and Reimann et al. (in press). Interestingly, of the seven data points with 'anomalously' high Cu:Ni ratio in C2, five were collected in late April or in May 1994, i.e. just after the snowmelt event, indicating flushing of the vadose zone with mobilisation of unusually large amounts of Cu relative to Ni.

For C5, the Cu:Ni ratio in groundwater is 1.22, i.e. close to what it is in snow meltwater (1.3, see Caritat et al., in prep.) or rainwater (1.4). This suggests that Cu and Ni are bound more or less equally efficiently in C5 (median Cu = 0.96 µg/l and Ni = 0.76 µg/l in snow meltwater and median Cu = 1.8 µg/l and Ni = 1.31 µg/l in rainwater, decreasing to median Cu = 0.7 µg/l and Ni = 0.6 µg/l in groundwater), with perhaps a slightly greater binding capacity for Cu in this case as well.

The Si-EC diagram (Fig. 11e) shows a positive correlation for C2, suggesting that silicate weathering directly influences the groundwater ionic content or salinity. In C5, EC varies quite greatly within a narrow range of Si concentrations. This may indicate that Si solubility is constrained by silica saturation and that, for example, carbonate dissolution is responsible for the high EC values, as discussed above.

6.2. Comparison with other groundwaters

Despite being located within, and on the margins of, an area with some of the world's most intense emission of SO₂ (Gunn et al., 1995) and accompanying trace element spectrum, the median concentrations of the 'standard' heavy metals in C2 and C5 groundwaters are within or below the published 'background' concentration ranges for groundwater (Allard, 1995) for Cr, Ni (C5 only), Cu, As, Cd and Pb. C2 groundwater is above the quoted 'background' only for Ni (by a factor of 10).

Since the published 'background' levels only apply to very few elements, it is interesting to also compare (hardrock) groundwater from C2 with the hardrock groundwaters from Norway recently analysed by Reimann et al. (1996). They reported the concentration of 64 elements in 145 raw (unfiltered) bedrock groundwater samples from the Oslo and Bergen regions. Possibly because the groundwater samples from C2 were filtered, many elements are much

more abundant in the Norwegian study, for instance, comparing median values, Cu (by a factor of 11.3), B (11), Li (7.9), Mo (7.4), Na (5.1) and Al (3.8). More interesting here, is the suite of elements more abundant in filtered groundwater from C2 than in the raw Oslo/Bergen groundwaters: Ni (by a factor of 7.8), Co (3.9), Fe (2.8) and Mn (1.8). Thus, two metals (Ni, Co) possibly from the sulphide ore being smelted in Monchegorsk, and two elements (Fe, Mn) of likely geogenic origin (mineral weathering accelerated under intense acid deposition, plus role of Eh-pH conditions) are clearly present in anomalous proportions in the groundwater near Monchegorsk.

Median groundwater composition from C2 and C5 is below the Dutch A-value ('reference level') as given in Ewers (1991, Tab. I.20b-14) for As, Ba, Cd, Co, Cr, Cu, Mo, Ni and Pb. Even when using our maximum values, only two instances exceeding the Dutch A-value are found: Ni in C2 and Mo in C5. For Cu and Cr, the maximum values in C5 comes close to (>half) the Dutch A-value.

6.3. Comparison with drinking water standards

Drinking water standards (DWS) and guidelines (GL) collated by Ewers (1991, Tab. I.20b-7) and including data from the World Health Organization (WHO), the Council of the European Communities (CEC) and the United States Environmental Protection Agency (U.S. EPA) are all (well) above any detected concentrations in C2 or C5 groundwaters for Ag, As, Ba, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, Pb, Sb, Se and Sr. The only exceedences (all given here in µg/l) noted are for Al (maximum C5 = 463 vs. DWS = 200), Fe (median C2 = 70, maximum C2 = 1230 and maximum C5 = 310 vs. CEC GL = 50 and DWS = 200 or 300) and Mn (maximum C2 = 142 and maximum C5 = 53.7 vs. CEC GL = 20 and DWS = 50 or 100).

The issue of incipient groundwater contamination by industrial emissions is a serious one in an area like Monchegorsk because of the already advanced stage of surface water pollution there (Moiseenko, 1994, Moiseenko et al., 1995, Olsen, 1996, Väisänen et al., in press, Caritat et al., 1996a,b). If groundwater can not be considered a safe alternative source of potable water, serious drinking water supply problems may follow, as transport of water in pipe-lines over long distances is precluded by climatic and ground conditions in these arctic regions. Therefore, the groundwater resources of the region should be carefully protected and managed.

6.4. Comparison between groundwater and stream water

The geochemistry of the stream water in all eight catchments of the Kola Ecogeochemistry project is described in detail elsewhere (Caritat et al., 1996a,b). Accordingly, stream water and groundwater quality is compared here with focus especially on groundwater processes.

The composition of stream water and groundwater in C2 is compared in Fig. 9b, and in Tables 1 and 2. Parameters higher in stream water compared to groundwater are (parameters are ranked in order of decreasing ratio, and if ratio <2 the parameter is given in parenthesis) Cu (by a factor of 40), Ni (40), Co (29), Al, Cd, V (3.4), As, NO₃, Cr (>2.5), Sb, Mo, (Ag), (U), (Mg), (Mn), (Ba), (Sr), (S), (B), (Pb), (SO₄), (Li), (EC) and (Si), whilst those higher in groundwater are Cl (2.4), (Fe), (Na), (Rb), (K) and (Ca).

The fact that the three most important sulphide metals, Ni, Cu, Co, together with S and a suite of other trace metals typical of the ore, are (much) more abundant in stream water than in groundwater in C2 is taken as an indication of a much less severe contamination level of the aquifer than of surface water bodies. Many other elements are also more abundant in stream water because of enhanced weathering reaction in the upper soil layers due to acid deposition (SO₂, NO_x). Not surprisingly, of the few elements more abundant in groundwater, all but Cl (and partly Na) likely find their origin in weathering of rock-forming minerals. The relatively high Cl concentration in groundwater (9.5 mg/l) is partly explained by evaporative upconcentration of emission-contaminated surface water (4 mg/l).

The composition of stream water and groundwater in C5 is compared in Fig. 9c, and in Tables 1 and 2. Parameters higher in stream water compared to groundwater are Ca (by a factor of 4.4), As (4.3), Fe, Br, EC, (SO₄), (Ba), (Sr), (S), (Ni), (Cu), (Mg), whilst those higher in groundwater are Co (>3), Pb, Al (2.5), Si, Mn, (K), (Mo), (V), (B), (Na), (Rb), (Li), (Cl) and (pH).

The higher abundance of typical geogenic elements (Ca, Fe, Mg, Sr) in stream water than in groundwater, together with the opposite relationship for typical seaspray elements (Na, Cl), suggest that these two waters are in very good communication with one another in C5. The bedrock, which includes limestone, and the Quaternary deposits here are known to be generally Ca-rich (Melezhic, 1995, Olsen, 1995, Caritat, 1995 a,b, Pavlov et al., 1996). Perhaps the occasional acid precipitation events (up to 3 mg SO₄/l) as recorded in the rain samples (Reimann et al., 1997) cause leaching of carbonate and other Ca-bearing minerals in the upper soil layers, the acidity of the infiltrating water being progressively consumed as it percolates down to the aquifer (pH groundwater > stream water).

The median Cl content of groundwater (2.45 mg/l) is slightly higher than in stream water (2.32), and this small difference is explained by evapotranspiration. The maximum Cl concentrations show clearly the influence of seasalt transported during storms onto the catchment and its surface water reservoir. Sodium can have a geogenic component (Nafeldspar, etc.), in addition to the seasalt source, hence explaining its higher (median and maximum) concentration in groundwater than in stream water.

Arsenic is only slightly enriched in rain in C5 compared to the background catchments of the Kola project (Reimann et al., 1997), and thus partly finds its source in the technogenic airborne contaminant load. However, as seen above, As increases in concentration down the aquifer in C5, suggesting also a geogenic source, consistent with bedrock and Quaternary deposit compositions here (Pavlov et al., 1996).

Higher abundance of Co in groundwater in C5 than in stream water has a natural cause here: both bedrock and Quaternary deposits have unusually elevated Co content (Pavlov et al., 1996). For Pb, the relative enrichment in groundwater is more problematic, as seen above: the content in rocks and overburden is not unusual. If Pb was deposited as an anthropogenic pollutant, one would expect it to be strongly bound to the humus layer (Lewis, 1977, Wang et al., 1995), and not be mobilised either to surface or groundwater.

Other elements result clearly from weathering of alumino-silicates in the soil and aquifer: Al, Si, Mn, K and Li.

To further give an impression of which elements are part of the emission spectrum of the Monchegorsk smelter, it is interesting to compare the median geochemistry of the two streams (Tab. 2, Fig. 9d). Parameters greater in C2 than in C5 are Co (by a factor of 341!), Ni (241), Cu (42), NO₃, Mn (8.8), Cd, S/SO₄ (4.2), Al, Mg, V, Mo (2.9), Cr, Sb, Si (2.2), Li, (Ag), (Cl), (B), (Ba), (Rb),(Sr), (K), (Na), (Pb) and (EC), whilst those greater in C5 are V (3), (Ca), (As) and (pH).

6.5. Acidification status

Figure 11f shows the distribution of non-marine hardness (Ca* + Mg*) vs. alkalinity, where both variables are given in meq/l. Non-marine hardness is calculated by assuming Cl to be conservative and exclusively of marine origin; although this is an unjustified assumption for C2 in the light of what has been said above, it results in underestimates of acidification effects. Alkalinity is calculated by charge balance; a linear regression between the 17

available measured values of alkalinity from C5 and the corresponding calculated values yielded a slope of 0.96 and a correlation coefficient $r^2 = 0.987$.

The hardness-alkalinity plot is commonly used to assess the acidification status of surface or ground waters (Jacks and Knutsson, 1981, Jacks et al., 1984, Brömssen, 1989, Caritat, 1995c). Slopes of 1:1 on this diagram are typical of waters in equilibrium with atmospheric CO₂ and minerals (e.g. carbonates) in the soil, surficial deposits or bedrock. Slopes of 2:1 or greater reflect the influence of strong acids, usually interpreted to be of anthropogenic origin. In Figure 11f, we see that all groundwaters from C5 fall near the 1:1 line, regardless of whether they are extracted from the shallow sandy aquifer or the deeper gravel aquifer. This reflects the low acid loadings in combination with the abundance of easily weatherable minerals, such as the carbonates known to be present in the catchment.

In C2, however, the groundwater samples plot close to or above the 2:1 line, testifying to the impact of strong acids in the system. Given the extreme sulphate emission rates from the nearby smelting industry in Monchegorsk, we suspect sulphuric acid of anthropogenic origin to be the cause for this behaviour. Thus, the groundwater in C2 clearly has been acidified by industrial activity and resulting pollution in the immediate vicinity. Note that by using the hardness values corrected for marine influence, we have underestimated the effects of acidification; the total (uncorrected) hardness would be much higher since Cl concentrations are high (6 to 11.5 mg/l) here, and so a best-fit slope would be greater than 2.

The acid neutralising capacity (ANC) of a water can be calculated as follows:

$$\text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) - (\text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-),$$

where all concentrations are expressed in $\mu\text{eq/l}$ (Stumm, 1992) and its 'acidification' (Aci), defined as the loss of alkalinity, by:

$$\text{Aci} = 0.93(\text{Ca}^* + \text{Mg}^*) - 14 - \text{Alk} + \text{Al},$$

where all concentrations are expressed in $\mu\text{eq/l}$ (Henriksen, 1980, Henriksen and Kirkhusmo, 1986, and Henriksen et al., 1989). Figure 11g shows the relationships of ANC to Aci for the two aquifers of C2 and C5. Groundwater from C2 has relatively low ANC values (100 to 600 $\mu\text{eq/l}$) and high Aci values (200 to 450 $\mu\text{eq/l}$). This suggests that although the groundwater has been acidified in C2, it still has some potential to neutralise acids (ANC is still positive), presumably as a result of the mafic nature of the aquifer rocks and loose deposits. In C5, groundwater has not been significantly acidified: Aci values are low or indeed negative (-200 to 150 $\mu\text{eq/l}$), and ANC values range from 100 $\mu\text{eq/l}$ in the shallow sandy part of the aquifer

to 1300 µeq/l in the deeper gravel layer. Again, interactions between easily weatherable minerals and water seeping through the soil, Quaternary deposits and fractured bedrock ensure effective neutralisation of the mostly natural (CO₂) acidity of the precipitation here.

7. CONCLUSIONS

The composition of groundwater from two catchments in the Barents region (C2 in NW Russia and C5 in NE Norway) is reported in terms of pH, electrical conductance, plus concentration of Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Li, Mg, Mn, Mo, Na, Ni, NO₃, P, Pb, PO₄, Rb, S, Sb, Se, Si, SO₄, Sr, Th, Ti, Tl, U, V and Zn as determined by state-of-the-art (e.g. ICP-MS) analysis of 185 samples collected over the period April 1994 to November 1995. C2 is adjacent to the Monchegorsk industrial centre, which is a major SO₂ and trace metal emission source, whilst C5 is located further away and off-wind from the smelter in Nikel and the ore roasting plant of Zapoljarniy.

Median concentrations in groundwater (Tab. 1, Fig. 9) are >2 times higher in C2 than C5 for Ni (by a factor of 10.3), Fe, SO₄, S (5.3), NO₃, Co (4), Cl, Ca, Mg (2.8) and Mn. These elements are either components of the ore being smelted in nearby Monchegorsk (Ni, S, Co), otherwise part of the emission cocktail of this industry (NO₃, Cl), or base cations mobilised by weathering (possibly intensified under acid deposition) (Ca, Mg) or mobilised under reducing conditions (Fe, Mn). As a result, EC is also much higher in groundwater from C2 than C5.

Median concentrations in groundwater are >2 times higher in C5 than C2 for Al (by a factor of 6.1), U (>6) and Pb (3.2). These elements all dominantly have a subsurface source here and are thought to owe their high solubility to the Eh-pH conditions in the aquifer. Al and U probably originate exclusively from natural, geogenic sources, whereas Pb may partly have its origin in an existing minor subsurface waste deposit (ammunition and battery storage during World War 2).

Compared with published 'background' composition ranges for groundwaters (Allard, 1995) only median Ni in C2 exceed 'background' (by a factor of 10). Cr, Cu, As, Cd and Pb concentrations are all below 'background'.

Compared with 145 raw (unfiltered) hardrock groundwaters from Oslo and Bergen recently analysed (Reimann et al., 1996), the (filtered) hardrock groundwater of C2 contains more Ni (by a factor of 7.9), Co (3.9), Fe (2.8) and Mn (1.8). The two first metals are possibly derived from the sulphide ore smelted at Monchegorsk, the latter two are likely geogenic in origin.

The median content of As, Ba, Cd, Co, Cr, Cu, Mo, Ni and Pb in groundwater from C2 and C5 are all below the Dutch A-value for groundwater. The maximum values reported for Ni in C2 and for Mo in C5 exceed the Dutch A-value.

The only elements found to exceed drinking water standards or guidelines in any one instance or more are Al, Fe and Mn. Given that surface waters around Monchegorsk are under severe environmental stress due to the level of airborne contamination here, groundwater could prove a viable alternative for the source of drinking water. However, the first results for the groundwater in C2 presented here clearly indicate the groundwater resources are experiencing incipient stages of (inorganic) contamination.

Median stream water in C2 contains 40 times more Cu and Ni, and 29 times more Co than the groundwater here, and 341 times more Co, 241 times more Ni and 42 times more Cu than stream water in C5. Thus, at least in terms of Ni and Co, the groundwater in C2 is significantly more enriched than even stream water in C5.

Groundwater in C2 has been acidified by the industrial emission of sulphur compounds, but thanks to the abundance and mafic nature of the minerals in the soil, loose deposits and underlying bedrock here, the capacity to neutralising incoming acidity has not yet been exhausted. In C5, groundwater has not been acidified and has a partly very high acid neutralising capacity; this is a result of low acid deposition rates here combined with high weatherability of the minerals present (including carbonates).

The nature of the geological substrate (Quaternary deposits, bedrock) of a catchment controls to a large extent the sensitivity of its groundwater to human impacts, even when these are as extreme as in C2.

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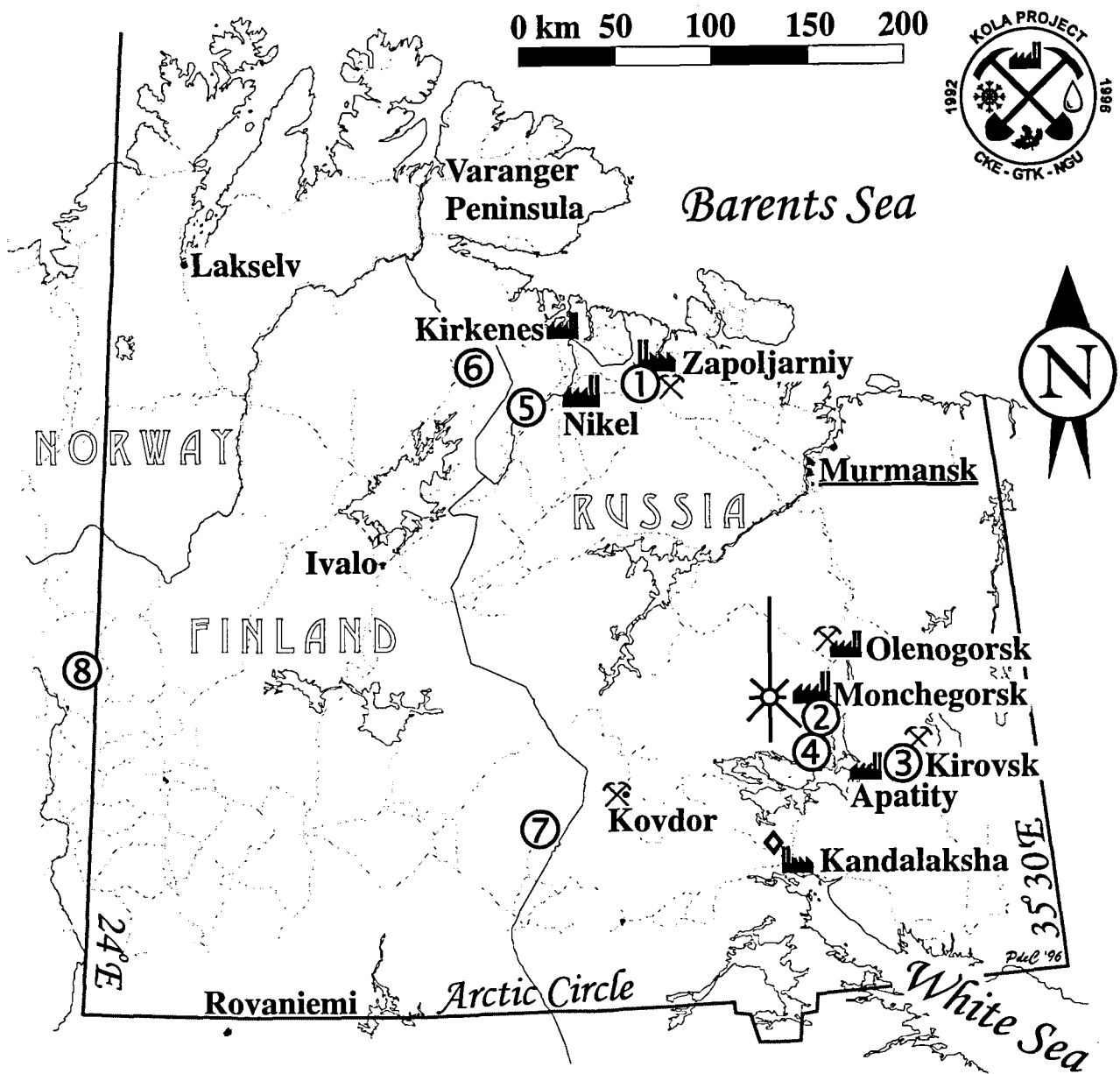


Figure 1. Location map of catchments in Russia (C1: Zapoljarniy, C2: Monchegorsk, C3: Kirovsk and C4: Kurka), Norway (C5: Skjellbekken) and Finland (C6: Kirakka, C7: Naruska and C8: Pallas). Important industrial centres include Kirkenes (open-pit iron mine and mill), Monchegorsk (nickel-copper smelter, cobalt smelter, etc.), Nikel (nickel-copper smelter), and Zapoljarniy (nickel-copper ore roasting plant).

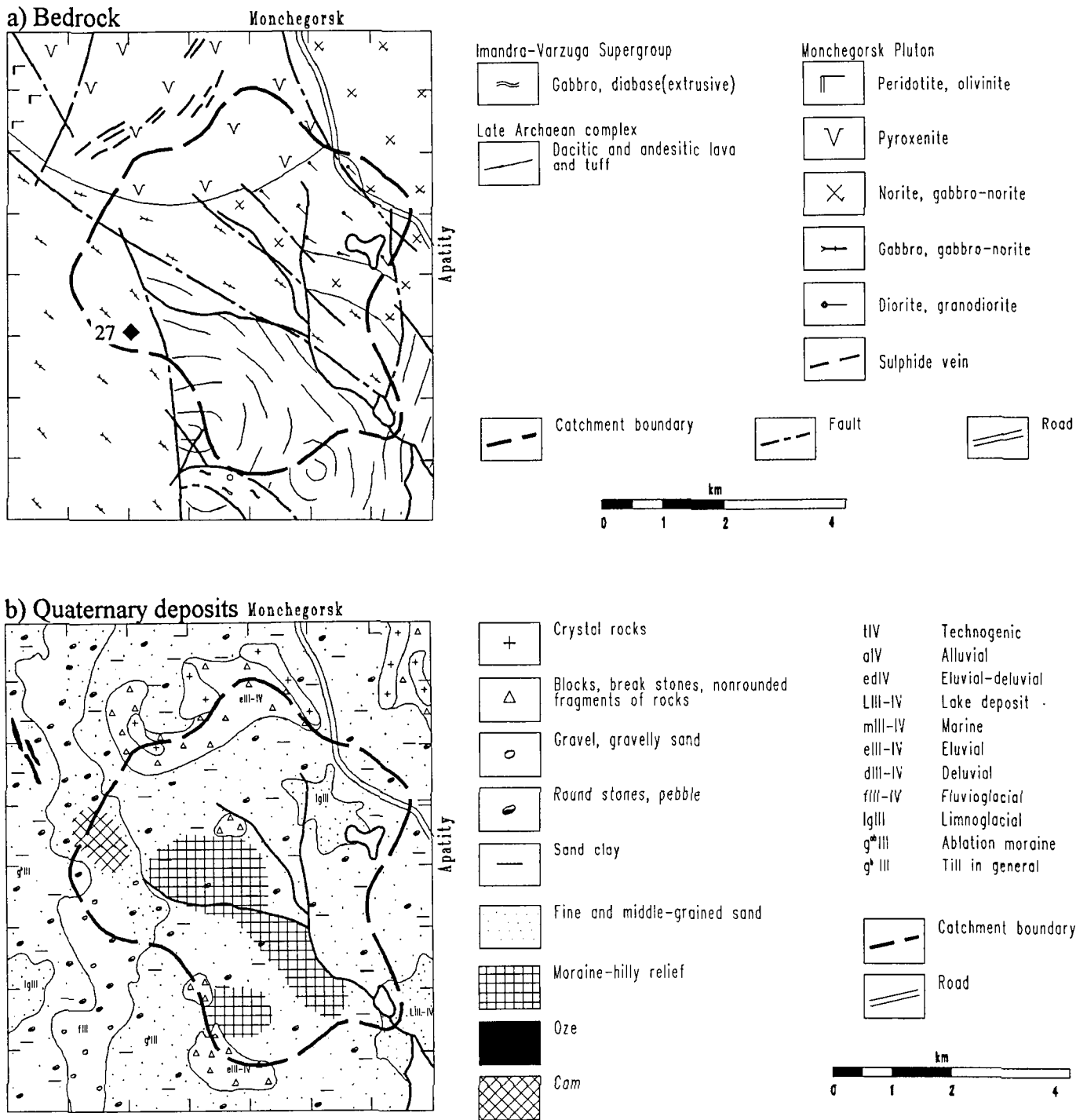
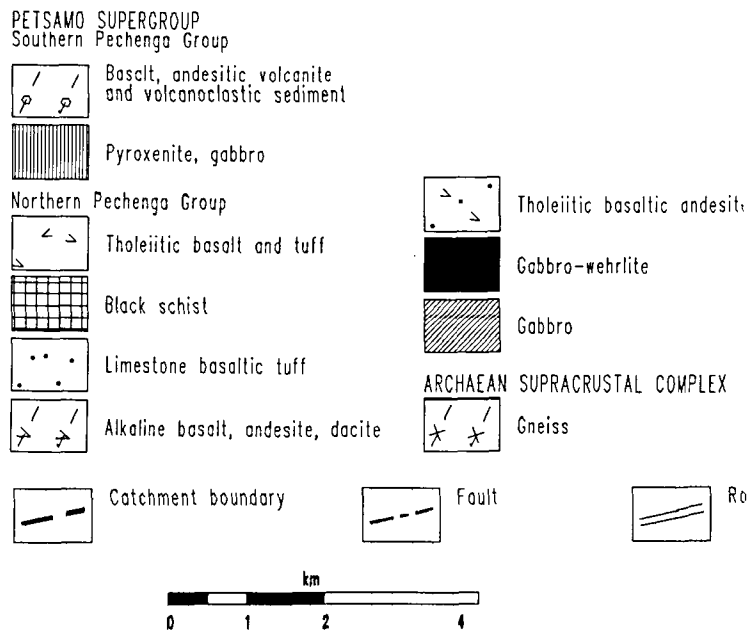
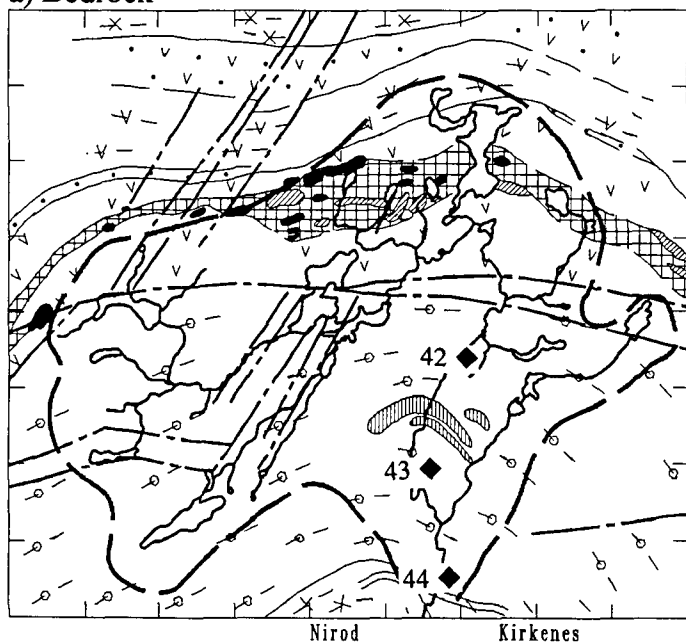


Figure 2. Bedrock (a) and Quaternary deposits (b) maps of C2. Location of groundwater well (Loc. 27) is shown on the bedrock map only for clarity.

a) Bedrock



b) Quaternary deposits

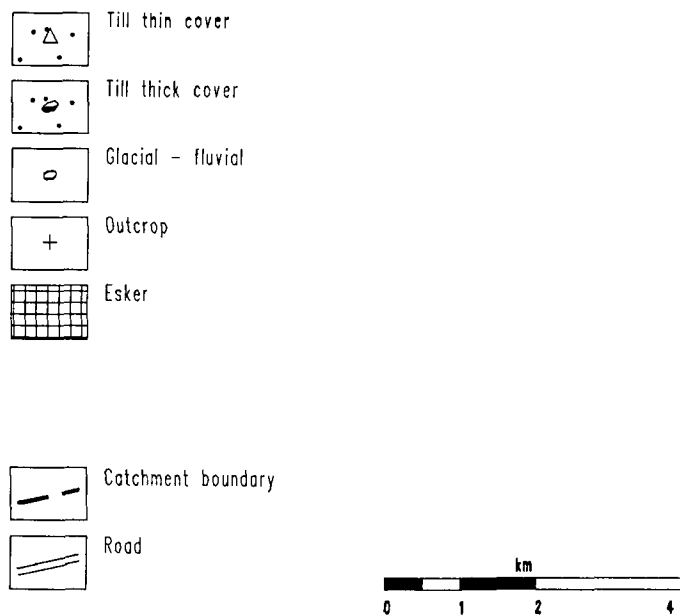
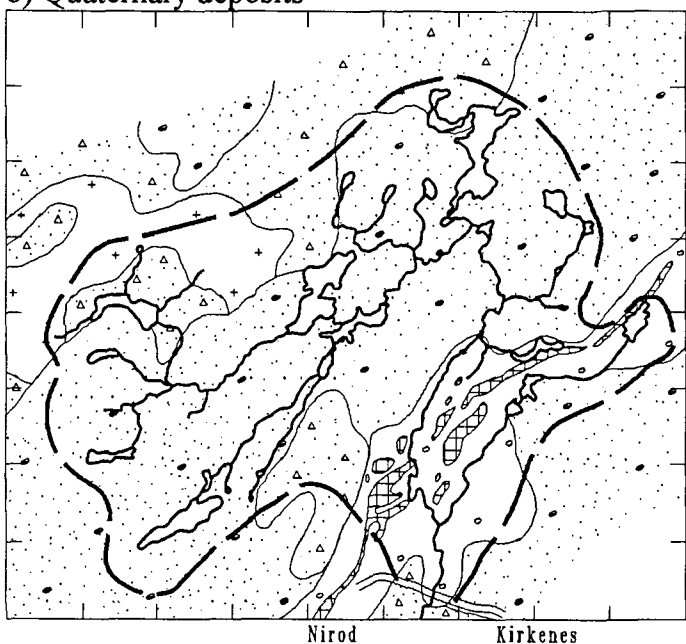


Figure 3. Bedrock (a) and Quaternary deposits (b) maps of C5. Location of groundwater wells (Loc. 42, 43, 44) is shown on the bedrock map only for clarity.

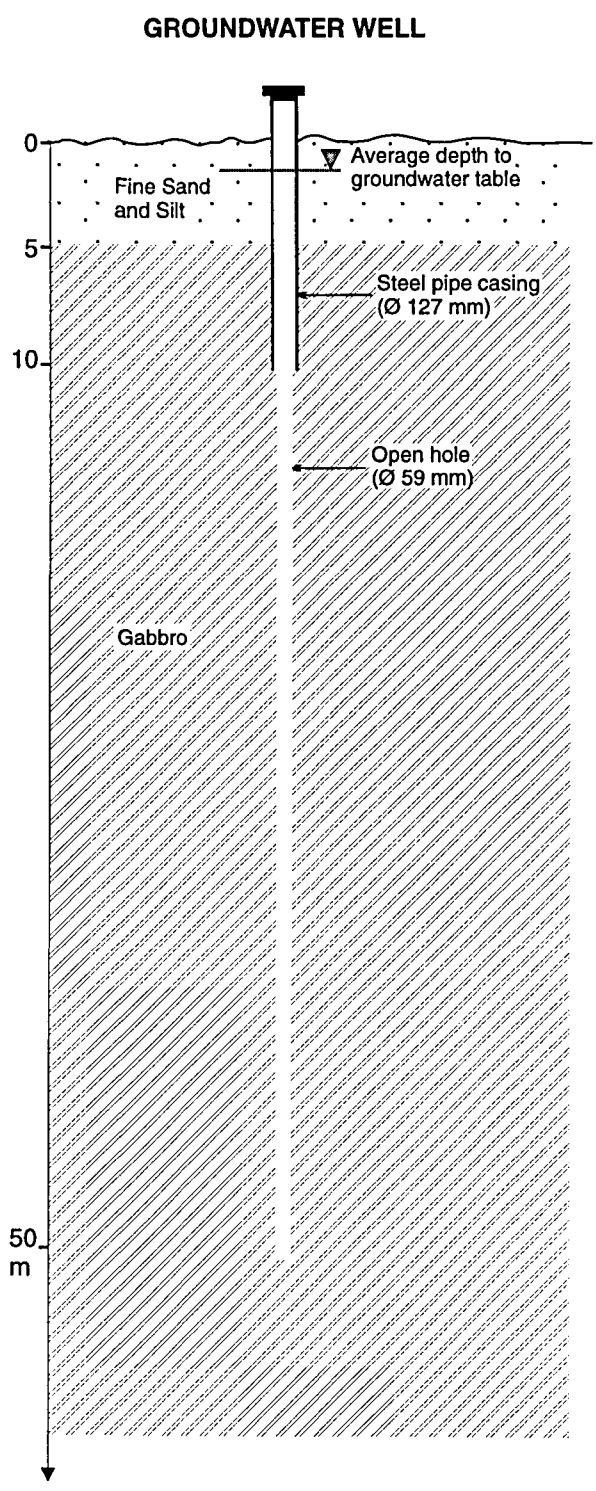


Figure 4. Cross-section of groundwater well in C2 (Loc. 27).

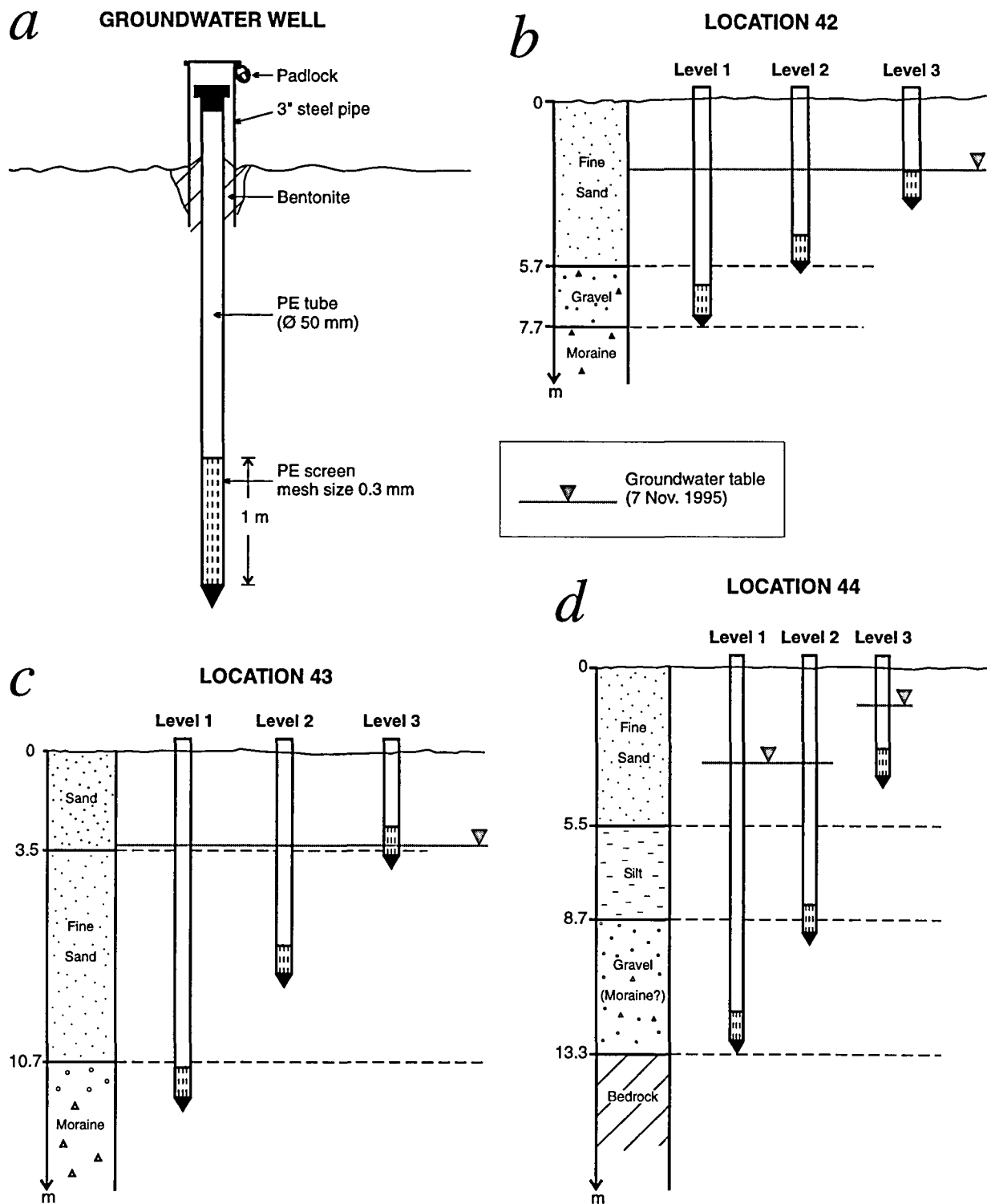


Figure 5. Cross-section of groundwater wells in C5 (Loc. 42, 43, 44).

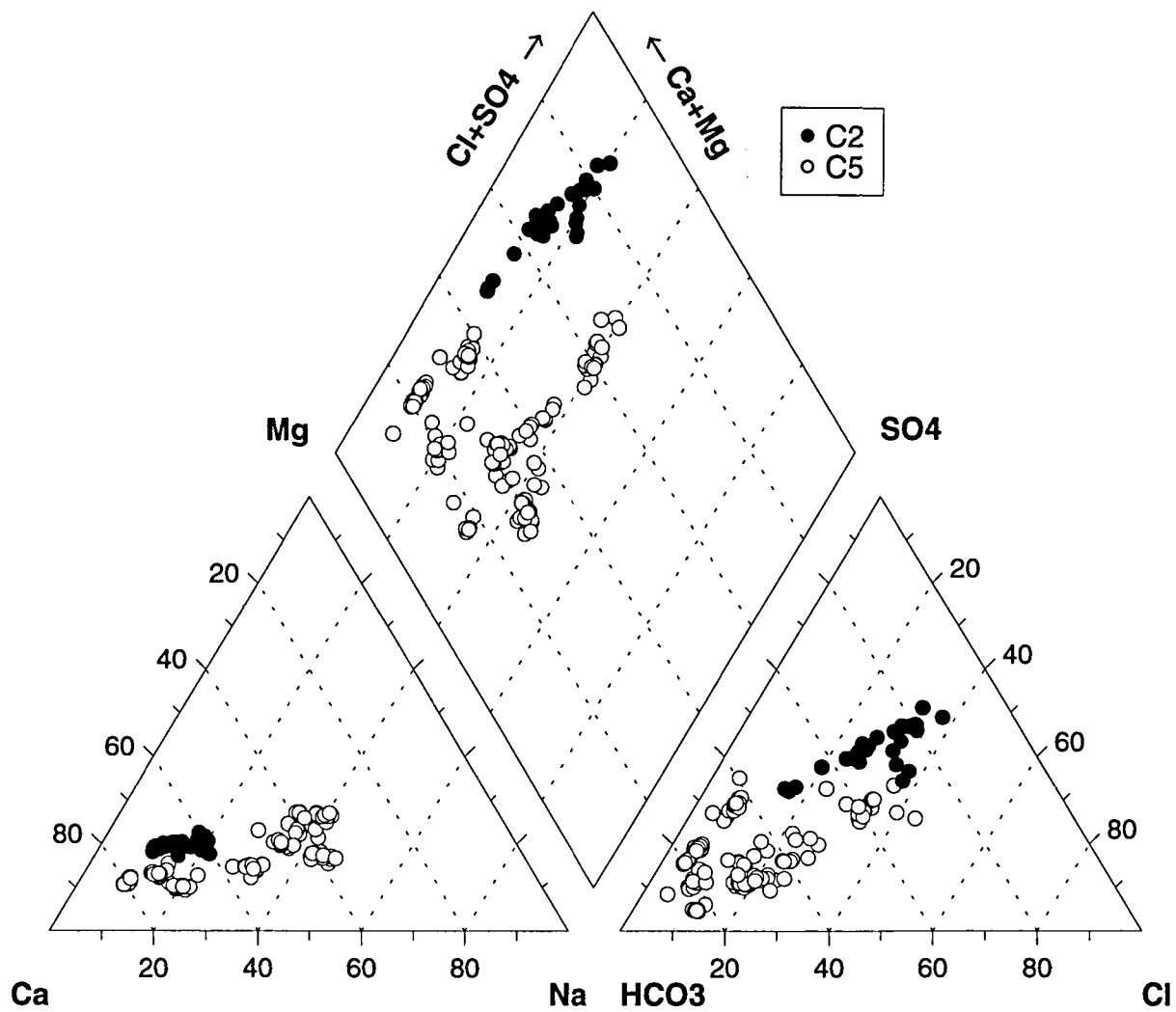


Figure 6. Piper diagram of the groundwaters from C2 and C5.

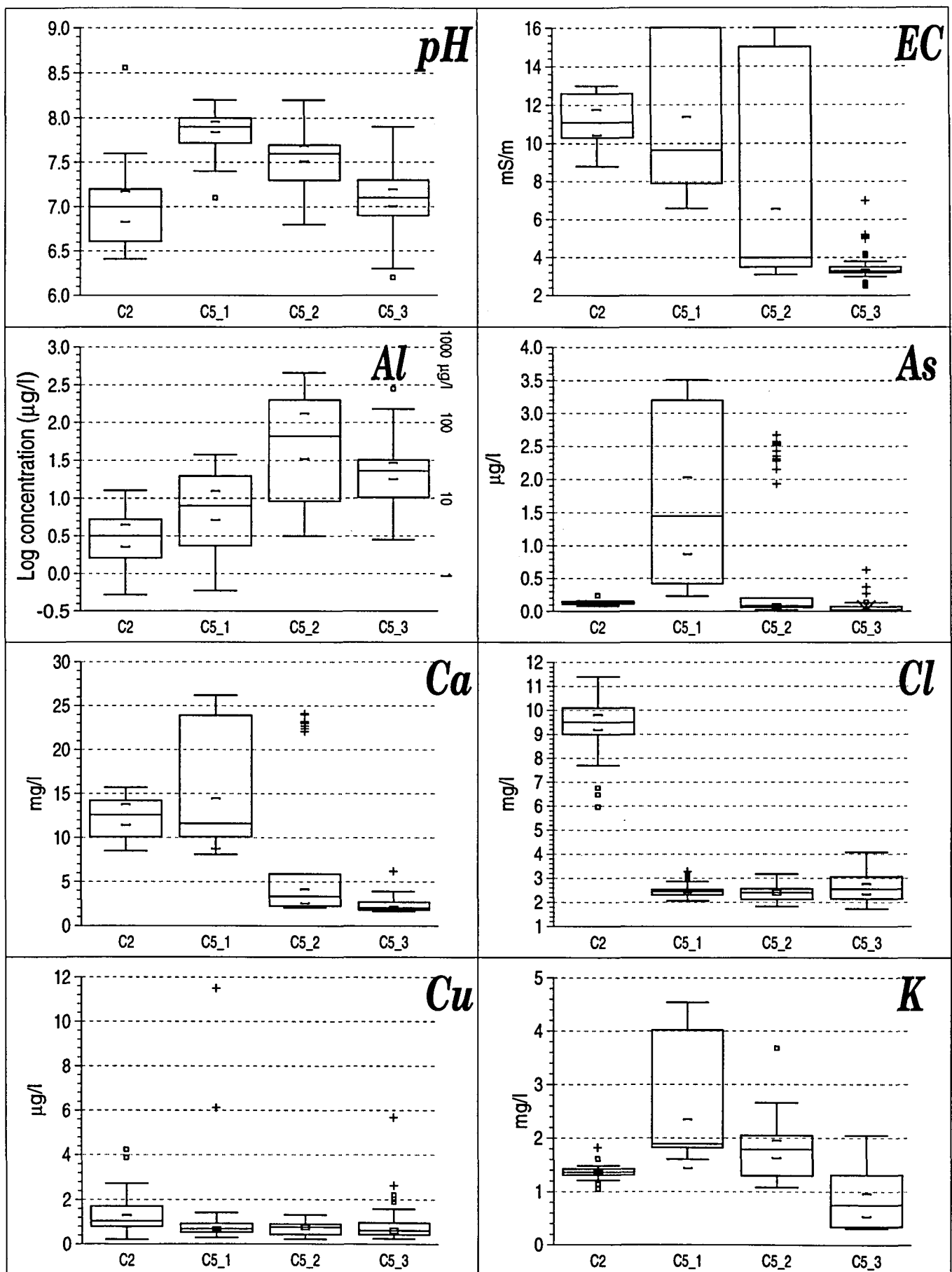


Figure 7 (part 1 of 2) Boxplot comparison of selected groundwater parameters from C2 and the deep (C5_1), intermediate (C5_2) and shallow (C5_3) wells from C5 (see Fig. 5). Each rectangular box is delimited by the 25th and 75th percentile of the data, while the horizontal strike inside the box represents the 50th percentile (median).

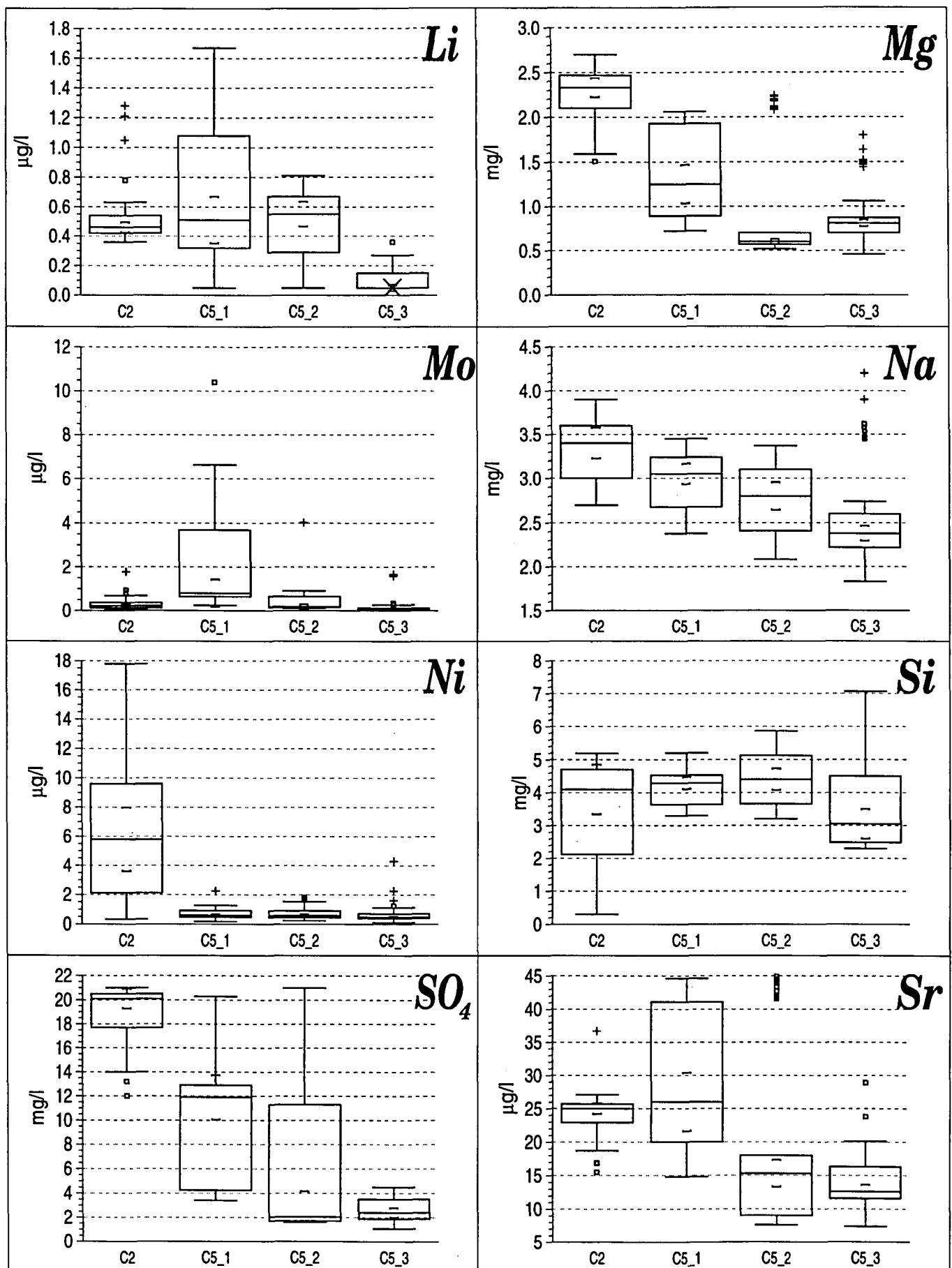


Figure 7 (part 2 of 2) Boxplot comparison of selected groundwater parameters from C2 and the deep (C5_1), intermediate (C5_2) and shallow (C5_3) wells from C5 (see Fig. 5). Each rectangular box is delimited by the 25th and 75th percentile of the data, while the horizontal strike inside the box represents the 50th percentile (median).

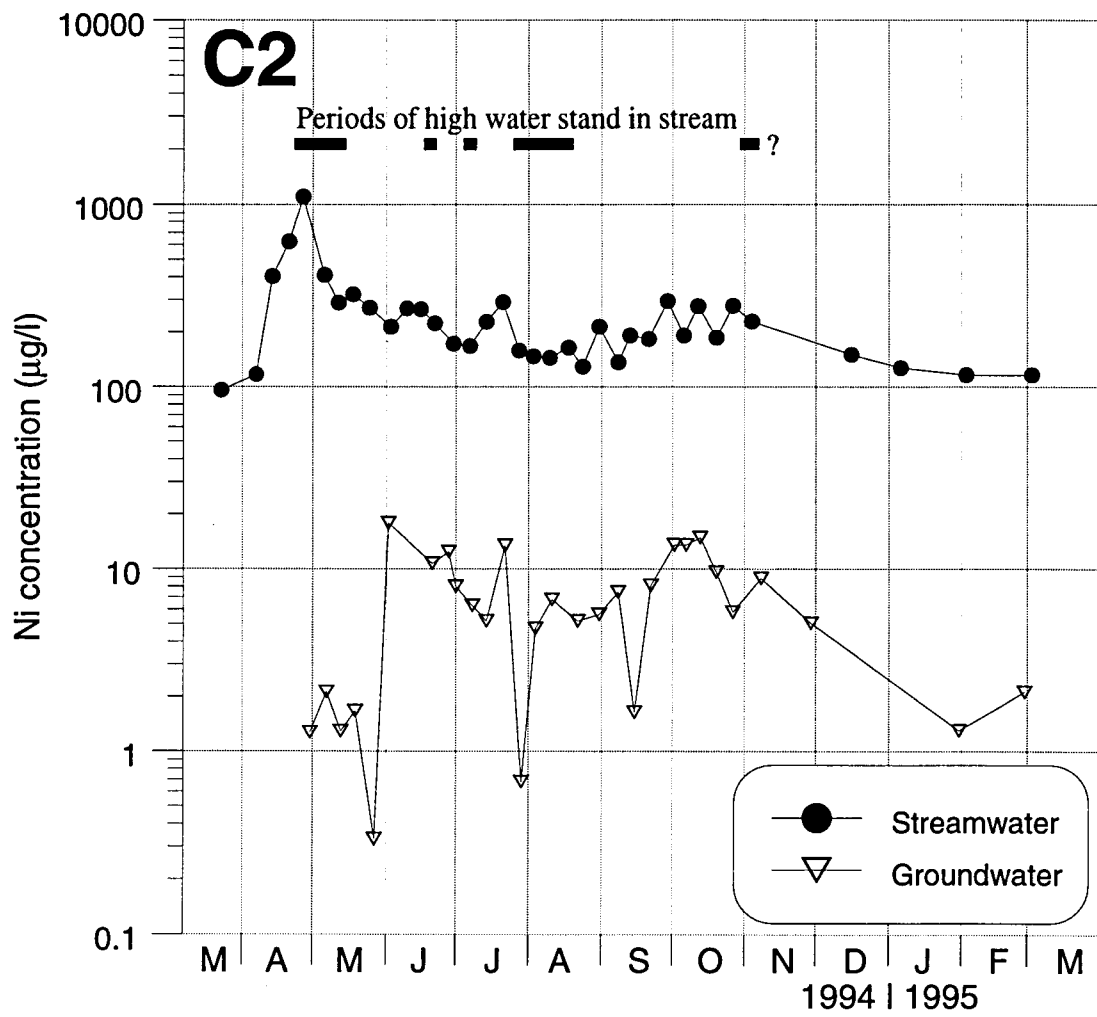


Figure 8. Time-series of Ni concentration in stream water and groundwater from C2.

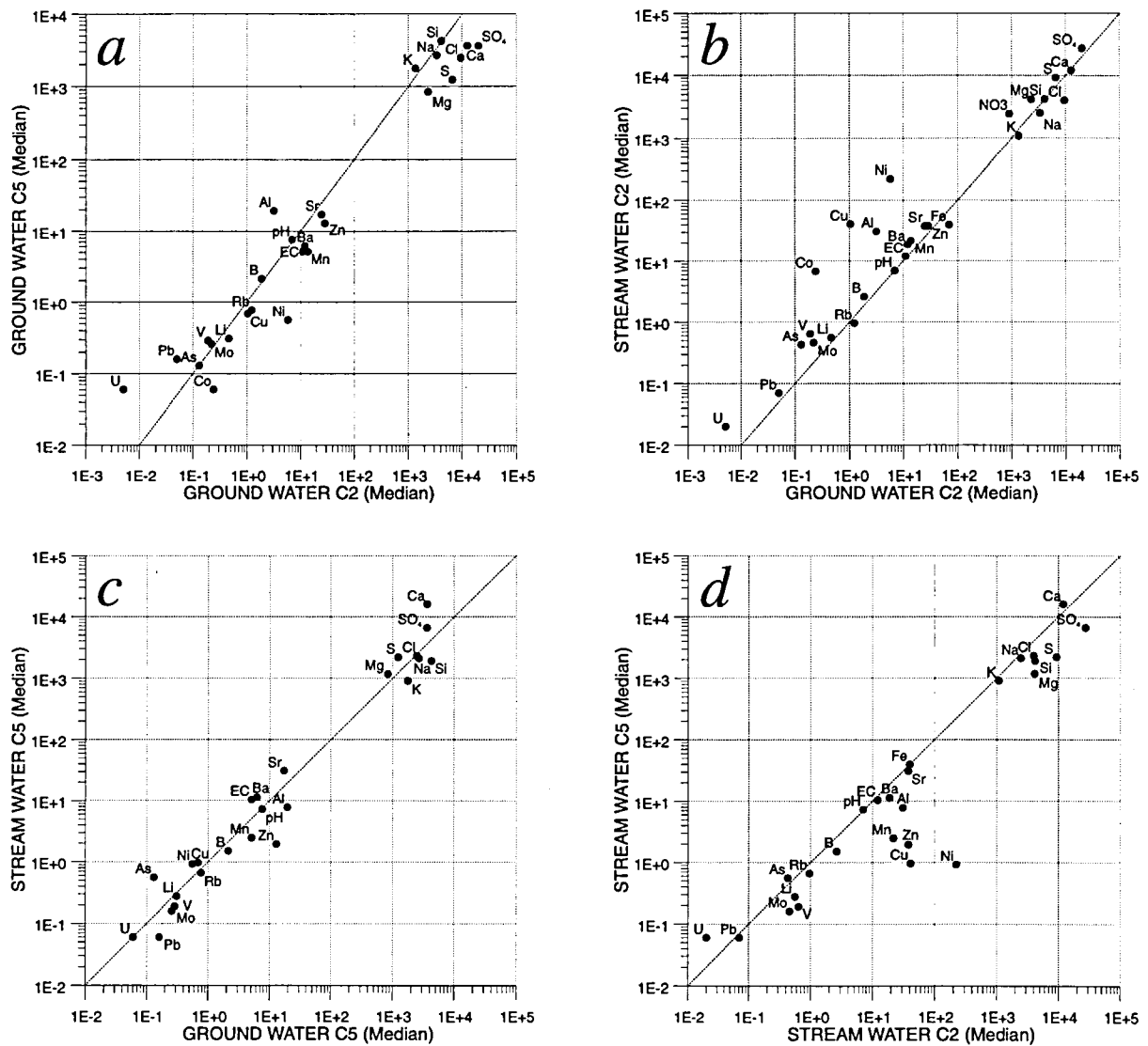


Figure 9. Median composition of groundwater in C5 vs. groundwater in C2 (a), stream water in C2 vs. groundwater in C2 (b), stream water in C5 vs. groundwater in C5 (c), and stream water in C5 vs. stream water in C2 (d). Units in $\mu\text{g/l}$, except for EC, in mS/m , and pH, in pH-units.

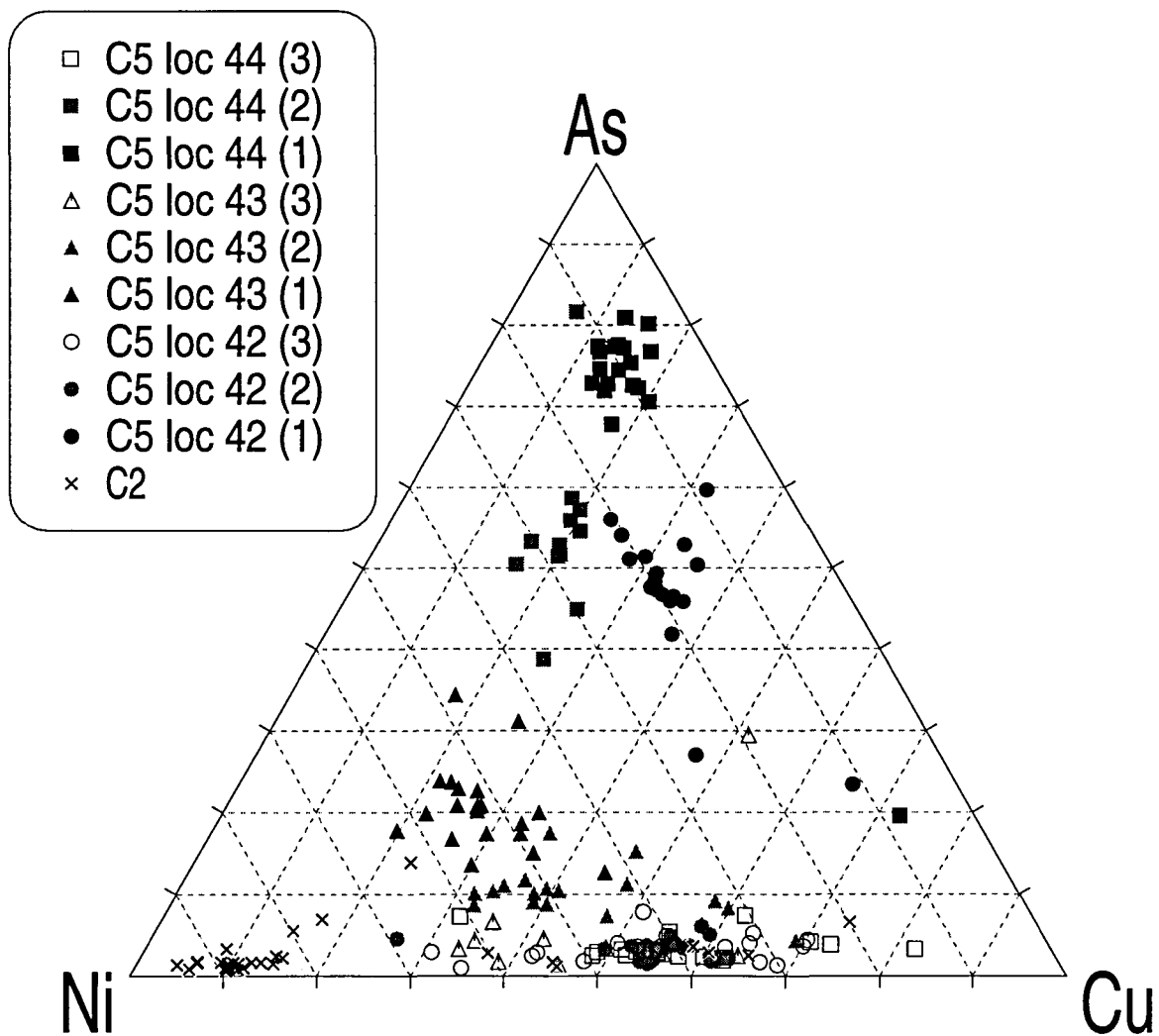


Figure 10. As-Ni-Cu ternary plot of the groundwaters in C2 and C5 (basis: concentrations in $\mu\text{g/l}$).

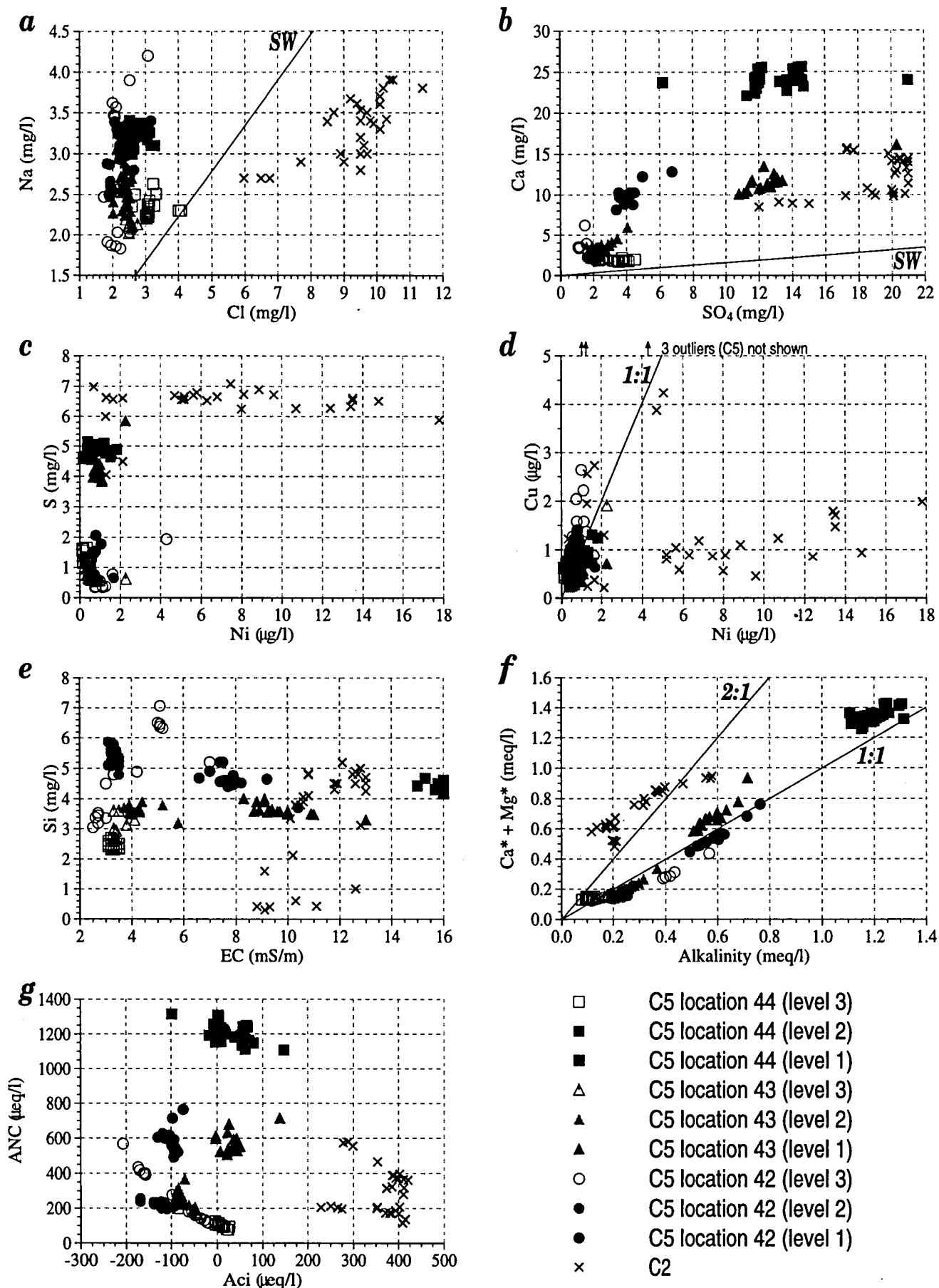


Figure 11. Scatterplots of groundwater composition in C2 and C5: Na vs. Cl (a), Ca vs. SO₄ (b), S vs. Ni (c), Cu vs. Ni (d), Si vs. EC (e), non-marine hardness vs. alkalinity (f), and acid neutralising capacity vs. acidification (g). See text for discussion. stream water represents the seawater dilution line.

Table 1: Statistical summary of the parameters determined in groundwater
(concentrations in µg/l, pH in pH-units, EC in mS/m at 25°C)

Detection	Limit	GROUNDWATER C2 (n=28; 30 Apr. 1994-28 Feb. 1995)					GROUNDWATER C5 (n=157; 20 Sep. 1994-7 Nov. 1995)				
		Min	Median	Mean	Std.Dev.	Max	Min	Median	Mean	Std.Dev.	Max
Ag	0.01	<0.01	<0.01	0.01	0.02	0.1	<0.01	<0.01	0.01	0	0.03
Al	0.1	0.52	3.18	4.07	3.41	12.6	0.59	19.4	49.24	81.17	463
As	0.05	0.08	0.13	0.13	0.03	0.24	<0.05	0.13	0.85	1.16	3.51
B	0.5	<0.5	1.86	3.83	11.36	62.8	<0.5	2.12	2.30	1.16	6.7
Ba	0.04	4.25	12.1	12.58	5.40	22.9	1.42	6.22	8.81	5.70	20.8
Be	0.1	<0.1	<0.1	<0.1		0.11	<0.1	<0.1	<0.1		<0.1
Bi	0.03	<0.03	<0.03	<0.03		<0.03	<0.03	<0.03		<0.03	<0.03
Br	30/100	<100	<100	<100		<100	<30	<30	40	36	120
Ca	10	8500	12600	12113	2350	15700	1620	3630	8900	8377	26200
Cd	0.02	<0.02	<0.02	0.02	0.01	0.06	<0.02	0.02	0.03	0.03	0.16
Cl	100	5970	9500	9290	1216	11400	1730	2450	2491	397	4080
Co	0.02	<0.02	0.24	0.27	0.20	0.67	<0.02	0.06	0.11	0.22	2.31
Cr	0.2	<0.2	<0.2	<0.2		0.42	<0.2	<0.2	<0.2		0.87
Cu	0.04	0.21	1.04	1.32	0.99	4.24	0.22	0.69	0.87	1.11	11.5
F	50	<50	<50	<50		310	<50	<50	<50		83
Fe	10	<10	70	134	224	1230	<10	<10	31	49	310
K	10	1050	1360	1363	141	1820	310	1760	1795	1074	4540
Li	0.1	0.36	0.46	0.54	0.24	1.28	<0.1	0.31	0.42	0.35	1.67
Mg	10	1510	2330	2230	333	2700	460	840	1098	557	2240
Mn	0.02	1.38	13.8	26.94	31.79	142	0.16	5.09	9.60	11.67	53.7
Mo	0.03	0.06	0.22	0.34	0.36	1.78	<0.03	0.26	0.95	1.69	10.4
Na	100	2700	3400	3317	371	3900	1830	2660	2767	466	4200
Ni	0.06	0.33	5.79	6.73	4.87	17.8	0.11	0.56	0.69	0.47	4.3
NO ₃	200	<200	900	880	485	2100	<200	<200	<200		1210
P	50	<50	<50	<50		<50	<50	<50	<50		<50
Pb	0.03	<0.03	0.05	0.05	0.04	0.19	<0.03	0.16	0.32	0.52	4.48
PO ₄	20/100	<20	<20	32	60	260	<100	<100	<100		<100
Rb	0.01	0.71	1.23	1.24	0.31	1.84	0.19	0.77	0.92	0.57	2.7
S	50	4050	6550	6285	751	7080	340	1230	2132	1775	5850
Sb	0.025	<0.025	<0.025	<0.025		0.09	<0.025	<0.025	0.03	0.03	0.23
Se	0.5	<0.5	<0.5	<0.5		<0.5	<0.5	<0.5	<0.5		0.68
Si	100	300	4100	3397	1695	5190	2300	4240	4087	1023	7060
SO ₄	200	12000	20100	18907	2505	21000	1070	3620	6125	5022	21000
Sr	0.1	15.5	25	24.05	3.92	36.7	7.35	17.2	21.39	12.15	44.9
Th	0.02	<0.02	<0.02	<0.02		<0.02	<0.02	<0.02	0.03	0.05	0.3
Ti	5	<5	<5	<5		<5	<5	<5	<5		10
Tl	0.02	<0.02	<0.02	<0.02		<0.02	<0.02	<0.02	<0.02		<0.02
U	0.01	<0.01	<0.01	0.01	0.01	0.04	<0.01	0.06	0.14	0.15	0.71
V	0.02	0.1	0.19	0.34	0.26	0.94	0.06	0.29	0.41	0.31	1.29
Zn	0.1	2.24	28.9	75.24	132.54	616	0.71	12.9	72.56	275.33	1970
EC		8.8	11.1	11.30	1.34	13	2.5	5.1	7.49	4.89	16
pH		6.41	7	7.01	0.46	8.56	6.2	7.6	7.53	0.44	8.2

Table 2: Statistical summary of the parameters determined in stream water
(concentrations in µg/l, pH in pH-units, EC in mS/m at 25°C)

<i>Detection</i>	<i>Limit</i>	STREAM WATER C2 (n=45; 23 Mar. 1994-2 Jun. 1995)					STREAM WATER C5 (n=55; 18 Mar. 1994-7 Nov. 1995)				
		<i>Min</i>	<i>Median</i>	<i>Mean</i>	<i>Std.Dev.</i>	<i>Max</i>	<i>Min</i>	<i>Median</i>	<i>Mean</i>	<i>Std.Dev.</i>	<i>Max</i>
Ag	0.01	<0.01	0.02	0.03	0.02	0.08	<0.01	<0.01	0.01	0	0.03
Al	0.1	6.02	31.1	55.26	131.08	895	1.9	7.83	9.18	5.71	24.8
As	0.05	0.23	0.43	0.59	0.49	2.39	0.35	0.56	0.57	0.09	0.83
B	0.5	0.6	2.62	2.63	0.88	5.27	0.52	1.52	1.48	0.62	2.82
Ba	0.04	13.9	18.9	18.98	2.97	26.9	7.41	11.4	11.78	2.46	19.7
Be	0.1	<0.1	<0.1	<0.1		0.22	<0.1	<0.1	<0.1		<0.1
Bi	0.03	<0.03	<0.03	<0.03		<0.03	<0.03	<0.03	<0.03		<0.03
Br	30/100	<100	<100	<100		<100	<100	<100		<100	
Ca	10	4900	12000	11036	2605	14600	7650	16100	15209	3156	19400
Cd	0.02	0.05	0.15	0.35	0.54	2.51	<0.02	<0.02	<0.02		0.03
Cl	100	1880	4000	3828	768	5500	1440	2320	2613	1945	16500
Co	0.02	1.57	6.81	12.82	16.38	83.8	<0.02	<0.02	<0.02		0.03
Cr	0.2	<0.2	0.5	0.55	0.32	1.98	<0.2	<0.2	<0.2		0.21
Cu	0.04	16.5	41	93.10	169.34	1100	0.25	0.97	0.98	0.34	2.24
F	50	<50	<50	<50		80	<50	<50	<50		50
Fe	10	10	40	48	45	240	10	40	42	24	130
K	10	730	1080	1157	336	2600	530	905	885	190	1230
Li	0.1	0.15	0.56	0.68	0.41	1.99	<0.1	0.275	0.30	0.18	1.04
Mg	10	1640	4150	3801	904	4940	590	1175	1113	224	1500
Mn	0.02	9.91	21.8	44.58	44.45	166	1.03	2.49	2.70	1.18	6.16
Mo	0.03	0.15	0.46	0.45	0.13	0.79	0.09	0.16	0.16	0.03	0.21
Na	100	1000	2500	2365	517	3700	1170	2100	2038	355	2900
Ni	0.06	96	223	261.84	171.74	1100	0.41	0.925	1.00	0.26	1.64
NO ₃	200	1400	2430	2829	1109	5500	<200	<200	219	228	1470
P	50	<50	<50	<50		<50	<50	<50	<50		<50
Pb	0.03	<0.03	0.07	0.12	0.14	0.57	<0.03	0.06	0.07	0.05	0.25
PO ₄	20/100	<20	<20	10	2	20	<20	<20	<20		<20
Rb	0.01	0.47	0.96	1.05	0.40	2.15	0.45	0.665	0.68	0.07	0.85
S	50	5600	9230	9169	1400	12500	1450	2190	2244	337	2980
Sb	0.025	<0.025	0.06	0.06	0.03	0.15	<0.025	<0.025	<0.025		0.03
Se	0.5	<0.5	<0.5	0.50	0.32	1.4	<0.5	<0.5	<0.5		0.6
Si	100	1600	4200	4071	891	5500	1170	1900	1970	595	3400
SO ₄	200	14600	27500	27496	4978	39000	4040	6600	6647	1028	9100
Sr	0.1	20.2	38	36.79	6.48	48.5	13.6	31.1	28.70	6.81	39
Th	0.02	<0.02	<0.02	<0.02		<0.02	<0.02	<0.02	<0.02		<0.02
Ti	5	<5	<5	<5		<5	<5	<5	<5		<5
Tl	0.02	<0.02	<0.02	0.02	0.01	0.07	<0.02	<0.02	<0.02		<0.02
U	0.01	<0.01	0.02	0.02	0.01	0.05	0.02	0.06	0.06	0.02	0.09
V	0.02	0.47	0.64	0.72	0.29	1.86	0.11	0.19	0.20	0.04	0.32
Zn	0.1	6.45	38.1	181.63	638.48	3820	0.42	1.97	4.69	5.54	25
EC		6	12.1	11.52	2.19	14.8	5.3	10.4	9.95	1.99	13.3
pH		5.78	7	6.96	0.44	7.6	6.65	7.3	7.40	0.39	8.1