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Abstract

Sulphide concentrations in groundwater play a key role in the long term reliability of the metal canisters containing the radioactive waste within a disposal facility for nuclear waste. This is because sulphide in the groundwaters circulating in the vicinity of the deposition tunnels can react with copper in the canisters causing corrosion and therefore reducing their expected lifetime; in a worst case scenario erosion of the bentonite buffer material will expose the canister more rapidly to the fracture groundwater.

Sulphide in the groundwater is predominantly microbially produced and thereby controlled by the content of oxidised sulphur sources, organics (carbon sources), reductants (mainly Fe(II), DOC, H_2 and CH_4), and also flow. In addition, achieved saturation in respect to amorphous Fe-monosulphide will control the possible maximum values and thus limit the Fe^{2+} and S^{2-} values in the groundwater.

The aim of this report is to assess realistic, representative and reliable sulphide groundwater concentrations at present conditions in Laxemar to be considered for use in (future) safety assessments. To achieve this, an evaluation is performed of all the sulphide related data reported from the Laxemar site investigations /Laaksoharju et al. 2009/ and later monitoring campaigns, all of which are stored in the Sicada database. This evaluation shows that values from the Complete Chemical Characterisation (CCC) (i.e. *in situ* sampling from one or more borehole sections using mobile equipment) are usually lower than those measured during the monitoring phase (i.e. *in situ* sampling from one borehole section using permanently installed equipment). An exception is borehole KLX01, where values generally lie within the same range as the monitoring samples. For most of the CCC and monitoring sections the last sample in the time series is suggested as representing the 'best possible' sulphide value. When both initial values from CCC (or samples taken with the hydrotest equipment) and monitoring values are available from one borehole section, two values are chosen, one representing an early sampling in the borehole history (i.e. CCC/hydrotest equipment) and the other representing permanent borehole installation conditions after several years (i.e. monitoring equipment). When sampling time series are measured in the monitoring sections, the sulphide values are generally much higher in the downhole tubing and in the borehole section compared with the formation groundwater from the surrounding fractures. This persists even though before taking the final samples in each time series occasion considerable amounts of water have been removed by pumping (about 10 to more than 500 section volumes). Despite such volumes, however, there still prevails some suspicion that, at least in some cases, the removed volumes may be inadequate to guarantee stable representative values. Nevertheless, it is assumed that the two groundwater samples from the same water conducting structures, i.e. the sample from the monitoring and the sample from the CCC/hydrotest equipment sampling, the latter usually showing lower sulphide, spans the interval of representative sulphide values in the formation water.

Practically all sulphide concentrations at Laxemar are ≤ 0.03 mmol/L (~0.9 mg/L). There is, however, a probability that for some locations at repository depth groundwaters may have sulphide concentrations as high as 0.08 mmol/L (~2.5 mg/L).

Sammanfattning

Mängden sulfid i grundvattnet har central betydelse för kopparkapslarnas livslängd i ett förvar för använt kärnbränsle. Sulfiden skulle kunna reagera med kopparn och därmed minska kapslarnas livslängd. Sulfid i grundvattnet produceras i huvudsak via mikrobiella reaktioner (sulfatreduktion) och är därför relaterad till mängden sulfat, organiskt material (som kolkälla), samt tillgängliga reduktanter (till exempel Fe(II), DOC, H_2 och CH_4) och grundvattenflöde. Mängden löst sulfid i grundvattnet kommer att begränsas genom mättnad med avseende på amorf Fe-monosulfid, vilket också medför att mängderna löst Fe(II) och sulfid är relaterade till varandra.

Syfte med föreliggande rapport är att ange realistiska och trovärdiga sulfidvärden för de olika grundvattentyperna i Laxemar under nuvarande förhållanden. För att uppnå syftet med rapporten har det gjorts en förnyad genomgång av de sulfidrelaterade parametrarna som redovisades i /Laaksoharju et al. 2009/ samt en noggrann genomgång av alla data från den senare grundvattenmoniteringen till och med 2009. All data har inhämtats från SKB:s databas Sicada. Sulfidvärdena från den kompletta kemiska karakteriseringen (CCC) (som är tagna ”in situ” i en eller flera sektioner med mobil utrustning) är vanligtvis lägre än de från moniteringsprogrammet med undantag för mätningarna i KLX01, vilka i stället visar värden i samma intervall som moniteringsproverna (som är tagna med utrustning som är stationär i borrhålet). Från vissa sektioner finns analyser både från CCC (eller från hydrotest provtagningen) och den senare moniteringen tillgängliga från samma vattenförande struktur i ett och samma borrhål, och i dessa fall visar moniteringsvärdena med något enstaka undantag betydligt högre värden än de som erhållits vid CCC-provtagningen. Det kan emellertid antas att sulfidhalterna i den vattenförande strukturen representeras av spannet mellan CCC-provet och moniteringsprovet. Under moniteringen, vår och höst 2008 och 2009, gjordes en mer omfattande provtagning i samband med moniteringen, där en tidsserie om 5–7 prover analyserades. I de flesta fall visade de första proven (representerande volymen som stått i kontakt med utrustningen och själva borrhålssektionen) betydligt högre sulfidvärden än de som representerade formationsvatten från sprickor i omgivande berg. För de flesta borrhålssektionerna valdes det sista provet i tidsserien. Den totala pumpade volymen uppgår till mellan 10 till mer än 500 sektionsvolymer. Trots detta kvarstår en misstanke om otillräcklig pumpning i några sektioner.

Praktiskt taget alla sulfidhalter i grundvattnet i Laxemar visar värden ≤ 0,03 mmol/L (~0,9 mg/L). Det finns emellertid en möjlighet att grundvattnet i enstaka sprickor på förvarsdjup kan ha högre koncentrationer, upp till 0,08 mmol/L (~2,5 mg/L).

Contents

1 Introduction

1.1 Background

This report forms part of the overall SR-Site safety assessment /SKB 2011/ for a repository in Forsmark based on the KBS-3 concept (cf. Figure 1-1). Only conditions at the Laxemar area are described and the objective is to compare and provide support for the main Forsmark background document by /Tullborg et al. 2010/ where the focus is on concentrations of sulphide and sulphide related parameters. The final purpose is to provide a groundwater sulphide dataset for use in the long term safety assessment modelling to be carried out on the Forsmark site /SKB 2011/.

In the safety assessment perspective for nuclear waste disposal, sulphide concentrations in groundwater play a key role in the long term stability of the copper canisters containing the waste. Sulphide in the fracture groundwaters circulating in the vicinity of the deposition tunnels can react with the copper in the canisters causing corrosion and therefore reducing their expected lifetime. As long as the bentonite buffer remains intact, sulphide formed by Sulphate Reducing Bacteria (SRB) in the groundwater at the boundary between the rock and the compacted bentonite buffer only reaches the container by diffusion with very little or no sulphate reduction taking place in the bentonite matrix /King et al. 1999, Pedersen 2010/, although sulphide will react with available Fe on its way through the bentonite. However, rapid access to the canisters can result from erosion of the bentonite buffer material along water conducting fractures intersecting the disposal borehole.

The chemical reaction of the copper corrosion process can be described as:

$$2Cu(s) + HS^- + H^+ \leftrightarrow Cu_2S(s) + H_2(aq) \qquad 1\text{-}1$$

In the presence of sulphate and sulphate reducing bacteria (SRB), the hydrogen produced will be converted to additional sulphide according to:

$$\tfrac{1}{4}\,SO_4^{2-} + H_2(aq) + \tfrac{1}{4}\,H^+ \rightarrow \tfrac{1}{4}\,HS^- + H_2O(l) \qquad 1\text{-}2$$

so that the overall reaction becomes:

$$2Cu(s) + 0.25\,SO_4^{2-} + 0.75\,HS^- + 1.25\,H^+ \rightarrow Cu_2S(s) + H_2O(l) \qquad 1\text{-}3$$

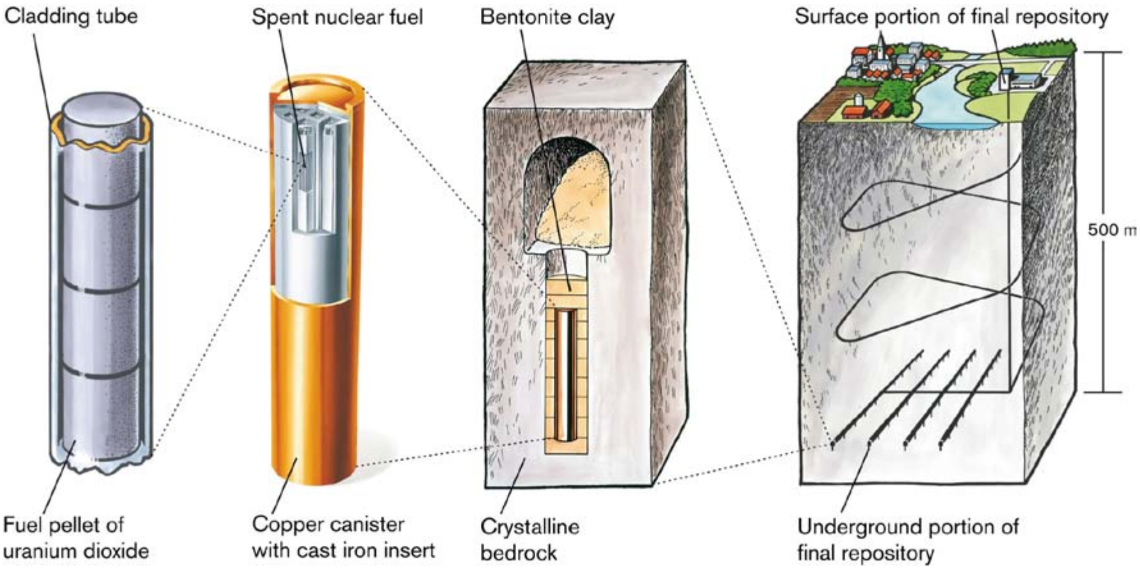

Figure 1-1. *The KBS-3 concept for a repository for spent nuclear fuel in crystalline bedrock, cf. /Gunnarsson et al. 2006/.*

Within the SR-Site project there is a need to judge if present day sulphide data selected for the Forsmark site are realistic, representative and reliable /SKB 2011/. In this context, not only the Forsmark sulphide data are considered /Tullborg et al. 2010/ but also the Laxemar site data are included here to provide a wider hydrogeochemical perspective to test for sulphide applicability. 'Representative' refers to a selected sulphide value that satisfies a number of criteria which reflect the complexity of the systems being studied, for example, taking into account the hydrogeochemistry, hydrogeology and fracture geometry of the sampled borehole section, and indirectly microbial effects. In addition, the potential influence of the downhole isolation and sampling equipment as potential sources of contamination has also played a major role.

Not only do the sulphide concentrations at present need to be defined, but the expected changes during a glacial cycle are also required in order to evaluate the extent of the corrosion of the canisters over long time periods. In order to estimate the changes in sulphide concentrations it is necessary to have a good understanding of the processes behind sulphide production (e.g. by sulphate reduction). Because the temperature in the repository (outside the canisters) is not expected to exceed 100°C, the production of sulphide can only proceed through microbial processes. Therefore, it is important to understand the conditions and limiting factors for microbial sulphate reduction based on, for example, the available amounts of sulphate, organic carbon and reactive gases such as hydrogen and methane. Of importance is also the contents of Fe(II) in the groundwaters because the saturation of amorphous monosulphide will provide an upper limit for the content of sulphide and ferrous iron in the groundwater. The same could be said with respect to the presence of Fe(III)-oxyhydroxides as their reductive dissolution by H_2S may also provide both an additional source of Fe(II) and an additional sink of dissolved sulphide (cf. Section 2.2).

1.2 Aim and scope

The aim of this report is to provide dependable sulphide groundwater concentrations for present day conditions at the Laxemar site to compare and provide support for the main Forsmark site background dataset, and to comment on the associated uncertainties for the SR-Site safety assessment analyses.

Sulphide in the groundwater is predominantly microbially produced and thereby controlled by the content of oxidised sulphur sources, organics (carbon sources), reductants (mainly Fe(II), DOC, H_2 and CH_4), and also flow. In addition, achieved saturation with respect to amorphous Fe-monosulphide will control the possible maximum values and will also bind the Fe^{2+} and S^{2-} values in the groundwater. Each of these factors will be addressed emphasising their potential influence on the content or presence of dissolved sulphide in the groundwaters.

To achieve these aims, an evaluation was performed of all the sulphide related data reported from the Laxemar site investigations /Laaksoharju et al. 2009/ and later monitoring campaigns, all of which are stored in the Sicada database. This present report includes all the groundwater data from Laxemar where sulphide has been analysed and extracted from Sicada. From this dataset, a reduced set of representative sulphide groundwater concentrations has been selected for Laxemar that can be used in subsequent modelling of canister corrosion within the SR-Site during "undisturbed" temperate periods. Data from other sites are sometimes used to support arguments made, for example in Figure 5-10, but only Laxemar data have been evaluated in this report. For site intercomparison purposes, refer to the Forsmark data in /Tullborg et al. 2010/.

It was first discovered from the preinvestigation studies at the Äspö Hard Rock Laboratory (HRL) that long delays between drilling boreholes and the subsequent Complete Chemical Characterisation (CCC) investigations (i.e. time gaps of approximately four months to one year) resulted in high sulphide concentrations in CCC samples (cf. Section 3.1.5). A thorough discussion on conceptual and representativity uncertainties of the selected sulphide data are an important part of this work.

1.3 Report structure

This study represents the integration of several disciplines which are interdependent and complex, and the report has been structured to systematically introduce each discipline and discuss the interrelationships between them. Some repetition between chapters is inevitable but generally this is considered to facilitate the reader.

The introduction to the study is detailed in Chapter 1 under background, aim and scope, report structure and finally an outline of the hydrogeochemical background to the Laxemar site emphasising groundwater evolution, composition and redox conditions. Chapter 2 introduces the major processes contributing to the production of sulphide and the control of sulphide contents in the groundwaters involving microbial activity and water/rock interaction.

A critical part of the present study has been to establish and explain the sampling uncertainties surrounding the different methods used for groundwater sampling and analysis. Sampling methods and conditions may, to a varying extent, result in the interaction of hydrogeochemistry, hydrogeology, microbiology, downhole equipment materials and sample extraction rates and time. These are summarised in Chapter 3 and, when applicable, are discussed in relation to other field studies carried out at Laxemar and Äspö. Chapter 4 details the selection criteria of 'representative' sulphide values for the Laxemar site. A thorough documentation of the selection procedure is presented in Appendix 1 and diagrams produced to visualise the sensitive changes in sulphide chemistry that occurred during sampling of the groundwater time series data are given in Appendix 2.

To put the selected sulphide values into a broader perspective, Chapter 5 provides an overview of present day hydrogeochemical conditions at Laxemar. The major groundwater types are introduced and then systematically the different chemical processes relevant to sulphide production are described and discussed. When it comes to gases (methane, carbon dioxide and hydrogen) the number of analyses available from Laxemar is relatively small and therefore results from Forsmark and Olkiluoto have been included for comparison. Also evaluated is the correlation of sulphide with hydrogeological parameters. Finally in this chapter, the results of a comprehensive literature study of sulphate production rates in different hydrogeological environments is summarised based on Appendix 3 in /Tullborg et al. 2010/.

The main conclusions as bullets are presented in Chapter 6, the acknowledgements in Chapter 7 and references in Chapter 8.

There is a necessity to explain the units used in the report. For sulphide and other groundwater compositions given in the tables (Appendix 1), in the scatter plots (Appendix 2) and in Table 4-1 (which represents data direct from Sicada), 'mg/L' has been retained. However, in order to facilitate comparison of different concentrations of sulphur compounds, mmol/L has been used in Chapters 4 and 5. Generally, it takes 1 methane or DOC + 1 sulphate to produce 1 molecule of sulphide.

When referring to a specific section in a borehole, the mid elevation of this section is given in metres above sea level, for example KLX03: –379.85 masl.

1.4 Hydrogeochemical background of the Laxemar site

1.4.1 Groundwater evolution

During the site investigation at Laxemar, explorative analyses and modelling of groundwater chemistry data measured in samples from cored boreholes, percussion boreholes, shallow soil boreholes and rock matrix porewaters were used to evaluate the hydrogeochemical conditions at the site /Laaksoharju et al. 2009/.

The four major groundwater types identified were: Fresh water (< 200 mg/L Cl), Brackish Glacial (200–10,000 mg/L Cl; Mg <25 m/L; δ^{18}O < –13.0‰ V-SMOW), Brackish Marine (2,000 to 6,000 mg/L Cl and Mg > 100 mg/L) and Brackish to Saline Non-marine groundwater with Cl ranging from 4,000 to 16,000 mg/L and Mg < 25 mg/L. Mixing between these four groups occurred in several of the sampled sections, for example, mixing between Fresh, Brackish Glacial and Brackish Marine waters in the interval 200 to 2,000 mg/L are labelled "Mixed Brackish". Mixing between

Brackish Glacial and/or Brackish Non-marine and Brackish Marine groundwaters are referred to as "Transition type" where Cl ranges from 2,000–10,000 mg/L, Mg from 25–100 mg/L and $\delta^{18}O >$ –13.0‰ V-SMOW. The distribution of these groundwater types are shown in the conceptual model in Figure 1-1 and described in /Laaksoharju et al. 2009/.

Several groundwater types which are now present in the bedrock can be associated with past climatic events in the late Pleistocene, including interglaciations, glaciations, deglaciations, and associated changes in the shoreline in connection with marine transgressions and regressions. Among these, the last glaciation and post glacial period are the most important for the groundwater development in the Fennoscandian shield, especially in terms of land uplift and shore level displacement as well as the development of the Baltic Basin.

The post glacial development reveals that when the continental ice melted and retreated from the Simpevarp area around 12,000 BC, glacial meltwater was hydraulically injected under considerable head pressure into the bedrock. The exact penetration depth is unknown, but, according to hydraulic simulations depths exceeding several hundred metres are possible. Although the last deglaciation of the Simpevarp area coincided with the end of the Yoldia period, there are no signs of Yoldia Sea water in the bedrock. The Ancylus Lake (8800 to 7500 BC) was lacustrine and developed after the deglaciation. This period was followed by the brackish Littorina Sea (7500 BC to present). During the Littorina Sea stage, the salinity was considerably higher than the Baltic Sea at present, reaching a maximum of about 15‰ in the period 4500 to 3000 BC. Dense brackish sea water from the Littorina Sea initially penetrated most of the rock in the Simpevarp subarea, and subsequently probably a more diluted variety penetrated the eastern and south-eastern parts of the bedrock at Laxemar (low topographic areas and along valleys). This resulted in a density intrusion that affected the groundwater in the more conductive parts of the bedrock. In the areas not covered by the Littorina Sea water, meteoric water circulation became established around 12,000 BC forming a freshwater layer on top of the older saline water. Driven by the land uplift, this meteoric water started to gradually flush out the older groundwater types. However, this has been limited, and consequently post-glacial water dominates at depths of about 20–300 m and remnants of glacial water still dominate within the approximate 300–600 m depth interval.

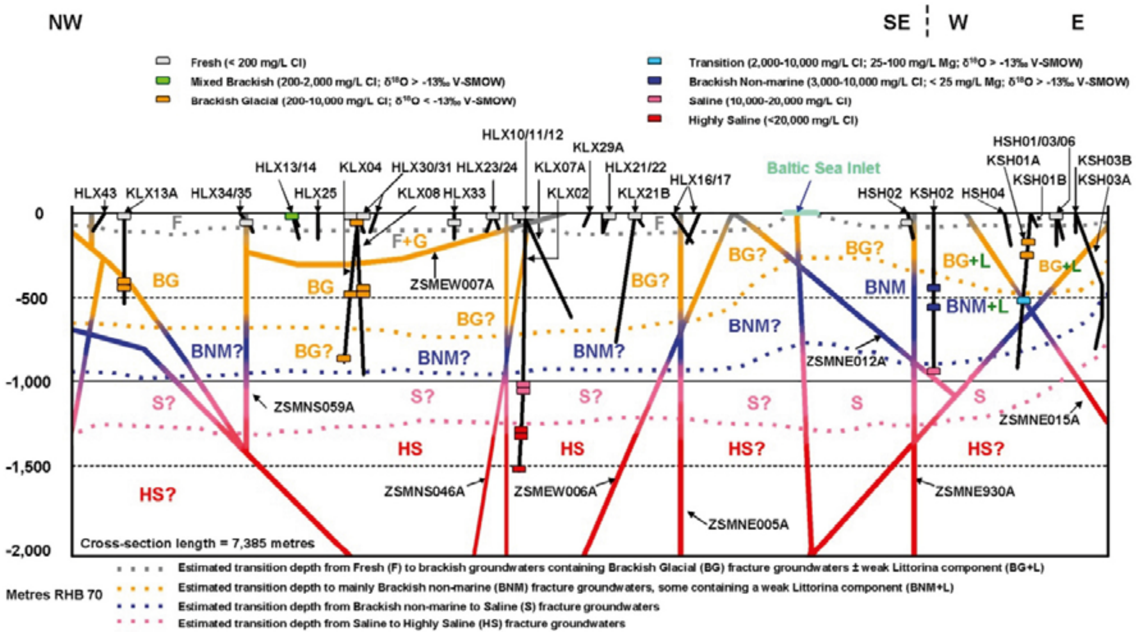

Figure 1-2. *Approximately NW-SE/W-E cross-section through the Laxemar-Simpevarp area. Shown are: a) the location of the boreholes and the sections which have undergone hydrochemical sampling, b) the main fracture groundwater types (colour coded) which characterise the site, and c) the chloride distribution with depth along the major deformation zones. The dotted lines in different colours represent the approximate depths of penetration of the various fracture groundwater types along hydraulically active deformation zones. The main regional groundwater flow direction is from the west (recharge) to the east (discharge), approximately parallel to the section. (Cross-section length = 7,385 metres) /Laaksoharju et al. 2009/.*

The Holocene evolution dominates the groundwater chemistry in the Laxemar-Simpevarp area, but at greater depths (>600 m) this is not restricted to post glacial time. At these depths the hydrochemistry of the Laxemar-Simpevarp area cannot be explained without recognising an older groundwater component. The present groundwaters therefore are a result of mixing and reactions over a long period of geological time. The interfaces between different groundwater types are not sharp and reflect the anisotropy in the bedrock hydrostructural properties.

1.4.2 Groundwater composition and redox conditions

The major hydrochemical features of the groundwaters can be summarised as follows:

The 0–20 m depth interval is hydrogeologically active (residence times in the order of years to decades) and dominated by recharge meteoric water or Fresh groundwater (< 200 mg/L Cl) of Na-Ca-HCO_3 (SO_4) type showing large variations in pH and redox conditions.

The 20–250 m depth interval is dominated by Fresh–Mixed Brackish–Brackish Glacial groundwaters of Na-Ca-HCO_3 (SO_4) to Na-Ca-Cl-HCO_3 type, showing a transition to stable reducing conditions with increasing depth. The upper approximately 150 m is characterised by modern meteoric recharge water with measurable tritium (1–5 TU); groundwaters at greater depths are either tritium free or record 1–4 TU possibly due to contamination. Down to about 200 m high bicarbonate (> 150 mg/L HCO_3) characterises the groundwaters. This is partly due to calcite dissolution but even more importantly ongoing organic decomposition in combination with microbial reduction of iron, manganese or sulphate. The residence times of the groundwaters are in the order of decades to several thousands of years.

The 250–600 m depth interval is dominated by Brackish Glacial–Brackish Non marine–Transition groundwaters of Na-Ca-Cl-(HCO_3) type. Redox conditions are reducing and low Eh values (–245 to –303 mV) are typically controlled by the interplay between the iron and especially the sulphur systems. The significant portions of glacial waters at this depth interval, and the significant increase of non-marine groundwaters with depth, indicate that groundwaters older than 14,000 years are becoming increasingly important.

The 600–1,200 m depth interval is dominated by Brackish Non marine–Saline (±Brackish Glacial and Transition) groundwater of Na-Ca Cl-(SO_4) to Ca-Na Cl-(SO_4) type. This groundwater shows very low magnesium values and they are clearly reducing (–220 to –265 mV). Interpretation of chlorine-36 measurements on these saline groundwaters indicates long residence times of hundreds of thousands of years further suggested by the low flow to stagnant hydraulic conditions.

Groundwater pH values are between 7.2 and 8.6 and they do not show any clear variation trend with depth. The pH is mainly controlled by calcite dissolution-precipitation reactions and, probably, by microbial activities. Of secondary importance is the influence of other common chemical processes, such as aluminosilicate dissolution-precipitation or cation exchange.

Rock matrix porewaters have been analysed from boreholes representing sampled depths from about 600 to 1,000 m. Taken together, similarities in the preserved porewater compositions indicate a clear change from waters of temperate meteoric origin, to glacial waters and finally to much older saline waters with increasing depth. Generally, this is in good agreement with the surrounding fracture groundwater compositions and the hydraulic properties of the bedrock.

1.4.3 Changes in redox conditions and available redox buffer capacity

Concerning the available redox and pH buffer provided by the fracture minerals present along the groundwater pathways, it can be concluded that:

- The most efficient pH buffer is calcite which is present in most of the fractures and deformation zones although in lower amounts in the upper 10–20 m.
- The main inorganic redox buffer is Fe(II), which is present in chlorite, clay minerals and in pyrite grains. The redox buffer has only been significantly decreased in the very near surface fractures (upper 20 metres) but may be partly lowered in the upper 50 m.
- Despite earlier oxidising hydrothermal events and potential increased introduction of oxidising glacial water during the Quaternary glaciations, there still remains a large redox buffer capacity provided by the fracture and wall rock minerals.

2 Sulphide related processes

2.1 Microbial sulphide producing processes

2.1.1 Metabolism

Sulphate reducing prokaryotes (organisms lacking cell nucleus), such as Bacteria and Archaea, play a key role in marine and brackish systems for the terminal oxidation of organic material to CO_2 /Muyzer and Stams 2008/ and have been isolated from shallow and deep groundwaters in the Fennoscandian shield (e.g. /Pedersen et al. 2008/). The metabolic pathway of sulphate reduction, using either H_2 or an organic energy source, is known for Archaea and Bacteria. Hydrogen sulphide, here used to indicate the species H_2S, HS^- and S^{2-}, is produced in the enzymatic reduction of sulphate (SO_4^{2-}), sulphite (SO_3^{2-}), and thiosulphate ($S_2O_3^{2-}$). Few Archaea and Bacteria can also reduce elemental sulphur to hydrogen sulphide. A more recently discovered pathway involves the disproportionation of elemental sulphur, thiosulphate, and sulphite /Finster et al. 1998/.

2.1.2 Energy and carbon sources

Sulphate reducing bacteria (SRB) conserve energy by ATP (adenosine triphosphate) synthesis through transmembral proton dislocation. The electrons for the reduction of sulphate are transported by membrane-associated cytochromes. Sulphate reducing prokaryotes can use a large variety of electron donors ranging from H_2 over short chain fatty acids (lactate, formate, propionate, butyrate) to aromatic compounds (benzene, benzoate) to alkanols, alkanoic acids and alkanes /Muyzer and Stams 2008/. The rates of sulphide production in many aquatic systems are therefore critically dependent on the rates of production of the potential electron donors in preceding fermentation reactions. Several SRB are known to be autotrophic and to utilise H_2 and CO_2 (e.g. most notable being the various *Desulfovibrio* species).

Sulphate-reducing prokaryotes can also be involved in the corrosion of metallic iron (e.g. /Dinh et al. 2004/). Both direct and indirect iron corrosion mechanisms have been proposed, the most common explanation being an indirect corrosion process called "hydrogen embrittlement" that occurs as a result of the oxidation of metallic iron with hydrogen sulphide (produced by microbiological sulphate reduction) according to the reaction: $Fe + H_2S \rightarrow FeS + H_2$. The ready consumption of the H_2 by sulphate reducing bacteria drives this reaction. Waters with high concentrations of biodegradable organics may, therefore, promote the corrosion of iron. Sulphate reducing prokaryotes may also be directly involved in corrosion, i.e. a cell surface active cytochrome may serve as an electron shuttle and participate in the electron transport from metallic iron to reduce protons to H_2. The oxidation of H_2, in turn, drives the reduction of sulphate /Dinh et al. 2004/.

An important process for sulphate reduction is the anaerobic reduction of sulphate by methane. Most existing evidence suggests that this process is catalysed by a syntrophic anaerobic consortium of methane-oxidising Archaea that transfer a reactive intermediate (possibly methanethiol) to the sulphate reducing partner /Knittel and Boetius 2009/. In this case the sulphate reducers live off the product from the methane-oxidisers. In the marine environment, this process oxidises globally up to 95% of all methane formed biogenically in the marine subsurface.

Despite their name, sulphate reducing bacteria neither are exclusively dependent on sulphate or other dissolved sulphur compounds, nor are they always obligate anaerobic bacteria. Some SRB, for example, several *Desulfovibrio* species and *Desulfobulbus propionicus*, can use nitrate (NO_3^-) as an alternative electron acceptor, and reduce NO_3^- to NH_4^+ /Widdel and Pfennig 1982/. Few sulphur bacteria even have been shown to perform oxygen respiration. However, aerobic respiration does not support growth and is probably a means of removing O_2 when it is present in an environment otherwise suitable for growth of SRB /Madigan et al. 2000/. Reduction of iron(III) has rarely been observed for sulphate reducers.

Since most sulphate reducers are anaerobic heterotrophs, their activity relies on the concomitant production of suitable low molecular weight organic electron donors that can be taken up across the cell membrane and are needed for energy conservation. In most aquatic settings, the rate of sulphate reduction is, therefore, limited by the availability of suitable electron donors and many SRB live in intimate syntrophic associations with fermenting bacteria or with other electron donor producing partners /Plugge et al. 2002, Harmsen et al. 1993/. Sulphate reduction is thought to be limited when electron donor or acceptor concentrations fall below the so-called thermodynamic energy threshold.

2.1.3 Adaptations

Sulphate reducing bacteria have been isolated from a wide range of physical and chemical environments /Rabus et al. 2006/. Sulphate reducing bacteria occur in environments of low permeability, but also in systems of slow flow such as fine grained sand aquifers. It is generally poorly understood whether SRB are mainly associated with solid surfaces or free-living. In systems with low permeability, SRB are likely to be associated with particles and rely on the molecular diffusion of substrate to the cell. In flowing systems, the bacteria are also likely to be free living as indicated by successful enrichments from pumped groundwater /Pedersen et al. 2008/. Sulphate reducing bacteria have been found often attached to mineral or other solid surfaces and are part of biofilms /Pedersen et al. 1996, Santegoeds et al. 1999/. It is important to emphasise that in any given environment, the proportion between free living and surface attached bacteria, for example in deep groundwaters, is generally poorly established. The greatest restriction to sulphate reducing microbial activity is the presence of consistently high concentrations of molecular oxygen, since reactive oxygen species such as peroxide and superoxide can damage or destroy reactive centres and redox sensitive proteins. At concentrations of oxygen of less than 1 μM, activity of sulphate reducers was sustained and oxygen may even have been used as an alternative electron acceptor /Krekeler et al. 1997/.

2.1.4 Methods to analyse microbial populations

There are many microbiological methods in use for the analysis of sulphide producing processes. The most common method involves bacterial enrichments and most probable number (MPN) counting. Common nucleic acid based methods include 16S-rDNA/rRNA- or functional gene based finger printing methods to assess microbial community composition, or microarray based gene sequence analyses /Muyzer and Stams 2008/. Generally, however, these molecular methods cannot be used to quantify microbial population size.

Microbiological analyses of the Laxemar (and Forsmark) groundwaters were carried out using the most probable number (MPN) method to determine nitrate, manganese, iron, and sulphate reducing bacteria, as well as autotrophic and heterotrophic acetogens, and autotrophic and heterotrophic methanogens.

2.2 Water-rock reactions

The reduction of sulphate to sulphide in natural systems may occur both inorganically (thermochemical sulphate reduction, TSR) and bacterially mediated (bacterial sulphate reduction, BSR) but in mutually exclusive thermal regimes; TSR at temperatures higher than 100–140 ºC and BSR at lower temperatures (e.g. /Machel 2001/ and references therein). Thus, the presence of dissolved sulphide in low temperature aqueous environments is undoubtedly related to SRB activity. However, additional factors other than SRB activity, and mainly related to the iron system, may participate in the control of dissolved sulphide contents in low temperature groundwaters.

Different inorganic, kinetically fast reactions that may play important roles in the control of dissolved sulphide contents in reducing groundwaters are the precipitation of ferrous sulphide and the inorganic reductive dissolution of iron (or manganese) oxyhydroxides by the dissolved sulphide.

Ferrous sulphide formation in low temperature environments is intimately linked to the activity of sulphate reducing bacteria (SRB) as a source of H_2S. It is a potentially important process as it can control dissolved sulphide (and iron) concentrations, limiting their mobility in anaerobic aquifers. The "amorphous" iron monosulphide (more properly termed disordered mackinawite or nanocrystalline mackinawite (cf. /Gimeno et al. 2009/ and references therein) is the first phase to precipitate in most natural aqueous environments because it is the most soluble of the ferrous sulphide phases, according to the reaction:

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \qquad 2\text{-}1$$

Its precipitation rate is very fast compared to other sulphides and the nanocrystalline character of this first precipitate /Wolthers et al. 2003, 2005, Rickard 2006/ may induce the formation of colloidal phases. Recrystallisation (ripening) towards more ordered, crystalline mackinawite is also a fast process that can affect the composition of the surrounding waters, which would quickly reequilibrate with respect to this less soluble and more crystalline mackinawite /Chen and Liu 2005/.

Apart from SRB activity, a source of iron is needed in order to surpass the IAP (Ion Activity Product) of the amorphous monosulphides, allowing their precipitation. The relative importance of these two factors (SRB activity and iron availability) would give rise to waters with high dissolved sulphide contents (if there is no source of iron) or low sulphide contents in spite of the SRB activity (if the amorphous ferrous monosulphides precipitate).

The activity of iron reducing bacteria (IRB) may serve as a source of Fe(II) but the reductive dissolution of iron oxyhydroxides by H_2S may also provide both an additional source of Fe(II) and an additional sink of dissolved sulphide. The inorganic reductive dissolution of iron oxyhydroxides by the dissolved sulphide (sulphidisation of iron minerals), proceeds via the oxidation of dissolved sulphide at the mineral surface (e.g. according to /Pyzik and Sommer 1981, Yao and Millero 1996, Poulton et al. 2004/:

$$H_2S + 2FeOOH + 4H^+ \rightarrow S^0 + 2Fe^{2+} + 4H_2O \qquad 2\text{-}2$$

This reaction promotes the release of Fe(II) to solution and its subsequent reaction with additional dissolved sulphide to produce FeS according to reaction (1). The extent to which iron minerals are able to control dissolved sulphide contents depends on the reactivity and abundance of the particular minerals present. Iron minerals display a wide variability in terms of their reactivity towards dissolved sulphide, ranging from reactive Fe(III) oxyhydroxides (with very fast kinetics) to essentially unreactive Fe-silicates (/Gimeno et al. 2009/ and references therein).

Similarly, dissolved sulphides may quickly react with manganese oxides (if present) according to /Yao and Millero 1993/:

$$H_2S + MnO_2 \rightarrow S^0 + Mn^{2+} + 2OH^- \qquad 2\text{-}3$$

$$H_2S + 4MnO_2 + 2H_2O \rightarrow SO_4^{2-} + 4Mn^{2+} + 4OH^- \qquad 2\text{-}4$$

Thus, the availability of iron (e.g. hematite) and manganese oxyhydroxides in the fracture fillings may play an important role in the buffering of the dissolved sulphide in groundwaters and this potential role would merit further study.

3 Sampling uncertainties

3.1 Different methods for groundwater sampling and analysis

The groundwater data in the Sicada database originate from groundwaters sampled under quite different conditions in terms of possible influence from drilling, hydraulic tests and other borehole activities /Smellie and Tullborg 2009/. Furthermore, they are sampled in different ways which may severely influence the results of certain parameters (e.g. trace elements such as Cu, Mo, As and Cr and the lanthanides). This may also be the case for elements involved in microbial or inorganic redox reactions, for example, Fe(II)/Fe(III), S(-II)/S(VI) and Mn(II)/Mn(IV). Below are listed the sequence of borehole activities carried out and the different sampling techniques. Their possible influence on the sulphide system in particular is described in /Tullborg et al. 2010/.

3.1.1 Investigation sequence in cored boreholes

During the site investigations in Laxemar, in common with Forsmark, bedrock groundwater samples for sulphide analyses were mainly collected by two different methods, *Complete Chemical Characterisation (CCC)* most often relatively soon after borehole completion, and subsequent regular periodic *Monitoring Sampling*. No earlier sulphide data were obtained from packed-off borehole sections in percussion boreholes, only from selected sections during the later monitoring sampling programme.

Microbial production of sulphide is probably influenced by borehole activities /Hallbeck and Pedersen 2008a, b, c/. In particular, heavy pumping or conditions causing mixing of groundwaters from different aquifers may disturb or promote microbial activity. Therefore, it is necessary to consider also the sequence of borehole events that have preceded each sampling occasion. Important to mention in this context is the rigorous demands on cleaning the downhole equipment prior to use and on the correct choice of lubricants, especially for activities early in the sequence before the CCC sampling programme commenced. The bioaccessibility of all chemical products used have been thoroughly addressed.

In general, the different geoscientific investigation activities carried out in the cored boreholes within the Laxemar and Forsmark site investigations were conducted in the following order (cf. /Tullborg et al. 2010/):

- Drilling and contemporaneous mammoth pumping.
- Additional pumping (if required) to remove the remaining drilling water from the borehole.
- Different downhole activities, for example, BIPS (Borehole Image Processing System), geophysical loggings, differential flow logging etc.
- Complete Chemical Characterisation (CCC) /SKB 2001/ using the special SKB mobile chemistry units*.
- Hydraulic injection tests (only in selected boreholes and borehole sections)*.
- Groundwater flow measurements (only in selected boreholes and borehole sections) using the dilution test equipment and injected tracers*.
- Installation of stationary monitoring equipment for groundwater level monitoring, groundwater sampling as well as groundwater flow measurements in packed-off borehole sections.
- Groundwater sampling performed yearly, alternatively twice a year within the hydrochemical monitoring programme*
- Monitoring of groundwater flow using the tracer dilution technique

The asterisk (*) indicates the occasions when groundwater samples are sampled and implications of these different methods on sulphide values are presented and discussed in detail in /Tullborg et al. 2010/. The exception to this is the potential impact of sampling using the PSS (Pipe String System) hydraulic testing (or hydrotest) equipment (i.e. Hydraulic injection tests) and sampling using the dilution test equipment for groundwater flow measurements. There are six samples from Laxemar which have been sampled using this equipment (Boreholes KLX04, KLX06, KLX19A and KLX11A) and thus a description is warranted here.

Groundwater sampling with the PSS equipment implies pumping the groundwater from the sampled borehole section through a pipe string made of aluminium (inner diameter = 21 mm), generally at a flow rate of several litres per minute. The section length is fixed and can be either 5, 20 or 100 m. The pump used in this equipment is not suitable for low flow rates below 5 L/min and therefore in borehole sections with a low water yield the pumped water has to be recirculated back to the pump to avoid pump failure. The sampling method is considered unsuitable for on-line measurements of Eh at the surface and therefore since sulphide is a redox sensitive component, the sulphide concentrations may also be affected by this method. Furthermore, the generally high flow rate, the pumping system and the large aluminium surface area in contact with the sampled waters, are factors that may result in sampling artefacts.

Groundwater sampling using the dilution test equipment resembles the CCC sampling since the water is pumped from the borehole section (flexible length) at similar flow rates and through an umbilical hose similar in type to the CCC equipment. On-line redox measurements may be performed if a flow through measurement cell is connected to the pumped water outlet at the surface and the success rate is similar to corresponding CCC measurements.

Both types of equipment may be used for collecting single samples as well as sample time series. Generally, in the Laxemar case, three samples in series were initially collected but only one was selected and sent for a complete set of analyses.

An additional complication which is relevant for both sampling methods is whether the sampling was performed before or after the injection tests or the groundwater flow measurements. Both of these tasks involve the addition of water which may not be *in situ* as well as tracer compounds to the borehole section which may contaminate the groundwater, add foreign microbes and affect the redox conditions. The actual sampling method for each borehole section is stated, when possible, in Appendix 1.

Table 3-1 provides a summary of the sampling conditions which characterise the CCC and monitoring programmes.

Table 3-1. Summary of sampling conditions characterising the CCC and monitoring programmes.

Condition	CCC sampling	Monitoring sampling
Frequency.	On one occasion.	Once a year from 2006–2007 and twice a year during 2008–2009.
Time between completion of drilling and sampling.	2–12 months.	From 4 months to several years delay before the first sampling occasion.
Typical borehole settling/stabilised period prior to pump start*.	In the order of 3–14 days.	4–6 months.
Typical exchanged volume prior to first sample/sampling.	Water channel volume in the 1,000 m long umbilical hose**= 25 L.	3–5 borehole section volumes up to 2007. During 2008–2009 sampling was conducted based on time series and total volumes pumped are exemplified by the data from 2008 /Table 3-4 and 3-5/.
Section volume/section + tube volume.	15–25 L/40–50 L	11–65 L/26–73 L.
Sample water flow rate.	50–270 mL/min.	50–270 mL/min (is dependent on the hydraulic transmissivity of the borehole section and therefore a low flow rate during CCC implies a low flow rate also during monitoring sampling).
Main difference from contamination aspects.	The groundwater is always flowing through the equipment during operation and the equipment is removed when not in use.	Stationary equipment in borehole section and close to stagnant groundwater present in the complex monitoring system for several months between sampling occasions.
Number of time-series samples taken during continuous pumping.	A total of 44 time series from 44 borehole sections were compiled	2 series in December 2007, 12 in March 2008, 11 in November 2008, 11 in April 2009 and 8 in November 2009.

* If clean up pumping is performed in the borehole section to be investigated using the CCC equipment as an initial measure to lower the drilling water content, there will be no settling/resting period.

** Furthermore, the removed water volume from the borehole section will amount to a 1–4 m^3.

3.1.2 Complete Chemical Characterisation (CCC)

The equipment for CCC consists of a hose unit with facilities for lowering and raising the approximately 1,000 m long umbilical hose carrying the downhole units which consist of: 1) Upper and lower packers used to isolate a predetermined borehole section. 2) Downhole piston pump controlled by a pump unit at the ground surface. 3) Probe for *in situ* measurements of pH, Eh, pressure and water temperature. 4) Downhole sampler for collecting *in situ* samples at maintained pressure. The investigations are performed in one borehole section at a time using downhole equipment which has been internally rinsed and filled with deareated and deionised water before use and where the outside of the equipment is cleaned/wiped using 70% ethanol when being lowered into the borehole. Despite this cleaning, sterile conditions can not be assumed to prevail and foreign microbes may be introduced by the equipment.

Prior to sampling, the sample water is first pumped through the downhole units and further through the Tecalan tube housed in the umbilical hose to the ground surface where sample portions are collected for sulphide (and other components) analysis. All contact surfaces are either composed of polyamide or high quality stainless steel, and lubricants (generally Teflon spray but also vaseline) are used sparsely on O-rings in valves and other different types of connections.

During the site investigations in Laxemar, the CCC sampling campaign generally was performed between two to twelve months after drilling of the borehole was completed. The lengths of the packed-off borehole sections varied between 11 and 50 m. The volume of the borehole sections was in the order of 15–25 L but depends on section length and configuration of the downhole equipment, and the water-conducting part of the approximately 1,000 long umbilical tube adds an additional 25 L. The pumping flow rate was between 50 to 270 mL/min depending of water yield, and the pumping periods were a minimum of three weeks; however, pumping was often prolonged due to unacceptably high drilling water contents. Generally, two samples per week were collected and all were analysed for sulphide. Duplicate samples were collected in Winkler bottles and immediately conserved with sodium hydroxide and zinc acetate in the field. The analytical method for sulphide, based on /Grasshoff and Chan 1971/, is the Swedish Standard SIS 02 81 15 SIS 1976, and the analyses were conducted by two reliable certified laboratories.

Advantages with the CCC sampling method as used during the PLU site investigations:

- Shorter contact time between the sampled water and equipment compared to monitoring sampling, where stationary, long term borehole installations are used.
- The advanced equipment is specially designed to minimise contamination risks and other disturbances.
- Collection of sample time series including at least six samples during continuous pumping permits judgement concerning the stability of the groundwater composition and especially the sulphide concentration.
- Investigation activities involving injection of water (injection tests and groundwater flow measurements) generally had not been performed in the borehole prior to the CCC campaign.
- The boreholes are most often relatively new and quite recently filled with groundwater from the bedrock fractures, and the rock surfaces of the borehole may still be fresh. This was not always the case in Laxemar (compared to Forsmark) and exceptions with time delays of up to 12 months exist.

Disadvantages with the CCC sampling method as used during the PLU site investigations include:

- Of all the borehole activities that may disturb or promote microbial production of sulphide, the actual drilling combined with heavy mammoth pumping and the use of drilling water is probably the most serious cause of perturbation. Removal of large water volumes (i.e. during drilling procedures and subsequent clean up pumping) shortly before the sampling campaign may decrease the microbial sulphide production according to /Hallbeck and Pedersen 2008a, b, c/.
- In common with most downhole activities, the lowering of the CCC equipment into the borehole may cause mixing of different water types and may also introduce foreign microbes despite the rigorous cleaning and sterilisation procedures.

- Diffusion of oxygen (from the air) into the water conducting part of the approximately 1,000 m long umbilical hose, or subsequently through connections and tubing in the sample water line, may change the redox conditions and cause oxidation of sulphide. Such conditions, however, have proved to be irrelevant if negative Eh values are measured in the flow through cell at the surface. An amorphous black precipitate on the outside of the downhole equipment has occasionally been observed when raising it from the borehole. However, there was no such evidence in the sampled groundwater.

3.1.3 Hydrochemical monitoring in boreholes

Regular hydrochemical monitoring in packed-off borehole sections requires the installation of stationary and long term downhole equipment. This equipment includes a packer system dividing the borehole into a maximum of ten sections for groundwater level monitoring. Each borehole section is connected by tubing to a stand pipe (ø 34/23.5 mm) in the wider, upper part of the telescopic borehole. This stand pipe includes a pressure transducer for groundwater pressure monitoring. A maximum of two sections are also connected to a second larger diameter stand pipe (ø 66/53.5 mm) for chemical sampling and groundwater flow measurements. The different materials in contact with the sampled water (cf. Figure 3-1) are listed in Table 3-2.

The large diameter stand pipes allow lowering of a pump connected to a 50 µm filter (polyamide) and a mini packer for isolating the stand pipe from the atmosphere In order to collect samples, pumping is conducted in the closed stand pipe. When the pressure decreases, groundwater from the connected borehole section is sucked into the stand pipe and pumped to the ground surface.

Figure 3-1. *Water sampling from a circulation section (the wide stand pipe) in one of the cored drillholes at Laxemar during the monitoring campaign in March 2008.*

Table 3-2. Equipment details and material.

Equipment	Materials
Water stand pipe	PEHD (High density polyethene) in the upper pipes and stainless steel in the bottom pipe.
Tubing	Tecalane (polyamide)
Casing rubber	Polyuerethane
Connection pipes and supporting frame	Stainless steel
Dummy	PEHD
Other details	Tape, pump, filter (polyamide yarn)

The packed-off borehole sections that were included in the monitoring programme in Laxemar varied in length between 9 m and 31 m. Dummies (PEHD) were installed in all the sections to reduce the section volumes and facilitate exchange of water in the sections. The section volumes varied between 11 and 65 litres and the total volumes including tubing between the stand pipe and borehole section amounted to between 26 and 73 litres.

Before pumping sample water from the connected borehole section the pump was always rinsed by pumped water from the upper part of the stand pipe for a few minutes. The pumping flow rate used for water exchange and sampling amounted to between 20 and 300 L/min depending on the hydraulic transmissivity of the borehole section. The sample treatment and analytical methods used were identical to the ones previously described for CCC. (Note: When the borehole section being monitored is the same as that sampled earlier during CCC, the pump rates used are similar as they are both determined by the same bedrock with the same hydraulic properties.)

The major advantage with the monitoring method as used during the PLU site investigations and subsequent monitoring phase is that:

- It provides the possibility to verify the major groundwater chemistry over long periods of time.
- The same equipment can be used for several purposes, i.e. continuous groundwater pressure registrations, groundwater sampling for chemical analyses and groundwater flow measurements.
- For more delicate hydrochemical studies such as trace element analyses, and also involving redox sensitive elements such as Fe(II), Mn(II) and S(-II).

However, there are several problems associated with the hydrochemical monitoring which include:

- Long contact time between groundwater and the stationary borehole equipment.
- Generally, if only one sample is collected from each sampling location, at each sampling occasion (in Laxemar once a year up to 2007), this sample is collected after removing at least three but generally five section volumes of groundwater.
- The stand pipes, the tubing connecting each stand pipe to the corresponding borehole section, and probably also the sections themselves, contain after some time a dirty, smelling stagnant water with a high microbe content and high TOC and sulphide concentrations /Rosdahl et al. 2010, Nilsson et al. 2010/, all of which may contaminate the samples. The only way to minimise contamination is to ensure a sufficient exchange of groundwater into the borehole section before sampling.
- The need to remove large volumes of water from the borehole section in order to prevent contamination from stagnant water initially present in the borehole section, or in the stand pipe, may affect a large bedrock volume with one or more sources of groundwater from different aquifers. This may result in questionable representativity of the sampled water due to mixing which, in turn, may also impact on the sulphide concentration.
- The equipment constitutes a complex system and the contribution from trapped stagnant water to the samples from the borehole section or from tubing may be difficult to avoid, in spite of long pumping periods and removal of large water volumes before sampling.
- A pump connected to a 50 µm filter has to be lowered through the dirty water to the bottom of the stand pipe in order to sample the connected borehole section. However, the pump is rinsed first with this water to avoid contamination from the previously sampled borehole. During sampling, therefore, the filter will most probably catch solid amorphous material that may contaminate subsequently collected samples.

- The lowering and raising of equipment in the two stand pipes connected to each circulation section creates pressure differences and water movements that probably propagate down to the borehole section being sampled. The sounding of the groundwater level each month in the narrow stand pipe for pressure measurements is a frequently repeated activity that in the long run may impact on conditions in the borehole section.
- Remains from dead insects and vegetation and even mice are often present on top of the packers sealing off the stand pipes. It is not unreasonable to believe that some of these materials reach the water in the stand pipes when the packers are released and lifted to the surface. Furthermore, transport of this material further down to the borehole section by gravity is likely to occur.

3.1.4 Hydrochemical monitoring at Laxemar

This section describes the introduction of a modified monitoring approach which commenced with a few borehole sections in the Autumn of 2007 and was extended during 2008 and 2009 to include time series sampling data collected from 12 different borehole sections in cored drillholes and 4 sections from percussion drillholes

The first groundwater sampling campaign within the monitoring programme for cored and percussion boreholes was conducted in 2006 /Askling and Nilsson 2006/. Up to 2007, sampling was performed once a year (a single sample from each included borehole section) and the first time series sampling was carried out in December 2007 when only KLX15A: –462.63 masl and KLX19A: –410.52 masl were sampled for sulphide. The sampling of each borehole section continued until a stable chloride concentration and electrical conductivity was achieved. This was assumed adequate in order to assure that the last sample in each series represented groundwater directly from the bedrock formation and not water occupying the borehole section since the previous sampling occasion. During 2008 and 2009 time series samples were collected twice a year and sampling was based on procedures where the first samples in the series comprise the tube and first section volumes. Thereafter, samples were collected after removal of two and three section volumes, respectively. Pumping continued and electrical conductivity was monitored to verify that stable conditions were established and then at least two additional samples were collected. The results from the time series sampling are reported in /Regander and Thorvaldsson 2008, Regander et al. 2009, Regander and Bergman 2010/. Since the number of sampled boreholes and borehole sections varied at each sampling occasion during the time period 2006–2009, a summary listing the sampled borehole sections at each sampling occasion is given in Table 3-3, and the volumes of water removed during the sampling in 2008 and 2009 are listed in Table 3-4.

Table 3-3. Sampled borehole sections (single samples or time series) during the time period 2006–2009.

Borehole section (masl)	Single samples 2006–2007	Time series Dec 2007	Time series Spring 2008	Time series Autumn 2008	Time series Spring 2009	Time series Autumn 2009
KLX02: –1,129.14	X	–	–	–	–	–
KLX04: –491.94	X	–	X	–	–	–
KLX04: –854.86	–	–	X	–	–	–
KLX05: –204.94	X	–	X	–	–	–
KLX06: –221.18	X	–	–	–	–	–
KLX06: –475.27	X	–	–	–	X	–
KLX07: –569.69	X	–	X	–	–	–
KLX08: –504.90	X	–	X	X	X	X
KLX08: –539.39	X	–	X	–	–	–
KLX10: –338.43	X	–	X	X	X	X
KLX10: –676.19	–	–	X	X	X	X
KLX12A: –501.12	X	–	X	X	X	X
KLX15A: –192.74	–	–	X	X	X	X
KLX15A: –469.27	–	X	X	X	X	X
KLX18A: –452.87	–	–	X	X	X	X
KLX19A: –413.86	X	X	X	X	X	X
KLX20A: –183.32	–	–	X	–	–	–

Table 3-4. Sampled borehole sections during the Spring and Autumn of 2008–2009. Given is the water volume in the borehole section and the approximate total pumped volume of water /Regander et al. 2009, Regander and Bergman 2010/.

Borehole section (masl)	Section volume	Total pumped vol. 2008 Spring	2008 Autumn	2009 Spring	2009 Autumn
KLX04: –491.94	24.5	4,500			
KLX04: –854.86	33.3	370			
KLX05: –204.84	15.3	3,600			
KLX07A: –569.69	33.3	8,000			
KLX08: –500.90	32.9	5,700	4,900	5,000	3,900
KLX08: –539.39	65.5	5,700			
KLX10A: –338.43	18.9	4,000	4,500	5,000	4,000
KLX10A: –679.19	26.6	1,400	910	1,500	710
KLX12A: –501.12	14.2	1,300	980	900	1,500
KLX15A: –192.74	13.9	5,700	7,900	5,000	5,300
KLX15A: –469.27	21.6	5,600	5,600	5,200	3,500
KLX18A: –452.87	13.9	730	720	713	750
KLX19A: –413.86	11.7	6,500	5,700	6,500	5,200
KLX20A: –183.32	40.1	5,000			

The examples from the sampling time series during Autumn and Spring 2008 and 2009, shown in Table 3-4, underline not only that in most cases large amounts of water have been removed during these two sampling occasions, but also in those cases with duplicate data, that good stability has been maintained between both sampling occasions. However, as mentioned above, the removal of considerable amounts of water may affect a large bedrock volume with one or more sources of groundwater from different aquifers possibly influencing the sulphide contents. On the other hand, it may also increase the probability that the sampled waters are representative of formation groundwaters free from any of the contamination possibilities discussed above in Section 3.1.3.

Discussion

The resulting sulphide data from the time series monitoring campaign generally show decreasing trends within each sample series, and the final sulphide values generally verify the concentrations obtained from the previous monitoring campaign where there is a absence of time series data.

Typical sulphide trends in boreholes, where repeated time series have been collected within the monitoring programme, are presented in Figure 3-2. The initially high sulphide contents recorded when starting each sample time series, followed by a gradual decrease in values during continued pumping, is a common observation in most of the boreholes and may in some samples coincide with increased values of DOC and HCO_3 in the initial samples.

On a smaller scale, the effect of short term variation in sulphide contents related to sampling intervals has been reported earlier from the MICROBE project /Hallbeck and Pedersen 2008b/ at the Äspö HRL (Hard Rock Laboratory).

As mentioned above, one possible reason for the observed enhanced sulphide concentrations with time is the contribution to the samples from the initial stagnant water present in the borehole section prior to pump start. These residual section waters may contain high sulphide concentrations reflecting changes in borehole conditions with time. This hypothesis was tested at Forsmark by estimating the percentage of borehole section water in each sample in the sample time series and comparing these with the corresponding sulphide concentrations /Nilsson et al. 2010, Tullborg et al. 2010/.

Taking into account all possible errors in the calculations, a comparison between different sulphide concentration trends and the corresponding calculated admixture of formation water, supports the hypothesis that residual initial borehole section stagnant water is causing enhanced sulphide concentrations. Generally, the different sulphide trends (i.e. rate of decrease), correspond quite well to the increases of formation groundwater contribution (or decreases of initial borehole section stagnant

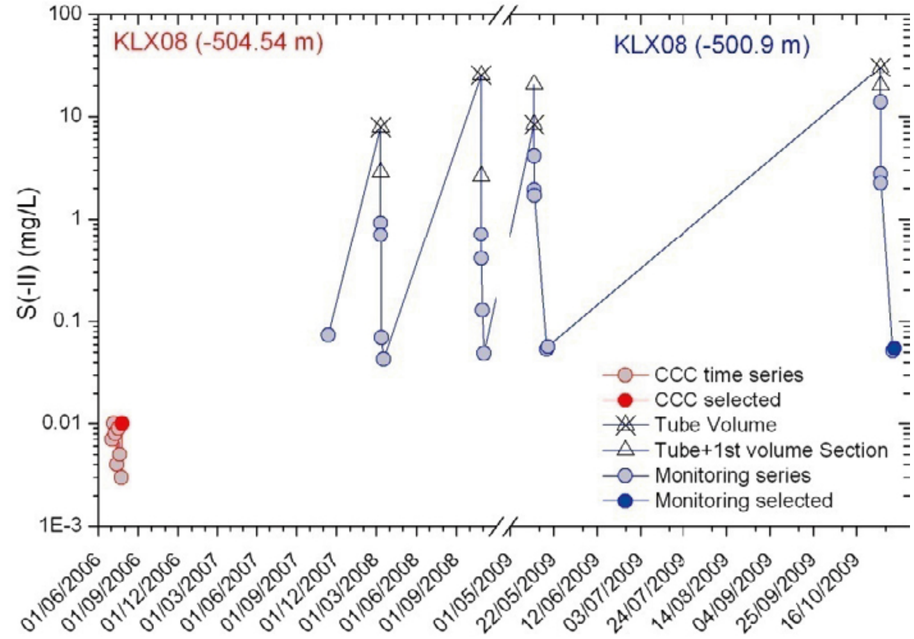

Figure 3-2. *Sulphide concentration plotted versus sample time series in borehole KLX08. Decreasing sulphide concentrations (mg/L) are observed during groundwater sampling and an increase in sulphide concentrations between the sampling occasions.*

water contribution) for Forsmark /Nilsson et al. 2010/ and for the 'Sulphide Project' focussed on borehole KLX06 /Rosdahl et al. 2010/. Some preliminary calculations have also been made for the monitoring time series sampling from Laxemar. These are not as detailed as the ones for Forsmark, but there are still some interesting observations. Firstly, when comparing the total volume of water pumped before the last sample was taken in each sampling series with the calculated volume needed to ensure 100% formation water, it can be concluded that the ratio of estimated volume of water necessary to be removed to the actual volume of water removed, varied from 0.8 to 125 (cf. Figure 3-3). This means that with only one exception the actual pumped volume should be enough to ensure formation water (cf. Appendix 1 for details).

Secondly, when plotting the sulphide values versus the volumes of water removed prior to sampling during the monitoring campaign (from 370 to 8,000 L), corresponding to approximately 10 to 500 section volumes, it is obvious that the highest sulphide values are found in borehole sections were the pumping volumes are on the low side (Figure 3-3). The explanation may be that; 1) more pumping was needed to get rid of all the stagnant water, i.e. the section may be more complicated than shown by the PFL logging and the sulphide values in some of the samples may be, in such cases, still too high, or, 2) the very large volumes pumped from some of the sections may cause disturbances and short circuiting that may, for some borehole sections, result in too low values.

3.1.5 Other experience and observations

The two described sampling methods have been used in other SKB projects and also under somewhat different conditions from the ones accounted for above.

The CCC method was used already during the preinvestigation phase within the Äspö Hard Rock Laboratory project from 1986–1990 /Smellie and Laaksoharju 1992/ with similar equipment. Also in these early investigations, similar to the present programme in Laxemar, the time delay between the drilling and the hydrochemical investigation campaign (CCC) was up to a year. The sulphide concentrations encountered were often relatively high and the reason for this is not fully understood but may involve differences in drilling and sampling routines, for example, cleaning of the equipment and excessive volumes of water pumped before sampling (e.g. KLX02) etc. This, together with the long delay after the drilling and before the sampling occasion, may be the explanation for the high sulphide values. Samples with sulphide concentrations exceeding 1 mg/L (and a few concentrations as high as 7 mg/L) were measured in borehole KLX01 some eight months after being drilled.

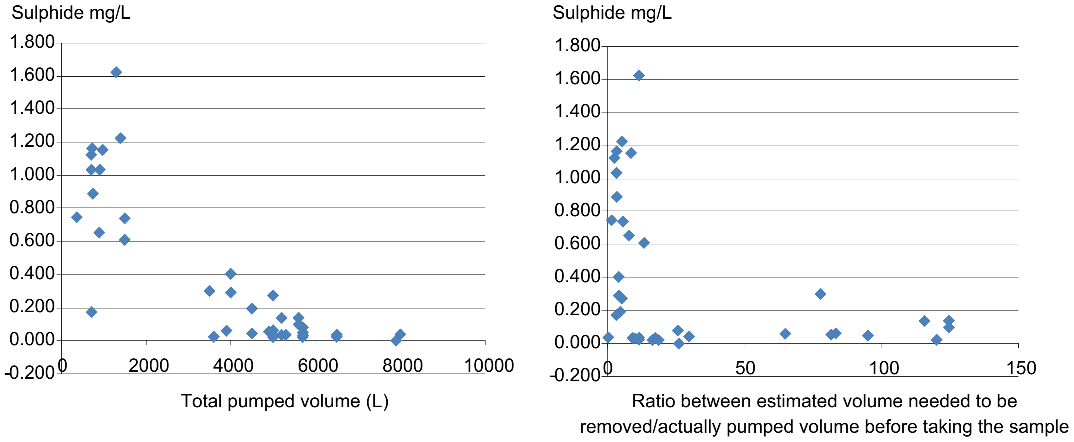

Figure 3-3. *Sulphide contents in monitoring sections from cored boreholes in Laxemar. The samples represent the last sample in each time series from Spring and Autumn in 2008 and 2009.*

3.1.6 *In situ* studies to investigate sulphide production processes in groundwaters at Äspö and Laxemar

In order to better understand the variations in sulphide contents (and especially the very high values) obtained during the monitoring sampling at Laxemar and Forsmark, one borehole from the Laxemar area (KLX06) was selected to study the variation in sulphide during a longer period of continuous sampling (up to 145 section volumes). During this period, 13 samples were analysed and after a pause of two and a half months the sampling was repeated again when only 7 borehole section volumes were pumped and 4 samples were analysed (cf. Figure 3-4). The two sampling series show identical behaviour with the highest sulphide contents present in the first section volume, i.e. where the water is exposed to both the fracture walls and the downhole equipment. With continued pumping, the sulphide contents decreased significantly but stable values were measured only first after 60 borehole section volumes of water were removed.

Analyses from two boreholes at Äspö (KAS03 and KAS09) drilled during 1988 and 1989 were also included in the study. Aging of equipment (from the early 1990’s) and long water exposure times of the borehole walls have been suggested as a possible trigger to sulphide production. In both boreholes the equipment was subsequently removed and the nature of the corrosion and the dark amorphous precipitate covering the downhole parts could be observed /Rosdahl et al. 2010/. Some unrealistically high values of sulphide and DOC (>100 mg/L) were measured and attributed to the addition of partly solid material passing through the filter. This is in line with the observations of turbid samples where particulate sulphide may be included in the analyses.

Important observations and lessons learned during the project are:

- In KLX06 the entire groundwater chemistry differs in the first samples collected in the time series. The reason for more dilute water in the first samples may be due to a leakage in a standpipe connection or a connection in one of the tubes leading to the test section. Since the water pressure is higher in the uppermost section than in the tested section, such a leakage may transport shallow water to the test section via the tubes.
- From the long time series in KLX06 it is evident that only after 60 section volumes have been removed does the water reach stable sulphide values; this is also reflected by Fe. When repeating the sampling after several months an identical decrease in sulphide was detected (cf. Figure 3-4). Only four samples were taken during this sampling event and it is obvious from the plot that stable values were not achieved. As discussed in /Tullborg et al. 2010/, the extent of the pumping required is section-specific and different volumes may need to be removed to achieve stable values that are representative of the fracture groundwater. It is worth noting that the plug flow calculation on the section sampled in KLX06 corresponds very well with the obtained results, in agreement with the Forsmark studies /Tullborg et al. 2010/.

- The section sampled in KLX06 is especially unfavourable from the water exchange point of view since the dominating flow anomaly is located in the middle of the borehole and a second anomaly, with very low hydraulic transmissivity, is present close to the bottom. This geometry explains the extremely slow stabilisation of the sulphide concentration.
- The study confirms earlier indications from borehole sampling that the aging of the borehole and borehole equipment makes it increasingly more difficult to obtain reliable values of especially trace and redox sensitive elements. This study, together with the results from the time series measurements at Forsmark, shows that a time series of 5 borehole section volumes removed by pumping can be assumed to be far too low in many cases to obtain reliable sulphide values from the fracture groundwaters.

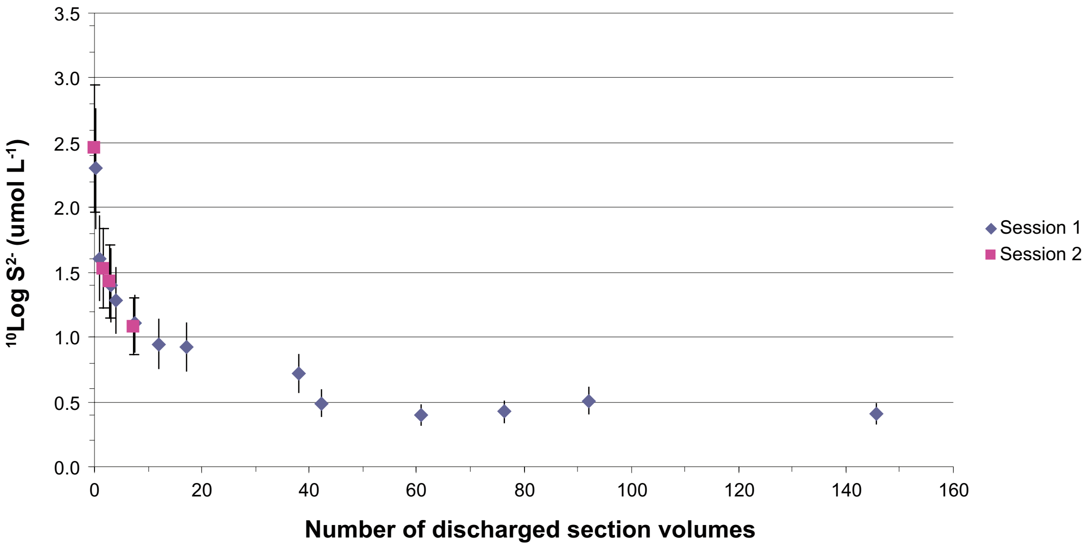

Figure 3-4. *Sulphide contents in groundwaters from KLX06: –475 masl versus number of pumped borehole section volumes removed. First time series,blue symbols (2009-02-09 to 2009-02-23), was extended to 145 pumped borehole section volumes removed. Second time series, pink symbols, started after 2.5 months and comprised only 7 pumped borehole section volumes removed. The error bars represent the measurement uncertainty at ± 25% (2σ). From /Rosdahl et al. 2010/.*

4 Evaluation of the sulphide data from Laxemar

4.1 Introduction

The evaluation of the Laxemar dataset intends to establish as close as possible the natural, undisturbed groundwater sulphide contents. This considers not only the measured sulphide contents, but also the amount and variation of the reductant species, i.e. mainly Fe and DOC, but Mn (as a further redox indicator) and HCO_3 (as a further indicator of microbial sulphate reduction) also have been used.

Prior to the evaluation in Section 4.6, Sections 4.2, 4.3, 4.4 and 4.5 briefly summarise some of the background information relating to the evaluation of the sulphide data, i.e. the data sources available, a brief mention of some of the sampling difficulties involved, and a short summary of the sampling strategy.

4.2 Data sources and availability

The evaluation discussed below is based on the dataset extracted and delivered from Sicada (Sicada-10-093) which includes *all* the groundwater samples from percussion and cored boreholes analysed for sulphide from Laxemar. Three sources of sulphide data are available: 1) Complete Chemical Characterisation (CCC) data. 2) Data from sampling using the hydrotest equipment; this is made in connection to regular hydrotests performed after drilling and no sample time series data are available. Both the CCC sampling and sampling using the hydrotest equipment are restricted to the cored boreholes of the site characterisation programme (i.e. Laxemar Extended 2.3 data freeze /Laaksoharju et al. 2009, Smellie and Tullborg 2009/) that includes the earlier established categorisation of the samples based on groundwater type and major ion chemistry. 3) Data from the monitoring of selected borehole sections in percussion and cored boreholes initiated at different times during and following the site characterisation programme up to October 2009. Figure 4-1 shows sulphide content (with analytical error bars) versus elevation for the entire Laxemar dataset. It is important to note that detection levels for sulphide have varied during the site investigations from 0.002 to 0.006 mg/L (0.06 to 019 µmol/L) and during the late 1980's and 1990's at 0.01 mg/L (0.3 µmol/L), in this last case restricted to the KLX01 and KLX02 CCC results. The overall quality of the Laxemar groundwater samples has been categorised already as 1–5 (i.e. highest to lowest quality) for the hydrogeochemical site descriptive modelling /Smellie and Tullborg 2009/ and will not be repeated here, but it is important to note that these criteria relate mostly to major ions and the important environmental isotopes. Because of the increased sensitivity of many minor elements to drilling and sampling procedures, sometimes their element values may either be missing or obviously wrong when compared to the rest of the data. This refers mainly to the redox sensitive elements (e.g. S^{2-}, Fe^{2+} and Mn^{2+}), which are of special importance for the SR-Site safety case. The sulphide values recorded during the CCC sampling are generally low compared with those measured when monitoring has been carried out subsequently in the same sections. However, because different sampling techniques have been employed on these occasions, introducing contrasting types of disturbances and uncertainties (cf. Chapter 3 for details), evaluating the "true" sulphide values is therefore a very difficult task.

4.3 Analytical uncertainties

The inclusion of analytical uncertainties in plots and diagrams are often requested and these are included in the sulphide plots in Figure 4-1 above and 4-3 below and are also commented upon in the foot note of Table 4-1. It is important to keep in mind that the sampling uncertainties are generally much larger than the reported analytical uncertainties and therefore the analytical uncertainties are not included in all diagrams in Chapter 5 as it may give a false picture of the reliability of the values.

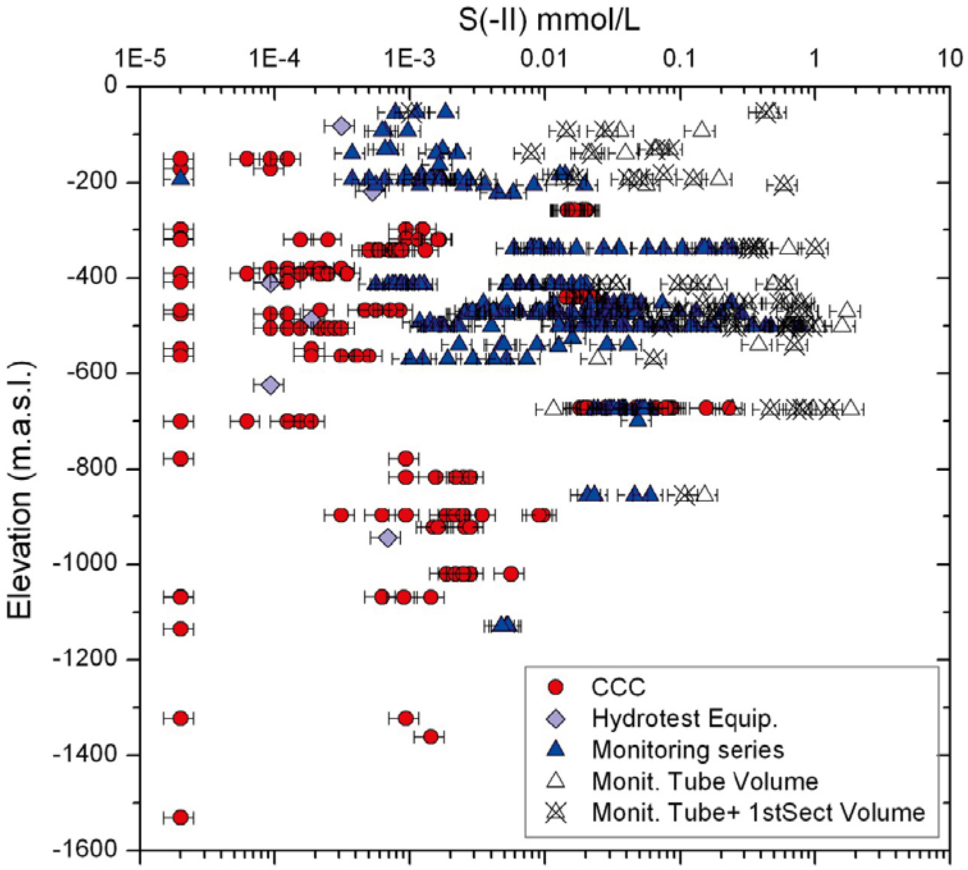

***Figure 4-1.** Sulphide versus elevation from cored and percussion boreholes. Data below the detection limit of the analyses (2σ i.e. 0.006 mg/L or 0.19 µmol/L) are shown in this diagram at $2 \cdot 10^{-5}$ mmol/L. The highest CCC values at Laxemar are from borehole KLX01 sampled during the 1980's, i.e. they do not belong to the later sampling and drilling programme performed during 2002 to 2008.*

4.4 Sampling strategy

Only cored boreholes have been sampled in the CCC programme, whilst both cored and percussion boreholes form part of the monitoring programme. Sampling in all boreholes is carried out in packed-off borehole sections.

The differences between the two sampling methods are described in Chapter 3. When considering the output of data from the two contrasting types of sampling campaigns it is important to remember that: 1) Sampling in the CCC programme has been conducted normally on a single occasion in a cored borehole section where there is usually a long time series of data extending over some weeks. 2) Sampling in the monitoring programme in most cases has been conducted at several occasions from the same cored borehole section (usually periodically after at least six months or more and using the same permanently installed equipment) and where the time series data can vary from a single value to, in many cases, a series of 4–6 values extending over some days, but never to the same extent as the CCC programme. At Laxemar, six sections from boreholes KLX04, KLX06 and KLX19 have been sampled using the hydrotest equipment. These samples are collected shortly after the drilling during the hydraulic testing of the of the borehole and no time series are available.

In some cases the selected monitoring sections coincide, at least closely with those sampled earlier for CCC, thus providing the possibility to compare sulphide values over even longer time intervals. It is important in this context to note that when the borehole section being monitored is the same as that sampled earlier during CCC, the pump rates used are similar as they are both determined by the same bedrock with the same hydraulic properties.

With respect to the percussion boreholes, five borehole sections from five different boreholes have been monitored chemically using packed-off sections which are generally less than 20 m in length, with the exception of HLX37 where the entire lower part of the boreholes was sampled (150–199.8 m). These percussion boreholes were initially investigated to geographically extend the area covered by the investigations. Time series comprising 2 to 3 samples were collected during Spring and Autumn 2009. The time series sampling comprises the tube+first section volume, first section volume and finally the last sample collected following the removal of about 5 borehole section volumes of water in order to access suitable formation groundwater quality. From borehole HLX20 there is only one single sample available collected in 2008. Two of the borehole sections show stable conditions (HLX37 and -39) and the other three indicate slight instability concerning major groundwater chemistry (HLX20, HLX28 and HLX35). The instability in the groundwater chemistry is due to interactions in the near surface fracture network although all samples from the percussion boreholes are classified as fresh groundwaters.

4.5 Selection criteria

Because some borehole sections have been sampled and analysed for sulphide more often than others, a bias would be introduced if all sulphide data deemed as representative were selected. In order to avoid this bias, the approach has been to select a single groundwater sample (with a sulphide value) that can be assumed to be representative for a given section. When time series data during sampling are available, variations of the reductant species, together with sulphide, can be carefully assessed to provide some insight into presently active sulphide producing microbial conditions and/or degrees of anthropogenic contamination from pumping/sampling activities.

Evaluation and selection of groundwater samples with respect to the representativity of the sulphide values are based on:

- The stability of the major ion and isotope groundwater chemistry throughout the sampling period. For the CCC samples this is already judged from the earlier categorisation (cf. /Smellie and Tullborg 2009/) and in these samples the contamination of drilling fluid is one important parameter in that evaluation.
- For the monitoring samples, in contrast, the potential portions of drilling fluid in many cases cannot be evaluated due to the use of uranine introduced earlier as part of the hydraulic tracer test programme which has been conducted in, or nearby, the same borehole section being monitored.
- The charge balance should be less than ±5%. A large difference in charge balance indicates that something is seriously wrong with the analytical or the sampling programmes.
- The samples should not show supersaturation in respect of amorphous monosulphide. It is assumed that the precipitation of amorphous monosulphide is very rapid and a groundwater showing significant supersaturation of this phase cannot exist. It therefore indicates a serious analytical error in either the sulphide or ferrous iron analyses, or both.
- The combined variation of one or more of S^{2-}, Fe^{2+}, Mn^{2+}, DOC, HCO_3^- and SO_4^{2-} in the time series may also be an important criteria. Concerning the CCC samples, these elements usually show stable values in the time series measurements for the Category 1–3 samples. For the monitoring samples, however, the situation is quite different and time series samples generally show systematic trends in the behaviour of these elements. The rationale behind these trends is discussed in Chapter 3 and will not be repeated here. Generally, the lowest sulphide values are selected which usually correspond to the lowest DOC and HCO_3^- values and also that there is a general stabilising trend towards lower values with increased sampling time.

Detailed documentation of this evaluation and the chosen sulphide values to be used in the modelling exercises are presented in Appendix 1 in table format. These tables include the total range of S^{2-}, Fe^{2+}, Mn^{2+} and DOC and the values for the selected sample are also recorded. In addition, time series data of these elements comprising three or more values in a single sampling sequence (or over longer time periods from the same borehole section) have been recorded with respect to increasing, decreasing or absence of compositional trends with time. Information on groundwater type, chloride content and stability of the major ion chemistry, and the rationale behind the choice of sulphide values, is also given.

4.6 Evaluation

4.6.1 Cored boreholes

Introduction

Based on the derived dataset, a graphical framework has been produced to visualise the sensitive changes in chemistry that occurred during sampling of the groundwater time series data, thus leading to a better understanding of the processes involved. The parameters that have been plotted against time (i.e. sampling date) for each of the selected borehole sections sampled are listed in Table 4-1 and described below, and the complete set of plots for all sections where time series are available are included in Appendix 2.

The parameters in question are: S^{2-}(mg/L), Fe^{2+} (mg/L), Mn (mg/L), FeS (amorphous) Saturation Index, Cl (mg/L), SO_4^{2-} (mg/L), δS^{34} (‰ CDT), Mg (mg/L), HCO_3^- (mg/L), DOC (mg/L), Calcite Saturation Index and pH.

When sampling data using both CCC/hydrotest and monitoring equipment are available from the same water conducting structure, these are shown also in the same diagrams. This is only the case for three sets of analyses; KLX02: –1,134.60 masl (CCC)/–1,129.14 masl (monitoring), KLX08: –504.54 masl (CCC)/–500.90 masl (monitoring), and KLX15A: –467.22 masl (CCC)/–469.27 masl (monitoring). In all of these sections the groundwater chemistry is largely stable, which is also the case for the 3 sets of analyses where a first sample is taken using hydrotest equipment and then later monitoring of the same section is performed; KLX04: –486.52 masl (hydrotest equipment)/ –491.94 masl (monitoring), KLX06: –218.52 masl (hydrotest equipment)/ –221.18 masl (monitoring), and KLX19: –410.52 (hydrotest equipment)/ –413.86 masl (monitoring).

CCC data

The initial evaluation step is based on the assumption that groundwaters already judged from the site investigations to be representative from an analysis of the major ions and the important environmental isotopes, would also include the minor elements (e.g. S^{2-}, Fe and Mn). Most of the selected CCC sulphide values therefore correspond to groundwater samples previously selected as being representative (i.e. Categories 1–3). Sulphide contents for these varied from below detection to 0.09 mg/L (0.003 mmol/L), with the exception of the groundwater samples from KLX01 which shows significantly higher values, up to 2.5 mg/L (almost 0.08 mmol/L). These samples were collected during the preinvestigation phase within the Äspö Hard Rock Laboratory investigations from 1986–1990 /Smellie and Laaksoharju 1992/ using similar sampling equipment as later used during the site investigations at Laxemar from 2002–2008. However, not all routines were similar during drilling and sampling and high sulphide values have not been detected during CCC sampling in the site investigations programme at Laxemar.

A number of sections earlier judged as less representative (Category 4 and 5) have been reinterpreted and the sulphide values have been selected as representative. This is the case for three sections from KLX01: –817.20 masl/–897.09 masl and –1,019.9 masl where the reason for allocating a Category 4 was the lack of environmental isotope analyses. The sulphide values were, however, judged representative. For KLX02: –1,134.60 masl a Category 5 was earlier allocated due to some instability in the time series and also questionable isotopic results. However, later monitoring confirmed the results and now this section has been judged to be representative. KLX08: –150.43 masl was allocated a Category 5 due to the risk of short circuiting and draw down of surface waters to deeper levels. In the light of monitoring results from the upper 150 m in the bedrock, this section was reinterpretated to be representative.

Samples collected using the hydrotest equipment

This sampling was performed during the hydraulic testing programme carried out soon after drilling and cleaning of the borehole. Six boreholes sections were sampled and all were allocated a Category 4 because of the lack of time series data. However, the groundwater chemistry was later verified by monitoring in the same water conducting structures or by the overall understanding of the site /Smellie and Tullborg 2009/. The sulphide values of these samples at $0.2–0.7 \cdot 10^{-3}$ mmol/L (0.006–0.022 mg/L) do not deviate significantly from the CCC samples (cf. Section 3.1.1).

Monitoring data

For the monitoring data, the groundwater major ions and isotopes are sometimes unstable when each different sampling occasion is compared, and they may also differ from earlier representative CCC sampling in the same borehole section (if present).

At Laxemar, all but two of the monitoring sections have time series data. However, the routines for monitoring sampling have changed during the site investigations and the number of samples from each monitoring section varies considerably (cf. Table 3-3). An initial pulse of fresh water is commonly observed during each sampling occasion; the explanation for this may be the same as that suggested for KLX06: –475 masl studied within the sulphide project /Rosdahl et al. 2010/ and referred to above in Section 3.1.6 (i.e. a leakage in a standpipe connection or a connection in one of the tubes leading to the test section). Since the water pressure is higher in the uppermost section than in the tested section due to the hydraulic gradient (inforced by the topography), such a leakage may transport shallow groundwater to the test section via the tubes. Concerning the selected sulphide data, the values are generally much higher compared with CCC; mainly 0.0006–0.035 mmol/L (0.018–1.12 mg/L). All the measurements from the tube+first section volume are even higher, always above some mg/L (>0.05 mmol/L) and in one sample as high as 58 mg/L (1.8 mmol/L). The variation during each time series sampling occasion is also much larger when compared to the CCC data. Allocating a 'representative' sulphide value is therefore a difficult task especially when only one sample is analysed at each sampling occasion. In some favourable cases from the monitoring samples (less so from the CCC samples), the data show a clear and systematic time dependent inverse relationship during sampling between sulphide (decreasing with time) and ferrous iron (increasing with time). Systematic changes in DOC/TOC, sulphate and bicarbonate are indicated in some samples. Collectively, these observations probably reflect the greater differences in microbial processes taking place in the downhole tubings and monitoring sections compared with the processes ongoing in the bedrock fractures.

The final sulphide value of the time series data showing a systematic decrease in sulphide, which is a major trend of importance for this evaluation, is selected as being the 'best possible' representative sample available. When adequate data are available for both CCC samples and later monitoring samples from the same borehole section, and there are higher values for the monitoring samples which is the normal case, two values have been selected from these sections; one from the CCC sample (corresponding to the earlier selected representative and categorised sample) and one value selected from the monitoring.

4.6.2 Percussion boreholes

For the sulphide dataset from the percussion boreholes there are no original values compatible with the CCC for any of the sampled sections, and time series are restricted to three samples during two occasions in 2009 (HLX28, HLX35, HLX37 and HLX38), and only one sample from HLX20 in 2007. As mentioned above, the major ion groundwater chemistry is largely stable and the groundwater type corresponds to fresh water in all of the sampled sections in the percussion boreholes. Because information from the upper approximately 150 metres of bedrock, based on the cored boreholes, is very limited, the sulphide data from the percussion boreholes make a useful contribution, not least in helping to determine the fresh groundwater type.

4.7 Recommendations

The values from the CCC sampling are generally lower (below detection to 0.09 mg/L) than those measured during the monitoring phase (0.018–1.12 mg/L). There is, however, one anomaly, that of KLX01 which cannot be adequately explained. In this borehole the CCC sulphide values range, with one exception at 2.50 mg/L, from 0.180–0.53 mg/L which is within the range of the monitoring phase at 0.018–0.884 mg/L if the highest value of 1.12 mg/L is ignored. As pointed out in Section 3.1.5, the reason for this is not fully understood but it may involve any combination of possibilities including differences in drilling and sampling routines (e.g. cleaning of equipment and pumping different volumes of water prior to sampling) used some 20 years ago compared with present protocols, Furthermore, the difference cannot be explained simply by the time elapsed between drilling and sampling as the KLX01 CCC sampling was carried out after a similar lapse of time as that from KLX03 onwards (i.e. from 2002–2008) and found to show similar trends. Additional important factors may include the high volumes of water pumped prior to the hydrochemical sampling etc.

The other anomaly is why does KLX02, which was drilled and sampled also some 20 years ago, not show similar high sulphide trends to KLX01? One reason may be that KLX02 was excessively pumped during hydraulic testing over a long period of time and the system may not have equilibrated prior to the hydrochemical sampling for some of the samples.

When sulphide values from the CCC/hydrotest equipment and monitoring sampling are available from one borehole section, two values are used, one representing each of the sampling methods.

When time series are measured in the monitoring sections, the sulphide values are higher in the downhole tubes and in the borehole section compared with groundwater from the surrounding fractures. During each time series a considerable volume of water has been removed; up to 370–8,000 litres equivalent to 10–570 borehole section volumes. This should guarantee that formation water has been sampled, but for some sections where < 1,500 litres have been removed, there is still some doubt as to whether only formation water has been collected. For most of the sections, therefore, the last sample in the time series is suggested as representing the 'best possible' value.

For the percussion boreholes, only monitoring data are available; time series of two or three samples were performed during Spring and Autumn 2009 (HLX28, HLX35, HLX37 and HLX39). Selected samples/values for the sulphides refer usually to the last sample in the time series. For HLX20 one sample was taken at one occasion during 2007.

The finally selected samples and values of key parameters are shown in Table 4-1. Note that in Chapter 5 only the selected samples shown in Table 4-1 are considered.

Table 4-1. Sulphide and related parameters of the selected samples from the CCC sampling and the monitoring sections.

Borehole	Sample #	Sample type	Elev. masl	S^{2-} mg/L	Fe mg/L	Cl mg/L	SO_4 mg/L	Mg mg/L	HCO_3 mg/L	Mn mg/L	DOC mg/L	S^{34} (SO_4) ‰ CDT	CO_2 ml/L	CH_4 ml/L	H_2 μl/L	SRB cells/mL	ATP fmol/mL	siFeS (am)	SI Calcite
HLX20	11923	Monit.	–54.46	0.025	0.0342	50.2	36.9	3.4	198	0.044	3.1	27.3	n.a	n.a	n.a	n.a	n.a	–1.58	0.006
HLX28	15979	Monit.	–53.69	0.036	0.108	89.9	60	4.68	216	0.093	7.2	12.6	n.a	n.a	n.a	n.a	n.a	–1.21	0.009
HLX35	19114	Monit.	–92.56	0.031	0.0665	221	61.9	6.21	247	0.080	6	27.3	n.a	n.a	n.a	n.a	n.a	–1.39	0.013
HLX37	19108	Monit.	–131.06	0.021	0.0066	43.2	37.9	1.2	213	0.011	3.2	26.9	n.a	n.a	n.a	n.a	n.a	–3.01	0.006
HLX39	19117	Monit.	–139.09	0.05	0.0389	56.2	4.65	2.37	277	0.048	7.3	37.3	n.a	n.a	n.a	n.a	n.a	–1.33	0.007
KLX01	11209	TTMonit	–163.26	0.053	4.3	110	105	5.8	277	0.352	9	28.3	n.a	n.a	n.a	n.a	n.a	0.03	0.012
KLX01	1537	CCC	–257.06	0.53	0.129	2,050	48	28	83	0.200	1.5	n.a	n.a	0.11	n.a	n.a	n.a	0.01	0.068
KLX01	1516	CCC	–672.95	2.5	0.032	4,870	351	23	24	0.200	1.2	n.a	0.29	0.22	n.a	n.a	n.a	–0.5	0.181
KLX01	1761	CCC	–817.2	0.07	0.219	9,180	670	15.4	6	0.110	n.a	n.a	0.62	0.031	n.a	n.a	n.a	–0.82	0.349
KLX01	1773	CCC	–897.09	0.29	0.053	11,200	770	9.6	6	0.090	n.a	n.a	n.a	n.a	n.a	n.a	n.a	–0.61	0.427
KLX01	1785	CCC	–1,019.91	0.18	0.364	12,600	695	6.9	12	0.050	n.a	n.a	n.a	n.a	n.a	n.a	n.a	–0.12	0.489
KLX02	2722	CCC	–1,068.24	<0.003		15,800	1,010	2.1	8	0.010	1.1	n.a	n.a	n.a	n.a	n.a	n.a	—	0.604
KLX02	2934	CCC	–1,134.6	<0.003	1.035	15,130	860	5	11.8	0.247	10	n.a	n.a	n.a	n.a	n.a	n.a	—	0.574
KLX02	11145	TTMonit	–1,129.14	0.165	1.36	15,000	813	8.3	17.3	0.540	1.2	11.4	n.a	n.a	n.a	n.a	n.a	–0.74	0.586
KLX02	2931	CCC	–1,322.81	<0.003	0.2	31,230	1,024	2.7	9	0.080	98	n.a	n.a	n.a	n.a	n.a	n.a	—	1.197
KLX02	3038	CCC	–1,360.93	0.046	3.438	36,970	1,205	1.2	42	1.110	n.a	n.a	n.a	n.a	n.a	n.a	n.a	–1.07	1.518
KLX02	2731	CCC	–1,530.98	<0.003	0.405	45,500	832	2.7	9	0.140	0.9	n.a	n.a	n.a	n.a	n.a	n.a	—	1.887
KLX03	7952	CCC	–170.82	0.003	0.294	260	36.4	5	335	0.063	21	36.3	1.4	0.87	<0.5	<2.3	53,880	–1.76	0.015
KLX03	10091	CCC	–379.85	0.007	0.408	1,390	127	10.8	189	0.107	13	15.1	1.8	0.62	110	220	n.a	–1.38	0.053
KLX03	10076	CCC	–922.45	0.09		10,500	758	2.1	7.7	0.016	1.4	11.1	<0.07	0.059	<0.5	<2.3	17,041.0	—	0.405
KLX04	15421	Monit.	–854.86	0.742	0.043	3,790	475	5	10.1	0.090	2.2	10.2	n.a	n.a	n.a	n.a	n.a	–1.36	0.140
KLX04	7856	Hydrot.Eq	–81.9	0.01	0.158	23.5	15.9	5.9	324	0.162	9.9	n.a	n.a	n.a	n.a	n.a	n.a	–1.83	0.007
KLX04	7776	Hydrot.Eq	–486.52	0.006	0.09	1,480	104	6.9	51.4	0.109	2.2	12.7	n.a	n.a	n.a	n.a	n.a	–2.27	0.050
KLX04	15380	Monit.	–491.94	0.038	0.114	1,690	102	10.4	33.1	0.196	2.1	16.9	n.a	n.a	n.a	n.a	n.a	–1.46	0.058
KLX04	7752	Hydrot.Eq	–944.38	0.022	0.155	7,910	845	5	8.48	0.074	<0.3	9.1	n.a	n.a	n.a	n.a	n.a	–1.95	0.296
KLX05	15450	Monit.	–204.84	0.018	0.368	657	155	8	185	0.063	6	24.9	n.a	n.a	n.a	n.a	n.a	–1.47	0.028
KLX06	10122	Hydrot.Eq	–218.51	0.017	0.0592	36.8	34.3	1.2	226	0.012	n.a	n.a	n.a	n.a	n.a	n.a	n.a	–1.37	0.006
KLX06	11464	TTMonit.	–221.18	0.186	0.057	58.7	40.6	1.3	224	0.012	3.5	30.9	n.a	n.a	n.a	n.a	n.a	–0.37	0.007
KLX06	14726	Monit.	–475.27	0.082	0.257	1,430	685	11.5	32.5	0.144	2	8.6	n.a	n.a	n.a	n.a	n.a	–1.78	0.064
KLX07A	15415	Monit.	–569.69	0.032	0.359	2,930	317	27.1	24.2	0.411	2	14.7	n.a	n.a	n.a	n.a	n.a	–1.36	0.105

Borehole	**Sample #**	**Sample type**	**Elev. masl**	**S^{2-} mg/L**	**Fe mg/L**	**Cl mg/L**	**SO_4 mg/L**	**Mg mg/L**	**HCO_3 mg/L**	**Mn mg/L**	**DOC mg/L**	**S^{34} (SO_4) ‰ CDT**	**CO_2 ml/L**	**CH_4 ml/L**	**H_2 µl/L**	**SRB cells/mL**	**ATP fmol/mL**	**siFeS (am)**	**SI Calcite**
KLX08	10649	CCC	–150.43	0.004	0.104	12.6	12.8	3.9	296	0.085	7.7	39.4	n.a	n.a	n.a	2.3	821,287	–2.06	0.006
KLX08	11143	CCC	–390.71	0.004	0.265	1,560	130	6.7	32.2	0.089	2.9	15.4	0.13	0.029	46	50	15,000	–2.23	0.055
KLX08	11228	CCC	–504.54	0.01	0.0202	2,030	145	8	20.5	0.089	1.8	13.2	0.071	0.025	<0.5	n.a	n.a	–2.35	0.070
KLX08	19160	Monit.	–500.9	0.055	0.083	1,980	134	8.03	19.8	0.089	2.2	15	n.a	n.a	n.a	n.a	n.a	–1.01	0.068
KLX08	15397	Monit.	–539.39	0.074	0.0754	2,250	149	7.9	16.6	0.080	1.6	14	n.a	n.a	n.a	n.a	n.a	–1	0.076
KLX10	19131	Monit.	–338.43	0.286	0.187	2,190	190	44.9	65.4	0.257	2.7	22.8	n.a	n.a	n.a	n.a	n.a	–0.22	0.075
KLX10	19153	Monit.	–676.19	1.12	0.0506	3,550	250	29.3	21.3	0.227	2	20.1	n.a	n.a	n.a	n.a	n.a	–0.49	0.126
KLX11A	11921	TTMonit.	–542.07	0.403	0.0228	1,040	130	1.7	42.6	0.019	2.3	14	n.a	n.a	n.a	n.a	n.a	–0.45	0.036
KLX12A	15895	Monit.	–501.12	0.649	0.0339	4,210	363	18.3	12.8	0.177	2.3	13	n.a	n.a	n.a	n.a	n.a	–1.59	0.147
KLX13A	11607	CCC	–408.01	0.004	0.0024	744	36.8	3.1	73.9	0.027	2.7	29	0.75	0.015	0.5	2.3	10,700	–3.47	0.025
KLX13A	11542	CCC	–474.99	0.003	0.223	769	47.3	4.4	83.7	0.061	2.6	n.a	n.a	n.a	n.a	n.a	n.a	–1.8	0.026
KLX15A	19098	Monit.	–192.74	0.029	0.212	3,270	85.5	78.6	50.6	0.611	1.9	25.6	n.a	n.a	n.a	n.a	n.a	–1.24	0.113
KLX15A	15008	CCC	–467.22	0.007	0.537	5,890	425	54	14.1	0.549	1.5	17.3	0.14	0.021	<0.5	130	12,800	–1.88	0.214
KLX15A	15355	Monit.	–469.27	0.133	0.286	5,690	377	54.7	17.8	0.522	1.6	19	n.a	n.a	n.a	n.a	n.a	–0.93	0.205
KLX17A	11809	CCC	–342.32	0.028	0.791	565	22.9	9.4	122	0.099	3.4	31.3	0.71	0.07	<0.5	300	82,500	–0.49	0.021
KLX18A	19167	Monit.	–452.87	0.884	0.0457	1,720	154	15.3	33	0.087	3.7	16.8	n.a	n.a	n.a	n.a	n.a	–0.06	0.060
KLX19A	11604	Hydrot.Eq	–410.52	0.003	0.063	1,780	114	8.8	38.5	0.071	1.5	22.6	n.a	n.a	n.a	n.a	n.a	–2.39	0.056
KLX19A	15699	Monit.	–413.86	0.025	0.0487	1,930	116	10.2	25.9	0.066	1.4	21.9	n.a	n.a	n.a	n.a	n.a	–3.37	0.062
KLX19A	11569	Hydrot.Eq	–624.78	0.003	0.146	3,520	196	2.5	55.3	0.036	3.1	18.6	n.a	n.a	n.a	n.a	n.a	–2.36	0.119
KLX20A	15477	Monit.	–183.32	0.03	0.0403	614	59.1	2.6	107	0.019	3.5	36.1	n.a	n.a	n.a	n.a	n.a	–1.31	0.022
KLX27A	15587	CCC	–562.96	<0.003	0.007	1,700	108	1.4	13.1	0.013	1.4	20.1	n.a	n.a	n.a	n.a	n.a	–1.58	0.054

Note that the gas and SRB and ATP values given in italics are imported from a sample in the same time series.

The analytical uncertainties differ for the different elements; major elements (e.g. Cl^-, HCO_3^-, SO_4^{2-}) lie within the 5–10% interval; minor elements such as S(−II), Fe(II) and Mn(II) within the 12–20% interval; gas analyses within the 30–100% interval depending on concentration; stable isotope analyses for sulphur in sulphate are ±0.4 (1σ) ‰.

5 Overview of Laxemar data for present day conditions

5.1 Introduction

This chapter discusses the variation of certain factors of importance for sulphide production. Because some of the elements described vary between the different groundwater types (cf. Section 1.4.1), the plots have been colour coded according to the subdivision described below:

Fresh (Light Grey colour code ⬜)

Water type: Fresh (<200 mg/L Cl; <1.0 g/L TDS); Mainly meteoric in origin, i.e. Na(Ca)-$HCO_3(SO_4)$ in type, $\delta^{18}O = -12.0$ to $-10.5‰$ V-SMOW.

Mixed Brackish (Light Green colour code 🟩), not a specific groundwater type

Waters of mixed Fresh ± Brackish Glacial (± Brackish Marine) origin (200–2,000 mg/L Cl; 1.0–3.5 g/L TDS); it is usually sampled at 20–150 m depth and may be the result of natural and/or anthropogenic mixing during drilling activities and sampling.

Brackish Glacial (Dark orange colour code 🟧)

Water type: Brackish Glacial (200–10,000 mg/L Cl; < 1.0–18 g/L TDS; $\delta^{18}O \leq -13.0‰$ V-SMOW). Last Deglaciation meltwater + Brackish Non-marine or Brackish Marine to Saline component; Ca-Na-Cl (SO_4); Mg < 25 mg/L; $\delta^{18}O < -13.0‰$ V-SMOW.

Transition water samples (Turquoise code 🟦), not a specific water type

Transition type representing a mixture of Brackish Glacial and/or Brackish Non-marine groundwaters with a variable component of Brackish Marine. These waters range from 2,000–10,000 mg/L Cl and from 25–100 mg/L Mg; $\delta^{18}O > -13.0‰$ V-SMOW. They may be the result of natural and/or anthropogenic mixing during drilling activities and sampling.

Brackish Non-marine (Medium blue colour code 🟦)

Water type: Brackish Non-marine (3,000–10,000 mg/L Cl; 5–18 g/L TDS; Mg <25 mg/L); Old Meteoric ± Old Glacial ± Last Deglaciation meltwater ± Saline component, i.e. Na-Ca-Cl (SO_4) in type, $\delta^{18}O > -13.0‰$ V-SMOW.

Saline (Medium lilac colour code 🟪)

Water type: Saline (10,000–20,000 mg/L Cl; 18–35 g/L TDS); Old Meteoric ± Old Glacial ± Last Deglaciation meltwater ± Highly saline component, i.e. Ca-Na-Cl (SO_4) in type, $\delta^{18}O = -13.0$ to $-10.0‰$ V-SMOW.

This is the same subdivision used within the hydrogeochemical site model for Laxemar /Laaksoharju et al. 2009/. However, the groundwaters classified as Brackish Marine *sensu stricto* are not present at Laxemar, but components of brackish marine waters are included in the groundwaters classified as Transition type.

***Note*:** In order to facilitate comparison of different concentrations of sulphur compounds, mmol/L have been preferred over the previously used mg/L. Generally it takes 1 methane or DOC + 1 sulphate to produce 1 molecule of sulphide.

5.2 The sulphur system

The available sulphur sources for interaction with the bedrock aquifers comprise, for example, dissolved species in groundwaters or precipitates along fracture walls or in wall rock adjacent to flowing fractures. The different oxidation states of the sulphur compounds together with the available sources of organic materials (e.g. reductants and carbon sources), and finally the supply of gases (e.g. methane and carbon dioxide) that can contribute to microbial activity, provide the framework for sulphide production in the bedrock groundwater system. In this section, the different sulphur sources are discussed.

5.2.1 Sulphate concentrations in groundwater

In general, sulphate constitutes the largest sulphur pool in bedrock groundwaters and may have very different origins depending on the groundwater history. The main sources in fresh waters are usually the result of atmospheric deposition and oxidation of sulphides or dissolution of possible sulphates in the overburden. Deeper in the bedrock fracture system pyrite is relatively common. In addition, some sulphate minerals (gypsum and barite) have been observed, especially at depth below 300 metres /Drake and Tullborg 2009/. Water of marine origin (e.g. Littorina Sea at Laxemar) initially carries elevated sulphate contents with a specific isotopic signature when entering the bedrock or the overlying sediments. However, subsequently this content may be lowered to various degrees due to microbially mediated sulphate reduction thus modifing the sulphur isotope signatures (generally enriched in ^{34}S) in the remaining sulphate. Brackish and saline waters at greater depths characterised by long residence times in the bedrock have sulphate contents of mixed origins and the addition of sulphate from dissolution of sulphate minerals is indicated. It should be noted that these waters may also have sulphate from older marine sources, or from very old brine groundwaters (potentially of sedimentary origin). Furthermore, the sulphate contents may also be modified by permafrost freeze-out processes (i.e. formation and dissociation of mirabilite).

Figure 5-1 gives an overall picture of the variation in sulphate content in the different groundwaters at Laxemar versus elevation. Only the selected samples from CCC and monitoring sampling, respectively, are shown in the plots. Generally, the sulphate content increases with depth and correlates also with the increase in chloride content /Laaksoharju et al. 2009/. The fresh groundwaters dominating the upper 200 metres are low in sulphate as expected. Groundwaters of transition type (with components of brackish marine groundwaters) show higher sulphate contents than non-marine groundwaters at the same depth. One exception is the brackish glacial water at –475 masl in borehole KLX06 which has a high SO_4 content (around 7 mmol/L) compared with other brackish waters at intermediate depth.

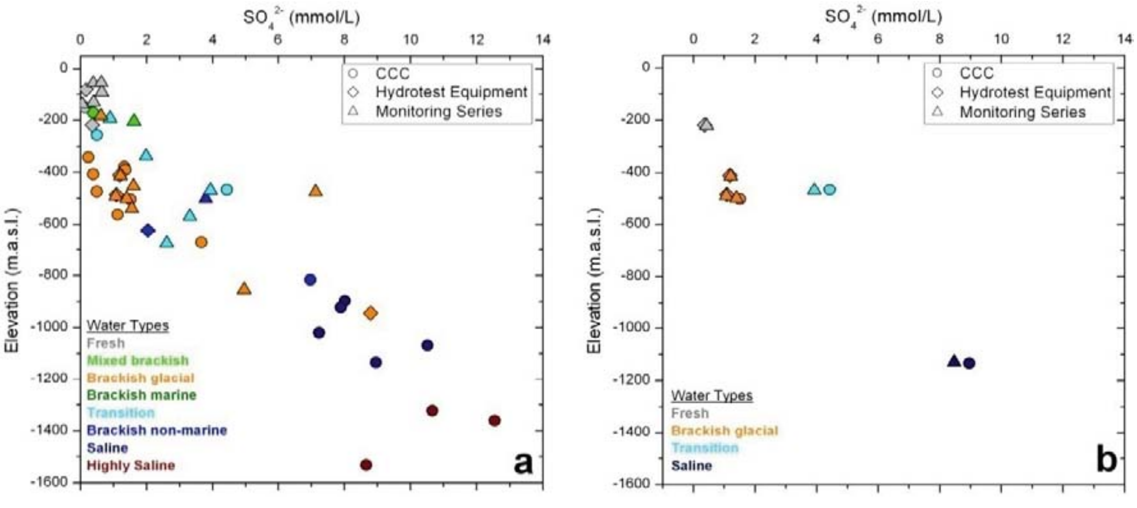

Figure 5-1. *(a) SO_4 in groundwaters from percussion and cored boreholes sampled using CCC, hydrotest equipment and monitoring versus elevation (masl).(b) Only CCC (or hydrotest equipment) and monitoring samples from the same water conducting structure are shown in order to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC or sampling using hydrotest equipment) overlapping to the monitoring period.*

In contrast to Forsmark where the main sulphate source is marine (Littorina Sea water), the intrusion of Littorina Sea water was more restricted in the Laxemar area, both in time and space. The main sulphate source at Laxemar is the deep saline water with components both of old brine and from the interaction with the sulphate fracture minerals. The fact that sulphate minerals are present in the fracture systems means that sulphate will be contributed to the groundwater by sulphate reduction processes at repository depths.

When comparing CCC samples with later monitoring results from the same water conducting structures it can be concluded that the changes in sulphate contents with time are very small.

δ^{34}S in sulphate

Stable sulphur isotope ratios, expressed as δ^{34}S CDT (Canyon Diablo Troilite), can be used not only to trace the origin of the sulphur sources for the sulphate but also to study processes such as biogenic sulphur reduction which can modify the isotope ratios. Sulphur isotopes were determined in sulphate from surface waters and groundwaters during the site investigations and reported in /Tröjbom et al. 2008/ (shallow waters) and /Laaksoharju et al. 2009/ (groundwaters). The evaluation of possible origins of sulphur (SO_4) in the surface water system showed that atmospheric deposition and oxidation of sulphides in the soil cover constitute the most important sources, together with marine sulphate /Tröjbom et al. 2008/. These sulphate contents are, however, generally low (~1 mmol/L).

The available δ^{34}S from the selected samples are plotted versus depth (Figure 5-2) and versus chloride and sulphate (Figure 5-3). The δ^{34}S values range between +8.6.1 to +39.4‰ CDT. Values higher than marine (~ 21‰ CDT) are found in groundwaters with chloride contents < 20 mmol/L and at depths above 400 m. The highest δ^{34}S values correspond to samples of low dissolved sulphate concentrations (Figure 5-3b), and these are interpreted as being produced *in situ* by sulphate reducing bacteria /Laaksoharju et al. 2009/. The origin of this sulphate is not clear but it involves most probably different sources including some marine sulphate.

Below 350 m depth a switch towards lower δ^{34}S values and correspondingly higher sulphate contents can be seen, although some high δ^{34}S values (> +29‰ CDT) are present down to about 400 m.

One explanation for the low δ^{34}S values measured at depths exceeding 400 metres is the dissolution of sulphate minerals present in the fracture system. This is supported by sulphur isotope analyses in fracture gypsum samples from > 400 m depth (cf. Section 5.2.2 and Figure 5-4).

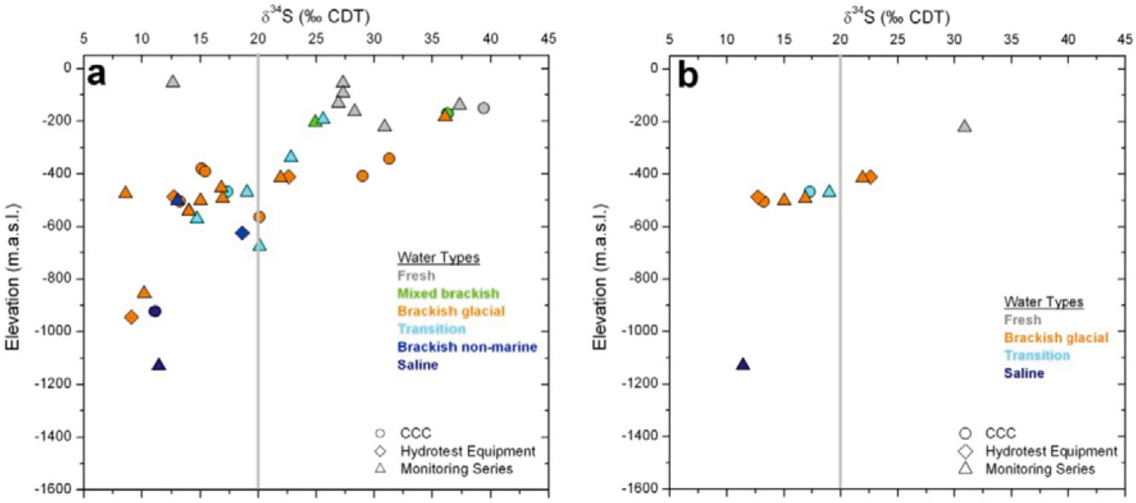

***Figure 5-2.** (a) $\delta^{34}S_{(SO4)}$ in groundwaters from percussion and cored boreholes sampled using CCC/hydrotest equipment and monitoring versus elevation (masl). (b) Only CCC/hydrotest equipment and monitoring samples from the same water conducting structure are shown to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period. Marine cut-off δ^{34}S values at ~21‰ CDT are indicated.*

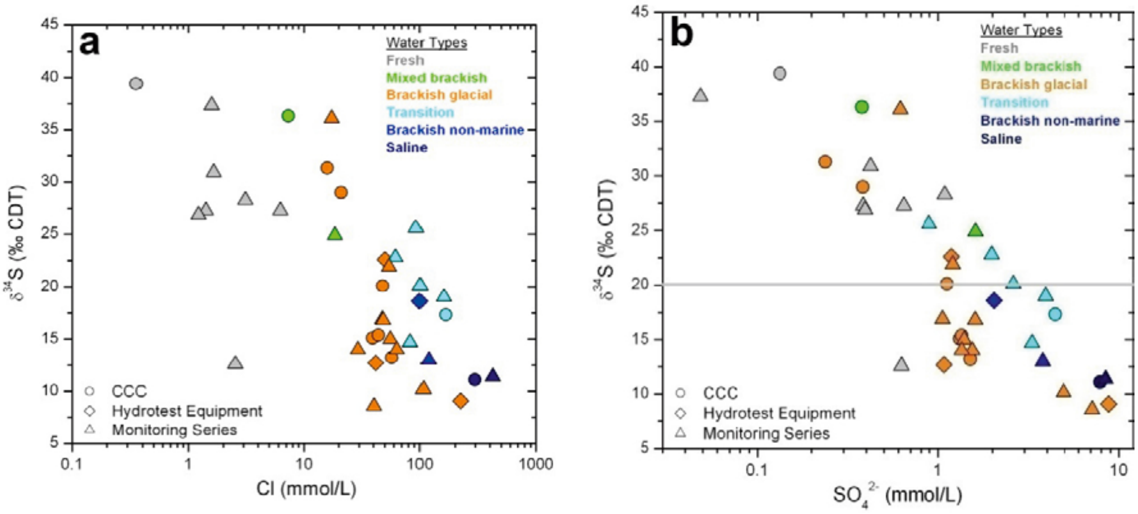

Figure 5-3. *$\delta^{34}S_{(SO4)}$ in groundwaters from percussion and cored boreholes versus chloride content (a) and sulphate (b). Marine cut-off $\delta^{34}S$ values at ~21‰ CDT are indicated in (b).*

5.2.2 Solid sulphates and sulphides

Sulphur minerals identified at Laxemar include different sulphides such as chalcopyrite and galena and the overall most frequently mapped pyrite; sulphate minerals such as barite and gypsum are also found. Barite is frequently observed but usually only as very small grains (small amounts), whilst gypsum is only detected below 300 metres depth and occurrences are relatively scarce based on core mapping /Drake and Tullborg 2009/. It must, however, be kept in mind that gypsum found together with, for example calcite, can easily be overlooked during the regular core mapping. During the detailed fracture mineral investigations which were an integral part of the site investigations at Laxemar, sulphide isotope ratios have been determined in a number of fracture mineral samples, including sulphides (pyrite) and sulphates (gypsum and barite) /Drake and Tullborg 2009/. Two different generations of pyrite were analysed; a) hydrothermal pyrite with $\delta^{34}S$ values in the range –3 to +5‰ CDT; these pyrites are older than 1 Ga, and b) younger pyrite with ages from the Late Palaeozoic up to the present time. This latter pyrite shows an extremely large variation in $\delta^{34}S$ values (from –45 to +55 5‰ CDT) with most of the samples plotting in the interval of +5 to + 35‰ CDT (cf. Figure 5-4). The large variation in $\delta^{34}S$ values indicate microbial sulphate reduction. The highest values are found in the upper 300 m which indicates that these pyrites may have formed from a system similar to the present, where the highest values in the sulphate are found at depths down to 350 m.

The analysed gypsum samples are all from depths > 400 m in more near surface intervals most gypsum has been dissolved. The $\delta^{34}S$ values ranges from +5 to + 15‰ CDT (Figure 5-4), i.e. lower than present day marine sulphate at around 20‰ CDT. These low values are in line with the proposed dissolution of gypsum as a source for SO_4 in the deep groundwaters. It is suggested that the gypsum is formed from warm brine present in the bedrock during the Palaeozoic.

The few analysed barite samples show somewhat higher values (+10 to +20‰ CDT) than the analysed gypsum. The barite is not cogenitic with the gypsum and may be younger (e.g Late Palaeozoic).

In conclusion, the origin of the sulphate in the shallow groundwaters is that expected with the surface and near surface waters (including atmospheric deposition, oxidation of sulphides, leaching of marine clays etc.), but the original isotopic signature is significantly modified by microbial sulphate reduction. This is most prominent down to depths between about 300 to 400 m depending on location. At greater depths, the sulphate content increases and the origin of this sulphate can be attributed mostly to dissolution of sulphate minerals (gypsum), although some of marine origin may still be present.

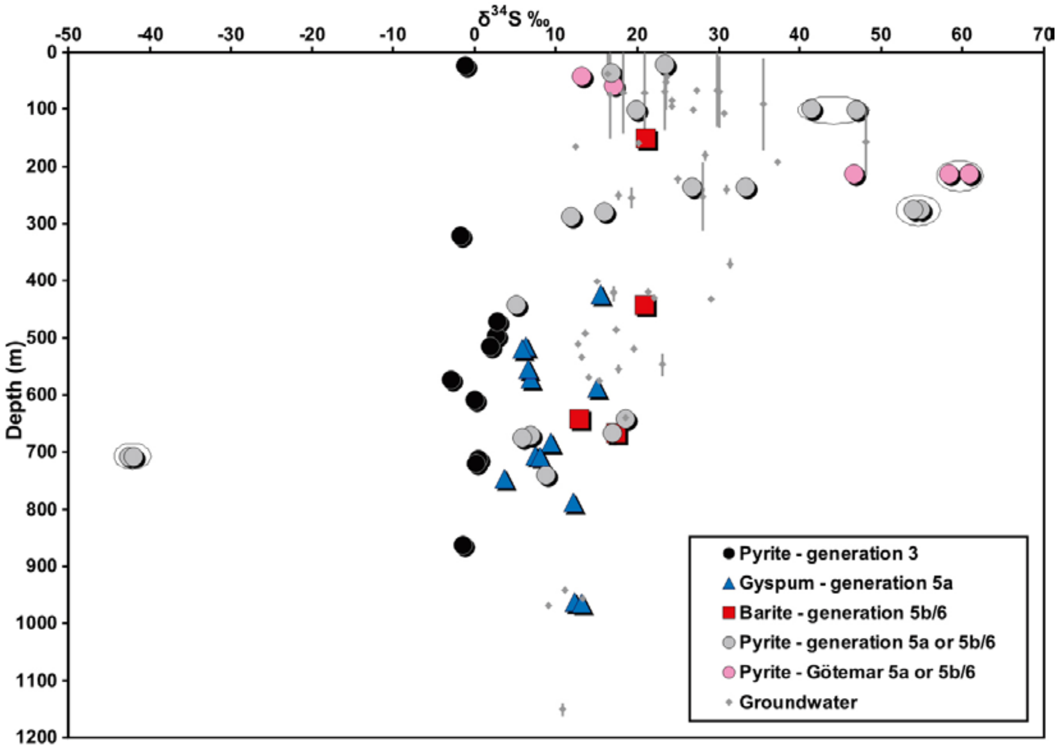

Figure 5-4. *$\delta^{34}S$ in fracture filling pyrite,gypsum and barite versus vertical depth. Samples are from the Laxemar and Simpevarp subareas and from the Götemar granite (plotted separately). Encircled values comprise two analyses of material from the same fracture surface. $\delta^{34}S$ in groundwater samples is also shown and the y-axis bars define the borehole length of each section sampled (data from the Laxemar 2.3 groundwater dataset). Analytical errors are within the size of the symbols. The generations refer to the sequence of events outlined for the fracture mineral formations. Generation 3 corresponds to a hydrothermal event related to the intrusion of the Götemar granite. Generation 5a corresponds to mineral precipitation from a warm brine period during the Palaeozoic. Generations 5b to 6 represent low temperature precipitates formed from the Late Palaeozoic up to the present. Data from /Drake and Tullborg 2009/.*

5.2.3 Sulphide in groundwaters

Chapter 3 has addressed the problems associated with the derivation of reliable sulphide contents during groundwater sampling. Nevertheless, from present measured values it has been possible to extract sulphide data that have been very useful in the interpretation of the borehole sections sampled because they give the most probable intervals for naturally occurring sulphide values. CCC/hydrotest equipment data and monitoring data are compared and described below in terms of their compositional variation and depth trends, and potential correlation with the different groundwater types.

The sulphide values measured in the groundwaters during CCC/hydrotest equipment and subsequent monitoring show, as pointed out in Section 4.6, a large variation, and the possible reasons for this are discussed. For example, only samples taken during CCC/hydrotest equipment give sulphide concentrations below or close to detection limit ($1 \cdot 10^{-4}$ mmol/L), whereas the lowest values measured during monitoring sampling are about $5 \cdot 10^{-4}$ mmol/L. There are a few relatively high values ($> 5 \cdot 10^{-3}$ mmol/L) from the CCC sampling as well but these all belong to the sampling in KLX01 carried out during 1988 and 1989 (cf. discussions in Section 4.7). Most of the sulphide samples are from above 700 m depth and the general pattern is that the sulphide values from the monitoring samples are one to two orders of magnitude higher than the ones measured during the CCC/hydrotest equipment sampling (cf. Figure 5-5b) where only CCC/hydrotest equipment samples from the same water conducting structure are shown in order to facilitate comparison. These observations are also in agreement with the observations from Forsmark /Tullborg et al. 2010/. At depths below 700 m the measurements are too few (only two monitoring sections) to make any conclusions. The indication is, however, that the difference between the monitoring and the CCC/hydrotest equipment values are less pronounced if taking all measurements into consideration (Figure 5-5a); this is in accordance with the observations at Forsmark.

Because the sulphide values span three orders of magnitude the values are displayed in logarithmic scale for the two diagrams in Figure 5-5; in total, 9 samples are below or close to detection limit. It is not possible to detect any correlation between groundwater type and the sulphide values.

In conclusion, the sulphide contents measured and shown in Figure 5-5 span about three orders of magnitude, with the majority of the CCC samples plotting on the lower side and the monitoring samples on the higher side of which some show values higher than >0.01 mmol/L. Uncertainties involved in the monitoring sampling programme include the possibility of an anthropogenic increase in sulphide production associated with the downhole equipment and the exposed borehole walls, and the resulting sulphide content in the water is in turn related to the different borehole section volumes of water removed (cf. Chapter 3). Based on these uncertainties, it can be concluded that, in many cases, the volume of water pumped before the last sample collected (usually the one selected as most representative) has not been sufficient to remove all the contaminated stagnant water from the borehole section sampled (cf. the plug flow calculations referred to in Section 3.1.4 and also the experience from the sulphide monitoring project /Rosdahl et al. 2010/).

The iron content in the groundwater is important to interpret the dissolved sulphide in the samples because the dissolved sulphide may be controlled by precipitation of iron sulphide. Figure 5-6a shows Fe(II) in groundwater plotted versus depth which shows no evident depth trend and no obvious pattern in the Fe(II) contents in the monitoring samples compared with the CCC samples as, for example, indicated for sulphide (cf. Figure 5-5). Calculation of the saturation indices for amorphous FeS (Figure 5-6b) shows about ten samples that are at, or close to saturation in respect of FeS(am). Two important observations are evident; a) in samples at or close to saturation the measured Fe^{2+} and S^{2-} values in a single sample are interconnected, and b) the solubility of FeS(am) consequently sets an upper limit for these species in the groundwater (cf. Figures 5-6b and 5-7). Actual precipitation of FeS(am) has not been possible to demonstrate, but an opportunity to study this will take place during 2010/2011 when downhole monitoring equipment will be removed from some of the boreholes at Laxemar, and possible precipitates on this equipment will be investigated. If precipitation of FeS is observed to have taken place, it means that more sulphide than the contents measured in the water have been produced during a certain time interval. If effective enough, this process should in such cases have resulted in a significant lowering of the sulphate content combined with increased δ^{34}S values in a specific water volume, for example the sampled borehole section.

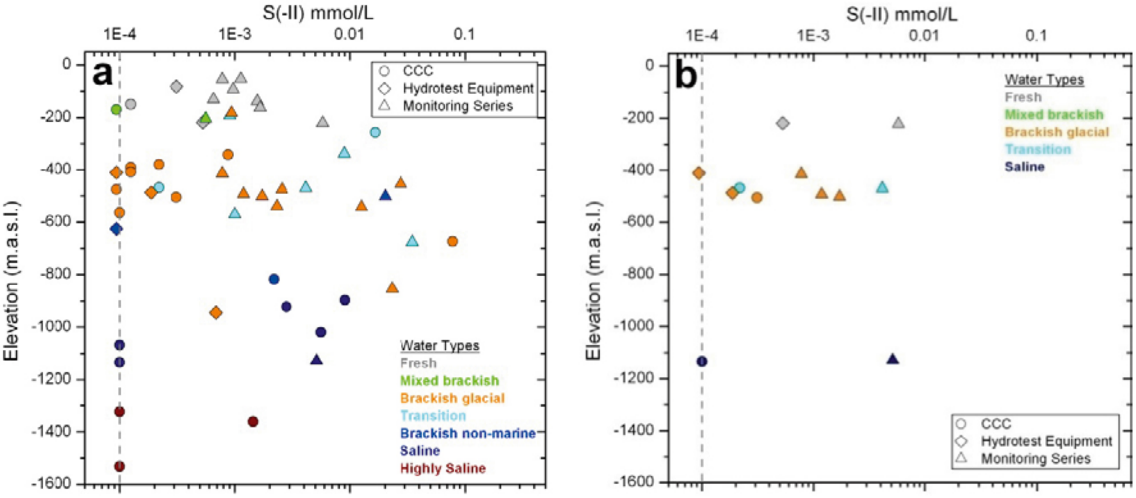

Figure 5-5. *(a) Dissolved S(-II) in groundwaters from percussion and cored boreholes from sampling using CCC/hydrotest equipment and monitoring versus elevation (masl). (b) Only CCC/hydrotest equipment and monitoring samples from the same water conducting structure are shown in order to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period.*

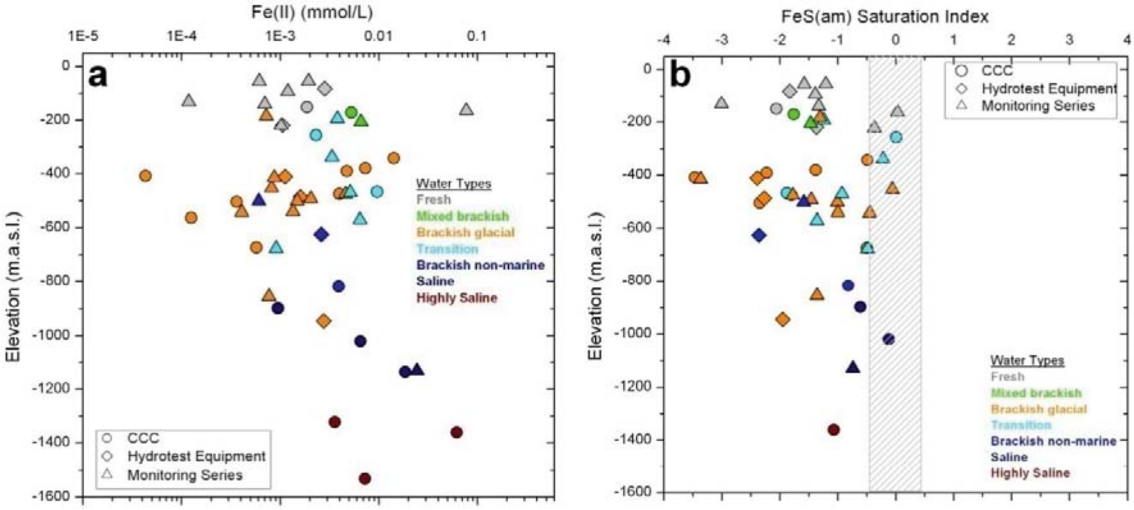

Figure 5-6. (a) Dissolved Fe in groundwaters from percussion and cored boreholes sampled using the CCC/hydrotest equipment and monitoring versus elevation (masl). (b) Saturation index for amorphous monosulphide versus elevation.

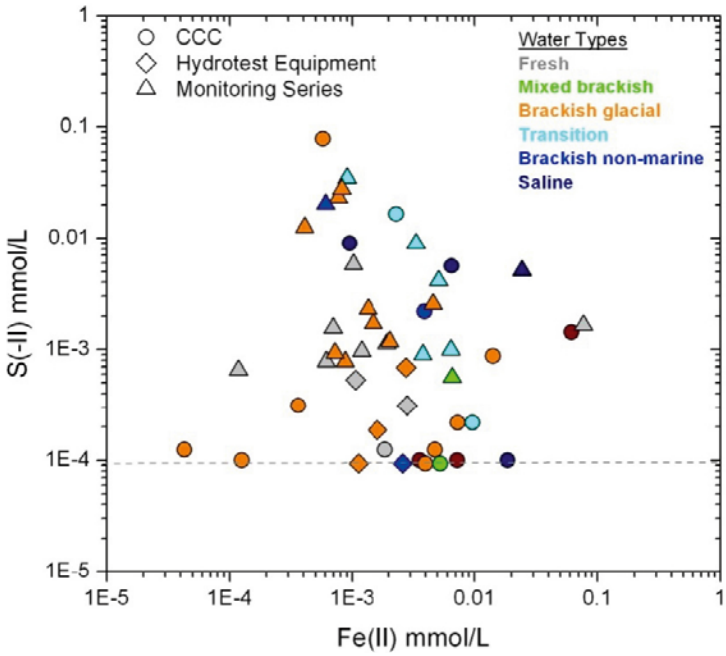

Figure 5-7. Sulphide versus dissolved Fe(II) in groundwaters from percussion and cored boreholes sampled using the CCC/hydrotest and monitoring equipment.

5.2.4 Concluding remarks

Because sulphate is needed for microbial sulphide production, the sulphate sources are of paramount interest. At Laxemar these sources are related to the surface water (oxidation of sulphides in the soil and leaching of marine sediments), partly to brackish marine waters (Littorina type), but the largest part to the contribution from dissolution of sulphate minerals (mainly gypsum) and mixing with deep saline water with brine type components /Laaksoharju et al. 2009/. The amount of sulphate contributed by marine (i.e. Littorina Sea) waters is far more limited at Laxemar than at Äspö and Forsmark.

Evidence from mineralogical /Drake and Tullborg 2009/ and groundwater /Laaksoharju et al. 2009/ data at Laxemar show that microbial sulphate reduction has been active in the bedrock since at least the Palaeozoic onwards.

The recorded sulphide values measured during CCC/hydrotest equipment and the monitoring programmes show large variations (three orders of magnitude) with the CCC samples generally characterised by lower values than from the monitoring when samples from the same borehole section can be compared. These differences are significant down to 700 m depth. Time series measurements during the monitoring programme show decreasing sulphide values during each time series, i.e. the pumped volumes have not been large enough to ensure stable values in all of the sampled sections representing the bedrock fracture groundwaters (cf. Section 3.1.4). On the other hand, very low sulphide values were measured during the CCC sampling and it is possible that some of these are due to artefacts from the drilling and heavy pumping carried out in the boreholes.

Saturation in respect of FeS(am) is reached for about ten sections (including both monitoring and CCC samples). In samples at or close to saturation, the measured Fe^{2+} and S^{2-} values in a single sample are interconnected and consequently the solubility of FeS(am) sets an upper limit for these species in the groundwater.

5.3 Organic carbon

Organic materials in the groundwaters have been analysed and are presented either as TOC (Total Organic Carbon) or as DOC (Dissolved Organic Carbon) if filtered through a 0.4 µm filter before being analysed. In a number of samples both TOC and DOC have been analysed (Figure 5-7), and these generally show a good correlation which implies that almost all organic carbon is present as molecules less than 0.4 µm in size. However, the analyses of organic matter in deep groundwaters is a complicated task for sampling and analytical reasons, and obtained results need to be interpreted with caution.

5.3.1 Concentrations

The DOC values at depth are expected to be close to the detection limit of 0.1 mmol/L (1 mg/L) but generally the more dependable CCC values at depths greater than 100 m still vary between 0.1 to 0.4 mmol/L (1 and 5 mg/L) with a few exceptions where the values are even higher (Figure 5-9a).

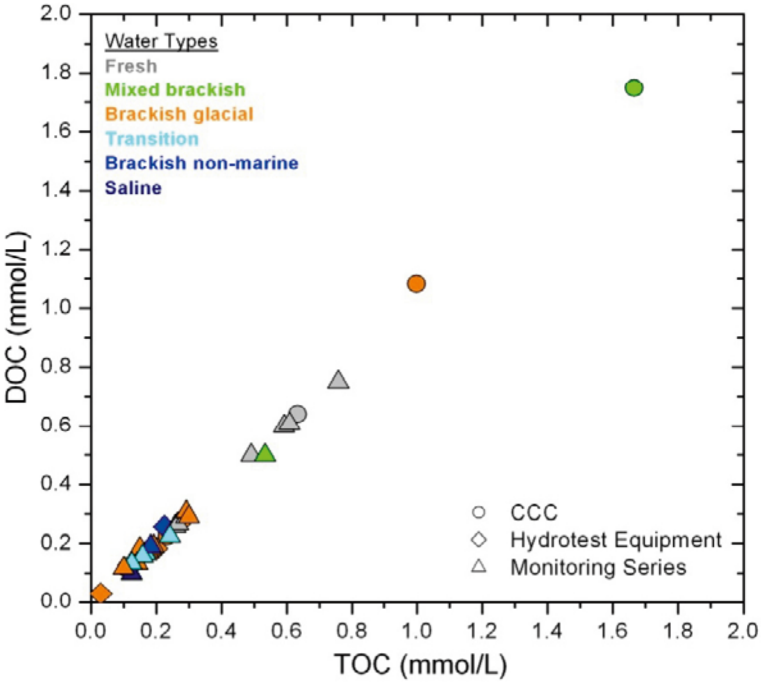

Figure 5-8. Dissolved organic carbon (DOC) plotted versus total organic carbon (TOC) for the Laxemar groundwaters.

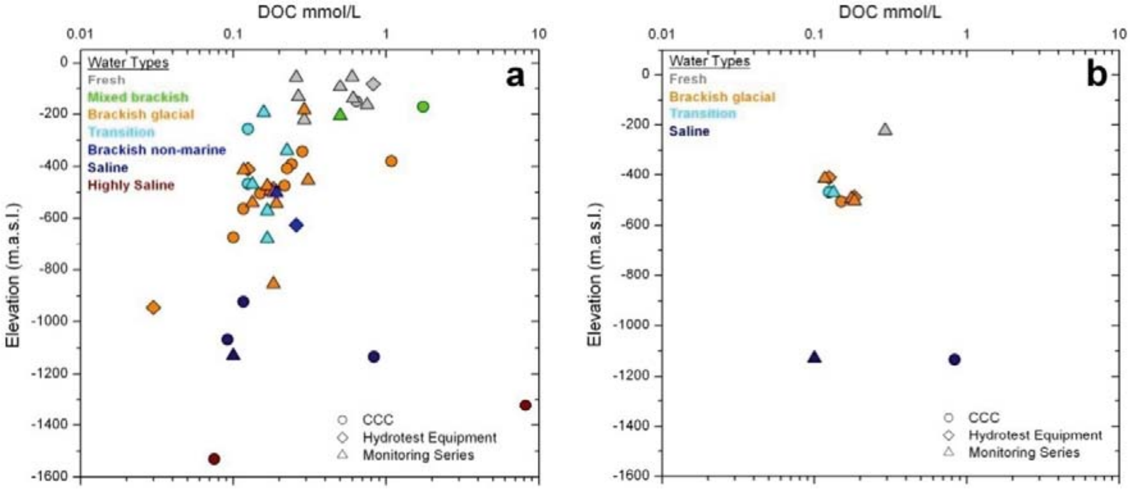

Figure 5-9. *(a) DOC in groundwaters from percussion and cored boreholes from sampling using CCC and monitoring versus elevation (masl). (b) Only CCC/hydrotest equipment and monitoring samples from the same water conducting structure are shown to facilitate comparison and elucidate the evolution of composition from the initial sampling (CCC) overlapping to the monitoring period.*

This observation also was commented upon in /Laaksoharju et al. 2009/. The reason for these slightly increased values (also found in Forsmark and elsewhere in the Nordic sites, cf. /SKB 2010/) is not known. Contamination during drilling/sampling, new routines for cleaning the equipment etc. have been discussed. It was hoped that additional data from the monitoring programme would help to clarify the long term behaviour of DOC, but unfortunately this has not materialised. In this context it has been noted also (e.g. Figure 5-9) that deep saline and highly saline groundwaters of old age at great depth (> 700–800 m) tend to have enhanced DOC (and sometimes clearly erroneously high) contents which so far have not been satisfactorily explained. One of the very high values (close to 1 mmol/L) from the CCC sampling in KLX02: –1,134.6 masl was subsequently followed by a one magnitude lower value measured during the monitoring of the same structure (KLX02: –1,129.14 masl; cf. Figure 5-9b). For the majority of samples there is an indication of lower DOC with depth.

However, for most samples there are no major differences between the values obtained during the CCC and the monitoring sampling programmes. When considering the time series from the monitoring, in many cases the first samples (from the tube and the first section volume) are higher in DOC and in some sections a correlation with sulphide can be observed (e.g. KLX10A: –338.43 masl; Figure 5-10).

5.3.2 Stable isotopes

In seven different borehole sections organic material was collected for carbon isotope analysis during the site investigations (CCC sampling). This included ^{14}C (pmC) in order to provide some age constraints on the material and δ^{13}C to give information on the origin of the organic material (Table 5-1). For all but one sample the ^{14}C contents varied between 64.6 to 83.7 pmC and there is no trend with depth or groundwater type. The δ^{13}C values are generally low (−23.4 to −27.8‰ PDB) indicating a terrestrial rather than a marine origin /Faure and Mensing 2005/. Generally, it can be concluded that the origin of the DOC in the samples is clearly post-glacial, in some of the cases maybe in the range of a few thousand years. The small number of analyses and obvious risk of contamination does not allow any further conclusions to be made.

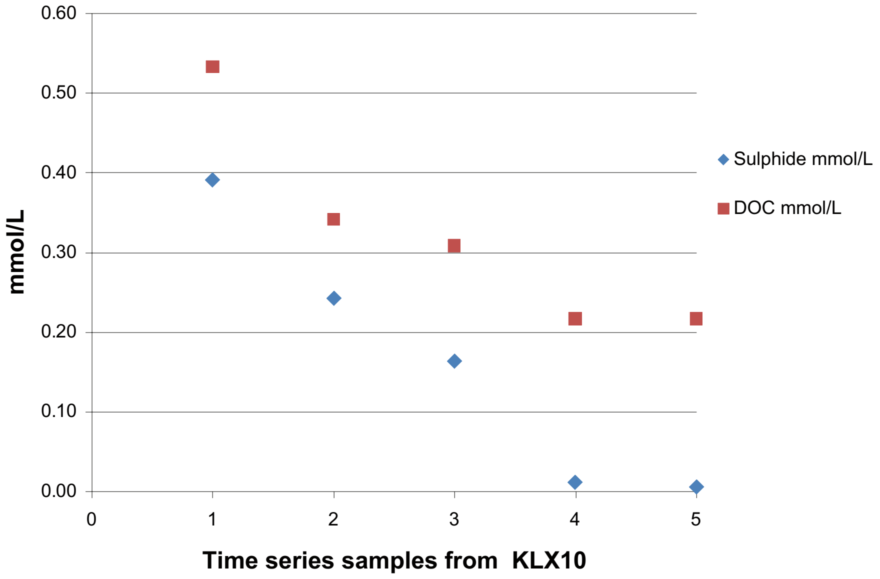

Figure 5-10. *Dissolved organic carbon (DOC) and sulphide (mmol/L) plotted versus sample number in a sampling time series from KFM10A: –338.43 masl, Autumn 2008. Sample 1 represents water from the first section volume and sample 2 and 3 represent removal of two and three section volumes whereas the last sample (5) is taken after removal of more than 200 section volumes. The final section volume recorded 0.006 mmol/L (0.19 mg/L) sulphide.*

Table 5-1. Carbon isotope analyses of organic material from groundwaters at Laxemar. Data from the CCC samples.

Borehole	Elevation (masl)	pmC (%)	$\delta^{13}C$ (‰ PDB)	Groundwater type
KLX03	−170.82	68.7	−26.3	Mixed brackish
KLX03	−379.85	65.22	−27.1	Brackish glacial
KLX03	−922.45	81.4	−23.4	Saline
KLX08	−150.43	83.7	−26.7	Fresh
KLX08	−390.71	64.6	–27.8	Brackish glacial
KLX15A	−467.22	3.6	−26.4	Transition type
KLX17A	−342.32	71.0	−26.8	Brackish glacial

5.4 Hydrogen, methane and carbon dioxide

As stated earlier in the report, the amount of sulphide not only depends on sources such as dissolved sulphate and available sulphate- and sulphide-bearing minerals, but also on the presence of reductants which includes methane and hydrogen; carbon dioxide is also included here because it can provide a food source for potential bacterial activity and is therefore relevant to the discussion.

In general, relatively few analyses of H_2, CH_4 and CO_2 are available from the Laxemar site, even when including results from the nearby Äspö and Simpevarp, and unfortunately there are no time series data and no monitoring data. Additional data from the Olkiluoto site in Finland and from the Forsmark site in Sweden are included therefore for comparison and discussion purposes. The values are given as mmol dissolved gas per litre of groundwater. The Laxemar gas analyses have earlier been reported by /Hallbeck and Pedersen 2008c/ and the Forsmark analyses have been reported in /Hallbeck and Pedersen 2008a/. The laboratory reports < 20% measurement uncertainty for the analyses and separation of the gases from the water. However, based on repeated sampling and analyses for the Swedish samples, the uncertainty is estimated to 30–100% depending on the concentration of the gas component.

5.4.1 Methane

At the Laxemar/Simpevarp/Äspö sites, Figure 5-11b, almost all data plot between 10^{-3} to 10^{-2} mmol/L. However, the highest values (> 10^{-2} mmol/L) all relate to Laxemar but appear to be independent of groundwater type and depth and no significant trends can be seen. This is similar to the Forsmark site where all methane values are between 10^{-3} to 10^{-2} mmol/L with one exception; KFM01D: −445 masl shows a methane value of about $2 \cdot 10^{-1}$ mmol/L (cf. Figure 5-11a).

The Olkiluoto data, in contrast, clearly show an increasing methane trend with depth (Figure 5-11c), especially from close to the bedrock surface to about –500 masl where values, despite showing a degree of scattering down to about –350 masl, increase systematically from about 10^{-2} to 10 mmol/L. From about –500 to –650 masl the methane content remains quite constant at about 10 mmol/L, but shows even slightly more increased values at depth below –750 masl. This clear trend shows also a well defined change in groundwater type with increasing depth (Figure 5-11c).

5.4.2 Hydrogen

Most of the groundwaters from the Laxemar/Simpevarp/Äspö sites, Figure 5-12b, plot at or close to detection. The remaining five groundwaters, three from Laxemar and two from Simpevarp, show values between $2 \cdot 10^{-3}$ and $9 \cdot 10^{-3}$ mmol/L.

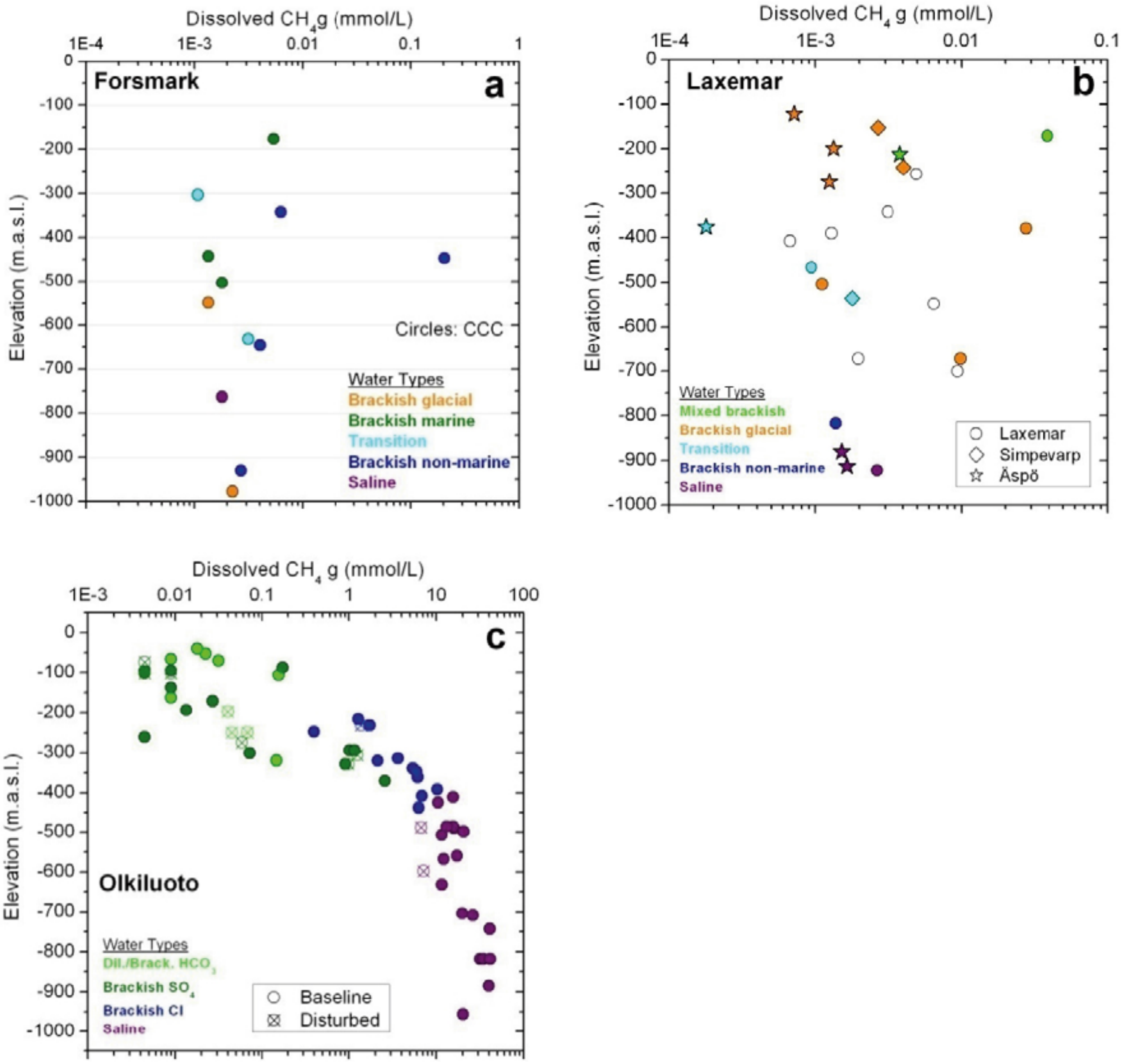

Figure 5-11. Methane concentrations (dissolved gas) in groundwaters from: a) Forsmark, b) Laxemar/Simpevarp/Äspö, and c) Olkiluoto.

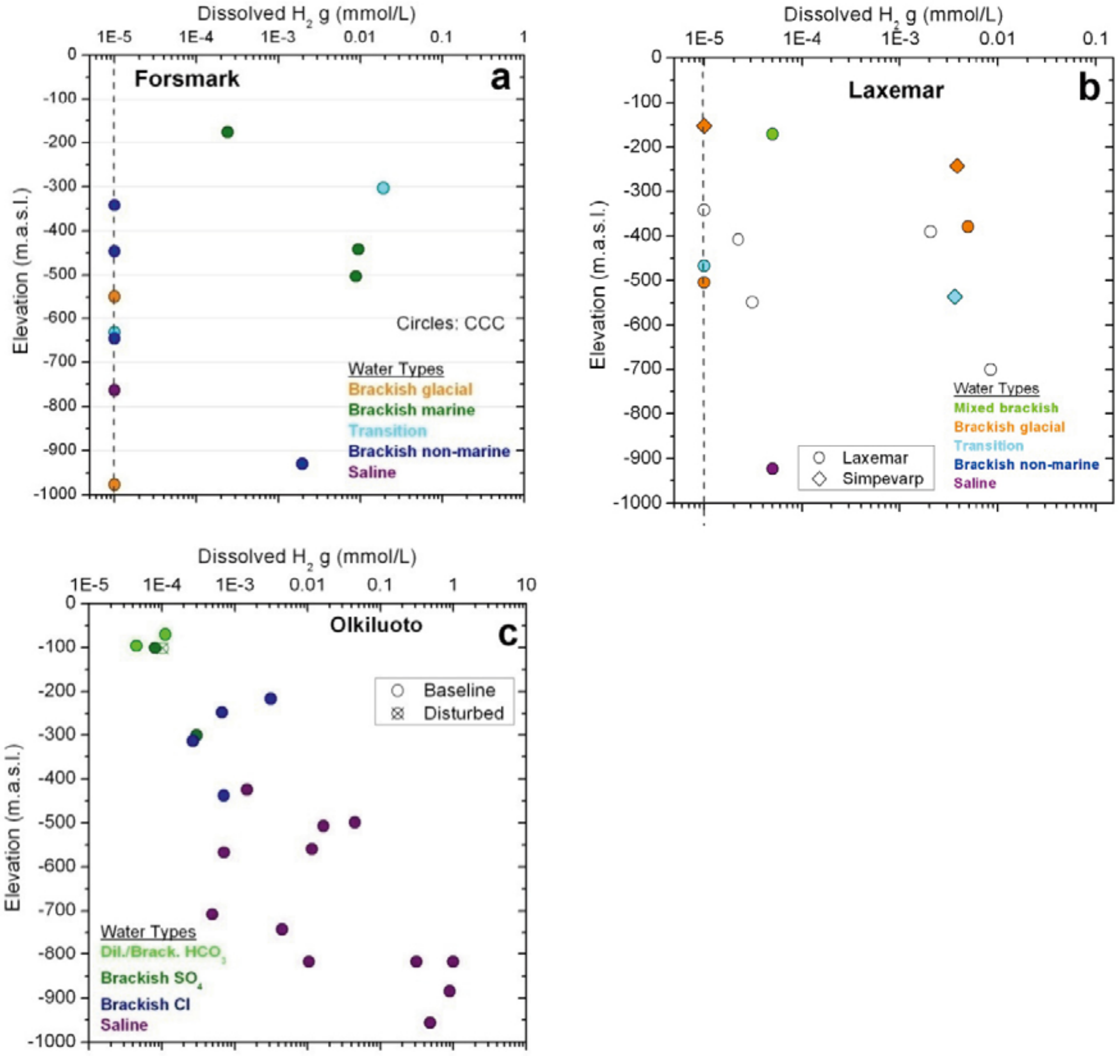

Figure 5-12. Hydrogen concentrations (dissolved gas) in groundwaters from: a) Forsmark, b) Laxemar/Simpevarp/Äspö, and c) Olkiluoto.

More than half of the Forsmark data, Figure 5-12a, are at or close to the detection limit of $2 \cdot 10^{-5}$ mmol/L; the remaining 5 groundwater samples representing depths from –170 masl to –950 masl show hydrogen values from $2 \cdot 10^{-4}$ to $2 \cdot 10^{-2}$ mmol/L.

The groundwaters at Olkiluoto, Figure 5-12c, show a scattered distribution, but nevertheless an increase in hydrogen from $4.5 \cdot 10^{-5}$ to 1 mmol/kg is suggested with increasing depth (i.e. –100 to –900 masl).

5.4.3 Carbon dioxide

For the Laxemar/Simpevarp/Äspö site, Figure 5-13b, most carbon dioxide data from the depth interval sampled (between –100 to –950 masl) plot within the range of 10^{-2} to 10^{-1} mmol/L. One Äspö sample at –212 masl records the highest value at $2 \cdot 10^{-1}$ mmol/L, and a group of four samples (mostly Laxemar) at intermediate depths of about –400 to –550 masl show the lowest values from $3 \cdot 10^{-3}$ to $6 \cdot 10^{-3}$ mmol/L. This group of four represent brackish glacial (with one transition) groundwater types generally not associated with bacterial activity.

Despite the Forsmark data, Figure 5-13a, showing a large scatter in carbon dioxide content from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-1}$ mmol/L, suggests a weak indication of a decrease with increasing depth. The highest values are found in the brackish marine waters and characteristically indicate a product of bacterial activity often associated with these marine groundwaters.

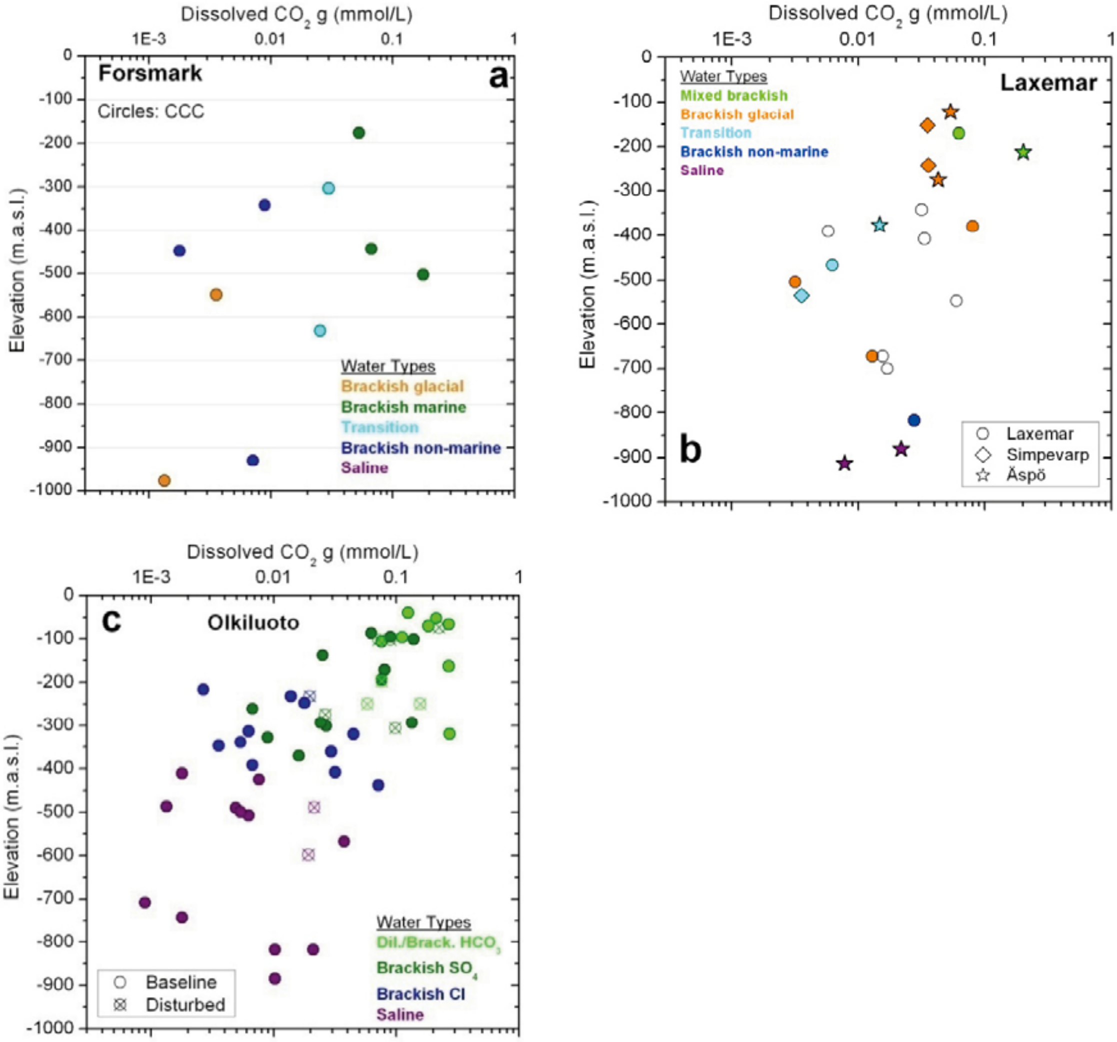

Figure 5-13. *Carbon dioxide concentrations (dissolved gas) in groundwaters from: a) Forsmark, b) Laxemar/Simpevarp/Äspö, and c) Olkiluoto.*

At Olkiluoto, Figure 5-13c, the upper 350 m of bedrock has the largest spread and highest carbon dioxide values, the latter associated mainly with the dilute, brackish bicarbonate groundwater types (and some of the brackish sulphate types) associated with bacterial activity. From –400 masl to the maximum depths sampled, there is a sharp decrease in carbon dioxide to less than $5\cdot10^{-2}$ mmol/L with many values at or near detection limit; this depth interval is dominated by the deeper saline groundwaters.

5.4.4 General comments

The analyses of gas dissolved in groundwater at Laxemar/Simpevarp/Äspö and Forsmark generally show a lack of strong depth trends, especially for methane and hydrogen. At Olkiluoto the increase in methane with depth suggests a deep input of abiogenic methane, and the two highest outlier values at intermediate depths may represent biogenic sources. The decrease in hydrogen with depth observed at Olkiluoto is not shown in the datasets from Forsmark and Laxemar/Äspö/Simpevarp. On the other hand, the number of analyses are much less in the Swedish dataset and many of the values are below detection limit. An overall decrease of carbon dioxide with depth is indicated at all sites.

In the absence (or at very low amounts) of superficial organic carbon, deep-sourced H_2 and CH_4 may be the key factors in the possible control of sulphate reduction. Sulphate reduction activity in groundwaters may be supported directly by H_2-utilising SRB (with or without coupling with anaerobic methane oxidation) or, indirectly, by suitable organic matter liberated by other H_2-utilising microorganisms (e.g. autotrophic acetogens). These type of microbial activities would be limited by the flux of H_2 and CH_4.

As stated above, the detected amounts of these gases in Forsmark and Laxemar are very low and fluxes and maximum productions of methane and hydrogen have been estimated based on these groundwater gas contents /Delos et al. 2010/. The calculated fluxes range from 0.2 to 1.2 10^{-10} mol/(m^2 yr) for CH_4 and from 0.5 to $9.0 \cdot 10^{-10}$ mol/(m^2 yr) for H_2 and, thus, sulphate reduction rates would be very low, in the range of 10^{-6} to 10^{-8} mM/year (assuming all CH_4 and H_2 is used up by sulphate reducing activity). This range is in agreement with the estimated values for the deep and old groundwaters in Laxemar and Forsmark and with the values of sulphate reduction rates for H_2-utilising SRB found in the literature (for further discussion see /Tullborg et al. 2010, Appendix 3/

5.5 Sulphate reducing bacteria (SRB) and adenosine-tri-phosphate (ATP)

Data of total cell counts, ATP concentrations, and most probable number (MPN) for sulphatereducing bacteria (SRB), exist for 10 samples out of the 598 samples (cf. Figure 5-14). SRB counts in sample #11692 (KLX17A: –547.97 masl) are high (3,000 cells/mL) compared with the rest of the samples, which suggests different environmental conditions of this sample compared to the remaining samples. This could be explained by intrusion of shallow water resulting in increased growth due the addition of organic material. This interpretation is also in accordance with the high ATP levels (222,000 fmol/L) in this sample and suggests an active community of heterotrophic sulphate reducers. SRB numbers are lower than 300 cell/mL in the rest of the samples. Comparison of the SRB cell numbers estimated with the MPN technique with the total numbers of directly measured cells indicate that SRB contributed generally less than 4.8% to the total bacterial cell numbers. These numbers are comparable to estimates with the same method from other sulphate reducing environments. Compared to studies that used molecular methods, however, the relative proportion of SRB to the total bacterial community determined here is relatively low. For example, in a deep marine biosphere study with active bacterial sulphate reduction, /Leloup et al. 2009/ estimated, based on real time PCR of the functional gene dsrAB (which shows how active the SRB are), that sulphate reducers comprised up to 22% of the total bacterial community. The lower numbers in Laxemar groundwaters could be due to selective enrichment of bacteria adapted to high substrate concentrations (i.e. more electron donors than in the natural environment favour some SRB) in the medium chosen in the MPN method.

As discussed in the Laxemar report /Hallbeck and Pedersen 2008c/ prolonged pumping could have affected sulphide concentrations and bacterial cell numbers so that a significant uncertainty is associated with the cell counts. Overall, DOC concentrations, dissolved sulphate and sulphide concentra-

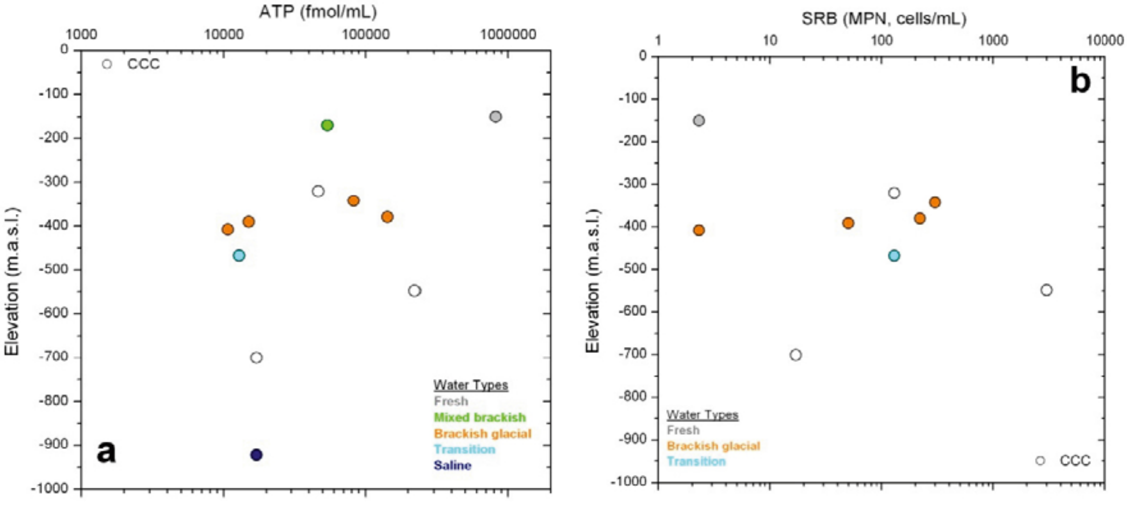

Figure 5-14. *ATP production (a) and most probable numbers of SRB (b) versus depth for groundwaters at Laxemar. Note that these plots only show the CCC dataset. The plot includes all the samples analysed for microbes but only the ones selected as representative are coloured.*

tions, and stable sulphur isotope composition of sulphate, were poorly correlated with cell numbers of SRB /Hallbeck and Pedersen 2008c/. This may be partly due to the fact that dissolved sulphide was buffered by iron (II) leading to the removal of sulphide as iron sulphide In support of this, counts of iron reducing bacteria (IRB) were elevated in some samples with higher counts of sulphate reducing bacteria. An alternative explanation could be that sulphate reducing activity was suppressed in the environment due to the coexistence of heterotrophic nitrate reducing bacteria, or that the sulphate reducing bacteria enriched by the MPN method also possessed the ability to reduce nitrate or nitrite. In support of this, NRB counts of nitrate reducers were the highest in the same samples that had high counts of SRB. In the absence of supporting phylogenetic information, it is not clear whether the same organisms were enriched with these two electron acceptors. The very low levels of nitrate and nitrite may thus be attributed to the consumption of these electron acceptors to their energy thresholds. A third explanation for the lack of correlation with sulphide levels may be that chemolithotrophic, nitrate reducing bacteria catalyse the oxidation of sulphide by reduction of nitrate to N_2 /Greene et al. 2004/. However, based on the existing dataset it is not clear if this pathway that is used in many oil reservoirs for sulphide remediation is active in the groundwaters at Laxemar.

5.6 Sulphide reduction rates

Sulphate reduction rate (SRR) in sedimentary and crystalline aquifers has been reviewed and some SRR calculations have been performed for the Laxemar and Forsmark groundwater systems (Figure 5-15; cf. Appendix 3 in /Tullborg et al. 2010/ for details).

In deep and long residence time groundwaters from sedimentary aquifers, the SRR is extremely low, as low as that observed in deep highly oligotrophic subseafloor marine settings. The main control of such SRR is the low availability of suitable, surface derived organic matter. In crystalline aquifer systems, where the availability of this type of organic matter is much more limited, SRR values must be equal to (or even lower than) those in deep sedimentary aquifers. Thus:

- The estimated SRR values for groundwaters at repository level with residence times of 3,000–15,000 years are between 10^{-4} and 10^{-5} mM/year, the lower value being the most probable, as the higher one corresponds to Littorina-enriched groundwaters from Olkiluoto, i.e. inside the range of values for deep sedimentary aquifers.
- In deeper (600–1,000 m depth) and longer residence time groundwaters from Laxemar and Forsmark, the SRR would be of the order of 10^{-6}–10^{-8} mM/year (Appendix 3 in /Tullborg et al. 2010/), in agreement with the few available values in crystalline systems at these depths, and lower than the values for deep sedimentary aquifers (Figure 5-15).

Metabolisms, based on deep sourced H_2 and CH_4, may participate in the control of sulphate reduction rates in crystalline systems. This type of microbial activity is limited by the flux of H_2 and CH_4 and, with the presently available data on these fluxes, the SRR would be in the range of 10^{-6} to 10^{-8} mM/year. These values are compatible with independent calculations based on dissolved sulphide contents in old deep groundwaters from Laxemar and Forsmark and in agreement with the few data found in the literature (cf. Appendix 3 in /Tullborg et al. 2010/).

The presence of dissolved Fe(II) sources, mainly iron oxhydroxides, exert a major control on the dissolved sulphide produced by the SRB activity. In the absence of these Fe(II) sources, local accumulation of dissolved sulphide occurs in some points of the groundwater systems. At the low SRR values typical of pristine conditions in deep sedimentary and crystalline systems, build up of meaningful concentrations of dissolved sulphide would need long periods of time. In any case, more detailed data on the spatial variability of Fe(II) mineral sources would be necessary to estimate the “buffering” capacity for dissolved sulphide at repository levels.

In this context, the SRR values obtained from the dissolved sulphide “peaks” during the monitoring programme or in experimental setups in crystalline systems (e.g. the MICROBE experiment; Figure 5-15) are too high to be considered representative of the pristine conditions. SRR values as high as those obtained in the monitoring programme are only observed in shallow aquifers enriched in organic matter. This fact, as well as other lines of evidence, supports an enhancement of SRB activity by additional, human induced sources of organic matter.

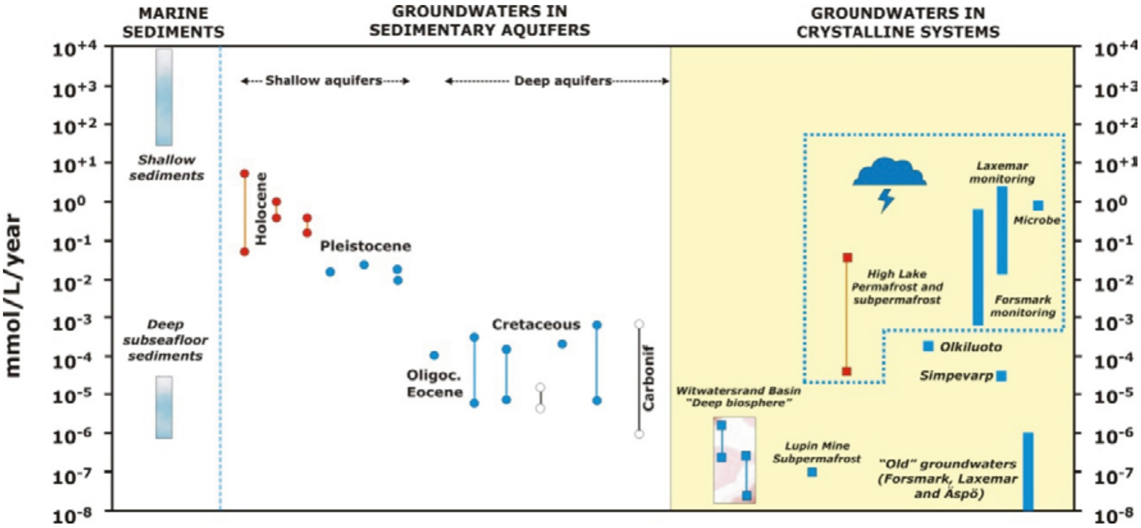

***Figure 5-15.** Compilation of published sulphate reduction rates (the sources of information are listed in Figure A3-1 /Tullborg et al. 2010/) including those values calculated in this study (Littorina enriched groundwaters from Olkiluoto; brackish non-marine groundwaters from Simpevarp at 250–500 m depth; and old, deep (>600 m depth) saline groundwaters from Forsmark, Laxemar and Äspö). Conflictive or unrealistic rates are included within the dotted area. Full references are given in Appendix 3 /Tullborg et al. 2010/.*

Sulphate reducing bacteria have been identified in the Forsmark and Laxemar groundwater systems but their amounts (as most probable numbers, MPN) are not homogeneously distributed with depth. SRB data do not show any clear trend with respect to the amounts of dissolved sulphate and no significant correlations exist with respect to DOC, TOC and hydrogen (cf. references in Appendix 3). Thus, factors conditioning the presence and distribution of SRB, the size of their populations and the distribution of SRR values in a more detailed level in the sites, are still poorly known.

The ultimate limiting factor on the rate of sulphate reduction is not necessarily the amounts of electron donor and sulphate (cf. references in Appendix 3 in /Tullborg et al. 2010/). Energy availability (ΔG) constitutes a primary control on the distribution and rate of microbial sulphate reduction in nature that needs to be evaluated in the studied systems.

5.7 Correlation between sulphide contents and hydrogeological observations

This section is devoted to the analysis of possible correlations between dissolved sulphide concentrations and hydrogeological parameters or the rock mass itself. All the boreholes with sulphide samples and geological data in the same range of elevation were compared. A total of 39 sulphide concentration measurements were used from the following boreholes: KLX02, KLX03, KLX04, KLX06, KLX07A, KLX08, KLX10, KLX11A, KLX12A, KLX13A, KLX15A, KLX17A, KLX18A, KLX19A and KLX20A (cf. Appendix 1). However, due to incomplete hydrogeological data, some of the sulphide data could not be used: HLX20: –54.46 masl, HLX28: –53.69 masl, HLX35: –92.56 masl, HLX37: –131.06 masl, HLX39: –139.09 masl, KLX01 (all sections), KLX02: –1,530.98 masl and KLX27A: –562.96 masl.

The hydrogeological parameters compared against sulphide concentrations are; a) the rock type (Figure 5-18), b) the pumping flow rate during sampling (Figure 5-19), c) the natural flow rate (in Figure 5-20), and d) the transmissivity (Figure 5-21). The study of hydrogeological parameters and sulphide along each one of the individual boreholes was also carried out (cf. Appendix 3).

Figure 5-18 shows the observed sulphide concentrations related to each major rock type. It seems that the types of rock with highest sulphide concentrations are; 1) granite to quartz monzodiorite, generally porphyritic, and 2) quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic.

However, it is worth noting that the first rock type is the most common in the Laxemar site and so there are more samples corresponding to this than to any of the others.

As shown in Figure 5-17, the pumping flow rate during sampling does not appear to correlate with the sulphide measurements, although the highest sulphide concentrations coincide when the pumping flow rate is lower than 1,00E^{-6} m^3/s.

An interesting result is that all the samples showing the highest sulphide contents coincide with borehole sections having a negligible natural flow rate (cf. Figure 5-18). It is worth noting that these sections must correspond to water conducting fractures (otherwise sampling is not possible), and that a very low natural hydraulic gradient must occur in order to explain such 'pseudo-stagnant' conditions. Furthermore, these conditions may favour the microbial activity needed to drive the sulphate reduction processes at low temperatures.

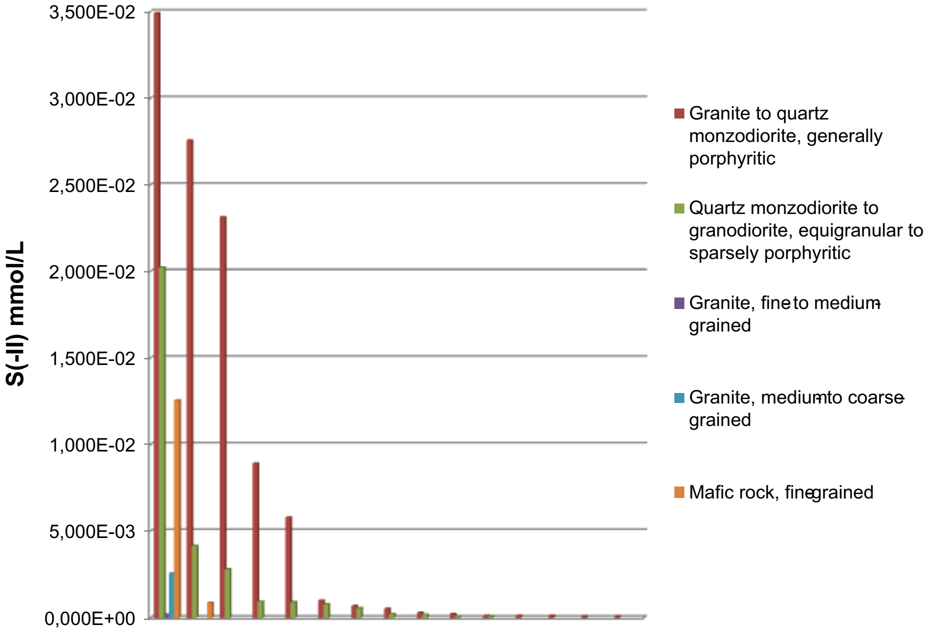

Figure 5-16. *Rock type plotted against dissolved sulphide concentration in the Laxemar boreholes.*

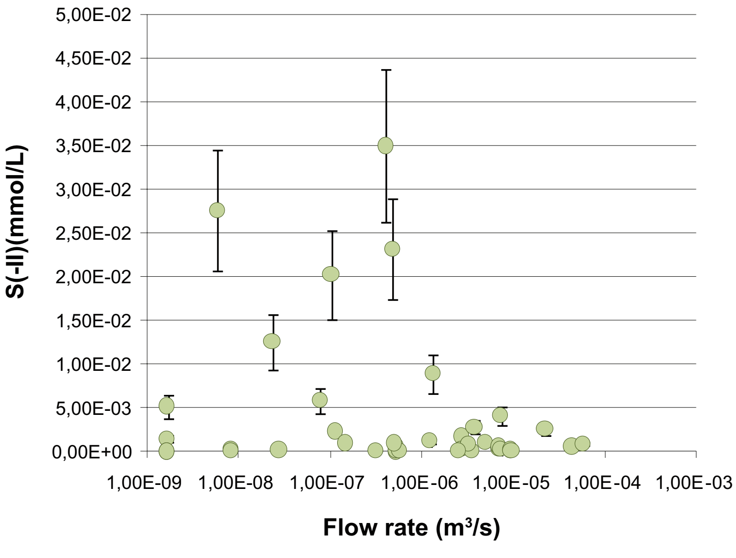

Figure 5-17. *Pumped flow rate plotted against dissolved sulphide concentrations in the Laxemar boreholes (error bars indicate the analytical uncertainty in sulphide measurements).*

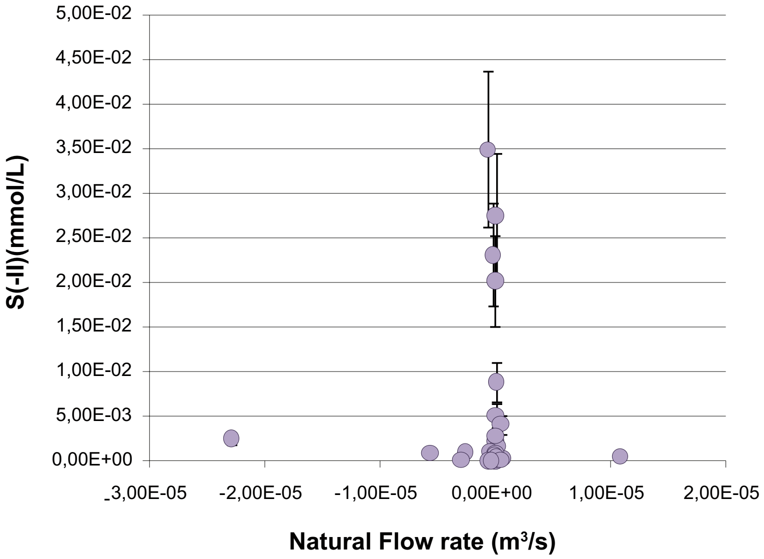

***Figure 5-18.** Natural flow rate plotted against dissolved sulphide in the Laxemar boreholes (error bars indicate the analytical uncertainty in sulphide measurements).*

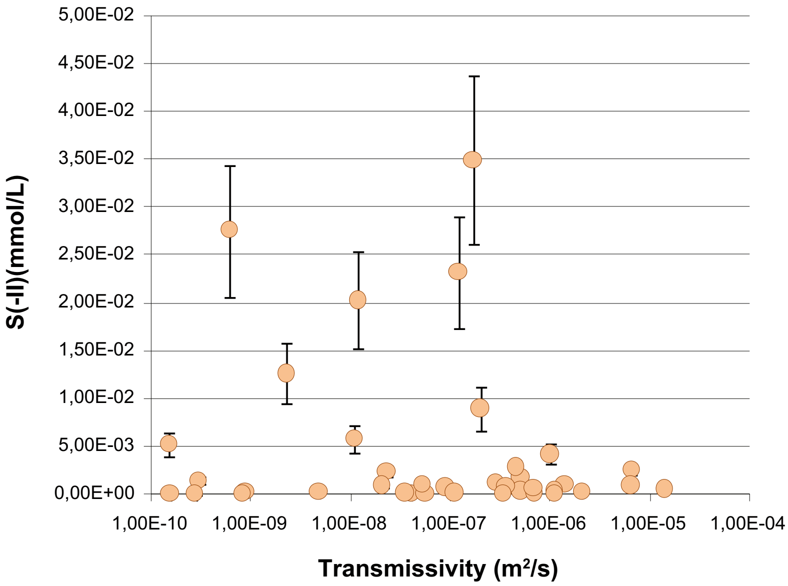

***Figure 5-19.** Transmissivity plotted against dissolved sulphide concentrations in Laxemar boreholes (error bars indicate the analytical uncertainty in sulphide measurements).*

Figure 5-19 appears to show a lack of correlation between transmissivity values and the sulphide contents, although the highest sulphide concentrations coincide always with transmissivity values lower than $1.7 \cdot 10^{-7}$ m²/s.

The main conclusions that can be extracted from these hydraulically related plots are:

- There is no apparent correlation between the sulphide contents in the groundwater and the rock transmissivity, although high sulphide values are always measured in borehole sections with transmissivities lower than $1.7 \cdot 10^{-7}$ m²/s.
- The highest sulphide contents are measured at elevations ranging from –400 to –700 masl, and in borehole sections showing negligible natural flow rate (pseudo-stagnant conditions). This might be related to the fact that microbial activity could be more active in such borehole sections under near stagnant groundwater conditions.

6 Conclusions

The problem with identifying reliable sulphide values was recognised at an early stage in the site investigations (PLU) from both Laxemar and Forsmark when the large variation in values between CCC and monitoring samples was observed, and also the very large variation within the monitoring time series.

The selection of "best possible" values has been handled accordingly: 1) For the CCC samples, the assumption is that groundwaters already judged from the site investigations to be representative from an analysis of the major ions and the important environmental isotopes, would also include the minor elements such as Fe, DOC, and S^{2-}. Most of the selected CCC sulphide values therefore correspond to groundwater samples previously selected as being representative (i.e. Categories 1–3 with the addition of some Category 4 and 5 samples where the groundwater chemistry has later been verified by monitoring results). 2) For the monitoring samples, in most cases during the time series measurements the sulphide values are higher in the downhole tubes and in the borehole section compared with formation groundwaters from the surrounding fractures. During the monitoring time series measurements carried out in Spring and Autumn 2008 and 2009, considerable volumes of water were removed before the final samples in each time series were selected (in the order of 10 to 500 section volumes depending on the borehole section). However, even when only considering these last samples, which should be dominated by formation water, there are still large variations (in many cases more than one order of magnitude) with the CCC samples, generally characterised by lower values when samples from the same borehole section can be compared. These differences are significant down to 650 m depth. However, taking into account only the CCC samples, there is an increase in sulphide below about 650 m which is not evident in the monitoring samples.

As mentioned above, time series measurements recorded during the monitoring programme show in most cases decreasing sulphide values. Furthermore, in sections where the monitoring values seems to have levelled out, there is still a discrepancy between this value and the lower CCC sulphide value. This either means that; a) the last groundwater sample from the borehole section sampled still has not reached 100% formation groundwater, or, b) the CCC values may reflect too low values due to artefacts from drilling and heavy pumping carried out in the boreholes prior to sampling, or, c) it may be almost impossible to avoid minor contamination to the monitoring samples from the section stagnant water with high sulphide content, irrespective as to how much water is pumped out, due to the geometry of the section or design of the equipment, or, d) differences in pumping time may cause an imbalance in hydraulic/hydrochemical conditions within the same aquifer.

It can, however, be assumed that the two selected groundwater samples from the same water conducting structures, i.e. the "best possible" sample from the monitoring and the sample from the CCC sampling, the latter usually showing lower sulphide, spans the interval of representative sulphide values in the formation water.

Saturation in respect of FeS(am) is achieved for some monitoring samples but only for one CCC sample. In samples at or close to saturation, the measured Fe^{2+} and S^{2-} values in a single sample are interdependent and consequently the solubility of FeS(am) sets an upper limit for these species in the groundwater.

It is worth noting that the plug flow calculations performed for the monitored sections at Forsmark /Nilsson et al. 2010, Tullborg et al. 2010/ and for borehole KLX06 in Laxemar /Rosdahl et al. 2010/ can be very useful in the planning and execution of groundwater sampling strategy (by knowing) the individual sampling schemes for each borehole section. However, for the majority of the Laxemar borehole sections sampled during the monitoring time series, only qualitative estimations of section water volumes removed was possible. Therefore, when comparing the volume needed to be removed with the actual volume pumped, the indications were that sufficient water (and often much more) was removed to ensure formation water was sampled. However, the results showed that sulphide values > 0.016 mmol/L (> 0.5 mg/L) were restricted to four sections which had been pumped 2 to 14 times more than the estimated volume calculated. One explanation may be that these borehole sections are more complex hydrogeologically than indicated by the calculations based on the differential flow log data. Another possibility is that the sulphide values measured are representative. Additional *in situ* tests over longer periods of time with tighter sampling protocols are required to help resolve these issues.

The plot below (Figure 7-1) compares the sulphide values from the earlier SR-Can safety assessment and the presently selected distribution for the SR-Site Forsmark (left-hand plot) and Laxemar (right-hand plot) studies. All sulphide concentrations (apart from one) at Forsmark are ≤ 0.013 mmol/L (0.4 mg/L); for Laxemar, six samples show values above 0.013 mmol/L.

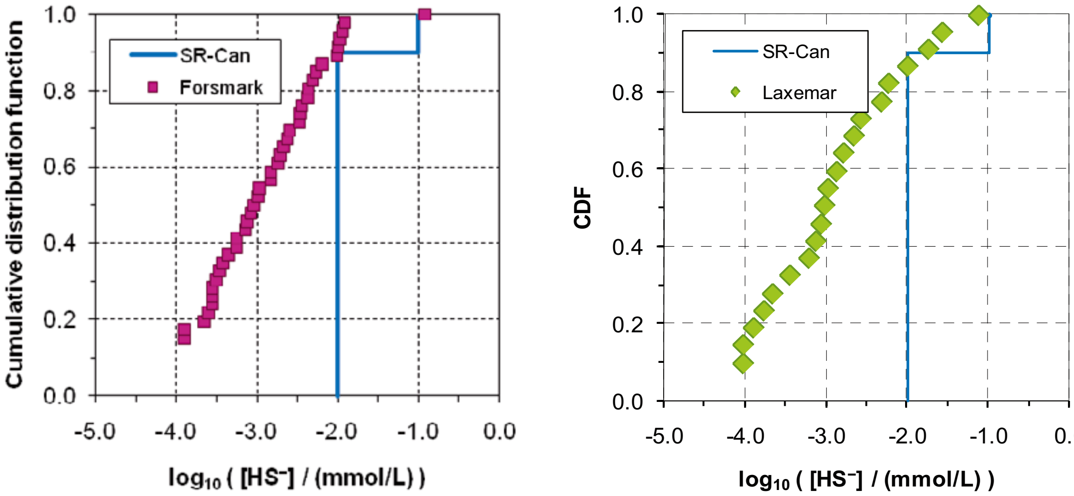

***Figure 6-1.** Cumulative distribution curve showing the selected sulphide values for groundwaters to be used for Forsmark /Tullborg et al. 2010/ to the left and Laxemar (present report) to the right. The blue curve shows the values used in the earlier performed safety assessment (SR-Can). The distribution function describes the probability that a sulphide concentration will be found to be less than, or equal to, a given value. The data show, for example, that the probability of finding a sulphide value ≤ 0.001 mM is ≈50%.*

7 Acknowledgements

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8 References

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Appendix 1

Tables

This appendix contains tables reviewing the S^{2-}, Fe^{2+}, Mn^{2+} and DOC/TOC contents for all the analyses from percussion and cored boreholes in Laxemar where sulphide has been analysed. Groundwater type and chloride content are also given.

Data from two different types of sampling are used: a) Complete Chemical Characterisation (CCC) data from cored boreholes of the site characterisation programme (i.e. 'Extended data freeze Laxemar 2.3' of December 4th, 2007 /Laaksoharju et al. 2009/) that includes the earlier established categorisation of the samples, and b) data from the monitoring of selected borehole sections in percussion and cored boreholes initiated at different times during and following the site characterisation programme up to November 2009. In addition, some groundwater data taken during hydraulic testing ('Sampled using Hydrotest Equipment') of individual borehole sections are included. This hydraulic testing combined with groundwater sampling have usually been carried out soon after completion of the borehole drilling and therefore prior to the CCC and monitoring campaigns. Furthermore, groundwater samples have been taken during tracer tests carried out in some borehole sections as part of the Laxemar site investigations. These were carried out following the CCC campaign but prior to the monitoring campaign, and have been included and described under the 'Monitoring Section' tables ('Monitoring section (tracer test)') as they can be considered an early monitoring stage of specific borehole sections.

Some of the CCC/hydrotest and monitoring equipment sections correspond to each other (i.e. the same water conducting fracture is sampled) and in such cases the corresponding section is referred to in the table heading.

It is also commented upon if the major ion chemistry has been stable during the sampling period, and for the monitoring samples corresponding to a CCC/hydrotest sampled section it is recorded if the groundwater chemistry deviates from the earlier sampled CCC/hydrotest values. Concerning the measured sulphide values given, it is important to note that detection levels for sulphide have varied during the site investigations from 0.002 to 0.006 mg/L, and that during some periods a "reporting limit" of 0.03 mg/L (equal to 10σ) has been used when the measured values are included in the database. For each measured sulphide value selected, there is also an explanation as to why it has been chosen.

Two different methods have been used for analyses of iron content; the total iron content was measured using ICP (Fe), and spectrophotometry was used to determine both total Fe (Fe(tot)) and Fe(II). There is usually a good correlation between all three values. The values for Fe(ICP) are mostly chosen in the present study because these are measured for almost all samples and constitute, therefore, the largest dataset. In some cases spectrophotometry values are used and these are indicated in the documentation.

The organic content is given as DOC (analysed for most of the samples) and its correlation with TOC (if analysed) is noted. The groundwater sample for TOC (Total organic Carbon) is not filtered and the sample for DOC (Dissolved Organic Carbon) is filtered through a 0.4 µm disposable filter. The samples are stored immediately in the freezer and transported to the laboratory in isolated bags with cooling blocks. The analytical method used includes: 1) Acidification to remove inorganic carbon and volatile organic carbon. 2) UV-oxidation to convert all the carbon present to carbon dioxide which is flushed through scrubber tubes to remove chlorine gas and water vapour. 3) Detection and quantification using an Infrared Detector.

HLX20

Monitoring section: 71.0 to 75.5 m

Elevation sec mid:

–54.46 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Samples collected from 2007-06-18.	Only one sample but considered representative for the sample depth.
Groundwater type.	Na-HCO_3 (Cl, SO_4) type. Cl is 50.20 mg/L.	Fresh groundwater type. Uncertain major ion stability.	Selected sample: #11923 (2007-06-18); 50.20 mg/L Cl.
S^{2-}	0.025 mg/L	Only a single measured value.	0.025 mg/L
Fe	0.0342 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.0342 mg/L
Mn	0.044 mg/L		0.044 mg/L
DOC	3.1 mg/L	Good correlation between DOC and TOC.	3.1 mg/L

Note: Because of the shallow nature of the borehole, the sampled section may respond to a well connected fracture system of high transmissivity.

HLX28

Monitoring section: 70.00 to 90.00 m

Elevation sec mid:

–53.69 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	5 samples.	Samples collected during 2 occasions: 2009-06-16 to 2009-06-24 (2 samples), and 2009-10-14 to 2009-10-20 (3 samples).	Sample selected because of stable values during the first sampling occasion.
Groundwater type.	Na-HCO_3 (Cl, SO_4) type. Cl varies from 89.9 to 60.0 mg/L.	Fresh groundwater type. Uncertain major ion stability due to limited data.	Selected sample: #15979 (2009-06-24); 89.9 mg/L Cl.
S^{2-}	0.033 to 15.700 mg/L	Selection based on first sampling with a similarly low value to the final sample selected (0.059 mg/L).	0.036 mg/L
Fe	0.072 to 0.108 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Chosen values correspond to the last sampling on both occasions. No systematic decrease with time.	0.108 mg/L
Mn	0.069 to 0.093 mg/L	Chosen values correspond to the last sampling on both occasions. No systematic decrease with time.	0.093 mg/L
DOC	7.2 to 7.4 mg/L	Good correlation between DOC and TOC. Chosen values correspond to the last sampling on both time series occasions. No systematic decrease with time.	7.2 mg/L

Note: Because of the shallow nature of the borehole, the sampled section may respond to a well connected fracture system of high transmissivity.

HLX35

Monitoring section: 120.00 to 135.00 m
Elevation sec mid:
–92.56 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 3 occasions: 2008-10-04, 2009-05-18 to 2009-05-26 (3 samples), and 2009-10-27 to 2009-11-02 (3 samples).	Sampling during 2009 shows a similar repetitive pattern during the two sampling series and the final sample was chosen as being suitable.
Groundwater type.	Na-HCO$_3$-Cl (SO$_4$) type. Cl varies from 177.0 to 221.0 mg/L.	Fresh groundwater type. Largely stable major ion chemistry.	Selected sample: #19114 (2009-11-02); 221.0 mg/L Cl.
S^{2-}	0.020 to 4.61 mg/L	Selected sample is based on the lowest values for each sampling occasion (0.020 to 0.031 mg/L). The actual sample selected from the final time series sampling is based on greater groundwater stability and a more acceptable sulphur isotope value. No systematic decrease with time.	0.031 mg/L
Fe	0.058 to 0.056 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic decrease with time.	0.066 mg/L
Mn	0.072 to 0.080 mg/L	No systematic decrease with time.	0.080 mg/L
DOC	5.7 to 6.0 mg/L	Good correlation between DOC and TOC. No systematic decrease with time.	6.0 mg/L

Note: Because of the shallow nature of the borehole, the sampled section may respond to a well connected fracture system of high transmissivity.

HLX37

Monitoring section: 150.0 to 199.80 m
Elevation sec mid:
–131.06 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	6 samples.	Samples collected during 3 occasions: 2008-10-22, 2009-06-16 to 2009-06-23 (2 samples), and 2009-10-14 to 2009-10-21 (3 samples).	The selected sample represents the final value taken from the last sampling series occasion which showed a good systematic decrease with time.
Groundwater type.	Na-HCO$_3$ (Cl, SO$_4$) type. Cl varies from 43.2 to 70.1 mg/L.	Fresh groundwater type. Stable major ion chemistry suggesting local discharge (i.e. low TU and relatively low ^{14}C).	Selected sample: #19108 (2009-10-21); 43.2 mg/L Cl.
S^{2-}	0.021 to 2.650 mg/L	The last sampling occasion was chosen because of the longer time series (3 samples). The final sample was selected (0.021 mg/L). Systematic decrease during the time series (2.650 to 0.021 mg/L).	0.021 mg/L
Fe	0.007 to 0.020 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic decrease with time.	0.007 mg/L
Mn	0.009 to 0.038 mg/L	No systematic decrease with time.	0.011 mg/L
DOC	2.3 to 3.2 mg/L	Good correlation between DOC and TOC. No systematic decrease with time.	3.2 mg/L

Note: Because of the shallow nature of the borehole, the sampled section may respond to a well connected fracture system of high transmissivity.

HLX39

Monitoring section: 187.00 to 199.30 m
Elevation sec mid:
–139.09 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 3 occasions: 2008-11-04, 2009-05-18 to 2009-05-25 (3 samples), and 2009-10-28 to 2009-11-02 (3 samples).	The selected sample represents the final value taken from the last sampling series occasion which showed a systematic decrease with time.
Groundwater type.	Na-HCO_3 (Cl) type.	Fresh groundwater type.	Selected sample: #19117 (2009-11-20); 56.2 mg/L Cl.
	Cl varies from 56.2 to 74.3 mg/L.	Stable major ion chemistry.	
S^{2-}	0.012 to 1.26 mg/L	The final sample was selected.	0.050 mg/L
		Last sampled time series occasion shows a systematic decrease (0.709–0.050 mg/L).	
Fe	0.037 to 0.042 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.039 mg/L
		No systematic decrease with time.	
Mn	0.048 to 0.065 mg/L	No systematic decrease with time.	0.048 mg/L
DOC	7.2 to 7.6 mg/L	Good correlation between DOC and TOC.	7.3 mg/L
		No systematic decrease with time.	

Note: Because of the shallow nature of the borehole, the sampled section may respond to a well connected fracture system of high transmissivity.

KLX01

Monitoring section (tracer test): 171.00 to 190.00 m
Elevation sec mid:
–163.26 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2006-07-05.	Only one sample but considered representative for the sample depth.
Groundwater type.	Na(Ca)-Cl (SO_4)type.	Fresh groundwater type.	Selected sample: #11209 (Category 3*, 2003-07-05); 110.0 mg/L Cl.
	Cl is 110.0 mg/L.		
S^{2-}	0.053 mg/L		0.053 mg/L
Fe	4.3 mg/L (spectrometry value)	Good correlation between Fe(tot) and Fe(II).	4.3 mg/L
		Note higher value than normal.	
Mn	0.352 mg/L		0.352 mg/L
DOC	9.0 mg/L	Good correlation between DOC and TOC.	9.0mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX01

CCC section: 272.00 to 277.00 m
Elevation sec mid:
–257.06 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	10 samples.	Samples collected during 1 occasion: 1988-11-25 to 1988-12-09.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na(Ca)-Cl type. Cl varies from 1,640 to 2,080 mg/L.	Transition groundwater type. Relatively stable major ion chemistry especially for the final 4 samples.	Selected sample: #1537 (Category 3*, 1988-12-08); 2,050 mg/L Cl.
S^{2-}	0.470 to 0.650 mg/L	No systematic time change.	0.530 mg/L
Fe	0.079 to 0.559 mg/L (spectrometry values)	Good correlation between Fe(tot) and Fe(II). No ICP values measured. No systematic decrease with time.	0.129 mg/L
Mn	0.20 to 0.23 mg/L	**Note:** higher detection limit. No systematic decrease with time.	0.20 mg/L
DOC	1.5 to 2.3 mg/L	Only two measured values. No TOC measurement.	1.5 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX01

CCC section: 456.00 to 461.00 m
Elevation sec mid:
–440.73 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	10 samples.	Samples collected during 1 occasion: 1988-11-08 to 1988-11-23.	None selected because of Category 5 groundwater type.
Groundwater type.	Na(Ca)-Cl-SO_4 type. Cl varies from 1,650.0 to 1,700.0 mg/L.		
S^{2-}	Below 0.460 to 0.730 mg/L.	Systematic change with time (0.730 to 0.460 mg/L).	None selected.
Fe	0.029 to 0.088 mg/L (spectrometry values)	Relatively good correlation between Fe(tot) and Fe(II); no ICP value. No systematic decrease with time.	None selected.
Mn	0.14 to 0.17 mg/L	No systematic decrease with time.	None selected.
DOC	1.4 to 2.6 mg/L	Values from three samples. TOC not analysed. No systematic decrease with time.	None selected.

KLX01

CCC section: 680.00 to 702.11 m
Elevation sec mid:
–672.95 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	17 samples.	Samples collected during 2 occasions: 1988-10-05 to 1988-11-03 (9 samples) and 1989-10-23 to 1989-11-01 (8 samples). **Note:** This borehole section was sampled two times on different occasions with a gap of one year. The earlier occasion showed higher sulphide contents but was chosen to be more suitable because the major groundwater composition is considered representative for this depth.	Selected sample corresponds to the earlier CCC categorised groundwater and considered more representative.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 2,460 to 4,870 mg/L.	Brackish glacial groundwater type. This groundwater type is believed representative for this depth.	Selected sample: #1516 (Category 3*, 1988-11-03); 4,870 mg/L Cl.
S^{2-}	0.58 to 7.4 mg/L	No systematic time change.	2.5 mg/L.
Fe	0.019 to 0.435 mg/L (spectrometry values)	Only Fe(tot) and Fe(II) analysed; good correlation. No systematic time change.	0.032 mg/L
Mn	0.19 to 0.23 mg/L	No systematic time change.	0.20 mg/L
DOC	0.8 to 7.0 mg/L	TOC is not measured. No systematic time change.	1.2 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX01

CCC section: 830.00 to 841.00 m
Elevation sec mid:
–817.20 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples	8 samples.	Samples collected during 1 occasion: 1990-09-24 to 1990-10-09.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type	Ca-Na-Cl(SO_4) type. Cl varies from 9,120 to 9,250 mg/L.	Brackish non-marine groundwater type.	Selected sample: #1761 (Category 3*, 1990-10-09); 9,180 mg/L Cl.
S^{2-}	0.030 to 0.090 mg/L	No systematic time change.	0.070 mg/L
Fe	0.226 to 3.23 mg/L (spectrometry values)	No ICP analyses; good correlation between Fe(tot) and Fe(II). No systematic time change.	0.219 mg/L (Fe (tot) value).
Mn	0.11 to 0.12 mg/L	No systematic time change.	0.11 mg/L
DOC		No TOC or DOC values.	

***** see documentation in /Smellie and Tullborg 2009/.

KLX01

CCC section: 910.00 to 921.00 m
Elevation sec mid:
–897.09 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	10 samples.	Samples collected during 1 occasion: 1990-10-12 to 1990-10-30.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 10,000 to 11,200 mg/L.	Saline groundwater.	Selected sample: #1773 (Category 4*, 1990-10-30); 11,200 mg/L Cl.
S^{2-}	0.010 to 0.310 mg/L	Systematic increase with time.	0.290 mg/L
Fe	0.017 to 0.528 mg/L (spectrometry values)	No ICP analyses. Good correlation between Fe(tot) and Fe(II). No systematic decrease with time.	0.053 mg/L (Fe(tot) value).
Mn	0.09 to 0.12 mg/L	No systematic variation with time.	0.09 mg/L
DOC		No TOC and DOC values measured.	

* see documentation in /Smellie and Tullborg 2009/.

KLX01

CCC section: 999.0 to 1,077.99 m
Elevation sec mid:
–1,019.91 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	10 samples.	Samples collected during 1 occasion: 1990-11-05 to 1990-11-19.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Ca-Na-Cl(SO_4) type. Cl varies from 12,400 to 12,600 mg/L.	Saline groundwater type with variable marine components.	Selected sample: #1785 (Category 4; 1990-11-19); 4,570 mg/L Cl.
S^{2-}	0.070 to 0.180 mg/L	No systematic time change.	0.180 mg/L
Fe	0.364 to 0.786 mg/L (spectrometry values)	No ICP analyses. Good correlation between Fe(tot) and Fe(II). No systematic time change.	0.364 mg/L
Mn	0.05 to 0.06 mg/L	No systematic time change.	0.06 mg/L
DOC		No TOC or DOC values measured.	

* see documentation in /Smellie and Tullborg 2009/.

KLX02

CCC section: 315.00 to 321.50 m
Elevation sec mid:
–298.57 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	3 samples.	Samples collected during 1 occasion: 1994-01-31 to 1994-02-10.	Not representative for the sampling depth (Category 5).
Groundwater type.	Na-HCO_3(Cl, SO_4) type. Cl varies from 33.0–73.0 mg/L.	Fresh groundwater type.	None selected.
S^{2-}	Below detection limit of 0.01 up to 0.04 mg/L.		None selected.
Fe	1.060 to 1.880 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	None selected.
Mn	0.150 to 0.200 mg/L		None selected.
DOC	5.5 to 5.7 mg/L	No TOC measured.	None selected.

KLX02

CCC section: 335.00 to 340.80 m
Elevation sec mid:
–318.13 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	2 samples.	Samples collected during 1 occasion; 1993-11-04 to 1993-11-08.	Not representative for the sampling depth (Category 5).
Groundwater type.	Na-Ca-HCO_3-Cl(SO_4) type. Cl is 178.0 and 235.0 mg/L.	Fresh groundwater type.	None selected.
S^{2-}	One value below detection limit (0.010 mg/L) and the other 0.030 mg/L.		None selected.
Fe	0.465 and 0.675 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	None selected.
Mn	0.140 and 0.180 mg/L		None selected.
DOC		No DOC or TOC measurements made.	

KLX02

Monitoring section (tracer test): 452.00 to 494.00 m
Elevation sec mid:
–452.50 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	2 samples.	Single samples collected during 2 occasions; 2006-06-04 and 2006-10-30.	Not representative for the sampling depth (i.e. Category 5).
Groundwater type.	Na(Ca)-Cl-SO_4 (HCO_3) type. Cl is 563.0 and 645.0 mg/L.	Mixed brackish groundwater type. Unstable major ion chemistry.	None selected.
S^{2-}	0.112 and 0.370 mg/L		None selected.
Fe	8.79 and 15.00 mg/L Fe(ICP)	Extremely high values. Good correlation between Fe(ICP), Fe(tot) and Fe(II).	None selected.
Mn	0.536 and 0.712 mg/L		None selected.
DOC	47.0 and 140.0 mg/L	TOC also measured and shows corresponding higher values to DOC. Extremely high values.	None selected.

KLX02

CCC section: 798.00 to 803.80.
Elevation sec mid:
–778.18 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	4 samples.	Samples collected during 1 occasion; 1993-11-11 to 1993-11-23.	Not representative for the sampling depth (i.e. Category 5).
Groundwater type.	Na(Ca)-Cl-HCO_3-SO_4 type. Cl varies from 87.0 and 717.0 mg/L.	Unstable groundwater showing variation from fresh to mixed brackish.	None selected.
S^{2-}	From below detection at 0.010 to 0.030 mg/L.		None selected.
Fe	0.585 to 1.830 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	None selected.
Mn	0.092 and 0.390 mg/L		None selected.
DOC	5.0 mg/L	No TOC measurements.	None selected.

KLX02

CCC section: 1,090.00 to 1,096.20 m (Section corresponds to a later CCC sampling section: 1,090.00 to 1,097.00 m)
Elevation sec mid:
–1,068.24 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	4 samples.	Samples collected during 1 occasion: 1993-12-07 to 1993-12-16.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type	Ca-Na-Cl(SO_4) type. Cl varies from 14,600 to 15,800 mg/L.	Saline groundwater type.	Selected sample #2722 (Category 3*, 1993-12-16); 15,800 mg/L Cl.
S^{2-}	Below detection limit (0.010 mg/L) to 0.020 mg/L.	No systematic time change.	Below 0.010 mg/L
Fe	Under detection limit (0.008 mg/L) to 0.034 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Systematic decrease with time.	Below 0.008 mg/L
Mn	0.010 to 0.020 mg/L	No systematic time change.	0.010 mg/L
DOC	1.1 mg/L	TOC not measured. No systematic time change.	1.1 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX02

CCC section: 1,090.00 to 1,097.00 m (Section corresponds to an earlier CCC sampling section: 1,090.00 to 1,096.20 m)
Elevation sec mid:
–1,068.64 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	3 samples.	Samples collected during 1 occasion: 1993-09-27 to 1993-10-28.	Not representative for the sampling depth (Category 5). Previous sampled section was chosen as being representative for this packed-off section.
Groundwater type.	Ca-Na-Cl(SO_4) type. Cl varies from 1,010 to 4,739 mg/L.	Very unstable major ion chemistry.	None selected.
S^{2-}	From below detection limit (0.010 mg/L) to 0.046 mg/L.		None selected.
Fe	6.04 to 12.40 mg/L Fe(ICP)	Very high values. Good correlation between Fe(ICP) and Fe(tot) but both significantly lower (2.01 to 3.43 mg/L) than Fe(II).	None selected.
Mn	1.03 to 1.54 mg/L	High values.	None selected.
DOC	15.1 and 16.0 mg/L	Two samples measured. TOC not measured.	None selected.

KLX02

Monitoring section (tracer test): 1,145.00 to 1,164.00 m (Corresponds to CCC section 1,155.00 to 1,165.00 m).
Elevation sec mid:
–1,129.14 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	3 samples.	Samples collected during 3 occasions: 2006-06-21, 2006-10-31 and 2007-07-10.	All values are suitable; first sample selected.
Groundwater type.	Ca-Na-Cl(SO_4) type. Cl is 15,500 mg/L for all three samples.	Saline groundwater type. Stable major chemistry.	Selected sample: #11145, (2006-06-21); 15,000 mg/L Cl.
S^{2-}	0.152 to 0.171 mg/L	No systematic decrease with time.	0.165 mg/L
Fe	1.590 to 1.780 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic decrease with time.	1.360 mg/L **Note:** Fe(tot) and Fe(II) values are slightly lower than the ICP value.
Mn	0.540 to 0.683 mg/L	No systematic decrease with time.	0.540 mg/L
DOC	1.20 to 2.30 mg/L	Good correlation between DOC and TOC. No systematic decrease with time.	1.20 mg/L.

KLX02

CCC section: 1,155.00 to 1,165.00 m (Corresponds to Monitoring Section: 1,145.00 to 1,164.00 m).
Elevation sec mid:
–1,134.60 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	3 samples.	Samples collected during 1 occasion: 1999-09-01 to 1999-09-15.	One sample from this Category 5 series has been selected (final value) because of support from later monitoring data from an overlapping section.
Groundwater type.	Ca-Na-Cl(SO_4) type. Cl from 14,220 to 15,130 mg/L.	Saline groundwater type.	Selected sample: #2934 (Category 5, 1999-09-15); 15,130 mg/L Cl.
S^{2-}	All values below detection limit (0.010 mg/L).	No systematic time change.	< 0.010 mg/L
Fe	1.060 to 2.780 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Systematic decrease with time.	1.035 mg/L (Spectrometer value).
Mn	0.247 to 0.418 mg/L	Systematic decrease with time.	0.247 mg/L
DOC	10.0 to 13.0 mg/L	No TOC measurements. No systematic decrease with time.	10.0 mg/L

KLX02

CCC section: 1,345.00 to 1,355.00 m
Elevation sec mid:
–1,322.81 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	3 samples.	Samples collected during 1 occasion: 1999-07-19 to 1999-08-10.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Ca-Na-Cl(SO_4) type. Cl varies from 31,060 to 31,590 mg/L.	Highly saline groundwater.	Selected sample: #2931 (Category 3, 1999-08-10); 31,230 mg/L Cl.
S^{2-}	Below detection limit (0.010 mg/L) to 0.030 mg/L.	No systematic time change.	0.010 mg/L
Fe	0.200 to 2.110 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.200 mg/L
Mn	0.080 to 0.209 mg/L	No systematic time change.	0.080 mg/L
DOC	89.5 to 181.0 mg/L	DOC not considered representative. TOC not measured. No systematic time change.	98.0 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX02

CCC section: 1,385.00 to 1,392.00 m
Elevation sec mid:
–1,360.93 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 1999-12-06.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl is 36,970 mg/L.	Highly saline groundwater type.	Selected sample: #3038 (Category 4*, 1999-12-06); 35,970 mg/L Cl.
S^{2-}	0.046 mg/L		0.046 mg/L
Fe	22.00 (Fe(mg/L)) by ICP 3.438 (Fe(tot)) 3.453 (Fe(II))	Fe(tot) value selected for modelling purposes.	3.438 mg/L
Mn	1.110 mg/L		1.110 mg/L
DOC		DOC and TOC not analysed.	

***** see documentation in /Smellie and Tullborg 2009/.

KLX02

CCC section: 1,420.00 to 1,700.50 m
Elevation sec mid:
–1,530.98 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	4 samples.	Samples collected during 1 occasion: 1993-12-28 to 1994-01-17.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 42,200 to 45,500 mg/L.	Highly saline groundwater type.	Selected sample: #2731 (Category 3*, 1994-01-17); 45,500 mg/L Cl.
S^{2-}	All below detection limit (0.010 mg/L).		0.010 mg/L
Fe	0.401 to 0.405 mg/L Fe(ICP)	Stable values of Fe(ICP), Fe(tot) and Fe(II). **Note:** The last three samples (measured by ICP) were only considered because of their groundwater stability. No systematic time change.	0.405 mg/L
Mn	0.120 to 0.140 mg/L	Small systematic increase with time.	0.140 mg/L
DOC	1.4 to 0.9 mg/L	**Note:** DOC measured in the first and last sample. No TOC values. No systematic time change.	0.9 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX03

CCC section: 193.50 to 198.37 m
Elevation sec mid:
–170.82 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 1 occasion: 2004-11-29 to 2004-12-15.	Selected sample corresponds to the earlier CCC categorised groundwater. Sample represents the second last in the Category 1 time series to include a modelling value. **Note:** Gas analyses and microbe data imported from #7953.
Groundwater type.	Na(Ca)-HCO_3-Cl type. Cl varies from 259.0 to 279.0 mg/L.	Mixed brackish groundwater type.	Selected sample: #7952 (Category 1*, 2004-12-13), 260.0 mg/L Cl.
S^{2-}	Below detection limit (0.002 to 0.003 mg/L).	No systematic time change	0.003 mg/L
Fe	0.209 to 0.359 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.294 mg/L
Mn	0.062 to 0.065 mg/L	No systematic time change.	0.063 mg/L
DOC	19.0 to 22.0 mg/L	DOC measured for all samples; TOC from 4 samples. Good correlation between DOC and TOC. No systematic time change.	21.0 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX03

CCC section: 408.00 to 415.30 m
Elevation sec mid:
–379.85 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 1 occasion: 2005-02-21 to 2005-03-22.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na(Ca)-Cl(HCO_3, SO_4) type. Cl varies from 1,040 to 1,430 mg/L.	Brackish glacial groundwater type.	Selected sample #10091 (Category 3*, 2005-03-22), 1,390 mg/L Cl.
S^{2-}	0.003 to 0.010 mg/L	No systematic time change.	0.007 mg/L
Fe	0.355 to 1.030 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.408 mg/L
Mn	0.106 to 0.131 mg/L	No systematic time change.	0.107 mg/L
DOC	13.0 to 17.0 mg/L	DOC measured in all samples; TOC in 3 samples. DOC and TOC show good correlation. No systematic time change.	13.0 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX03

CCC section: 735.50 till 748.04 m (Overlap with Monitoring Section: 729.00 to 751.00 m)
Elevation sec mid:
–700.60 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 1 occasion: 2005-04-01 to 2005-04-25.	None selected because of Category 5 groundwater type.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 2,250 and 3,940 mg/L.	Not representative.	
S^{2-}	From below detection limit (0.002 mg/L) to 0.006 mg/L.	No systematic time change.	None selected.
Fe	0.839 to 1.800 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Generally slightly lower values using ICP. No systematic time change.	None selected.
Mn	0.257 to 0.345 mg/L	No systematic time change	None selected.
DOC	4.0 to 9.8 mg/L	DOC measured in all samples; TOC in 3 samples. DOC and TOC show good correlation. No systematic time change.	None selected.

KLX03

Monitoring section (tracer test): 735.50 to 748.04 m (Overlap with CCC section: 729.00 to 751.00 m).
Elevation sec mid:
–698.88 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	1 sample.	Sample collected from 2006-11-28.	None selected because of Category 5 groundwater type.
Groundwater type.	Na-Ca-Cl (HCO_3, SO_4) type. Cl is 1,660 mg/L.	Not representative.	
S^{2-}	1.560 mg/L		None selected.
Fe	0.094 mg/L Fe(ICP)	Relatively good correlation between Fe(ICP), Fe(tot) and Fe(II).	None selected.
Mn	0.227 mg/L		None selected.
DOC	11.0 mg/L	Good correlation between DOC and TOC.	None selected.

KLX03

CCC section: 964.50 to 975.15 m
Elevation sec mid:
–922.45 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	5 samples.	Samples collected during 1 occasion: 2005-01-25 to 2005-02-14.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Ca-Na-Cl (SO_4) type. Cl varies from 10,400 to 10,500 mg/L.	Saline groundwater type.	Selected sample #10076 (Category 1*, 2005-02-14), 10,500 mg/L Cl.
S^{2-}	0.048 to 0.090 mg/L	There is a systematic increase with time.	0.090 mg/L
Fe	All ICP samples are below detection limit at 0.004 mg/L.	One sample shows Fe(tot) and Fe(II) at 0.077 mg/L; the others are below detection limit. No systematic time change.	< 0.004 mg/L
Mn	From below detection limit up to 0.016 mg/L.	No systematic time change.	0.016 mg/L
DOC	1.4 to 2.1 mg/L	DOC measured for all samples; TOC for 2 samples. No systematic time change.	1.4 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX04

Sampled using Hydrotest Equipment: 104.00 to109.00 m
Elevation sec mid:
–81.90 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	1 sample.	Sample collected from 2004-09-30.	Only one sample but considered representative for the sample depth.
Groundwater type.	Na-(Ca)-HCO_3 type. Cl is 23.5 mg/L.	Fresh groundwater type.	Selected sample: #7856; (Category 4*, 2004-09-30); 23.5 mg/L Cl.
S^{2-}	0.010 mg/L		0.010 mg/L
Fe	0.158 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.158 mg/L
Mn	0.162 mg/L		0.162 mg/L
DOC	9.9 mg/L	TOC not analysed.	9.9 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX04

Sampling using hydrotest equipment: 510.56 to 515.56 m (Overlaps with Monitoring Section: 507.00 to 530.00 m).
Elevation sec mid:
–486.52 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2004-09-29.	Only one sample but considered representative for the sample depth.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl is 1,480 mg/L.	Brackish glacial groundwater type.	Selected sample: #7776; (Category 4*, 2004-09-29); 1,480 mg/L Cl.
S^{2-}	0.006 mg/L	Value close to detection limit.	0.006 mg/L
Fe	0.090 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.090 mg/L
Mn	0.109 mg/L		0.109 mg/L
DOC	2.2 mg/L	Good correlation with TOC.	2.2 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX04

Monitoring section: 507.00 to 530.00 m (Corresponds to Hydrotest section: 510.56 to 515.56 m).
Elevation sec mid:
–491.94 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 2 occasions: 2006-11-14, and 2008-03-06 to 2008-03-13 (6 samples). **Note:** First sampling occasion represents a tracer test.	The selected sample represents the final value taken from the last sampling series occasion which showed a systematic decrease with time.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 1,480 to 1,690 mg/L.	Brackish glacial groundwater type. Uncertain stability; lack of systematic data.	Selected sample: #15380; (2008-03-13); 1,690 mg/L Cl.
S^{2-}	0.038 to 5.43 mg/L	Shows a systematic decrease with time for 6 samples during the second sampling occasion.	0.038 mg/L
Fe	0.114 to 0.302 mg/L Fe(ICP)	ICP is only measured for the very first and last samples. For the remaining samples there is a good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.114 mg/L
Mn	0.196 to 0.355 mg/L	No systematic time change.	0.196 mg/L
DOC	2.1 to 4.7 mg/L	DOC and TOC show a good correlation for the second sampling series. No systematic time change.	2.1 mg/L

KLX04

Monitoring section: 870.00 to 897.00 m
Elevation sec mid:
–854.86 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	6 samples.	Samples collected during 1 occasion: 2008-03-17 to 2008-03-27.	Sample selected from the final sampling because of complete chemistry.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 3,470 to 3,790 mg/L.	Brackish glacial groundwater type. Uncertain stability; lack systematic of data.	Selected sample: #15421; (2008-03-27); 3,790 mg/L Cl.
S^{2-}	0.660 to 4.84 mg/L	Shows a decreasing trend with time.	0.742 mg/L
Fe	0.0430 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.0430 mg/L
Mn	0.090 mg/L		0.090 mg/L
DOC	1.7 to 3.8 mg/L	DOC and TOC analysed for 5 samples showing a good correlation. No systematic time change.	2.2 mg/L

KLX04

Sampling using hydrotest equipment: 971.21 to 976.21 m
Elevation sec mid:
–944.38 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2004-09-16.	Only one sample but considered representative for the sample depth.
Groundwater type.	Ca-Na-Cl(SO_4)type. Cl is 7,910 mg/L.	Brackish glacial groundwater type.	Selected sample: #7752; (Category 4*,2004-09-16); 7,910 mg/L Cl.
S^{2-}	0.022 mg/L		0.022 mg/L
Fe	0.155 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.155 mg/
Mn	0.074 mg/L		0.074 mg/L
DOC	Under detection (–1.0 mg/L).	Good correlation with TOC.	–1.0 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX05

Monitoring section: 241.00 to 255.00 m
Elevation sec mid:
–204.84 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	8 samples.	Samples collected during 3 occasions: 2006-10-24, 2007-08-14, and 2008-03-17 to 2008-03-20 (6 samples).	The selected sample represents the final value taken from the last sampling series occasion which showed a systematic decrease with time.
Groundwater type.	Na(Ca)-Cl(HCO_3, SO_4) type. Cl varies from 592 to 657 mg/L.	Mixed brackish groundwater type. Stable major ion chemistry.	Selected sample: #15450; (2008-03-20); 657 mg/L Cl.
S^{2-}	0.018 to 18.90 mg/L	Systematic decrease with time in the last sampling occasion.	0.018 mg/L
Fe	0.363 to 0.709 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). There is a weak decreasing trend with time during the last sampling occasion.	0.368 mg/L
Mn	0.063 to 0.101 mg/L	No systematic time change.	0.063 mg/L
DOC	6.0 to 7.6 mg/L	DOC and TOC show a good correlation. No systematic time change.	6.0 mg/L

Note: There is also a slight negative correlation with HCO_3 and SO_4 in each sampling series.

KLX06

Sampling using hydrotest equipment: 260.00 to 265.00 m (Corresponds to Monitoring Section: 256.00 to 275.00 m).
Elevation sec mid:
–218.51 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2005-03-09.	Only one sample but considered representative for the sample depth.
Groundwater type.	Na-HCO_3(Cl, SO_4) type. Cl is 36.8 mg/L.	Fresh groundwater type.	Selected sample: #10122; (Category 3*, 2005-03-09); 36.8 mg/L Cl.
S^{2-}	0.017 mg/L		0.017 mg/L
Fe	0.059 mg/L Fe(ICP)	Fe(II) is lower (0.031 mg/L) than Fe(ICP) and Fe(tot).	0.059 mg/L
Mn	0.012 mg/L		0.012 mg/L
DOC	No value for DOC.	TOC records 3.0 mg/L.	3.0 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX06

Monitoring section (tracer test): 256.00 to 275.00 m (Corresponds to Hydrotest Section: 260.00 to 265.00 m)
Elevation sec mid:
–221.18 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	2 samples.	Samples collected during 2 occasions: 2006-07-04 and 2006-10-24.	Both values are suitable; last sample selected.
Groundwater type.	Na-HCO_3-(Cl, SO_4) type. Cl varies from 57.7 to 58.7 mg/L.	Fresh groundwater type.	Selected sample: #11464 (Category 3*, 2006-10-24); 58.7 mg/L Cl.
S^{2-}	0.143 and 0.186 mg/L		0.186 mg/L
Fe	0.057 and 0.062 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.057 mg/L
Mn	0.012 and 0.015 mg/L		0.012 mg/L
DOC	3.3 and 3.5 mg/L	DOC and TOC show a good correlation.	3.5 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX06

Monitoring section: 554.00 to 570.00 m (Note: Sulphide Project; /Rosdahl et al. 2010/.)
Elevation sec mid:
–475.27 masl

	Groundwater chemistry	**Comment**	**Selected sample/value**
Number of samples.	22 samples.	Samples collected during 4 occasions: 2006-07-04, 2006-10-24, 2009-02-09 to 2009-02-23 (14 samples), and 2009-05-05 to 2009-05-07 (6 samples).	Final sample selected from the first sampling time series because of: a) complete chemical data, and b) clear levelling out of the sulphide values.
Groundwater type.	Na-Ca-Cl-SO_4 type. Cl varies from 58.3 to 1,480 mg/L. (**Note**: low initial value reflects inadequate removal of non-representative water volumes).	Brackish glacial groundwater type. The two time-series sampling occasions approach similar values when terminated, but this is no guarantee that they are representative.	Selected sample: #14726 (2009-02-23); 1,430 mg/L Cl.
S^{2-}	0.080 to 9.18 mg/L	A decreasing trend with time is observed in both of the time-series sampling occasions.	0.082 mg/L
Fe	From below detection (0.020 mg/L) to 0.2450 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). An increasing trend with time is observed in both of the time-series sampling occasions.	0.239 mg/L
Mn	0.065 to 0.163 mg/L	Weak increase correlating with Fe.	0.144 mg/L
DOC	2.0 to 22.9 mg/L (**Note:** the highest values from 22.8 to 367 mg/L have been omitted as they indicate contamination from tubing).	Good correlation between TOC and DOC. Systematic decrease with time.	2.0 mg/L

KLX07A

Monitoring section (tracer test): 753.00 to 780.00 m
Elevation sec mid:
–569.69 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	9 samples.	Samples collected during 3 occasions: 2006-06-20, 2007-06-13 to 2007-06-27 (2 samples), and 2008-03-13 to 2008-03-25 (6 samples). **Note:** First two sampling occasions represent tracer tests.	The selected sample represents the final value taken from the last sampling series occasion which showed a systematic decrease with time.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 318 to 2,930 mg/L.	Brackish non-marine transition groundwater type. Unstable major ion chemistry with possible short-circuiting.	Selected sample: #15415 (2008-03-25); 2,930 mg/L Cl.
S^{2-}	0.032 to 2.02 mg/L	Systematic decreasing trend in the final sampling occasion.	0.032 mg/L
Fe	0.359 to 0.535 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Weak increasing trend (Spectrophotometry values) with time in the final sampling occasion.	0.359 mg/L
Mn	0.230 to 0.411 mg/L	No systematic time change.	0.411 mg/L
DOC	1.6 to 3.6 mg/L	Good correlation between TOC and DOC. No systematic time change.	2.0 mg/L

KLX08

CCC section: 197.00 to 206.65 m
Elevation sec mid:
–150.43 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	6 samples.	Samples collected during 1 occasion: 2005-12-01 to 2005-12-19.	One sample from this Category 5 series has been selected (final value) because of: a) complete chemical data, and b) support from later monitoring data from surrounding boreholes.
Groundwater type.	Na(Ca)-HCO_3 type. Cl varies from 12.5 to 12.8 mg/L.	Fresh groundwater type.	Selected sample: #10649 (Category 5, 2005-12-19); 12.6 mg/L Cl.
S^{2-}	Under detection limit; 0.002 to 0.004 mg/L.	No systematic time change.	0.004 mg/L
Fe	0.104 to o.248 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Systematic decrease with time.	0.104 mg/L
Mn	0.085 to 0.102 mg/L	A decreasing time trend can be observed.	0.085 mg/L
DOC	7.5 to 7.9 mg/L	TOC is analysed for every other sample. Good correlation between TOC and DOC. No systematic time change.	7.7 mg/L

KLX08

CCC section: 396.00 to 400.87 m
Elevation sec mid:
–320.03 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	8 samples.	Samples collected during 1 occasion: 2006-02-07 to 2006-03-06.	None selected because of Category 5 groundwater type.
Groundwater type.	Na(Ca)-HCO_3 type. Cl varies from 14.3 to 15.6 mg/L.	This groundwater is identical to the preceding section and is considered non-representative.	
S^{2-}	From below detection limit (0.002 mg/L) to 0.053 mg/L.	No systematic time change.	None selected.
Fe	0.0267 to 1.03 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	None selected.
Mn	0.023 to 0.070 mg/L	No systematic time change.	None selected.
DOC		DOC and TOC not analysed.	None selected.

KLX08

CCC section: 476.00 to 485.65 m and 476.00 to 485.62 m
Elevation sec mid:
–390.73 and –390.71 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	14 samples.	Samples collected during 2 occasions: 2006-01-10 to 2006-01-12 (2 samples), and 2006-05-22 to 2006-06-26 (12 samples). The first sampling occasion is not considered because of high drilling water content.	Selected sample corresponds to the earlier CCC categorised groundwater from the second sampling occasion. To ensure a sulphide value, an alternative sample from the same sample series was selected. **Note:** Gas analyses and microbe data imported from #11183
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 1,480 to 1,600 mg/L.	Brackish glacial groundwater type.	Selected sample: #11143 (Category 2*, 2006-06-12); 1,560 mg/L Cl.
S^{2-}	From under detection limit (0.02 mg/L) to 0.011 mg/L.	No systematic time change.	0.004 mg/L
Fe	0.220 to 0.853 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II. No systematic time change.	0.265 mg/L
Mn	0.064 to 0.105 mg/L (**Note:** first two values were omitted because of excess drilling water and therefore not representative).	No systematic time change.	0.089 mg/L
DOC	2.5 to 6.4 mg/L	DOC values for all samples; TOC from every other sample. Good correlation between TOC and DOC. No systematic time change.	2.9 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX08

CCC section: 609.00 to 618.51 m (Corresponds to Monitoring Section: 594.00 to 625.00 m)
Elevation sec mid:
–504.54 masl.

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	8 samples.	Samples collected during 1 occasion: 2006-07-03 to 2006-07-26.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 2,010 to 2,030 mg/L.	Brackish glacial groundwater type.	Selected sample: #11228 (Category 3*, 2006-07-26); 2,030 mg/L Cl.
S^{2-}	0.003 to 0.010 mg/L	No systematic time change.	0.010 mg/L
Fe	0.006 to 0.251 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.020 mg/L
Mn	0.079 to 0.095 mg/L	No systematic time change.	0.089 mg/L
DOC	1.7 to 1.9 mg/L	DOC and TOC when measured together show a good correlation. No systematic time change.	1.8 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX08

Monitoring section: 594.00 to 625.00 m (Corresponds to the CCC section: 609.00 to 618.51 m)
Elevation sec mid:
–500.90 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	27 samples.	Samples collected during 5 occasions: 2007-11-12, 2008-03-11 to 2008-03-18 (6 samples), 2008-10-27 to 2008-11-03 (6 samples), 2009-05-12 to 2009-05-19 (7 samples), and 2009-10-27 to 2009-11-03 (7 samples).	Sampling shows a similar repetitive pattern during the four sampling series. The final sample of the last occasion was chosen as being generally suitable.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 1,900 to 2,060 mg/L.	Brackish glacial groundwater type. Stable groundwater chemistry.	Selected sample: #19160 (2009-11-03); 1,980 mg/L Cl.
S^{2-}	0.043 to 30.40 mg/L	All the sampled series show a clear systematic decrease with time.	0.055 mg/L
Fe	Less than detection limit (0.02 mg/L) to 0.102 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). There is an increasing trend with time.	0.070 mg/L
Mn	0.054 to 0.097 mg/L	No systematic time change.	0.089 mg/L
DOC	1.7 to 8.1 mg/L	DOC and TOC show a good correlation. There is a decreasing trend with time.	2.2 mg/L

KLX08

Monitoring section: 626.00 to 683.00 m
Elevation sec mid:
–539.39 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	8 samples.	Samples collected during 3 occasions: 2007-08-15, 2007-11-05, and 2008-03-11 to 2008-03-19 (6 samples).	The selected sample represents the final value taken from the last sampling series occasion, which showed a complete chemistry and a systematic decrease with time.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 2,200 to 2,290 mg/L.	Brackish glacial groundwater type. Stable major ion chemistry.	Selected sample: #15397 (2008-03-19); 2,250 mg/L Cl.
S^{2-}	0.074 to 22.6 mg/L	Systematic decrease with time.	0.074 mg/L
Fe	0.075 to 0.137 mg/L Fe(ICP)	Good correlation, when measured, between Fe(ICP), Fe(tot) and Fe(II). Systematic decrease with time.	0.075 mg/L
Mn	0.080 to 0.099 mg/L	No systematic time change.	0.080 mg/L
DOC	1.6 to 2.8 mg/L	DOC and TOC show a good correlation. No systematic time change.	1.6 mg/L

KLX10

Monitoring section (tracer test): 351.00 to 368.00 m
Elevation sec mid:
–338.43 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	27 samples.	Samples collected during 5 occasions: 2007-06-28, 2008-03-19 to 2009-03-26 (6 samples), 2008-10-20 to 2008-10-28 (6 samples), 2009-05-11 to 2009-05-20 (7 samples), and 2009-10-20 to 2009-10-27 (7 samples). **Note:** First sampling occasion represents a tracer test.	Sampling shows a similar repetitive pattern during the four sampling series. The final sample selected from the last occasion was chosen therefore as it showed the same complete chemistry and systematic decrease with time.
Groundwater type.	Na(Ca)-Cl(SO_4,HCO_3), type. Cl varies from 1,090 to 2,210 mg/L.	Transition groundwater type. Final major ion values are stable within each sampling occasion.	Selected sample: #19131 (2009-10-27); 2,190 mg/L Cl.
S^{2-}	0.188 to 32.2 mg/L	Shows a systematic decrease with time in each sampling series.	0.286 mg/L
Fe	0.043 to 0.214 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Shows a systematic increase with time in each sampling series.	0.187 mg/L
Mn	0.196 to 0.264 mg/L	No systematic time change	0.257 mg/L
DOC	2.5 to 6.4 mg/L	DOC and TOC show a good correlation. Decreasing trend with time in each sampling series.	2.7 mg/L

KLX10

Monitoring section: 689.00 to 710.00 m
Elevation sec mid:
–676.19 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	26 samples.	Samples collected during 4 occasions: 2008-03-12 to 2008-03-26 (6 samples), 2008-10-21 to 2008-10-30 (6 samples), 2009-05-11 to 2009-05-26 (7 samples), and 2009-10-20 to 2009-10-27 (7 samples).	Sampling shows a similar repetitive pattern during the four sampling series. The final sample selected from the last occasion was considered suitable as it showed the same complete chemistry and systematic decrease with time.
Groundwater type.	Na-Ca-Cl(SO_4) type. Cl varies from 3,160 to 3,750 mg/L.	Transition groundwater type. Final major ion values are relatively stable within each sampling occasion.	Selected sample: #19153 (2009-10-27); 3,550 mg/L Cl.
S^{2-}	0.369 to 58.8 mg/L	Shows a general decreasing trend in each time series.	1.12 mg/L
Fe	0.022 to 0.062 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Shows a general increasing trend in each time series.	0.051 mg/L
Mn	0.183 to 0.234 mg/L	No systematic time change.	0.227 mg/L
DOC	1.0 to 3.2 mg/L	DOC and TOC show a good correlation. No systematic time change.	2.0 mg/L

KLX11A

Monitoring section (tracer test): 516.50 to 519.50 m
Elevation sec mid:
–465.97 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2007-07-24.	None selected because it was not considered representative.
Groundwater type.	Na(Ca)-HCO_3(Cl) type. Cl is 105 mg/L.	Shallow fresh groundwater type. Unstable.	
S^{2-}	1.46 mg/L		None selected.
Fe	0.66 mg/L Fe(ICP)	Fe(tot) and Fe(II) have a good correlation with Fe (ICP).	None selected.
Mn	0.102 mg/L		None selected.
DOC	9.6 mg/L	DOC and TOC show a good correlation.	None selected.

KLX11A

Monitoring section (tracer test): 579.00 to 584.00 m
Elevation sec mid:
–526.01 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2007-04-02.	None selected because it was not considered representative.
Groundwater type.	Na(Ca)-HCO_3(Cl) type. Cl is 35.1 mg/L.	Shallow fresh groundwater type. Unstable.	
S^{2-}	0.511 mg/L		None selected.
Fe	0.198 mg/L Fe(ICP)	Fe(tot) and Fe(II) show slightly higher values than the Fe(ICP).	None selected.
Mn	1.56 mg/L		None selected.
DOC	7.5 mg/L	DOC and TOC show a good correlation.	None selected.

KLX11A

Monitoring section (tracer test): 598.00 to 599.00 m
Elevation sec mid:
–542.07 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2007-06-13.	Only one sample but considered representative for the sample depth in the central and western parts of the Laxemar area.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl is 1,040 mg/L.	Brackish glacial groundwater type. Unclear stability.	Selected sample: #11921 (2007-06-13); 1,040 mg/L Cl.
S^{2-}	0.403 mg/L		0.403 mg/L
Fe	0.023 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II).	0.023 mg/L
Mn	0.019 mg/L		0.019 mg/L
DOC	2.3 mg/L	DOC and TOC show a good correlation.	2.3 mg/L

KLX12A

Monitoring section: 535.00 to 545.00 m
Elevation sec mid:
–501.12 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	26 samples.	Samples collected during 5 occasions: 2006-11-14, 2008-03-17 to 2008-03-27 (5 samples), 2008-10-21 to 2008-10-29 (6 samples), 2009-05-06 to 2009-05-14 (7 samples), and 2009-10-21 to 2009-11-02 (7 samples).	Sampling shows a similar repetitive pattern during the four sampling series with a similar complete chemistry and systematic decrease with time. The sample selected was from the fourth occasion because of a more stable major chemistry.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 2,220 to 4,230 mg/L.	Brackish non-marine groundwater type. Final major ion values are stable within each time series sampling occasion.	Selected sample: #15895 (2009-05-14); 4,210 mg/L Cl.
S^{2-}	0.403 to 51.0 mg/L	Shows a systematic decrease with time in each sampling series.	0.649 mg/L
Fe	Below detection limit (0.020 mg/L) to 0.172 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Shows an increasing trend with time in each sampling series.	0.034 mg/L
Mn	0.137 to 0.193 mg/L.	No systematic changes with time.	0.177 mg/L
DOC	2.0 to 6.6 mg/L	DOC and TOC show a good correlation. Shows a decreasing trend with time in each sampling series.	2.0 mg/L

Note: There is also a negative correlation with HCO_3 and SO_4 in each sampling series.

KLX13A

CCC section: 432.0 to 439.16 m
Elevation sec mid:
–480.01 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	7 samples.	Samples collected during 1 occasion: 2006-12-18 to 2007-01-21.	Selected sample corresponds to the earlier CCC categorised groundwater. **Note:** Gas analyses and microbe data imported from #11609.
Groundwater type.	Na(Ca)-Cl(HCO_3) type. Cl varies from 728 to 762 mg/L.	Very dilute glacial groundwater type.	Selected sample: #11607 (Category 3*, 2007-01-11); 744 mg/L Cl.
S^{2-}	From detection limit (0.006 mg/L) up to 0.004 mg/L.	No systematic time change.	0.004 mg/L
Fe	0.0017 to 0.383 mg/L Fe(ICP)	Values are generally very low and close to detection. No systematic time change.	0.0024 mg/L
Mn	0.027 to 0.035 mg/L	No systematic time change.	0.027 mg/L
DOC	2.6 to 4.0 mg/L	Good correlation between DOC and TOC when measured. No systematic time change.	2.7 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX13A

CCC section: 499.50 to 506.66 m
Elevation sec mid:
–474.99 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	4 samples.	Samples collected during 1 occasion: 2006-11-23 to 2006-12-11.	Selected sample corresponds to the earlier CCC categorised groundwater. To ensure a sulphide value, an alternative sample from the same sample series was selected.
Groundwater type.	Na(Ca)-Cl(HC0$_3$) type. Cl varies from 678 to 769 mg/L.	Very dilute brackish glacial groundwater type.	Selected sample: #11542; (Category 4*, 2006-11-30); 769 mg/L Cl.
S^{2-}	From below detection limit (0.006 mg/L) to 0.004 mg/L.	No systematic time change.	<0.003 mg/L.
Fe	0.030 to 1.520 mg/L Fe(ICP)	Good correlation between Fe (ICP), Fe(tot) and Fe(II). Shows decreasing trend with time.	0.223 mg/L
Mn	0.052 to 0.182 mg/L	Weak systematic decrease trend with time.	0.061 mg/L
DOC	2.6 to 4.1 mg/L	No TOC measurements. No systematic time change.	2.5 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX15A

Monitoring section: 260.00 to 272.00 m
Elevation sec mid:
–192.74 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	26 samples.	Samples collected during 4 occasions: 2008-02-27 to 2008-03-05 (6 samples), 2008-10-15 to 2008-10-27 (6 samples), 2009-05-07 to 2009-05-14 (7 samples), and 2009-10-15 to 2009-10-22 (7 samples).	Sampling shows a similar repetitive pattern during the four sampling series with a similar complete chemistry and systematic decrease with time. The sample selected was from the last occasion because of a more stable major chemistry.
Groundwater type.	Na-Ca(Mg)-Cl(SO$_4$, HCO$_3$) type. Cl varies from 2,580 to 3,270 mg/L.	Transition groundwater type. Final major ion values are relatively stable within each time series sampling occasion.	Selected sample: #19098; (2009-10-22) 3,270 mg/L Cl.
S^{2-}	From below detection limit (0.006 mg/L) to 6.18 mg/L.	Shows a systematic decrease in each sampling series.	0.029 mg/L
Fe	0.200 to 1.050 mg/L Fe(ICP)	Good correlation between Fe (ICP), Fe(tot) and Fe(II) when measured. Shows a decreasing trend with time in each sampling series.	0.534 mg/L
Mn	0.469 to 0.611 mg/L	No systematic time change.	0.611 mg/L
DOC	1.7 to 3.5 mg/L	Good correlation between DOC and TOC. Weak decrease in each sampling series.	1.9 mg/L

Note: There is also a negative trend with bicarbonate in each sampling series.

KLX15A

CCC section: 623.0 to 634.51 m (Correlates with Monitoring Section 623.00 to 640.00 m)
Elevation sec mid:
–467.22 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	10 samples.	Samples collected during 2 occasions: 2007-06-28 to 2007-08-06.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na-$Ca(Mg)$-$Cl(SO_4)$ type. Cl varies from 5,670 to 5,920 mg/L.	Transition groundwater type.	Selected sample: #15008; (2009-10-22, Category 2*) 5,890 mg/L Cl.
S^{2-}	From below detection limit (0.006 mg/L) to 0.027 mg/L.	No systematic time change.	0.007 mg/L
Fe	0.288 to 0.721 mg/L Fe(ICP)	Good correlation between Fe (ICP), Fe(tot) and Fe(II). No systematic time change.	0.537 mg/L
Mn	0.509 to 0.553 mg/L	No systematic time change.	0.549 mg/L
DOC	1.4 to 1.5 mg/L.	Good correlation between DOC and TOC when measured. No systematic time change.	1.5 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX15A

Monitoring section: 623.00 to 640.00 m (Correlates with CCC section: 623.00 to 634.51 m).
Elevation sec mid:
–469.27 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	31 samples.	Samples collected during 5 occasions: 2007-12-04 to 2007-12-12 (5 samples), 2008-02-26 to 2008-03-10 (6 samples), 2008-10-15 to 2008-10-28 (6 samples), 2009-05-07 to 2009-05-19 (7 samples), and 2009-10-09 to 2009-10-27 (7 samples). Final major ion values are relatively stable within each time series sampling occasion.	Slightly lower salinity than the CCC samples. This section also showed some instability during the CCC sampling. Sampling shows a similar repetitive pattern during the five sampling series with a similar complete chemistry for the last sample in each series, and a systematic decrease with time within each series. Selected is the final sample from the second occasion because of the similarity to the CCC sample with higher salinity and slightly more depleted O-18.
Groundwater type.	Na-$Ca(Mg)$-$Cl(SO_4)$ type. Cl varies from 3,670 to 5,690 mg/L.	Transition groundwater type. Final sample in each sampling series indicates major chemistry stability.	Selected sample: #15355 (2008-03-10); 5.690 mg/L Cl.
S^{2-}	0.093 to 55.4 mg/L	Shows a systematic decrease in each sampling series, and coming close to the same values.	0.133 mg/L
Fe	0.099 to 0.383 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.286 mg/L
Mn	0.487 to 0.559 mg/L	No systematic time change.	0.522 mg/L
DOC	1.0 to 62.0 mg/L.	Good correlation between DOC and TOC when measured. Significant higher values during the first sampling occasion. Significant increase with time in the first and second sampling occasions; otherwise only a weak decreasing trend.	1.6 mg/L

KLX17A

CCC Section: 416.00 to 437.51 m
Elevation sec mid:
–342.32 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	11 samples.	Samples collected during 1 occasion: 2007-03-12 to 2007-04 23.	Selected sample corresponds to the earlier CCC categorised groundwater. **Note:** Gas analyses and microbe data imported from #11810.
Groundwater type.	Na(Ca)-Cl(HCO_3) type. Cl varies from 254 to 591 mg/L.	Very dilute brackish glacial groundwater type.	Selected sample: #11809 (Category 3*, 2007-04-12); 565 mg/L Cl.
S^{2-}	0.016 to 0.042 mg/L	No systematic time change.	0.028 mg/L
Fe	0.791 to 2.36 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.791 mg/L
Mn	0.082 to 0.119 mg/L	No systematic time change.	0.099 mg/L
DOC	3.3 to 17.0 mg/L	Good correlation between DOC and TOC when measured. No systematic time change.	3.4 mg/L

* see documentation in /Smellie and Tullborg 2009/.

KLX17A

CCC Section: 642.00 to 701.08 m
Elevation sec mid:
–547.97 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	8 samples.	Samples collected during 1 occasion: 2007-02-01 to 2007-02 28.	None selected because of Category 5 groundwater type.
Groundwater type.	Na-HCO_3 type. Cl varies from 17.1 to 340 mg/L.	Fresh to dilute brackish groundwater type.	None selected.
S^{2-}	At or below detection limit (0.006 mg/L).	No systematic time change.	None selected.
Fe	0.324 to 2.370 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	None selected.
Mn	0.012 to 0.054 mg/L	No systematic time change.	None selected.
DOC	4.1 to 7.6 mg/L	Good correlation between DOC and TOC when measured. No systematic time change.	None selected.

* see documentation in /Smellie and Tullborg 2009/.

KLX18A

Monitoring Section (tracer test): 472.00 to 489.00 m
Elevation sec mid:
–452.87 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	29 samples.	Samples collected during 6 occasions: 2007-07-03, 2007-11-07, 2008-02-27 to 2008-03-05 (6 samples), 2008-10-22 to 2008-10-29 (6 samples), 2009-05-06 to 2009-05-13 (8 samples), and 2009-10-21 to 2009-10-28 (7 samples). **Note:** First sampling occasion represents a tracer test.	Sampling shows a similar repetitive pattern during the six sampling series with a similar complete chemistry and systematic decrease with time. Simply, the final sample from the last occasion was selected.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 1,480 to 1,730 mg/L.	Brackish glacial groundwater type. Stable major ion chemistry.	Selected sample: #19167 (2009-10-28); 1,720 mg/L.
S^{2-}	0.0167 to 25.4 mg/L	Shows a systematic decrease in the third and fourth sampling series, but final values in the last two occasions show a small increase.	0.884 mg/L
Fe	From below detection limit (0.02 mg/L) to 0.061 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.046 mg/L
Mn	0.077 to 0.096 mg/L	No systematic time change.	0.087 mg/L
DOC	2.9 to 8.0 mg/L	Good correlation between DOC and TOC when measured. Tendency to decrease slightly in each time series.	3.7 mg/L

Note: There is an increase of SO_4 and decrease of HCO_3 in each sampling series.

KLX19A

Sampling using hydrotest equipment: 499.00 to 519.00 m (Corresponds to Monitoring section: 509.00 to 517.00 m)
Elevation sec mid:
–410.52 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2007-01-08.	One sample but considered representative for the sampling depth.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl is 1,780 mg/L.	Brackish glacial groundwater type.	Selected sample: #11604 (Category 3* 2007-01-08); 1,780 mg/L.
S^{2-}	0.003 mg/L	No systematic time change.	0.003 mg/L
Fe	0.063 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.063 mg/L
Mn	0.071 mg/L	No systematic time change.	0.071 mg/L
DOC	1.5 mg/L	Good correlation between DOC and TOC. No systematic time change.	1.5 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX19A

Monitoring Section: 509.00 to 517.00 m (Corresponding to Hydrotest Section: 499.00 to 519.00 m)
Elevation sec mid:
–413.86 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	31 samples.	Samples collected during 7 occasions: 2007-06-13, 2007-08-21, 2007-12-03 to 2007-12-11 (5 samples), 2008-02-26 to 2008-03-04 (6 samples), 2008-10-14 to 2008-10-22 (6 samples), 2009-06-15 to 2009-06-24 (6 samples), and 2009-10-14 to 2009-10-21 (7 samples).	Sampling shows a similar repetitive pattern during the seven sampling series with a similar complete chemistry for the last sample in each series, and a systematic decrease with time within each series. Selected is the final sample from the third occasion because of a more stable groundwater chemistry (e.g. when considering Cl and O-18).
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 1,690 to 2,020 mg/L.	Brackish glacial groundwater type. Largely stable major chemistry.	Selected sample: #15699 (2008-10-22); 1,930 mg/L.
S^{2-}	0.022 to 19.0 mg/L	Shows a systematic decrease in each sampling series.	0.025 mg/L
Fe	0.049 to 0.140 mg/L Fe(ICP)	Good correlation between Fe(ICP), Fe(tot) and Fe(II). Systematic decrease in the fourth sampling series; otherwise only a weak decreasing trend.	0.049 mg/L
Mn	0.059 to 0.125 mg/L	Weak decreasing trend with time.	0.066 mg/L
DOC	1.2 to 4.5 mg/L	Good correlation between DOC and TOC when measured. Tendency to decrease slightly in each sampling series.	1.5 mg/L

Note: There is sometimes an increase of SO_4 and always a decrease of HCO_3 in each sampling series.

KLX19A

Sampling using hydrotest equipment: 764.00 to 769.00 m
Elevation sec mid:
–624.78 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	1 sample.	Sample collected from 2006-12-05.	Considered representative for this depth.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl is 3,520 mg/L.	Brackish non-marine groundwater type.	Selected sample: #11569 (Category 4*, 2006-12-05); 3,520 mg/L.
S^{2-}	0.003 mg/L	No systematic time change.	0.003 mg/L
Fe	0.146 mg/L Fe(ICP)	Approximate correlation between Fe(ICP), Fe(tot) and Fe(II). No systematic time change.	0.146 mg/L
Mn	0.036 mg/L	No systematic time change.	0.036 mg/L
DOC	3.1 mg/L	Good correlation between DOC and TOC. No systematic time change.	3.1 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

KLX20A

Monitoring Section: 260.00 to 293.00 m
Elevation sec mid:
–183.32 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	6 samples.	Samples collected during 1 occasion: 2008-03-19 to 2008-03-26.	The selected sample represents the final value taken from the sampling series which showed a systematic decrease with time.
Groundwater type.	Na-Cl(HCO_3, SO4) type. Cl varies from 484 to 616 mg/L.	Brackish glacial groundwater type. Slightly unstable major ion chemistry; some variation during sampling.	Selected sample: #15477 (2008-03-26); 614 mg/L.
S^{2-}	0.030 to 2.400 mg/L	Shows a systematic decrease in the sample series.	0.030 mg/L
Fe	0.040 mg/L (ICP) 0.035 to 0.128 mg/L Fe(tot)	Good correlation between Fe(ICP), Fe(tot) and Fe(II) when measured. Values show a decrease in the sample series.	0.046 mg/L (**Note:** Spectrophotometry values).
Mn	0.019 mg/L		0.019 mg/L
DOC	3.5 to 4.6 mg/L	Good correlation between DOC and TOC. No systematic time change.	3.5 mg/L

Note: There is an increase of Cl and SO_4 and a decrease of HCO_3 in the sampling series.

KLX27A

CCC Section: 641.50 to 650.56 m
Elevation sec mid:
–562.96 masl

	Groundwater chemistry	Comment	Selected sample/value
Number of samples.	17 samples.	Samples collected during 1 occasion: 2008-03-18 to 2008-06-05.	Selected sample corresponds to the earlier CCC categorised groundwater.
Groundwater type.	Na(Ca)-Cl(SO_4) type. Cl varies from 1,670 to 1,710 mg/L.	Dilute brackish glacial groundwater type.	Selected sample: #15587 (Category 1*, 2008-06-05); 1,700 mg/L Cl.
S^{2-}	From under detection (0.006 mg/L) to 0.016 mg/L.	No systematic time change.	<0.006 mg/L
Fe	From under detection (0.006 mg/L) to 0.037 mg/L. (Spectrophotometry values).	No systematic time change. Fe(ICP) only measured for the first eight samples in the time series. All values are close to detection limit.	0.007 mg/L (**Note:** Spectrophotometry value).
Mn	0.011 to 0.013 mg/L	No systematic time change.	0.013 mg/L
DOC	1.0 to 1.4 mg/L	Good correlation between DOC and TOC when measured. No systematic time change.	1.4 mg/L

***** see documentation in /Smellie and Tullborg 2009/.

Appendix 2

A number of diagrams have been produced to visualise the sensitive changes in chemistry that occurred during sampling of the groundwater time series data. The parameters that have been plotted against time (i.e. sampling date) for each of the selected borehole sections sampled include chemical data, isotopic data and modelling results and they are: Cl (mg/L), Mg (mg/L), SO_4 (mg/L), S^{2-}(mg/L), Fe(II) (mg/L), FeS(amorphous) Saturation Index, $\delta^{34}S$ (‰ CDT), HCO_3 (mg/L), Mn (mg/L), Calcite Saturation Index, and DOC (mg/L).

These data correspond to the excel table *Laxemar_AllGW_SecondVersion_20101227.xlsx*, where only the data analysed for sulphide have been extracted from Sicada.

Therefore, only the samples in which sulphide has been analysed are shown in the plots (even if some of the values are below detection limit). The rest of the sections have not been included (indicated in the list below) and there is only a mention when the amount of data is scarce.

Samples are shown with different colours and symbols depending on the sampling procedure:

CCC (Complete Chemical Characterisation; SDM)	Red circles
Hydrotest Equipment	Lilac circles
Monitoring series	Blue circles
Tube volume	*Open triangle + enclosed 'X'*
Tube + 1st section volume of removed water	*Open triangle*

Selected samples for any of the previous groups are plotted as solid symbols with the corresponding colour. The remaining sample series are indicated by a light grey colour.

The plots show the evolution of different parameters (when available) subdivided as follows:

- Cl, SO_4^{2-}, Mg, Mn, HCO_3^-, DOC
- S(-II), Fe(II) and $\delta^{34}S$, and the FeS(am) and calcite saturation indices.

Borehole sections plotted in this Appendix are:

- KLX01: -257.06, -440.73, -672.95, -817.2, -897.09 and -1,019.91 masl
- KLX03: -379.85, -700.6 and -922.45 masl
- KLX04: -491.94 and -854.86 masl
- KLX05: -204.84 masl
- KLX06: -218.51 and -475.27 masl
- KLX07: -569.69 masl
- KLX08: -150.43, -320.03, -390.71, -500.9, -504.54 and -539.39 masl
- KLX10: -338.43 and -676.19 masl
- KLX12: -501.12 masl
- KLX13: -408.01 and -474.99 masl
- KLX15: -192.74 and-467.22 masl
- KLX17: -342.32 and -547.97 masl
- KLX19: -413.86 masl
- KLX20: -183.32 masl
- KLX27: -562.96 masl

Note: The given elevation values correspond to the centres of the borehole sections.

Excluded are the following borehole sections:

- KLX01 (-163.26 masl): Only one value for sulphide at 0.053 mg/L
- KLX03 (-170.82 masl): Seven values for sulphide all record -0.002 mg/L except for the second last one which records 0.003 mg/L
- KLX04 (-81.9 masl): Only one value for sulphide at 0.01 mg/L
- KLX04 (-922.45 masl): Only one value for sulphide at 0.022 mg/L
- KLX11 (-465.97 masl): Only one value for sulphide at 1.46 mg/L
- KLX11 (-526.01 masl): Only one value for sulphide at 0.511 mg/L
- KLX11 (-542.07 masl): Only one value for sulphide at 0.403 mg/L
- KLX19 (-624.78 masl): Only one value for sulphide at 0.003 mg/L

Additional comments

For each borehole section the pH and Eh values are indicated. In some cases the pH corresponds to 'Chemmac measurements', but in other cases it has been measured at the surface in the field (indicated as 'Field/surface measurement') or in the laboratory ('Laboratory measurements'). The Eh values are presented either as direct *in situ* downhole measurements ('Chemmac measurements') or they have been calculated using the redox pair S(-II)/S(VI) ('Calculated using the S(-II)/S(VI) redox couple').

Estimates based on plug flow calculations of the number of borehole section volumes of water needed to be removed in order to obtain 100% formation groundwater have been carried out /Tullborg et al. 2010/. In Figure A-1, the ratio between the calculated volumes and the actual pumped volumes are plotted versus the sulphide content in the sample.

Large volumes have been pumped (370 to 8,000 litres). In Figure A-1 it is shown that the highest sulphide values are measured in some of the samples where the pumped volumes are in the order of 2-14 times the estimated volume needed to be removed. It is suspected that in these borehole sections the hydrogeological situation may be more complex than indicated by the differential flow log data and thus not reflected in the plug flow calculations, and therefore the volumes pumped are still too low to give representative sulphide values. Another possibility is that the measured sulphide values reflect natural variations. Additional *in situ* tests over longer periods of time with tighter sampling protocols are required to help resolve these issues.

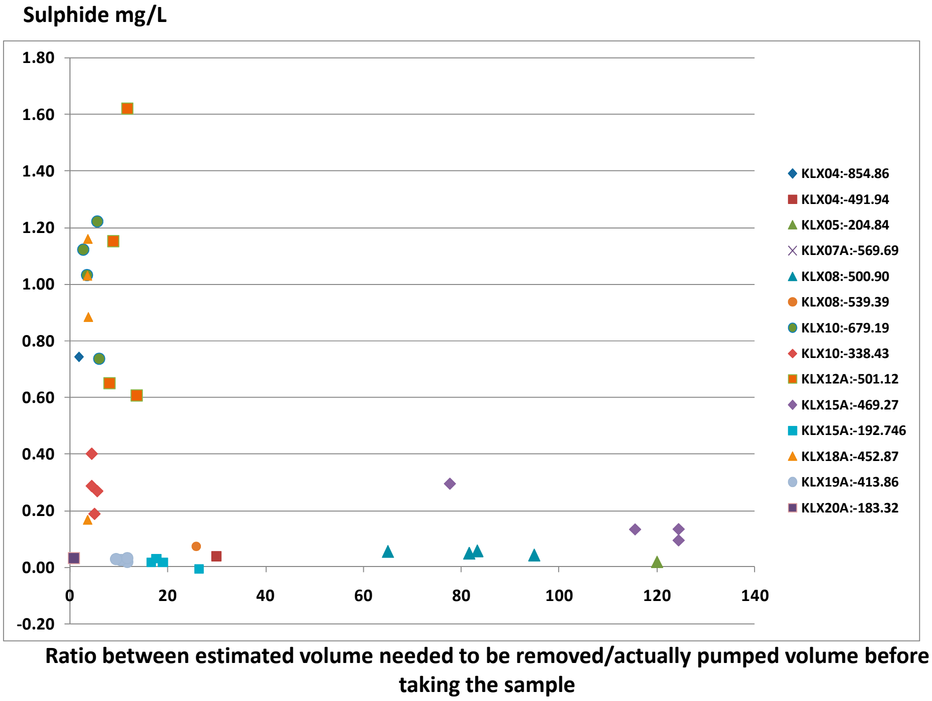

Figure A-1*: Dissolved sulphide in cored borehole sections from Laxemar plotted versus the ratio between the estimated volume of borehole section water needed to be removed before obtaining 100% formation groundwater, and the actual pumped volume removed. The data represent the monitoring sampling during Spring and Autumn 2008 and 2009. The final sample in each time series is shown in the plot.*

BOREHOLE KLX01 (-257.06 masl)

Eh ≈ -230 mV (Calculated using the S(-II)/S(VI) redox couple)

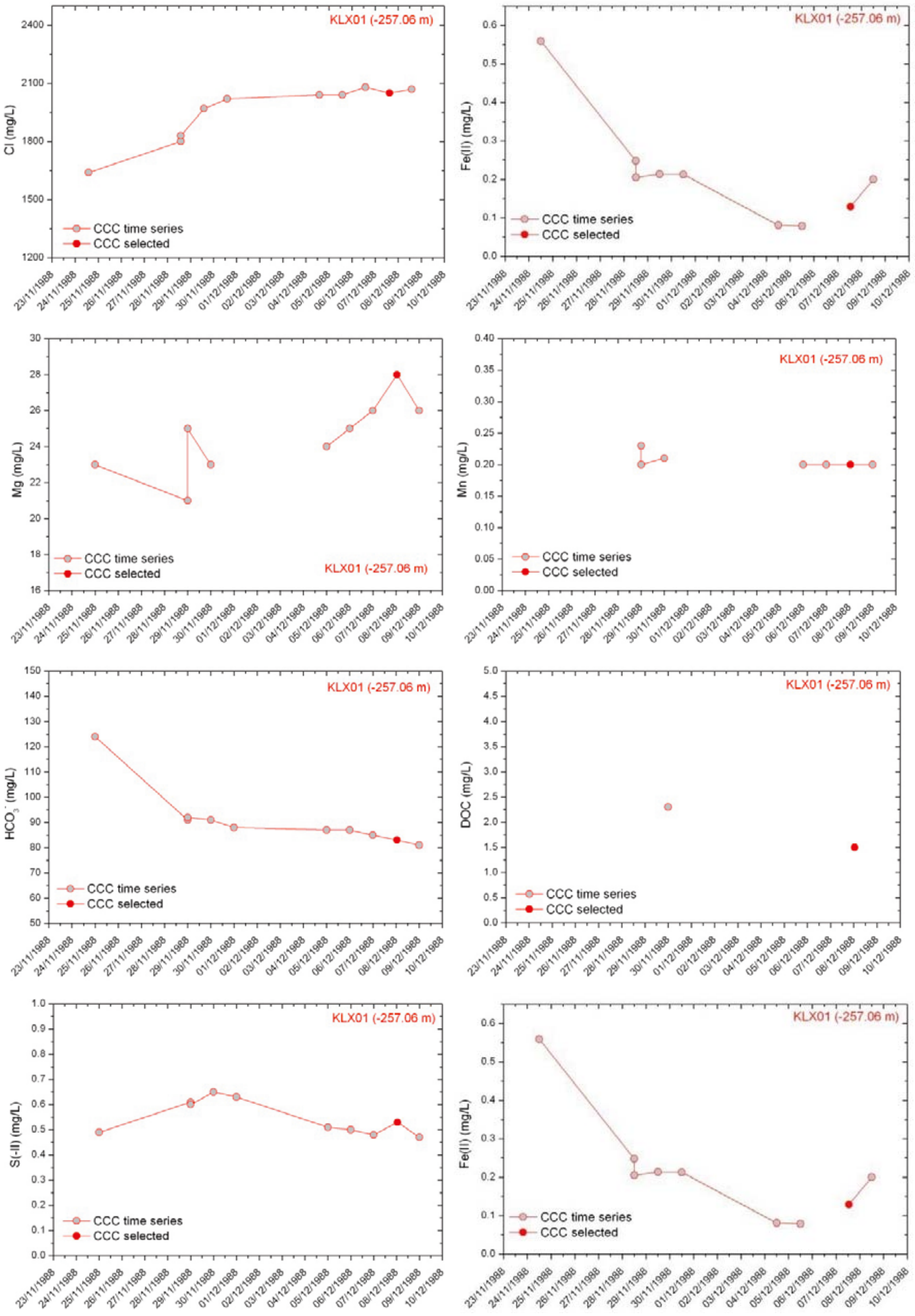

Figure A-2. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^-, DOC, S(-II) and Fe(II).*

BOREHOLE KLX01 (-440.73 masl)

Chemmac measurements:
pH = 8.6
Eh = -280 mV

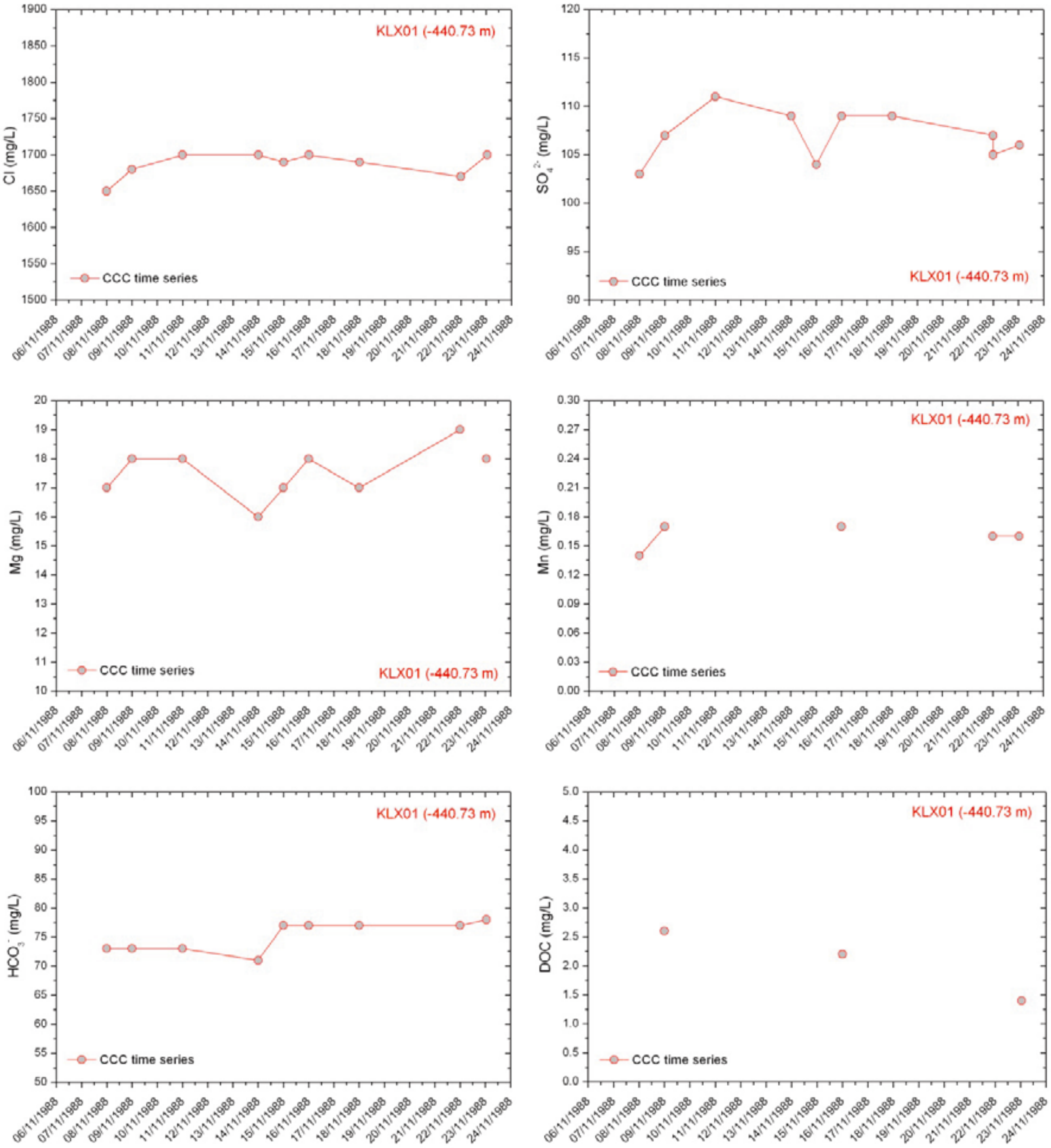

Figure A-3. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX01 (-440.73 masl)

Chemmac measurements:
pH = 8.6
Eh = -280 mV

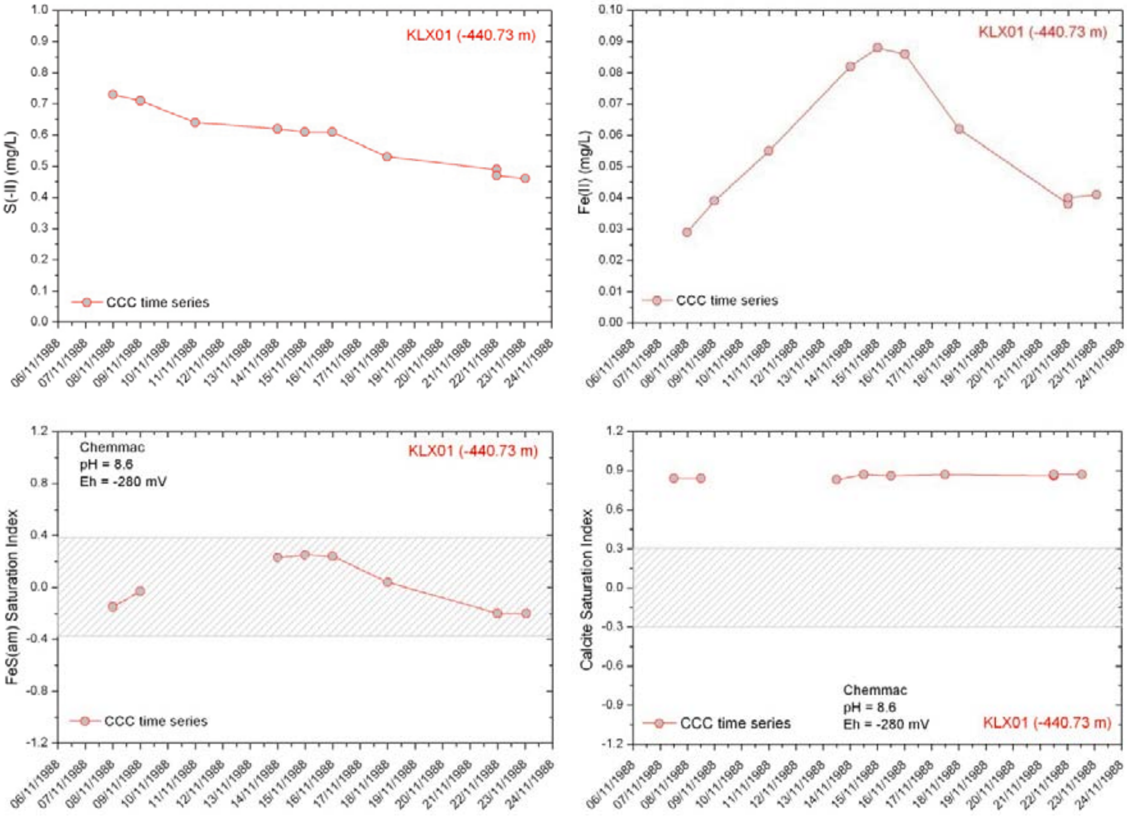

Figure A-4. *Evolution with time for S(-II), Fe(II) and the FeS(am) and calcite saturation indices.*

BOREHOLE KLX01 (-672.95 masl)

Chemmac measurements:
pH = 7.8
Eh = -265 mV

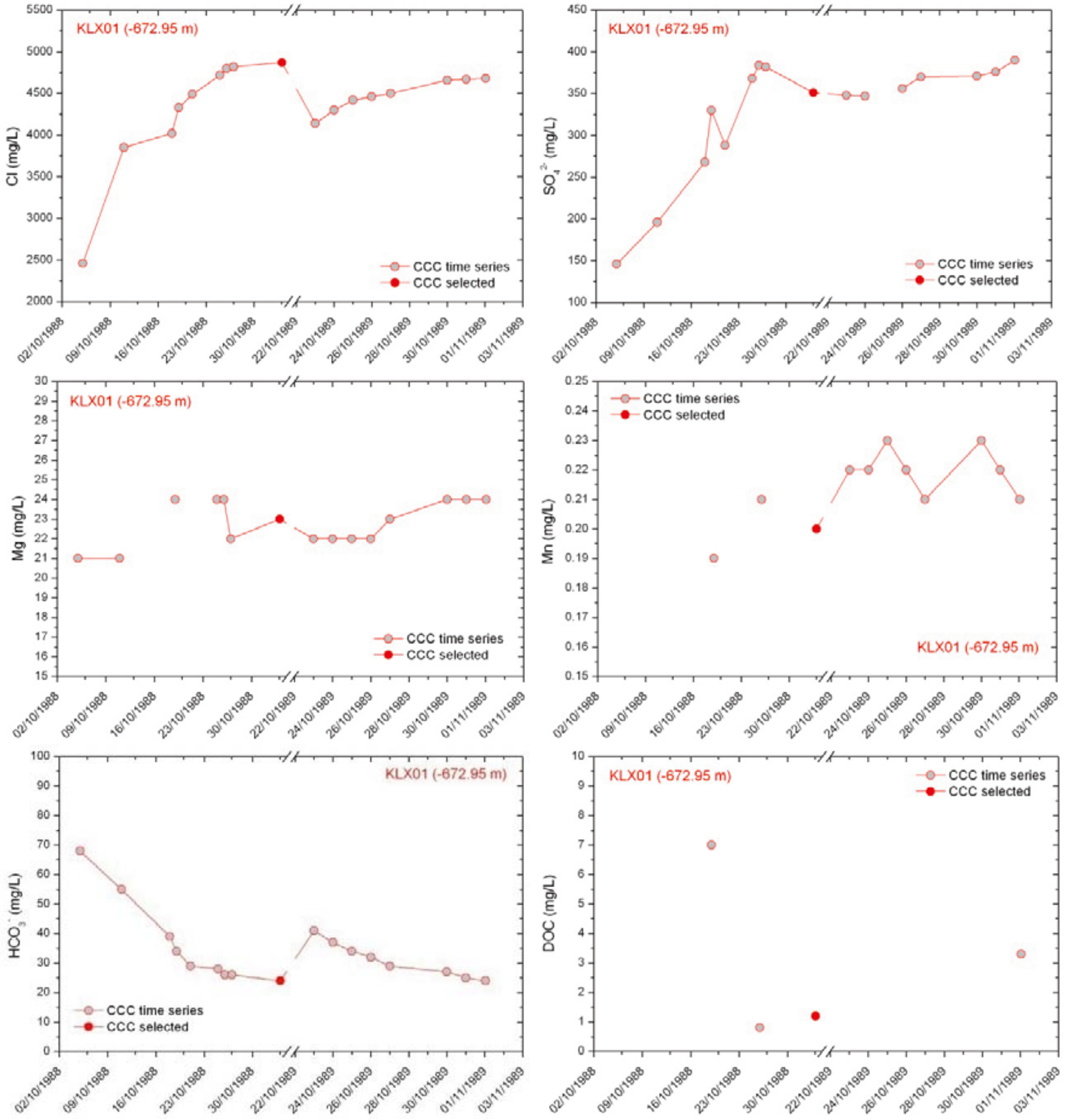

Figure A-5. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX01 (-672.95 masl)

Chemmac measurements:
pH = 7.8
Eh = -265 mV

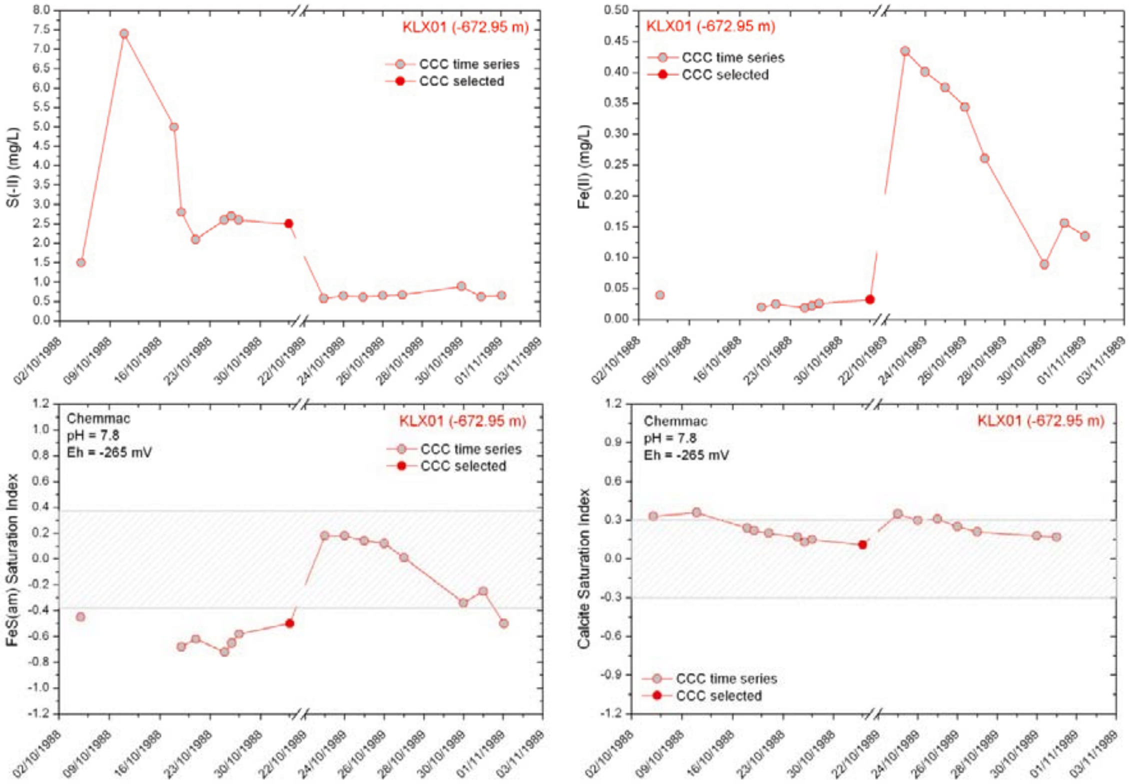

Figure A-6. *Evolution with time for S(-II), Fe(II) and the FeS(am) and calcite saturation indices.*

BOREHOLE KLX01 (-817.2 masl)

pH (lab) = 7.8-8.1 (range)
Eh ≈ -220 mV (Calculated using the S(-II)/S(VI) redox couple)

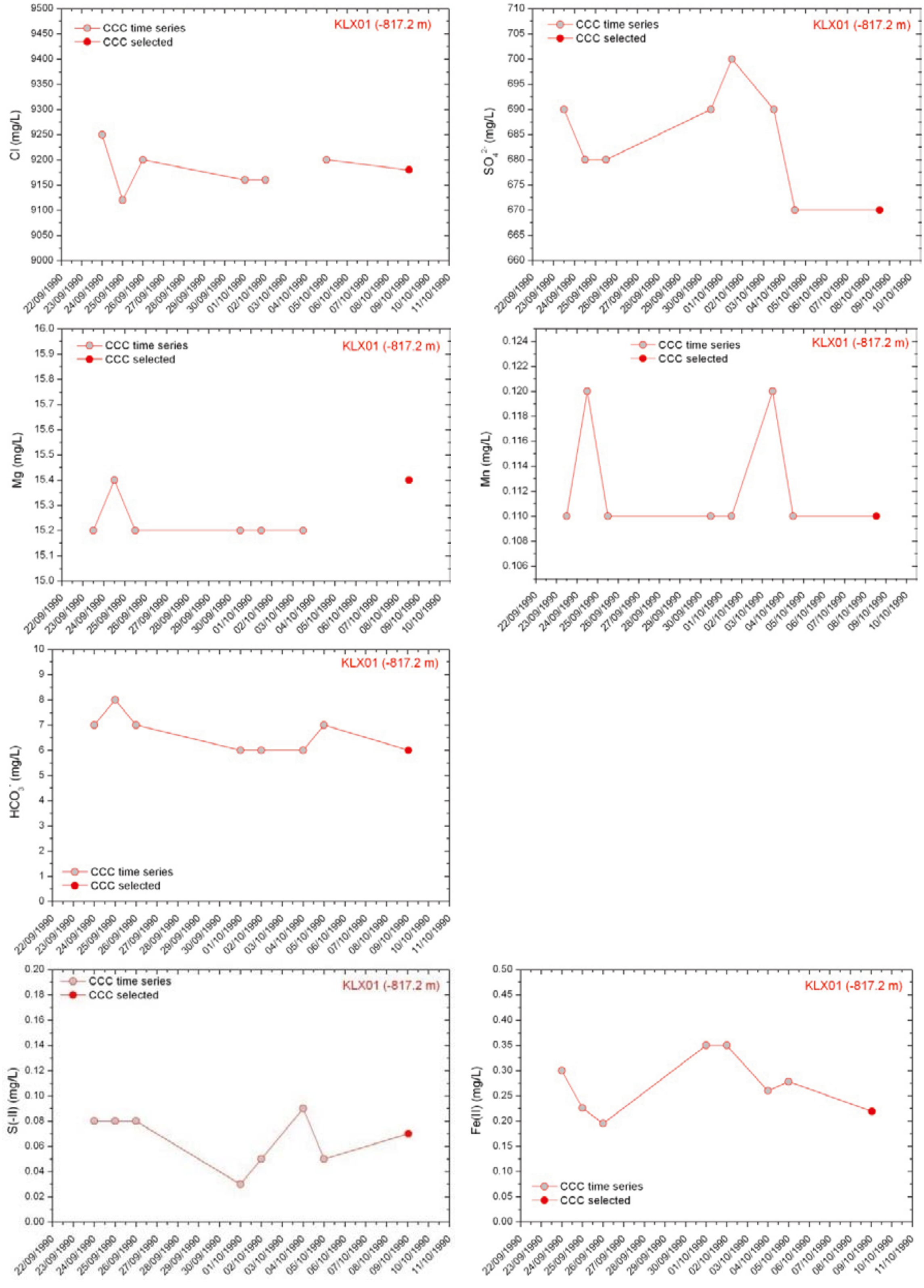

Figure A-7. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^-, S(-II) and Fe(II).*

BOREHOLE KLX01 (-897.09 masl)

pH = 8.4 (Chemmac measurement)
Eh ≈ 250 mV (Calculated using the S(-II)/S(VI) redox couple)

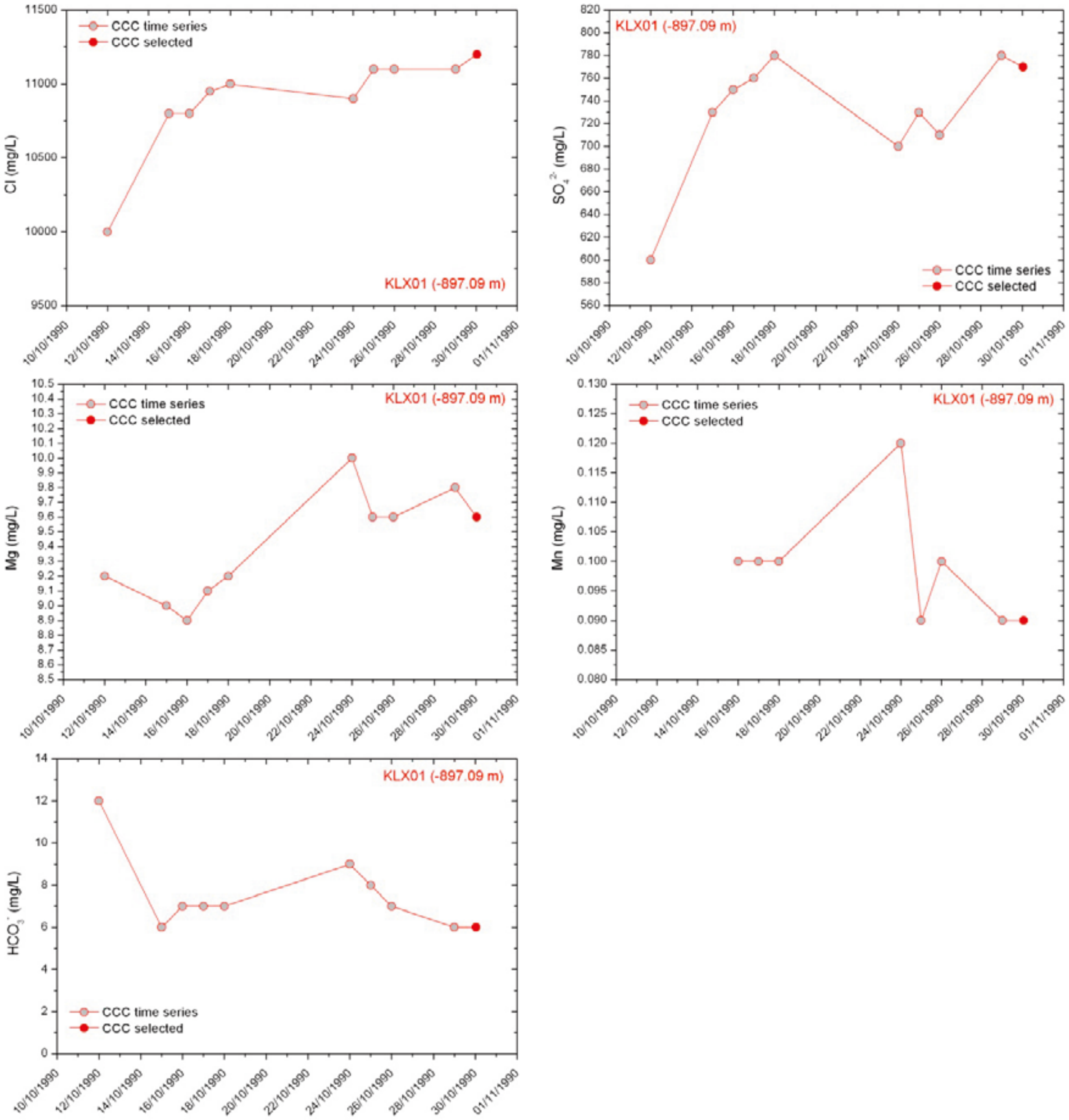

Figure A-8. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn and HCO_3^-.*

BOREHOLE KLX01 (-897.09 masl)

pH = 8.4 (Chemmac measurement)
Eh ≈ -250 mV (Calculated using the S(-II)/S(VI) redox couple)

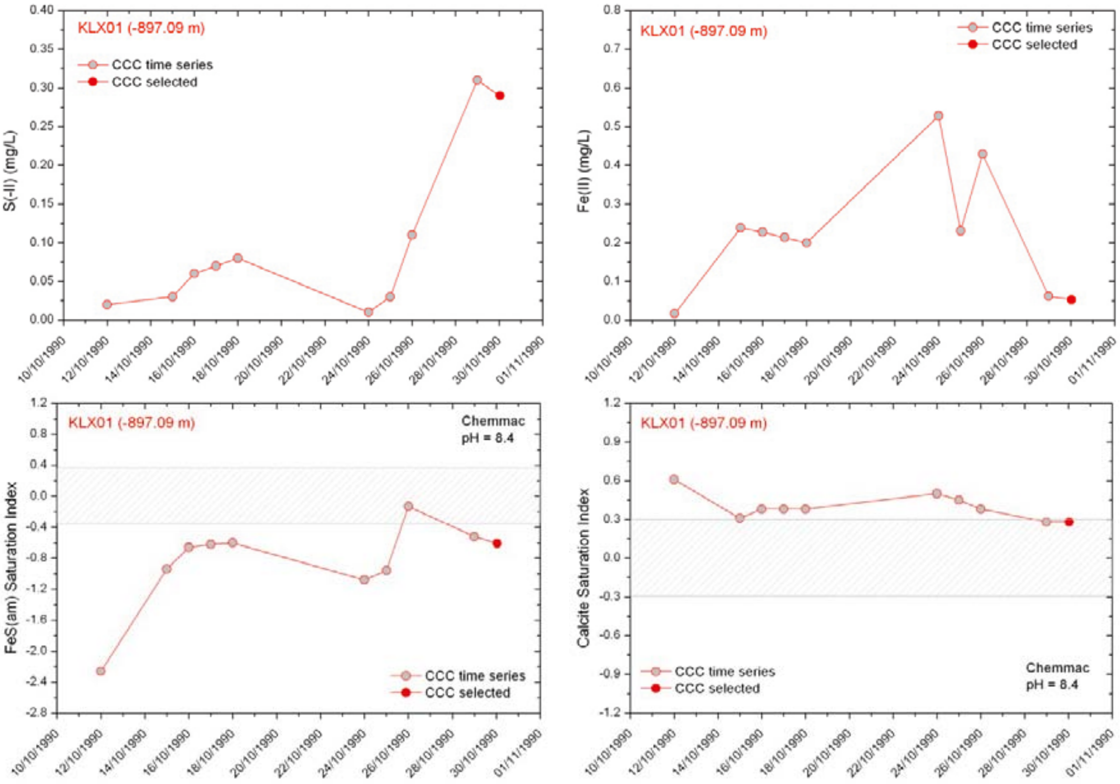

Figure A-9. *Evolution with time for S(-II), Fe(II) and the FeS(am) and calcite saturation indices.*

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BOREHOLE KLX01 (-1,019.91 masl)

Eh ≈ -235 mV (Calculated using the S(-II)/S(VI) redox couple)

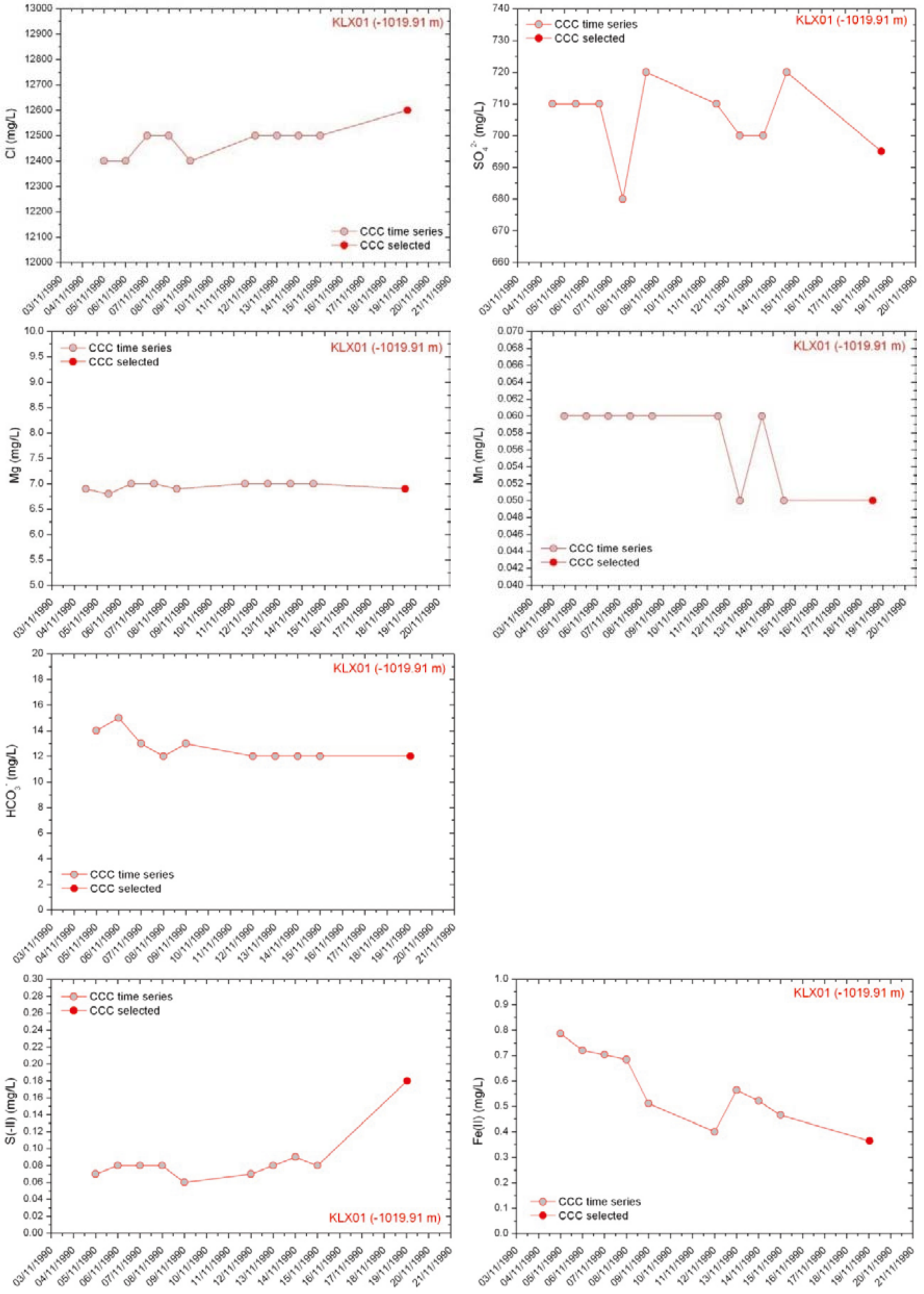

Figure A-10. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^-, S(-II) and Fe(II).*

BOREHOLE KLX02 (-1,068.24 masl)

pH = 8.6 (Chemmac measurement)
Eh ≈ -275 mV (Calculated using the S(-II)/S(VI) redox couple)

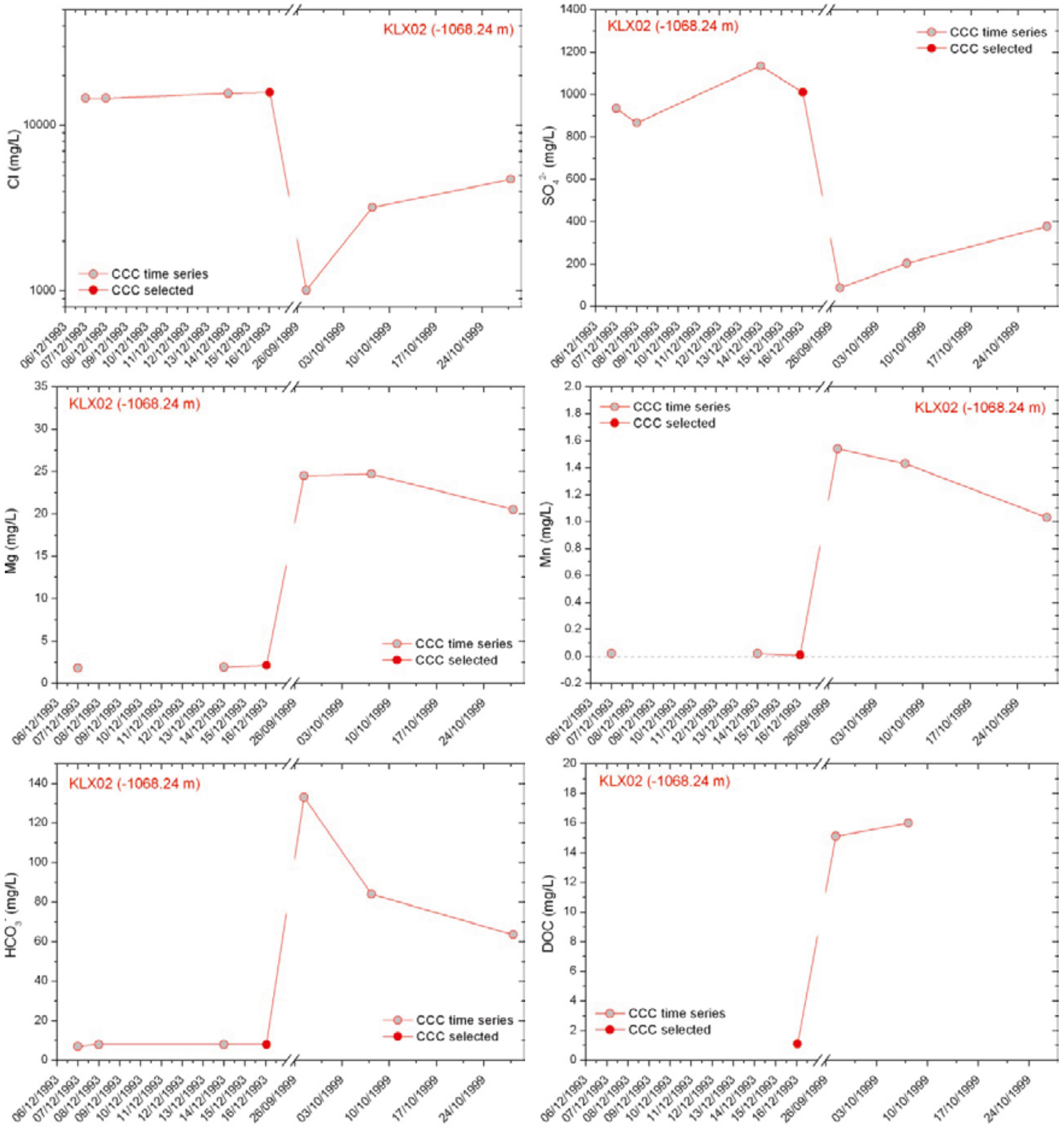

Figure A-11. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX02 (-1,068.24 masl)

pH = 8.6 (Chemmac measurement)
Eh ≈ -275 mV (Calculated using the S(-II)/S(VI) redox couple)

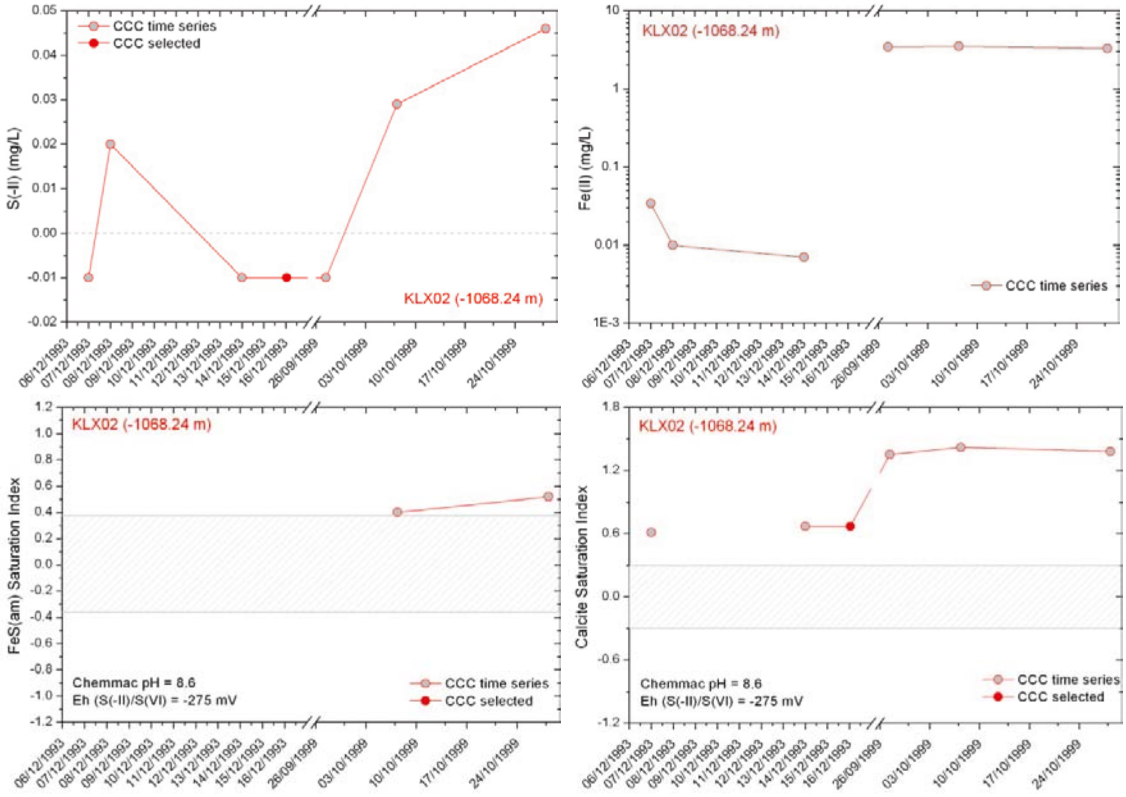

Figure A-12. *Evolution with time for S(-II), Fe(II) and the FeS(am) and calcite saturation indices.*

BOREHOLE KLX02 (-1,134.6 masl and -1,129.14 masl)

pH = 7.1-7.46 (Chemmac measurements)
Eh ≈ -180 mV (Calculated using the S(-II)/S(VI) redox couple)

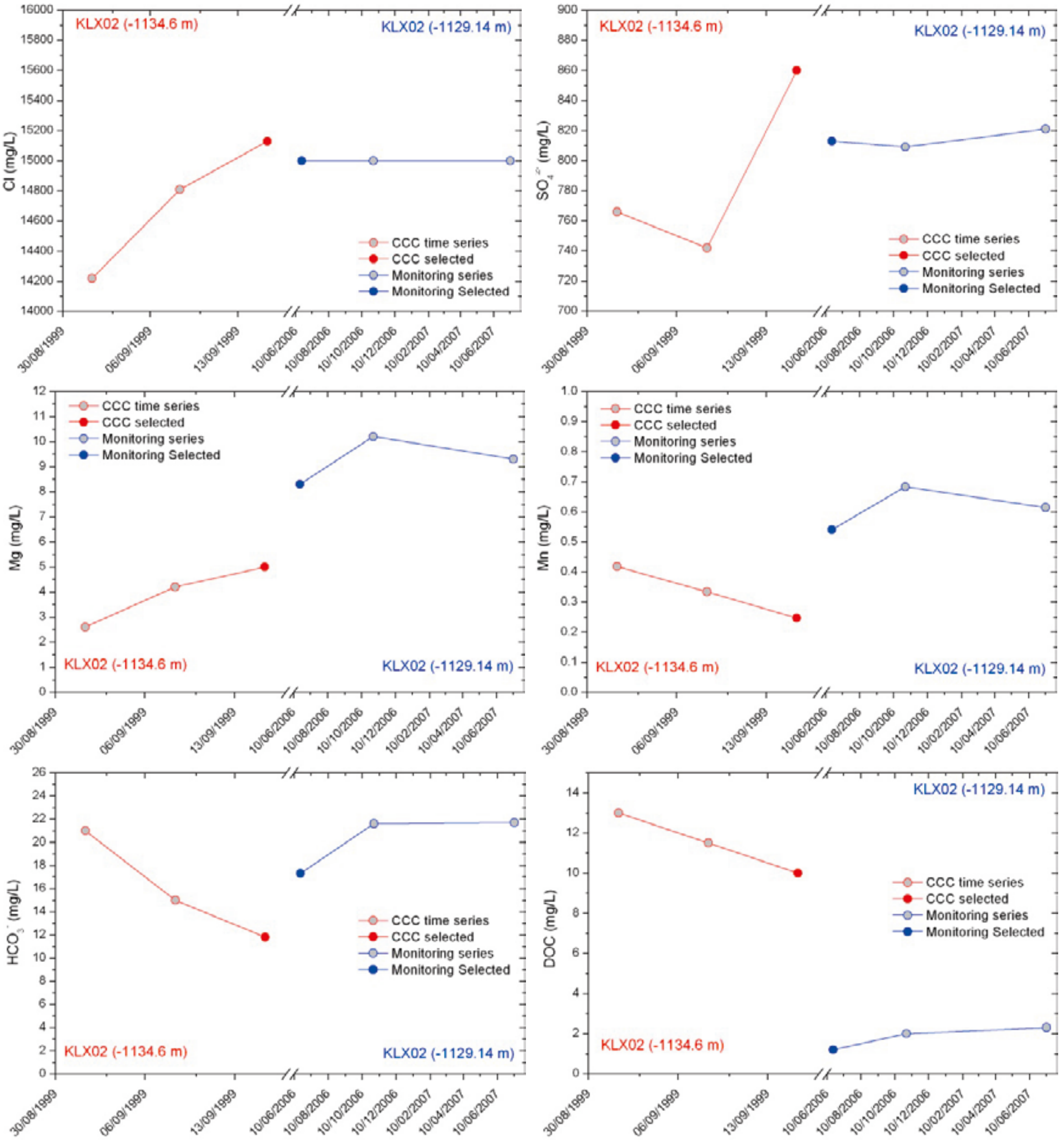

Figure A-13. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX02 (-1,134.6 masl and -1,129.14 masl)

pH = 7.1-7.46 (Chemmac measurements)
Eh ≈ -180 mV (Calculated using the S(-II)/S(VI) redox couple)

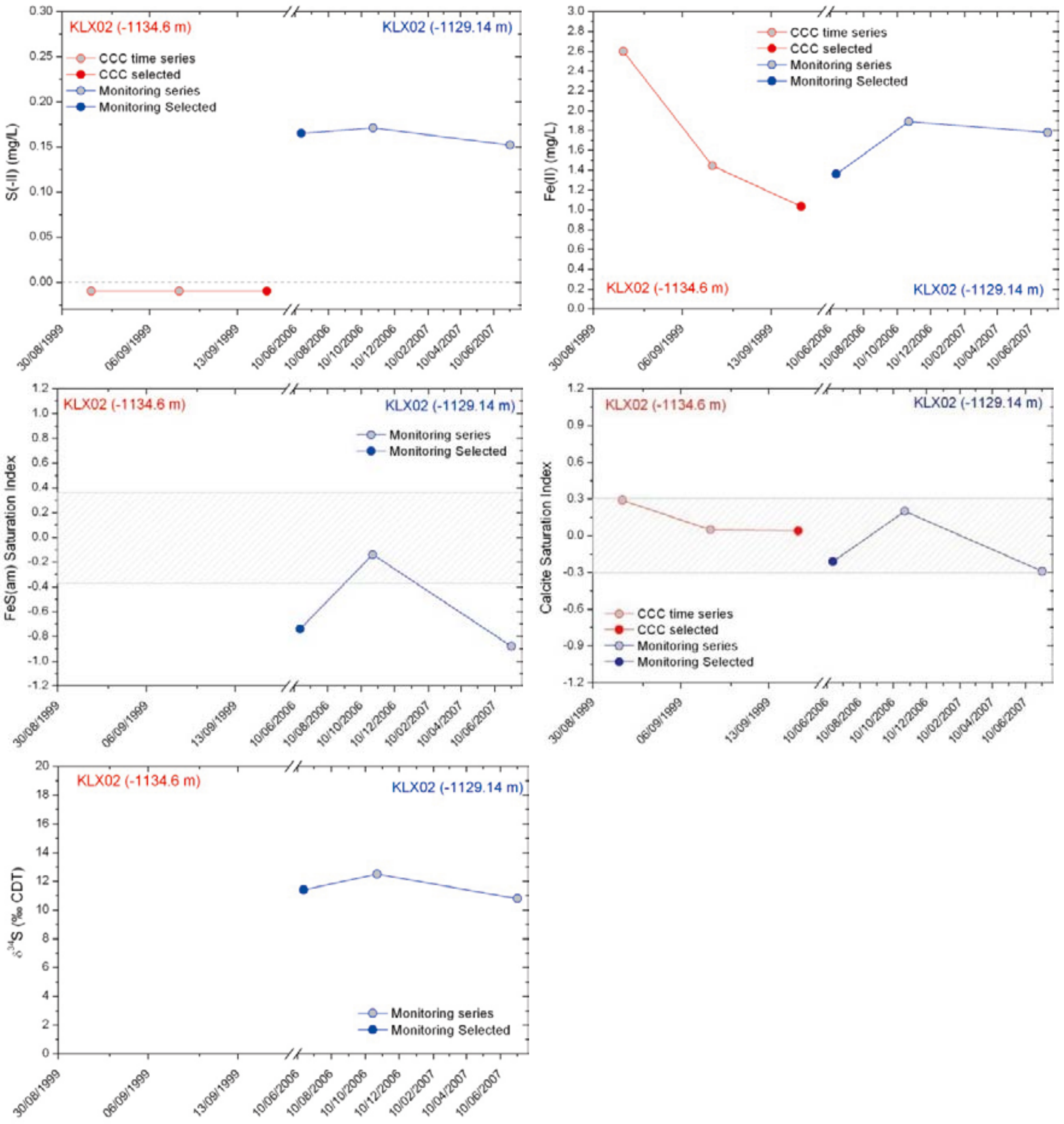

Figure A-14. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and* $\delta^{34}S$.

BOREHOLE KLX03 (-379.85 masl)

Chemmac measurements:
pH = 8.1
Eh = -270 mV

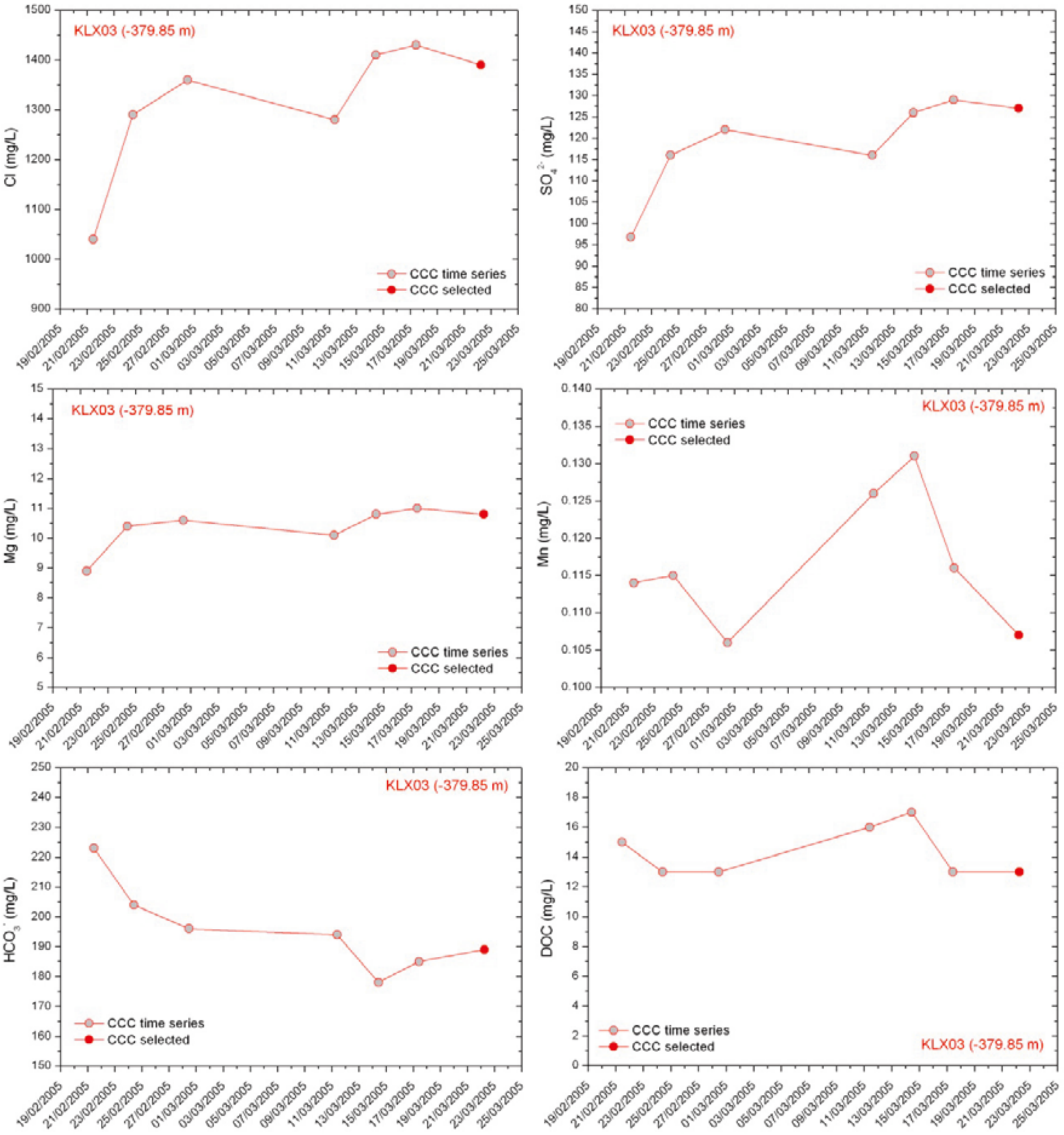

Figure A-15. Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.

BOREHOLE KLX03 (-379.85 masl)

Chemmac measurements:
pH = 8.1
Eh = -270 mV

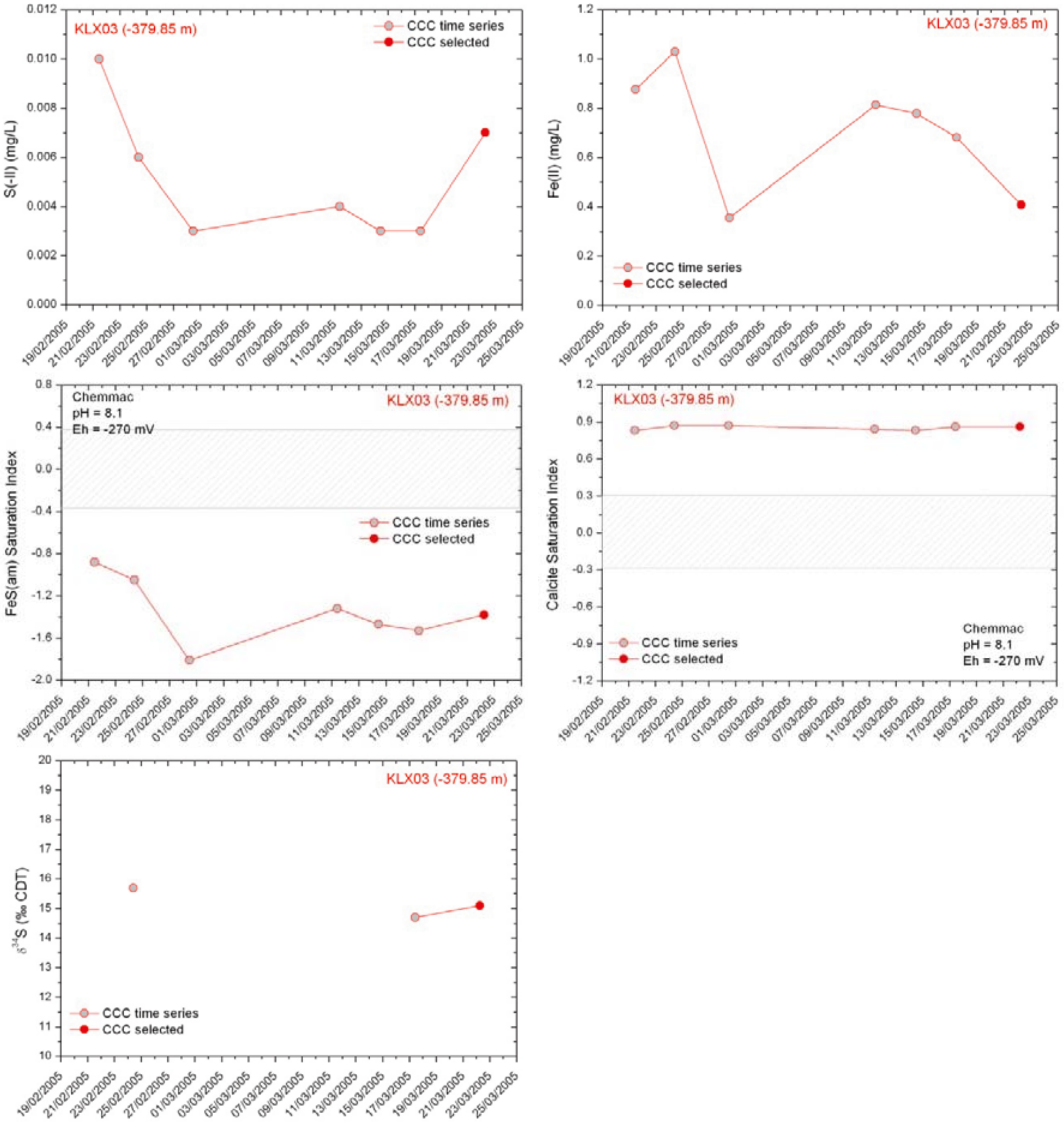

Figure A-16. *Evolution with time for S(-II) and Fe(II), the FeS(am) calcite saturation indices and* $\delta^{34}S$.

BOREHOLE KLX03 (-700.6 masl)

Chemmac measurements:
pH = 7.5
Eh = -220 mV

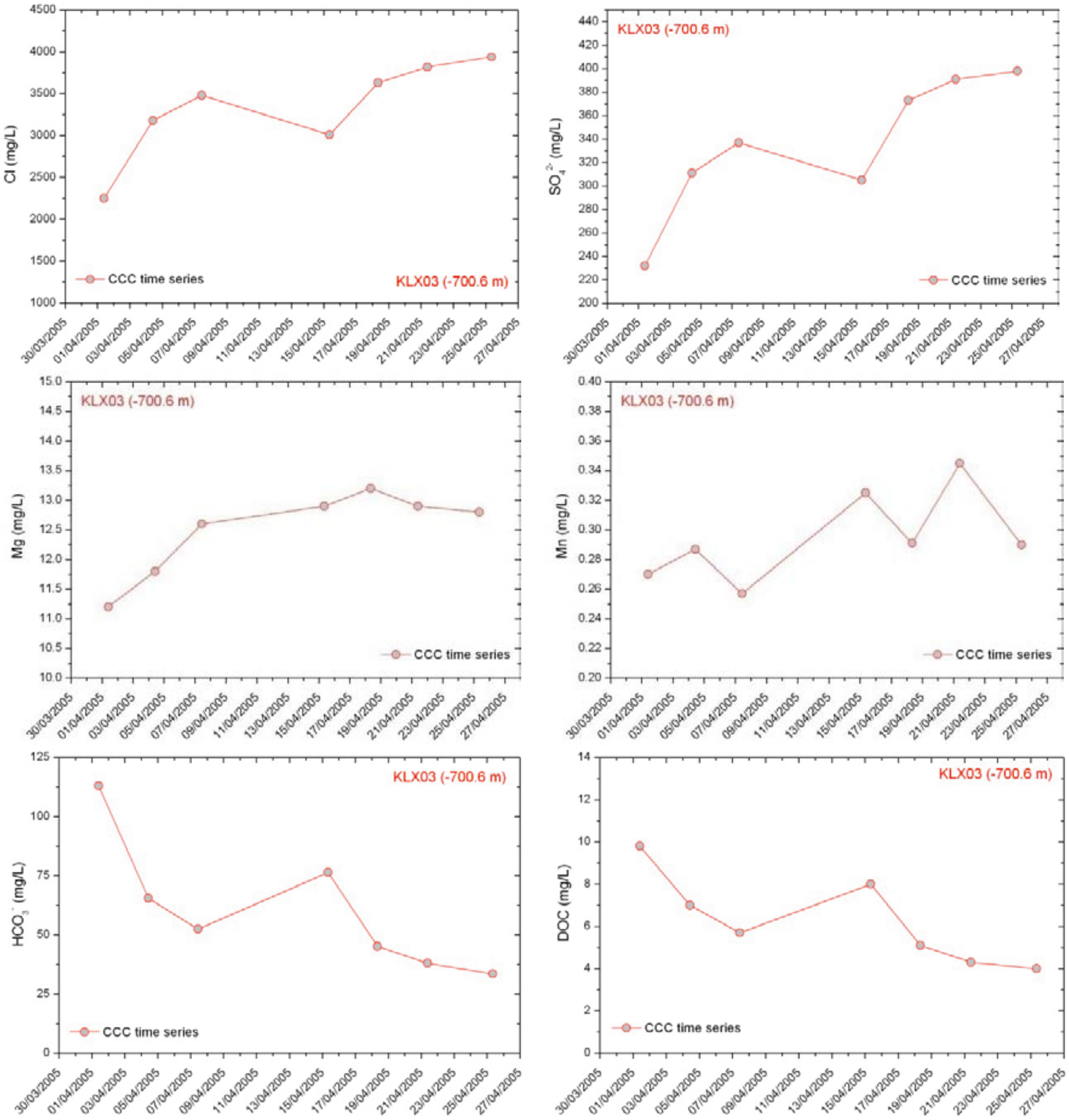

Figure A-17. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX03 (-700.6 masl)

Chemmac measurements:
pH = 7.5
Eh = -220 mV

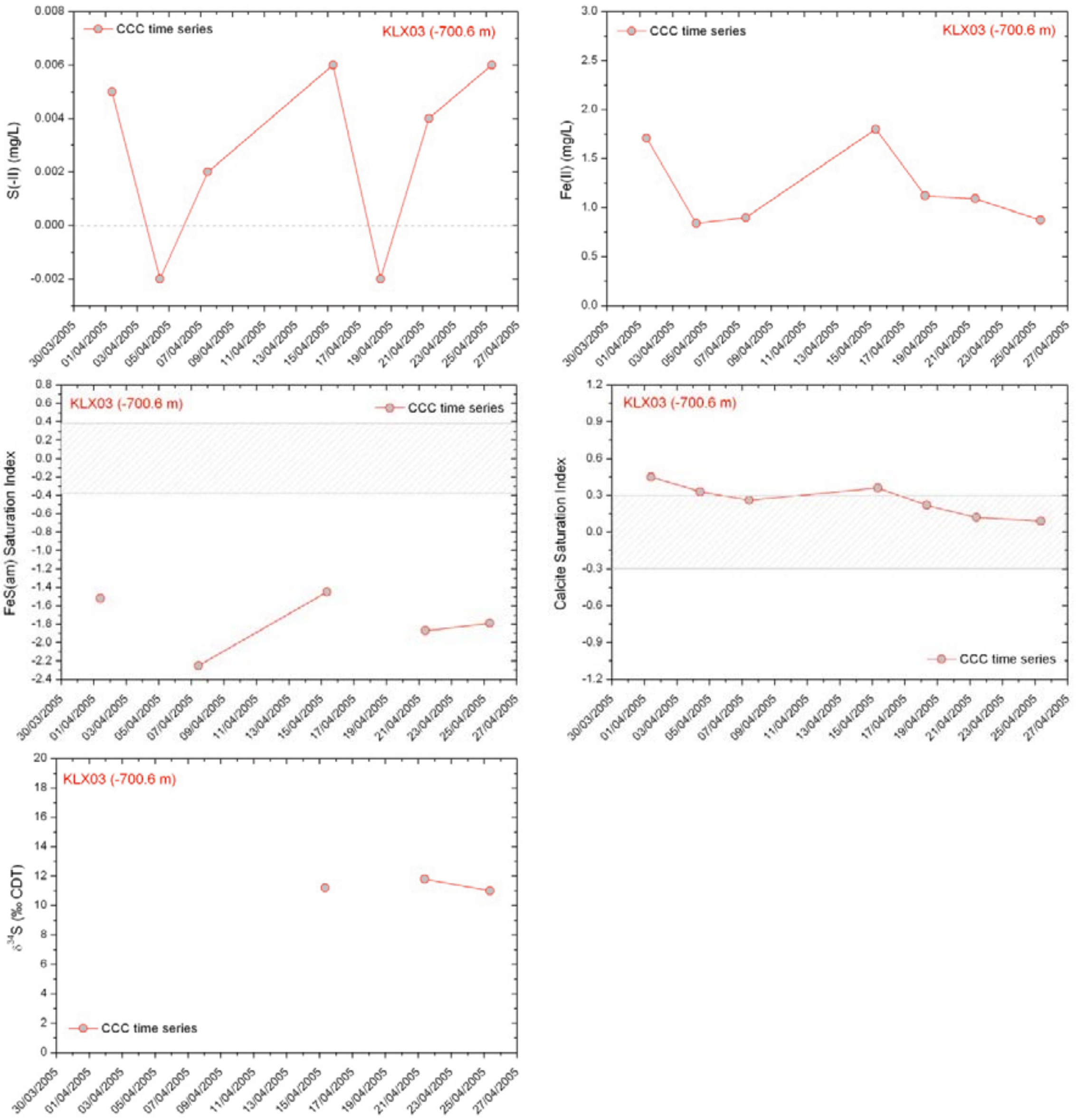

Figure A-18. *Evolution with time for S(-II), Fe(II), FeS(am), calcite saturation indices and δ^{34}S.*

BOREHOLE KLX03 (-922.45 masl)

pH = 8.4 (Chemmac measurement)
Eh ≈ -275 mV (Calculated using the S(-II)/S(VI) redox couple)

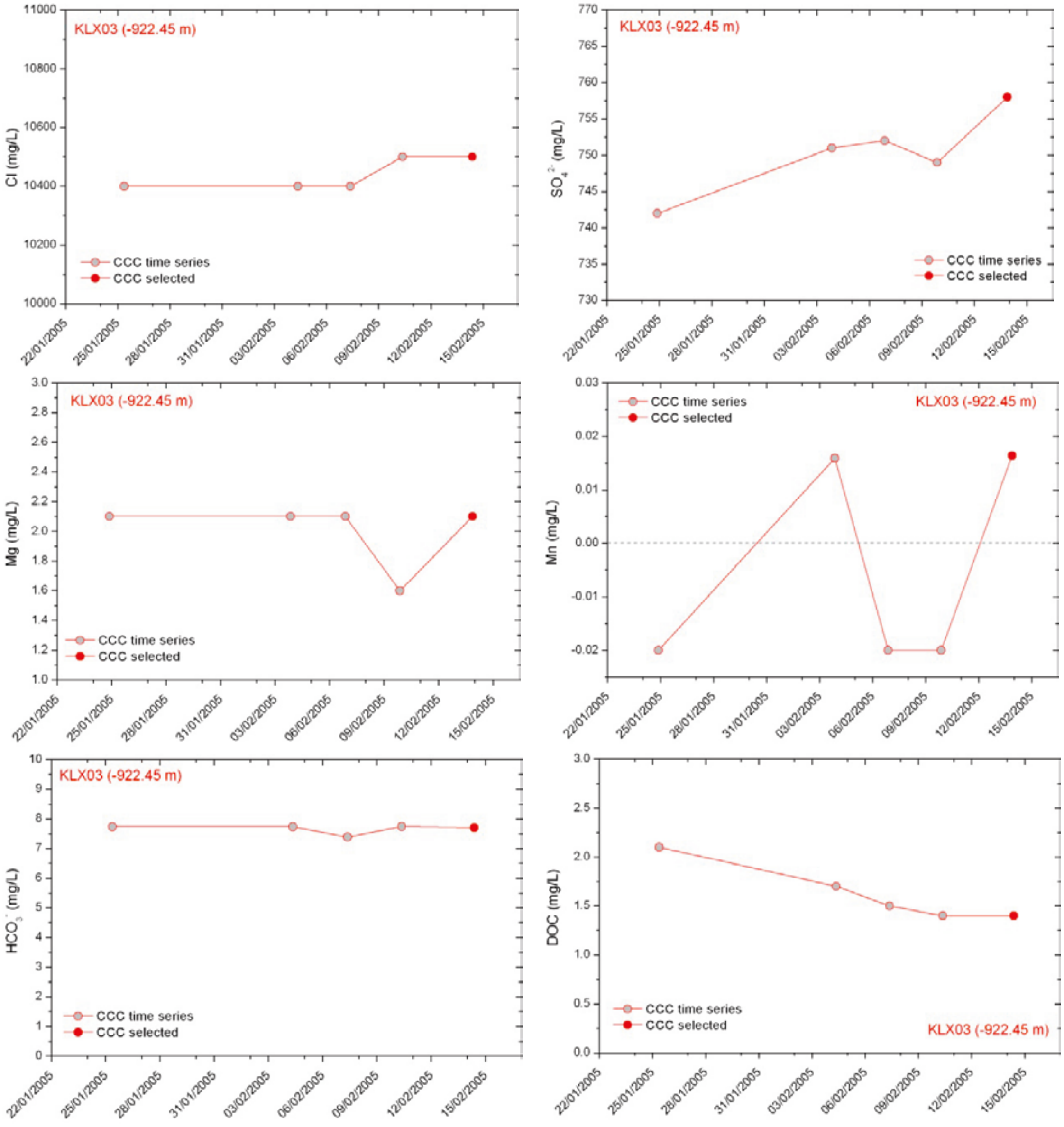

Figure A-19. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX03 (-922.45 masl)

pH = 8.4 (Chemmac measurement)
Eh ≈ -275 mV (Calculated using the S(-II)/S(VI) redox couple)

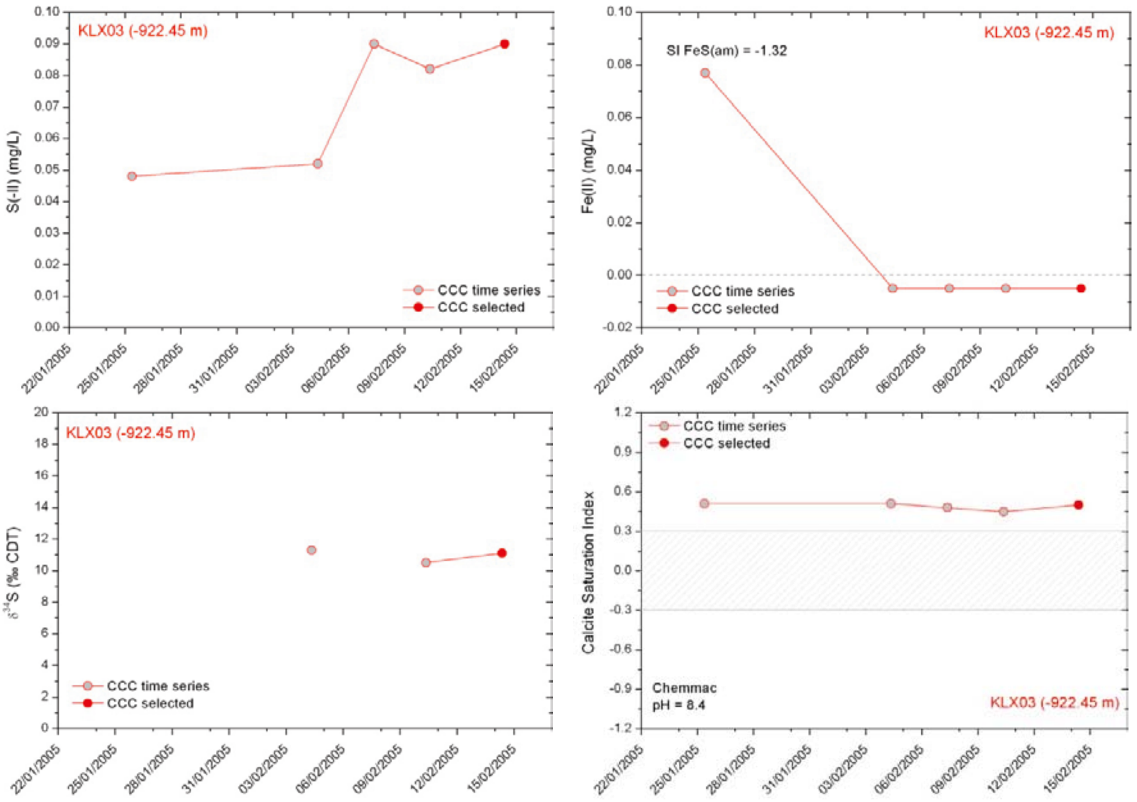

Figure A-20. *Evolution with time for S(-II), Fe(II), δ^{34}S and the calcite saturation indices.*

BOREHOLE KLX04 (-487.52 masl, CCC; -491.94 masl, Monitoring)

Incomplete chemical analysis

pH = 7.26-7.85 (Field/surface measurements)
Eh ≈ -200 mV (Calculated using the S(-II)/S(VI) redox couple)

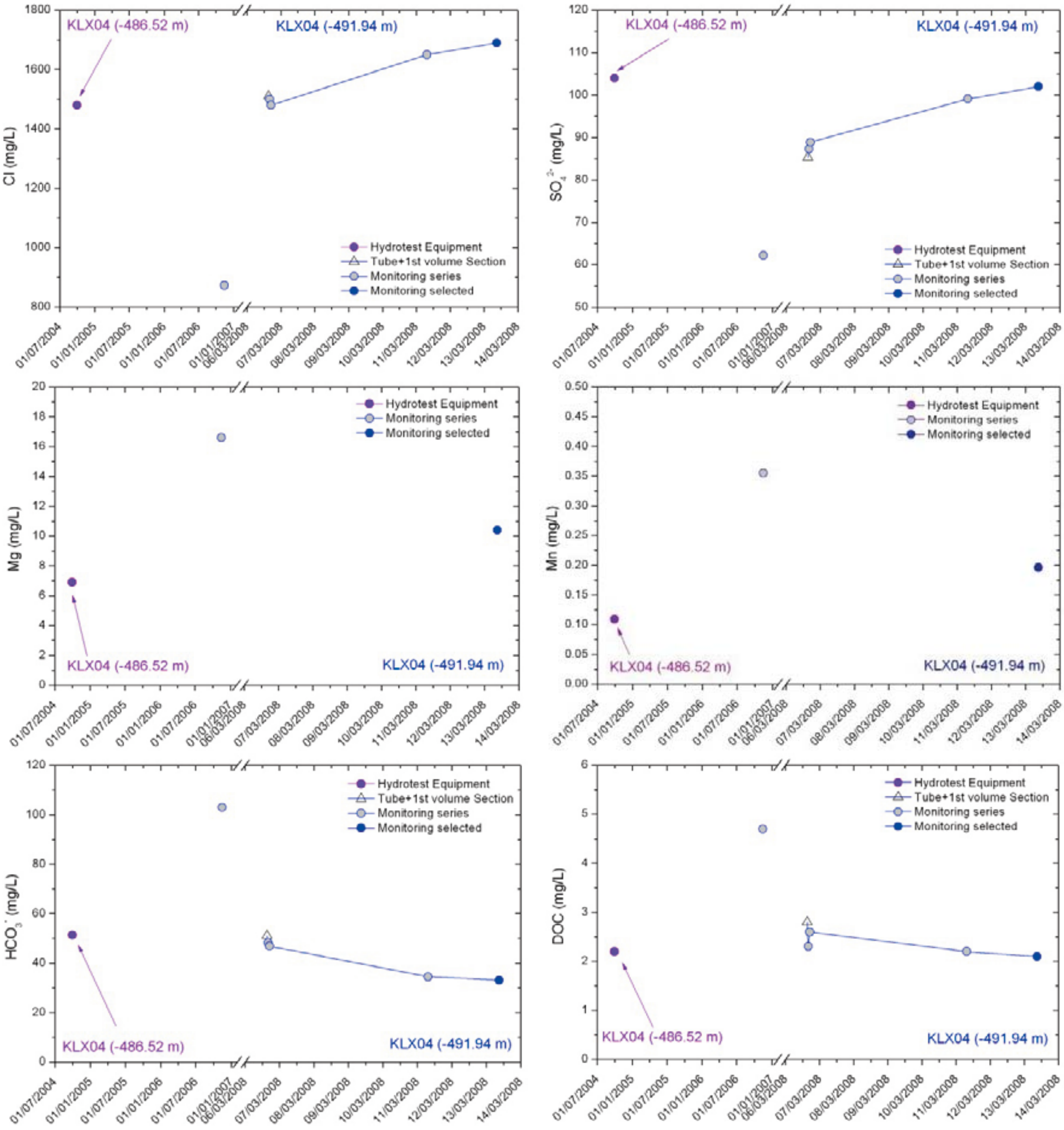

Figure A-21. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX04 (-487.52 m, CCC; -491.94 m, Monitoring)

Incomplete chemical analysis

pH = 7.26-7.85 (Field/surface measurements)
Eh ≈ -200 mV (Calculated using the S(-II)/S(VI) redox couple)

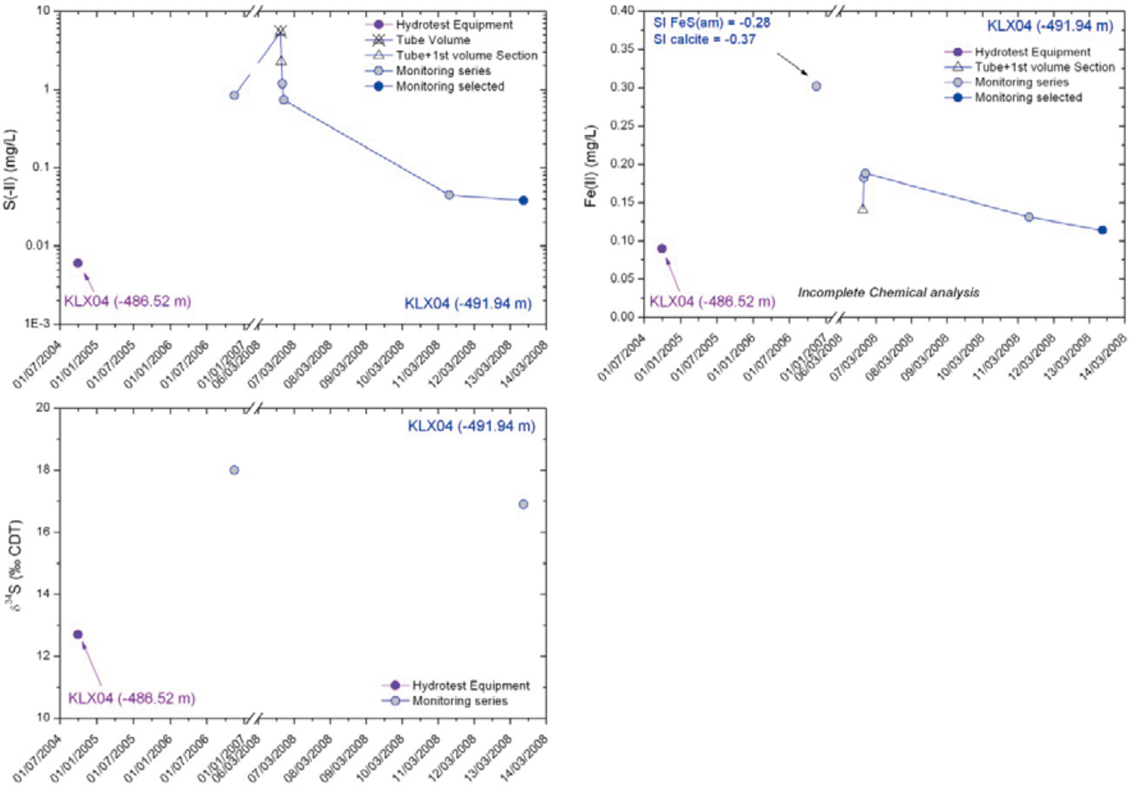

Figure A-22. *Evolution with time for S(-II), Fe(II) and δ^{34}S.*

BOREHOLE KLX04 (-854.86 masl)

Incomplete chemical analysis

pH = 6.83-7.74 (Field/surface measurements)

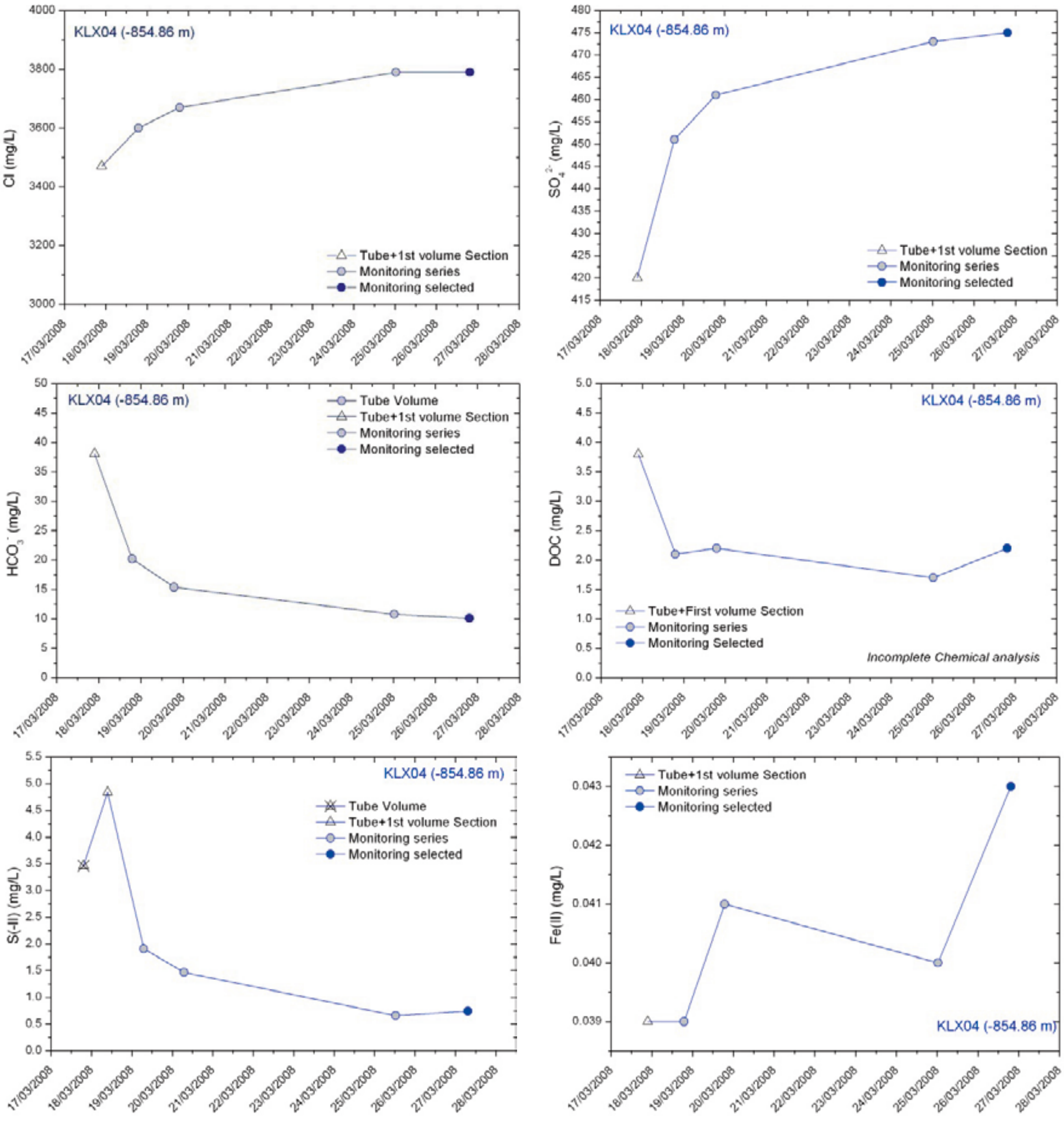

Figure A-23. *Evolution with time for Cl, SO_4^{2-}, HCO_3^-, DOC, S(-II) and Fe(II).*

BOREHOLE KLX05 (-204.84 masl)
Incomplete chemical analysis

pH = 7.03-8.42 (Field/surface measurements)
Eh ≈ range -193 to -263 mV (Calculated using the S(-II)/S(VI) redox couple)

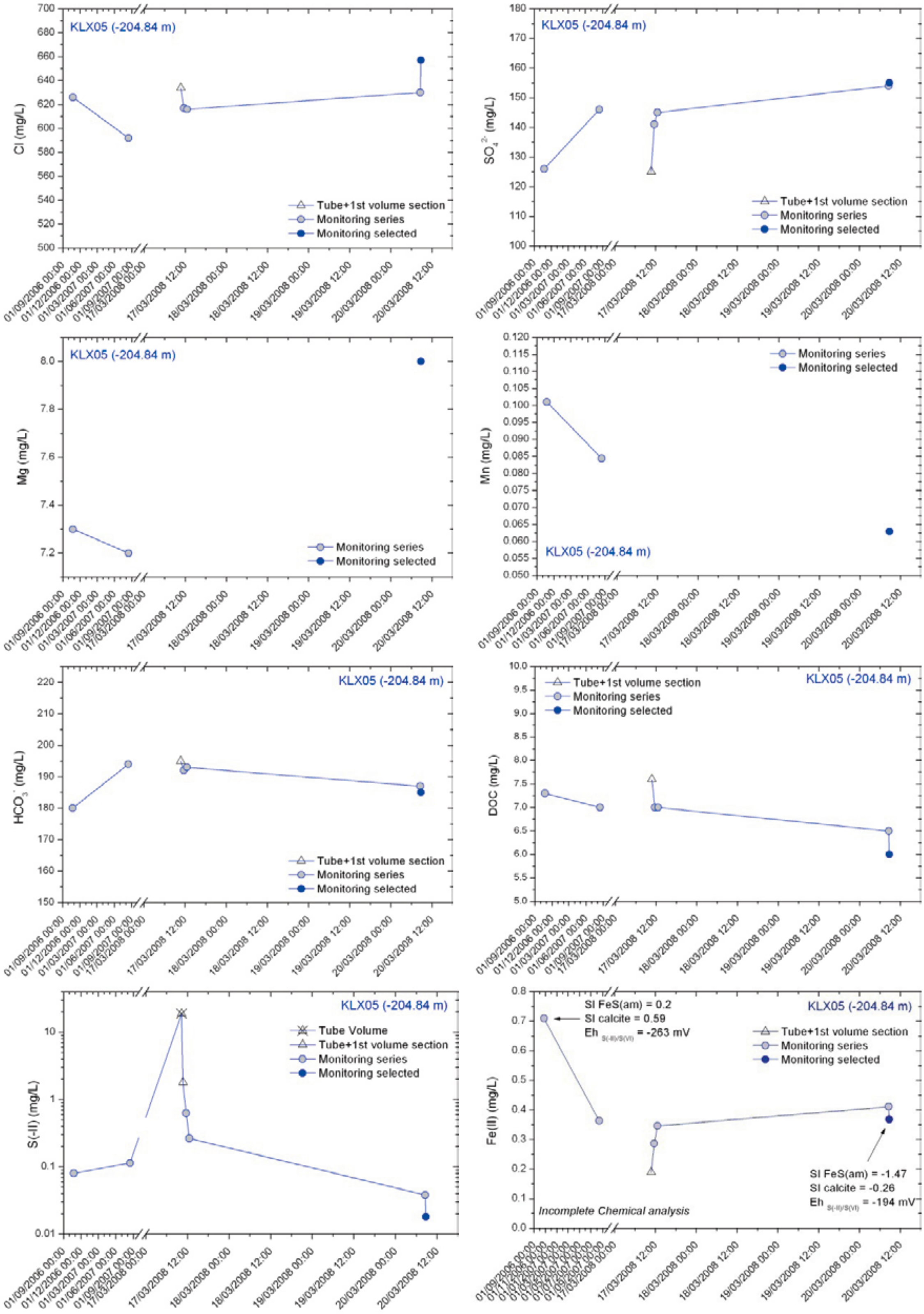

Figure A-24. *Evolution with time for Cl,* SO_4^{2-}*, Mg, Mn,* HCO_3^-*, DOC, S(-II) and Fe(II) .*

BOREHOLE KLX06 (-218.51 masl, Hydrotest equipment; -221.18 masl, Monitoring)

pH = 8.44-8.83 (Field/surface measurements)
Eh ≈ -280 mV (Calculated using the S(-II)/S(VI) redox couple)

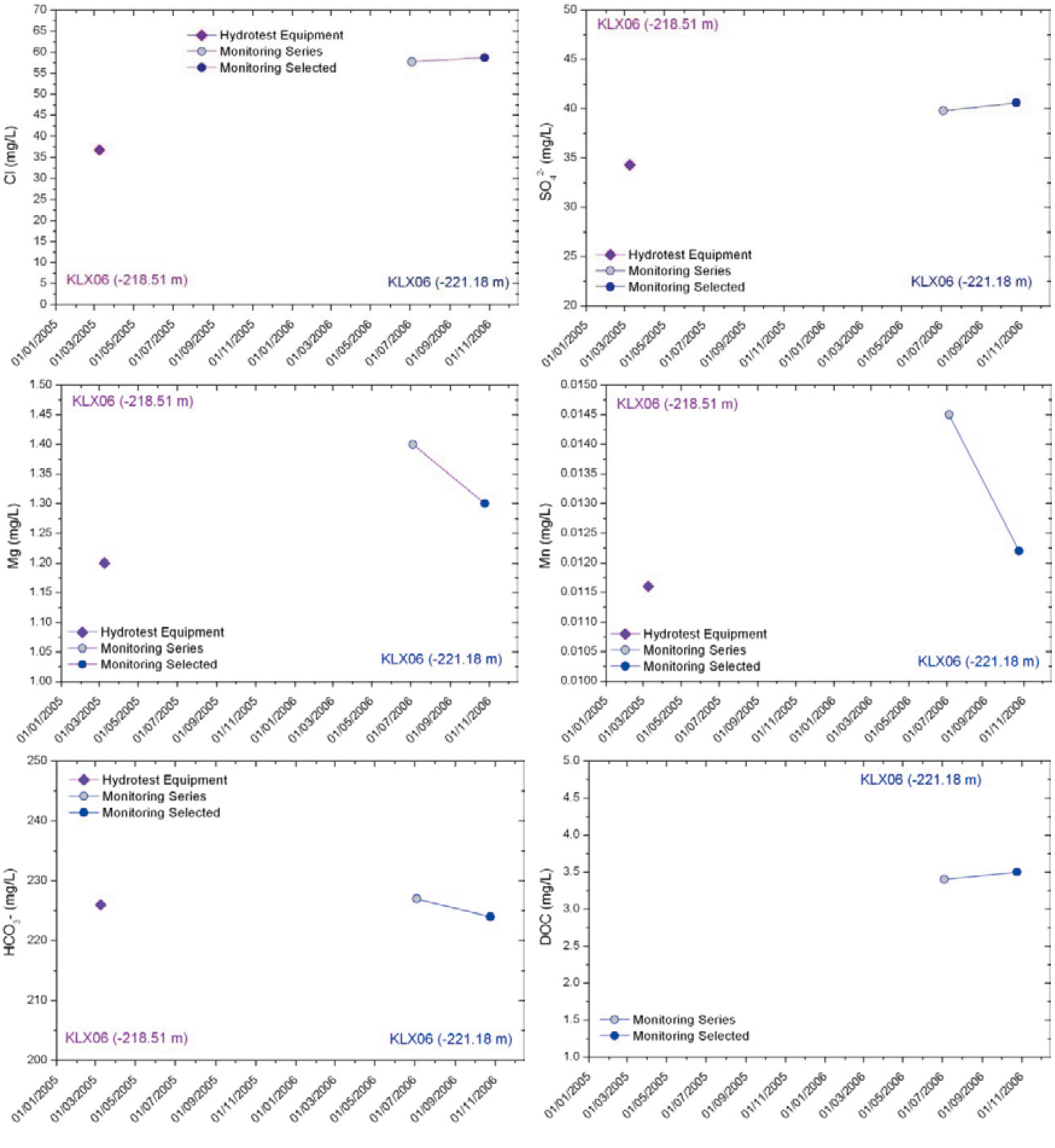

Figure A-25. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX06 (-218.51 masl, Hydrotest equipment; -221.18 masl, Monitoring)

pH = 8.44-8.83 (Field/surface measurements)
Eh ≈ range -193 to -263 mV (Calculated using the S(-II)/S(VI) redox couple)

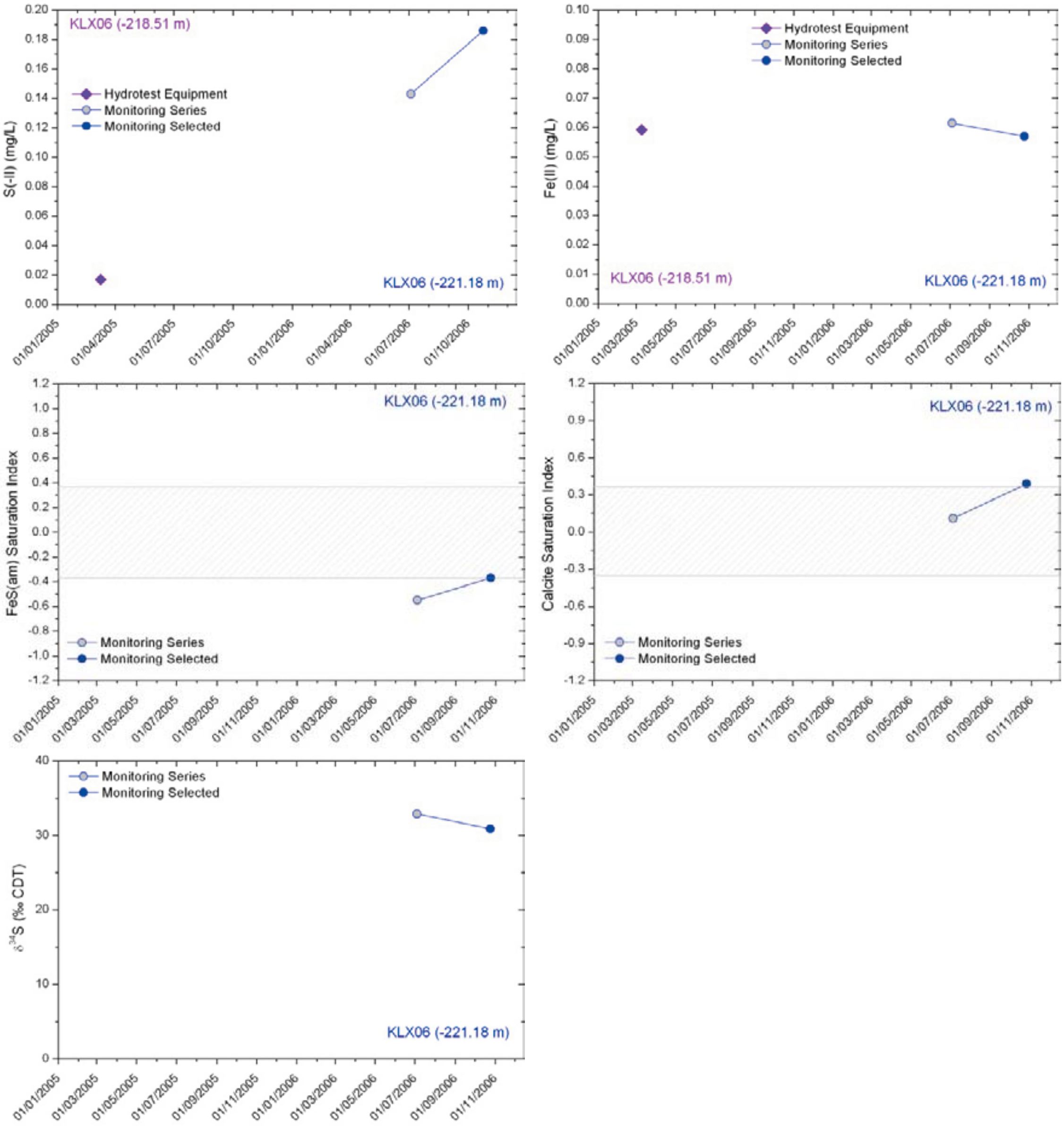

Figure A-26. *Evolution with time for S(-II) and Fe(II), the FeS(am)* and *calcite saturation indices and* $\delta^{34}S$.

BOREHOLE KLX06 (-475.27 masl)

pH = 7.73-8.62 (Field/surface measurements); Eh ≈ range -162 mV to -277 mV(Calculated using the S(-II)/S(VI) redox couple)

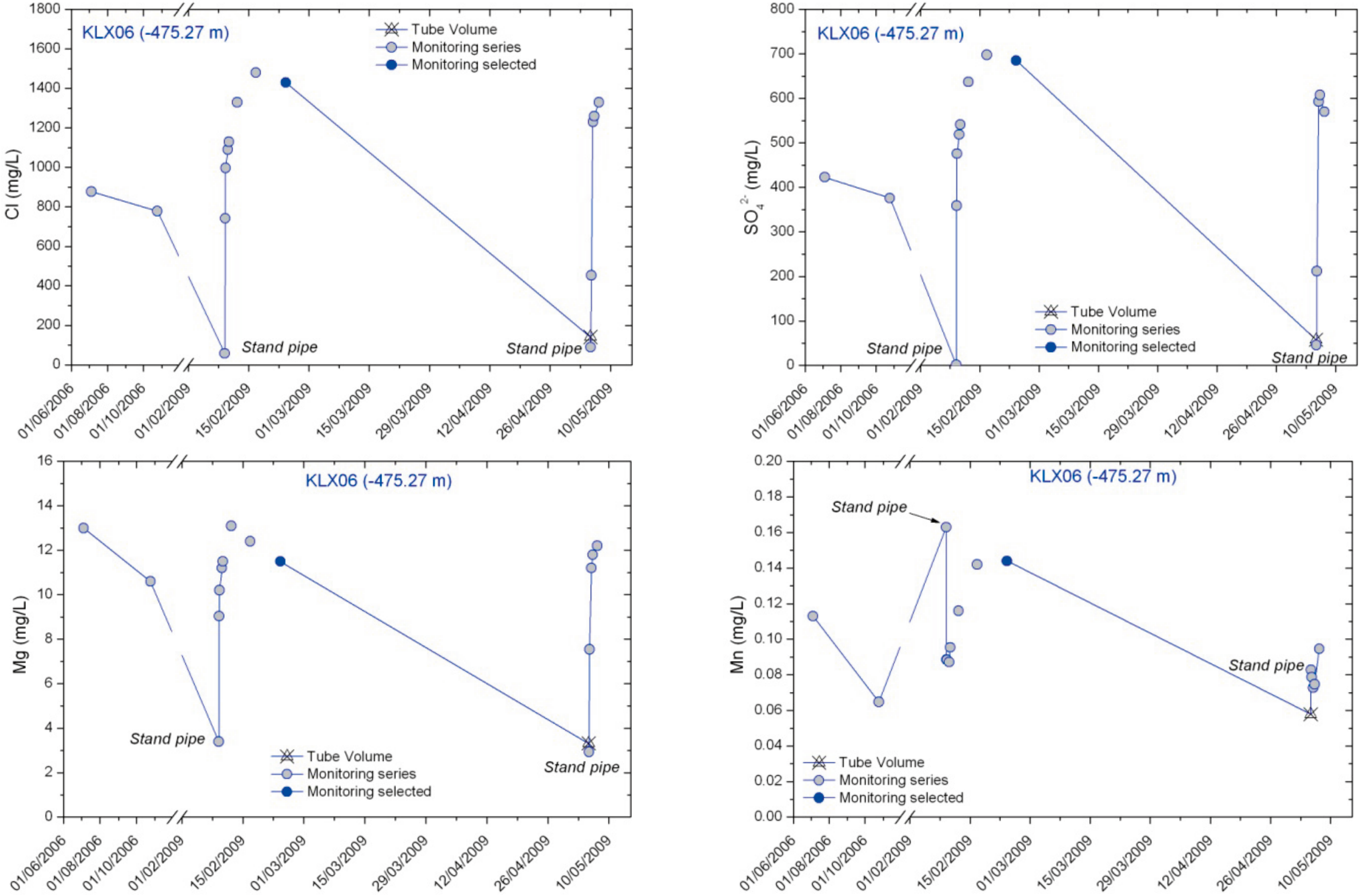

Figure A-27. *Evolution with time for Cl, SO$_4^{2-}$, Mg and Mn.*

BOREHOLE KLX06 (-475.27 masl)

pH = 7.738.62 (Field/surface measurements); Eh ≈ range -162 mV to -277 mV (Calculated using the S(-II)/S(VI) redox couple)

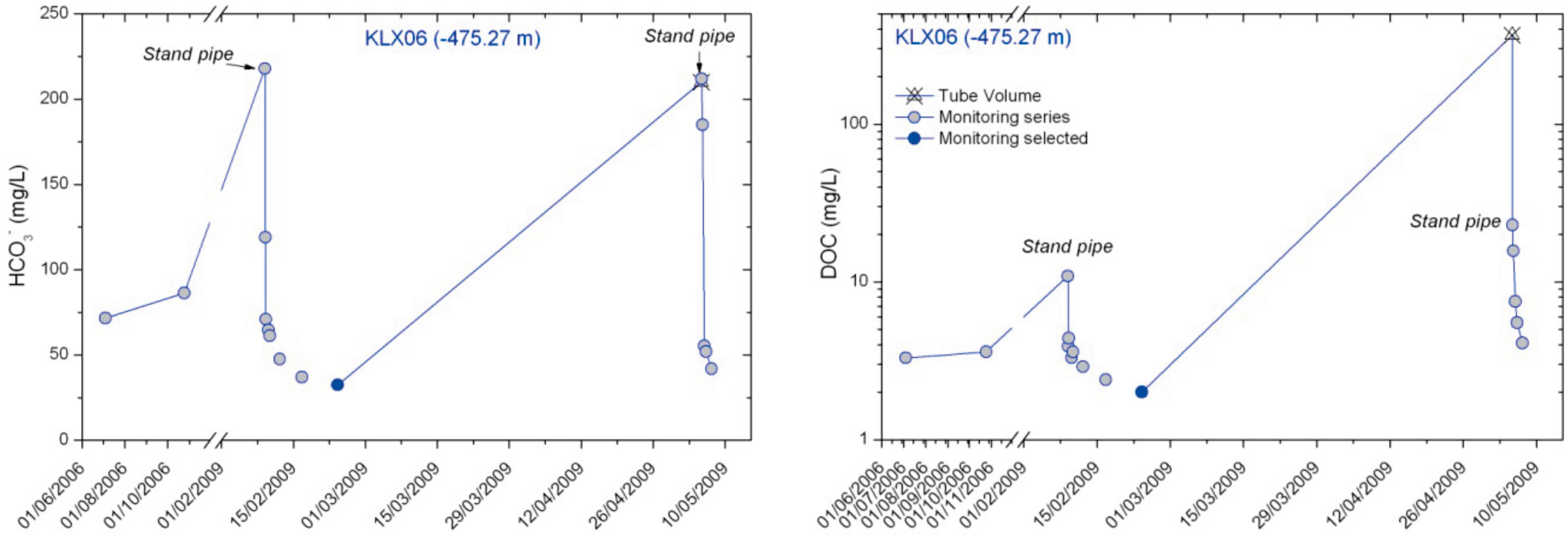

Figure A-28. *Evolution with time for* HCO_3^- *and DOC.*

BOREHOLE KLX06 (-475.27 masl)

pH = 7.73-8.62 (Field/surface measurements); Eh ≈ range -162 mV to -277 mV (Calculated using the S(-II)/S(VI) redox couple)

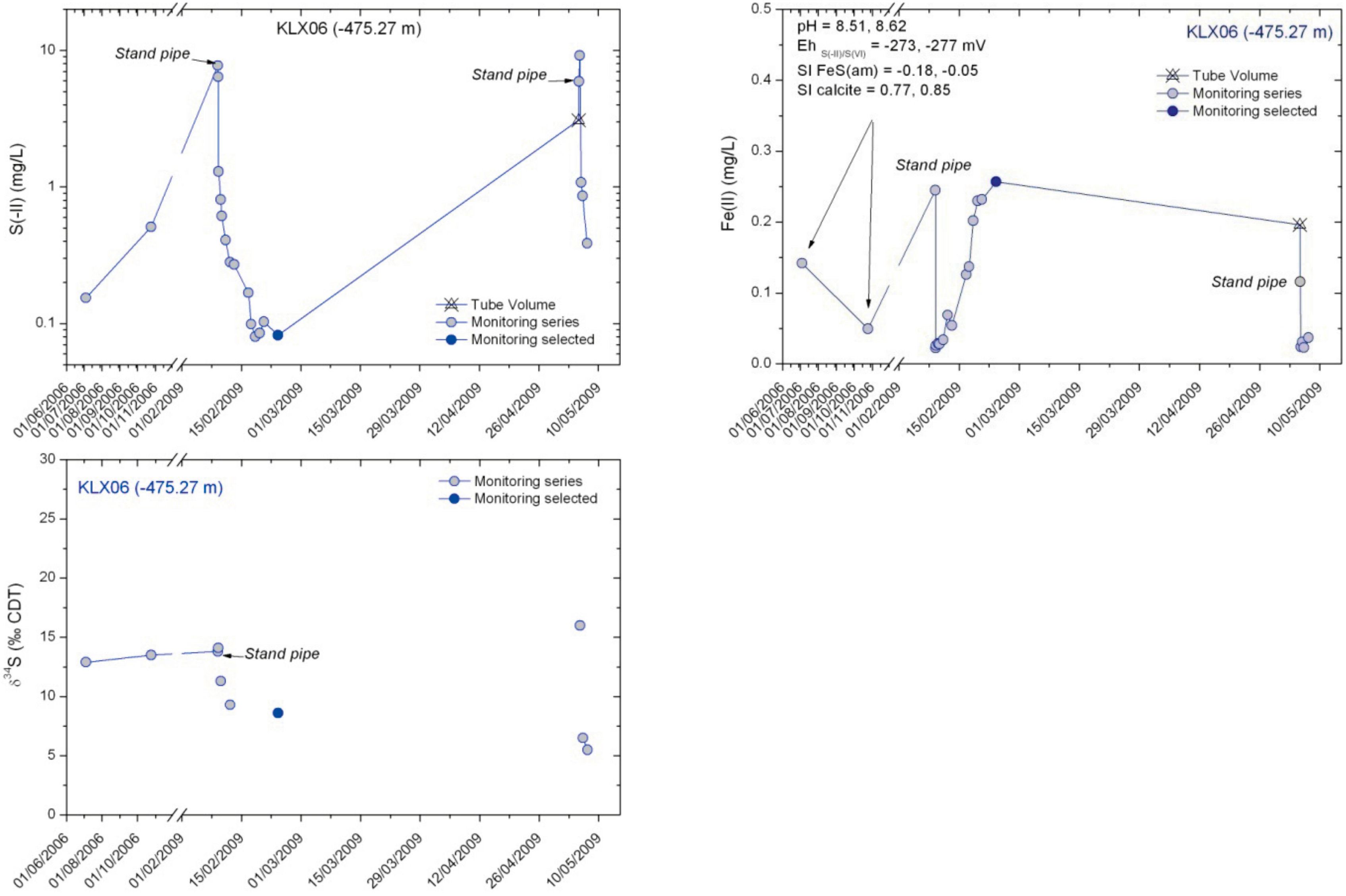

Figure A-29. *Evolution with time for S(-II) and Fe(II), the FeS(am) and saturation indices and $\delta^{34}S$.*

BOREHOLE KLX07 (-569.69 masl)

pH = 7.34-7.87 (Field/surface measurements)
Eh ≈ -210 mV (Calculated using the S(-II)/S(VI) redox couple)

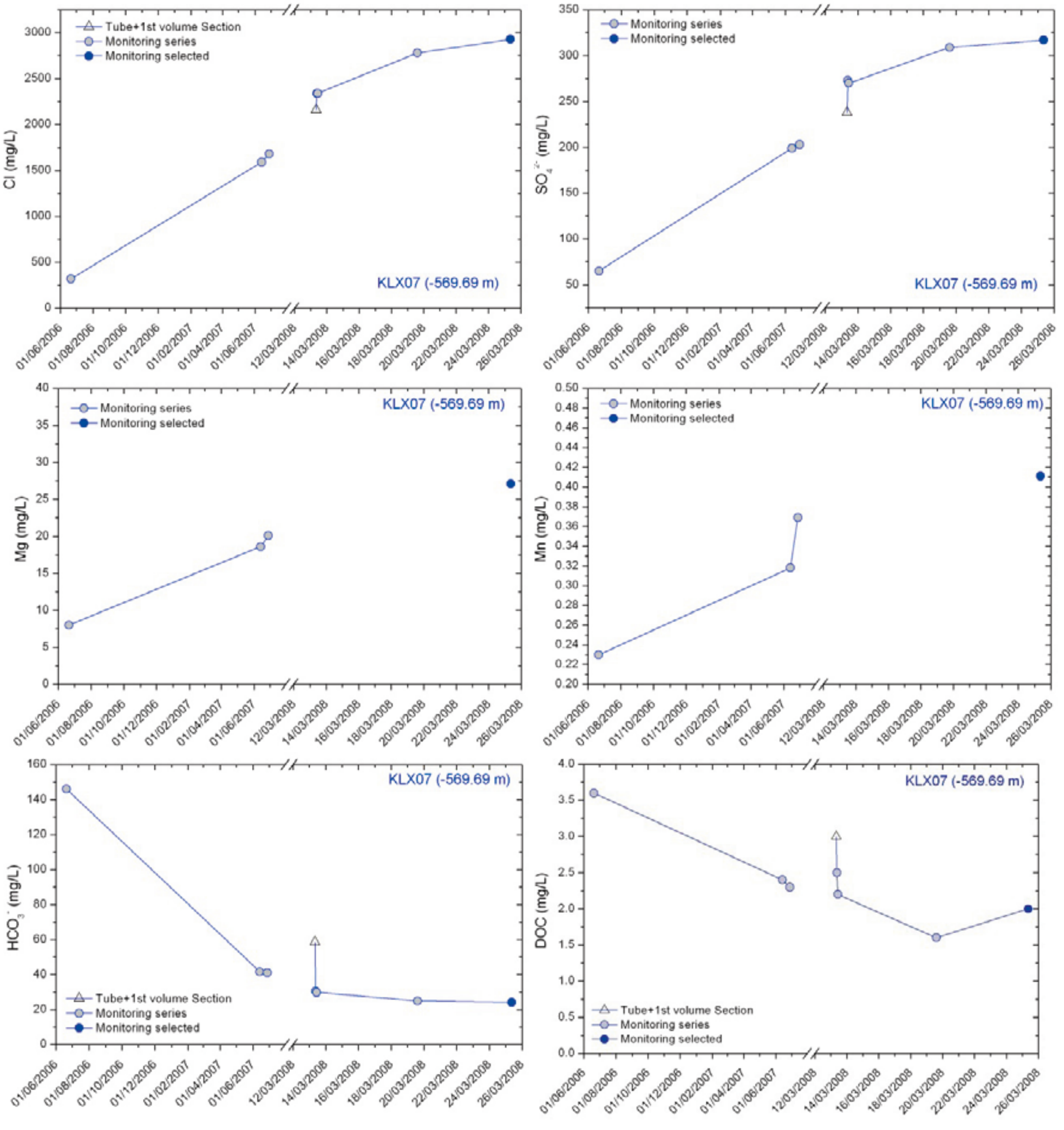

Figure A-30. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX07 (-569.69 masl)

Incomplete Chemical analysis

pH = 7.34-7.87 (Field/surface measurements)
Eh ≈ -210 mV (Calculated using the S(-II)/S(VI) redox couple)

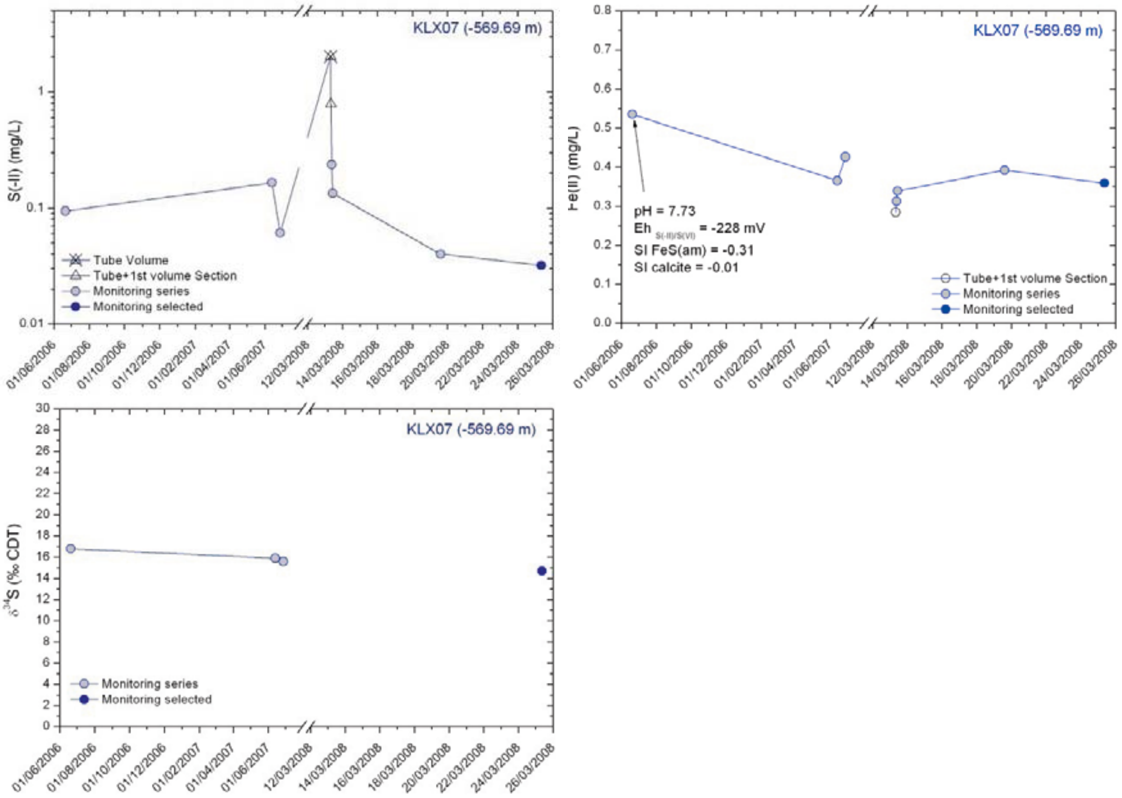

Figure A-31. *Evolution with time for S(-II), Fe(II and δ^{34}S.*

BOREHOLE KLX08 (-150.43 masl)

Chemmac measurements:
pH = 8.1
Eh = -235 mV

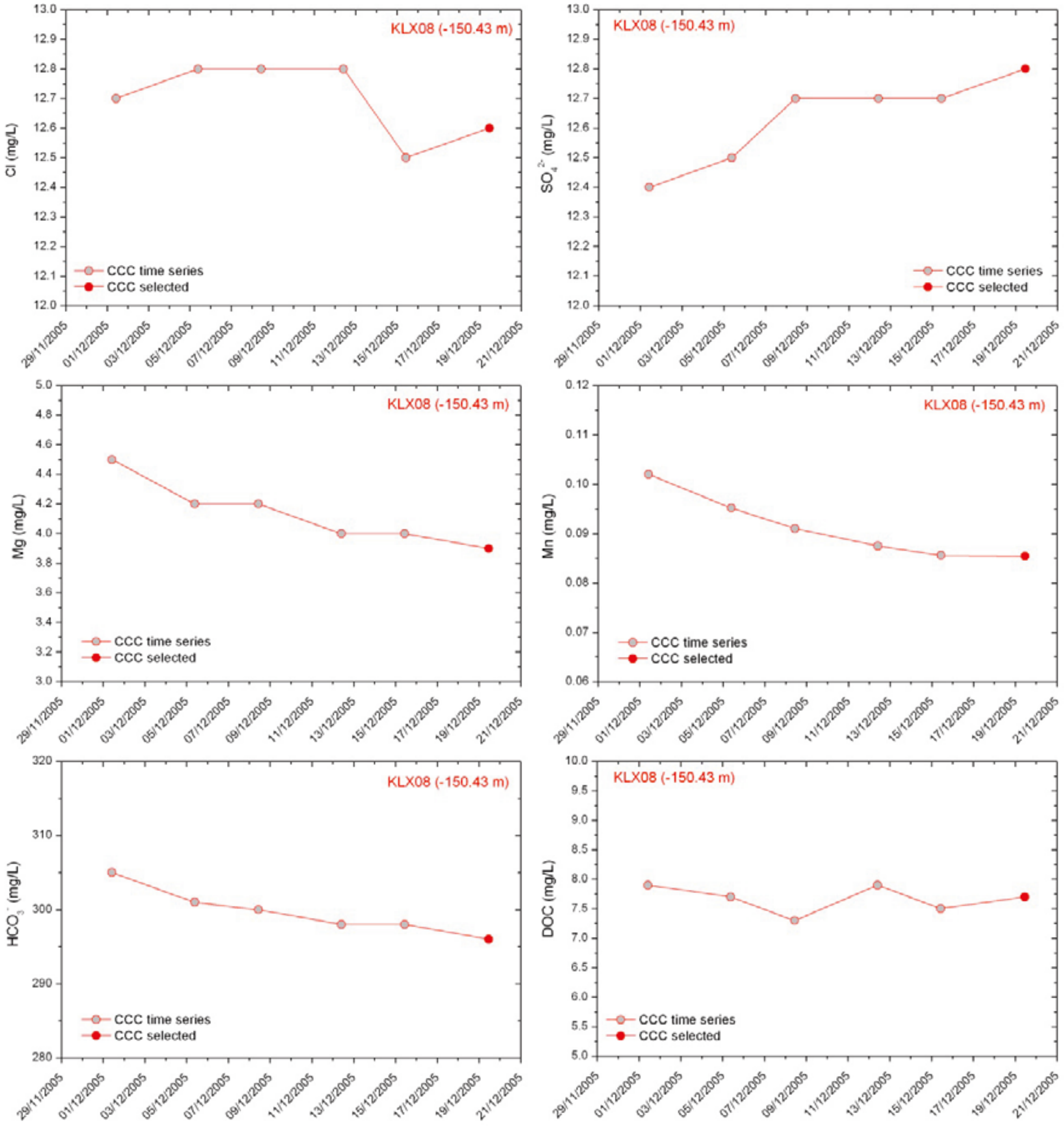

Figure A-32. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX08 (-150.43 masl)

Chemmac measurements:
pH = 8.1
Eh = -235 mV

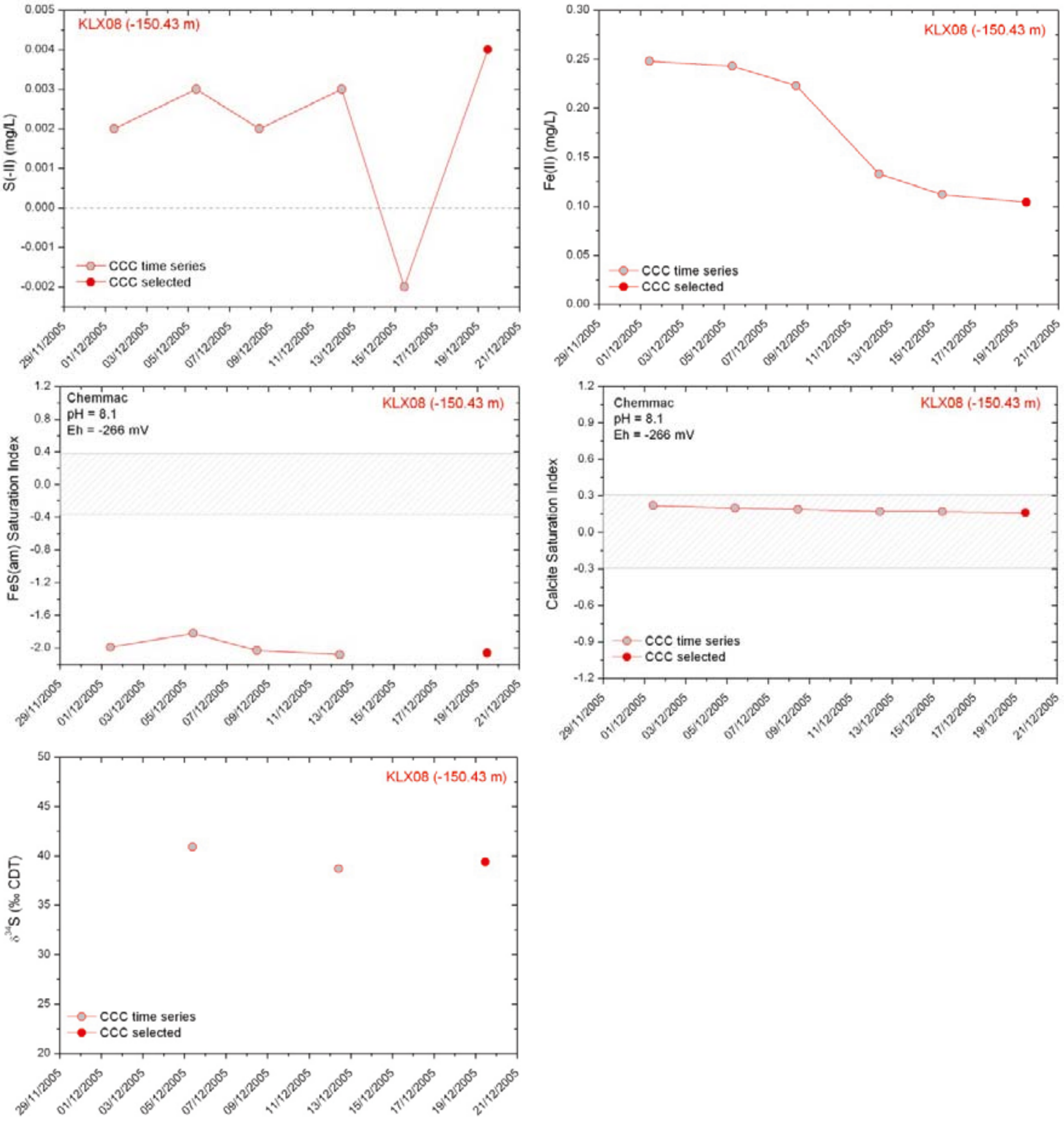

Figure A-33. *Evolution with time for S(-II), Fe(II), FeS(am), calcite saturation indices and* $\delta^{34}S$.

BOREHOLE KLX08 (-320.03 masl)

Chemmac measurements:
pH = 8
Eh = -245 mV

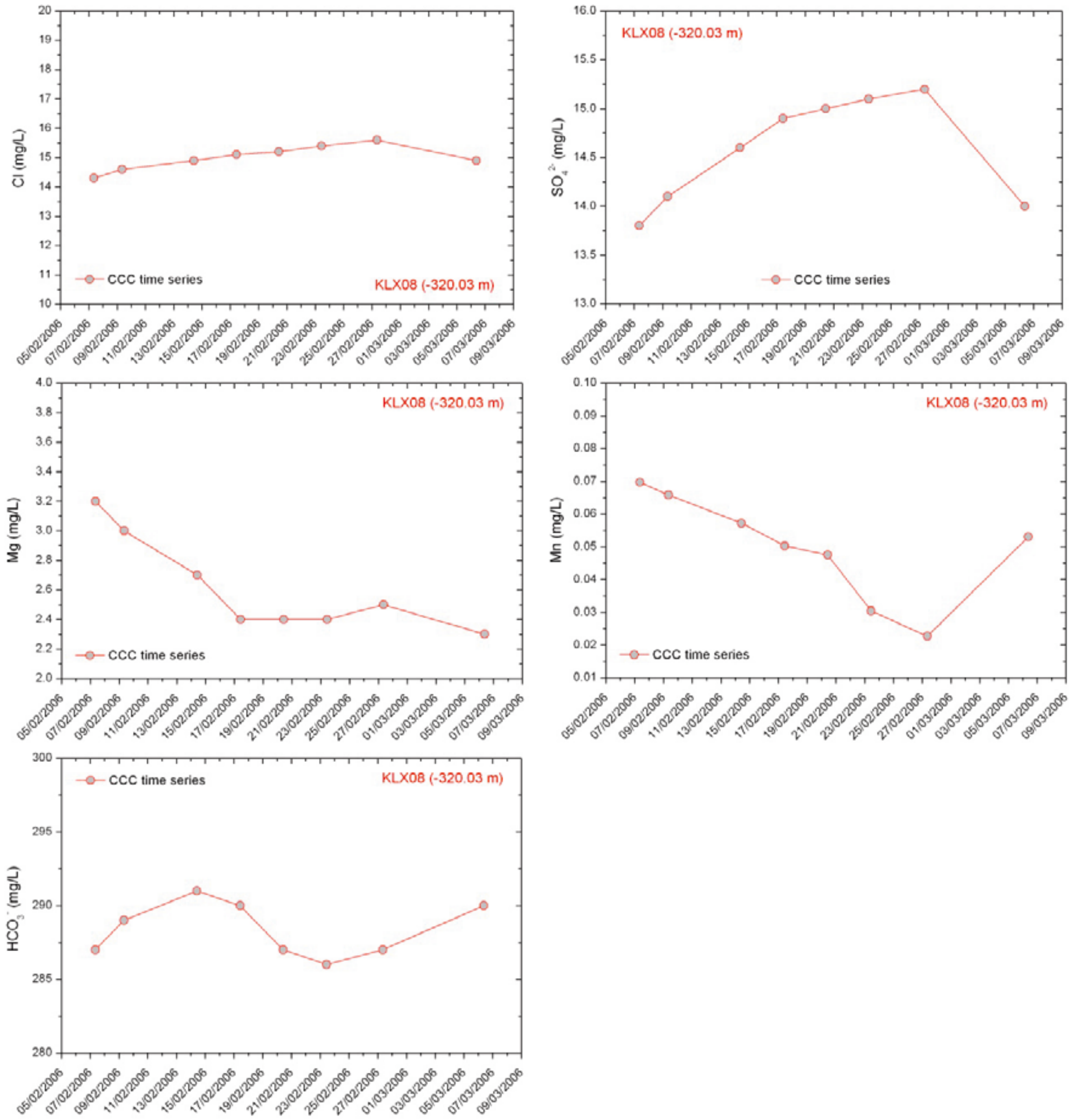

Figure A-34. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn and HCO_3^-.*

BOREHOLE KLX08 (-320.03 masl)

Chemmac measurements:
pH = 8
Eh = -245 mV

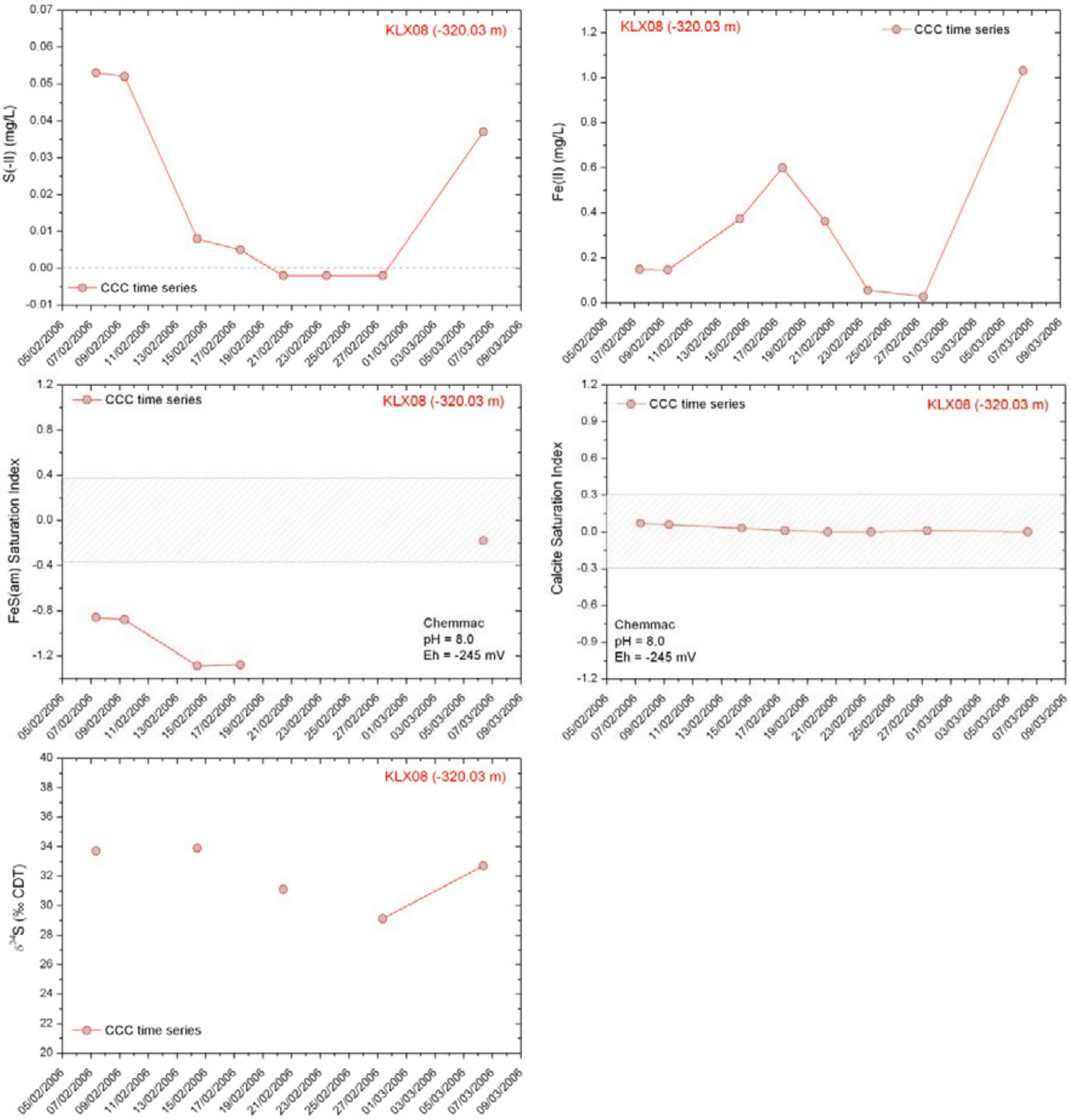

Figure A-35. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and* δ^{34}*S.*

BOREHOLE KLX08 (-390.71 masl)

pH = 7.6 (Chemmac measurement)
Eh ≈ -208 mV (Calculated using the S(-II)/S(VI) redox couple)

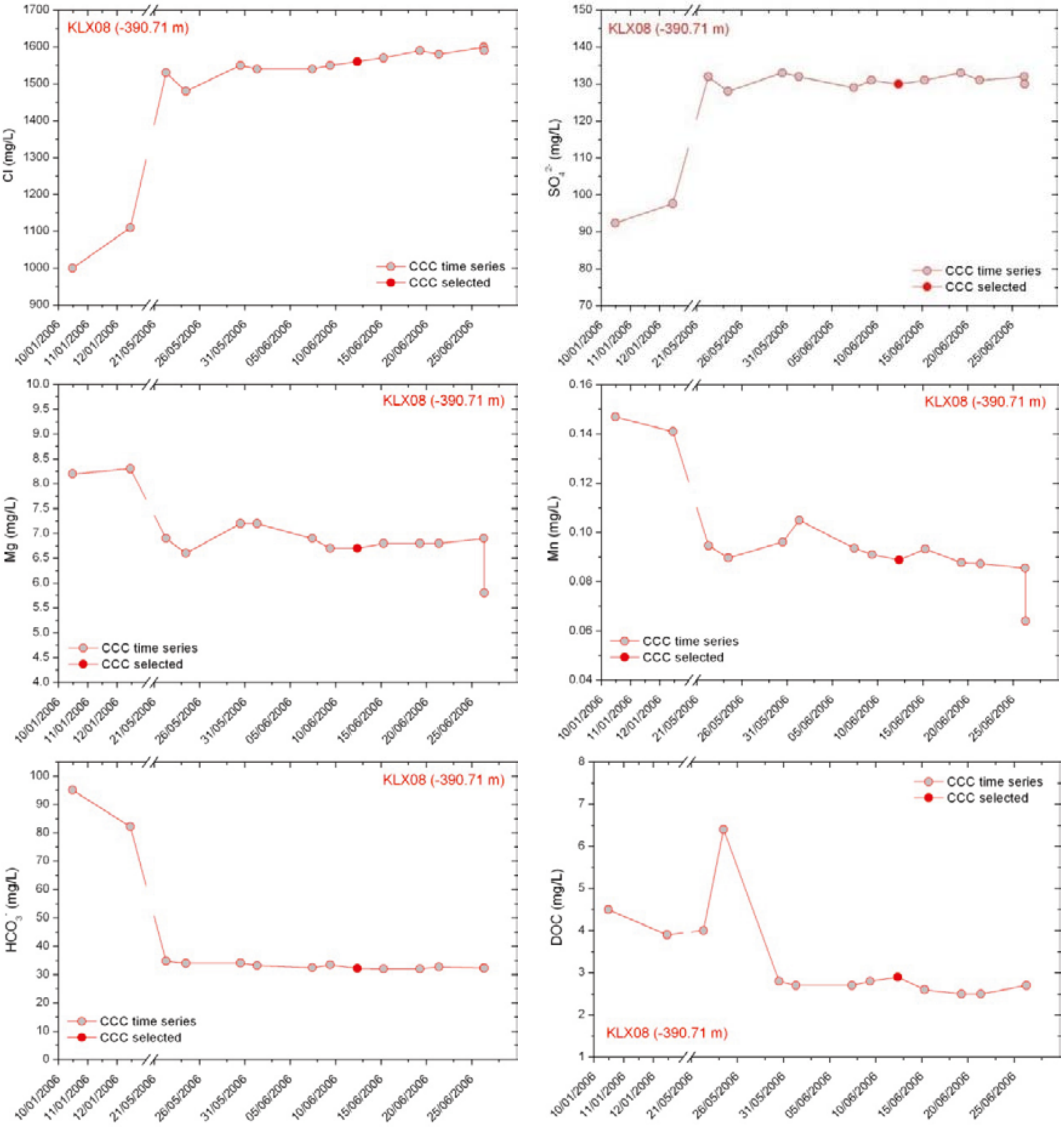

Figure A-36. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX08 (-390.71 masl)

pH = 7.6 (Chemmac measurement)
Eh ≈–208 mV (Calculated using the S(-II)/S(VI) redox couple)

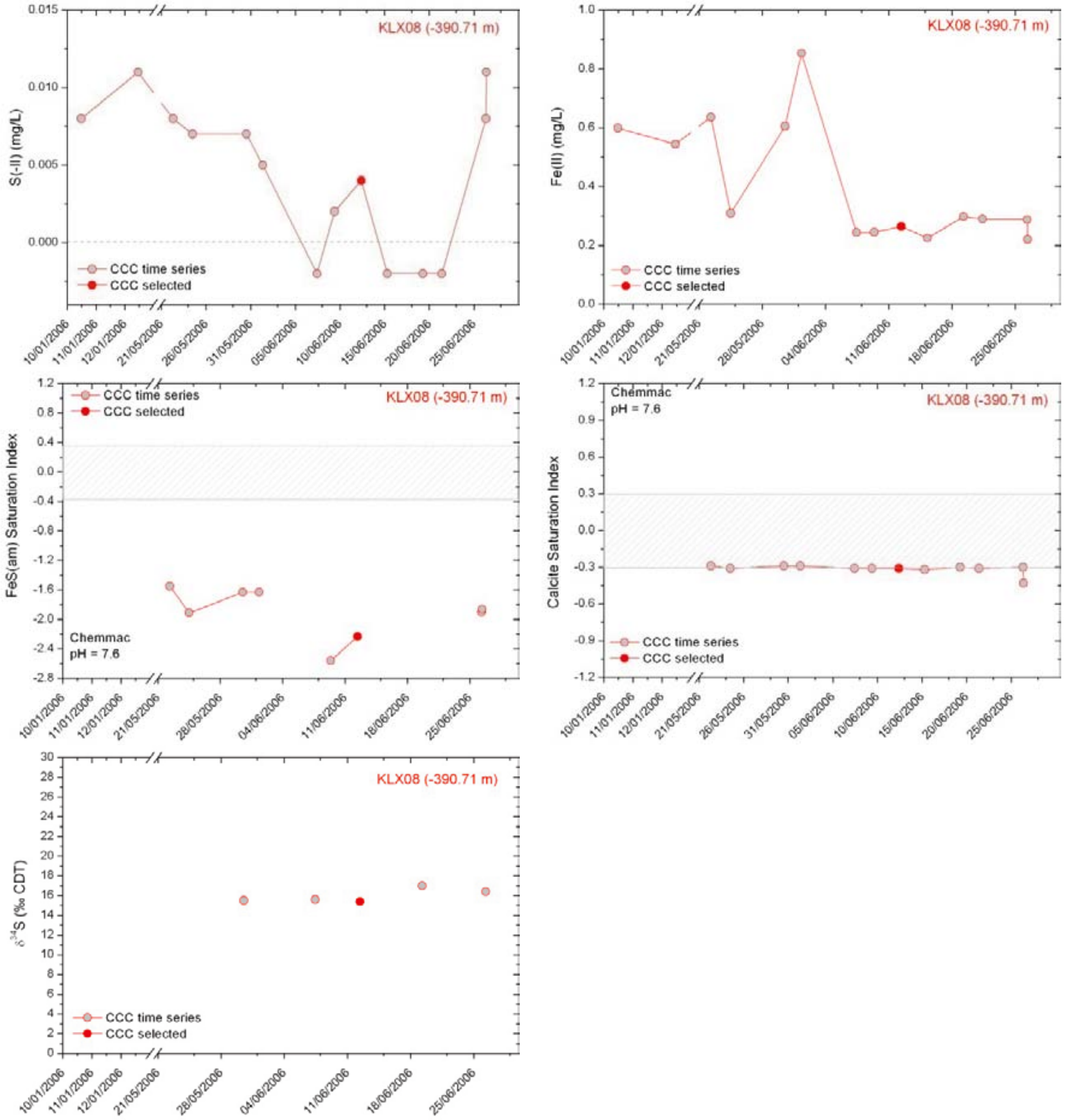

Figure A-37. Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and d^{34}S.

BOREHOLE KLX08 (-504.54 masl and -500.9 masl)

pH = 8.3 (Chemmac measurement, CCC) 6.11-8.3 (Field/surface measurements, Monitoring); Eh ≈ range -107 to -264 mV (Calculated using the S(-II)/S(VI) redox couple)

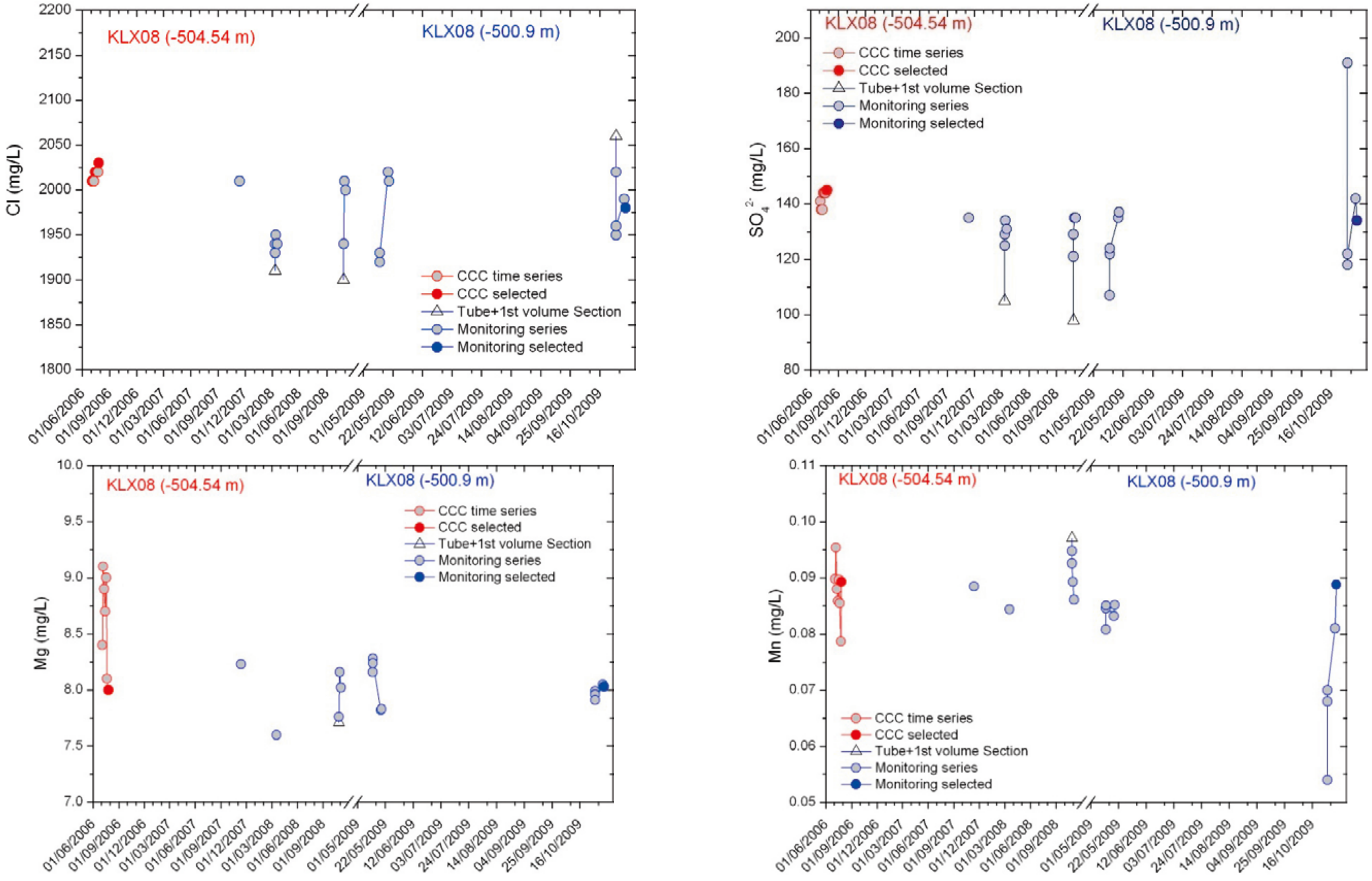

Figure A-38. *Evolution with time for Cl, SO_4^{2-}, Mg and Mn.*

BOREHOLE KLX08 (-504.54 masl and -500.9 masl)

pH = 8.3 (Chemmac measurement, CCC) 6.11-8.3 (Field/surface measurements, Monitoring); Eh ≈ range -107 to -264 mV (Calculated using the S(-II)/S(VI) redox couple)

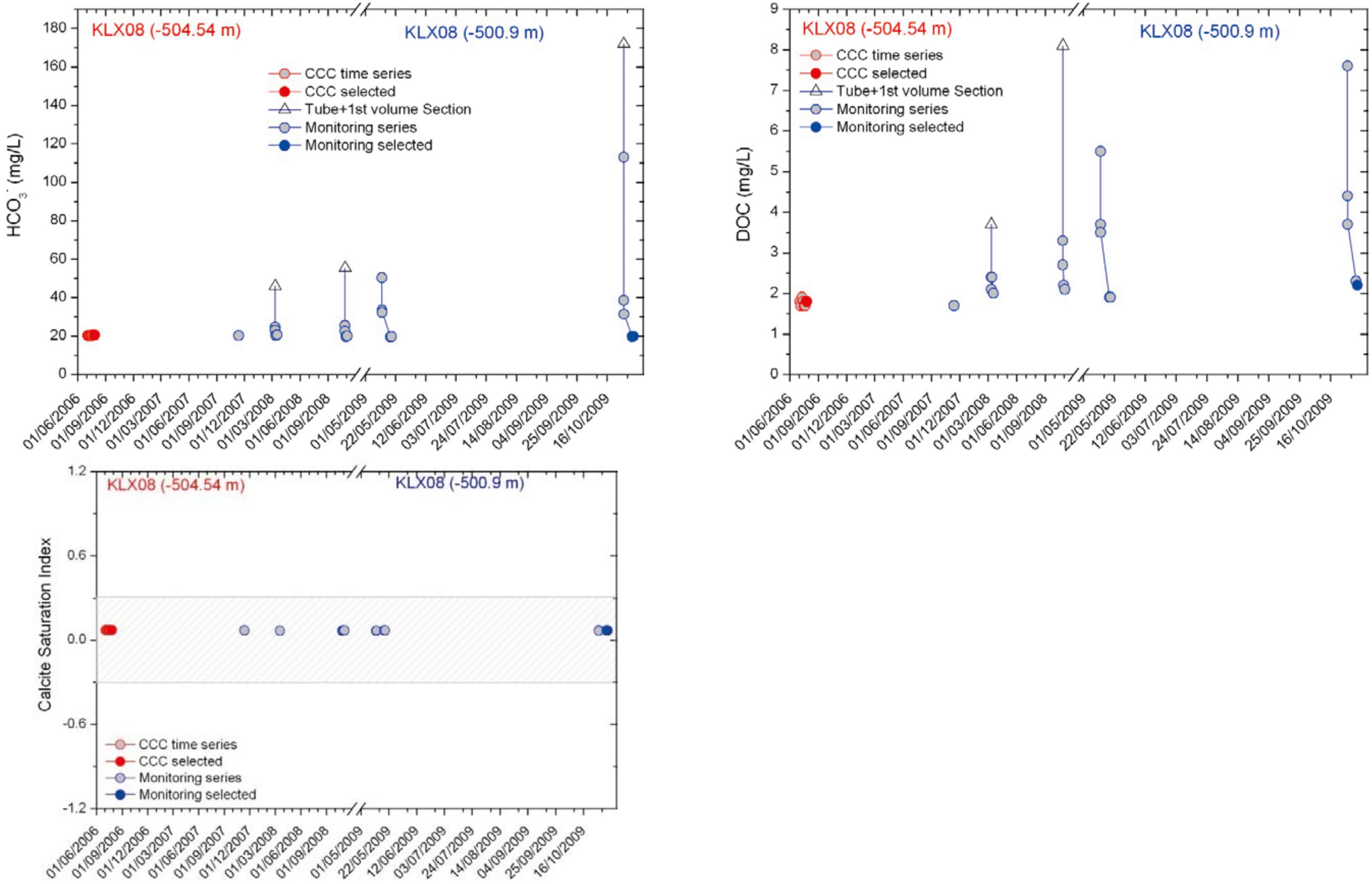

Figure A-39. *Evolution with time for HCO_3^-, DOC and the calcite saturation index.*

BOREHOLE KLX08 (-504.54 masl and -500.9 masl)

pH = 8.3 (Chemmac measurement, CCC) 6.11-8.3 (Field/surface measurements, Monitoring); Eh ≈ range -107 to -264 mV (Calculated using the S(-II)/S(VI) redox couple)

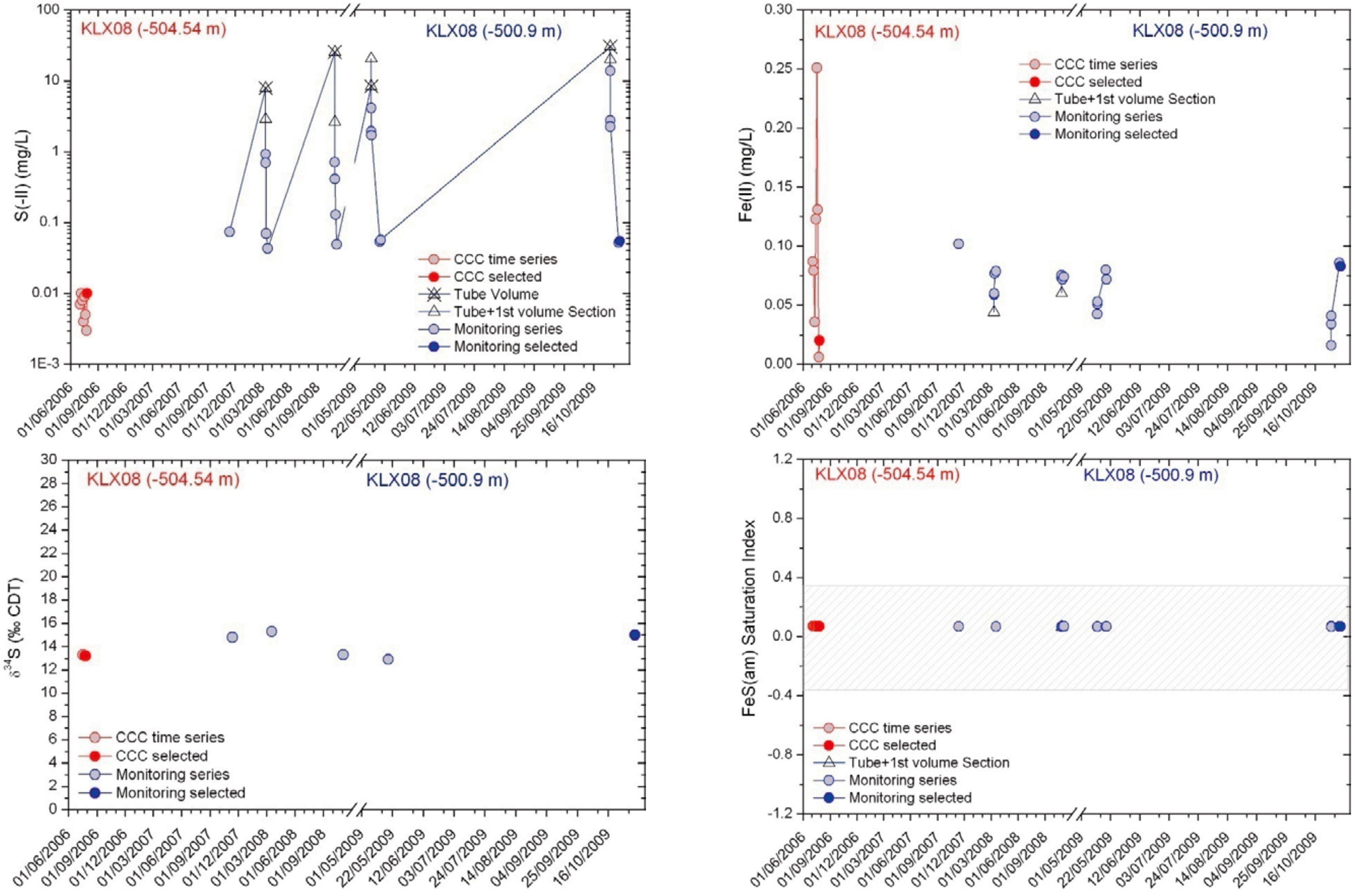

***Figure A-40**. Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and δ^{34}S.*

BOREHOLE KLX08 (-539.39 masl and -500.9 masl)

pH = 7.89-8.46 (Field/surface measurements)
Eh ≈ -241 mV (Calculated using the S(-II)/S(VI) redox couple)

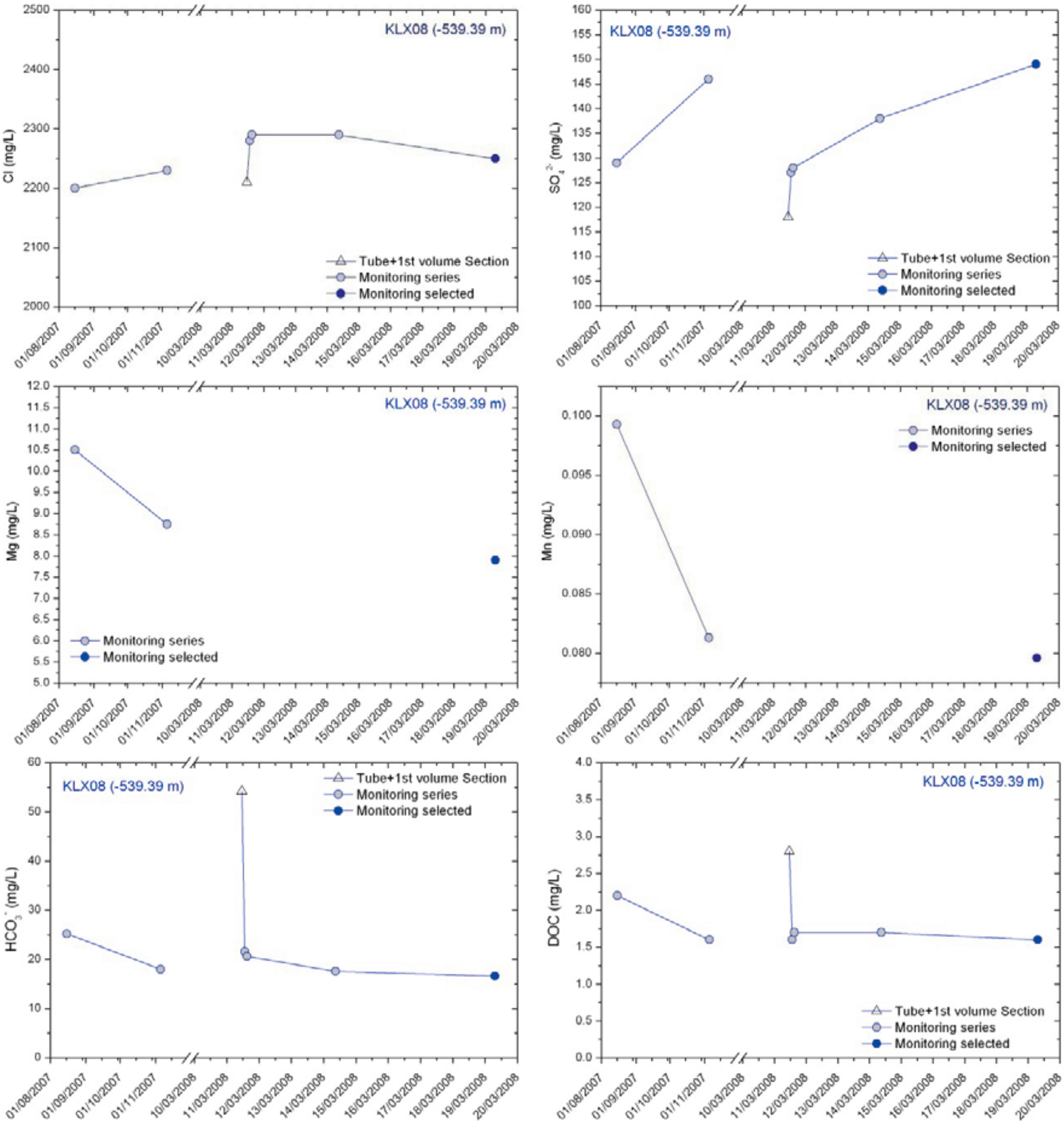

Figure A-41. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX08 (-539.39 masl and -500.9 masl)

pH = 7.89-8.46 (Field/surface measurements)
Eh ≈ –241 mV (Calculated using the S(-II)/S(VI) redox couple)

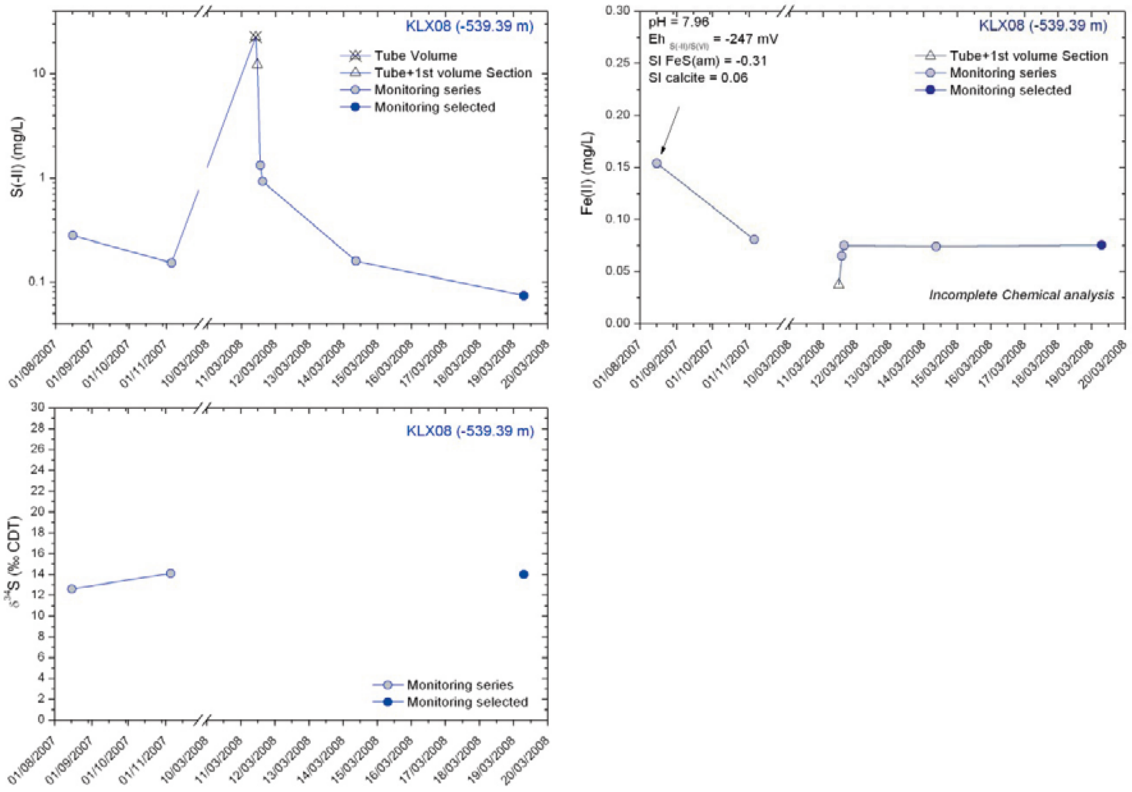

__Figure A-42.__ Evolution with time for S(-II), Fe(II) and δ^{34}S.

BOREHOLE KLX10 (-338.43 masl)

pH = 7.49-8.48 (Field/surface measurements); Eh ≈ range -200 to -308 mV (Calculated using the S(-II)/S(VI) redox couple)

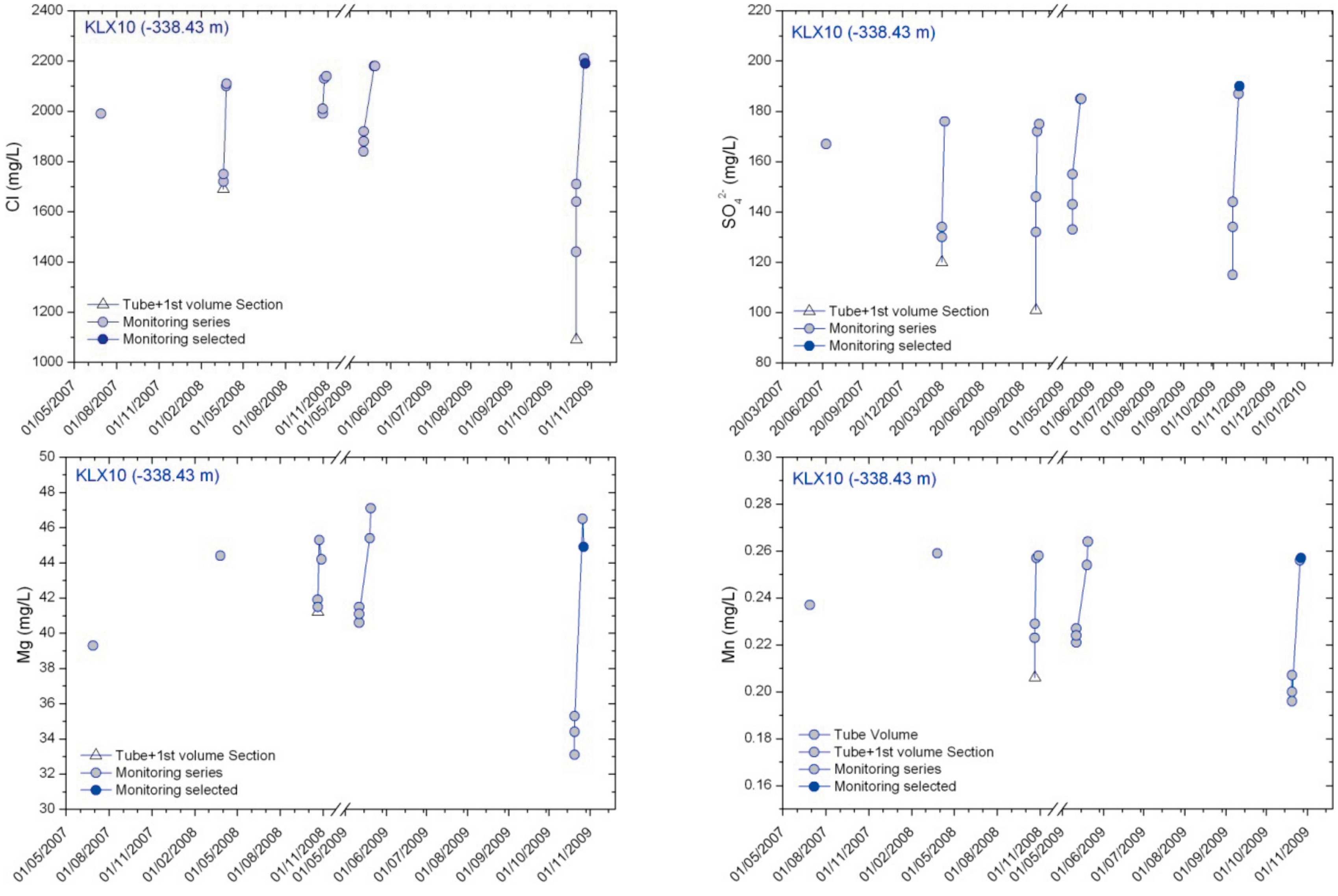

Figure A-43. *Evolution with time for Cl, SO_4^{2-}, Mg and Mn.*

BOREHOLE KLX10 (-338.43 masl)

pH = 7.498.48 (Field/surface measurements); Eh ≈ range -200 to -308 mV (Calculated using the S(-II)/S(VI) redox couple)

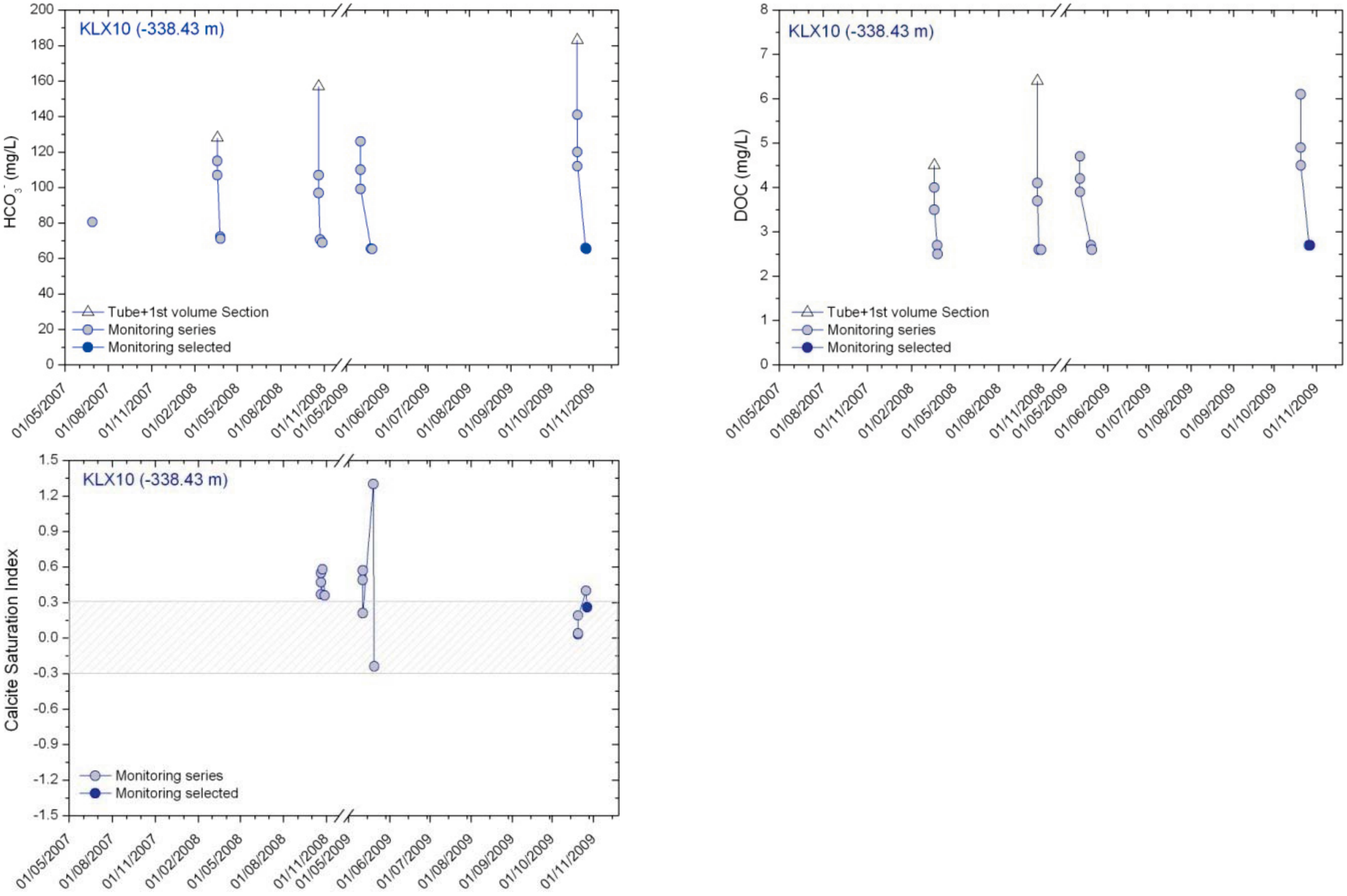

Figure A-44. *Evolution with time for* HCO_3^-*, DOC and the calcite saturation index.*

BOREHOLE KLX10 (-338.43 masl)

pH = 7.49-8.48 (Field/surface measurements); Eh ≈ range -200 to -308 mV (Calculated using the S(-II)/S(VI) redox couple)

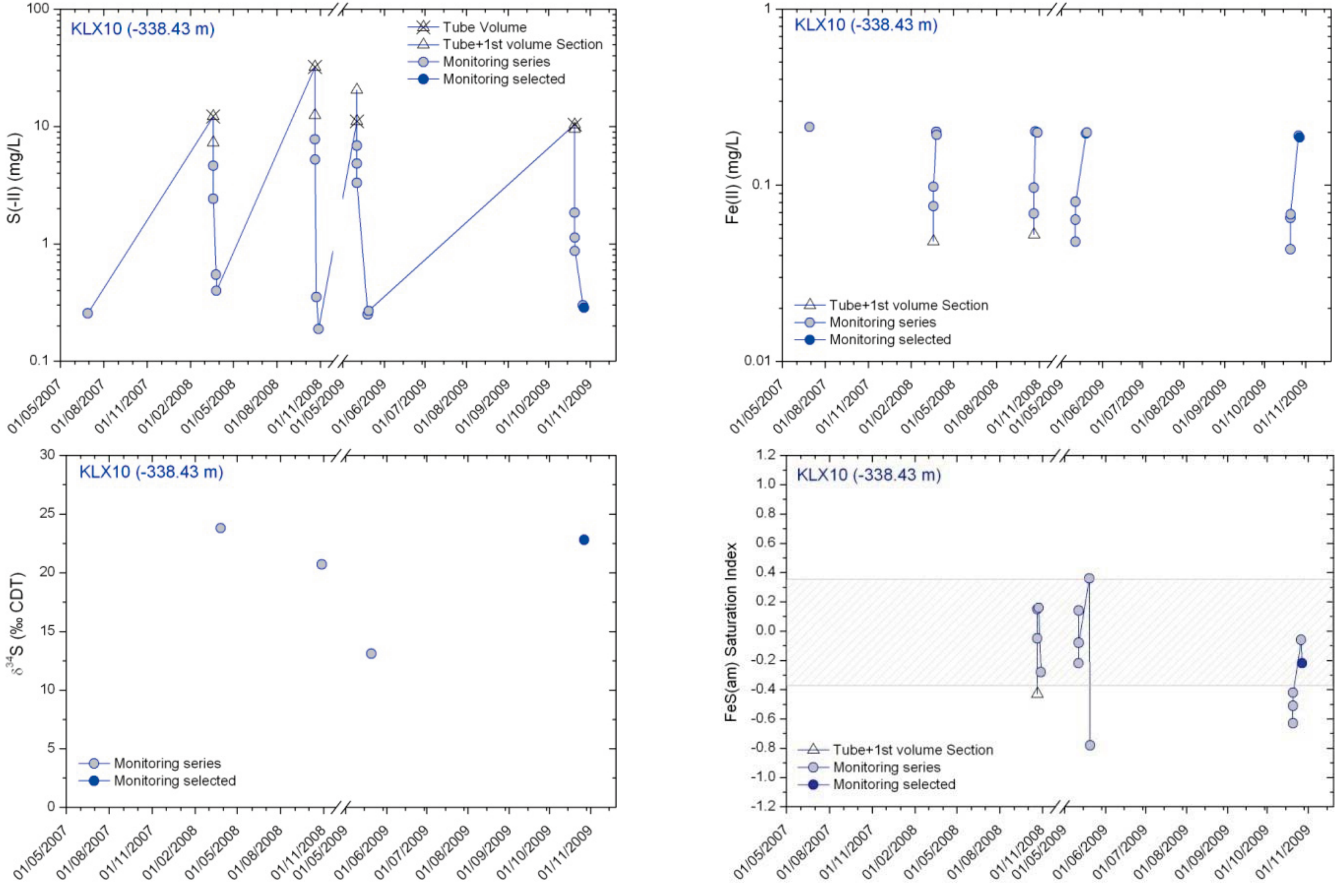

Figure A-45. *Evolution with time for S(-II), Fe(II), the FeS(am) saturation index and δ^{34}S.*

BOREHOLE KLX10 (-676.19 masl)

pH = 6.68-8.26 (Field/surface measurements); Eh ≈ range -213 to -259 mV (Calculated using the S(-II)/S(VI) redox couple)

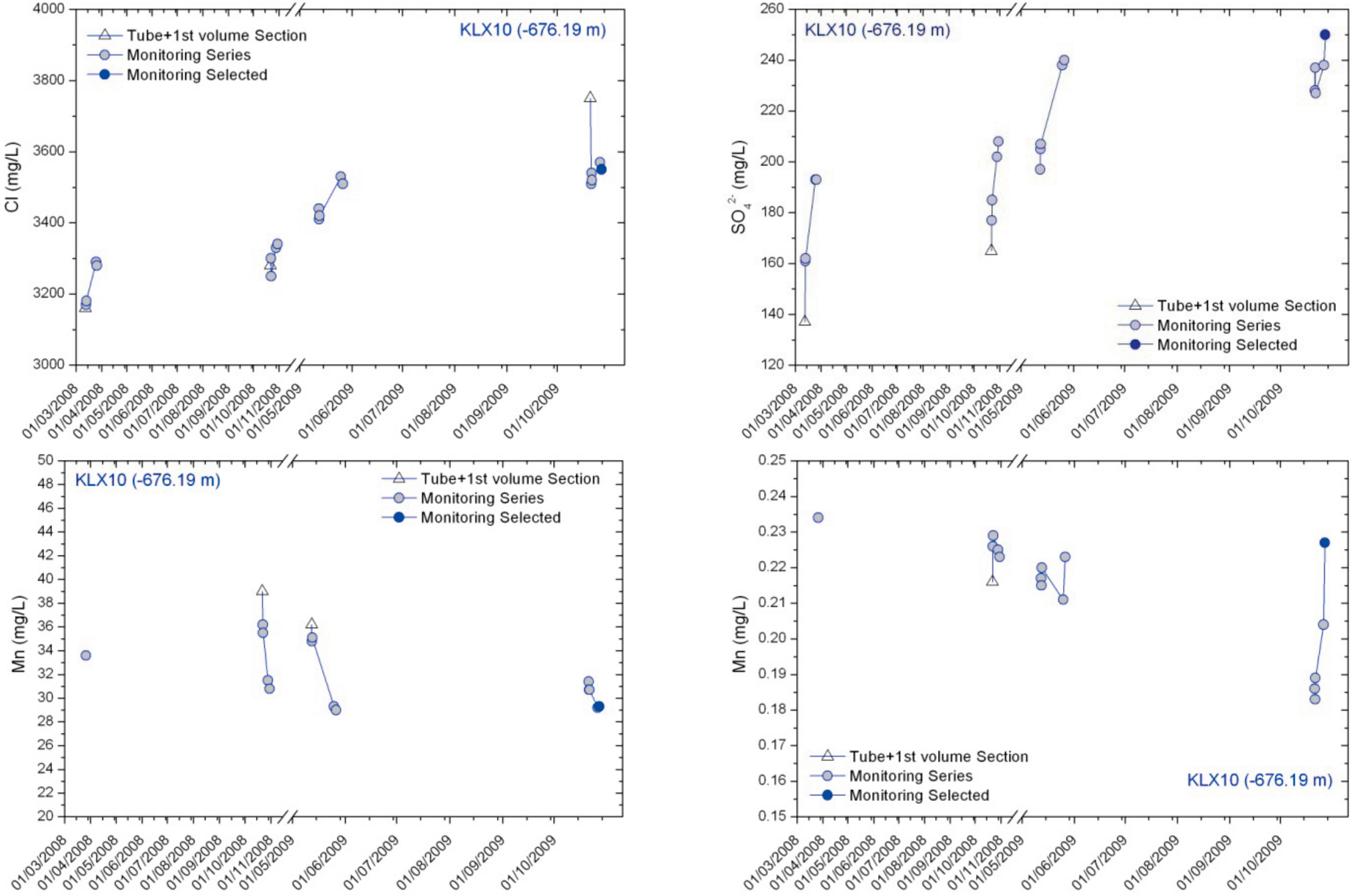

Figure A-46. *Evolution with time for Cl, SO$_4^{2-}$, Mg and Mn.*

BOREHOLE KLX10 (-676.19 masl)

pH = 6.68-8.26 (Field/surface measurements); Eh ≈ range -213 to -259 mV (Calculated using the S(-II)/S(VI) redox couple)

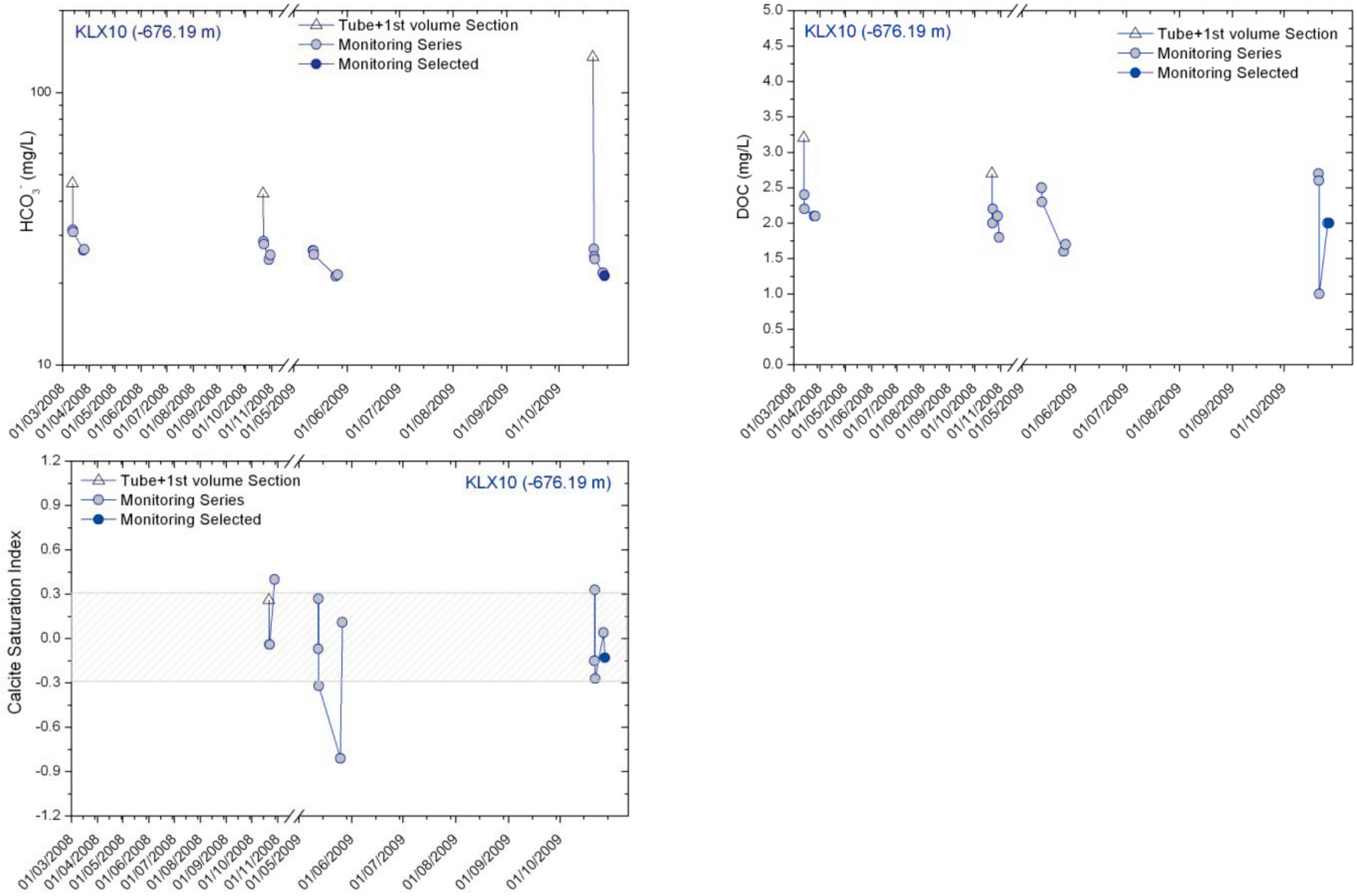

Figure A-47. Evolution with time for HCO_3^-, DOC and the calcite saturation index.

BOREHOLE KLX10 (-676.19 masl)

pH = 6.68-8.26 (Field/surface measurements); Eh ≈ range -213 to -259 mV (Calculated using the S(-II)/S(VI) redox couple)

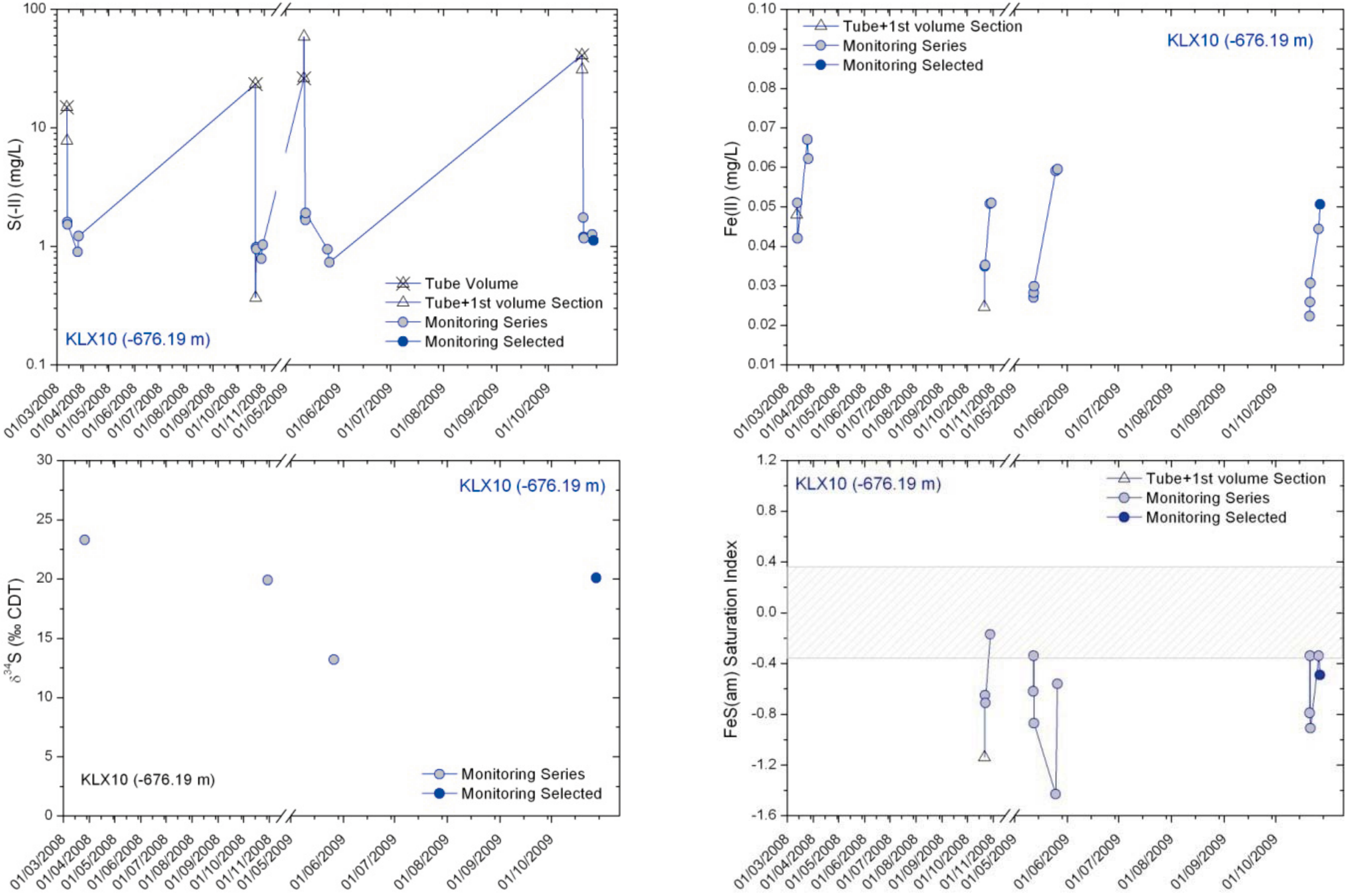

Figure A-48. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and* $\delta^{34}S$.

BOREHOLE KLX12 (-501.12 masl)

pH = 6.03-7.92 (Field/surface measurements); Eh ≈ range -78 to -228 mV (Calculated using the S(-II)/S(VI) redox couple)

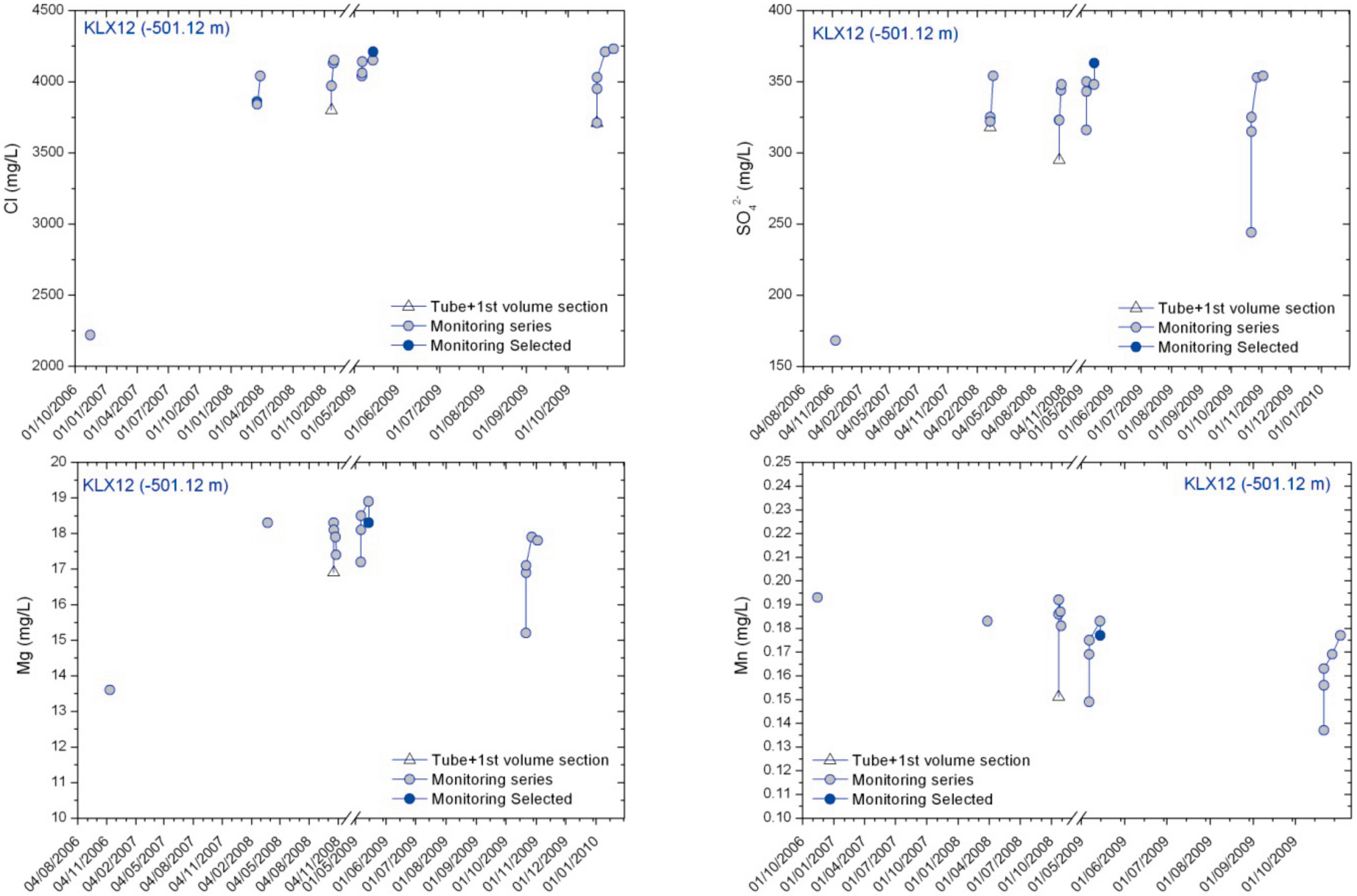

Figure A-49. *Evolution with time for Cl, SO_4^{2-}, Mg and Mn.*

BOREHOLE KLX12 (-501.12 masl)

pH = 6.03-7.92 (Field/surface measurements); Eh ≈ range -78 to -228 mV (Calculated using the S(-II)/S(VI) redox couple)

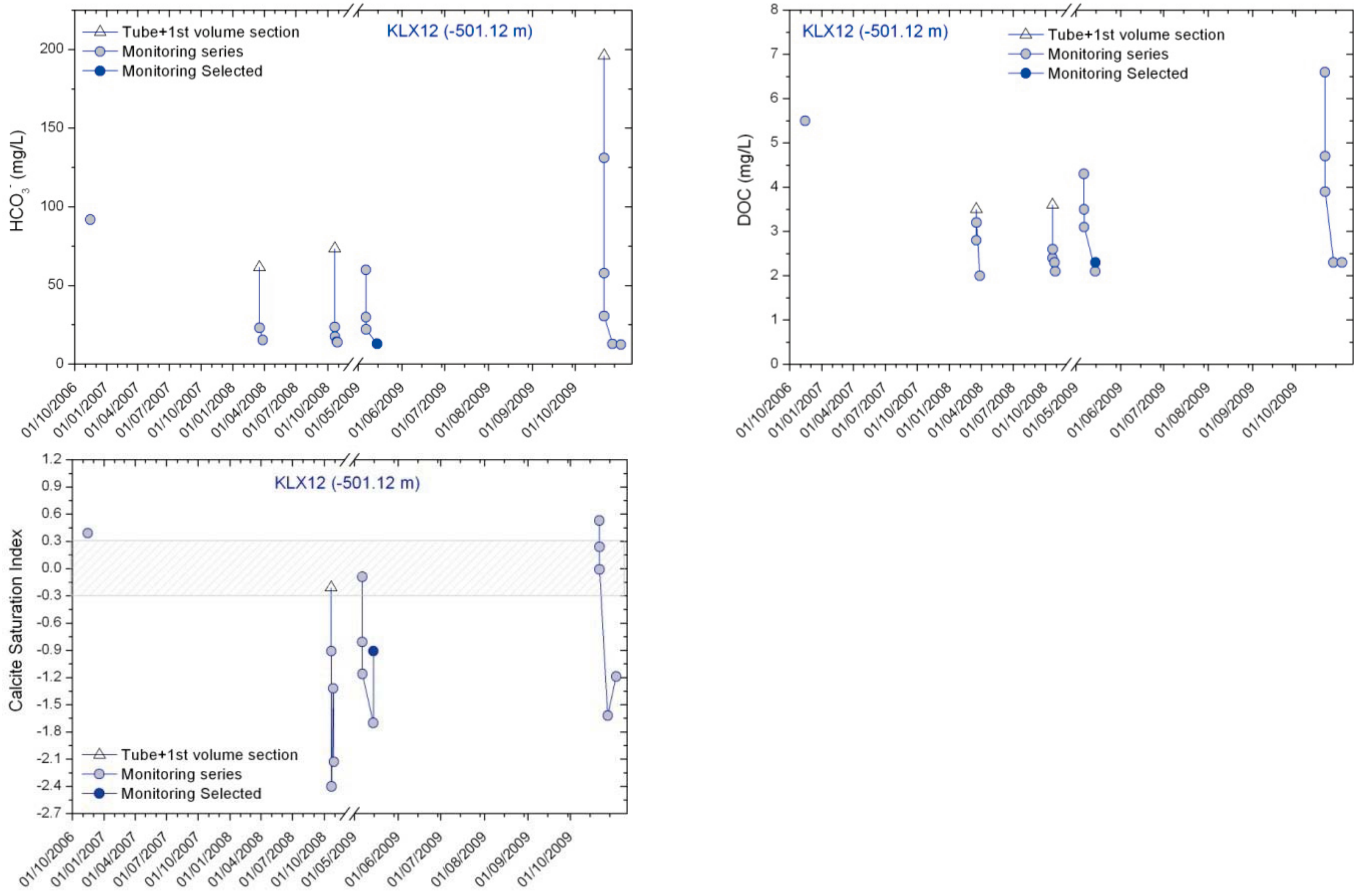

Figure A-50. *Evolution with time for HCO_3^-, DOC and the calcite saturation index.*

BOREHOLE KLX12 (-501.12 masl)

pH = 6.03-7.92 (Field/surface measurements); Eh ≈ range -78 to -228 mV (Calculated using the S(-II)/S(VI) redox couple)

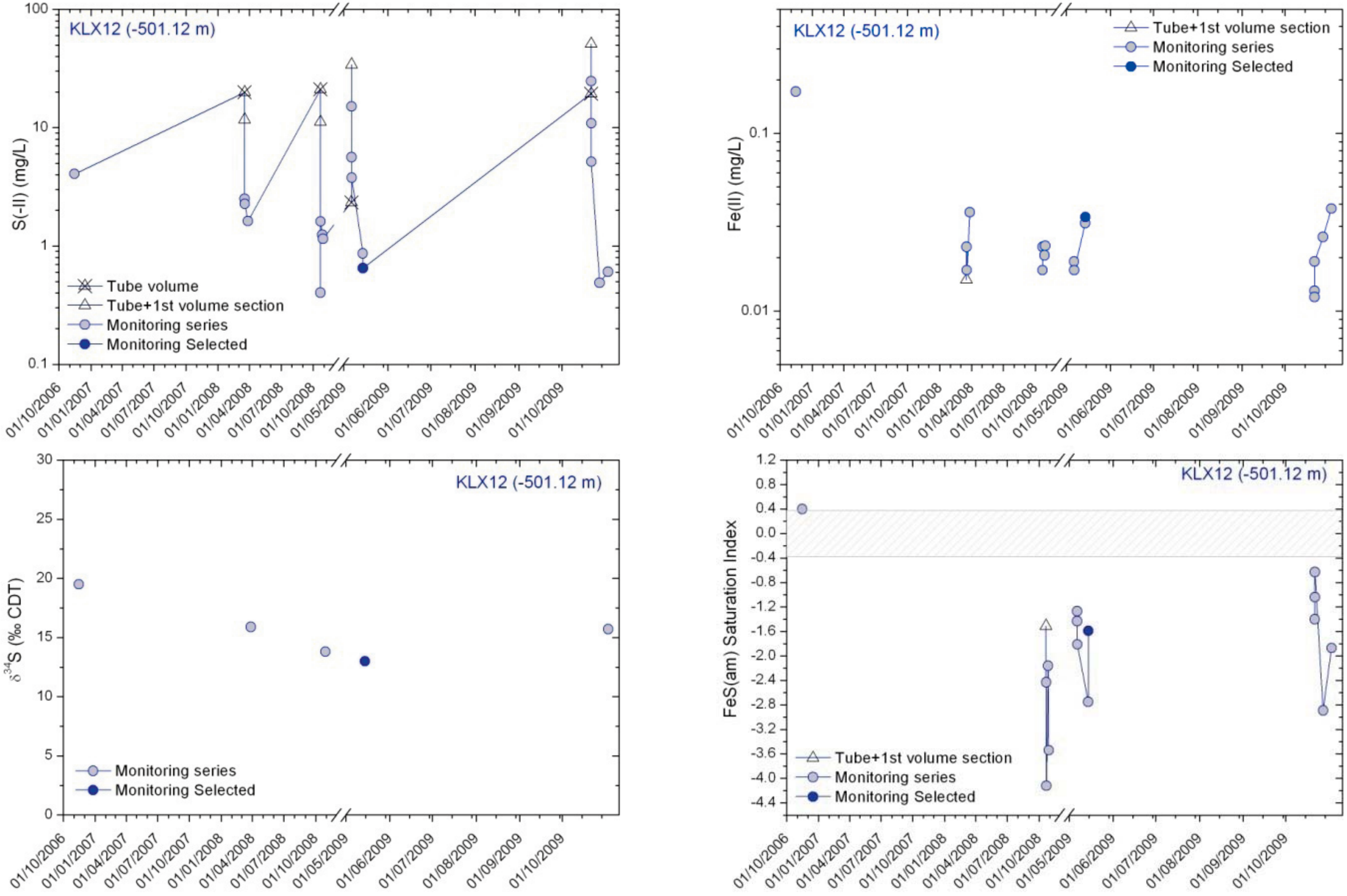

Figure A-51. *Evolution with time for S(-II), Fe(II), the FeS(am) and calcite saturation indices and* δ^{34}*S.*

BOREHOLE KLX13 (-408.01 masl)

Chemmac measurements:
pH = 8.45
Eh = -287 mV

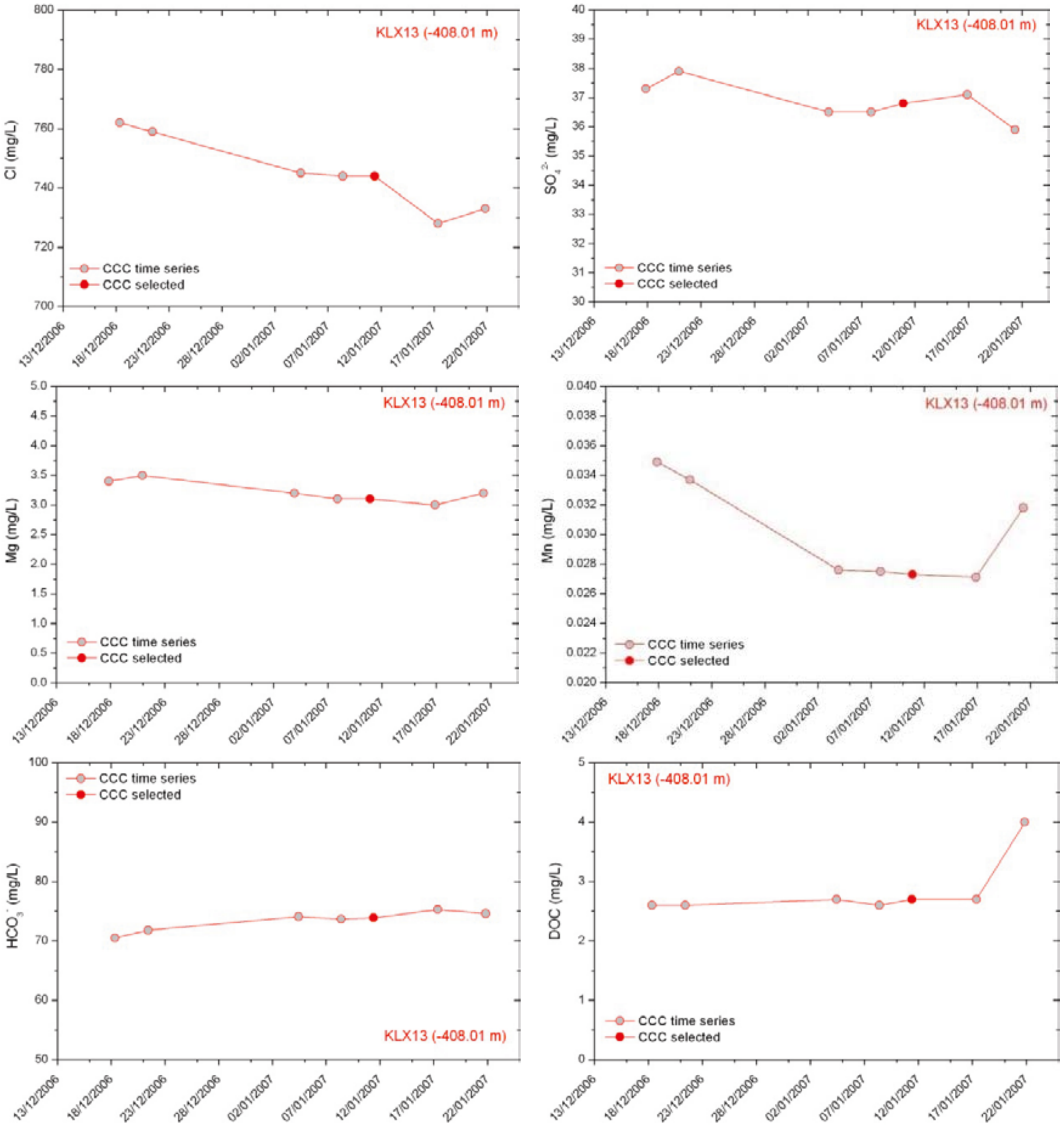

Figure A-52. Evolution with time for Cl, SO$_4^{2-}$, Mg, Mn, HCO$_3^-$ and DOC.

BOREHOLE KLX13 (-408.01 masl)

Chemmac measurements:
pH = 8.45
Eh = -287 mV

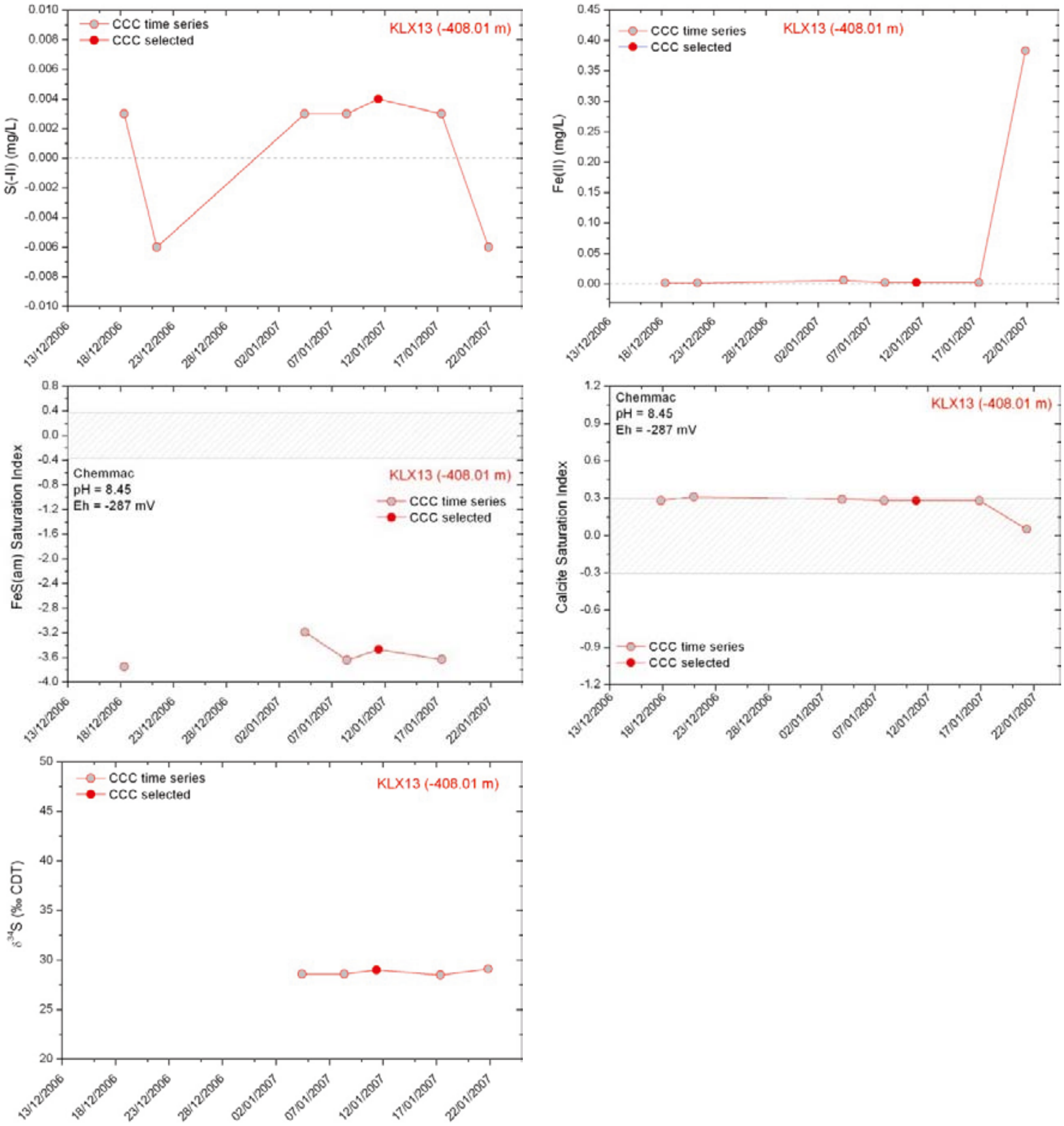

Figure A-53. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and* δ^{34}*S.*

BOREHOLE KLX13 (-474.99 masl)

Chemmac measurements:
pH = 8.2
Eh = -277 mV

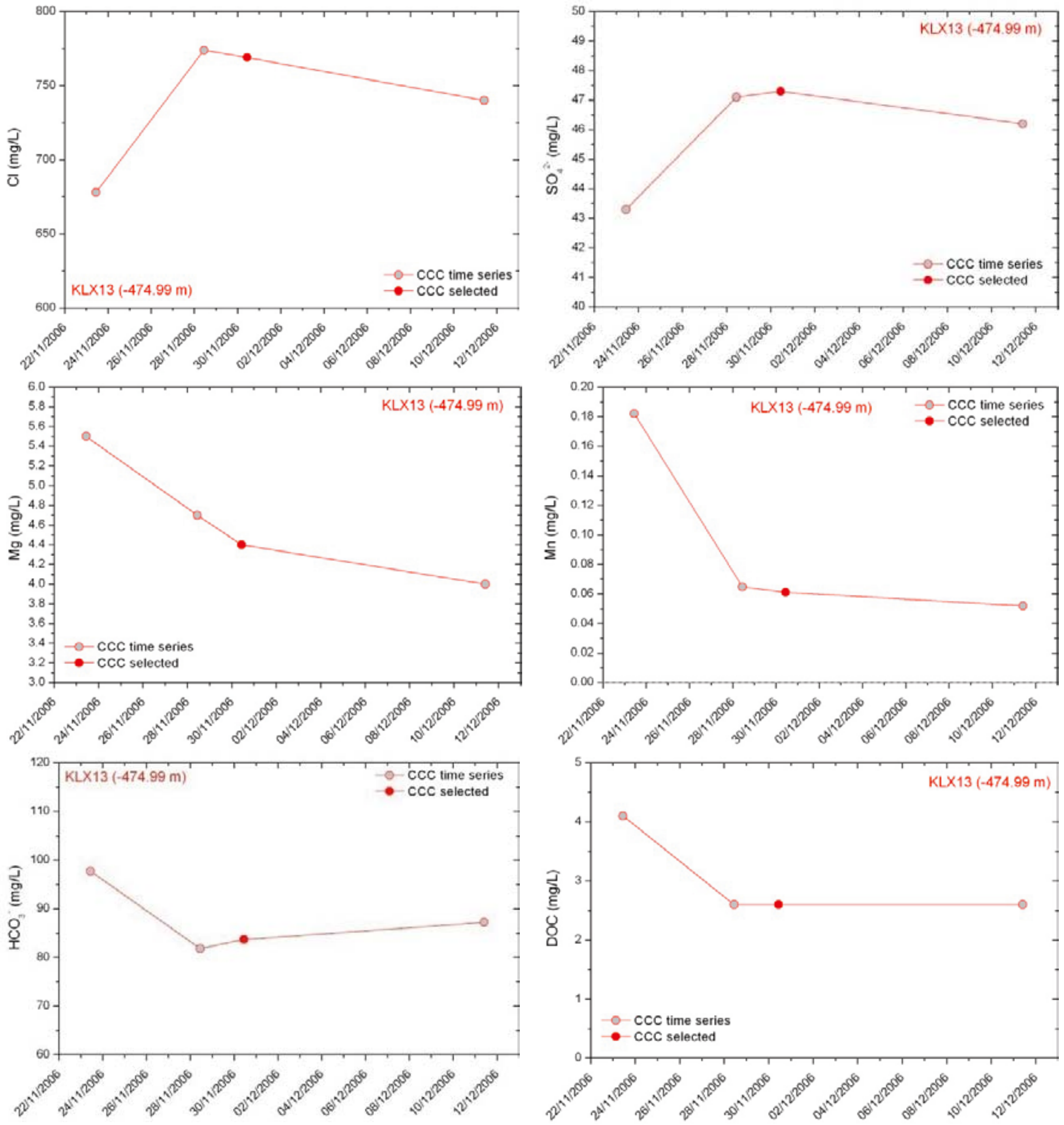

Figure A-54. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX13 (-474.99 masl)

Chemmac measurements:
pH = 8.2
Eh = -277 mV

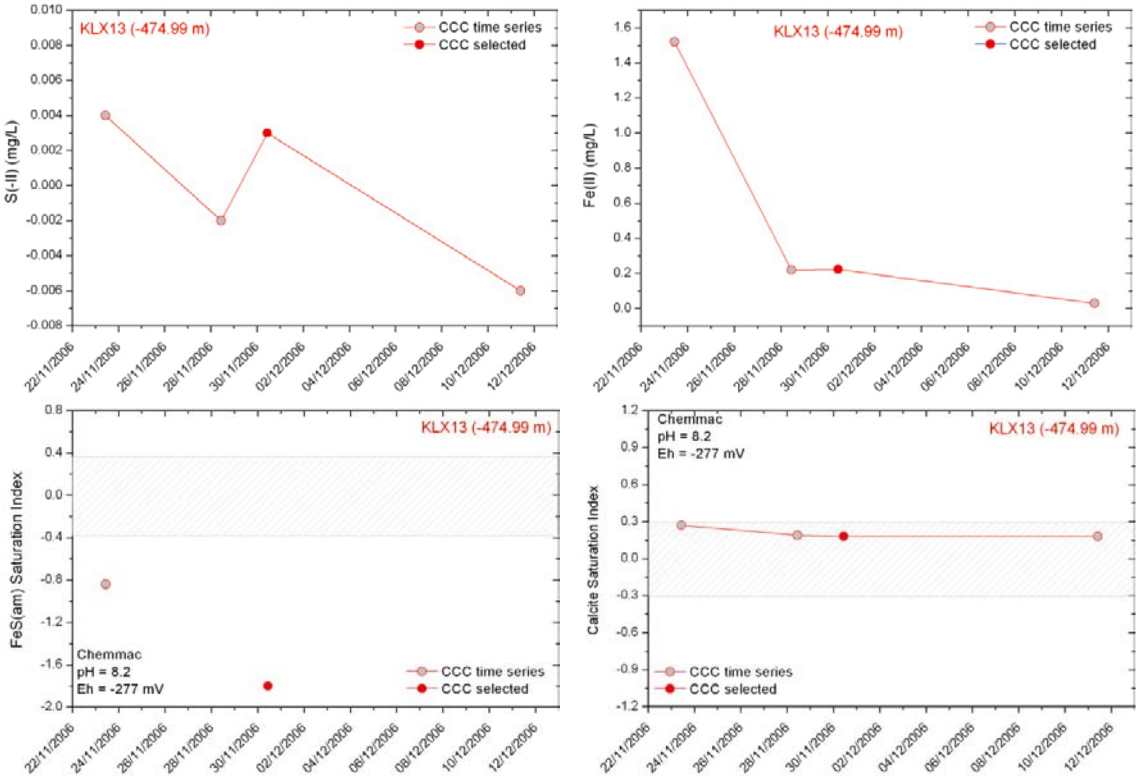

Figure A-55. *Evolution with time for S(-II), Fe(II) and the FeS(am) and calcite saturation indices.*

BOREHOLE KLX15 (-192.74 masl)

pH = 6.46-9.97 (Field/surface measurements); Eh ≈ range -128 to -346 mV (Calculated using the S(-II)/S(VI) redox couple)

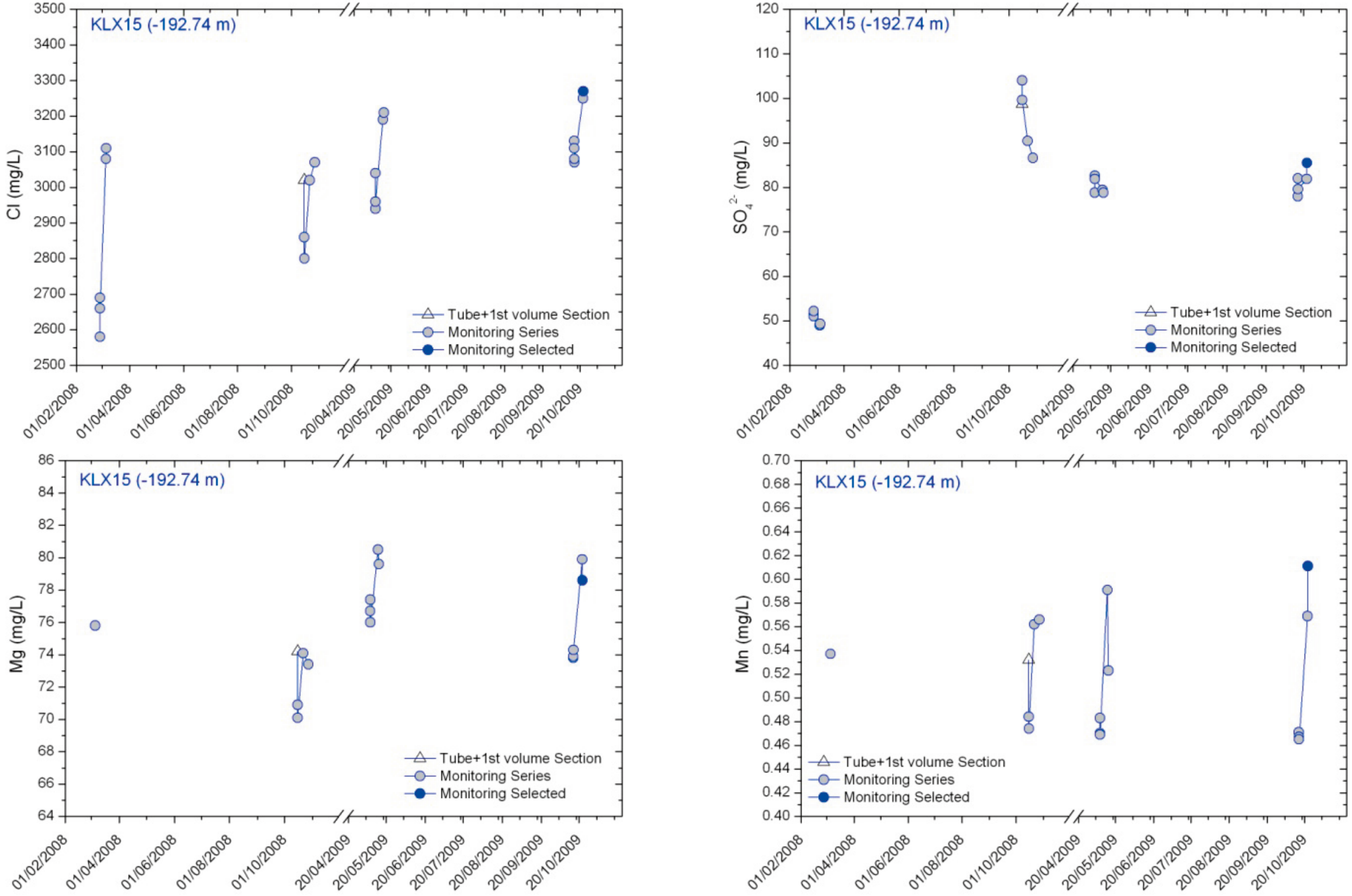

Figure A-56. Evolution with time for Cl, SO$_4^{2-}$, Mg and Mn.

BOREHOLE KLX15 (-192.74 masl)

pH = 6.46-9.97 (Field/surface measurements); Eh ≈ range -128 to -346 mV (Calculated using the S(-II)/S(VI) redox couple)

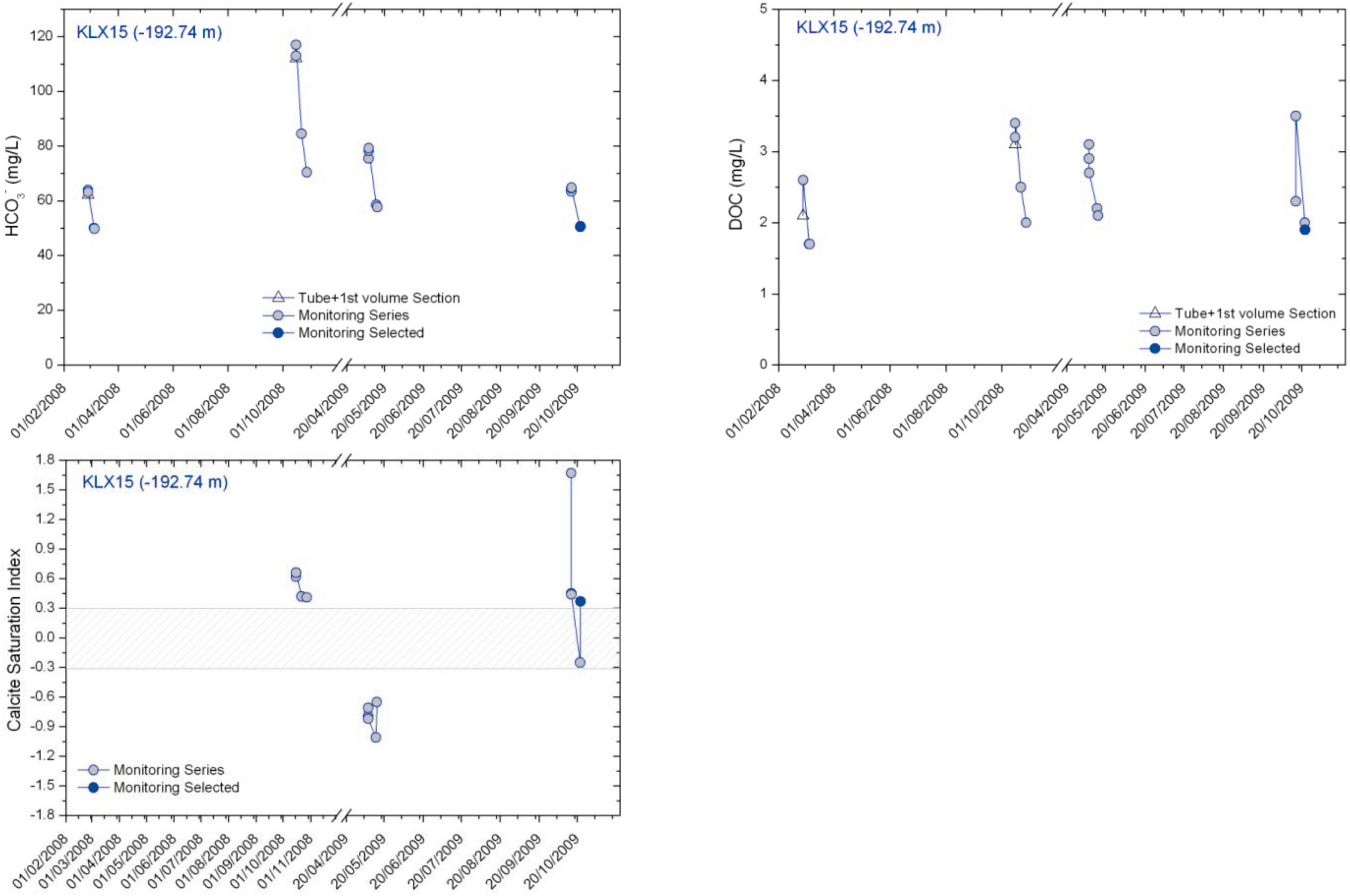

Figure A-57. *Evolution with time for HCO_3^-, DOC and the calcite saturation index.*

BORREHOLE KLX15 (-192.74 m)

pH = 6.46-9.97 (Field/surface measurements); Eh ≈ range -128 to -346 mV (Calculated using the S(-II)/S(VI) redox couple)

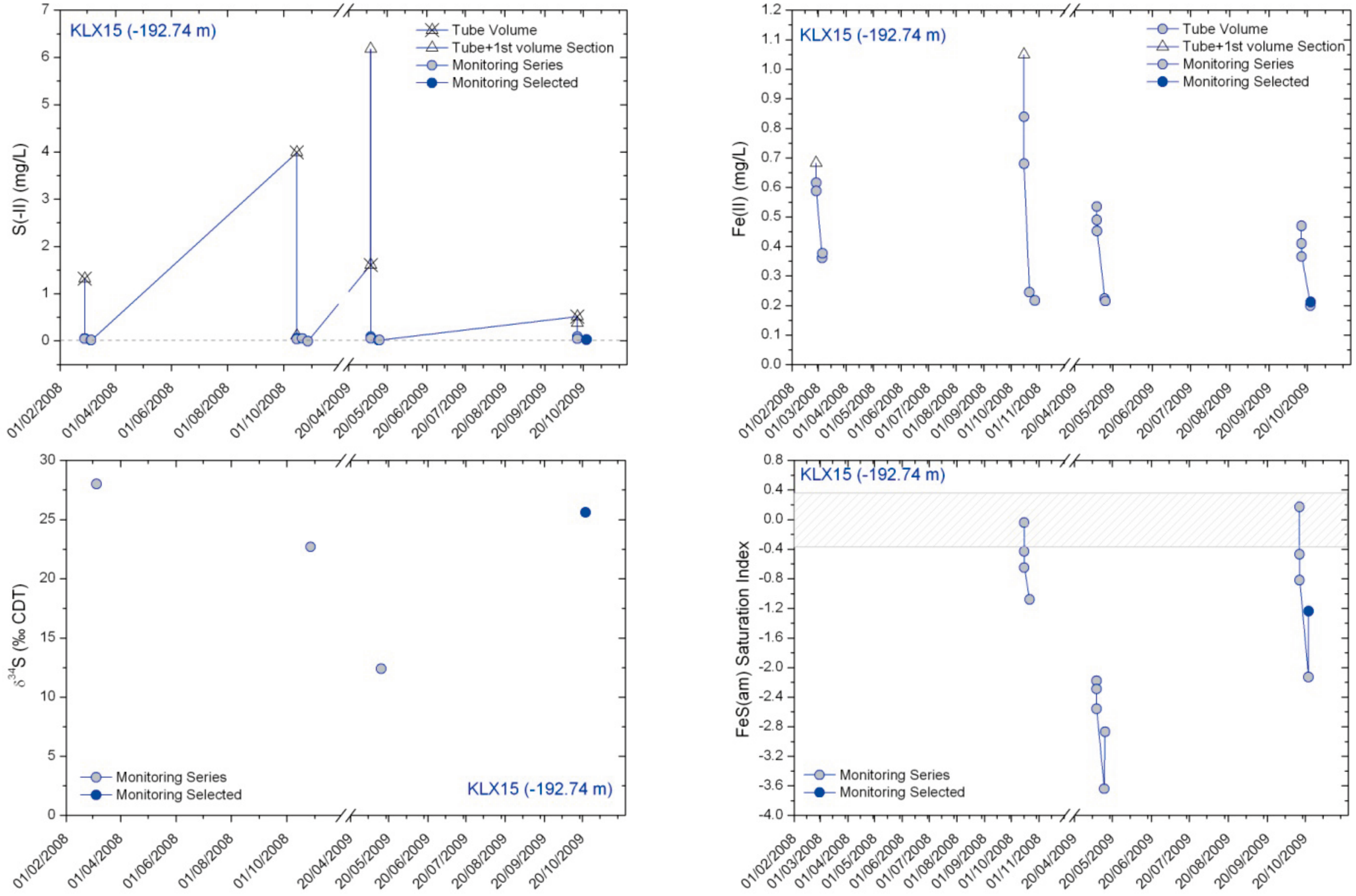

Figure A-58. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and* $\delta^{34}S$.

BOREHOLE KLX15 (-467.22 masl, CCC; 469.27 masl, Monitoring)

pH = 7.6 (Chemmac measurement; CCC); range 5.47-8.15 (Field/surface measurement; Monitoring)

Eh (Chemmac measurement; CCC) = -208.8 mV; Eh (Monitoring) ≈ range -71 to -238 mV (Calculated using the S(-II)/S(VI) redox couple)

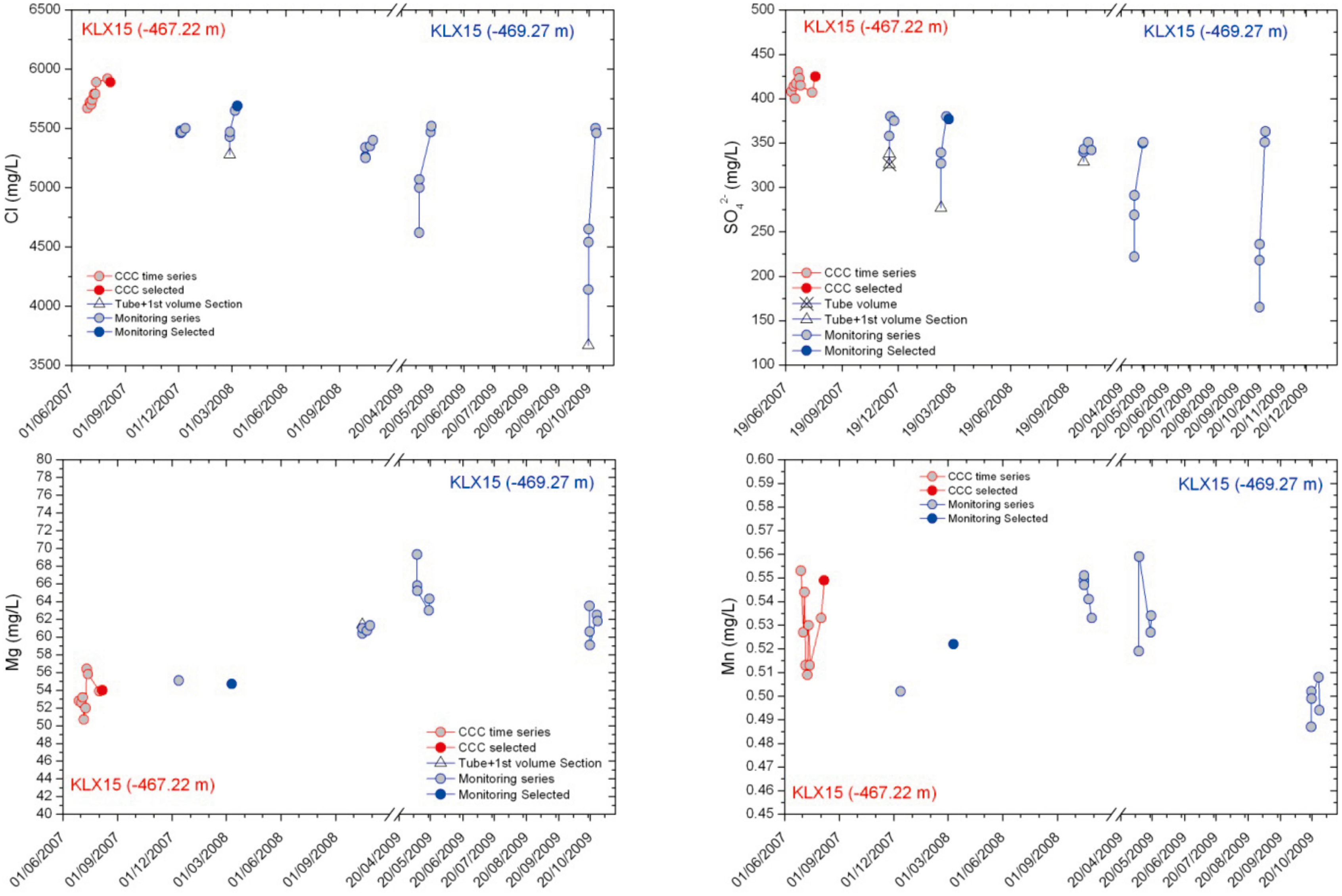

Figure A-59. *Evolution with time for Cl,* SO_4^{2-}*, Mg and Mn.*

BOREHOLE KLX15 (-467.22 masl, CCC; -469.27 masl, Monitoring)

pH = 7.6 (Chemmac measurement; CCC) range 5.47-8.15 (Field/surface measurement; Monitoring)

Eh (Chemmac measurement; CCC) = -208.8 mV; Eh (Monitoring) ≈ range -71 to -238 mV (Calculated using the S(-II)/S(VI) redox couple)

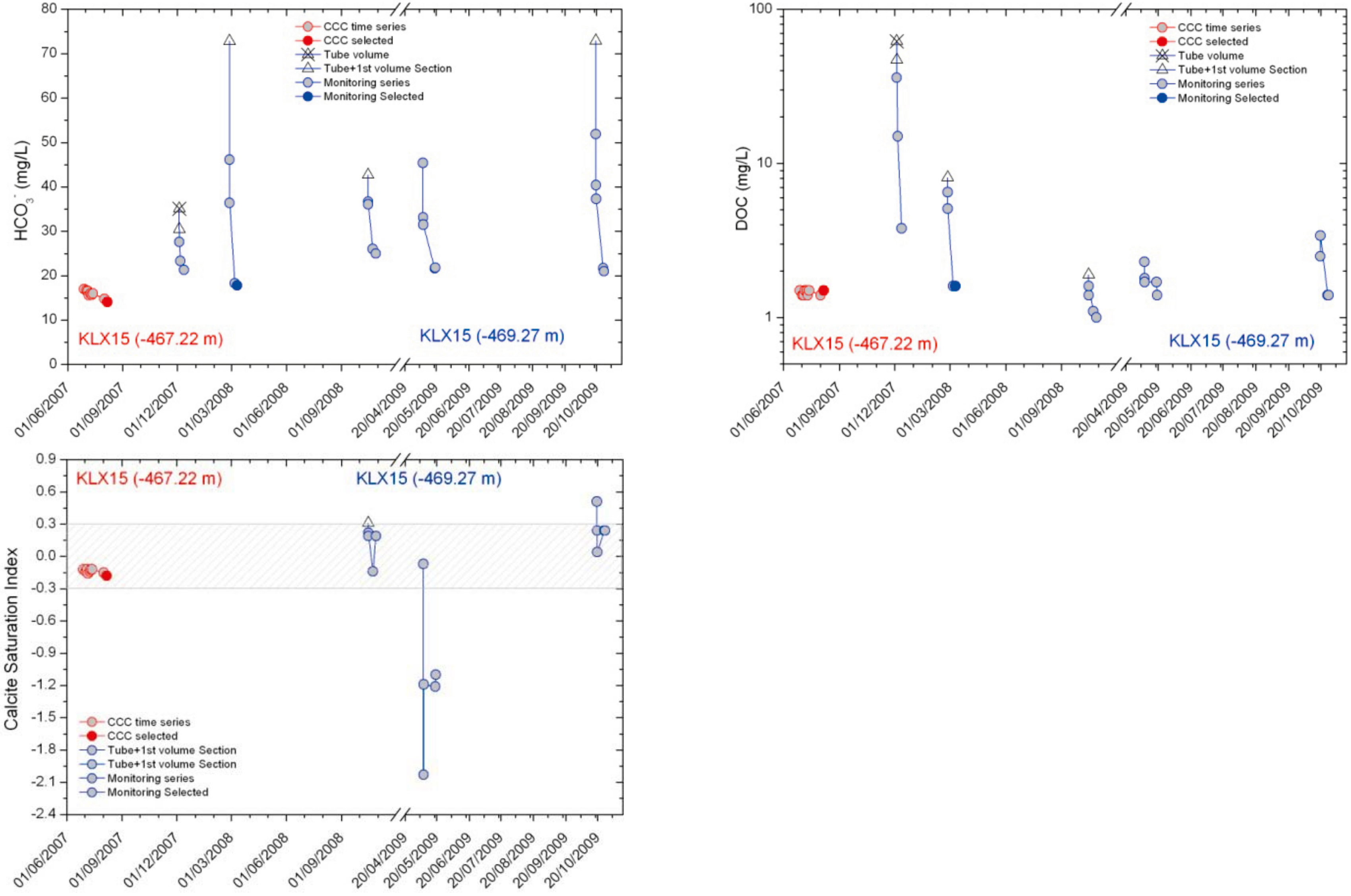

Figure A-60. Evolution with time for HCO_3^-, DOC and the calcite saturation index.

BOREHOLE KLX15 (-467.22 masl, CCC; -469.27 masl, Monitoring)

pH = 7.6 (Chemmac measurement; CCC); range 5.47-8.15 (Field/surface measurement; Monitoring)

Eh (Chemmac measurement; CCC) = -208.8 mV; Eh (Monitoring) ≈ range -71 to -238 mV (Calculated using the S(-II)/S(VI) redox couple)

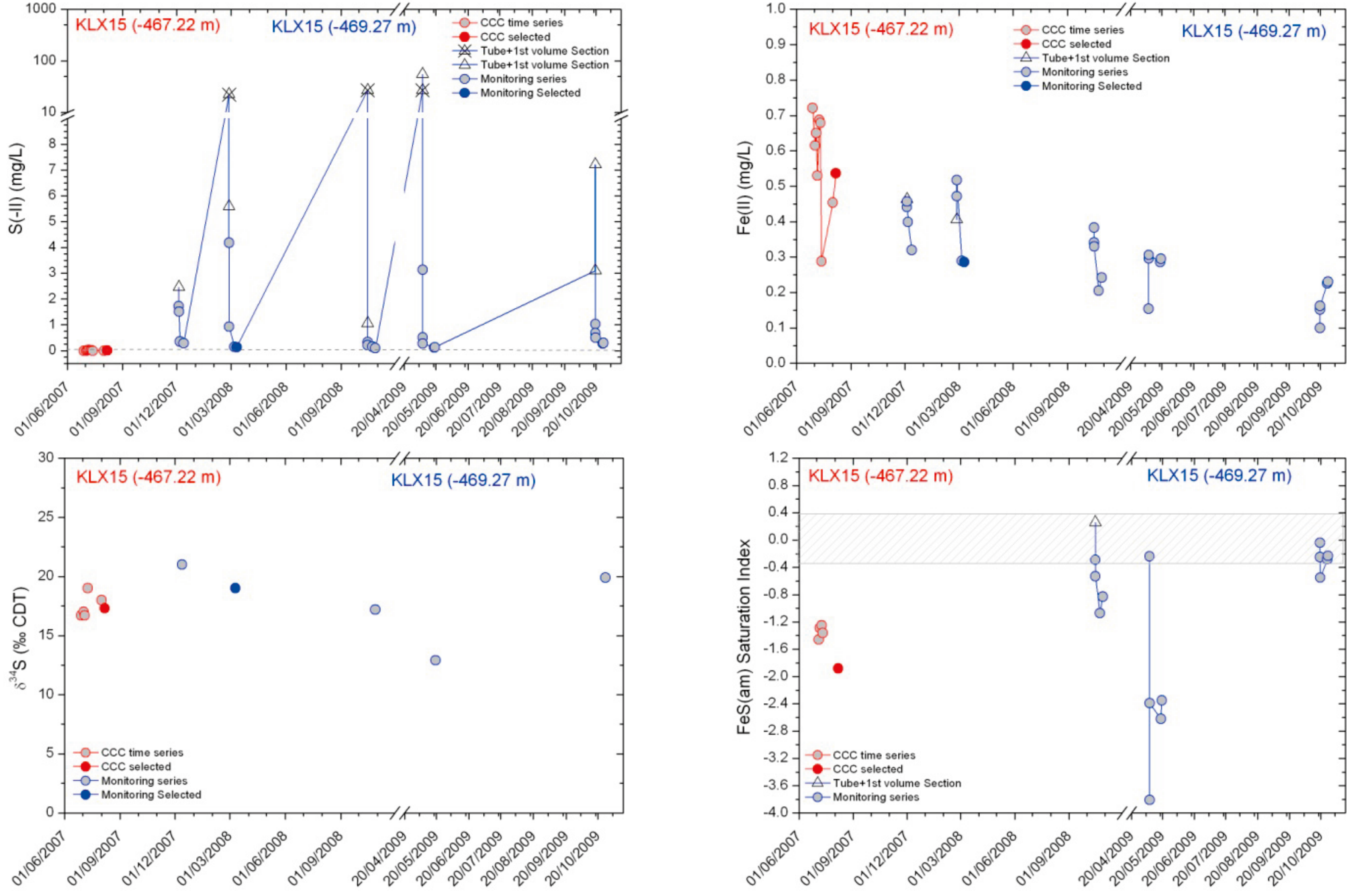

Figure A-61. Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and δ^{34}S.

BOREHOLE KLX17 (-342.32 masl)

Chemmac measurements:
pH = 7.92
Eh = -285 mV

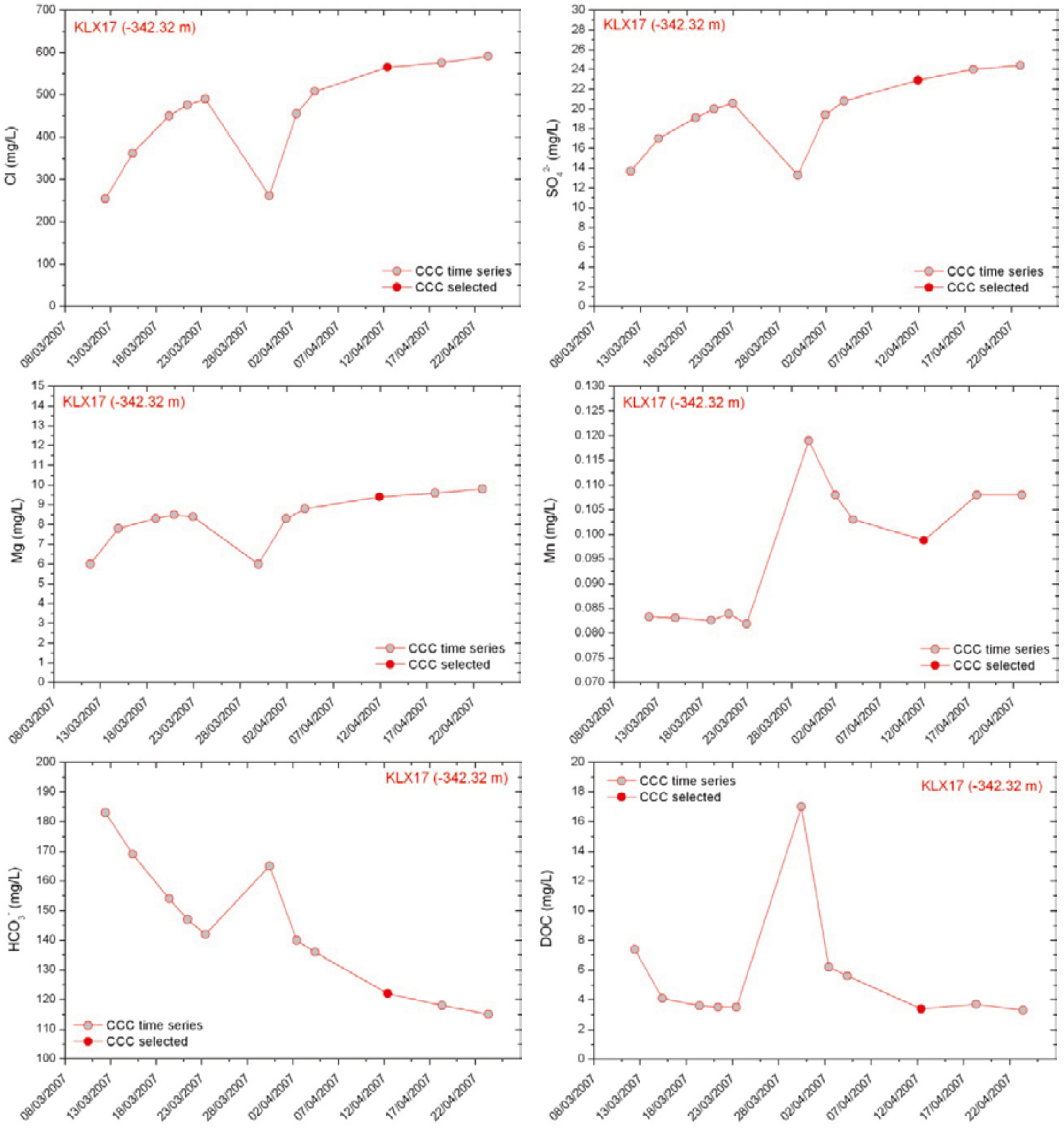

Figure A-62. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX17 (-342.32 masl)

Chemmac measurements:
pH = 7.92
Eh = -285 mV

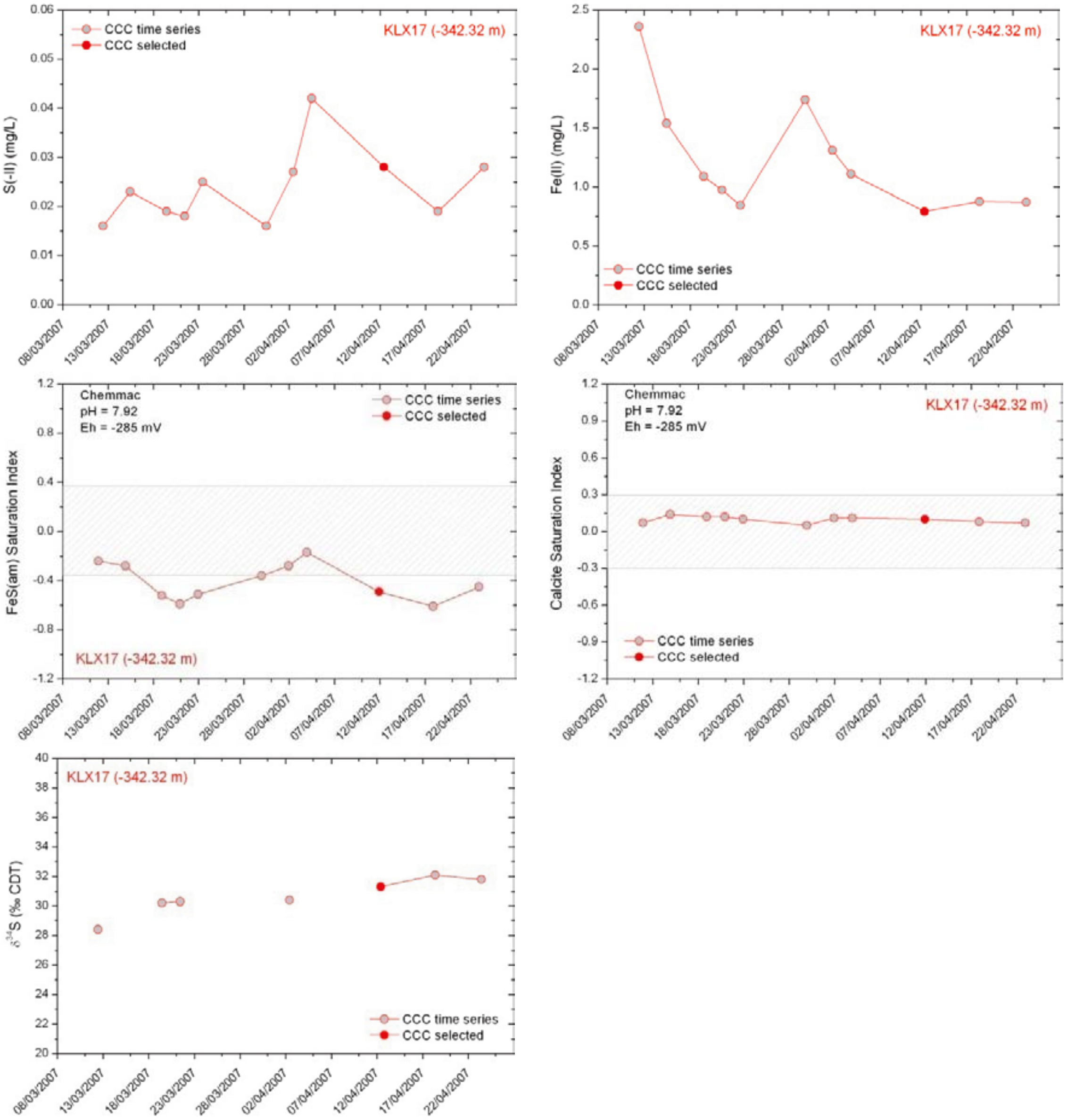

__Figure A-63.__ Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and δ^{34}S.

BOREHOLE KLX17 (-547.97 masl)

Chemmac measurements:
pH = 8.36
Eh = -303 mV

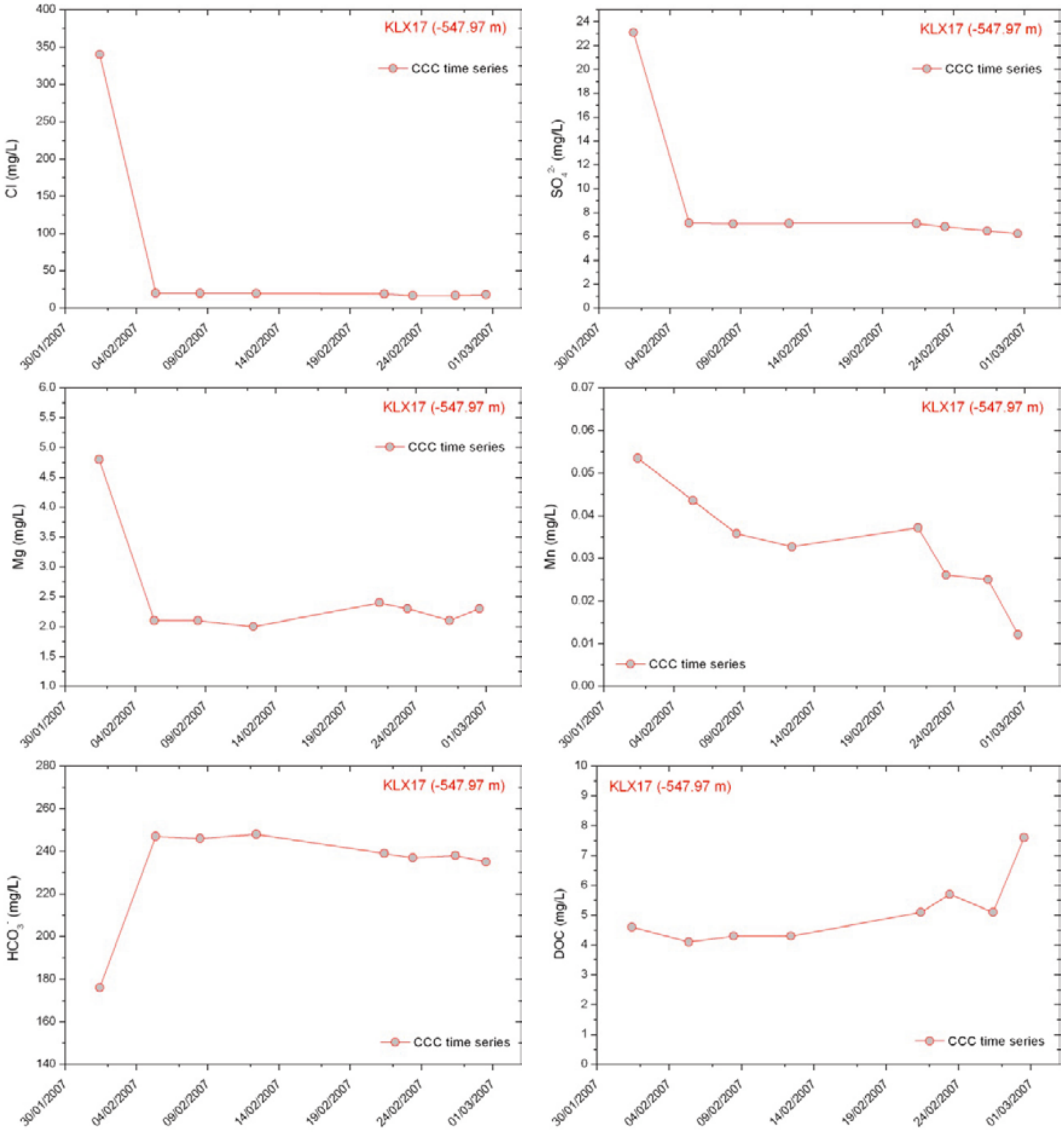

Figure A-64. *Evolution with time for Cl, SO_4^{2-}, Mg, Mn, HCO_3^- and DOC.*

BOREHOLE KLX17 (-547.97 masl)

Chemmac measurements:
pH = 8.36
Eh = -303 mV

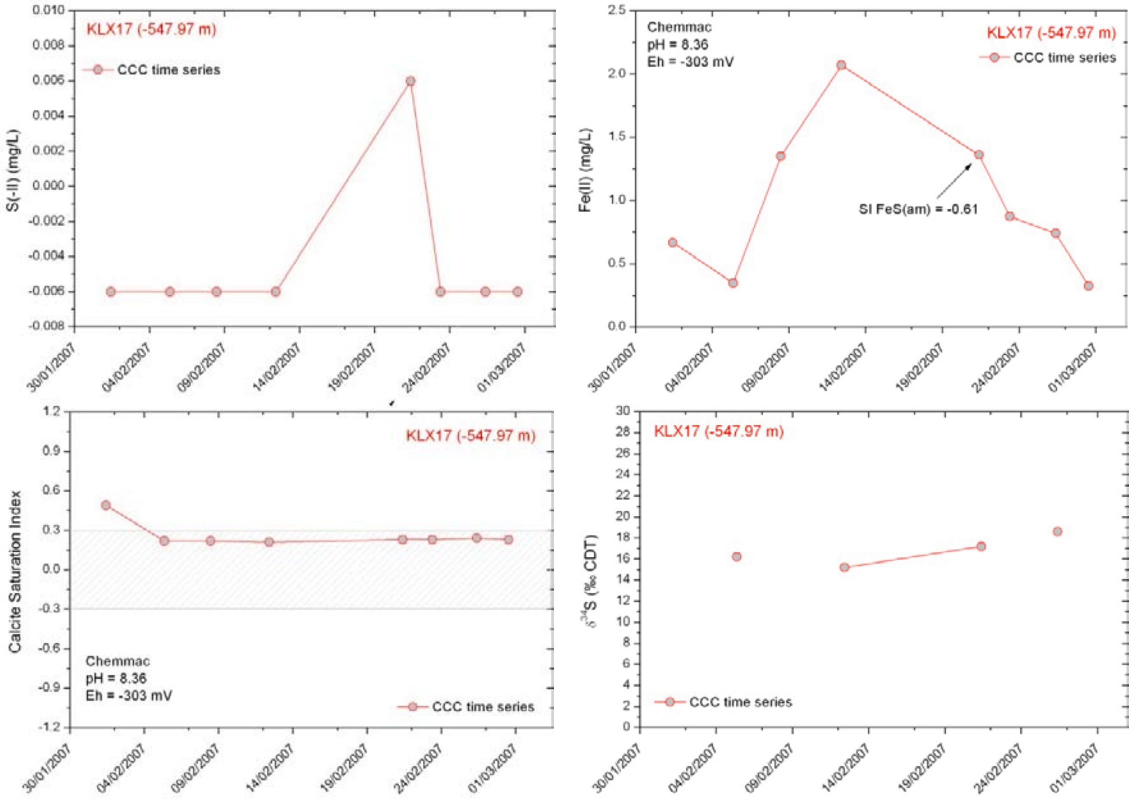

Figure A-65. *Evolution with time for S(-II) and Fe(II), the calcite saturation index and δ^{34}S.*

BOREHOLE KLX18 (-452.87 masl)

pH = 6.52-8.27 (Field/surface measurements); Eh ≈ range -147 to -252 mV (Calculated using the S(-II)/S(VI) redox couple)

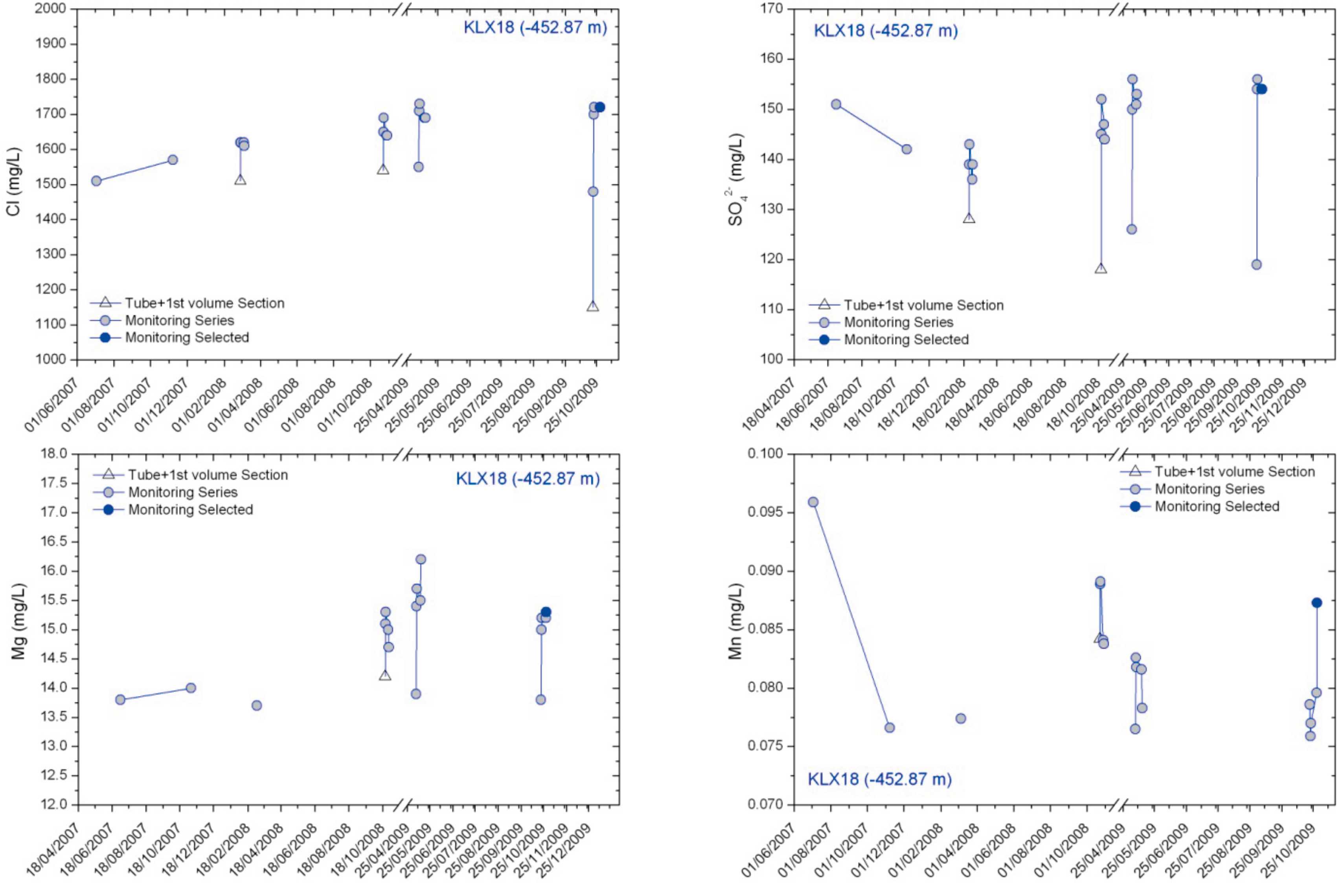

Figure A-66. *Evolution with time for Cl, SO_4^{2-}, Mg and Mn.*

BOREHOLE KLX18 (-452.87 masl)

pH = 6.52-8.27 (Field/surface measurements); Eh ≈ range -147 to -252 mV (Calculated using the S(-II)/S(VI) redox couple)

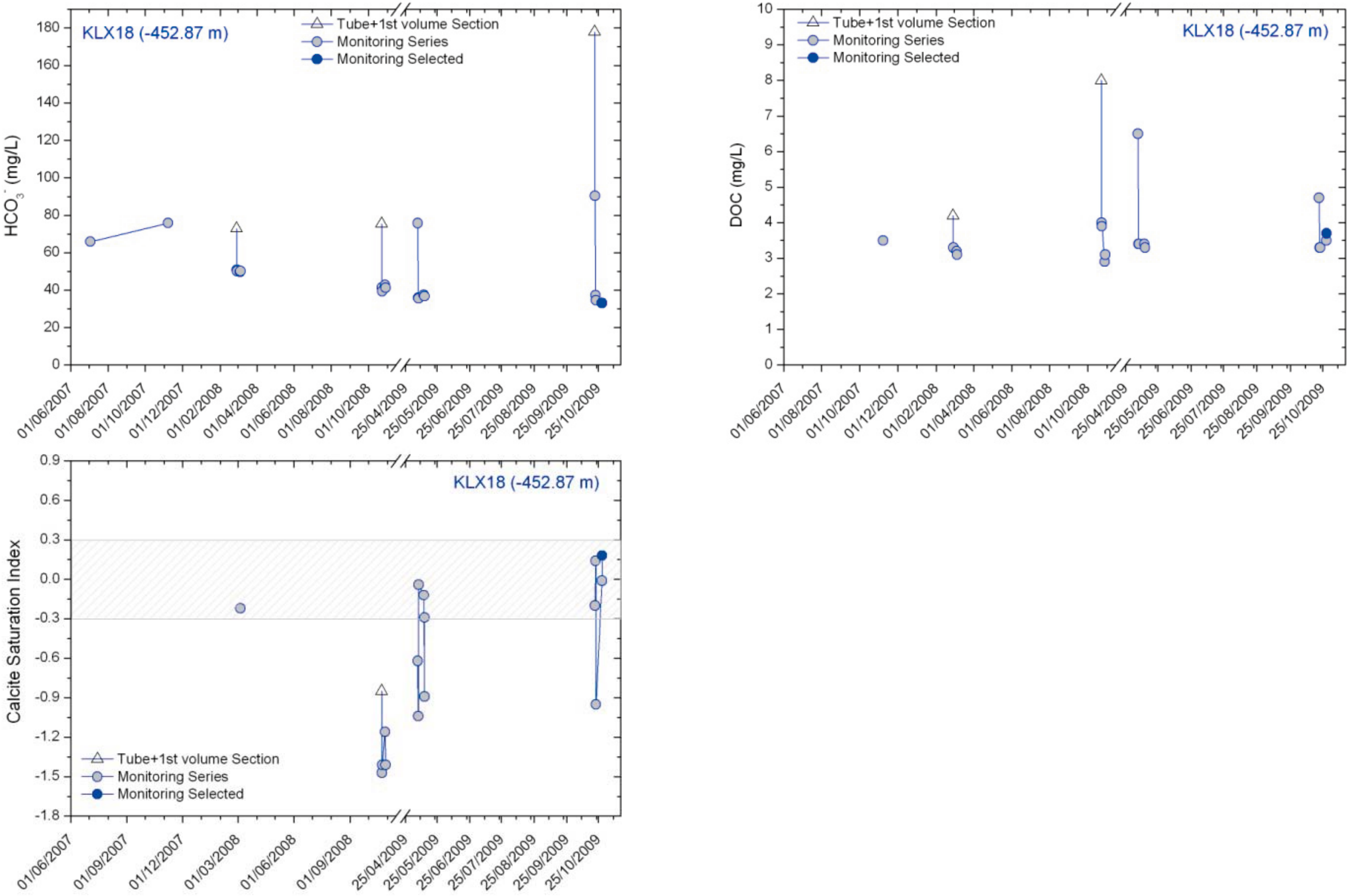

Figure A-67. *Evolution with time for HCO_3^-, DOC and the calcite saturation index.*

BOREHOLE KLX18 (-452.87 masl)

pH = 6.52-8.27 (Field/surface measurements); Eh ≈ range -147 to -252 mV (Calculated using the S(-II)/S(VI) redox couple)

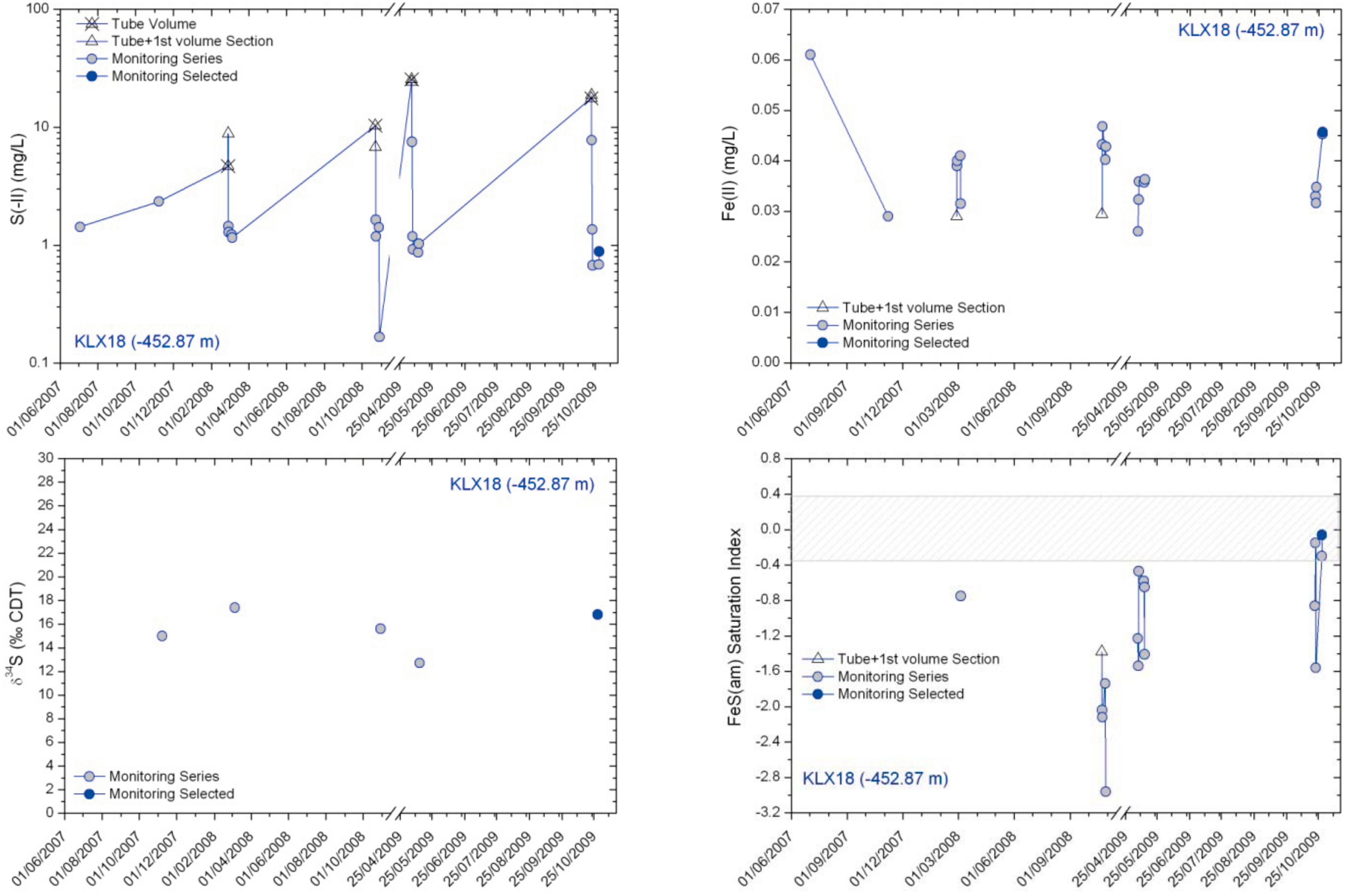

Figure A-68. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and* δ^{34}*S.*

BOREHOLE KLX19 (-410.52 masl, Hydrotest equipment; -413.86 masl, Monitoring)

pH = 6.32-8.52 (Field/surface measurements); Eh ≈ range -132 to -269 mV (Calculated using the S(-II)/S(VI) redox couple)

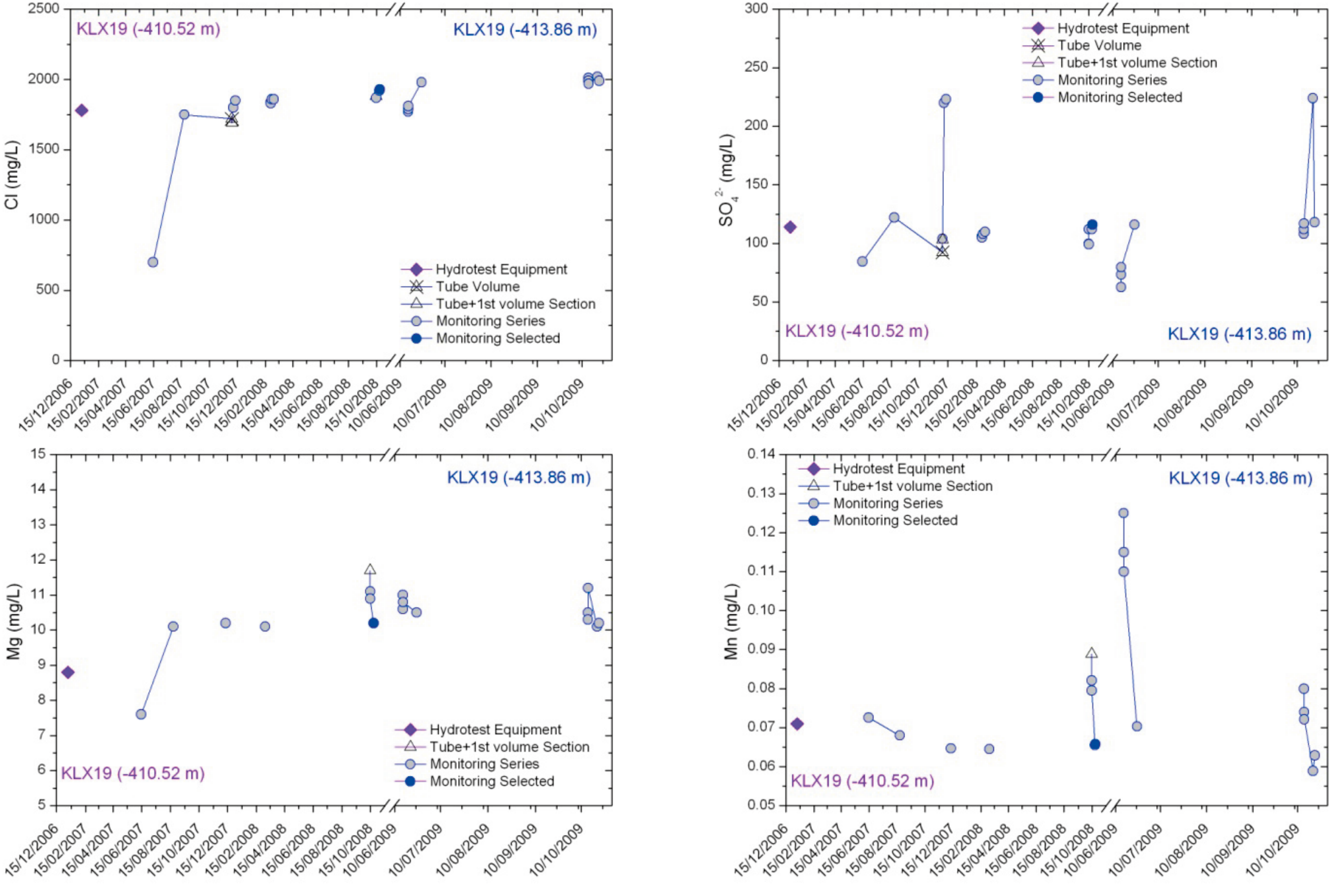

Figure A-69. *Evolution with time for Cl, SO_4^{2-}, Mg and Mn.*

BOREHOLE KLX19 (-410.52 masl, Hydrotest equipment; -413.86 masl, Monitoring)
pH = 6.32-8.52 (Field/surface measurements); Eh ≈ range -132 to -269 mV (Calculated using the S(-II)/S(VI) redox couple)

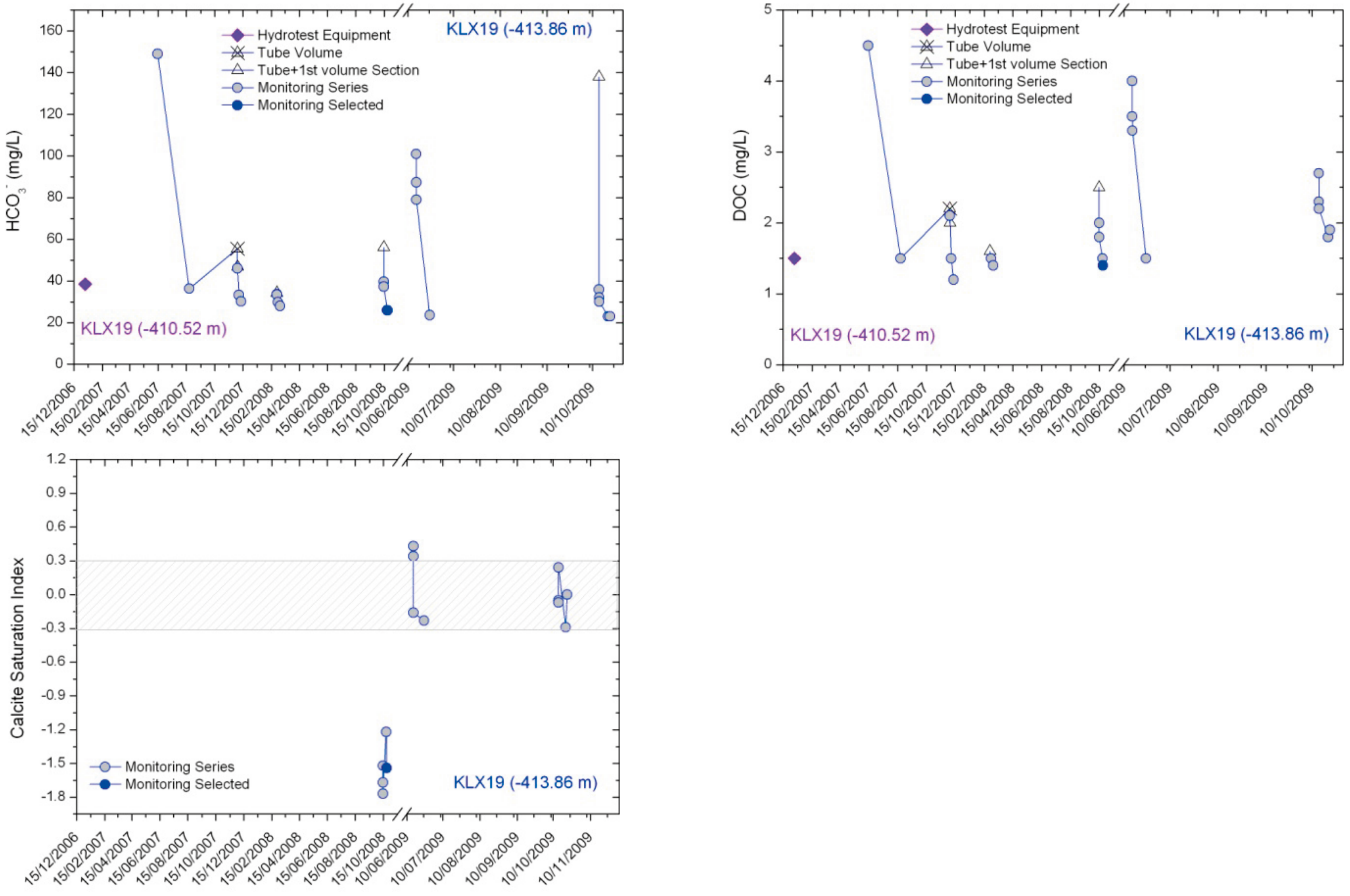

Figure A-70. *Evolution with time for* HCO_3^-*, DOC and the calcite saturation index.*

BOREHOLE KLX19 (-410.52 masl, Hydrotest equipment; -413.86 masl, Monitoring)

pH = 6.32-8.52 (Field/surface measurements); Eh ≈ range -132 to -269 mV (Calculated using the S(-II)/S(VI) redox couple)

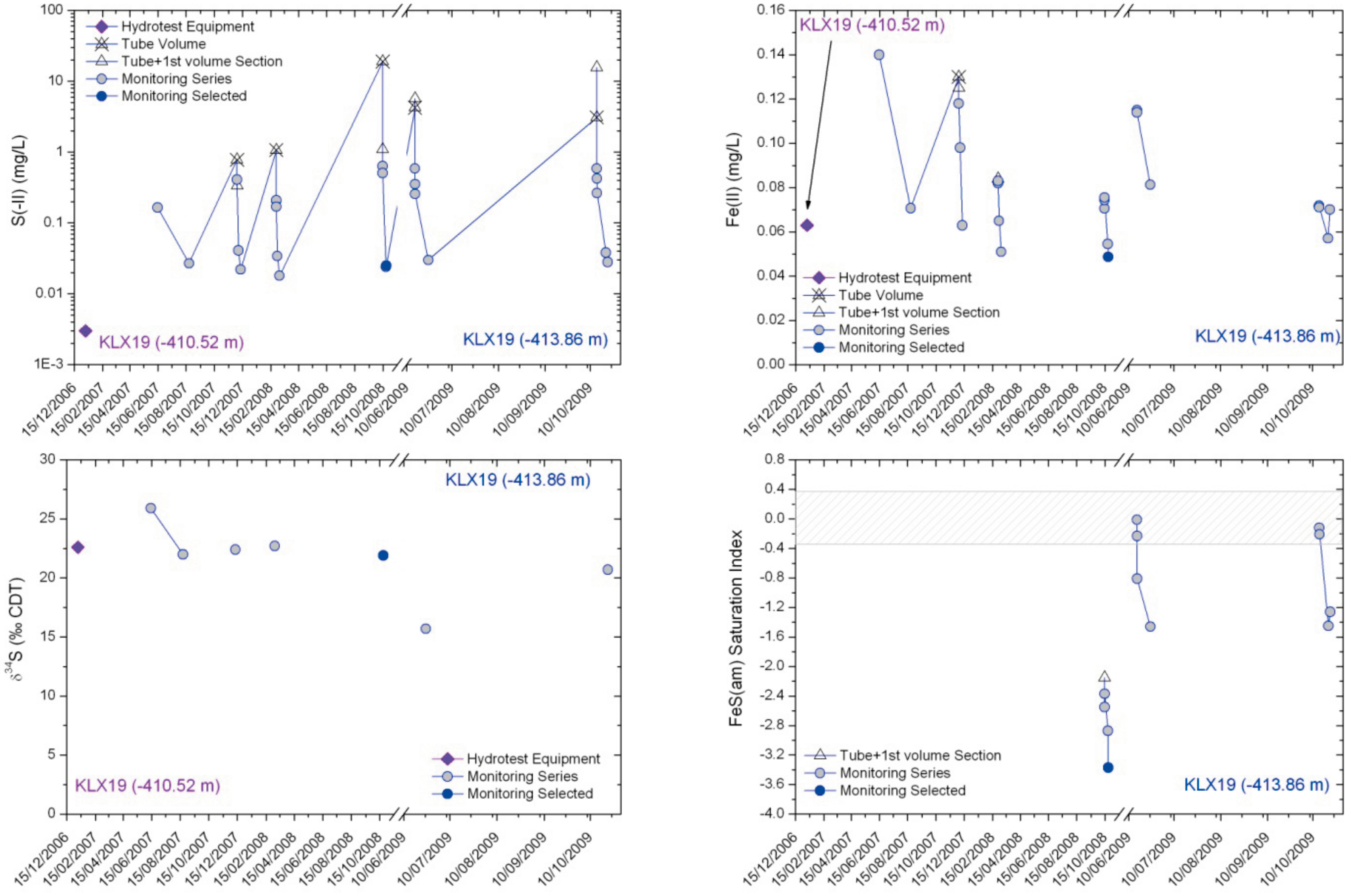

Figure A-71. *Evolution with time for S(-II) and Fe(II), the FeS(am) and calcite saturation indices and δ^{34}S.*

BOREHOLE KLX20 (-183.32 masl)

pH = 7.47-8.43 (Field/surface measurements)
Eh ≈ -259 mV (Calculated using the S(-II)/S(VI) redox couple)

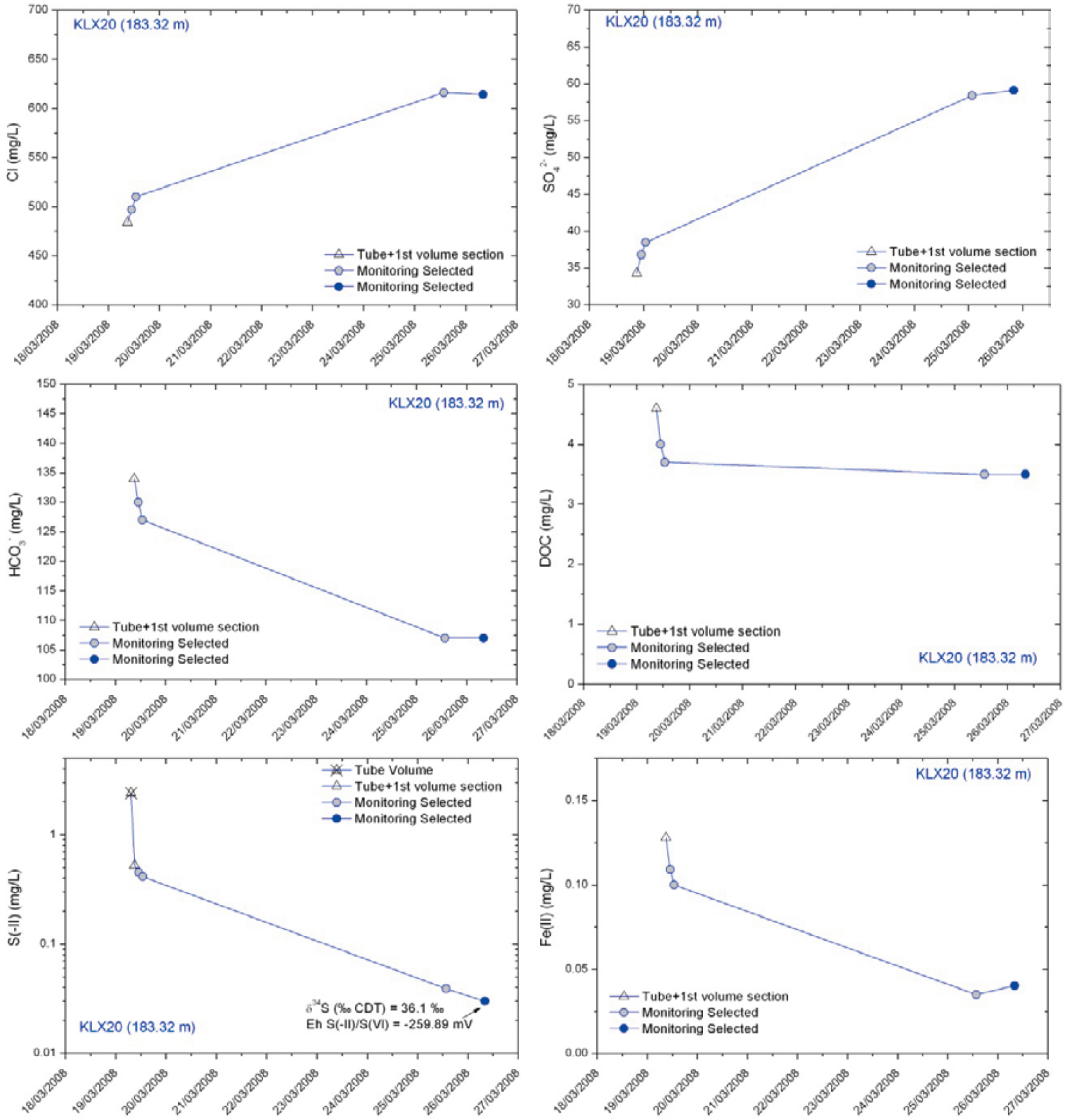

Figure A-72. *Evolution with time for Cl, SO_4^{2-}, HCO_3^-, DOC, S(-II) and Fe(II).*

BOREHOLE KLX27 (-562.96 masl)

pH ≈ 8.8 (Laboratory)
Eh ≈ -270 mV (Calculated using the S(-II)/S(VI) redox couple)

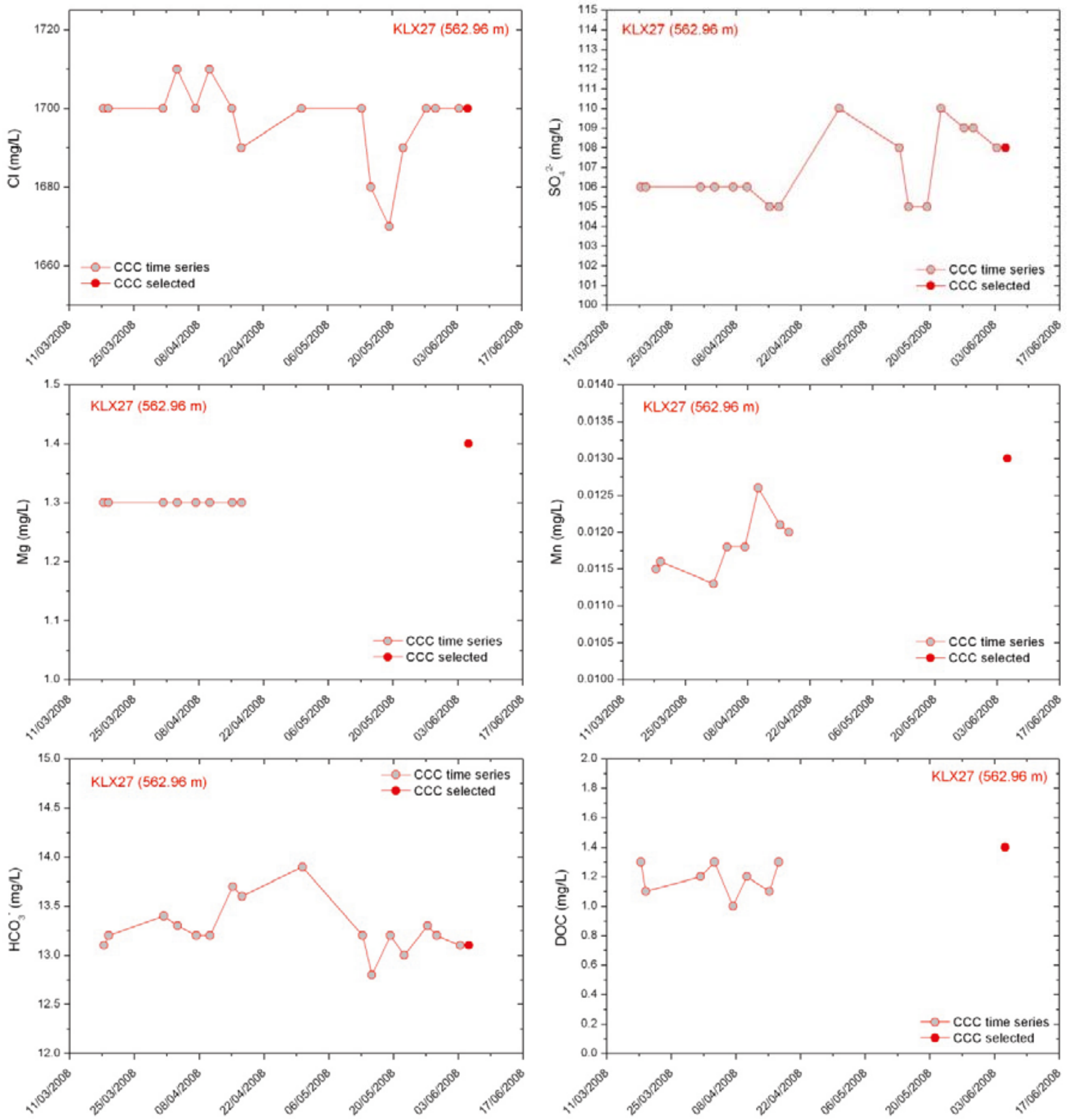

Figure A-73. *Evolution with time for Cl, SO_4^{2-}, HCO_3^-, DOC, S(-II) and Fe(II).*

BOREHOLE KLX27 (-562.96 masl)

pH ≈ 8.8 (Laboratory measurement)
Eh ≈ -270 mV (Calculated using the S(-II)/S(VI) redox couple)

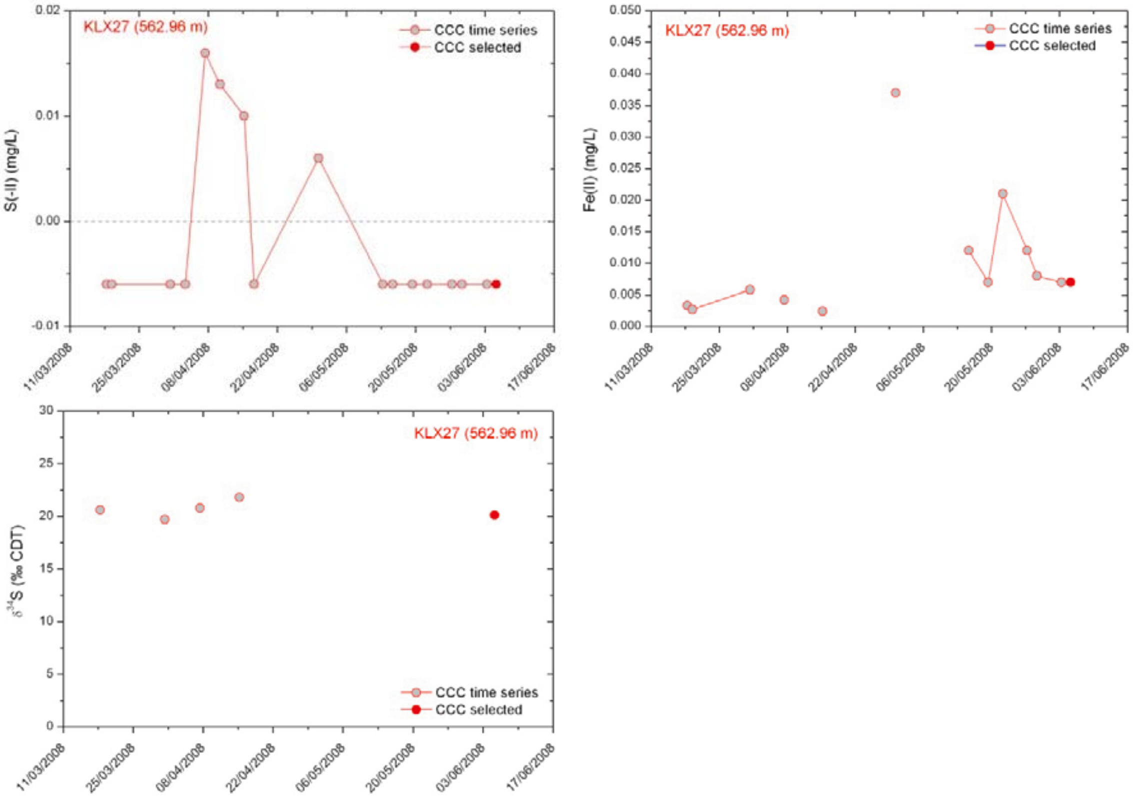

Figure A-74. *Evolution with time for S(-II), Fe(II) and δ^{34}S.*

Appendix 3

The data provided below, taken directly from the Sicada database, represent hydrogeological parameters corresponding to the sections with selected representative sulphide values.

Hydrogeological and sulphide database used in the analysis.

IDCODE	Elevation SecMid	S2(mg/l)	S_2_mol_L	ELEVATION_FROM_LENGTH	type rock name	ROCK_NAME1	OPEN_FRAC1	NATURAL_FLOW_RATE_Q0	FLOW_RATE_Q1	TRANSMISSIVITY_TD
KLX02	-1129,14	0,165	5,1458E-06	-1128,53			0	1,6700E-009	1,6700E-009	1,50E-010
KLX02	-1360,93	0,046	1,43459E-06	-1360,50			0	1,6700E-009	1,6700E-009	3,01E-010
KLX02	-1068,24	near 0	#¡VALOR!	-1068,99			0	-7,8678E-009	5,2002E-007	4,08E-008
KLX02	-1134,60	near 0	#¡VALOR!	-1134,49			0	1,6700E-009	1,6700E-009	1,54E-010
KLX02	-1322,81	near 0	#¡VALOR!	-1321,83			0	1,6700E-009	1,6700E-009	2,77E-010
KLX08	-539,39	0,074	2,30781E-06	-541,07	3	Diorite to gabbro	0	8,3333E-009	1,1300E-007	2,30E-008
KLX08	-500,90	0,055	1,71527E-06	-502,54	3	Diorite to gabbro	4	2,6900E-007	2,7800E-006	5,10E-007
KLX04	-491,94	0,038	1,18509E-06	-494,00	3	Diorite to gabbro	1	-4,7200E-007	1,2400E-006	2,90E-007
KLX08	-504,54	0,010	3,11867E-07	-502,54	3	Diorite to gabbro	4	2,6900E-007	2,7800E-006	5,10E-007
KLX10	-676,19	1,120	3,49291E-05	-674,44	1	Granite to quartz monzodiorite, generally porphyritic	1	-7,0300E-007	4,0300E-007	1,70E-007
KLX18A	-452,87	0,884	2,7569E-05	-452,08	1	Granite to quartz monzodiorite, generally porphyritic	5	8,3300E-009	5,8300E-009	6,10E-010
KLX04	-854,86	0,742	2,31405E-05	-852,48	1	Granite to quartz monzodiorite, generally porphyritic	2	-2,1000E-007	4,8600E-007	1,20E-007
KLX10	-338,43	0,286	8,91938E-06	-336,36	1	Granite to quartz monzodiorite, generally porphyritic	3	2,6400E-008	1,3400E-006	2,00E-007
KLX06	-221,18	0,186	5,80072E-06	-222,19	1	Granite to quartz monzodiorite, generally porphyritic	0		7,8300E-008	1,10E-008
KLX07A	-569,69	0,032	9,97973E-07	-570,50	1	Granite to quartz monzodiorite, generally porphyritic	7	-2,6000E-006	4,9700E-006	1,40E-006
KLX04	-944,38	0,022	6,86106E-07	-941,90	1	Granite to quartz monzodiorite, generally porphyritic	1	2,7800E-008	5,2300E-007	9,00E-008
KLX06	-218,51	0,017	5,30173E-07	-217,74	1	Granite to quartz monzodiorite, generally porphyritic	1	1,0800E-005	4,4400E-005	1,40E-005
KLX04	-81,90	0,010	3,11867E-07	-80,62	1	Granite to quartz monzodiorite, generally porphyritic	4	6,2200E-007	7,0900E-006	1,10E-006
KLX03	-379,85	0,007	2,18307E-07	-379,91	1	Granite to quartz monzodiorite, generally porphyritic	0	8,3300E-009	8,3300E-009	8,80E-010
KLX13A	-408,01	0,004	1,24747E-07	-406,95	1	Granite to quartz monzodiorite, generally porphyritic	0	-3,2200E-008	3,1900E-007	3,50E-008
KLX08	-390,71	0,004	1,24747E-07	-391,06	1	Granite to quartz monzodiorite, generally porphyritic	6	-2,7800E-008	5,2800E-007	1,10E-007
KLX08	-150,43	0,004	1,24747E-07	-149,73	1	Granite to quartz monzodiorite, generally porphyritic	11	-2,2800E-008	3,5300E-006	6,90E-007
KLX03	-170,82	0,003	9,356E-08	-171,29	1	Granite to quartz monzodiorite, generally porphyritic	0	2,2200E-008	5,7200E-007	5,64E-008
KLX13A	-474,99	0,003	9,356E-08	-476,42	1	Granite to quartz monzodiorite, generally porphyritic	0	8,3300E-009	8,3300E-009	8,20E-010
KLX04	-486,52	0,006	1,8712E-07	-489,01	4	Granite, fine- to medium-grained	0	2,7800E-008	2,7800E-008	4,80E-009
KLX06	-475,27	0,082	2,55731E-06	-475,24	5	Granite, medium- to coarse-grained	0	-2,2900E-005	2,2400E-005	6,60E-006
KLX11A	-542,07	0,403	1,25682E-05	-543,13	6	Mafic rock, fine-grained	0		2,3300E-008	2,30E-009
KLX17A	-342,32	0,028	8,73226E-07	-343,94	6	Mafic rock, fine-grained	4	-5,6700E-006	5,8900E-005	6,50E-006
KLX12A	-501,12	0,649	2,02401E-05	-503,22	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	0	-8,8900E-009	1,0300E-007	1,20E-008
KLX15A	-469,27	0,133	4,14782E-06	-468,57	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	11	4,5300E-007	7,3600E-006	1,00E-006
KLX03	-922,45	0,090	2,8068E-06	-920,08	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	1	1,6700E-008	3,7800E-006	4,56E-007
KLX20A	-183,32	0,030	9,356E-07	-184,44	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	0	1,9400E-008	5,1100E-007	5,20E-008
KLX15A	-192,74	0,029	9,04413E-07	-192,16	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	2	8,3300E-009	1,4700E-007	2,10E-008
KLX19A	-413,86	0,025	7,79666E-07	-414,78	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	0	-1,0900E-007	3,2500E-006	3,60E-007
KLX05	-204,84	0,018	5,6136E-07	-203,17	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	0	9,2800E-008	6,9700E-006	6,80E-007
KLX15A	-467,22	0,007	2,18307E-07	-468,57	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	11	4,5300E-007	7,3600E-006	
KLX04	-486,52	0,006	1,8712E-07	-484,03	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	1	-2,9700E-006	9,5300E-006	2,10E-006
KLX19A	-624,78	0,003	9,356E-08	-622,88	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	1	-6,2200E-007	2,5400E-006	3,40E-007
KLX19A	-410,52	0,003	9,356E-08	-410,58	2	Quartz monzodiorite to granodiorite, equigranular to sparsely porphyritic	2	-3,4400E-007	9,5600E-006	1,10E-006

Note that the number of open fractures does not reflect all flowing features of each borehole section.

Individual analysis of sulphide contents and hydrogeologic parameters along the different boreholes were carried out in order to see if there was any evident correlation. No clear correlations are seen with depth and natural flow rate, as explained in the main text. All the plots of the corresponding boreholes are presented in this appendix.

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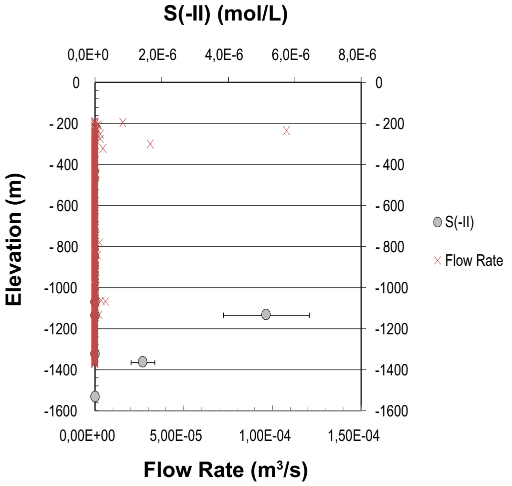
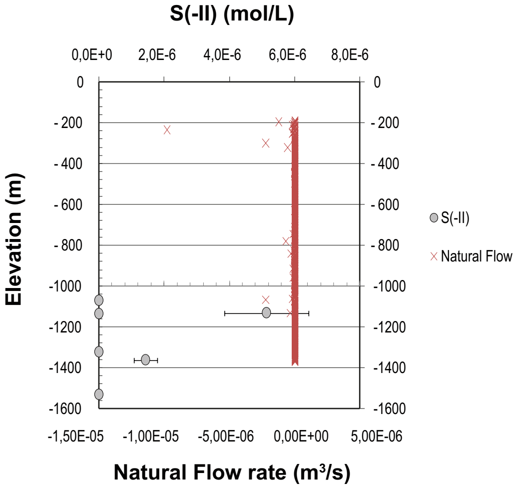
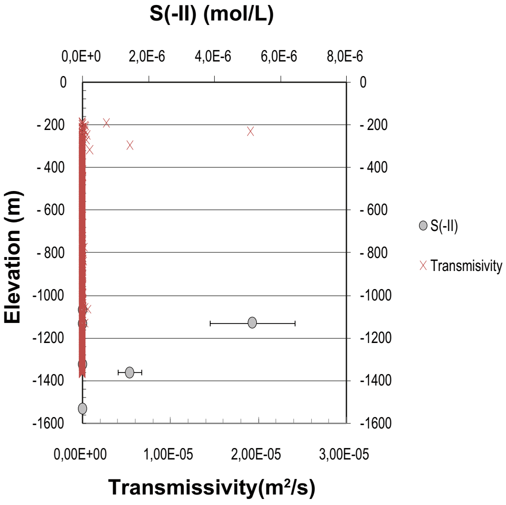
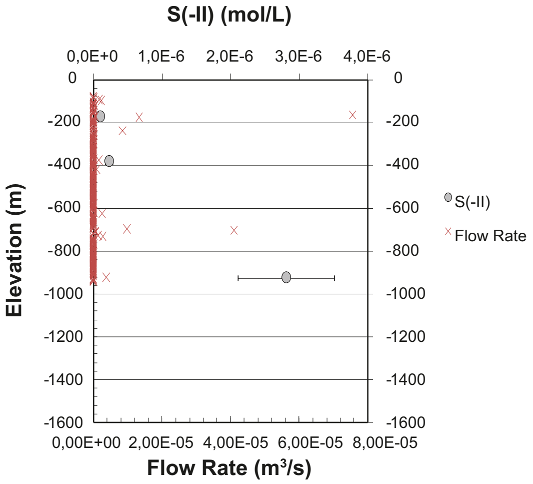
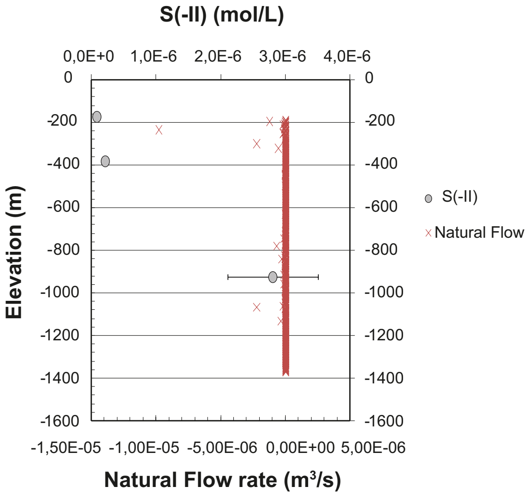


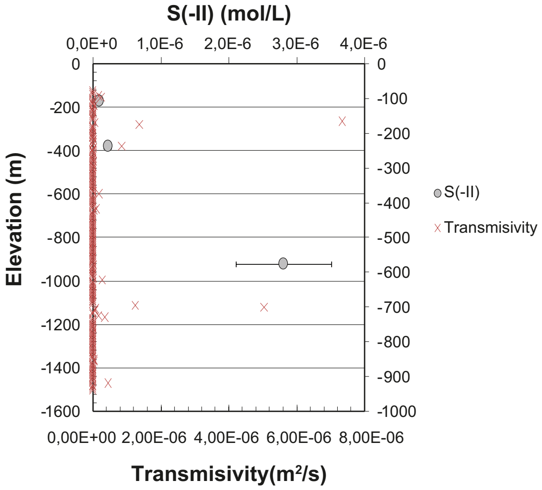




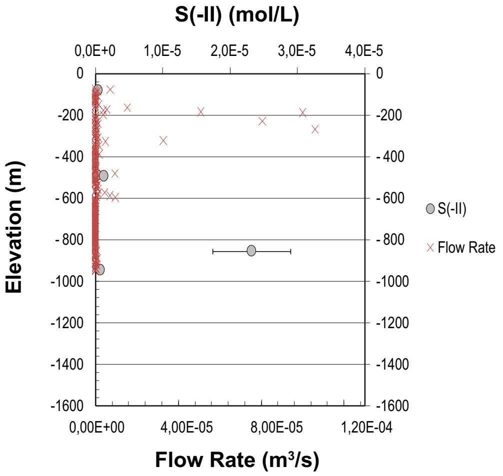
Borehole KLX03

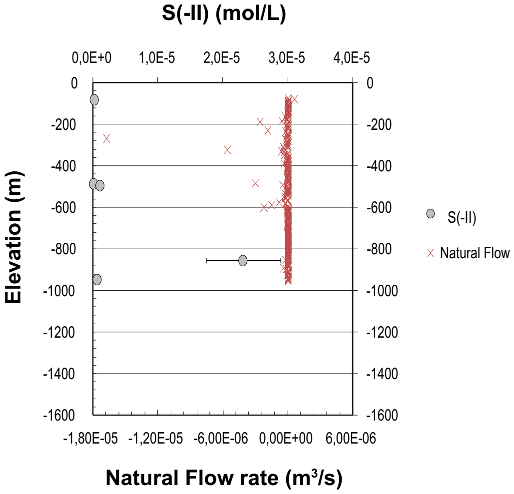


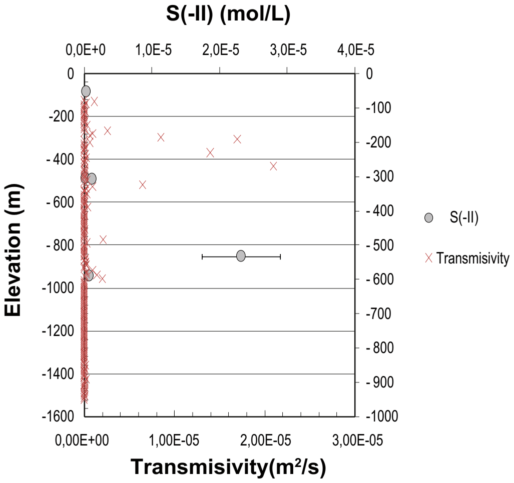




Borehole KLX04







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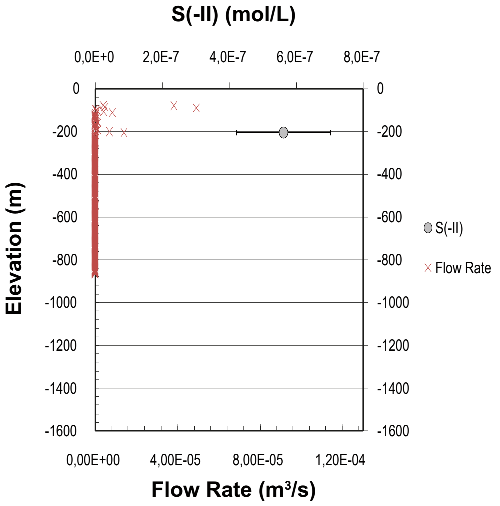
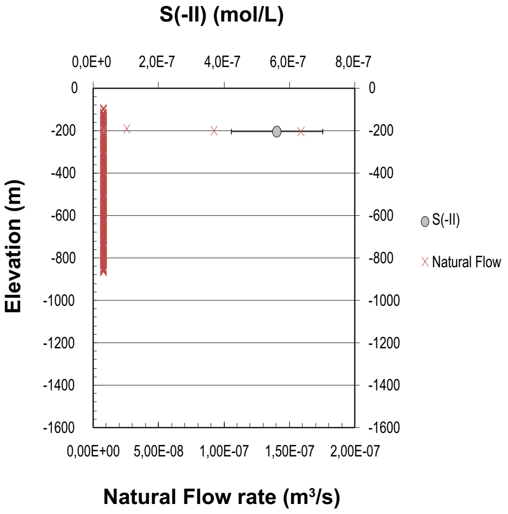
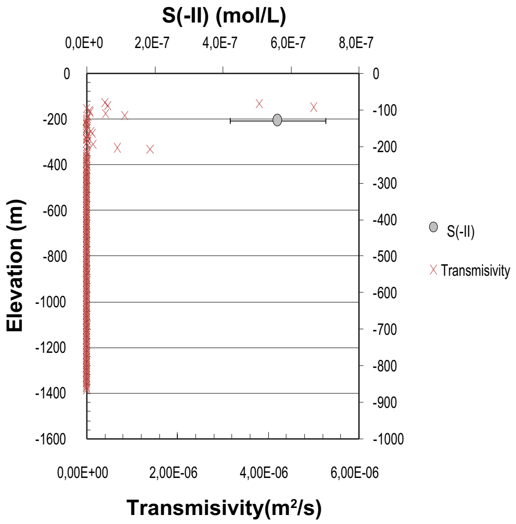
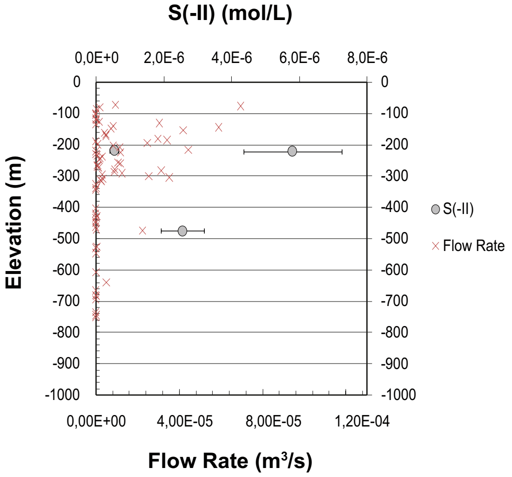
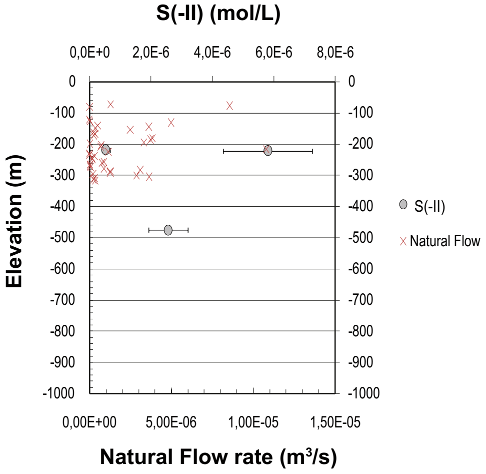


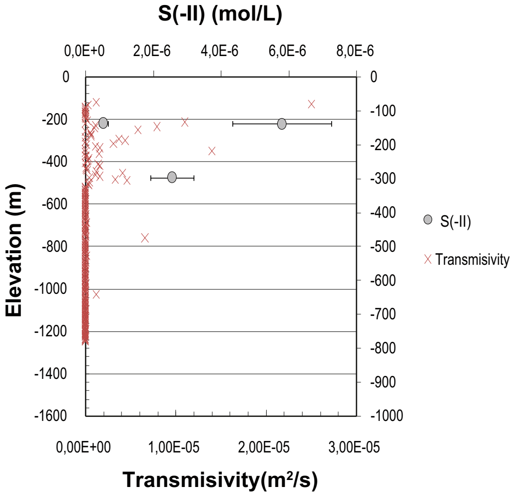




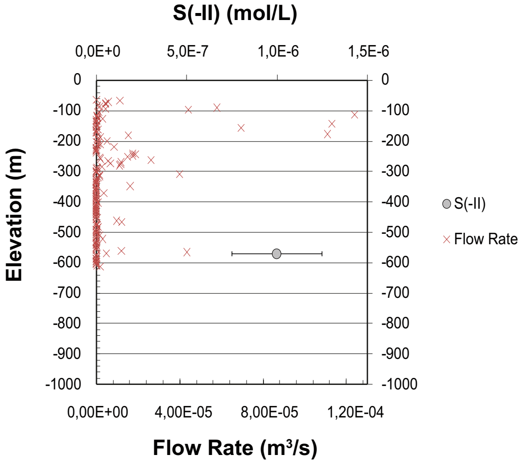
Borehole KLX06

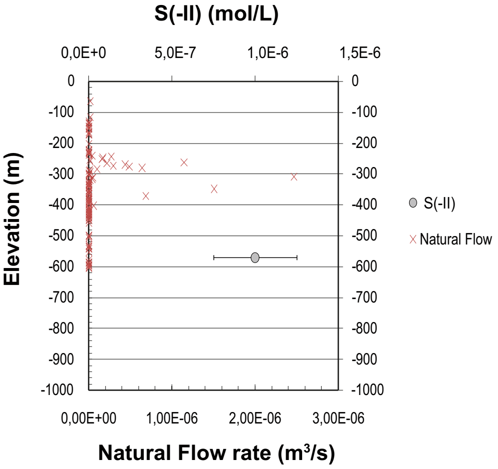


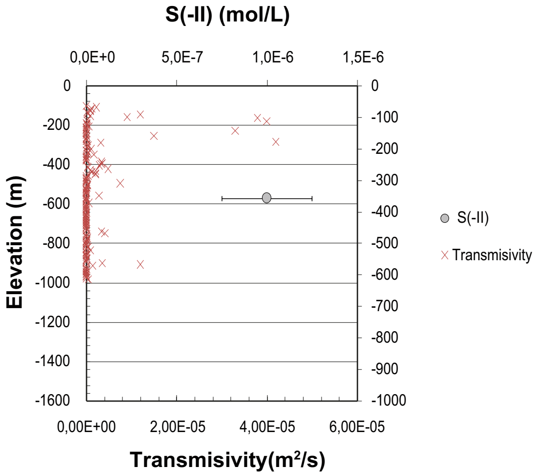




Borehole KLX07A







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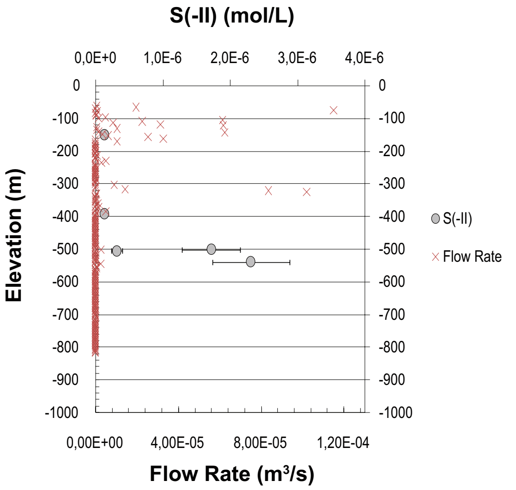
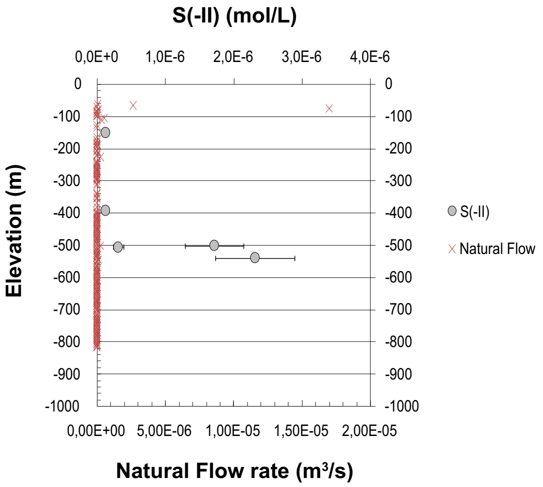
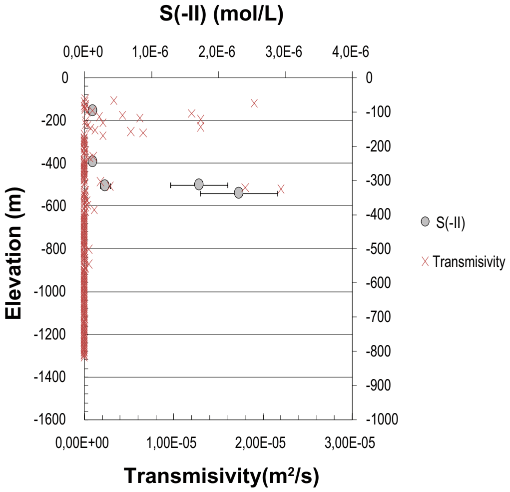
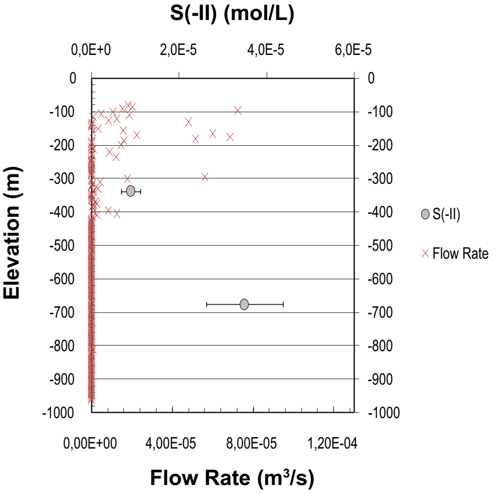
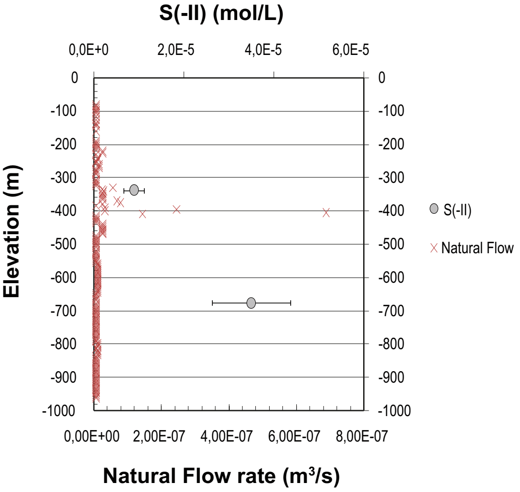


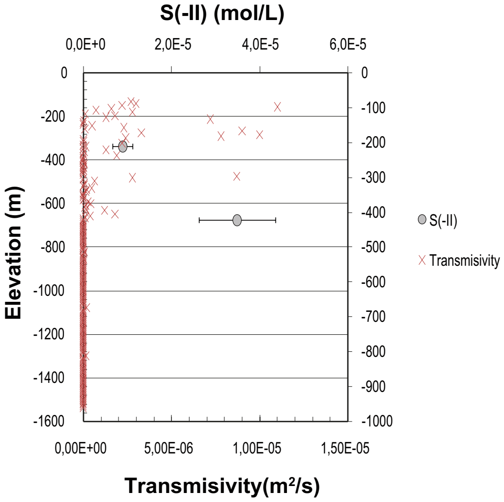




Borehole KLX10







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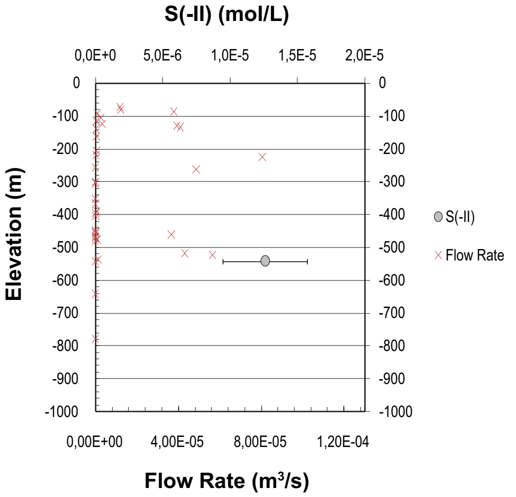

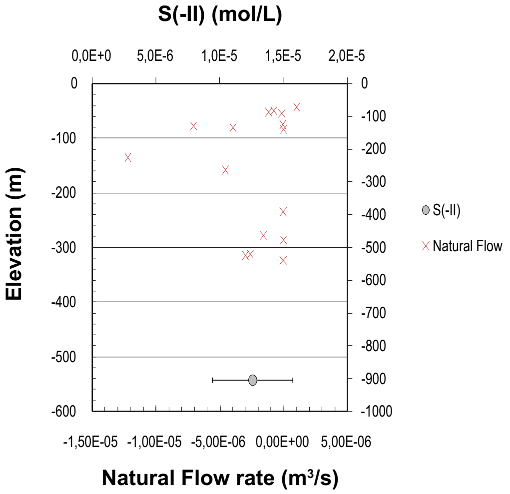

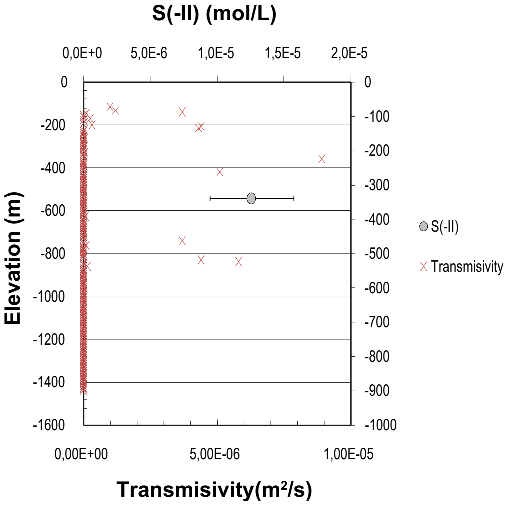

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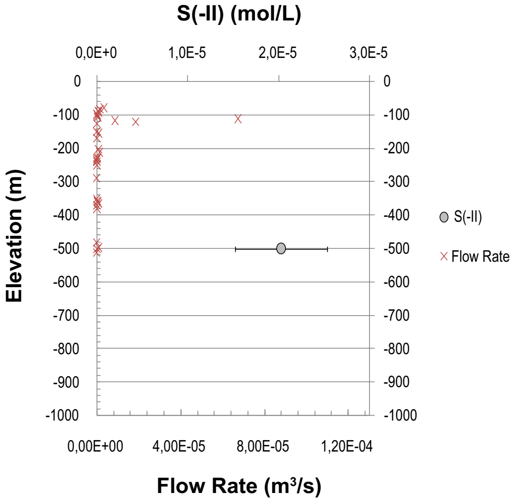
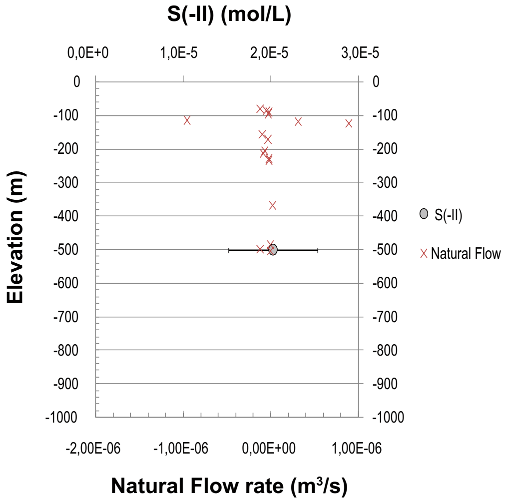
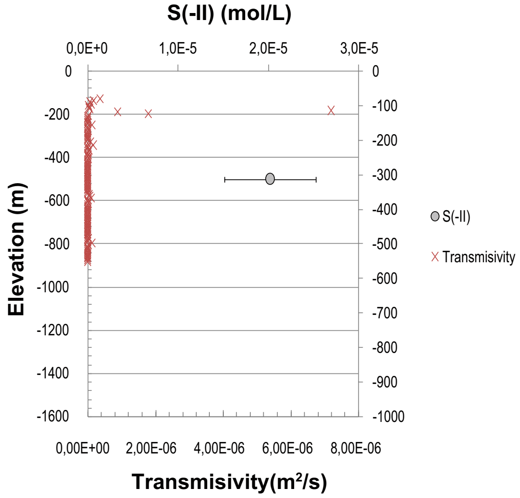
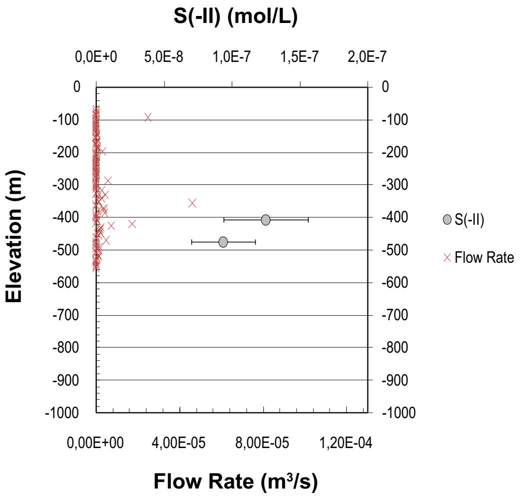
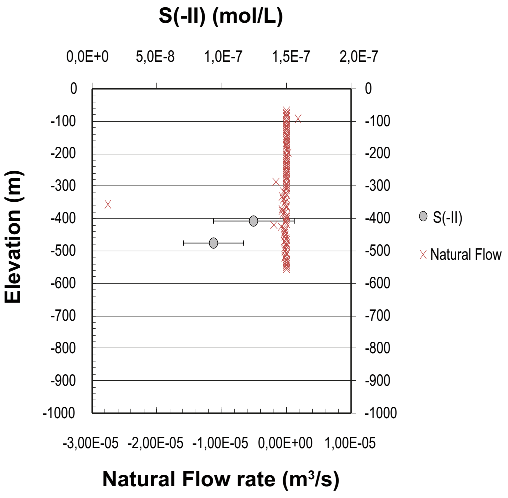


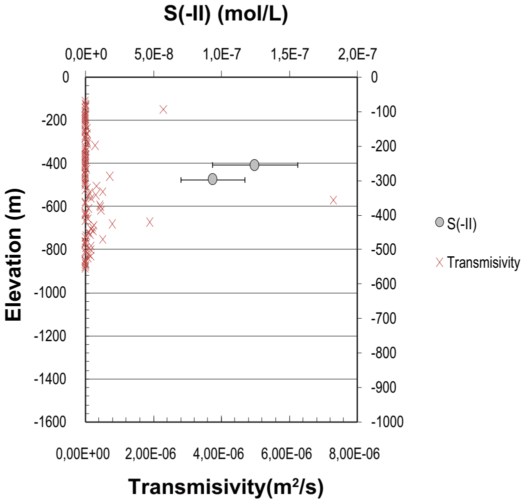




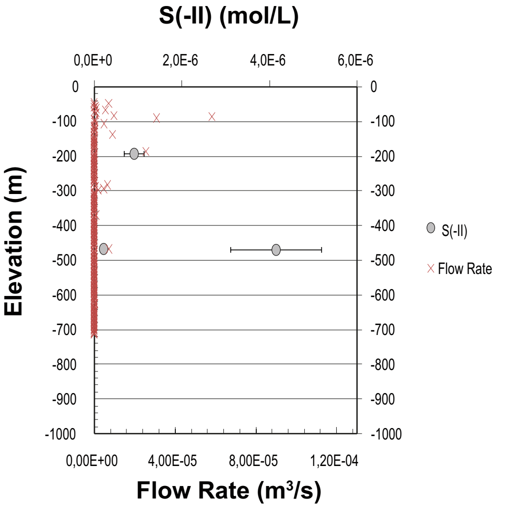
Borehole KLX13A

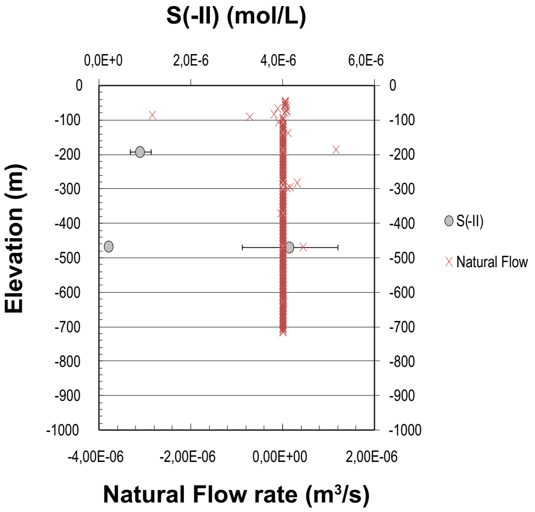


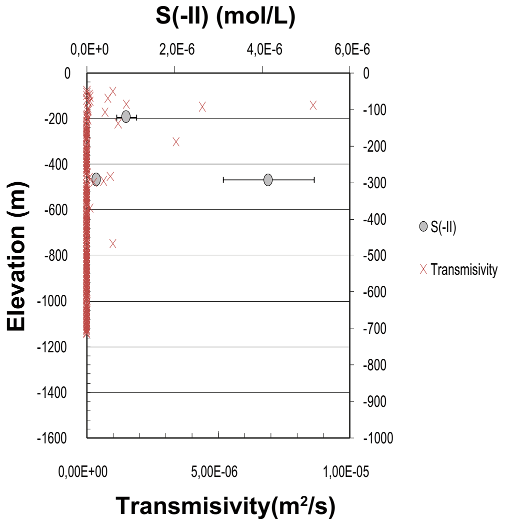




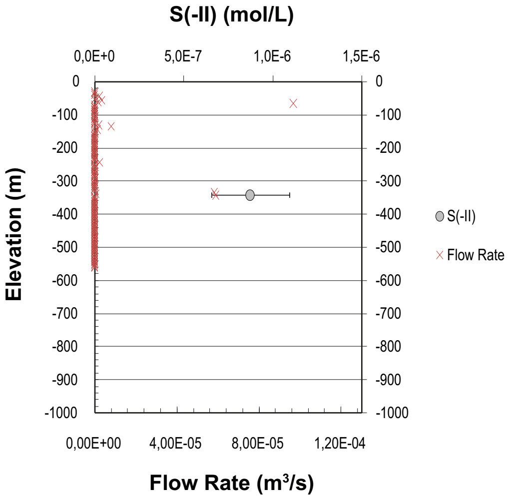
Borehole KLX15A

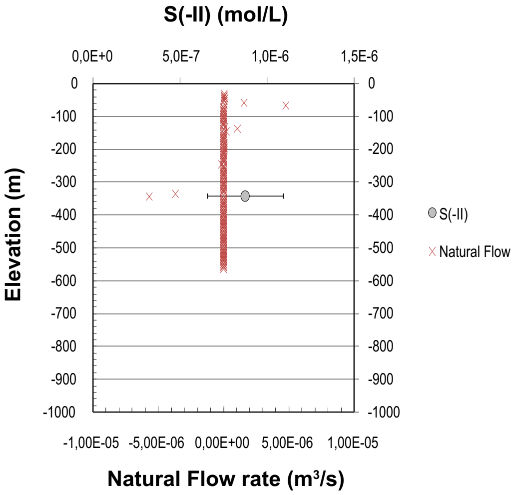


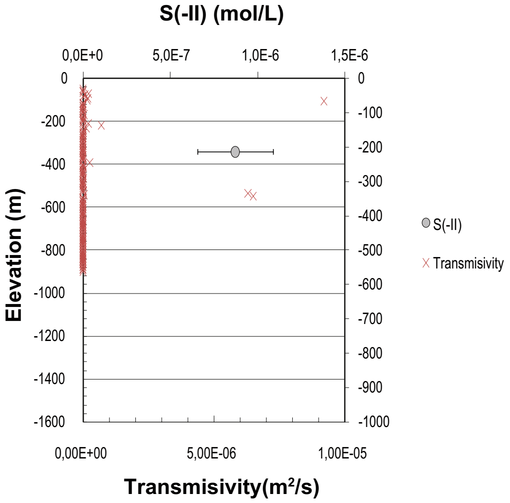




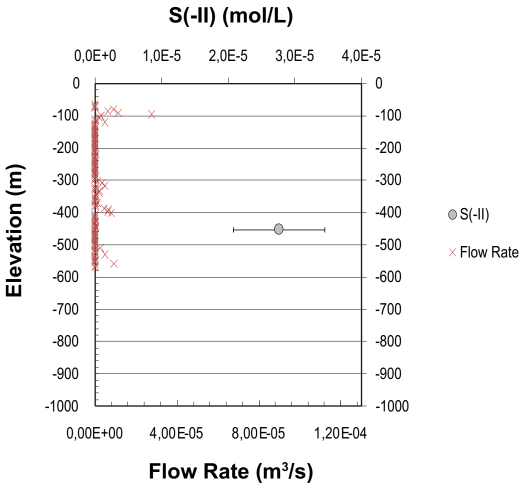
Borehole KLX17A

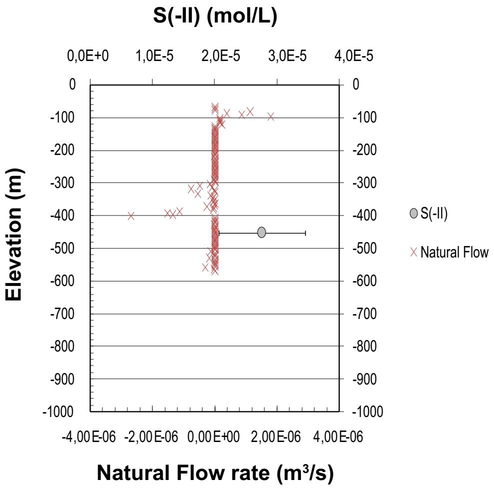


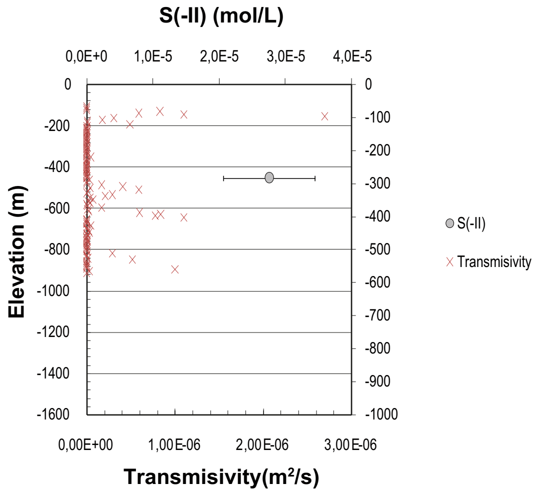




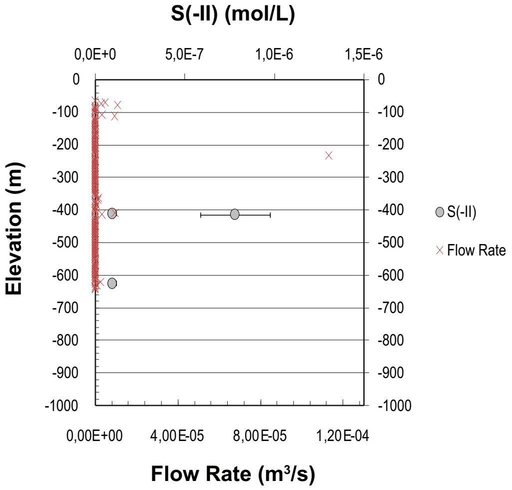
Borehole KLX18A

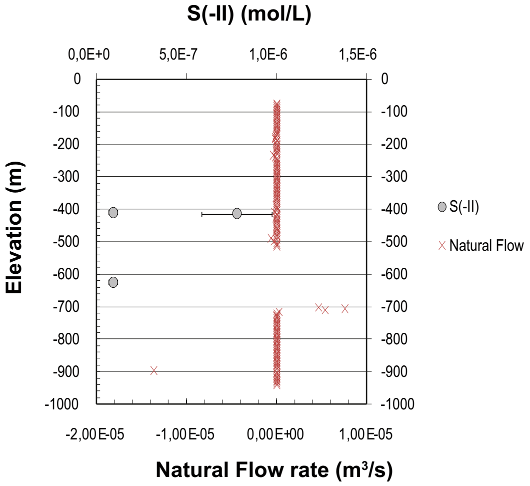


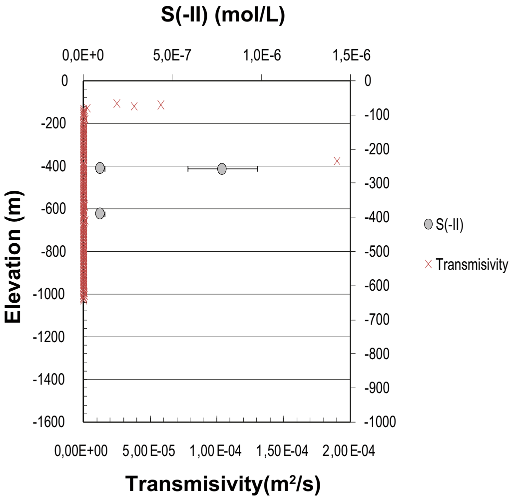




Borehole KLX19A







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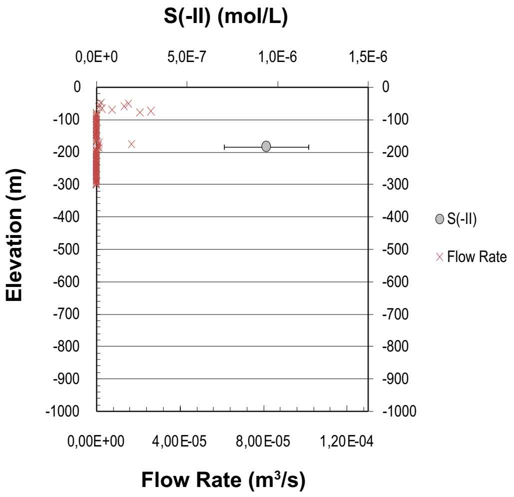

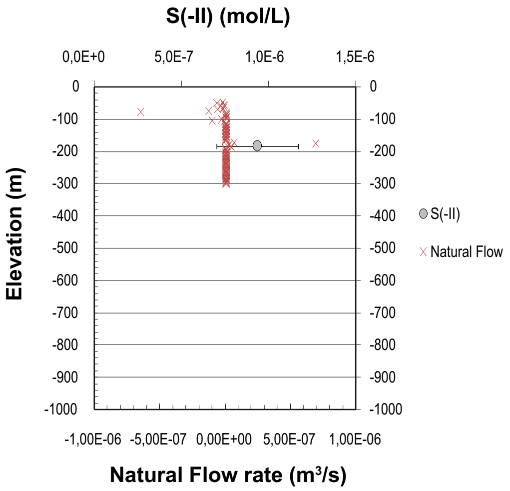

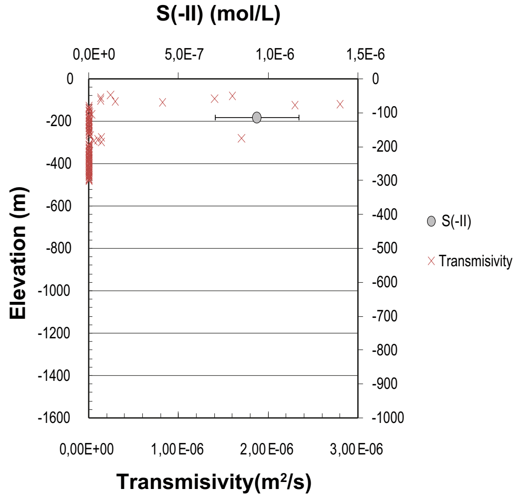

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