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Evaluating hydrochemical data from shallow groundwater in Forsmark from a microbiological perspective

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Abstract

Oxygen is one of the chemical species that can corrode a copper canister in a KBS-3 repository. It is therefore important to determine whether oxygen dissolved in precipitation or groundwater could reach repository depth by groundwater transport. This matter can be determined by gaining an understanding of the oxygen-consuming microbial processes that take place in shallow groundwater in the area of interest.

This report evaluates hydrogeochemical data from shallow groundwater in the Forsmark area from a microbiological perspective. Hydrogeochemical data were gathered from soil pipes at depths from 1.6 to 9.6 m and from percussion-drilled boreholes having mid-point depths of between c. 30 and c. 180 m. Only a few of the percussion-drilled boreholes had packers installed. The sampled sections were therefore very long, allowing groundwater from many different depths to mix.

Oxygen and oxidation-reduction potential (ORP) were measured in groundwater in soil pipes but not in percussion-drilled boreholes. The poor quality of the oxygen data made it difficult to identify the depth of origin of completely oxygen-free groundwater. Parameters that indicated ongoing anaerobic microbial processes, such as nitrite, ferrous iron, dissolved manganese, and sulphide, were found in many soil pipes.

The soil pipes displayed individual chemical profiles in terms of chemical species related to microbial activity. The microbial activity could not be linked to the classes of soil pipe, i.e. recharge, discharge, or intermittent.

Existing soil pipes and percussion-drilled boreholes could be used for additional sampling of microbial parameters. Such sampling would benefit from careful hypothesis-driven description of the sampling parameters and experience-guided choice of sampling methods.

Sammanfattning

Syre är ett kemiskt ämne som kan korrodera en kopparkapsel i ett KBS-3-förvar. Därför är det viktigt att bestämma om syre som är löst i nederbörd eller i grundvatten kan transporteras med grundvatten ner till förvarsdjup. För att förstå detta bör de syrekonsumerande mikrobiella processerna som pågår i de grunda grundvattnen i området av intresse studeras.

Syftet med den här rapporten var att från ett mikrobiologiskt perspektiv utvärdera hydrogeokemiska data från grunda grundvatten i Forsmarksområdet. Hydrogeokemiska data har samlats in från jordrör med djup från 1,6 till 9,6 m och från hammarborrade borrhål med ett medeldjup av ca 30 m till ca 180 m. Få hammarborrade hål hade packers installerade och därför var många av de provtagna sektionerna från dessa hål väldigt långa och innehöll förmodligen en blandning av grundvatten från olika djup.

Syre och ”oxidation-reduction potential” (ORP) mättes i jordrör men inte i hammarborrade hål. Den låga kvaliteten på syremätningarna gjorde det svårt att definiera det djup där grundvattnet var helt syrefritt. Mätbara halter av kemiska parametrar som indikerade att anaeroba mikrobiella processer pågick, t ex nitrit, tvåvärt järn, löst mangan och sulfid, fanns i flera av jordrören.

Jordrören uppvisade individuella kemiska karaktärer med avseende på kemiska specier som är relaterade till mikrobiell aktivitet. Den mikrobiella aktiviteten kunde inte kopplas till utflödes- eller inflödeszoner.

De befintliga jordrören och borrhålen kan användas för ytterligare provtagningar av mikrobiella parametrar. En sådan provtagning bör vara hypotesdriven och provtagningarna och valet av parametrar och provtagningsmetoder väljas utifrån erfarenhet från liknade uppdrag.

Contents

1 Introduction

One of the most important conditions for a KBS-3 type repository /Anonymous 1983/ for radioactive waste in the bedrock in Sweden is maintenance of anoxic and reduced conditions. The source of oxygen that could reach the repository is air that dissolves in precipitation or directly into groundwater. The oxygen could then theoretically reach down to repository depth of 500 m by transport of the groundwater.

Oxygen in shallow groundwater is effectively consumed by microorganisms during the degradation of organic matter, as oxygen functions as an electron acceptor in the microbial metabolism. Compounds other than organic ones, such as methane, sulphide, ammonium, iron, and manganese, can also be used by microorganisms as energy sources, when coupled with the reduction of oxygen. All such microbially catalyzed reactions will rapidly consume the available oxygen; when oxygen is depleted, the degradation of organic matter will be continued by anaerobic microorganisms. These organisms use other compounds as electron acceptors. They follow a thermodynamic hierarchy, depending on the energy exchange with the available electron donors and acceptors (see Figure 1-1).

As can be seen in Figures 1-1 and 1-2, the manganese- and iron-reducing bacteria (MRB and IRB, respectively) will follow when the oxygen is gone. Their source of electron acceptors is oxidized iron and manganese, which are solid phases found on fracture surfaces. They are active only if such mineral phases are present. One group of iron and manganese reducers (including the genus Shewanella) is very versatile and can use an array of different electron acceptors ranging from oxygen and nitrate to highly crystalline iron oxides; these microbes are facultatively anaerobic.

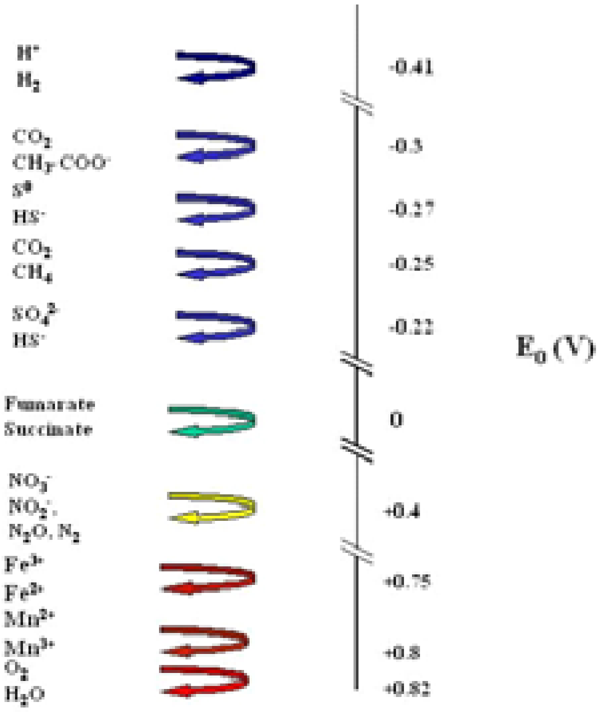


Figure 1-1. *Redox couples found in deep groundwater.*

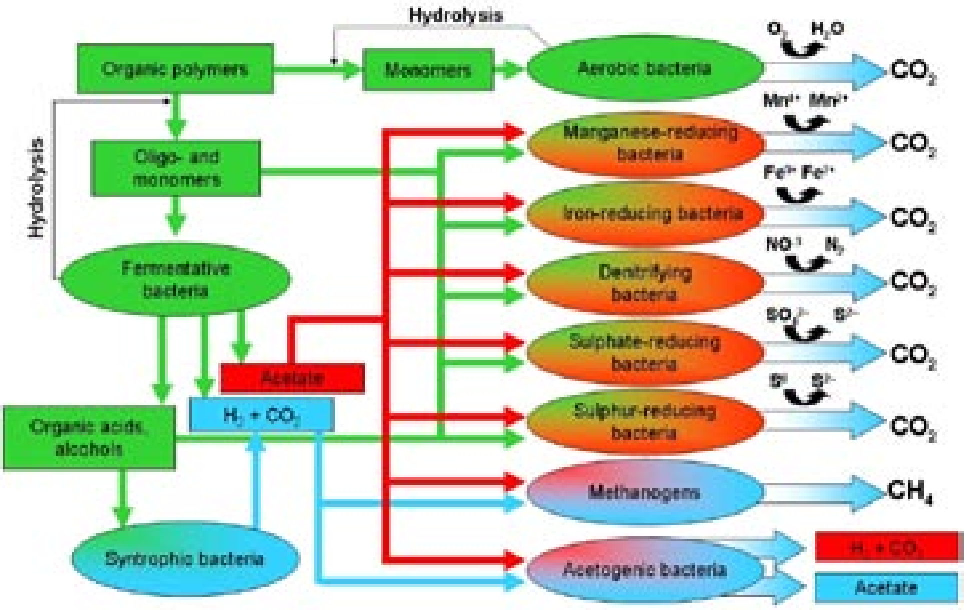


Figure 1-2. *Possible pathways for the flow of carbon in the subterranean environment. Organic carbon is respired with oxygen, if present, or else fermentation and anaerobic respiration occur using an array of different electron acceptors.*

The manganese and iron reducers are followed by nitrate-reducing bacteria (NRB). This group is also often facultatively anaerobic, meaning that members of it can use both oxygen and nitrate as electron acceptors. The next organism group comprises the sulphate-reducing bacteria (SRB), which use sulphate as an electron acceptor and reduce the sulphur atom in sulphate to sulphide, S^{2-}. Sulphate reducers are present in almost all waters, though in different numbers.

Along with the anaerobic microbes described above, fermenting microorganisms are also active. Fermentation consists of degradation pathways that do not require external electron acceptors; instead, electrons are shuffled around within the degraded molecule that has been split into two or more compounds. The degradation products consist of both more reduced and more oxidized organic molecules, such as organic acids, ketones, alcohols, and hydrogen gas. The hydrogen is an important energy source for the autotrophic microorganisms that thrive in groundwater. Apart from fermentation, hydrogen also comes from sources deeper in the bedrock /Apps and Van de Kamp 1993/. Two important groups of autotrophic organisms that can use hydrogen in groundwater are methanogens and acetogens. The end product of methanogens is methane and the end product of acetogens is acetate. Both groups fix carbon dioxide using the energy in hydrogen (see Equations 1-1 and 1-2).

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ Equation 1-1

$4H_2 + 2CO_2 \rightarrow CH_3COO^- + H^+ + 2H_2O$ Equation 1-2

There are also microorganisms that can use one or two organic carbon compounds and produce acetate and methane. Table 1-1 presents a summary of the different organism groups and their effect on the environment.

The site investigation in Forsmark has included studies of microbial populations in core-drilled boreholes from depths of 112 m to 978 m. Unfortunately, no microbial data are available for the interval from the ground surface to a depth of 112 m. On the other hand, *chemical* data are available from soil pipes and percussion-drilled boreholes for the interval from a depth of 1.6 m to c. 180 m. Some of the soil pipes yield data that can give clues as to the redox conditions, and thus information about the active microbial populations in the groundwater.

Table 1-1. Activities and effects of the different physiological groups of microorganisms found in deep groundwater.

Metabolic groups of microorganisms	Activity	Effect on the environment
Aerobic respiration	Oxidation of organic material by means of oxygen reduction	Depletion of oxygen and organic material Increase in alkalinity Lowering of redox potential
Anaerobic respiration	Oxidation of organic material along with the reduction of compounds other than oxygen	See below for each specific group of bacteria
Iron-reducing bacteria	Oxidation of organic material along with ferric iron reduction	Depletion of organic material and ferric iron Increase in ferrous iron concentration and alkalinity Lowering of redox potential
Manganese-reducing bacteria	Oxidation of organic material along with manganese(IV) ion reduction	Depletion of organic matter and manganese(IV) Increase in manganese(II) concentration and alkalinity Lowering of redox potential
Sulphate-reducing bacteria	Oxidation of organic material along with sulphate reduction	Depletion of organic matter and sulphate Increase in sulphide concentration and alkalinity Lowering of redox potential
Methanogenesis		
Heterotrophic methanogens	Convert short-chained organic material to methane and carbon dioxide	Depletion of organic material Increase in methane gas and carbon dioxide (alkalinity) concentrations Redox not influenced
Autotrophic methanogens	Oxidation of hydrogen gas and reduction of carbon dioxide to methane gas	Depletion of hydrogen gas and alkalinity Increase in methane gas concentration Redox lowered
Acetogenesis		
Heterotrophic acetogens	Convert organic material to acetate	Depletion of organic material other than acetate Increase in acetate concentration Redox not influenced
Autotrophic acetogens	Oxidation of hydrogen gas along with reduction of carbon dioxide to acetate	Depletion of hydrogen gas and alkalinity Increase in acetate concentration Redox lowered

The parameters influenced by microbial activity and therefore of interest are oxygen, redox potential or oxidation-reduction potential (ORP), nitrogen species, ferrous iron and manganese, sulphate and sulphide, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and hydrogen carbonate. In addition, stable isotope data for inorganic carbon and sulphate can give information about microbial processes.

Many of these parameters were measured in the soil pipes, but not all parameters on all occasions and not in all soil pipes. In some soil pipes, there are measurements covering quite long periods and covering seasonal variations over the year. Chemical data from the percussion-drilled boreholes are much fewer than those from the soil pipes: oxygen and ORP were not measured in any percussion-drilled boreholes; manganese, ferrous iron, DOC, sulphate, and sulphide were measured in some of them, but on few occasions.

This study aimed to answer the following questions raised at the start of the study with the help of available data:

- Is it possible to determine from area-specific chemistry and the results of the microbe investigation in Olkiluoto, Finland, what microbial processes are active in different parts of the Forsmark area?
- Which process or processes dominate the degradation of organic matter? Do different processes dominate in different areas and/or depths? Could the area be divided into subareas based on depth, recharge/discharge areas, or other factors?
- Is it possible to establish a depth limit for the presence of oxic groundwater? Does this limit vary over the course of the year or between years? Where is the oxygen consumed, if it is not transported down to the bedrock?
- Are we still missing some chemical parameters necessary for a full understanding of the microbiology in the oxic/anoxic zone in Forsmark?

This report will evaluate the available data with respect to microbial activity. It is hoped that the evaluation will reveal seasonal variations, environmental variations, and depth variations present in shallow groundwater in Forsmark.

2 Data evaluation

The data used in this report are from measurements made in soil pipes and percussion-drilled boreholes. The data were compiled by Mats Tröjbom and are the same as used in the SKB report R-07-55 /Tröjbom et al. 2007/.

2.1 Sampling depths

For the soil pipes, the depth of the midpoint of the 1–2 m long screen in each pipe was defined as sampling depth in this work. Based on this definition, the sampling depth of the shallowest soil pipe was 1.6 m and that of the deepest soil pipe that provided a sufficient amount of data was 9.6 m. Most of the soil pipes had sampling depths in the range 3–6 m.

Also for the percussion-drilled boreholes, the midpoints of the sampled depth intervals were defined as sampling depths. Since some of these borehole intervals were very long, especially in the boreholes that had no packers installed, this implies a relatively large uncertainty concerning the actual sampling depth (i.e. what depth the water came from). In the boreholes without packers, the sampled sections were in some cases as long as 200 m. Water samples from such boreholes may therefore be a mixture of shallow and deep groundwater. Furthermore, the important parameters oxygen and ORP were not measured in percussion-drilled boreholes.

Using the section midpoints to define the sampling depths, the shallowest percussion-drilled borehole section providing data to the present work had a sampling depth of c. 30 m and the deepest section was at a depth of c. 180 m. This indicates that no data were available from depths between 10 and 25 m. This is unfortunate, since this depth interval is where the greatest decrease of oxygen in Olkiluoto groundwater has been observed to occur, as can be seen in Figure 2-1 taken from /Pedersen 2006/. This figure also shows the difference in oxygen concentration between spring and autumn in samples from soil pipes and boreholes in Olkiluoto, Finland.

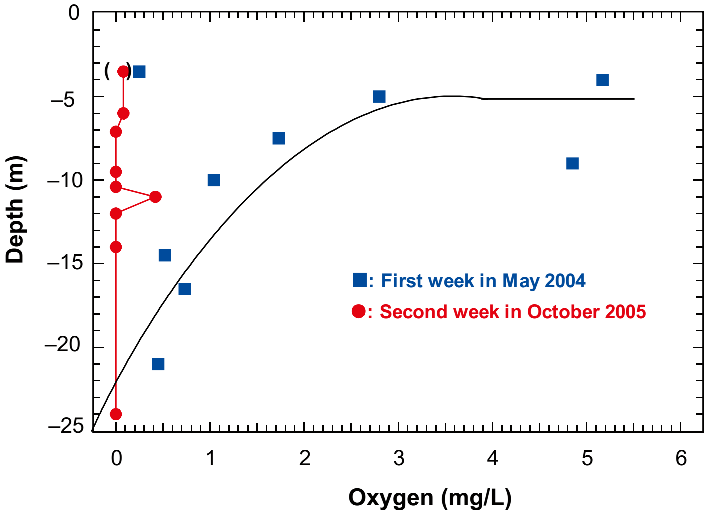


Figure 2-1. *The concentration of dissolved oxygen in shallow groundwater in Olkiluoto, Finland, analysed using Winkler titration in the laboratory /from Pedersen 2006/.*

Concerning Forsmark, it should be noted that many of the borehole sections sampled there included the shallow part of the rock; in particular, several open boreholes covered the whole interval from the ground surface to c. 200 m depth. However, due to the uncertainty regarding the actual sampling depths discussed above data from these boreholes could not be used to describe the hydrochemical conditions in the potentially important 10–25 m depth interval (or any other specific interval). In either case, oxygen and ORP were not available from boreholes deeper that c. 10 m.

2.2 Oxygen

Measuring oxygen concentrations is complicated and is done using two main approaches. They can be measured in the field using an oxygen electrode or in the laboratory using a modified Winkler method, as described in detail in /Carritt and Carpenter 1966/. In the Winkler method, groundwater is carefully sampled in 115 mL, glass-stoppered Winkler bottles; the dissolved oxygen is immediately precipitated as manganese-hydroxide-oxide ($MnO(OH)_2$) by adding manganese ions in an alkaline medium. With the oxygen bound in the precipitate, the samples can be stored and the actual analysis is done in the laboratory; the following are the reactions that take place during sampling and analysis.

$2Mn(OH)_2 + O_2 \Rightarrow 2MnO(OH)_2$ Equation 2-1

The manganese hydroxide is dissolved in the laboratory with acid and reduced by iodine ions, as follows:

$MnO(OH)_2 + 4H_3O^+ + 3I^- \Rightarrow Mn^{2+} + I_3^- + 7H_2O$ Equation 2-2

Finally, the I_3^- ions produced are determined by titration, using thiosulphate ions and soluble starch as the titration indicator, as follows:

$2S_2O_3^{2-} + I_3^- \Rightarrow S_4O_6^{2-} + 3I^-$ Equation 2-3

The field measurements in Forsmark were made using two multiparameter sondes, YSI 600 QS and YSI 6600 EDS, which measured pH, water temperature, oxygen, ORP, and electrical conductivity. The measurements were made in a simple flow-through cell, and the sonde used for measuring oxygen was a membrane electrode. This method for measuring oxygen is somewhat less reliable than the Winkler titration method. /Nilsson and Borgiel 2005/ concluded that if an electrode measurement indicated a value of 4 mg L^{-1}, the true value might well be below the detection limit or even zero. This is a very rough estimate and the detection limit should be much lower.

The membrane electrode used in the monitoring program, YSI Rapid Pulse™ Dissolved Oxygen, has a measurement range of 0–50 mg L^{-1} with a resolution of 0.01 mg L^{-1}; the accuracy of the electrode is ±0.2 mg L^{-1} over the 0–20 mg L^{-1} range. This type of electrode needs continuous calibration and maintenance, for example, the membrane needs to be changed on a regular basis. There is another type of oxygen electrode available, which uses luminescence to detect oxygen and is easier to handle. In sampling shallow groundwater at Olkiluoto, Finland, both types of electrodes were used, but on different occasions. The conclusion was that the HQ10 Hach Portable LDO™ Dissolved Oxygen Meter, Cat. No. 51815-00 (Hach, Stockholm, Sweden) gave lower and more reliable results and was easier to handle than the pIONeer 20 portable oxygen meter equipped with a DOX20T-T oxygen probe /Pedersen 2007/. For all measurements of oxygen in water with low or zero values, it must be established that a zero value can indeed be measured by making a reference measurement in completely oxygen-free water.

Figure 2-2 shows oxygen values versus depth in groundwater from soil pipes in Forsmark. If the criterion proposed by /Nilsson and Borgiel 2005/ of a detection limit of 4 mg L^{-1} is applied to the dataset, there will not be many data points above this limit. The precision of the data above the detection limit is also very uncertain. Since the oxygen was mostly measured in

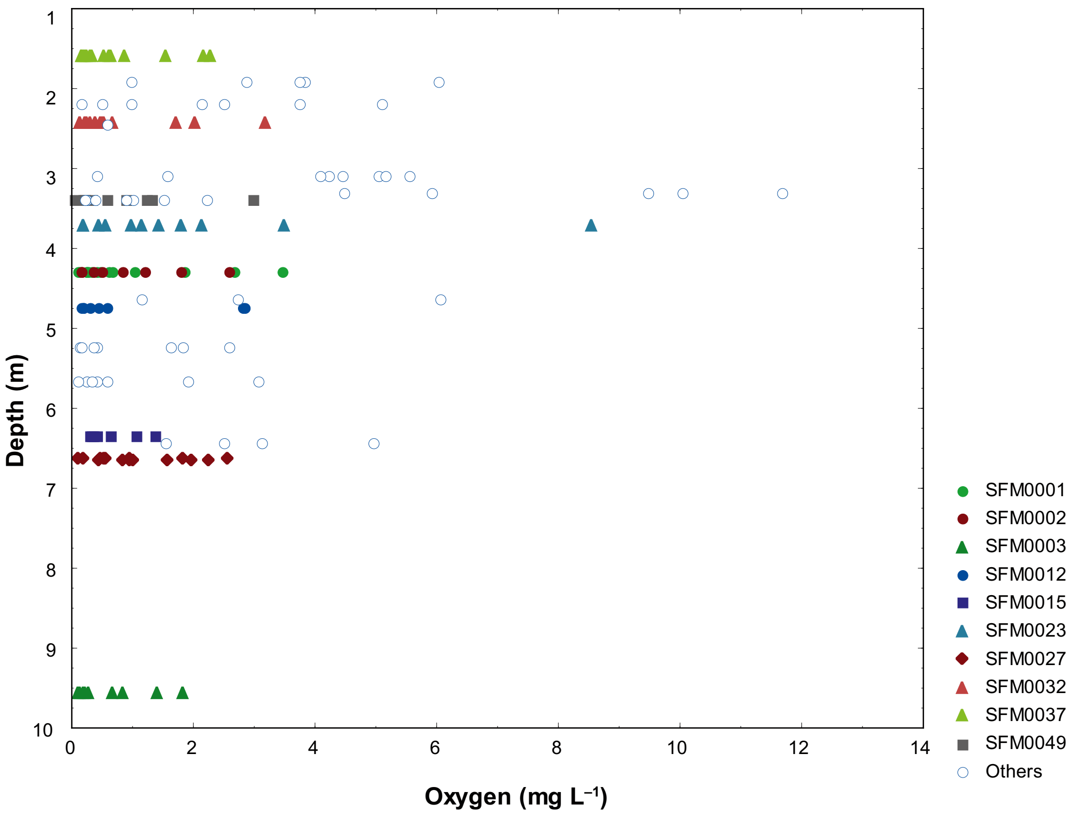


Figure 2-2. *Field measurements of oxygen versus depth in shallow groundwater in Forsmark***.**

the field using an electrode, it is important to be careful when evaluating the results in relation to other redox-sensitive parameters. This matter is examined in greater detail in the following paragraphs.

2.3 Oxidation-reduction potential

2.3.1 Methods and parameters

The oxidation-reduction potential (ORP) is measured using one electrode, often made of a precious metal such as gold, silver or platinum, with a silver–silver chloride reference electrode. This parameter is used in the SKB surface system program. When sampling deep groundwater, several electrodes are used instead of only one as in the ORP measurements. The data from the deep sampling are reported as the redox potential (E_h) which is the recalculated potential against the hydrogen reference electrode. In this report, the ORP values are used. The E_h value can be calculated using the following equation:

$$E_h = E_{meas} + E_{ref} \qquad \text{Equation 2-4}$$

where E_h is the redox potential, E_{meas} is the ORP value, and E_{ref} is the potential of the electrode against the hydrogen electrode. The potential of the used electrode at 15°C is +214 mV.

Redox potential or oxidation-reduction potential is a measure of a system’s tendency to donate electrons. Negative values indicate a high tendency to donate electrons and positive values a low tendency and that the system more likely accepts electrons.

2.3.2 Comparison of oxygen data with ORP, ferrous iron, and sulphide

To evaluate the field oxygen data, these were plotted versus the ORP data (see Figure 2-3). This figure indicates no obvious relationship between the parameters, a relationship that would have been clear if the data quality had been satisfactory.

Ferrous iron (Fe^{2+}) and sulphide (S^{2-}) are two reduced species that rapidly oxidize if oxygen is present. If these two species are present, there should be no oxygen. In Figure 2-4 and Figure 2-5, ferrous iron and sulphide are plotted against oxygen in groundwater from the soil pipes. In both cases, oxygen is found together with the reduced species of iron and sulphide, which is unlikely. Ferrous iron and sulphide are only present in anoxic systems at the pH found in groundwater in Forsmark, which was approximately 7. Figure 2-6 shows oxygen versus ORP in identified soil pipes (see Section 3). No specific groups of data can be seen.

No oxygen or ORP data are available for the percussion-drilled boreholes. Therefore, no comparison could be made for the deeper part of the system.

2.4 Conclusions

The conclusions of the data evaluation can be summarized as follows:

- Oxygen and ORP data from the 10–25 m depth interval were missing from the dataset. This made evaluating oxygen penetration difficult, since it was in this depth range that the oxygen depletion occurred in Olkiluoto, Finland. Oxygen and ORP data were missing for the percussion-drilled boreholes.
- The quality of the oxygen and ORP data was not good enough to allow us to make conclusions as to what parameters (e.g. area, season, and depth) determined the oxygen depletion. It is suggested that a luminescence electrode be used for measuring oxygen.
- The presence of reduced species of iron and sulphur, ferrous iron, and sulphide indicate that anoxic conditions were present at some point in the sampled soil pipes.

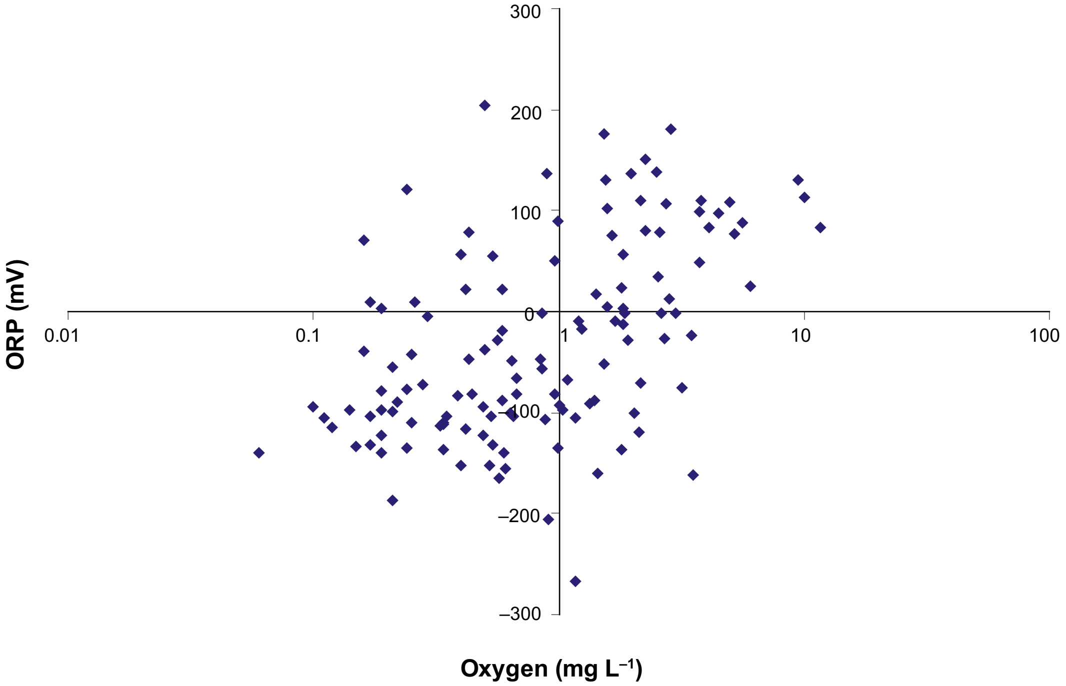


Figure 2-3. ORP values versus field oxygen values in shallow groundwater in Forsmark.

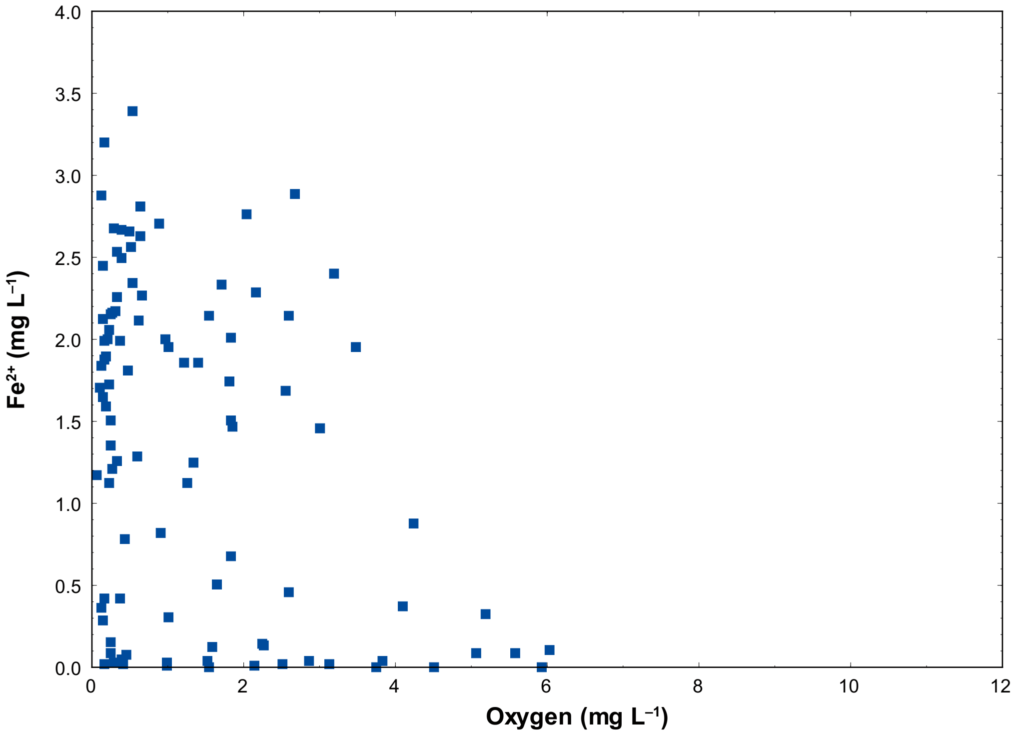


Figure 2-4. Field oxygen data versus ferrous iron in shallow groundwater in Forsmark.

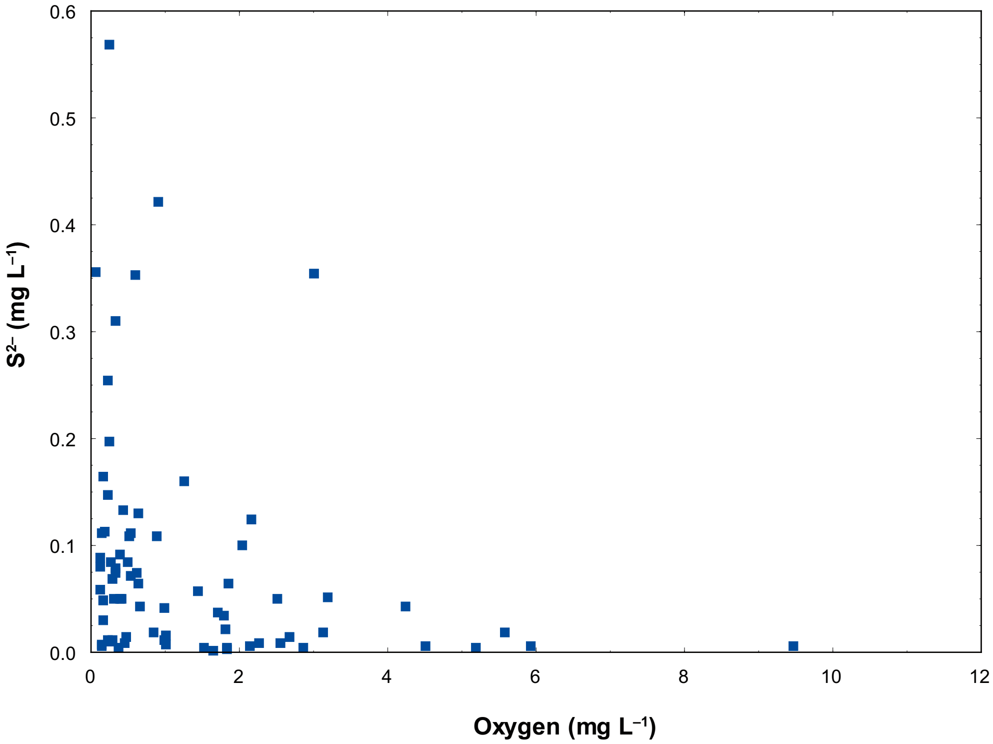


Figure 2-5. Field oxygen versus sulphide in shallow groundwater in Forsmark.

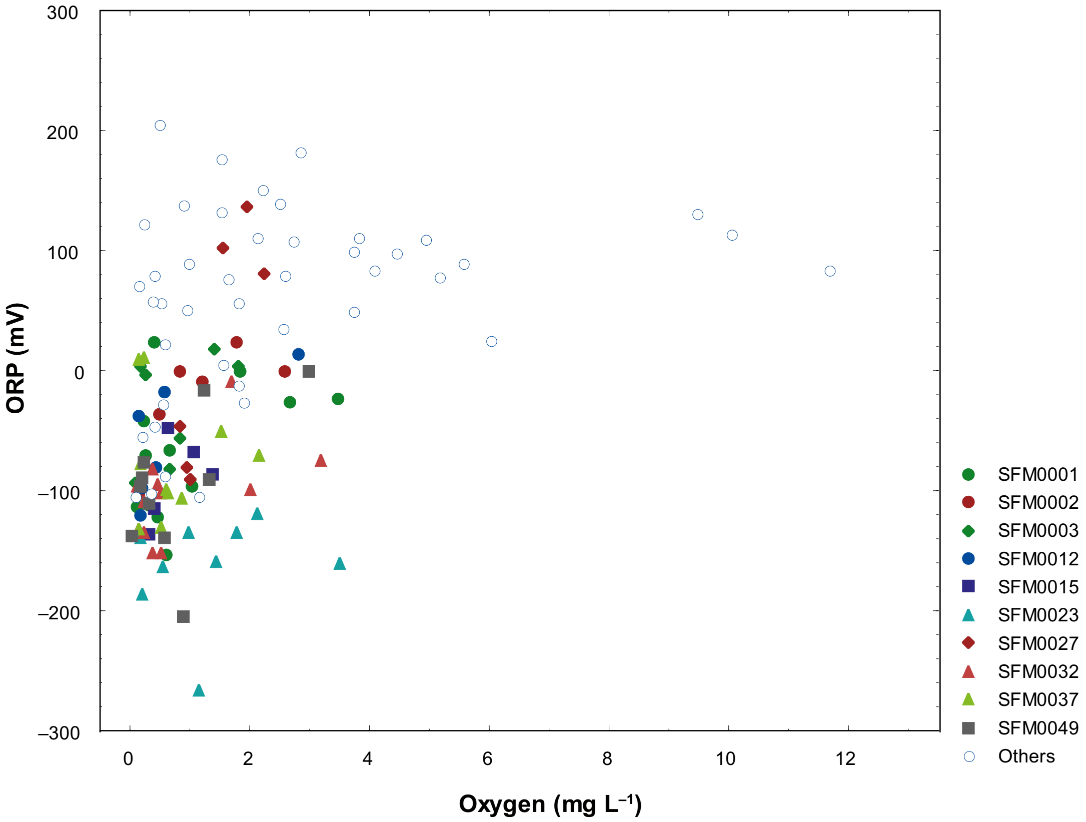


Figure 2-6. *Field oxygen data versus oxidation-reduction potential (ORP) in groundwater from the soil pipes in Forsmark.*

3 Characterization of soil pipes and percussion-drilled boreholes

3.1 Overview of data and sampled boreholes

Since one of the questions to be answered by this study was whether there were any differences between soil pipes with discharging or recharging groundwater, initial analyses focused on these two groups of soil pipes. Several plots were made in which oxygen, DOC, DIC, chloride, and time were plotted with the data divided into discharge and recharge groups. All the plots from these studies are compiled in the Appendix. No obvious trends were found when the data were analyzed in this way. A study of shallow groundwater in Olkiluoto, Finland /Pedersen 2008/, found that most of the soil pipes sampled had chemical characteristics that remained stable from season to season and from one year to another.

When some of the parameters measured in Forsmark were plotted against each other, a borehole-specific chemical composition pattern became evident. The chosen soil pipes were those sampled in the now-ongoing monitoring programme, and because of that had data series for most of the parameters. In Table 3-1 the biotope and characteristics of the identified boreholes are compiled. When suitable, figures from a previous unpublished study of soil pipes have been used to illustrate seasonal changes over the course of the year. This unpublished study was made as a basis for a proposed microbial investigation of shallow groundwater in Forsmark. Data in these figures come from both the boreholes identified in Table 3-1 and the boreholes in the "other group", i.e. the following soil pipes: SFM0005, -06, -08, -09, -10, -11, -13, -14, -16, -17, -18, -19, -20, -21, -22, -24, -25, -26, -28, -29, -30, -31, -34, -36, -57, -60, -61, -62, -63, -65, and -74.

The data from percussion-drilled boreholes were much scarcer, no oxygen, ORP, or DIC data being available for these boreholes. Ferrous iron, manganese, and nitrogen species were measured only in some boreholes on a few occasions. Data for chloride, hydrogen carbonate, $\partial\ ^{13}C$, sulphate, and $\partial\ ^{34}S$ were available for all boreholes and measured over longer periods.

Table 3-1. Depth, main biotopes, and symbols for well-characterized soil pipes in Forsmark.

Soil pipe	Depth (m)	Main biotype	Symbol in figures
SFM0001	4.3	Forest	●
SFM0002	4.3	Open landscape	●
SFM0003	9.6	Forest	◆
SFM0012	4.7	Lake Gällsboträsket	●
SFM0015	6.3	Lake Eckarfjärden	■
SFM0023	3.7	Lake Bolundsfjärden	▲
SFM0027	6.7	Forest	●
SFM0032	2.4	Open landscape	▲
SFM0037	1.6	Forest	▲
SFM0049	3.4	Open landscape	●

As described in Section 2.1, many of the percussion-drilled boreholes had no packers installed, which means that the water sampled was a mixture of water from many different depths. The section midpoints used to define the sampling depths in the percussion-drilled boreholes in this study were in the interval 30–180 m. Although shallower depths were included in the sampled sections in many boreholes (about 15 boreholes were open up to the ground surface and others had relatively shallow packed-off sections), it was uncertain whether the potentially important depth interval between 10 m and 25 m was represented in the dataset.

3.2 Dissolved organic carbon and dissolved inorganic carbon

In Figure 3-1, the dissolved organic carbon (DOC) and the dissolved inorganic carbon (DIC) are plotted versus each other. The soil pipes had DOC and DIC data that were typical of each soil pipe, and soil pipes placed in similar environments displayed data coherence from one sampling occasion to another. The typical DOC and DIC profiles seem to be linked to the biotope where the soil pipes were placed. Soil pipes SFM0001 and SFM0037 were both located in areas with 60–70% forest cover and 30–40% open land in the closest 100 × 100 m surrounding area, but differed in the closest 20 × 20 m area in that SFM0037 was located in more open area. On the other hand, SFM0037 was 1.6 m deep and hence shallower than SFM0001 with a depth of 4.3 m. These soil pipes had the highest DOC values as well as high DIC values.

The data are grouped into two clusters, one of which represents autumn and winter data and the other spring and summer data. This is consistent with the degradation of organic matter being high in autumn and the mineralization being highest in winter. The DIC values should therefore be higher in winter and the DOC values slightly lower than in spring and summer when the biomass production is higher. SFM0003 was also located in a forested area, but its groundwater was sampled at a greater depth. The DOC was lower in this soil pipe, probably because more

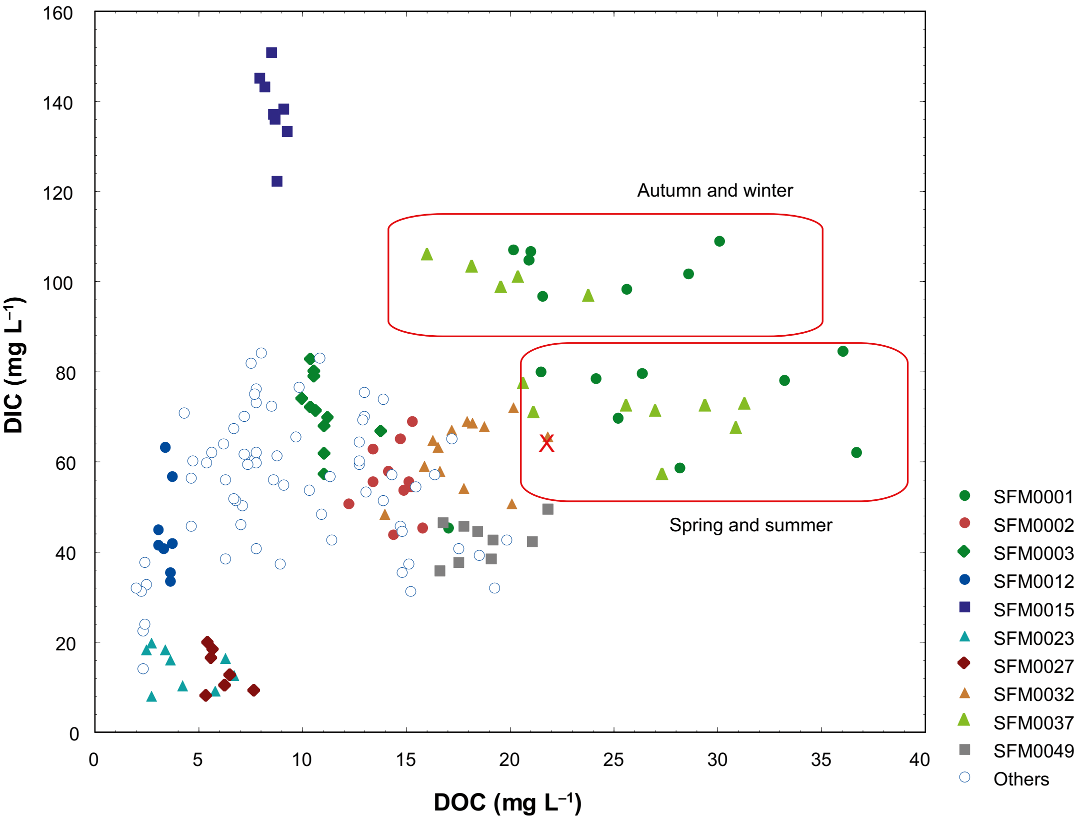


Figure 3-1. *DOC versus DIC in groundwater from soil pipes in Forsmark. The red × indicates that this point does not belong to soil pipes SFM001 or SFM037.*

of the organic matter had become degraded on its way from the surface to the sample depth. In addition, SFM0027 was placed in a forested area, but at a depth of 6.7 m, so the low DOC values there may be explained by heavier degradation occurring in this borehole.

Soil pipe SFM0015 is located in lake sediment in Lake Eckarfjärden and was distinguished by its high DIC values. SFM0012 and SFM0023 are also located in lake sediments, in Lake Gällsboträsket and Lake Bolundsfjärden, respectively. SFM0023 had a marine signature, containing approximately 3,700 mg chloride L^{-1}. Soil pipes SFM0002, SFM0032, and SFM0049 are located in mostly open landscapes and displayed a moderate content of DOC and DIC compared to the other characterized soil pipes.

DOC was measured in some of the percussion-drilled boreholes on a few occasions. Figure 3-2 shows the distribution of DOC versus depth for all the soil pipes and percussion-drilled boreholes. It can be seen that many measurements were made in the soil pipes but far fewer in the deeper boreholes. The range of DOC values in the upper ten metres is 2–36 mg L^{-1}; in the deeper groundwater the DOC is also high, between 2 and 13 mg L^{-1}. The value of 35 mg L^{-1} DOC found at a depth of 175 m is spectacular and is accompanied by a very high sulphide value of 1.57 mg L^{-1} as well as high ferrous iron and manganese values of 5.36 and 1.93 mg L^{-1}, respectively. These samples are all from the relatively well-defined 168–182 m section in HFM019. This will be discussed more in later sections.

Biological processes discriminate against heavy isotopes, and this can be seen in the isotopic fractionation of, for example, dissolved organic carbon in groundwater. Photosynthesis makes organic carbon in plants and microorganisms lighter than the carbon dioxide in the atmosphere. This light composition is also seen in the hydrogen carbonate in shallow groundwater that originates from the degradation of organic matter from the ground surface. The isotopic carbon compositions of different carbon reservoirs on Earth are depicted in Figure 3-3. It is important to note that the isotopic composition tells nothing about when the fractionation took place. As well, mixtures of waters having different isotope signatures can obscure the picture. To be certain of what processes are currently ongoing, the microbial communities must be investigated.

Figure 3-4 shows $\partial\ ^{13}C$ versus DIC in groundwater from soil pipes in Forsmark. The ^{13}C is compared with a standard, the Vienna Pee Dee Belemnite (PDB) carbonate, having a specific isotopic composition. The soil pipe with the heaviest inorganic carbon was SFM0015, with $\partial\ ^{13}C$ values from 6 to 8‰ (PDB). This soil pipe is located below the sediment in Lake Eckarfjärden.

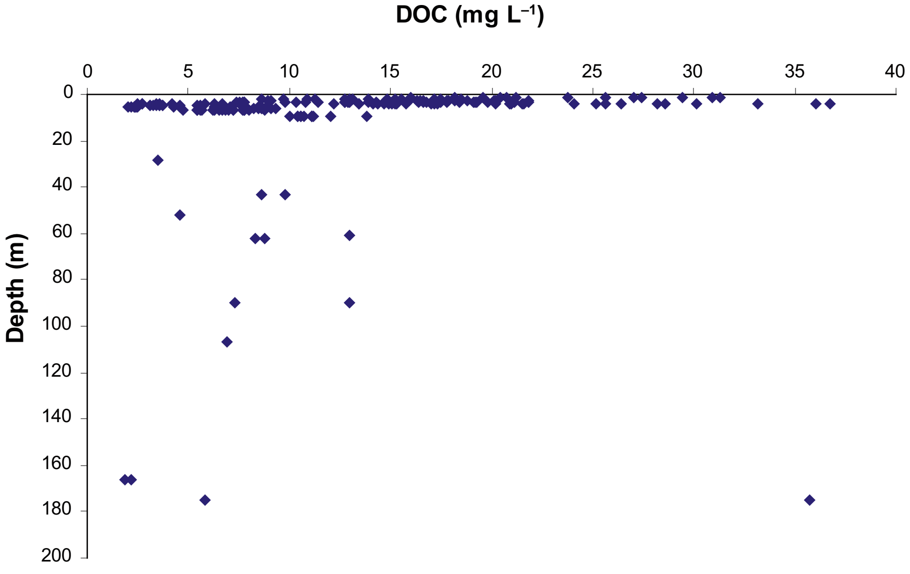


Figure 3-2. Dissolved organic carbon (DOC) versus depth in groundwater from soil pipes and percussion-drilled boreholes in Forsmark.

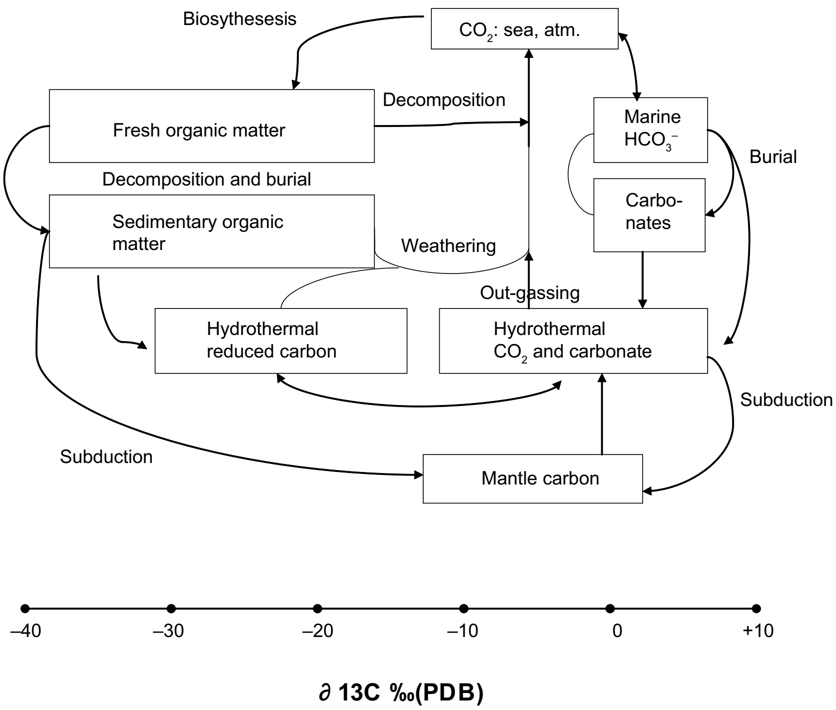


Figure 3-3. *Carbon isotopic composition of carbon reservoirs (modified from /Des Marais 1996/).*

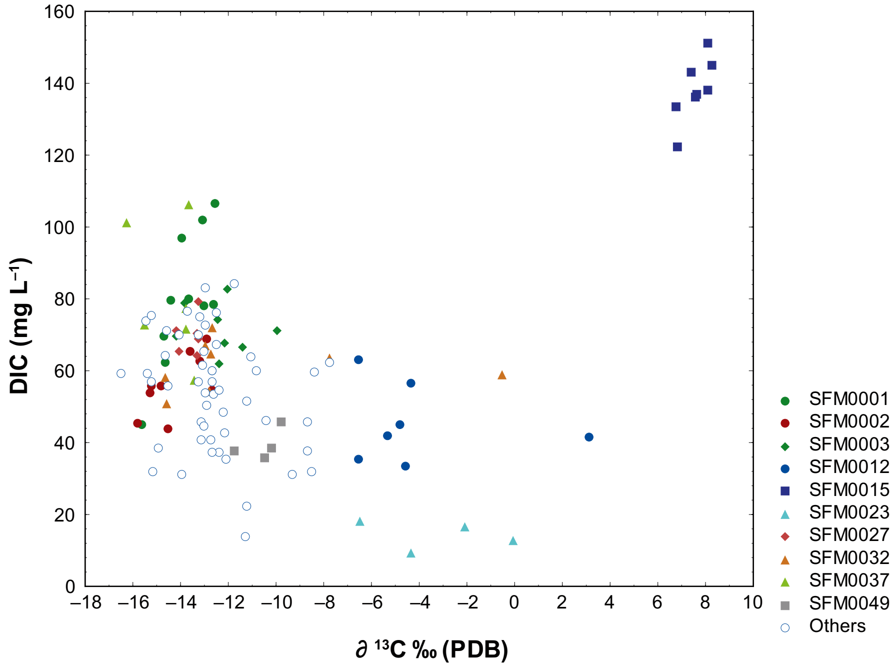


Figure 3-4. *∂ ^{13}C versus DIC in groundwater from soil pipes in Forsmark.*

Other soil pipes with distinct ∂^{13}C values between –6 and 0 are SFM0023 and SFM0012. SFM0023 is located below the bottom sediment in Lake Bolundsfjärden and is exposed to saline groundwater. SFM0012 is also located below the lake sediment, but in Lake Gällsboträsket.

There are at least two different explanations for the heavy observed ∂^{13}C signature. The first is that ongoing autotrophic processes, such as methanogenesis and/or acetogenesis, may discriminate against the heavy carbon dioxide. The second explanation is that there could be ongoing calcite dissolution in these lakes. The very low ∂^{13}C values in SFM0015 indicate that methanogenesis is more likely the origin. Since stable isotope measurements do not indicate when the process occurred, they must be complemented with microbial studies and analyses of groundwater gases. The soil pipes placed in forest and open landscape have inorganic carbon with light ∂^{13}C signatures, which reveals the photosynthetic origin of the degraded organic matter.

Figure 3-5 shows the carbon isotopic composition of inorganic carbon versus hydrogen carbonate measured in samples from percussion-drilled boreholes. No distinct pattern was evident for the different boreholes, but there was a trend towards lighter carbon in groundwater containing a higher concentration of hydrogen carbonate. It should be noted that in some boreholes, sampling was not consistently done at the same depths on different sampling occasions. Figure 3-6, on the other hand, presents ∂^{13}C versus depth in the percussion-drilled boreholes. It indicates that the lighter carbon was found at shallower depths, together with higher hydrogen carbonate concentrations than were found at greater depths.

3.3 Anaerobic microbial processes in groundwater

3.3.1 Nitrate reduction

It can now be concluded that there is variation in the amount of DOC and DIC in groundwater from soil pipes. In samples from some pipes, the DOC content is higher and there is degradation, especially in autumn and winter. Because of the varying quality of the oxygen data, they

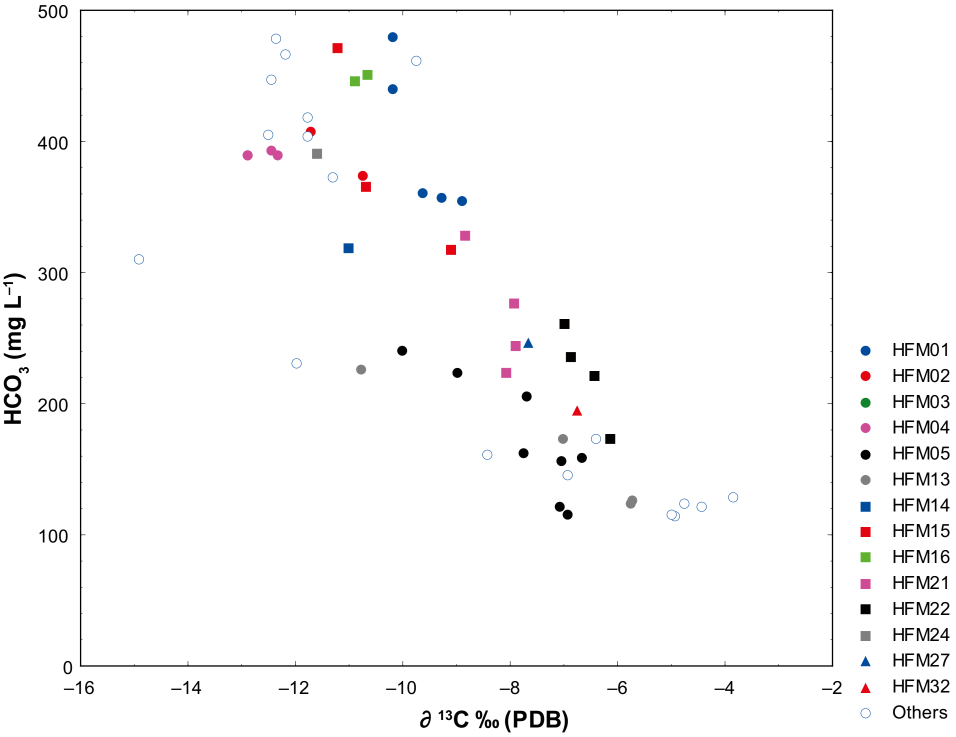


Figure 3-5. *Carbon isotopic composition of inorganic carbon versus HCO$_3^-$ in groundwater from percussion-drilled boreholes in Forsmark.*

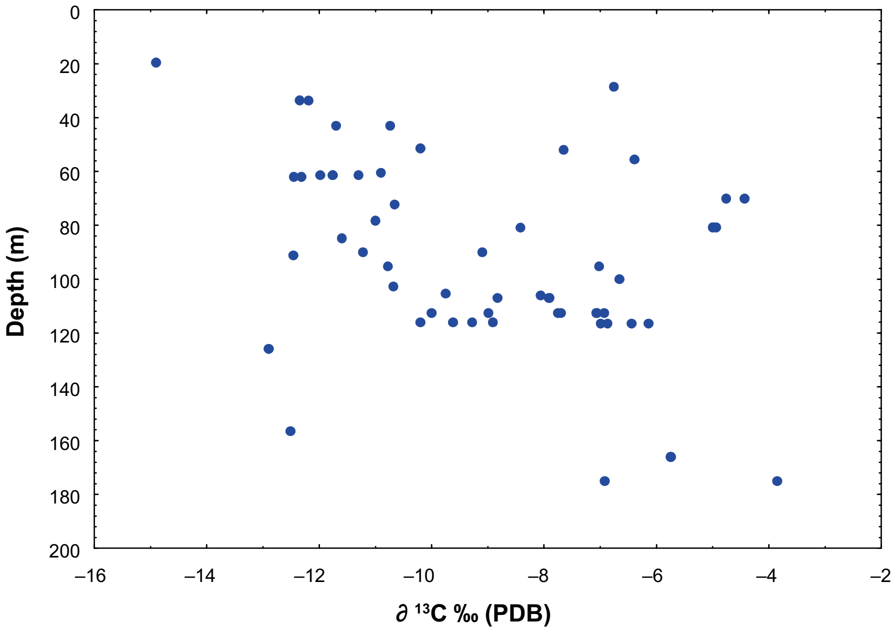


Figure 3-6. *Carbon isotopic composition of inorganic carbon versus depth in groundwater from percussion-drilled boreholes in Forsmark.*

cannot be used to determine the depth at which the oxygen is depleted. This means that the alternate electron acceptor used when oxygen is consumed and anaerobic degradation takes place, namely, nitrate, will be used. Many aerobic microorganisms have the ability to use nitrate as an alternate electron acceptor when oxygen is depleted, and for this reason are called facultative anaerobes.

Concentrations of nitrate are often low in groundwater, depending on how frequently the nitrate is used as an electron acceptor by microorganisms and as nitrogen source for plants and microorganisms. The end product of nitrate reduction is often nitrogen gas, but this cannot be used as an indication of ongoing nitrate reduction because of its high background concentration in air and groundwater. Some microorganisms that use nitrate oxidize it only partially to nitrite and not completely to nitrogen gas. Thus, the presence of nitrite can be an indicator of ongoing nitrate reduction. In Figure 3-7, nitrate is plotted versus nitrite for groundwater from soil pipes in Forsmark.

The detection limit for nitrite is 0.0003 mg L^{-1} and for nitrate approximately 0.001 mg L^{-1} (different values are found in SKB's database SICADA). Some points in Figure 3-7 are below the detection limit for one or both of the parameters. Some data, belonging to the "other" group, are relatively high in nitrate, up to 3 mg L^{-1}. When they were checked, it was clear that the high values came from several soil pipes but from one sampling occasion in April 2005. One explanation for this unusually high reading may be that the degradation and mineralization of organic matter in autumn and winter were close to complete, no nitrate reduction was occurring, and the vegetative growth period had not yet started. On the same occasion, oxygen was measured both in the field using an electrode and in the lab using the Winkler method. Measurable amounts of oxygen were found in most of the soil pipes, which explains the absence of nitrate reduction and thus the high nitrate values.

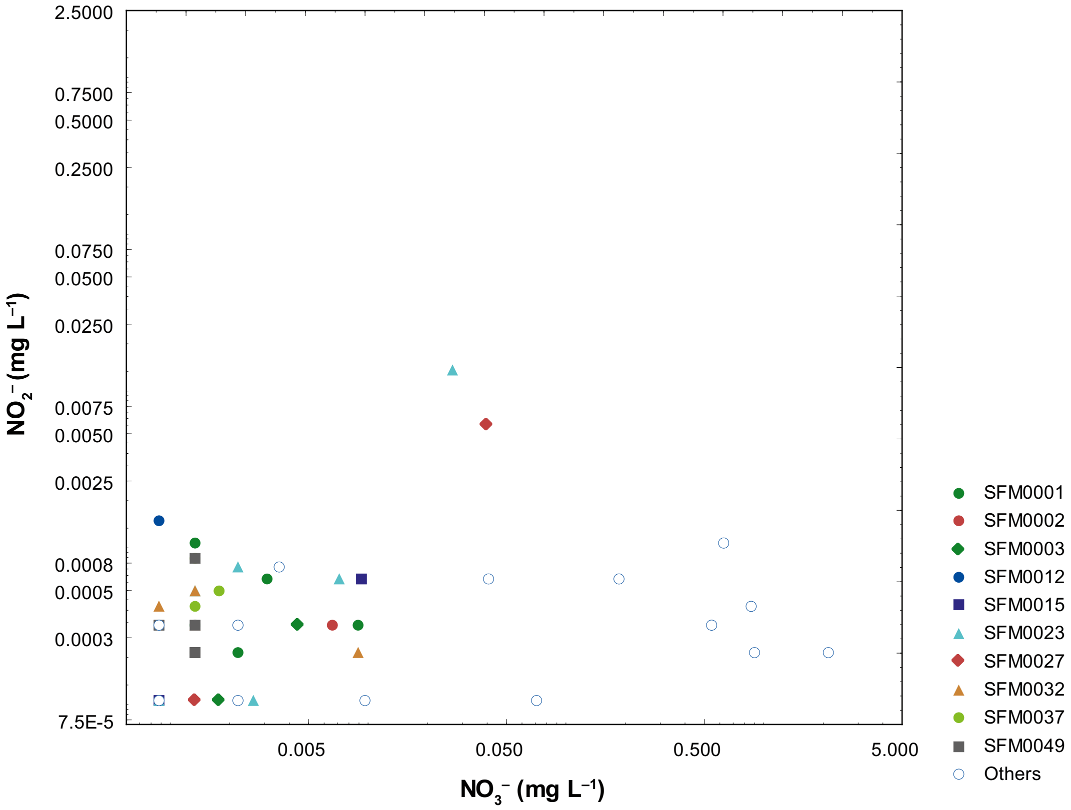


Figure 3-7. *Nitrate versus nitrite in groundwater from soil pipes in Forsmark.*

For some soil pipes, the nitrate/nitrite data were plotted versus the sampling date to elucidate whether any seasonal variation was evident in the dataset (see Figure 3-8). This plotting indicates that in late winter and spring the nitrate concentration rises above the detection limit and that in summer and autumn nitrate is consumed.

The investigations in Olkiluoto in Finland revealed that the greatest variation in the number of nitrate-reducing bacteria was between different soil pipes and not between samples from different seasons /Pedersen 2008/.

3.3.2 Iron and manganese reduction

The group of anaerobic bacteria that follow the nitrate-reducing bacteria after the nitrate is depleted is the iron- and manganese-reducing bacteria. Activity of this group of microorganisms is dependent on the presence of solid ferric iron or manganese phases, and results in elevated ferrous iron and manganese levels in the groundwater. Figure 3-9 shows the ferrous iron concentration versus depth and Figure 3-10 the manganese concentration versus depth for groundwater samples from soil pipes in Forsmark. There was no obvious trend in either the ferrous iron or manganese concentrations against depth. The concentrations seem to be more soil pipe related than depth related. This is clearly evident in Figure 3-11, where ferrous iron is plotted against manganese. In this plot it can be seen that both species were related in several of the soil pipes. The highest concentrations were found in the soil pipes with the highest DOC values, i.e. SFM0001 and SFM0037, which were located in or near forest areas.

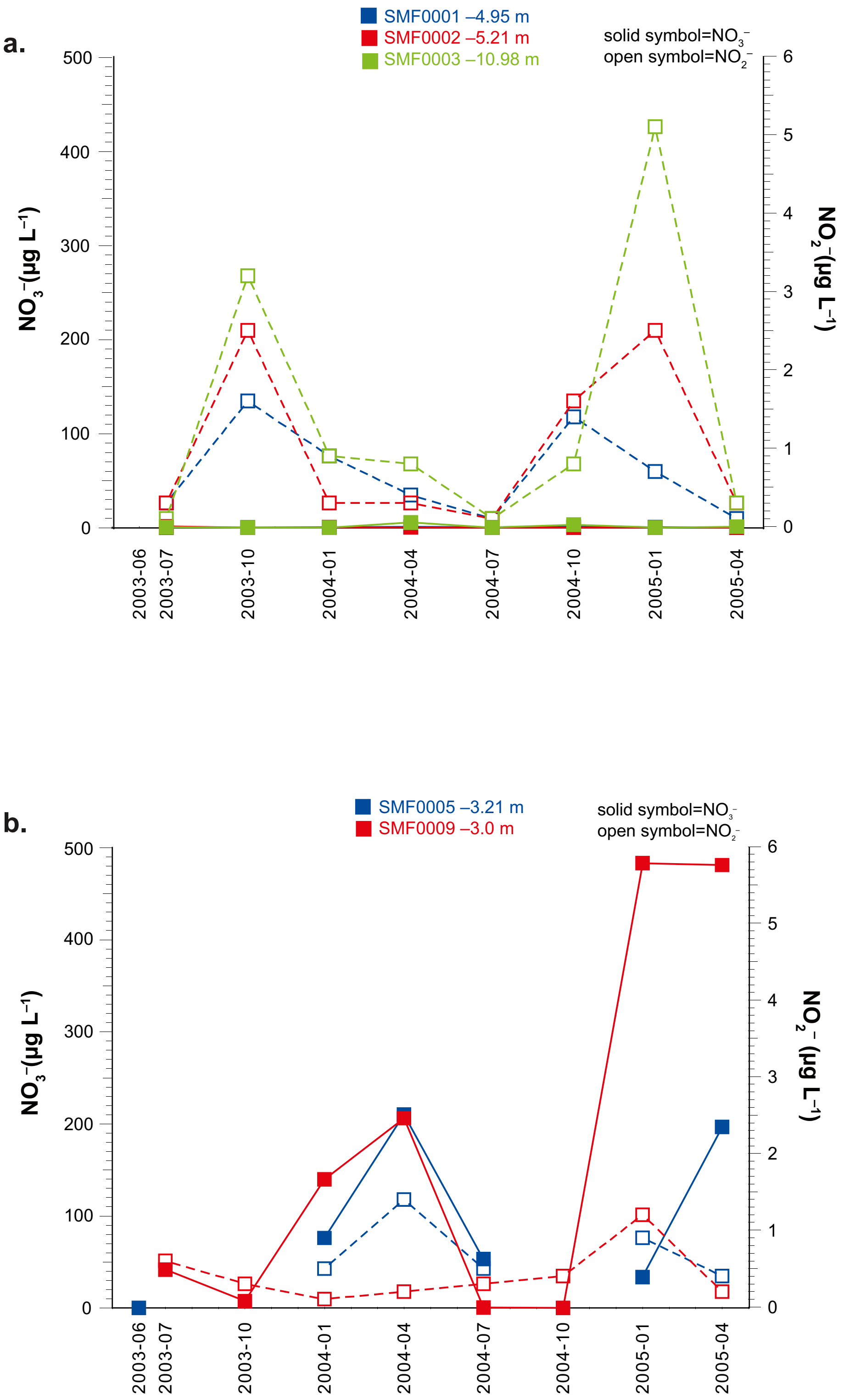


Figure 3-8 a–b. *Nitrate and nitrite over time in groundwater from soil pipes in Forsmark.*

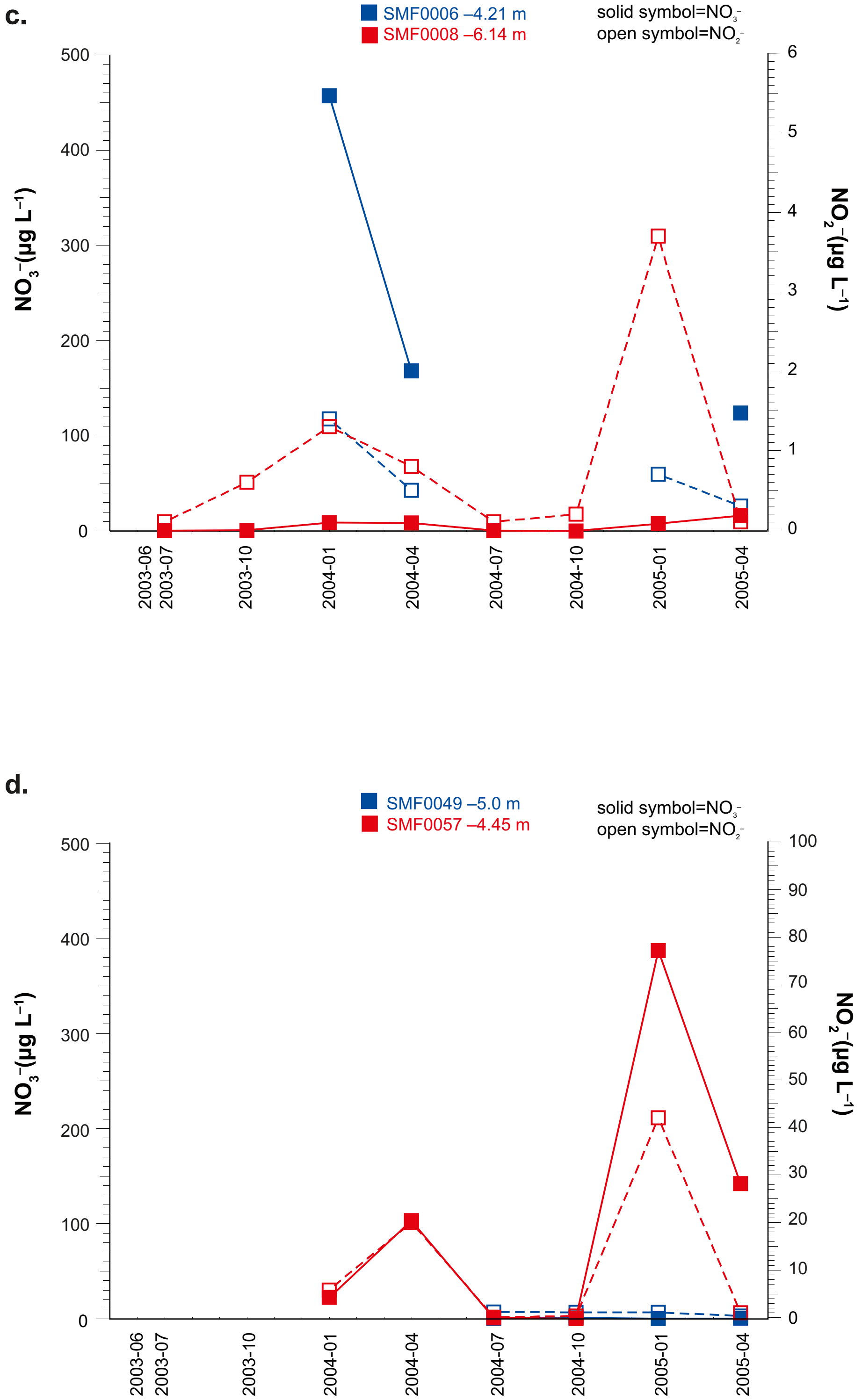


Figure 3-8 c–d. *Nitrate and nitrite over time in groundwater from soil pipes in Forsmark.*

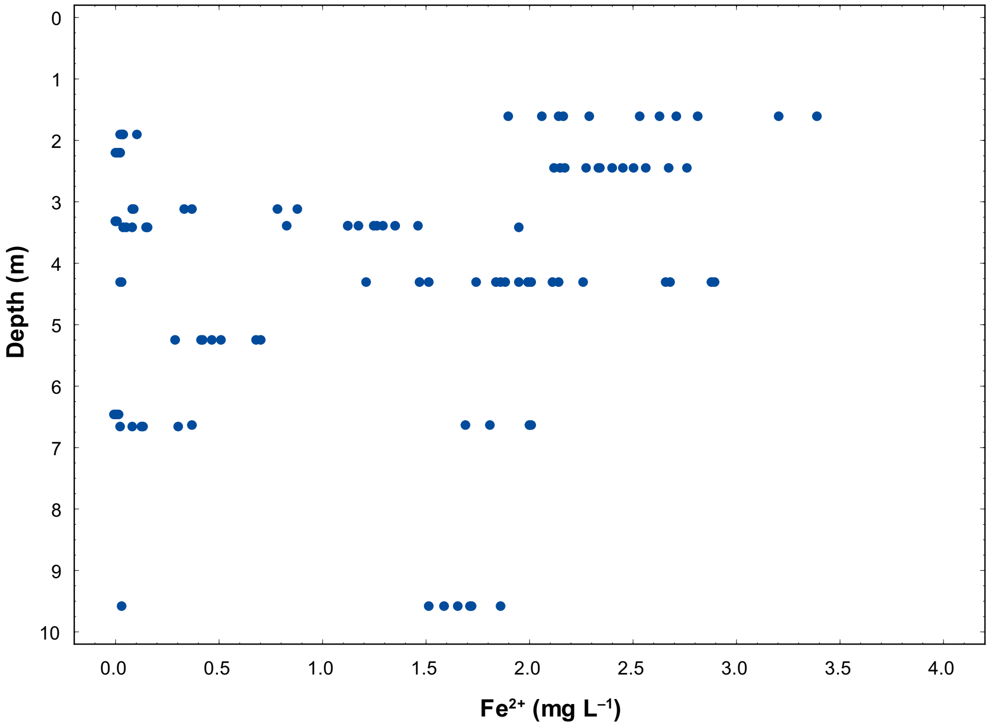


Figure 3-9. *Ferrous iron versus depth in groundwater from soil pipes in Forsmark.*

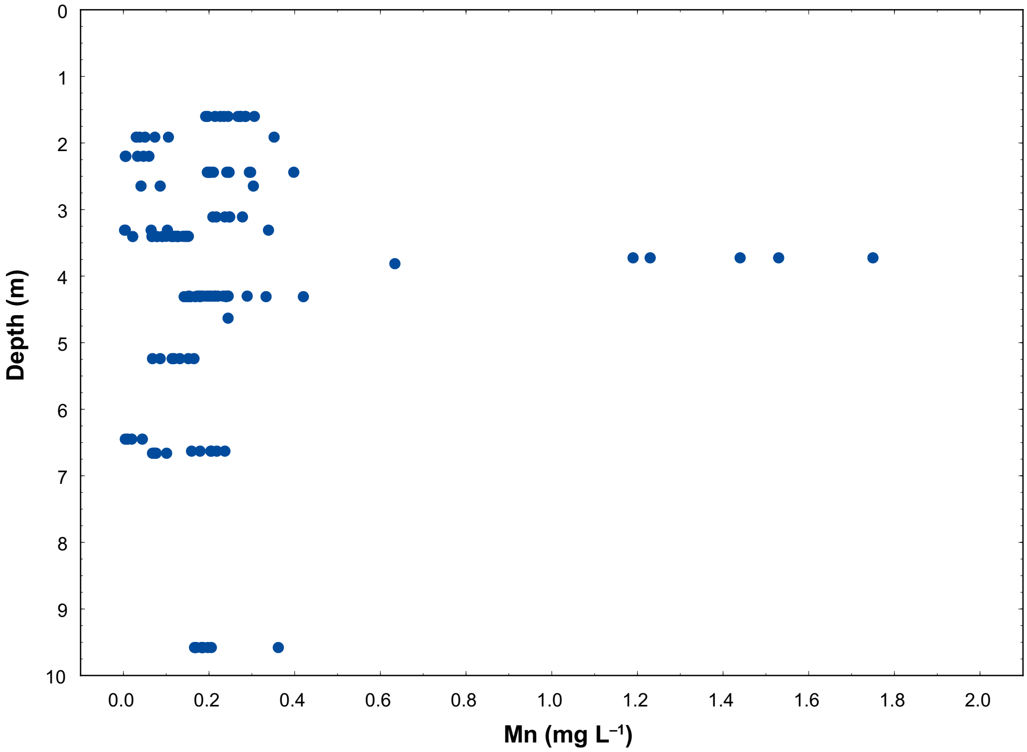


Figure 3-10. *Manganese versus depth in groundwater from soil pipes in Forsmark.*

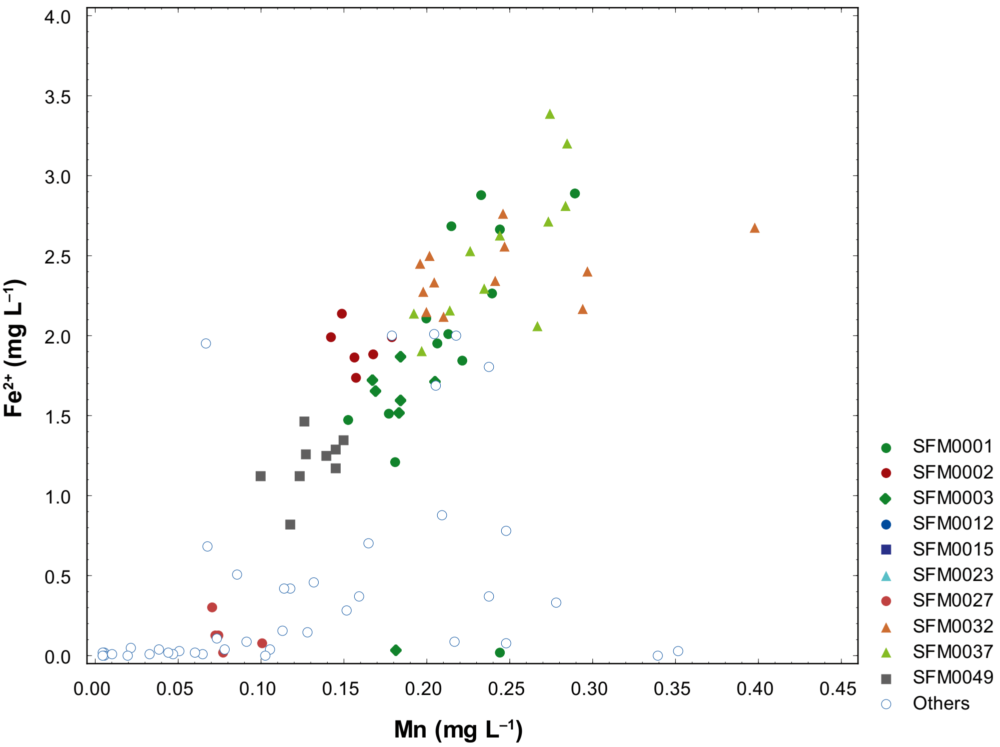


Figure 3-11. *Iron versus manganese in groundwater from soil pipes in Forsmark.*

These soil pipes are followed by SFM0032, which was located in a more open area. Note that some of the soil pipes were not included in Figure 3-11 because of missing data. Soil pipe SFM0023 displayed manganese values over 1.0 mg L^{-1}, which is a level unique in this data set. This is consistent with the high salinity and marine signature of groundwater from this soil pipe. There are several reports of ferromanganese concretions found on the floor of the Baltic Sea /Anufriev and Boltenkov 2007, Ghiorse and Hirsch 1982, Zhang et al. 2002/. The sediment and groundwater in Lake Bolundsfjärden has its origin in former sea sediment, as approximately 100 years ago this lake was part of the Baltic Sea /Tröjbom et al. 2007/. There were no reliable ferrous iron data from this borehole.

The microbial investigation of shallow groundwater in Olkiluoto, Finland demonstrated that iron- and manganese-reducing bacteria decreased in number with depth, but that between depths of 300 and 350 m, the numbers increased to approximately 1,000 cells mL^{-1}. The concentrations of ferrous iron decreased with depth /Pedersen 2008/.

Samples from the investigation of deeper groundwater in Forsmark displayed high numbers of iron- and manganese-reducing bacteria in the upper part of the investigated depths and a decreasing trend with depth (see Figure 3-12). The concentration of ferrous iron followed the decreasing trend with depth (data not shown; see hydrogeochemistry report SDM-Site Forsmark /Laaksoharju et al. 2008/ and /Hallbeck and Pedersen 2008).

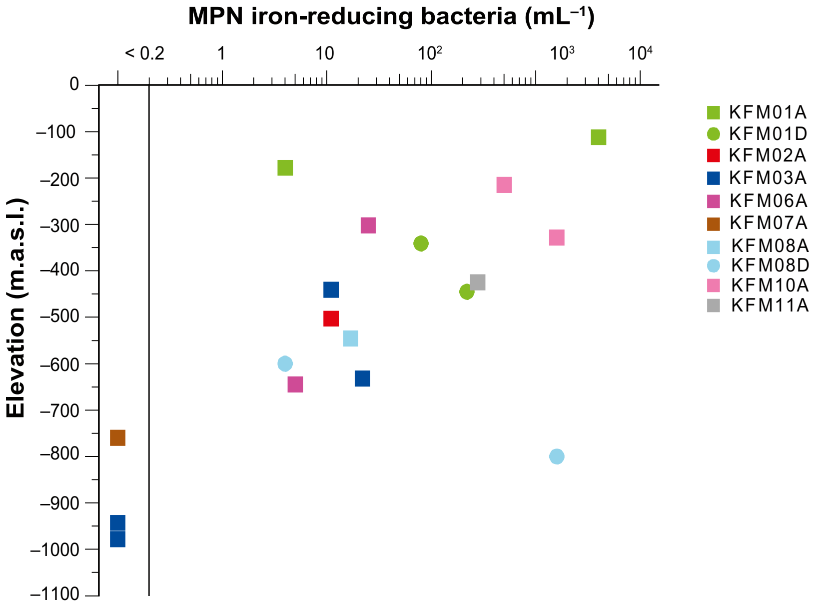
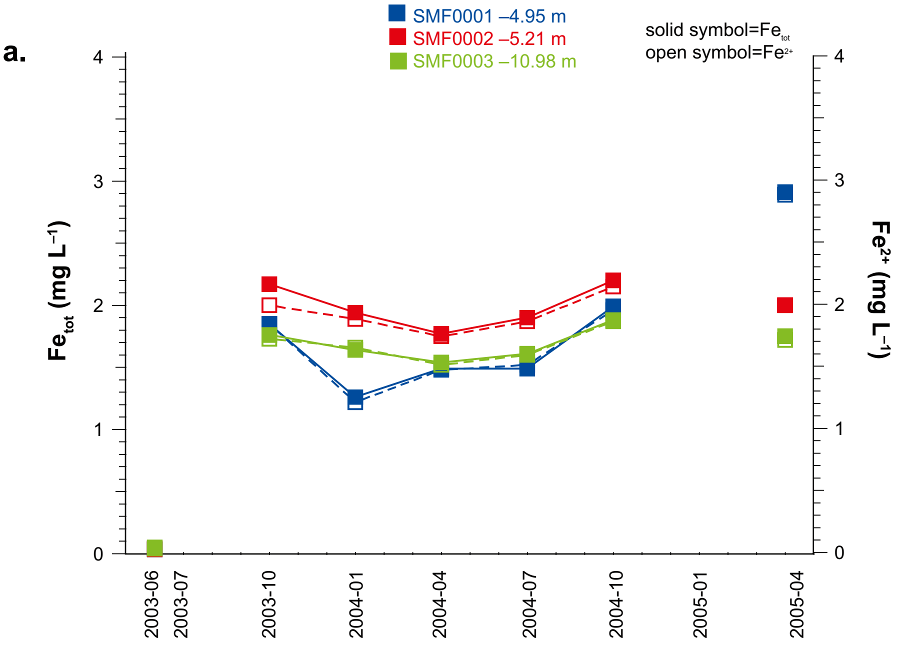


Figure 3-12. *Most probable number (MPN) of iron-reducing bacteria (IRB) in groundwater from core-drilled boreholes in Forsmark.*

Figure 3-13 and Figure 3-14 show total and ferrous iron and manganese contents in groundwater samples from eight soil pipes over time. SFM0001, SFM0002, and SFM0003 displayed higher iron and manganese values than the other soil pipes. These soil pipes are located near drill site 1, which is situated near Lake Bolundsfjärden, the lake with the high manganese and iron concentrations in groundwater below the bottom sediment. No trend over the course of the year could be seen. Total and ferrous iron levels followed each other over the year, suggesting that the reduced conditions were stable.

3.3.3 Sulphate reduction

Sulphate-reducing bacteria often follow the iron and manganese reducers when oxidized iron and manganese phases are depleted. These two groups of microorganisms utilize the same carbon and energy sources, i.e. short-chained organic acids or hydrogen. The sulphate reducers are often found in high-salinity environments that often include high sulphate concentrations. The sulphate concentrations in groundwater from soil pipes in Forsmark are shown in Figure 3-15. Soil pipe SFM0023 in Bolundsfjärden had the highest sulphate concentrations, between 300 and 400 mg L^{-1}. The sulphate concentrations in SFM0001 and SFM0037 varied the most. The values in SFM0001 ranged from 100 to 160 mg L^{-1}. Either this variation depends on dilution by precipitation over the year or it represents the effect of ongoing sulphate reduction.



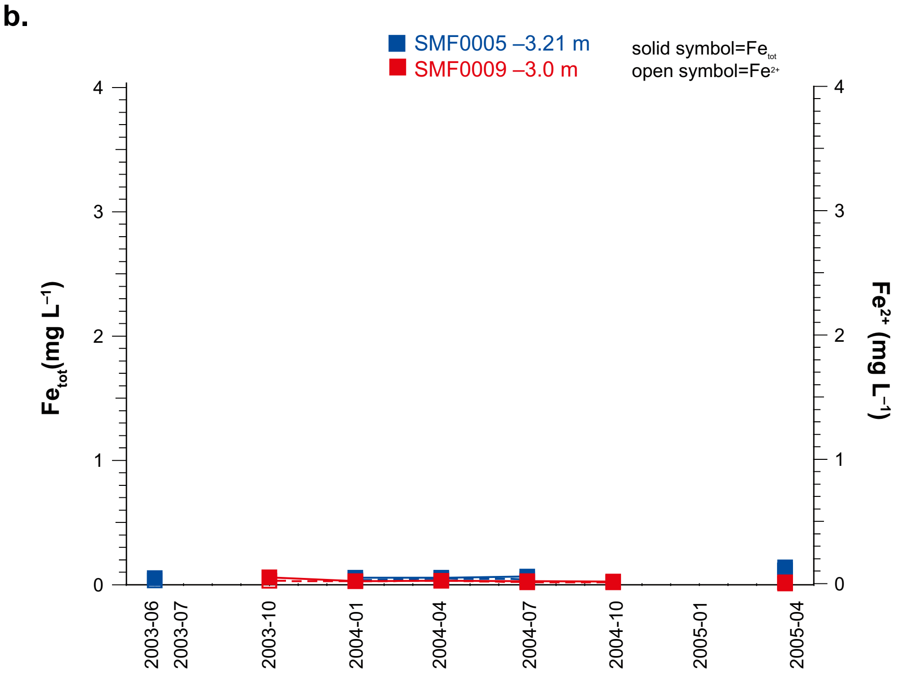
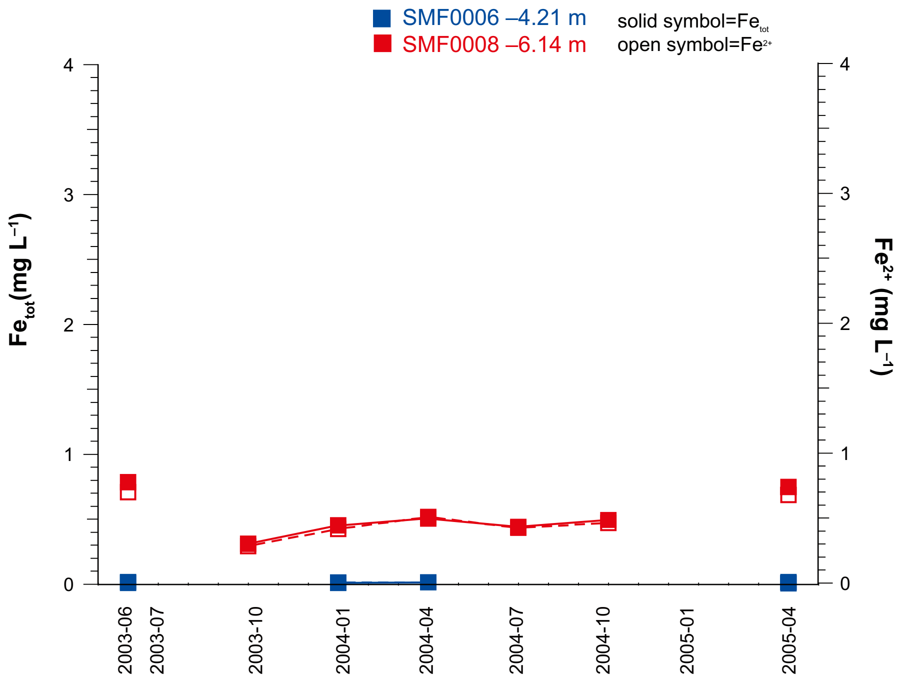


Figure 3-13 a-b. *Total and ferrous iron over time in groundwater from soil pipes in Forsmark.*

c.



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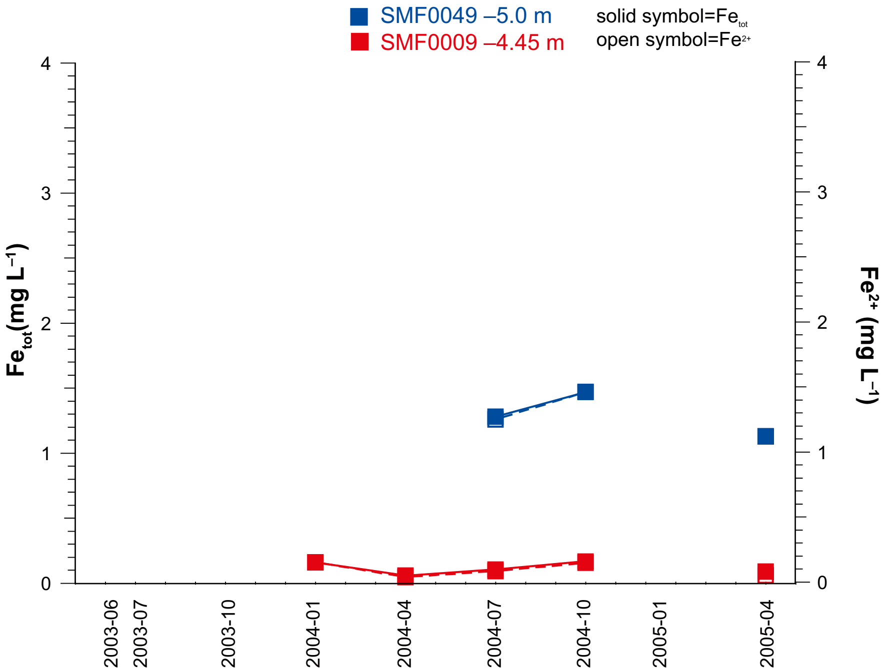

Figure 3-13 c-d. *Total and ferrous iron over time in groundwater from soil pipes in Forsmark.*

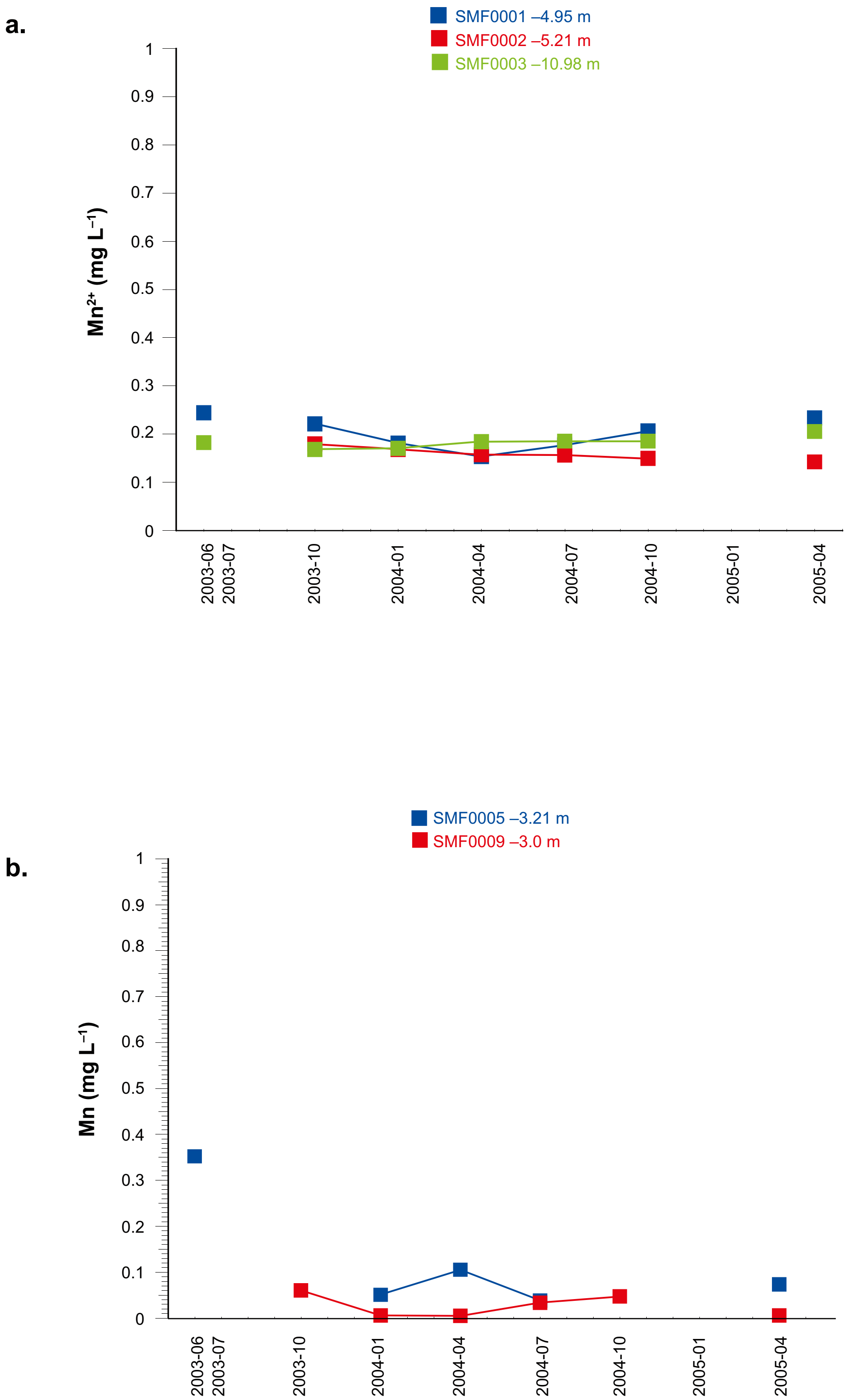

Figure 3-14 a-b. *Manganese over time in groundwater from soil pipes in Forsmark.*

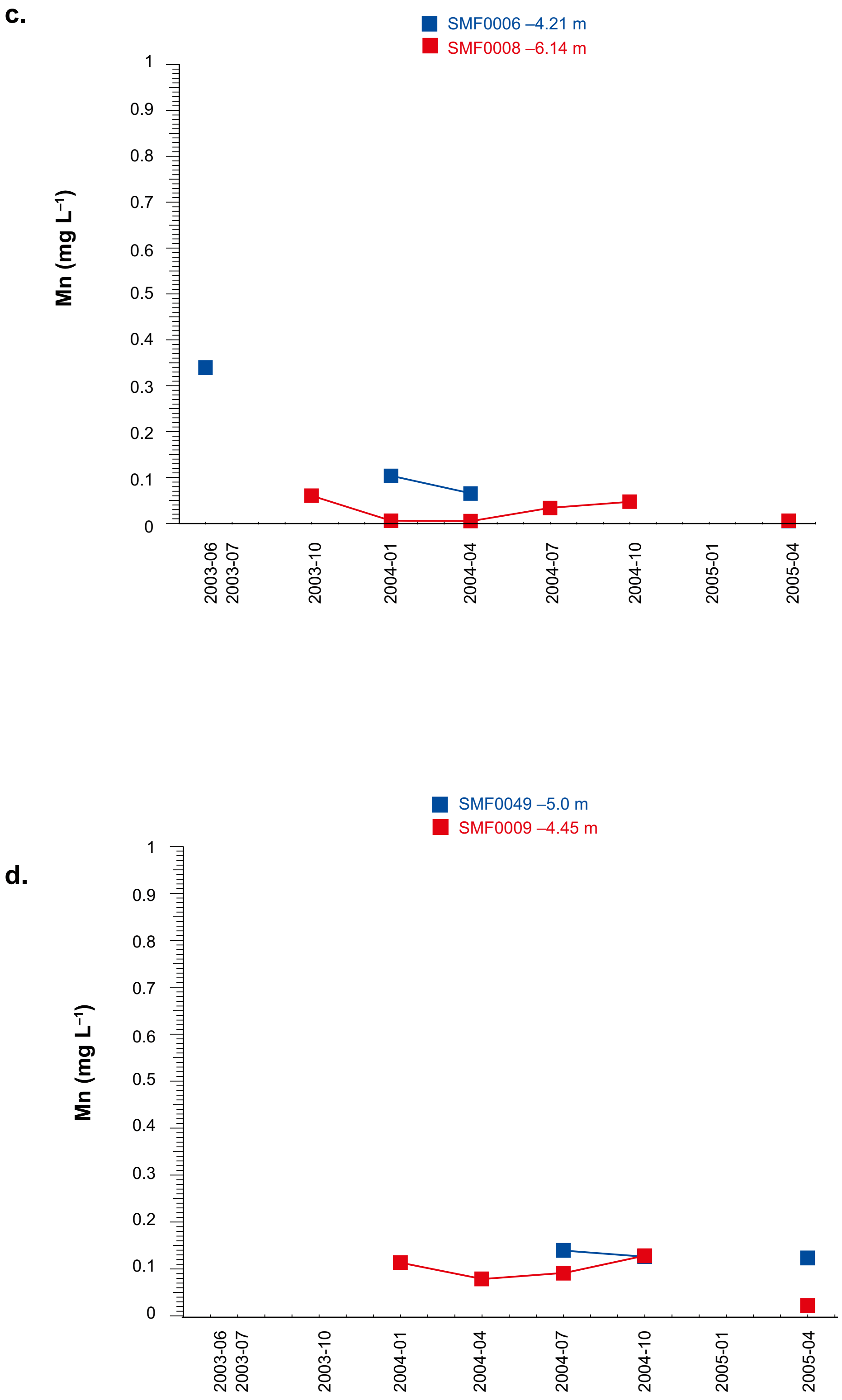

Figure 3-14 c-d. *Manganese over time in groundwater from soil pipes in Forsmark.*

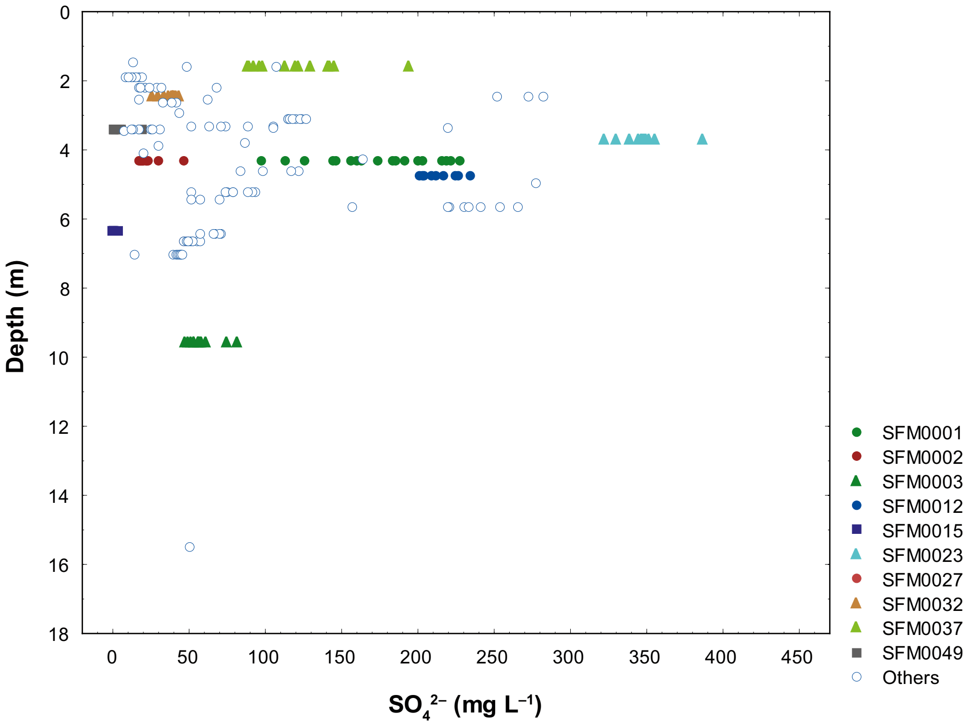

Figure 3-15. Sulphate versus depth in groundwater from soil pipes in Forsmark.

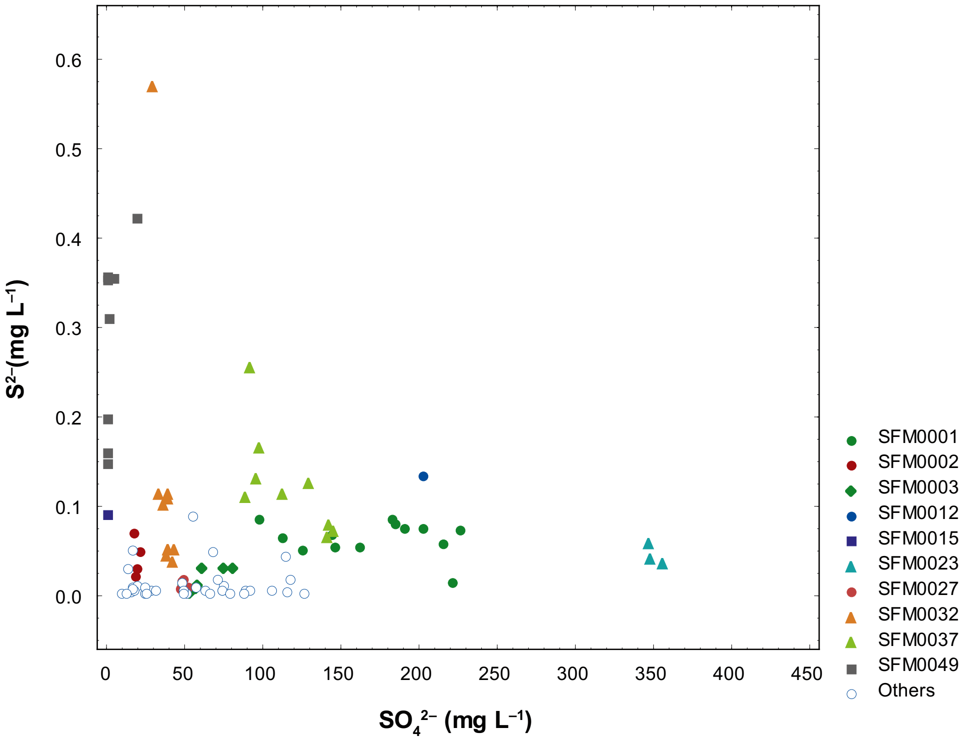

Figure 3-16. Sulphate versus sulphide in groundwater from soil pipes in Forsmark.

When the sulphate values were plotted against the chloride values for this soil pipe, it was clear that the change in sulphate was due to dilution and not to microbial sulphate reduction (data not shown). On the other hand, Figure 3-18a presents sulphate and sulphide values against time for groundwater from SFM0001 and two other soil pipes. Here it can be seen that the sulphide values increased when the sulphate decreased; this was probably the effect of a supply of organic matter following the infiltrating rainwater. The presence of sulphide indicated that the groundwater conditions in this soil pipe were reducing. Figure 3-16 shows the measured sulphide values versus sulphate in groundwater in the other soil pipes in Forsmark.

During the Forsmark and Laxemar site investigations and the studies in the Äspö tunnel, it was obvious that sulphide is a parameter that is sensitive to pumping. Since the sulphide is produced by microorganisms, the pump rate and pumped volume can cause a "wash out" of both microorganisms and sulphide. The result is that measurements made near the pumping point display low sulphide values. Depending on the number of sulphate-reducing bacteria, the volume of the sulphide-producing water, and the inflow of substrates, producing enough sulphide to reach the initial concentrations can take up to several months. Sulphide data should therefore be interpreted with caution, because the levels they indicate are probably lower than they would be under undisturbed conditions. Figure 3-16 shows sulphate versus sulphide in groundwater from soil pipes in Forsmark. The highest sulphide values were found in SFM0049, which had the lowest sulphate values, and in one measurement occasion in SFM0012.

During sulphate reduction a fractionation of sulphate isotopes takes place leaving heavy sulphate isotopes in the groundwater. Figure 3-17 shows the $\partial\ {}^{34}$S in sulphate, compared to that in a standard, Canon Diablo meteoritic troilite (CDT), versus sulphate in groundwater from soil pipes in Forsmark. Some of the soil pipes displayed very specific sulphate fractionation properties. SFM0023 had the highest sulphate values and also the heaviest isotope fraction, close to 30‰ (CDT); in addition, SFM0012 had the same isotopic composition. One explanation of this is that sulphate reduction may have occurred at some point, while another possibility is that sulphate reduction was ongoing at the time of sampling.

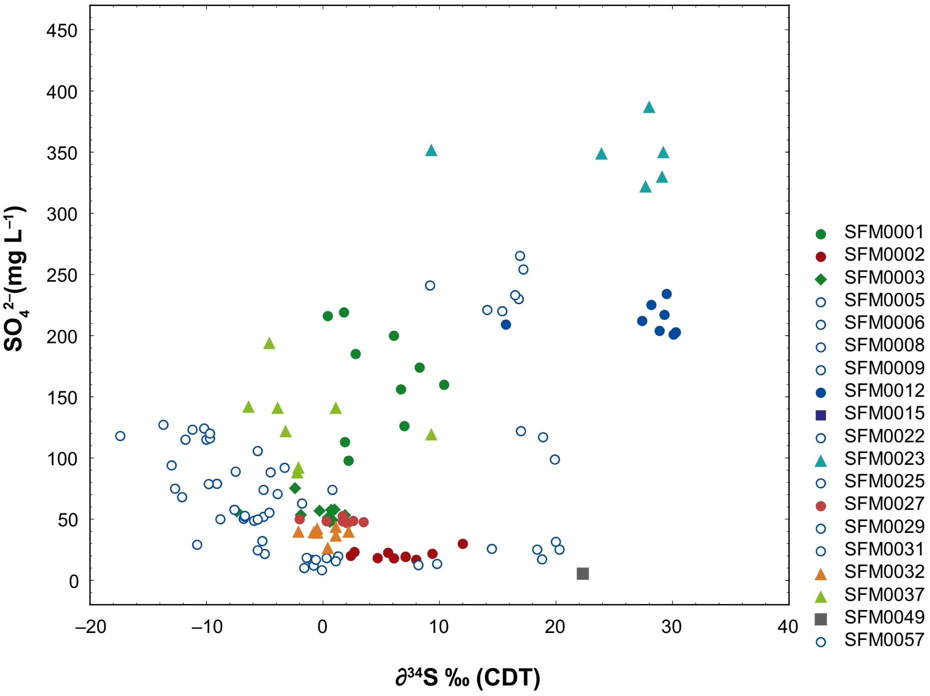

Figure 3-17. *The stable 34S isotope in sulphate versus sulphate in groundwater from soil pipes in Forsmark. The open symbols are the ones that belong to the "other" group in most of the figures in this report.*

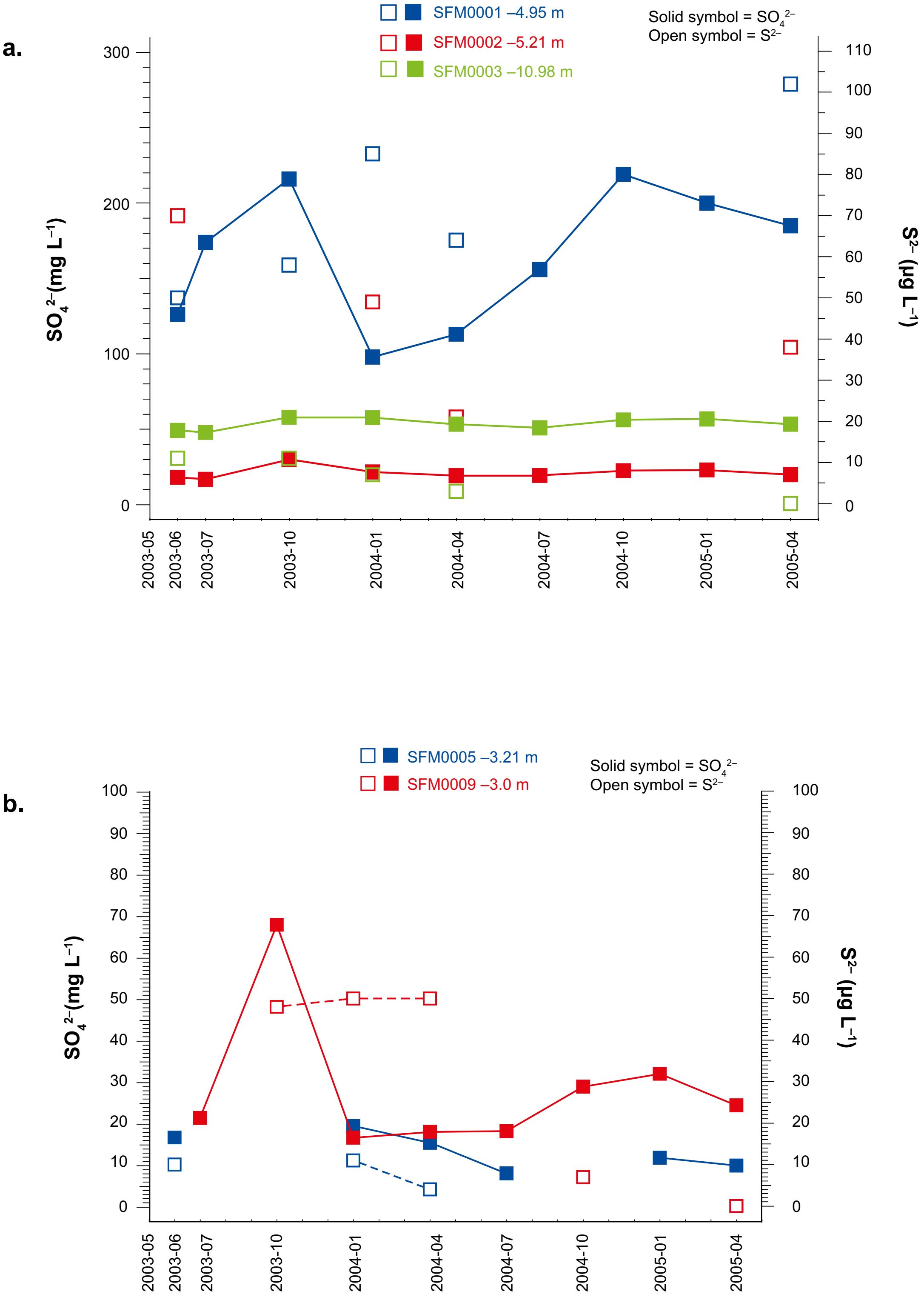

Figure 3-18 a-b. *Sulphate and sulphide versus time in groundwater from soil pipes in Forsmark.*

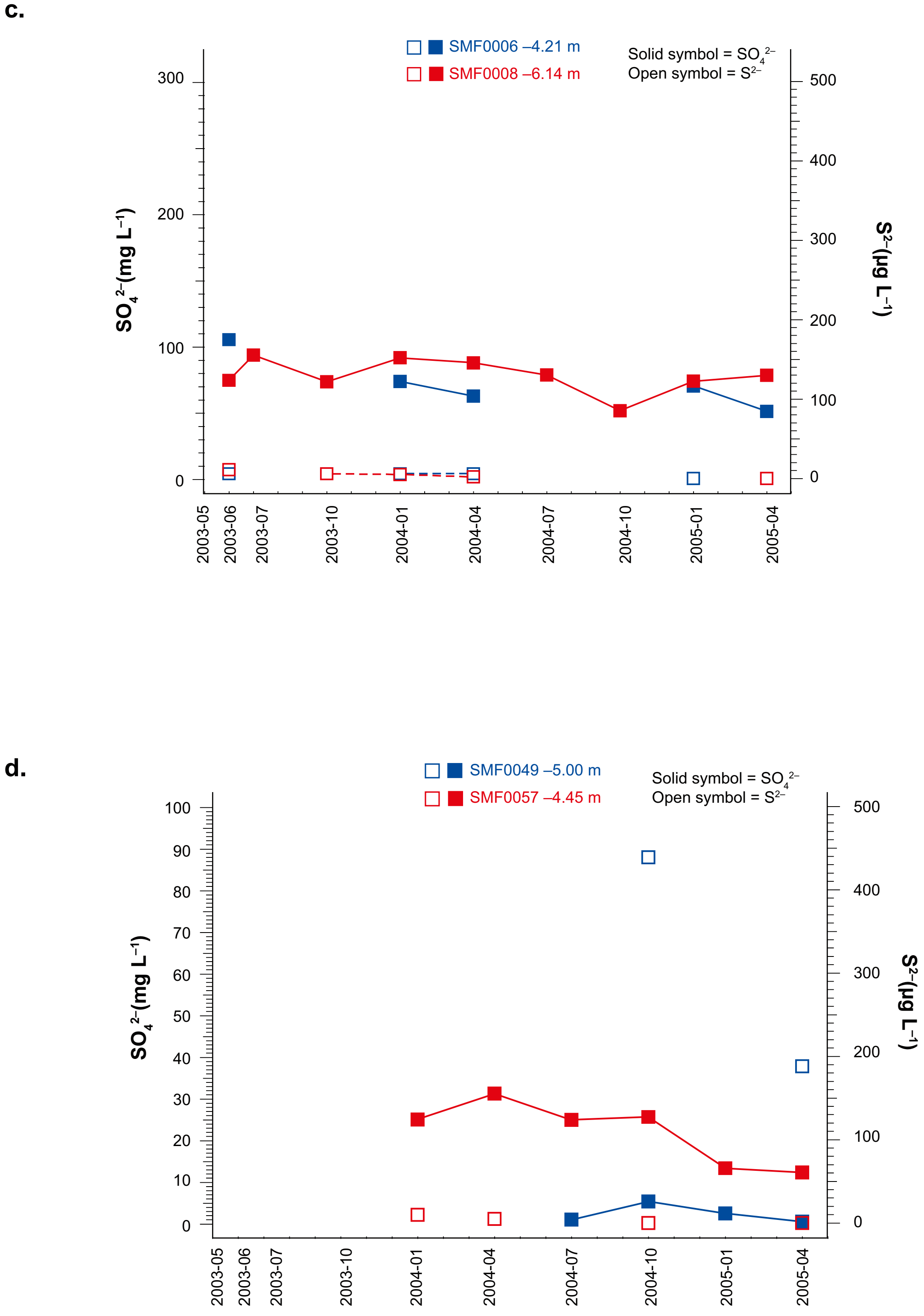

Figure 3-18 c-d. *Sulphate and sulphide versus time in groundwater from soil pipes in Forsmark.*

Unfortunately, in groundwater from some soil pipes, most of the parameters involved in sulphate reduction were missing and it was therefore impossible to determine whether or not sulphate reduction was ongoing. One such soil pipe was SFM0015, which had a unique DOC/DIC profile and $\partial\ ^{13}C$ values. On the other hand, in this borehole, both sulphate and sulphide levels were low and there was probably no ongoing sulphate reduction in the groundwater.

Figure 3-18 shows sulphate and sulphide data over time for groundwater from some of the soil pipes. The sulphide values were generally low, as discussed above. SFM0001 displayed a tendency to seasonal variation, also discussed above.

In Olkiluoto in Finland, the numbers of sulphate-reducing bacteria range from zero to 1,000 mL^{-1} in groundwater in soil pipes and shallow boreholes down to depths of 25 m /Pedersen 2008/. This indicates that the presence of various microbial groups is more site specific, i.e. soil pipe or borehole related, than generally depth related.

The DOC levels were high in some deep borehole groundwaters, and along with this, the numbers of sulphate reducers were also high. This can be compared with the DOC level of 35 mg L^{-1} and sulphide level of 1.57 mg L^{-1} found at a depth of 175 m mentioned in Section 3-1.

3.4 Methanogenesis and acetogenesis

Methanogens and acetogens are important organisms that merit study in the context of oxygen consumption. They are aerobic microorganisms that oxidize methane, and hence are called methanotrophic microorganisms. Acetate is an intermediary molecule in most microbial metabolisms and will be consumed in both aerobic and anaerobic metabolisms. Both methane and acetate will be oxidized with oxygen but by different organism groups.

In an ecosystem in which all possible electron acceptors are present, for example, sea or lake sediment, the last microbial process that takes place is methanogenesis. In this process, fermentatively produced hydrogen is oxidized with carbon dioxide as the electron acceptor and methane as the end product (see also Section 1). There is also another group of microorganisms, the acetogens, which uses the same components as methanogens do but produce acetate instead of methane. In some environments (e.g. moss and bog environments), methanogenesis and fermentation are almost the sole microbial processes that take place. *Sphagnum* moss produces large amounts of organic matter, but the environments in which it grows contain nearly no available electron acceptors with which aerobic or anaerobic microorganisms can degrade this organic material. The fermenting organisms produce short organic molecules together with hydrogen, which the methanogens use in their metabolism. Methane concentrations are therefore high in groundwater from mosses.

The groundwater of the Fennoscandian Shield contains relatively large amounts of hydrogen produced by various processes in the deep bedrock /Apps and Van de Kamp 1993/. Studies of microbiology in deep groundwater in Forsmark and in shallow and deep groundwater in Olkiluoto in Finland have demonstrated that acetogens are present in all sampled groundwater. As well, a study of deep groundwater demonstrated the presence of acetogens in all sampled boreholes. Methanogens, on the other hand, were also present in groundwater in Olkiluoto and in Forsmark but in much lower numbers /Pedersen 2008/.

The investigation of shallow groundwater in Olkiluoto also examined the presence of methanotrophic bacteria, the distribution of which is shown in Figure 3-19. This indicates that methane oxidizers are part of the oxygen-consuming microbial population in shallow groundwater in Olkiluoto and possibly in the Forsmark shallow groundwater system.

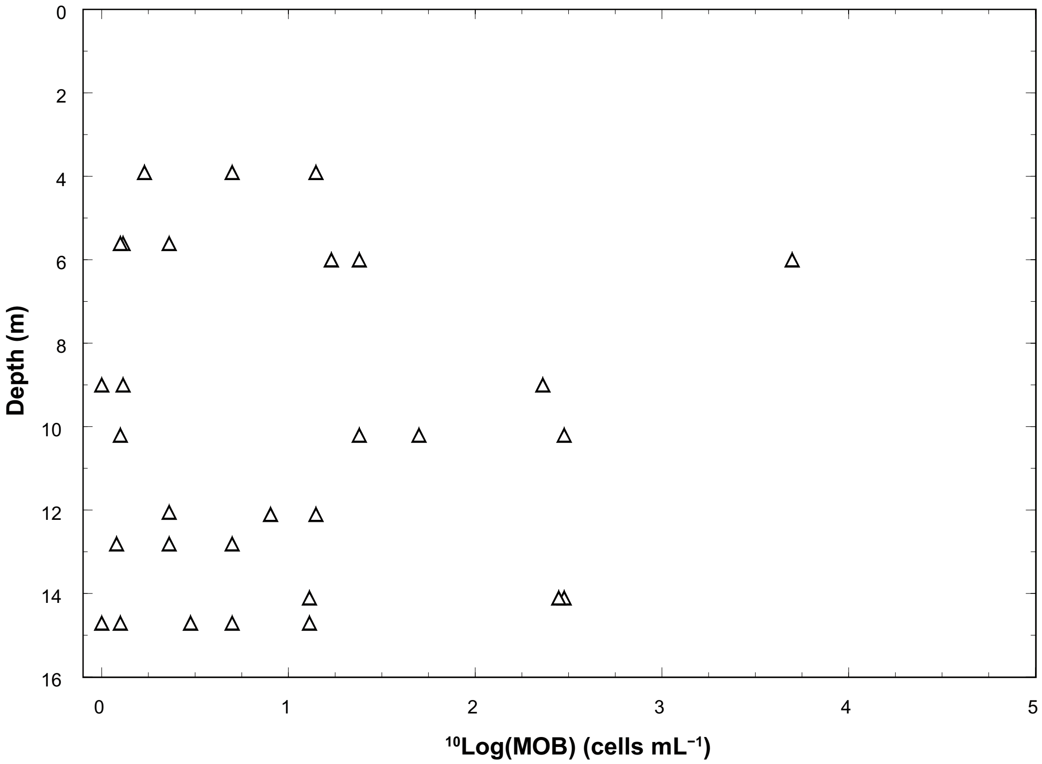

Figure 3-19. *The distribution of methane-oxidizing bacteria (MOB) versus depth in shallow Olkiluoto groundwater /Pedersen 2008/.*

4 Conclusions

Investigating and evaluating the available data from shallow groundwater in Forsmark demonstrated that: 1) different soil pipes had individual chemical characteristics in terms of the chemical species related to microbial activities, and 2) microbial activity could not be linked to the class of soil pipe, i.e. recharge, discharge, or intermittent.

Groundwater from soil pipes placed at SFM0023, and at the SFM0001, SFM0002, SFM0003, SFM0032, and SFM0037 sites, at Lake Bolundsfjärden, displayed more ongoing iron- and manganese-related biogeochemical reactions (in other words, iron and manganese reduction) than did other areas. This could be because there were iron and manganese precipitates left from when this area was the floor of the Baltic Sea. This area is a relatively young mass of land, less than 100 years old. In areas that have been above sea level for longer periods, the oxidized iron and manganese precipitates may already have been depleted by microbial iron and manganese reduction.

Because of the variable quality of the oxygen analyses and the ORP data, it is difficult to draw any conclusions as to the presence of oxygen other than *if* oxygen was present in the shallow groundwater it was in low concentrations. Based on the presence of the reduced species ferrous iron and sulphide, it can be concluded that reduced conditions prevailed at most sampled depths. There was a seasonal variation controlled by the DOC amounts. Soil pipes placed in similar biotopes displayed similar chemical signatures regarding DOC, while soil pipes in forested areas generally displayed evidence of high DOC.

The aim of this study was to answer the following questions, raised at the outset (the answers are given in italics after each question):

- Is it possible to determine from area-specific chemistry and the results of the microbe investigation in Olkiluoto, Finland, what microbial processes are active in different parts of the Forsmark area?

Active microbial processes could not be conclusively identified, but the chemistry gave a clear indication that DOC had been consumed by aerobic microorganisms and that various anaerobic processes had taken place. Autotrophic anaerobic processes, such as methanogenesis or acetogenesis, may be ongoing, but the proper microbial data on which to base conclusive statements were not available.

- Which process or processes dominate the degradation of organic matter? Do different processes dominate in different areas and/or depths? Could the area be divided into subareas based on depth, recharge/discharge areas, or other factors?

The unsatisfactory quality of the available oxygen and ORP data meant it was impossible to make any conclusions. Microbial activity and processes seemed mostly to be linked to the specific characteristics of the studied boreholes and to the biotope in which they are situated. A direct relationship between microbial processes and depth and recharge/discharge area could not be identified.

- Is it possible to establish a depth limit for the presence of oxic groundwater? Does this limit vary over the course of the year or between years? Where is the oxygen consumed, if it is not transported down to the bedrock?

A depth limit for oxygen penetration could not be established from this set of data, because of the poor quality of the oxygen data and because dissolved oxygen data were missing for the 10–25 m depth interval (the interval where the limit for oxygen intrusion was established from data in Olkiluoto, Finland). Oxygen data were also missing for greater depths, since neither oxygen nor ORP was measured in percussion-drilled boreholes. The particular soil *pipes and boreholes sampled varied from sampling occasion to sampling occasion, and the parameters measured on the different occasions varied as well. This variability in the analytical program created a very problematic discontinuity in the dataset, which severely hampered the interpretation and conceptual analysis. In addition, many of the percussion-drilled boreholes were not packed off, and because of that, the sampled sections were too extended to give useful information.*

- Are we still missing some chemical parameters necessary for a full understanding of the microbiology in the oxic/anoxic zone in Forsmark?

Precise and reproducible measurements, made over seasonal time scales, of the oxygen content and redox potential of groundwater in selected soil pipes and boreholes over the whole depth range, including the 10–25 m interval, could return a more accurate model of oxygen reduction with depth in Forsmark. It is crucial that the measurements cover the whole depth range from the ground surface to a depth of approximately 100 m, where the deep CHEMNET investigations start. All parameters related to microbial processes, such as oxygen, ferrous iron, sulphide, and DOC, are sensitive to sample disturbances. They must be measured with confidence and reproducibility on repeated sampling occasions over the course of a year to amass a complete dataset. In addition, gas data should be gathered on the same sampling occasions, preferably together with isotopic composition.

There is generally no need for more soil pipes or percussion-drilled boreholes. The existing ones could be used if sampling points are carefully chosen and a cautious sampling procedure is devised. To gather useful information from percussion-drilled boreholes, distinct fractures need to be packed off. Some soil pipes placed at the bottoms of lakes, however, are made of steel, and these will particularly affect the iron data gathered. Therefore, it is suggested that new pipes should replace the old steel ones or that new ones be installed.

It is strongly recommended that future sampling programs in shallow groundwaters be hypothesis driven, rather than oriented towards the mass production of data that end up harbouring great uncertainties. Hypotheses can be constructed concerning questions such as: What microbial processes are expected, and how can they be mapped with respect to rates and extent? What processes merit investigation with respect to repository safety (e.g. oxygen intrusion and biogeochemistry related to radionuclide migration processes)?

5 References

Anonymous, 1983. Final storage of spent nuclear fuel, KBS-3 Final Report, Vols. I–IV, 1–100, Svensk Kärnbränslehantering AB.

Anufriev G S, Boltenkov B S, 2007. Ferromanganese nodules of the Baltic Sea: composition, helium isotopes, and growth rate. Lithology and Mineral Resources, 42, 267–272.

Apps J A, Van de Kamp P C, 1993. Energy gases of abiogenic origin in the Earth's crust: the future of energy gases. US Geological Survey Prof. Pap. 1570, 81–132.

Des Marais D, 1996. Stable light isotope biogeochemistry of hydrothermal systems. In: Evolution of hydrothermal ecosystems on Earth (and Mars?). Ciba Foundation Symposium 202. John Wiley & Sons, Chichester.

Carritt D E, Carpenter J H, 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in sea water: a NASCO Report. Journal of Marine Research, 24, 286–318.

Ghiorse W C, Hirsch P, 1982. Isolation and properties of ferromanganese-depositing budding bacteria from Baltic Sea ferromanganese concretions. Applied and Environmental Microbiology, 43, 1464–1472.

Hallbeck L, Pedersen K, 2008. Explorative analysis of microbes, colloids and gases. SDM-Site Forsmark. SKB R-08-85, Svensk Kärnbränslehantering AB.

Laaksoharju M, Smellie J, Tullborg E-L, Gimeno M, Hallbeck L, Molinero J, Waber N, 2008. Bedrock hydrogeochemistry Forsmark. Site descriptive modelling. SDM-Site Forsmark. SKB R-08-47, Svensk Kärnbränslehantering AB.

Nilsson A C, Borgiel M, 2005. Forsmark site investigation. Sampling and analyses of near surface groundwaters. Results from sampling of shallow soil monitoring wells, BAT pipes, a natural spring and private wells, May 2003–April 2005. SKB P-05-171, Svensk Kärnbränslehantering AB.

Pedersen K, 2006. Microbiology of transitional groundwater of the porous overburden and underlying shallow fractured bedrock aquifers in Olkiluoto 2004, Finland. Posiva Working Report 2006-09, Posiva OY, Finland.

Pedersen K, 2007. Microbiology of transitional groundwater of the porous overburden and underlying shallow fractured bedrock aquifers in Olkiluoto, Finland. Posiva Working Report 2007-20, Posiva OY, Finland.

Pedersen K, 2008. Microbiology of Olkiluoto groundwater, 2004–2006. Posiva Report 2008-02, Posiva OY, Finland.

Tröjbom M, Söderbäck B, Johansson P O, 2007. Hydrochemistry in surface water and shallow groundwater. Site descriptive modelling. SDM-Site Forsmark. SKB R-07-55, Svensk Kärnbränslehantering AB.

Zhang F S, Lin C Y, Bian L Z, Glasby G P, Zhamoida V A, 2002. Possible evidence for the biogenic formation of spheroidal ferromanganese concretions from the eastern Gulf of Finland, the Baltic Sea. Baltica, 15, 23–29.

Appendix

Figures A-1 to A-15 summarise the oxygen, DOC, DIC and chloride data from soil pipes in Forsmark. The grouping into "recharge", "discharge" and "intermittent" soil pipes refer to the hydrological field classification of the pipes.

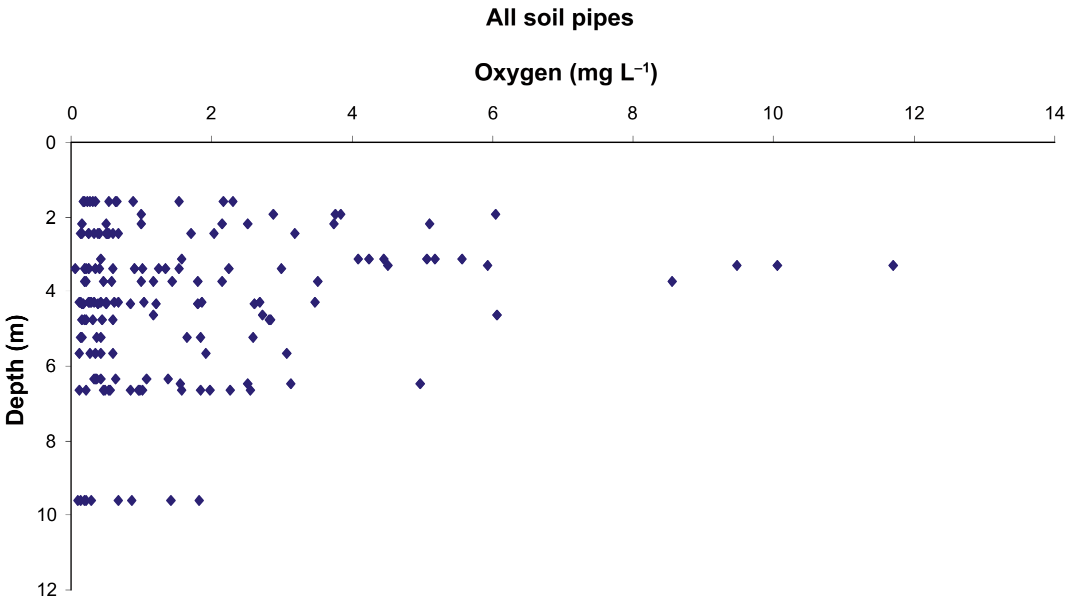

Figure A-1. *Oxygen versus depth; groundwater from all soil pipes.*

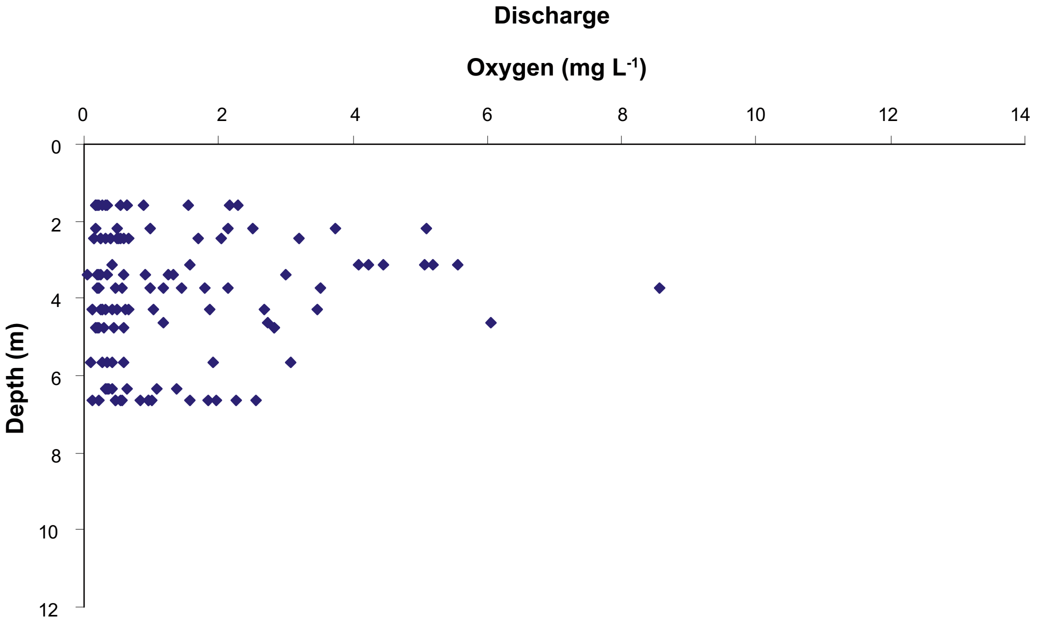

Figure A-2. *Oxygen versus depth; groundwater from discharge soil pipes.*

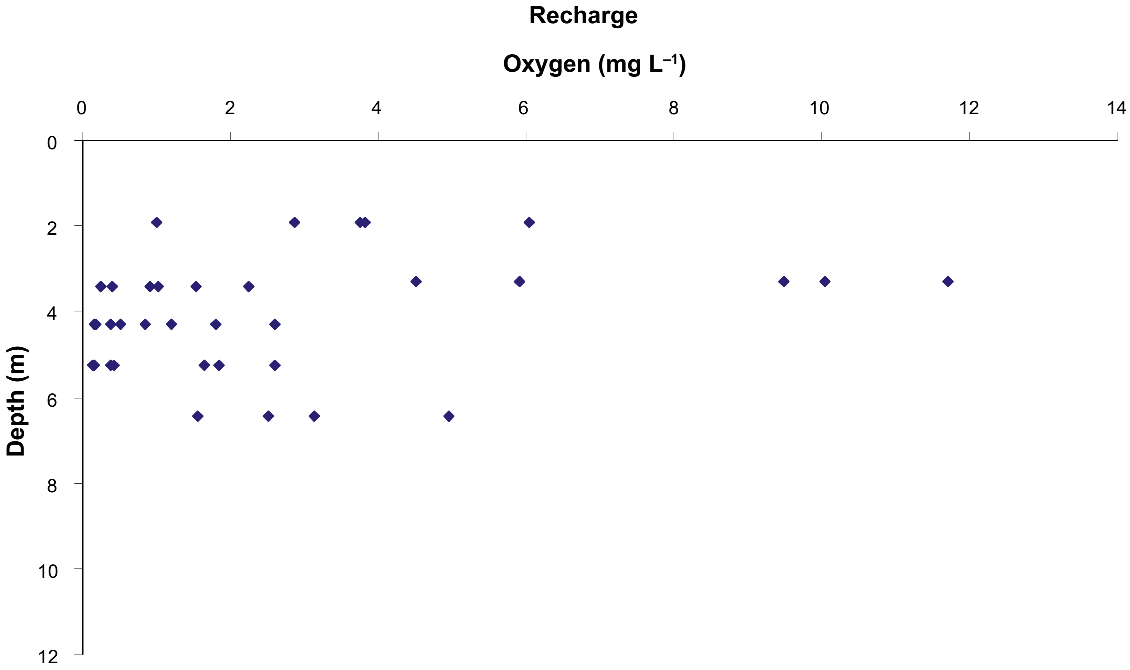

Figure A-3. *Oxygen versus depth; groundwater from recharge soil pipes.*

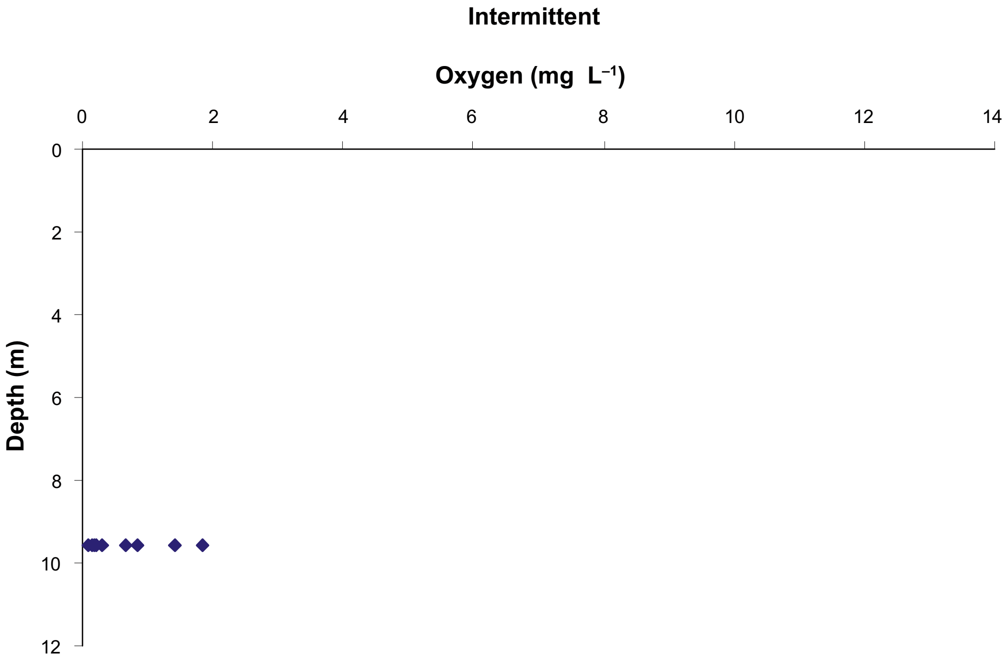

Figure A-4. *Oxygen versus depth; groundwater from one intermittent soil pipe.*

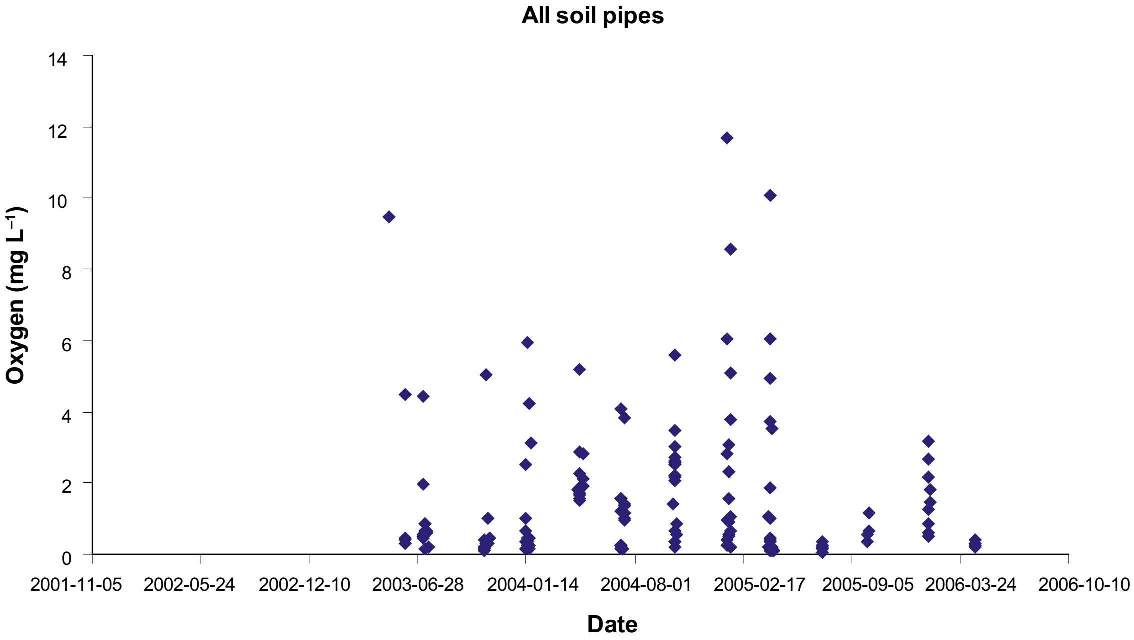

Figure A-5. *Oxygen versus sampling date; groundwater from all soil pipes.*

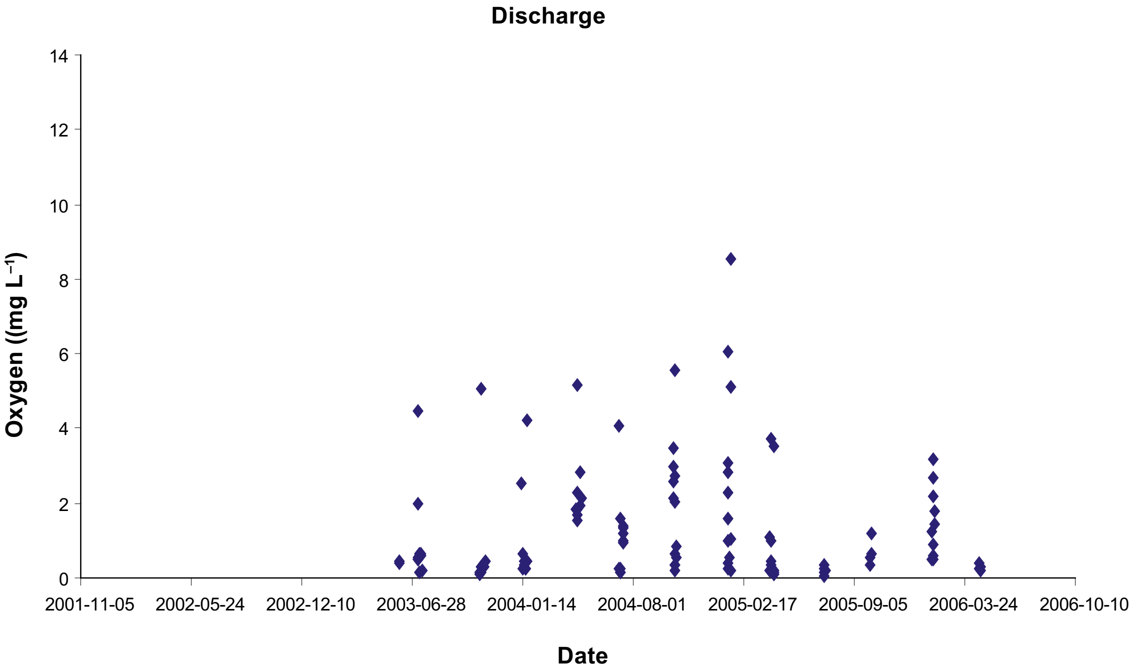

Figure A-6. *Oxygen versus sampling date; groundwater from discharge soil pipes.*

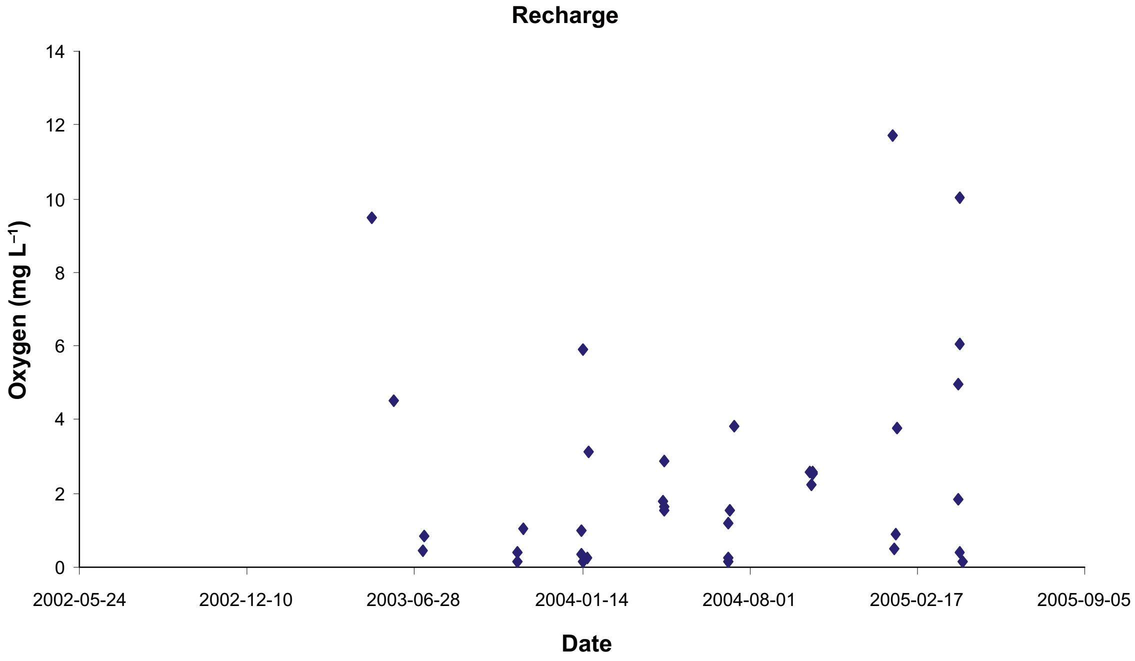

Figure A-7. *Oxygen versus sampling date; groundwater from recharge soil pipes.*

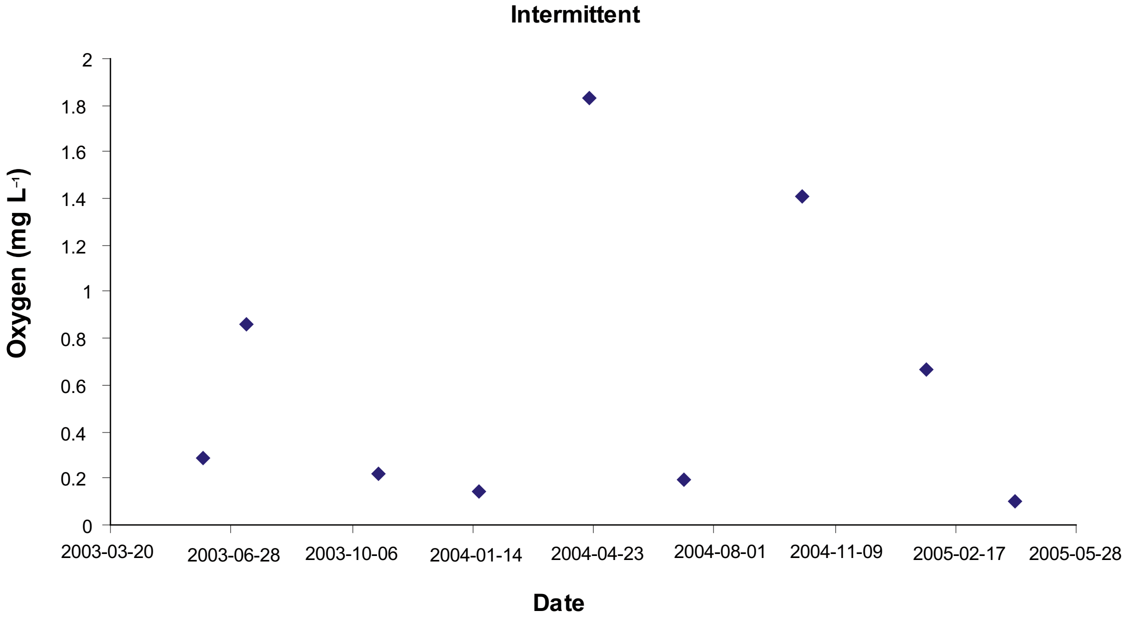

Figure A-8. *Oxygen versus sampling date; groundwater from one intermittent soil pipe.*

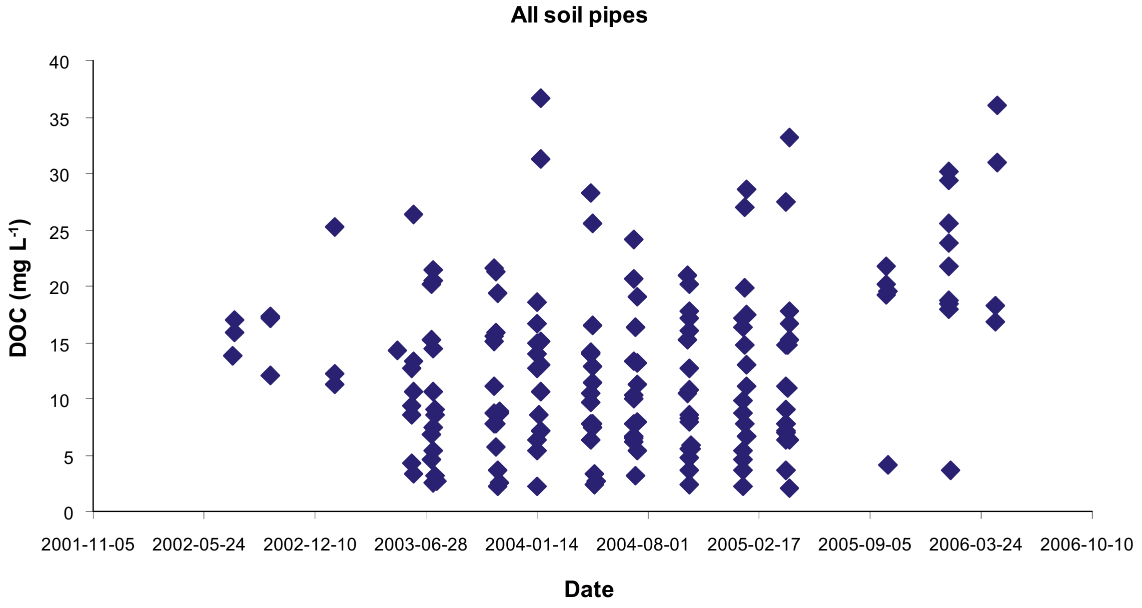

Figure A-9. *DOC versus sampling date; groundwater from all soil pipes.*

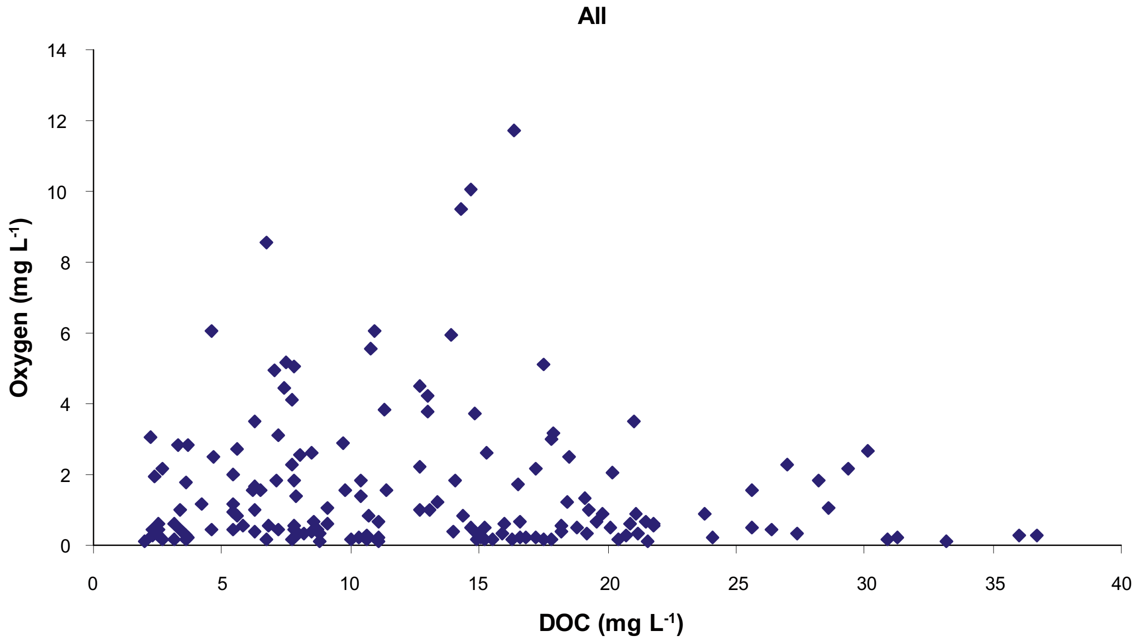

Figure A-10. *DOC versus oxygen; groundwater from all soil pipes.*

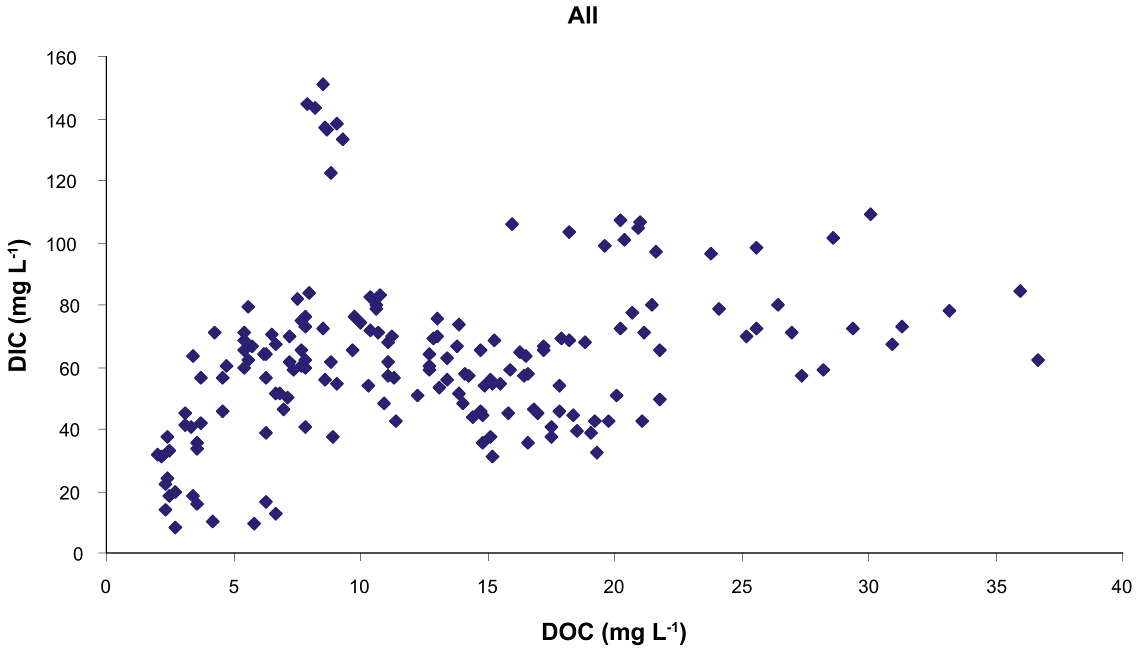

Figure A-11. *DOC versus DIC; groundwater from all soil pipes.*

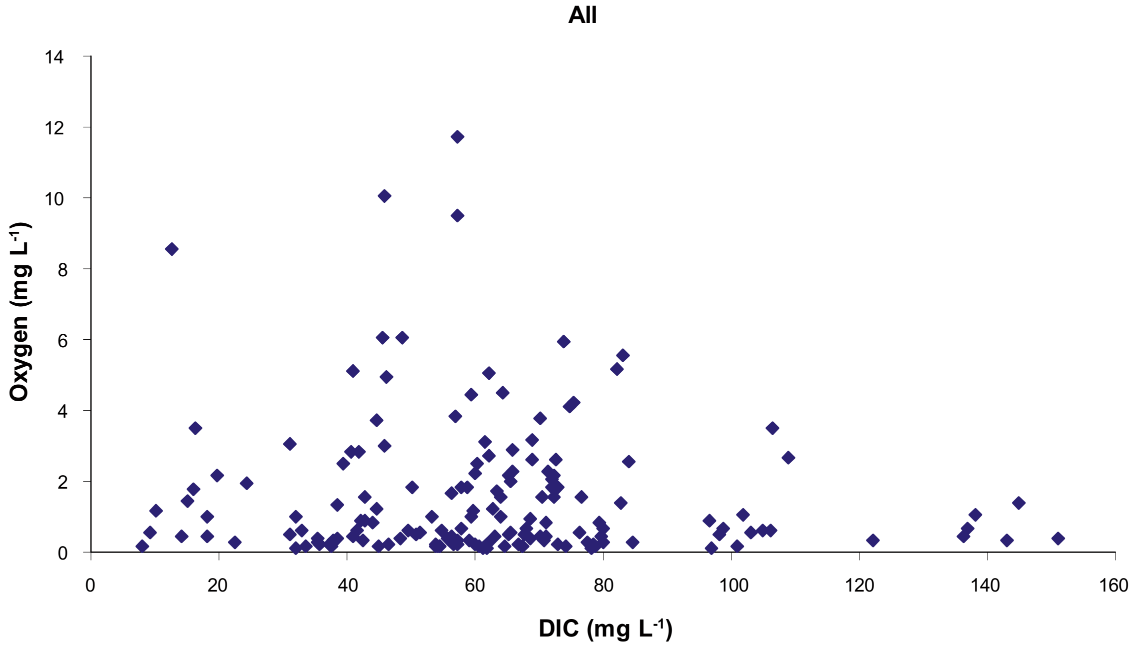

Figure A-12. *DIC versus oxygen; groundwater from all soil pipes.*

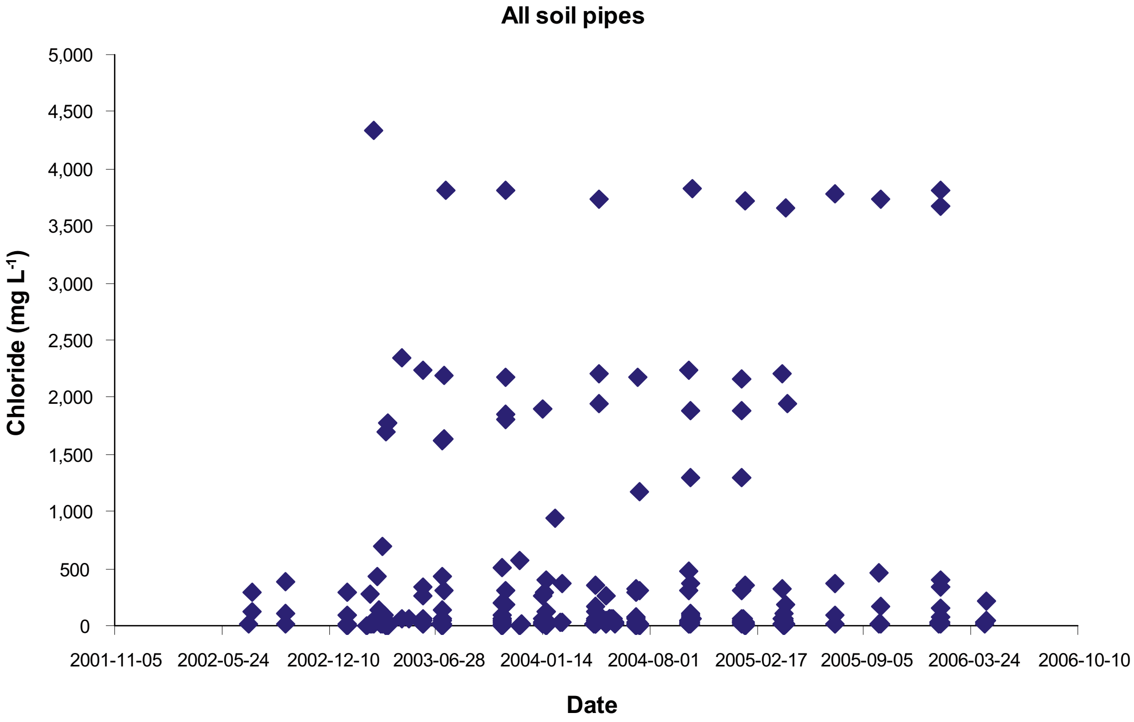

Figure A-13. *Chloride versus time; groundwater from all soil pipes.*

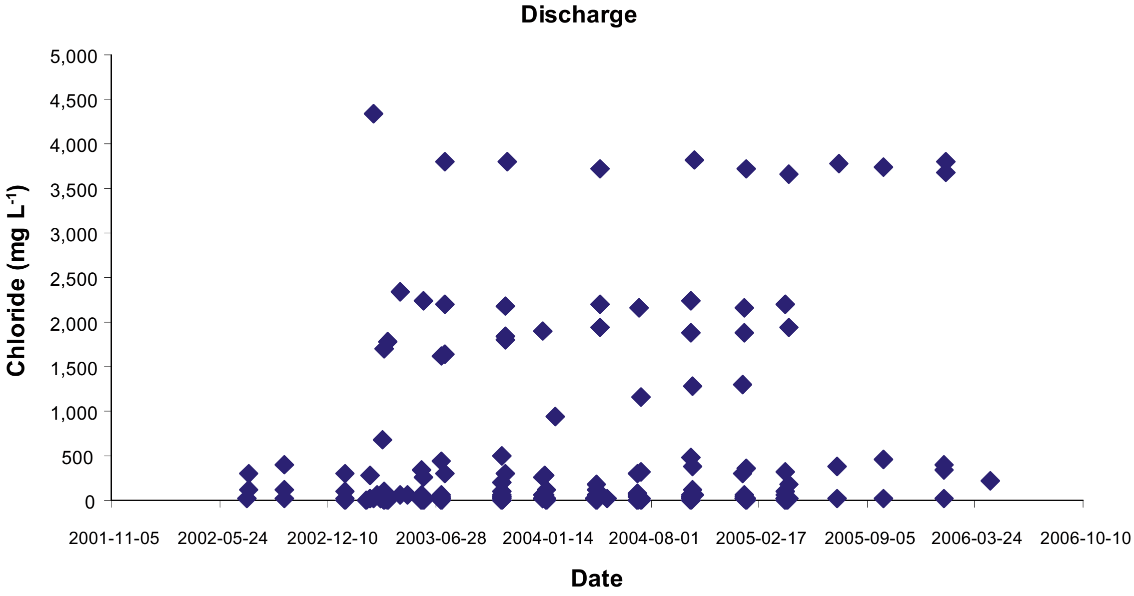

Figure A-14. *Chloride versus time; groundwater from discharge soil pipes.*

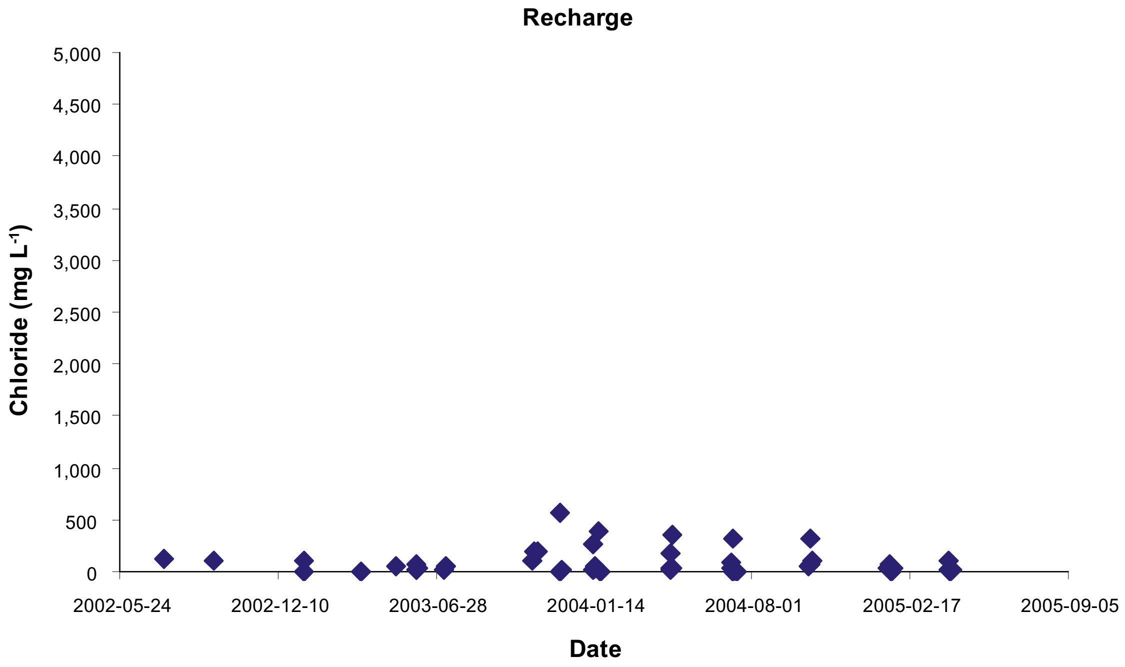

Figure A-15. *Chloride versus time; groundwater from recharge soil pipes.*